

## Review

# Biogeochemical Controls on Methane Generation: A Review on Indian Coal Resources

Tushar Adsul <sup>1</sup>, Santanu Ghosh <sup>2</sup>, Susheel Kumar <sup>3</sup>, Balram Tiwari <sup>1</sup>, Subir Dutta <sup>1</sup> and Atul Kumar Varma <sup>1,\*</sup><sup>1</sup> Coal Geology and Organic Petrology Laboratory, Department of Applied Geology, Indian Institute of Technology (Indian School of Mines), Dhanbad 826004, Jharkhand, India<sup>2</sup> Department of Geology, Mizoram University, Aizawl 796004, Mizoram, India<sup>3</sup> Centre for Petroleum Exploration, Mizoram University, Aizawl 796004, Mizoram, India

\* Correspondence: atul@iitism.ac.in

**Abstract:** Coal bed methane (CBM) extraction has astounding effects on the global energy budget. Since the earliest discoveries of CBM, this natural gas form has witnessed ever-increasing demands from the core sectors of the economy. CBM is an unconventional source of energy occurring naturally within coal beds. The multiphase CBM generation during coal evolution commences with microbial diagenesis of the sedimentary organic matter during peatification, followed by early to mature thermogenic kerogen decomposition and post-coalification occurrences. Indeed, the origin of the CBM and, moreover, its economically valuable retention within coal seams is a function of various parameters. Several noticeable knowledge gaps include the controls of coal make-up and its physico-chemical position on the CBM generation and genetic link through fossil molecular and stable isotopic integration with the parent coal during its evolution. Therefore, this manuscript reviews the origin of CBM; the influences of coal properties and micropetrographic entities on CBM generation and storage; and its genetic molecular and stable isotope compositions in India and the world's major coal reservoirs. Moreover, analyses of and outlooks on future development trends in the exploration, production, and application of coalbed methane are also addressed. Finally, as India has the fifth largest proven coal reserves, this brief review of the recent CBM discoveries and developments provides a plausible scope for microbially enhanced CBM production from these basins.

**Keywords:** methanogenesis; microbially enhanced–coalbed methane; compound specific stable isotope; petrographic evidence; molecular signals; gas mixing; Indian coal resource plays



**Citation:** Adsul, T.; Ghosh, S.; Kumar, S.; Tiwari, B.; Dutta, S.; Varma, A.K. Biogeochemical Controls on Methane Generation: A Review on Indian Coal Resources. *Minerals* **2023**, *13*, 695. <https://doi.org/10.3390/min13050695>

Academic Editor: Thomas Gentzis

Received: 7 March 2023

Revised: 14 April 2023

Accepted: 17 May 2023

Published: 19 May 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Coal is made up of elements in their purest form, with carbon being the dominant element. Carbon naturally combines with other elements to form products of economic significance. Among these products, coal bed methane (CBM) has drawn tremendous attention in the energy market as a clean energy resource because it produces fewer greenhouse gases than other conventional sources [1]. Coal bed methane (CH<sub>4</sub>) occurs naturally within coal beds and is usually trapped within the coal matrix due to adsorption. Coal acts as both a source and a reservoir for methane; therefore, it is considered a storehouse for CBM. This clean energy resource has been given more importance than ever due to its benevolent properties. Moreover, the current levels of CO<sub>2</sub> emission are at a record high due to the consumption of conventional fossil fuels. Therefore, nodal agencies such as the Intergovernmental Panel on Climate Change (IPCC) are on alert and recommend alleviating the dependence on these resources. Scientists are also more vocal than ever about carbon dioxide sequestration to mitigate the augmented anthropogenic global warming [2]. Keeping this in view, many countries are stepping up to choose alternate energy resources such as green hydrogen, shale gas, and coal bed methane. Evidently, India, too, has commercialized its CBM resources and explored the CBM recovery potential of its coal

resources. At present, commercial production of coal bed methane in India has reached about 2% of the domestic natural gas production to fulfill the energy demand.

Indian coal deposits are diversified in terms of depth of occurrence [3,4]. The majority of coal deposits seated up to 600 m depth are mineable, whereas coal seams beyond that depth are uneconomical with current technologies [4]. Although numerous technologies are being used to benefitiate those deep-seated coal deposits, their economic viability is debatable. The coal gasification technique converts coal into syngas; however, it requires higher temperatures and pressure regimes that are deemed to be non-viable for commercialized use [5]. Moreover, other factors, such as controls on the gas supply and gas quality, solvent recyclability, solvent leakage into water bodies, and high catalyst cost preclude its economic execution [6]. In addition, the conversion of coal to synthetic fuel (liquefaction) is another aspect of coal beneficiation; its commercial production is parochial, mainly because it attracts higher costs in coal-to-oil processing. In fact, the efficiency and overall yield of these conversion techniques in the Indian coal scenario seem apocryphal due to the higher ash yield in these coals. However, these deep-seated coal beds can be subjected to CO<sub>2</sub> sequestration for enhanced CBM recovery [7].

The widespread occurrence of coal in the Indian subcontinent accounts for approximately a 13% share of the global coal reserves [8]. India holds the fifth position in terms of the largest coal reserves and is ranked second in total coal production [8]. However, the mining and extraction of coal invite several economic and environmental consequences. Therefore, it is imperative to explore alternative strategies to utilize the coal deposits with a safeguard for the environment. The reasonably large amount of coal deposits in India gives leverage for CBM recovery. India currently possesses 2600 billion cubic meters (BCM) of total CBM reserves, and CBM has been produced commercially since 2007 [1,9–12]. According to the Directorate General of Hydrocarbons [13], CBM resources in the Indian Coal Basin are identified as having an area of 26,000 km<sup>2</sup> and ~91.8 TCF (trillion cubic feet). CBM is reported to be present in this areal extent. Among other states, Jharkhand has the largest estimated CBM resource, at 25.5 TCF. The average CBM production in the financial year of 2020–2021 stood at 1.76 MMSCMD (million metric standard cubic meters per day) from 4 CBM blocks [13], while the annual production reached 642 MMSCM (million metric standard cubic meters). Further, cumulative CBM production up to 2024–2025 is estimated to reach 8 BCM (billion cubic meters). As per the recent study, CBM is being produced from only four blocks, namely, the Jharia block in Jharkhand by Oil and Natural Gas Corporation (ONGC), Raniganj East in West Bengal by Essar Oil Ltd., Raniganj South in West Bengal by Great Eastern Energy Corporation, and Sohagpur West in Madhya Pradesh by the Reliance Industries Limited (RIL) at the commercial scale [13].

Since the earliest discoveries of CBM, it has been held as a promising alternative energy source around the globe. Moreover, the depletion of conventional fossil fuel resources is pushing economies to adopt unconventional energy sources. Therefore, nations are now recognizing the importance of unconventional forms of energy, such as coal bed methane. As the world enters the golden age of gas, India, too, has stepped up to explore alternative energy sources. Therefore, this review comprehensively assesses. Therefore, this review comprehensively assesses CBM prospect of Indian coal resources. A brief background is illustrated on the originating pathways of the CBM and its storage in coal beds. Further, the influences of different coal properties on the CBM generation and storage mechanism are highlighted. The gas molecular ratio and evidence of a compound-specific stable isotope are additionally illustrated for the purpose of elucidating the origin and genetic types of CBM from its parent coal. This thorough review concludes with an overview of the potential of CBM in Indian coal basins and a note on microbially enhanced coal bed methane (ME-CBM) recovery.

## 2. Origin of Methane in Coal Beds

The origin of coal bed methane (CBM) can be distinguished broadly into (a) primary microbial (PM), (b) thermogenic (T), and (c) mixed sources [14–20]. Meanwhile, microbial

methane is present primarily in low-rank coals, while high-rank coals often comprise secondary late mature microbial gas [15,19–25]. Thermogenic gas can also be divided into early mature thermogenic gas (EMT) and late mature thermogenic gas (LMT) [22] based on its mode of origin. The origin of CBM can be evidenced by (a) the gas molecular ratio (methane/(ethane + propane):  $\text{CH}_4/(\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8)$ ); (b) the stable carbon and deuterium isotopes of methane ( $\delta^{13}\text{C}-\text{CH}_4$  and  $\delta\text{D}-\text{CH}_4$ ); (c) the stable carbon isotope of carbon dioxide ( $\delta^{13}\text{C}-\text{CO}_2$ ); (d) the stable deuterium and oxygen isotopes of coal seam water ( $\delta\text{D}-\text{H}_2\text{O}$  and  $\delta^{18}\text{O}-\text{H}_2\text{O}$ ); (e) the stable carbon isotopic discrimination factor ( $\alpha_{\text{CO}_2-\text{CH}_4}$ ); and (f) the carbon isotopic difference between  $\text{CO}_2$  and  $\text{CH}_4$  ( $\Delta^{13}\text{C}_{\text{CO}_2-\text{H}_4}$ ), [15–17,20,22,24,26–29].

### 3. Coal Make-Up Controls the Storage of Methane in Coal Beds

Methane generated from the microbial diagenesis and/or thermogenic degradation of organic components is accommodated as (a) sorbed gas on macerals and mineral surfaces; (b) free gas in pores and fractures; and (c) dissolved gas in bitumen, water, and kerogen. In unconventional reservoirs, pores can be classified into four types, i.e., (a) ultra-micropores (<0.8 nm), (b) micropores (<2 nm), (c) mesopores (2–50 nm), and (d) macropores (>50 nm) [30,31], and these types are present in variable abundances in coal beds. The various sorption mechanism is a function of the pore size distribution in coal. Ultra-micropores and micropores, primarily, get saturated with methane to their full extent in coal beds [30,32,33]. On the other hand, in the mesopores and macropores, only surface wall adsorption, which acts as a methane transport conduit in coal, dominates [30,34]. The types and abundances of macerals and mineral matter; the degree of organic metamorphism; thermal alternations, etc., control the adsorption of the gas on the micropores [35–38]. The pore size distribution and the surface area of pores directly influence the CBM sorption mechanism [30,34]. The ratio of free gas to adsorbed gas alleviates with the decrease in the pore size [39]. Chalmers et al. [40] suggested that interconnection among the pores and fractures governs the matrix permeability of methane. Methane is transported through diffusion in the micropores [41], while in the nanopore networks, the methane flow is controlled by pore wall–molecule interactions, molecule–molecule interactions, and diffusion [38,42]. The maceral content and total organic carbon (TOC) content in coals also influence the adsorption of methane on micropores [10,43–45]. With the advent of coal rank, hydrocarbon production from the thermal degradation of organic matter forms the organic intraparticle pores [35,46]. The formation of these intraparticle micropores enhances the gas adsorption capacity of the high-rank coals [35]. The maceral abundances also have profound influences on CBM generation and adsorption. The vitrinite macerals comprise more micropores than the inertinite; hence, they are suitable sites for CBM adsorption. Additionally, large concentrations of lignocellulosic vitrinite grains may lead to a higher amount of methane generation through the demethylation of functional groups. Additionally, a large number of macropores can be observed at the low volatile bituminous rank, although they decrease with the increase in micropores with thermal maturation [38]. In high-rank coals, thermal cracking of kerogen produces methane and unplugs the pores that can adsorb the generated methane, which leads to higher gas content in these high-rank coals compared to the low-rank [47].

Further, in an attempt to derive the gas diffusion equations in coal, Gawor et al. [48] introduced the term “accumulation kinetics” to understand the temporal kinetics of the gas molecule transportation in sorption processes. They suggested that the amount of gas sorption and, consequently, the gas transport in coal depends on the pore size distribution. According to them, the gas transfer phenomenon within the porous matrix of coal takes place as a seepage process occurring within the mesopores and macropores. This occurs due to the pressure gradient and diffusion process prevailing in the ultra-micropores and micropores because of the concentration gradient [49]. However, they emphasized that diffusion is the predominant transport process within coals, owing to their ultra-microporous characteristics, as coal contains a dominant pore distribution of <1 nm, leading to abundant empty spaces [30]. Additionally, Norbert et al. [50], in the study

of coal sorption analyses around gas outburst zones, upheld the idea that the diffusion process is the dominant factor in the coal gas transport mechanism. Moreover, in methane emission studies, Wierzbicki et al. [51] asserted that the diffusion model is the governing aspect of methane emission from coal. In a nutshell, the diffusion process is a crucial gas transport mechanism in the porous matrix of coal, especially that of micropores, among other discussed transport means.

Further, the coal rank has promising effects on CBM storage. Lignite is a heterogeneous mixture of plant remains with abundant moisture and volatile contents. These large amounts of moisture and volatile contents remain sorbed in the pore spaces. However, as rank increases, the lignites undergo dehydration due to overburdening pressure and a geothermal gradient, resulting in a loss of moisture and, to some extent, the volatile contents from the porous structure of the coal. At this stage, primary microbial methane is accommodated in those pores. Furthermore, increasing the rank toward the subbituminous stage elevates the storage capacity for secondary biogenic methane.

#### 4. Methanogenesis

##### 4.1. Microbial Methanogenesis: An Overview

Microbial methanogenesis is the ultimate phase of organic matter biodegradation, which yields methane and carbon dioxide [18]. The microbial decomposition of organic matter involves geopolymer conversion to low-molecular-weight hydrocarbons ( $C_{LMW}$ ) within the coal beds. Microbially mediated transformations of the  $C_{LMW}$  compounds yield methane precursors, i.e., methanol, formate,  $H_2$ , acetate, carbon monoxide, etc. [25,52]. The obligate anaerobes, such as methanogenic archaea, facilitate the final stage of biodegradation and yield methane. Carbon dioxide is a subsidiary product of microbial methanogenesis that is required by the electron balance of the  $C_{LMW}$  compounds [18,22]. The methane precursor compounds donate an electron to the methanogenic archaea in a syntrophic association in the final stage of biodegradation. However, direct electron transfer from microbes to methanogens may also occur without requiring the intermediary  $H_2$  precursor [53,54]. Methanogens, including *Methanospirillum*, *Methanococcus*, and *Methanobacterium*, can utilize the  $H_2$  and  $CO_2$  precursors, whereas only *Methanosaeta* and *Methanosarcina* archaea can utilize the acetate. *Methanosarcina* utilizes either acetate or  $CO_2 + H_2$  [52]. Assessments based on the DNA of the microbial communities suggest that their archaeal diversity is less than that of the bacteria in unconventional reservoirs [32,55,56]. Proteobacteria, Bacteroidetes, Firmicutes, and Actinobacteria are abundant in coal beds [56–60], and are capable of metabolizing and decomposing kerogen and hydrocarbons. Meanwhile, *Methanobacteriales*, *Methanomicrobiales*, and *Methanosarcinales* reflect the archaeal diversity in CBM basins [61,62].

##### 4.2. Pathways of Primary Microbial Methanogenesis

Methanogenic archaea proliferate in oxygen-poor anoxic redox conditions. In addition, thermogenic constraints influence microbial methanogenesis. Competitive substrates, such as formate, acetate, and  $H_2$  [20], are scavenged by heterotrophic microbes that intercede in the iron, nitrate, and sulfate reduction pathways. These non-methanogenic pathways produce more free energy per mole of the substrate than the methanogenic route [18]. Microbial methanogenesis takes place primarily through two ways in water free of alternative electron acceptors (such as sulfate): (a) the hydrogenotrophic or  $CO_2$ -reduction pathway (Equation (1)), which involves  $H_2$  as an electron donor and  $CO_2$  as an electron acceptor; and (b) acetate fermentation, or the acetoclastic route (Equation (2)), which is characterized by the reduction of a methyl group to methane and the oxidation of a carboxylic group to carbon dioxide [15,18,29,52,63].



The hydrogenotrophic and acetoclastic methanogenesis involve terminal enzymatic activities, and these pathways engage the methyl-coenzyme M reductase. Meanwhile, during hydrogenotrophic methanogenesis, primary activation and transfer of the C1 unit from the substrate uses the methanofuran coenzyme [52]. Further, in the acetoclastic pathway, methane production from acetate is activated by acetyl-coenzyme A. Subsequent enzymatic procedures form methyl-coenzyme M, which is further reduced to methane. The presence of transition metals, such as cobalt and nickel, also influences the enzymatic activities during methanogenesis [64,65]. These two transition metals are present as trace elements in coal beds, and, thus, may have a considerable effect on CBM production. Both of these methanogenic pathways are exogenic and yield free energy, and the gain in free energy is used to synthesize adenosine triphosphate (ATP). Oremland et al. [66] reported that the free energy yield during hydrogenotrophic methanogenesis ( $-135 \text{ kJ mol}^{-1}$ ) is much higher compared to acetoclastic methanogenesis ( $-31 \text{ kJ mol}^{-1}$ ). This free energy gain during hydrogenotrophic methanogenesis is sufficient to synthesize at least one molecule of ATP. The terminal enzymatic activities involving the methyl-coenzyme M reductase help to conserve energy. These enzymatic activities are crucial for preserving the methanogenic society, and also favor energetically efficient metabolisms in energetically inadequate environments [52].

Methanogenesis using methylamines and methanol by *Methanobolus* has also been reported in addition to the acetoclastic and hydrogenotrophic pathways. Demethoxylation produces ranges of methylated compounds, which can be utilized as non-competitive substrates [25,55,67,68]. Meanwhile, in the presence of microbially-reducible iron oxides or sulfates, methylated substrates are used by methylotrophs when bacteria surpass the methanogens in utilizing the competitive substrates. Sulfate abundance may adversely affect methanogenesis by restricting the methanogens from utilizing the competitive substrates. In the presence of sulfur, sulfate-reducing microbes efficiently scavenge the acetate, making hydrogenotrophic methanogenesis the dominant pathway in marine sediments. On the other hand, acetoclastic methanogenesis is dominant in freshwater sediments that lack sulfur [20,29,52,69]. A lack of sulfate-reducing microbes promotes the formation of short-chain-length volatile fatty acids and acetate, which offer a proper substrate for acetoclastic methanogenesis in a freshwater environment [19,20]. In addition, the methylotrophic pathway is also considered to be dominant in marine sediment due to the abundance of sulfate in seawater [70,71]. Furthermore, salinity and temperature control the growth, proliferation, and extent of biodegradation of organic matter. Methanogenic activities are hindered at temperatures  $> \sim 80^\circ\text{C}$  [72]. Further, freshwater recharge can induce methanogenesis in coal beds [23,73–75]. Salinity may also influence the archaea, as the energy needed to remove salts from bacterial cells alleviates the methanogenic potential [18]. Hydrogenotrophic methanogenesis can tolerate higher salinity, while acetate precursor is scavenged at lower salinity conditions by methanogens [76,77]. Meanwhile, methylotrophic methanogenesis that utilizes a methylated substrate persists at a greater level of salinity than acetoclastic and even hydrogenotrophic methanogenesis [78]. Moreover, it is also observed that hydrogenotrophic methanogenesis tolerates more salt compared to the acetoclastic pathway at low temperatures ( $\leq 30^\circ\text{C}$ ), while at  $60^\circ\text{C}$ , both methanogenic routes become less tolerant to salt [72].

#### 4.3. Secondary Microbial Methanogenesis

Secondary microbial gases may occur in the medium- to high-rank coals and may alter the primary thermogenic methane isotopic fingerprints if mixing occurs [15,24]. The secondary microbial methanogenesis may occur either by the hydrogenotrophic or acetoclastic pathway. Weathering of coal seams, atmospheric exposure, and mixing between meteoric water and coal bed formation water may introduce microbes into the coal beds, which metabolize residual kerogen and have previously produced wet gases to generate methane. In hydrogen-rich coals or petroliferous coal reservoirs, the biodegradation of liquid hydrocarbons may also generate secondary microbial gases. The carbon dioxide



formed along with these gases shows  $^{13}\text{C}$  enrichment and is, thus, isotopically heavier than primary microbial gases [79]. Low-rank coals often possess higher gas content than high-rank coals, which may further indicate a plausible influence of secondary microbial methanogenesis. The microbial communities introduced into coal beds through the aforementioned pathways may utilize the hydrocarbons and residual labile kerogen to yield methane. If this secondary microbial methane is present in considerable abundance, it may re-saturate the coal to adsorption isotherm [80]. The stable isotopic differences between the primary and secondary microbial methane (discussed in the following sections) were documented by Milkov and Etiope [81] in their proposed gas genetic diagrams.

## 5. Thermogenic Methanogenesis

Thermogenic methanogenesis involves the thermal breakdown of kerogen during coalification, which yields variable abundances of methane, ethane, propane, butane, pentane, isobutane, isopentane, and carbon dioxide based on the coal rank. Thermogenic gas is primarily divided into early mature thermogenic gas (EMT) and late mature thermogenic gas (LMT). These two types of gases can be distinguished using the gas molecular ratio,  $\delta^{13}\text{C}-\text{CH}_4$ ,  $\delta\text{D}-\text{CH}_4$ , and  $\delta^{13}\text{C}-\text{CO}_2$  compositions [81].

### 5.1. Early Mature Thermogenic Gas (EMT)

Early mature thermogenic gases are formed from the hydrogen-rich macerals in lignite to a high volatile bituminous C rank [14,16,22]. The hydrogen-rich macerals, such as liptinites and perhydrous vitrinites/huminites, often crack at the early stages of coalification due to their high reactivity and lower thermal susceptibility, and produce substantial concentrations of wet gases, such as ethane, propane, etc. [22,80]. Decarboxylation and dehydration reactions associated with the cleavage of the heteroatomic bonds produce large amounts of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

### 5.2. Late Mature Thermogenic Gas (LMT)

Late mature thermogenic gases (LMT) are produced from medium- to high-rank coals at elevated temperatures through the thermal degradation of kerogen. With the advent of coal rank, the organic carbon becomes more aromatic in the residual organic matter with the expulsion of low-molecular-weight hydrocarbons, such as methane, ethane, etc., along with carbon dioxide and water [82]. Progressive coalification leads to the disproportionation of the organic hydrogen pool due to the liberation of hydrogen-enriched liquid and gaseous hydrocarbons during their peak expulsion phases. Consequently, aromatization and aromatic ring condensation occur in the residual organic matter. The peak phase of wet gas generation coincides with the boundary between bituminous C and bituminous B ranks (mean random vitrinite reflectance ( $\bar{R}_r$ ) = ~1.1%; Gao et al. [14]). The wet gas generation is drastically alleviated at  $\bar{R}_r > \sim 1.2\%$ , with a concomitant increase in methane generation (dry gas). At this rank, the residual aliphatic functionalities and previously produced hydrocarbons with greater than two carbon atoms ( $\text{C}_{2+}$ ) thermally crack to produce  $\text{CH}_4$ . The production of  $\text{CH}_4$  continues within the effective dry gas window up to  $\bar{R}_r = \sim 1.8\%$  (bituminous A rank), but terminates at  $\bar{R}_r = \sim 3.0\%$  (dry gas floor; anthracite C–B rank) when thermo-polycondensation leads to an inert coal microstructure. The theoretical amounts of methane generation were estimated based on coal rank and composition. Berner and Faber [83] theoretically quantified the methane generation from coals using Equation (3):

$$\text{CH}_4 = 9.1 \ln \bar{R}_r + 93.1 \quad (3)$$

At  $\bar{R}_r > 0.7\%$  (bituminous C rank), large amounts of methane are produced from coalified organic matter, and the threshold of peak thermogenic methane generation coincides with the boundary between the bituminous C and bituminous B ranks ( $\bar{R}_r = \sim 1.0\%$ ) [84]. The LMT gas originating at  $\bar{R}_r > 1.2\%$  is drier and contains lower quantities of  $\text{CO}_2$  than the EMT gas, as wet gases are prone to forming methane through thermal degradation [14].

