

**GEOCHEMICAL EVIDENCE FOR BIOGENIC GAS PLAYS IN UPPER DEVONIAN
AND UPPER ORDOVICIAN ORGANIC-RICH SHALES: WESTERN NEW YORK AND
THE APPALACHIAN BASIN
Final Report**

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ABSTRACT

This study investigated the geochemistry of formation waters, gas, and core materials in Devonian and Upper Ordovician shales and reservoir sandstones across the northern margin of the Appalachian Basin, including New York State, to determine the origin and distribution of natural gas – an economically important energy resource. The vast majority of produced gases sampled in the Devonian organic-rich shales and adjacent reservoir sandstones in western New York and Pennsylvania are thermogenic in origin, based on the gas composition, carbon and hydrogen isotope values of methane, higher chain hydrocarbons and carbon dioxide, and formation water chemistry. Similarly, dissolved natural gas sampled from domestic water supply wells screened in the Upper Ordovician Utica Shale in New York is primarily thermogenic in origin with minor amounts of microbial methane. Limited accumulations of microbial methane were also observed in domestic water supply wells screened in the Upper Devonian organic-rich shale subcrop near Lake Erie. The lack of extensive microbial gas plays in the northern Appalachian Basin, unlike the adjacent Michigan and Illinois basins, may be due to the paucity of formation waters in organic-rich shales, decreased bioavailability of shale organic matter with increased thermal maturity, and/or high sulfate and chloride levels.

Key Words: Devonian, Ordovician, shale, microbial gas, thermogenic gas, methane

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SUMMARY

Natural gas resources are becoming increasingly economically-important with growing populations, rising energy demands and higher fuel costs worldwide. Fractured organic-rich shales in sedimentary basins host large accumulations of natural gas generated by geologic (thermogenic) and/or microbial processes. Determining the extent and mechanism of shale gas generation is critical for exploration and production strategies, and gas resource estimates. Our study investigated the origin and distribution of natural gas in Devonian and Upper Ordovician organic-rich shales and adjacent reservoir sandstones across the northern margin of the Appalachian Basin, including New York State.

Thermogenic gas is typically generated at high temperatures and pressures at depth in basins over geologic timescales (i.e. millions of years). Microbial gas is generated by a consortium of microorganisms (including methanogens) that degrade organic matter to produce methane and carbon dioxide, typically at shallow depths along basin margins. Microbial methane may have been generated in the geologic past; however, recent studies have shown that methanogenic populations are still active in sedimentary basins, such as the Michigan, Illinois and Powder River basins, and have generated natural gas resources within the last ~18,000 years. This leads to the intriguing possibility that these microbial communities may be stimulated to produce new gas resources. It is estimated that ~80% of natural gas resources in sedimentary basins worldwide are thermogenic in origin, while ~20% are microbial in origin.

The first commercial use of natural gas in the United States began in the 1820's near Fredonia, New York with the installation of the first shale gas well. Despite a long history (almost 200 years) of oil and gas production in the Appalachian Basin, relatively little is known about the extent and origin of natural gas resources in the basin. The majority of natural gas production has been limited to the central and western basin, where thermogenic gas is dominant. There is evidence of microbial gas from one well sampled in the Upper Devonian organic-rich shale near Lake Erie, Pennsylvania. Recent exploration targeting Devonian organic-rich shales (i.e. Marcellus Shale) in New York and Pennsylvania emphasizes the need for a better understanding of shale gas resources in the basin.

To determine the origin of natural gas in Devonian and Upper Ordovician organic-rich shales across the northern Appalachian Basin, we collected co-produced formation waters and gas samples from 43 shale gas wells in New York and Pennsylvania. It is important to note that many of the shale gas wells did not produce any water; the presence of water in shale fracture networks is critical for microbial methane generation. Additional formation water and gas samples (17 total) were collected from the Mississippian Berea Sandstone, Silurian Medina Sandstone, and Ordovician Trenton Black River Group in New York, Ohio, Pennsylvania and eastern Kentucky for comparison.

In regions without active shale gas production, such as the Devonian organic-rich shale along Lake Erie and the Upper Ordovician Utica Shale in central New York, we sampled dissolved gases and groundwater from domestic water supply wells (19 total) screened in the organic-rich shales. Gas samples were analyzed for molecular and isotopic composition at Isotech Laboratories. Water samples were analyzed for elemental and isotopic composition at the University of Arizona.

The vast majority of produced gases sampled in the Devonian organic-rich shales and adjacent reservoir sandstones in western New York and Pennsylvania are thermogenic in origin, based on the gas composition, carbon and hydrogen isotope values of methane, ethane, propane, and carbon dioxide, and formation water chemistry. Similarly, dissolved natural gas sampled from domestic water supply wells screened in the Upper Ordovician Utica Shale in New York is primarily thermogenic in origin with minor amounts of microbial methane. Limited accumulations of microbial methane were also observed in domestic water supply wells screened in the Upper Devonian organic-rich shale subcrop near Lake Erie. The lack of extensive microbial gas plays in the northern Appalachian Basin, unlike the adjacent Michigan and Illinois basins, may be due to the paucity of formation waters in organic-rich shales, decreased bioavailability of shale organic matter with increased thermal maturity, and/or high sulfate and chloride levels. These hypotheses still need to be tested.

Results of this study should be of interest to the oil/gas industry, policy makers and governmental agencies, and the general public. In addition, this study helped to constrain environmental conditions necessary for microbial generation of methane, and further developed research tools to distinguish between microbial and thermogenic gas resources.

INTRODUCTION TO STUDY

Section 1

Upper Devonian organic-rich fractured shales from the midcontinent region of the United States (U.S.), including the Appalachian, Illinois, and Michigan basins, host large economic accumulations of natural gas. These reservoirs accounted for approximately 84% of the total U.S. shale gas production in 1999 (~380 bcf/year; Curtis, 2002). A significant portion of these shale gas resources (~20%; Rice and Claypool, 1981) have been shown to be microbial in origin – generated by an active community of microbes that degrade complex organic matter to CO₂ – and may be stimulated to generate new methane on human timescales.

Pleistocene glacial recharge enhanced microbial methane generation (methanogenesis) in organic-rich shales along the shallow margins of the Michigan and Illinois basins by diluting formation water salinity and likely transporting in microorganisms from near surface environments (Martini et al., 2003; McIntosh et al., 2004). In contrast, thermogenic gas resources are generated by thermal degradation of organic matter at depth within sedimentary basins, and are often associated with saline fluids (>~2 mole/L chloride). Distinguishing the origin of natural gas in fractured shales is critical for gas exploration and production strategies and for making reasonable resource estimates.

Although the first known commercial gas production in the United States was from an Upper Devonian black shale in Chautauqua County, western New York, in 1821 (Hill and Nelson, 2000), very little research has been done on the potential for microbial methane in fractured black shales in the Appalachian Basin. In addition, no systematic study has been conducted on the potential for freshwater recharge to fractured shales in western New York driven by Pleistocene glaciation.

Laughrey and Baldassare (1998) report one anomalous Ohio Shale gas sample from near Lake Erie (PA) that had high CH₄ concentrations and low $\delta^{13}\text{C}$ values of CH₄, compared to deeper basin-centered thermogenic gas samples. They suggested that the methane-rich gas might have been generated by microbial activity. Milici (1993) also proposed a biogenic origin for Devonian shale gases along Lake Erie, where the black shales are thermally-immature. Since the early 1800's, shale gas production in the basin has targeted deeper thermogenic gas reservoirs in eastern Kentucky and West Virginia. The few wells that were drilled in the Upper Devonian Ohio Shale along the northern basin margin have been producing gas for over 100 years. Recent exploration in the Ordovician Trenton/Black River Group in New York, and throughout the Appalachian basin, has stimulated interest in the overlying Upper Ordovician Utica Shale as a possible target for fractured shale gas plays (Shirley, 2001). The lack of published formation water and gas chemistry from Upper Devonian and Upper Ordovician shales in the Appalachian basin has prevented

an adequate assessment of the source of natural gas, and has precluded comparative studies with other fractured shale gas plays in adjacent Paleozoic basins.

A systematic study of formation water and gas geochemistry in Devonian and Upper Ordovician organic-rich shales was conducted across the northern margin of the Appalachian Basin, including New York State, to determine the origin of natural gas. Although the vast majority of natural gas resources were found to be thermogenic in origin, microbial methane was detected in dissolved gas samples from domestic water supply wells screened in the Devonian shale subcrop. Microbial methane accumulations appear to be limited at depth in Devonian shales by the presence of sulfate, elevated chloride, paucity of formation waters, and/or bioavailability of the organic matter. Dissolved gases and formation water chemistry of the Upper Ordovician organic-rich shale (Utica) in central New York State show the dominance of thermogenic gas with potential minor contributions from microbial methane. Results of this study have important implications for the exploration and development of fractured shale gas plays in New York State and the Appalachian Basin region as an energy resource.

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CHEMICAL AND ISOTOPIC TRACERS OF THE CONTRIBUTION OF MICROBIAL GAS IN DEVONIAN ORGANIC-RICH SHALES AND RESERVOIR SANDSTONES, NORTHERN APPALACHIAN BASIN

Section 2

The following section summarizes the results of our study on the origin and distribution of natural gas in Devonian organic-rich shales in western New York State, eastern Ohio, and western Pennsylvania. The results have been published in the journal *Applied Geochemistry* (Osborn and McIntosh, 2010). A copy of the *Applied Geochemistry* manuscript is inserted below.

We originally proposed to extend our study to eastern Kentucky (E. KY) and southeastern Ohio (S.E. OH) to investigate the importance of glacial recharge on microbial generation of natural gas. Devonian shale natural gas wells in unglaciated portions of the western Appalachian Basin (E. KY and S.E. OH) were to be sampled and analyzed to determine the origin of natural gas, and compared to results from the glaciated northern margin of the basin (e.g. western New York State). Ph.D. student, Stephen Osborn, spent five days in Kentucky meeting with gas companies and making ~70 phone calls in summer of 2007 and 2008. At that time there were no Devonian shale wells producing gas or formation waters. Meetings with geologists at the Kentucky Geological Survey confirmed these results. Two gas and water samples were collected from the Mississippian Berea Sandstone in E. KY. We are still attempting to gain access to hardcopy Devonian shale water and gas data from the Kentucky Geological Survey. Similar to Kentucky, there were no producing gas wells available to sample in E. OH in 2007-2008, as confirmed by the Ohio Department of Mineral and Gas Resources. Given the paucity of Devonian shale wells to sample in E. KY and E. OH, we concentrated our efforts in western New York State and western Pennsylvania on Devonian shale and Upper Ordovician shale gas wells and domestic water supply wells, as discussed below and in Section 2.

ABSTRACT

In this study, we investigated the geochemistry and origin of natural gas and formation waters in Devonian age organic-rich shales and reservoir sandstones across the northern Appalachian Basin margin (western New York, eastern Ohio, northwestern Pennsylvania, and eastern Kentucky). Additional samples were collected from Mississippian Berea Sandstone, Silurian Medina Sandstone, and Ordovician Trenton/Black River Group oil and gas wells for comparison. Dissolved gases in shallow groundwaters in Devonian organic-rich shales along Lake Erie contain detectable methane (0.01 to 50.55 mole%) with low $\delta^{13}\text{C}\text{-CH}_4$ values (-74.68 to -57.86‰) and no higher chain hydrocarbons, characteristics typical of microbial gas. Nevertheless, these groundwaters have only moderate alkalinity concentrations (1.14 to 8.72 meq/kg) and relatively low $\delta^{13}\text{C}$ values of dissolved inorganic carbon (DIC) (-24.8 to -0.6‰), suggesting that microbial

methanogenesis is limited. The majority of natural gases in Devonian organic-rich shales and sandstones at depth (>168 m) in the northern Appalachian Basin have a low methane to ethane and propane ratios (3-35 mole%; C₁/C₂+C₃) and high δ¹³C and δD values of CH₄ (-53.35 to -40.24‰, and -315.0 to -174.6‰, respectively), which increase with depth, reservoir age and thermal maturity; the molecular and isotopic signature of these gases show that methane was generated via thermogenic processes. Despite this, the geochemistry of co-produced brines shows evidence for microbial activity. High δ¹³C values of DIC (>+10‰), slightly elevated alkalinity concentrations (up to 12.01 meq/kg) and low SO₄ values (<1 mmole/L) in select Devonian organic-rich shale and sandstone formation water samples suggest the presence of methanogenesis, while low δ¹³C-DIC values (<-22‰) and relatively high sulfate concentrations (up to 12.31 mmole/L) in many brine samples point to sulfate reduction, which likely limits microbial methane generation in the Appalachian Basin. Together the formation water and gas results suggest that the vast majority of methane in the Devonian organic-rich shales and sandstones across the northern Appalachian Basin margin is thermogenic in origin. Small accumulations of microbial methane are present at shallow depths along Lake Erie and in western NY.

INTRODUCTION

Fractured organic-rich shales in midcontinent United States Paleozoic basins are important source rocks for natural gas, and are estimated to account for up to 53% of the total U.S. shale gas production in 2010 (Energy Information Administration, 2009). Previous studies of the Upper Devonian Antrim and New Albany shales in the Michigan and Illinois basins have demonstrated that the vast majority of these gas resources were generated by microbial methanogenesis at the shallow (<550 m depth) basin margins where organic-rich shales are thermally-immature (vitrinite reflectance values less than 0.6) and basinal brines were diluted by subglacial recharge from melting Pleistocene ice sheets. Thermogenic gas deposits are present at depth (>550 m) in both basins (Martini et al., 1996, 1998; McIntosh et al., 2002, 2004) (Figure 2-1). The northern margin of the adjacent Appalachian Basin was glaciated during the Pleistocene and contains age-equivalent organic-rich shales with copious natural gas reserves (70 trillion cubic feet of undiscovered gas; Milici et al., 2003). Thus, we hypothesize that natural gas in the northern Appalachian Basin Devonian organic-rich shales was generated by both microbial and thermogenic processes, and is related to the thermal maturity of source rocks and aqueous environmental conditions, such as formation water salinity and availability of electron acceptors (e.g. SO₄).

To determine the origin and distribution of natural gas in Devonian organic-rich shales and reservoir sandstones at the shallow northern Appalachian Basin margin, herein we present combined gas and co-produced formation water geochemistry. Additional samples are included from Mississippian Berea Sandstone, Silurian Medina Sandstone and Ordovician Trenton/Black River Group reservoirs for comparison. This regional study has broader implications for targeted exploration of natural gas in other sedimentary basins and controls on subsurface microbial methanogenesis.

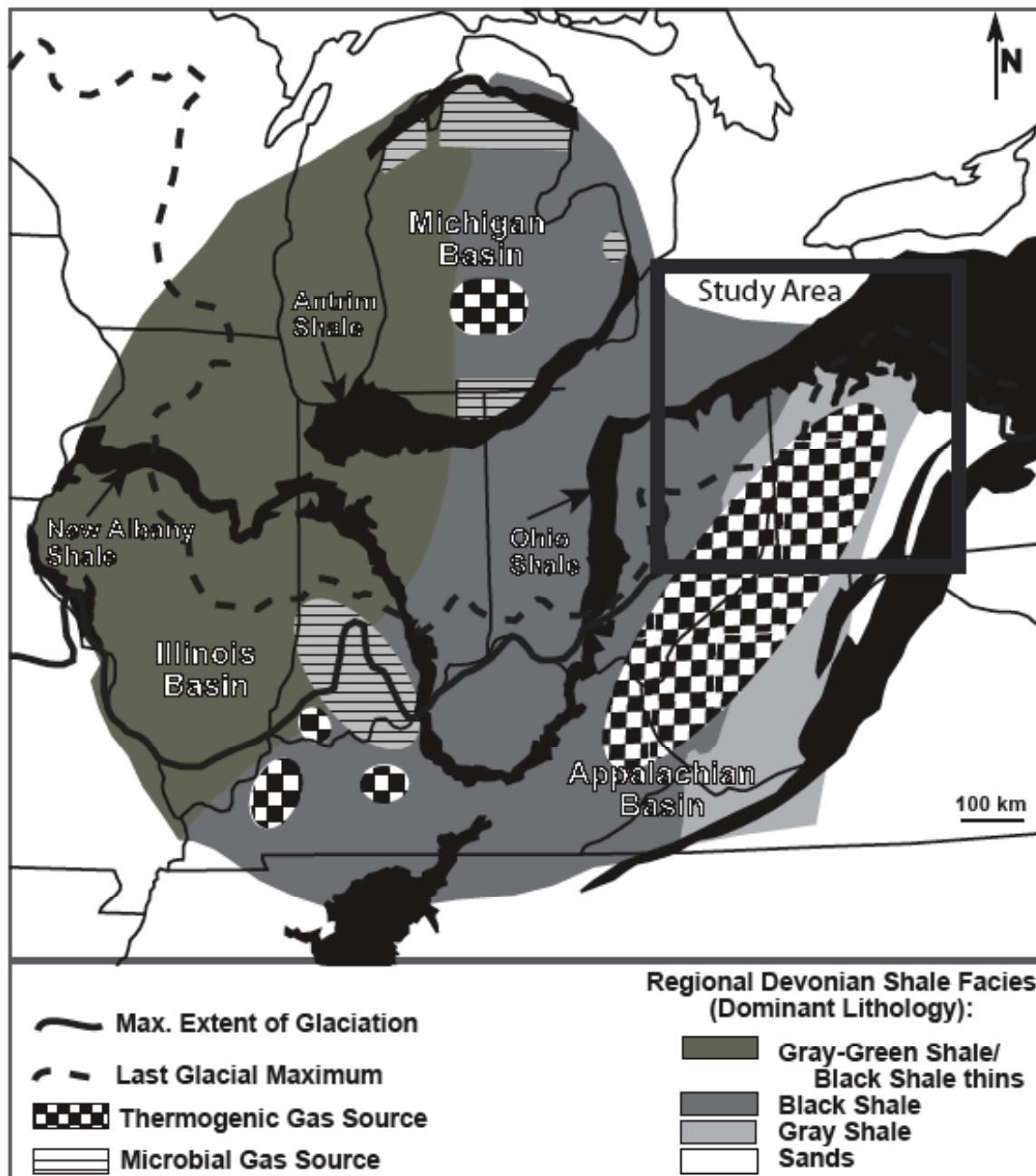


Figure 2-1. Generalized geologic map of the Great Lakes region depicting the location of known microbial and thermogenic gas sources in the Appalachian, Michigan, and Illinois basins in relation to the extent of Pleistocene glaciation (modified from McIntosh and Martini, 2008).

Indicators for Origin of Natural Gas from Produced Gases

Distinguishing between microbial and thermogenic methane is important for natural gas exploration and production strategies, and improved resource estimates. Thermogenic gas has a greater proportion of higher chain hydrocarbons (ethane, propane, butane, and pentane) relative to methane than microbial gas, which dominantly contains CH₄ and CO₂ (Schoell, 1980). Thus, gas composition may be used as a first

order approximation distinguishing between microbial and thermogenic gas. Multiple post genetic processes, such as microbial oxidation and migration, may alter gas contents, however (Prinzhofer and Huc, 1995; Prinzhofer and Pernaton, 1997; Whiticar, 1999).

Carbon and hydrogen isotopes of methane are widely used to further constrain the origin of natural gas. Schoell (1980) suggested that $\delta^{13}\text{C-CH}_4$ values less than -64‰ and ethane concentration less than 0.5 mole% may represent a purely microbial gas end-member, where as more positive $\delta^{13}\text{C-CH}_4$ values (up to approximately -50‰) may represent an admixture of thermogenic and microbial gas. The ratio of methane to higher chain hydrocarbons with values greater than approximately 1000 and carbon isotope values of methane ($\delta^{13}\text{C-CH}_4$) less than approximately -50‰ have been used as an indication of microbial gas generation (Bernard, 1978; Schoell, 1980; Whiticar et al., 1986). Jenden (1985) noted a poor correlation between the carbon isotope values of co-genetic methane and ethane and postulated that it was likely related to post genetic processes affecting the $\delta^{13}\text{C-CH}_4$ such as microbial oxidation and mixing between gases from different sources. The relatively good correlation between carbon isotopes of ethane ($\delta^{13}\text{C-C}_2$) and propane ($\delta^{13}\text{C-C}_3$) and thermal maturity of source rocks has been used qualitatively to identify thermogenic gas (Jenden, 1985, Martini et al., 1998). Thus, subsequent studies on thermogenic gas generation have largely focused on higher chain hydrocarbons to distinguish the genetic evolution of gas in sedimentary basins (Chung et al., 1988; Prinzhofer and Huc, 1995).

Chung et al. (1988) proposed a kinetic fractionation model (natural gas plot) that assumed a linear correlation between carbon isotope values ($\text{C}_1\text{-C}_5$) and the reciprocal carbon number as a qualitative indicator of purely thermogenic gas. Deviations from linearity in the heavier hydrocarbons ($\text{C}_2\text{-C}_5$) may be interpreted as a mixture of different thermogenic gas end-members and/or reflecting the heterogeneity within a single organic matter source. Depleted carbon isotope values of methane relative to a linear thermogenic end-member may result from mixed thermogenic and microbial gas. Carbon isotopes in the source organic matter become progressively enriched with increasing thermal maturity (kinetic isotope fractionation) resulting in a convergence of the $\delta^{13}\text{C}$ values (C_1 through C_5) in the gas phase and a relatively shallow slope to the gas plot. The sole use of gas composition and $\delta^{13}\text{C}$ values to determine the origin of natural gas is complicated by microbial production of higher chain hydrocarbons (i.e., ethane and propane) and secondary modifications during microbial oxidation and diffusive fractionation and mixing between multiple gas sources (Barker and Fritz, 1981; Prinzhofer and Pernaton, 1997; Boetius et al., 2000; Taylor et al., 2000; Martini et al., 2003; Hinrichs et al., 2006). Thus, additional indicators from formation water geochemistry are necessary to further constrain the origin of natural gas.

Indicators for Origin of Natural Gas from Produced Waters

Methanogens extract hydrogen from shale organic matter and in-situ formation waters to produce methane. The covariance of hydrogen isotope values of water and methane have been used as a strong indicator of methanogenesis, as well as identifying the predominant metabolic pathways for methane generation, as CO_2 reducing methanogens impart a different hydrogen isotope fractionation factor ($\alpha_{\text{CH}_4\text{-H}_2\text{O}}$) than acetate fermenting methanogens (Schoell, 1980; Whiticar et al., 1986; Martini et al., 1996). In addition, methanogens and associated microbial communities produce and consume CO_2 , imparting a strong ^{13}C - CO_2 fractionation; Martini et al. (1998) show that microbial gas accumulations contain high concentrations of CO_2 (up to 14.82 mole%) with very positive $\delta^{13}\text{C}\text{-CO}_2$ values ($>+20\text{‰}$). Production of CO_2 causes formation waters associated with methanogenesis to be enriched in alkalinity (>10 meq/kg), and have very positive $\delta^{13}\text{C}$ values of dissolved inorganic carbon (DIC) ($>10\text{‰}$).

