Laboratory NMR

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Aarhus, Denmark

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RUTGERS
NEWARK

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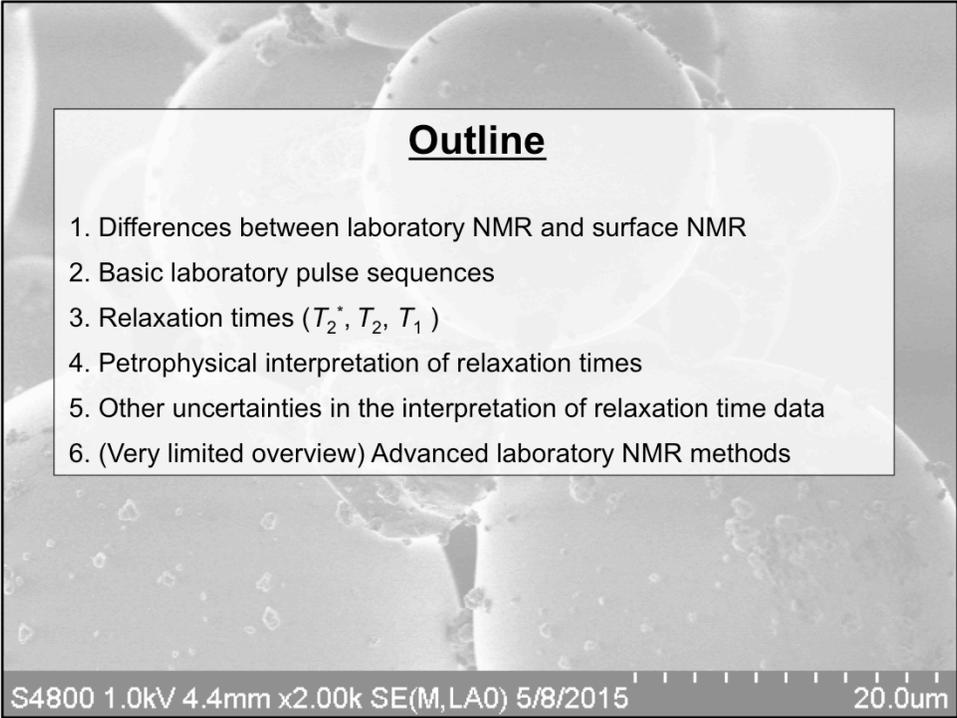
Outline

1. Differences between laboratory NMR and surface NMR

2. Basic laboratory pulse sequences

3. Relaxation times (T_2^*, T_2, T_1)

4. Petrophysical interpretation of relaxation times

5. Other uncertainties in the interpretation of relaxation time data

6. (Very limited overview) Advanced laboratory NMR methods

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1. Laboratory versus Surface NMR

Surface NMR	Laboratory NMR
Field strength (in terms of f_0) ~2000 kHz	Field Field strength (in terms of f_0) ~2000 kHz to 80 MHz (typically 2000 kHz to 2 MHz for geophysics)
Low Field Inhomogeneities (due to low field strength)	Large field inhomogeneities (Due to large field strength)
Most common pulse sequence FID	Most common pulse sequence CPMG (T_2)
Pulse duration > 5 ms	Pulse duration ~20 μs
Dead time > 4 ms	Dead time < 10 μs
Minimum Echo Spacing > 100 ms	Minimum Echo Spacing < 100 to 200 μs

