Microbial methane from in situ biodegradation of coal and shale: A review and reevaluation of hydrogen and carbon isotope signatures

David S. Vinson [a,*], Neal E. Blair [b,g], Anna M. Martini [c], Steve Larter [d], William H. Orem [f], Jennifer C. McIntosh [e,f]

[a] University of North Carolina at Charlotte, Charlotte, NC, USA
[b] Northwestern University, Department of Civil & Environmental Engineering, Evanston, IL, USA
[c] Amherst College, Department of Geology, Amherst, MA, USA
[d] University of Calgary, PRG, Department of Geosciences, Calgary, Canada
[e] University of Arizona, Department of Hydrology & Atmospheric Sciences, Tucson, AZ, USA
[f] U.S. Geological Survey, Eastern Energy Resources Science Center, Reston, VA, USA
[g] Northwestern University, Department of Earth & Planetary Sciences, Evanston, IL, USA

ARTICLE INFO

ABSTRACT

Stable carbon and hydrogen isotope signatures of methane, water, and inorganic carbon are widely utilized in natural gas systems for distinguishing microbial and thermogenic methane and for delineating methanogenic pathways (acetoclastic, hydrogenotrophic, and/or methylotrophic methanogenesis). Recent studies of coal and shale gas systems have characterized in situ microbial communities and provided stable isotope data (δD-CH_4, δD-H_2O, $\delta^{13}C$-CH_4, and $\delta^{13}C$-CO_2) from a wider range of environments than available previously. Here we review the principal biogenic methane-yielding pathways in coal beds and shales and the isotope effects imparted on methane, document the uncertainties and inconsistencies in established isotopic fingerprinting techniques, and identify the knowledge gaps in understanding the subsurface processes that govern H and C isotope signatures of biogenic methane. We also compare established isotopic interpretations with recent microbial community characterization techniques, which reveal additional inconsistencies in the interpretation of microbial metabolic pathways in coal beds and shales. Collectively, the re-assessed data show that widely-utilized isotopic fingerprinting techniques neglect important complications in coal beds and shales.

Isotopic fingerprinting techniques that combine $\delta^{13}C$-CH_4 with δD-CH_4 and/or $\delta^{13}C$-CO_2 have significant limitations: (1) The consistent ~160‰ offset between δD-H_2O and δD-CH_4 could imply that hydrogenotrophic methanogenesis is the dominant metabolic pathway in microbial gas systems. However, hydrogen isotopes can equilibrate between methane precursors and coexisting water, yielding a similar apparent H isotope signal as hydrogenotrophic methanogenesis, regardless of the actual methane formation pathway. (2) Non-methanogenic processes such as sulfate reduction, Fe oxide reduction, inputs of thermogenic methane, anaerobic methane oxidation, and/or formation water interaction can cause the apparent carbon isotope fractionation between $\delta^{13}C$-CH_4 and $\delta^{13}C$-CO_2 ($\alpha^{13}C_{CO2\text{-}CH4}$) to differ from the true methanogenic fractionation, complicating interpretation of methanogenic pathways. (3) Where little-fractionating non-methanogenic bacterial processes compete with highly-fractionating methanogenesis, the mass balance between CH_4 and CO_2 is affected. This has implications for $\delta^{13}C$ values and provides an alternative interpretation for net C isotope signatures than solely the pathways used by active methanogens. (4) While most of the reviewed values of δD-H_2O - δD-CH_4 and $\alpha^{13}C_{CO2\text{-}CH4}$ are apparently consistent with hydrogenotrophic methanogenesis as the dominant pathway in coal beds and shales, recent microbial community characterization techniques suggest a possible role for acetoclastic or methylotrophic methanogenesis in some basins.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

1.1. Importance of distinguishing biogenic sources of methane

Microbial degradation of organic matter in the subsurface has been estimated to contribute to ~20% of natural gas resources worldwide, whereas ~80% of economically significant gas is thought to be thermogenic, produced from thermal cracking of organic matter (Rice and

* Corresponding author.
E-mail address: dsvinson@uncc.edu (D.S. Vinson).