Microbial methane generation is inhibited at high salinities and sulfate concentrations. A salinity level of approximately 2,000 mmole/L chloride has been proposed as a boundary for the onset of toxicity for methanogens, however, a range of tolerances is observed up to 4,000 mmole/L (Zinder, 1993; Ollivier et al., 1994; Waldron et al., 2007). Sulfate reducing bacteria (SRB) begin to out-compete methanogens in freshwater sediments for hydrogen and acetate at sulfate concentrations greater than 1 mmole/L (Lovley and Klug, 1982). These prior results demonstrate the importance of a combined gas and formation water approach for constraining the origin of natural gas in sedimentary basins.

GEOLOGIC BACKGROUND

The Appalachian Basin is a northeast trending foreland basin (Figure 2-1), which extends along its long axis from the Canadian Shield in Quebec and Ontario, Canada southwest to the northern portions of Alabama and Georgia in the United States. The western margin of the Appalachian Basin is relatively tectonically undeformed, while the eastern margin (Blue Ridge Province) is highly folded and faulted resulting from the Grenville, Taconic, Acadian, and Alleghanian orogenies (Popov et al., 2001). Paleozoic rocks lap onto structural highs (Findlay and Cincinnati arches) at the western and northwestern margins separating the Appalachian Basin from the Michigan and Illinois basins. The northern Appalachian Basin deepens and thickens to the east and southeast.

The Appalachian Basin has comparable stratigraphy to the adjacent Michigan and Illinois basins, resulting from similar depositional environments during the Paleozoic (Roen, 1993) (Figure 2-2A). The Paleozoic section of all three basins broadly consists of a cyclic sequence of carbonates, shales, siltstones and sandstones (Roen, 1984). This study focuses on the formation waters and gas in Devonian organic-rich shales and reservoir sandstones. The Devonian organic-rich shales and sandstones are major source rocks and reservoirs, respectively, in the Appalachian Basin. Select samples were also collected from the Lower

A)

SYSTEM	SERIES	FORMATION Illinois Basin	FORMATION Michigan Basin	FORMATION Appalachian Basin (E. OH) W. Penn./W. New York.
PERMIAN				
PENN.		Mississippian-Pennsylvanian Clastic and Carbonates	Mississippian-Pennsylvanian Clastic and Carbonates	Conemaugh Grp Allegheny Grp Burgoon Fm Murrysville Sand
MISS.		Borden Grp	Colswater/Sunberry Sh Cusworth/Berea/Bedford	Sunberry Sh Hera Ss
DEVONIAN	Upper	New Albany Shale	Antrim Shale	Ohio Shale Venango Grp. Bradford Grp. Rhinstreet Sh. Genesee Grp.
	Middle	Mudcatuck Grp	Trevose Grp Dundee Ls	Columbus Ls Hicksville Ls Oriskany Ss Marcellus Fm
	Lower	New Harmony Grp	Rock Blaine Ls Detroit River Grp Bass Islands Dol	Oriskany Ss Helderberg Grp
SILURIAN	Upper	Bainbridge Grp	Salina Grp	Salina Grp
	Middle		Niagara Grp Lockport Dol	Lockport Dol
	Lower	Sexton Creek Ls	Manitouville Grp Burrill Bluff Grp/ Catawba Grp	Rochester Sh & Dayton Dol Clinton Grp
ORDOVICIAN	Upper	Maquoketa Sh	Queenston Sh Utica Sh	Queenston Sh Reedsville Sh Utica Sh
	Middle	Trenton & Black River Grp	Trenton & Black River Grp	Trenton & Black River Grp
	Lower	St. Peter Ss Prairie du Chien Grp	St. Peter Ss Prairie du Chien Grp	Beekmantown Dol Little Falls Dol
CAMBRIAN	Upper	Munising Grp	Munising Grp	Beekmantown Dol Knox Dol/Nose Run Ss Barnes Fm Potsdam
	Middle	Mount Simon Ss	Mount Simon Ss	Home Fm Potsdam
	Lower		Precambrian	Potsdam Ss
PRE C.		Precambrian	Precambrian	Precambrian

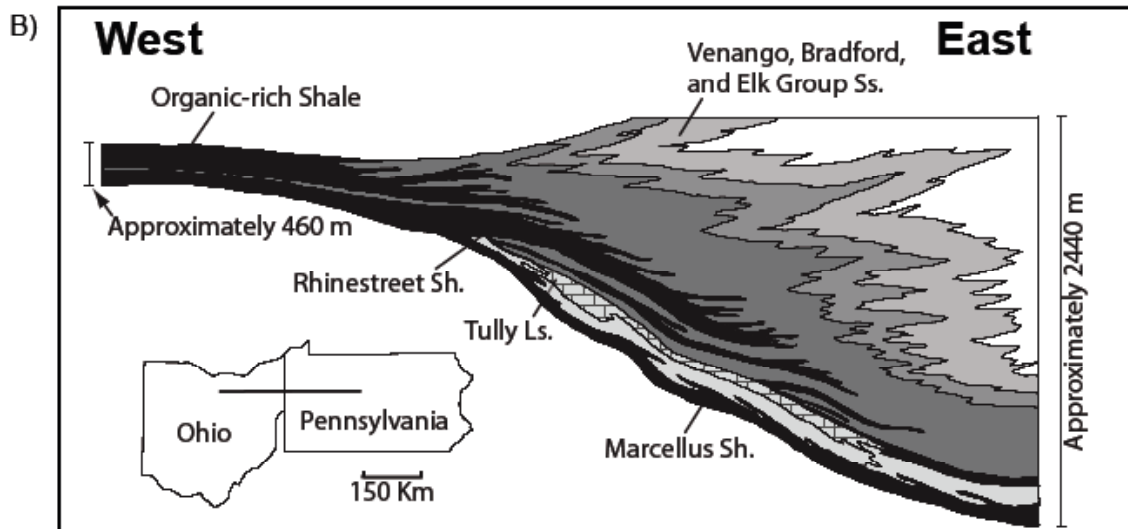


Figure 2-2. A) Stratigraphy of the Appalachian, Michigan and Illinois basins (modified from Shaver et al. (1986) and Laughrey and Baldassare (1998)). Geologic formations sampled as part of this study in the Appalachian Basin are identified by various symbols, which correspond to the sample location map and data figures. B) Regional cross-section (west-east) of the northern Appalachian Basin depicting the distribution of organic-rich shales and reservoir sandstone units of the Devonian section (modified from Harper and Laughrey (1987)).

Mississippian Berea Sandstone, Lower Silurian Medina Sandstone, and Middle Ordovician Trenton/Black River Group for comparison.

The Middle Ordovician Trenton and Black River Group limestones are deep oil/gas reservoirs in the Appalachian Basin, confined by Upper Ordovician shales (Utica, Reedsville, and Queenston shales) (Figure 2-2A). Oil and thermogenic gas accumulations in the overlying Lower Silurian Medina Group have been extensively developed along the northwestern margin of the basin. A series of Silurian and Lower Devonian carbonates, sandstones and bedded evaporites (Salina Group) separate the Lower Silurian Medina Group from the Upper Devonian organic-rich shales. The Upper Devonian Ohio Shale is composed of multiple organic-rich shales, including the Cleveland and Huron members. The Upper Devonian Venango, Bradford, and Elk Group sandstones are important hydrocarbon reservoirs that have historically had producing wells since the late 1800's (Boswell et al., 1996a,b). The Lower Mississippian to Upper Devonian Berea Sandstone overlies the Upper Devonian Ohio Shale and has been a target of oil and gas production historically in the Appalachian Basin.

The Devonian organic-rich shales are interbedded with grey shales and siltstones at the western basin margin near Lake Erie, which grade into coarser gray shales, siltstones, and sandstones (of the Venango, Bradford, and Elk groups) to the east and south (Figure 2-2B). The Devonian organic-rich shales have total organic carbon contents up to 4.5% and thermal maturity values that range from immature to over-mature for the generation of hydrocarbons, based on the vitrinite reflectance and conodont alteration index (CAI) (GRI, 2000; Milici, 1993).

HISTORY OF GAS PRODUCTION AND RESEARCH IN THE APPALACHIAN BASIN

The first known gas well in the United States was completed in the Upper Devonian organic-rich shales in Dunkirk, New York, in 1821. Exploration and production of natural gas in the Appalachian Basin has largely targeted thermogenic gas reservoirs toward the basin center (Figure 2-1) with little published research combining fluid and gas geochemistry to investigate the contribution and distribution of microbial gas accumulations at the northern basin margin. Published formation water data is largely limited to studies from the Silurian and some from the Devonian sections of the basin in northeast Ohio, western New York, and northwest Pennsylvania (Breen et al., 1985; Dresel, 1985; Lowry et al., 1988; Siegel et al., 1990; Sanders, 1991). In addition, gas studies by Jenden et al. (1993) and Laughrey and Baldassare (1998) in northwest Pennsylvania and western New York do not report co-produced formation water chemistry (Jenden et al., 1993; Laughrey and Baldassare, 1998).

Milici (1993) speculated that microbial methane may exist at the Appalachian Basin margin along Lake Erie, where organic-rich shales are thermally immature and relatively shallow. Subsequent shale gas studies in western New York and northwest Pennsylvania have determined that natural gas in the Appalachian Basin is dominantly thermogenic in origin based on carbon and hydrogen isotope values of

methane, ethane, and propane (Jenden et al, 1993; Laughrey and Baldassare, 1998). Laughrey and Baldassare (1998) reported five samples collected from the Upper Devonian Venango and Bradford formations and three Pennsylvania coal gas samples that have carbon isotope values of methane between -48.9 and -55.1‰ that may be interpreted as mixed microbial and thermogenic gas based on the definition

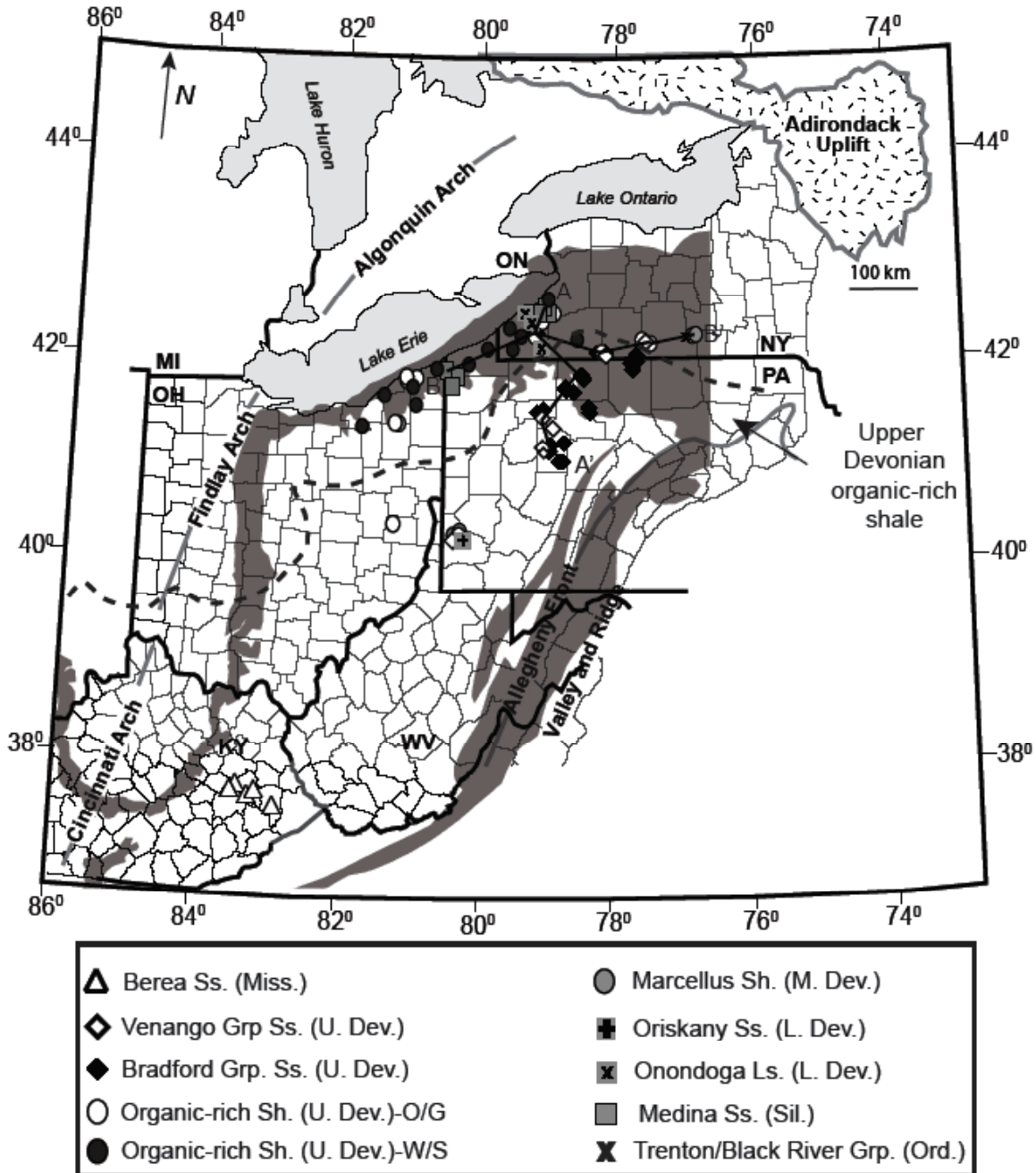


Figure 2-3. Map depicting the location of water and gas samples collected for this study from oil/gas (O/G) production wells and domestic water supply (W/S) wells in the Appalachian Basin. The extent of the Upper Devonian organic-rich shale subcrop (shaded area) and the maximum extent of Pleistocene glaciation (dotted line) are shown for reference. Lines of cross-section are outlined from north to south (A-A') and west to east (B-B'). Miss.=Mississippian; U. Dev. = Upper Devonian; M. Dev. = Middle Devonian; L. Dev. = Lower Devonian; Sil. = Silurian; Ord. = Ordovician.

by Schoell (1980). Laughrey and Baldassare (1998) interpreted these samples as likely resulting from low $\delta^{13}\text{C-CH}_4$ values that reflect the early migration of wet gas into the reservoirs.

METHODS

In order to constrain better the origin of natural gas resources in Devonian fractured shales and reservoir sandstones at the shallow northern Appalachian Basin margin, 61 natural gas samples were collected from active oil and gas wells producing from Mississippian through Ordovician age formations (50 samples from Devonian formations) in western New York, northwestern Pennsylvania, eastern Ohio, and eastern Kentucky (Figure 2-3; Table 2-1). Twenty-four co-produced formation water samples were also collected (20 from Devonian formations). There is anecdotal evidence that the majority of oil and gas wells at the northern Appalachian Basin margin do not produce formation water and was evidenced during fieldwork (i.e., only 24 formation water samples were able to be collected from a total 61 wells sampled). Samples were collected across thermal maturity gradients at the northern basin margin, from areas of low to high CAI (Figure 2-4). The depth of shale oil and gas wells sampled ranged from 137 to 2,256 m. Thirteen groundwater samples were also collected from shallow (<122 m depth) domestic and municipal drinking water supply wells screened in the Devonian shale sub-crop along Lake Erie from northwest Ohio through Erie county Pennsylvania and into western New York. Seven of the thirteen drinking water wells were sampled for dissolved gases.

Sampling Procedures and Field Analyses

Formation water samples were collected from oil and gas wellheads or from dedicated brine storage tanks where waters had been purged within 24-hours of sampling. Groundwater samples from domestic drinking water wells were collected from the wellhead or a faucet closest to the well and prior to any water treatment or storage tank. Temperature, conductivity, and dissolved oxygen were monitored during purging of the well and recorded after readings had stabilized. Water samples were then filtered through a 0.45 μm nylon filter into pre-cleaned sample containers. The pH was measured in the field with an Oakton 110 series pH meter and Orion Ross Combination electrode (precision, ± 0.01 pH units).

Samples for alkalinity and anion analyses were collected in 30 ml high density polyethylene (HDPE) bottles with no headspace. Samples for cation analyses were collected in 30 ml HDPE bottles and preserved with concentrated nitric acid to a pH of less than 2. Sample aliquots for carbon isotopes of DIC were collected in 30 ml capped glass serum vials with no head space and preserved with copper chloride to prevent microbial degradation. Samples for oxygen and hydrogen isotope analyses were collected in 30 ml glass scintillation vials with no head space. All formation water samples were kept on ice while in the field and refrigerated in the lab at 4°C until analyses were completed. Alkalinity was measured by the Gran-Alk titration method within 12 hours of sampling (Gieskes and Rogers, 1973) (precision, $\pm 0.6\%$).

Natural gas samples were collected from producing oil and gas wells into Isotubes[®] using a gas sampling manifold provided by Isotech Laboratories[®] (Champaign, Illinois) and in accordance with their instructions. Dissolved gases in groundwaters were collected into 1-L polyethylene terephthalate (PET) bottles pretreated with bacteriocide and in accordance with Isotech[®] instructions.

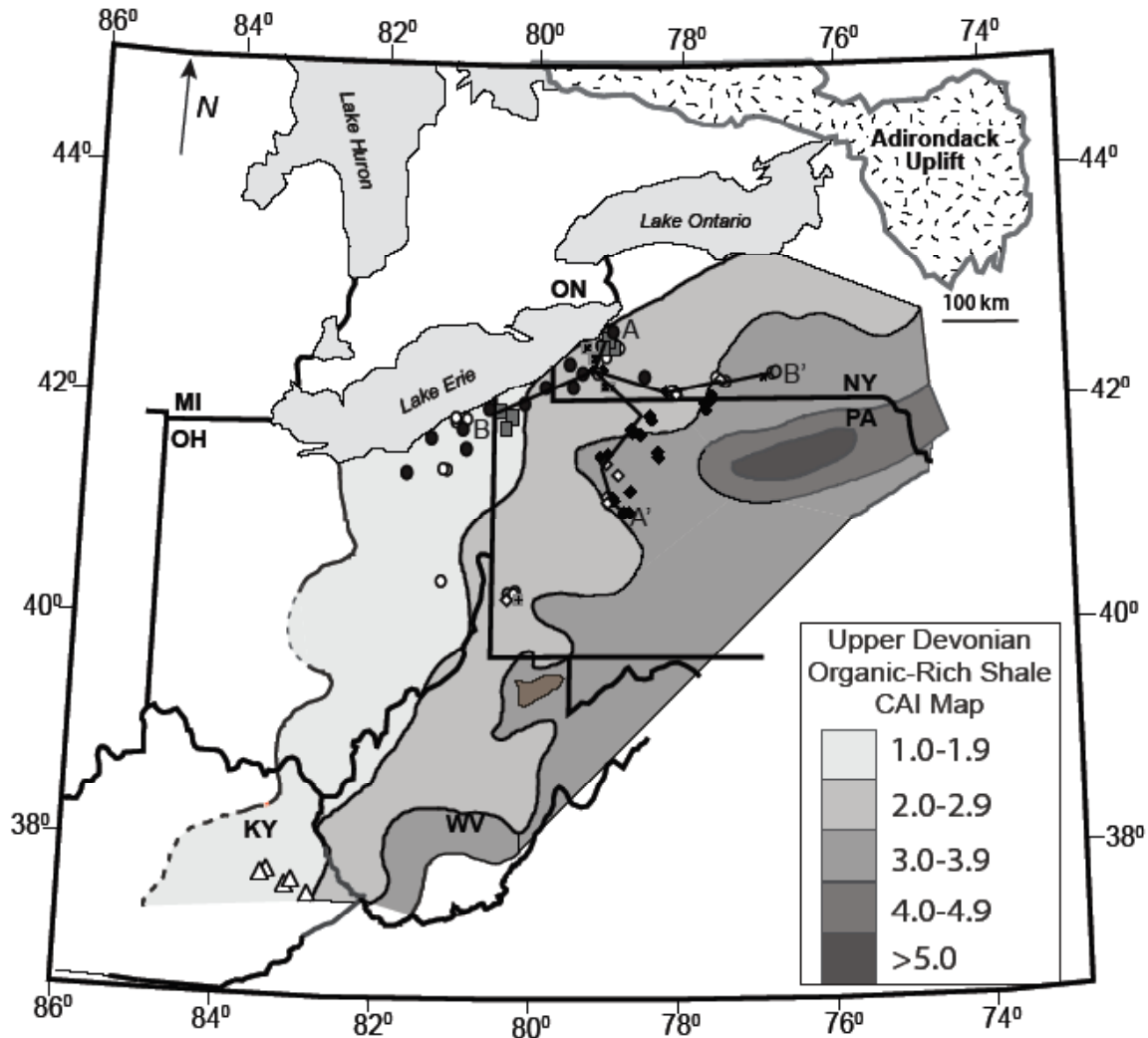


Figure 2-4. Map showing the conodont alteration index (CAI) of Upper Devonian organic-rich shales (modified from Repetski et al. (2006)), which is an indicator of thermal maturity; higher CAI values represent higher thermal maturities. Sample locations and cross-section lines are overlain for reference. Well symbols are the same as in Figure 2-3.

Laboratory Analyses of Gas and Formation Waters

Major and minor elemental chemistry of formation waters and groundwaters were analyzed in the Department of Hydrology and Water Resources at the University of Arizona (UA). Cation chemistry was measured by a Perkin Elmer Inductively Coupled Plasma Optical Emission spectrometer (ICP-OES)

Model Optima 5300 DV (precision, $\pm 2\%$). Anion chemistry was measured on a Dionex Ion Chromatograph Model ICS-3000 with an AS23 column (precision, $\pm 1\%$). Stable isotopes of oxygen, hydrogen, and carbon were measured in the Environmental Geochemistry Laboratory in the Geoscience Department (UA). The $\delta^{18}\text{O}$ and δD measurements were completed on a Finnigan Delta S gas-source isotope ratio mass spectrometer (precision, $\pm 0.9\%$ or better for hydrogen and $\pm 0.08\%$ or better for oxygen). The $\delta^{13}\text{C}$ -DIC was measured on a ThermoQuest Finnigan Delta Plus XL continuous-flow gas ratio mass spectrometer (precision, $\pm 0.30\%$ or better). Produced natural gas and dissolved gas samples were analyzed at Isotech Laboratories[®] for gas composition and compound specific isotopes. Gas composition analyses were measured on a custom-configured Carle Gas Chromatograph (GC) system ($\pm 2\%$ error) and based on the ASTM D1945 method. An offline preparation system and dual inlet mass spectrometer were used to analyze the carbon and hydrogen isotopic values of hydrocarbon components in gas samples (precision, $\pm 0.1\%$ for carbon isotopes and $\pm 2\%$ for hydrogen isotopes).

