Using NMR to Assess Extent of Shale Fracture Biomineralization

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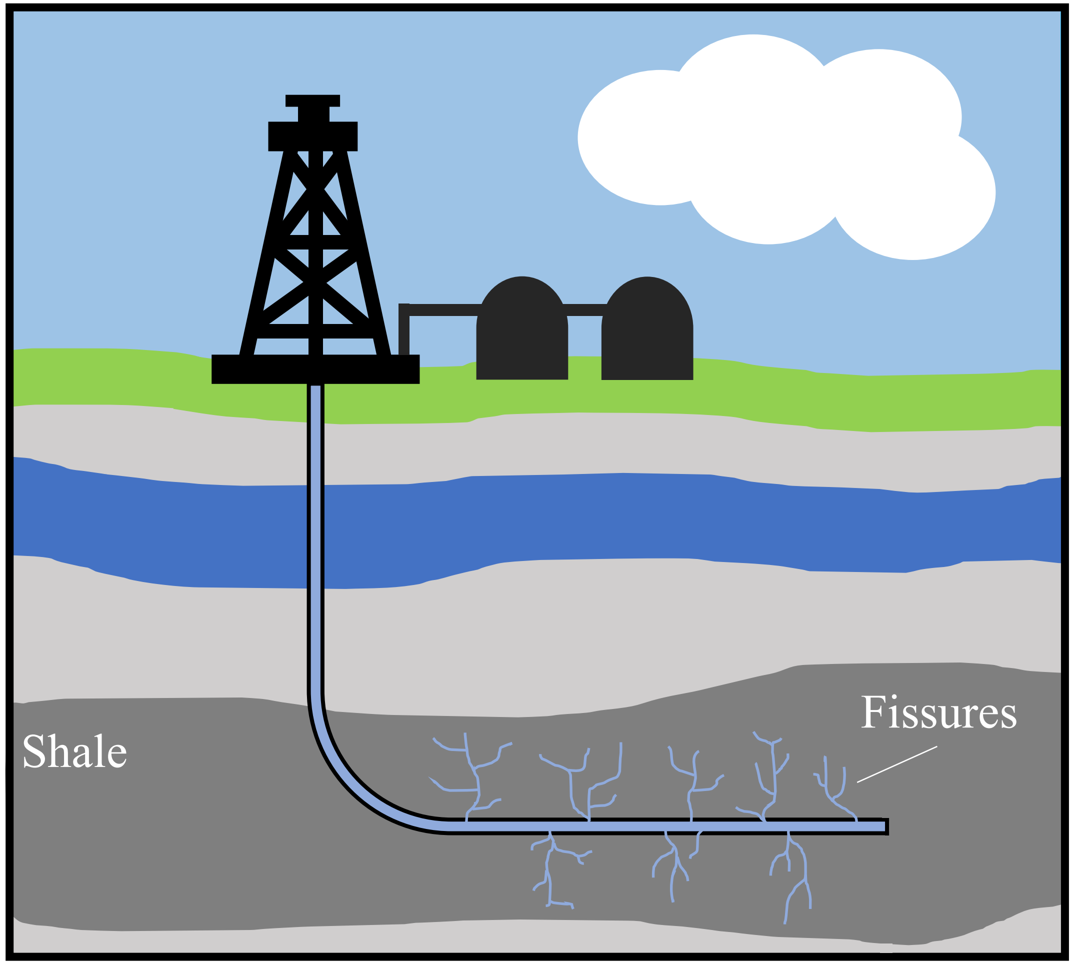
MONTANA STATE UNIVERSITY

Mountains & Minds

Background

Shale rock characteristics

- Low permeability } Caprock for CCS
- Natural gas reserves } Energy source



Hydraulic fracturing ("fracking")

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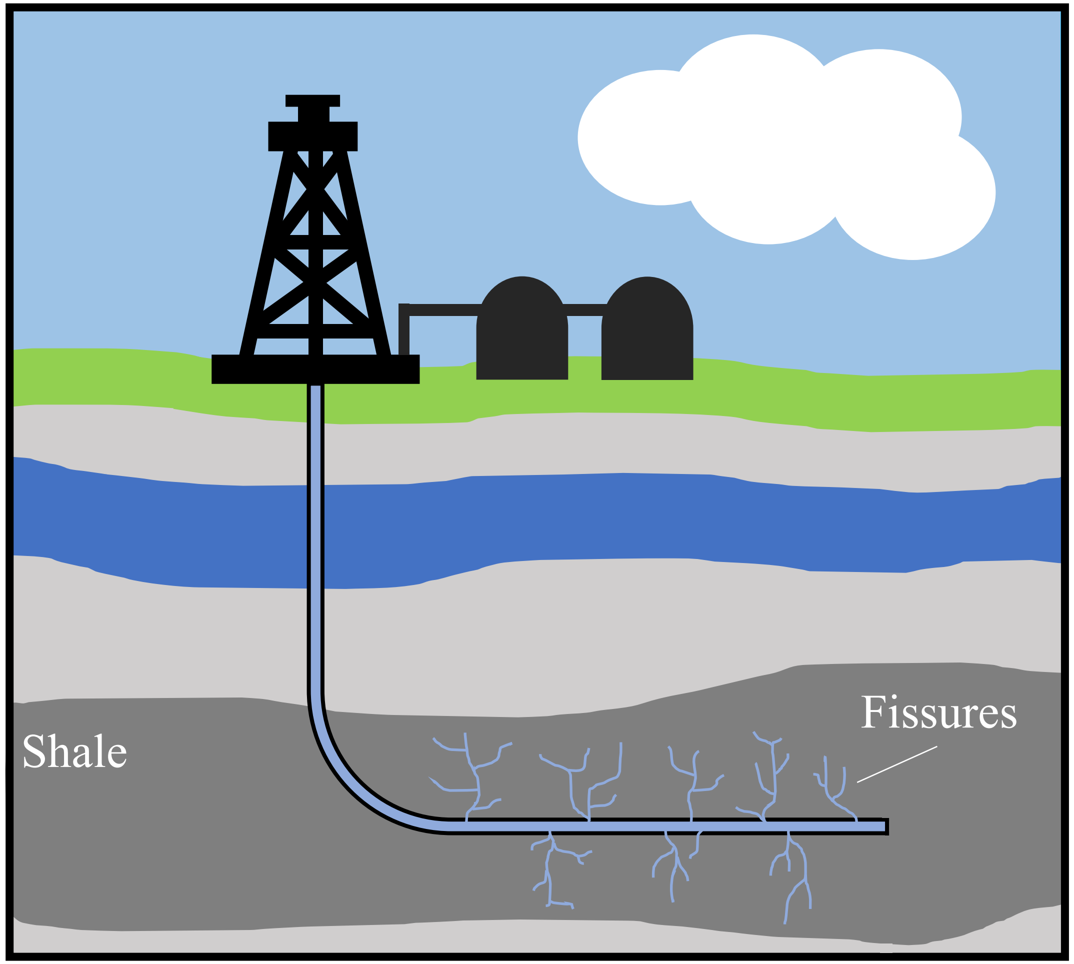
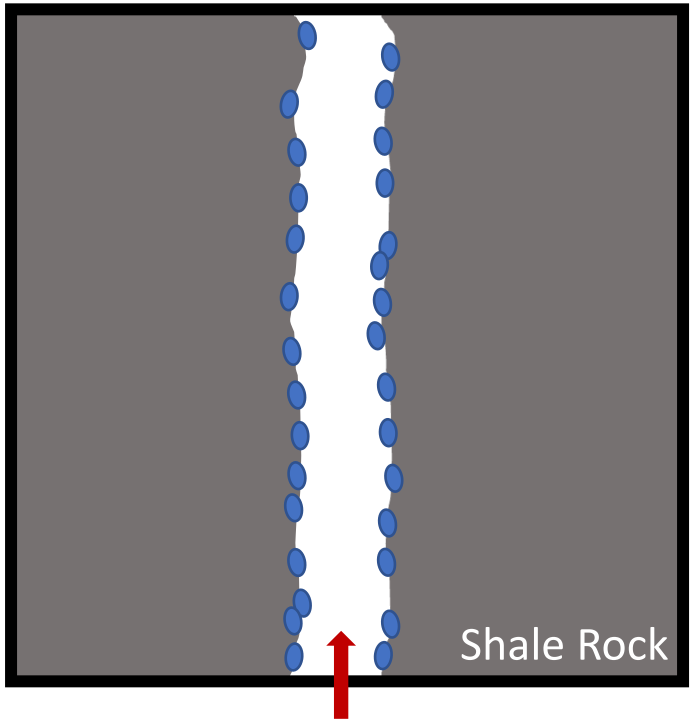
Need for methods to control shale permeability



Hydraulic fracturing (“fracking”)

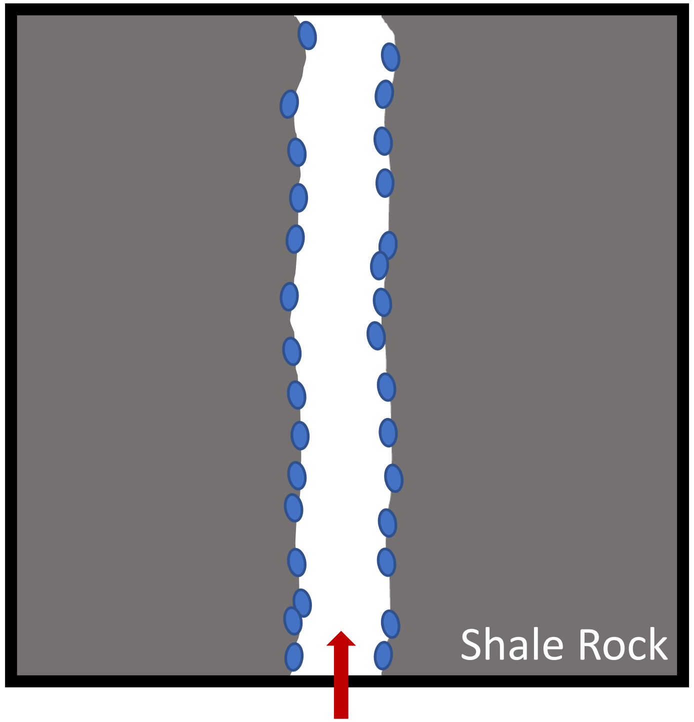
Microbially-induced calcium carbonate precipitation (MICP)



Step 1: Inject microbes
(*S. pasteurii*)

Microbially-induced calcium carbonate precipitation (MICP)

$$CO(NH_2)_2 + 2H_2O + Ca^{2+} \xrightarrow{urease} 2NH_4^+ + CaCO_3(s)$$



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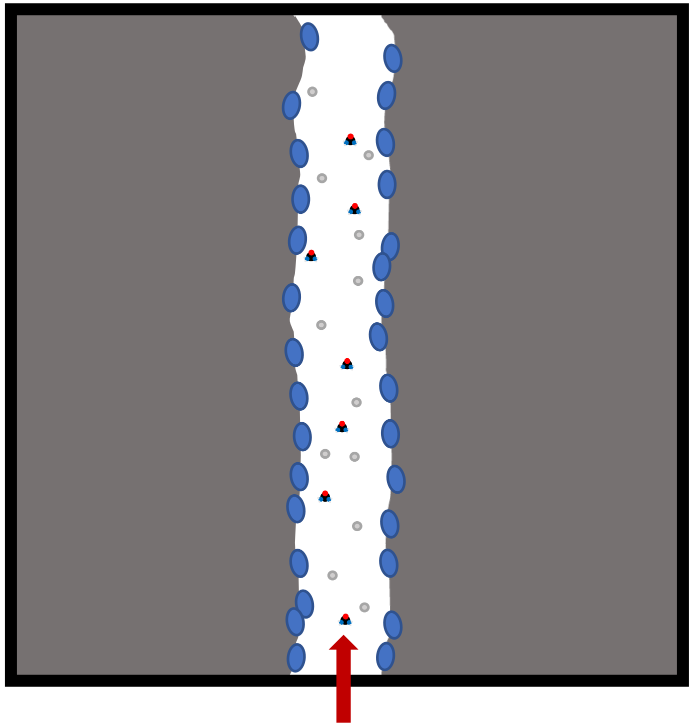

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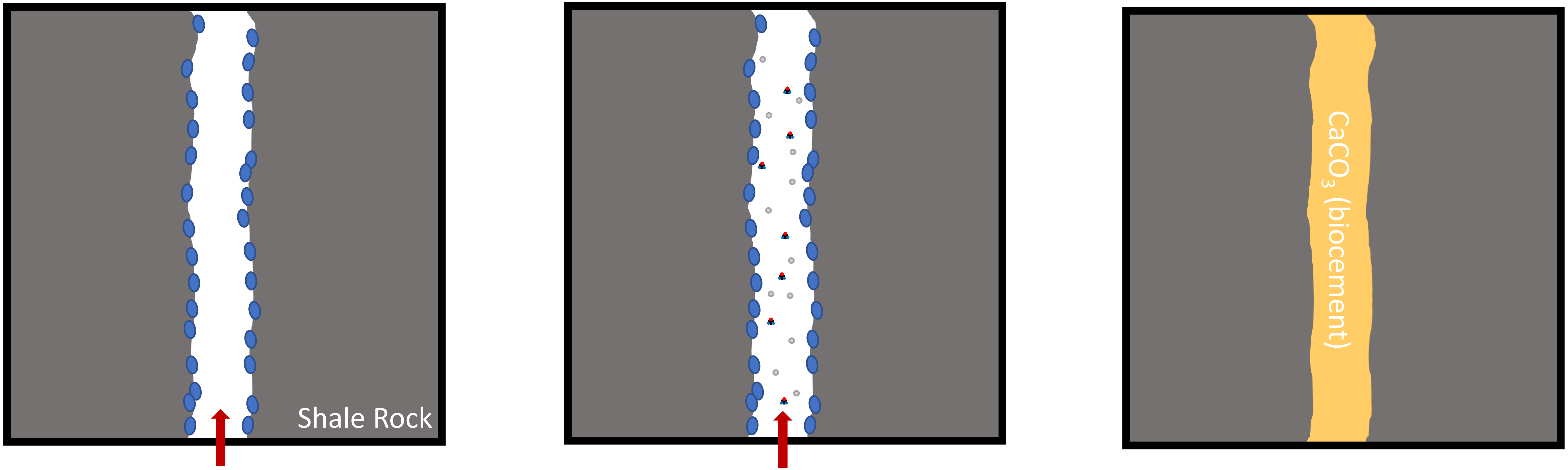
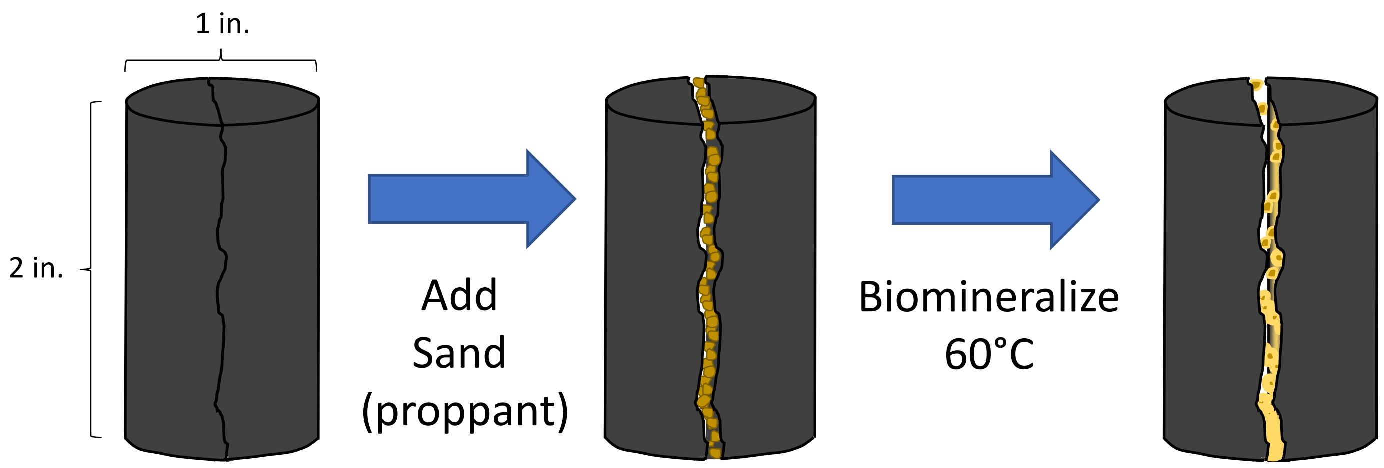


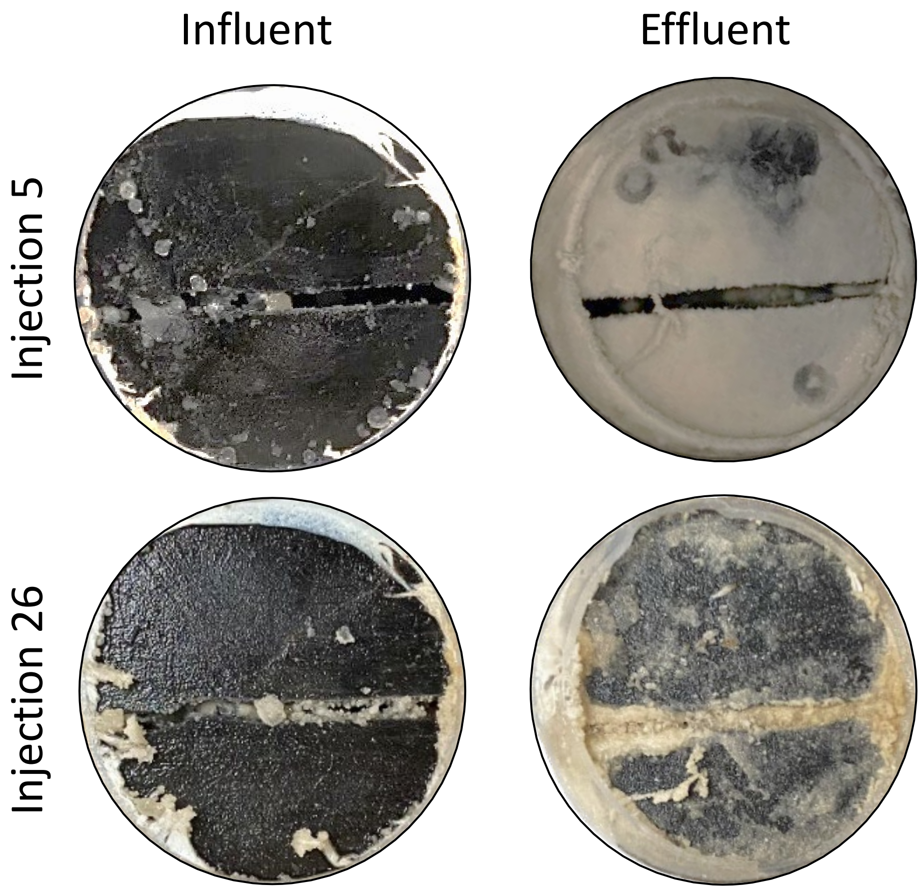
Step 1: Inject microbes (*S. pasteurii*)

Step 2: Add reactants (urea and calcium)

Step 3: Repeat

Assessing potential of shale biomineralization





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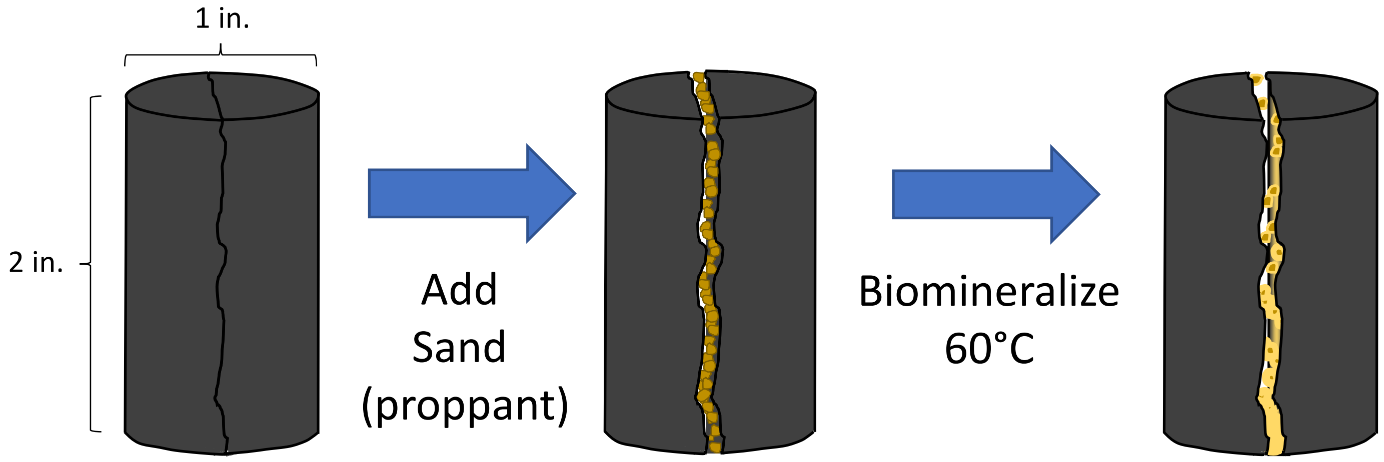
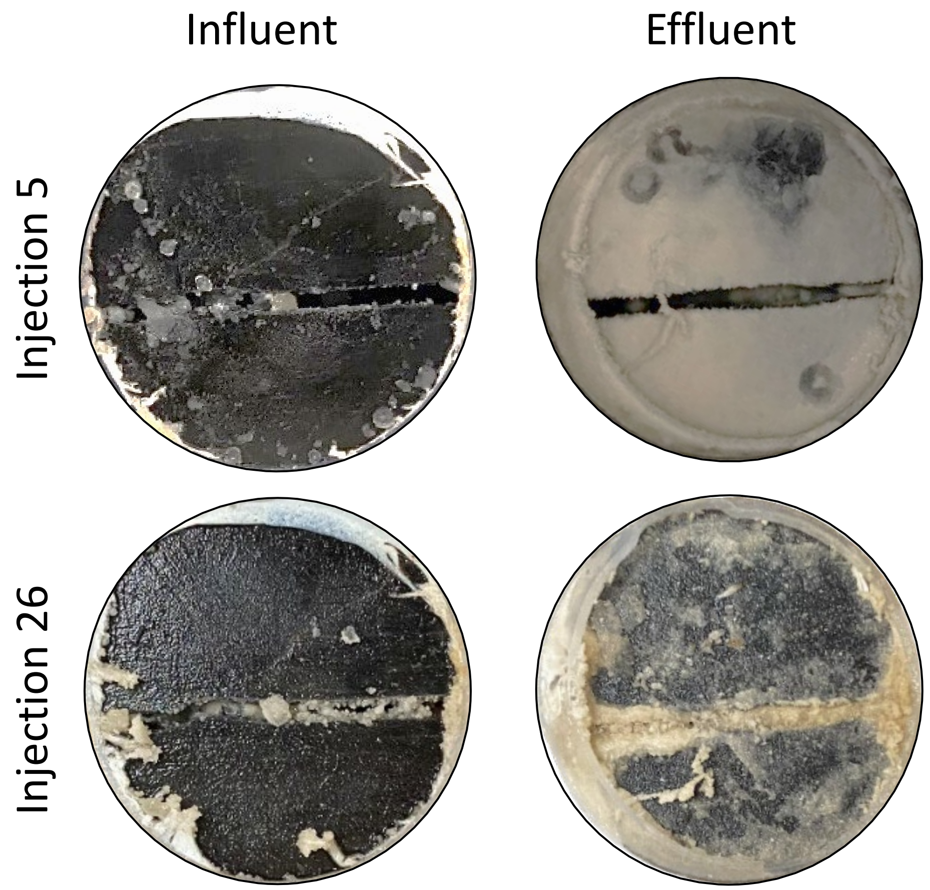


