# Enhanced Formation Evaluation of Shales Using NMR Secular Relaxation*

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## Abstract

Determining the porosity associated with organic and inorganic components of shales is an important but difficult part of formation evaluation in unconventional resources. Nuclear magnetic resonance (NMR) measurements offer a means of quantifying organic and inorganic porosity by separating the inorganic porosity, where proton relaxation occurs by paramagnetic interactions, from the organic porosity, where proton relaxation occurs by intermolecular dipole interactions. We performed laboratory measurements on preserved Bakken and Eagle Ford samples with a 2.2 MHz nuclear magnetic resonance (NMR) core analysis system. Additional measurements were performed on a Barnett sample in the as-received state. We constructed two-dimensional maps of T1 and T2 with different echo spacings for the T2 measurement and computed distributions of T1/T2 ratio and the secular relaxation rate, which is the difference between the transverse and longitudinal relaxation rates. Based on the distribution of T1/T2 ratios and the change in secular relaxation rate with echo spacing, we were able to differentiate organic porosity, inorganic porosity, and the relaxation signal from the organic material itself. The differentiation is based on theoretical consideration of relaxation times due to paramagnetic and dipole interactions. The T2 values we found for the organic material and associated porosity are generally shorter than 1 ms while the T1 values are generally 1–10 ms, indicating that T1 measurements may be a feasible means of quantifying organic material downhole.

## Reference Cited

Passey, Q.R., K.M. Bohacs, W.L. Esch, R. Klimentidis, and S. Sinha, 2010, From Oil-Prone Source Rock to Gas-Producing Shale Reservoir - Geologic and Petrophysical Characterization of Unconventional Shale-Gas Reservoirs: SPE 131350, 29 p.

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# *Enhanced formation evaluation of shales using NMR secular relaxation*


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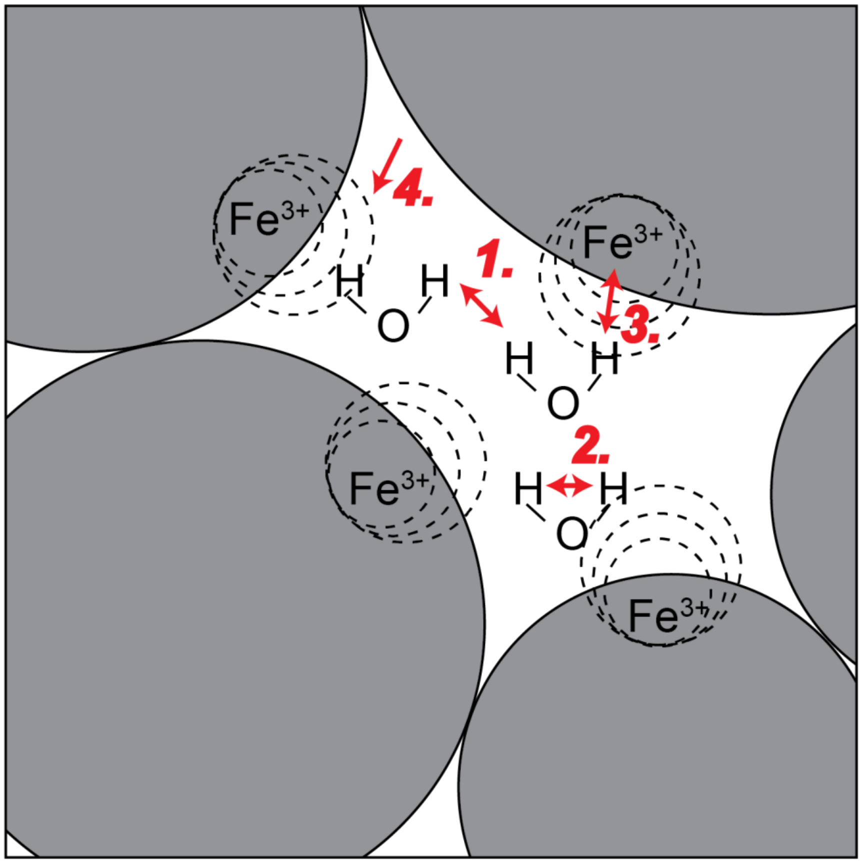
# Key points

- Shales are challenging for $^1H$ NMR because hydrocarbons are present as liquids and (semi)solids
- Relaxation times at pore walls vary in predictable ways depending on the type of pore wall material (inorganic or organic)
- We can combine standard relaxation time measurements and separate the pore space into inorganic & organic porosity

