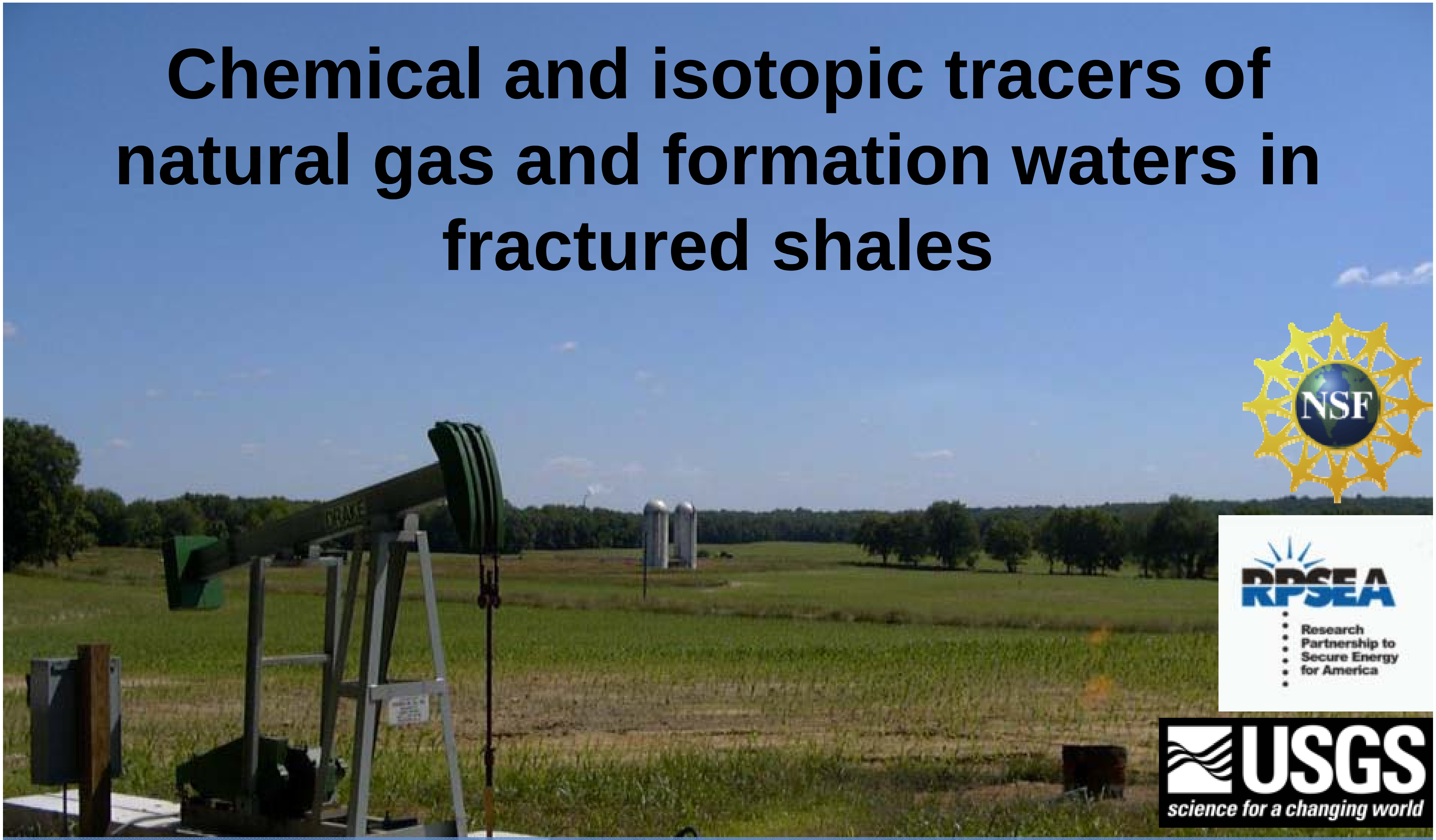
Chemical and isotopic tracers of natural gas and formation waters in fractured shales



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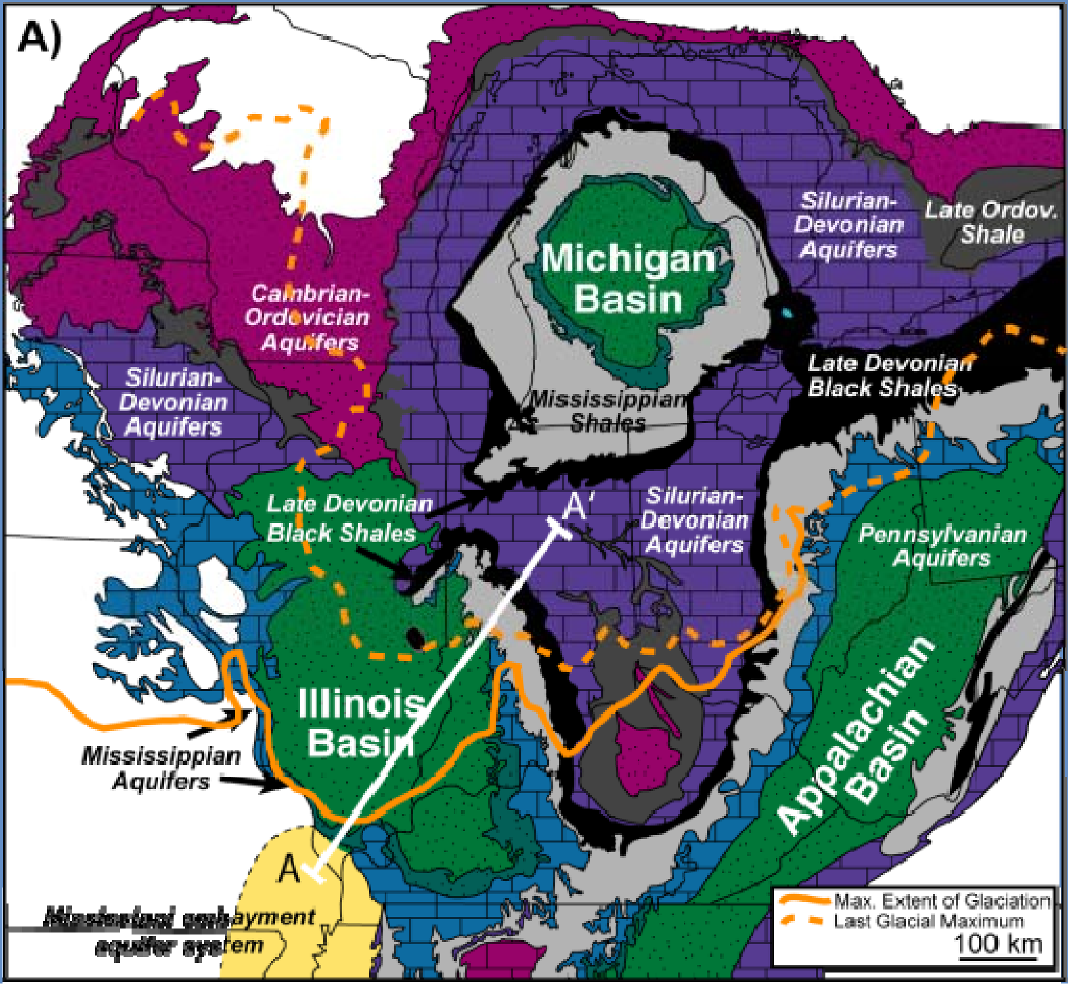
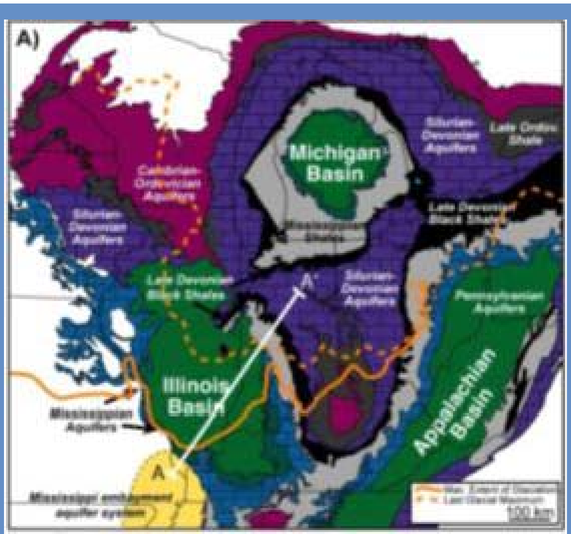
EPA Technical Workshop Feb 24-25, 2011