Measuring effect of MICP Treatment:



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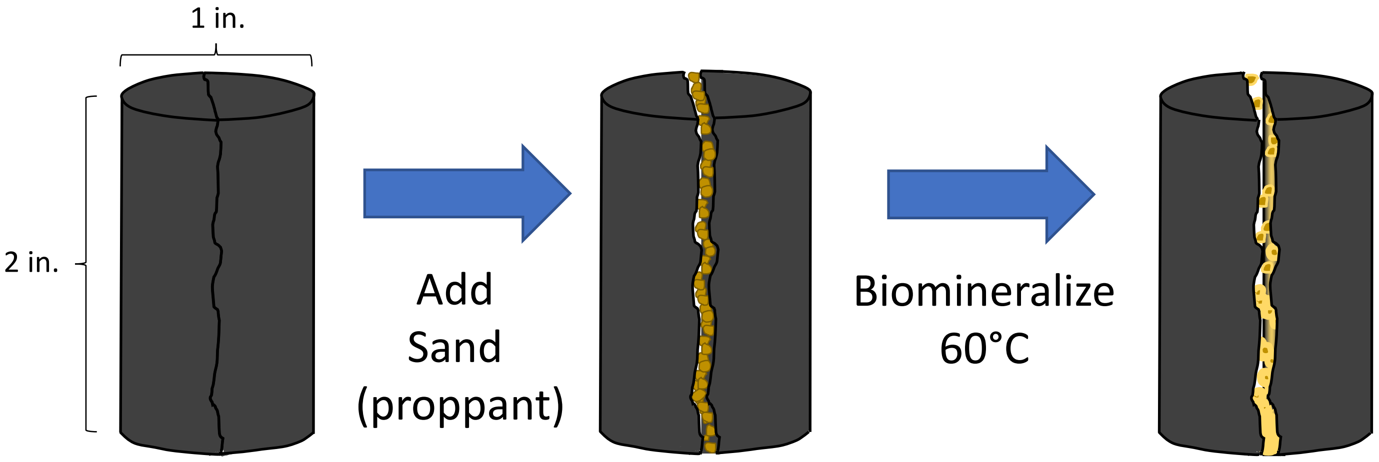
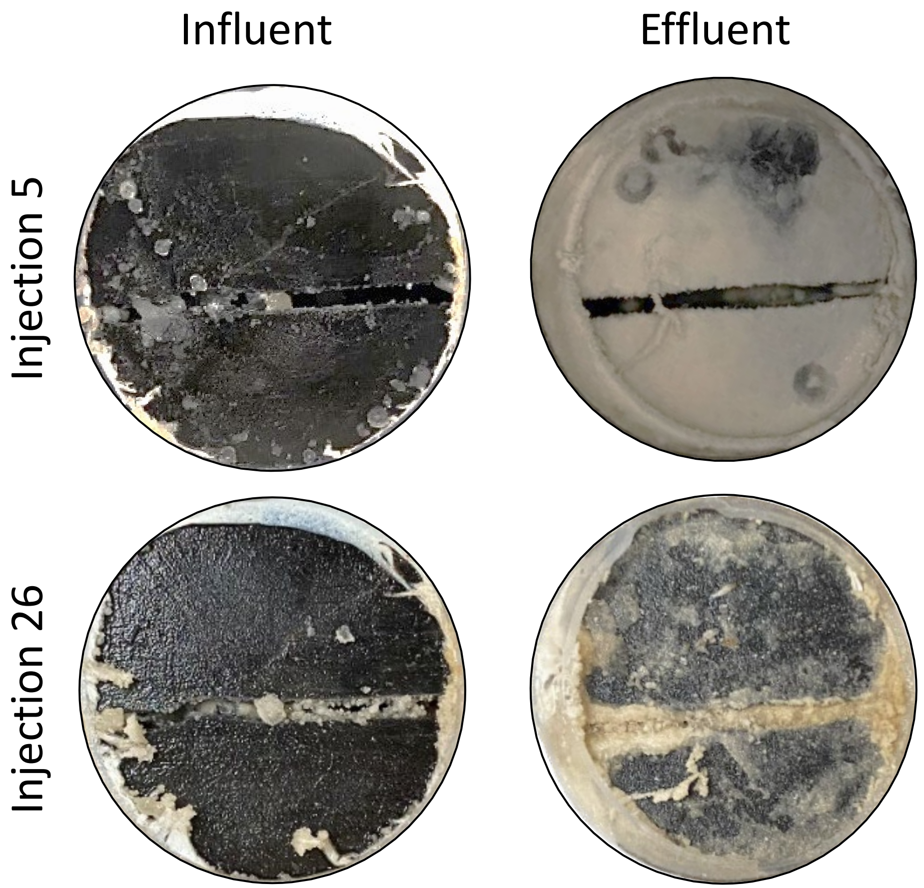


Measuring effect of MICP Treatment:

- Permeability reduction
- Tension testing*
- Extent of biomineralization



*Bedey, Kayla. "Developing Methods to Assess Changes in Mechanical Properties of Shale Modified by Engineered Mineral Precipitation." MS03.

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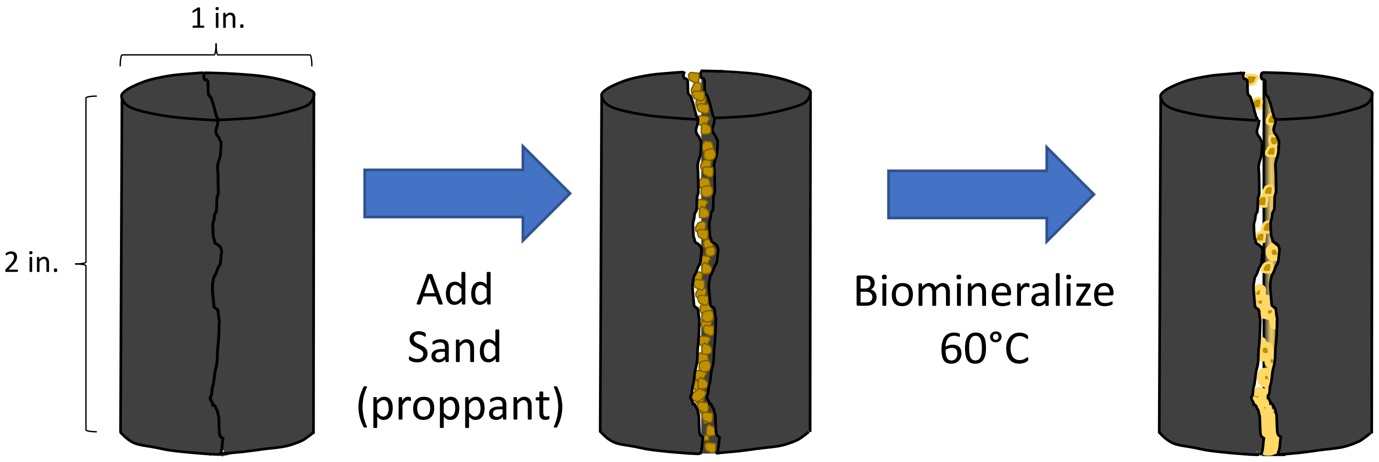

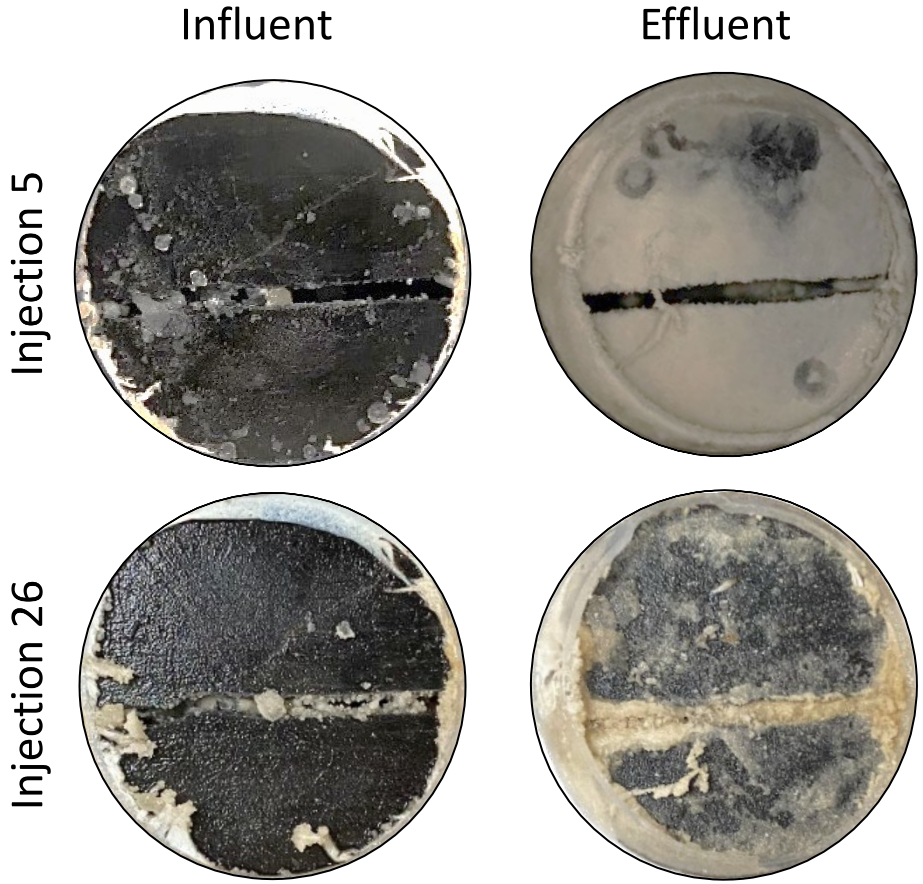

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<u>Non-invasive tools needed (NMR)</u>

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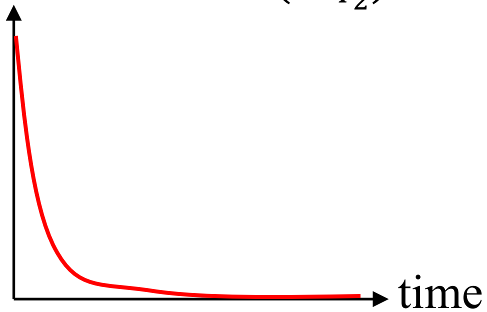
Low-Field Nuclear Magnetic Resonance (NMR)

$$S(t) = S_0 \exp\left(-\frac{t}{T_2}\right)$$



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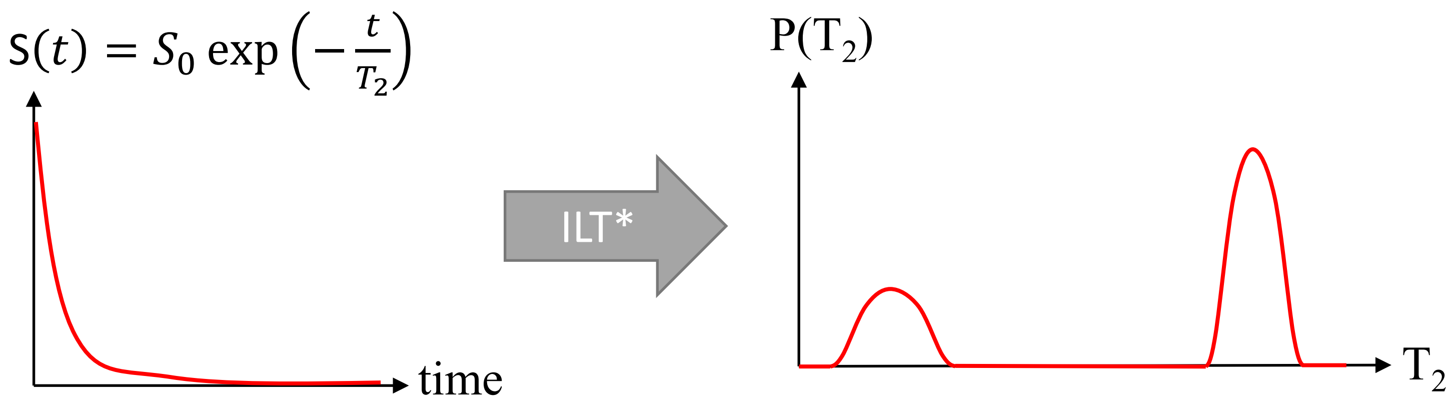

*Inverse Laplace Transform

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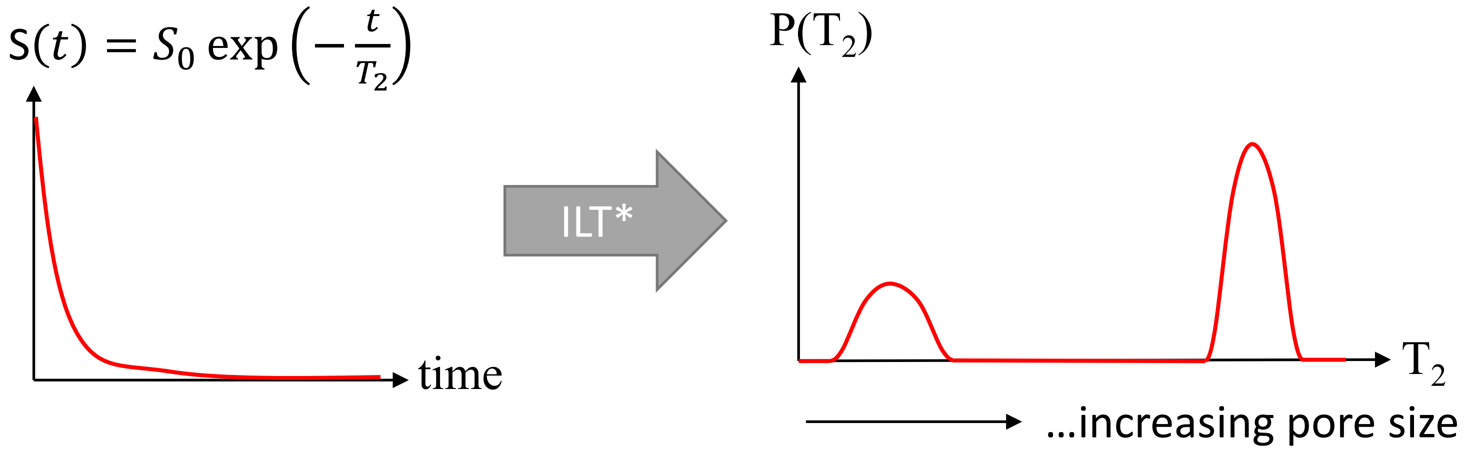

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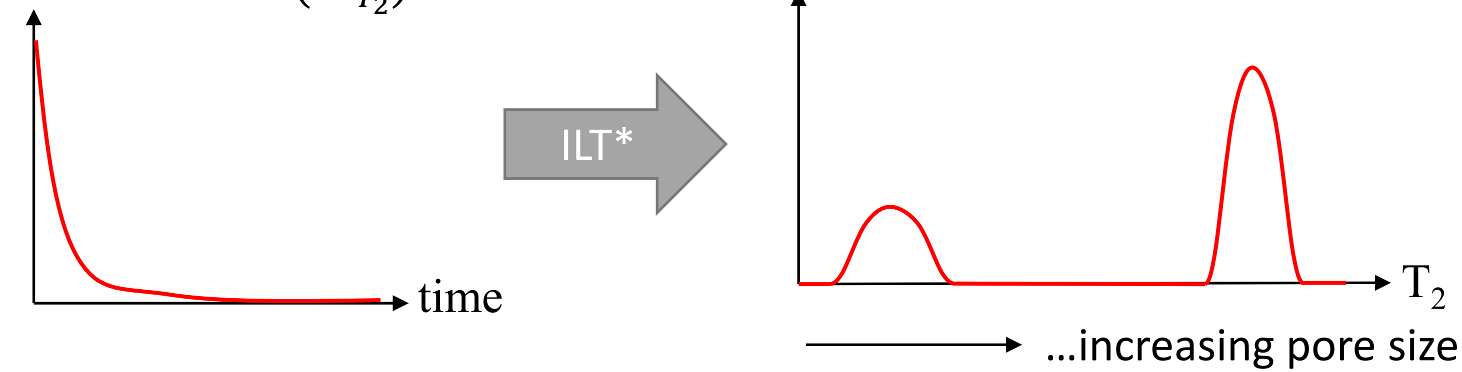

T_2 profiles reveal distribution of pore/fracture sizes.

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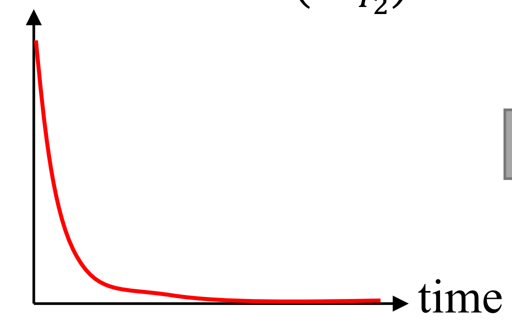

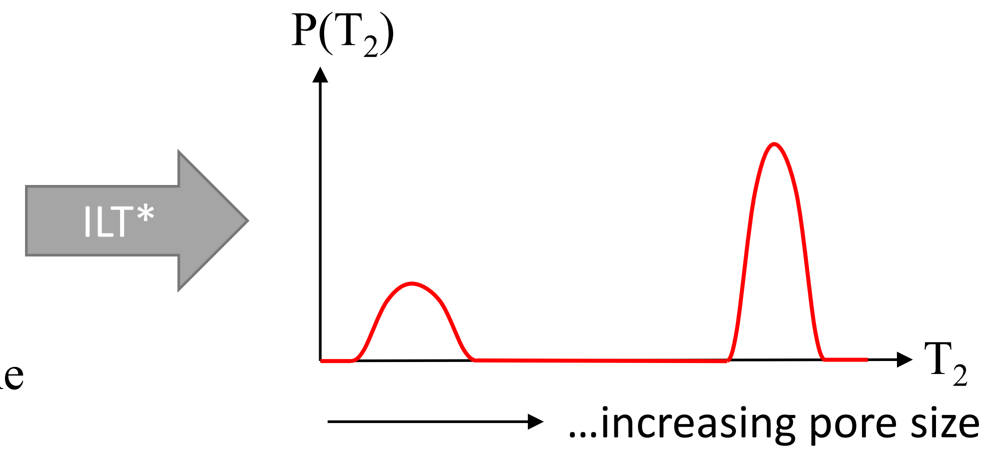

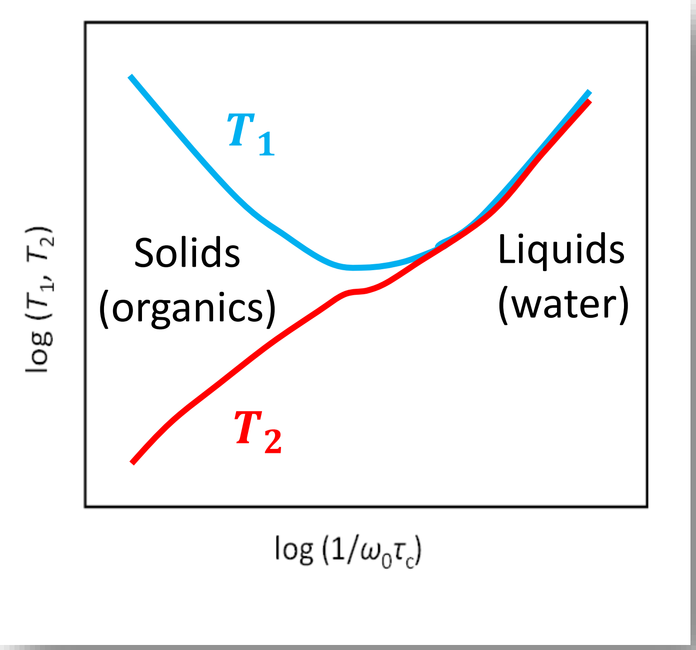

T_1/T_2 Relaxation Profile

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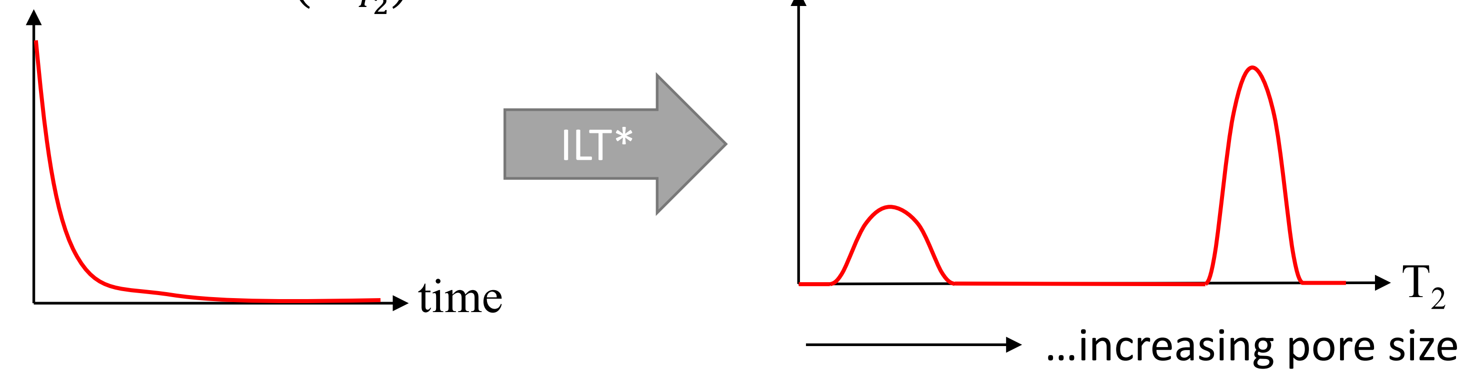