# NMR relaxation mechanisms



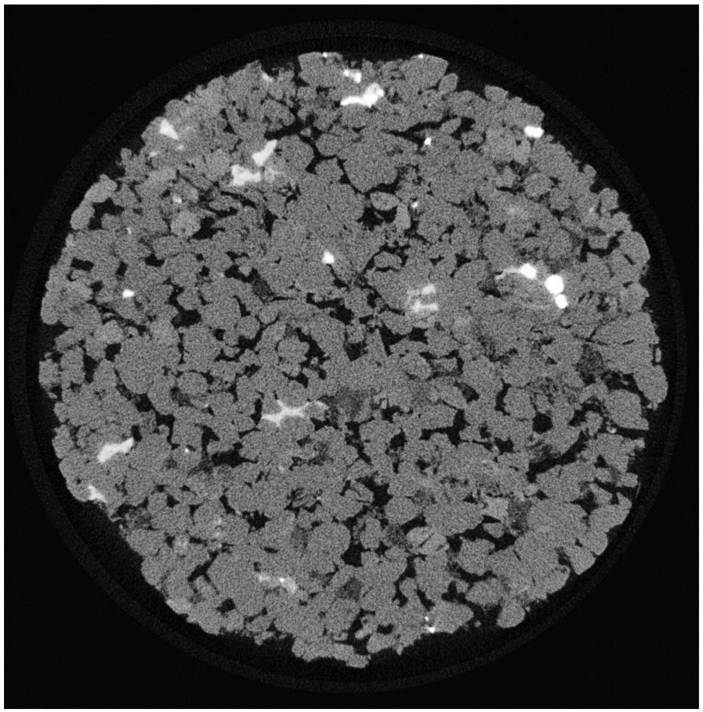

**1.** Intermolecular dipolar coupling
**2.** Intramolecular dipolar coupling
} Bulk relaxation

**3.** Interactions with paramagnetic ions on pore wall (Surface relaxation)

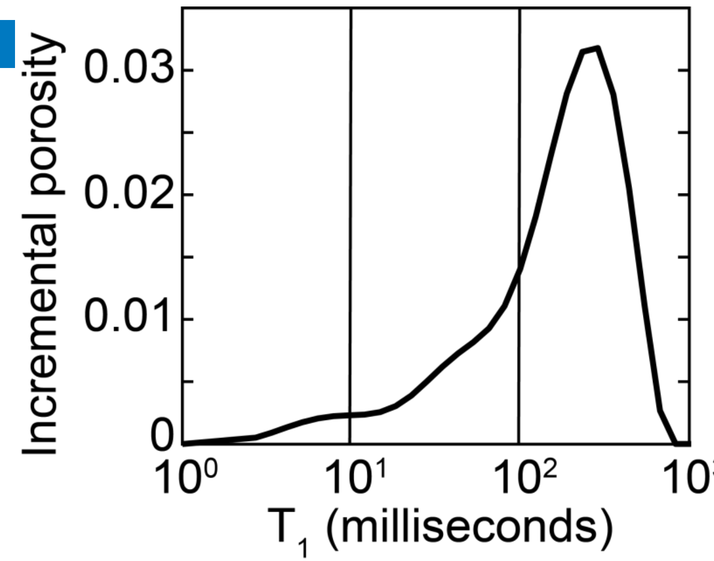
**4.** Diffusion in internal field gradients (Diffusion relaxation) ($T_2$ only)

