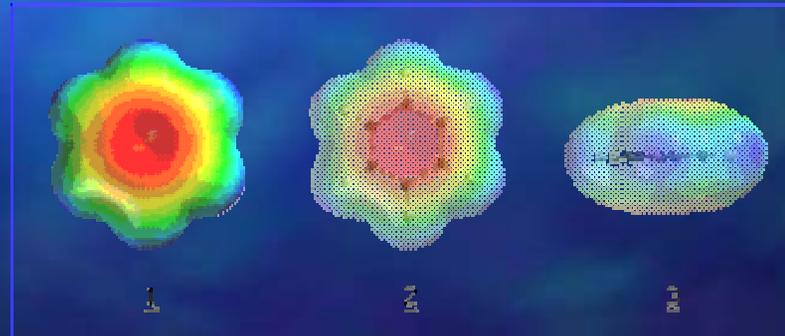


GEOCHEMISTRY OF TRENTON/BLACK RIVER GASES IN THE APPALACHIAN BASIN

A PRELIMINARY REPORT



ACKNOWLEDGEMENTS

- **COMPANIES**

- Isotech Laboratories
- Triana Energy and CNR
- Fortuna Energy Inc.
- Hay Exploration
- K Petroleum
- CGAS Exploration/Enervest

- *Colleagues*

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- Jeff Bowers (Fortuna)
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- Bill Grubaugh (Enervest)
- Katharine Lee Avery (WVGS)
- Dave Harris (KGS)
- Larry Wickstrom (OGS)
- Dennis Coleman and Martin Schoell (Isotech)

OUTLINE

- **Utility of isotope geochemistry in natural gas exploration and development**
- **Purpose of Trenton/Black River natural gas study**
- **Natural gas sample distribution**
- **Results to date**
- **Preliminary conclusions and future work**



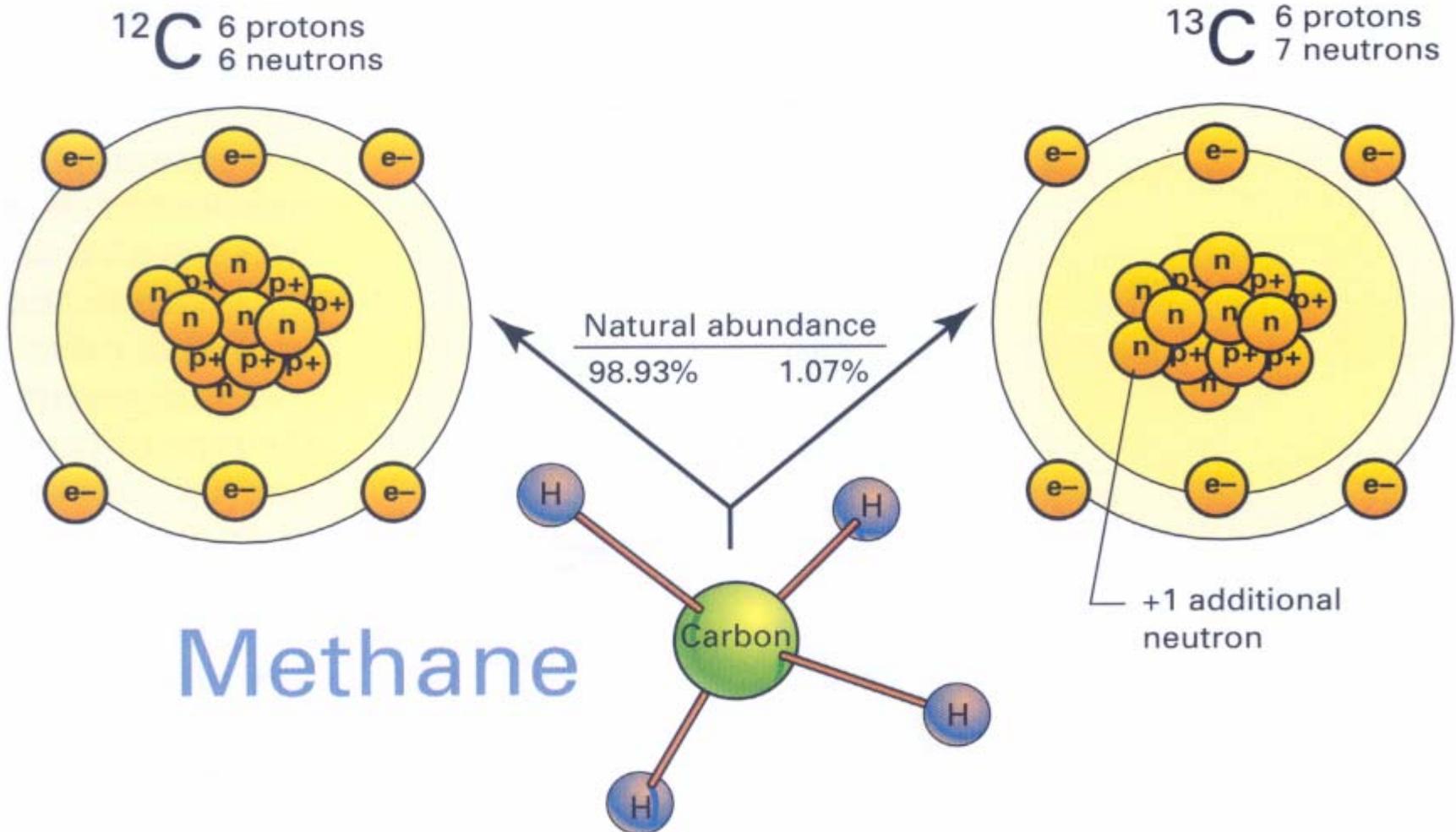
UTILITY OF ISOTOPE GEOCHEMISTRY IN NATURAL GAS EXPLORATION AND DEVELOPMENT

- **Genetic Information**
- **Recognize and Quantify Gas Mixing**
- **Reservoir Identification**
- **Fault Block Mapping**