Outline of Presentation

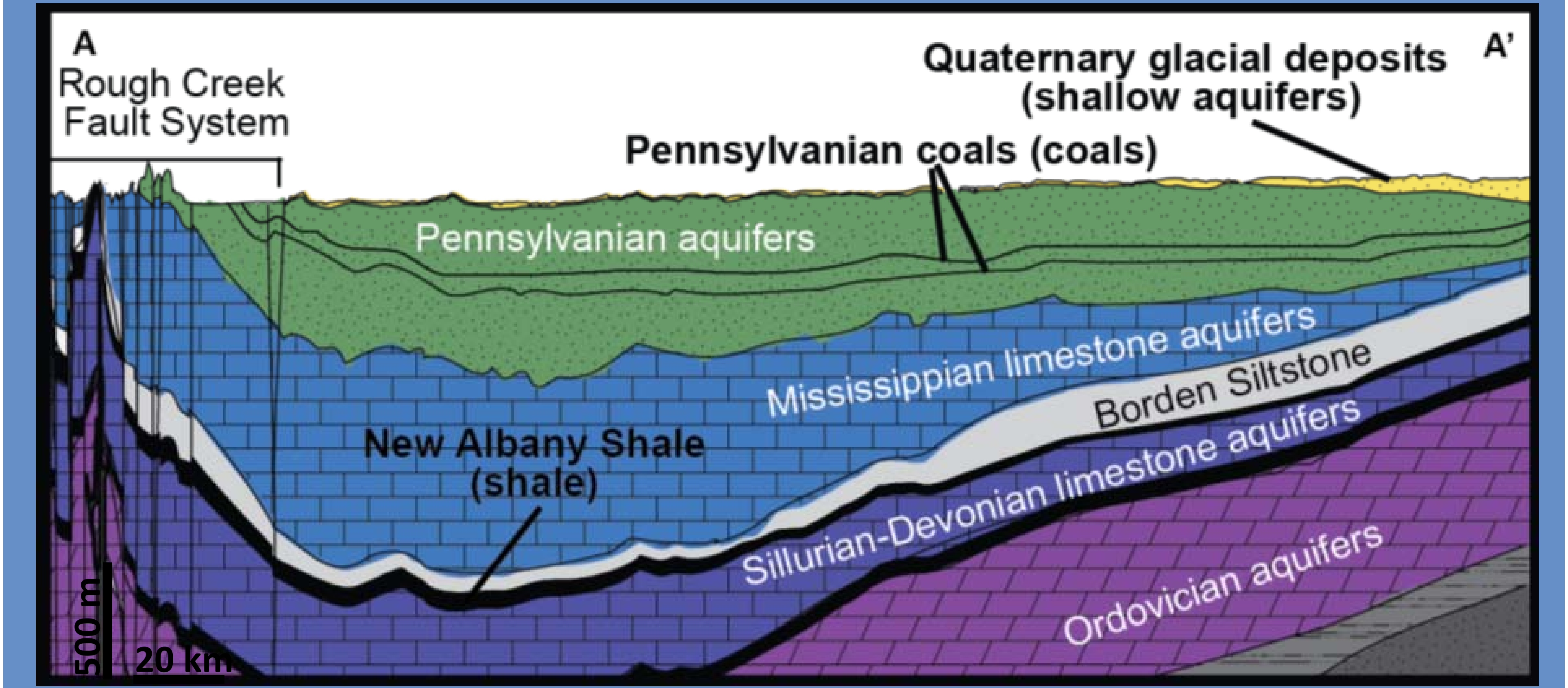
1) What is the chemical and isotopic signature of formation waters and natural gas in fractured shales?
2) How does it compare with shallow drift aquifers, coalbeds, and other deep geologic formations?



Illinois Basin-Case Study



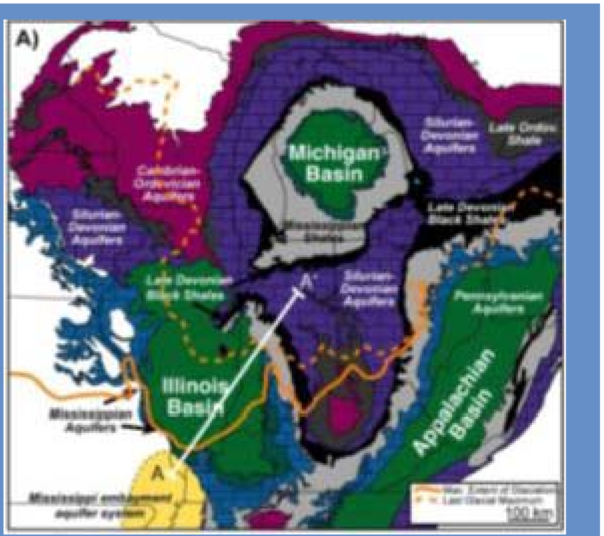
- 3 organic-rich formations: glacial drift, Penn. coal, & Dev. fractured shale
- organic-rich Ordov. Shale, not part of this study

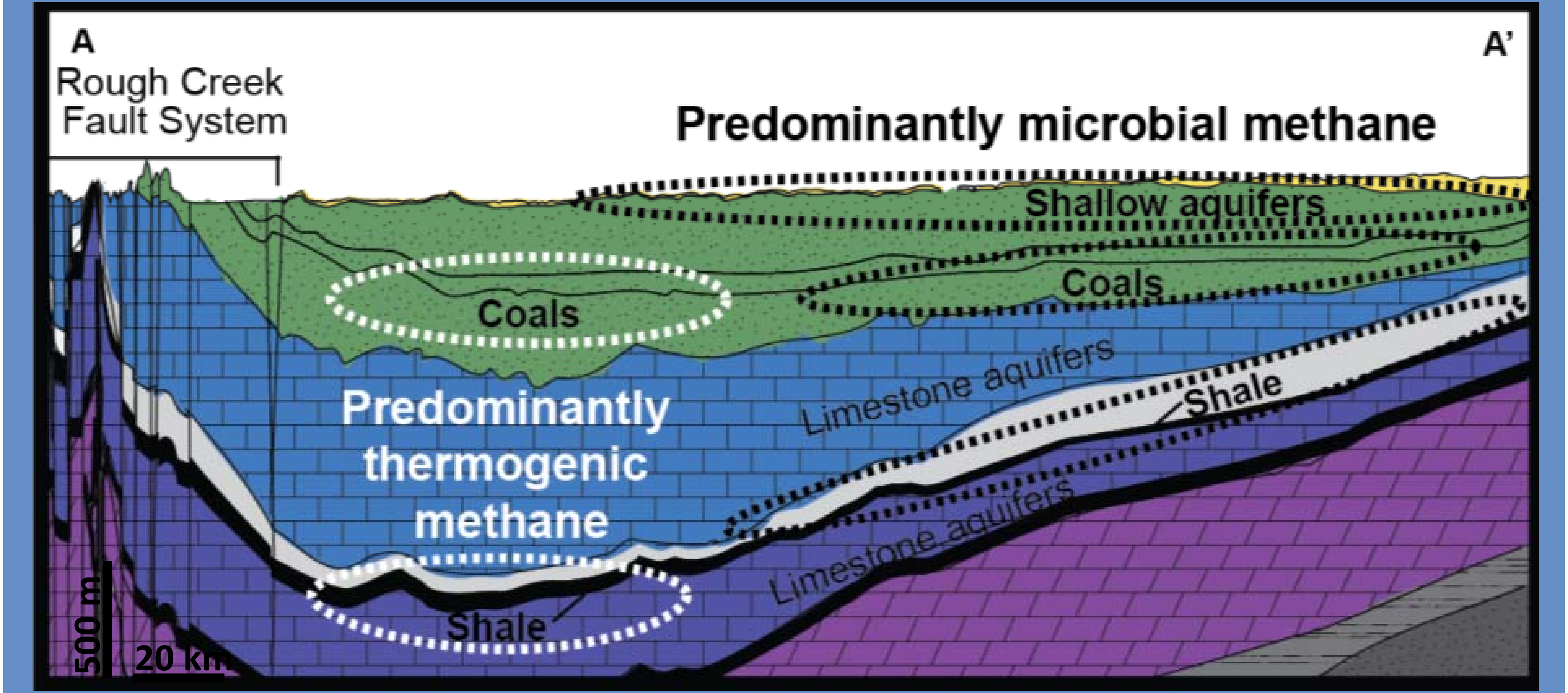


Schlegel et al. (in press, 2011, Geochimica et Cosmochimica Acta)

