



Chemical compound classes supporting microbial methanogenesis in coal



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ABSTRACT

Microbial generation of coalbed methane (CBM) occurs in numerous basins worldwide. This study identifies specific classes of chemical compounds in two high volatile bituminous coals from the Illinois Basin in southwestern Indiana, USA that are being degraded during methanogenesis. Springfield Coal is rich in vitrinite (92.2 vol.% vitrinite in coal) whereas Lower Block Coal contains larger contributions of liptinite and inertinite and contains only 66.2 vol.% vitrinite. Anaerobic bioreactors used in the experiments contained a mineral-salts medium, operationally-defined coal extracts, and a microbial inoculum composed of an endemic microbial consortium that was obtained from co-produced water from an active CBM well. Our experiments investigated degradation of organic matter (OM) and concurrent methanogenesis using water-soluble, methanol (CH₃OH)-soluble, and dichloromethane (CH₂Cl₂)-soluble fractions of extracted OM from coal as the sole carbon sources. Only methanol and dichloromethane were found to be effective solvents to extract sufficient OM from coals for biodegradation. The methane yield over time was small (1.7 to 8.7 μmol in total headspace) and less than 1% of carbon added to bioreactors in organic extracts was converted into methane. Extracts of vitrinite-rich Springfield Coal yielded relatively more methane than extracts of Lower Block Coal. The preference of methanogenic microbial consortia for extracts from vitrinite-rich Springfield Coal may be related to the fact that the organic matter in vitrinite is rich in functional groups containing organic nitrogen, sulfur and oxygen (NSO) that provide chemical sites with low activation energies to initiate biodegradation. A comparison of the molecular compositions of the initial organic extracts with their biodegraded residues after incubation of the bioreactors for 24 weeks indicated that biodegradation of *n*-alkanes and aromatic hydrocarbons occurred concurrently, whereas hopanes proved to be far more refractory. Our study documents significant biodegradation of *n*-alkanes (14 to 91% by GC/MS peak intensity) from coal extracts. It is particularly noteworthy that biodegradation also eliminated 6 to 58% of aromatic biomarkers, although the pool of *n*-alkanes was not exhausted. This significant early biodegradation of aromatic hydrocarbons in coal extracts contrasts starkly with the biodegradation pattern of petroleum where similar aromatic compounds are degraded only after *n*-alkanes have been severely depleted. This evidence may support the hypothesis that microbial communities engaged in coal biodegradation do not express a strong preference for either aliphatic or aromatic carbon sources, in contrast to biodegradation patterns typical of petroleum. CH₃OH-extracted organic matter from coal was generally more biodegradable than CH₂Cl₂-extracted organic matter from the same coal, probably because CH₃OH extracts contained lower concentrations of longer straight aliphatic chains allowing faster microbial degradation.

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Abbreviations: SPR, Springfield Coal; LBC, Lower Block Coal; FTIR, Fourier transform infrared spectroscopy; AR, aromaticity; LAC, length of aliphatic chains; DOS, degree of substitution of aromatic sites by alkyl groups; CAR, condensation of aromatic rings; Ar, aromatic; Al, aliphatic; ν , stretching vibration; δ , deformation vibration in plane; γ , deformation vibration out of plane; as, asymmetric vibration; s, symmetric vibration; tfu, Fort Union Formation; tw, Wasatch Formation from the Powder River Basin; HVB, high-volatile bituminous coal; La, lignite coal; SB, sub-bituminous coal; c–b–a, are subdivisions of increasing coal rank; R_o (%), vitrinite reflectance.

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1. Introduction

ExxonMobil's long-term predictions of the world's energy demand indicate a greater use of natural gas by more than 60% through 2040 relative to 2010 (ExxonMobil, 2012). The U.S. National Mining Association estimates that 13% of the area of the United States has underground coal deposits (National Mining Association, 2012) that contain natural gas, often referred to as coal bed methane (CBM). By 2009 the U.S. annual CBM production was 53.8×10^9 m³, i.e., ~1.9 TCF (trillion cubic feet), and is projected to increase further (U.S. Department of Energy, Energy Information Administration, 2010). This accounts for about 8.3% of the 648×10^9 m³ (~22.9 TCF)

of natural gas consumed in the United States in 2009 (U.S. DOE EIA, 2012).

Several prominent examples of coal-bearing sedimentary basins with microbial gas production are shown in Table 1. Active methanogenesis in organic-rich sediments is not surprising since the presence of robust and diverse microbial populations at depths exceeding hundreds of meters has been demonstrated in both aquifers and porous, consolidated rock (Krumholz et al., 1997; Fredrickson and Onstott, 2001). Indeed, biodegradation of crude oil in petroleum reservoirs, previously attributed only to aerobic microbes, has recently been also clearly linked to anaerobic communities and active methane production. It is therefore tempting to consider the coal beds as potential subsurface bioreactors for production of natural gas. Although large plays of secondary biogenic methane in many sedimentary environments prove that moderately mature sedimentary organic matter (OM) can support substantial, *in situ* generation of biogenic gas (Scott et al., 1994; Faiz and Hendry, 2006; Ulrich and Bower, 2008), surprisingly little is known about the limiting constraints of microbial gas production and anaerobic C metabolism in coal beds.