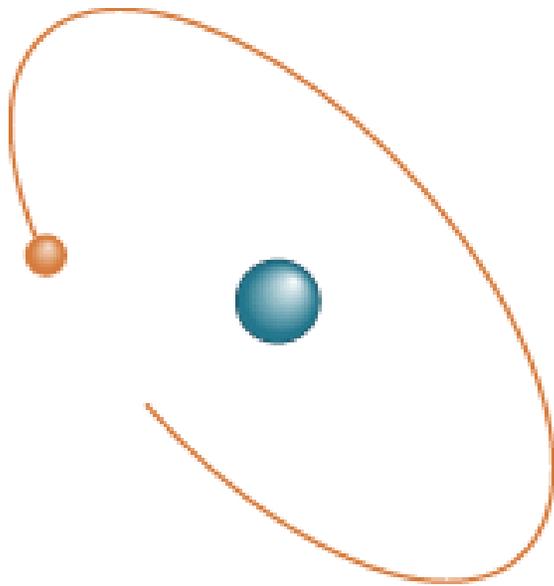
GENETIC INFORMATION

TWO STABLE ISOTOPES OF CARBON

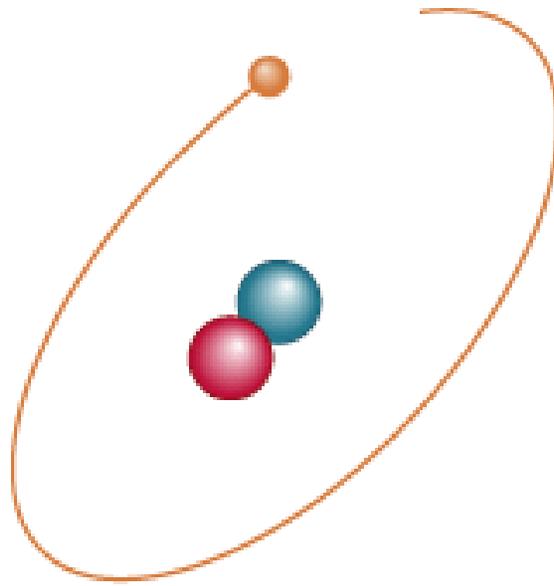
Fig. 4



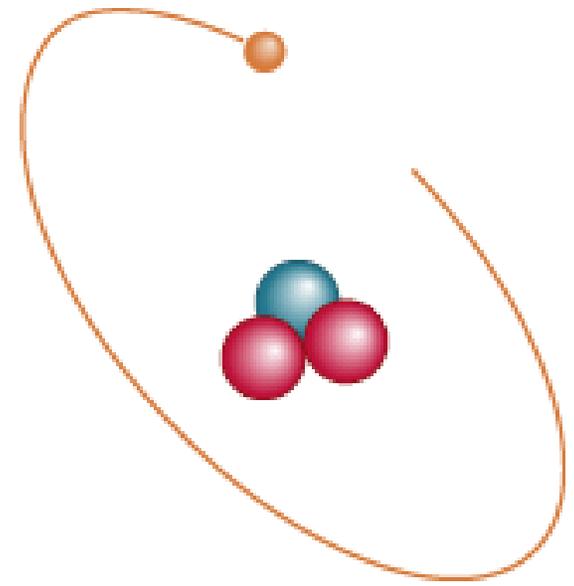
GENETIC INFORMATION



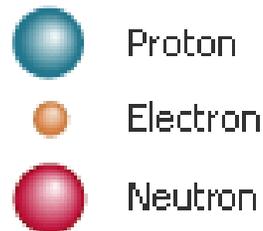
Protium



Deuterium

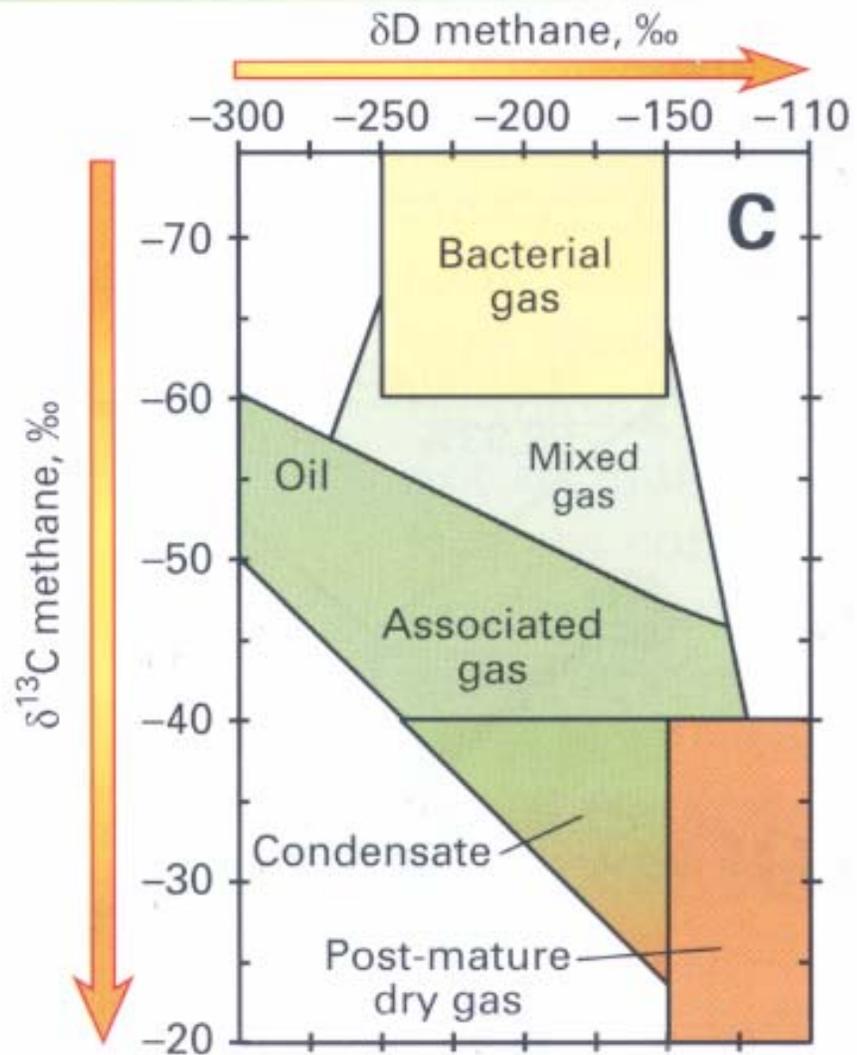
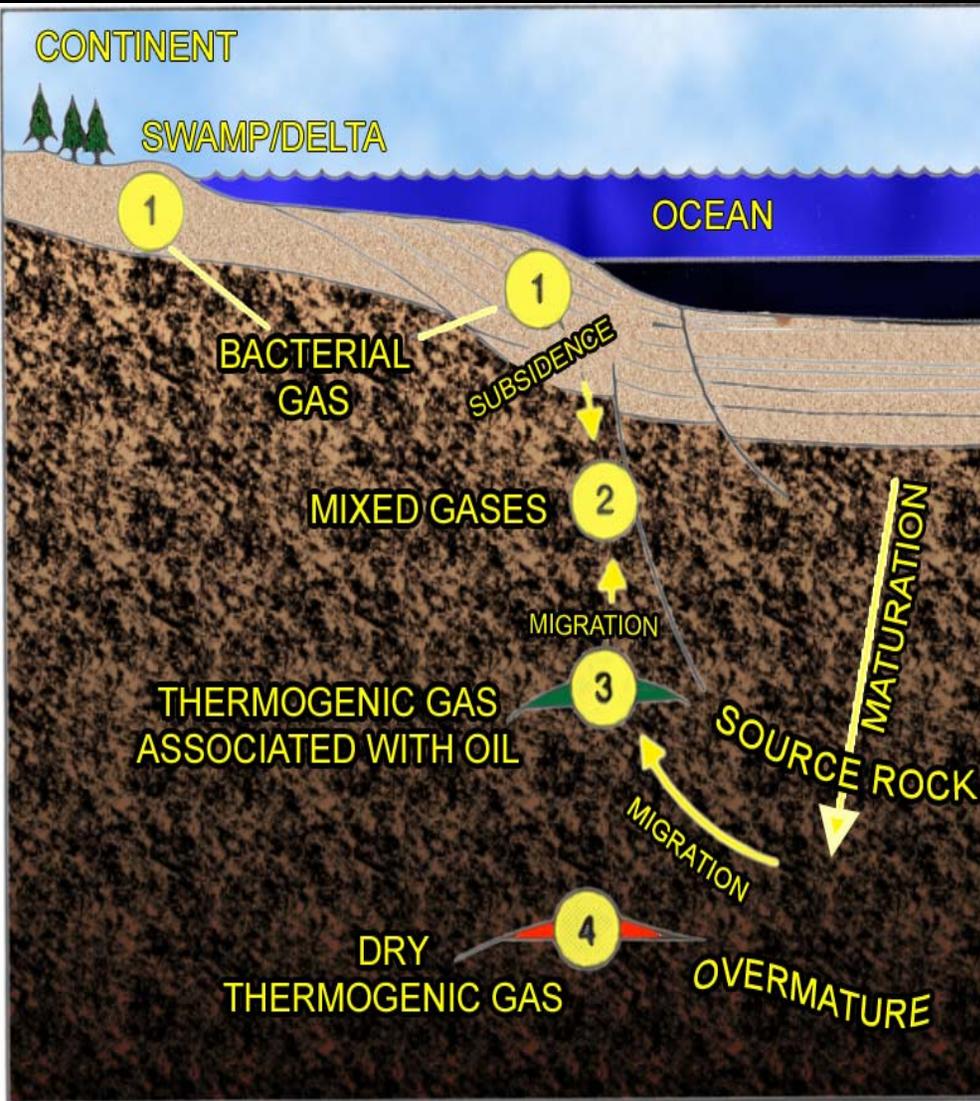


Tritium



Hydrogen

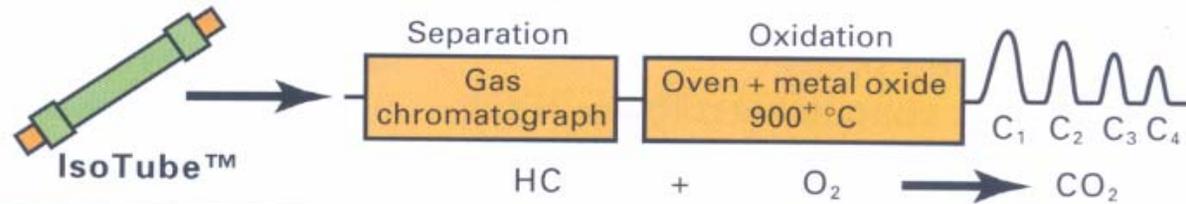
GENETIC INFORMATION



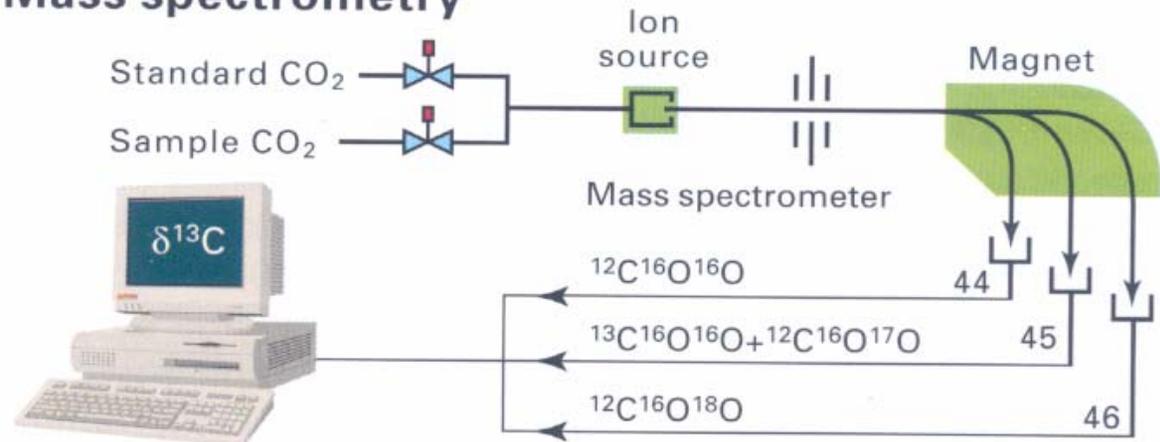
GENETIC INFORMATION



Chromatography and combustion



Mass spectrometry



UTILITY OF ISOTOPE GEOCHEMISTRY IN NATURAL GAS EXPLORATION AND DEVELOPMENT

Natural gases vary in chemical and isotope composition as a function of their formation and migration history.