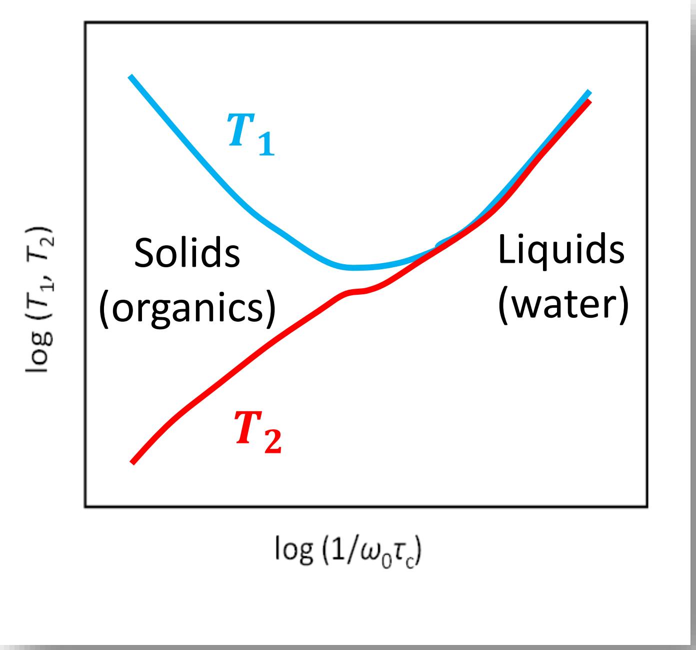

T_1/T_2 Relaxation Profile

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T_1-T_2 correlations help separate signal from water and organics.

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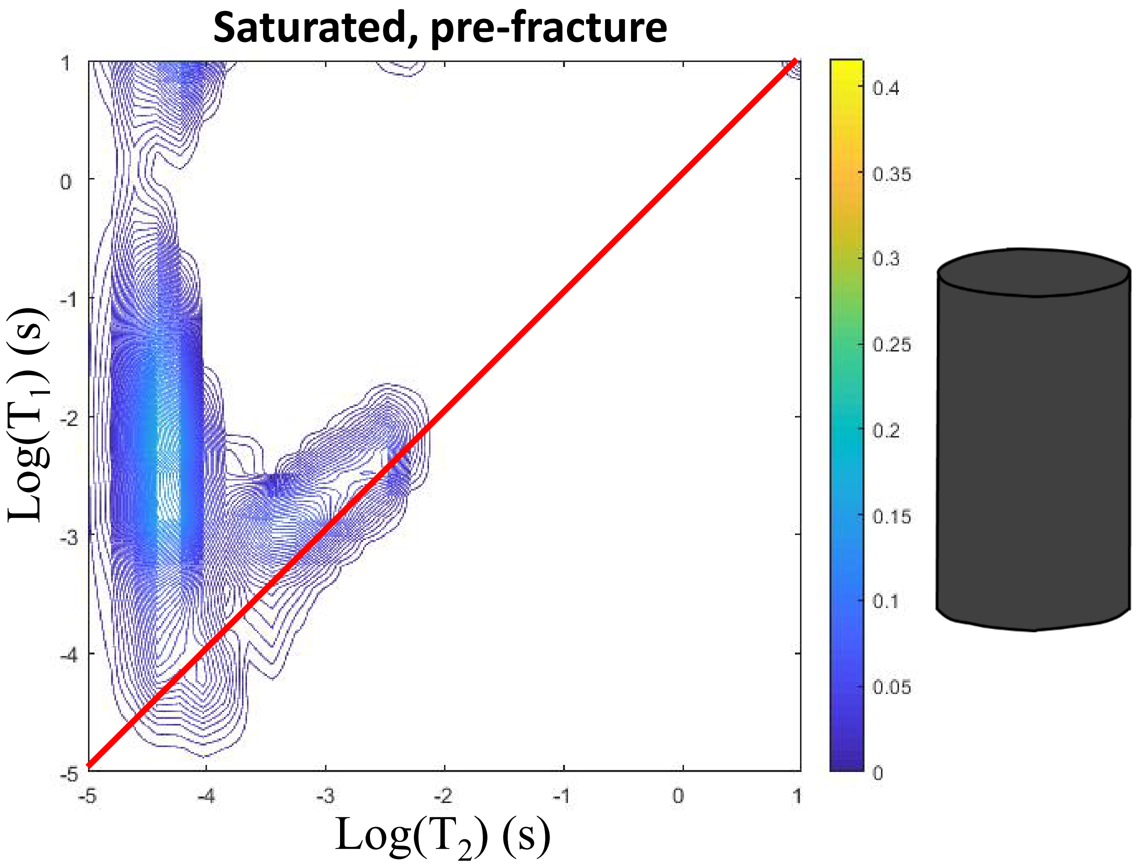
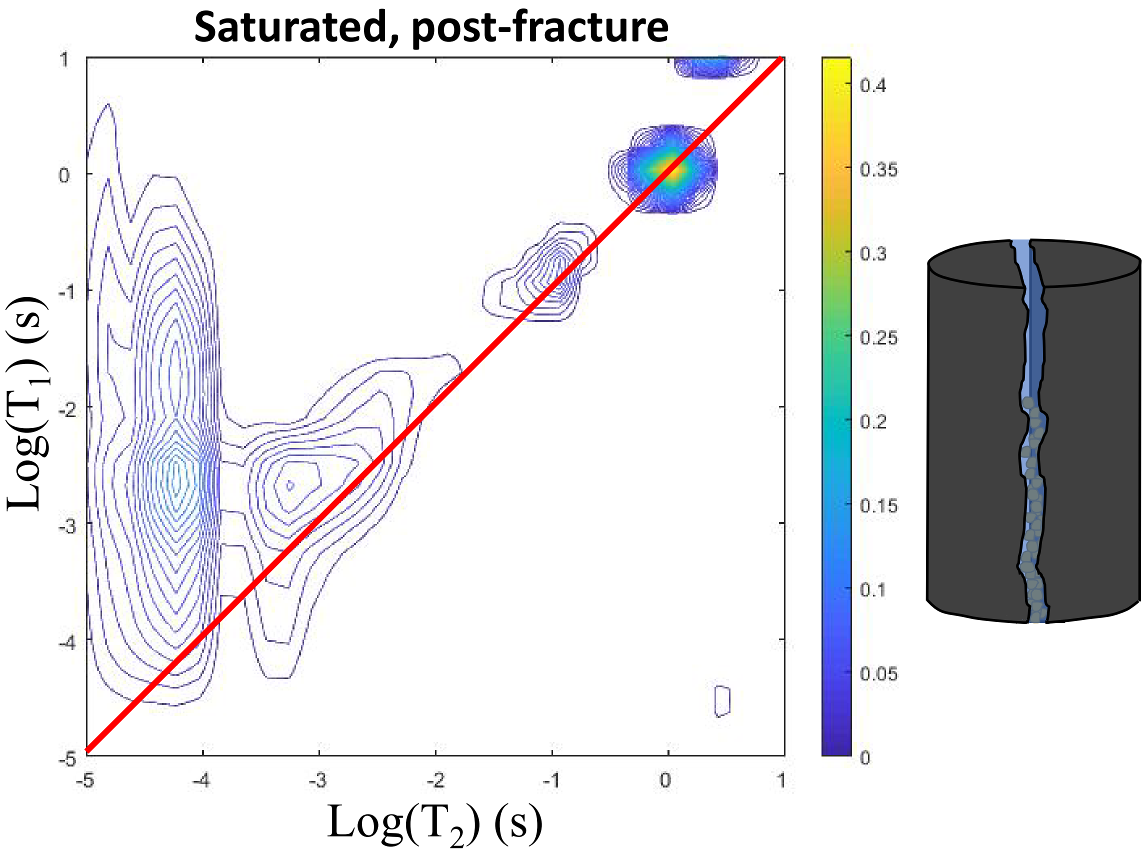
T_1-T_2 correlation



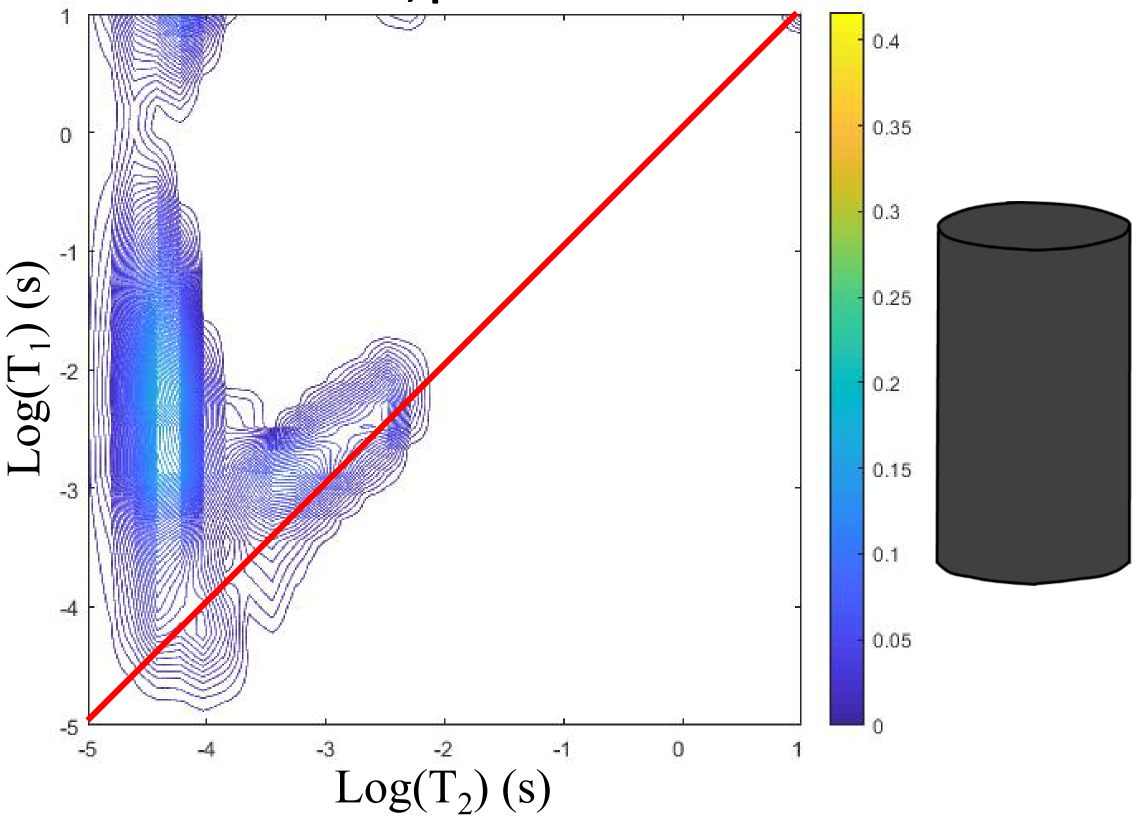


T_1-T_2 correlation

Hydrogen populations:

Bitumen & Kerogen | Structural & adsorbed water | Oil | Pore water | Fracture water

Saturated, pre-fracture



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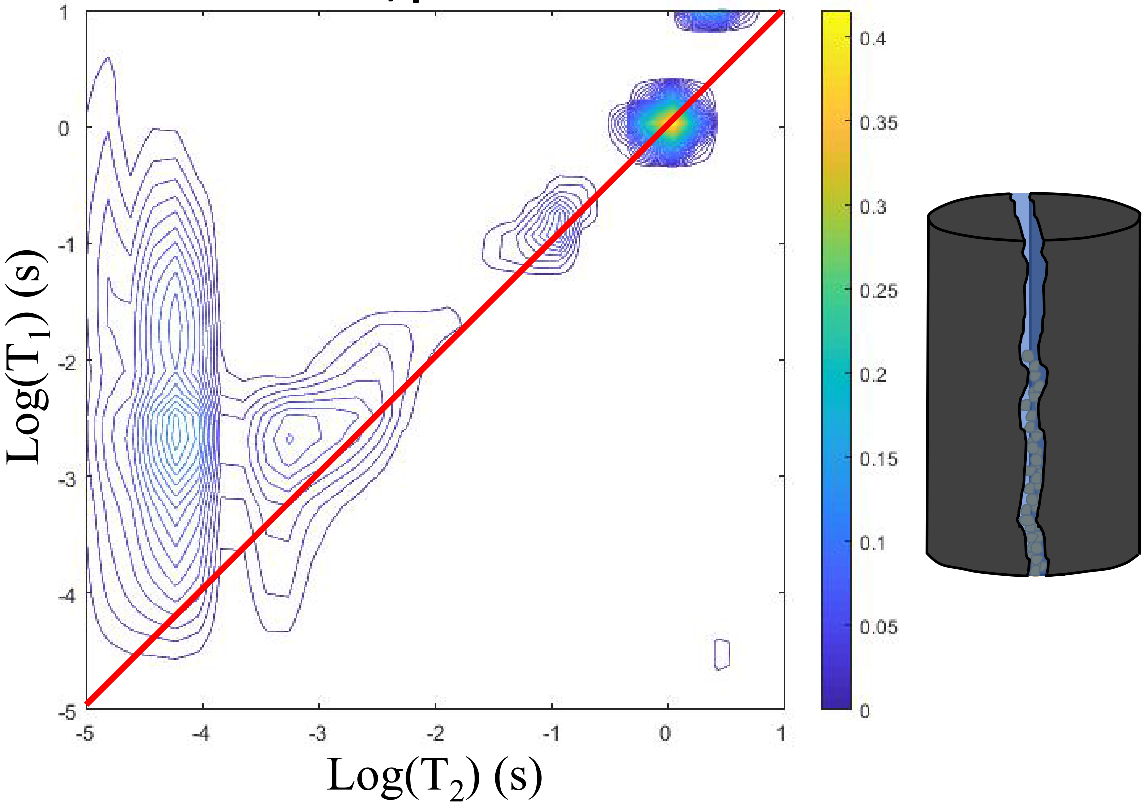

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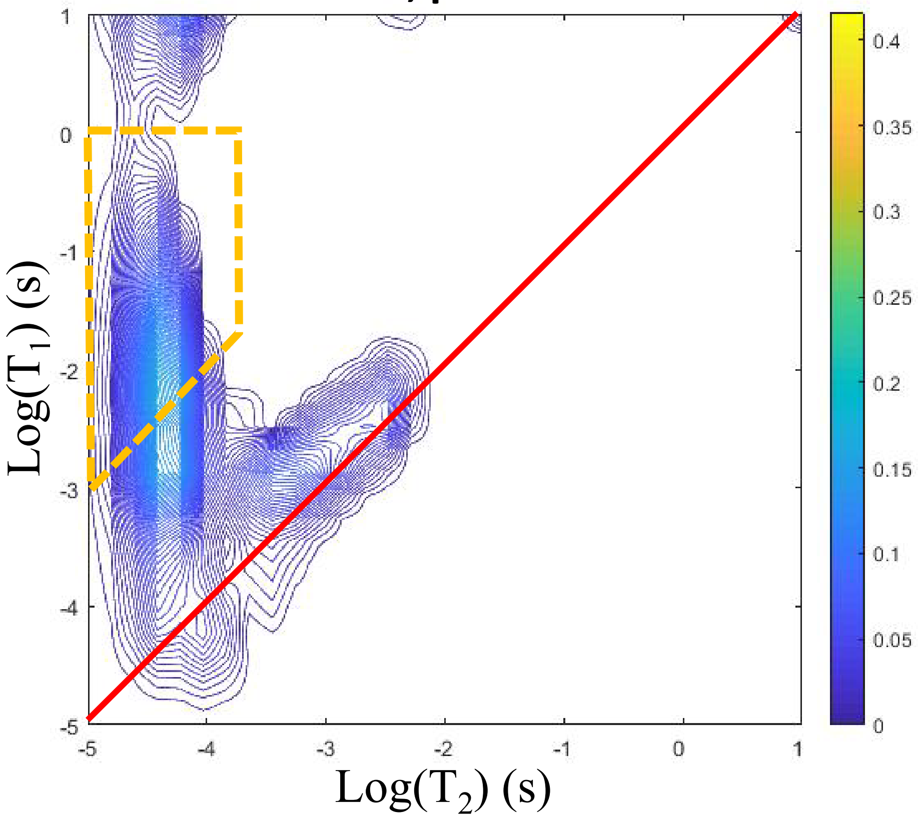

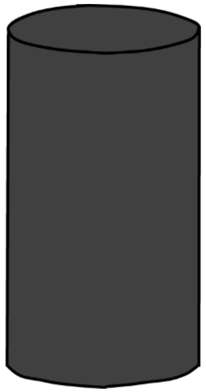

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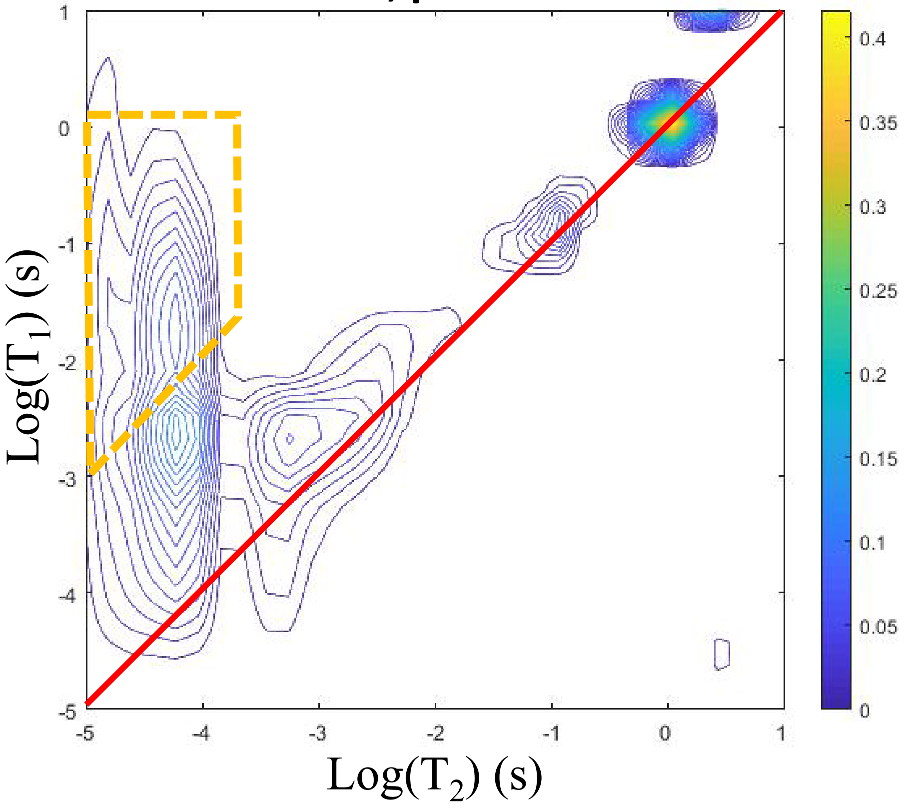