RESULTS

Gas and formation water samples collected for this study are divided into ten groups based on the age of the targeted geologic formation and type of well sampled: (1) Ordovician Trenton-Black River Group (gas well), (2) Silurian Medina Sandstone (oil/gas wells), (3) Lower Devonian Onondoga limestone (oil/gas wells), (4) Lower Devonian Oriskany Sandstone (oil/gas wells), (5) Middle Devonian Marcellus organic-rich shale (oil/gas wells), (6) Devonian organic-rich shales (oil/gas wells), (7) Devonian organic-rich shales (domestic water supply wells), (8) Upper Devonian Bradford Group sandstone (oil/gas wells), (9) Upper Devonian Venango Group sandstone (oil/gas wells), and (10) Mississippian Berea Sandstone (oil/gas wells). Well location, type, depth information are provided in Table 2-1. Gas molecular and isotopic compositions are presented in Table 2-2. Formation water chemistry is provided in Table 2-3.

Molecular and Isotopic Composition of Natural Gas

Methane is the dominant gas component in all natural gas samples from producing oil/gas wells, ranging in concentration from 59.24 to 98.47 mole% (Table 2-2 and Figure 2-5). The dominant dissolved gas component in all water supply wells (Devonian organic-rich shales), except for sample D58, is nitrogen with values ranging between 42.09 and 90.33 mole%. Methane is the dominant gas component in sample D58 at 50.55 mole%. Measured dissolved methane concentrations in water supply wells range between 0.01 and 50.55 mole%. Ethane concentrations in all natural gas samples range from 0.73 to 16.88 mole% and are all less than their respective methane concentrations (Table 2-2). Ethane was not detected in any samples from the water supply wells, except for sample D58 (0.01 mole%). Propane concentrations in all gas samples are less than their respective ethane concentrations, and range from 0.03 to 8.29 mole% (Table 2-2). Propane was not detected in any water supply well sample. The highest methane to ethane and propane ratios (C_1/C_2+C_3) were measured in dissolved gas samples from the shallow water supply wells in the Devonian organic-rich shales with values of 10 to 24,420 (Table 2-2 and Figure 2-5). Sample O74

from the Ordovician Trenton/Black River Group has a methane to ethane and propane ratio of 130. The remaining samples from oil and gas wells have methane to ethane and propane ratios between 2 and 35. Two gas samples (D11 and D42) have high nitrogen and oxygen concentrations (71.90 and 26.27 mole% N₂, and 21.35 and 6.66 mole% O₂, respectively), likely from atmospheric contamination. Thus, samples

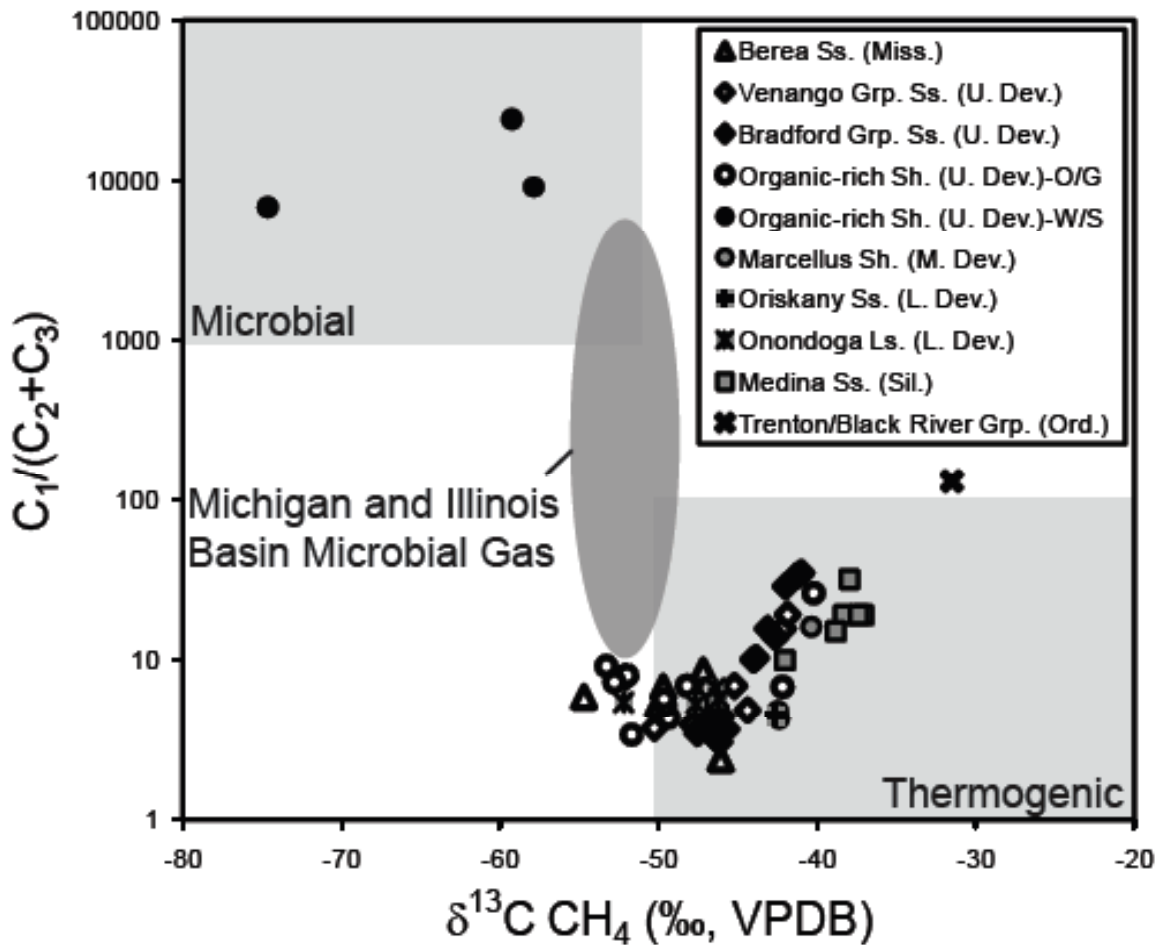


Figure 2-5. Plot of methane (C₁) to ethane (C₂) plus propane (C₃) ratio versus the carbon isotope value of methane. Typical fields for microbial and thermogenic gases (Schoell, 1980; Whiticar et al., 1986) are outlined. The range of microbial gas samples from the Michigan and Illinois basin margins are also shown for reference (Martini et al., 1998; McIntosh et al., 2002).

D11 and D42 are excluded from the discussion of gas composition, and methane to ethane and propane ratios above.

Carbon dioxide concentrations in all of the natural gas samples from oil/gas wells were too low (<0.170 mole%) to be analyzed for carbon isotope composition. Dissolved gas samples from the shallow Devonian organic-rich shales (water supply wells) contain between 0.270 and 5.250 mole% CO₂, with δ¹³C values of -29.19 to -11.76‰. Carbon and hydrogen isotope values of CH₄ across all natural gas samples range from -54.74 to -31.53 ‰ and -315.0 to -156.6 ‰, respectively (Table 2-2; Figures 2-5 and 2-9). The most

positive $\delta^{13}\text{C}$ and δD values of CH_4 were measured in the Ordovician Trenton/Black River Group gas sample (-31.53 ‰ and -156.6‰, respectively). The Devonian organic-rich shale water supply well samples have $\delta^{13}\text{C}$ and δD values of dissolved methane between -74.68 to -57.86‰ and -250.1 to -190.2‰, respectively. Carbon isotope values of methane gas samples collected from oil/gas wells generally become more positive with depth and laterally towards the basin center (Figure 2-6A,B).

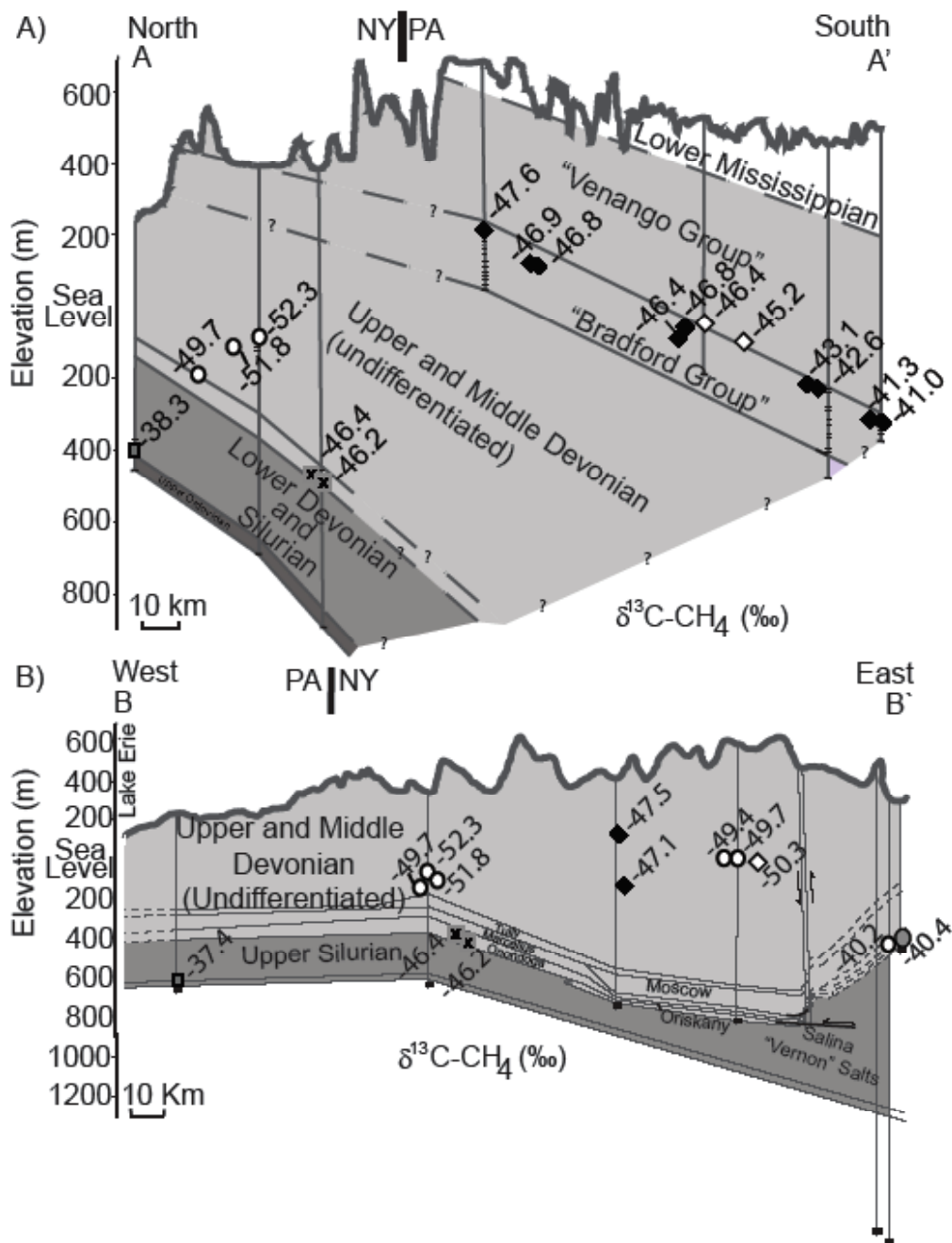


Figure 2-6. Carbon isotope values of methane plotted on the north-south (A) and west-east (B) cross-sections (transect lines shown in Figures 2-3 and 2-4). Values generally become more positive with depth and toward the basin center.

Except for the Ordovician Trenton/Black River Group sample (O74), carbon isotope values of ethane across all natural gas samples are more positive than their respective $\delta^{13}\text{C-CH}_4$ values, ranging between -47.53 and -31.37‰ (Table 2-2). The $\delta^{13}\text{C-C}_2$ value for the Ordovician Trenton/Black/River Group sample is -38.96‰, which is more negative than its corresponding $\delta^{13}\text{C-CH}_4$ value (-31.53‰). Sample M3 from the Mississippian Berea Sandstone in Kentucky has the most negative carbon isotope values of methane and ethane (-54.74 and -47.53‰, respectively).

Six gas samples (D6, D13, D14, D28, D31, and D38) were selected from the Upper Devonian organic-rich shales (oil/gas), Bradford Group sandstones and Venango Group sandstones for an extend carbon isotope analyses of propane and butane. The carbon isotope values of propane ($\delta^{13}\text{C-C}_3$) for these samples are more positive than their respective $\delta^{13}\text{C-C}_2$ values, ranging between -37.0 and -29.4‰ (Table 2-2 and Figures 2-7 and 2-8). The carbon isotope values of butane ($\delta^{13}\text{C-C}_4$) exhibit a similar trend with respect to $\delta^{13}\text{C-C}_3$. The $\delta^{13}\text{C-C}_4$ values range between -34.5 and -27.4‰ (Table 2-2 and Figures 2-7 and 2-8).

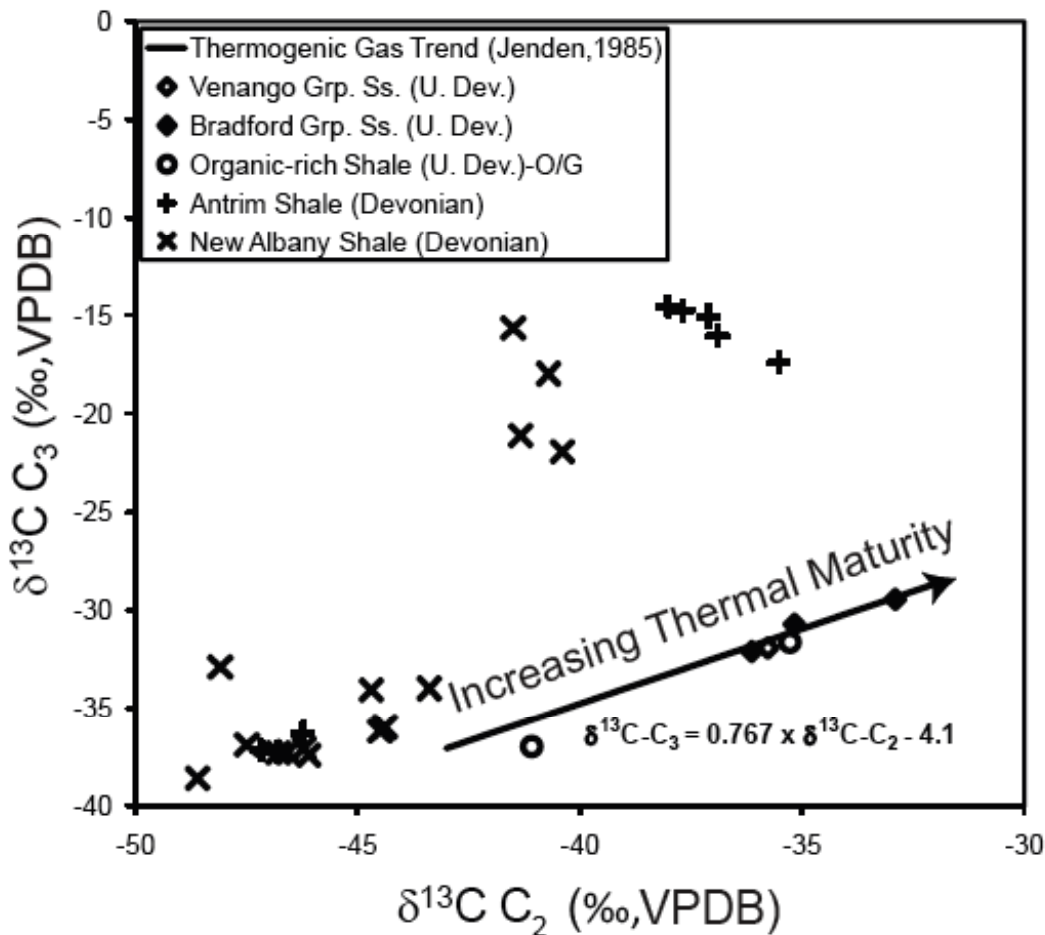


Figure 2-7. Plot of carbon isotope values of ethane (C_3) versus propane (C_2). The black arrow depicts the typical trend for thermogenic gases with increasing thermal maturity (Jenden, 1985). Microbial gas data from Devonian organic-rich shales in the Michigan (Antrim Shale) and Illinois (New Albany Shale) basins are provided for reference (Martini et al., 1998; McIntosh et al., 2002).

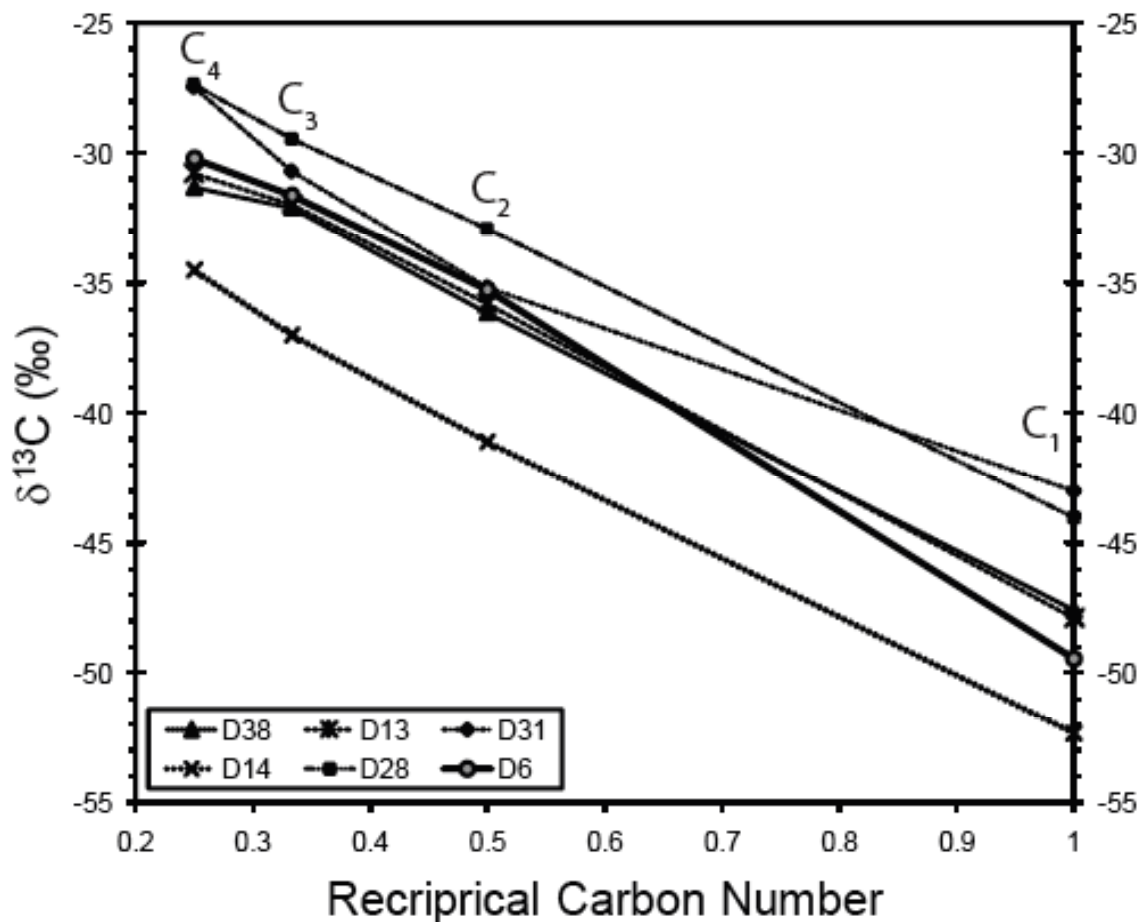


Figure 2-8. Plot of carbon isotope values of methane (C₁), ethane (C₂), propane (C₃), and butane (C₄) versus the reciprocal carbon number of select gas samples. Most samples plot along a relatively straight line consistent with thermogenic gas. Sample D6 has a depleted carbon isotope value of methane relative to its straight-line (thermogenic) end-member and may be interpreted as resulting from mixed microbial and thermogenic gas.

Formation Water Geochemistry

Formation waters collected from oil and gas wells are referred to as brine throughout the remainder of the paper, to distinguish them from formation waters collected from the shallow domestic water supply wells (referred to as groundwaters). The temperature of all brines ranges between 12.1 and 29.6 °C, and the pH ranges from 4.30 to 7.53 (Table 2-3). Groundwaters have temperature and pH values between 11.3 to 15.6 °C, and 7.01 to 8.41, respectively. Alkalinity concentrations in brines range from 0.13 to 12.01 meq/kg (Figure 2-9). Groundwaters have alkalinity values ranging from 1.14 to 8.72 meq/kg.

Chloride is the dominant anion in all brine samples, with values from 919 to 4,496 mmole/L. Seven brine samples (M1, D6, D10, D14, D24, D27, and D37) out of 24 measured have chloride concentrations less than 2,000 mmole/L (methanogens are known to be inhibited at high salinities, starting at ~2,000 mmole/L Cl⁻; Zinder, 1993; Ollivier et al., 1994; Waldron et al., 2007) (Figure 2-10A). Chloride concentrations of

groundwaters range from 0.091 to 12.558 mmole/L. Chloride concentrations generally increase with depth and from west to east (Figure 2-11).