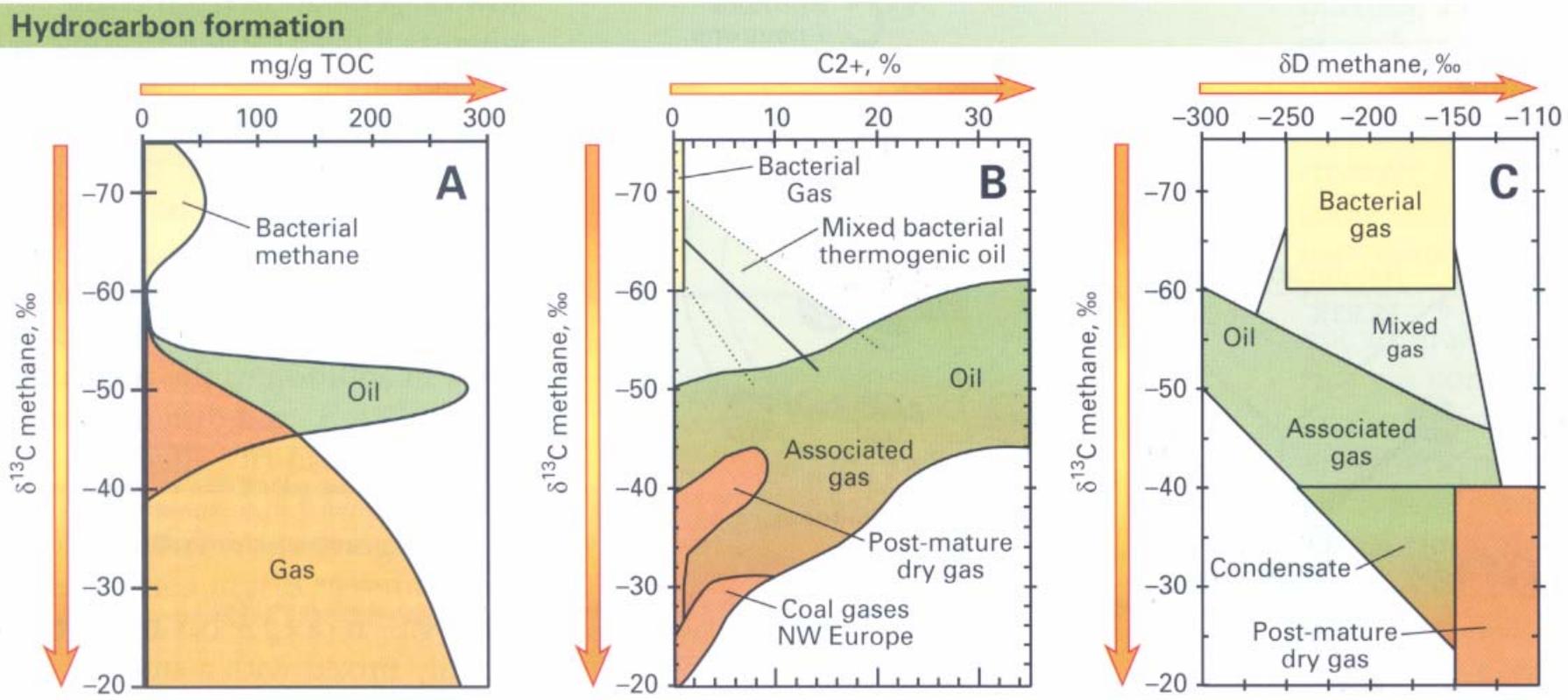
Individual gas components (CH_4 , C_2H_6 , etc.) can be characterized by their stable carbon ($^{13}\text{C}/^{12}\text{C}$) and hydrogen ($^2\text{H}/^1\text{H}$) isotopic compositions

$$\delta^{13}\text{C} \text{ (permil)} = \left[\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{sample}} / \left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{PDB}} - 1 \right] 1000$$

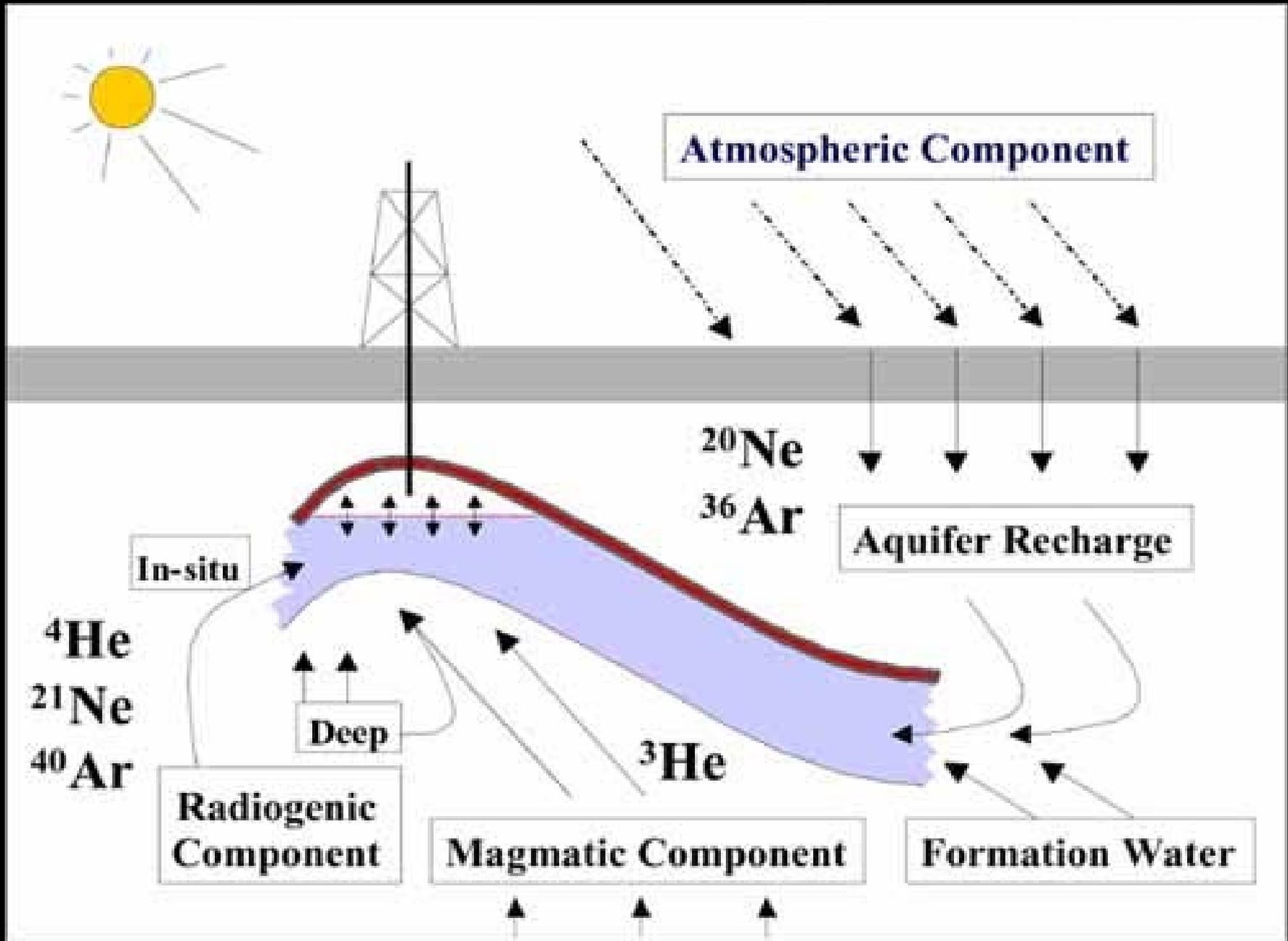
$$\delta \text{D} \text{ (permil)} = \left[\left(\frac{\text{D}}{\text{H}} \right)_{\text{sample}} / \left(\frac{\text{D}}{\text{H}} \right)_{\text{SMOW}} - 1 \right] 1000$$

