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Enhancing Microbial Gas From Unconventional Reservoirs: Geochemical And Microbiological Characterization Of Methane-Rich Fractured Black Shales

FINAL REPORT

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13. ABSTRACT (Maximum 200 words)
A geochemical and microbial survey was conducted of formation waters of two active shale gas reservoirs: the northern producing trend of the Antrim Shale [ANPT] (Michigan) and the Forest City Basin [FCB] (Kansas). Enrichment experiments established which metabolic roles may be present in these formation waters (i.e. bacterial sulfate reduction, acetate fermentation, ferric iron reduction, CO_2 reduction, etc.). DNA analysis provided information on types of microorganisms in these reservoirs, genetic and metabolic diversity, and phylogenetic relationships with other organisms. Geochemical analyses confirmed microbial methanogenesis as the dominant methane source in ANPT formation waters, and revealed significant microbial methane generation in FCB formation waters. Microbial methanogenesis has not previously been documented for this reservoir. Active (rather than relict or ancient) methane generation was confirmed in enrichment and microcosm experiments using waters from both reservoirs. This has significant implications for gas exploration. Genetic information obtained from DNA isolated from ANPT formation waters indicates a microbial community comprised of acetogenic Bacteria acting in syntrophy with both acetate-fermenting and CO_2-reducing methanogenic Archaebacteria. Thus, active microbial methanogenesis in sedimentary basins may not depend on external supply of electron acceptors (e.g. sulfate, ferric iron), but instead reflects internal control limited by formation water hydrology, geochemistry, and organic matter composition.

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RESEARCH SUMMARY

Natural gas produced from black shale and coal bed deposits is of increasing importance due to economic and political realities. At present these unconventional gas resources account for nearly 10% of total U.S. natural gas production. From 1988 to 2002, shale gas production in particular has increased by more than 60%, due primarily to a single new play: the Antrim Shale in the Michigan Basin. Like many shale gas plays, the Antrim produces a mixture of thermogenic and microbial (biogenic) gas. Understanding the dominant origin of shale gas is fundamental in guiding future reservoir exploration and production and in stimulating recovery in underproducing areas. This research examined the origin of natural gas in an established microbial gas resource (the northern producing trend of the Antrim Shale, Michigan Basin [ANPT]) and a reservoir in which microbial gas production had not yet been confirmed (the Forest City Basin [FCB]).

This study comprised several goals, including:
1. identifying the active, modern-day community of subsurface microorganisms responsible for current methane production in shale gas plays, recognizing that methanogenesis is only the end product of a cascade of microbial metabolic functions,
2. establishing which environmental parameter(s) limit microbial growth and activity, and thus methane generation, in shale gas reservoirs, and
3. stimulating microbial growth and gas generation in poorly producing wells based on identification of microbial communities.

Geochemical analyses confirmed microbial methanogenesis as the dominant methane source in ANPT formation waters, and revealed significant microbial methane generation in FCB formation waters.. Active (rather than relict or ancient) methane generation was confirmed in enrichment as well as microcosm experiments using waters from both reservoirs, a finding that has significant implications for gas production prediction. Genetic information obtained from DNA isolated from ANPT formation waters indicates a microbial community comprised of acetogenic Bacteria acting in syntrophy with both acetate-fermenting and CO_2-reducing methanogenic Archaebacteria. Thus, active microbial methanogenesis in sedimentary basins may not depend on external supply of electron acceptors (e.g. sulfate, ferric iron), but instead reflects internal control limited by formation water hydrology, geochemistry, and organic matter composition.

The results of this seed project involving microbial community analysis in shale gas plays strongly indicate that microbial methane generation in sedimentary basins is an active process, with a high potential for stimulation and thus extension of projected well production histories. Application of these results has a direct relationship with potential targets of exploration and gas production in other sedimentary basins where methanogenesis may occur or in the future, be stimulated. Thus, this research may contribute towards development of technologies to enhance methane production in shale gas plays, and help secure natural gas resources from the extensive occurrence of fractured black shales and coal beds found throughout the U.S.A.

