

Distinguishing the source of natural gas accumulations with a combined gas and co-produced formation water geochemical approach: A case study from the Appalachian Basin

By:

Stephen Osborn, Duke University
Post-doctoral research associate
(stephen.osborn@duke.edu)

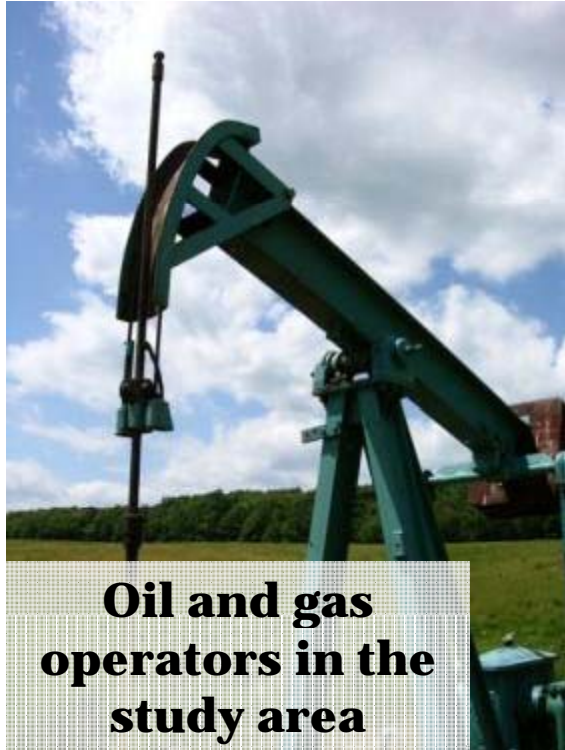
and

Jennifer McIntosh, University of Arizona
(mcintosh@hwr.arizona.edu)

EPA Technical Workshop, February 24-25 2011



Acknowledgements:



THE GEOLOGICAL SOCIETY
OF AMERICA®



American Association of Petroleum Geologists

An International Geological Organization



Robert Jackson (Duke)
Avner Vengosh (Duke)
Nathaniel Warner (Duke)



Duke
UNIVERSITY

Introduction

- Strong interest in Devonian age organic-rich shales of the northern Appalachian basin.

*“Appalachian Basin’s Marcellus – the new target”
-AAPG Explorer (March 2008)*

“There’s Gas in Those Hills” -N.Y. Times (April 2008)

- Some concern on the potential environmental impact to shallow groundwater
- Distinguishing the source of natural gas may provide some insight into understanding mechanisms associated with oil/gas operations, if any.

Objective

- Discuss the use of gas and co-produced formation water geochemistry for identifying the source of natural gas
- Present gas geochemistry for the northern Appalachian Basin

“Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin”

-Osborn, S.G. and McIntosh J.C., Applied Geochemistry, 25, pp. 456-471.”

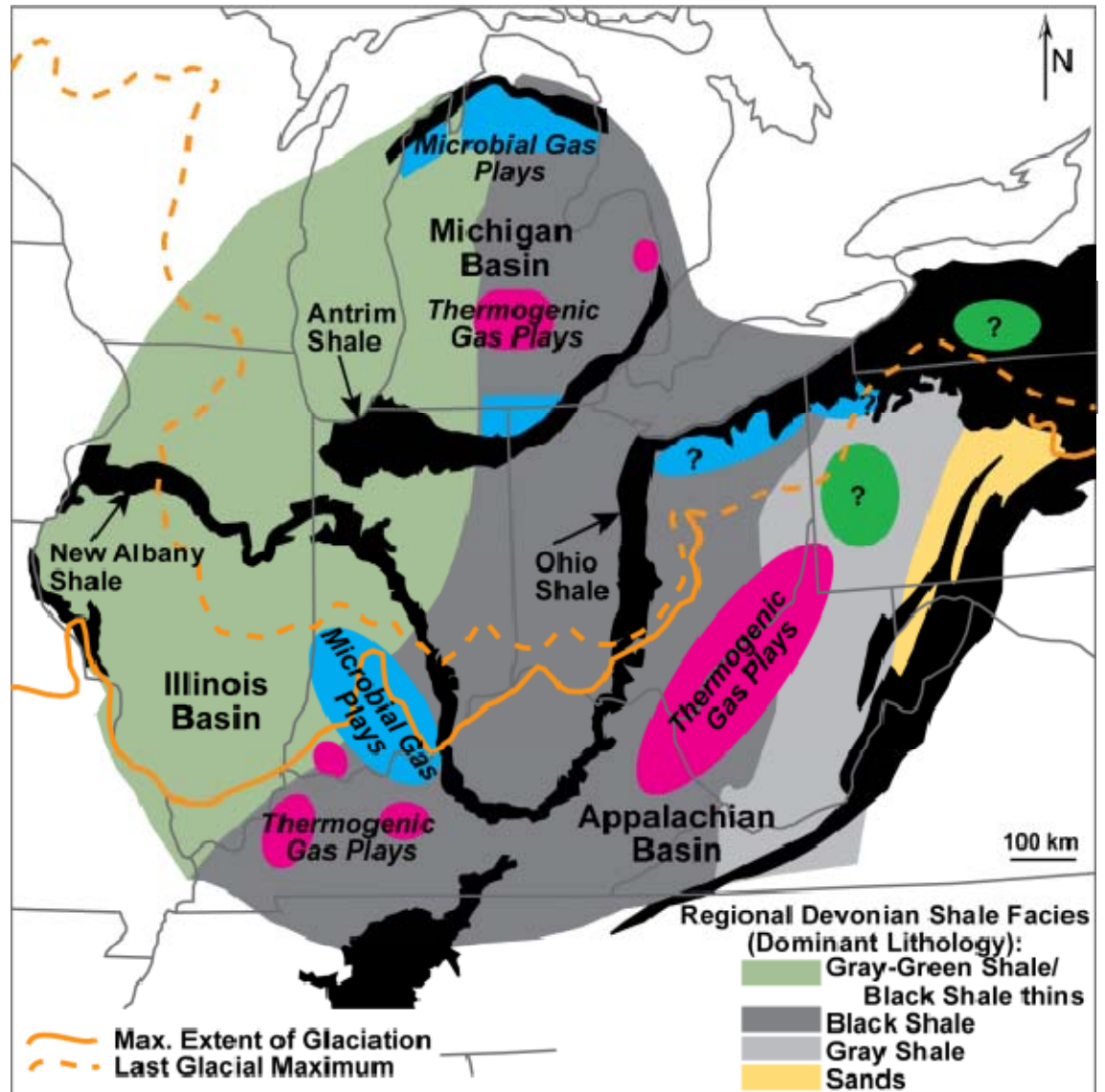
Regional Geologic Setting

- Microbial gas is actively generated at the shallow margins of the glaciated Michigan and Illinois basins

Northern Appalachian Basin:

- Similar glacial history and litho-stratigraphic relationships
- Important differences?