Illinois Basin-Case Study

- microbial methane in all 3 units
- thermogenic methane in shale and coal





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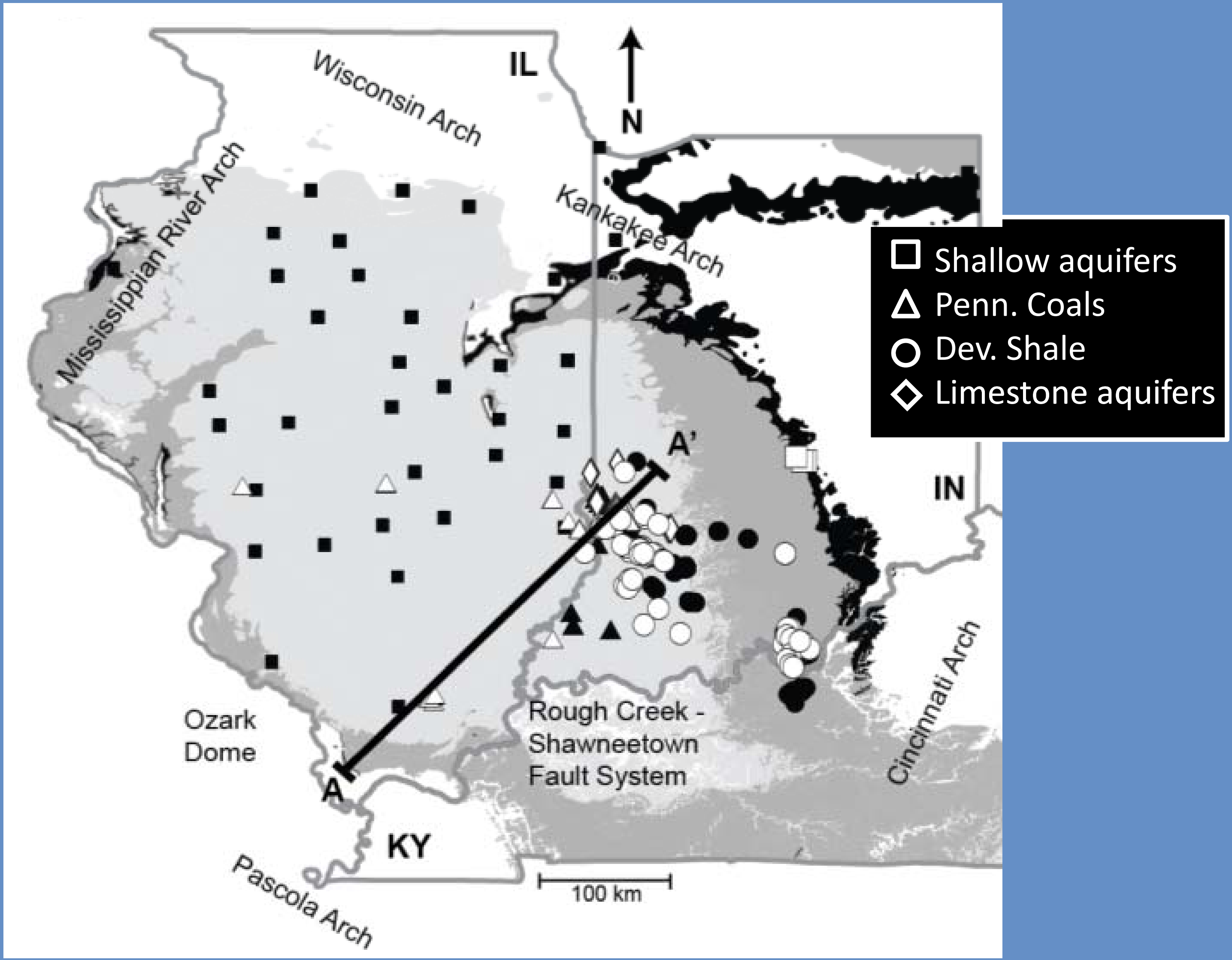
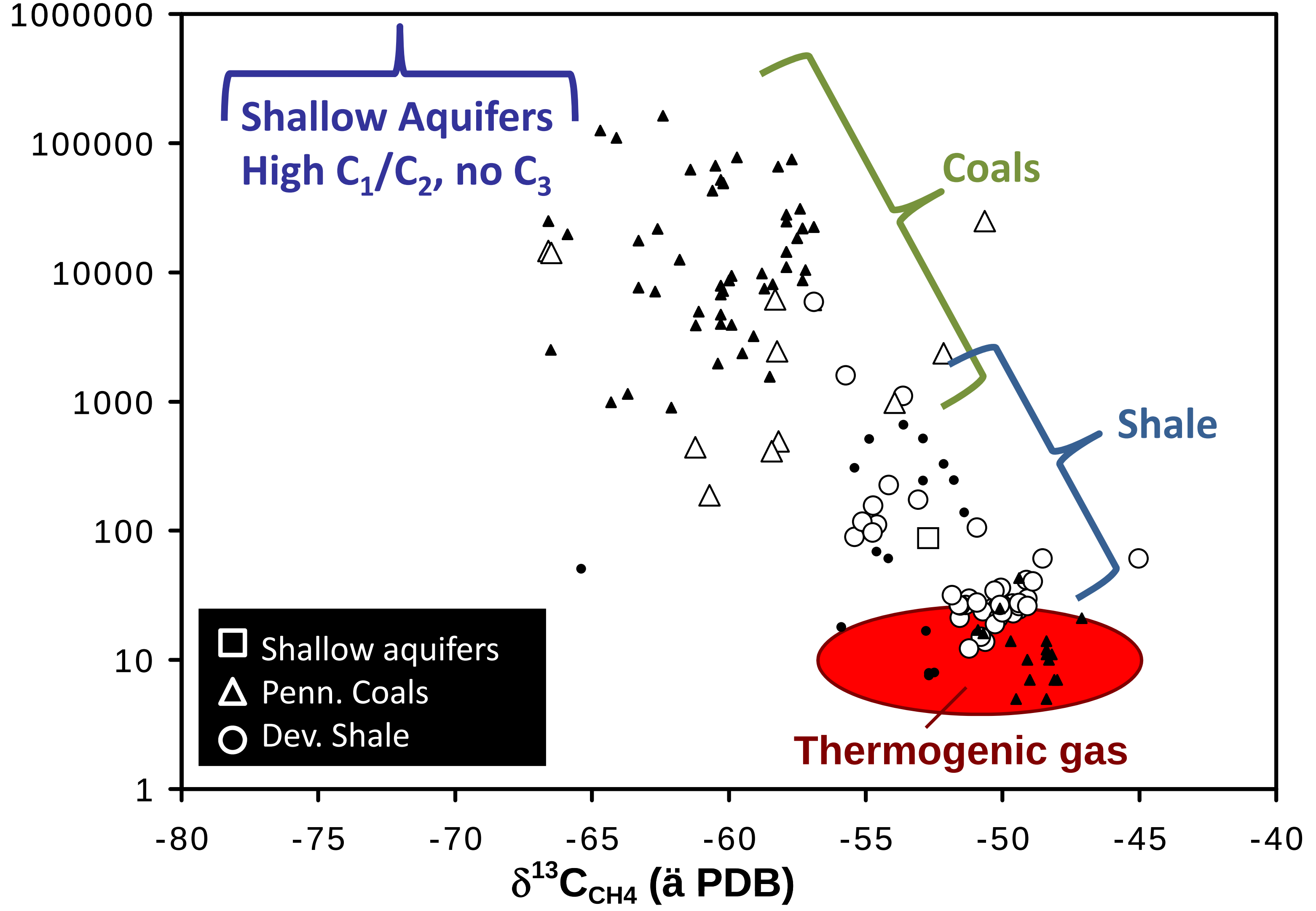
Illinois Basin - water & gas samples



- ✓*New data (white symbols): Schlegel et al. (in press)*
- ✓*Previous data (black symbols): McIntosh et al., 2002; Strąpoć et al., 2007, 2008a,b; Coleman et al, 1988*

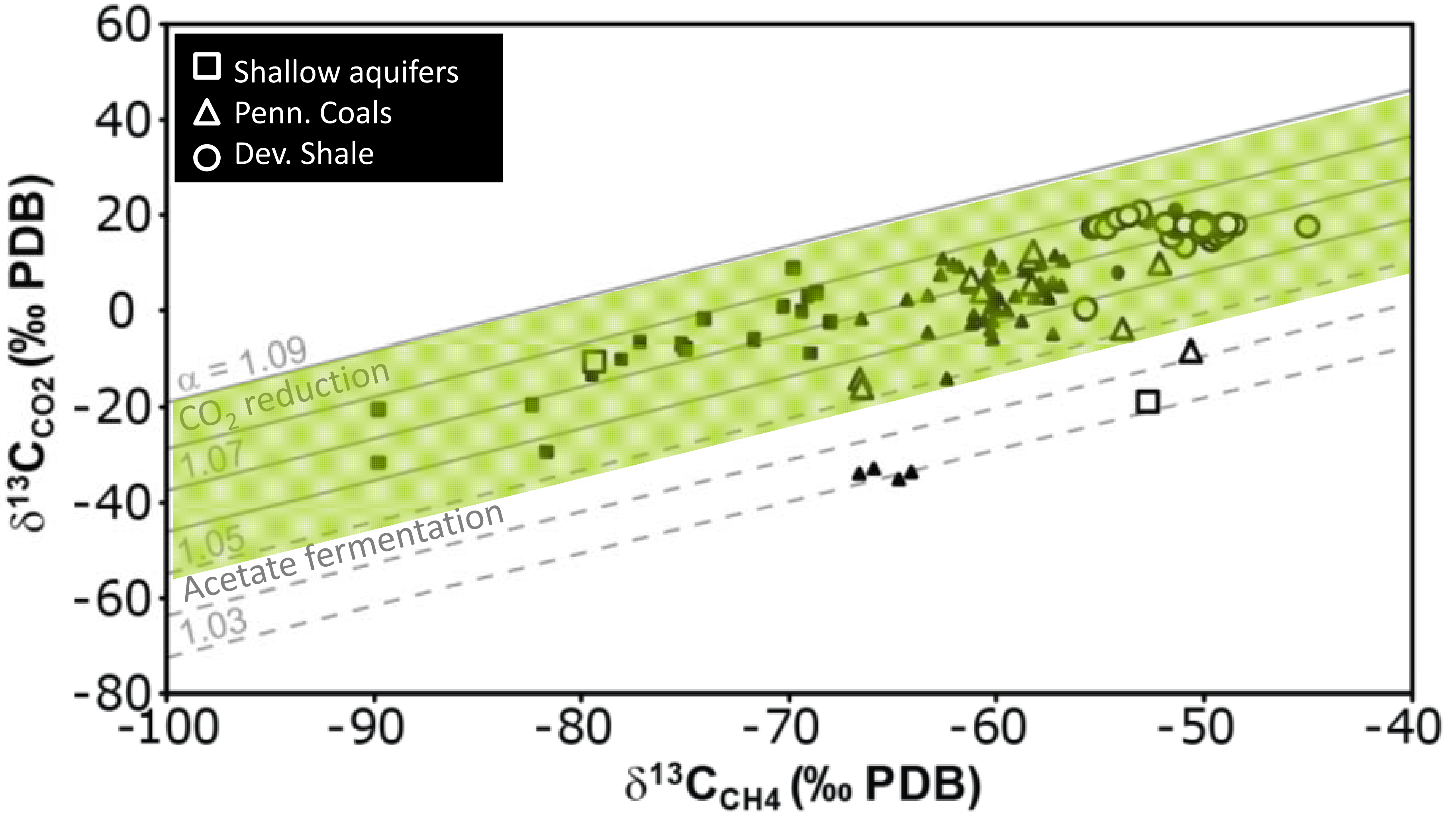
Fingerprint of natural gases



✓*In general, 3 organic-rich units have different gas compositions (C_1/C_2+C_3) and δ^{13}C-CH_4 values.*