INTRODUCTION

With demand for natural gas on a steady rise (~30% increase in the past 15 years), unconventional gas deposits, such as those produced from coalbeds and shales, are receiving attention from both small independent operators and the major energy companies. In unconventional plays, the origin of gas is fundamental to assessing a natural gas reservoir and in guiding exploration strategies. In general, a thermogenic gas play is expected to be most productive in the deeper sections of a basin where the organic material has experienced more thermal cracking. However, in an unconventional play where the gas is predominantly microbial, the margins of the basin where the organic matter is less mature and hydrologic flow systems are active would be the target of exploration. Given the extensive occurrence and abundance of fractured black shales and coalbeds throughout sedimentary basins in the U.S., there is a significant economic incentive to understand the microbial origin of the gas. This knowledge may then be applied to stimulating and enhancing recovery of natural gas from these deposits.

The organic-rich shales of the eastern U.S. have a long history of production and recent development and account for nearly 2% of U.S. natural gas production. Since 1988, shale gas production has increased by over 60%, due primarily to a single new black shale play, the Antrim Shale in the Michigan Basin (Figure 1)[1]. Given its importance as one of the most productive and recent black shale gas plays, the Antrim Shale, Michigan Basin (Figure 2) provides an ideal setting in which to study microbial methanogenesis and modification of thermogenic gas. The Michigan Basin has a long history of thermogenic gas production from deep Devonian-Cambrian strata. It is only since the mid-1980s that shallow black shales became a target of rapid development, beginning with 100 wells in 1985 to over 12,000 wells today. Our proposed research focused on wells located along the northern margin of the Michigan Basin. This region has the highest natural gas production rates, strongest geochemical indicators of microbial activity, and sharpest chemical gradients in formation water composition[2-4]. Furthermore, production histories of wells in the region strongly suggest active methane generation, rather than relict methane generated in the geologic past.

In addition, development in the Forest City Basin (Four Corners region, Iowa-Missouri-Kansas-Nebraska) has revealed this play as a potential source of microbial gas. This research investigates the source of microbial gas in the Forest City Basin and uses modern molecular identification of microorganisms as a tool to aid enhanced gas generation and recovery strategies in both regions.

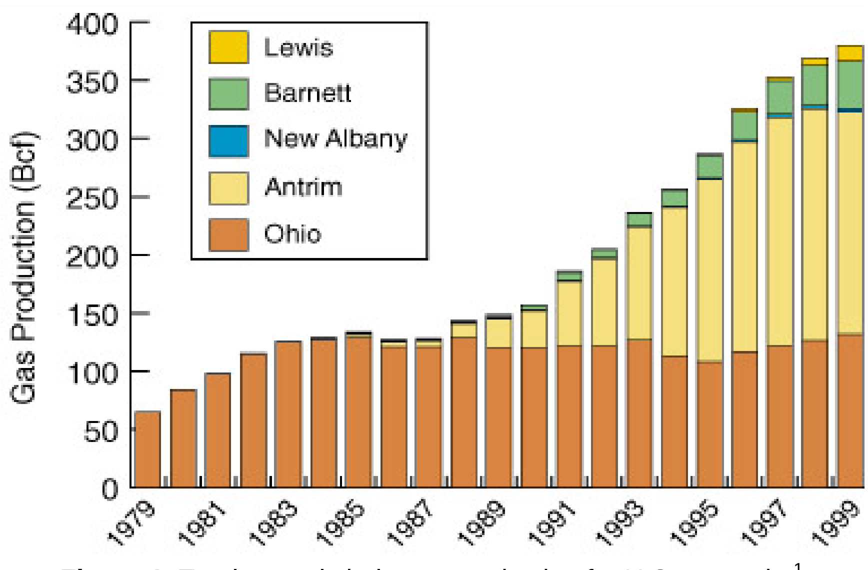


Figure 1: Total annual shale gas production for U.S reservoirs[1].