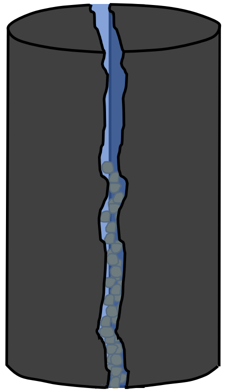

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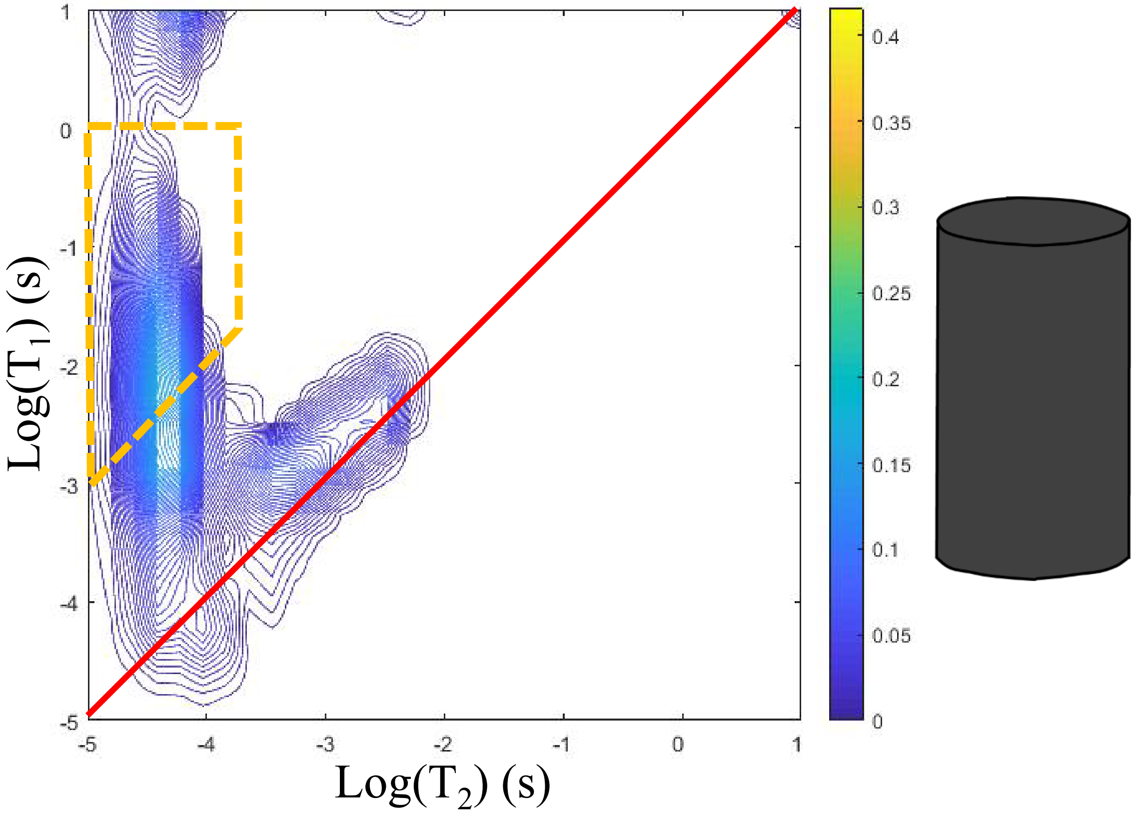

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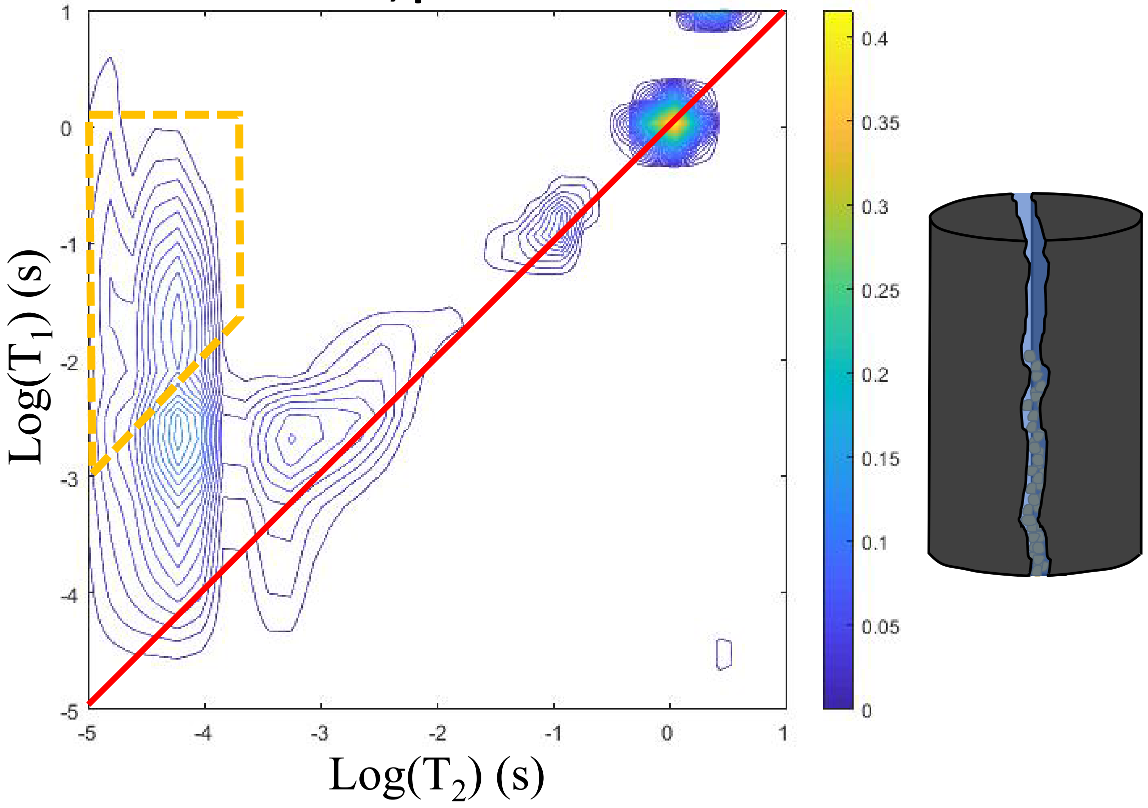

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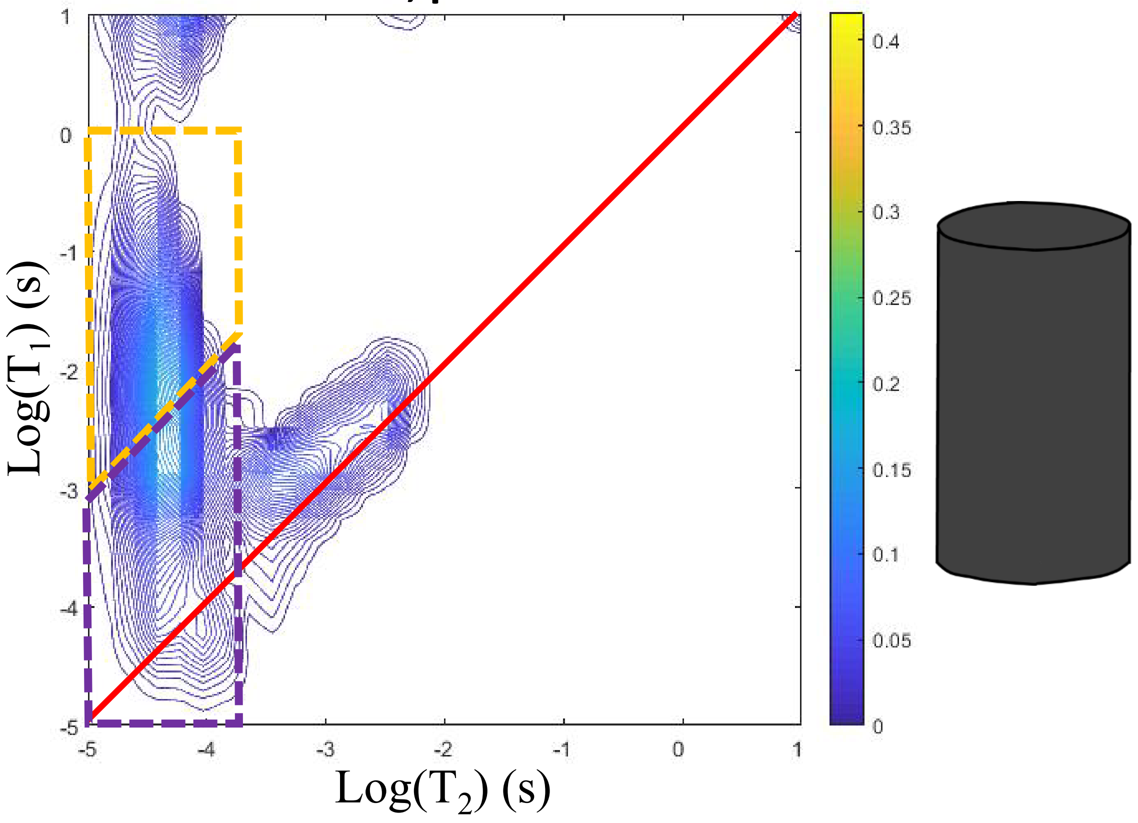

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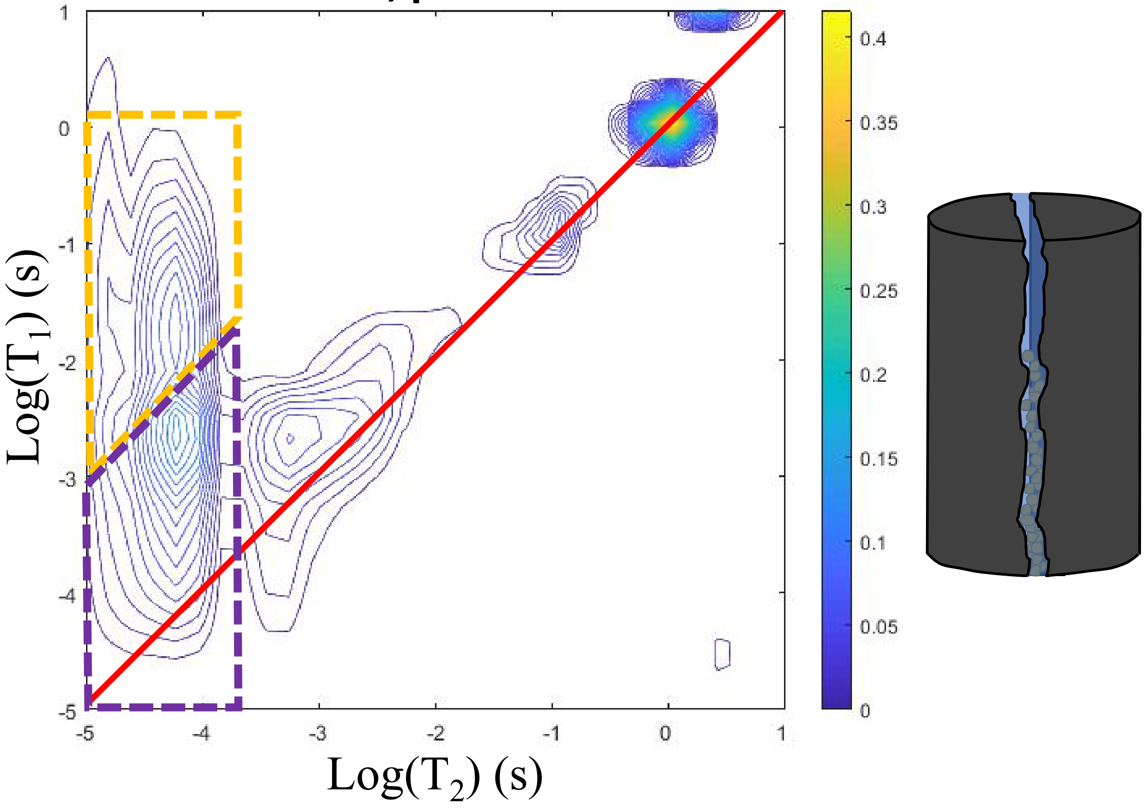

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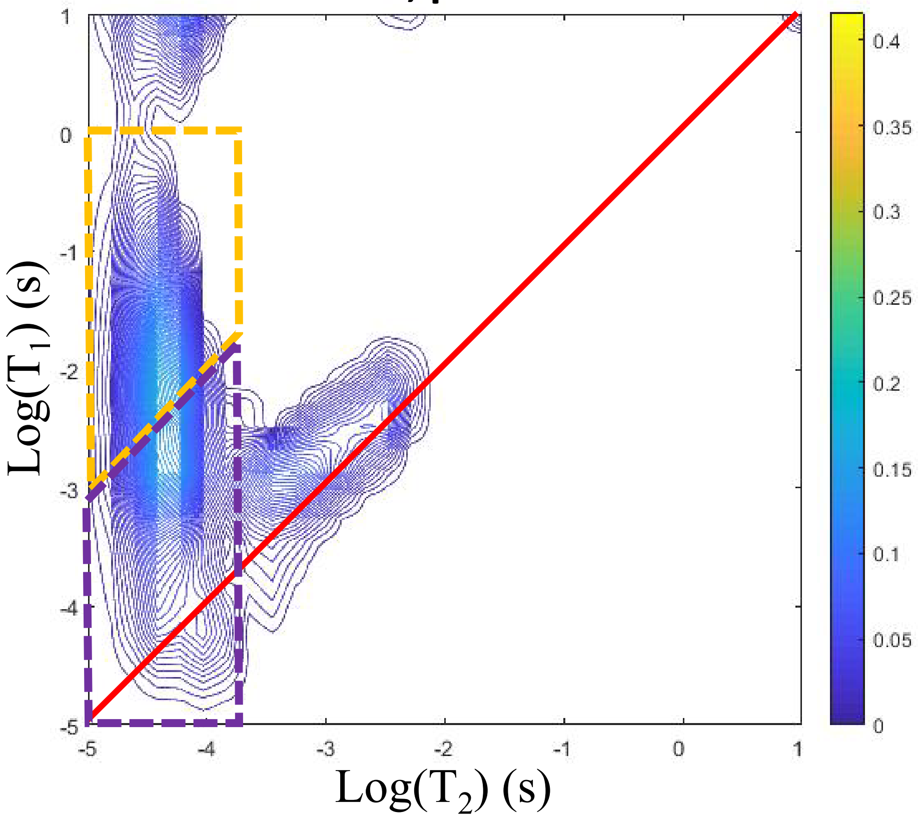

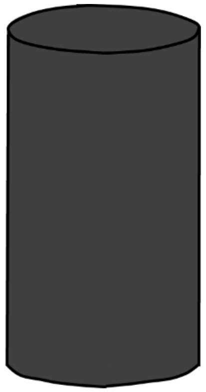

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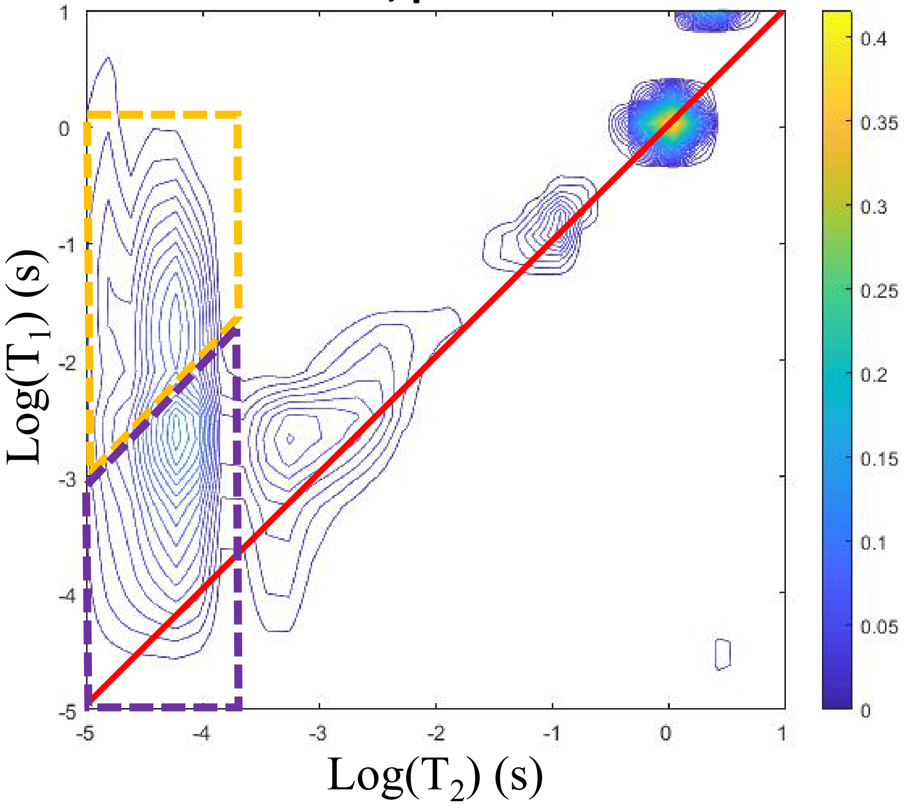

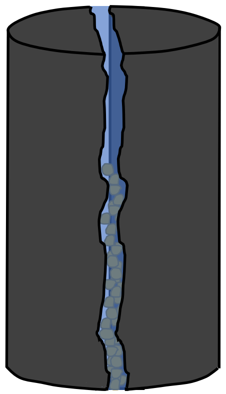

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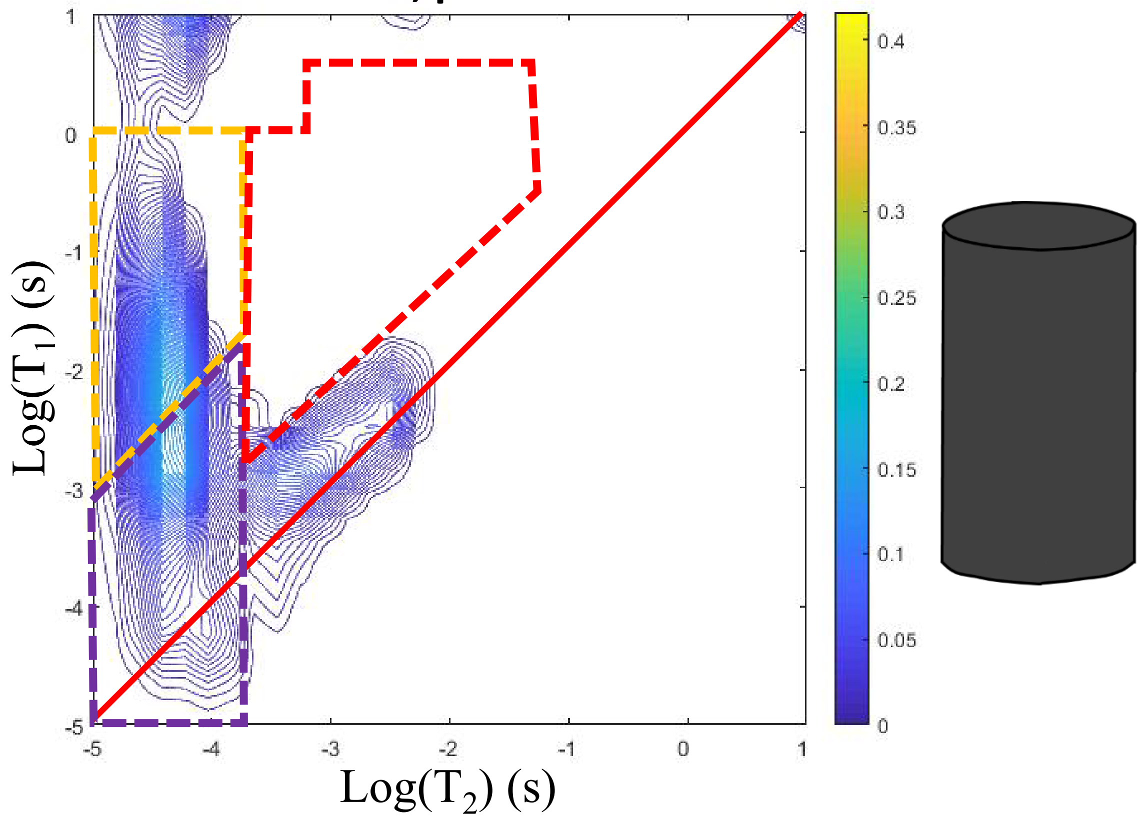

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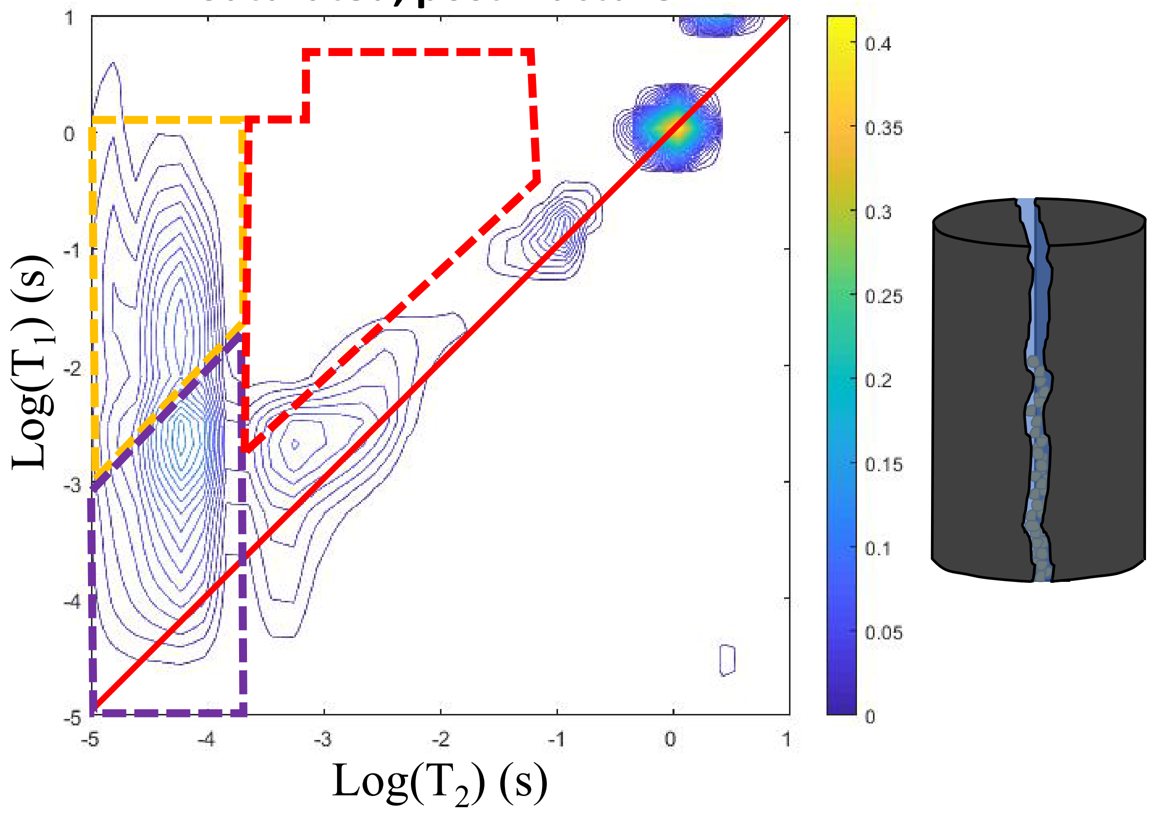