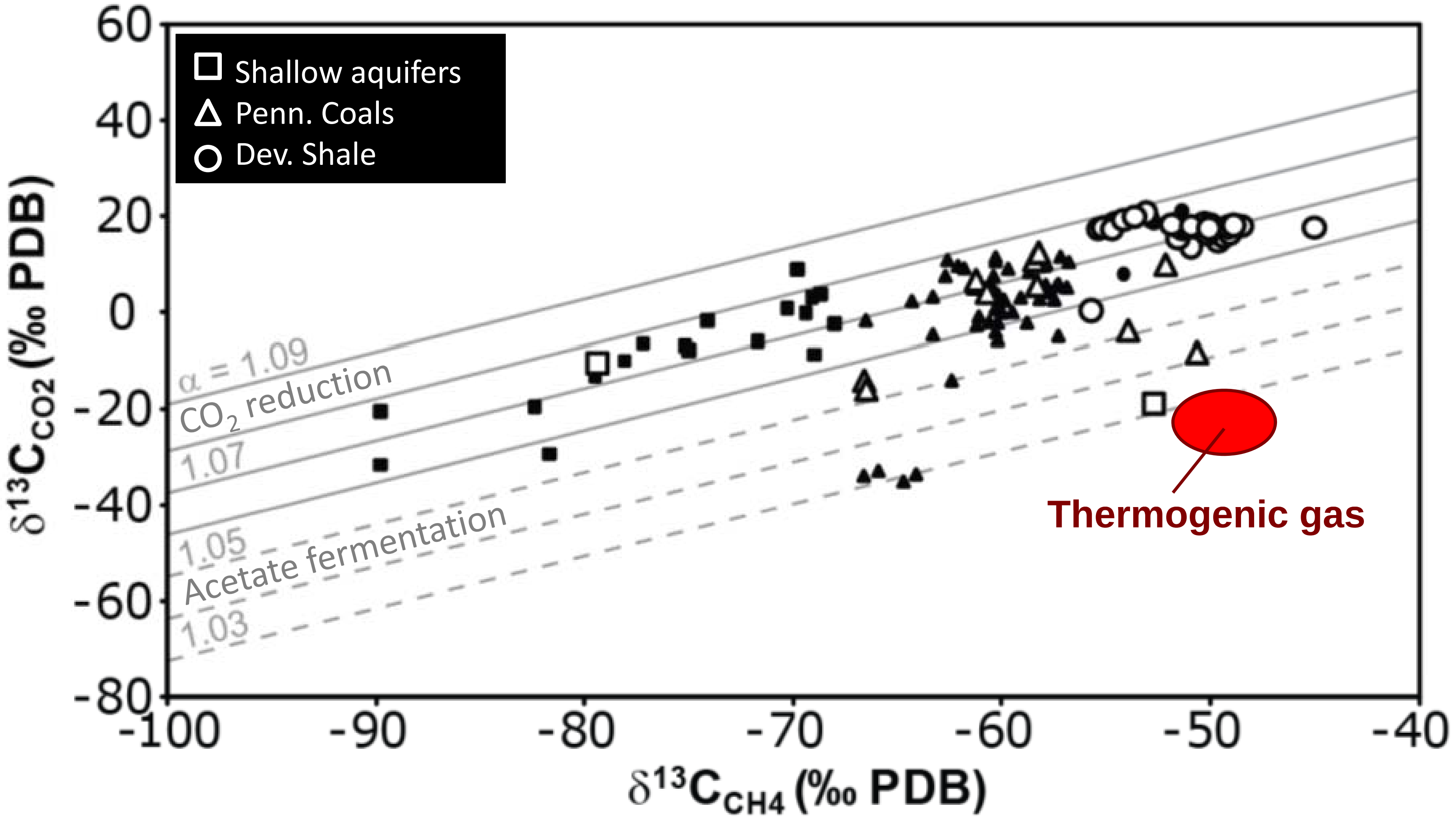
✓*Cannot distinguish thermogenic from microbial CH_4 in Dev. Shales using carbon isotopes alone.*

Differences in C isotopes of gas



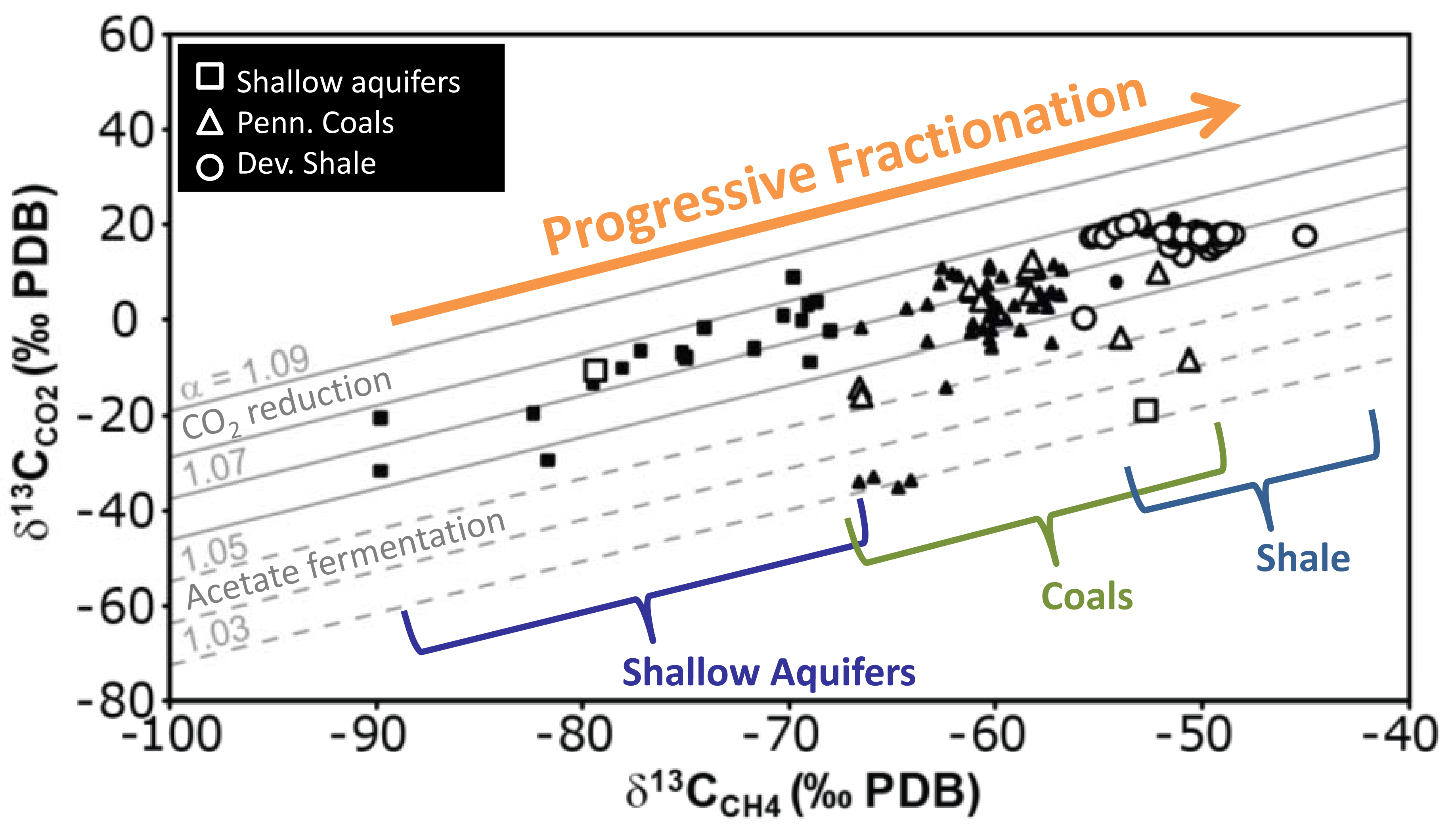
✓Microbial methane from shallow glacial drift, coalbeds and fractured shales all plot along carbon isotope fractionation line of ~1.05 to 1.09, except for a few coal samples influenced by methane oxidation/sulfate reduction (Strapoc et al., 2008), and one outlier glacial drift sample.

Differences in C isotopes of gas



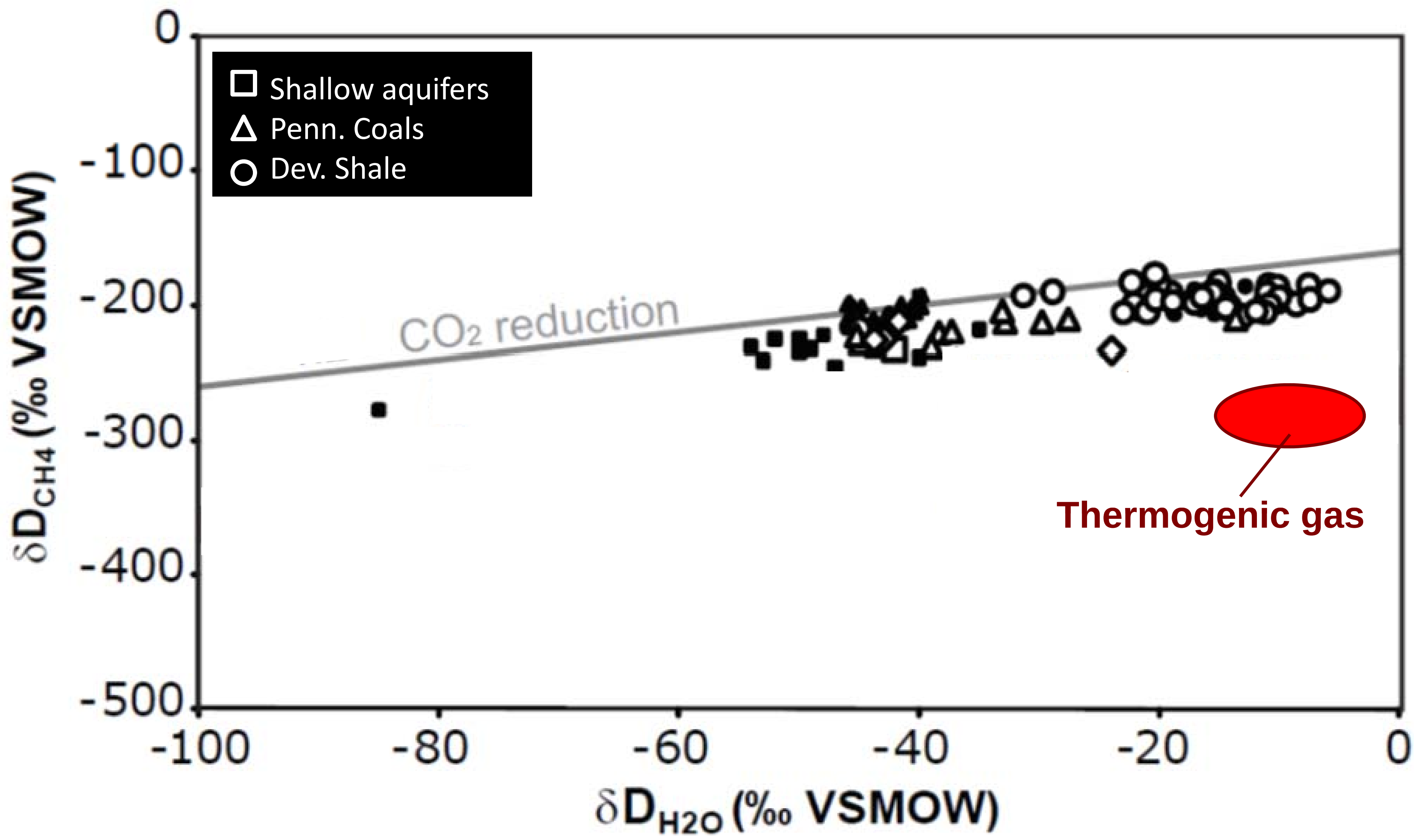
- ✓ *Thermogenic gas in Penn. coalbeds is distinct from microbial gas, with lower* δ^{13}*C-CO*$_2$ *and higher* δ^{13}*C-CH*$_4$ *values.*
- ✓ *Thermogenic gas in the Dev. fractured shales contains very little CO*$_2$ *(<0.1 mole%) - not shown.*