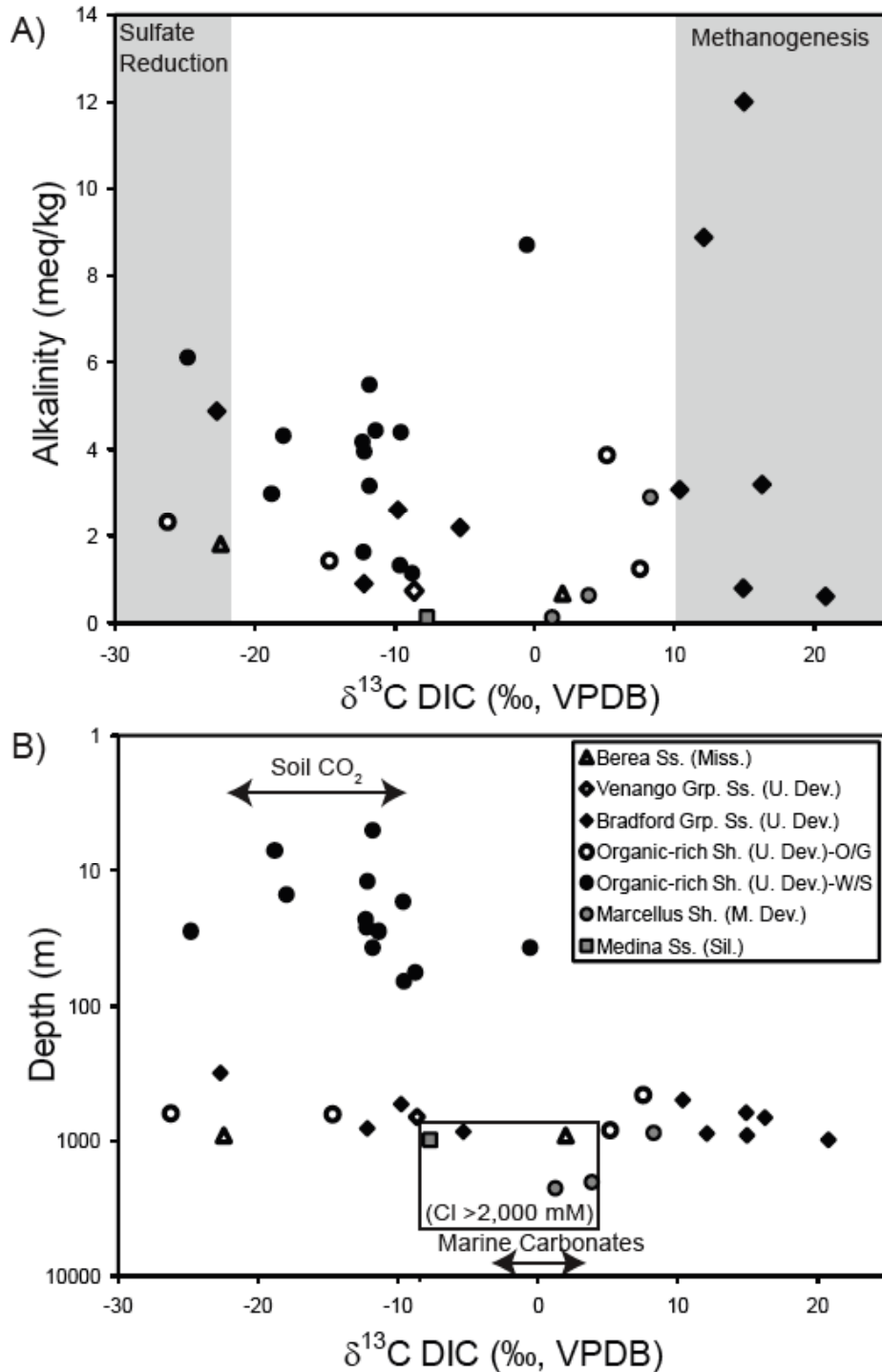


Figure 2-9. A) Plot of alkalinity versus carbon isotope values of dissolved inorganic carbon (DIC) in formation waters. B) Plot of $\delta^{13}\text{C}$ -DIC values with depth. Ranges in carbon isotope values for methanogenesis, sulfate reduction, soil CO_2 , and marine carbonates are taken from Clark and Fritz (1997). Formation waters at depth with chloride concentrations greater than 2,000 mmole/L and $\delta^{13}\text{C}$ -DIC values near 0 ‰ are typical of saline fluids that have not been affected by microbial activity.

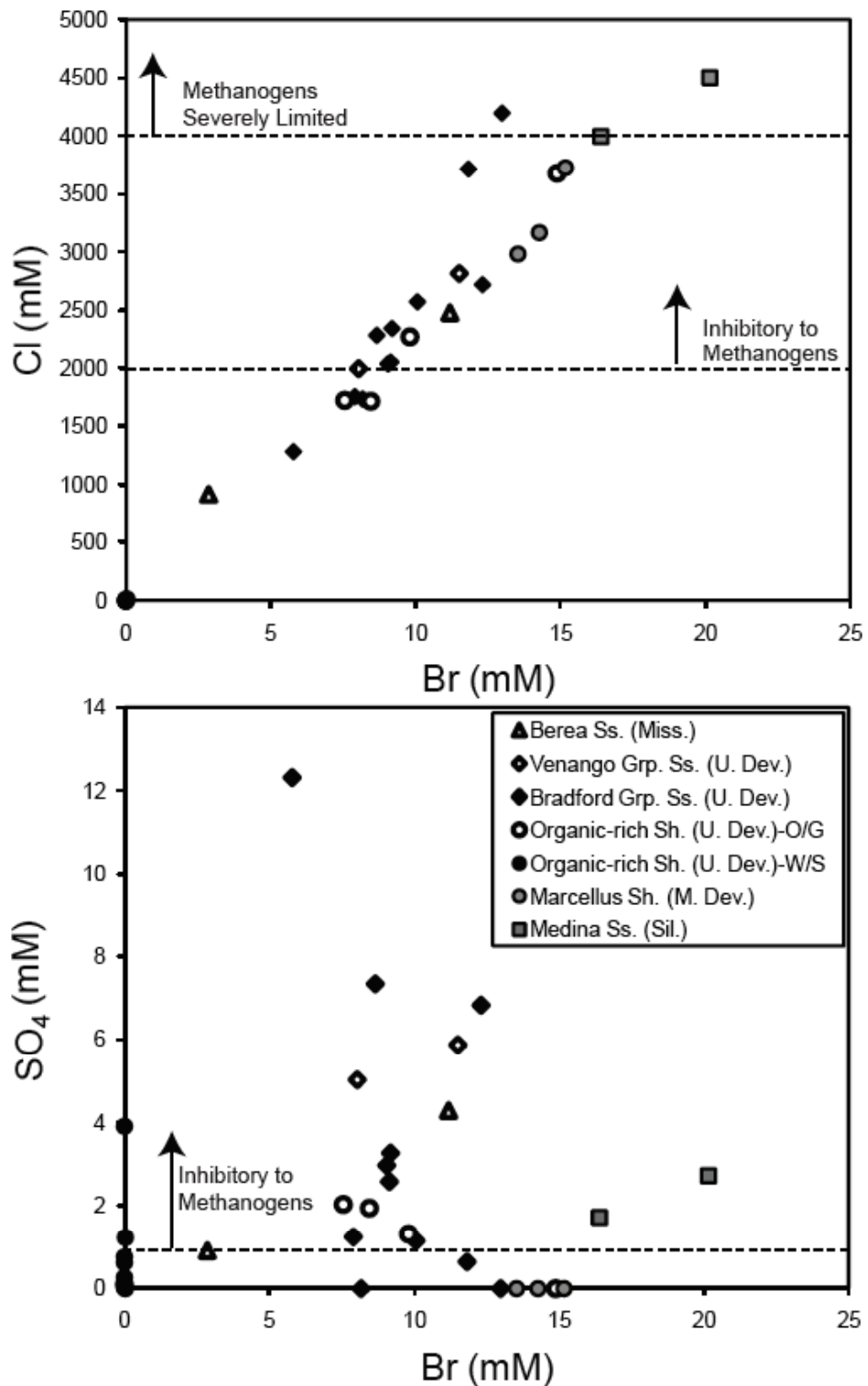


Figure 2-10. A) Plot of chloride versus bromide concentrations in formation waters. Chloride concentrations above ~2000 mmole/L are typically inhibitory for microbial metabolism (Zinder, 1993; Ollivier et al., 1994). Methanogens are severely limited above ~4000 mmole/L (Waldron et al., 2007). B) Plot of sulfate versus bromide concentrations in formation waters. Sulfate reducing bacteria typically out compete methanogens at sulfate concentrations above ~1 mmole/L (Lovley and Klug, 1982).

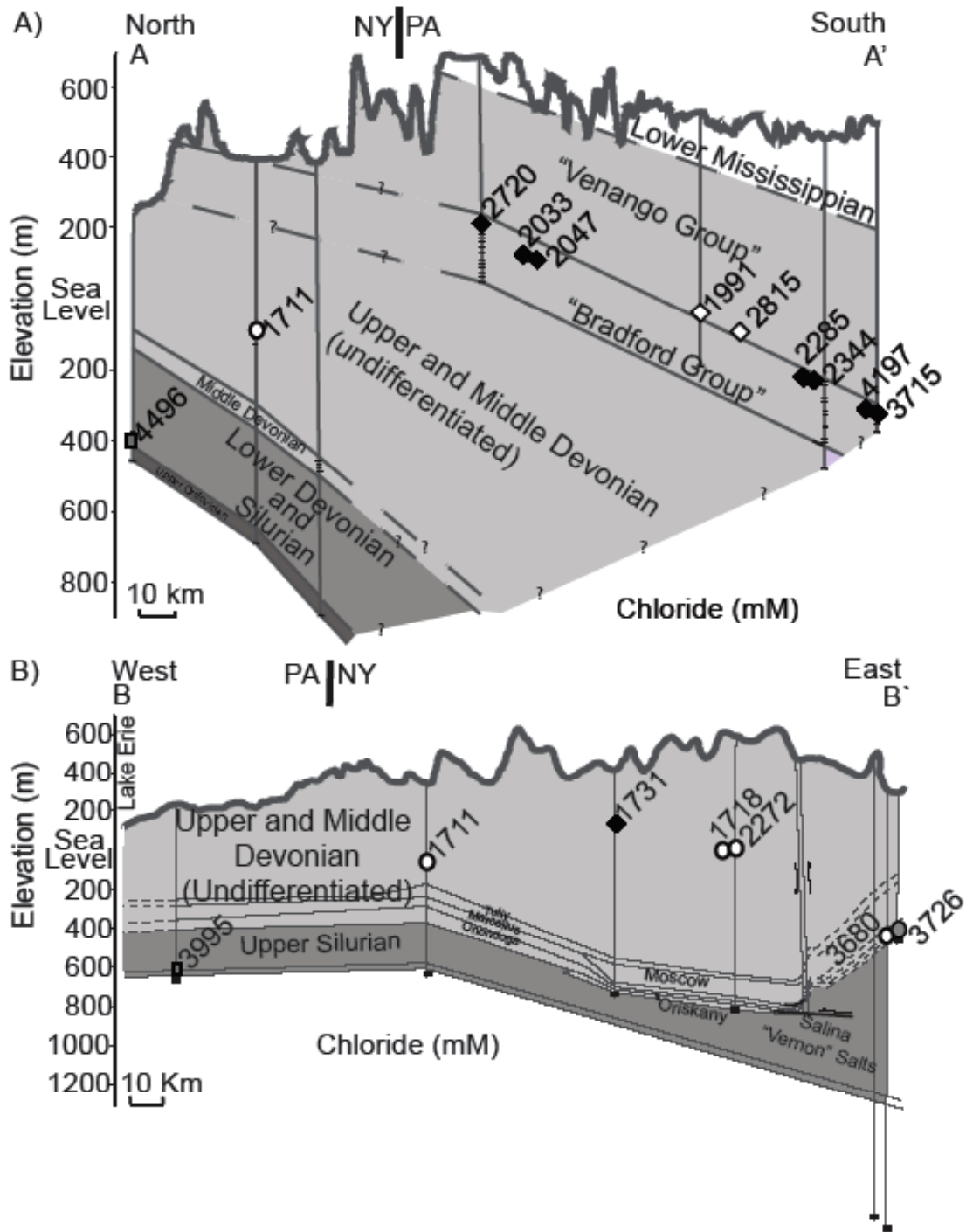


Figure 2-11. Chloride concentrations of formation waters overlain on the north-south (A) and west-east (B) cross-sections. In general, chloride increases with depth, excluding some local variations, to values that are inhibitory to microbial metabolism (>~2,000 mmole/L; Zinder, 1993; Ollivier et al., 1994).

Bromide concentrations in brine samples range between 2.85 and 20.14 mmole/L, while SO_4 concentrations range from below detection to 12.31 mmole/L. There are eight brine samples (M1, D10, D17, D29, D30, D60, D61, and D62) with sulfate concentrations less than 1 mmole/L – the approximate limit above which sulfate reducing bacteria typically outcompete methanogens (Lovley and Klug, 1982; Figure 2-10B). Groundwaters have Br and SO_4 concentrations less than 0.0340, and 3.895 mmole/L, respectively.

There is a wide range of carbon isotope values of DIC in groundwater and brine samples. Groundwaters have $\delta^{13}\text{C}$ -DIC values between -24.8 and -0.6‰, while brines at depth range between -26.2 and +20.8‰ (Table 2-3, Figure 2-9A,B). Oxygen and hydrogen isotope values of brines range between -7.1 and -0.4‰ and -55.6 and -30.2‰, respectively (Figure 2-12). The $\delta^{18}\text{O}$ and δD values of Devonian organic-rich shale groundwaters range from -11.6 to -9.1‰ and -76.6 to -56.9‰, respectively, more negative than the brine samples at depth.

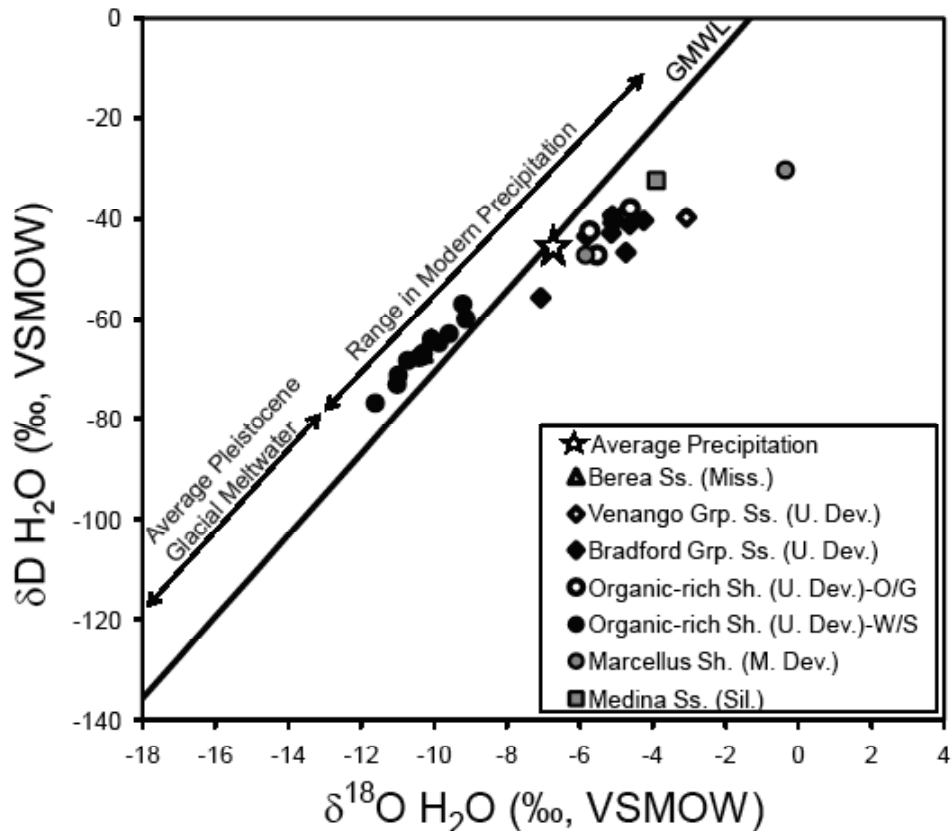


Figure 2-12. Plot of oxygen and hydrogen isotope values of formation waters relative to the Global Meteoric Water Line (GMWL; Craig, 1961). The local meteoric water line overlaps the GMWL and is not shown in this figure. The $\delta^{18}\text{O}$ value of mean annual weighted precipitation in the study area (Northern Lake Erie) is -6.7‰, and the range of precipitation $\delta^{18}\text{O}$ values is -12.2 to -3.7‰ (Huddart et al., 1999). Pleistocene glacial meltwaters, which have been shown to be an important source of recharge to shales in the Illinois and Michigan basins, are depleted in ^{18}O and ^2H , with $\delta^{18}\text{O}$ values ranging from less than -16‰ to approximately -12‰ (Martini et al., 1998; McIntosh et al., 2002).

DISCUSSION

In general, there were no prominent differences observed in the formation water and gas geochemistry of samples collected from oil and gas wells in the Upper Devonian organic-rich shales, Upper Devonian Venango Group sandstones, Upper Devonian Bradford Group sandstones, Middle Devonian Marcellus organic-rich shale, Lower Devonian Oriskany Sandstone, and Lower Devonian Onondoga limestone. This is based on the methane to ethane and propane ratios, $\delta^{13}\text{C-CH}_4$, $\delta^{13}\text{C-DIC}$, δD , $\delta^{18}\text{O}$, and elemental analyses. Thus, all of the data from oil and gas wells in the Devonian section (shale and sandstone reservoirs) are treated as a petroleum system and discussed as a whole, regardless of the different formation ages and lithologies. The Mississippian Berea Sandstone, Silurian Medina Sandstone and Ordovician Trenton/Black River Group data exhibit some observable differences with the Devonian section oil and gas wells and with each other. These geologic sections are discussed separately when these differences are pronounced. The gas and formation water data collected from the shallow Devonian organic-rich shale domestic water supply wells are treated separately in the discussion from the oil and gas well data.

Dominance of Thermogenic Gas

Natural gas samples collected from the Devonian section, Mississippian Berea Sandstone, Silurian Medina Sandstone and Ordovician Trenton/Black River Group oil and gas wells are dominantly thermogenic in origin, based on the relatively high concentrations of higher chain hydrocarbons (e.g. ethane, propane), relatively positive carbon isotope values of methane ($>-50\text{‰}$), and low methane to ethane and propane ratios (<35) that increase with depth and toward the basin center (Table 2-2 and Figures 2-5 and 2-6). Additional evidence of thermogenic gas at the northern Appalachian basin margin is the low CO_2 concentrations (<0.170 mole% for all oil and gas wells), covariance between $\delta^{13}\text{C-C}_2$ and $\delta^{13}\text{C-C}_3$ (Figure 2-7), systematically more positive $\delta^{13}\text{C}$ values of the higher chain hydrocarbons with increasing carbon number (Table 2-2 and Figure 2-8), and the apparent absence of a relationship between the hydrogen isotopes of methane and water, which would be expected for gas generated via microbial methanogenesis (Figure 2-13).

Most natural gas samples (with $\delta^{13}\text{C-CH}_4$ values $>-50\text{‰}$) plot within the thermogenic gas field in Figure 2-5, along a trend of increasing methane to ethane and propane ratios and $\delta^{13}\text{C-CH}_4$ values that appear to relate to reservoir age, depth and distance towards the basin center (Figure 2-6A,B). The Ordovician Trenton/Black River Group gas sample has the most positive $\delta^{13}\text{C-CH}_4$ value and highest methane to ethane and propane ratio of the gas samples collected for this study. The Silurian Medina Sandstone samples have $\delta^{13}\text{C-CH}_4$ values that are generally more positive than the Devonian and Mississippian sections, and higher methane to ethane and propane ratios. Gas samples from the Mississippian Berea Sandstone have $\delta^{13}\text{C-CH}_4$ values that are lower than only eight gas samples from the Devonian section and all of the Silurian section samples. Jenden et al. (1993) interpret similar trends (increasing $\delta^{13}\text{C-CH}_4$ and

C_1/C_2+C_3) in their Appalachian Basin gas data as resulting from a mixture of thermogenic gas sourced from organic matter with significantly different thermal maturities. The average concentration of methane for all oil and gas wells increases with increasing formation age, while the reverse trend is observed in ethane and propane relative concentrations (Section 5.1). Data reported by Laughrey and Baldassere (1998) collected closer to the structural front of the Blue Ridge Province in central and western Pennsylvania from coal beds (Pennsylvanian), and shales (Devonian and Silurian) exhibit no apparent trend in the average methane concentration with increasing formation age. However, there is a slight increasing trend in average ethane and propane concentrations as might be expected for early thermogenic gas production.

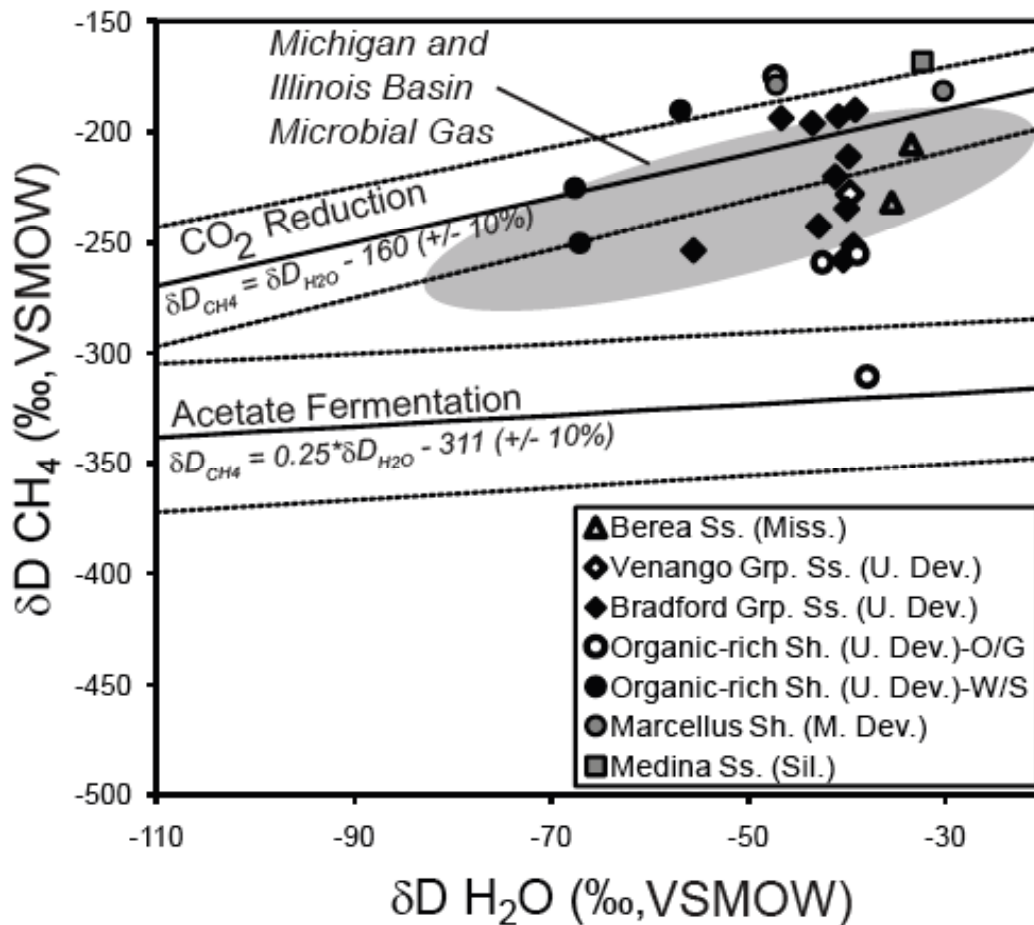


Figure 2-13. Hydrogen isotope composition of co-produced methane and water. Fractionation lines for microbial methanogenesis via CO_2 reduction and acetate fermentation are shown for reference (Whiticar et al., 1986). The range of microbial gas data from the Illinois and Michigan basins (Martini et al., 1998; McIntosh et al., 2002) is highlighted in the grey oval.