Thermogenic methane production and its storage in coal beds depend on the coal rank, distribution, basin tectonics, structural geometry, depth of the coal beds, permeability, intergranular porosity, maceral distributions, gas content, hydrology, and hydrodynamics [85–87]. The thickness of coal beds and their geological extent are related to depositional and structural settings, and substantially influence the methane distribution routes [86,88]. Furthermore, thermal stress from geothermal gradients and intrusive igneous bodies also affects CBM production and storage [89,90]. Although the deep burial of coal beds is ideal for the thermogenic cracking of kerogen, the unusual and high amplitude of heat flow induced by the contact metamorphism of coal seams may also generate methane at shallower depths [14,91]. Additionally, erosion of the overlying lithology and/or basin upliftment may lead to migration and subsequent gas loss from coal beds, affecting the bulk gas content. CBM production also depends on the capability of methane to be transported along cleats and other fractures of coal beds to the collection site. The in situ stress directions in a productive basin strongly affect CBM exploration [85,88]. The abundance of open cleats and fractures governs methane's permeability in coal beds to the production well. High permeability eases the transport of desorbed CBM, while extremely high permeability leads to augmented water production [14]. Furthermore, the gas content in coal beds varies widely in different basins, and depends on reservoir's characteristics and the basin's hydrogeological properties. Gas generated in coal beds is trapped primarily by the hydrostatic pressure of formation water, which is pumped out from coal beds to alleviate the water pressure and consequent desorption of methane. It also causes the expansion of the free gas phase and builds a pressure gradient that triggers the flow of free gas to the production well [14]. Hence, the hydrogeological properties of coal beds have a profound effect on CBM storage and exploration.

## 6. Geochemical Proxies for CBM Investigations

### 6.1. Gas Molecular Ratio

The gases produced from coal beds usually comprise variable abundances of methane, ethane, propane, and other components, such as carbon dioxide and nitrogen, depending on the coal rank and other geological conditions. The composition of the CBM can be inferred through the gas molecular ratio, which is determined by the ratio of methane ( $C_1$ ) concentrations to the summed abundances of ethane ( $C_2$ ) and propane ( $C_3$ ) ( $C_1/(C_2 + C_3)$ ). Often, gas dryness is estimated using the ratio of methane to the summation of methane to pentane abundances ( $C_1/(C_1 + C_2 + C_3 + C_4 + C_5)$ ). Hence, dry gas shows ( $C_1/(C_1 + C_2 + C_3 + C_4 + C_5) > 97\%–98\%$  [82], while ( $C_1/(C_2 + C_3) > 50\%$  [26,92]. Meanwhile, the gas wetness is estimated by the ratio of the summed concentrations of ethane to propane to the summation of methane to propane ( $(C_2 + C_3)/(C_1 + C_2 + C_3 + C_4 + C_5)$ ) [93]. Moreover, the gas molecular ratio ( $C_1/(C_2 + C_3)$ ) is often integrated with the  $\delta^{13}\text{C}-\text{CH}_4$  values to determine the gas dryness and distinguish between microbial and thermogenic gases [25,94,95]. A ( $C_1/(C_2 + C_3) < 100$ ) indicates thermogenic wet gas, while ( $C_1/(C_2 + C_3) > 1000$ ) signifies dry microbial gas [15,19,23–25,94–99]. Often, mixing between microbial and thermogenic gases may result in intermediate values of this ratio [22]. The gas genetic diagram constructed with the gas molecular ratio and  $\delta^{13}\text{C}-\text{CH}_4$  [81] may discriminate the origin of the methane. This diagram suggests that the acetoclastic and hydrogenotrophic primary microbial pathways and the secondary microbial methanogenesis yield dry gas irrespective of different carbon isotopic signatures. Further, LMT gas is drier than the EMT variety produced by the early breakdown of hydrogen-rich macerals in coals. The gas molecular ratio varies vertically and laterally in coal basins. This ratio is often observed to lessen with the depth of the coal basin, as thermogenic wet gas is generated at a greater depth [86]. In addition, in shallower coal beds, secondary microbial methanogenesis induced by meteoric recharge may alter the primary gas molecular ratio [15].

Wet gas production occurs through kerogen decomposition and/or solid/liquid bitumen degradation at the peak wet gas window, following catagenesis. While, in general, the gas generation almost ceases around  $\bar{R}_r = 3.0\%$  (anthracite C–B rank), humic coals may pos-

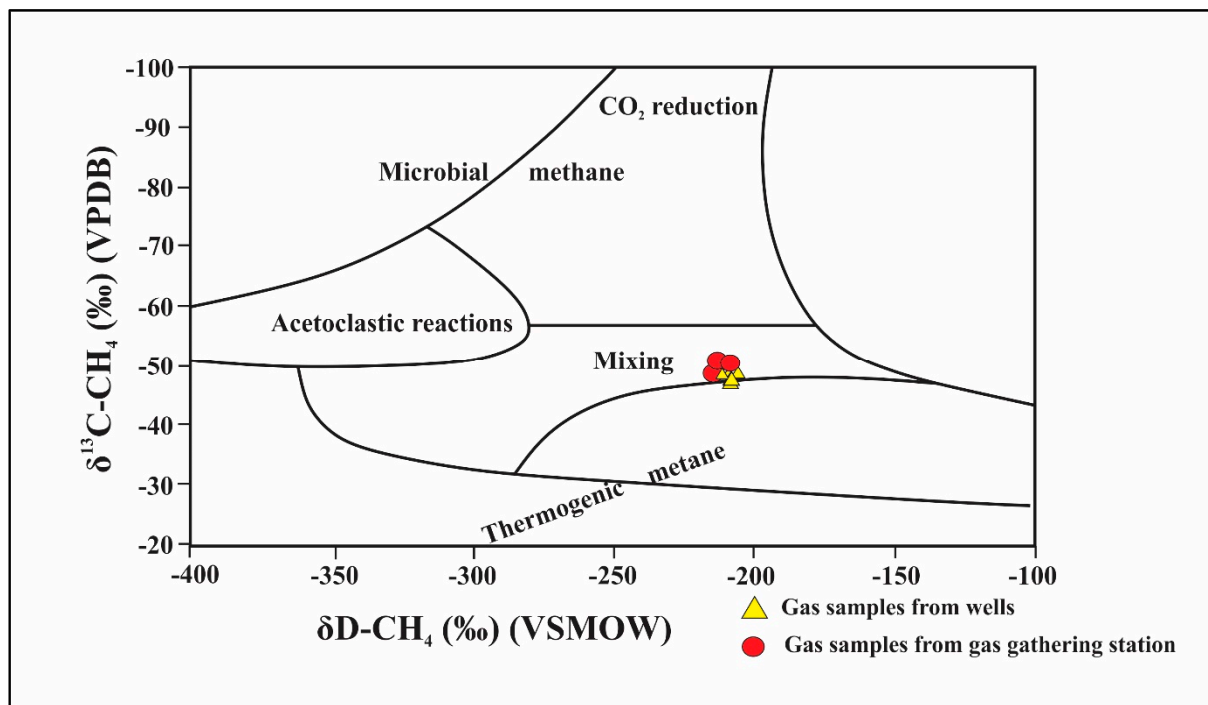
sess ~18% residual methane generation potential at  $\bar{R}_r > 6.0\%$  (meta-anthracite) [100]. The microbial pathways produce dry gas with occasional trace amounts of ethane-dominated wet gas [66,101,102] at low temperatures ( $<80\text{ }^{\circ}\text{C}$ ) [103]. Meanwhile, the thermogenic wet gas signature overprints the microbial wet gas fingerprints. Wet gas generation is controlled by organic matter sources, thermal maturity [82], biodegradation [103,104], fractionation during migration [105,106], and adsorption/desorption properties [86,107]. Thermogenic CBM generally comprises 20% wet gas, which may occasionally rise up to 70% [86]. In coal beds, wet gas is generated at intermediate maturity, while dry gas is produced at low and high ranks. In addition, the coal composition affects the gas wetness. Coals comprising hydrogen-rich macerals produce wet gas over a broader maturity range than coals consisting of lignocellulosic type III kerogen [15,86]. The peak thermogenic wet gas generation at high coal ranks may be related to the liquid hydrocarbon retention and transition from oil to wet gas cracking [15].

## 6.2. Stable Carbon Isotopic Fingerprints of Methane

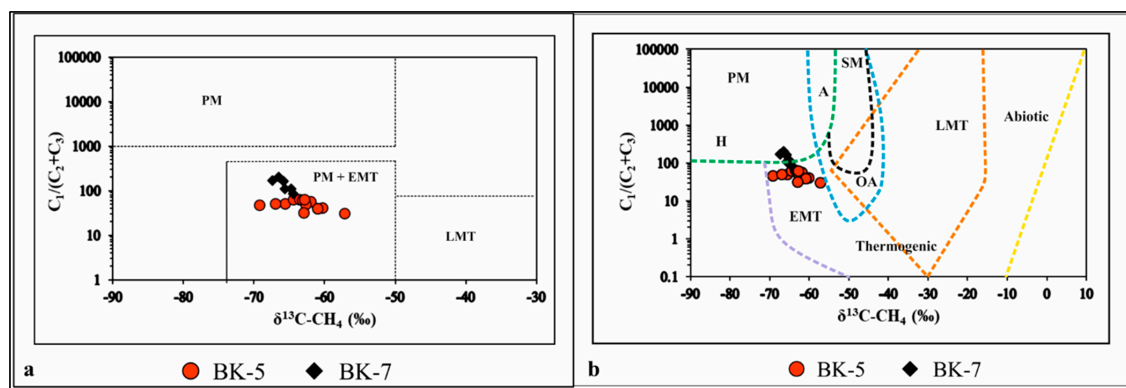
The stable carbon isotopic composition of methane ( $\delta^{13}\text{C}\text{-CH}_4$ ) is a widely used proxy to determine the origin of CBM. The formation of methane from source coals is a classic example of a kinetic isotopic fraction, where the  $^{12}\text{C}$ -rich, isotopically lighter substrates are utilized at a higher rate than the  $^{13}\text{C}$ -rich, isotopically heavier varieties, leading to much lighter isotopic compositions of the generated methane [27,29,108,109]. Thermogenic gas possesses  $\delta^{13}\text{C}\text{-CH}_4$  values lower than  $-50\text{‰}$ , while hydrogenotrophic methanogenesis has  $\delta^{13}\text{C}\text{-CH}_4$  values lighter than  $60\text{‰}$  and the acetoclastic pathway is characterized by  $\delta^{13}\text{C}\text{-CH}_4 < -50\text{‰}$  [15,19,25,29,110,111]. Furthermore, a gas molecular ratio  $< 100$  with  $\delta^{13}\text{C}\text{-CH}_4$  values  $> -50\text{‰}$  marks the thermogenic wet gas, while  $((\text{C}_1/(\text{C}_2 + \text{C}_3)) > 1000$  with  $\delta^{13}\text{C}\text{-CH}_4$  values  $< -50\text{‰}$  indicates microbial methanogenesis that primarily produces dry gas. However, the boundary of the thermogenic gas field may often vary depending on the influence of the coal rank on the carbon isotopic and gas molecular compositions [19,74,99].

Meanwhile, intermediate  $\delta^{13}\text{C}\text{-CH}_4$  values ranging from  $-50$  to  $-60\text{‰}$  may imply solid/liquid bitumen cracking, water stripping, mixing between primary thermogenic gas and secondary microbial methane, as well as mixing of EMT gas and primary microbial methane [19,22–24,98,112–115]. Often, progressive substrate depletion in a partially closed system (often linked to the groundwater residence time) may alter the primary microbial methane signature and unequivocally depict thermogenic gas characteristics [116]. Ghosh et al. [24] found that post-mature secondary microbial methane had altered the isotopic signatures of primary thermogenic gas, resulting in intermediate isotopic signatures of the bituminous coal beds in the Raniganj Basin, India (Figure 1). Further, Dutta et al. [22] modified Bernard's plot by introducing a new field that accommodated the geochemical signatures of methane originating from the primary microbial pathway and early mature degradation of perhydrous organic matter in Eocene lignites (Figure 2a). They observed that hydrogenotrophic methanogenesis yielded the primary microbial methane, which was mixed with EMT gas showing intermediate  $\delta^{13}\text{C}\text{-CH}_4$  signatures between  $-57.20$  and  $-69.30\text{‰}$  (Figure 2b). Moreover, mixing trends between microbial and thermogenic gases, as well as the integrated influence of methanogenic routes and coal rank on the carbon isotopic and molecular compositions of CBM, was modeled by Strapoc et al. [25]. The mixing lines in those models mark the relative concentrations of microbial and thermogenic methane. Dutta et al. [22] also utilized this model to assess the extent of mixing between the primary microbial and EMT gases (Figure 3).

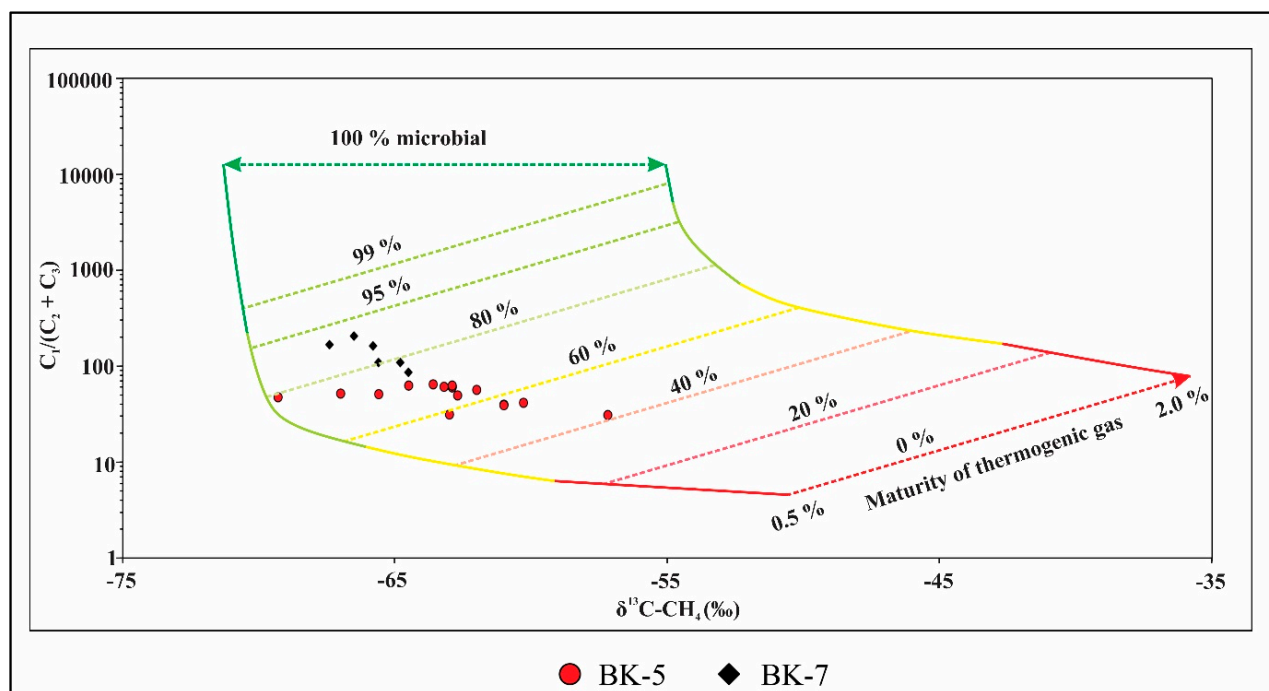




**Figure 1.** Whiticar-style plot constructed using the stable deuterium and carbon isotopic compositions of methane, showing mixing between primary thermogenic gas and secondary microbial gas (after Ghosh et al. [24]; reuse of this figure is permitted by Elsevier and Copyright Clearance Center; license number: 5472060707164; dated 18 January 2023). **Explanations:**  $\delta^{13}\text{C}-\text{CH}_4$  = stable carbon isotopic composition of methane; VPBD = Vienna Pee dee Belemnite;  $\delta\text{D}-\text{CH}_4$  = stable deuterium isotopic fingerprint of methane; VSMOW = Vienna Standard Mean Ocean Water.



**Figure 2.** (a) Mixing between primary microbial and early mature thermogenic gases led to the introduction of a new field (PM + EMT) in Bernard's plot and (b) more detailed evidence of mingling between methane generated through hydrogenotrophic methanogenesis and early mature thermogenic breakdown of perhydrous organic matter in Eocene lignites from India (after Dutta et al. [22]; reuse of this figure is permitted by Elsevier and Copyright Clearance Center; license number: 5472060428554; dated 18 January 2023). **Explanations:** BK-5 and BK-7 are the lignite wells in the Eocene Tharad Formation of the Sanchor Sub-Basin, Gujarat, India; PM = primary microbial gas, EMT = early mature thermogenic gas; LMT = late mature thermogenic gas, H = hydrogenotrophic methanogenesis, A = acetoclastic methanogenesis; SM = secondary microbial gas, OA = oil-associated gas;  $C_1/(C_2 + C_3)$  = ratio of methane ( $C_1$ ) concentrations to the summed abundances of ethane ( $C_2$ ) and propane ( $C_3$ );  $\delta^{13}\text{C}-\text{CH}_4$  = stable carbon isotopic composition of methane.



**Figure 3.** Mixing between microbial and thermogenic gases in Strapoč's model [25], evidenced in the Eocene lignites of India (after Dutta et al. [22]; reuse of this figure is permitted by Elsevier and Copyright Clearance Center; license number: 5472060428554; dated 18 January 2023). **Explanations:** BK-5 and BK-7 are the lignite wells in the Eocene Tharad Formation of the Sanchor Sub-Basin, Gujarat, India;  $C_1/(C_2 + C_3)$  = ratio of methane ( $C_1$ ) concentrations to the summed abundances of ethane ( $C_2$ ) and propane ( $C_3$ );  $\delta^{13}\text{C}-\text{CH}_4$  = stable carbon isotopic composition of methane.

### 6.3. Stable Deuterium Isotopic Composition of Methane

The deuterium isotopic fingerprint of CBM ( $\delta\text{D}-\text{CH}_4$ ) is estimated from the deuterium isotope of coexisting coal bed formation water and methanogenic pathways [15,29,111]. The  $\delta\text{D}-\text{CH}_4$  collaborated with the  $\delta^{13}\text{C}-\text{CH}_4$  values in the Whiticar-style plot to discriminate between the CBM sources. In general, hydrogenotrophic methanogenesis is associated with heavier  $\delta\text{D}-\text{CH}_4$  and lighter  $\delta^{13}\text{C}-\text{CH}_4$  values than acetoclastic methanogenesis [29]. On the other hand, thermogenic methane shows a broader range of  $\delta\text{D}-\text{CH}_4$  values. This Whiticar-style plot (Figure 1) also reflects any mixing between the thermogenic and microbial gases [15,24]. Methanogens acquire a particular fraction of hydrogen from water to produce methane. During hydrogenotrophic methanogenesis, all the hydrogen is scavenged from the coexisting coal bed formation water, while a fraction of hydrogen is derived from the water during acetoclastic methanogenesis. Further, [117] opined that the  $\delta\text{D}-\text{CH}_4$  is controlled by the enzyme-mediated incorporation of hydrogen from water, but not by the precursor hydrogen present in the methyl group. This enzymatic process is active in both hydrogenotrophic and acetoclastic methanogenesis. The relation between the deuterium isotopic signatures of methane and coexisting coal bed formation water ( $\delta\text{D}-\text{CH}_4$  and  $\delta\text{D}-\text{H}_2\text{O}$ ) can be established using the following equation:

$$\delta\text{D}-\text{CH}_4 = m \times (\delta\text{D}-\text{H}_2\text{O}) - \beta \quad (4)$$

The value of  $m$  is 0.25 for methylated substrate fermentation, and 1 for hydrogenotrophic methanogenesis. The  $\beta$  value depends on the abstraction and transfer of hydrogen. The deuterium isotopic fractionation during hydrogenotrophic methanogenesis shows consistency around 160‰ [15]; thus, the  $\delta\text{D}-\text{CH}_4$  parameter in this methanogenic pathway is related to the  $\delta\text{D}-\text{H}_2\text{O}$  by the following equation:

$$\delta\text{D}-\text{CH}_4 = (\delta\text{D}-\text{H}_2\text{O}) - 160\text{‰} \quad (5)$$

Thus, hydrogenotrophic methanogenesis, utilizing the coal bed formation water in intermediate latitudes with  $\delta D-H_2O$  ranging from  $-40$  to  $-80\text{‰}$ , will yield methane with  $\delta D-CH_4$  values of  $-200$  to  $-240\text{‰}$  ( $\pm 10\text{‰}$ ), whereas utilizing high-latitude water with  $\delta D-H_2O$  lighter than  $-80\text{‰}$  will generate methane with mixed isotopic signatures.

On the other hand,  $\beta$  has no specific value for acetoclastic methanogenesis, but is significantly greater than hydrogenotrophic methanogenesis [20]. Moreover, in fresh water, enzyme-interceded hydrogen exchange between water and the methyl group during acetoclastic methanogenesis may enhance the  $\delta D-CH_4$  values [118]. Hence, in a sulfate-depleted freshwater environment, the  $\delta D-CH_4$  and  $\delta D-H_2O$  parameters are related by the following equation [118]:

$$\delta D-CH_4 = 0.675 \times (\delta D-H_2O) - 284 (\pm 6)\text{‰} \quad (6)$$

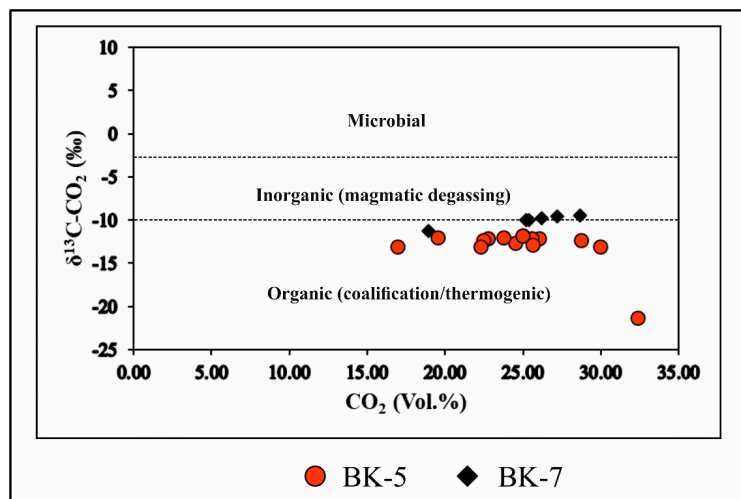
Hence, acetoclastic methanogenesis that utilizes coal bed formation water from intermediate latitudes with  $\delta D-H_2O$  ranging from  $-40$  to  $-80\text{‰}$  will produce methane with  $\delta D-CH_4$  values varying between  $-311$  and  $-351\text{‰}$ . On the other hand, utilizing high-latitude, isotopically lighter water generates methane with  $\delta D-CH_4$  values in the area of the bacterial fermentation field in the Whiticar-style plot. Thus, the Whiticar-style plot should be cautiously applied while determining the microbial CBM origin when high-latitude coal bed formation water is involved in the methanogenesis [15].