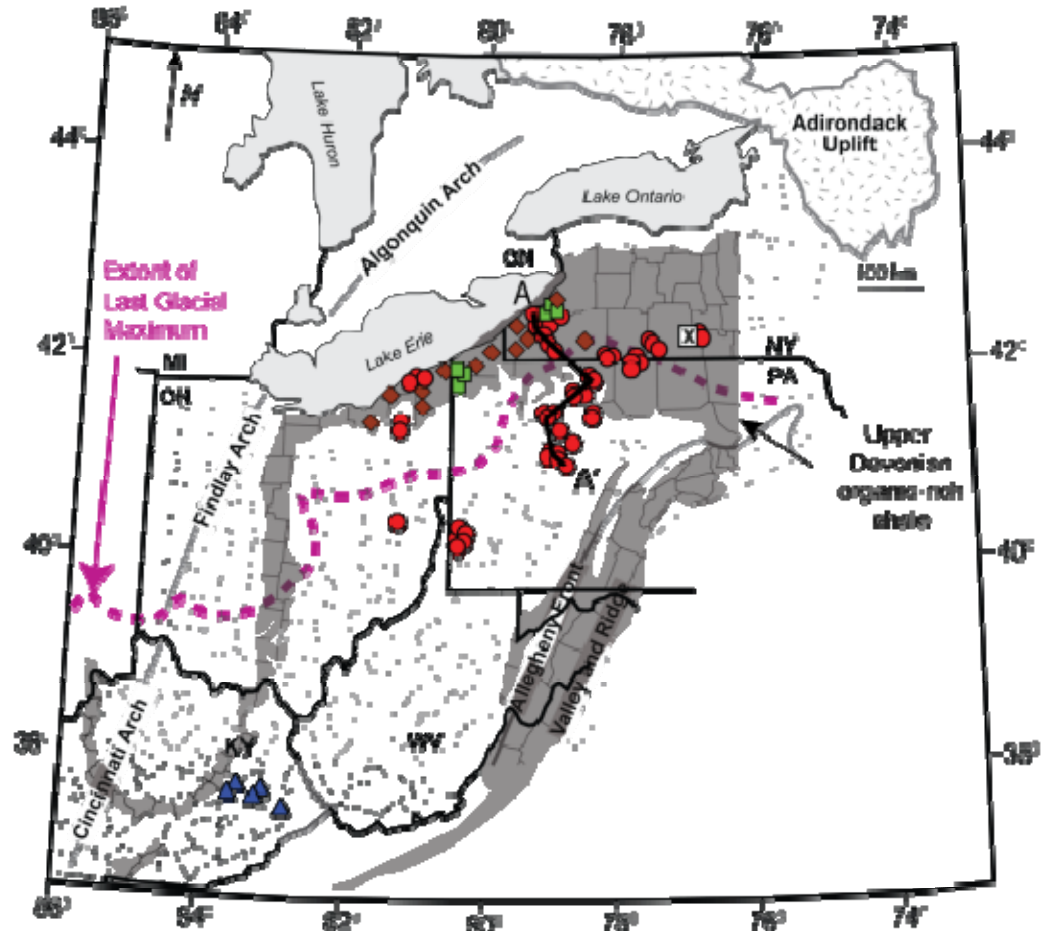
Upper Devonian Fractured Black Shale Gas Plays



(modified from McIntosh and Martini, 2007)

Research Area

SYSTEM	MEMBER	FORMATION		
		Appalachian Basin (E. Old)	W. Penn./N. New York	
PROTEROZOIC				
PENNSYLVANIAN			Conemaugh Gp. Allegheny Gp. Burgoon Fm. Murrysville Sand	
		Sunberry Sh Berea Ss		
DEVONIAN	Upper	Ohio Shale	Venango Gp. Bradford Gp. Huron Sh. Elk Gp. Rhinecliff Sh.	
			Hamilton Gp.	
			Marcellus Fm.	
			Onondoga Ls.	
	Middle	Columbus Ls. Bois Blanc Ls.	Ridgeley Ss.	
	Lower	Oriskany Ss. Bass Islands Dol.	Helderberg Gp.	
	SILURIAN	Upper	Salina Gp.	Salina Gp.
		Middle	Lockport Dol.	Lockport Dol.
		Lower	Rochester Sh & Dayton Dol.	Clinton Gp.
ORDOVICIAN	Upper	Clinton Ss.	Medina Gp.	
		Queenston Sh.	Queenston Sh.	
		Reedsville Sh.	Reedsville Sh.	
	Middle	Utica Sh.	Utica Sh.	
	Lower	Trenton & Black River Ls.	Trenton & Black River Ls. Beekmantown Dol.	
CAMBRIAN	Upper	Beekmantown Dol/ Knox Dol/Rose Run Ss.	Gatesburg Fm. Warrior Fm.	
	Middle	Rome Fm. Potsdam	Potsdam Ss. Pleasant Hill Fm.	
	Lower	Precambrian	Precambrian	
PRE-CAMBRIAN			Precambrian	