GENETIC CHARACTERIZATION OF GASES

Fig. 5

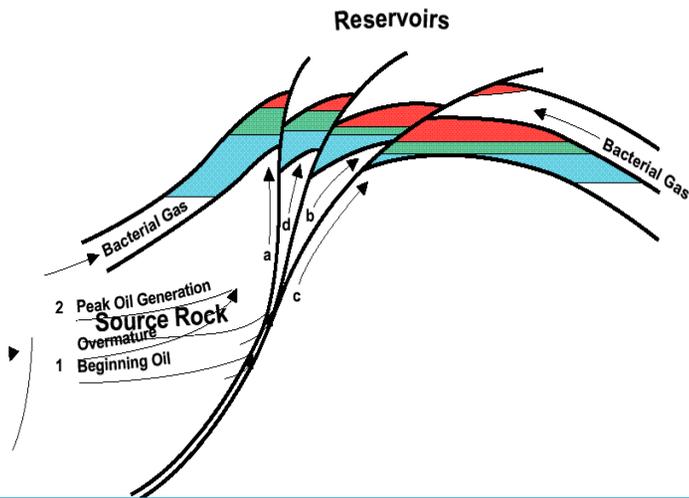


GENETIC INFORMATION

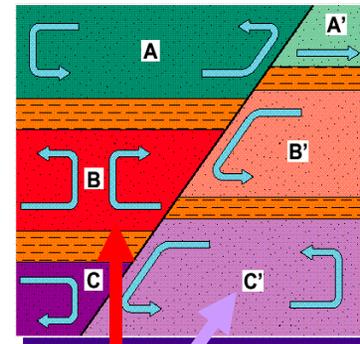


RESERVOIR COMPARTMENTALIZATION AND FAULT BLOCK MAPPING

Concept of Episodic Migration of Oil and Gas
and Multiple Filling of Reservoirs

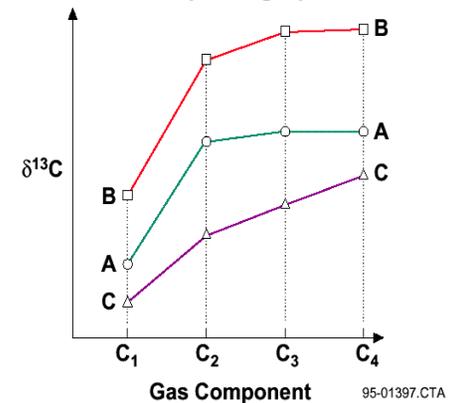


Reservoir Compartmentalization Principle



Flow Units

Gas Isotope Fingerprints



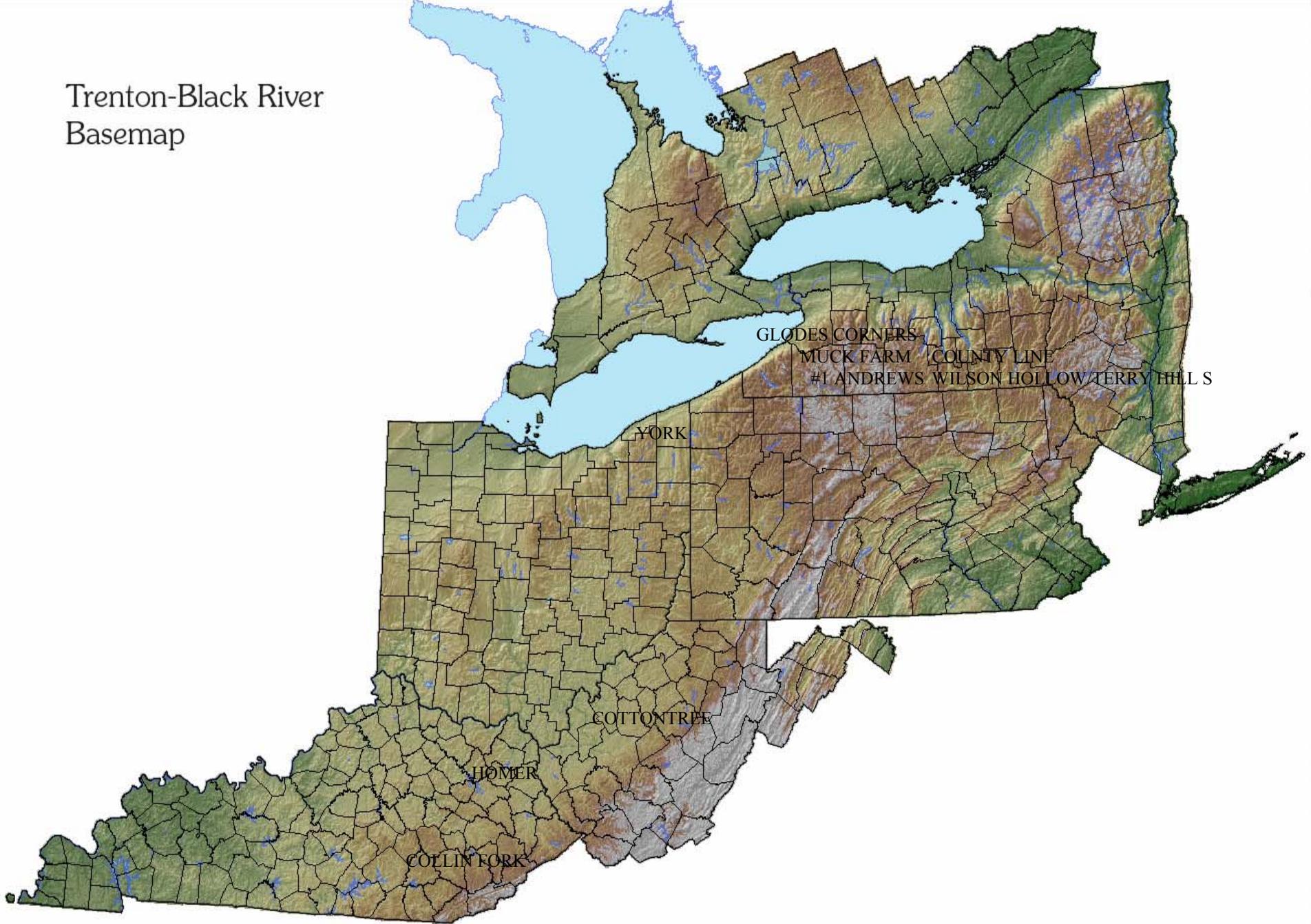
Geochemical
Flow Unit
Definition

Schoell, 2003 personal
communication

PURPOSE OF TRENTON/BLACK RIVER NATURAL GASES STUDY

- Source Rock and Thermal Maturation Data
- Recognize and Quantify Gas Mixing
- Recognize Reservoir Compartmentalization
- Fault Block Mapping

Trenton-Black River
Basemap



Natural Gas Sample Distribution

- Glodes Corners Field, Steuben Co., NY: 5 samples
- Muck Farm Field, Steuben Co., NY: 1 sample
- Wilson Hollow Field, Steuben and Chemung Co., NY: 1 sample
- County Line Field, Chemung Co., NY: 1 sample
- Terry Hill South Field, Chemung Co., NY: 1 sample
- #1 Andrews well, Steuben Co., NY: 1 sample