Claypool, 1981). Biogenic gas has been detected in conventional hydrocarbon systems and in unconventional settings, such as coal beds and shales. In an examination of conventional natural gas, Milkov (2011) estimated that 3–4% of recoverable gas is of primary microbial origin, derived from biodegradation of sedimentary organic matter, and another 5–11% is secondary, derived from biodegradation of thermogenic hydrocarbons. However, the estimates of Milkov (2011) did not address unconventional gas hosted in coal and shales. Coalbed methane is estimated to represent 9% of United States natural gas production (Gao et al., 2014). In coal beds and shales, the generated gas is largely retained by adsorption to water-saturated coal and shale, then released when the formation is depressurized, such as by pumping during production (Martini et al., 1998, 2008; Pashin, 2014). As with other gas resources, coal and shale gas can be thermogenic, secondary biogenic, primary biogenic, or a mixture of these sources. Here we focus on generation of microbial gas from in situ biodegradation of coal- and shale-derived organics, that is, primary biogenic gas. Primary biogenic gas depends on steady-state biodegradation of the coal and shale source materials, producing low molecular-weight intermediates and methane precursors, coupled to microbial methanogenesis that yields CH_4 and CO_2. While gas samples may record a long gas accumulation history, this linked (syntrophic) metabolism is in many cases thought to represent organisms and/or metabolic pathways that remain active in sedimentary basins.

Reliably identifying biogenic natural gas in the subsurface has numerous implications, such as assessing the origins of methane, evaluating natural gas resources, and understanding the environmental footprint of production practices: (1) Methanogenesis is the terminal step in organic matter biodegradation, yielding the greenhouse gases CH_4 and CO_2. The active methanogenic metabolic pathway(s) are linked to the history of organic matter deposition and to upstream biogeochemical reactions that produce substrates needed by methanogens. Therefore, in a variety of environments, identifying methanogenic pathways is a significant part of understanding organic matter decomposition and fluxes of carbon compounds (e.g. Formolo, 2010; Hornibrook and Aravena, 2010). (2) In basins with complex thermal histories or hydrologic settings, mixed biogenic-thermogenic gas may be present, and elucidating this gas mixture is a long-standing problem (Scott et al., 1994; Martini et al., 1998, 2003, 2008; Cheung et al., 2010; McIntosh et al., 2010; Osborn and McIntosh, 2010; Golding et al., 2013; Stolper et al., 2015). (3) In systems with active microbial methanogenesis, there is interest in stimulating underlying processes to yield additional gas resources, which requires understanding of organic matter biodegradation and methane generation (Jones E.J.P. et al., 2008; Jones et al., 2010; Ulrich and Bower, 2008; Papendick et al., 2011; Strąpoć et al., 2011b; Barnhart et al., 2013; Schlegel et al., 2013; Ritter et al., 2015). (4) As unconventional natural gas extraction from hydrocarbon-bearing formations grows in economic importance, tools and techniques are needed to assess potential environmental impacts of production practices (Vidic et al., 2013; Jackson et al., 2013; Brantley et al., 2014; Darrah et al., 2014; Vengosh et al., 2014). Formations containing biogenic gas are among the shallowest targets for hydraulic fracturing in the USA (e.g. Antrim Shale in Michigan Basin; Jackson et al., 2015), so the detection of biogenic gas in the near-surface environment is of significant interest.