Differences in C isotopes of gas



- ✓*Microbial CH_4 from shallow aquifers, coalbeds, and fractured shales have distinct δ^{13}C-CH_4 values, which corresponds to increasing fractionation of CO_2 reservoir during CO_2 reduction.*
- ✓*C isotopes of CH_4 and CO_2 may be used to distinguish sources of methane.*

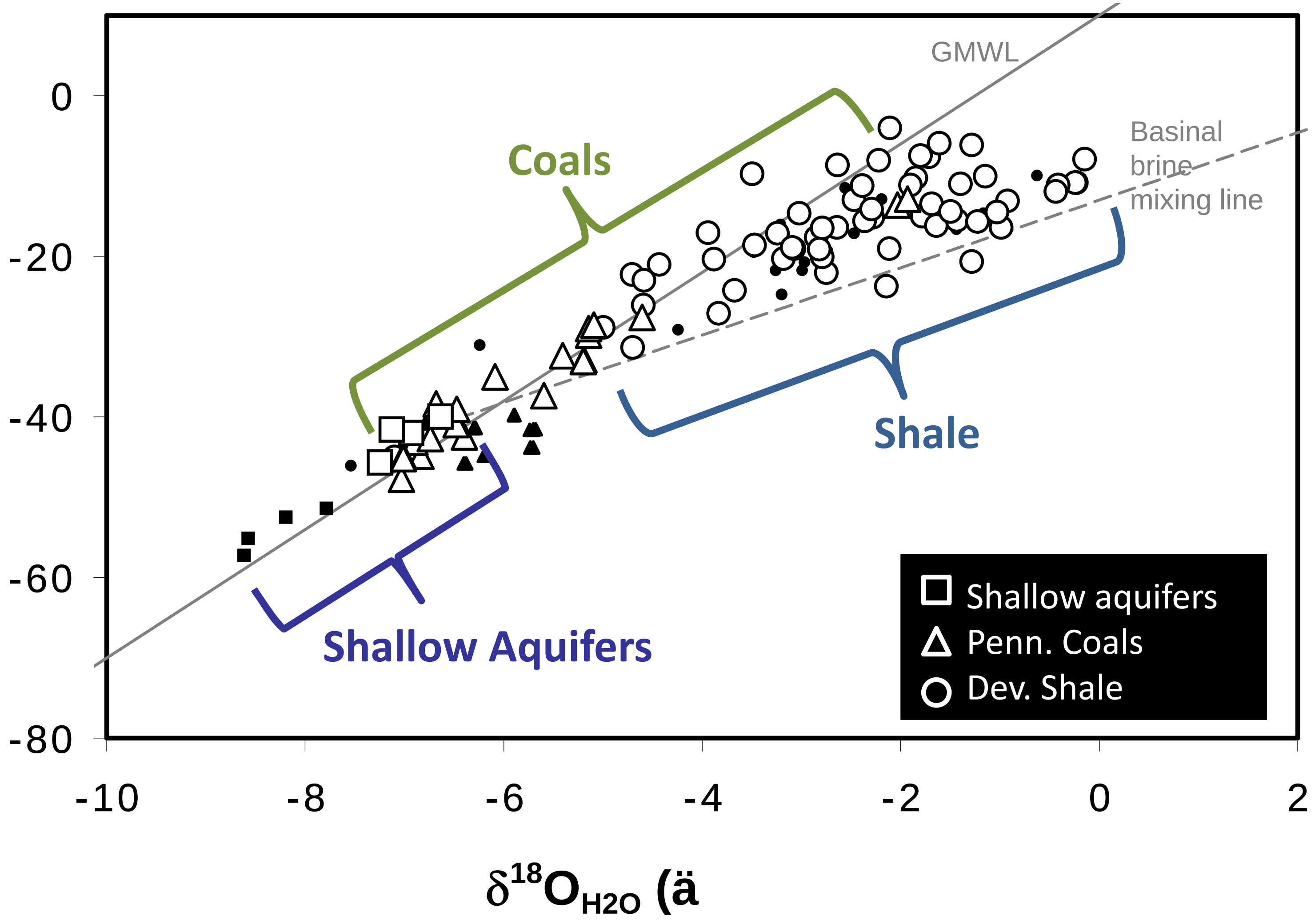
Differences in H isotopes of gas/water



✓ δD-CH_4 not useful in distinguishing gas sources; Microbial CH_4 from shallow aquifers, coalbeds, and fractured shales have similar δD-CH_4 values.

✓ Major difference is in H isotope values of formation waters - related to meteoric water/brine mixing

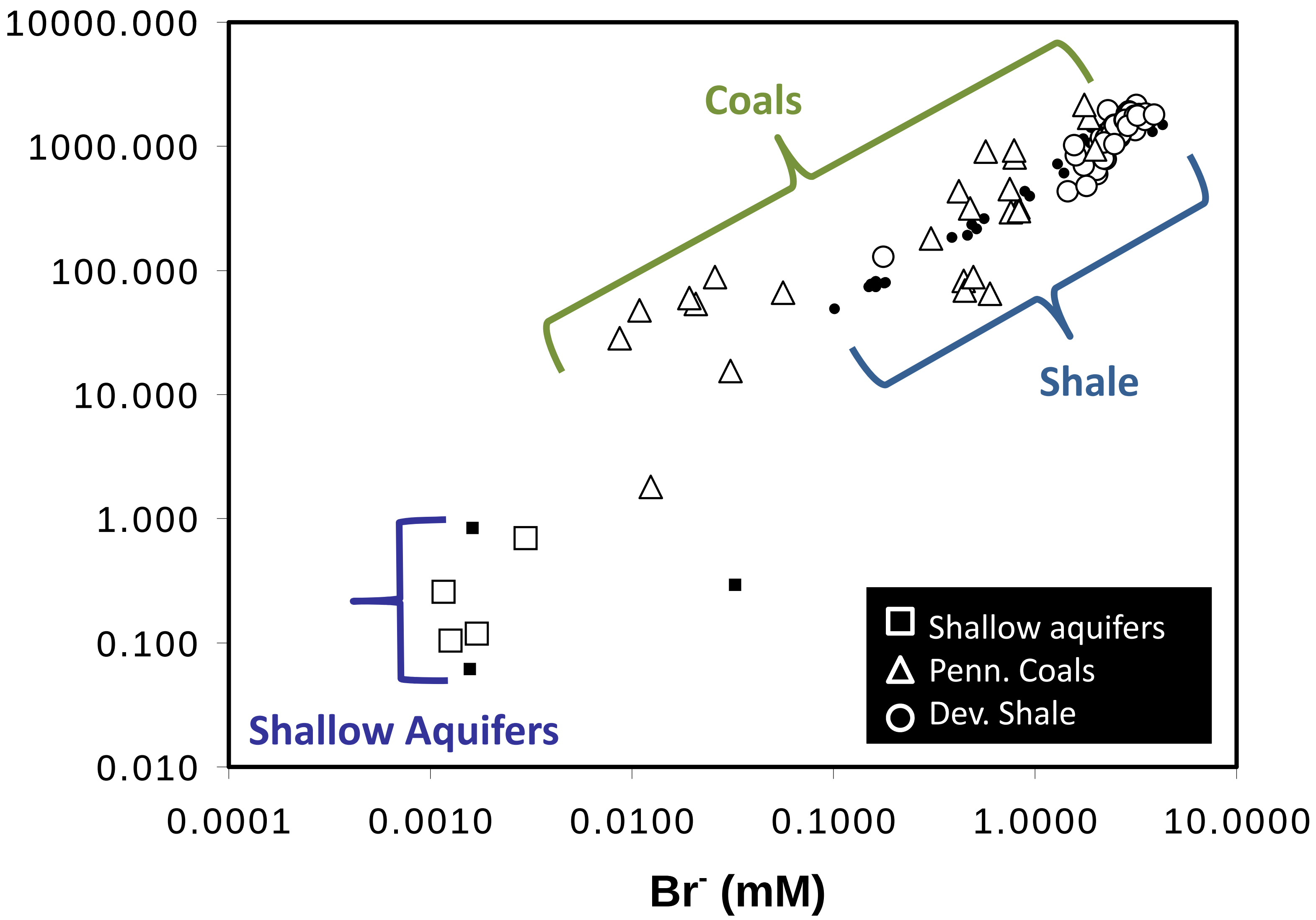
Fingerprint of formation waters



✓*In general, formation waters associated with fractured shales are more enriched in ^{18}O and ^{2}H than shallow (drinking water) aquifers*