#### 6.4. Carbon Dioxide Content and Its Stable Carbon Isotopic Signatures

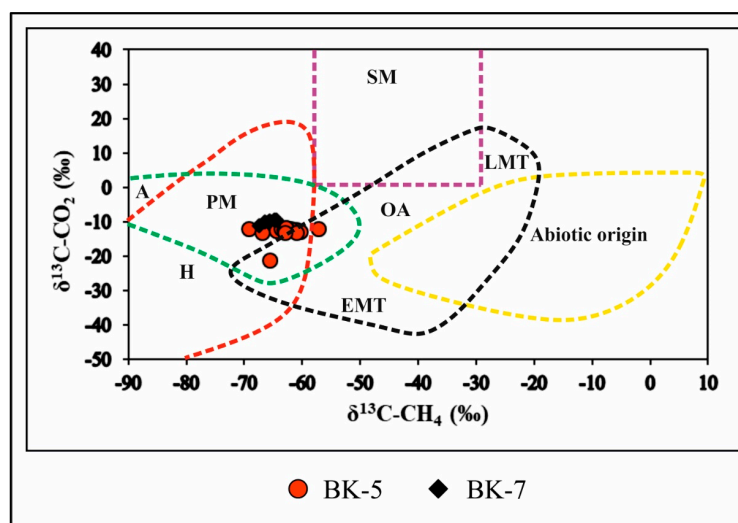
Carbon dioxide ( $CO_2$ ) has variable abundance in microbial and thermogenic gases. As it is an additional product of microbial methanogenesis,  $CO_2$  is associated with dry microbial gas. Carbon dioxide concentrations may reach  $>10$  vol.% when associated with dry gas production [80]. The bacterial communities that metabolize coal kerogen to produce methane both generate and consume  $CO_2$  [15], resulting in ambiguous abundances of  $CO_2$  in microbial gases. The  $CO_2$  in coal bed gases may derive from coalification, early mature thermogenic degradation of kerogen, thermal degradation of carbonates and organic substrates, magmatic degassing, or atmosphere [15,22,119]. The origin of  $CO_2$  in coal beds can be inferred from the correlation between its abundance and stable carbon isotopic ( $\delta^{13}C-CO_2$ ) compositions (Figure 4) [120]. Magmatic  $CO_2$  shows  $\delta^{13}C-CO_2$  ranging from  $-3$  to  $-10\text{‰}$ , with  $>10$  vol.% abundance in coal beds. Gases with  $<10$  vol.% of  $CO_2$  exhibit a wide range of  $\delta^{13}C-CO_2$  values. Thermogenic  $CO_2$  originating from organic matter's coalification shows an isotopically lighter signature, while methanogenesis produces isotopically heavier  $CO_2$  ( $>-3\text{‰}$ ). Additionally, a  $CO_2$  abundance level of  $<10$  vol.% with a  $\delta^{13}C-CO_2$  range between  $-3$  and  $-10\text{‰}$  may derive from gas mixing or microbial influence on thermogenic  $CO_2$ . Further, the primary magmatic origin of  $CO_2$  is often altered by  $CO_2$  derived from coalification and/or thermogenic sources [22]. Moreover,  $CO_2$  derived during coalification shows a  $\delta^{13}C-CO_2$  signature varying from  $-20$  to  $-10\text{‰}$  [15]. The type of kerogen also influences  $CO_2$  generation. The catagenesis and metagenesis of type III kerogen in humic coals produce substantial amounts of  $CO_2$ , while type I/II kerogen in sapropelic organic matter generates an insignificant amount of  $CO_2$  [92].

The cross-plot between the  $\delta^{13}C-CO_2$  and  $\delta^{13}C-CH_4$  can decipher the origin of CBM [22,81]. Hydrogenotrophic methanogenesis yields lighter  $\delta^{13}C-CO_2$  than the acetoclastic methanogenesis, while the secondary microbial gases exhibit positive  $\delta^{13}C-CO_2$  signatures heavier than the primary microbial methane. Further, EMT gases have a lighter  $\delta^{13}C-CO_2$  signal compared to LMT gases. This plot (Figure 5) can also be used to document the mixing between microbial and thermogenic gases [22,81]. The isotopic discrimination factor  $\alpha_{CO_2-CH_4} = (1000 + \delta^{13}C-CO_2)/(1000 + \delta^{13}C-CH_4)$ , following Whiticar et al. [29]), varies from 1.039 to 1.058 in the acetoclastic pathway and from 1.049 to 1.095 in hydrogenotrophic methanogenesis (Figure 6; Vinson et al. [18]). Methylo-trophic methanogenesis that utilizes dimethyl sulfide, methanol, and trimethylamine substantially influences substrate-to-methane fractionations compared to the acetoclastic pathway [27,109]. Therefore, the methylo-trophic pathway may overlap the  $\alpha_{CO_2-CH_4}$  values of the hydrogenotrophic

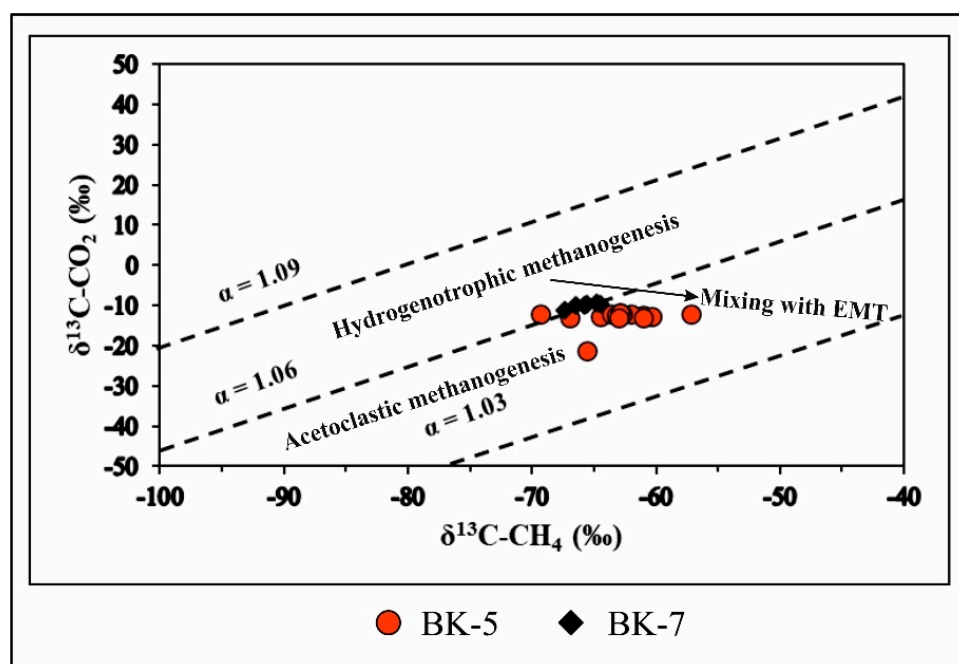
methanogenesis [109]. Often, mixing between microbial and thermogenic gases may yield  $\alpha_{\text{CO}_2\text{-CH}_4}$  values that overlap the signatures of both hydrogenotrophic and acetoclastic methanogenesis [22].



**Figure 4.** Abundance and stable carbon isotopic compositions of carbon dioxide, depicting its multiple sources (after Dutta et al. [22]; reuse of this figure is permitted by the Elsevier and Copyright Clearance Center; license number: 5472060428554; dated 18 January 2023). **Explanations:** BK-5 and BK-7 are the lignite wells in the Eocene Tharad Formation of the Sanchor Sub-Basin, Gujarat, India;  $\delta^{13}\text{C-CO}_2$  = stable carbon isotopic composition of carbon dioxide;  $\text{CO}_2$  = carbon dioxide.



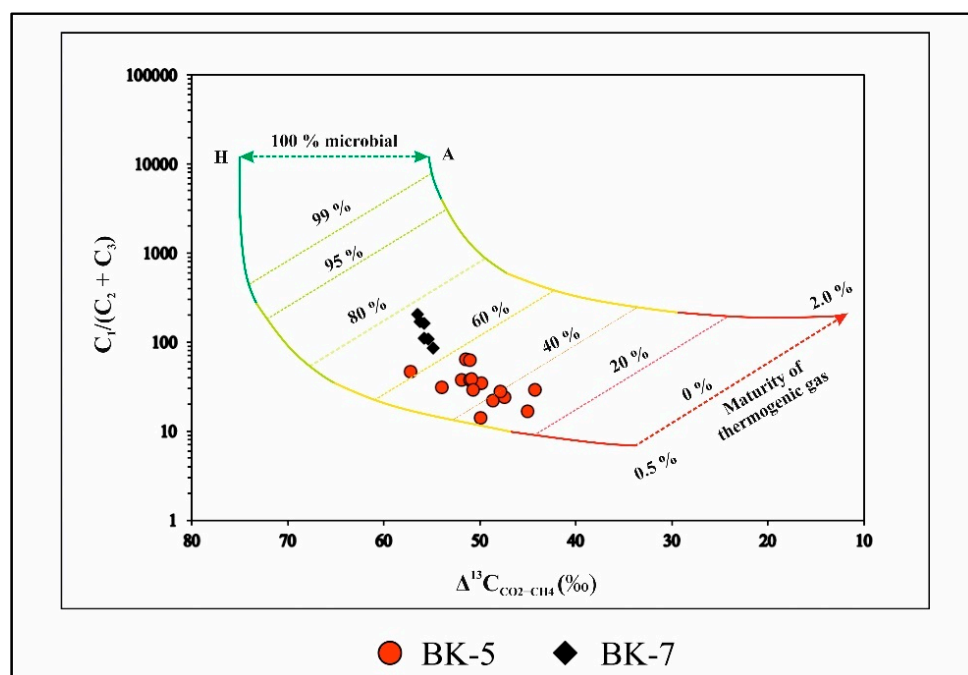
**Figure 5.** Mixing between primary microbial and EMT methane in Eocene lignite, evidenced by the stable carbon isotopic fingerprints of methane and carbon dioxide (after Dutta et al. [22]; reuse of this figure is permitted by Elsevier and Copyright Clearance Center; license number: 5472060428554; dated 18 January 2023). **Explanations:** BK-5 and BK-7 are the lignite wells in the Eocene Tharad Formation of the Sanchor Sub-Basin, Gujarat, India; PM = primary microbial gas, EMT = early mature thermogenic gas; LMT = late mature thermogenic gas, H = hydrogenotrophic methanogenesis, A = acetoclastic methanogenesis; SM = secondary microbial gas, OA = oil-associated gas;  $\delta^{13}\text{C-CO}_2$  = stable carbon isotopic composition of carbon dioxide;  $\delta^{13}\text{C-CH}_4$  = stable carbon isotopic composition of methane.



**Figure 6.** Mixing between primary microbial and EMT methane in Eocene lignite, evidenced by the carbon isotopic discriminant factor (after Dutta et al. [22]; reuse of this figure is permitted by Elsevier and Copyright Clearance Center; license number: 5472060428554; dated 18 January 2023). **Explanations:** BK-5 and BK-7 are the lignite wells in the Eocene Tharad Formation of the Sanchar Sub-Basin, Gujarat, India;  $\delta^{13}\text{C-CO}_2$  = stable carbon isotopic composition of carbon dioxide;  $\delta^{13}\text{C-CH}_4$  = stable carbon isotopic composition of methane.

In microbial methanogenesis, the covariance of the stable carbon isotopic compositions of  $\text{CO}_2$  and  $\text{CH}_4$  occurs when methanogens utilize the hydrogenotrophic pathway [15]. Further, methanogens and methanotrophs produce and metabolize  $\text{CO}_2$  and  $\text{CH}_4$  during microbial methanogenesis, and the methanogenic pathways control the stable carbon isotopic fractionation [20]. Therefore, the stable carbon isotopic compositions of carbon dioxide and methane ( $\Delta^{13}\text{C}_{\text{CO}_2-\text{CH}_4} = \delta^{13}\text{C}_{\text{CO}_2} - \delta^{13}\text{C}_{\text{CH}_4}$ ) can be used to distinguish between the microbial methanogenic pathways. The  $\Delta^{13}\text{C}_{\text{CO}_2-\text{CH}_4}$  values in hydrogenotrophic methanogenesis range from 49 to >100‰ (commonly 60‰–80‰) [20,29,121], while in the acetoclastic methanogenesis, this parameter varies from 40 to 55‰ [20]. However, this parameter is also influenced by the mixed origin of  $\text{CH}_4$  and  $\text{CO}_2$  and alterations to their primary signatures [22]. The cross-plot between the  $(\text{C}_1/(\text{C}_2 + \text{C}_3))$  and  $\Delta^{13}\text{C}_{\text{CO}_2-\text{CH}_4}$  modeled by Strapoc et al. [25] can also discriminate between microbial and thermogenic origins of CBM, as well as the microbial methanogenic pathways. Evidence of such mixing between the primary microbial gas originated through the hydrogenotrophic methanogenesis and the EMT degradation of labile organic matter has been demonstrated by Dutta et al. [22] in Eocene lignites (Figure 7).

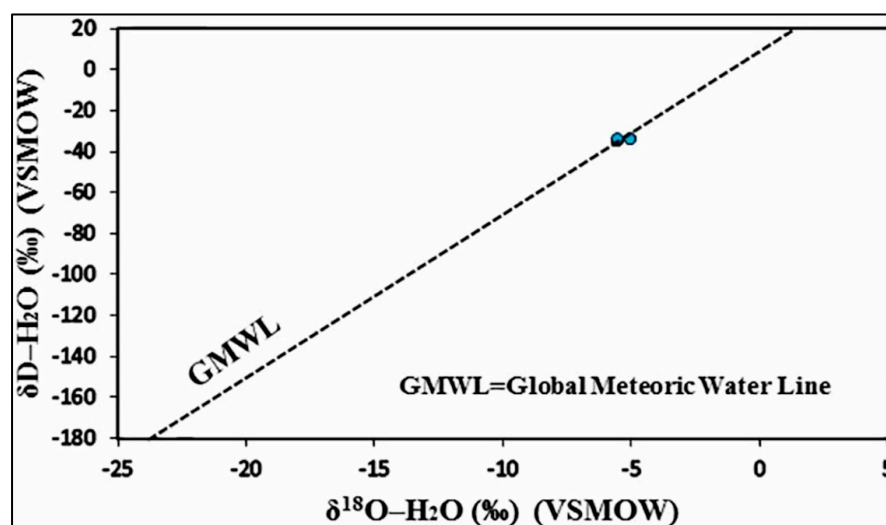




**Figure 7.** Mixing between microbial and thermogenic gases using the gas molecular ratio and carbon isotopic difference between carbon dioxide and methane which was evidenced in the Eocene lignites of India (after Dutta et al. [22]; reuse of this figure is permitted by Elsevier and Copyright Clearance Center; license number: 5472060428554; dated 18 January 2023). **Explanations:** BK-5 and BK-7 are the lignite wells in the Eocene Tharad Formation of the Sanchor Sub-Basin, Gujarat, India;  $(C_1/(C_2 + C_3))$  = ratio of methane ( $C_1$ ) concentrations to the summed abundances of ethane ( $C_2$ ) and propane ( $C_3$ );  $\Delta^{13}C_{CO_2-CH_4}$  = carbon isotopic difference between carbon dioxide and methane.

#### 6.5. Stable Hydrogen and Oxygen Isotopes of Coal Bed Formation Water

The stable deuterium and oxygen isotopes ( $\delta D-H_2O$  and  $\delta^{18}O-H_2O$ ) of the coal bed formation water or produced water from the CBM fields are equally important in characterizing the CBM origin in coal basins. The  $\delta D-H_2O$  and  $\delta^{18}O-H_2O$  values in the CBM fields usually lie to the right of the global meteoric water line (GMWL) [15]. Meanwhile, the stable isotopic compositions of the water produced from the highly productive CBM wells plot above or left of the GMWL [17,114]. Intercalation of meteoric water with brines or seawater, high-temperature fluid–rock interaction, evaporation, etc., shift the isotopic compositions of the coal bed formation water to plot on the right side of the GMWL. Contrastingly, coal bed formation water with  $\delta D-H_2O$  and  $\delta^{18}O-H_2O$  values to the left of the GMWL may result from low-temperature water–rock interactions; open-system  $CO_2$  exsolution from  $CO_2$ -enriched groundwater or spring water; or the utilization of water-derived hydrogen by the methanogens during microbial methanogenesis, leaving the residual water rich in deuterium [20,122,123]. Moreover, carbonate and clay precipitation in cleats and feldspars, as well as lithic alterations in interburden sandstones, may lead to the enrichment of deuterium in the residual fluid, which may affect the  $\delta D-H_2O$  and  $\delta^{18}O-H_2O$  parameters. Further, hydrogenotrophic methanogenesis may plot the coal bed formation water to the right of the GMWL. In this case, the methanogens utilize all the hydrogen from the groundwater, leading to the enrichment of deuterium in the residual water [114]. Often, mixing between the meteoric water and saline coal bed formation water may plot the coal bed formation water just above the GMWL. This mixing can often lead to secondary microbial methanogenesis that may alter the stable carbon and deuterium isotopes of methane (Figure 8) [24]. Moreover, lighter  $\delta D-H_2O$  and  $\delta^{18}O-H_2O$  values of the production water than the meteoric water often suggest older water that represents glacial paleoclimatic conditions [15].



**Figure 8.** Mixing between meteoric water and coal bed formation water in Permian bituminous coals from the Raniganj Basin, India, evidenced by the stable deuterium and oxygen isotopic compositions of the formation water samples (after Dutta et al. [22]; reuse of this figure is permitted by Elsevier and Copyright Clearance Center; license number: 5472060707164; dated 18 January 2023). **Explanations:**  $\delta\text{D-H}_2\text{O}$  = stable deuterium isotope composition of the coal bed formation water or produced water from the CBM;  $\delta^{18}\text{O-H}_2\text{O}$  = stable oxygen isotope composition of the coal bed formation water or produced water from the CBM; VSMOW = Vienna Standard Mean Ocean Water.

#### 6.6. Chemistry of Coexisting Coal Seam Formation Water

Coal beds are fractured aquifers confined by lithology, and have less permeability. CBM extraction requires the injection of a huge amount of water that lowers the pressure built up in coal beds and facilitates methane desorption. The water is mixed with the coal bed formation water and extracted from wells other than those used for CBM production. The production of formation water alleviates with the increase in methane production. The water produced from the CBM field is composed of a myriad of total dissolved solids, sodium, bicarbonate, and chloride ions, with minor abundances of magnesium and calcium and an ultra-trace amount of sulfate [15,114,124]. Bicarbonate ions are produced by the methyl fermentation pathway found in deep coal beds, and with the increase in the abundance of bicarbonate, magnesium and calcium ions precipitate from water. Furthermore, water produced in highly productive CBM fields with microbial or mixed origins of gas consists of a higher abundance of sodium and dissolved inorganic carbon, and possesses high alkalinity with subordinate concentrations of magnesium and calcium. On the other hand, water produced from thermogenic CBM fields possesses low concentrations of dissolved inorganic carbon and low alkalinity, with higher abundances of wet gas components [15]. Moreover, the sodicity or sodium abundances in the produced water can be calculated according to the sodium adsorption ratio (SAR) [114]:

$$\text{SAR} = \{[\text{Na}^+]/([\text{Ca}^{2+}] + [\text{Mg}^{2+}])/2\} \exp 0.5 \quad (7)$$

The sodicity of water has been observed to rise with the depth of coal beds, and low sodic water at the shallow subsurface may indicate a meteoric recharge [114]. Moreover, salinity and total dissolved solids in produced water exhibit lower abundances near the recharge zones, which elevates with increasing distance from these zones [15,114,125–127]. Additionally, the alkalinity of subsurface waters and the calcium/magnesium ratio aid in the reactions in carbonate dissolution and subsequent precipitation, as well as the degree of methanogenesis. The extent of microbial methanogenesis can be inferred from rising alkalinity with the stable carbon isotopic compositions of the dissolved inorganic

carbon [116,128]. Thus, in summary, alkalinity in produced water rises during microbial methanogenesis and declines in the case of thermogenic methane production.

## 7. A Note on the Age Controls of Methane Generation

Myriad natural processes are responsible for CBM generation. The decomposition of organic matter in an oxygen-poor environment is a vital methane generation mechanism. However, the methane generation rate is a function of various factors, including the age of organic detritus. Recent research has shown that the age of organic matter can significantly impact the methane generation rate. It is believed that the methane generation rate in older organic matter is comparatively slower than in its younger counterparts. OM exposed to sufficient geological time decomposes and breaks down the carbon bonds, leaving less carbon with which methanogens can produce methane. Younger coal, on the other hand, such as that from the Tertiary period, tends to have higher methane content than older coal, such as that from the Carboniferous period. This is because younger coals have not had as much time to lose their methane through the process of coalification. Additionally, younger coals are typically more rich in volatile matter and porous, which can facilitate the migration of CBM. Further, paleofloral evolution may influence the gas wetness in coal. Cenozoic and Mesozoic coal yields greater amounts of thermogenic wet gases than Paleozoic coal, possibly due to the abundance of perhydrous macerals in the former [86].

## 8. Petrographic Evidence

Macerals are inherent organic constituents of coal. The influence of macerals on CBM generation and storage in coals has been studied previously by various researchers [35,44,129–131]. The ligno-cellulosic organic matter of vitrinites plays a crucial role in CBM generation, whereas liptinites contribute to a lesser extent. The demethylation reaction of the methoxy groups present in ligno-cellulosic terrestrial organic matter is the principal mechanism for methane generation from humic coals. Although inertinite macerals are inert and their contribution to methane generation is minimal, these groups of macerals play a key role in methane storage. Therefore, the overall maceral composition has pronounced control of the sorption properties of coal. Studies have found that vitrinite-dominated coal has more adsorption potential compared to inertinite-rich coal of a similar rank [35–37,44,130–134]. Vitrinite macerals comprise more micropores than the inertinite; hence, they are suitable sites for CBM adsorption. Specifically, collotelinite is enriched in large volumes of micro- and mesopores, whereas collodetrinite contains lower meso- and micropore volumes. On the other hand, inertinite macerals are rich in mesopores [33]. The relationship between methane sorption capacity and the petrographic associations of different coal ranks was studied by Chalmers and Bustin [44]. Interestingly, they reported the highest sorption capacities in higher-rank coals. Their report additionally suggested insignificant sorption differences between the bright and dull bands of low-rank coals. On the contrary, the bright bands in high-rank coals portray maximum sorption potential compared to the dull bands. Further, the same authors examined methane sorption ability in liptinite-rich coals and reported reasonably higher sorption potential in liptinite-rich boghead coal types. They argued that the methane was held as a solution gas in liptinite-rich boghead coals. Furthermore, the methane sorption trend with reactive inertinites in their study revealed a positive correlation due to the dominance of microporosity in those reactive inertinite grains. Overall, their findings advocate that the different groups of macerals bear diverse methane sorption capabilities depending on their pore size distributions. Moreover, the gas diffusion rates also differ significantly within the coal matrix depending on the maceral composition and rank [135]. In low- to medium-rank coals, the gas diffusion rates in inertinites show a positive correlation. In contrast, the diffusion rates are subdued at higher ranks and become independent of coal ranks and composition. However, vitrinites are believed to play a positive role in the diffusion time of spreading gas in the coal matrix. Therefore, in low- to medium-rank coals, vitrinite and inertinite abundances have significant implications for gas penetration within the structure of the coal. Furthermore,

the gas diffusion rate plays an important role in regulating the production of CBM. As discussed, coal comprises different lithotypes of alternating bright- and dull-colored bands. These bands vary in their overall chemical and maceral compositions. Usually, bright bands contain a vitrinite group of macerals, whereas dull bands represent inertinite-rich substrates. The desorption in bright coal is mainly controlled by its distribution of micropores, while in dull coal, it is a function of a bi-dispersed pore system. As a consequence, these bands possess different gas retention capacities. The usefulness of these bands for storing gas was studied by Crosdale and Beamish [136] using applications of organic petrography. They suggested that the gas desorption potential of dull bands varies due to differential concentrations of inertinite sub-macerals. According to them, dull bands rich in fusinite and semifusinite desorb precipitously, whereas inertodetrinite-rich dull bands desorb at a relatively slower pace. Moreover, the vitrinite-rich, bright bands in their study were also found to desorb slowly. Additionally, Laxminarayana and Crosdale [37] studied the effect of maceral composition on gas diffusion rates in Australian coal. Their results also suggest that the inertinite-rich coals show a faster gas diffusion rate than vitrinite-rich coals. Moreover, they compared gas diffusion rates between the low and high-rank coals and suggested an inverse correlation of gas diffusion with increasing rank. The pore size distribution could explain the potential for faster gas diffusion of inertinite-rich coals. The inertinites are enriched in macropores compared to other macerals, resulting in increased gas diffusion [136–139]. This was further supported by the observation of Karacan [140], in which the author studied the sorption kinetic on coal lithotypes using X-ray CT. They found faster diffusion rates through the coal's inert region than in vitrinite-rich regions. Further, using infrared spectroscopy, the gas sorption properties of coal were studied by Mastalerz et al. [141]. Their reports also suggest that inertinite-rich coals diffuse gas much more easily than vitrinite-rich coals. Moreover, Staib et al. [142] also agreed with the higher gas diffusion capacity of inertinite-rich coals compared to vitrinite-rich coals.