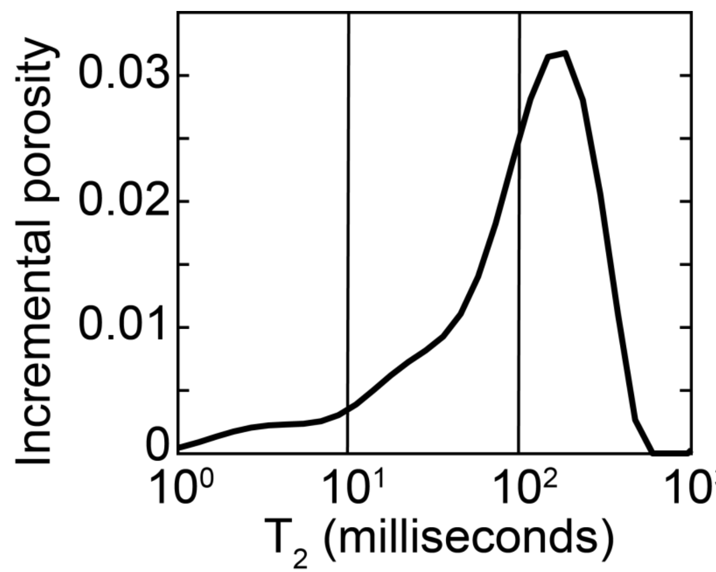
**In general, $T_1 \geq T_2$**

# NMR in conventional rocks



2.54 cm

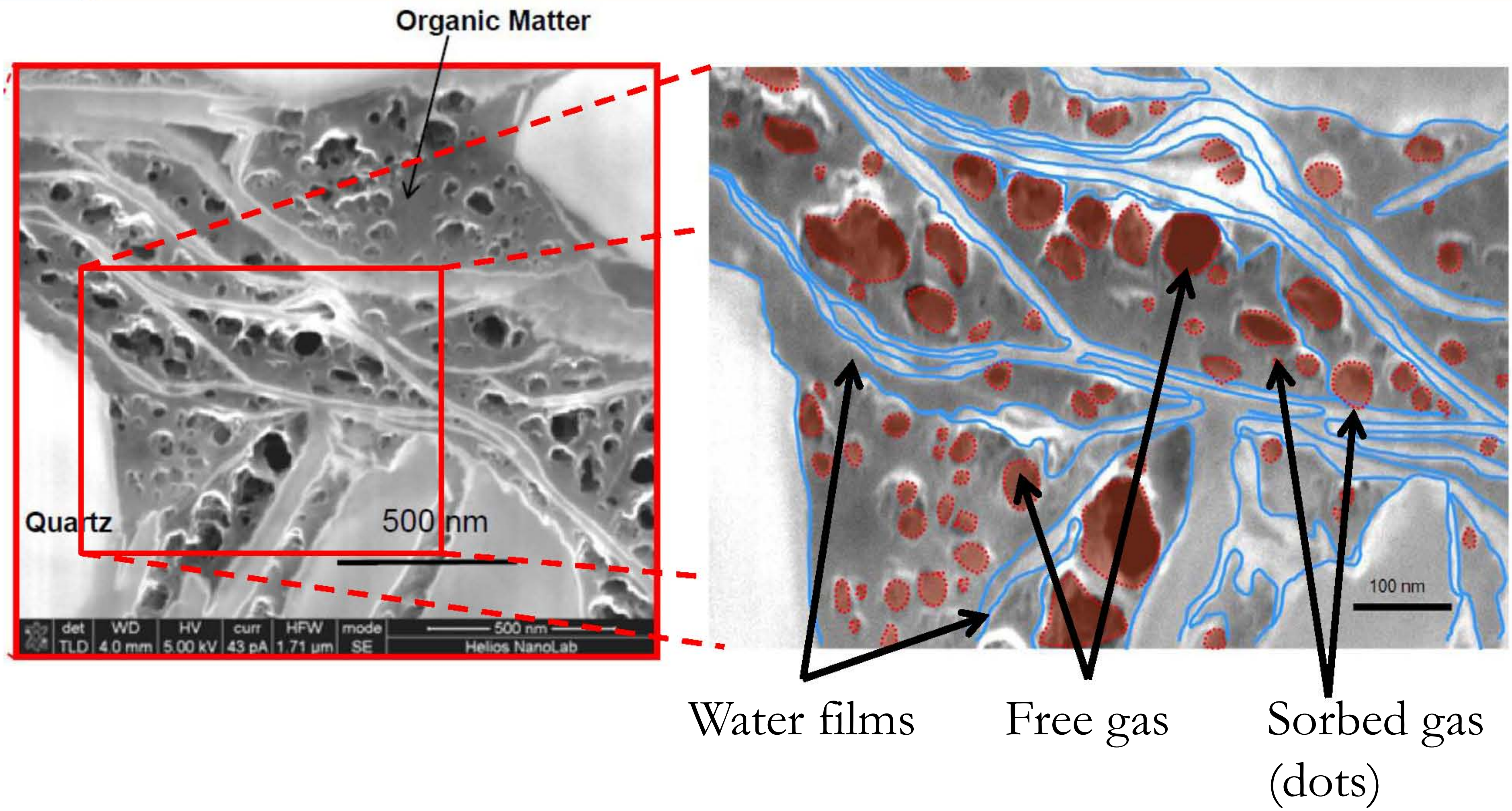



Bulk & diffusion relaxation can be ignored

$$T_{1,2} \sim r$$

# Pores and fluids in the Barnett




Passey et al., SPE 131350, 2010

+viscous hydrocarbons associated with kerogen

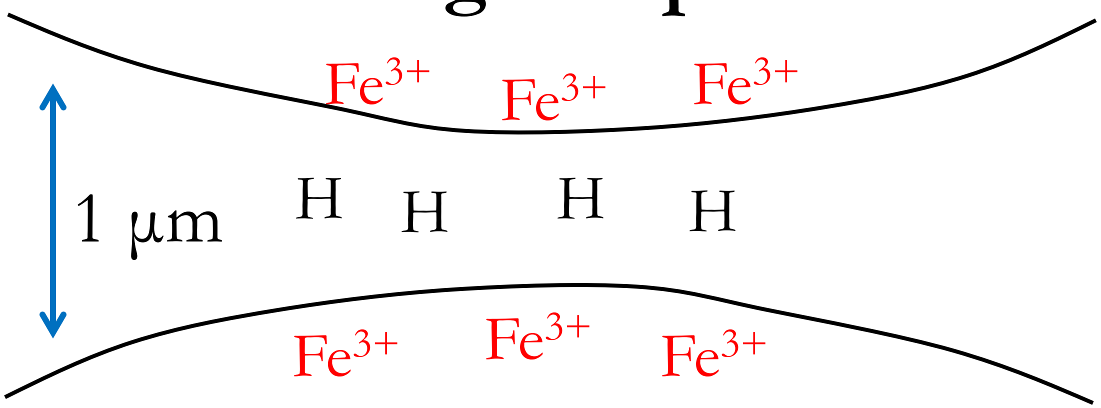
# Key differences in shales (for NMR)

- Pores are very small
- Porosity in organic <u>and</u> inorganic matter
- Viscous hydrocarbons present