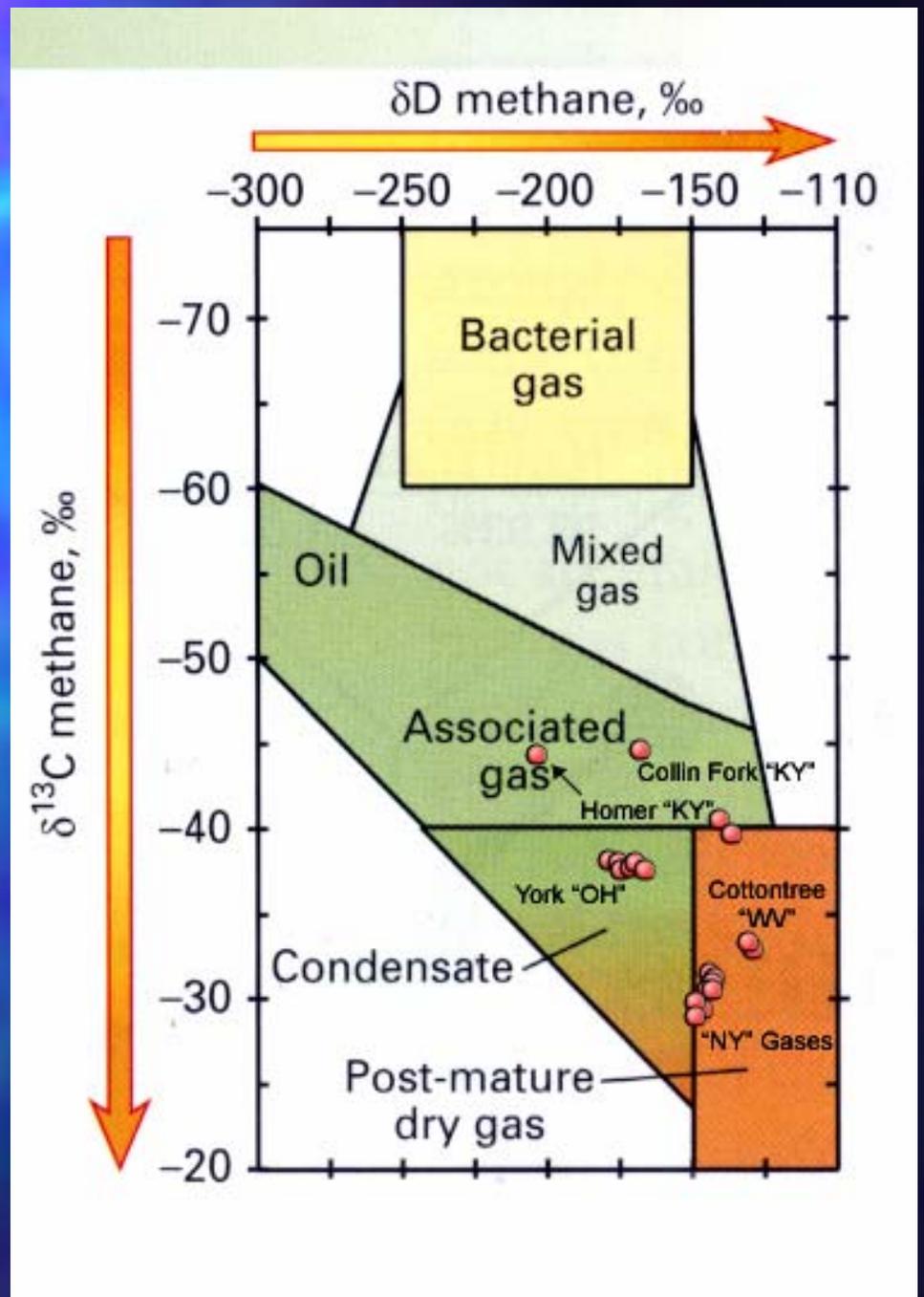


Natural Gas Sample Distribution

- York Field, Ashtabula Co., OH: 6 samples
- Cottontree Field, Roane CO., WV: 2 samples
- Homer Field, Elliott Co., KY: 2 samples
- Clay Co., KY: 1 sample

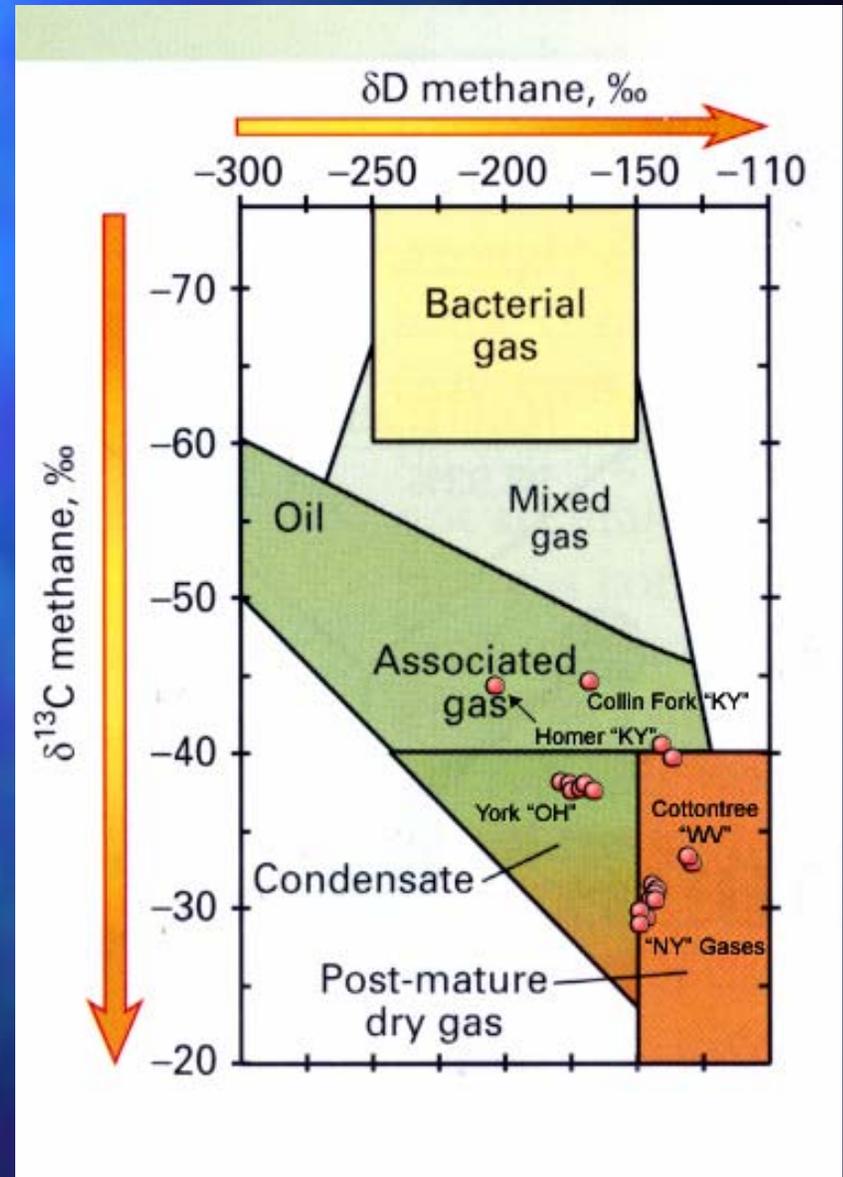


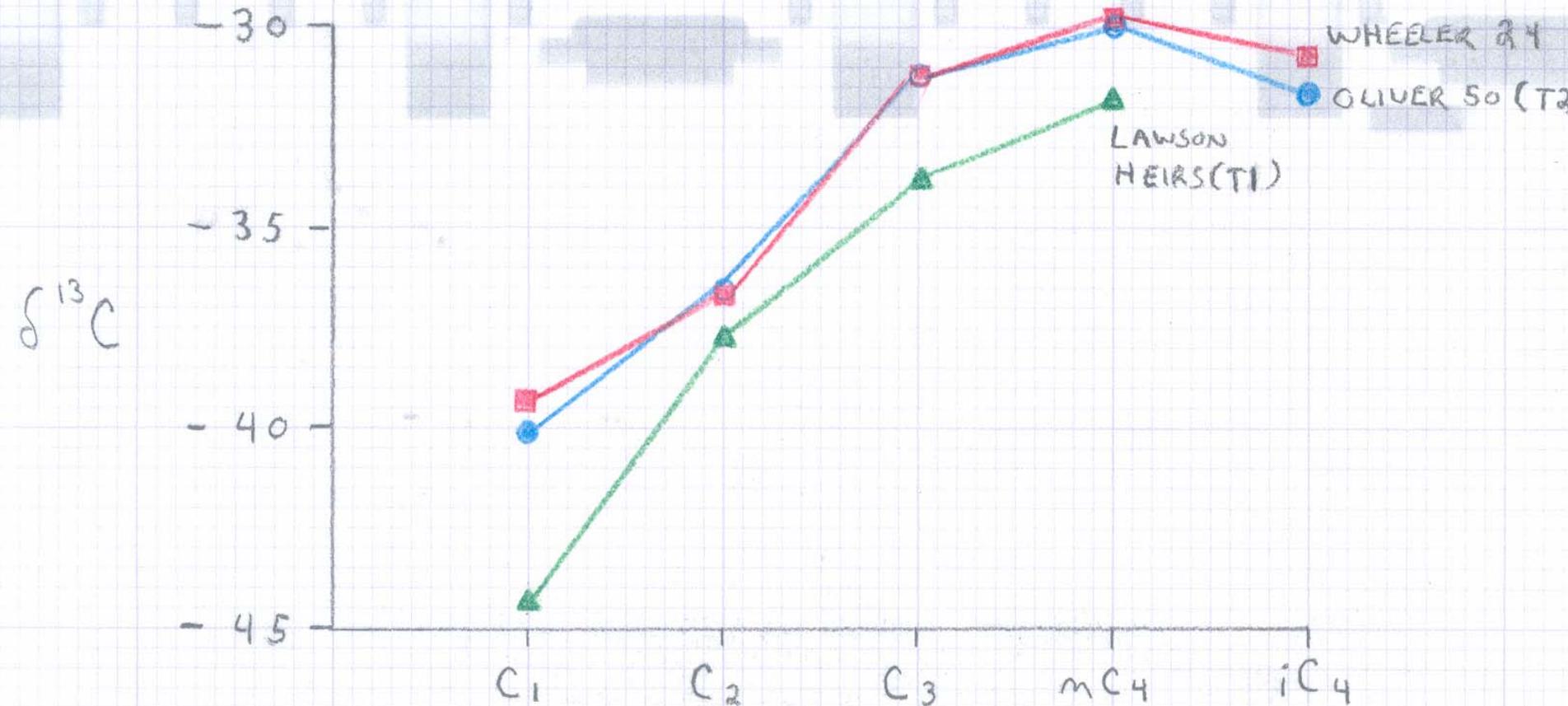
RESULTS TO DATE



RESULTS TO DATE

- Collin Fork Field, Clay Co. KY.
 - Early-mature, associated gas
 - High N₂
- Homer Field, Elliott Co. KY
 - At least two distinct natural gases:
 - Early-mature, associated gas
 - Late-mature, non-associated gas
 - Reservoir compartmentalization
 - High N₂