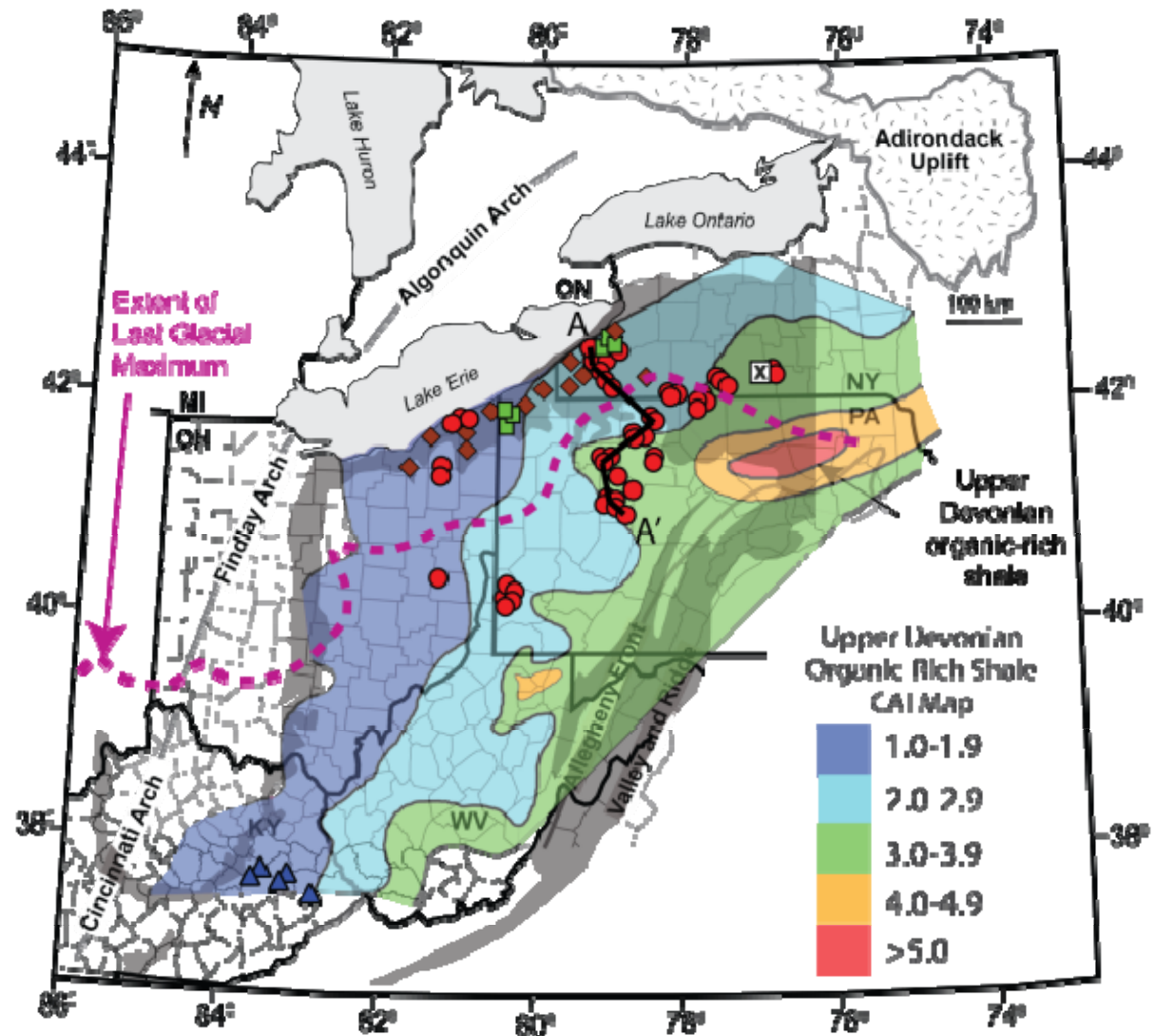


- ▲ Berea Ss. (Miss.)
- Devonian Sh. and Ss.
- Medina Ss. (Sil.)
- ◆ Devonian Sh. - W/S Wells
- X** Trenton/Black River (Ord.)

(modified from Shaver et al., 1986; Laughrey and Baldassare, 1998)