| 1	2	3	4	5	6

1. Laboratory versus Surface NMR
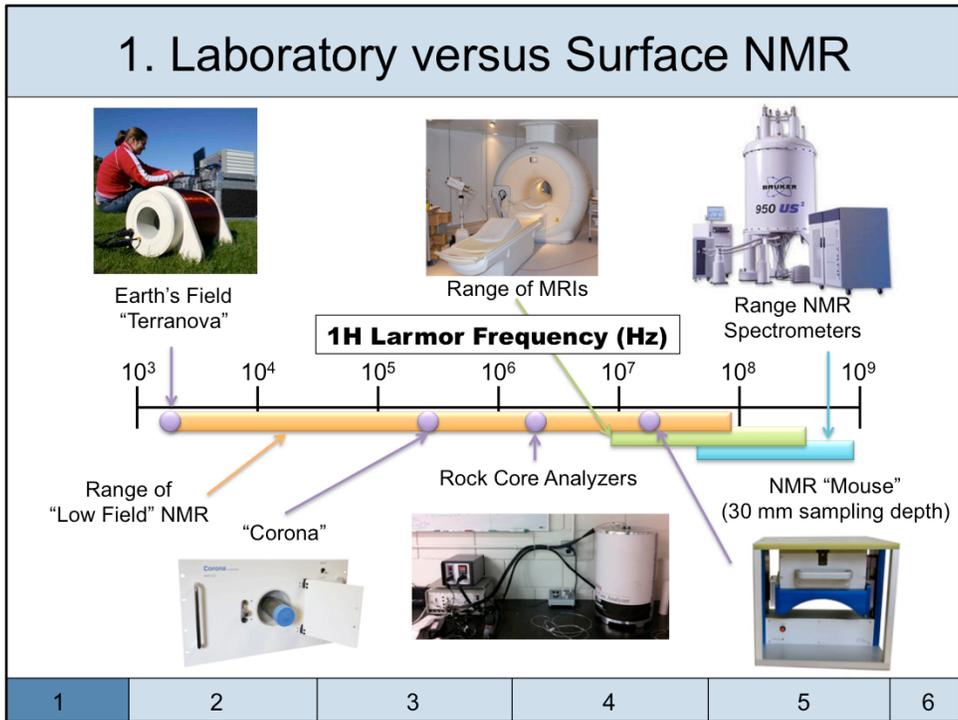
NMR Equipment

The 1H (proton) Larmor frequency associated with laboratory instruments varies over multiple orders of magnitude. Spectrometers have 1H frequencies from~42 to >900 MHz. MRI (Magnetic resonance Imaging) equipment typically ranges from 8 to 300 MHz. "Low field" NMR are classified as anywhere from the Earth's Magnetic field (~2 kHz) to 100 MHz. Rock physics measurements are typically collected at a frequency of 2MHz, to be consistent with the borehole tools used in the oil industry. However, instruments also exist that can be used to collect measurements at 250 kHz, similar to the borehole tools used for near surface investigation, or at frequencies of ~2 kHz associated with the earth's magnetic field.

As you increase frequency it becomes more and more difficult to have a homogeneous B0 field, so the measured sample size decreases. However, the signal amplitude increases with B0 so this is typically not a problem. 2 MHz systems have bores that range from 1.5 to 4 in in diameter, 250 kHz and Earth's field systems have bores that are ~ 4 in in diameter.

Relevant equipment Manufactures for low field laboratory NMR systems: Vista Clara Inc., Magritek, Oxford Instruments, Bruker (mini spec),