## 9. A Global Overview of the Exploitation and Development of CBM

By far, the US-based CBM industry is at the most mature stage globally, with Australia and Canada lining up to match that level. The CBM industry was first developed in the USA, and it is progressing successively with time compared to other countries [143]. The Cenozoic coal-bearing horizons of the Rocky Mountains comprise ~84.2% of the CBM resources of the USA. At the same time, the remaining amount is stored between the Appalachian Mountains and Carboniferous coal-bearing basins in the central part of the country [144]. Fourteen coal basins have been targeted in the country for CBM development since the 1980s. The present recoverable CBM reserves in the USA add up to  $3 \times 10^{12} \text{ m}^3$ . Additionally, in 2009, the total explored CBM rose to  $542 \times 10^8 \text{ m}^3$  from  $2.83 \times 10^8 \text{ m}^3$  of gas explored in 1985 [145–147]. Preferable geological conditions, cutting-edge research and development, superior gas piping, advanced engineering network, the natural gas market, and constructive government policies have favored the rapid development of CBM industries in the USA. The Canadian CBM industry is also catching up with the trend. Commencing CBM exploration in 1987, it scaled up rapidly in 2002. A total of 7700 mines were reported to be producing  $60 \times 10^8 \text{ m}^3$  of CBM in 2009 from Canada. The CBM resources of Australia are primarily restricted to the Bowen, Sydney, and Surat basins. The Australian CBM industry is also progressing drastically. In addition, the CBM industry in China is developing due to favorable government policies, advantageous price conditions, tax breaks, advanced resource management, research and development subsidies, a CBM development plan, and mining rights protections [144]. CBM-producing companies, i.e., PetroChina ( $3 \times 10^{12} \text{ m}^3$ ), the Jincheng Anthracite Mining Group (JAMG;  $9 \times 10^8 \text{ m}^3$ ), China CBM, and the China National Offshore Oil Corporation (CNOOC;  $50 \times 10^4 \text{ m}^3$ , daily), are successfully exploring CBM in China. The total gas-in-place resources buried at <2000 m depth are estimated to be about 29.8 trillion cubic meters (TCM) of CBM. However, the technically recoverable resource is around 12.5 TCM [148].

Furthermore, India is well known for being the fifth largest coal reserve in the world, and may be a significant prospect for coal bed methane resources. About 98 percent of the coal resources of India are found in Gondwana sediments of the Permian age, and the remaining in Tertiary sediments, which are geographically distributed mainly in the eastern and central regions and the northeastern region. In India, states with Gondwana coal deposits, particularly Jharkhand and West Bengal, are the best prospective areas for CBM development due to their vast coal reserves and geologically favorable conditions for CBM generation, although other states, viz. Madhya Pradesh, Chhattisgarh, Odisha, Gujarat, Rajasthan, and Tamil Nadu have also reported significant prospects for CBM resources. The CBM resources of the Tertiary coal deposits distributed in the northeastern coalfields of India have not yet been fully explored. India is actively looking to maximize CBM resources in order to enhance the domestic production of natural gas and, thus, fulfill growing energy demand and ensure the safety of coal mining operations. There are, in total, 33 CBM blocks used for extracting CBM from coal beds in India [4].

The gas content values in the following discussions are based on Kim's correlation [149]. The Jharia coal seams have the maximum gas content capacity in India, i.e., about 239.37 billion m<sup>3</sup>, followed by the Raniganj Basin, with an estimated CBM volume of 175.06 billion m<sup>3</sup>. The amounts of gas held in the West Bengal coal basins vary from 3.07 to 10.54 cm<sup>3</sup>/g of coal, with significant gas quantities present in the Raniganj Basin (6 to 10.5 cm<sup>3</sup>/g of coal) [150]. The majority of the CBM is found within 600 meters of depth. The Raniganj coal is unique in terms of moisture, volatile matter, ash, and fixed carbon contents compared to other coalfields of the West Bengal region [151]. Interestingly, the lower moisture level in Raniganj coal (avg. 1.35%) provides space for the accumulation of CBM in the porous matrices of these coals. Further, in Jharkhand state, among other noteworthy coal mines, the highest CBM resources are found in the Jharia coal mines due to its higher fixed carbon contents [152]. The total CBM estimates range from 11.7 to 14.01 cm<sup>3</sup>/g [153]. Other significant CBM resources of Jharkhand include East Bokaro (7.25 to 12.79 cm<sup>3</sup>/g coal), West Bokaro (7.25 to 10.46 cm<sup>3</sup>/g coal), North Karanpura (4.78 to 6.96 cm<sup>3</sup>/g coal), South Karanpura (3.33 to 5.90 cm<sup>3</sup>/g coal), and Auranga Basin (2.49 to 4.44 cm<sup>3</sup>/g coal) [154]. Furthermore, in Chhattisgarh, the Korba coals indicate suppressed gas contents of 2.13–3.14 cm<sup>3</sup>/g due to high ash yields, whereas Tatapani–Ramkola coals possess high gas contents of 4.05–5.88 cm<sup>3</sup>/g due to the high fixed carbon and lower moisture level [155]. Similarly, Pathakhera coals from Madhya Pradesh (MP) retain about 5.49–7.94 cm<sup>3</sup>/g coal due to their lower moisture content, and Singrauli mine coals are relatively less saturated with CBM (1.91–3.48 cm<sup>3</sup>/g coal) due to high amounts of ash [155]. Coals from Maharashtra are medium- to low-grade, as the region is characterized by relatively higher moisture, volatile, and ash content, with low fixed carbon values [156]. Therefore, their gas retention capacity is also lower. The estimates suggest that the amount of gas held by Maharashtra coals is in the range of 2.19 to 3.93 cm<sup>3</sup>/g coal. Further, the CBM richness in the Odisha coalfields is considerably lower due to the high amounts of inorganic matter, with average ash yields of about 45 wt% [155]. Additionally, among the northeastern coalfields, the gassiness in the coals from Assam is relatively higher, in the ranges of 6.33 to 9.31 cm<sup>3</sup>/g coal, due to the low amounts of moisture and the ash yields [157].

From the above discussion, it can be understood that the inherent character of coal and its technological properties, such as moisture, ash yield, volatile matter yield, and fixed carbon contents, affect the amount of gas retention on coal seams. As previously discussed, methane generated through various pathways is accommodated in coal seams as sorbed gas on macerals and mineral surfaces; free gas in pores and fractures; and dissolved gas in bitumen, water, and kerogen. However, moisture plays a crucial role in the free gas retention capacities of a substrate. The large amounts of moisture may acquire space in the pores and fractures of coals, resulting in limited gas retention capacities in the coal bed. Likewise, the large amounts of volatile matter and ash yields may suppress the fixed carbon content, leading to alleviated gas sorption efficiencies. These properties are typical of low-rank coals such as lignites; thus, lignites often exhibit lower CBM retention capacity. The best example is represented by the Tamil Nadu lignites, which, despite having remarkable



potential for CBM recovery (36.56 billion tons) [158], possess a gas capacity varying from 0.28 to 0.56 cm<sup>3</sup>/g coal. These lignites are high in moisture (avg. 45 wt%) and low in fixed carbon (avg. 20 wt%). Other notable lignite deposits are from Rajasthan (0.29 to 0.57 cm<sup>3</sup>/g coal), Gujarat (0.54 to 0.83 cm<sup>3</sup>/g coal), and Jammu and Kashmir (0.27 cm<sup>3</sup>/g of coal).

## 10. A Global Sketch of Coal Bed Methane Geochemistry

### 10.1. United States of America (USA)

The commercial production of CBM in the United States of America was initiated in late 1980, and it was mainly concentrated with the highly matured coal of the San Juan (e.g., Fruitland coal), Black Warrior, and Bowen basins for the production of thermogenic methane [15,25]. Later on, immature coal of the Powder River and Illinois basins was found to produce thermogenic methane [15]. In addition, mixing secondary microbial methane with thermogenic gas was discovered in the northern part of the San Juan Basin, where the coal is relatively matured [80,159]. Source paradigms of microbial or thermogenic methane in both low- and high-maturity coals triggered the gas molecular and compound-specific stable isotopic studies to identify the genesis process of methane. Isotopic values of CO<sub>2</sub> and methane are routinely used to distinguish between microbial and thermogenic gases, along with documenting the genetic pathways of microbial methane, i.e., CO<sub>2</sub> reduction (hydrogenotrophic) or acetoclastic methanogenesis. The Powder River Basin, San Juan Basin, Black Warrior Basin, and Illinois Basin, to name a few, are considered to be prospective sources of CBM in the USA. Most of the microbial methane in the USA has been discovered in Powder River Basin and Illinois Basin [160]. Natural gas from the lignite to sub-bituminous coal of the Powder River Basin, with a depth range generally less than 2500 feet, is produced by a methyl-type fermentation pathway [86]. Along the eastern margin of the Illinois Basin, geochemical evidence points to the microbial origin of methane rather than the thermogenic variety [60]. With time, the importance of secondary microbial methane was recognized first in the San Juan Basin [161,162]. Geochemical and isotopic data suggest that thermogenic gases prevailed in the northern part of the San Juan Basin. In contrast, the southern part of this basin is dominated by microbial gas formed through acetate fermentation [163]. However, Scott et al. [80] later suggested that the Fruitland Formation produces early thermogenic, main-stage thermogenic, and secondary microbial gases. Secondary microbial gases are generated by microbes introduced after burial, coalification, and subsequent upliftment. Interestingly, saline water's influence in microbial methane formation was discovered in the Paleocene–Eocene Wilcox Group coal zone of northern Louisiana and south-central Mississippi, Gulf of Mexico Basin, where the maturity of the coal spans from lignite to high volatile C bituminous ranks [164]. Moreover, Flores et al. [98] demonstrated the impact of Pleistocene water recharge in the formation of secondary microbial methane in the Powder River Basin. Further, meteoric water recharge and basin upliftment influenced the generation of secondary microbial methane in the San Juan Basin. Basinal uplift-induced secondary microbial methane was additionally documented in the Black Warrior Basin. In the southern part of the Illinois Basin, thermogenic methane generation is associated with deeper burial and the possible impact of hydrothermal fluids. In contrast, the immature coal of the eastern part exclusively generates microbial methane [25]. Furthermore, the southern part of the San Juan Basin produces wet gases with oil, while the northern part is dominated by dry gases, including a significant amount of carbon dioxide [163,165]. The gases generated from high volatile A to low volatile bituminous coals of the Black Warrior Basin (west-central Alabama) are interpreted to be primarily thermogenic in origin, and are altered later on by mixing with microbial gas and oxidizing heavier hydrocarbons [86].

### 10.2. Australia

The initial idea of CBM in Australia came after the explosions, fires, and fatalities in Australian coal mines. Later on, with the reduction in the production cost and the depletion of conventional energy resources, the CBM was rapidly developed in Australia and the first

commercial production commenced in 1996 in Queensland. The Bowen, Surat, and Sydney basins are the main producers of CBM in Australia. High volatile bituminous to low volatile bituminous coals of the Sydney Basin with mean random vitrinite reflectance values in the range of 0.7 to 1.9% generally yield CH<sub>4</sub>, with a minor amount of other, higher hydrocarbon components as well as CO<sub>2</sub> and N<sub>2</sub>, except in a few places, where the CO<sub>2</sub> content goes up to 90% [166]. Thermogenic origin and secondary microbial methanogenesis are two important sources of methane found in the Sydney Basin [96,167,168]. Sub-bituminous to high volatile bituminous coals of the Surat Basin generally produce methane at a depth range of 200–600 m [169]. In the Dalby and Roma fields of the Surat Basin, the Walloon Subgroup generates mainly microbial methane via the hydrogenotrophic pathway. However, some intermediate carbon isotopic compositions probably reflect mixing with migrated Permian thermogenic gases or in situ early mature thermogenic (EMT) gases generated from the Walloons coals [170]. On the other hand, bituminous coals of the Bowen Basin generate CH<sub>4</sub> through the CO<sub>2</sub> reduction pathway [96]. The gas composition reveals that CO<sub>2</sub> (<1%) and other higher components of hydrocarbons form a subordinate part. Meanwhile, Kinnon et al. [114], while working on the isotopic compositions of CBM produced in Bowen Basin, found that methane produced from two bituminous coal seams was both microbial and thermogenic in origin.

### 10.3. China

After the successful development of CBM in the USA and Australia, commercial CBM development began in China in the late 90s. The Qinshui Basin of northern China is the largest basin where commercial development of CBM occurs in its southern area [171,172]. The coal of the Qinshui Basin is of high rank and mainly produces thermogenic methane, with a meager yield of the microbial variety [172]. In this basin, the magmatic thermal event is the principal controlling factor for methane enrichment [173]. Wei et al. [174] indicated that the genetic type of methane was predominately thermogenic, secondarily followed by microbial methane produced by the CO<sub>2</sub> reduction pathway in the Panxie Coal Mining Area, Anhui Province, China. In the Ordos Basin, CBM is well-established towards its eastern margin. In this basin, the rank of the coal progressively increases from high volatile bituminous to low volatile bituminous from the northern to the southern direction. The methane produced in this basin is typically thermogenic, with a plausible influence of secondary microbial methanogenesis [175].

### 10.4. India

#### 10.4.1. Raniganj Basin

The Raniganj Basin, comprising ~26.68 billion tons of Permian coal [158], is one of the most CBM-productive basins in India [176,177]. The coal beds vary from 26 to 1250 m in depth, and the gas exploration occurs primarily in the south, northeast, and north-central blocks [176]. The Great Eastern Energy Corporation Ltd. (GEECL) produces about 0.80 million cubic meters of CBM from 80 wells, whereas Essar Oil Exploration produces around 0.82 mmscmd from 200 wells. The original gas-in-place volume of CBM in the Raniganj south block was ~2.62 trillion cubic feet in 2022, as reported by the GEECL. The Permian coal in this basin is of bituminous C to bituminous B rank [178], with its mean random vitrinite reflectance ( $\bar{R}_r$ ) reaching up to 1.0% [90]. The prolonged progressive elevation in the geothermal gradient (4–5 °C/100 m) gradually increased the coal rank [89], while sudden thermal stress from the intrusive igneous bodies (lamprophyre dyke and sills) occasionally enhanced the coal rank, reaching even greater than 1.5% vitrinite reflectance [90]. The impact of thermal aureole asymmetry on the hydrocarbon generation of the Raniganj coals was successfully demonstrated by Misra et al. [90] by organic petrological and geochemical proxies. Other investigations have also depicted the gas-prone nature of these coal beds, as they comprise mainly type III kerogen derived from lignocellulosic plant tissues.

Furthermore, Ghosh et al. [24] studied the gas isotopic fingerprints of the Raniganj coal. They applied the  $\delta^{13}\text{C}\text{-CH}_4$  and  $\delta\text{D}\text{-CH}_4$  of the coal bed gas samples, along with the

$\delta\text{D-H}_2\text{O}$  and  $\delta^{18}\text{O-H}_2\text{O}$  of the coal bed formation water, to determine the origin of the CBM. The stable carbon isotope of methane revealed an intermediate signature ranging from  $-49.5$  to  $-47.4\text{‰}$ , indicating a plausible mixing between thermogenic and microbial gas. Primary microbial methanogenesis at that coal rank ( $\bar{R}_r \sim 1.0\%$ ) is very unlikely, as methanogens and methanogenic archaea can barely survive a temperature that high. Hence, the gas is primarily thermogenic in nature. Meanwhile, the secondary microbial methane altered the primary thermogenic gas signatures. In addition, the  $\delta\text{D-CH}_4$  parameter of the gas samples varied from  $-207$  to  $-211\text{‰}$ , which, in collaboration with the  $\delta^{13}\text{C-CH}_4$  values, additionally implied that mixing occurred between primary thermogenic and secondary microbial gases. Moreover, the deuterium and oxygen isotopic compositions ( $\delta\text{D-H}_2\text{O}$  and  $\delta^{18}\text{O-H}_2\text{O}$ ) of the coal bed formation's water samples ranged from  $-34$  to  $-35\text{‰}$  and from  $-5$  to  $-5.5\text{‰}$ . The deuterium isotopic difference between the water and methane, along with the cross-plot between the  $\delta\text{D-CH}_4$  and  $\delta\text{D-H}_2\text{O}$  parameters, pointed towards the hydrogenotrophic pathway of secondary microbial methane generation. Additionally, the  $\delta\text{D-H}_2\text{O}$  and  $\delta^{18}\text{O-H}_2\text{O}$  values of the coal bed formation's water samples placed them just above the GMWL (Figure 8), which marked a plausible interaction between meteoric water and coal bed formation water, along with a possible introduction of microbes and consequent metabolism of residual kerogen and thermogenic wet gas. This study is a novel portrait of alterations in primary thermogenic gas signatures by secondary microbial methanogenesis in various Indian basins.

#### 10.4.2. Sanchor Sub-Basin

The Sanchor Sub-Basin of Gujarat, India, comprises a huge deposit of Eocene lignite. These lignite deposits are primarily confined to the Eocene Tharad Formation [179]. This sub-basin is situated at the northern tip of the Cambay Basin and the southern end of the Barmer Basin, which are the main hydrocarbon-producing on-land basins of western India [11]. Therefore, the isochronous lignite deposit at the Sanchor Sub-Basin has significant economic significance. The lignite deposits comprise a substantial volatile matter yield, a high moisture content, low calorific values, and an  $R_r$  range from  $0.28$  to  $< 0.40\%$  [179]. Until now, a few sporadic wells have been drilled by various operators in Sanchor Sub-Basin; however, they have yet to achieve any success. Nevertheless, Dutta et al. [22] studied the gas samples from two wells, and the results were interpreted to determine the genesis processes of methane and carbon dioxide.

Lignite comprises organic matter that has shown intermediate thermal maturity in the course of coalification, and soluble bitumen extract from lignite consists of partially de-functionalized aromatic and saturated compounds [180]. These compounds include labile functionalities, cyclic compounds with 1–2 aromatic rings, unsaturated cyclic functionalities with 1–2 double bonds, heterocycles, etc. [180–186]. Biochemical coalification at this rank involves alkylation, the loss of methoxyl groups by dehydroxylation and demethylation processes, and the cleavage of aryl ether bonds [25]. Hence, lignite rank preserves the labile kerogen available for microbial metabolism and/or thermal cracking at the early mature phase. Furthermore, the mean random vitrinite reflectance and peak palaeotemperature ranges ( $\sim 35$  to  $< 60\text{ °C}$ ; estimated from the Barker and Pawlewicz equation [187]) suggest that microbial methanogenesis occurs in these lignite deposits.

Dutta et al. [22] employed the gas molecular ratio ( $\text{C}_1/(\text{C}_2 + \text{C}_3)$ ),  $\delta^{13}\text{C-CH}_4$ ,  $\delta^{13}\text{C-CO}_2$ , and  $\text{CO}_2$  content to document the origin of methane in the Tharad lignite beds. The ( $\text{C}_1/(\text{C}_2 + \text{C}_3)$ ) ratio and the  $\delta^{13}\text{C-CH}_4$  varied from  $14.32$ – $64.61$  and from  $-69.30$  to  $-57.20\text{‰}$  in the BK-5 well, while in the BK-7 well, these parameters ranged from  $85.63$  to  $204.65$  and from  $-67.40$  to  $-64.50\text{‰}$ . Bernard's plot, constructed with the gas molecular ratio and the  $\delta^{13}\text{C-CH}_4$  values, indicated an intermediate signature between the microbial and thermogenic gases. The late mature thermogenic gas (LMT), if present, would lead to heavier  $\delta^{13}\text{C-CH}_4$  values ( $> -50\text{‰}$ ), but the carbon isotope ranges suggested the presence of primary microbial methane. In addition, LMT gas generation is not feasible at such a low rank. Meanwhile, the presence of primary microbial methane alone would raise the

gas molecular ratio beyond 1000, but the ranges of this ratio implied a mixed signature. Hence, this mixing might result from intercalating primary microbial gas with early mature thermogenic gas (EMT). The labile kerogen in the lignites would comprise perhydrous macerals, which could crack at a very early stage of thermal maturation due to the low bond dissociation energy of the aliphatic functionalities. Thus, thermal cracking of this reactive organic matter at low temperatures might have generated the EMT that mixed with the primary microbial gas and altered its geochemical signatures. Dutta et al. [22] added a new field in Bernard's diagram (PM + EMT; Figure 2a) which accommodated these mixed gases. The gas genetic diagram (Figure 2b; after Milkov and Etiope [81]) additionally suggested that the primary microbial methane was generated through hydrogenotrophic methanogenesis and mixed with the EMT gas. Furthermore, the gas genetic diagram was integrated with Strapoc's model [25] to determine the extent of gas mixing. The gas samples fell within ~90% and ~40% mixing lines (Figure 3), signifying substantial mixing between the two sources of gas.

The CO<sub>2</sub> content ranged from 16.95 to 32.32 vol.% and from 18.91 to 28.60 vol.% in the BK-5 and BK-7 wells, respectively. Additionally, the  $\delta^{13}\text{C-CO}_2$  spanned from −21.30 to −11.80‰ in the BK-5 well and from −11.20 to −9.40‰ in BK-7 well, respectively. The interrelation between the  $\delta^{13}\text{C-CO}_2$  and the CO<sub>2</sub> content in these wells indicated both organic and inorganic sources of CO<sub>2</sub>. The BK-5 well consisted of CO<sub>2</sub> originating mainly from coalification, while the CO<sub>2</sub> in the BK-7 well exhibited a mixed magmatic and coalification source and/or an early mature thermogenic source. The volcanic degassing from the underlying Deccan Traps is the source of the inorganic magmatic CO<sub>2</sub> in these lignite beds. Furthermore, the microbial decay of organic matter, as well as decarbonylation and decarboxylation reactions during coalification and/or early mature thermal degradation of reactive functionalities, generate organic CO<sub>2</sub>. Dutta et al. [22] also suggested that the carbon dioxide generated during the coalification and/or early mature thermogenic processes would have altered the primary magmatic CO<sub>2</sub> signature, leading to a mixed isotopic fingerprint. In addition, the  $\Delta^{13}\text{C}_{\text{CO}_2\text{-CH}_4}$  and the  $\alpha_{\text{CO}_2\text{-CH}_4}$  parameters were applied to determine the methanogenic pathways involved in the Tharad lignite deposits. The  $\Delta^{13}\text{C}_{\text{CO}_2\text{-CH}_4}$  and  $\alpha_{\text{CO}_2\text{-CH}_4}$  values ranging from 44.30‰ to 57.30‰ and from 1.047 to 1.062 in the BK-5 well, as well as from 54.90‰ to 56.50‰ and from 1.059 to 1.061 in the BK-7 well, indicated that there was mixing between the hydrogenotrophic and acetoclastic types of methanogenesis. However, multiple sources of CO<sub>2</sub> and CH<sub>4</sub> and their impact on the stable carbon isotopic compositions also likely influenced these parameters, resulting in the pseudo-portrayal of intermixing between the microbial pathways. The relation between the  $\delta^{13}\text{C-CO}_2$  and  $\delta^{13}\text{C-CH}_4$  [81] further supported the mixing of methane generated through hydrogenotrophic methanogenesis and that generated by the EMT pathway (Figure 5). The relationship between the gas molecular ratio and the  $\Delta^{13}\text{C}_{\text{CO}_2\text{-CH}_4}$  parameter in Strapoc's model [25] additionally revealed around 20%–60% mixing in the BK-5 well and 60%–80% mixing in the BK-7 well (Figure 7). Hence, this complimented the mixing between the primary microbial and early mature thermogenic methane in the Eocene Tharad lignite deposits.