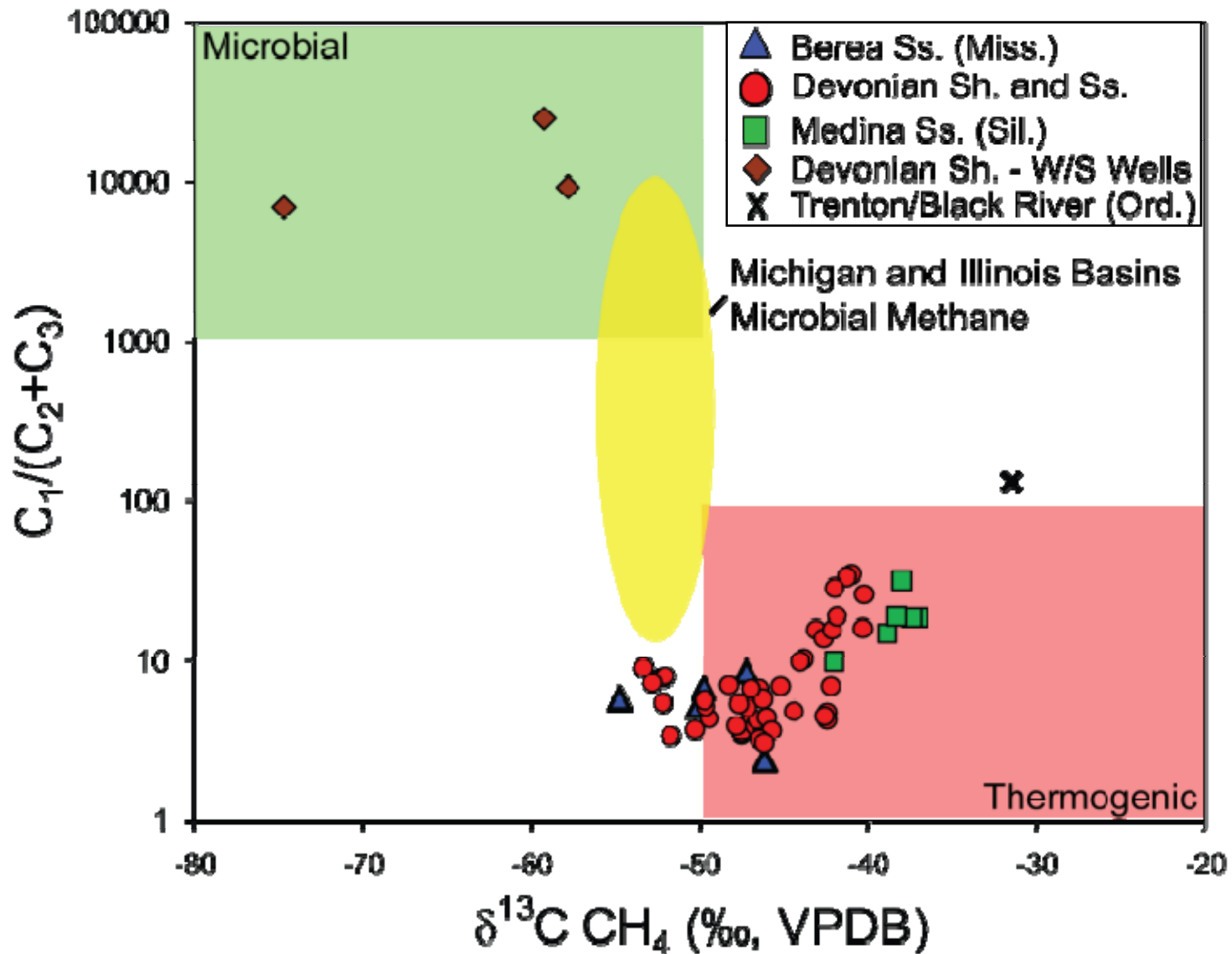
Quantity and Quality of Organic Matter

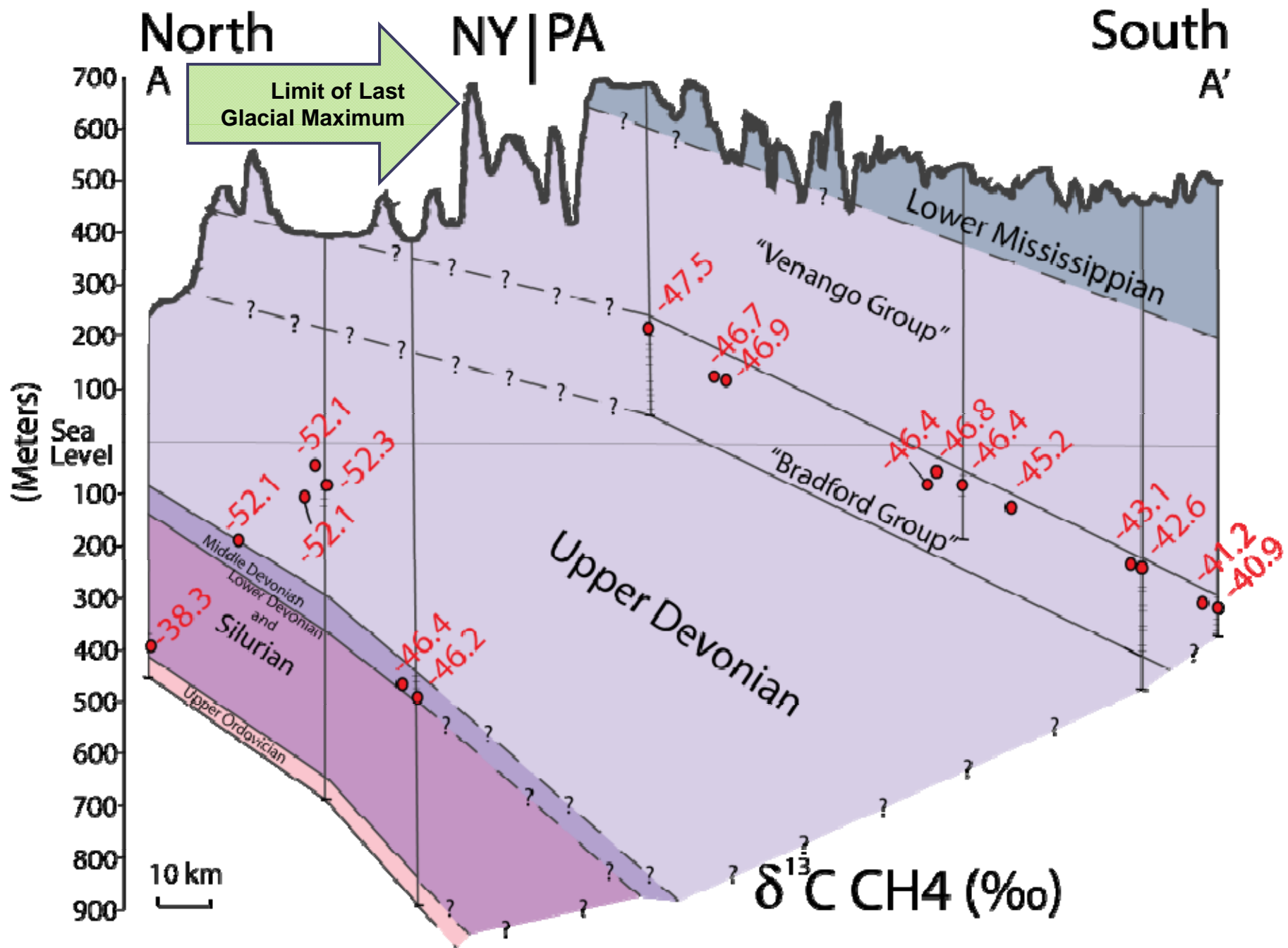