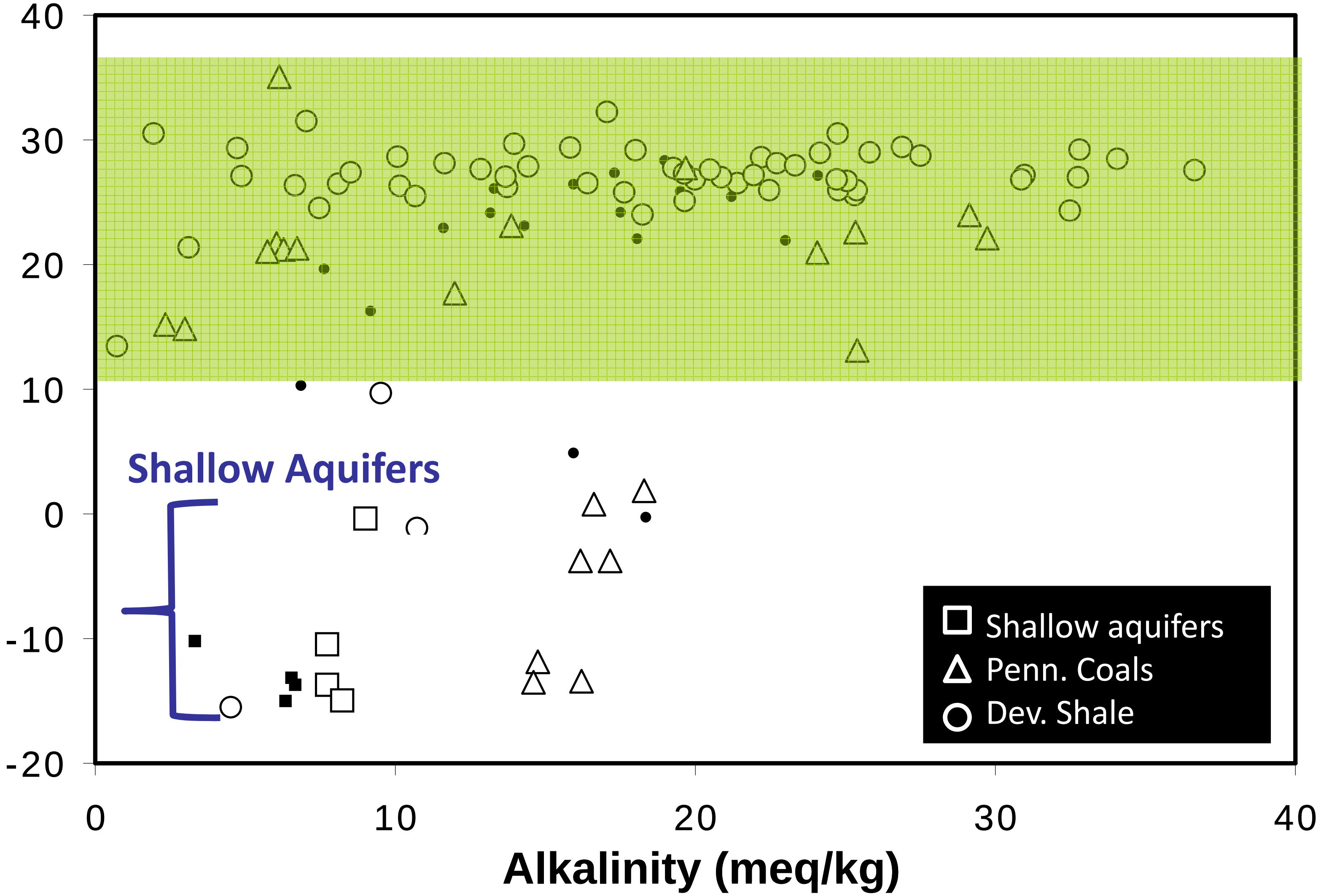
✓*Isotopic composition of coal waters overlap fractured shales and shallow aquifers*

Salinity differences in fluids



✓Formation waters associated with natural gas in coalbeds and fractured shales are enriched in Cl and Br (and other solutes) relative to shallow (drinking water) aquifers

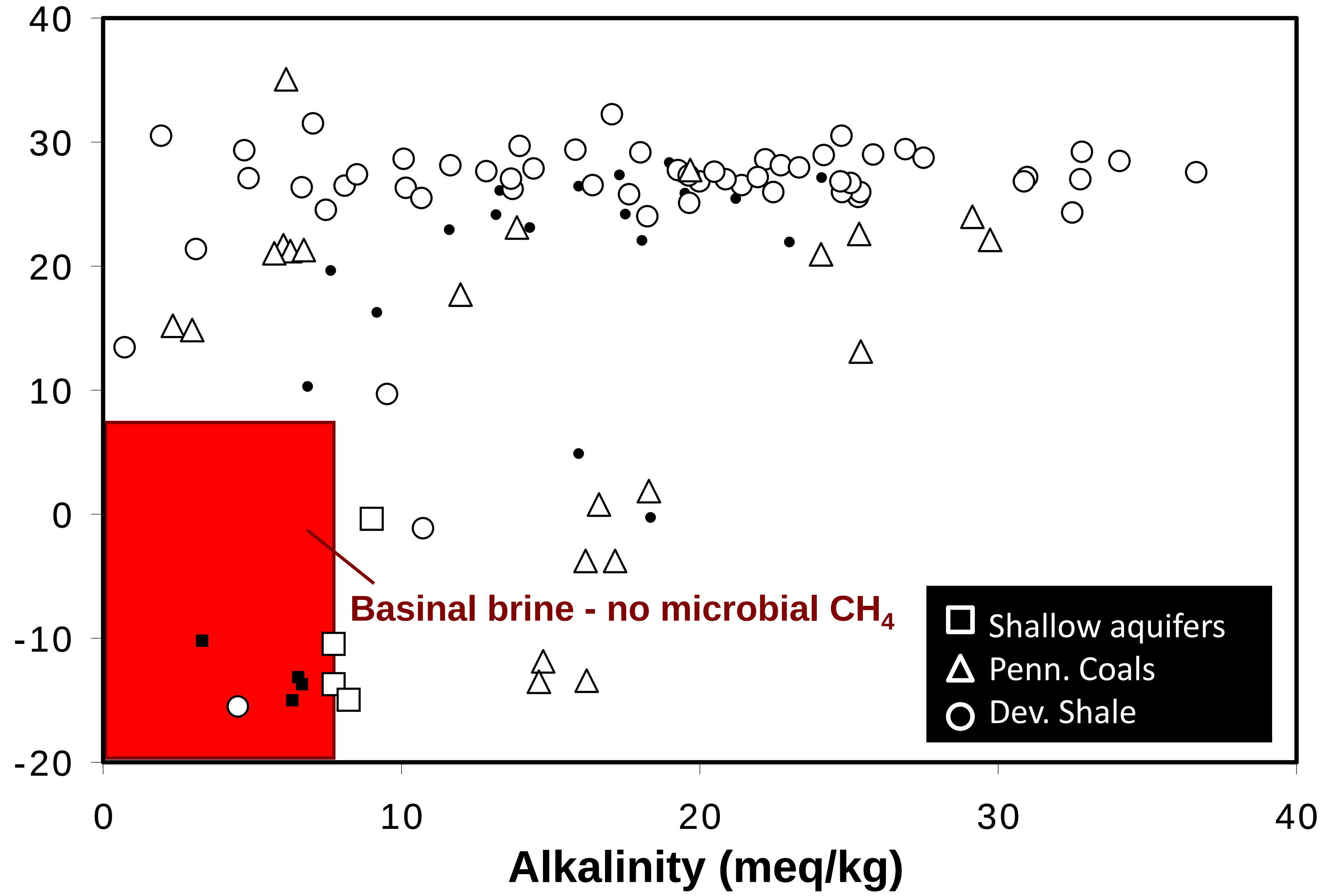
Fingerprint of formation waters



✓*Formation waters associated with microbial CH_4 in shales or coalbeds typically have high δ^{13}C-DIC values (>10 per mil), and variable alkalinities (<5 to 37 meq/kg)*

✓*Shallow aquifers have alkalinities <10 meq/kg, and low δ^{13}C-DIC values (<0 per mil)*

Fingerprint of formation waters

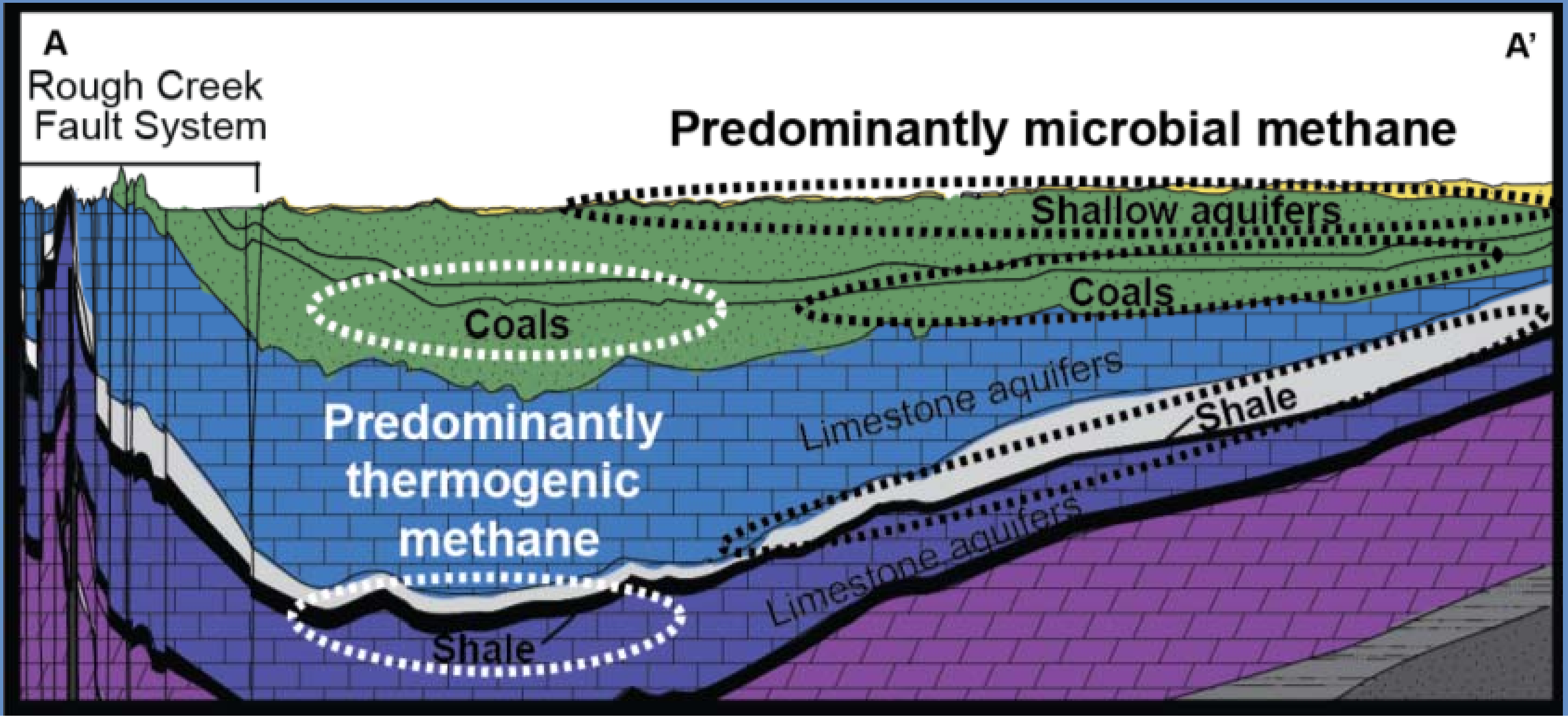


✓Basinal brines not associated with microbial methane have low alkalinities (<8 meq/kg) and low δ^{13}C-DIC values (most near 0 per mil)