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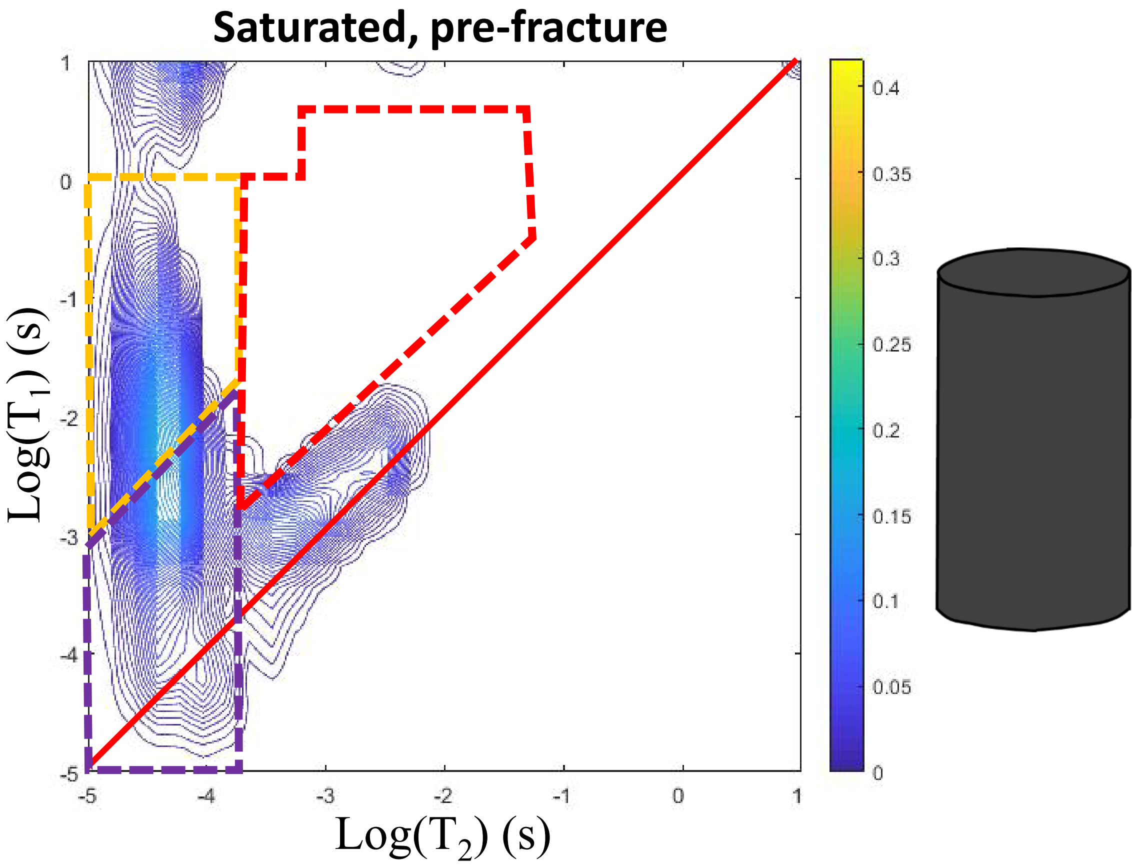

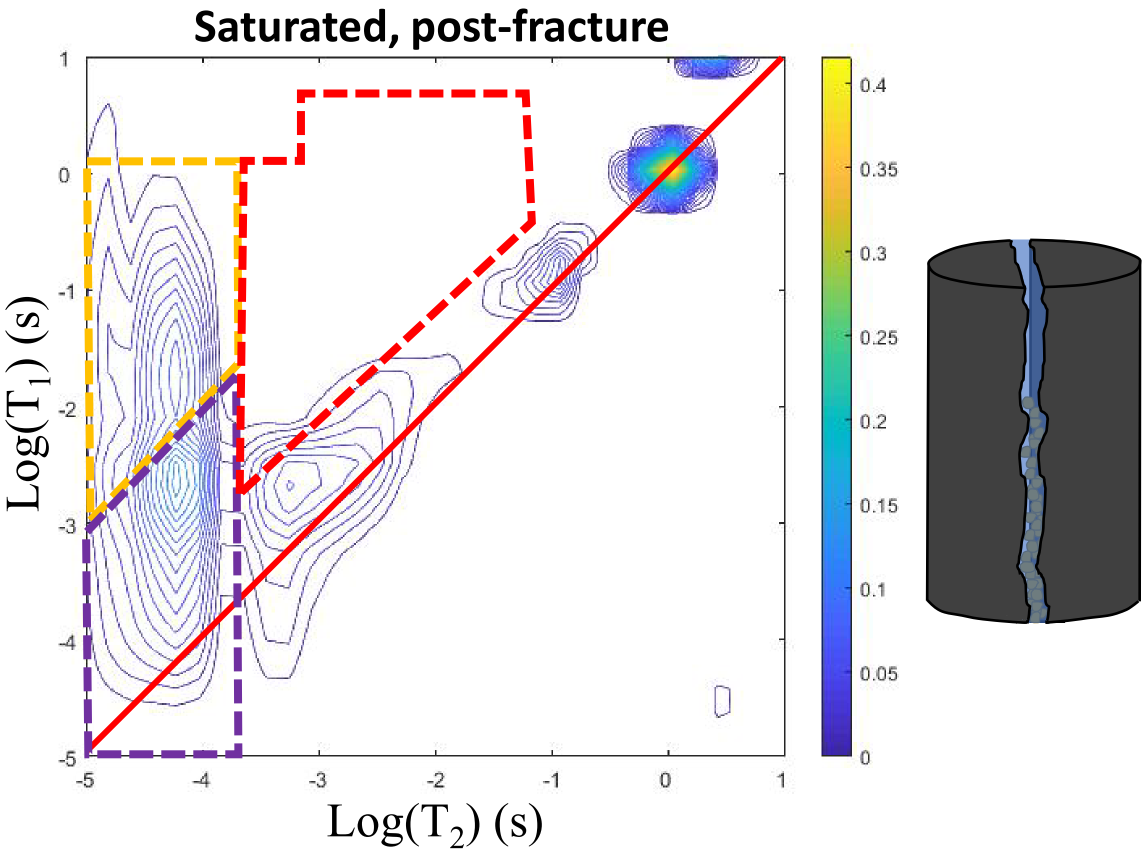

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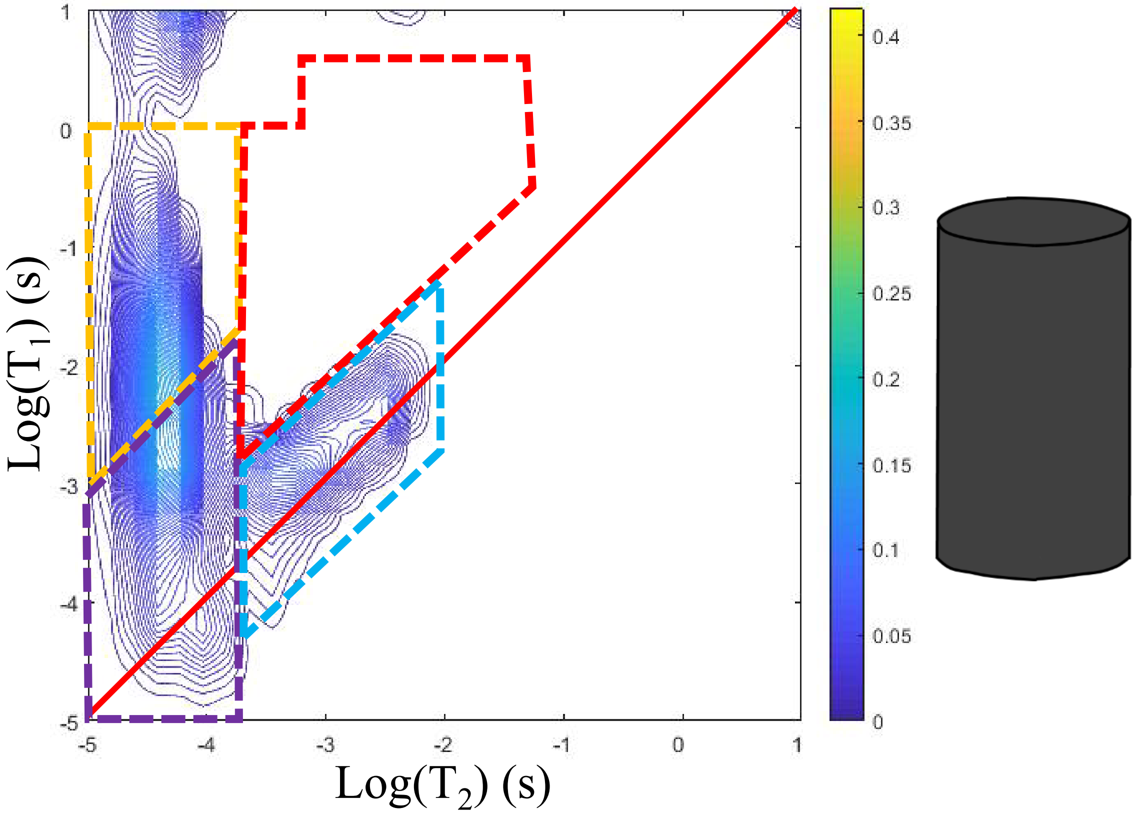

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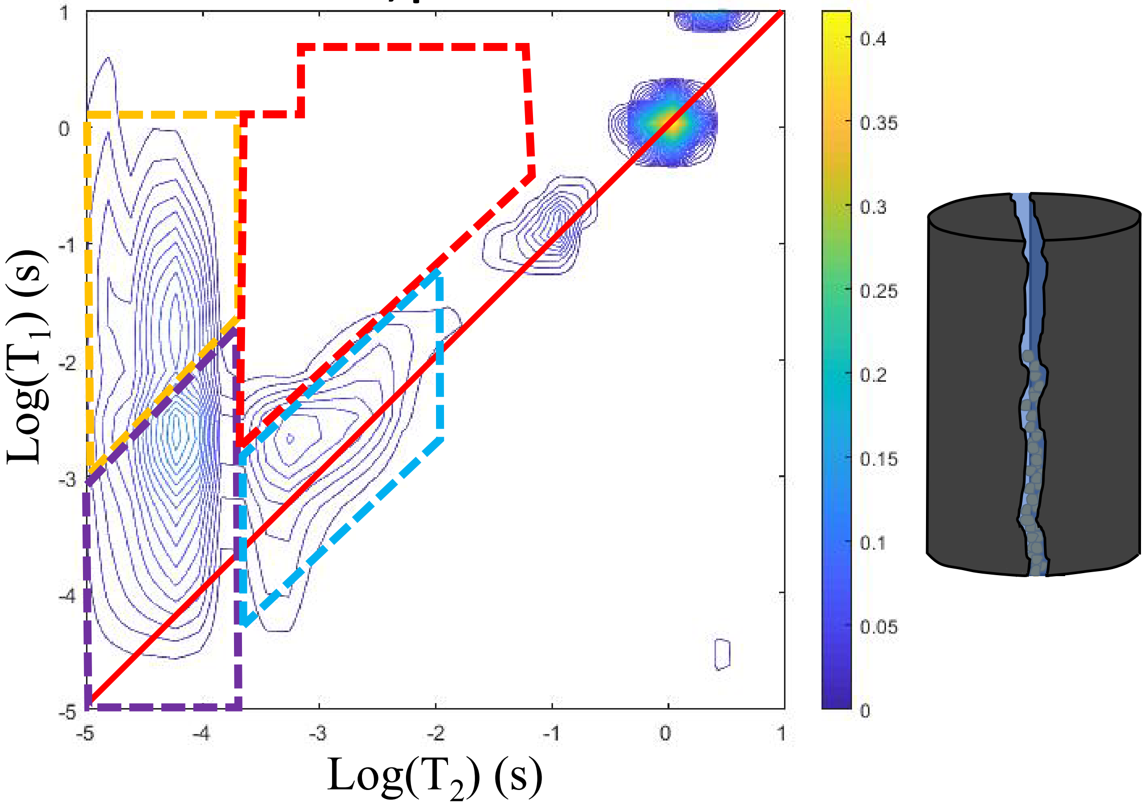

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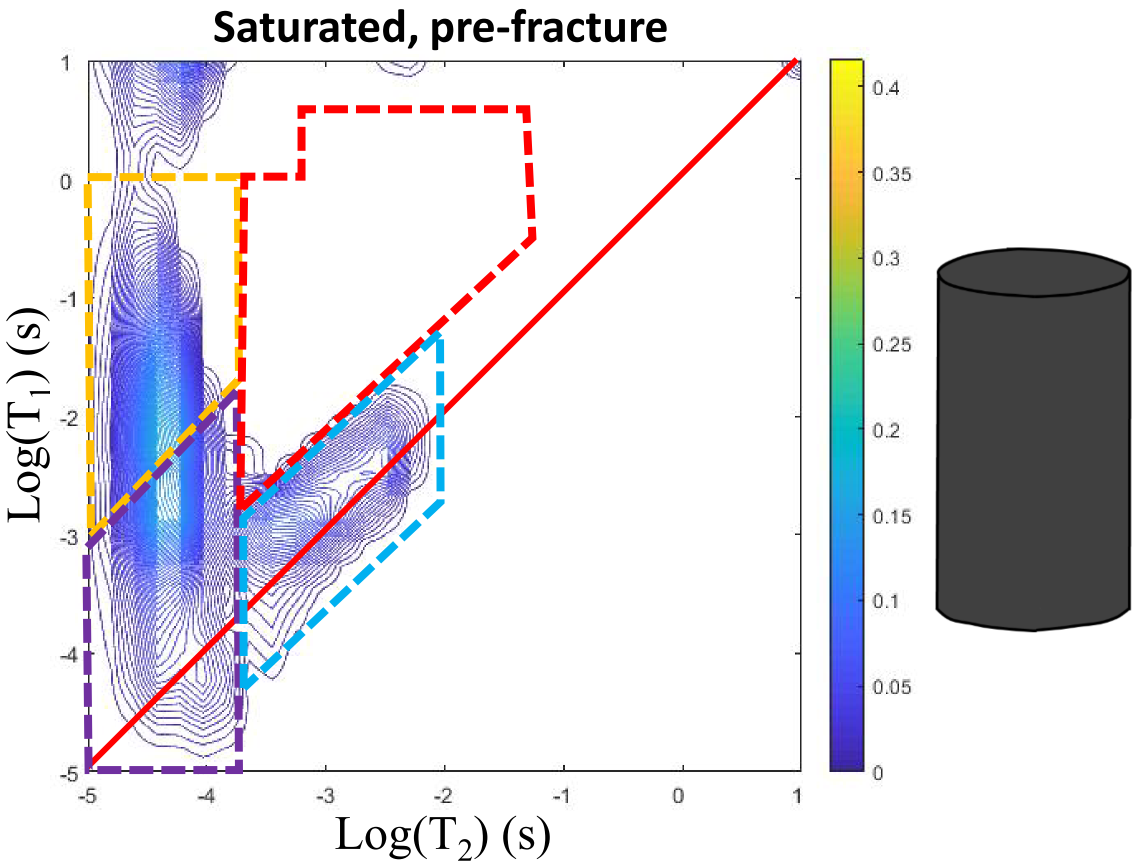

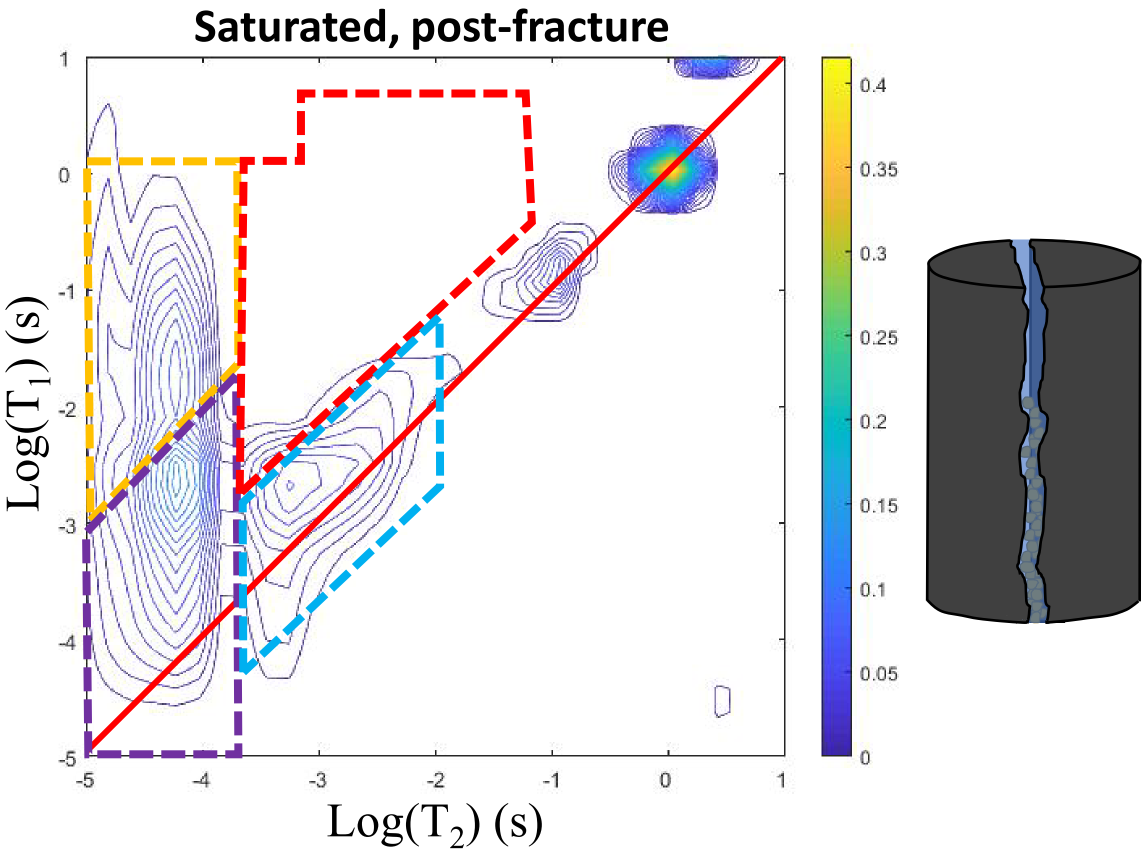

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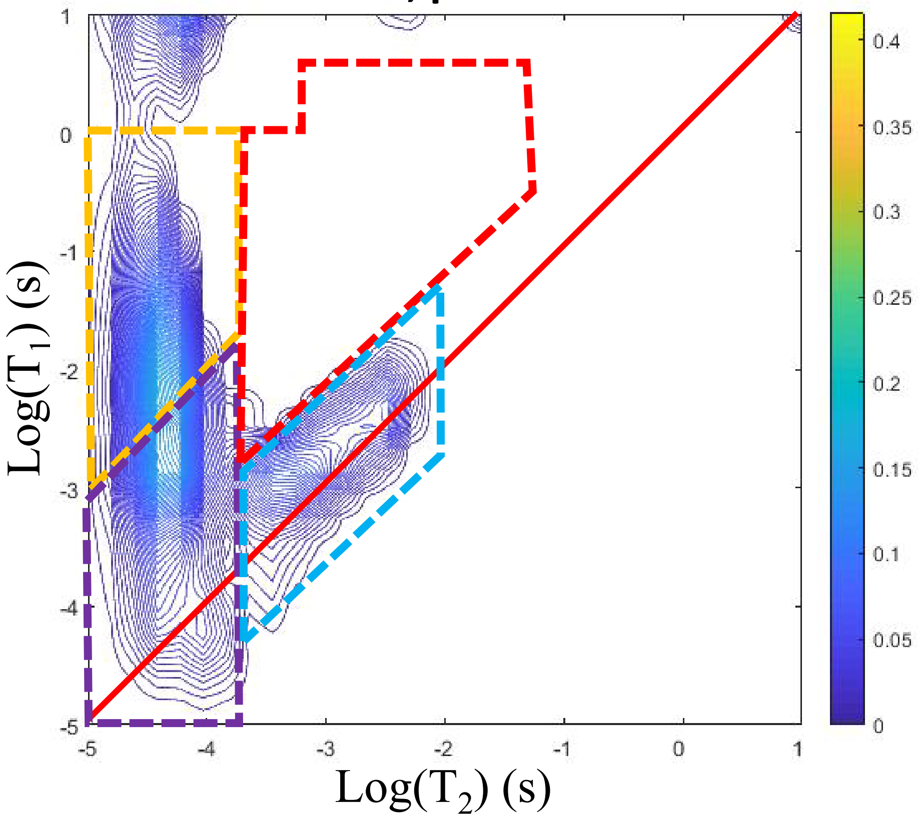