**These differences can be used to our advantage.**

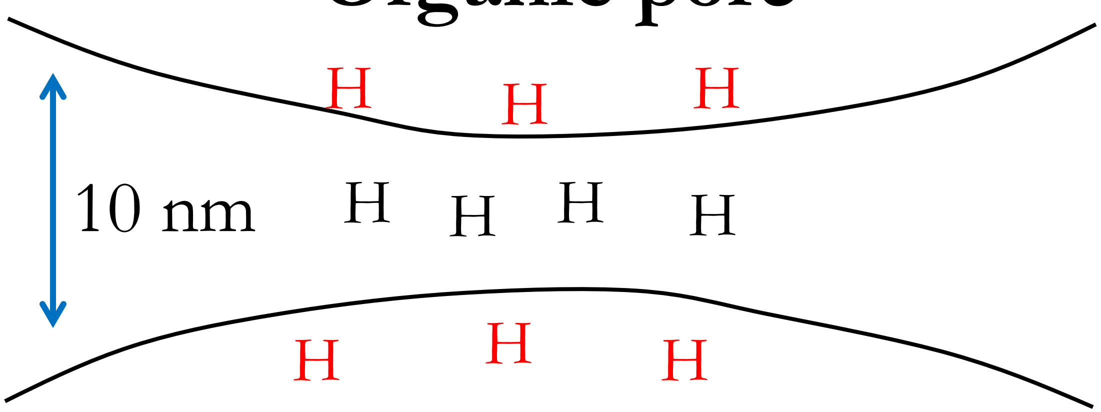
# Different relaxation mechanisms

**Inorganic pore**




Paramagnetic ions
Diffusion in internal gradients

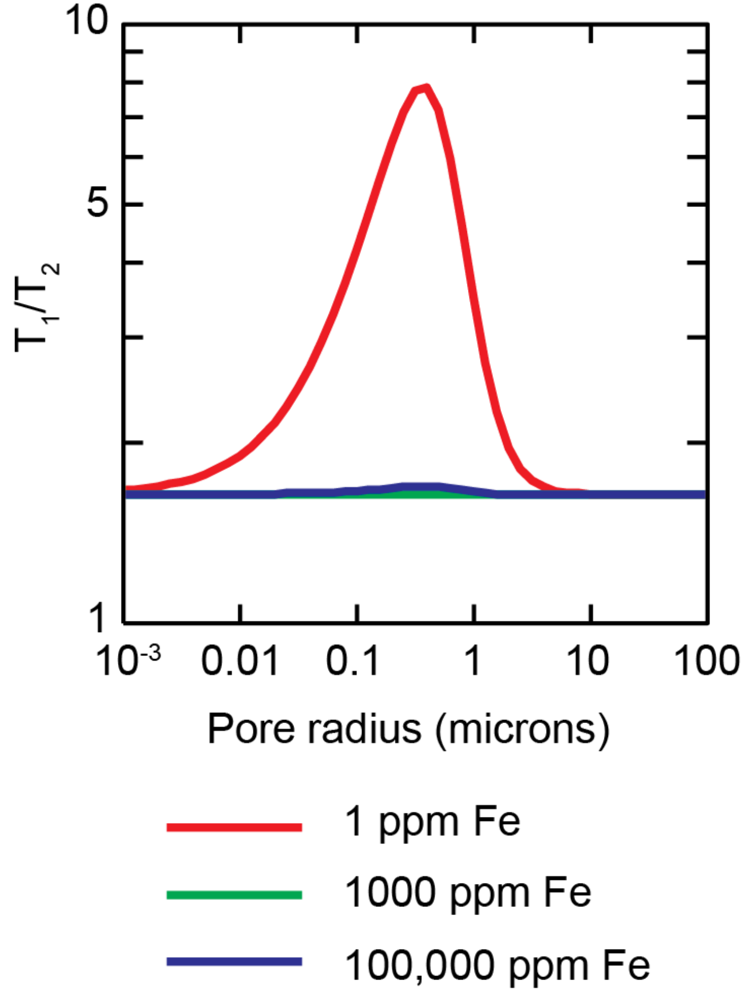
**Organic pore**



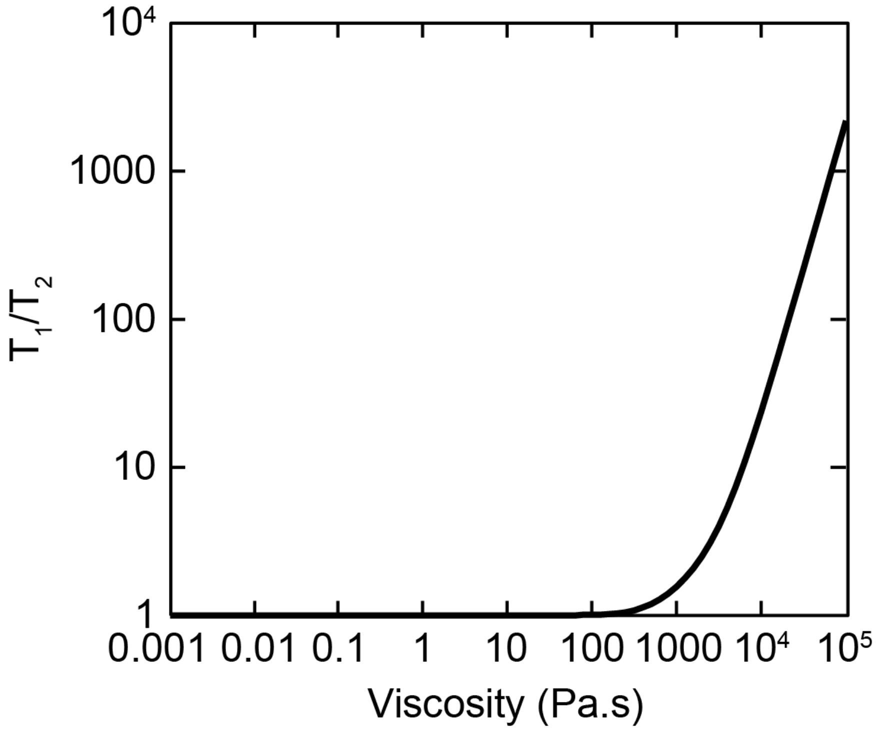

Proton-proton relaxation
Diffusion restriction due to pore size
*$CH_4$ diameter is about 0.4 nm