Summary

✓*Natural gas (microbial & thermogenic) from shales and coalbeds can be distinguished from microbial methane in glacial drift aquifers based on gas composition and $\delta^{13}C$ values of CH_4 and CO_2.*

✓*Formation waters from Dev. fractured shales can be distinguished from shallow glacial drift aquifers using major ion chemistry (Cl, Br, other solutes) and stable isotopes (^{18}O,^{2}H,^{13}C).*



For more information

Schlegel, M.E., McIntosh, J.C., Bates, B., Kirk, M., Martini, A.M. (*in press, 2011*) Comparison of fluid geochemistry and microbiology of multiple organic-rich reservoirs in a sedimentary basin: evidence for controls on methanogenesis and microbial transport. *Geochimica et Cosmochimica Acta*.

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Chemical and Isotopic Tracers of Natural Gas and Formation Waters in Fractured Shales

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Introduction

Fingerprinting the chemical and isotopic composition of formation waters and natural gas associated with organic-rich shales is critical for evaluating potential environmental impacts of hydraulic fracturing for gas production. This paper summarizes recent results from Schlegel et al. (in press) comparing the chemical and isotopic composition of formation waters and natural gas in an organic-rich shale (Devonian New Albany Shale) in the Illinois Basin to other gas accumulations in overlying Pennsylvanian coalbeds and shallow glacial drift aquifers (Figure 3) to determine the best analytical tools for distinguishing gas and fluid sources. Previous data are included from Coleman et al. (1988), Strąpoć et al. (2007), and McIntosh et al. (2002).

Geologic Background

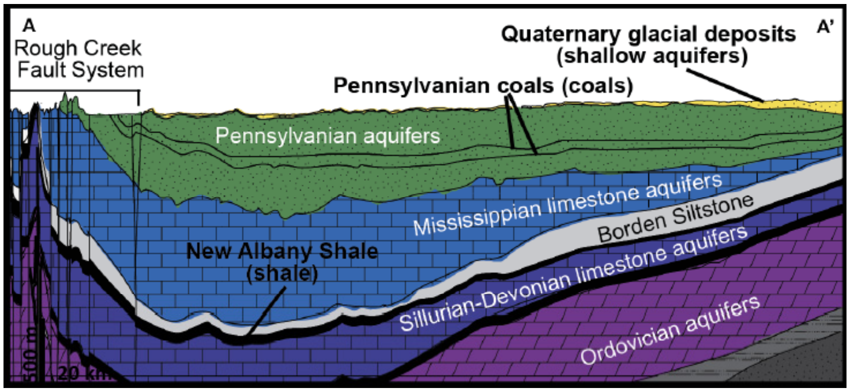

Figure 3. Cross-section of Illinois Basin from Schlegel et al. (in press)

The New Albany Shale is an organic-rich (black) shale along the eastern margin of the Illinois Basin and grades into a grey-green shale along the western margin (Barrows and Cluff, 1984; Hassenmueller, 1993). The shale contains predominantly type-II kerogen (sapropelic-marine), with up to 16 wt% total organic carbon (TOC) and has low thermal maturity (R_o <0.6%; e.g. Barrows and Cluff, 1984) except in the south near the Shawneetown-Rough Creek fault system where the shale reaches R_o values >1% (Fig. 3b; Cluff and Byrnes, 1991). Previous studies have shown that the shale contains both microbial and thermogenic gas. Thermogenic gas is distributed throughout the basin, while microbial gas is predominantly located along the northeastern and eastern margins of the basin where meteoric water infiltration likely stimulated microbial methanogenesis by decreasing formation water salinity and transporting in near-surface microbial communities into paleo-pasteurized sediments (McIntosh et al., 2002; Schlegel et al., in press). New Albany Shale wells in areas of predominantly microbial methane typically contain copious amounts of formation waters, which must be removed for gas production.

Pennsylvanian coalbeds are composed of type-III kerogen (typical of terrestrial organic matter; Hatch et al., 1991), and have low thermal maturity (R_o <0.6%) except in the south where tectonic activity locally increased the geothermal gradient and produced higher coal maturity (R_o ~0.7 to 0.8%; Fig. 3a; Drobniak et al., 2004; Hower et al., 2005). Pennsylvanian coals contain thermogenic gas in the central and southern basin with little to no co-produced formation waters. The coals contain microbial gas, associated with variable salinity formation waters, across the northern and northeastern basin margins (Strąpoć et al., 2007).

Glacial drift sediments containing detrital organic matter overlie much of the northern portion of the Illinois Basin; these sediments are up to 120m thick and constitute an aquifer with high quality drinking water (Swann, 1968). The glacial sediments contain up to 17.2 wt% TOC, which is relatively thermally immature (Glessner and Roy, 2009). Many water supply wells screened in glacial drift aquifers contain dissolved methane that is microbial in origin, and sourced from biodegradation of in-situ organic matter and/or in underlying shallow Paleozoic sediments (Coleman et al., 1988).

Chemical and Isotopic Fingerprint of Natural Gas

In general, gas accumulations in the Devonian New Albany Shale, Pennsylvanian coalbeds, and shallow glacial drift aquifers have different hydrocarbon compositions (methane (C_1) to ethane (C_2) and propane (C_3) ratios; Figure 4). Dissolved gas in the shallow aquifers is predominantly comprised of CH_4 with some C_2 (in addition to atmospheric-derived gases, such as N_2 and Ar), and no detectable C_{3+}. Natural gas in the shale has much lower C_1/C_2+C_3 ratios (12-5931), compared to the shallow aquifers ($>10^6$), due to the presence of thermogenic gas in addition to microbial methane. Coals have C_1/C_2+C_3 ratios (188-163,361) that plot roughly between the shallow aquifers and shale.

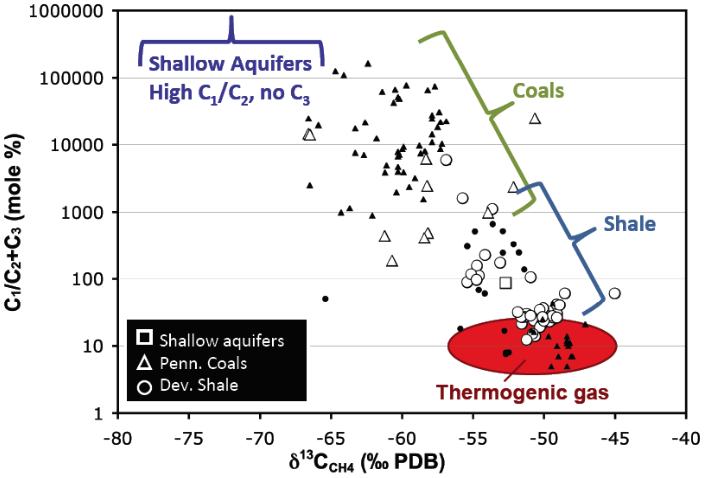

Figure 4. Methane to ethane + propane ratios versus carbon isotopes of methane for various gas

The carbon isotope values of methane accumulations are also distinct between the three organic-rich formations. Shallow aquifers have very low δ^{13}C-CH_4 values (-90 to -68‰), consistent with early stage methanogenesis where the CO_2 reservoir has not been significantly depleted. In contrast, δ^{13}C values of CH_4 from the Devonian shale are much higher (-57 to –45‰) likely due to mixing with isotopically-enriched thermogenic gas, and significant depletion of the CO_2 reservoir during microbial methanogenesis via CO_2 reduction (Schlegel et al., in press). Importantly, microbial CH_4 from the Devonian shales has similar δ^{13}C values to thermogenic CH_4 (-55.9 to –52.7‰), suggesting that carbon isotope of CH_4 alone cannot distinguish mechanisms of shale gas generation. In contrast, δ^{13}C values of thermogenic and microbial CH_4 in the Pennsylvanian coals are distinct (Strąpoć et al., 2007). In addition, δ^{13}C values of microbial CH_4 (-67 to –51‰) in the coals plot between the shallow aquifers and Devonian shale with little overlap (Figure 4).

Microbial methanogenesis produces (and consumes) CO_2 in addition to CH_4, with high δ^{13}C-CO_2 values. Carbon isotope fractionation factors ($\alpha_{CO2\text{-}CH4}$) for methanogenesis via CO_2 reduction typically range from 1.05 to 1.09 (Figure 5), while $\alpha_{CO2\text{-}CH4}$ values for acetate fermentation typically range from 1.03 to 1.05 (Whiticar et al., 1986). The majority of CO_2 and CH_4 from the Devonian shale, Pennsylvanian coals, and shallow aquifers plot along a carbon isotope fractionation line of ~1.05 to 1.09, except for a few coal samples influenced by methane oxidation and sulfate reduction (Strapoc et al., 2007), and one outlier glacial drift sample. Thermogenic gas in the Devonian shale was not analyzed for δ^{13}C-CO_2 as it contains very little CO_2 (<0.1 mole %). Thermogenic gas in the Pennsylvanian coals has much lower δ^{13}C-CO_2 values than microbial gas, within the range of C_3-type organic matter.