Jenden (1985) observed a correlation ($r^2=0.88$) between the carbon isotope values of ethane and propane and noted that the isotopic fractionation between ethane and propane decreases with increasing thermal maturity of the source organic matter. The six gas samples from the Upper Devonian organic-rich shale,

Bradford and Venango Group sandstones oil and gas wells were analyzed for extended carbon isotope analyses ($\delta^{13}\text{C-C}_2$ and $\delta^{13}\text{C-C}_3$) and plot in Figure 2-7 along the thermal maturity trend of Jenden (1985). This result may indicate that increasing thermal maturity of the source organic matter rather than microbial oxidation in these gas samples has a major control on the $\delta^{13}\text{C}$ value of CH_4 . The same samples for the extended carbon isotope analyses were used to construct a natural gas plot (Figure 2-8). Linear to sub-linear trends in samples D13, D14, D28, and D38 may be interpreted as typical of thermogenic gases based on the definition by Chung et al. (1988). The result from sample D31 has carbon isotope values of propane and butane that are more positive than a linear end-member and may be interpreted as mixing between different thermogenic end-members. This is consistent with results by Jenden et al. (1993) in western New York. Sample D6, collected in western New York near Lake Erie, exhibits low $\delta^{13}\text{C-CH}_4$ values relative to a purely thermogenic linear end-member and has a sub-linear trend in the higher chain hydrocarbons ($\text{C}_2\text{-C}_4$), which may be interpreted as resulting from the addition of microbial gas depleted in ^{13}C .

Combined Gas and Water Evidence for Microbial Methane Generation

Three of the seven dissolved gas samples collected along Lake Erie from Devonian organic-rich shales (water supply wells) contained methane above trace levels (9.16, 24.42, and 50.55 mole%). A trace amount of ethane was detected only in sample D58 with no higher chain hydrocarbons detected in any dissolved gas sample. The three dissolved gas samples with significant methane concentrations plot within the microbial gas field in Figure 2-5 with high methane to ethane and propane ratios (<6,831) and relatively negative $\delta^{13}\text{C-CH}_4$ values (-57.86 to -74.68‰). Although it is possible that these samples may be thermogenic in origin and the carbon isotope values have been fractionated during migration from depth (Prinzhofer and Pernaton, 1997), the lack of measureable higher chain hydrocarbons (except for D58) supports a microbial origin. It is interesting that sample D58 had measureable ethane (0.01 mole%). Microbial ethane production in anoxic sediments and shallow groundwater systems has been proposed by Oremland et al. (1988), Taylor et al. (2000) and Hinrichs et al. (2006). Taylor et al. (2000) showed that significant microbial methane and ethane is produced in dissolved gas samples collected from relatively shallow water supply wells. Ethane was a minor component in their study with reported methane to ethane ratios (CH_4/C_2) between 875 and 11,714 and $\delta^{13}\text{C-CH}_4$ values between -90.3 and -69.2‰. Although the $\delta^{13}\text{C-C}_2$ was not measured for sample D58, the CH_4/C_2 value is greater than 5,000 and the $\delta^{13}\text{C-CH}_4$ value (-74.68‰) is consistent with a microbial origin of methane and possibly ethane based on Taylor et al. (2000).

Eleven natural gas samples from all oil/gas wells with $\delta^{13}\text{C-CH}_4$ values less than -50‰, display a trend of increasing methane to ethane and propane ratios and decreasing $\delta^{13}\text{C-CH}_4$ values (Figure 2-5). Although these samples have low methane to ethane and propane ratios, this trend may reflect mixing between minor amounts of microbial gas and a larger reservoir of thermogenic gas. Laughrey and Baldassare (1998) report several samples from the Upper Devonian Venango and Bradford groups in central-western

Pennsylvania (south and east of the study area reported herein) that plot within the mixed microbial and thermogenic gas based on Schoell (1980). They interpreted these samples as reflecting the early migration of low methane to ethane and propane gases into the sampled reservoirs. Sample D6 from this study was interpreted above as resulting from mixing between biogenic gas and a larger reservoir of thermogenic gas based on the extended carbon isotope values of the gas (Chung et al., 1988). This sample, however, has a $\delta^{13}\text{C-DIC}$ value of -26.2 ‰ that is consistent with sulfate reduction. Furthermore, the δD value of methane and co-produced waters for D6 do not plot within a range consistent with microbial methanogenesis (Figure 2-13).

There is no apparent correlation between the δD values of CH_4 and co-produced formation water across all samples (oil/gas and water supply wells), which would be expected if microbial methanogenesis by CO_2 reduction or acetate fermentation were present (Figure 2-13). However, there are some samples that have $\delta\text{D-CH}_4$ values within the range of microbial methane from the Michigan and Illinois basins (Martini et al., 1998; McIntosh et al., 2002). In summary, the gas results suggest that if microbial methane is present in Devonian shales in the northern Appalachian Basin, it is likely only in minor amounts relative to much larger accumulations of thermogenic gas.

Elemental and isotopic chemistry of co-produced brines and groundwaters provide further constraints on the presence of microbial methanogenesis, and possible limitations on microbial activity. Brines and groundwaters in Devonian organic-rich shales and sandstones have a wide range of carbon isotope values of DIC (-26.2 to 20.8‰), with no apparent trend with alkalinity (Figure 2-9A). In contrast, brines associated with microbial methane in the Michigan and Illinois basins show a strong trend of increasing $\delta^{13}\text{C-DIC}$ values with increasing alkalinity (up to >20‰ and ~64 meq/kg, respectively; Martini et al., 1998; McIntosh et al., 2002). The large variation in $\delta^{13}\text{C-DIC}$ values of Appalachian Basin brines and groundwaters may be interpreted as a mixture of methanogenesis, sulfate reduction, soil CO_2 (likely less a factor with depth) and carbonate dissolution. End-member values for these carbon sources are highlighted in Figure 2-9A. The alkalinity concentration of groundwaters and brines is less than 12.01 meq/kg, considerably lower than alkalinity values measured in the Michigan and Illinois basin microbial gas plays (up to 64 meq/kg; Martini et al., 1998; McIntosh et al., 2002). Several Appalachian Basin brine samples have very positive $\delta^{13}\text{C-DIC}$ values (D27, D30, D31, D32, D38, D39) that can only be explained by microbial methanogenesis, yet alkalinity values are relatively low, which may result from: 1) the initial stages of methanogenesis, where by alkalinity from microbial methanogenesis has not accumulated, and/or 2) possibly from an open hydrologic flow system where alkalinity concentrations are diluted by input of new waters.

Groundwaters in shallow Devonian organic-rich shales (water supply wells, <65 m depth) have variable $\delta^{13}\text{C-DIC}$ values (-24.8 to -0.6‰) within the range of sulfate reduction, soil CO_2 , and carbonate dissolution

(Figure 2-9B). These wells contained dissolved methane with carbon isotope values (-74.68 to -57.86‰) indicative of methanogenesis. It appears that some microbial methane has been generated in the shallow Devonian organic-rich shales, but possibly not enough to dominant the groundwater carbon chemistry.

In Figure 2-9B, we have outlined the brine samples from the Silurian Medina Sandstone, Middle Devonian Marcellus organic-rich shale, Bradford Group sandstone, and Mississippian Berea Sandstone that were collected from the greatest depths (>900 m) in the basin and had chloride concentrations greater than 2,000 mmole/L (M4, D62, D63, and S73). These samples have $\delta^{13}\text{C-DIC}$ values close to 0‰, consistent with the dissolution of marine carbonates, which are ubiquitous throughout the northern Appalachian Basin (Colton, 1970). There is no indication of microbial activity in these samples, as evidenced by the low alkalinity values (0.13 to 0.69 meq/kg).

Brine samples collected from an intermediate depth zone (168 to 900 m; Figure 2-9B) in the Silurian Medina Sandstone, Middle Devonian Marcellus organic-rich shale, Upper Devonian organic-rich shales, Bradford Group sandstone, Venango Group sandstone, and Mississippian Berea Sandstone exhibit a wider range of $\delta^{13}\text{C-DIC}$ values that indicate that sulfate reduction, marine carbonate dissolution, and/or microbial methanogenesis may be occurring. Processes in this intermediate zone are likely controlled by the presence of electron acceptors such as sulfate that may limit methanogenesis in favor of sulfate reduction, and/or formation water salinity, although several brine samples (D30, D31, D32, D38, and D39) have $\delta^{13}\text{C-DIC}$ values indicative of methanogenesis at chloride concentrations greater than 2,000 mmole/L. Additional potential controlling factors that need to be investigated include the absence of a consortium of microbes in the Devonian organic-rich shales supportive of methanogenesis, the lack of formation waters in the shales necessary for microbial activity (as observed during sampling), and/or the thermal maturity of the source organic matter. Laughrey (2008) recently suggested that Devonian shales in the northern Appalachian Basin may be more thermally matured than the vitrinite reflectance or CAI measurements conclude, which would decrease the availability of the organic matter for microbial metabolism.

Potential Inhibitors of Microbial Methanogenesis

Chloride to bromide relations of Appalachian Basin brines and shallow groundwaters show a mixing trend between a saline end-member enriched in Cl and Br, likely from evaporated Paleozoic seawater, and dilute meteoric water (Figure 2-10A). All groundwaters from the basin margin, along Lake Erie, one Mississippian Berea Sandstone, one Venango Group sandstone, three Bradford Group sandstone, and two Upper Devonian organic-rich shale samples have chloride concentrations below 2,000 mmole/L, indicating that salinity is unlikely to inhibit microbial activity in these wells (Zinder, 1993; Ollivier et al., 1994, and Waldron et al., 2007). The remainder of the brines samples have high chloride concentrations (>2000 mmole/L), which may strongly inhibit methanogenesis, as observed in the Upper Devonian Antrim Shale in the Michigan Basin (Waldron et al., 2007).

Chloride concentrations in brines generally increase from less than 1,300 mmole/L at the shallow basin margin to greater than 2,000 mmole/L with depth (Figure 2-11A). The same increasing chloride trend in brines is apparent from the basin margin (1,711 mmole/L Cl) near Lake Erie east toward central New York (3,715 mmole/L Cl) (Figure 2-11B). Brines in the underlying Silurian Medina Sandstone have higher chloride concentrations (3,995 to 4,496 mmole/L).

Only one brine sample (D27) out of the six that have $\delta^{13}\text{C-DIC}$ values greater than +10‰ (indicative of methanogenesis) has a Cl concentration less than 2,000 mmole/L; the other five samples have chloride values between 2,033 and 4,197 mmole/L. Zinder (1993), Ollivier et al. (1994) and Waldron et al. (2007) show that acetoclastic methanogens are limited at chloride concentrations above 2,000 mmole/L, but that CO_2 reducing methanogens can survive up to ~4,000 mmole/L. Our results suggest that chloride is not the dominant factor controlling microbial activity at the northern Appalachian Basin margin.

There is no apparent trend between sulfate and bromide (Figure 2-10B), indicating the non-conservative nature of sulfate in these brine samples. Sulfate may be sourced from gypsum dissolution, pyrite oxidation and/or remnant marine waters, and lost via sulfate reduction or mineral precipitation. Several Appalachian Basin brine samples have low $\delta^{13}\text{C-DIC}$ values suggestive of sulfate reduction (Figure 2-9A). Although, H_2S was not measured for this study, Jenden et al. (1993) observed one sample in the Middle Devonian Onondaga limestone of western New York with H_2S concentrations of 260 ppm that they hypothesized may have been a result of microbial sulfate reduction. Furthermore, H_2S has been observed by oil and gas industry field personnel (personal communication). Thus, there is anecdotal evidence for H_2S in the Appalachian basin. It may be possible that much of this has been released from the subsurface and trace amounts are being produced. Never the less, it has been observed. Without data, it would be difficult to speculate where the H_2S has gone. Extensive gypsum deposits, pyrite and other sulfide ores have been noted within the Devonian section at the relatively shallow northern basin margin (Colton, 1970; Craig and Vokes, 1992; Formolo and Lyons, 2007, Perkins et al., 2008).

Lovley and Klug (1982) showed that sulfate reducing bacteria begin to out-compete methanogens for available substrates at sulfate concentrations above approximately 1 mmole/L. The majority of brine samples (16 samples out of 24) have sulfate concentrations that are greater than 1 mmole/L, and two of these samples (M1 in eastern Kentucky and D10 in western New York) have low $\delta^{13}\text{C-DIC}$ values within the range of sulfate reduction. Groundwaters from the shallow domestic water supply wells have sulfate concentrations less than 1 mmole/L, except for samples D49 and D52, which have sulfate values of 3.895 and 1.239 mmole/L, respectively. Of the eight brine samples that have low sulfate concentrations below 1 mmole/L, two samples (M1 and D10) have corresponding chloride concentrations less than 2,000 mmole/L that may indicate most favorable environmental conditions for methanogenesis. However, these samples

have $\delta^{13}\text{C}$ -DIC values that are fairly negative (-22.5 and -22.7‰), in the range of sulfate reduction. The high concentrations of sulfate and low $\delta^{13}\text{C}$ -DIC values observed in the Devonian organic-rich shale at depth in the northern Appalachian Basin, coupled to the dominance of thermogenic gas, suggest that sulfate reduction may be a primary inhibitor of methanogenesis.

Evidence for Meteoric Recharge to Basin Margin

Pleistocene meteoric recharge has been shown to be important for stimulating methanogenesis in Devonian organic-rich shales along the margins of the Michigan and Illinois basins (Martini et al., 1998; McIntosh et al., 2002). Chloride versus bromide trends in the Appalachian Basin formation waters show evidence for dilution of saline brines by a fresh groundwater end-member (Figure 2-10A). Unlike the Michigan and Illinois basins, however, there does not appear to be any stable isotope evidence for recharge of Pleistocene glacial meltwaters in Appalachian Basin formation waters. Oxygen and hydrogen isotope values of brine samples from the Mississippian Berea Sandstone, Devonian organic-rich shales and sandstones (oil/gas), and Silurian Medina Sandstone range from -7.1 to -0.4‰ and -55.6 to 30.2‰, respectively. The brines plot to the right of the global and local meteoric water lines along an apparent mixing trend with meteoric waters with similar isotopic values to modern precipitation (-6.7‰ $\delta^{18}\text{O}$; Huddart et al., 1999) (Figure 2-12). Stable isotope values of Pleistocene subglacial meltwaters are much more negative (-25 to -9‰ $\delta^{18}\text{O}$; Person et al., 2007). Formation waters associated with microbial methane in Devonian organic-rich shales in the Michigan and Illinois basins have low $\delta^{18}\text{O}$ values (-16.2 to +0.4‰), likely due to mixing of Pleistocene subglacial recharge, basinal brines and modern precipitation (Martini et al., 1998; McIntosh et al., 2002). Groundwaters have $\delta^{18}\text{O}$ and δD values that plot parallel to the global and local meteoric water lines, with $\delta^{18}\text{O}$ values between -9.1 and -11.6‰ (Figure 2-12). These values are within the range of modern precipitation, but slightly more negative than the mean-weighted annual average value for the Lake Erie area (-6.7‰ $\delta^{18}\text{O}$; Huddart et al., 1999).

CONCLUSIONS

The combined water and gas results suggest that natural gas in Devonian organic-rich shales and reservoir sandstones at the northern Appalachian Basin margin is largely thermogenic in origin and has, in part, mixed with small shallow reservoirs of microbial methane along Lake Erie (Figure 2-14). The evidence for the dominance of thermogenic gas is based on the relatively positive carbon isotope values of methane (>-50‰) and low methane to ethane and propane ratios (<130) in the majority of natural gas samples.

Additionally, the correlation of $\delta^{13}\text{C}$ -C₂ and $\delta^{13}\text{C}$ -C₃ along a thermogenic gas trend and systematic increase of the carbon isotope values of the higher chain hydrocarbons is consistent with natural gas generated via thermal maturation of organic matter. There is no apparent correlation between the δD values of methane and co-produced formation waters, and only trace amounts of CO₂ are present. In contrast, dissolved gases in groundwaters from shallow Devonian organic-rich shales along Lake Erie have relatively negative $\delta^{13}\text{C}$

values of CH_4 (-74.68 to -59.24‰) and high methane to ethane and propane ratios (up to 24,420), within the range of microbial methanogenesis.

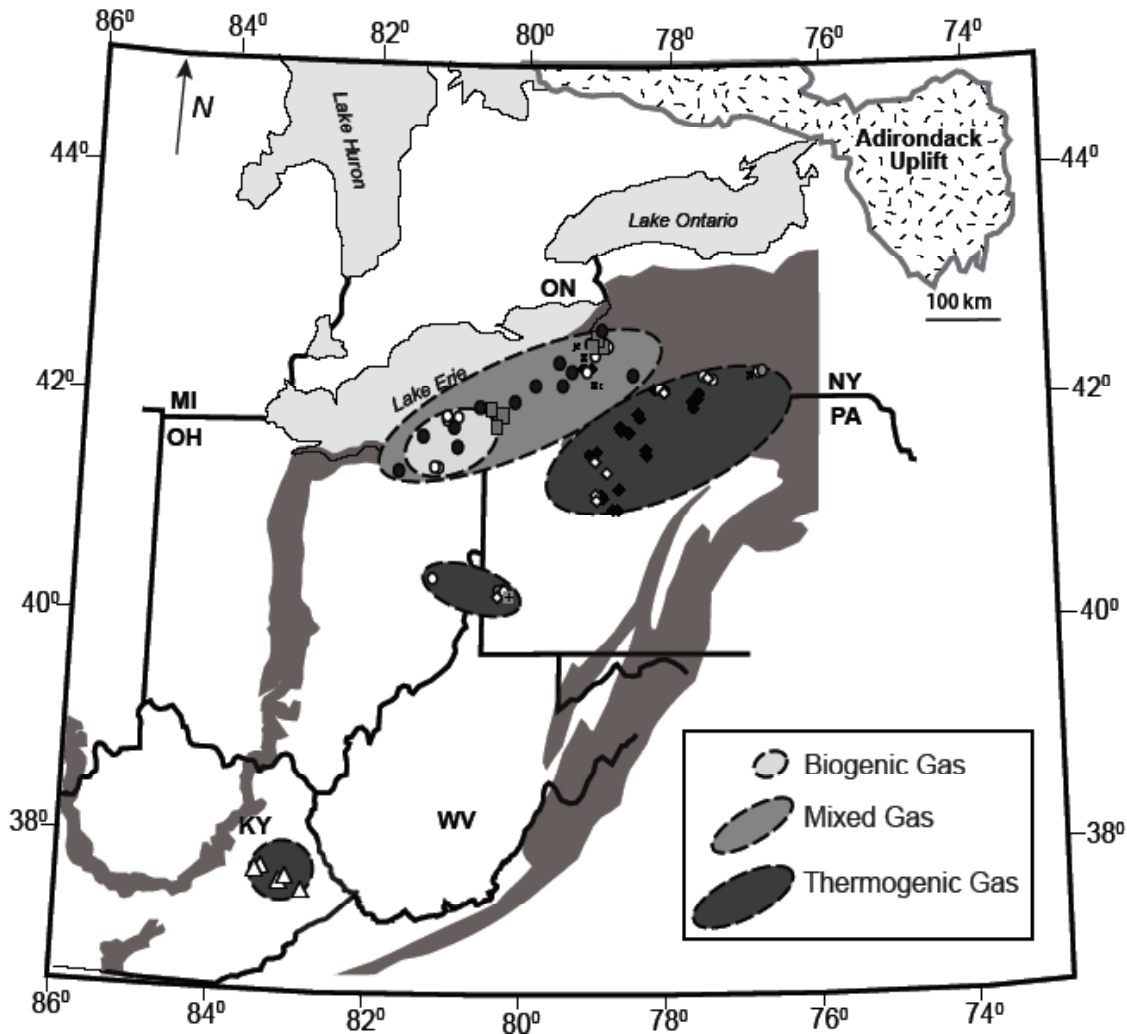


Figure 2-14. Approximate spatial distribution of natural gas in Devonian organic-rich shales across the northern Appalachian Basin margin generated by dominantly microbial or thermogenic processes, or a combination of the two processes (“mixed”). Well locations are shown for reference.

Chloride to bromide trends show evidence for dilution of brines at depth by meteoric water recharge, with $\delta^{18}\text{O}$ values within the range of modern precipitation; there is no isotopic evidence of Pleistocene recharge at depth. Twenty of the 37 formation water samples analyzed for this study have chloride levels that are non-inhibitory to microbial metabolism (<2,000 mmole/L); however, elevated sulfate concentrations (up to 12.31 mmole/L) and low $\delta^{13}\text{C-DIC}$ values (<-23‰) in several brine and groundwater samples indicate that sulfate reduction is likely an important process inhibiting methanogenesis. Positive $\delta^{13}\text{C-DIC}$ values (up to 20.8‰), elevated alkalinities (up to 12.01 meq/kg), and low SO_4 concentrations (<1 mmole/L) in select samples provide the strongest evidence for microbial methanogenesis in Devonian organic-rich shales and

reservoir sandstones. Additionally, a minor trend of increasing methane to ethane and propane ratios with decreasing $\delta^{13}\text{C-CH}_4$ values (<-50‰), and the depletion of $\delta^{13}\text{C-CH}_4$ values on the natural gas plot (Figure 2-8) relative to a linear thermogenic end-member, may provide evidence for the mixing of microbial gas with a larger reservoir of thermogenic gas.