# $T_1/T_2$ ratios by pore type

Inorganic: surface dominated




Organic: bulk fluid dominated

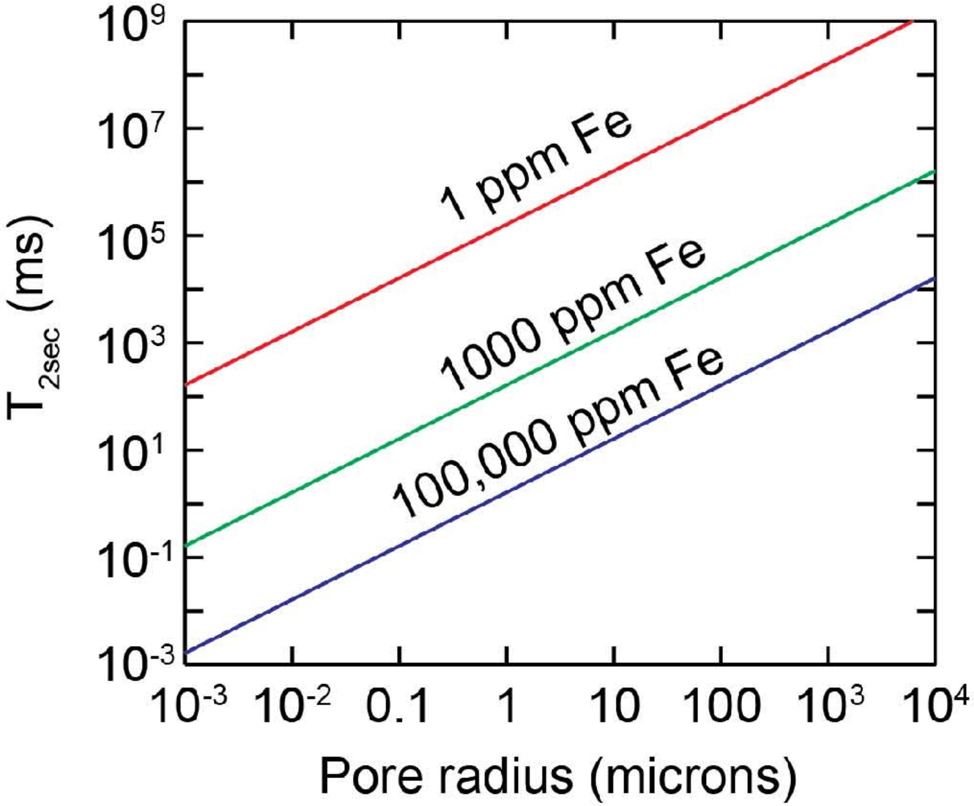


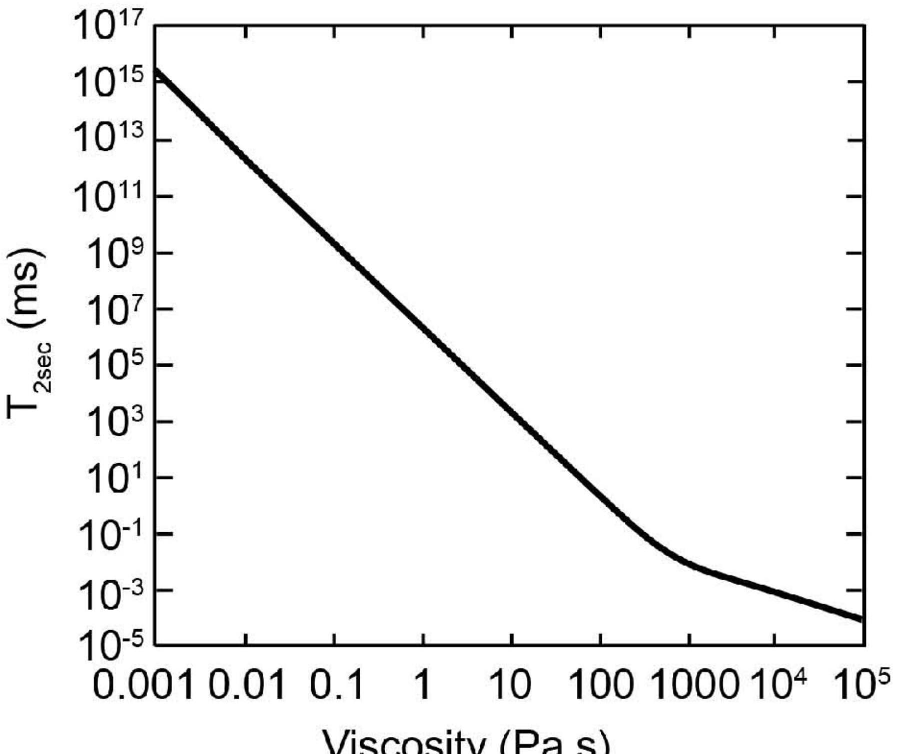

(or diffusion restriction in nanopores)

# Another dimension to add: secular relaxation

$$\frac{1}{T_{2sec}} = \frac{1}{T_2} - \frac{1}{T_1}$$

$$T_{2sec} = \frac{T_1}{\left(\frac{T_1}{T_2} - 1\right)}$$

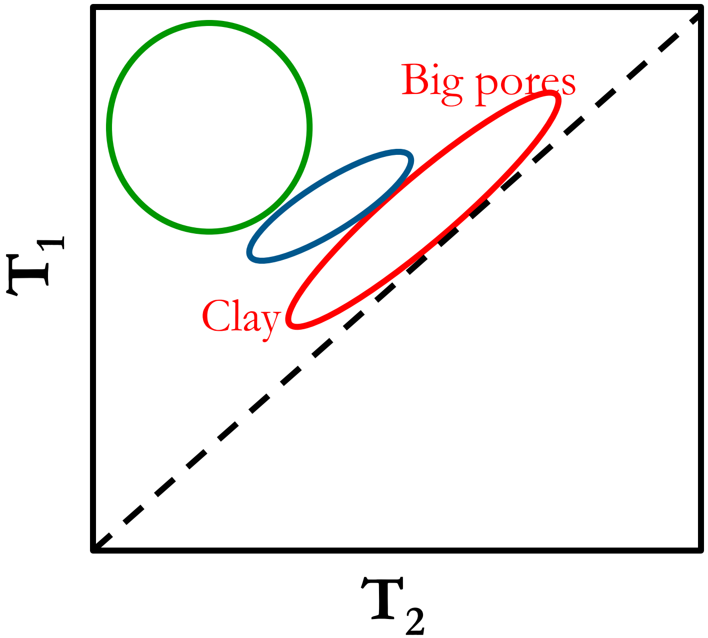


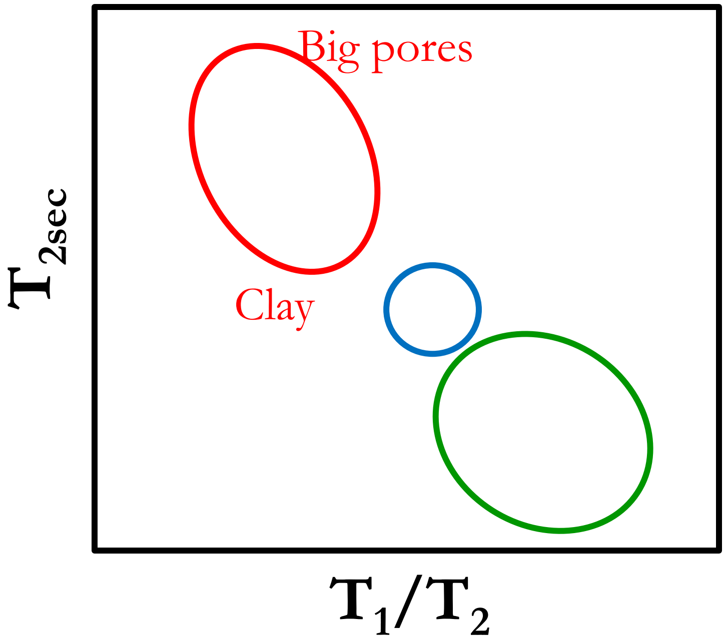




(or diffusion restriction in nanopores)