1. Laboratory versus Surface NMR
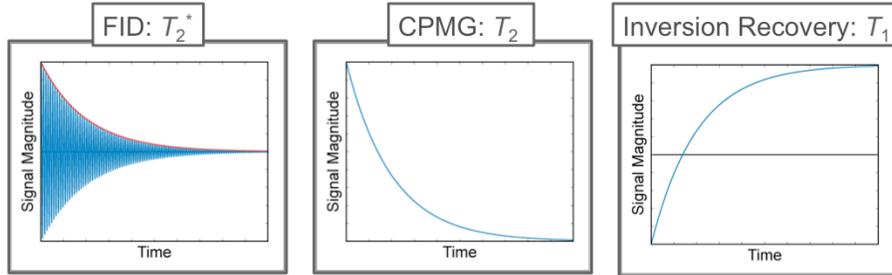
FID: T_2^*	CPMG: T_2	Inversion Recovery: T_1

Relaxation in bulk fluid or in a single pore

$$I_{xy}(t) = I_0\, e^{-t/T_2^*} \sin(2\pi f_0 t)$$

$$I_{xy}(t) = I_0\, e^{-t/T_2}$$

$$I_z(t) = I_0\left(1 - 2\,e^{-t/T_1}\right)$$

Relaxation in a porous system

$$I_{xy}(t) = I_0 \sum f_i\, e^{-t/T_{2i}^*} \sin(2\pi f_0 t)$$

$$I_{xy}(t) = I_0 \sum f_i\, e^{-t/T_{2i}}$$

$$I_z(t) = I_0\left(1 - 2\sum f_i\, e^{-t/T_{1i}}\right)$$

1	2	3	4	5	6

1. Laboratory versus Surface NMR

$T_2^* =$ transverse relaxation time

$T_2 =$ transverse relaxation time

$T_1 =$ longitudinal relaxation time

$\rho_2 =$ transverse surface relaxivity

$\rho_1 =$ longitudinal surface relaxivity

$T_{jML} =$ mean log relaxation time (j means 1, 2, or 2*)

$I_{xy}(t) =$ time varying transverse signal magnitude

$I_z(t) =$ time varying longitudinal signal magnitude

$I_0 =$ initial signal magnitude

$T_{ji} =$ Relaxation time in summation, (j means 1, 2, or 2*)

$f_i =$ Proporation of relaxation time relaxing with T_{ji}

$M_{xy}(t) =$ time varying transverse magnetization

$M_z(t) =$ time varying longitudinal magnetization

$BFI =$ Bound fluid index also called BVI

$FFI =$ Free fluid index

$S_s =$ Specific Surface Area

$T =$ Tortuosity

$g =$ acceleration of gravity

$D =$ Self diffusion coeficient of saturating fluid

$B_0 =$ Static magnetic field aligned in z-direction

$B_1(t) =$ Time varying excitation pulse

$r =$ pore radius

$\alpha =$ shape factor relating radius to S/V

$S/V =$ surface area to volume ratio

$\tau =$ interpulse delay

$t_E =$ Echo time

$T_{jB} =$ Bulk fluid relaxation time (j means 1 or 2)

$T_{jS} =$ Surface relaxation time (j means 1 or 2)

$T_{2D} =$ Diffusion (or dephasing) relaxation time

$T_{2IH} =$ Relaxation time due to inhomogeneities in B_0

$\Delta B =$ average magnetic field inhomogeneities

$G =$ average magnetic field gradient

$\kappa =$ control parameter

$k =$ permeability

$K =$ hydraulic conductivity

$\mu =$ dynmaic viscosity

$\rho =$ density of the fluid

| 1 | 2 | 3 | 4 | 5 | 6 |

Table with all variable definitions used in this presentation.

2. Laboratory NMR Pulse Sequences

Main Laboratory NMR pulse sequences:

FID (T_2^*)
Spin Echo (T_2)
CPMG (Carr-Purcell-Meiboom-Gill) (T_2)
Inversion Recovery (T_1)

Other relevant pulse sequences:
(only briefly covered here)

PGSE (Pulse Gradient Spin Echo) (D)
2D NMR pulse sequences (*e.g.* T_1-T_2 correlation and D-T_2 correlation)

| 1	2	3	4	5	6

2. Laboratory NMR Pulse Sequences

Free Induction Decay Pulse "Sequence"
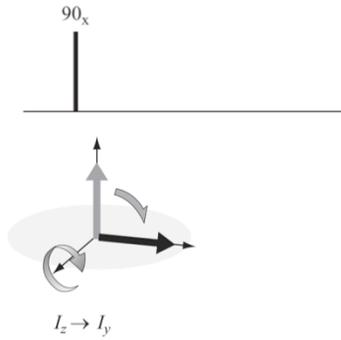
Measured Signal
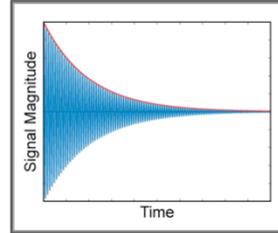
$$I_{xy}(t) = I_0 \sum f_i\, e^{-t/T_{2i}^*} \sin(2\pi f_0 t)$$

1	2	3	4	5	6

For the free induction decay, a 90 degree pulse is applied, which flips the spins into the xy plane. The decay in the xy-plane is measured over time. The resulting signal is an sinusoidal signal with an exponential decay envelope. The envelope is characterized by T2*. The decay due to an FID is strongly affected by magnetic field inhomogeneities.