#### 10.4.3. Jharia Basin

The Jharia Basin is situated in the eastern part of India. This sickle-shaped basin is about 38 km long and 18 km wide, with an aerial extent of 456 km<sup>2</sup> [188]. The Jharia Basin is a leading contributor to India's gross coal production, and is the only repository of prime coking coal in India. The Jharia Basin comprises ~19.53 billion tons of Gondwana bituminous coal deposits [158]. Significant coal deposits in this basin are limited to a depth of about 600 m (11.4 billion tons), whereas the rest of the deposits can be found at a depth of between 600 and 1200 m (5.2 billion tons). The majority of coal within the first 600 m of depth is viable for carrying out various types of coal-related research. As mentioned previously, the Jharia coal seams contain the largest volumes of CBM gas—about 239.37 billion m<sup>3</sup>. Laxminarayana and Crosdale [189] studied controls of moisture, mineral



matter, coal composition, and rank on the methane sorption capacities of Jharia coal. They reported that the mineral matter and the moisture influence methane adsorption inversely. On the other hand, they reported a positive correlation between the coal rank and the adsorption potential of this coal. Therefore, the largest CBM gas volumes in the Jharia coals are assumed to be due to the perfect blend of moisture, ash yield, coal composition, and rank. In support of this finding, the Jharia coals also contain the greatest estimated methane gas-holding capacity, at 11.7 to 14.01 cm<sup>3</sup>/g of coal. As a complementary study, Chatterjee and Paul [152] assessed the CBM recovery potential of the Jharia Basin using core samples and well log data. In their research, based on a hierarchical cluster analysis (HCA) of the coal parameters, including the coal seam thickness, gas content, and permeability, they classified coal seams in order of potentiality for efficient CBM exploration. Their results found that enhanced CBM recovery with CO<sub>2</sub> sequestration in the Jharia coalfields is important. The estimated CO<sub>2</sub> sequestration capacity of the Jharia coal seams stands at 881.8 million tons [4]. Therefore, the Jharia coal beds have a multitude of benefits. They are a good source of prime coking coal, and this coal has the most abundant CBM resources in India and an excellent CO<sub>2</sub> sequestration capacity.

## 11. Challenges in CBM Extraction

The exploration of coal bed methane is the ultimate task required to identify a natural gas reserve. Although the CBM has potential for green energy, its exploration and production pose numerous challenges. The characterization of the reservoir, including the accurate prediction of methane-rich coal seams and the estimation of the gas reserves contained in them, is initially the prime difficulty. The complex and heterogeneous nature of coal, its depth of occurrence, its thickness, and its associated structural features are among the most challenging geological constraints in identifying the most promising site for CBM exploration. Further, the successful recovery of CBM comes with a high cost of drilling and production. The coal deposits are mineable with current technologies up to a 600-m depth, but coal seams beyond this depth are uneconomical and thus, are considered for CBM exploration. Therefore, these deep-seated coalbeds incur high drilling costs. Moreover, using specialized equipment in hydraulic fracturing and horizontal drilling adds to the production costs. Apart from these operational challenges, CBM exploration poses environmental threats. CBM is a potent greenhouse gas (GHG), and its release into the atmosphere during exploration, production, and transport is harmful to the ozone layer. Moreover, due to underground exploration activities, the risk of groundwater contamination is always high. CBM production involves the removal of large amounts of water from underground, which may lead to land subsidence. In addition, the production water contains large amounts of salts and minerals, which are difficult to recycle and which incur additional costs. Therefore, water management imposes incremental challenges on CBM extraction [34]. Finally, the exploration and production of CBM are subject to various regulations, and navigating these regulations can be challenging and time-consuming. These challenges must be addressed in order to efficiently utilize CBM as an alternative energy source.

Coal bed methane exploration in Southeast Asian countries, which occurs exclusively in India and China, is facing serious trouble, unlike the USA, Australia, and Canada. Ambiguities in the coal composition, microstructure, rank, and hydrogeological conditions make the CBM exploration strategies of the USA incompatible with those of China. China's CBM industry struggles with exploration and development strategies [190] despite favorable governmental plans and policies. The geological conditions and high permeability levels of CBM-rich horizons; gas control factors; lack of proper production guides and critical technologies for suitable exploration under unfavorable geological circumstances; fracturing and extraction of gas in high-permeability fields; related equipment and technologies, etc., are hindering the progress of the CBM industry in China. The overlap of the coal mining and CBM exploration rights are also hurdles to executing gas extraction first and coal mining subsequently. Additionally, piping networks, overseas dependence, limitations on the privately-funded projects, geographic challenges, qualms in marketing CBM, low



return, and high production cost, among other factors, are holding back CBM exploration in China [144,148].

The development of CBM fields in India is facing many challenges, such as key exploration programs to identify coal deposits and the geological properties that are favorable for the generation and production of CBM, as well as the deficiency in the technology needed for CBM exploitation from different reservoirs, each with a specific geological framework. The development of CBM demands high investment, efficient production technology/skill, and a long recovery period. Additionally, environmental challenges are one of the most significant threats in India associated with CBM exploration and development. The major challenge related to the commercial development of CBM in India is technological crises in the economic management of co-produced water. However, many research programs and policies have been developed. CBM-produced water, mainly from the Damodar Valley Basin, contains relatively higher concentrations of dissolved sodium ( $\text{Na}^+$ ) and bicarbonate ( $\text{HCO}_3^-$ ), and may be categorized as Na–K type, Na– $\text{HCO}_3$  type, or  $\text{HCO}_3$  type. This water may serve several beneficial purposes after effective treatment. Moreover, CBM-produced water from the Raniganj Basin comprises bicarbonate, sodium, and fluoride that exceed the permissible limits of 10,500 for potable or drinking water and irrigation purposes. CBM-produced water could be a potential source of fresh water, although this will require more detailed information and efficient treatment technology.

The operational activities associated with CBM production certainly negatively impact the environment. A significant possible impact on the environment can occur at all phases of CBM exploitation, from the completion of drilling, to hydrofracturing, to extraction. Drilling and hydrofracturing operations may affect the groundwater quality due to seepage and the chemicals used in fracturing operations. Additionally, land acquisition for CBM well drilling is a crucial concern impacting agricultural and forest areas. Drilling CBM wells requires a huge amount of water, with bentonite clay to carry out drill cuttings and provide wellbore stability, which may cause surface pollution at drill sites and harm human and animal health. The environmental impact and risks that CBM development programs cause are exceptionally high; therefore, CBM exploration is advisable after performing a comprehensive environmental safety and risk assessment.

#### 11.1. Mine and Health Hazards of CBM Extraction

Although extraction of the CBM provides a valuable energy source, it poses a significant hazard to the mine workers and the environment. Therefore, addressing the adversities that come with the CBM extraction procedures is crucial. Some unfortunate events that can occur during extraction procedures are CBM gas outbursts, gas explosions, gas leakage, coal dust explosions, air and water pollution, land degradation, damage to the mine's infrastructure, and, most importantly, human health hazards. Such malignant incidents associated with methane extraction have long prevailed worldwide, and measured efforts are needed to mitigate these mishaps.

##### 11.1.1. Methane Gas Explosion

The risk of methane gas explosion has always been associated with CBM extraction procedures [191]. It incurs a severe safety hazard in the global coal mining industry [51,192]. Methane is a highly combustible, colorless, odorless gas that ignites easily [193]. Drilling CBM wells into coal seams is associated with releasing methane gas into the surrounding air. If the methane concentration in the air is too high, it creates an explosive atmosphere. This is particularly hazardous to the mine infrastructure and workers if the methane gas build ups in the confined space.

The earliest published records of a methane gas explosion date back to 1621, in Gateshead, England [194]. Since then, many practitioners have developed safety measures to mitigate methane explosions. However, numerous disasters still occur. For example, in the 20th century, 10,390 underground coal mine workers died in the USA alone in gas explosion-related disasters [194,195].

#### 11.1.2. Coal Dust Explosion

A coal dust explosion is usually associated with a coal mine gas outbreak. Consequently, this deleteriously affects the mine's infrastructure and human health [196]. Moreover, CBM associated with coal dust in suspension may exacerbate coal dust outbursts by several times. Dust explosions usually occur when fine coal dust particles are suspended in the air and ignited. These explosions can be particularly dangerous in coal mines, where large quantities of coal dust can accumulate. Dust explosions can also occur in processing and storage facilities, where dust can be generated during handling operations.

To prevent dust explosions, coal mines must take steps to control and minimize dust generation. This may include using water or other suppressants to prevent dust from becoming airborne and using dust collection systems to capture and remove dust. Moreover, careful rock dusting in an underground coal mine may help to alleviate the risk of coal dust accentuating gas explosions [194,196].

#### 11.1.3. CBM Outburst

CBM outburst is a dynamic incident referring to a strong and abrupt release of gas from a working coal seam. When gas accumulation occurs under a high-pressure coal seam, the pressure can exceed the coal strength, resulting in a coal seam burst which releases a large amount of gas [197]. The chances of a CBM outburst are highest during well drilling, as the pressure within the coal seam is reduced, which causes a quick release of methane, leading to a catastrophic, outburst-like event. Such gas outbursts are fatal to the mine workers and the mining infrastructure [50]. Gas outbursts in underground coal mining may also result in methane gas explosions and associated dust explosions. This disastrous event can be controlled by desorbing gas from a coal seam before drilling to reach a certain safe mining threshold [198]. Another essential aspect in preventing gas outbursts is monitoring and maintaining stable pressure during drilling activities.

#### 11.1.4. CBM Leakage

CBM leakage is escaping methane gas from the working coal seam to the surrounding environment. This can happen due to mining operations, natural fractures in the coal seam, or improperly sealed wells [194]. Methane leakage can occur at every stage of CBM extraction, from drilling and well completion to gas collection and transmission. A number of factors control the exact level of CBM leakage, including the geology of the coal seam, the quality of the equipment used, and the skill of the workers involved in the extraction process. However, even small amounts of methane leakage can significantly impact the environment and public health. CBM leakage can pose a significant risk to human health and the environment, as methane gas is a potent greenhouse gas and can displace oxygen in enclosed spaces [191,199]. To prevent CBM leakage, coal mines must take steps to contain the gas within the coal seam. This may include installing gas drainage systems, using well-sealing techniques that prevent gas from escaping, and monitoring the surrounding environment for signs of gas leakage [192,200]. Furthermore, improving the regulatory framework surrounding the industry is another key strategy for reducing methane leakage from CBM extraction. This includes stringent regulations on well construction and operation and requirements for regular testing and monitoring of methane emissions. Governments may also incentivize companies to invest in new technologies and practices that reduce methane leakage, such as using advanced sensors and leak detection systems.

#### 11.1.5. Potential Human Health Hazards of CBM Extraction

One of the most significant impacts of CBM extraction on human health is air pollution. In the CBM extraction process, methane gas, along with other harmful air pollutants such as nitrogen oxides, particulate matter, and volatile organic compounds (VOCs), leaks into the surrounding areas where mine workers, as well as people in nearby provinces, are at a greater risk of respiratory problems, cardiovascular disease, and other health issues [199].

Moreover, CBM extraction can also lead to water pollution. As discussed previously, in the process of extracting methane gas from coal seams, large amounts of water are pumped out of the ground along with the gas [34]. This water, often contaminated with salt, heavy metals, and other pollutants, can contaminate local water sources and threaten human health [193]. Drinking water contaminated with these pollutants can lead to various health problems, including gastrointestinal illness, kidney damage, and cancer. As another important aspect, CBM extraction can also be a significant source of noise pollution. The drilling, hydraulic fracturing, and transportation of CBM can create high levels of noise that can be disruptive to nearby communities. Exposure to high levels of noise can lead to hearing loss, sleep disturbance, and other health problems. Furthermore, CBM extraction may also lead to land degradation, which can impact human health in a number of ways. The process of drilling and hydraulic fracturing can damage local ecosystems and disrupt habitats, leading to a loss of biodiversity. This can have indirect effects on human health, such as disrupting food webs and reducing access to natural resources. Additionally, the disruption of the land can lead to soil erosion, crop deterioration, and land subsidence, which can pose a threat to infrastructure and human safety.

## 11.2. Measures to Mitigate Hazards Related to the CBM Extraction

### 11.2.1. Well Construction

A suitable well construction method is vital to averting the risks associated with CBM extraction. The wells should be designed and constructed with appropriate casing and cementing techniques to prevent gas or fluids from leaking out. [200]. The wellhead should also be secured and monitored regularly to detect any leaks or emissions. Proper well design and construction are crucial to mitigating the risks of gas explosions, outbursts, and leakage. In addition, the wells should be equipped with safety devices such as pressure relief valves, blowout preventers, and emergency shutdown systems. Routine maintenance and assessment of the wells are indispensable for detecting and addressing any possible threats. This includes inspecting the valves, wellhead, and pipelines for leaks, corrosion, and other damage that could lead to gas explosions, outbursts, or leakage. Routine testing of the pressure and temperature of the wells can also help to identify any likely dangers.

### 11.2.2. Efficient Water Management

CBM mining involves pumping significant volumes of water out of the coal seams to liberate trapped methane. This water may contain high levels of salt, minerals, and other contaminants that can have detrimental effects on the environment if not governed appropriately [34,193]. Effective water management strategies such as recycling, treatment, and disposal should be executed to reduce the impact on the environment and public health. CBM extraction can affect surface and groundwater quality; therefore, measures to protect these resources should be taken. Properly disposing of the produced water, regularly monitoring the water quality, and preventing spills or leaks can help to reduce the impact of CBM extraction on these resources.

### 11.2.3. Monitoring and Control of Emissions

CBM extraction releases many types of emissions, such as methane, volatile organic compounds (VOCs), and other air pollutants. Monitoring and controlling these emissions is essential in order to lessen the influence on air quality and climate change [201]. Techniques such as flare or capturing and utilizing methane can help reduce emissions. Monitoring gas levels in and around the wells is fundamental to noticing any latent hazards [193]. Gas detectors should be installed at strategic locations near the wells and in the surrounding areas to provide early warning of any gas leaks or concentrations. The gas levels should be monitored regularly, and appropriate action should be taken if any aberrations are identified. Proper ventilation is critical to preventing the buildup of explosive gas concentrations in underground mines. Adequate ventilation systems should be installed and maintained to ensure that the air in the mine is constantly circulating and that there is no gas buildup.

#### 11.2.4. Waste Disposal

The first step in proper CBM waste disposal is to separate the water from the other substances that are extracted during the extraction process. This water, known as produced water, is often highly saline and may contain many other contaminants. Produced water can be disposed of in a number of ways, including evaporation, surface discharge, and underground injection. In addition to produced water, CBM extraction also produces solid waste in the form of coal fines and other byproducts. This waste can be disposed of in several ways, including land application, landfilling, and reclamation. Reclamation is another vital aspect of CBM waste disposal. This involves restoring land that has been impacted by CBM extraction to its pre-existing condition or to a condition that is suitable for other uses, such as for agriculture or as a wildlife habitat. Reclamation can involve various activities, including soil stabilization, erosion control, and vegetation restoration. Furthermore, the waste generated from CBM extraction, such as drilling mud, should be appropriately disposed of to prevent environmental contamination. Proper storage, transportation, and disposal of hazardous and non-hazardous waste should be carried out according to regulatory requirements [193]. In addition to these practices, government regulations and oversight play an important role in ensuring proper CBM waste disposal. Governments can establish standards for waste disposal, require companies to obtain permits for waste disposal activities, and impose penalties for non-compliance. They can also invest in research and development for new waste disposal technologies and practices that minimize the environmental impacts.

#### 11.2.5. Community Engagement

Community engagement is a key component of CBM extraction, as it can help to identify and address the concerns and needs of the affected communities. Community members should be involved in decision making, and regular communication should be maintained throughout the extraction process. Training and education of workers are essential to avoid accidents related to CBM extraction. Workers should be trained on the hazards associated with CBM extraction, the proper use of equipment, and the safety procedures. Regular safety drills and emergency response training should also be conducted to ensure that workers are prepared to respond to any potential hazards.

#### 11.2.6. Emergency Response Plan

Proper emergency response plans should be formulated and applied to mitigate the risks of gas explosions, outbursts, and leakage. These plans should include procedures for shutting down wells, evacuating workers, and containing any gas leaks. Emergency response equipment such as gas detectors, breathing apparatus, and firefighting equipment should also be available and maintained in good condition.

In summary, CBM extraction promises to deliver a substantial energy source, but poses several hazards that must be carefully addressed. By executing suitable measures such as proper well construction, effective water management, monitoring and control of emissions, proper disposal of waste, and community engagement, the risks of CBM extraction can be curtailed, and the benefits can be amplified. Alleviating the jeopardies associated with gas explosions, outbursts, leakage, and related accidents in CBM extraction requires a comprehensive approach that includes regular maintenance and inspection, monitoring of gas levels, proper ventilation, training and education of workers, and proper emergency response plans.

### 12. An Outlook of Future Development Trends in the Exploration, Production, and Application of CBM

In order to counteract the challenges of CBM exploration and development, an array of research from different perspectives is immediately required. The high-depth coal seams must be investigated for their potential, storage behavior, adsorption and desorption characteristics, gas flow behavior, gas saturation, pore geometry, porosity, and permeability of

the strata, among others, for CBM development. A multi-angle approach is necessary in order to crack these issues and reach these high-depth coal seams for CBM exploration. Additional research should be performed to make drilling, hydraulic fracturing, gas extraction, proper pipeline conveying, etc., economical and less harmful to the environment and ecosystem. Implementing the pinnate horizontal well technique requires a lengthy investigation to enhance CBM extraction. In this technology, the horizontal well bore spreads evenly and widely in the coal beds and readily drops the stratum pressure, which amplifies the desorption and diffusion of methane, leading to enhanced CBM production [202].

Moreover, studies can be conducted on CBM extraction using CO<sub>2</sub>. As CO<sub>2</sub> shows greater sorption efficiency on coal than on methane, and at least two molecules of CO<sub>2</sub> can replace each methane molecule under optimal pressure and temperature conditions, CBM extraction using CO<sub>2</sub> injection in deep coal seams may be slightly improved. Amendments of policy measures; justified, scientific, and economic planning for CBM development; implementing research findings on gas production first, followed by coal mining (especially in China); improvements in market stability and security; and lowering of production costs, among others, are to be conducted soon to enhance CBM exploration. Further, enacting resource sharing, preventing unordered competition, and intensifying information channels are required to build an integrated information management system for CBM [144]. Additionally, improvements in government policies, as well as in the cooperation and understanding between coal mining and CBM exploration companies, as a way to raise the standards of financial subsidies, are necessary for the near future [148].

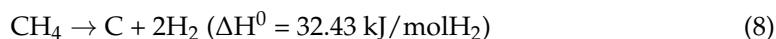
CBM exploration and development requires a huge, long-term financial investment and high risks to obtain the benefits. If the coal price is alleviated due to market fluctuations, CBM exploration and development funds decline. Hence, special funds for CBM exploration and development are necessary to keep the CBM industry on track for further development. Enterprises contributing significantly to CBM exploration, development, and application should be rewarded to stimulate their efforts, scheme, and eagerness; encourage investment; and loosen the financial constraints. Initiatives should be taken to invite various stakeholders to benefit from CBM exploration, development, and applications. For example, the Australian Government opted for the Commonwealth Greenhouse Gas Abatement Program to buoy up the extenuation of coal mine methane (CMM) emission and electricity generation from this methane [148]. The program was allotted USD 304 million and funds large-scale activities through a competitive method [203]. This program has funded many CBM/CMM projects in Australia, through which the proven reserves and output of CBM/CMM have experienced a rapid escalation in recent times [148].

In India, simulation studies are also underway to boost CBM exploration and development. As an example, Panwar et al. [204] established a three-dimensional excavation of CBM from reservoir simulation (COMET3) for the Sitarampur coal beds (Gondwana) of the Raniganj Basin. The Sitarampur block is a virgin and highly gassy coal block in the Burdwan district of West Bengal, India. It comprises a large amount of coal bed methane. The simulation investigation was conducted based on the vertical well degasification of the coal beds. The reservoir simulation was enacted to document the methane concentration in the coal matrix, the gas saturation in the fractures, and the production of water over time. The reservoir simulation was implemented for 25 years to recover methane from the coal beds. The results indicated that ~372 million cubic meters of carbon dioxide-equivalent greenhouse gas emissions could be mitigated by methane extraction with space and time. The simulation also revealed that a colossal amount of methane could be recovered from the Sitarampur coals with less water production. This immense amount of methane recovery may alleviate global warming and offer a potential alternative energy resource. The safety of the coal mines would also be improved through this process. Hence, ongoing and future research should also incorporate reservoir simulation techniques and artificial intelligence-based models in other CBM basins of India and other CBM-producing countries worldwide. Otherwise, researchers and industries are also looking for microbially enhanced CBM production from the existing and depleted wells through several techniques (discussed in

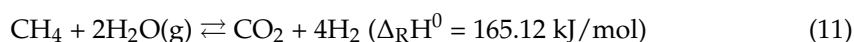
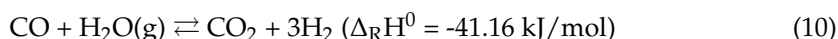
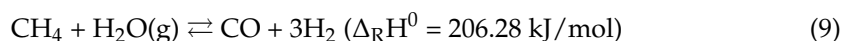


Section 13) to augment the methane recovery, and this technique will be one of the prime focuses for CBM exploration and development in the near future.

As the earth is progressing towards a green, sustainable future constituted by hydrogen energy, CBM can also be used to generate hydrogen through methane decarburization/decarbonization and the steam methane reforming process [205–207]. Methane decarbonization denotes splitting methane into solid carbon and hydrogen gas:



This reaction is endothermic, and ample energy is required to break the C-H bonds of high bond dissociation energy [208]. The methane decomposition commences at ~500 °C, and the high conversion rates are achieved beyond 1100 °C. Catalytic activities augment 10% conversion rates at 500 °C to 95% at 1050 °C [209]. Meanwhile, coke accumulation on the active surface of metal catalysts or alleviated superficial characteristics of carbonaceous catalysts may hinder the implementation of catalysts on an industrial scale [206]. The HYPRO technology, based on the fluidized bed reactor, was the most relevant practice for the catalytic thermal decarbonization of methane [210]. On the other hand, hydrogen gas is widely produced from methane through the steam methane reforming process. This process is highly efficient and causes less environmental pollution [207,211,212]. Steam methane reforming is primarily an endothermic process that employs nickel-based catalysts to react methane with high-temperature steam, generating hydrogen, carbon monoxide, and carbon dioxide at a temperature of 750–900 °C and a bar pressure >30 [207,213]:



The hydrogen generated from this steam-reforming process of methane is known as grey hydrogen, as a reasonable amount of CO<sub>2</sub> is released along with the hydrogen gas. Meanwhile, if this released CO<sub>2</sub> can be captured in organic matter and clay minerals [2], the produced hydrogen gas will be considered clean energy and termed as blue hydrogen [207]. Therefore, besides serving as a promising alternative energy resource in the coming days with progressive amplification of exploration and development, CBM can also offer a hydrogen-based economy and a greener sustainable future for the Earth and its inhabitants.

### 13. A Note on Microbially Enhanced Coal Bed Methane (ME-CBM) Recovery

Microbially enhanced coal bed methane recovery (ME-CBM) utilizes the ability of microorganisms to produce methane in coal beds [214,215]. The stimulation for in situ microbial methane generation in the coal resource has already been a research topic for scientists and engineers for a decade or two. Meanwhile, this in situ stimulation of microbial methane is controlled by several parameters, such as the availability of methanogens, the battle for methanogenic substrates, the rate and viability of methanogenesis, the availability of biodegradable organic matter, and the salinity and temperature of the formation, as well as the distributions of pores and fractures. Furthermore, several strategies have been proposed to stimulate microbial methane generation and amplify the CBM recovery from coal seams. These include bioaugmentation, biostimulation, enhancing the contact surface area of coals to the methanogens, and augmenting the proportion of bioavailable organic matter [32].