Organic-rich shales contain total organic carbon (TOC) up to 18%



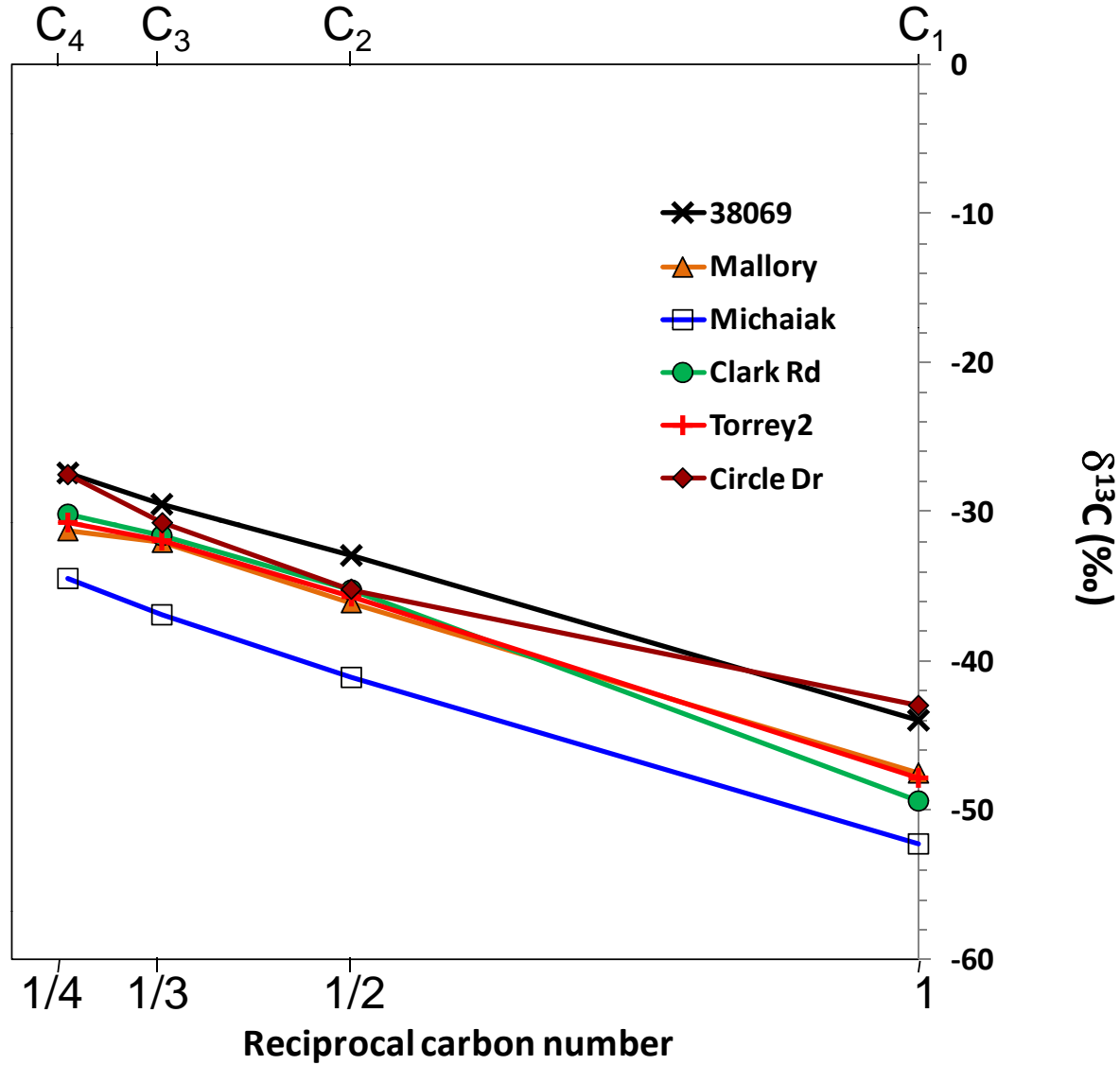
(Modified from Repetski et al., 2006)