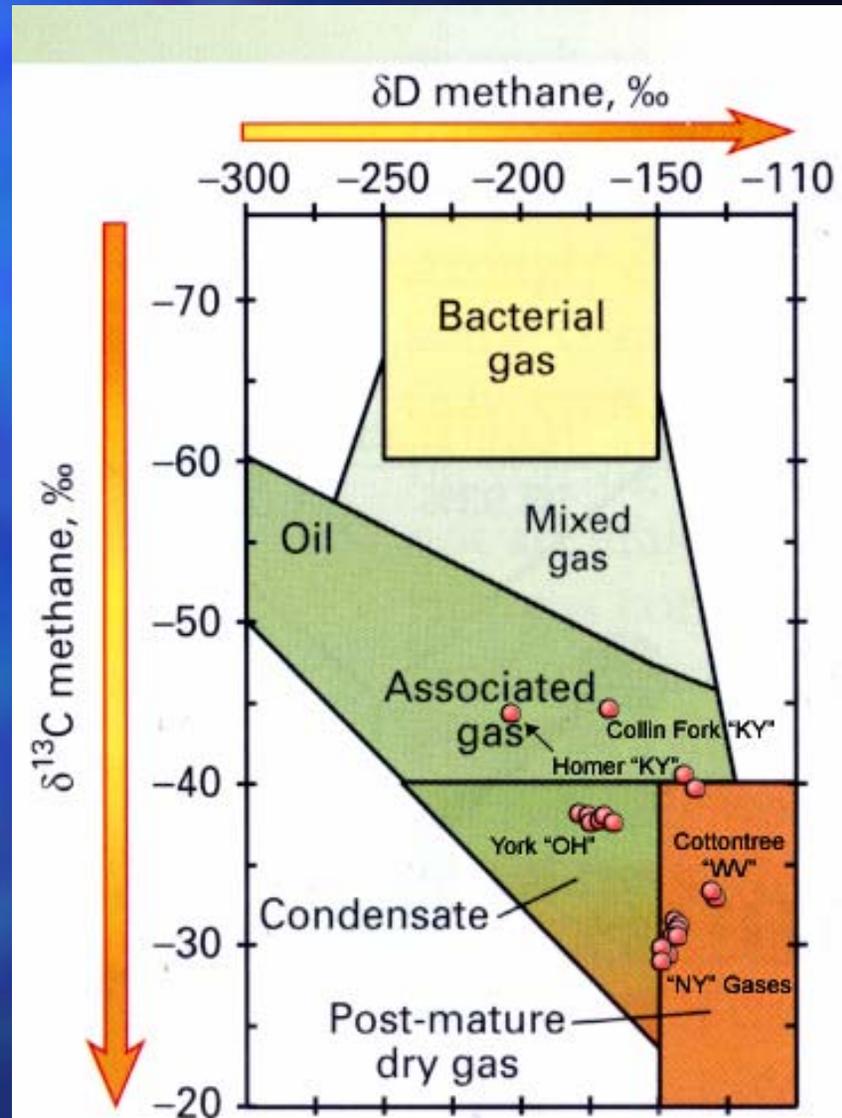


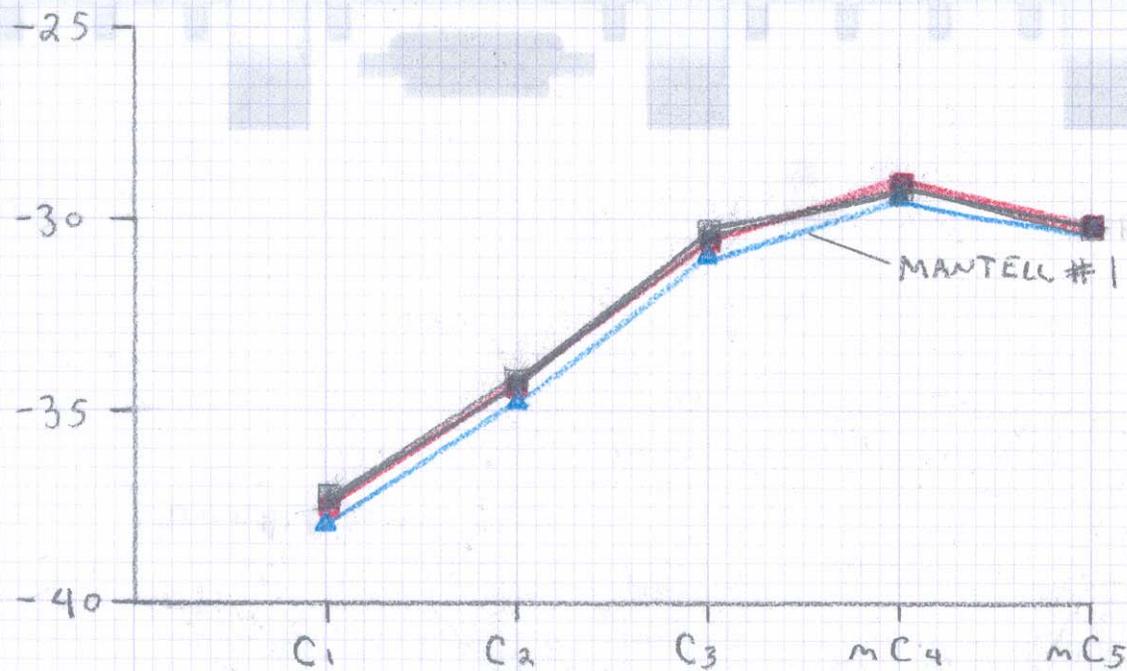


	$\delta^{13}C_1$	$\delta^{13}C_2$	$\delta^{13}C_3$	$\delta^{13}mC_4$	$\delta^{13}iC_4$ ‰
OLIVER 50 (T2)	-40.30	-36.67	-31.45	-30.22	-31.59
WHEELER 24	-39.50	-36.83	-31.36	-29.93	-30.95
LAWSON HEIRS (T1)	-44.41	-37.71	-33.92	-31.57	mm