Bioaugmentation denotes amplifying the in situ microbial activities in coal seams by injecting microorganisms [216]. This process may involve a single microorganism or a microbial consortium. However, introducing microbes into the subsurface coal seams may raise the risk of microbial contamination of groundwater, which may pose a severe environmental threat. Moreover, nutrients and/or electron receivers and donors are introduced to coal seams during biostimulation to accelerate methane production using the

native microbial communities. This method is highly useful in active microbial methane reservoirs or where the rate of methanogenesis is alleviated over time. At these particular sites, biostimulation can enhance the growth of methanogens and alter the redox conditions favorable for methanogenesis [55,217,218]. Stimulation of the primary and secondary fermenters induces geopolymer decomposition and the consequent expulsion of intermediate moieties, which are subsequently converted to methane by the methanogens. Biostimulation is a widely practiced technique in the commercial microbial methane stimulation process [32,217]. Additionally, laboratory simulation experiments employed yeast extract, synthetic nutrients, monosaccharides, etc. [58,219] to enhance methane recovery. Luca Technologies, INC, utilized a mixture of yeast extract, soy proteins, glycerol, weak organic acids, synthetic vitamins, etc., to amplify the CBM recovery in the Black Warrior Basin, San Juan Basin, and Uta Basin. Moreover, vitamins, trace metals, and non-carbonaceous nutrients were applied at different sites in India, Indonesia, and China by Next Fuel, INC [219], for the ME–CBM recovery.

In the coal seams, the methanogens are often restricted to the coal fractures as the pore networks are extremely tiny, too much so for their proliferation [87]. Hence, the limited accessibility of the coal surface area reduces the viability of methanogenesis. This issue can be resolved through hydraulic fracturing. The fracturing fluid exclusively comprises water and sand, with additives, such as acids, which are used to strip off drilling mud from the well bore, and biocides, to mitigate detrimental microbial bustle [220]. A fraction of this fluid remains within the coal seams after the completion of fracturing, which offers a reasonable chance for the introduction of the microbial consortium into the induced fracture networks. Enhanced permeability fracturing may help to develop microbial colonies in coal seams, particularly in coal matrix and pore networks, which can stimulate methane production. Furthermore, the bioavailability of organic matter in coal seams can be boosted by injecting chemicals to dissolve the coal matrix, such as hydrogen peroxide [221] or potassium permanganate [222]. However, these chemicals may often harm the microbial communities and decrease their activity. Any comprehensive utilization of this technique is lacking hitherto.

Research has shown that ME–CBM can significantly increase the amount of methane by 50 to 100% [5,215,218]. The selection of the microorganism is critical in ME–CBM recovery. Usually, methanogens that produce methane as a metabolic by-product are used. These microorganisms are naturally found within coalbeds; however, their numbers can be increased by injecting nutrients and other growth-promoting compounds [223]. Some of the most commonly used microorganisms in ME–CBM recovery include *Methanobacterium* sp., *Methanospirillum*, *Methanococcus*, *Methanobacterium*, *Methanosaeta thermophila*, *Methanothrix soehngenii*, and *Methanosarcina barkeri* [215]. Moreover, favorable environmental factors such as temperature, salinity, and pH levels also play essential roles in microbial growth [56,215]. Fuertez et al. [215], in their laboratory experiments, revealed that the feasible pH range for a microbe to grow and operate is between 4.2 to 6.8. In contrast, the optimum temperature for their efficiency ranges from 23 °C to 37 °C. On the other hand, a salt concentration between 3.7 mg/cm<sup>3</sup> and 9.0 mg/cm<sup>3</sup> is ideal for microbial functioning. Further, methane enhancement is increased by injecting water or CO<sub>2</sub> into coal beds, injection of surfactants to increase methane solubility, and applying electrical or thermal stimulation to release the methane. Surfactants can increase methane solubility, making it easier for the microorganisms to produce and release methane. Thermal stimulation is also an effective method for enhancing methane production. This involves heating the coal bed to temperatures between 70 and 150 °C, which can increase the activity of the methanogens and release methane from the coal. In conclusion, ME–CBM recovery promises to increase methane production from coal beds. Using microorganisms to stimulate the release of methane from the coal and methods such as water or carbon dioxide injection, surfactant application, and thermal stimulation to enhance methane production, it is possible to substantially improve the CBM recovery.

Although ME–CBM recovery is gaining attention in different coal basins nowadays, India is still looking for ways to successfully initiate it. Extensive biogeochemical investigations are required in India's productive coal basins to elucidate the methane's origin through primary/secondary microbial and/or thermogenic pathways. The Gondwana coal basins are generalized to contain late mature thermogenic gas due to their bituminous rank, although this may be imprecise, as Ghosh et al. [24] have already reported a fascinating finding regarding the secondary alteration of the primary thermogenic gas signatures in the Raniganj Basin. Thus, the microbes would have been introduced at the post-coalification stage in that case. Hydraulic fracturing is the principal CBM exploration method followed in this basin. So, if a microbial consortium can be introduced through the fracking liquid during this process, it may help augment the coal's surface area to favor microbial colonization. Additionally, the bioaugmentation process, as well as the injection of surfactants, nutrients, vitamins, trace metals, yeast extract, glycerol, and their mixtures, may help to enhance methane recovery from these coals. However, a potential risk assessment should be performed, and strategies should be developed to prevent the exposure of these synthetic communities to groundwater reservoirs before the application of these methods. The biogeochemical characteristics of the coal resources in other productive areas, such as the Jharia, Karanpura, and Bokaro coal fields, have been understudied until now, and the gas is generally designated as thermogenic. Thus, the feasibility of the ME–CBM recovery methods in these basins is still unknown. Additionally, the Tertiary coal and lignite fields are also devoid of any detailed gas geochemical investigations. Some sporadic information exists, but it can barely help to develop strategies for enhanced methane recovery. As already described, Dutta et al. [22] investigated the gas geochemical behavior of the Eocene Tharad lignites from the Sanchor Sub-Basin of Gujarat, India. The gas was primary microbial, and was mixed with the early mature thermogenic gas evolved from the hydrogen-rich biomolecules. In this case, biostimulation may be the ideal method to augment methane recovery. The nature and type of native microbial communities in these lignite seams, the formation temperature, the groundwater salinity, and the pore geometry of these lignites require thorough research. Only then should ME–CBM recovery strategies be developed, taking the risk assessment into consideration. Thus, in summary, the huge deposits of Indian coals and lignites require extensive biogeochemical, biological, and environmental investigations to construct any strategies for ME–CBM recovery.

#### 14. Concluding Remarks

Coal bed methane (CBM) is a naturally occurring gas in coal seams, and represents the chief resource for unconventional hydrocarbon energy in India hitherto. The CBM generates, through primary or secondary microbial methanogenesis and early and late mature thermogenic pathways, the degradation of organic matter. The primary microbial methanogenesis exclusively includes hydrogenotrophic and acetoclastic pathways. Several geological influences often lead to the mixing of microbial and thermogenic gases. The microbial methanogenic pathways, thermogenic degradation of organic matter, gas mixing, and hydrogeological conditions in coal seams are widely documented by the gas molecular ratio; stable carbon isotopic fingerprints of methane; carbon dioxide; the isotopic discrimination factor; the stable deuterium isotopic compositions of methane and coal bed formation water; and the stable oxygen isotopic signature of the co-produced water. The micropetrographic compositions, total organic carbon content, moisture content, ash yield, volatile matter yield, pore geometry of coals and lignites, coal rank, tectonic setting, geothermal gradient, and thermal stress from intrusive igneous bodies, among others, govern the generation, production, and storage of CBM.

Although the USA, Australia, and Canada are rapidly expanding their CBM industries, Southeast Asian countries, i.e., China and India, face numerous challenges in CBM exploration and development. A lack of proper mining technologies in unfavorable geological conditions, high production costs, geographic challenges, a dearth of proper strategies to develop CBM from deep coal seams, and market risk, among others, are hindering

China from following the trend of CBM exploration in developed countries. Furthermore, although having massive coal and lignite deposits to investigate these aspects, India's CBM exploration is still in its infancy. The production of CBM has not been reached, as was projected by the government of India. Plausible solutions, comprehensive and advanced investigations of the CBM behavior of deep-seated coal beds, proper drilling and fracturing techniques, pinnate horizontal well technology, reservoir simulations, environmental and economic risk assessment, etc., are required to escalate the development of the CBM industry, especially in India and China. Additionally, arranging special funding for the CBM industry, improving market security and relation, ensuring cooperation between the coal mining and CBM industries, increasing financial subsidies, and inviting investors to fund the ongoing and upcoming CBM projects should be utilized as ways to amplify the CBM exploration and development in Southeast Asia in the coming days. Moreover, besides its application as an alternative clean energy resource nowadays, CBM can be employed to generate hydrogen energy in the upcoming green and sustainable future. Hence, rapid CBM industry development is necessary and should be the primary focus of the upcoming research activities.

Recently, the government put forward policy guidelines for exploring CBM resources from several government agencies, namely, national oil companies, research institutes, and academic institutions, to develop the country's CBM resources. To produce coal bed methane (CBM) in India, the Government of India formulated a CBM policy in July 1997, wherein CBM, being a natural gas, was explored and exploited under the provisions of the Oil Fields (Regulation and Development) Act 1948 (ORD Act 1948) and the Petroleum and Natural Gas Rules 1959 (P&NG Rules 1959) administered by the Ministry of Petroleum and Natural Gas (MoP&NG). The government of India has approved the policy to permit the exploration and exploitation of unconventional hydrocarbons such as shale oil/gas, CBM, etc., under the existing production sharing contracts (PSCs), CBM contracts, and nomination fields to encourage the existing contractors in the licensed/leased area to unlock the potential of unconventional hydrocarbons in the existing acreages. The CBM industry in India may have enormous potential to become a vital energy resource in the future through improving our strategies and the economic conditions. The policies are modified annually by the Government of India to support the effective development of the CBM industry.

Although CBM has the potential to meet the world's renewable energy needs, it poses risks to the environment, infrastructure, ecosystem, and human health. Periodic methane outbursts, leaks, and explosions are linked to CBM extraction, and these events have an impact on the local ecosystem, infrastructure, agricultural land, environment, and public health. Many actions can be taken to reduce these hazards. These comprise installing ventilation systems to prevent gas accumulation, using sensors to assess methane levels, putting safety procedures in place, and training staff. Technologies such as directional drilling and hydraulic fracturing can further reduce the possibility of methane explosions and outbursts.

Moreover, ME–CBM recovery from Indian coal basins requires a long road prior to successful commercialization. The dearth of investigations and essential data restrict the researchers and engineers from developing any ME–CBM recovery strategies. Only two published reports on the Gondwana coal and Eocene lignites have revealed the biogeochemical characteristics of methane stored in these deposits. These investigations may shed light only on the microbe-induced recovery of methane. Additional widespread comprehensive research from scientific, technological, and environmental aspects is needed in all accessible coal and lignite fields of India to develop the ME–CBM recovery strategies efficaciously.

**Author Contributions:** Conceptualization, writing—original draft: T.A., S.G. and S.K.; writing—review and editing: A.K.V., S.D. and B.T.; supervision: A.K.V. All authors have read and agreed to the published version of the manuscript.

**Funding:** This investigation did not receive any funding.

**Data Availability Statement:** The data will be available on request.

**Acknowledgments:** The authors thank the learned Editor-in-Chief and three anonymous reviewers for their comments in improving the manuscript's quality. The authors would like to acknowledge Joan Esterle for arranging an occupational traineeship for Santanu Ghosh at the University of Queensland, Australia. The authors are grateful to Suzanne D. Golding and Kim A. Baublys, University of Queensland, Australia, for the compound-specific stable isotope analysis of the Raniganj CBM and production water samples.

**Conflicts of Interest:** The authors hereby declare that there is no conflict of interest or competing interest in the communication and publication of this article.

## References

1. Sinha, S.K.; Gupta, S.D. A geological model for enhanced coal bed methane (ECBM) recovery process: A case study from the Jharia coalfield region, India. *J. Pet. Sci. Eng.* **2021**, *201*, 108498. [CrossRef]
2. Ghosh, S.; Adsul, T.; Varma, A.K. Organic matter and mineralogical acumens in CO<sub>2</sub> sequestration. *Green Sustain. Process. Chem. Environ. Eng. Sci.* **2023**, 561–594. [CrossRef]
3. Khadse, A.; Qayyumi, M.; Mahajani, S.; Aghalayam, P. Underground coal gasification: A new clean coal utilization technique for India. *Energy* **2007**, *32*, 2061–2071. [CrossRef]
4. Prabu, V.; Mallick, N. Coalbed methane with CO<sub>2</sub> sequestration: An emerging clean coal technology in India. *Renew. Sustain. Energy Rev.* **2015**, *50*, 229–244. [CrossRef]
5. Park, S.Y.; Liang, Y. Biogenic methane production from coal: A review on recent research and development on microbially enhanced coalbed methane (MECBM). *Fuel* **2016**, *166*, 258–267. [CrossRef]
6. Taylor, G.H.; Teichmüller, M.; Davis, A.; Diessel, C.F.K.; Littke, R.; Robert, P. *Organic Petrology*; Gebrüder Borntraeger: Berlin, Germany, 1998; p. 704.
7. Wilcox, J. Introduction to Carbon Capture. In *Carbon Capture*; Springer: New York, NY, USA, 2012; pp. 1–34. [CrossRef]
8. BP PLC. *Statistical Review of World Energy 2021*; BP Energy Outlook 2021; BP PLC: London, UK, 2021; Volume 70, pp. 8–20.
9. Kumar, J.; Mendhe, V.A.; Kamble, A.D.; Bannerjee, M.; Mishra, S.; Singh, B.D.; Mishra, V.K.; Singh, P.K.; Singh, H. Coalbed methane reservoir characteristics of coal seams of south Karanpura coalfield, Jharkhand, India. *Int. J. Coal Geol.* **2018**, *196*, 185–200. [CrossRef]
10. Kumar, S.; Varma, A.K.; Mendhe, V.A.; Kumar, S.; Bhan, U. Geochemical and petrographical fingerprints of coal bed methane potential in the Son-valley Basin, India. *Arab. J. Geosci.* **2022**, *15*, 1705. [CrossRef]
11. DGH. *India's Hydrocarbon Outlook: 2016–17, A Report on Exploration & Production Activities*; The Directorate General of Hydrocarbon: New Delhi, India, 2017. Available online: <https://dghindia.gov.in/assets/downloads/ar/2016-17.pdf> (accessed on 6 March 2023).
12. MoPNG. *Indian Petroleum and Natural Gas Statistics*; Ministry of Petroleum and Natural Gas: New Delhi, India, 2017. Available online: <https://mopng.gov.in/en/petroleum-statistics/indian-png-statistics> (accessed on 6 March 2023).
13. General, D.; Gas, N. *Creation through a Government of India Resolution Dated to Promote Sound Management of the Oil and Natural Gas*; The Directorate General of Hydrocarbon: New Delhi, India, 2021. Available online: <https://dghindia.gov.in/> (accessed on 6 March 2023).
14. Gao, L.; Mastalerz, M.; Schimmelmann, A. The Origin of Coalbed Methane. In *Coal Bed Methane: From Prospect to Pipeline*; Elsevier Inc.: Amsterdam, The Netherlands, 2014; pp. 7–29. [CrossRef]
15. Golding, S.D.; Boreham, C.J.; Esterle, J.S. Stable isotope geochemistry of coal bed and shale gas and related production waters: A review. *Int. J. Coal Geol.* **2013**, *120*, 24–40. [CrossRef]
16. Hamilton, S.; Golding, S.; Baublys, K.; Esterle, J. Stable isotopic and molecular composition of desorbed coal seam gases from the Walloon Subgroup, eastern Surat Basin, Australia. *Int. J. Coal Geol.* **2014**, *122*, 21–36. [CrossRef]
17. Kinnon, E.; Golding, S.; Boreham, C.; Baublys, K.; Esterle, J. Stable isotope and water quality analysis of coal bed methane production waters and gases from the Bowen Basin, Australia. *Int. J. Coal Geol.* **2010**, *82*, 219–231. [CrossRef]
18. Vinson, D.S.; Blair, N.E.; Martini, A.M.; Larter, S.; Orem, W.H.; McIntosh, J.C. Microbial methane from in situ biodegradation of coal and shale: A review and reevaluation of hydrogen and carbon isotope signatures. *Chem. Geol.* **2017**, *453*, 128–145. [CrossRef]
19. Whiticar, M. Stable Isotope Geochemistry of Coals, Humic Kerogens and Related Natural Gases. *Int. J. Coal. Geol.* **1996**, *32*, 191–215. [CrossRef]
20. Whiticar, M.J. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chem. Geol.* **1999**, *161*, 291–314. [CrossRef]
21. Clayton, J. Geochemistry of coalbed gas—A review. *Int. J. Coal Geol.* **1998**, *35*, 159–173. [CrossRef]
22. Dutta, S.; Ghosh, S.; Varma, A.K. Methanogenesis in the Eocene Tharad lignite deposits of Sanchor Sub-Basin, Gujarat, India: Insights from gas molecular ratio and stable carbon isotopic compositions. *J. Nat. Gas Sci. Eng.* **2021**, *91*, 103970. [CrossRef]
23. Faiz, M.; Hendry, P. Significance of microbial activity in Australian coal bed methane reservoirs—A review. *Bull. Can. Pet. Geol.* **2006**, *54*, 261–272. [CrossRef]
24. Ghosh, S.; Golding, S.D.; Varma, A.K.; Baublys, K.A. Stable isotopic composition of coal bed gas and associated formation water samples from Raniganj Basin, West Bengal, India. *Int. J. Coal Geol.* **2018**, *191*, 1–6. [CrossRef]



25. Strapoć, D.; Mastalerz, M.; Dawson, K.; Macalady, J.; Callaghan, A.V.; Wawrik, B.; Turich, C.; Ashby, M. Biogeochemistry of Microbial Coal-Bed Methane. *Annu. Rev. Earth Planet. Sci.* **2011**, *39*, 617–656. [\[CrossRef\]](#)
26. Bernard, B.; Brooks, J.; Sackett, W. Natural gas seepage in the Gulf of Mexico. *Earth Planet. Sci. Lett.* **1976**, *31*, 48–54. [\[CrossRef\]](#)
27. Conrad, R. Quantification of methanogenic pathways using stable carbon isotopic signatures: A review and a proposal. *Org. Geochem.* **2005**, *36*, 739–752. [\[CrossRef\]](#)
28. Schoell, M. Multiple origins of methane in the Earth. *Chem. Geol.* **1988**, *71*, 1–10. [\[CrossRef\]](#)
29. Whiticar, M.; Faber, E.; Schoell, M. Biogenic methane formation in marine and freshwater environments: CO<sub>2</sub> reduction vs. acetate fermentation—Isotope evidence. *Geochim. Cosmochim. Acta* **1986**, *50*, 693–709. [\[CrossRef\]](#)
30. Pajdak, A.; Kudasik, M.; Skoczylas, N.; Wierzbicki, M.; Braga, L.T.P. Studies on the competitive sorption of CO<sub>2</sub> and CH<sub>4</sub> on hard coal. *Int. J. Greenh. Gas Control* **2019**, *90*, 102789. [\[CrossRef\]](#)
31. Rouquerol, J.; Avnir, D.; Fairbridge, C.W.; Everett, D.H.; Haynes, J.H.; Pernicone, N. Recommendations for the Characterization of Porous Solids. *Pure Appl. Chem.* **1994**, *66*, 1739–1758. [\[CrossRef\]](#)
32. Colosimo, F.; Thomas, R.; Lloyd, J.R.; Taylor, K.G.; Boothman, C.; Smith, A.D.; Lord, R.; Kalin, R.M. Biogenic methane in shale gas and coal bed methane: A review of current knowledge and gaps. *Int. J. Coal Geol.* **2016**, *165*, 106–120. [\[CrossRef\]](#)
33. Mastalerz, M.; Drobnia, A.; Strapoć, D.; Acosta, W.S.; Rupp, J. Variations in pore characteristics in high volatile bituminous coals: Implications for coal bed gas content. *Int. J. Coal Geol.* **2008**, *76*, 205–216. [\[CrossRef\]](#)
34. Moore, T.A. Coalbed methane: A review. *Int. J. Coal Geol.* **2012**, *101*, 36–81. [\[CrossRef\]](#)
35. Bustin, R.; Clarkson, C. Geological controls on coalbed methane reservoir capacity and gas content. *Int. J. Coal Geol.* **1998**, *38*, 3–26. [\[CrossRef\]](#)
36. Lamberson, R.M.B.M.N. Coalbed Methane Characteristics of Gates Formation Coals, Northeastern British Columbia: Effect of Maceral Composition. *Am. Assoc. Pet. Geol. Bull.* **1993**, *77*, 2062–2076. [\[CrossRef\]](#)
37. Laxminarayana, C.; Crosdale, P.J. Role of coal type and rank on methane sorption characteristics of Bowen Basin, Australia coals. *Int. J. Coal Geol.* **1999**, *40*, 309–325. [\[CrossRef\]](#)
38. Levine, J.R. Model study of the influence of matrix shrinkage on absolute permeability of coal bed reservoirs. *Geol. Soc. Spec. Publ.* **1996**, *109*, 197–212. [\[CrossRef\]](#)
39. Bustin, R.M.; Bustin, A.M.M.; Cui, A.; Ross, D.; Pathi, V.M. *Impact of Shale Properties on Pore Structure and Storage Characteristics. Presented at the SPE Shale Gas Production Conference, Fort Worth, TX, USA, 16 November 2008; Society of Petroleum Engineers (SPE): Richardson, TX, USA, 2008; pp. 32–59. [CrossRef]*
40. Chalmers, G.R.; Bustin, R.M.; Power, I.M. Characterization of gas shale pore systems by porosimetry, pycnometry, surface area, and field emission scanning electron microscopy/transmission electron microscopy image analyses: Examples from the Barnett, Woodford, Haynesville, Marcellus, and Doig units. *AAPG Bull.* **2012**, *96*, 1099–1119. [\[CrossRef\]](#)
41. Schlömer, S.; Krooss, B. Experimental characterisation of the hydrocarbon sealing efficiency of cap rocks. *Mar. Pet. Geol.* **1997**, *14*, 565–580. [\[CrossRef\]](#)
42. Javadpour, F. Nanopores and Apparent Permeability of Gas Flow in Mudrocks (Shales and Siltstone). *J. Can. Pet. Technol.* **2009**, *48*, 16–21. [\[CrossRef\]](#)
43. Chalmers, G.R.; Bustin, R.M. On the effects of petrographic composition on coalbed methane sorption. *Int. J. Coal Geol.* **2007**, *69*, 288–304. [\[CrossRef\]](#)
44. Chalmers, G.R.; Bustin, R.M. The organic matter distribution and methane capacity of the Lower Cretaceous strata of Northeastern British Columbia, Canada. *Int. J. Coal Geol.* **2007**, *70*, 223–239. [\[CrossRef\]](#)
45. Chalmers, G.; Bustin, R.M. Lower Cretaceous gas shales in northeastern British Columbia, Part I: Geological controls on methane sorption capacity. *Bull. Can. Pet. Geol.* **2008**, *56*, 1–21. [\[CrossRef\]](#)
46. Levy, J.H.; Day, S.J.; Killingley, J.S. Methane capacities of Bowen Basin coals related to coal properties. *Fuel* **1997**, *76*, 813–819. [\[CrossRef\]](#)
47. Raza, A.; Mahmoud, M.; Alafnan, S.; Arif, M.; Glatz, G. H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> Adsorption Potential of Kerogen as a Function of Pressure, Temperature, and Maturity. *Int. J. Mol. Sci.* **2022**, *23*, 12767. [\[CrossRef\]](#)
48. Gawor, M.; Skoczylas, N.; Pajdak, A.; Kudasik, M. Nonlinear and Linear Equation of Gas Diffusion in Coal—Theory and Applications. *Appl. Sci.* **2021**, *11*, 5130. [\[CrossRef\]](#)
49. Kudasik, M. Investigating Permeability of Coal Samples of Various Porosities under Stress Conditions. *Energies* **2019**, *12*, 762. [\[CrossRef\]](#)
50. Norbert, S.; Pajdak, A.; Koziel, K.; Braga, L.T.P. Methane Emission during Gas and Rock Outburst on the Basis of the Unipore Model. *Energies* **2019**, *12*, 1999. [\[CrossRef\]](#)
51. Wierzbicki, M.; Skoczylas, N.; Kudasik, M. The use of a unipore diffusion model to describe the kinetics of methane release from coal spoil in the longwall environment. *Stud. Geotech. Mech.* **2017**, *39*, 81–89. [\[CrossRef\]](#)
52. Formolo, M. The Microbial Production of Methane and Other Volatile Hydrocarbons. In *Handbook of Hydrocarbon and Lipid Microbiology*; Timmis, K.N., Ed.; Springer: Berlin/Heidelberg, Germany, 2010; pp. 113–126. [\[CrossRef\]](#)
53. Rotaru, A.-E.; Shrestha, P.M.; Liu, F.; Shrestha, M.; Shrestha, D.; Embree, M.; Zengler, K.; Wardman, C.; Nevin, K.P.; Lovley, D.R. A new model for electron flow during anaerobic digestion: Direct interspecies electron transfer to Methanosaeta for the reduction of carbon dioxide to methane. *Energy Environ. Sci.* **2013**, *7*, 408–415. [\[CrossRef\]](#)