The Antrim Shale and its formation waters

The Late Devonian Antrim Shale consists of finely laminated, silty, pyritic, OM-rich black shales interbedded with gray and green shales and carbonate units[5]. The shales contain dominantly Type I kerogen[6]. Antrim Shale kerogen ranges from 0.4% to 0.6% vitrinite reflectance (R_o) at the northern margin of the Michigan Basin, indicating low thermal maturity (pre-oil generation, <~80°C for entire history since burial)[7].

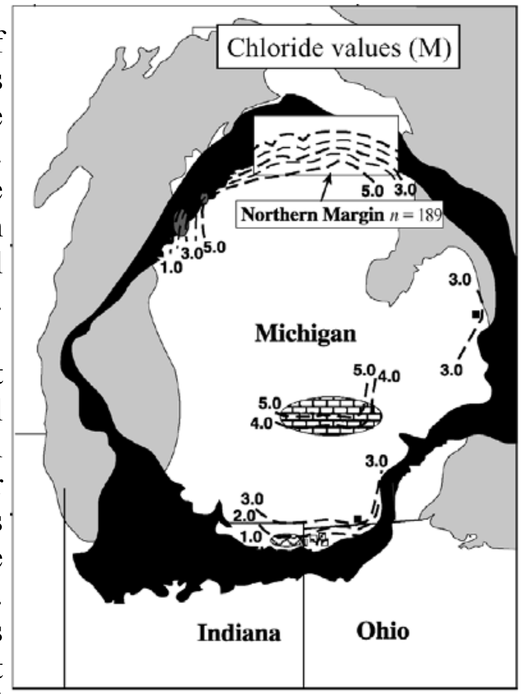


Figure 2: Location of Antrim Shale subcrop (black) in the Michigan Basin. Box on map defines northern producing trend and field area for this research. Gradients for Cl^- are shown *(2,3,4)*.

The Antrim Shale contains regional fractures that serve as conduits for migrating formation waters. Glacial moraines in the N and W margins form regional topographic highs that provide hydraulic head for recharge (Figure 3) driving flow from basin margins inward[2,3,8]. The shale may also be recharged from the underlying permeable, SO_4-bearing Traverse Limestone[9]. However, recharge rates and groundwater flow in this region are exceedingly slow[3]. A sharp salinity gradient occurs along basin margins where meteoric water and basin brines mix (Figure 2). Cl^- concentration ranges from <0.1 M at the basin margins to 5.9 M in the central basin. Microbial gas production in the northern margin of the Antrim Shale is focused in a narrow zone[3] with formation water salinity between 0.5 – 4 M Cl^-. This suggests that microbial methane production is impacted by infiltration of waters into the Antrim along the northern margin of the basin, and is inhibited by basin brines toward the south. Sulfate concentrations within the gas-producing region are low (<1 mM).

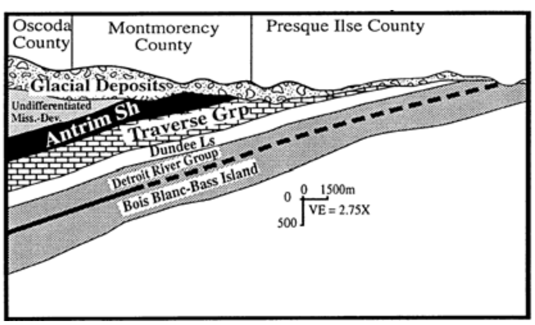
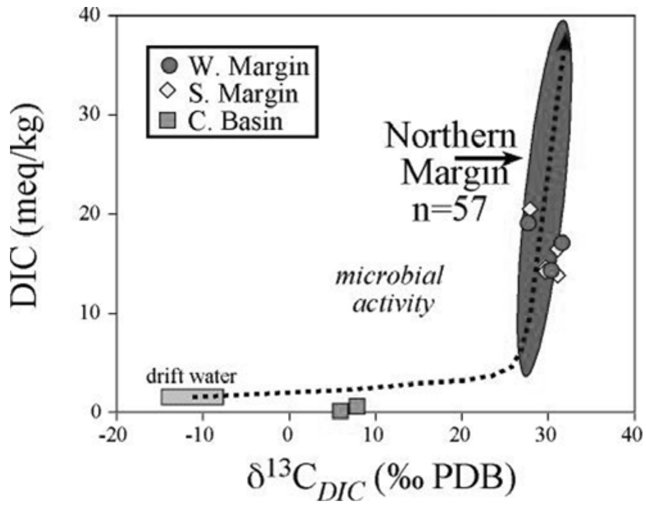