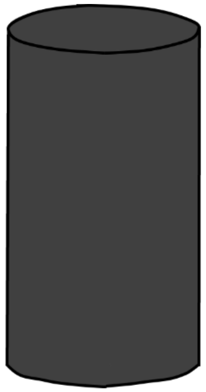

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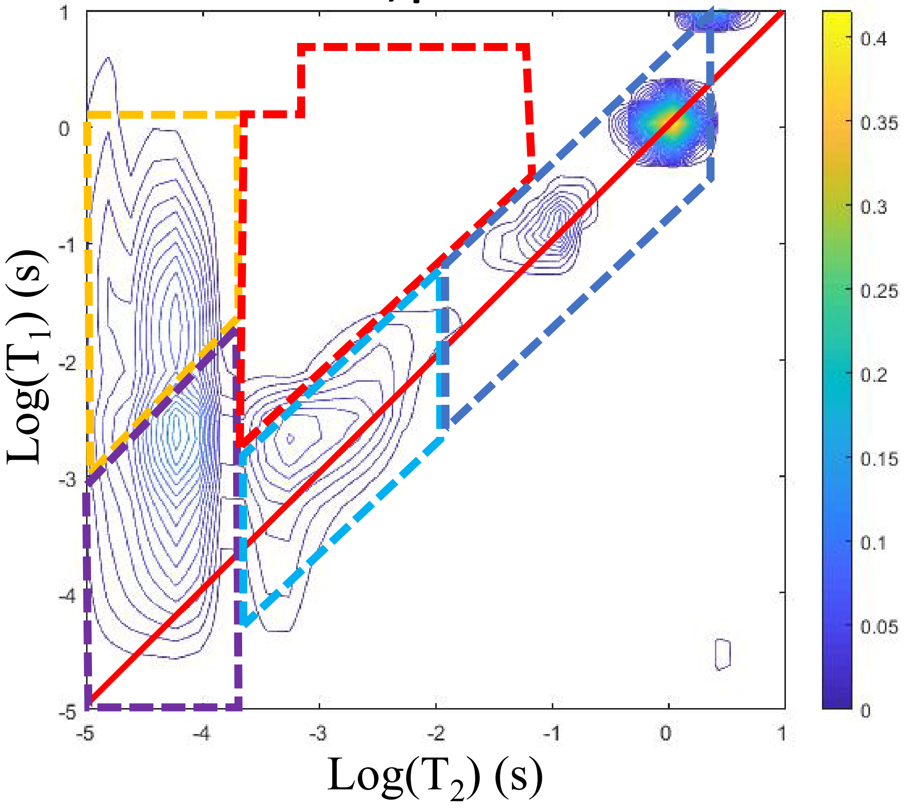

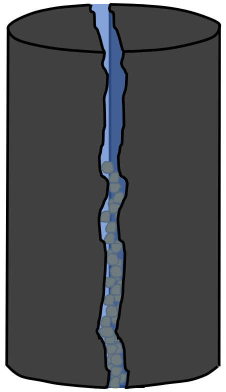

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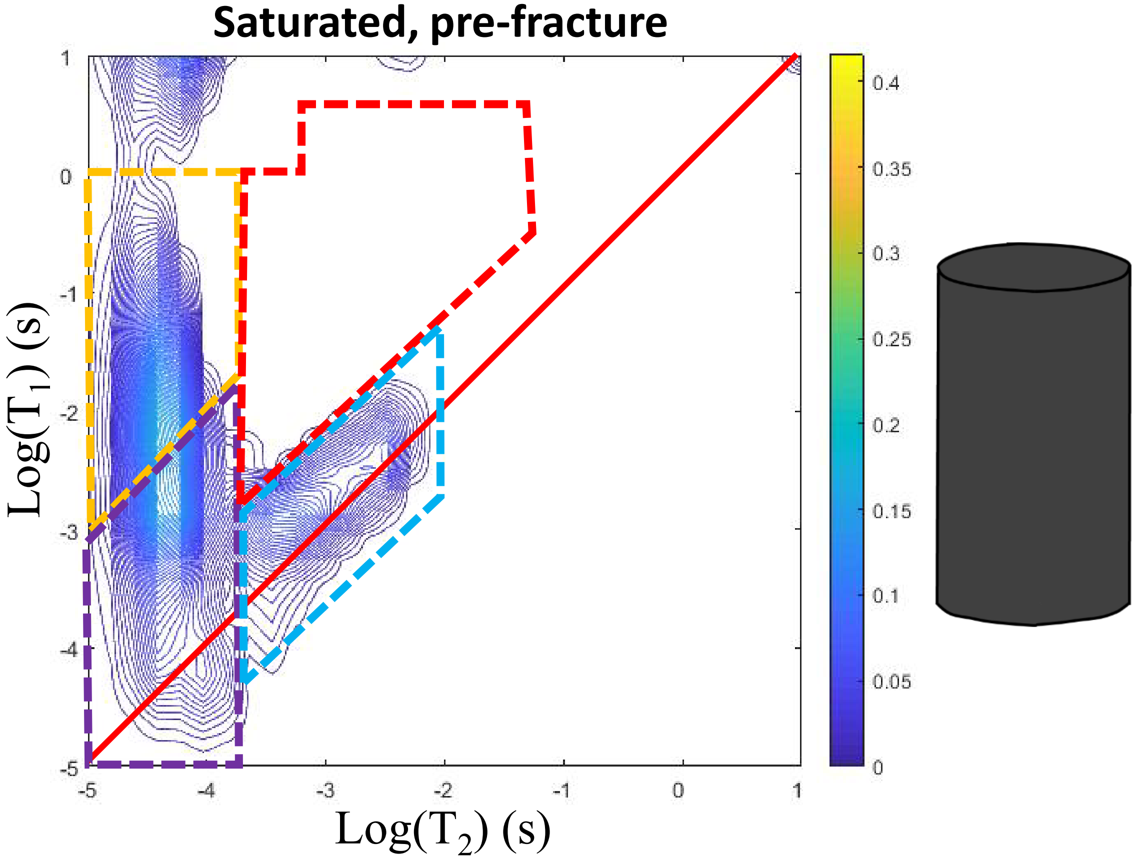
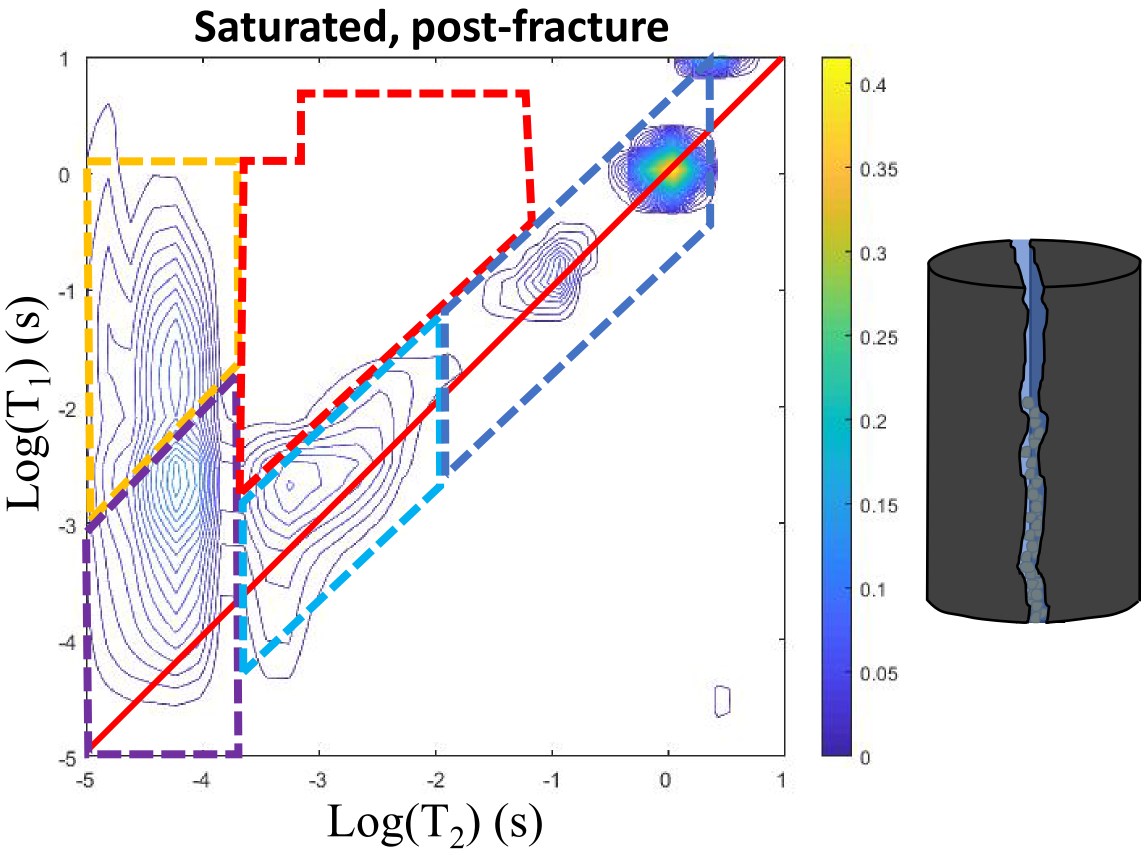
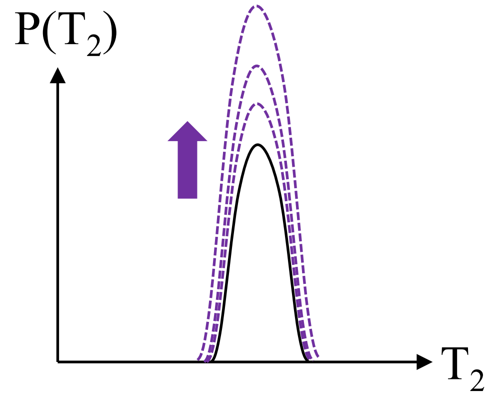
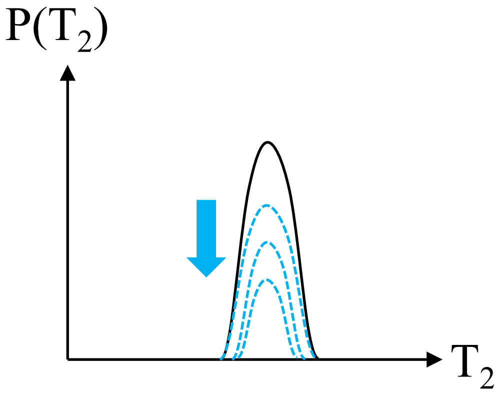




Interpreting NMR signal changes



More water in pore/fracture



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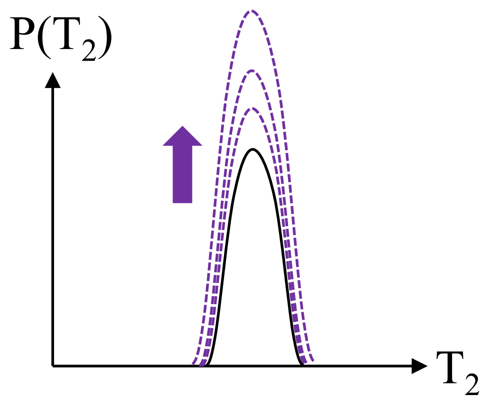

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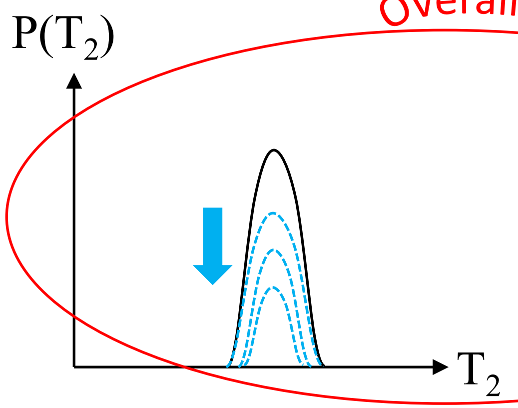
Overall reduction in signal



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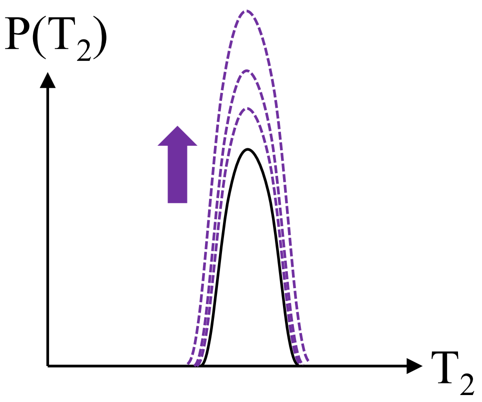

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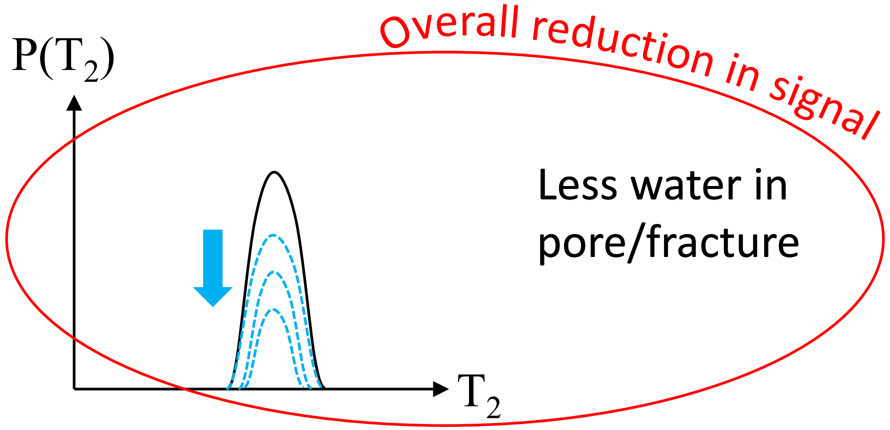

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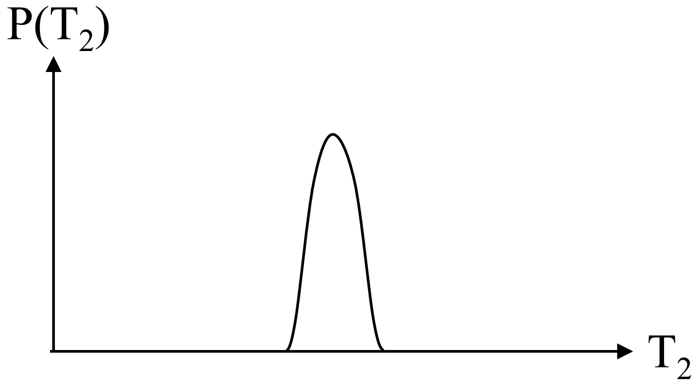
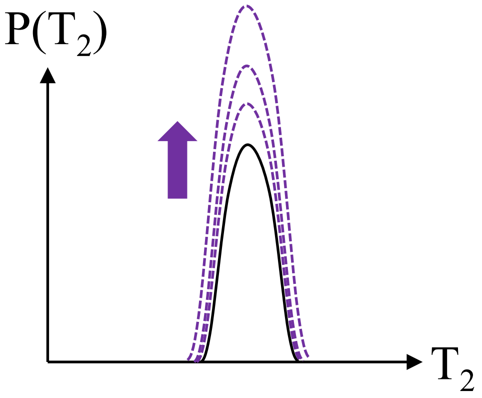


$$\frac{1}{T_2} = \frac{1}{T_{2,\,Bulk}} + \boldsymbol{\rho_2}\left(\frac{S}{V}\right)$$

Surface relaxivity of pore/fracture dominates T_2 relaxation

Interpreting NMR signal changes



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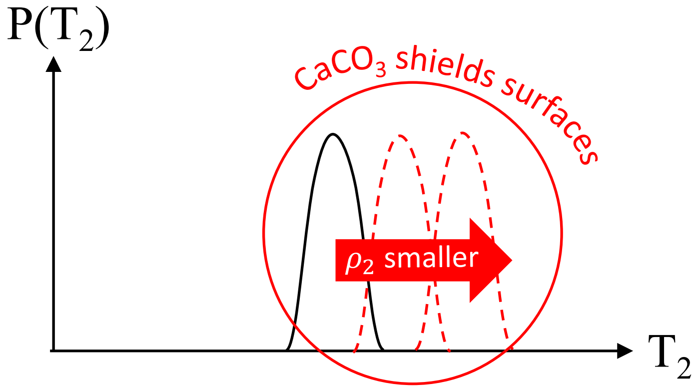
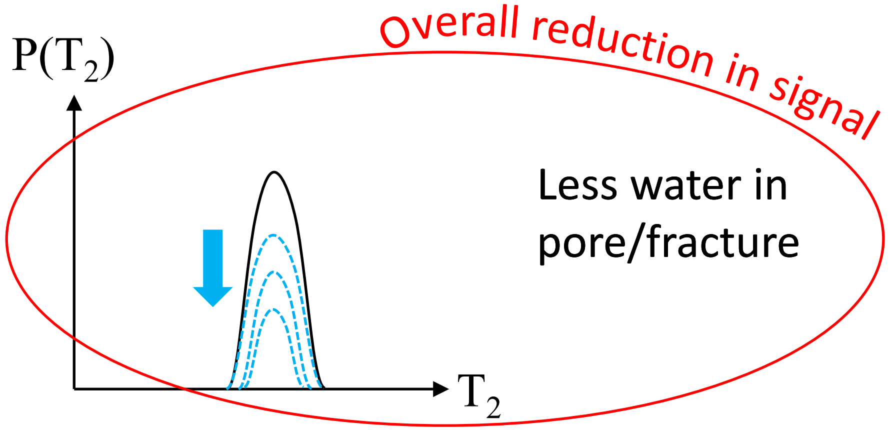
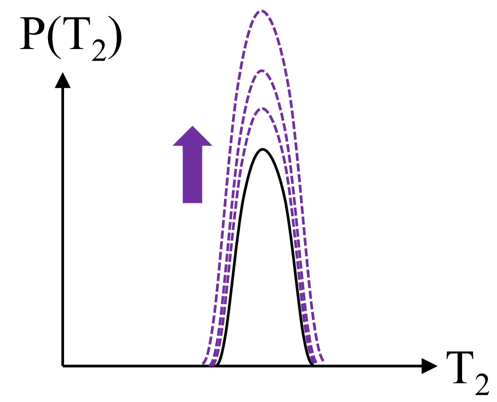


$$\frac{1}{T_2} = \frac{1}{T_{2,\,Bulk}} + \boldsymbol{\rho_2}\left(\frac{S}{V}\right)$$

Surface relaxivity of pore/fracture dominates T$_2$ relaxation



Interpreting NMR signal changes



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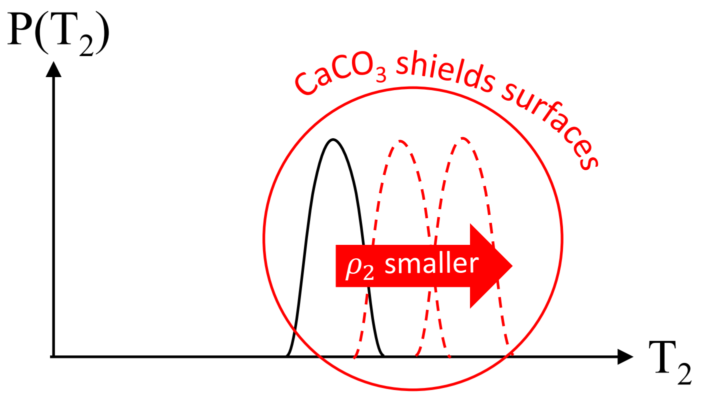

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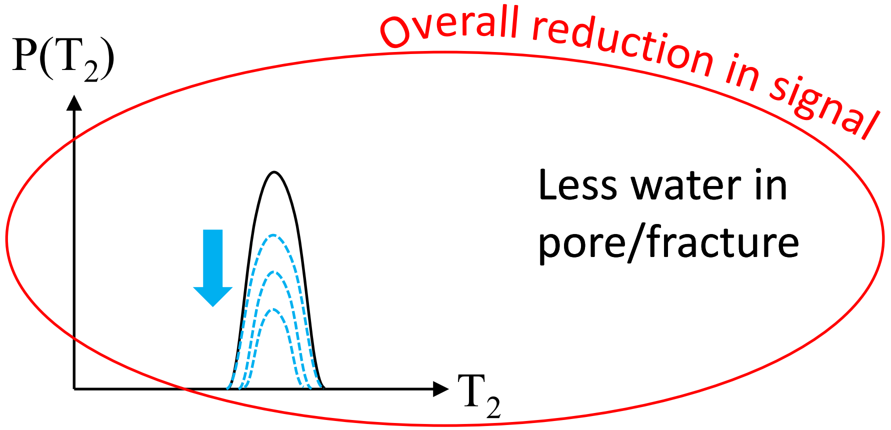

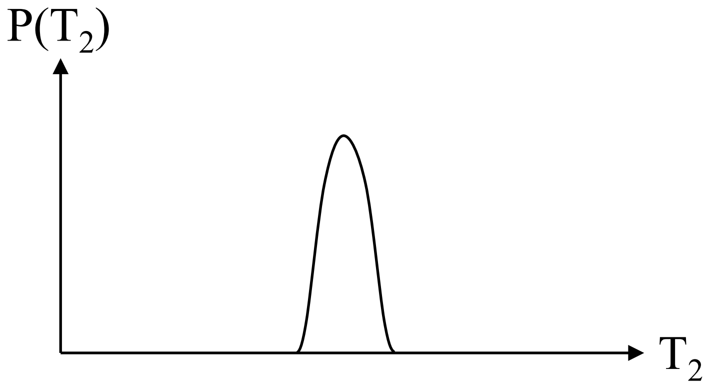

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Size of pore/fracture dominates T_2 relaxation

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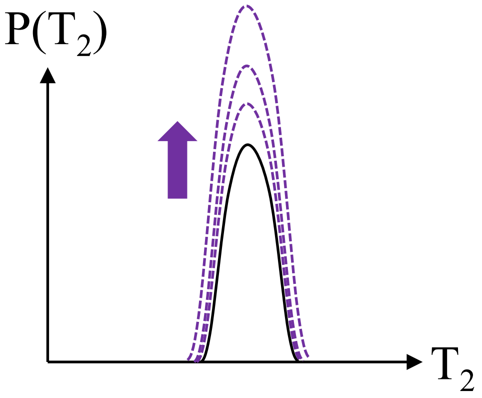