Unlike the Michigan and Illinois basins, there does not appear to be large accumulations of microbial methane in Devonian organic-rich shales at the northern Appalachian Basin margin, which may be due to: (1) the presence of sulfate reducing bacteria which outcompete methanogens; (2) absence of microbial consortium within the shales at depth; (3) lack of formation water in shales (as observed by the paucity of water production during sampling); and/or (4) decreased bioavailability of shale organic matter (shales may be more thermally-mature than previously thought, as proposed by Laughrey (2008)). These results offer important differences with the large Devonian shale biogenic gas plays in the adjacent Michigan and Illinois basins for comparison and prompt the need for additional work aimed at understanding the environmental controls on microbial methanogenesis.

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Table 1. Sample location, depth, and production type, Northern Appalachian Basin

Sample ID	Date	State	County	Formation ^(b)	Age ^(c)	Latitude	Longitude	Depth (m)	Well Type ^(d)
M1	7/3/07	KY	Floyd	Berea Ss.	L. Miss.	37.569	-82.649	915	O/G
M2	7/3/07	KY	Floyd	Berea Ss.	L. Miss.	37.643	-82.869	915	O/G
M3	7/3/07	KY	Floyd	Berea Ss.	L. Miss.	37.652	-82.880	915	O/G
M4	7/3/07	KY	Magoffin	Berea Ss.	L. Miss.	37.676	-83.132	915	O/G
M5	7/3/07	KY	Magoffin	Berea Ss.	L. Miss.	37.668	-83.142	915	O/G
D6	6/20/07	NY	Alleghany	Organic-rich Sh.	U. Dev.	42.125	-77.819	624	O/G
D7	6/20/07	NY	Alleghany	Organic-rich Sh.	U. Dev.	42.130	-77.819	640	O/G
D8	6/20/07	NY	Alleghany	Venango Grp. Ss.	U. Dev.	42.144	-77.760	625	O/G
D9	6/21/07	NY	Alleghany	Bradford Grp. Ss.	U. Dev.	42.001	-77.991	609	O/G
D10	6/21/07	NY	Cattaraugus	Bradford Grp. Ss.	U. Dev.	42.056	-78.408	314	O/G
D11	6/19/07	NY	Cattaraugus	Organic-rich Sh.	U. Dev.	42.521	-78.989	412	O/G
D12	6/19/07	NY	Cattaraugus	Organic-rich Sh.	U. Dev.	42.518	-78.988	412	O/G
D13	6/21/07	NY	Cattaraugus	Venango Grp. Ss.	U. Dev.	42.051	-78.404	572	O/G
D14	6/1/07	NY	Chautauqua	Organic-rich Sh.	U. Dev.	42.258	-79.315	457	O/G
D15	5/30/07	NY	Chautauqua	Bradford Grp. Ss.	U. Dev.	42.259	-79.329	427	O/G
D16	5/30/07	NY	Chautauqua	Bradford Grp. Ss.	U. Dev.	42.266	-79.313	427	O/G
D17	5/31/07	NY	Stueben	Organic-rich Sh.	U. Dev.	42.293	-77.069	832	O/G
D18	6/26/07	OH	Ashtabula	Organic-rich Sh.	U. Dev.	41.813	-80.865	168	O/G
D19	6/26/07	OH	Geauga	Organic-rich Sh.	U. Dev.	41.369	-81.096	366	O/G
D20	6/26/07	OH	Geauga	Organic-rich Sh.	U. Dev.	40.376	-81.139	366	O/G
D21	6/26/07	OH	Geauga	Organic-rich Sh.	U. Dev.	41.377	-81.131	366	O/G
D22	6/26/07	OH	Lake	Organic-rich Sh.	U. Dev.	41.792	-81.004	168	O/G
D23	6/26/07	OH	Lake	Organic-rich Sh.	U. Dev.	41.829	-81.006	168	O/G
D24	5/25/07	PA	Elk	Venango Grp. Ss.	U. Dev.	41.423	-79.225	609	O/G
D25	5/25/07	PA	Elk	Bradford Grp. Ss.	U. Dev.	41.468	-79.223		O/G
D26	5/25/07	PA	Elk	Bradford Grp. Ss.	U. Dev.	41.453	-79.226		O/G
D27	5/25/07	PA	Forrest	Bradford Grp. Ss.	U. Dev.	41.464	-78.601	668	O/G
D28	5/25/07	PA	Forrest	Bradford Grp. Ss.	U. Dev.	41.468	-78.609	854	O/G
D29	5/24/07	PA	Jefferson	Bradford Grp. Ss.	U. Dev.	41.007	-78.974	848	O/G
D30	5/24/07	PA	Jefferson	Bradford Grp. Ss.	U. Dev.	41.006	-78.979	972	O/G
D31	5/24/07	PA	Jefferson	Bradford Grp. Ss.	U. Dev.	41.107	-79.101	902	O/G
D32	5/24/07	PA	Jefferson	Bradford Grp. Ss.	U. Dev.	41.106	-79.105	874	O/G
D33	5/24/07	PA	Jefferson	Venango Grp. Ss.	U. Dev.	41.337	-79.083	663	O/G
D34	5/24/07	PA	Jefferson	Bradford Grp. Ss.	U. Dev.	41.156	-78.956	802	O/G
D35	5/24/07	PA	Jefferson	Venango Grp. Ss.	U. Dev.	41.106	-79.105	266	O/G
D36	5/24/07	PA	Jefferson	Venango Grp. Ss.	U. Dev.	41.107	-79.101	275	O/G
D37	5/30/07	PA	McKeen	Bradford Grp. Ss.	U. Dev.	41.820	-78.656	609	O/G
D38	5/30/07	PA	McKeen	Bradford Grp. Ss.	U. Dev.	41.860	-78.742	615	O/G
D39	5/25/07	PA	McKeen	Bradford Grp. Ss.	U. Dev.	41.727	-78.912	496	O/G
D40	5/25/07	PA	McKeen	Bradford Grp. Ss.	U. Dev.	41.738	-78.909	532	O/G
D41	5/25/07	PA	McKeen	Bradford Grp. Ss.	U. Dev.	41.730	-78.911	633	O/G
D42	6/21/07	PA	Potter	Bradford Grp. Ss.	U. Dev.	41.982	-78.035	427	O/G
D43	6/21/07	PA	Potter	Bradford Grp. Ss.	U. Dev.	41.971	-78.068	457	O/G
D44	6/21/07	PA	Potter	Bradford Grp. Ss.	U. Dev.	41.963	-78.097	427	O/G
D45	6/21/07	PA	Potter	Bradford Grp. Ss.	U. Dev.	41.985	-78.082	452	O/G
D46	5/23/07	PA	Washington	Venango Grp. Ss.	U. Dev.	40.266	-80.366	2256	O/G
D47	6/5/08	NY	Chautauqua	Organic-rich Sh.	U. Dev.	42.060	-79.527	17	WS
D48	6/5/08	NY	Chautauqua	Organic-rich Sh.	U. Dev.	42.290	-79.328	56	WS
D49	6/5/08	NY	Chautauqua	Organic-rich Sh.	U. Dev.	42.301	-79.662	5	WS
D50	6/6/08	NY	Cattaraugus	Organic-rich Sh.	U. Dev.	42.253	-78.801	26	WS
D51	6/3/08	NY	Chautauqua	Organic-rich Sh.	U. Dev.	42.505	-79.132	15	WS
D52	6/4/08	OH	Ashtabula	Organic-rich Sh.	U. Dev.	41.777	-80.923	28	WS
D53	6/4/08	OH	Ashtabula	Organic-rich Sh.	U. Dev.	41.620	-80.953	7	WS
D54	6/4/08	OH	Ashtabula	Organic-rich Sh.	U. Dev.	41.863	-80.605	28	WS
D55	6/3/08	OH	Geauga	Organic-rich Sh.	U. Dev.	41.384	-81.373	37	WS

Sample Date						Depth	Well		
ID ^(a)	Sampled	State	County	Formation ^(b)	Age ^(c)	Latitude	Longitude	(m)	Type ^(d)
D56	6/3/08	OH	Lake	Organic-rich Sh.	U. Dev.	41.695	-81.243	37	WS
D57	6/2/08	PA	Erie	Organic-rich Sh.	U. Dev.	41.886	-80.203	12	WS
D58	6/2/08	PA	Erie	Organic-rich Sh.	U. Dev.	41.885	-80.203	65	WS
D59	6/2/08	PA	Erie	Organic-rich Sh.	U. Dev.	42.030	-80.004	23	WS
D60	5/31/07	NY	Stueben	Marcellus Sh.	M. Dev.	42.281	-77.079	866	O/G
D61	5/23/07	PA	Washington	Marcellus Sh.	M. Dev.	40.283	-80.284	2233	O/G
D62	5/23/07	PA	Washington	Marcellus Sh.	M. Dev.	40.280	-80.292	2014	O/G
D63	5/23/07	PA	Washington	Oriskany Ss.	L. Dev.	40.283	-80.284	681	O/G
D64	6/25/07	NY	Chautauqua	Onondoga Ls.	L. Dev.	42.128	-79.199	762	O/G
D65	6/25/07	NY	Chautauqua	Onondoga Ls.	L. Dev.	42.131	-79.172	762	O/G
D66	6/25/07	NY	Chautauqua	Onondoga Ls.	L. Dev.	42.440	-79.378	338	O/G
D67	6/25/07	NY	Chautauqua	Onondoga Ls.	L. Dev.	42.390	-79.192	579	O/G
S68	5/30/07	NY	Cattaraugus	Medina Ss.	Sil.	42.521	-79.017	671	O/G
S69	5/30/07	NY	Chautauqua	Medina Ss.	Sil.	42.498	-79.238	610	O/G
S70	5/30/07	NY	Chautauqua	Medina Ss.	Sil.	42.532	-79.084	638	O/G
S71	6/22/07	PA	Crawford	Medina Ss.	Sil.	41.763	-80.387	1220	O/G
S72	6/22/07	PA	Erie	Medina Ss.	Sil.	41.880	-80.348	1372	O/G
S73	6/22/07	PA	Erie	Medina Ss.	Sil.	41.899	-80.474	980	O/G
O74	5/31/07	NY	Steuben	Trenton/Black River Grp.	Ord.	42.281	-77.079	2636	O/G

^(a) M (Mississippian), D (Devonian), S (Silurian), and O (Ordovician)

^(b) Ss = Sandstones; Ls = Limestones; Sh = Shales

^(c) L. Miss. = Lower Mississippian; U. Dev. = Upper Devonian; M. Dev. = Middle Devonian; L. Dev. = Lower Devonian
Sil. = Silurian; Ord. = Ordovician

^(d) O/G = Oil/Gas; WS = Water Supply

Table 2-2. Gas composition and compound specific isotopes

Sample ID	N ₂ mole %	O ₂ mole %	CH ₄ mole %	C ₂ mole %	C ₃ mole %	C ₁ /(C ₂ +C ₃)	CO ₂ mole %	δ ¹³ C _{CH4} (‰)	δD _{CH4} (‰)	δ ¹³ C ₂ (‰)	δ ¹³ C ₃ (‰)	δ ¹³ C ₄ (‰)	δ ¹³ CO ₂ (‰)
M1	8.23	2.10	59.24	16.88	8.21		2 0.024	-46.12	-205.6	-37.14			
M2	1.47	0.03	80.96	11.08	4.33		5 0.033	-50.07	-254.0	-43.10			
M3	2.87	0.10	80.96	9.57	4.25		6 0.036	-54.74	-280.9	-47.53			
M4	10.79	0.19	78.03	6.32	2.77		9 0.085	-47.23	-231.6	-42.55			
M5	5.93	0.02	80.22	8.07	3.78		7 0.000	-49.75	-247.4	-43.57			
D6	0.57	0.06	77.19	12.86	4.93		4 0.024	-49.42	-258.6	-35.26	-31.6	-31.2	
D7	0.60	0.05	81.03	11.74	3.86		5 0.022	-49.67	-255.1	-35.50			
D8	0.53	0.06	74.29	13.46	6.46		4 0.021	-50.31	-261.3	-34.08			
D9	1.97	0.44	78.41	11.58	3.94		5 0.042	-47.16	-238.6	-34.33			
D10	0.46	0.04	74.80	14.62	6.16		4 0.032	-47.54	-251.4	-35.70			
D11	71.90	21.35	4.30	0.95	0.33		3 0.063	-51.75	-315.0	-41.17			
D12	1.24	0.05	82.87	11.38	3.15		6 0.170	-49.74	-295.3	-38.63			
D13	0.53	0.05	76.66	14.13	5.34		4 0.073	-47.87	-258.4	-35.77	-31.9	-30.8	
D14	1.90	0.01	85.57	7.76	2.99		8 0.013	-52.31	-310.3	-41.08	-37.0	-34.5	
D15	1.92	0.01	85.35	7.86	3.05		8 0.017	-52.11	-310.1	-41.27			
D16	1.93	0.01	85.07	7.94	3.10		8 0.014	-52.17	-314.8	-41.28			
D17	2.71	0.01	93.49	3.28	0.27		26 0.015	-40.24	-174.6	-35.50			
D18	3.22	0.01	85.73	6.48	2.90		9 0.000	-53.35	-277.8	-41.30			
D19	3.28	0.04	82.45	9.06	3.31		7 0.000	-46.97	-251.5	-38.29			
D20	3.82	0.02	82.37	8.60	3.29		7 0.000	-48.25	-258.3	-39.26			
D21	3.58	0.25	80.81	8.46	3.41		7 0.014	-42.21	-212.8	-37.53			
D22	2.99	0.01	84.68	7.26	3.23		8 0.000	-52.03	-273.3	-40.71			
D23	2.60	0.03	84.10	8.07	3.51		7 0.000	-52.83	-281.7	-43.05			
D24	0.82	0.09	77.44	12.87	5.51		4 0.027	-46.45	-230.7	-34.40			
D25	0.67	0.03	77.09	13.15	5.63		4 0.023	-46.43	-226.4	-34.43			
D26	0.85	0.02	83.47	10.05	3.30		6 0.013	-46.88	-234.9	-34.27			
D27	0.37	0.01	89.63	7.11	1.61		10 0.020	-43.86	-220.0	-33.02			
D28	0.38	0.01	89.43	7.26	1.66		10 0.010	-44.02	-223.5	-32.90	-29.4	-27.4	
D29	0.53	0.02	96.05	2.30	0.45		35 0.021	-40.99	-195.9	-37.85			
D30	0.99	0.11	95.19	2.43	0.42		33 0.000	-41.28	-189.8	-39.01			
D31	0.65	0.02	92.41	4.70	1.22		16 0.034	-43.11	-192.8	-35.17	-30.7	-27.5	
D32	0.45	0.02	91.48	5.36	1.24		14 0.000	-42.64	-193.5	-34.99			
D33	0.59	0.05	85.09	9.69	2.65		7 0.033	-45.23	-227.8	-33.80			
D34	0.46	0.04	95.57	2.87	0.45		29 0.020	-41.98	-211.0	-36.55			
D35	0.49	0.02	92.79	4.91	1.01		16 0.014	-42.13	-194.8	-34.78			
D36	0.67	0.04	93.83	4.22	0.68		19 0.010	-41.85	-190.2	-35.22			
D37	0.77	0.04	75.05	13.16	6.45		4 0.033	-47.11	-253.8	-34.98			
D38	0.76	0.07	74.16	15.12	6.47		3 0.034	-47.56	-258.4	-36.13	-32.1	-31.3	
D39	0.70	0.04	77.20	13.19	5.52		4 0.017	-46.93	-242.7	-35.04			
D40	0.82	0.02	75.43	13.24	6.22		4 0.012	-46.75	-234.7	-34.97			
D41	0.85	0.01	77.84	12.88	5.32		4 0.012	-46.62	-232.4	-34.93			
D42	26.27	6.66	51.81	8.31	3.46		4 0.062	-46.05	-235.9	-34.31			
D43	5.36	1.30	68.71	12.53	6.36		4 0.063	-45.73	-230.4	-34.10			
D44	1.10	0.23	69.82	13.57	8.10		3 0.027	-46.44	-238.0	-34.39			
D45	2.43	0.57	67.48	14.01	8.29		3 0.140	-46.17	-231.7	-34.51			
D46	0.52	0.01	80.28	12.35	4.22		5 0.078	-44.39	-200.8	-33.62			
D48	87.79	7.97	0.02	<0.001	0.00		17* 2.590						
D51	84.73	8.57	0.03	<0.001	0.00		31* 5.080						
D52	90.33	6.96	0.07	<0.001	0.00		73* 0.930						
D55	73.27	0.54	24.42	<0.001	0.00		24420* 0.420	-59.24	-190.2				-29.19
D57	82.00	6.41	9.16	<0.001	0.00		9160* 0.850	-57.86	-225.0				-16.24
D58	42.09	6.39	50.55	0.01	0.00		6831 0.270	-74.68	-250.1				-11.76
D59	86.37	6.68	0.01	<0.001	0.00		10* 5.250						
D60	6.22	0.01	87.85	4.78	0.67		16 0.000	-40.37	-178.4	-32.15			
D61	0.96	0.20	79.53	12.57	4.06		5 0.086	-42.47	-181.1	-32.51			

Sample ID	N ₂ mole %	O ₂ mole %	CH ₄ mole %	C ₂ mole %	C ₃ mole %	C ₁ /(C ₂ +C ₃)	CO ₂ mole %	δ ¹³ C _{CH4} (‰)	δD _{CH4} (‰)	δ ¹³ C ₂ (‰)	δ ¹³ C ₃ (‰)	δ ¹³ C ₄ (‰)	δ ¹³ CO ₂ (‰)
D62	0.34	0.01	78.08	13.48	4.76	4	0.084	-42.43	-191.7	-31.45			
D63	0.40	0.01	79.32	13.44	4.30	4	0.073	-42.60	-186.9	-31.37			
D64	1.73	0.12	83.59	8.99	3.58	7	0.000	-46.47	-268.7	-36.64			
D65	1.27	0.01	82.41	10.58	3.69	6	0.000	-46.23	-265.9	-36.23			
D66	1.90	0.01	81.10	11.41	3.81	5	0.087	-47.69	-284.5	-37.35			
D67	1.51	0.11	81.46	11.00	3.98	5	0.026	-52.19	-314.0	-41.77			
S68	4.53	0.01	85.68	7.05	1.61	10	0.000	-42.02	-184.3	-33.55			
S69	3.70	0.02	92.92	2.48	0.45	32	0.011	-38.00	-160.1	-35.36			
S70	4.69	0.02	89.99	3.94	0.80	19	0.000	-38.33	-170.0	-34.72			
S71	5.40	0.01	87.55	4.37	1.46	15	0.011	-38.87	-175.0	-34.96			
S72	3.67	0.02	90.62	3.75	1.05	19	0.000	-37.10	-168.9	-35.96			
S73	3.94	0.02	90.35	3.76	1.04	19	0.000	-37.41	-168.4	-35.35			
O74	0.53	0.02	98.47	0.73	0.03	130	0.000	-31.53	-156.6	-38.96			

* Gas wetness values for samples D52, D55, D56, D59, D61, and D63 were calculated using the reported detection limit (0.001) for ethane.

Table 2-3. Elemental and stable isotope results for northern Appalachian Basin formation waters

Sample ID	Temp (°C)	Alkalinity (meq/kg)	Cl (mM)	Br (mM)	SO ₄ (mM)	Na (mM)	K (mM)	Ca (mM)	Mg (mM)	Sr (mM)	Fe (mM)	δ ¹³ C DIC (‰)	δ ¹⁸ O H ₂ O (‰)	δD H ₂ O (‰)	
M1	18.7	6.59	1.81	919	2.85	0.92	497	2.36	113	40	2.52	4.35	-22.5	-4.9	-33.5
M4	18.1	6.13	0.69	2479	11.19	4.29	1330	13.98	383	135	6.95	24.19	2.0	-2.7	-35.4
D6	13.1	6.70	2.31	1718	7.54	2.02	1106	2.01	239	66	1.40	1.34	-26.2	-5.7	-42.4
D7	13.8	6.26	1.43	2272	9.80	1.32	1332	2.50	309	85	2.05	0.64	-14.7	-4.7	-38.9
D10	12.1	6.99	4.88	1732	8.17	0.00	1013	2.84	216	75	0.97	1.16	-22.7	-5.1	-39.3
D14	13.4	7.13	1.24	1711	8.45	1.92	1017	2.50	250	79	1.19	1.27	7.5	-4.6	-37.9
D17		6.51	3.87	3680	14.88	0.00	1743	21.25	598	141	55.22	1.73	5.1	-5.5	-47.2
D24	21.8	5.08	2.55	1991	8.03	5.03	1199	2.29	273	74	1.95	0.29			
D27	12.9	7.21	3.20	1752	7.90	1.24	1066	2.00	279	60	0.96	0.00	16.2	-4.6	-41.2
D29	16.6	5.25	2.19	3715	11.82	0.65	1947	4.04	619	100	26.45	2.65	-5.4	-5.8	-43.5
D30	23.6	5.84	0.62	4197	12.98	0.00	2513	5.00	769	122	41.11	2.18	20.8	-4.7	-39.2
D31	19.2	5.51	12.01	2285	8.66	7.35	1300	3.17	317	75	0.84	9.11	14.9	-5.1	-40.9
D32	16.5	6.04	8.88	2344	9.19	3.27	1428	2.73	319	80	0.88	3.78	12.1	-4.7	-46.7
D33	14.2	5.72	0.74	2815	11.49	5.87	1507	3.28	468	96	1.46	0.20	-8.6	-3.1	-39.7
D34	20.8	5.55	0.91	2573	10.06	1.15	1315	3.73	395	88	3.71	0.27	-12.2	-4.5	-39.8
D37	16.1	7.53	0.85	1280	5.79	12.31	843	3.55	211	49	0.54	0.00		-7.1	-55.6
D38	13.3	7.15	0.81	2720	12.31	6.84	1517	2.91	402	100	1.44	0.03	14.9	-4.3	-40.4
D39	17.9	6.66	3.08	2033	9.05	2.98	1269	4.67	272	73	0.71	0.51	10.3	-5.1	-42.9
D40	18.7	6.47	2.61	2047	9.14	2.59	1194	3.11	274	69	0.59	1.40	-9.8	-5.1	-40.0
D47	12.4	7.43	1.33	0.091	0.0000	0.096	0.246	0.061	4.887	0.527	0.0025	0.0298	-9.7	-11.0	-71.0
D48	14.9	7.99	1.14	0.749	0.0044	0.040	2.490	0.044	0.336	0.123	0.0017	0.0000	-8.8	-11.6	-76.6
D49	15.6	7.01	3.17	0.432	0.0012	3.895	0.809	0.038	4.887	1.824	0.0033	0.0000	-11.9	-9.1	-59.8
D50	13.8	7.81	1.62	0.558	0.0010	0.119	0.420	0.024	1.521	0.338	0.0011	0.0000	-12.3	-11.0	-72.9
D51	12.7	7.36	4.31	1.984	0.0016	0.070	0.960	0.076	1.641	0.967	0.0063	0.0006	-18.0	-9.6	-62.9
D52	12.8	8.41	6.11	12.558	0.0340	1.239	18.877	0.088	0.253	0.142	0.0031	0.0007	-24.8	-9.2	-56.9
D53	11.3	7.11	2.98	0.529	0.0011	0.270	0.819	0.036	1.136	0.348	0.0011	0.0345	-18.8	-10.1	-63.8
D54	13.5	7.65	4.44	1.123	0.0014	0.633	0.503	0.036	2.259	0.839	0.0015	0.0017	-11.4	-10.3	-66.8
D55	15.0	8.29	8.72	8.064	0.0191	0.009	14.590	0.061	0.208	0.129	0.0019	0.0000	-0.6	-10.3	-67.0
D56	14.8	7.32	5.49	4.559	0.0016	0.771	1.881	0.043	3.399	1.232	0.0033	0.0170	-11.8	-9.9	-64.7
D57	12.3	7.78	3.95	0.105	0.0007	0.169	0.555	0.061	1.127	0.536	0.0029	0.0043	-12.2	-10.4	-67.5
D58	12.5	8.07	4.40	0.249	0.0016	0.080	1.842	0.062	0.858	0.395	0.0026	0.0095	-9.6	-10.7	-68.2
D59	14.3	8.14	4.18	0.134	0.0022	0.141	0.871	0.056	1.096	0.553	0.0040	0.0102	-12.3	-10.3	-67.3
D60	29.6	6.46	2.91	3726	15.18	0.00	1805	17.88	571	125	54.66	1.18	8.2	-5.9	-47.2
D61	24.6	6.84	0.14	2986	13.53	0.00	1650	6.22	529	90	22.54	1.52	1.2	-0.4	-30.2
D62	25.5	6.59	0.65	3170	14.29	0.00	1629	7.83	568	116	21.05	1.12	3.8		
S70	21.7	4.30	0.42	4496	20.14	2.73	2648	27.10	695	123	8.53	2.71			
S73	21.5	5.38	0.13	3995	16.41	1.71	2383	24.10	626	138	8.05	9.66	-7.7	-3.9	-32.3

GEOCHEMICAL EVIDENCE FOR ORIGIN OF NATURAL GAS IN UPPER ORDOVICIAN ORGANIC-RICH SHALES: WESTERN NEW YORK

Section 3

The following section summarizes the results of our pilot study to determine the origin of natural gas in the Upper Ordovician Utica Shale in central New York. These results have not been submitted for publication.