Figure 3: Cross section through the northern margin of the Michigan Basin.

Methanogenesis in the Antrim: geochemical evidence

One geochemical indicator of widespread microbial activity in the gas producing zone is extremely high concentration of dissolved inorganic carbon (DIC)[3]. Both groundwaters in the overlying glacial drift and deep central Antrim brines measure ~0-5 meq/L DIC (Figure 4). However, waters in the N, W, and S Margins all have DIC concentrations >>10 meq/L. This DIC gradient is not a mixing trend between drift waters and brine. Instead, these high DIC values are due to OM oxidation occurring within the Antrim Shale. In addition, $\delta^{13}C_{DIC}$ ratios require a large fraction of this DIC to be removed through CO_2 reduction. Very enriched $\delta^{13}C_{DIC}$ ratios (up to 34‰) are clear indicators of closed- or nearly closed-system Rayleigh distillation by a CO_2-fixing process with strong isotope discrimination. Similar values have been used to identify microbial activity in other basins[11,12]. Note that these alkalinities and $\delta^{13}C_{DIC}$ ratios are



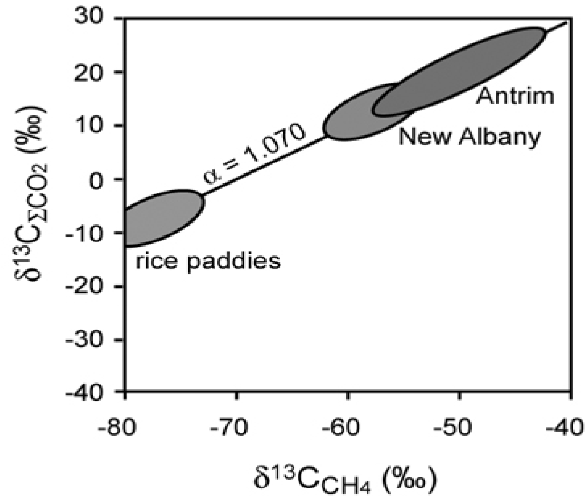


Figure 4: Alkalinity-$\delta^{13}C_{DIC}$ relationships for Antrim Shale formation waters and glacial drift recharge.

Figure 5: Carbon isotope ratios of CO_2 versus CH_4 in Antrim Shale[2-4], New Albany Shale[10], and rice paddies[76].

some of the highest ever measured in natural waters. The central Michigan basin, with little or no microbial activity, has low DIC concentrations that are far less enriched in ^{13}C than the margins.

The most common geochemical indicators to distinguish thermogenic from microbial gas are $\delta^{13}C_{CH4}$ ratios. Thermogenic CH_4 is depleted relative to bulk kerogen by 0-20‰[13,14]. Methanogenesis, however, results in CH_4 that is ~70‰ depleted relative to CO_2. In the Antrim Shale, $\delta^{13}C_{CH4}$ ratios of ~ 50‰ (~20 ‰ depleted relative to bulk kerogen) led early researchers to identify the gas as thermogenic, primarily because $\delta^{13}C_{DIC}$ was not measured but was assumed near 0‰. However, isotopic parameters once thought to uniquely identify gas generation processes can be obscured by secondary effects[3,13-16]. In these cases additional indicators are necessary.