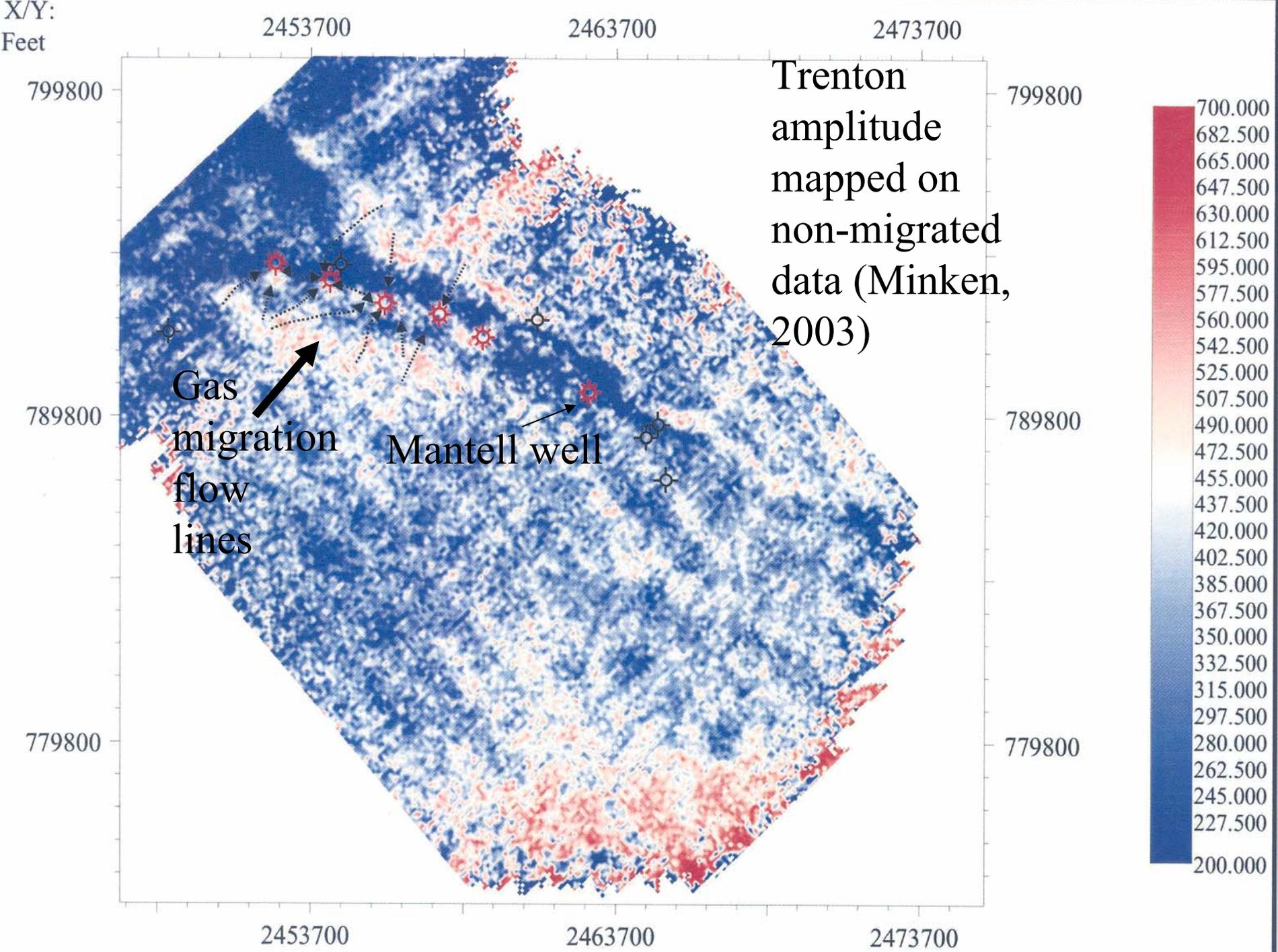
RESULTS TO DATE

- York Field, Ashtabula Co. OH
 - Condensate-associated gases
 - Late-mature
 - High N_2
 - Same source rocks
 - Compartmentalization?





	$\delta^{13}C_1$	$\delta^{13}C_2$	$\delta^{13}C_3$	$\delta^{13}mC_4$	$\delta^{13}iC_4$ ‰
RIFFLE#1	-37.41	-34.36	-30.48	-29.36	-30.32
DALIN#1	-37.50	-34.48	-30.59	-29.33	-30.31
YORK#1	-37.44	-34.44	-30.50	-29.34	-30.31
DOWNES#3	-37.37	-34.38	-30.50	-29.21	-30.30
DOWNES#1	-37.38	-34.37	-30.44	-29.25	-30.26
MANTELL#1	-38.04	-34.75	-30.83	-29.45	-30.40



X/Y:
Feet

2453700

2463700

2473700

799800

799800

789800

789800

779800

779800

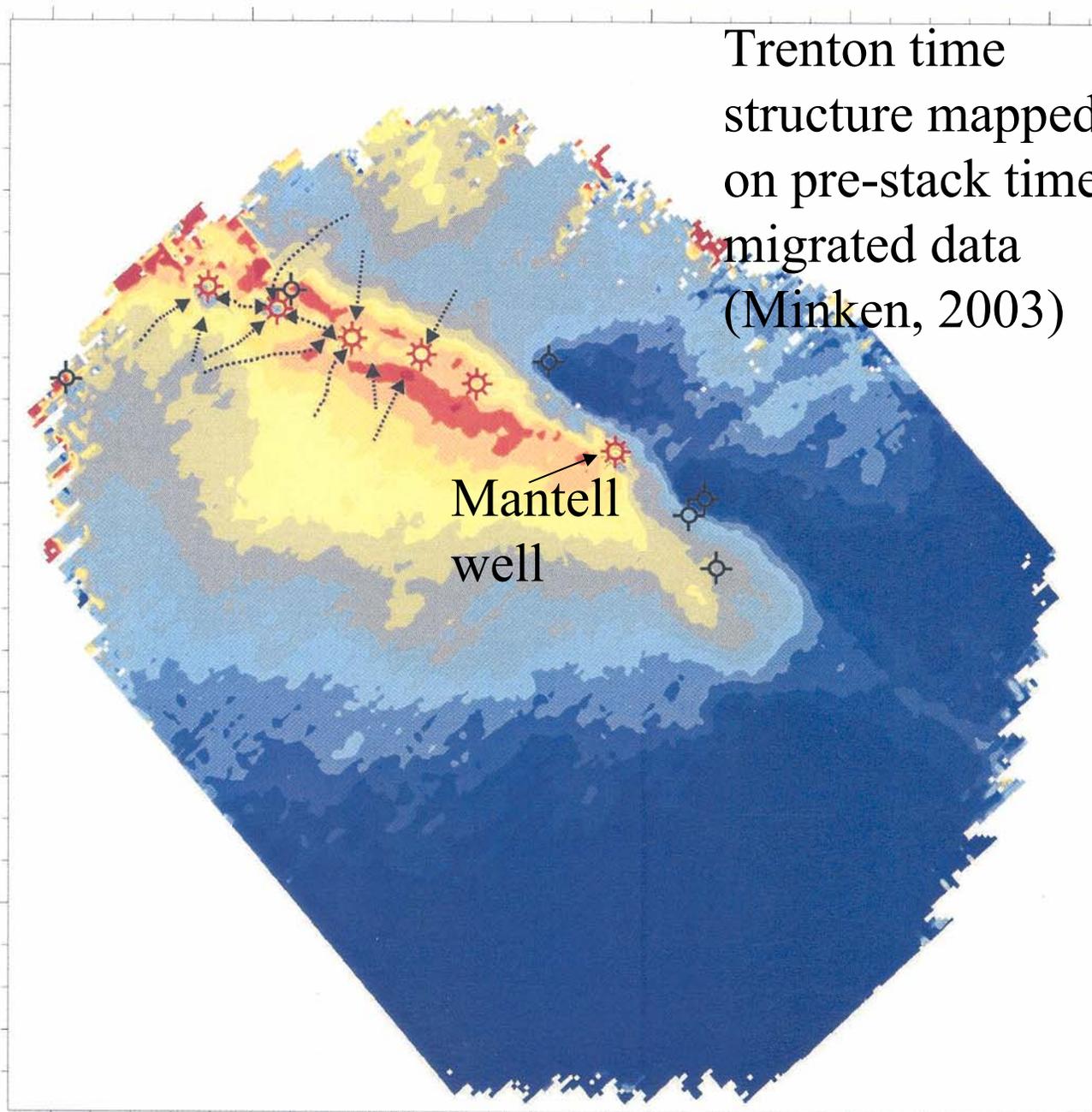
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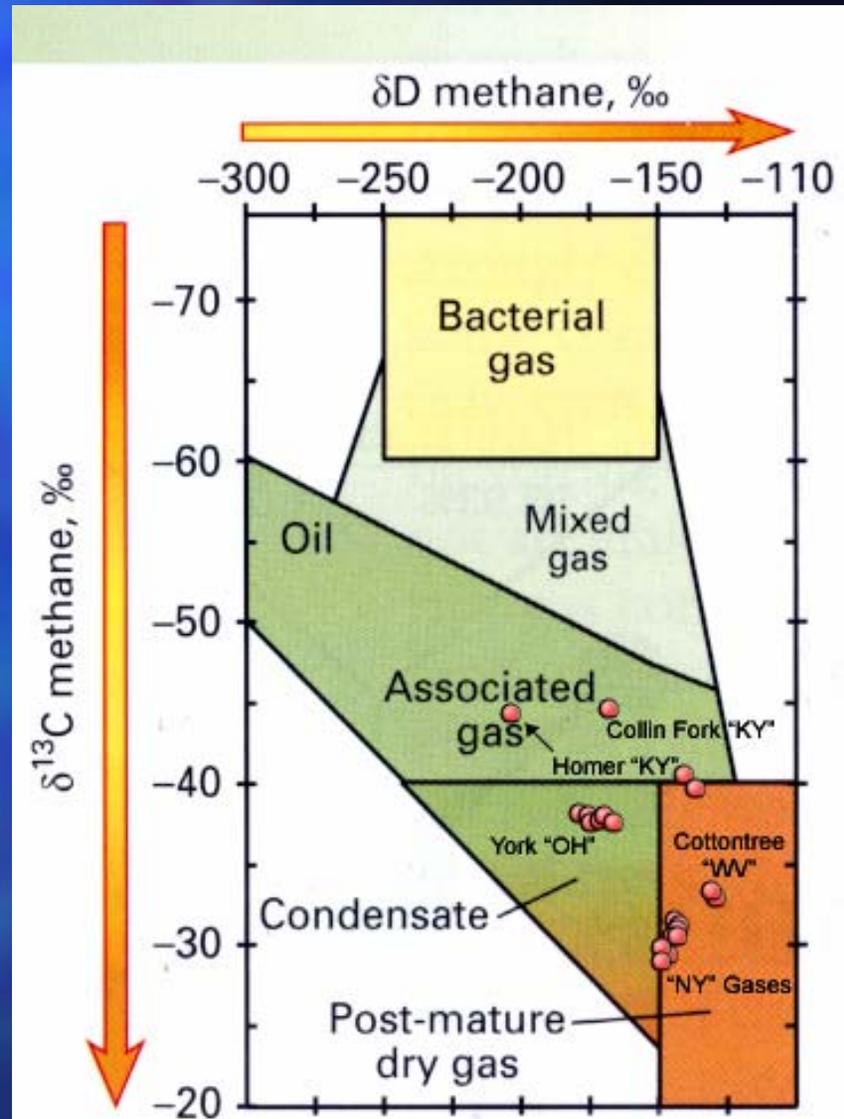
Trenton time
structure mapped
on pre-stack time
migrated data
(Minken, 2003)