2. Laboratory NMR Pulse Sequences

Spin Echo Pulse Sequence

Measured Signal

$$I(\tau) = I_0 \left(\sum f_i e^{-2\tau/T_{2i}} \right)$$
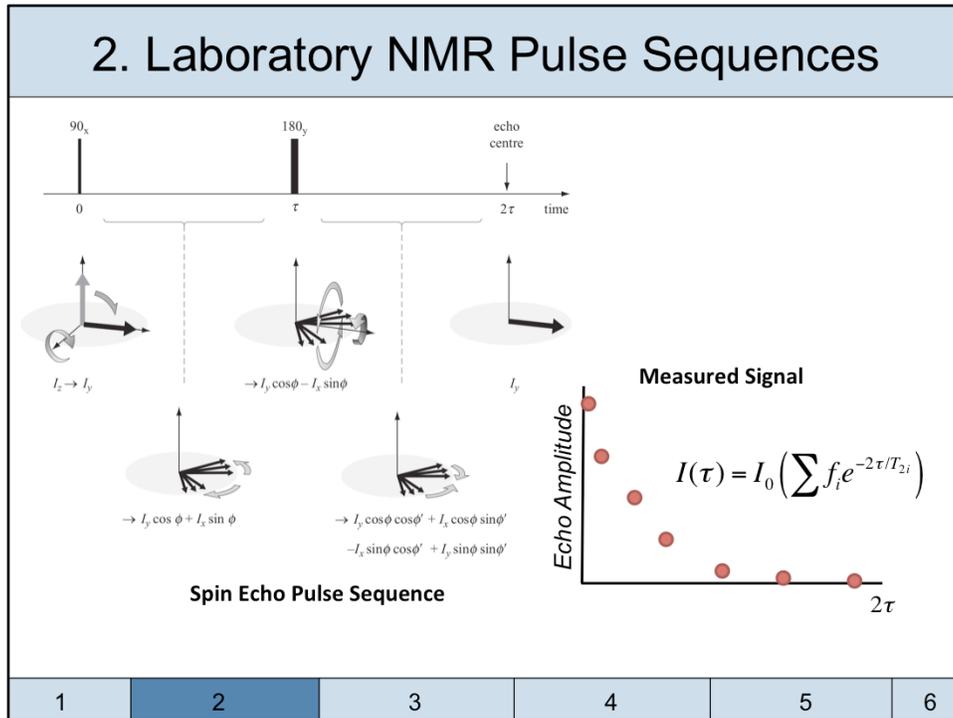
For the Spin Echo (or Hahn spin echo) Spin-echo pulse sequence showing the evolution of magnetization and the density matrix. Note that the 180 x pulse inverts the phase of each spin refocusing occurs at time t = 2tau. (Diagram from Callaghan, 2011). The signal is then measured at different tau spacing. If each measurement is stacked N times, and M values of tau are collected, then the measurements will take ~(NxMx(RD+2*tau). Where RD is the relaxation delay and is the time you wait between finishing the last measurement and starting the next measurement. RD should be greater than or equal to 3T1 to ensure that your sample returns to thermal equilibrium before starting the next measurement.

You typically want to collect data until the signal has fully decayed.