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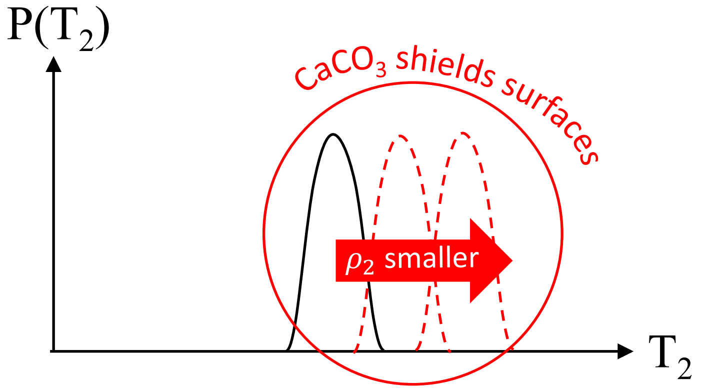

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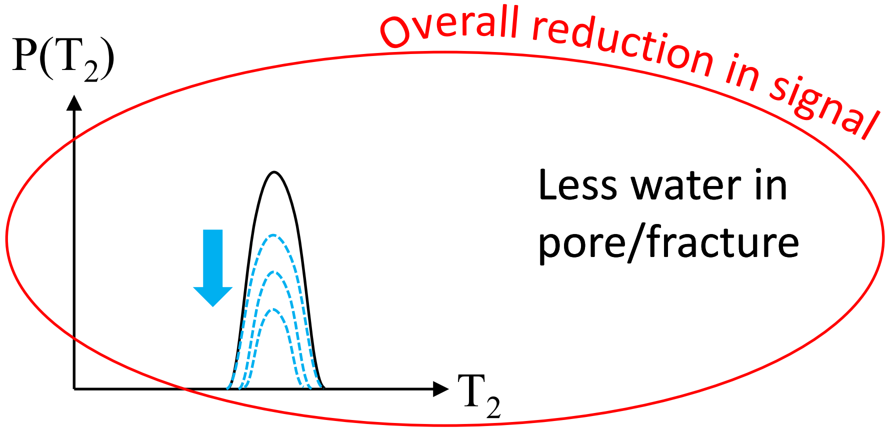

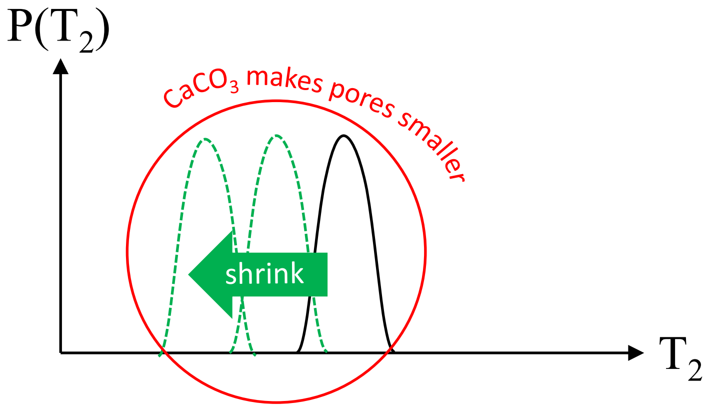

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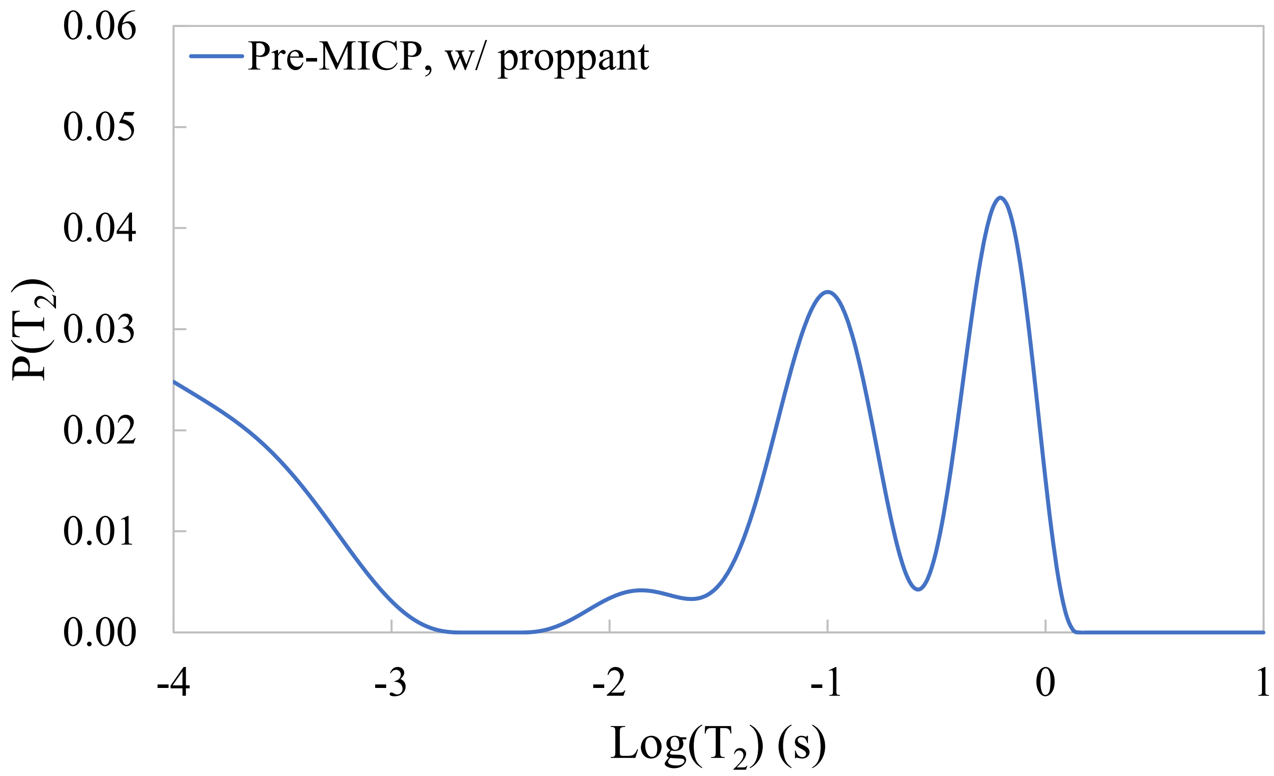
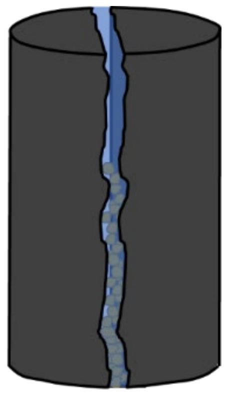
T_2 distribution

Three water populations appear in fracture.

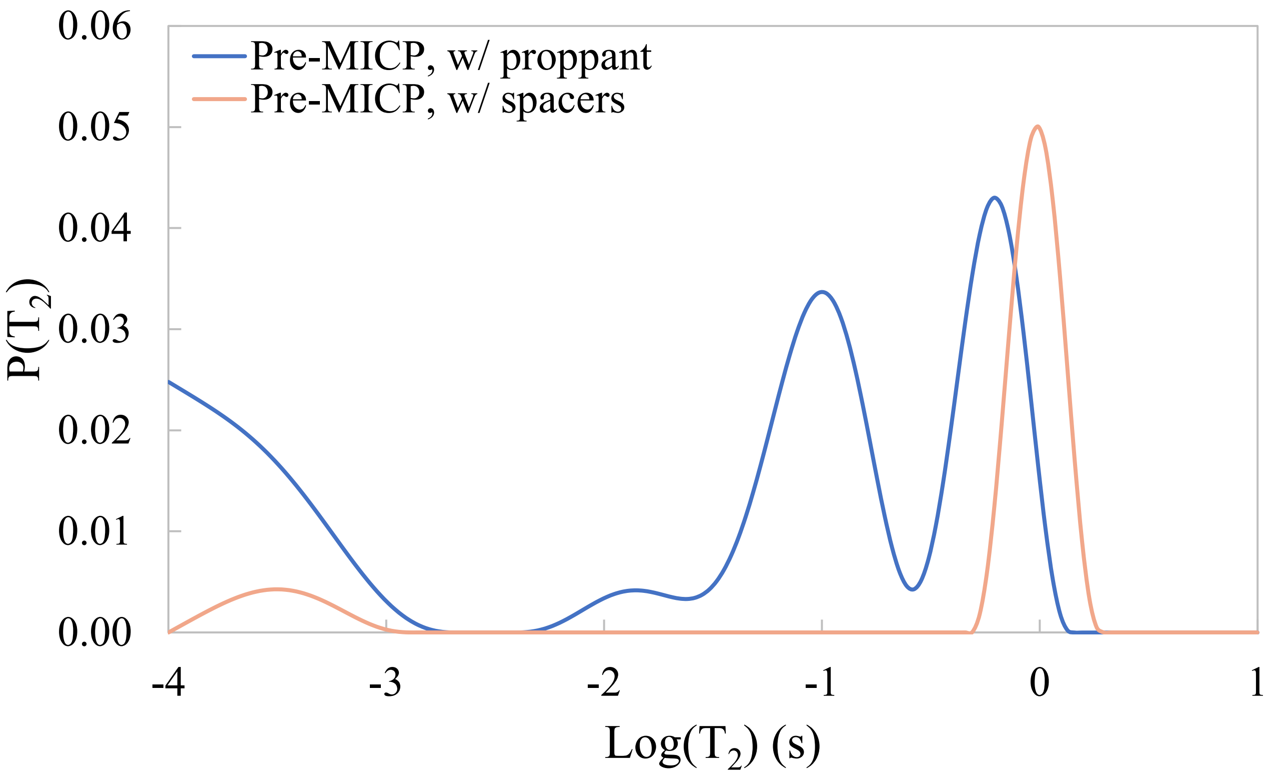


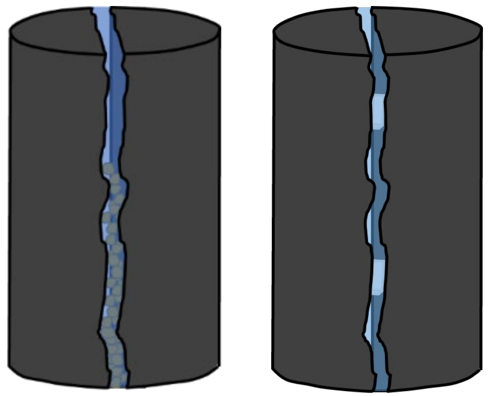


Pre-MICP
w/ proppant

T_2 distribution

Multiple water populations created by proppant.





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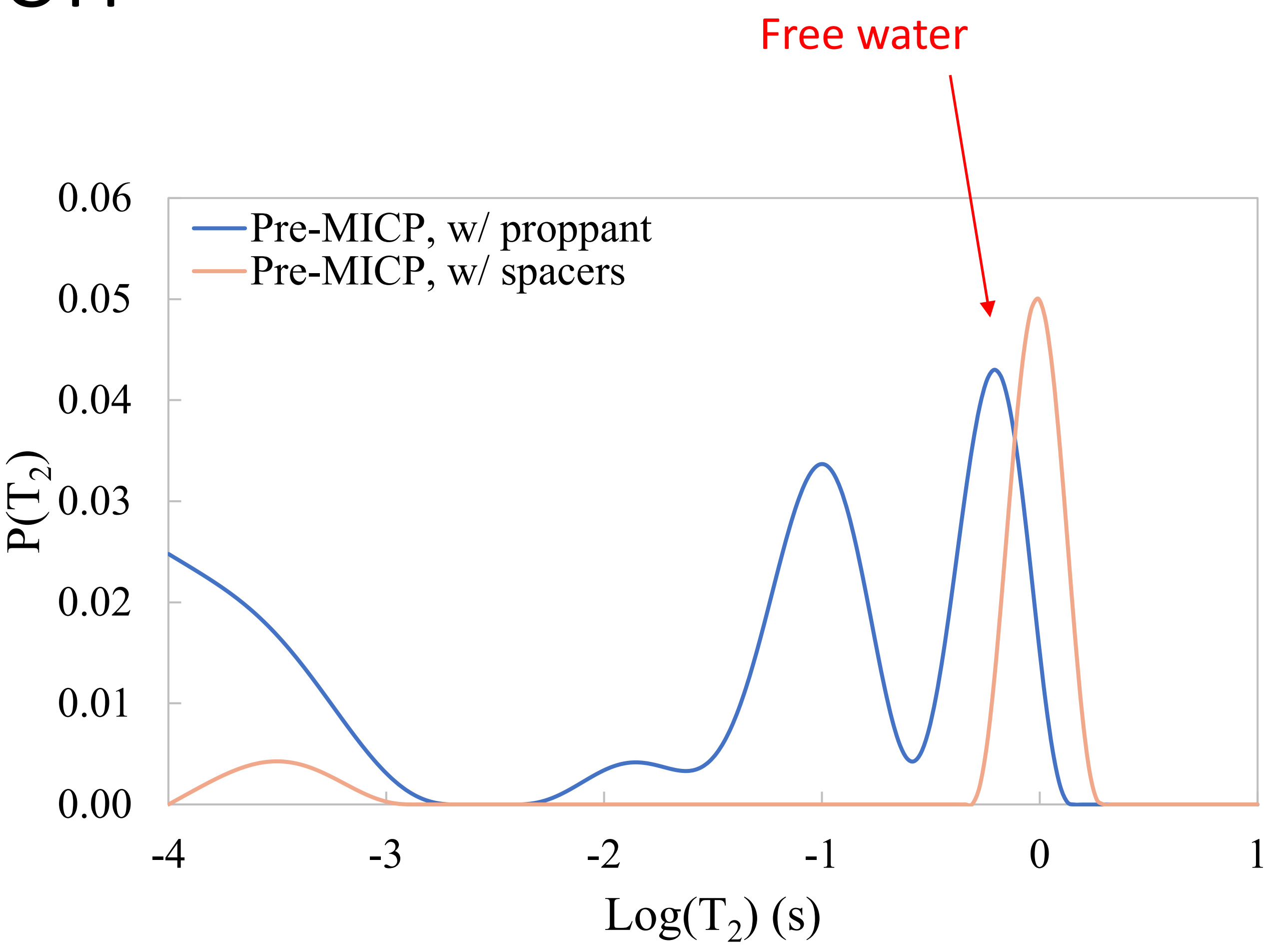

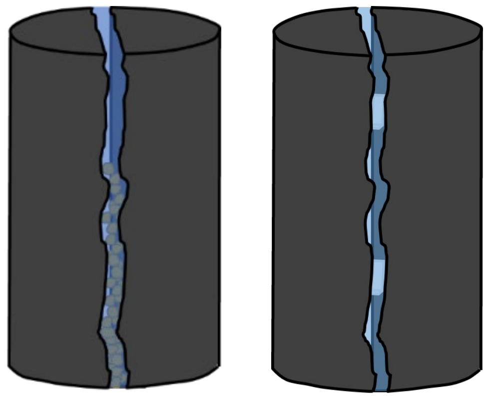

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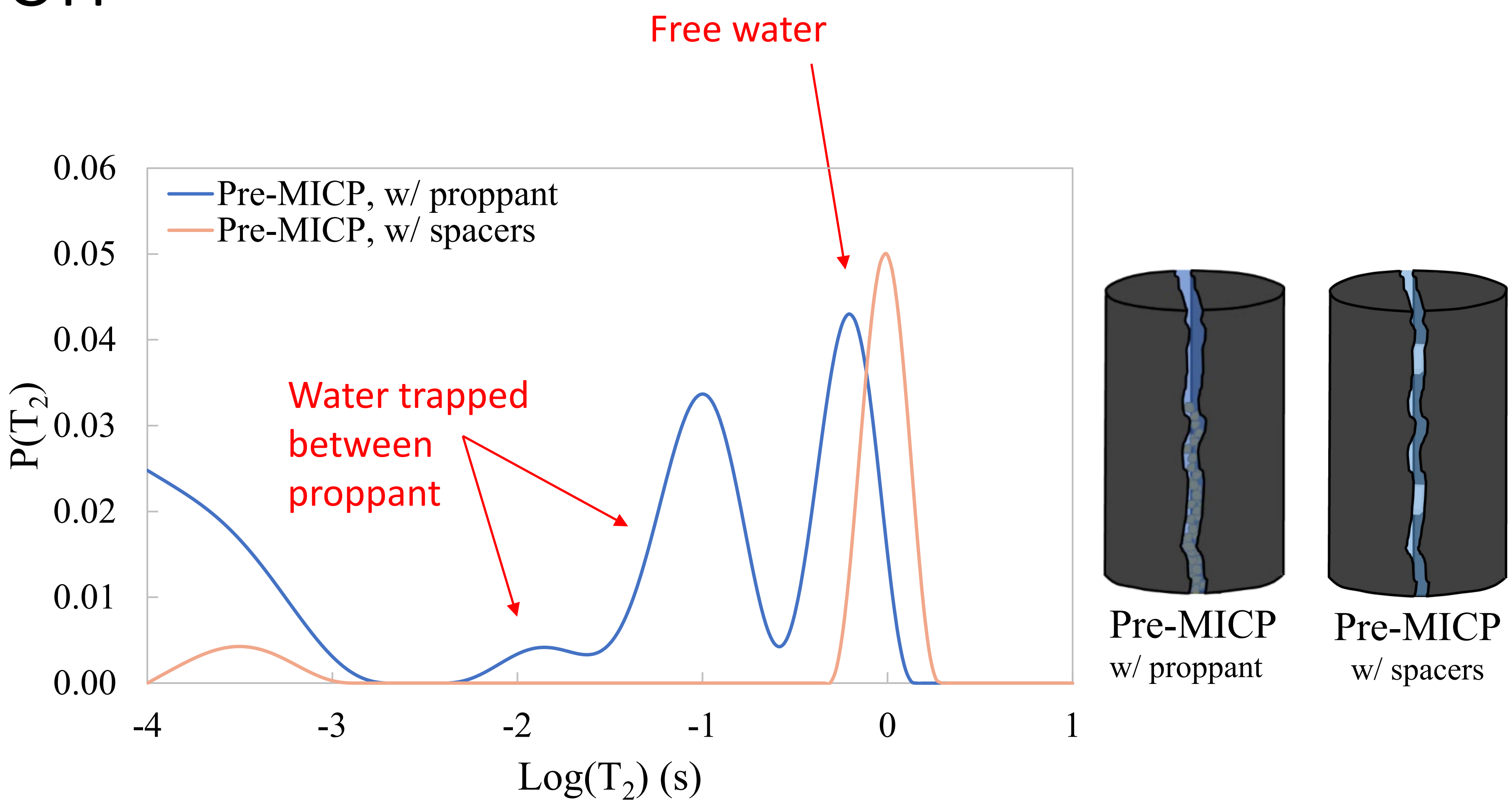

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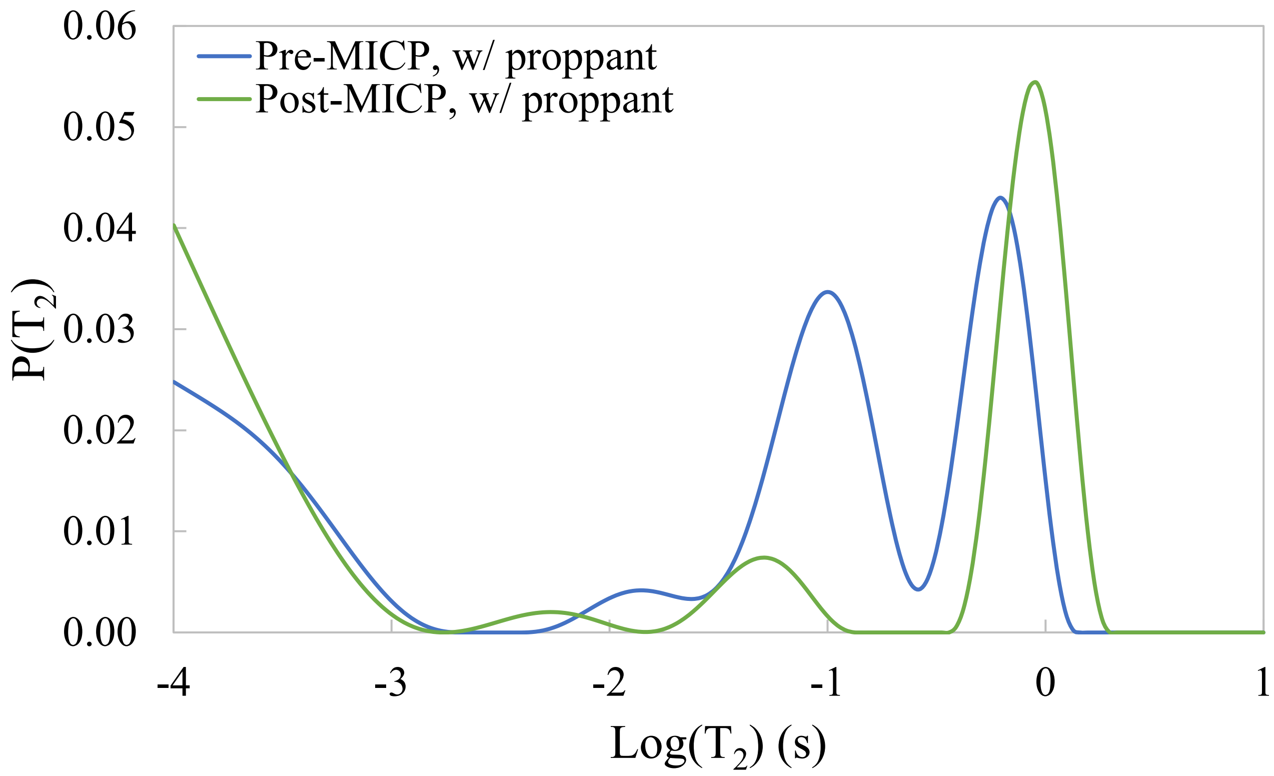
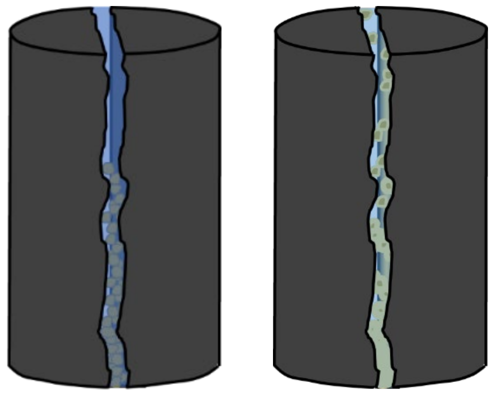