1.2. Need for critical re-examination of C and H isotope applications to biogenic gas

Geochemical and isotopic fingerprints utilizing stable carbon and hydrogen isotopes have been applied for decades to (1) identify microbial vs. thermogenic gas and (2) to distinguish pathways of microbial methane generation in natural gas systems. These C and H isotope techniques remain important for addressing established and emerging problems. Isotopic fingerprinting techniques are especially important in field-based studies where the active metabolic

pathway is not controlled experimentally and substrate concentrations alone do not point to an obvious dominant pathway. An improved understanding of the microbial controls on the C and H isotope composition of methane can provide insights on identifying in situ methanogenesis and quantifying inputs of microbial gas into groundwater and thermogenic-dominated gas systems. In addition, stable isotopic fingerprints and models have been used to assess methane leakage from gas infrastructure into the atmosphere (e.g. Townsend-Small et al., 2012; Phillips et al., 2013) and to shallow aquifers (e.g. Osborn et al., 2011; Révész et al., 2010; Jackson et al., 2013).

Widely-used geochemical and isotopic evidence of the microbial origin of gas includes: (1) ratios of methane to ethane and propane ($C_1/(C_2 + C_3)$), typically >1000 in samples of microbial gas (Bernard et al., 1976; Golding et al., 2013); (2) δ^{13}C-CH_4 values generally less than approximately −55‰ expected for biogenic gas (although showing considerable overlap with thermogenic gas in practice; Bernard et al., 1976; Whiticar et al., 1986; Schoell, 1988; Whiticar, 1999; Hornibrook and Aravena, 2010; Golding et al., 2013); (3) correlation of δD-CH_4 and δD-H_2O values as evidence of microbial methanogenesis and characteristic of metabolic pathways (Schoell, 1980; Whiticar et al., 1986; Whiticar, 1999; Golding et al., 2013); (4) plotting δ^{13}C-CH_4 vs. δD-CH_4 and comparing to diagnostic fields for biogenic and thermogenic gas (Schoell, 1980; Whiticar et al., 1986; Whiticar, 1999); (5) characteristic values of δ^{13}C-CO_2 > 0‰ in microbial gas systems (Scott et al., 1994; Martini et al., 2003, 2008; Golding et al., 2013); and (6) the difference between and δ^{13}C-CO_2 and δ^{13}C-CH_4 values as diagnostic of methanogenic pathways (Whiticar et al., 1986; Whiticar, 1999; Conrad, 2005; Golding et al., 2013).

Many of the data previously utilized to define the isotopic signatures of methanogenic pathways were from recent aquatic sediments or related cultures, combined with the available data from biogenic gas basins (e.g. Whiticar et al., 1986). However, the nature and time scale of biodegradation likely differ between modern and fossil C sources due to the preferential removal of easily-metabolized carbohydrates during sediment aging, differences in rate-limiting steps (e.g. H_2 production), and distinctive environmental conditions such as sulfate availability (e.g. Miyajima et al., 1997; Nakagawa et al., 2002a; Strąpoć et al., 2011b). Short-term seasonal hydrologic, temperature, and redox fluctuations (e.g. Blair et al., 1993; Blair and Aller, 1995; Avery et al., 1999), common in aquatic sediments, are not expected in gas-bearing formations. Moreover, methane oxidation, which would affect apparent isotopic signatures, is less likely to be significant in the persistently-anoxic deep subsurface than in shallow subsurface sediments. Collectively, these factors point to the need for data from consistent carbon sources and environmental conditions.

Since the 1990s, unconventional gas exploration has greatly expanded, including microbial coalbed methane and shale gas, making available recently-published data sets of paired water and gas isotopes from microbial gas systems. In addition, culturing and molecular microbial investigations have improved documentation of organisms and pathways that appear to be active in coal and shale biodegradation. Here we review the expected H and C isotope effects of methanogenic pathways and competing non-methanogenic pathways in coal beds and shales; compare these data to expected patterns derived from recent sediments and cultures; and document inconsistent interpretations of metabolic pathways using isotopic and microbial techniques. Evidence from recent studies demonstrates challenges in applying C and H isotopes to interpreting the in situ biogeochemical structure in coal beds and shales. In addition, discrepancies are apparent between observed methanogen populations and the pathways inferred from H and C isotopes of field-collected water and gas samples (see Table 1 for examples). These challenges call for a re-assessment of what phenomena are actually recorded by C and H isotopes in methanogenic coal beds and shales.