# Behavior in 2 dimensions

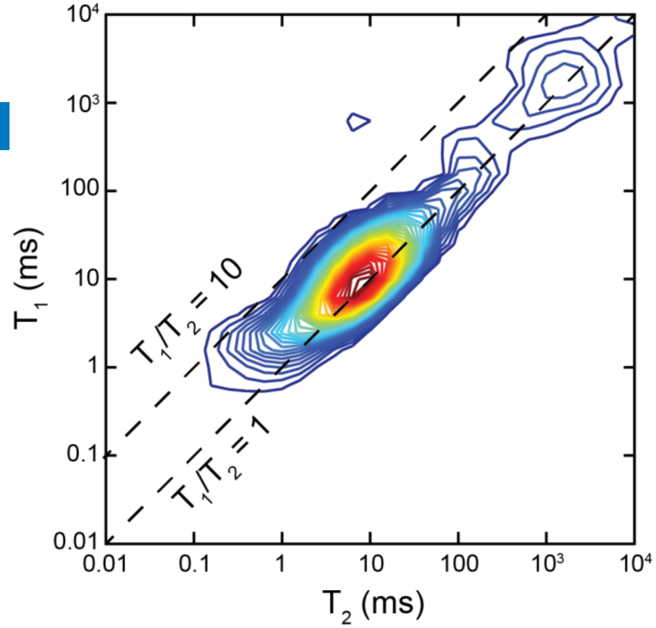
| | $T_1/T_2$ | $T_{2sec}$ |
|---|---|---|
| Inorganic pores | < 10 | 1 – 1000 ms |
| Organic pores | Moderate? | Moderate? |
| Fluids associated with organic matter | Large | Small |