Mantell
well



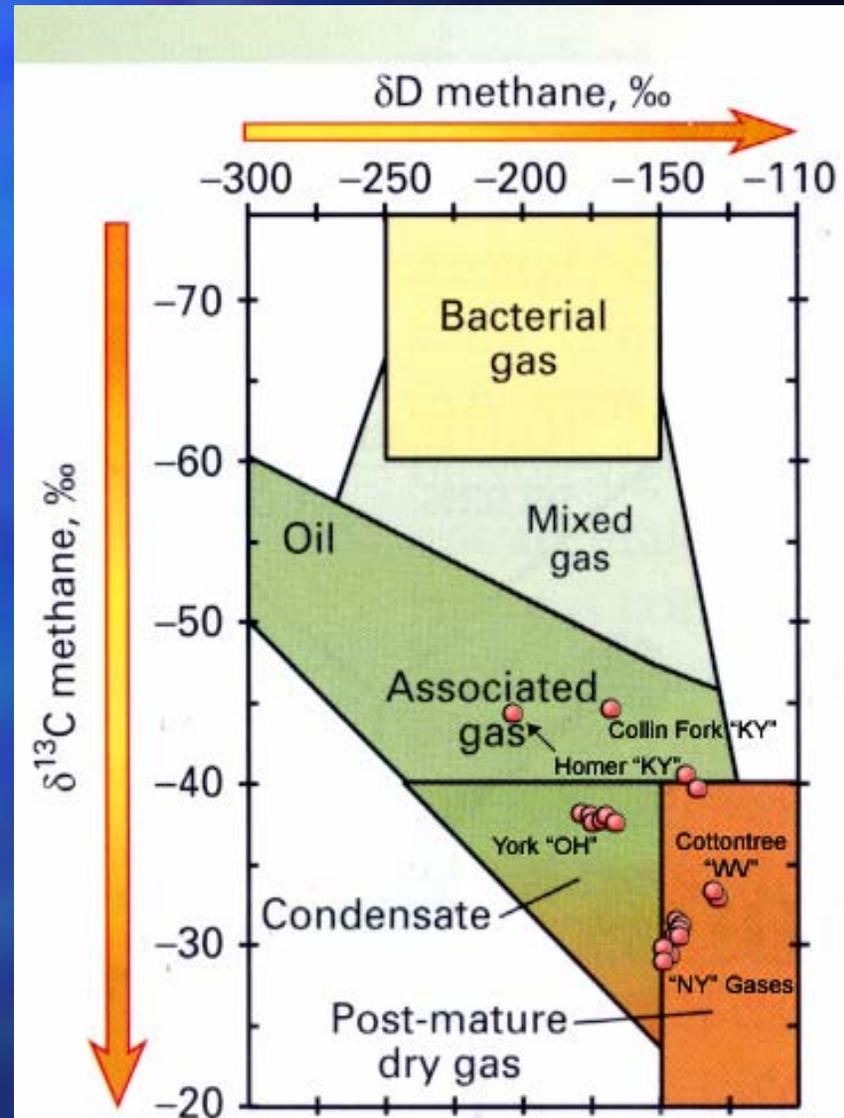
RESULTS TO DATE

- **Cottontree Field, Roane Co. WV**
 - Post-mature dry gas
 - Late-mature



RESULTS TO DATE

- **New York Gases**
 - Post-mature dry gases
 - Late-mature (source rock $R_o > 4.0$)
 - Very dry ($\geq 95\%$ CH_4)
 - **Isotopic reversals between methane and ethane**
 - **Notable N_2 at Glodes Corners and Muck Farm fields (1.18 – 2.41%)**



NITROGEN IN NATURAL GASES

- Origin of N₂ in natural gases poorly understood
- Magmatic gas component?
- Mantle outgassing?
- Oxidation of ammonia in the pore waters of sedimentary basins (maturation of organic matter)
- Atmosphere

“Integrated Hydrothermal Dolomite gas Conceptual Exploration Model and The Identification Of An Unrecognized Major Mg-Hydrocarbon Source”, S. Keith and others, 2003.

- Proposed a model to explain the generation, transport, and deposition and anomalous amounts of Mg and hydrocarbons that characterize HTD and MVT zinc deposits
- Based on surface geochemistry at Glodes Corners Field



“Integrated Hydrothermal Dolomite gas Conceptual Exploration Model and The Identification Of An Unrecognized Major Mg-Hydrocarbon Source”, S. Keith and others, 2003.

- Proposed Reaction Sequence:
 - Generation of methane and hydrocarbon-stable metagenic fluids from serpentinization of peridotite in intracratonic failed rifts or collision sutures in the basement
 - Initial low temperature dolomitization of shelf carbonates in overlying strata
 - Early HTD near depositional site
 - Late HTD, anhydrite formation, and CO₂ effervescence, H₂ loss, and CH₄ unmixing
 - Sulfide and hydrocarbon deposition
 - Deposition of late CaCO₃ and clay minerals
 - Gas-charged fluids may continue to ascend to higher stratigraphic levels where they deposit gas charge in shallower sandstones

Analytical Criteria for Identifying Mantle-Derived Hydrocarbons in Oil and Gas Fields (Jenden and others, 1993)

- Methane $\delta^{13}\text{C} > -25$ permil
- Isotopic reversals of the form methane $\delta^{13}\text{C} >$ ethane $\delta^{13}\text{C} >$ propane $\delta^{13}\text{C}$
- $^3\text{He}/^4\text{He} > 0.1 \text{ Ra}$

NY Gases

- Methane $\delta^{13}\text{C} = -29.56$ to 32.77 permil
- Methane $\delta^{13}\text{C}$ consistently $>$ than ethane $\delta^{13}\text{C}$ (gas mixing?)
- $^3\text{He}/^4\text{He} = 0.109$ to 0.196 Ra: suggests a dominantly crustal source of He in the gases, with a possible minor (1.2 – 2.3%) component of mantle-derived He
- Noble Gas Geochemistry:
 - $^4\text{He}/^{40}\text{Ar}$
 - $^{40}\text{Ar}/^{36}\text{Ar}$
 - He/Ne
 - $^{20}\text{Ne}/^{36}\text{Ar}$
 - N_2/Ar
 - $^{84}\text{Kr}/^{36}\text{Ar}$
 - $\text{CH}_4/^3\text{He}$

PRELIMINARY CONCLUSIONS AND FUTURE WORK

- Gases produced from Trenton/Black River reservoirs in the Appalachian basin are early-mature to post-mature. Maturity appears to correlate with burial and tectonic history.
- Gases produced at the Homer Field in Elliott County, KY are compartmentalized and originated from at least two different sources.
- Gases produced at York Field in Ashtabula County, OH also come from at least two discrete reservoir compartments; isotope geochemistry may reflect reserve potential.

PRELIMINARY CONCLUSIONS AND FUTURE WORK

- Gases produced from Trenton/Black River reservoirs in New York are post-mature, and exhibit isotopic reversals
 - Mixing?
 - Hydrothermal gases?
- Noble gas geochemistry of the NY gases indicates a predominantly crustal origin, with a minor ^3He component derived from the mantle

PRELIMINARY CONCLUSIONS AND FUTURE WORK

- Trenton/Black River gases produced in KY, OH, and NY contain notable N₂ (1.18 – 5.17%)
 - Magmatic component?
 - Future Work:
 - Interpret noble gas data
 - Construct plots to quantify gas mixing in the reservoirs
 - Compartmentalization and fault block mapping?
 - PA samples/data???
 - Look at H₂S and CO₂ in Trenton/Black River reservoirs