Origin of Methane

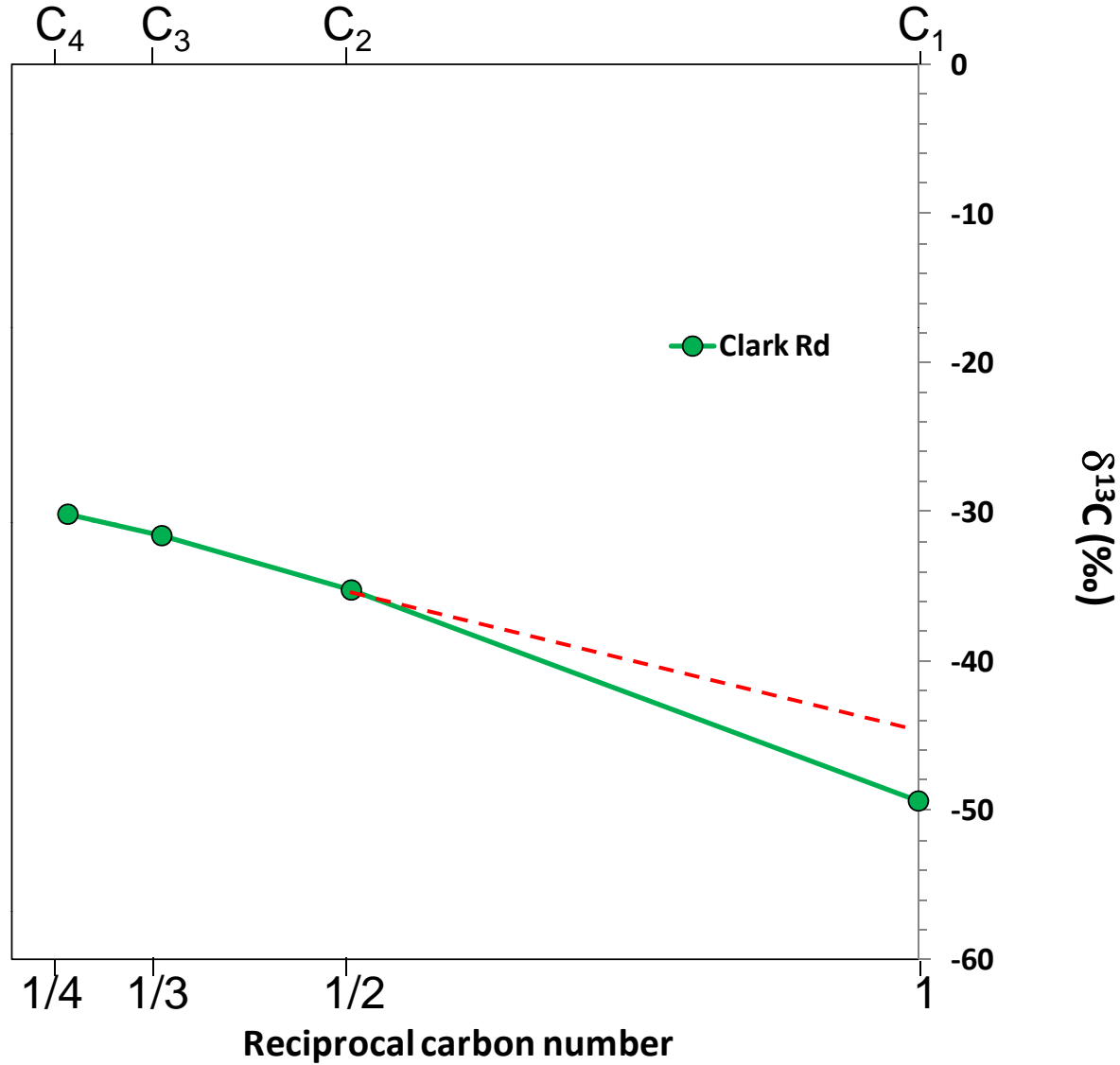




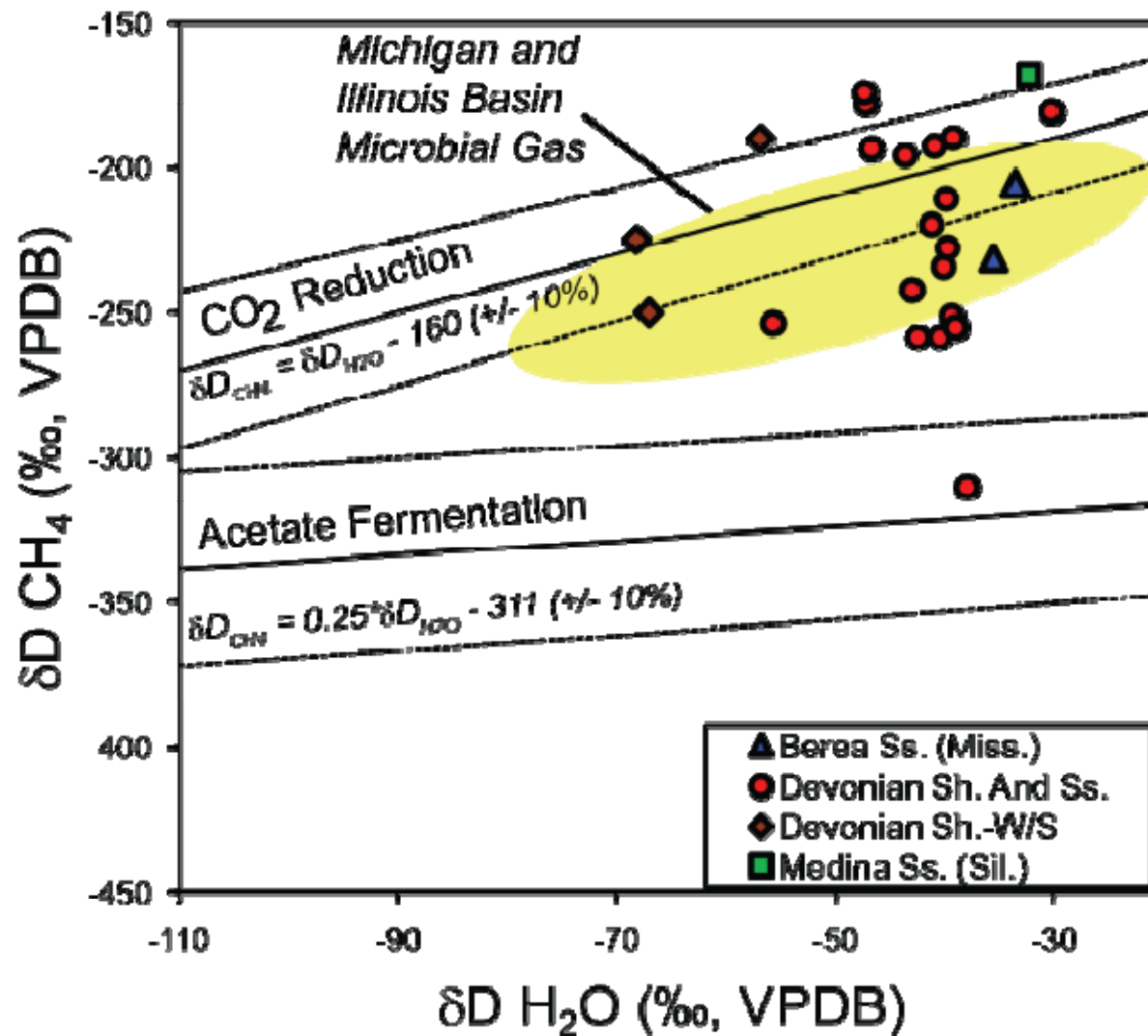
Carbon Isotopes C₁-C₄



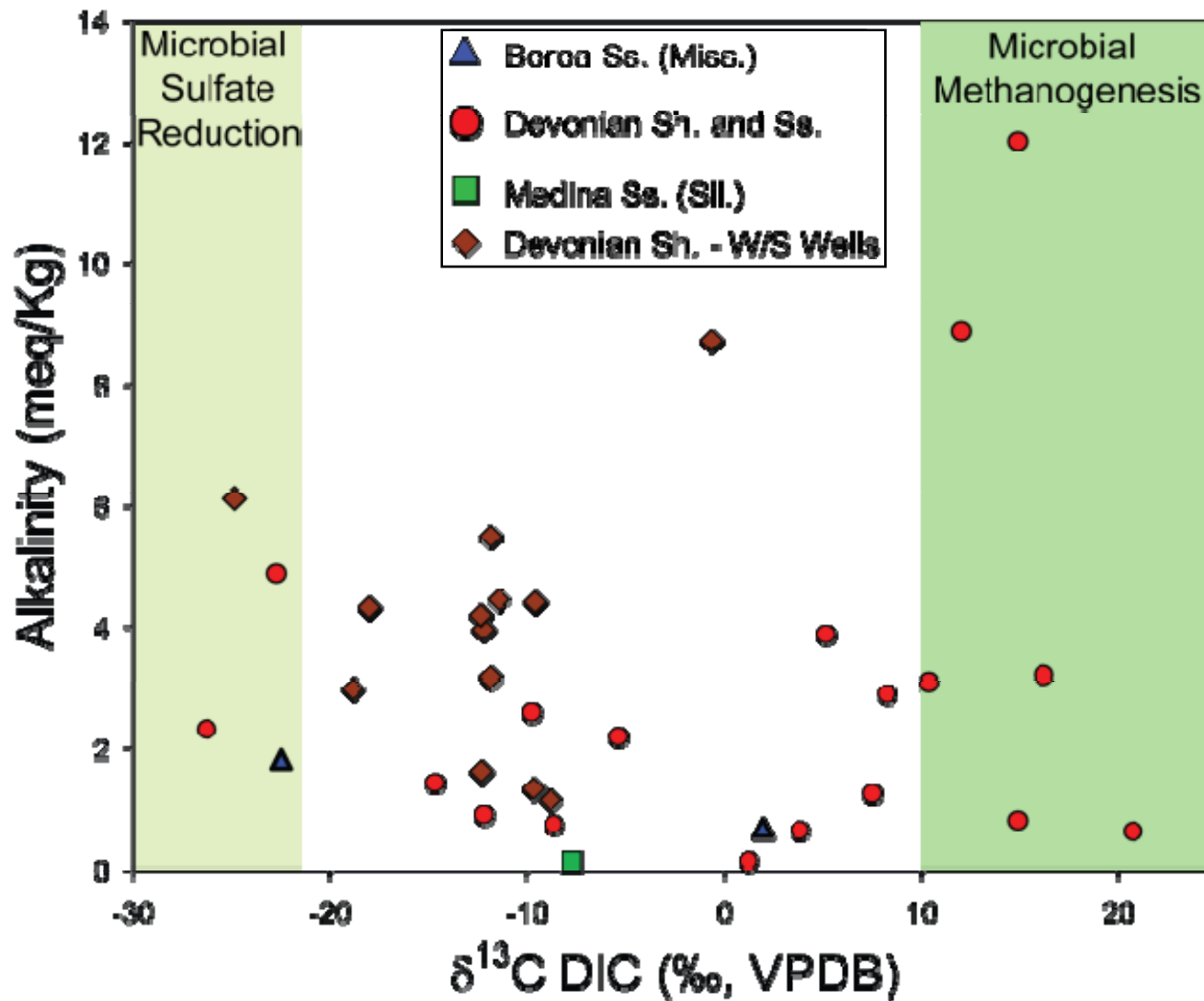
Carbon Isotopes C₁-C₄



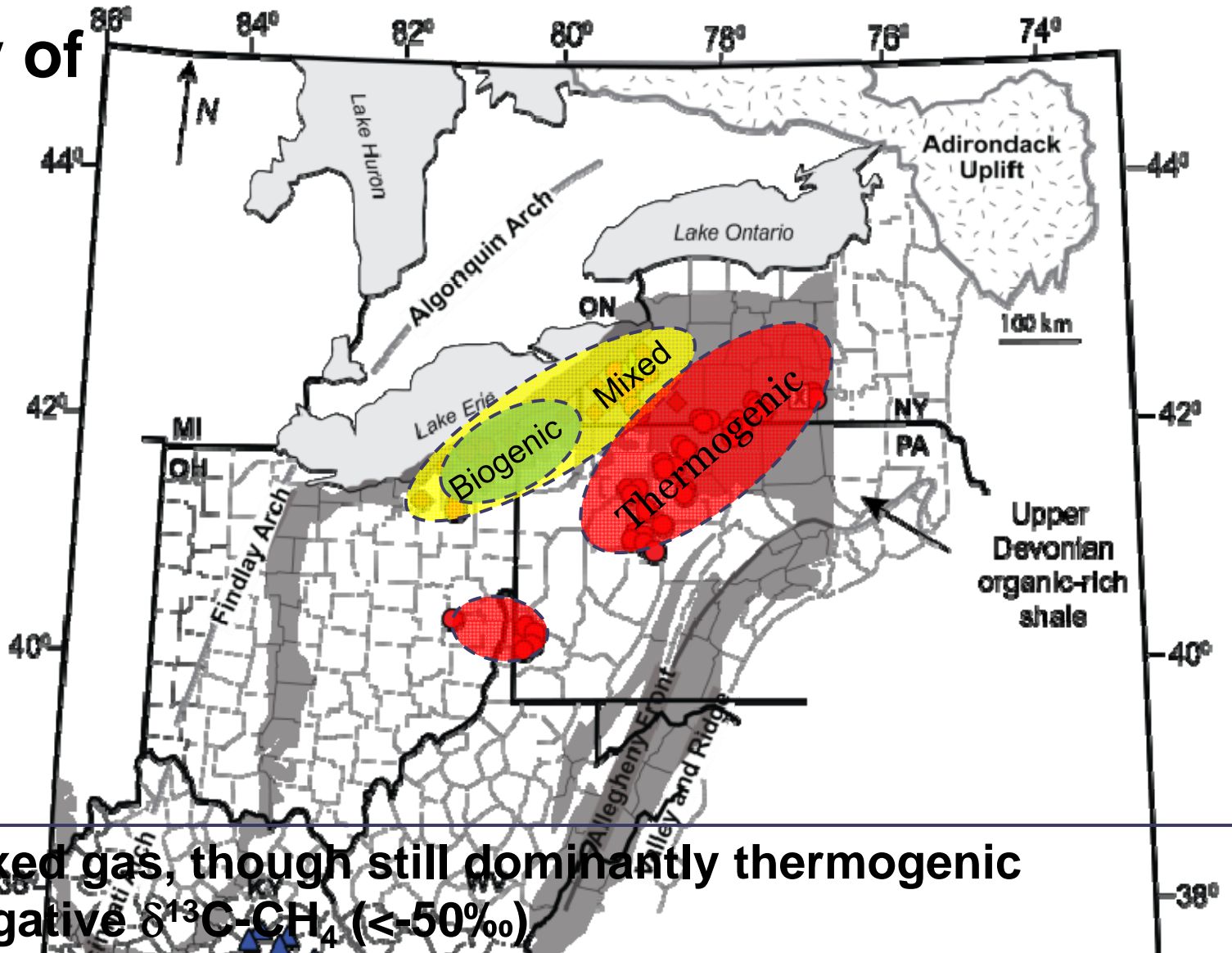
Hydrogen Isotopes of Water and Methane



Evidence for Microbial Methanogenesis and Sulfate Reduction



Summary of Results



Mixed gas, though still dominantly thermogenic

- slightly negative $\delta^{13}\text{C}-\text{CH}_4$ ($< -50\text{‰}$)
- low methane to ethane and propane ratios with increasing trend
- some positive $\delta^{13}\text{C}-\text{DIC}$ values
- low to moderate salinity

Take Home Message

- General indicators of thermogenic gas:
 - Presence of higher chain hydrocarbons (ethane, propane, butane) greater than 5% combined with,
 - Carbon isotope values of methane greater than $\sim -50\text{‰}$
 - Correlation between reciprocal carbon number and carbon isotope values of higher chain hydrocarbons
- Genetic and post-genetic considerations:
 - Organic matter source (effects carbon isotopic value)
 - Oxidation and Diffusion (fractionation of isotopes and gas composition)
 - Mixing of different thermogenic sources
- General indicators of biogenic gas:
 - Relatively Low salinity (less than $\sim 2-4$ M Cl)
 - Low concentration of alternative electron acceptors ($\text{SO}_4 > \sim 1\text{mM}$)
 - High $\delta^{13}\text{C-DIC}$ values ($> \sim +10\text{‰}$) and high Alkalinity ($> \sim 10$ meq/Kg)
 - Correlation of δD of methane and co-produced water

Distinguishing the Source of Natural Gas Accumulations with a Combined Gas and Co-produced Formation Water Geochemical Approach

Stephen Osborn¹ and Jennifer McIntosh²

¹Duke University, Center on Global Change

²University of Arizona, Hydrology and Water Resources

The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Introduction

Identifying the source of dissolved gas accumulations in shallow groundwater systems may provide some insight into potential impacts from underlying geologic formations targeted for natural gas production and associated with drilling and hydro-fracturing operations. This presentation describes a combined gas and formation water geochemical approach for distinguishing relatively shallow microbial methane and gas sourced from depth by the thermal-catalytic breakdown of organic matter (thermogenic gas). Recent results from the northern Appalachian Basin, detailed in Osborn and McIntosh (2010), will be presented and highlight this approach using gas composition and carbon isotope ($\delta^{13}\text{C}$) values of methane and higher chain hydrocarbons (ethane, propane, and butane) combined with elemental (major) and isotopic analyses ($\delta^{13}\text{C}$ -DIC) of formation waters.