2. Laboratory NMR Pulse Sequences

Video Demonstrating Spin Echo Pulse Sequence
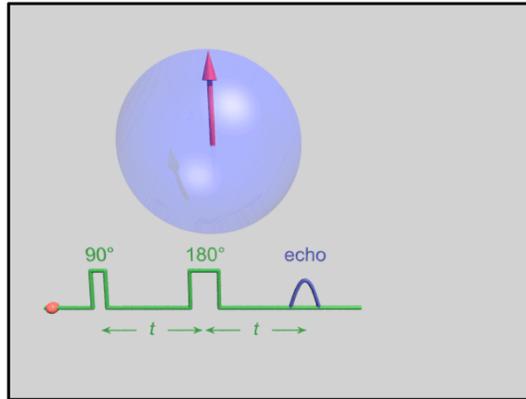

1	2	3	4	5	6

"HahnEcho GWM" by GavinMorley - Gavin W Morley. Licensed under CC BY-SA 3.0 via Wikimedia Commons - http://commons.wikimedia.org/wiki/File:HahnEcho_GWM.gif#/media/File:HahnEcho_GWM.gif

2. Laboratory NMR Pulse Sequences

CPMG Pulse Sequence and Associated Echo Train

90_x 180_y 180_y 180_y 180_y 180_y

0 τ 3τ 5τ 7τ 9τ time

echo envelope

signal

| 1 | 2 | 3 | 4 | 5 | 6 |
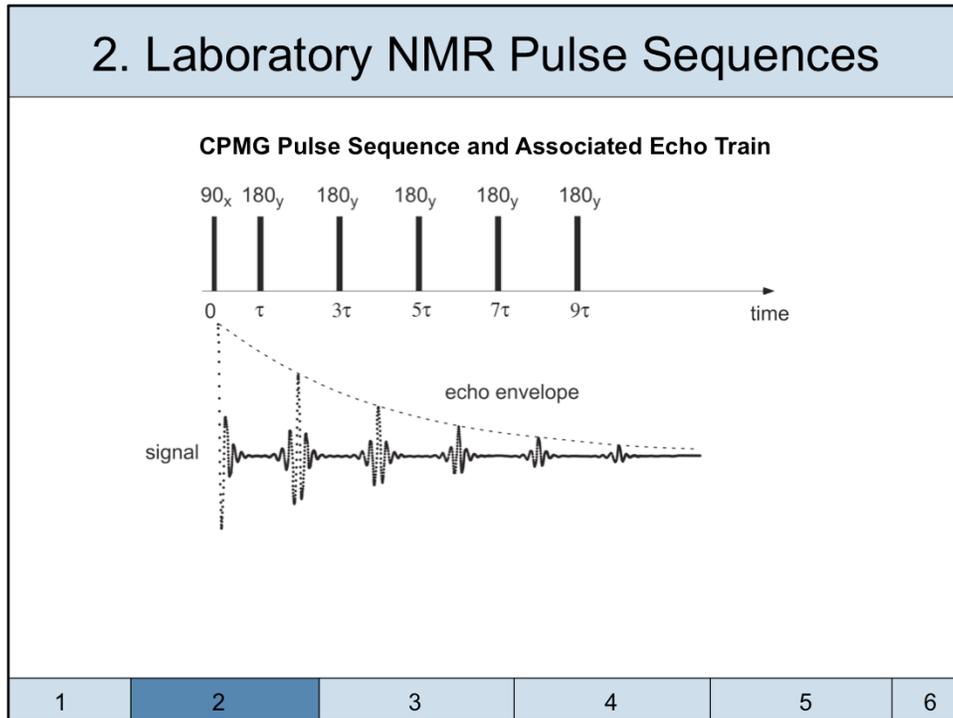
CPMG pulse sequence exhibiting multiple spin echoes at times $2n\tau$, modulated by a T2 relaxation envelope. (Callaghan, 2011).

The echo envelope is what is typically recorded. If we collect N stacks, and NE each stack, with a relaxation delay of RD, then the total time for each measurement will be N*(tau*2*NE + RD).

In the CPMG pulse sequence the echo spacing is denoted by te and is equal to 2*tau.