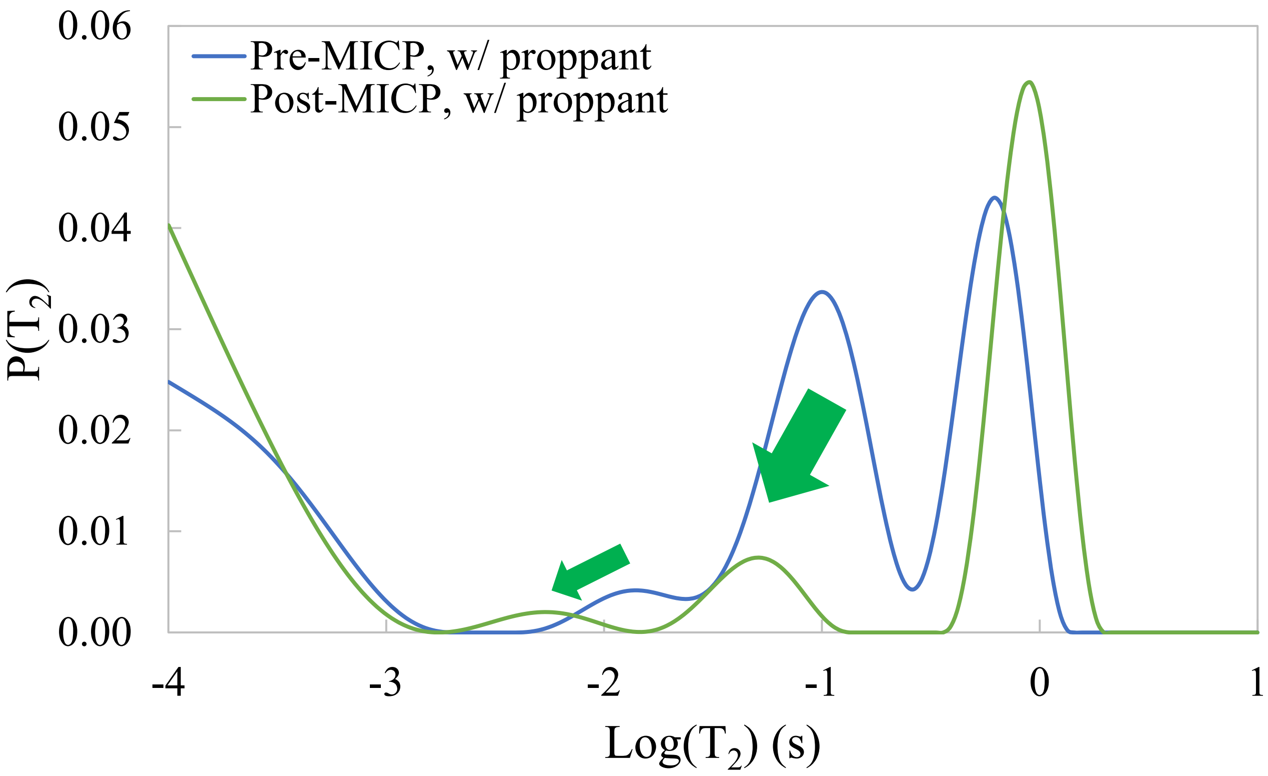


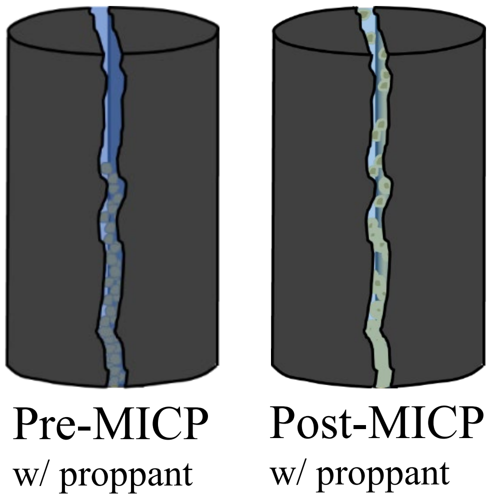
Pre-MICP
w/ proppant

Post-MICP
w/ proppant

T_2 distribution

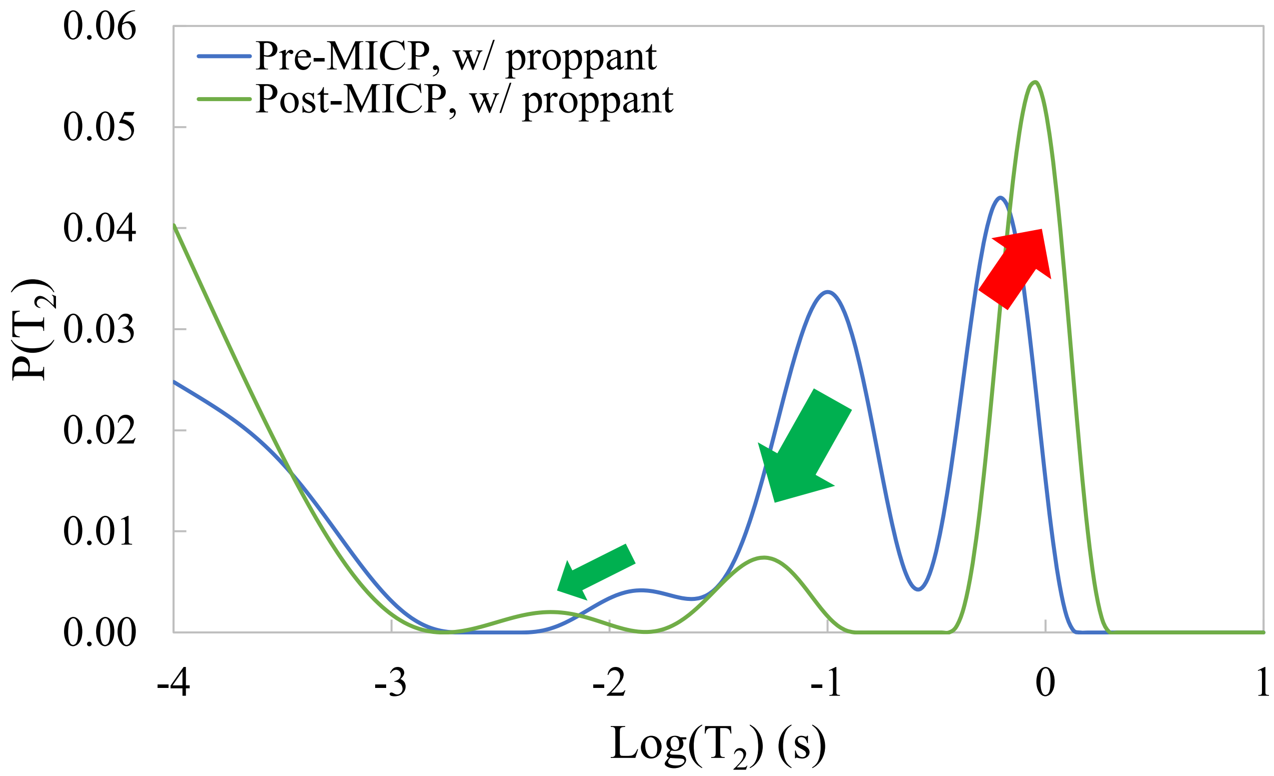
- T_2 peaks associated with proppant decreased

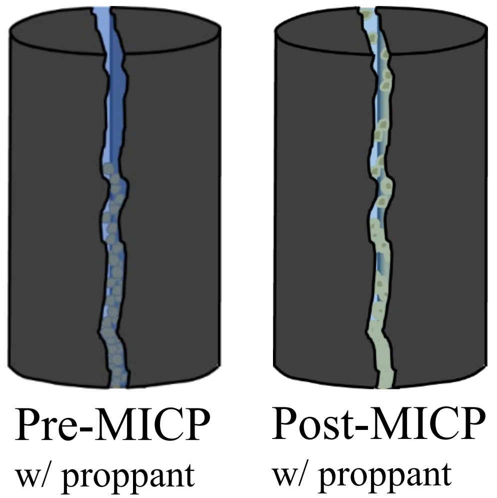




T_2 distribution

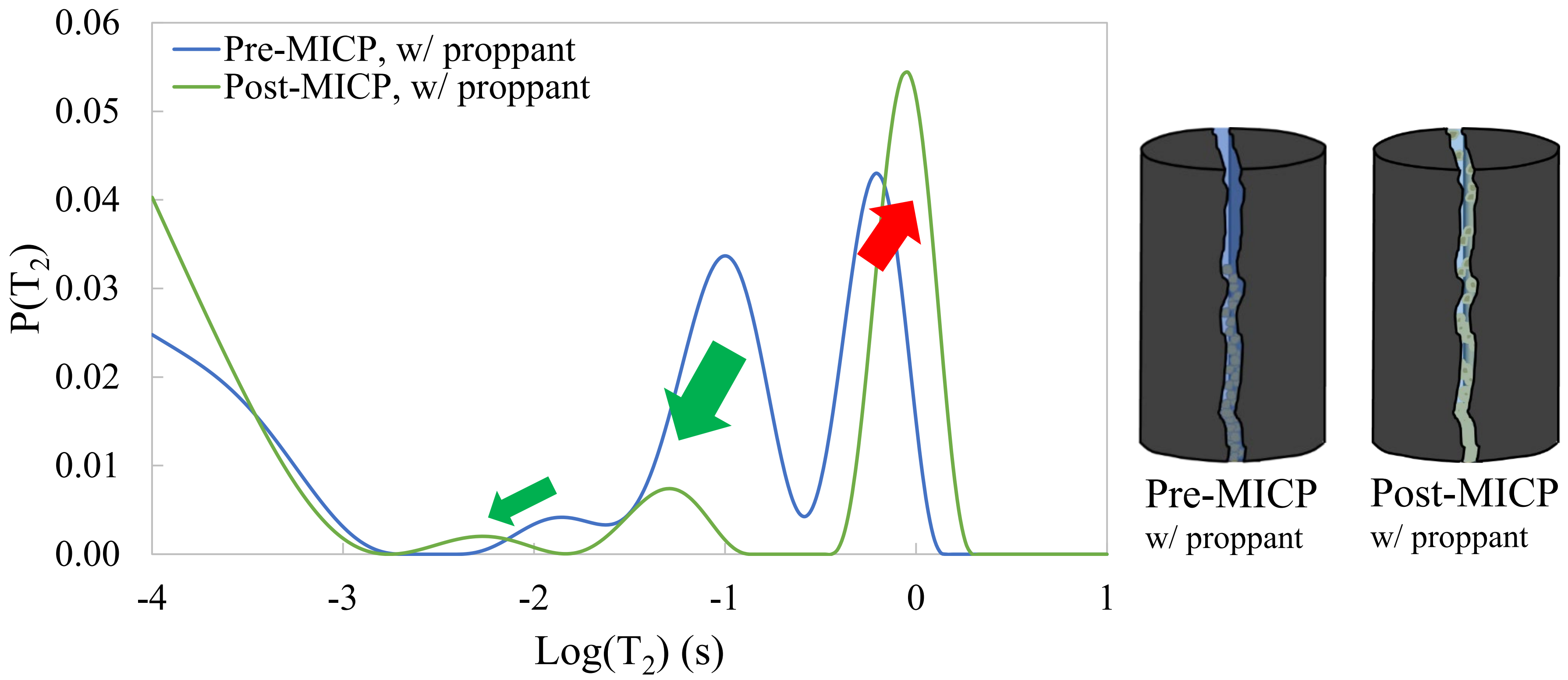
- T_2 peaks associated with proppant decreased
- T_2 peak associated with free water increased





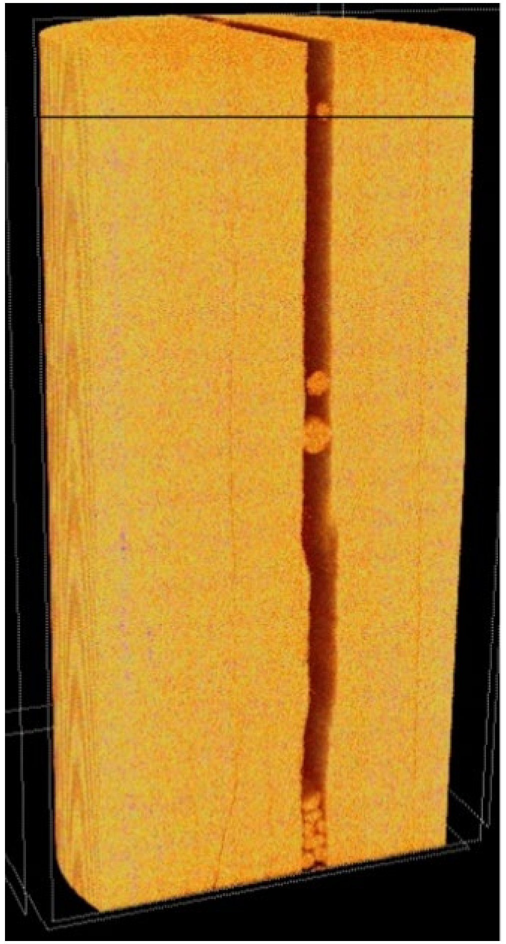
T_2 distribution

- T_2 peaks associated with proppant decreased
- T_2 peak associated with free water increased
- *Precipitation throughout fracture but concentrated around proppant & voids still present.*

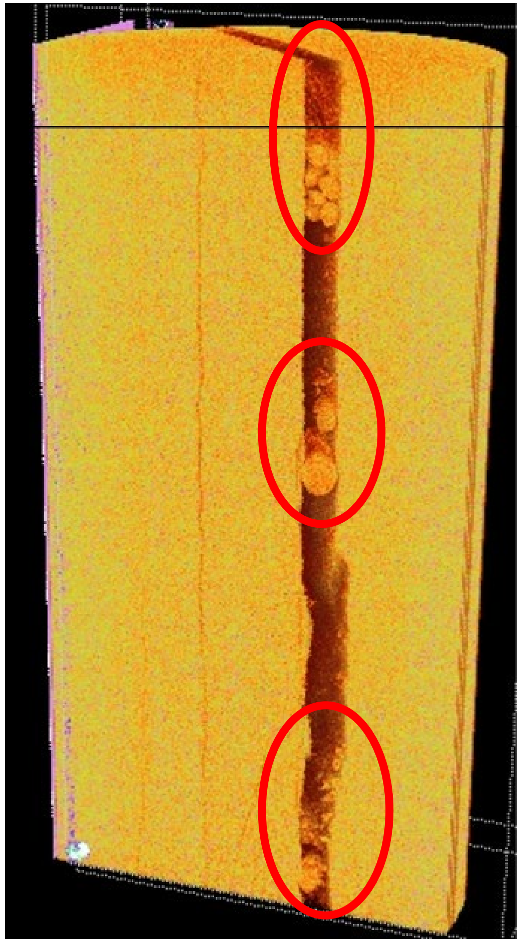


µ-CT analysis

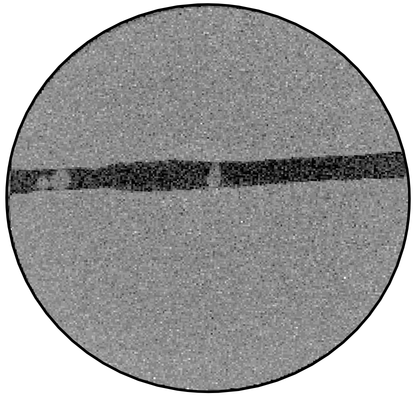
µ-CT shows biomineral accumulation around proppant, throughout most surfaces inside the fracture.



Pre-MICP



Post-MICP



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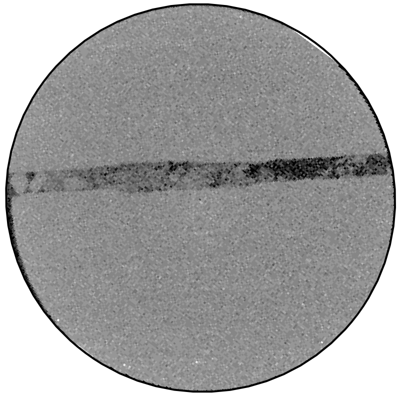

Post-MICP

Quantitative analysis

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Volume (mL)	NMR	μ-CT
$V_{pre-MICP}^{void}$	1.78	1.71
$V_{post-MICP}^{void}$	1.15	1.15
$V_{CaCO_3}^{solid}$	0.62	0.56

Conclusions

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- NMR T_2 experiments can be used to determine the extent of biomineralization within shale fractures by analyzing how peaks shift following MICP-treatment.
- µ-CT scanning provides important spatial information and confirmed NMR findings.
- NMR and µ-CT data can both be used to calculate the volume of solid biomineral formed inside the fracture.

Acknowledgements

NETL:
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MSU Team:
Kayla Bedey
Dr. Catherine Kirkland
Dr. Adrienne (Adie) Phillips
Dr. Laura Dobeck
Dr. Al Cunningham

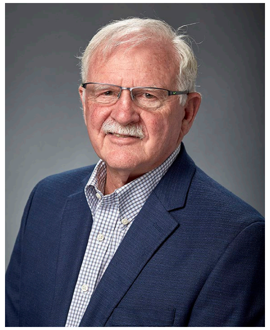
MONTANA STATE UNIVERSITY
NORM ASBJORNSON College of ENGINEERING

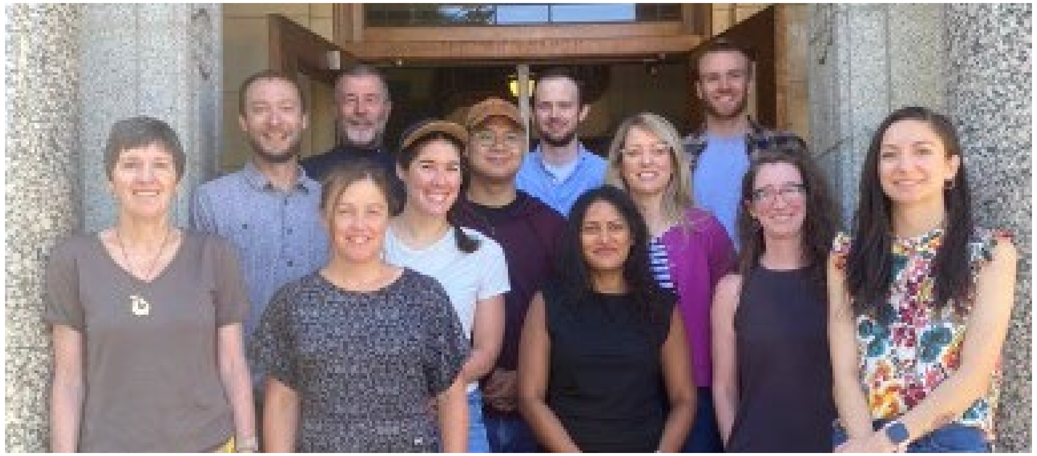
LBNL:
Dr. Jonny Rutqvist

BERKELEY LAB







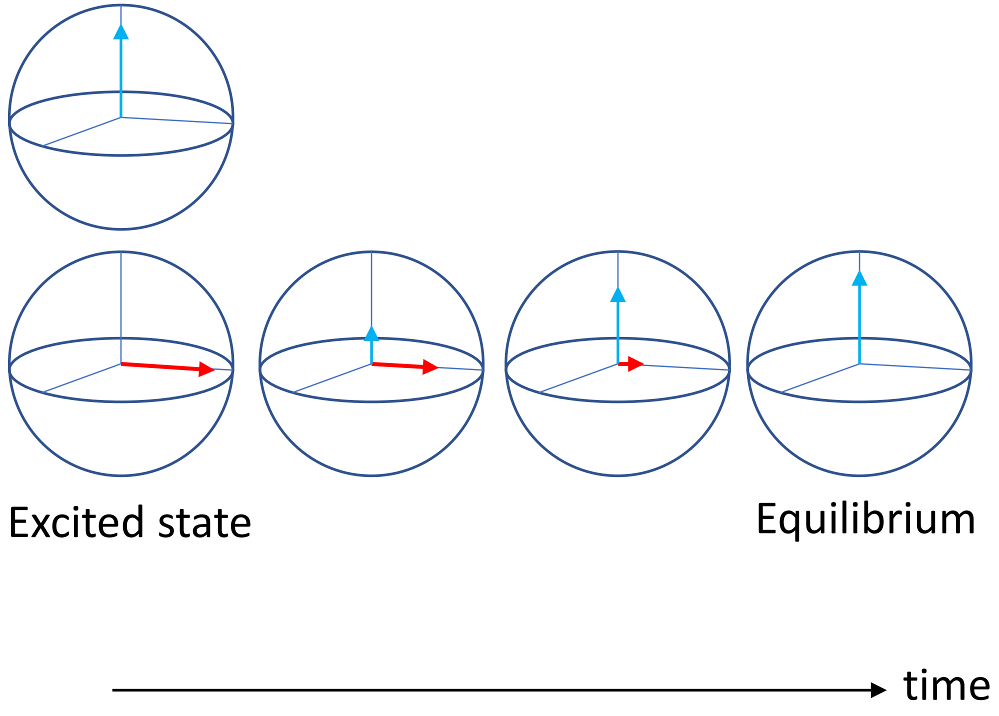


MSU Magnetic Resonance Lab

Thank You

Nuclear magnetic resonance

1. **NMR spectrometer magnetizes "spins" (^{1}H atoms) in sample**
2. **Excitation:** RF pulses push spins out of equilibrium
3. **Relaxation:** Recovery of magnetization to equilibrium
   - T_1: Longitudinal component
   - T_2: Transverse component



Extremely sensitive to signal from water and can detect organic material present in shale.

T_2 distribution

Shale/sand surfaces enhance relaxation to some extent.