INTRODUCTION

The Ordovician age Trenton/Black River Group hosts economic reservoirs of oil and natural gas, which have been a target of exploration in Western New York and northeast Ohio. The Utica organic-rich shale has been identified as the main source rock for gas accumulations in the Trenton/Black River Group (Dykstra and Longman, 1995; Ryder et al., 1998; Obermajer et al., 1999; Ryder and Zagorski, 2003). As a result, there is interest in the overlying Upper Ordovician Utica Shale as a possible target for fractured

shale gas plays in the region (Shirley, 2001). The Utica Shale contains less than 1% total organic carbon (TOC) in the northwestern portion of New York State, while TOC is greater than 1% towards the southwestern, central and north-central regions of New York (Coleman et al., 1995; Figure 3-1).

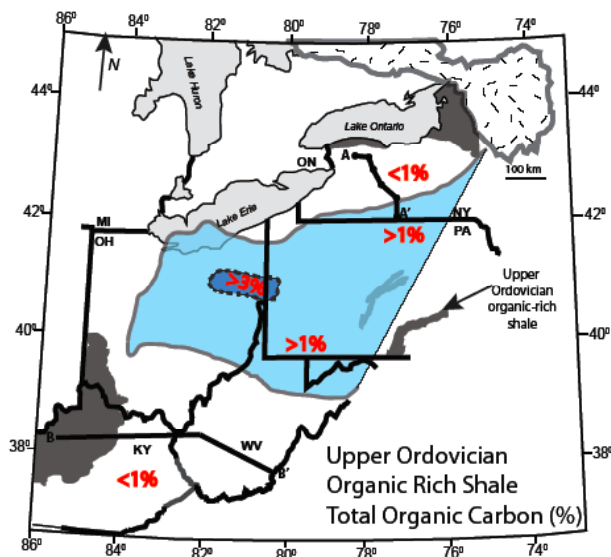


Figure 3-1. Map showing the total organic carbon (TOC) content of the Upper Ordovician organic-rich shales, modified from Coleman et al. (1995).

The thermal maturity of the Utica Shale generally increases towards the center of the Appalachian Basin, based on Conodont alteration index (CAI) values (Figure 3-2). CAI values increase with increasing thermal maturity (Epstein et al., 1977). Thus, based on TOC, thermal maturity, formation thickness, and proximity to the southern extent of Pleistocene glaciation, the Utica Shale in central New York State has the potential for containing accumulations of microbial methane.

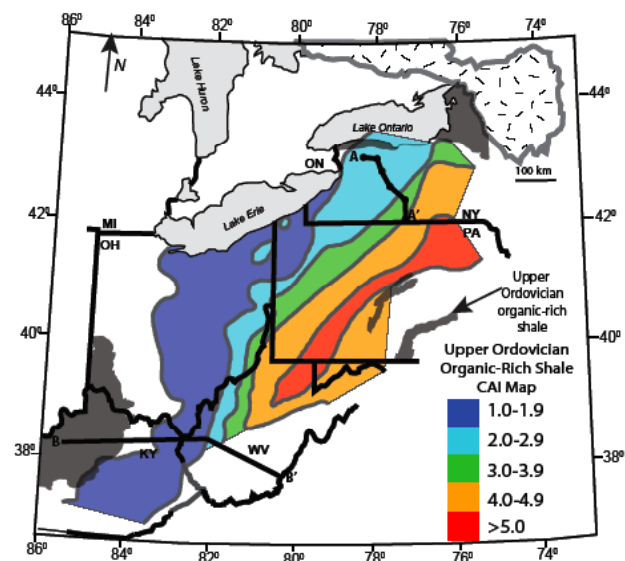


Figure 3-2. Map showing the Conodont Alteration Index (CAI) for the Upper Ordovician organic-rich shales, modified from Repetski et al. (2006).

There is little published research assessing the potential for microbial gas in the Utica organic-rich shale of central upstate New York, where the Utica subcrop is relatively shallow and may be part of an active hydrologic flow system. *We hypothesized that microbial methane may be generated in the Utica organic-rich shale in central upstate New York, where fresh water recharge may have depressed formation water salinity and the fractured shales contain high amounts of organic carbon.*

To address this hypothesis, we present herein, produced natural gas, dissolved gas, and formation water geochemistry collected from domestic water supply wells and one domestic gas well actively producing from the Upper Ordovician Utica organic-rich shale formation. We also collected core samples from the Devonian age Rhinestreet and the Ordovician age Utica organic-rich shales (analyses pending) to identify evidence for microbial degradation of the organic matter contained in the shales. This study offers limited evidence for localized microbial methane production in the Utica organic-rich shale, which are consistent with conclusions of Osborn and McIntosh (2010) for limited microbial methane in the shallow Devonian organic-rich shale in Western New York and along Lake Erie. In addition, these results expand upon recently published research on thermogenic gas production from the Utica Shale, primarily focused on core analyses from eastern Ohio and the Quebec Lowlands (Dykstra and Longman, 1995; Ryder et al., 1998; Obermajer et al., 1999; Ryder and Zagorski, 2003).

FIELD AND LABORATORY METHODS

Produced natural gas, dissolved gas, and formation water samples were collected in July 2008 in accordance with field procedures detailed in Osborn and McIntosh (2010). Water samples were analyzed for major and minor elemental chemistry, as well as stable isotopes of carbon, oxygen and hydrogen at the University of Arizona. Produced natural gas and dissolved gas samples were analyzed at Isotech Laboratories for gas composition, and carbon and hydrogen isotopes of CO₂ and CH₄. Sample locations are plotted in Figure 3-3. Core samples were collected from the Utica organic-rich shale in central upstate New York (inset, Figure 3-3) and the Devonian organic-rich shales of western New York (Figure 3-3). The shale core samples are being analyzed by Weatherford Laboratories in Texas for organic geochemistry (including the presence/absence of saturated alkanes to determine the extent of biodegradation) and are pending as of the date of this report. It is expected that results will be available in January and will be summarized in a supplement to this report upon receipt by our laboratory.

RESULTS

Since there were no oil/gas wells completed in the Utica Shale in central upstate New York at the time of sampling (personal communication with Richard Nyahay, New York State Museum), domestic water wells completed in the Utica organic-rich shale subcrop with gas shows were identified for sampling. One gas sample (O81) was collected from a dedicated domestic gas well in addition to the dissolved gas sample

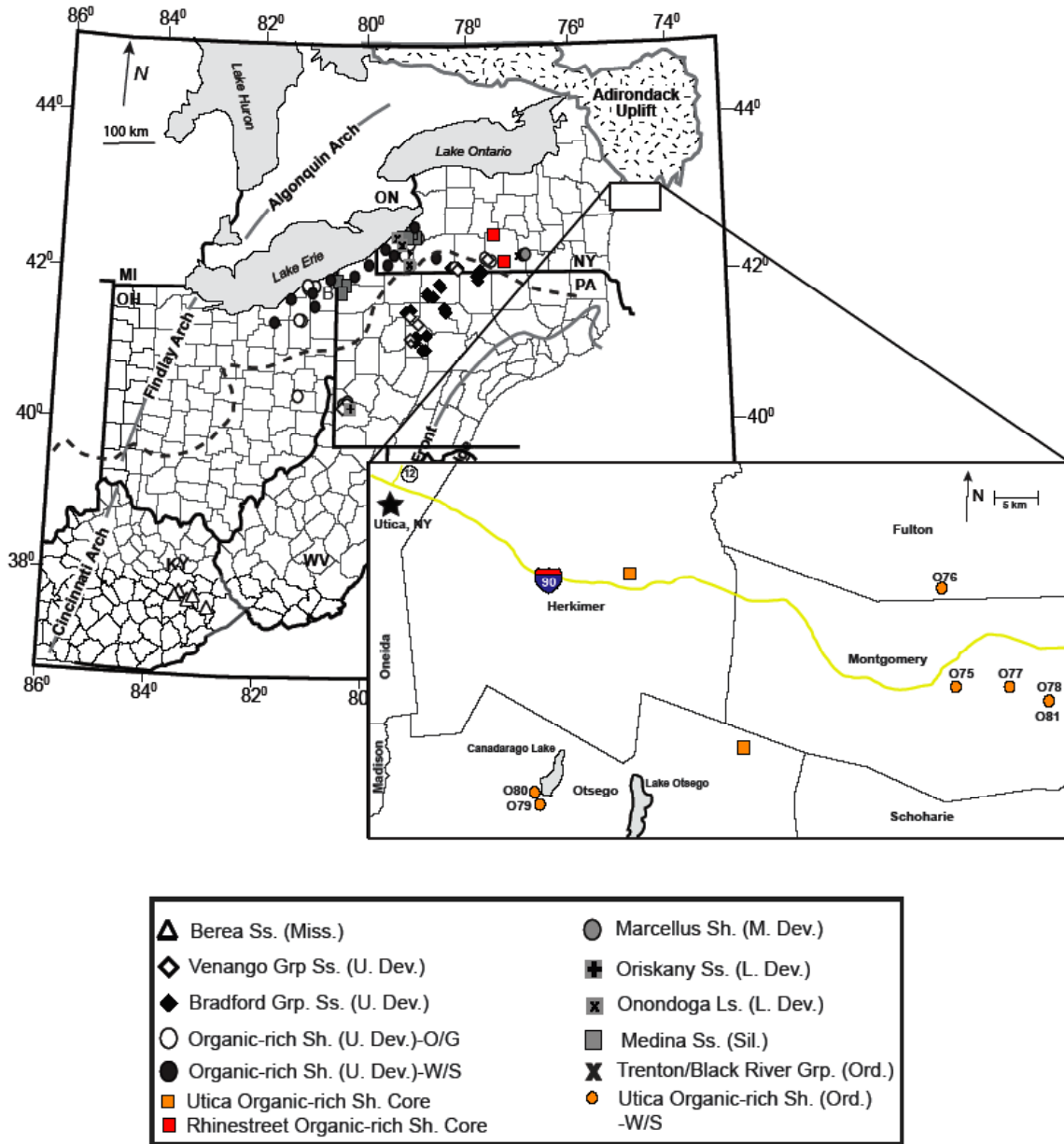


Figure 3-3. Map depicting the location of co produced water and gas/dissolved gas samples, and core samples collected for this study (map modified from Osborn and McIntosh, 2010). Core samples in western New York are from the Upper Devonian Rhinestreet organic-rich shale formation. Core samples (orange squares) in the inset from central up-state New York are from the Ordovician age Utica organic-rich shale.

collected (O78) at the same location. Wells sampled for this study ranged in depth between 26 and 122 m. Well location, type, depth information are provided in Table 3-1. Gas molecular and isotopic compositions are presented in Table 3-2. Formation water chemistry is provided in Table 3-3.

MOLECULAR AND ISOTOPIC COMPOSITION OF SHALE GAS

Methane is the dominant natural gas component in all produced and dissolved gas samples, except for O78. Methane concentrations ranged between 36.71 and 90.70 mole%. Nitrogen is the dominant gas in sample O78 with 60.39 mole%. Carbon dioxide and oxygen were low in all produced and dissolved gas samples, ranging from 0.019 to 0.85 mole% and 0.035 and 6.33 mole%, respectively. Ethane concentrations were lower than methane concentrations in all gas samples, ranging from 0.0155 to 0.118 mole%. No higher chain hydrocarbons were detected in the gas samples. The ratio of methane to ethane (C_1/C_2) ranged between 759 and 5497 (Figure 3-4). The carbon isotope values of methane ($\delta^{13}C-CH_4$) were between -58.27 and -41.12‰. Even though the molecular concentrations were measured in sample O79, the $\delta^{13}C-CH_4$ values were not measured due to a compromised sample container during storage at Isotech Laboratories.

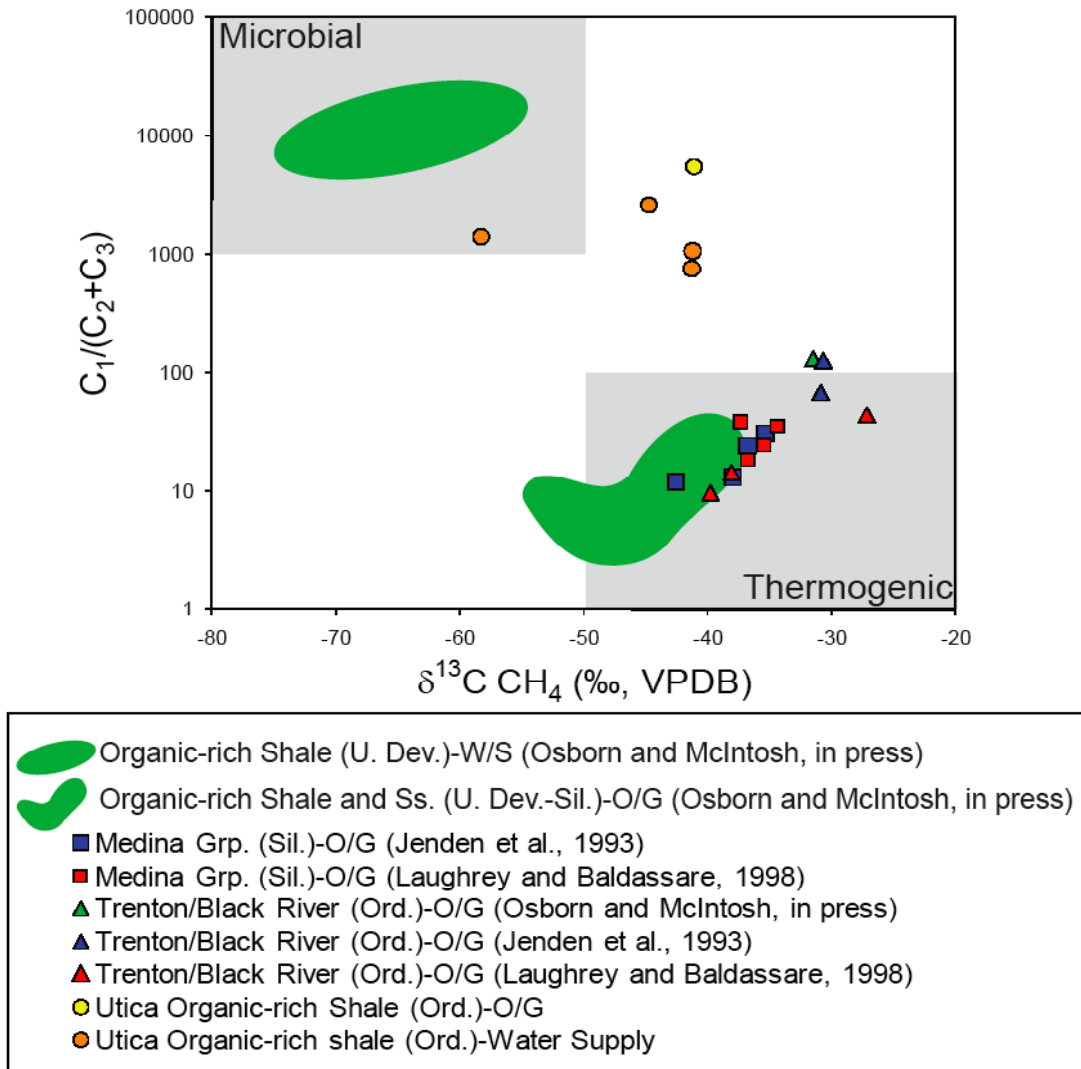


Figure 3-4. Plot of methane (C_1) to ethane (C_2) ratio versus the carbon isotope value of methane. Typical fields for microbial and thermogenic gases (Schoell, 1980; Whiticar et al., 1986) are outlined. Data from Osborn and McIntosh (2010) are outlined in green fields (labeled as Osborn and McIntosh, in press, in legend).

The hydrogen isotope values of methane ($\delta D-CH_4$) ranged between -251.7 and -182.0‰. Samples with the three highest CO_2 concentrations were measured for carbon isotopes of CO_2 ($\delta^{13}C-CO_2$) and had values ranging from -13.3 to -9.5‰.

FORMATION WATER GEOCHEMISTRY IN UTICA SHALE

The temperature of all formation water samples collected from the Utica Shale range between 15.6 and 16.7 °C, with pH values between 7.40 and 9.39. Alkalinity ranged from 5.66 to 10.95 meq/kg (Figure 3-5). Chloride and sodium are the dominant anion and cation species in all formation waters, respectively. Chloride ranged from 0.179 to 2.628 mmole/L, while sodium ranged from 3.855 to 12.633 mmole/L. Sulfate concentrations ranged between 0.010 to 0.631 mmole/L. The carbon isotope values of dissolved inorganic carbon ($\delta^{13}C-DIC$) were between -3.2 and +5.9‰ (Figure 3-5). The oxygen isotope values ($\delta^{18}O$) in formation waters from the Utica are between -11.0 and -9.9‰ with δD values between -72.0 and -66.0‰ (Figure 3-6).

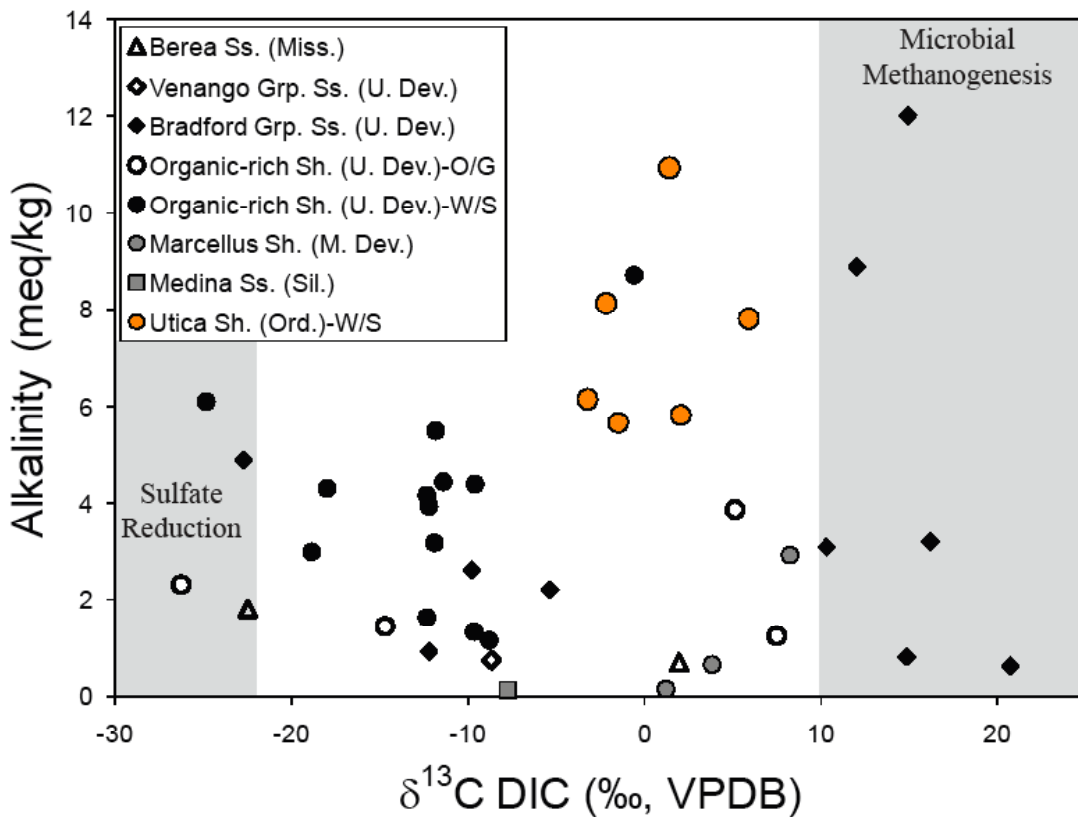


Figure 3-5. Plot of alkalinity versus carbon isotope values of dissolved inorganic carbon (DIC) in formation waters. Ranges in carbon isotope values for methanogenesis, sulfate reduction, soil CO_2 , and marine carbonates are taken from Clark and Fritz (1997). Data plotted in grey scale are from Osborn and McIntosh (2010).