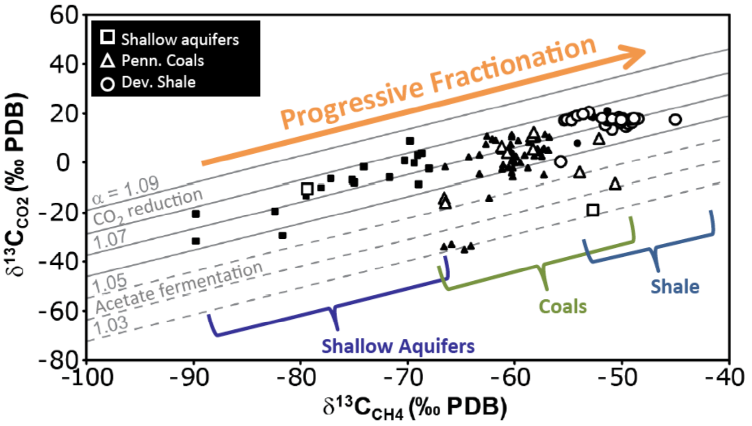

Figure 5. Carbon isotopes of carbon dioxide versus methane for various gas sources

Gas samples show a progression along the carbon isotope fractionation line (Figure 5) from more negative δ^{13}C values of CO_2 and CH_4 in the shallow aquifers to more positive values in the shale, with coal samples plotting in between. This may be due to mixing between a thermogenic and microbial methane source, or the progressive depletion of the carbon (CO_2) reservoir, causing increased $\delta^{13}C_{CO2}$ and $\delta^{13}C_{CH4}$. Mixing between microbial and thermogenic methane would be seen in an increasing trend of $\delta^{13}C_{CH4}$ versus C_{2+}%. Though the $\delta^{13}C_{CH4}$ of microbial and thermogenic methane for the shale have similar ranges (up to -47.1‰) (McIntosh and Martini, 2008), a slight increasing trend is observed in the shale from -53‰ to -47‰ for samples with <2% C_{2+}, however no such correlation is observed for the shallow aquifers or the coals. These trends suggest that though some thermogenic methane is mixing with microbial methane, the overall progression of carbon isotopes along the fractionation line may be due to the progressive depletion of the carbon (CO_2) reservoir under closed system conditions (Jones et al., 2008).

Together, the δ^{13}C values of CO_2 and CH_4, in combination with gas composition (including mole % CO_2, CH_4, C_2, C_{3+}), clearly distinguish microbial and thermogenic gas from the Devonian shale, Pennsylvanian coals, and shallow aquifers.

Chemical and Isotopic Fingerprint of Formation Waters

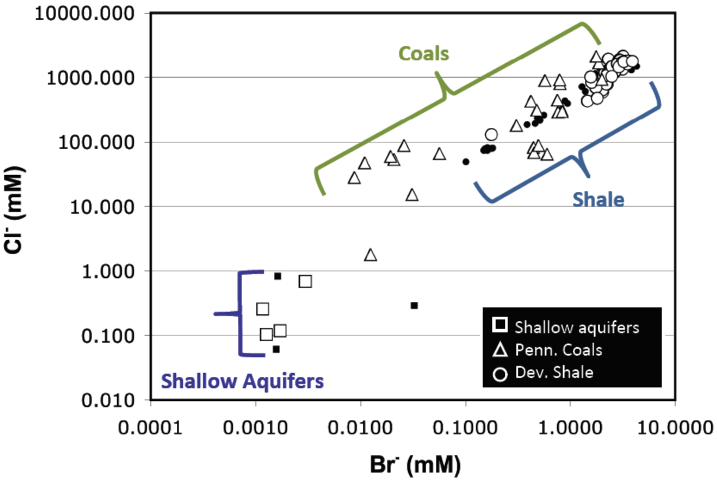

Figure 6. Chloride vs. bromide concentrations (log-scale) of formation waters associated with various gas sources

Formation waters associated with natural gas in coalbeds and fractured shales in the Illinois Basin are enriched in Cl and Br (>1.8 mM and >8.7 µM, respectively), as well as other solutes, relative to shallow aquifers (Figure 6). These saline fluids are likely remnant Paleozoic brines sourced from evaporation of seawater, which have been subsequently diluted by meteoric recharge and modified by water-rock-microbial reactions (McIntosh et al., 2002). In contrast, shallow aquifers contain dilute (Cl <0.8 mM), recently recharged meteoric waters (McIntosh and Walter, 2006).

Groundwaters from shallow aquifers have δ^{18}O and δD values, which plot along the global meteoric water line (GMWL) (-8.6 to –6.6‰, and –57 to –40‰, respectively; Figure 7). Saline fluids in the Devonian shale are more enriched in ^{18}O and ^{2}H (-7.5 to –0.14‰, and –46 to –8‰, respectively) than shallow aquifers, and plot to the right of the GMWL, along a mixing line between Illinois Basin brines and meteoric water. Stable isotopes of water may be useful for distinguishing between fluids sourced from the Devonian shale versus shallow aquifers. Formation waters in Pennsylvanian coals have δ^{18}O and δD values (-7.0 to –1.9‰, and –48 to –13‰, respectively) that overlap the shallow aquifers and Devonian shale, making it difficult to distinguish between water sourced from the coal versus water from the shale or shallow aquifers.

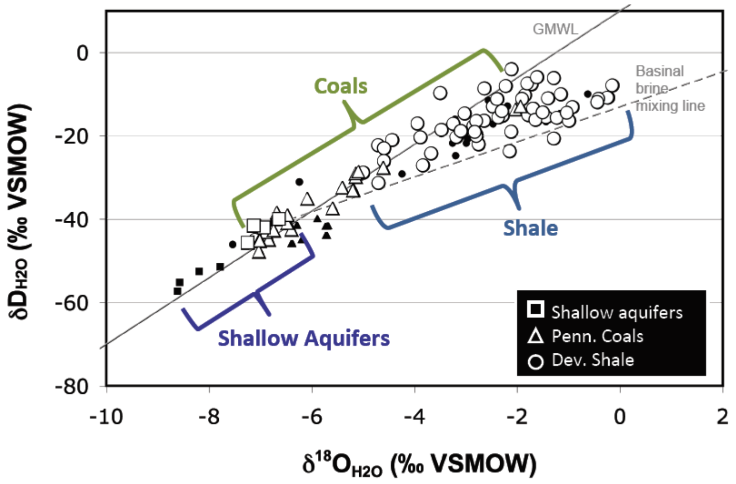

Figure 7. Stable isotopes of formation waters associated with natural gas accumulations

Alkalinity concentrations and carbon stable isotopes provide an additional tracer of fluid sources. Formation waters associated with microbial methanogenesis in the Devonian shale and Pennsylvanian coals typically have high δ^{13}C values of dissolved inorganic carbon (DIC; >10‰), and variable alkalinities (<5 to 37 meq/kg). Shallow aquifers have lower alkalinities (<10 meq/kg), and low δ^{13}C-DIC values (<0‰). Formation waters associated with thermogenic gas in the Devonian shale have low alkalinities (up to 2.4 meq/kg), and low δ^{13}C-DIC values (most near 0‰) (McIntosh et al, 2002).

In short, formation waters sourced from the Devonian shale are saline (with high Cl, Br, and other solute concentrations), enriched in ^{18}O and ^{2}H, and have high δ^{13}C-DIC and alkalinity values, compared to dilute meteoric waters in shallow aquifers. Formation waters from Pennsylvanian coals have similar solute concentrations (Cl, Br, alkalinity) and δ^{13}C-DIC values as Devonian shale fluids. In addition, their δ^{18}O and δD values overlap the Devonian shale and shallow aquifer samples, suggesting that it may be difficult to distinguish fluids sourced from Pennsylvanian coals versus fluids sourced from the Devonian shale.

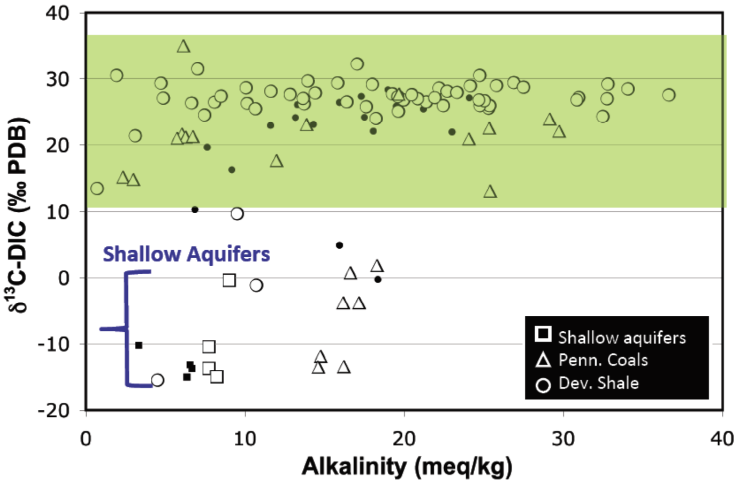

Figure 8. Carbon isotopes of dissolved inorganic carbon (DIC) versus alkalinity concentrations of formation waters associated with natural gas accumulations

Summary

Natural gas (microbial and thermogenic) from the Devonian shale and Pennsylvanian coals can be distinguished from microbial methane sourced from shallow glacial drift aquifers based on gas composition and δ^{13}C values of CH_4 and CO_2. Formation waters from the Devonian shale can be distinguished from dilute groundwater in shallow aquifers using major ion chemistry (Cl, Br, other solutes) and stable isotopes (^{18}O, ^{2}H, ^{13}C). It may not be possible to distinguish between formation waters sourced from Pennsylvanian coals versus the Devonian shale based on major ion chemistry and stable isotope compositions alone. These results are important for evaluation of potential environmental impacts of hydraulic fracturing of shales, such as the migration of brines and natural gas into shallow drinking water resources.

Acknowledgements

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