54. Rotaru, A.-E.; Shrestha, P.M.; Liu, F.; Markovaite, B.; Chen, S.; Nevin, K.P.; Lovley, D.R. Direct Interspecies Electron Transfer between *Geobacter metallireducens* and *Methanosarcina barkeri*. *Appl. Environ. Microbiol.* **2014**, *80*, 4599–4605. [[CrossRef](#)] [[PubMed](#)]
55. Barnhart, E.P.; De León, K.B.; Ramsay, B.D.; Cunningham, A.B.; Fields, M.W. Investigation of coal-associated bacterial and archaeal populations from a diffusive microbial sampler (DMS). *Int. J. Coal Geol.* **2013**, *115*, 64–70. [[CrossRef](#)]
56. Green, M.S.; Flanagan, K.C.; Gilcrease, P.C. Characterization of a methanogenic consortium enriched from a coalbed methane well in the Powder River Basin, U.S.A. *Int. J. Coal Geol.* **2008**, *76*, 34–45. [[CrossRef](#)]
57. Jones, E.J.; Voytek, M.A.; Warwick, P.D.; Corum, M.D.; Cohn, A.; Bunnell, J.E.; Clark, A.C.; Orem, W.H. Bioassay for estimating the biogenic methane-generating potential of coal samples. *Int. J. Coal Geol.* **2008**, *76*, 138–150. [[CrossRef](#)]
58. Jones, E.J.P.; Voytek, M.A.; Corum, M.D.; Orem, W.H. Stimulation of Methane Generation from Nonproductive Coal by Addition of Nutrients or a Microbial Consortium. *Appl. Environ. Microbiol.* **2010**, *76*, 7013–7022. [[CrossRef](#)]
59. Li, D.; Hendry, P.; Faiz, M. A survey of the microbial populations in some Australian coalbed methane reservoirs. *Int. J. Coal Geol.* **2008**, *76*, 14–24. [[CrossRef](#)]
60. Strapoć, D.; Mastalerz, M.; Schimmelmann, A.; Drobniak, A.; Hedges, S. Variability of geochemical properties in a microbially dominated coalbed gas system from the eastern margin of the Illinois Basin, USA. *Int. J. Coal Geol.* **2008**, *76*, 98–110. [[CrossRef](#)]
61. An, D.; Caffrey, S.M.; Soh, J.; Agrawal, A.; Brown, D.; Budwill, K.; Dong, X.; Dunfield, P.F.; Foght, J.; Gieg, L.M.; et al. Metagenomics of Hydrocarbon Resource Environments Indicates Aerobic Taxa and Genes to be Unexpectedly Common. *Environ. Sci. Technol.* **2013**, *47*, 10708–10717. [[CrossRef](#)] [[PubMed](#)]
62. Meslé, M.; Dromart, G.; Oger, P. Microbial methanogenesis in subsurface oil and coal. *Res. Microbiol.* **2013**, *164*, 959–972. [[CrossRef](#)] [[PubMed](#)]
63. Conrad, R.; Bak, F.; Seitz, H.J.; Thebrath, B.; Mayer, H.P.; Schütz, H. Hydrogen turnover by psychrotrophic homoacetogenic and mesophilic methanogenic bacteria in anoxic paddy soil and lake sediment. *FEMS Microbiol. Lett.* **1989**, *62*, 285–293. [[CrossRef](#)]
64. Hausrath, E.M.; Liermann, L.J.; House, C.H.; Ferry, J.G.; Brantley, S.L. The effect of methanogen growth on mineral substrates: Will Ni markers of methanogen-based communities be detectable in the rock record? *Geobiology* **2007**, *5*, 49–61. [[CrossRef](#)]
65. Kida, K.; Shigematsu, T.; Kijima, J.; Numaguchi, M.; Mochinaga, Y.; Abe, N.; Morimura, S. Influence of Ni<sup>2+</sup> and Co<sup>2+</sup> on methanogenic activity and the amounts of coenzymes involved in methanogenesis. *J. Biosci. Bioeng.* **2001**, *91*, 590–595. [[CrossRef](#)]
66. Oremland, R.S.; Whiticar, M.J.; Strohmaier, F.E.; Kiene, R.P. Bacterial ethane formation from reduced, ethylated sulfur compounds in anoxic sediments. *Geochim. Cosmochim. Acta* **1988**, *52*, 1895–1904. [[CrossRef](#)]
67. Doerfert, S.N.; Reichlen, M.; Iyer, P.; Wang, M.; Ferry, J.G. *Methanobolus zinderi* sp. nov., a methylotrophic methanogen isolated from a deep subsurface coal seam. *Int. J. Syst. Evol. Microbiol.* **2009**, *59*, 1064–1069. [[CrossRef](#)]
68. Wawrik, B.; Mendivelso, M.; Parisi, V.A.; Suflita, J.M.; Davidova, I.A.; Marks, C.R.; Van Nostrand, J.D.; Liang, Y.; Zhou, J.; Huizinga, B.J.; et al. Field and laboratory studies on the bioconversion of coal to methane in the San Juan Basin. *FEMS Microbiol. Ecol.* **2012**, *81*, 26–42. [[CrossRef](#)]
69. Hornibrook, E.R.; Longstaffe, F.J.; Fyfe, W.S. Evolution of stable carbon isotope compositions for methane and carbon dioxide in freshwater wetlands and other anaerobic environments. *Geochim. Cosmochim. Acta* **2000**, *64*, 1013–1027. [[CrossRef](#)]
70. King, G.M. Utilization of hydrogen, acetate, and “noncompetitive”; substrates by methanogenic bacteria in marine sediments. *Geomicrobiol. J.* **1984**, *3*, 275–306. [[CrossRef](#)]
71. Oremland, R.S.; Polcin, S. Methanogenesis and Sulfate Reduction: Competitive and Noncompetitive Substrates in Estuarine Sediments. *Appl. Environ. Microbiol.* **1982**, *44*, 1270–1276. [[CrossRef](#)] [[PubMed](#)]
72. Head, I.M.; Gray, N.; Larter, S. Life in the slow lane; biogeochemistry of biodegraded petroleum containing reservoirs and implications for energy recovery and carbon management. *Front. Microbiol.* **2014**, *5*, 566. [[CrossRef](#)] [[PubMed](#)]
73. Martini, A.M.; Budai, J.M.; Walter, L.M.; Schoell, M. Microbial generation of economic accumulations of methane within a shallow organic-rich shale. *Nature* **1996**, *383*, 155–158. [[CrossRef](#)]
74. Martini, A.; Walter, L.; Budai, J.; Ku, T.; Kaiser, C.; Schoell, M. Genetic and temporal relations between formation waters and biogenic methane: Upper Devonian Antrim Shale, Michigan Basin, USA. *Geochim. Cosmochim. Acta* **1998**, *62*, 1699–1720. [[CrossRef](#)]
75. McIntosh, J.; Walter, L.; Martini, A. Pleistocene recharge to midcontinent basins: Effects on salinity structure and microbial gas generation. *Geochim. Cosmochim. Acta* **2002**, *66*, 1681–1700. [[CrossRef](#)]
76. McIntosh, J.C.; Warwick, P.D.; Martini, A.M.; Osborn, S.G. Coupled hydrology and biogeochemistry of Paleocene–Eocene coal beds, northern Gulf of Mexico. *GSA Bull.* **2010**, *122*, 1248–1264. [[CrossRef](#)]
77. Schlegel, M.E.; McIntosh, J.C.; Petsch, S.T.; Orem, W.H.; Jones, E.J.; Martini, A.M. Extent and limits of biodegradation by in situ methanogenic consortia in shale and formation fluids. *Appl. Geochem.* **2013**, *28*, 172–184. [[CrossRef](#)]
78. Oren, A. Thermodynamic limits to microbial life at high salt concentrations. *Environ. Microbiol.* **2010**, *13*, 1908–1923. [[CrossRef](#)]
79. Milkov, A.V. Worldwide distribution and significance of secondary microbial methane formed during petroleum biodegradation in conventional reservoirs. *Org. Geochem.* **2011**, *42*, 184–207. [[CrossRef](#)]
80. Scott, A.R.; Kaiser, W.R.; Ayers, W.B., Jr. Thermogenic and Secondary Biogenic Gases, San Juan Basin, Colorado and New Mexico—Implications for Coalbed Gas Producibility. *Am. Assoc. Pet. Geol. Bull.* **1994**, *78*, 1186–1209. [[CrossRef](#)]
81. Milkov, A.; Etiope, G. Geochemistry of Shale Gases from around the World. In Proceedings of the 80th EAGE Conference and Exhibition 2018, Copenhagen, Denmark, 11–14 June 2018; EAGE Publications BV: Kosterijland, Bunnik, 2018; pp. 1–5. [[CrossRef](#)]

82. Tissot, B.P.; Welte, D.H. Diagenesis, Catagenesis and Metagenesis of Organic Matter. In *Petroleum Formation and Occurrence*; Springer: Berlin/Heidelberg, Germany, 1984; pp. 69–73. [CrossRef]
83. Berner, U.; Faber, E. Maturity related mixing model for methane, ethane and propane, based on carbon isotopes. *Org. Geochem.* **1988**, *13*, 67–72. [CrossRef]
84. Tang, Y.; Jenden, P.D.; Teerman, S.C. Thermogenic methane formation in low-rank coals—published models and results from laboratory pyrolysis of lignite. In *Organic Geochemistry—Advances and Applications in the Natural Environment*; Manchester University Press: Manchester, UK, 1991; pp. 329–331.
85. Ayers, W.B. Coalbed gas systems, resources, and production and a review of contrasting cases from the San Juan and Powder River basins. *Am. Assoc. Pet. Geol. Bull.* **2002**, *86*, 1853–1890. [CrossRef]
86. Rice, D.D.; Law, B.E. Composition and Origins of Coalbed Gas. *Hydrocarb. Coal AAPG Stud. Geol.* **1993**, *38*, 159–184. [CrossRef]
87. Scott, A.R. Improving Coal Gas Recovery with Microbially Enhanced Coalbed Methane. In *Coalbed Methane: Scientific, Environmental and Economic Evaluation*; Mastalerz, M., Glikson, M., Golding, S.D., Eds.; Springer: Dordrecht, The Netherlands, 1999; pp. 89–110. [CrossRef]
88. Scott, A.R. Hydrogeologic factors affecting gas content distribution in coal beds. *Int. J. Coal Geol.* **2002**, *50*, 363–387. [CrossRef]
89. Chandra, D.; Chakrabarti, N. Coalification trends in Indian coals. *Int. J. Coal Geol.* **1989**, *13*, 413–435. [CrossRef]
90. Misra, S.; Varma, A.K.; Hazra, B.; Biswas, S.; Samad, S.K. The influence of the thermal aureole asymmetry on hydrocarbon generative potential of coal beds: Insights from Raniganj Basin, West Bengal, India. *Int. J. Coal Geol.* **2019**, *206*, 91–105. [CrossRef]
91. Meissner, F.F. Cretaceous and lower Tertiary coals as sources for gas accumulations in the Rocky Mountain area. In *Hydrocarbon Source Rocks of the Greater Rocky Mountain Region*; Woodward, J., Meissner, F.F., Clayton, J.L., Eds.; Rocky Mountain Association of Geologists (RMAG): Denver, CO, USA, 1984; pp. 401–431.
92. Hunt, J.M. *Petroleum Geochemistry and Geology*, 2nd ed.; W.H. Free. Co.: New York, NY, USA, 1996; p. 332.
93. Zumberge, J.; Ferworn, K.; Brown, S. Isotopic reversal (‘rollover’) in shale gases produced from the Mississippian Barnett and Fayetteville formations. *Mar. Pet. Geol.* **2012**, *31*, 43–52. [CrossRef]
94. Bernard, B.B.; Brooks, J.M.; Sackett, W.M. Light hydrocarbons in recent Texas continental shelf and slope sediments. *J. Geophys. Res. Atmos.* **1978**, *83*, 4053–4061. [CrossRef]
95. Faber, W.S.E. Geochemical Surface Exploration for Hydrocarbons in North Sea. *Am. Assoc. Pet. Geol. Bull.* **1984**, *68*, 363–386. [CrossRef]
96. Smith, R.J.P.J.W. Microbial Origin of Australian Coalbed Methane. *AAPG Bull.* **1996**, *80*, 891–897. [CrossRef]
97. Dutta, S.; Mathews, R.P.; Singh, B.D.; Tripathi, S.M.; Singh, A.; Saraswati, P.K.; Banerjee, S.; Mann, U. Petrology, palynology and organic geochemistry of Eocene lignite of Matanomadh, Kutch Basin, western India: Implications to depositional environment and hydrocarbon source potential. *Int. J. Coal Geol.* **2011**, *85*, 91–102. [CrossRef]
98. Flores, R.M.; Rice, C.A.; Stricker, G.D.; Warden, A.; Ellis, M.S. Methanogenic pathways of coal-bed gas in the Powder River Basin, United States: The geologic factor. *Int. J. Coal Geol.* **2008**, *76*, 52–75. [CrossRef]
99. Osborn, S.G.; McIntosh, J.C. Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin. *Appl. Geochem.* **2010**, *25*, 456–471. [CrossRef]
100. Chen, J.; Sun, Y.; Deng, C. The limit of gas generation potential of highly to overmature humic coals: Theoretical consideration. In Proceedings of the AAPG Hedberg Research Conference—Natural Gas Geochemistry: Recent Developments, Applications and Technologies, Beijing, China, 9–12 May 2011. Available online: [https://www.searchanddiscovery.com/pdfz/abstracts/pdf/2011/hedberg-beijing/abstracts/ndx\\_chen02.pdf.html](https://www.searchanddiscovery.com/pdfz/abstracts/pdf/2011/hedberg-beijing/abstracts/ndx_chen02.pdf.html) (accessed on 6 March 2023).
101. Hinrichs, K.-U.; Hayes, J.M.; Bach, W.; Spivack, A.J.; Hmelo, L.R.; Holm, N.G.; Johnson, C.G.; Sylva, S.P. Biological formation of ethane and propane in the deep marine subsurface. *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 14684–14689. [CrossRef]
102. Sassen, R.; Curiale, J.A. Microbial methane and ethane from gas hydrate nodules of the Makassar Strait, Indonesia. *Org. Geochem.* **2006**, *37*, 977–980. [CrossRef]
103. Head, I.M.; Jones, D.M.; Larter, S.R. Biological activity in the deep subsurface and the origin of heavy oil. *Nature* **2003**, *426*, 344–352. [CrossRef]
104. Pallasser, R. Recognising biodegradation in gas/oil accumulations through the  $\delta^{13}\text{C}$  compositions of gas components. *Org. Geochem.* **2000**, *31*, 1363–1373. [CrossRef]
105. Lorant, F.; Prinzhofer, A.; Behar, F.; Huc, A.-Y. Carbon isotopic and molecular constraints on the formation and the expulsion of thermogenic hydrocarbon gases. *Chem. Geol.* **1998**, *147*, 249–264. [CrossRef]
106. Prinzhofer, A.A.; Huc, A.Y. Genetic and post-genetic molecular and isotopic fractionations in natural gases. *Chem. Geol.* **1995**, *126*, 281–290. [CrossRef]
107. Xia, X.; Tang, Y. Isotope fractionation of methane during natural gas flow with coupled diffusion and adsorption/desorption. *Geochim. Cosmochim. Acta* **2012**, *77*, 489–503. [CrossRef]
108. Blair, N.E.; Martens, C.S.; Marais, D.J.D. Natural Abundances of Carbon Isotopes in Acetate from a Coastal Marine Sediment. *Science* **1987**, *236*, 66–68. [CrossRef] [PubMed]
109. Penger, J.; Conrad, R.; Blaser, M. Stable Carbon Isotope Fractionation by Methylophilic Methanogenic Archaea. *Appl. Environ. Microbiol.* **2012**, *78*, 7596–7602. [CrossRef] [PubMed]
110. Sackett, W.M. Carbon and hydrogen isotope effects during the thermocatalytic production of hydrocarbons in laboratory simulation experiments. *Geochim. Cosmochim. Acta* **1978**, *42*, 571–580. [CrossRef]



111. Schoell, M. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochim. Cosmochim. Acta* **1980**, *44*, 649–661. [\[CrossRef\]](#)
112. Boreham, C.; Golding, S.; Glikson, M. Factors controlling the origin of gas in Australian Bowen Basin coals. *Org. Geochem.* **1998**, *29*, 347–362. [\[CrossRef\]](#)
113. Golding, S.D.; Baublys, K.A.; Glikson, M.; Uysal, I.T.; Boreham, C.J. Source and Timing of Coal Seam Gas Generation in Bowen Basin Coals. In *Coalbed Methane: Scientific, Environmental and Economic Evaluation*; Springer: Dordrecht, The Netherlands, 1999; pp. 257–269. [\[CrossRef\]](#)
114. Frape, S.K.; Fritz, P. The chemistry and isotopic composition of saline groundwaters from the Sudbury Basin, Ontario. *Can. J. Earth Sci.* **1982**, *19*, 645–661. [\[CrossRef\]](#)
115. Xia, X.; Chen, J.; Braun, R.; Tang, Y. Isotopic reversals with respect to maturity trends due to mixing of primary and secondary products in source rocks. *Chem. Geol.* **2012**, *339*, 205–212. [\[CrossRef\]](#)
116. Schlegel, M.E.; McIntosh, J.C.; Bates, B.L.; Kirk, M.F.; Martini, A.M. Comparison of fluid geochemistry and microbiology of multiple organic-rich reservoirs in the Illinois Basin, USA: Evidence for controls on methanogenesis and microbial transport. *Geochim. Cosmochim. Acta* **2011**, *75*, 1903–1919. [\[CrossRef\]](#)
117. Waldron, S.; Watson-Craik, I.A.; Hall, A.J.; Fallick, A.E. The carbon and hydrogen stable isotope composition of bacteriogenic methane: A laboratory study using a landfill inoculum. *Geomicrobiol. J.* **1998**, *15*, 157–169. [\[CrossRef\]](#)
118. Waldron, S.; Lansdown, J.; Scott, E.; Fallick, A.; Hall, A. The global influence of the hydrogen isotope composition of water on that of bacteriogenic methane from shallow freshwater environments. *Geochim. Cosmochim. Acta* **1999**, *63*, 2237–2245. [\[CrossRef\]](#)
119. Wycherley, H.; Fleet, A.; Shaw, H. Some observations on the origins of large volumes of carbon dioxide accumulations in sedimentary basins. *Mar. Pet. Geol.* **1999**, *16*, 489–494. [\[CrossRef\]](#)
120. Boreham, C.; Golding, S.D.; Glikson, M. Reply to Comment of Smith and Pallasser on “Factors controlling the origin of gas in Australian Bowen Basin coals”. *Org. Geochem.* **2001**, *32*, 207–210. [\[CrossRef\]](#)
121. Jenden, P.; Kaplan, I. Comparison of microbial\* gases from the Middle America Trench and Scripps Submarine Canyon: Implications for the origin of natural gas. *Appl. Geochem.* **1986**, *1*, 631–646. [\[CrossRef\]](#)
122. Cartwright, I.; Weaver, T.; Tweed, S.; Ahearne, D.; Cooper, M.; Czapnik, K.; Tranter, J. Stable isotope geochemistry of cold CO<sub>2</sub>-bearing mineral spring waters, Daylesford, Victoria, Australia: Sources of gas and water and links with waning volcanism. *Chem. Geol.* **2002**, *185*, 71–91. [\[CrossRef\]](#)
123. Kloppmann, W.; Girard, J.-P.; Négrel, P. Exotic stable isotope compositions of saline waters and brines from the crystalline basement. *Chem. Geol.* **2002**, *184*, 49–70. [\[CrossRef\]](#)
124. Van Voast, W.A. Geochemical signature of formation waters associated with coalbed methane. *Am. Assoc. Pet. Geol. Bull.* **2003**, *87*, 667–676. [\[CrossRef\]](#)
125. Bates, B.L.; McIntosh, J.C.; Lohse, K.A.; Brooks, P.D. Influence of groundwater flowpaths, residence times and nutrients on the extent of microbial methanogenesis in coal beds: Powder River Basin, USA. *Chem. Geol.* **2011**, *284*, 45–61. [\[CrossRef\]](#)
126. Cheung, K.; Sanei, H.; Klassen, P.; Mayer, B.; Goodarzi, F. Produced fluids and shallow groundwater in coalbed methane (CBM) producing regions of Alberta, Canada: Trace element and rare earth element geochemistry. *Int. J. Coal Geol.* **2009**, *77*, 338–349. [\[CrossRef\]](#)
127. Rice, C.; Flores, R.; Stricker, G.; Ellis, M. Chemical and stable isotopic evidence for water/rock interaction and biogenic origin of coalbed methane, Fort Union Formation, Powder River Basin, Wyoming and Montana, U.S.A. *Int. J. Coal Geol.* **2008**, *76*, 76–85. [\[CrossRef\]](#)
128. Rice, G.E.C.D.D. Generation, Accumulation, and Resource Potential of Biogenic Gas. *Am. Assoc. Pet. Geol. Bull.* **1981**, *65*, 5–25. [\[CrossRef\]](#)
129. Varma, A.K.; Biswas, S.; Patil, D.J.; Mani, D.; Misra, S.; Hazra, B. Significance of lithotypes for hydrocarbon generation and storage. *Fuel* **2019**, *235*, 396–405. [\[CrossRef\]](#)
130. Mardon, S.M.; Eble, C.F.; Hower, J.C.; Takacs, K.; Mastalerz, M.; Bustin, R.M. Organic petrology, geochemistry, gas content and gas composition of Middle Pennsylvanian age coal beds in the Eastern Interior (Illinois) Basin: Implications for CBM development and carbon sequestration. *Int. J. Coal Geol.* **2014**, *127*, 56–74. [\[CrossRef\]](#)
131. Crosdale, P.J.; Beamish, B.; Valix, M. Coalbed methane sorption related to coal composition. *Int. J. Coal Geol.* **1998**, *35*, 147–158. [\[CrossRef\]](#)
132. Clarkson, C.; Bustin, R. The effect of pore structure and gas pressure upon the transport properties of coal: A laboratory and modeling study. 1. Isotherms and pore volume distributions. *Fuel* **1999**, *78*, 1333–1344. [\[CrossRef\]](#)
133. Mastalerz, M.; Gluskoter, H.; Rupp, J. Carbon dioxide and methane sorption in high volatile bituminous coals from Indiana, USA. *Int. J. Coal Geol.* **2004**, *60*, 43–55. [\[CrossRef\]](#)
134. Hildenbrand, A.; Krooss, B.; Busch, A.; Gaschnitz, R. Evolution of methane sorption capacity of coal seams as a function of burial history—A case study from the Campine Basin, NE Belgium. *Int. J. Coal Geol.* **2006**, *66*, 179–203. [\[CrossRef\]](#)
135. Keshavarz, A.; Sakurovs, R.; Grigore, M.; Sayyafzadeh, M. Effect of maceral composition and coal rank on gas diffusion in Australian coals. *Int. J. Coal Geol.* **2017**, *173*, 65–75. [\[CrossRef\]](#)
136. Crosdale, P.J.; Beamish, B.B. Methane diffusivity at South Bulli (NSW) and Central (QLD) collieries in relation to coal maceral composition. In *International Symposium-Cum-Workshop on Management and Control of High Gas Emission and Outbursts in Underground Coal Mines*; Lama, R.D., Ed.; National Organising Committee of the Symposium: Wollongong, Australia, 1995; pp. 363–367.