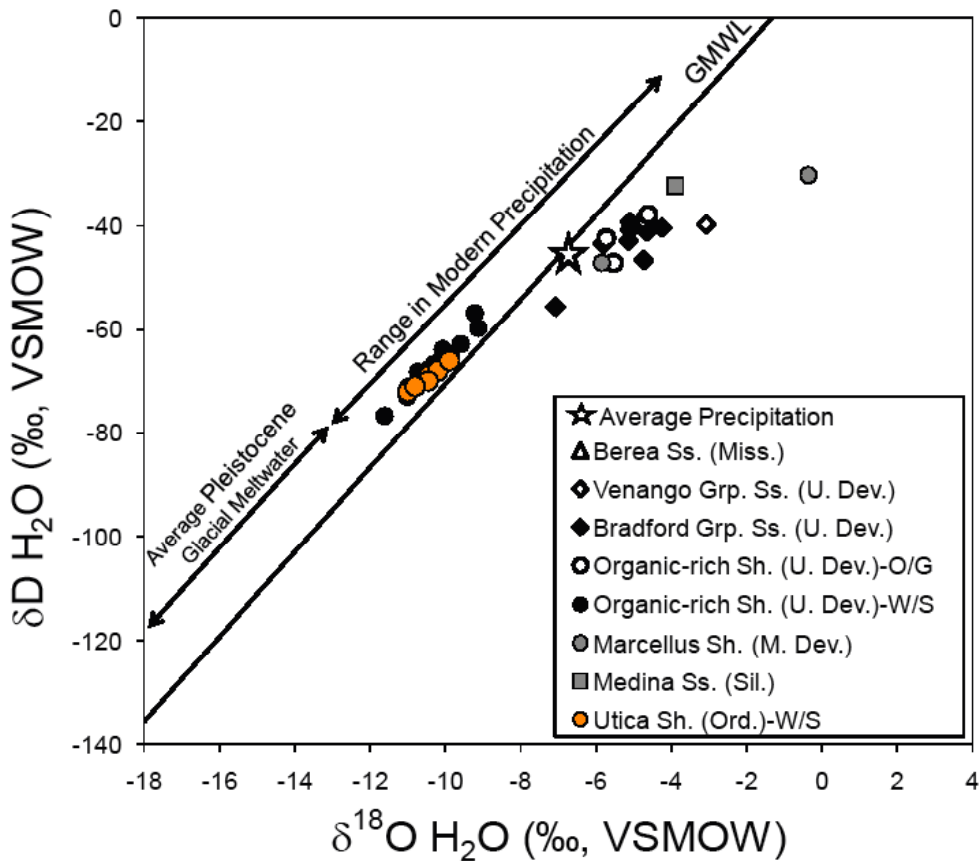


Figure 3-6. Plot of oxygen and hydrogen isotope values of formation waters relative to the Global Meteoric Water Line (GMWL; Craig, 1961).

DISCUSSION

The samples collected from the Utica organic-rich shale formations are plotted in figures modified from Osborn and McIntosh (2010) to compare with Devonian organic-rich shale data. Published data from the Trenton/Black River Group from Jenden et al. (1993) and Laughrey and Baldassare (1998) are also incorporated in the figures where applicable. A literature review was conducted to compile gas and formation water data from the Utica organic-rich shale in the Appalachian Basin; however, no coupled water and gas data were found. Heroux (1993) presented geochemical results for four gas samples from glacial drift overlying the Utica Shale in the Quebec Lowlands. The drift gas had $\delta^{13}\text{C}$ values of CH_4 from -74.7 to -36.6‰; he concluded that the low values (-74.7‰) represents microbial methane generated in the Pleistocene glacial drift, while the high values (-36.6‰) represents thermogenic gas that migrated from the underlying Utica Shale.

For a detailed description of the indicators and inhibitors of microbial methane and thermogenic gas, refer to section 1.0 of Osborn and McIntosh (2010). The methane to ethane ratios for produced and dissolved gas samples from the Utica organic-rich shale for this study plot with values greater than 1,000, except for

sample O76 (C_1/C_2 of 759). Natural gas with a C_1/C_2 ratio greater than 1,000 may be considered microbial in origin, based on Schoell (1980). Produced and dissolved gas samples from Silurian and Devonian formations in Western New York (Osborn and McIntosh, 2010) are plotted in Figure 3-4 for reference. Samples from the Utica Shale have C_1/C_2 ratios much higher than gas samples collected from Silurian and Devonian oil and gas wells. The respective $\delta^{13}C-CH_4$ values, except for sample O78, are relatively positive, in the range of thermogenic gas based on Schoell (1980). Sample O78 has a $\delta^{13}C-CH_4$ value that is fairly negative (-58‰) and may be considered within the range of a microbial or mixed gas origin based on Schoell (1980). The higher methane to ethane ratios and relatively positive $\delta^{13}C-CH_4$ values may be explained as an apparent mixing trend between thermogenic gas sourced from thermally mature organic matter (intermediate C_1/C_2 of approximately 100 and $\delta^{13}C-CH_4 > -50‰$) at depth and microbial gas (high C_1/C_2 of greater than 1,000 and $\delta^{13}C-CH_4 < -50‰$) produced in-situ.

Gas samples collected from the Trenton/Black River Group of the northern Appalachian basin from Jenden et al. (1993), Laughrey and Baldassare (1998), and Osborn and McIntosh (2010) are plotted for reference in Figure 3-4. Since gas samples from the Trenton/Black River Group are likely sourced from the Utica organic-rich shale formation based on Dykstra and Longman (1995), Ryder et al. (1998), Obermajer et al. (1999), and Ryder and Zagorski (2003), these samples may represent the thermogenic gas end-member sourced from the Utica formation at depth. It is interesting that none of the dissolved gas samples and the one gas sample collected from the Utica organic-rich shale have measureable concentrations of higher chain hydrocarbons past ethane. This observation is consistent with gas produced from organic matter of high thermal maturity (late thermogenic gas), such as the Utica Shale at depth. Microbial ethane production in anoxic sediments and shallow groundwater systems has been observed by Oremland et al. (1988), Taylor et al. (2000) and Hinrichs et al. (2006). Microbial production of higher chain hydrocarbons past ethane is unlikely to be significant and would largely be sourced, if present, from thermogenic gas produced from organic matter of relatively intermediate thermal maturity (early thermogenic gas). Thus, the lack of higher chain hydrocarbons in the Utica Shale past ethane may be a first order indicator of microbial methane generation locally and does not discount mixing with thermogenic gas produced from organic matter that has a high thermal maturity.

Relatively high CO_2 concentrations (up to approximately 14 mole %), positive $\delta^{13}C-CO_2$ values ($> +20‰$), and the covariance between δD values of methane and water have been used as additional indicators of microbial methanogenesis, and for identifying the predominate metabolic pathway (Martini et al., 1998). The CO_2 concentrations in the Utica Shale gas samples are fairly low (< 0.85 mole%) with negative $\delta^{13}C-CO_2$ values ($< -9.5‰$), counter to what would be expected for microbial methanogenesis based on Martini et al. (1998). Despite the fact that Utica Shale gas samples plot within the range of CO_2 reduction, there is little apparent covariance between the δD values of methane and water (Figure 3-7). This observation is

consistent with conclusions by Osborn and McIntosh (2010) for the Mississippian through Silurian section in western New York and elsewhere in the Northern Appalachian basin.

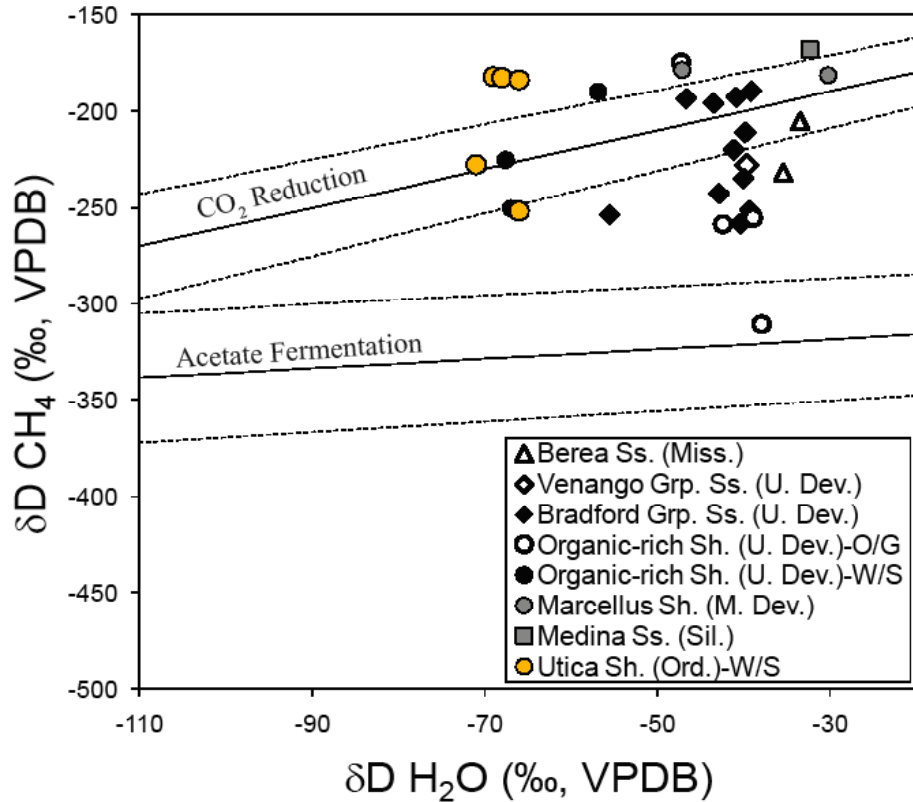


Figure 3-7. Hydrogen isotope composition of co-produced methane and water. Fractionation lines for microbial methanogenesis via CO₂ reduction and acetate fermentation are shown for reference (Whiticar et al., 1986).

High alkalinity concentrations and positive $\delta^{13}C$ -DIC values (> 5 to 10‰) may provide the strongest evidence for microbial methane generation in formation waters. The alkalinity concentrations measured in the Utica Shale formation waters are relatively high and have more positive $\delta^{13}C$ -DIC values as a whole compared to what was measured from the shallow Devonian subcrop water supply wells and the oil/gas wells (Osborn and McIntosh, 2010) (Figure 3-5). Alkalinity concentrations are, however, relatively low (5.66 to 10.95 meq/kg) compared to established microbial methane reservoirs in the Michigan and Illinois basins, which range between approximately 10 and 78 meq/kg (Martini et al., 1998; McIntosh et al., 2004). One sample (O75) has an alkalinity concentration greater than 10 meq/kg that may be considered consistent with the low end of alkalinity values for microbial methanogenesis. Since the Utica wells sampled for this study are relatively shallow and may be part of an active hydrologic flow system, the effect of soil respiration ($\delta^{13}C$ -DIC of between approximately -22 to -12‰), may control the $\delta^{13}C$ -DIC values of the Utica Shale formation waters. When compared to typical values for soil respiration of shallow waters and

the shallow water supply well samples in Osborn and McIntosh (2010) from the Devonian subcrop ($\delta^{13}\text{C-DIC}$ between -24.8 to -0.6‰), the formation waters from the Utica shale generally have $\delta^{13}\text{C-DIC}$ values that are more positive. This may be due to carbonate dissolution ($\delta^{13}\text{C-DIC}$ ~0‰) or microbial methanogenesis (>5 to 10‰). Sample O79 has the most positive $\delta^{13}\text{C-DIC}$ value (5.9‰), which may be considered high for values that are consistent with carbonate dissolution. A thorough assessment of microbial methanogenesis includes potential inhibitors such as salinity (i.e. chloride), sulfate concentrations, microbiology studies, and the bioavailability of organic matter substrates (core analyses that are pending).

Chloride concentrations are used as a strong proxy for inhibition of microbial methanogenesis. Microbial methanogenesis research has cited studies by Zinder (1993), Ollivier et al. (1994), and Waldron et al. (2007) for imposing salinity (>2,000 mmole/L chloride) constraints on microbial metabolism and methane production (McIntosh and Martini, 2008; Osborn and McIntosh, 2010). In addition, the presence of sulfate at a concentration greater than 1 mmole/L has been demonstrated to inhibit methanogenesis (Lovley and Klug, 1982). At high sulfate concentrations, sulfate reducing bacteria begin to out-compete methanogens for available electron donors and organic matter substrates necessary for metabolism. The chloride concentrations in Utica organic-rich shale formation waters are markedly less than the 2,000 mmole/L boundary inhibitory for microbes, indicating that salinity is not a factor controlling microbial methane production. Sulfate remains below the 1 mmole/L limit inhibitory for methanogenesis. The $\delta^{18}\text{O}$ and δD values are within the range of modern meteoric water and plot close to the local meteoric water line, but more negative than the average values measured in modern precipitation (Huddart et al., 1999, Figure 3-6). This may indicate that these shallow waters are part of a relatively active hydrologic flow system, as might be expected for relatively shallow formation waters. This is consistent with shallow formation waters collected from water supply wells in the Devonian section (Osborn and McIntosh, 2010). There is no isotopic evidence for the presence of Late Pleistocene waters in the Utica Shale. Analyses of organic matter in core materials from the Utica, as well as the upper Devonian organic-rich shales in western New York may shed some light on the bioavailability of organic matter and provide evidence for biodegradation. These results are pending from Weatherford Laboratories.

CONCLUSIONS

There is mixed evidence for limited reservoirs of microbial methane in the shallow Utica Shale subcrop, which also contains thermogenic gas produced from organic matter of high thermal maturity (likely the Utica Shale at depth). This conclusion is based on:

- 1) the relatively high C_1/C_2 values and the inverse relationship between increasing C_1/C_2 values and decreasing $\delta^{13}\text{C-CH}_4$ values, which suggests mixing of microbial and thermogenic gas;

- 2) lack of higher chain hydrocarbons above ethane in produced and dissolved gas samples, which maybe indicative of microbial gas or late stage thermogenic gas;
- 3) the upper end of alkalinity concentration and $\delta^{13}\text{C}$ -DIC values of some Utica Shale formation waters may be consistent with the lower end of values for microbial methanogenesis;
- 4) low chloride and low sulfate values, which suggest an environment conducive for methanogenesis.
- 5) Low CO_2 concentrations, relatively negative $\delta^{13}\text{C}$ - CO_2 values, and little covariance of δD values of methane and water provide little to no evidence for microbial methanogenesis.

These results indicate that methanogens, if present, may not be very active in the Utica Shale in the study area (central New York State), and is generally consistent with the conclusions of Osborn and McIntosh (2010) from the Devonian organic-rich shales in western New York and northwest Pennsylvania. If Utica Shale gas wells are drilled, we recommend future analyses of water, gas, and microbial materials (if present) to better understand the contribution of microbial methane and potential limitations on microbial activity.

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Table 3-1. Sample location, depth, and production type, Northern Appalachian Basin

Sample ID ^(a)	Date Sampled	State	County	Formation ^(b)	Age ^(c)	Latitude	Longitude	Depth (m)	Well Type ^(d)
O75	7/8/08	NY	Montgomery	Utica Organic-rich Sh.	Ord.	42.893	-74.431	122	W/S
O76	7/8/08	NY	Fulton	Utica Organic-rich Sh.	Ord.	42.998	-74.448	65	W/S
O77	7/8/08	NY	Montgomery	Utica Organic-rich Sh.	Ord.	42.891	-74.357	30	W/S
O78	7/8/08	NY	Montgomery	Utica Organic-rich Sh.	Ord.	42.877	-74.298	26	W/S
O79	7/8/08	NY	Otsego	Utica Organic-rich Sh.	Ord.	42.780	-75.032	105	W/S
O80	7/8/08	NY	Otsego	Utica Organic-rich Sh.	Ord.	42.794	-75.036	67	W/S
O81	7/8/08	NY	Montgomery	Utica Organic-rich Sh.	Ord.	42.877	-74.298	33	Gas

^(a) O (Ordovician)^(b) Sh = Shales^(c) Ord. = Ordovician^(d) W/S = Water Supply**Table 3-2. Gas composition and compound specific isotopes**

Sample ID	N ₂ mole %	O ₂ mole %	CH ₄ mole %	C ₂ mole %	C ₁ /C ₂	CO ₂ mole %	δ ¹³ C _{CH4} (‰)	δD _{CH4} (‰)	δ ¹³ CO ₂ (‰)
O75	31.73	0.0350	66.70	0.0625	1067	0.85	-41.23	-182.0	-12.5
O76	9.72	0.0180	89.59	0.118	759	0.34	-41.31	-182.6	-13.3
O78	60.39	1.86	36.71	0.0262	1401	0.043	-58.27	-251.7	
O79	9.50	0.315	89.96	0.0266	3382	0.019			
O80	52.16	6.33	40.22	0.0155	2595	0.21	-44.74	-227.4	-9.5
O81	8.33	0.726	90.70	0.0165	5497	0.073	-41.12	-183.6	

Table 3-3. Formation water geochemical results for water Supply wells in the Utica Fm.

Sample ID	Temp (°C)	pH	Alkalinity (meq/kg)	Cl (mM)	SO ₄ (mM)	Na (mM)	δ ¹³ C DIC (‰)	δ ¹⁸ O H ₂ O (‰)	δD H ₂ O (‰)
O75	16.4	8.29	10.95	0.741	0.631	12.633	1.4	-10.4	-69.0
O76	16.7	7.92	5.66	0.390	0.190	3.855	-1.5	-10.2	-68.0
O77	16.4	8.42	6.15	0.833	0.010	5.568	-3.2	-10.5	-70.0
O78	15.6	9.19	8.13	0.179	0.024	8.216	-2.1	-9.9	-66.0
O79	16.3	9.39	7.81	2.628	0.011	10.232	5.9	-11.0	-72.0
O80	15.6	7.40	5.82	0.896	0.102	7.014	2.1	-10.8	-71.0

EDUCATIONAL OPPORTUNITES PROVIDED BY THIS PROJECT

Section 4

On Ph.D. student, one Masters student, and three undergraduate students were supported by this project. Stephen Osborn, a Ph.D. student in the Department of Hydrology and Water Resources (HWR) at the University of Arizona was primarily supported by the NYSERDA project for 2 academic years. He was largely responsible for coordinating the fieldwork, analyzing the elemental chemistry of formation waters, collecting core materials from the New York State Museum, and interpreting the water and gas data, working closely with Dr. McIntosh (thesis advisor). Results from this project will form the basis for Stephen's Ph.D. dissertation (to be completed in June 2010).

We also hired two students as summer research assistants helping with both field and laboratory work. Justin Clark, an undergraduate student in HWR, worked with Stephen and Dr. McIntosh in the summer of 2007. Justin is currently a graduate student at the University of Waterloo. Keith Rogers, a M.S. student in HWR, worked with Stephen and Dr. McIntosh in the summer of 2008. Keith is now working for an environmental consulting company in North Carolina. In addition, two undergraduate students (Patrick Morgan and Matthew Travis) from the State University of New York (SUNY) at Genesso volunteered to assist with fieldwork in summer of 2008 to gain research experience.

The United States Geological Survey provided summer salary support for Stephen and Keith, as part of their cost-sharing contribution. They also provided summer salary support for Dr. McIntosh to advise the students on summer fieldwork campaigns and laboratory analyses.

PUBLICATIONS AND PRESENTATIONS RESULTING FROM THIS PROJECT

Section 5

The following section summarizes how results of this study have been disseminated to the scientific community and public through journal publications, presentations at national and international meetings, and magazine articles. We have also been in communication with the NYSERDA Senior Project Manager (Dr. John Martin) throughout the course of this project.

PAPERS PUBLISHED IN PEER-REVIEWED JOURNALS ON STUDY RESULTS

- McIntosh, J.C. and Martini, A.M. (2008) Hydrogeochemical indicators for microbial methane in fractured black shales: Case studies of the Antrim, New Albany, and Ohio shales. *In* Hill, D., Lillis, P., Curtis, J., eds, Gas Shale in the Rocky Mountains and Beyond, Rocky Mountain Association of Geologists 2008 Guidebook, p. 162-174.
- *Osborn, S., McIntosh, J.C. (2010) Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin. *Applied Geochemistry*, 122, 1248-1264.
- *Osborn, S.G., McIntosh, J.C. (*in prep*) Geochemistry of formation waters, gas, and core materials to determine origin of natural gas in Upper Ordovician organic-rich shales: northern Appalachian Basin. *To be submitted to AAPG Bulletin or Journal of Geochemical Exploration*.
- *Ph.D. student primarily supported by this project.

ABSTRACTS PRESENTED AT SCIENTIFIC MEETINGS ON STUDY RESULTS

- McIntosh, J.C. (2007) Hydrogeologic controls on microbial methane accumulations in organic-rich shales. Geological Survey of Canada, Calgary, Alberta – *invited talk*.
- Osborn, S.G., McIntosh, J.C. (2007) Fluid and gas geochemistry of organic-rich shales in the Appalachian Basin. American Association of Petroleum Geologists Eastern Section Meeting.
- Osborn, S.G., McIntosh, J.C. (2007) Origin and distribution of natural gas in Upper Devonian organic-rich shales, Appalachian Basin. Geological Society of America Conference.
- Osborn, S.G. and J.C. McIntosh (2008) Origin and Distribution of Natural Gas in Devonian Black Shales, Northern Appalachian Basin, AAPG NE regional conference, Pittsburgh, PA.
- McIntosh, J.C., Osborn, S.G., Schlegel, M.E. (2008) Distribution and controls on microbial methane generation in fractured organic-rich shales. International Geological Congress, Oslo, Norway – *invited talk*.

MEDIA COVERAGE OF RESEARCH

- “Taking the fossil out of fossil fuel,” by Phil McKenna. New Scientist magazine. July 20, 2007.
- “UA hydrologist studies huge natural gas reserves created by microbes”, by Ed Stiles. UANews.org. April 24, 2007.