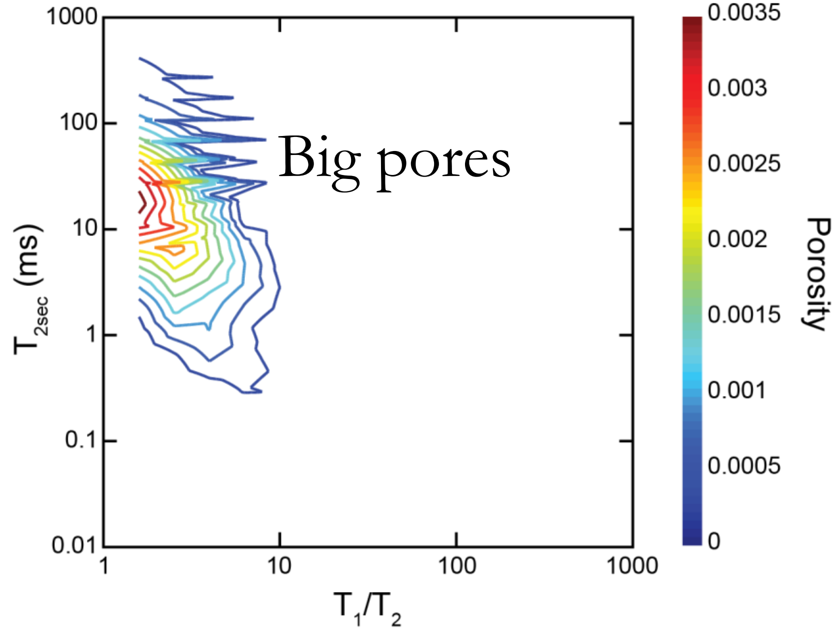


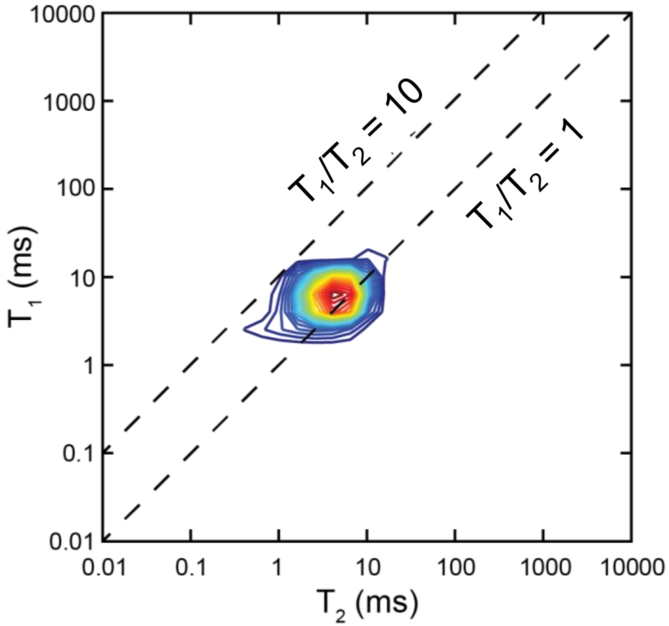
# Conventional rocks

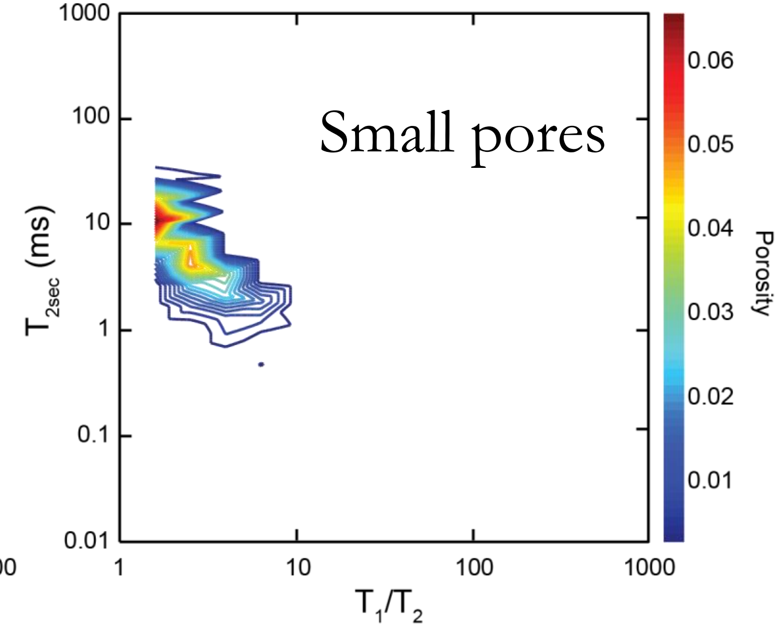
Wilcox Delta front




Marine Clay

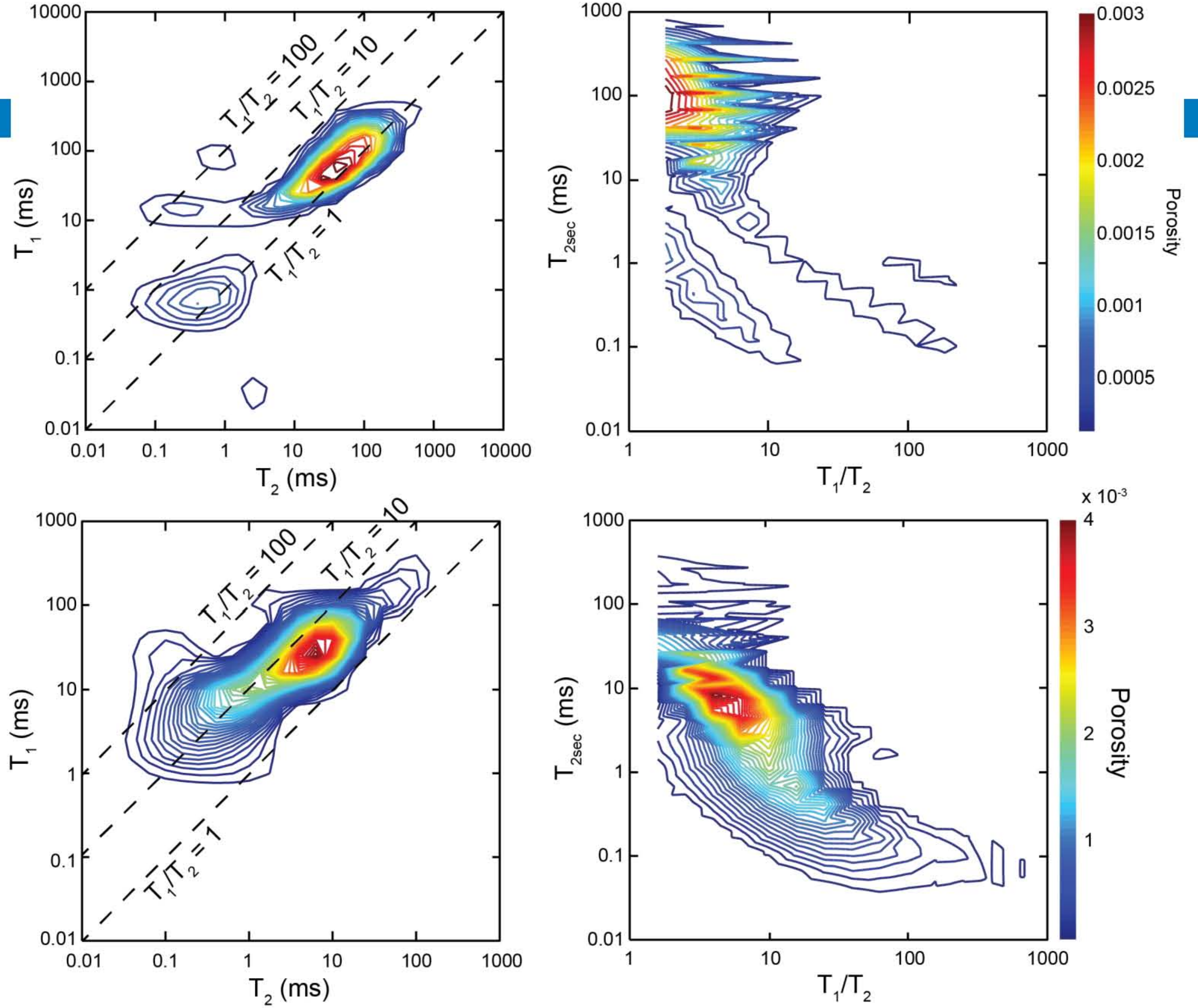


# Preserved shales

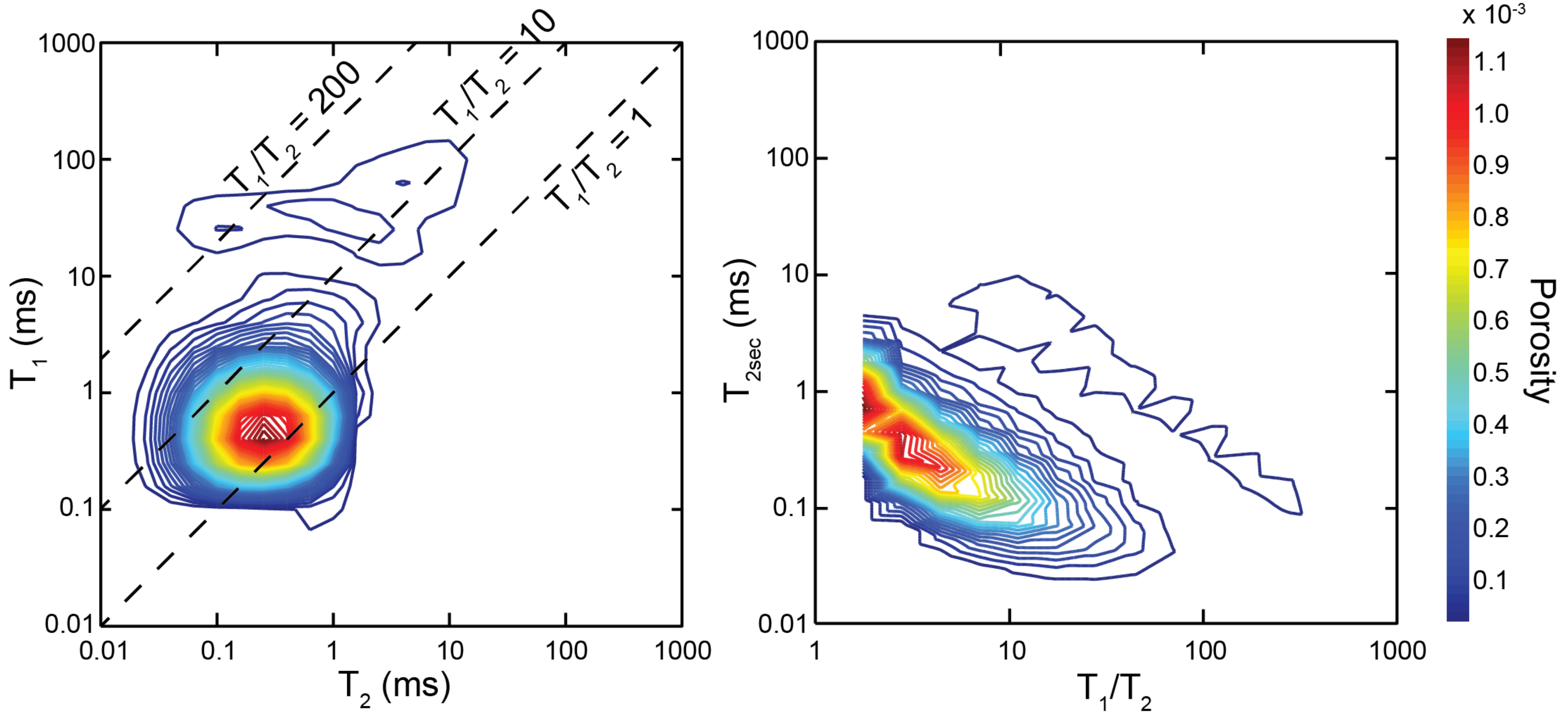
Bakken
TOC = 0%

Eagle Ford
TOC = 6%



# Unpreserved shale example (Barnett)

- Free fluids presumably not present
- Only have bound fluids and viscous hydrocarbons

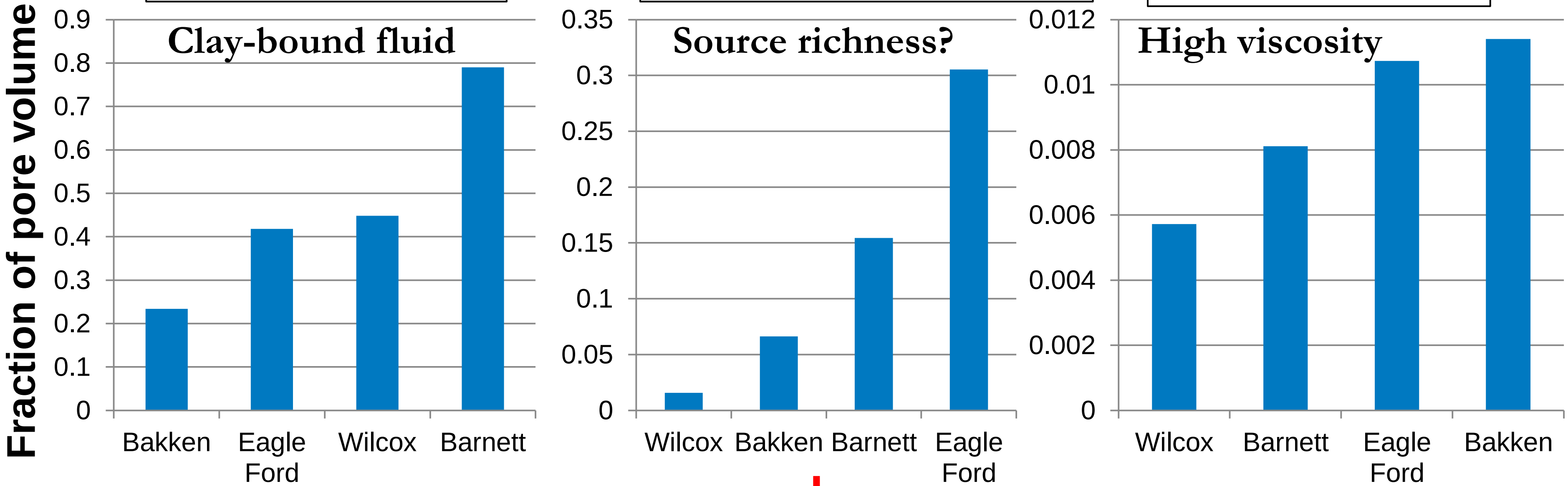