The relationship between carbon isotope ratios of CO_2 and CH_4 during methanogenesis is well defined, and follows the equation:

$$\alpha_C = (\delta^{13}C_{CO2} + 1000)/(\delta^{13}C_{CH4} + 1000) \approx 1.070$$

For the N, W, and S margins of the Antrim subcrop, the ~70‰ observed fractionation is consistent with methanogenesis, and reveals CO_2-reduction under nearly closed conditions (Figure 5). During methanogenesis there is also a direct link between D/H ratios of H_2O and microbial CH_4. A strong regional H-isotope gradient in Antrim waters (δD from -25‰ to -100‰) permits chemical tracing of hydrogen derived from H_2O[3]. For most of the W, N, and S margins, the $\delta D_{CH4-H2O}$ relationship $\delta D_{CH4} = \delta D_{H2O} + 160$ (± 10‰) (Figure 6) indicates the dominance of bacterial CO_2 reduction[13]. In contrast, CH_4 from the central basin has δD values consistent with a thermogenic origin and little evidence of equilibration with associated waters. These isotope signatures

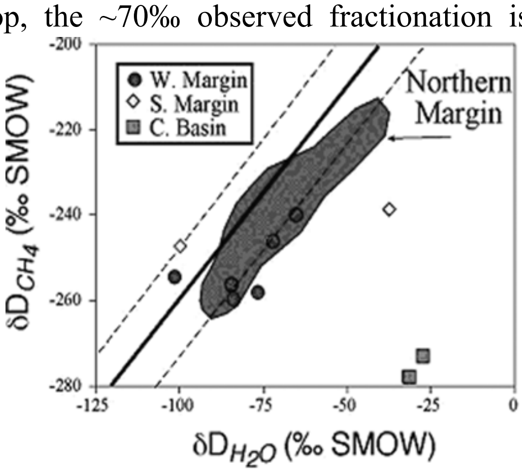


Figure 6: H-isotope ratios from methane and water, Antrim Shale, Michigan Basin. Slope follows equation from ref. *13*.

negate any thermogenic or radiogenic origin for gases along the basin margins; diffusion of produced gases would lead to isotopically depleted gases at basin margins leaving enriched gases towards the center, a feature not observed in the Antrim (Figure 6).

Although there is ample prior geochemical evidence suggesting a microbial origin for natural gas in the Antrim Shale, this report provides the first direct microbiological investigation of active Antrim Shale methanogenesis.

Forest City Basin sedimentary rocks and formation waters

The Late Paleozoic Forest City Basin extends through much of north-eastern Kansas and northwestern Missouri, separated from more deeply buried Paleozoic strata of the Cherokee basin (southeast Kansas – northeast Oklahoma) by the Bourbon Arch (Figure 7)[89]. The eastern margin of the basin is expressed as gently west-northwestward dipping rocks that onlap the Ozark Dome of southwestern Missouri; there is some suggestion of a slow regional recharge of relatively low salinity groundwater from the Ozark Uplift in the east into more saline Forest City brines to the west. The western margin of the basin is bounded by steeply-dipping faulted rocks of the Nemaha uplift. Rocks of the Cherokee and Marmaton Groups in the Forest City Basin comprise numerous thin interbedded siltstones, limestones, OM-rich shales ("coaly shales") and channel sandstones of Middle Pennsylvanian age, deposited in a variety of environments ranging from relatively deep marine to shallow marine and non-marine.[89-91] As in the Antrim, thermal maturity of the coal is low within much of the Forest City Basin, ranging from 0.5-0.6 % R_o throughout much of Basin. Although individual coal seams in the Forest City Basin are thin (most < 1m), the thickness of the entire Middle Pennsylvanian sequence is ~150 m. Modern burial depths in Miami County, KS, where this study was conducted, are ~100 m to the top of the sequence. Shallow burial depths and adjacent structural features to the south and west have resulted in an extensive and well-developed regional fracture system in the Basin, serving as conduits for slow groundwater movement within the Basin.[90-92]