Distinguishing the Source of Natural Gas

Thermogenic gas has a greater proportion of higher chain hydrocarbons (ethane, propane, butane, and pentane) relative to methane than microbial gas, which dominantly contains CH_4 and CO_2 (Schoell, 1980). Thus, gas composition may be used as a first order approximation distinguishing between microbial and thermogenic gas. Carbon isotope values of methane ($\delta^{13}\text{C}$ - CH_4) 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% (methane to higher chain hydrocarbon ratio greater than 1000) 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 (Bernard, 1978; Schoell, 1980; Whiticar et al., 1986). Methane to higher chain hydrocarbon ratios less than approximately 100 and $\delta^{13}\text{C}$ - CH_4 more positive than -50‰ have been interpreted as indicative of thermogenic gas (Bernard, 1978; Schoell, 1980; Whiticar et al., 1986). Studies on thermogenic gas have focused on higher chain hydrocarbons to understand mixing relationships among different sources of gas.

Chung et al. (1988) proposed a kinetic fractionation model (natural gas plot) that assumed a linear correlation between carbon isotope values of methane, ethane, propane, butane, and pentane (C₁-C₅); and the reciprocal carbon number as a qualitative indicator of purely thermogenic gas. Deviations from linearity in the heavier hydrocarbons (C₂-C₅) 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. 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.

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 methanogenesis, as well as identifying the predominant metabolic pathways for methane generation, as CO₂ 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). Production of CO₂ 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‰).

The geochemical conditions (salinity and redox) favorable for microbial metabolism are also important for identifying methanogenesis. 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).

Results from 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. This is based on the observation that 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 higher chain hydrocarbon ratio (3-35 mole%) with high $\delta^{13}\text{C}$ values of CH₄ (-53.35 to -40.24‰).

Dissolved gases in shallow groundwaters in Devonian organic-rich shales along Lake Erie contain detectable methane (0.01 to 50.55 mole%) with low $\delta^{13}\text{C}$ -CH₄ 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 geochemistry of co-produced brines shows evidence for microbial activity. High $\delta^{13}\text{C}$ values of DIC (>+10‰), slightly elevated alkalinity concentrations (up to 12.01 meq/kg) and low SO_4 values (<1 mmole/L) in select Devonian organic-rich shale and sandstone formation water samples suggest the presence of methanogenesis, while low $\delta^{13}\text{C}$ -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.

Conclusions

Results from this case study demonstrate the importance of a combined gas and formation water approach for constraining the origin of natural gas in sedimentary basins. This approach may provide useful in understanding the origin of natural gas accumulations in shallow groundwater systems that may be associated with drilling and hydro-fracturing operations.

Acknowledgements

Research support was provided by the New York State Energy Research and Development Authority, the American Chemical Society-Petroleum Research Fund (#45284-G2), and the United States Geologic Survey. We thank Robert Jackson, Avner Vengosh, and Nathaniel Warner from the Center on Global Change and the Earth and Ocean Science Department at Duke University for support during the preparation of this extended abstract.

References

- Barker, J.F., Fritz, P., 1981. Carbon isotope fractionation during microbial methane oxidation. *Nature* 293, 289-291.
- Bernard, B.B., 1978. Light hydrocarbons in marine sediments. Ph.D. Dissertation, Texas A&M University, College Station, Texas.
- Boetius, A., Ravensschlag, K., Schubert, C.J., Rickert, D., Widdel, F., Gleseke, A., Amann, R., Jergensen, B.B., Witte, U., Pfannkuche, O., 2000. A marine microbial consortium apparently mediating anaerobic oxidation of methane. *Nature* 407, 623-626.
- Chung, H.M., Gormly, J.R., Squires, R.M., 1988. Origin of gaseous hydrocarbons in subsurface environments: Theoretical considerations of carbon isotope distribution. *Chemical Geology* 71, 97-103.
- Hinrichs, K.U., Hayes, J.M., Bach, W., Spivack, A.J., Hmelo, L.R., Holm, N.G., Johnson, C.G., S.P. Sylva, 2006. Biological formation of ethane and propane in the deep marine subsurface. *PNAS* 103, no. 40, 14684-14689.
- Lovley, D.R., Klug, M.J., 1982. Sulfate Reducers Can Out-compete Methanogens at Freshwater Sulfate Concentrations. *Applied and Environmental Microbiology* 45, no. 1, 187-192.
- Martini, A.M., Budai, J.M., Walter, L.M., Schoell, M., 1996. Microbial generation of economic accumulations of methane within a shallow organic-rich shale. *Nature* 383, 155-158.
- Martini, A.M., Walter, L.M., Budai, J.M., Ku, T.C.W., McIntosh, J.C., Schoell, M., 2003. Microbial production and modification of gases in sedimentary basins: A geochemical case study from a Devonian Shale gas play, Michigan Basin. *AAPG Bulletin* 87, no. 8, 1355-1375.
- Ollivier, B., Caumette, P., Garcia, J.-L., Mah, R.A., 1994. Anaerobic bacteria from hypersaline environments. *Microbiology Reviews* 58, 27-38.
- Osborn, S.G. and 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*, 25, pp. 456-471.
- Prinzhofer, A, Pernaton, E., 1997. Isotopically light methane in natural gas: bacterial imprint or diffusive fractionation?. *Chemical Geology* 142, 193-200.
- Schoell, M., 1980. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochimica et Cosmochimica Acta* 44, 649-661.
- Taylor, S.W., Sherwood Lollar, B., Wassenaar, L.I., 2000. Bacteriogenic Ethane in Near-Surface Aquifers: Implications for Leaking Hydrocarbon Well Bores. *Environmental Science and Technology* 34, no. 22, 4727-4732.
- Whiticar, M.J., Faber, E., Schoell, M., 1986. Biogenic methane formation in marine and freshwater environments: CO₂ reduction vs. acetate fermentation – Isotope evidence. *Geochimica et Cosmochimica Acta* 50, 693-709.
- Whiticar, M.J., Faber, E., Schoell, M., 1986. Biogenic methane formation in marine and freshwater environments: CO₂ reduction vs. acetate fermentation – Isotope evidence. *Geochimica et Cosmochimica Acta* 50, 693-709.
- Zinder, S.H., 1993. Physiological ecology of methanogens. In: Ferry J.G. (Eds.), *Methanogenesis Ecology, Physiology, Biochemistry, and Genetics*. Chapman and Hall, 128-206.