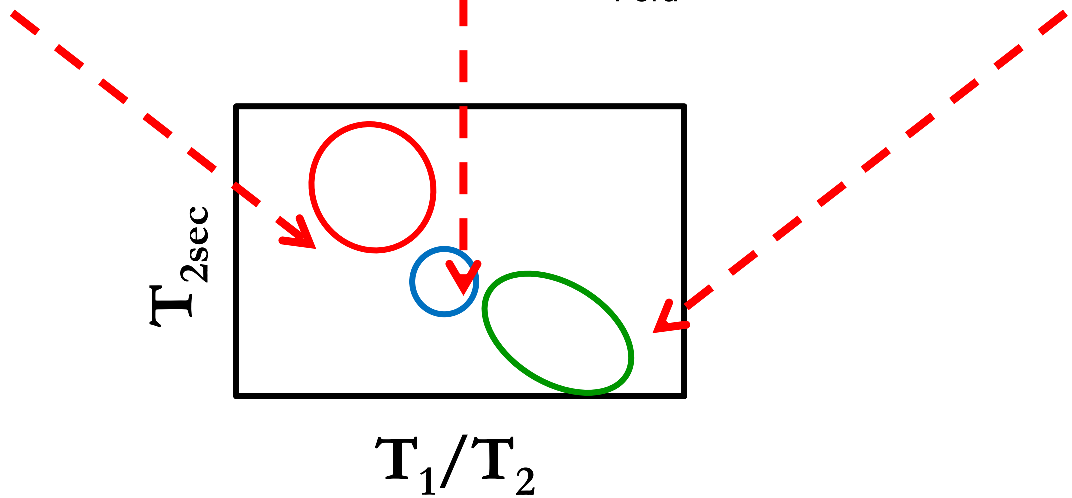
# Preliminary interpretation

$T_1/T_2 < 10$
$T_{2sec} < 10$ ms

$T_1/T_2 = 10 - 100$
$T_{2sec} < 10$ ms

$T_1/T_2 > 100$



# Summary

- Organic and inorganic surfaces relax $^1H$ spins in different, predictable ways
- This allows separation of pore space by comparing $T_1/T_2$ ratio and $T_{2sec}$
- Hydrocarbons in shales create significant features in $T_1$-$T_2$-$T_{2sec}$ diagrams
- Further work necessary (ongoing) to correlate what we see with fluids and pores