137. Smith, D.M.; Williams, F.L. Diffusion models for gas production from coal: Determination of diffusion parameters. *Fuel* **1984**, *63*, 256–261. [\[CrossRef\]](#)
138. Smith, D.M.; Williams, F.L. Diffusion models for gas production from coals: Application to methane content determination. *Fuel* **1984**, *63*, 251–255. [\[CrossRef\]](#)
139. Unsworth, J.F.; Fowler, C.S.; Jones, L.F. Moisture in coal: 2. Maceral effects on pore structure. *Fuel* **1989**, *68*, 18–26. [\[CrossRef\]](#)
140. Karacan, C. Heterogeneous Sorption and Swelling in a Confined and Stressed Coal during CO<sub>2</sub> Injection. *Energy Fuels* **2003**, *17*, 1595–1608. [\[CrossRef\]](#)
141. Mastalerz, M.; Schimmelmann, A.; Lis, G.; Drobnik, A.; Stankiewicz, A. Influence of maceral composition on geochemical characteristics of immature shale kerogen: Insight from density fraction analysis. *Int. J. Coal Geol.* **2012**, *103*, 60–69. [\[CrossRef\]](#)
142. Staib, G.; Sakurovs, R.; Gray, E.M.A. A pressure and concentration dependence of CO<sub>2</sub> diffusion in two Australian bituminous coals. *Int. J. Coal Geol.* **2013**, *116–117*, 106–116. [\[CrossRef\]](#)
143. Yao, G.X.; Wang, J.M. A glimpse of coalbed methane production overseas and reflections on accelerating coalbed methane development in China. *Sino-Glob. Energy* **2010**, *15*, 25–33.
144. Yun, J.; Xu, F.; Liu, L.; Zhong, N.; Wu, X. New progress and future prospects of CBM exploration and development in China. *Int. J. Min. Sci. Technol.* **2012**, *22*, 363–369. [\[CrossRef\]](#)
145. Cohen, D.M. Coalbed methane expansion stalls. *World Oil* **2007**, *228*, 91–93.
146. Cohen, D.M. US coalbed methane takes a dive. *World Oil* **2009**, *230*, 71–72.
147. Juvkam, H.C. US gas: Demand, supply and reserves. *World Oil* **2009**, *230*, 81–84.
148. Tao, S.; Chen, S.; Pan, Z. Current status, challenges, and policy suggestions for coalbed methane industry development in China: A review. *Energy Sci. Eng.* **2019**, *7*, 1059–1074. [\[CrossRef\]](#)
149. Kim, A.G. *Estimating Methane Content of Bituminous Coalbeds from Adsorption Data*; RI 8245; U.S. Department of the Interior, Bureau of Mines: Pittsburgh, PA, USA, 1977; pp. 1–22.
150. Mukherjee, A.; Alam, M.; Ghose, S. Gondwana coals of Bhutan Himalaya—Occurrence, properties and petrographic characteristics. *Int. J. Coal Geol.* **1988**, *9*, 287–304. [\[CrossRef\]](#)
151. Ghosh, R. The variation in thickness and composition of coal seams and its use in interpretation of palaeocurrents—A case study from the Raniganj Coalfield, West Bengal, India. *Int. J. Coal Geol.* **1987**, *9*, 209–220. [\[CrossRef\]](#)
152. Chatterjee, R.; Paul, S. Classification of coal seams for coal bed methane exploitation in central part of Jharia coalfield, India—A statistical approach. *Fuel* **2013**, *111*, 20–29. [\[CrossRef\]](#)
153. Mazumder, S.; Wolf, K.-H. An Overview of the Potentials and Prospects of Coalbed Methane Exploration and Exploitation in the Permo-Carboniferous Coal Measures of The Barakar Formation, Jharia Basin, India. *Geol. Belg.* **2004**, *7*, 147–156.
154. Datta, G.C.; Ghosh, T.K.; Basumatary, J.K. Evaluation of coal bed methane potential of the eastern part of North Karanpura CBM Block, Jharkhand, India. In Proceedings of the 9th Biennial International Conference & Exposition on Petroleum Geophysics, Hyderabad, India, 16–18 February 2012; pp. 1–5.
155. Iyengar, R.K.; Haque, R. Gasification of high-ash Indian coals for power generation. *Fuel Process. Technol.* **1991**, *27*, 247–262. [\[CrossRef\]](#)
156. Singh, R.; Singh, M.P.; Chandra, D. Occurrence, distribution and probable source of the trace elements in ghugus coals, wardha valley, districts chandrapur and yeotmal, maharashtra, India. *Int. J. Coal Geol.* **1983**, *2*, 371–381. [\[CrossRef\]](#)
157. Barooah, P.K.; Baruah, M.K. Sulphur in Assam coal. *Fuel Process. Technol.* **1996**, *46*, 83–97. [\[CrossRef\]](#)
158. Resources, N.E. Government of India Geological Survey of India (GSI): Indian Coal and Lignite Resources-2022. MISSION-IIB. 2022; pp. 25–28. Available online: [https://www.gsi.gov.in/webcenter/portal/OCBIS/pages\\_pageQuickLinks/pageMissionIIB](https://www.gsi.gov.in/webcenter/portal/OCBIS/pages_pageQuickLinks/pageMissionIIB) (accessed on 6 March 2023).
159. Zhou, Z.; Ballentine, C.J.; Kipfer, R.; Schoell, M.; Thibodeaux, S. Noble gas tracing of groundwater/coalbed methane interaction in the San Juan Basin, USA. *Geochim. Cosmochim. Acta* **2005**, *69*, 5413–5428. [\[CrossRef\]](#)
160. Ulrich, G.; Bower, S. Active methanogenesis and acetate utilization in Powder River Basin coals, United States. *Int. J. Coal Geol.* **2008**, *76*, 25–33. [\[CrossRef\]](#)
161. Ayers, W.B., Jr.; Ambrose, W.A.; Kaiser, W.R.; Laubach, S.E.; Scott, A.R.; Yeh, J.S.; Tremain, C.M.; Whitehead, N.H., III. Geologic and hydrologic characterization of coalbed methane reservoirs, Fruitland Formation, San Juan basin, Colorado and New Mexico. *AAPG Bull.* **1991**, *75*, 535.
162. Scott, A.R.; Kaiser, W.R.; Ayers, W.B., Jr. Composition, distribution, and origin of Fruitland and Pictured Cliffs Sandstone gases, San Juan basin, Colorado and New Mexico, in Coalbed Methane of Western North America. In *Rocky Mountain Association of Geologists (RMAG)*; Schwochow, S., Ed.; Guidebook: Denver, CO, USA, 1991; pp. 93–108. Available online: [https://archives.datapages.com/data/rmag/CBM\\_WNA\\_91/scott\\_b.htm](https://archives.datapages.com/data/rmag/CBM_WNA_91/scott_b.htm) (accessed on 6 March 2023).
163. Rice, D.D.; Clayton, J.L.; Pawlewicz, M.J. Characterization of coal-derived hydrocarbons and source-rock potential of coal beds, San Juan Basin, New Mexico and Colorado, U.S.A. *Int. J. Coal Geol.* **1989**, *13*, 597–626. [\[CrossRef\]](#)
164. Warwick, P.D.; Breland, F.C.; Hackley, P.C. Biogenic origin of coalbed gas in the northern Gulf of Mexico Coastal Plain, U.S.A. *Int. J. Coal Geol.* **2008**, *76*, 119–137. [\[CrossRef\]](#)
165. Clayton, C. Carbon isotope fractionation during natural gas generation from kerogen. *Mar. Pet. Geol.* **1991**, *8*, 232–240. [\[CrossRef\]](#)
166. Faiz, M.; Saghaei, A.; Sherwood, N.; Wang, I. The influence of petrological properties and burial history on coal seam methane reservoir characterisation, Sydney Basin, Australia. *Int. J. Coal Geol.* **2007**, *70*, 193–208. [\[CrossRef\]](#)



167. Faiz, M.; Hutton, A. Coal Seam Gas in the Southern Sydney Basin, New South Wales. *APPEA J.* **1997**, *37*, 415–428. [\[CrossRef\]](#)
168. Faiz, M.; Stalker, L.; Sherwood, N.; Saghafi, A.; Wold, M.; Barclay, S.; Choudhury, J.; Barker, W.; Wang, I. Bio-Enhancement of Coal Bed Methane Resources in the Southern Sydney Basin. *APPEA J.* **2003**, *43*, 595–610. [\[CrossRef\]](#)
169. Papendick, S.L.; Downs, K.R.; Vo, K.D.; Hamilton, S.K.; Dawson, G.; Golding, S.D.; Gilcrease, P.C. Biogenic methane potential for Surat Basin, Queensland coal seams. *Int. J. Coal Geol.* **2011**, *88*, 123–134. [\[CrossRef\]](#)
170. Draper, J.J.; Boreham, C. Geological Controls on Exploitable Coal Seam Gas Distribution in Queensland. *APPEA J.* **2006**, *46*, 343–366. [\[CrossRef\]](#)
171. Zhang, S.; Tang, S.; Li, Z.; Guo, Q.; Pan, Z. Stable isotope characteristics of CBM co-produced water and implications for CBM development: The example of the Shizhuangnan block in the southern Qinshui Basin, China. *J. Nat. Gas Sci. Eng.* **2015**, *27*, 1400–1411. [\[CrossRef\]](#)
172. Chen, B.; Stuart, F.M.; Xu, S.; Gyore, D.; Liu, C. Evolution of coal-bed methane in Southeast Qinshui Basin, China: Insights from stable and noble gas isotopes. *Chem. Geol.* **2019**, *529*, 119298. [\[CrossRef\]](#)
173. Yang, Q.; Tang, D.Z. Effect of coal metamorphism on methane content and permeability of coal in North China. *Earth Sci. China Univ. Geosci.* **2000**, *25*, 273–278.
174. Wei, Q.; Hu, B.; Fang, H.; Chen, S.; Feng, S.; Wu, C.; Zheng, C. Composition, Origin, and Accumulation Model of Coalbed Methane in the Panxie Coal Mining Area, Anhui Province, China. *ACS Omega* **2022**, *7*, 17929–17940. [\[CrossRef\]](#) [\[PubMed\]](#)
175. Li, Y.; Tang, D.; Fang, Y.; Xu, H.; Meng, Y. Distribution of stable carbon isotope in coalbed methane from the east margin of Ordos Basin. *Sci. China Earth Sci.* **2014**, *57*, 1741–1748. [\[CrossRef\]](#)
176. Mendhe, V.A.; Mishra, S.; Varma, A.K.; Singh, A.P. Coalbed methane-produced water quality and its management options in Raniganj Basin, West Bengal, India. *Appl. Water Sci.* **2015**, *7*, 1359–1367. [\[CrossRef\]](#)
177. Singh, A.P.; Gupta, S.K.; Mendhe, V.A.; Mishra, S. Variations in hydro-chemical properties and source insights of coalbed methane produced water of Raniganj Coalfield, Jharkhand, India. *J. Nat. Gas Sci. Eng.* **2018**, *51*, 233–250. [\[CrossRef\]](#)
178. ISO 11760; Classification of Coals. International Organization for Standardization: Geneva, Switzerland, 2018; pp. 1–7. Available online: <https://www.iso.org/standard/75705.html> (accessed on 6 March 2023).
179. Chakraborty, A.; Tiwari, P.K.; Singh, A.K. Coalbed methane exploration in a tertiary lignite basin, North Gujarat, India. In Proceedings of the 2nd South Asian Geosciences Conference and Exhibition, GEOIndia, Delhi, India, 12–14 January 2011; p. 509.
180. Fabiańska, M.J.; Kurkiewicz, S. Biomarkers, aromatic hydrocarbons and polar compounds in the Neogene lignites and gangue sediments of the Konin and Turoszów Brown Coal Basins (Poland). *Int. J. Coal Geol.* **2013**, *107*, 24–44. [\[CrossRef\]](#)
181. Behar, F.; Lorant, F.; Lewan, M. Role of NSO compounds during primary cracking of a Type II kerogen and a Type III lignite. *Org. Geochem.* **2008**, *39*, 1–22. [\[CrossRef\]](#)
182. Papanicolaou, C.; Dehmer, J.; Fowler, M. Petrological and organic geochemical characteristics of coal samples from Florina, Lava, Moschopotamos and Kalavryta coal fields, Greece. *Int. J. Coal Geol.* **2000**, *44*, 267–292. [\[CrossRef\]](#)
183. Peakman, T.; Haven, H.; Rechka, J.; De Leeuw, J.; Maxwell, J. Occurrence of (20R)- and (20S)- $\Delta^8(14)$  and  $\Delta^{14} 5\alpha(H)$ -sterenes and the origin of  $5\alpha(H)$ ,  $14\beta(H)$ ,  $17\beta(H)$ -steranes in an immature sediment. *Geochim. Cosmochim. Acta* **1989**, *53*, 2001–2009. [\[CrossRef\]](#)
184. Stefanova, M.; Magnier, C.; Velinova, D. Biomarker assemblage of some Miocene-aged Bulgarian lignite lithotypes. *Org. Geochem.* **1995**, *23*, 1067–1084. [\[CrossRef\]](#)
185. Stefanova, M.; Oros, D.R.; Otto, A.; Simoneit, B.R. Polar aromatic biomarkers in the Miocene Maritza-East lignite, Bulgaria. *Org. Geochem.* **2002**, *33*, 1079–1091. [\[CrossRef\]](#)
186. Stefanova, M.; Ivanov, D.A.; Utescher, T. Geochemical appraisal of palaeovegetation and climate oscillation in the Late Miocene of Western Bulgaria. *Org. Geochem.* **2011**, *42*, 1363–1374. [\[CrossRef\]](#)
187. Barker, C.E.; Pawlewicz, M.J. Calculation of Vitrinite Reflectance from Thermal Histories and Peak Temperatures—A Comparison of Methods. In *Vitrinite Reflectance as a Maturity Parameter. Applications and Limitations*; ACS Symposium Series; Mukhopadhyay, P.K., Dow, W.G., Eds.; ACS: Washington, DC, USA, 1994; Volume 570, pp. 216–229.
188. Paul, S.; Chatterjee, R. Determination of in-situ stress direction from cleat orientation mapping for coal bed methane exploration in south-eastern part of Jharia coalfield, India. *Int. J. Coal Geol.* **2011**, *87*, 87–96. [\[CrossRef\]](#)
189. Laxminarayana, C.; Crosdale, P.J.; Power, C.L. Controls on Methane Sorption Capacity of Indian Coals. *AAPG Bull.* **2002**, *86*, 201–212. [\[CrossRef\]](#)
190. Fengyin, X.; Shuguang, L.; Degui, W. Development trend of CBM exploration and development theories and technologies. *China Pet. Explor.* **2008**, *13*, 1.
191. Kędzior, S.; Dreger, M. Methane occurrence, emissions and hazards in the Upper Silesian Coal. *Int. J. Coal Geol.* **2019**, *211*, 103226. [\[CrossRef\]](#)
192. Cheng, J.; Mei, J.; Peng, S.; Qi, C.; Shi, Y. Comprehensive consultation model for explosion risk in mine atmosphere. *Saf. Sci.* **2019**, *120*, 798–812. [\[CrossRef\]](#)
193. Kumar, N.; Gupta, H. Methane: Risk assessment, environmental and health hazard. In *Hazardous Gases, Risk Assessment on the Environment and Human Health*, 1st ed.; Singh, J., Kaushik, R.D., Chawla, M., Eds.; Academic Press: Poole, UK, 2021; pp. 225–238. [\[CrossRef\]](#)

194. Cheng, J. *Explosions in Underground Coal Mines. Risk Assessment and Control*, 1st ed.; Springer: Cham, Switzerland, 2018; p. 208. [\[CrossRef\]](#)
195. CDC (Centre of Disease Control). *Morbidity & Mortality Weekly Report*; CDC: Atlanta, GA, USA, 2009; Volume 57, pp. 1379–1383.
196. Huang, Q.; Honaker, R. Recent trends in rock dust modifications for improved dispersion and coal dust explosion mitigation. *J. Loss Prev. Process. Ind.* **2016**, *41*, 121–128. [\[CrossRef\]](#)
197. Beamish, B.; Crosdale, P.J. Instantaneous outbursts in underground coal mines: An overview and association with coal type. *Int. J. Coal Geol.* **1998**, *35*, 27–55. [\[CrossRef\]](#)
198. Xu, L.; Jiang, C. Initial desorption characterization of methane and carbon dioxide in coal and its influence on coal and gas outburst risk. *Fuel* **2017**, *203*, 700–706. [\[CrossRef\]](#)
199. Mar, K.A.; Unger, C.; Walderdorff, L.; Butler, T. Beyond CO<sub>2</sub> equivalence: The impacts of methane on climate, ecosystems, and health. *Environ. Sci. Policy* **2022**, *134*, 127–136. [\[CrossRef\]](#)
200. Cheng, J.; Wang, Y.; Zhao, G.; Zheng, W.; Wang, H.; Lu, W.; Yang, H.; Wu, Y.; Wu, Y.; Sa, Z.; et al. Performance of New Inorganic Retarding Sealing Material for Gas Drainage Boreholes. *Min. Met. Explor.* **2022**, *39*, 1171–1187. [\[CrossRef\]](#)
201. Marek, U. Monitoring of methane and rockburst hazards as a condition of safe coal exploitation in the mines of Kompania Weglowa SA. *Procedia Earth Planet. Sci.* **2009**, *1*, 54–59. [\[CrossRef\]](#)
202. Zhang, D.; Wang, X. Mechanism of production increasing of coalbed gas for the pinnate horizontal well and sensitivity effect of parameters on gas production. *Chin. Sci. Bull.* **2005**, *50*, 163–170. [\[CrossRef\]](#)
203. ESMAP (Energy Sector Management Assistance Program). *A Strategy for Coal Bed Methane (CBM) and Coal Mine Methane (CMM) Development and Utilization in China*; World Bank: Washington, DC, USA, 2007; pp. 1–109.
204. Panwar, D.S.; Chaurasia, R.C.; Saxena, V.K.; Singh, A.K. Modeling and Forecasting of Coal Bed Methane Reservoir from Raniganj Coalfield, India. *Methane* **2022**, *1*, 229–242. [\[CrossRef\]](#)
205. Abánades, A.; Ruiz, E.; Ferruelo, E.M.; Hernández, F.; Cabanillas, A.; Martínez-Val, J.M.; Rubio, J.A.; López, C.; Gavela, R.; Barrera, G.; et al. Experimental analysis of direct thermal methane cracking. *Int. J. Hydrogen Energy* **2011**, *36*, 12877–12886. [\[CrossRef\]](#)
206. Abánades, A.; Rubbia, C.; Salmieri, D. Technological challenges for industrial development of hydrogen production based on methane cracking. *Energy* **2012**, *46*, 359–363. [\[CrossRef\]](#)
207. Ghosh, S.; Varma, A.K. Geothermal Energy-Driven Hydrogen Production Systems. In *Materials for Hydrogen Production, Conversion, and Storage*; Inamuddin, A.T., Adnan, S.M., Amin, M.A., Eds.; Willey Scrivener Publishing LLC: Hoboken, NJ, USA, 2023; pp. 343–395. [\[CrossRef\]](#)
208. Abánades, A. Natural Gas Decarbonization as Tool for Greenhouse Gases Emission Control. *Front. Energy Res.* **2018**, *6*, 47. [\[CrossRef\]](#)
209. Maag, G.; Zanganeh, G.; Steinfeld, A. Solar thermal cracking of methane in a particle-flow reactor for the co-production of hydrogen and carbon. *Int. J. Hydrogen Energy* **2009**, *34*, 7676–7685. [\[CrossRef\]](#)
210. Pohlenz, J.B.; Scott, N.H. Method for Hydrogen Production by Catalytic Decomposition of a Gaseous Hydrocarbon Stream. U.S. Patent number 3,284,161, 8 November 1966.
211. Ball, M.; Weeda, M. The hydrogen economy: Vision or reality? *Int. J. Hydrogen Energ.* **2015**, *40*, 7903–7919. [\[CrossRef\]](#)
212. Ursua, A.; Gandia, L.M.; Sanchis, P. Hydrogen Production from Water Electrolysis: Current Status and Future Trends. *Proc. IEEE* **2012**, *100*, 410–426. [\[CrossRef\]](#)
213. Schneider, S.; Bajohr, S.; Graf, F.; Kolb, T. Verfahrensübersicht zur Erzeugung von Wasserstoff durch Erdgas-Pyrolyse. *Chem. Ing. Tech.* **2020**, *92*, 1023–1032. [\[CrossRef\]](#)
214. Bao, Y.; Huang, H.; He, D.; Ju, Y.; Qi, Y. Microbial enhancing coal-bed methane generation potential, constraints and mechanism—A mini-review. *J. Nat. Gas Sci. Eng.* **2016**, *35*, 68–78. [\[CrossRef\]](#)
215. Fuertez, J.; Nguyen, V.; McLennan, J.D.; Adams, D.J.; Han, K.-B.; Sparks, T.D. Optimization of biogenic methane production from coal. *Int. J. Coal Geol.* **2017**, *183*, 14–24. [\[CrossRef\]](#)
216. da Silva, M.L.B.; Alvarez, P.J.J. Bioaugmentation. In *Handbook of Hydrocarbon and Lipid Microbiology*; Timmis, K.N., Ed.; Springer: Berlin/Heidelberg, Germany, 2010; pp. 4531–4544. [\[CrossRef\]](#)
217. Fallgren, P.H.; Zeng, C.; Ren, Z.; Lu, A.; Ren, S.; Jin, S. Feasibility of microbial production of new natural gas from non-gas-producing lignite. *Int. J. Coal Geol.* **2013**, *115*, 79–84. [\[CrossRef\]](#)
218. Ritter, D.; Vinson, D.; Barnhart, E.; Akob, D.M.; Fields, M.W.; Cunningham, A.B.; Orem, W.; McIntosh, J.C. Enhanced microbial coalbed methane generation: A review of research, commercial activity, and remaining challenges. *Int. J. Coal Geol.* **2015**, *146*, 28–41. [\[CrossRef\]](#)
219. Davis, K.J.; Gerlach, R. Transition of biogenic coal-to-methane conversion from the laboratory to the field: A review of important parameters and studies. *Int. J. Coal Geol.* **2018**, *185*, 33–43. [\[CrossRef\]](#)
220. Davies, R.J. Methane contamination of drinking water caused by hydraulic fracturing remains unproven. *Proc. Natl. Acad. Sci. USA* **2011**, *108*, E871. [\[CrossRef\]](#)
221. Jones, E.J.; Harris, S.H.; Barnhart, E.P.; Orem, W.H.; Clark, A.C.; Corum, M.D.; Kirshtein, J.D.; Varonka, M.S.; Voytek, M.A. The effect of coal bed dewatering and partial oxidation on biogenic methane potential. *Int. J. Coal Geol.* **2013**, *115*, 54–63. [\[CrossRef\]](#)

- 
222. Huang, Z.; Urynowicz, M.A.; Colberg, P.J. Stimulation of biogenic methane generation in coal samples following chemical treatment with potassium permanganate. *Fuel* **2013**, *111*, 813–819. [[CrossRef](#)]
223. Rönsch, S.; Schneider, J.; Matthischke, S.; Schlüter, M.; Götz, M.; Lefebvre, J.; Prabhakaran, P.; Bajohr, S. Review on methanation—From fundamentals to current projects. *Fuel* **2016**, *166*, 276–296. [[CrossRef](#)]

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.