Microbial CBM production is ultimately a result of methanogenic archaea able to convert a limited range of low-molecular-weight compounds into methane (Hedderich and Whitman, 2006; Ferry, 2010). This group of microbes can be broadly classified into H₂-utilizing (or CO₂-reducing) methanogens able to utilize H₂ and CO₂ as substrates, acetoclastic methanogens which utilize acetate, and methylotrophic methanogens that utilize C1 compounds such as formate or methanol. In complete contrast to the simple compounds used by methanogens, coal is a complex, cross-linked, operationally-defined, and variable assemblage of geomacromolecules that must first be broken down into simple methane precursors by complex, anaerobic communities of fermentative bacteria, acetogenic bacteria, and other microorganisms (Ferry, 2011). Although numerous laboratory and field studies of microbial methanogenesis, e.g., Flores et al., 2008; Green et al., 2008; Harris et al., 2008; Jones et al., 2008, 2010; Orem et al., 2010, have been reported in recent years using coals from different locations, results have varied. Some studies have suggested that biogenic methane primarily results from acetoclastic methanogens, e.g., (Beckmann et al., 2011), whereas other reports have suggested that CO₂ reduction is the primary methane-producing process, e.g., Harris et al. (2008).

Regardless of whether acetate or H₂ is the substrate which archaea utilize to produce CH₄, the 'upstream' biogeochemical processes that break down complex coal macromolecules are very poorly characterized. Hypotheses about carbon biotransformation pathways under

anaerobic conditions in coal beds must therefore be primarily based on our knowledge of carbon cycling in other, largely dissimilar environments. It is not known if bacteria in coal beds are able to metabolize only soluble substrates that slowly dissolve from organic matter or if they have access to water-insoluble oil droplets or poorly-soluble compounds at and near the coal surface. It is not at all clear which compound classes in the coal are the primary sources of H₂ or acetate, the likely immediate precursors for CBM production.

The chemical complexity and physical nature of coal make it difficult to design laboratory biodegradation experiments using bulk coal to assign methanogenesis to degradation of specific compound classes. The use of organic carbon extracted from coal, however, offers the potential to study biodegradation of an operationally-defined, subset of compounds in the absence of the likely-nondegradable, larger mass of solid material present in the coal. Although organic extracts have been used to characterize coal organic matter in laboratory studies of methanogenesis from powdered coal (Harris et al., 2008) and in field studies of coal biodegradation at various depths (Formolo et al., 2008), coal extracts, to our knowledge, have not themselves been previously used as substrates for studies of methanogenesis.

Here we report laboratory experiments that examined methane production in bioreactors using coal extracts as sole carbon and energy sources for biodegradation by microbial communities obtained from water produced from Indiana coal beds. Coal extracts were prepared using two different coals and either water, methanol, or dichloromethane as the solvent. These solvents were chosen to selectively extract organic matter that varied in water solubility and hydrophobicity since these characteristics may be key factors in determining overall rates of biodegradation and methanogenesis. By avoiding the use of coal in bioreactors, we eliminated the possibility of pre-existing methane that had been trapped in coal pores. Our approach also allowed analysis of specific molecular changes in the extracted organic matter that occurred during methanogenesis. For this purpose, we examined the biodegradation of three biomarker groups: normal alkenes and acyclic isoprenoids, hopanes, and aromatic hydrocarbons.

2. Materials and methods

2.1. Sample collection

The overall design and work flow of the experiments and the major laboratory procedures are illustrated in Fig. 1. The investigations

Table 1
Examples of coal basins with methanogenic gas generation.

Coal basin	Age	Coal rank R _o (%)	Depth	Source
Illinois Basin: IL, IN	Carboniferous: Pennsylvanian	HVB c,b ~0.6%	60–200 m (197–656 ft)	Strapoć et al. (2007, 2008b); Drobniak et al. (2004); Mastalerz et al. (2009)
Powder River Basin: WY tfu	Tertiary	SB c	915 m	Tang et al. (1996); Meissner (1984);
Powder River Basin: WY tw	Paleogene Paleocene	L a	(<3000 ft)	Ayers (2002); Formolo et al. (2008); Harris et al. (2008)
Forest City Basin: IO,MI,KS	Pennsylvanian	HVB c,b,a ~0.49–>0.86%	488 m (max 1600 ft)	McIntosh et al. (2008)
Gulf of Mexico Basin: LA, MS	Paleocene–Eocene	SB c–HVB c	300–1675 m (980–5500 ft)	Warwick et al. (2008)
New Zealand coalfields:	Eocene	SB b–a ~0.45%	cores from:	Butland and Moore (2008)
Huntly	Cretaceous	SB c–a ~0.5%	338.7–358.2 m	
Ohai	Cretaceous	HVB a ~0.6%	254.9–416.0 m	
Graymouth			309.6–358.2 m	
N San Juan Basin Colorado kfd	Upper Cretaceous–early Eocene	LVB	2175 m	Scott et al. (1994); Ayers (2002); Meissner (1984);
S San Juan Basin New Mexico kmv	(~80 to 40 Ma)	HVBc	(max 6630 ft), burial during the Miocene	Meissner (1984)

States: IL – Illinois, IN – Indiana, WY – Wyoming; IA – Iowa, MO – Missouri, KS – Kansas, LA – Louisiana, MS – Mississippi. Formation symbols: tfu – Fort Union, tw – Wasatch, kfd – Fruitland, kmv – Mesaverde. Coal ranks: HVB – high-volatile bituminous, LVB – low-volatile bituminous; La – lignite; SB – sub-bituminous; c–b–a are subdivisions of increasing coal rank.

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