2. Laboratory NMR Pulse Sequences

Measured Signal

$$I_y(\tau) = I_0\left(1 - 2\sum f_i e^{-\tau/T_{1i}}\right)$$

Inversion Recovery Pulse Sequence

$I_z \rightarrow -I_z$ $-I_z \rightarrow -I_y$

| 1	2	3	4	5	6
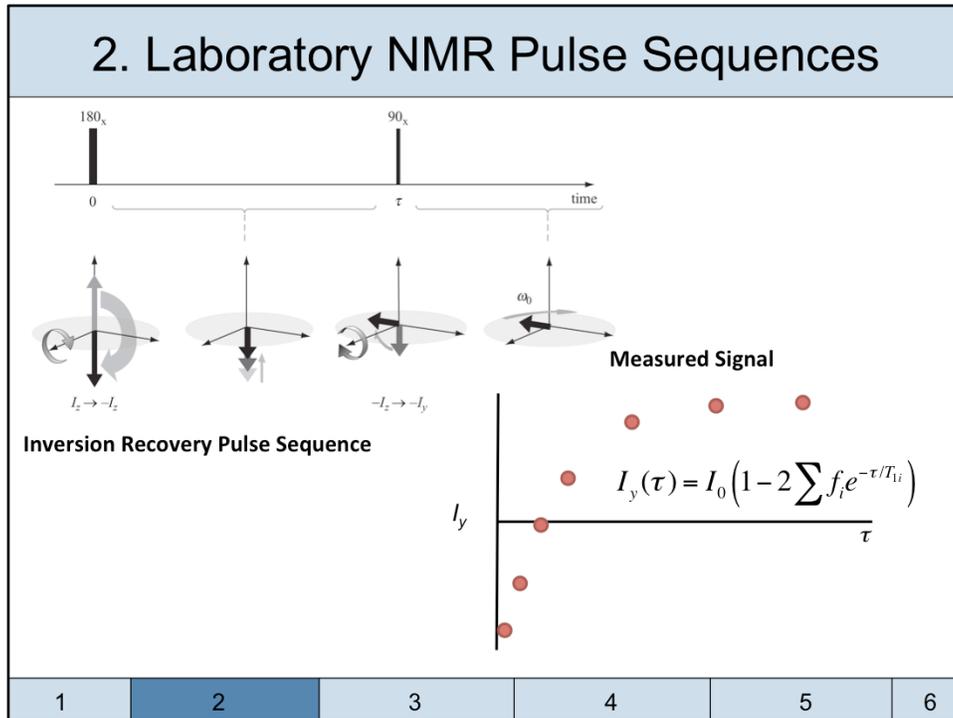
Inversion recovery pulse sequence and magnetization trajectories. At each RF pulse the grey arrow represents the magnetization prior to the pulse. The black vector represents the magnetization after the pulse. Also shown is the evolution of the density matrix under the action of the pulse sequence. (Callaghan, 2011). The set of pulse sequences is stacked (N times), and then the value of tau is varied (collect M different tau spacings). If the relaxation delay is RD then the total measurement time will be NxMx(RD+tau), similar to a spin echo measurement and much greater than the measurement time for the CPMG pulse sequence. This is why CPMG pulse sequences, and T2 measurements are more often collected than T1 measurements.

You typically want to collect data until the signal has fully returned to equilibrium.

Another way of measuring T1 is using the saturation recovery pulse sequence, which is a 90degree pulse followed by a second 90 degree pulse. The signal for a saturation recovery is: I(t) = I0(1-\Sum(fi exp(-t/T1i))). The inversion method has a larger dynamic range, and so is easier to measure; however, the saturation recovery sequence can be faster as it allows for arbitrarily short delays between the two pulse pairs and an infinite train of 90 degree pulses can be applied that after reaching a steady state, the signal after each pulse is given by I(t) = I0(1-\Sum(fi exp(-t/T1i))) (Dunn et al., 2002).

3. T_2^*, T_2, T_1 Relaxation

FID

90$_x$

0

T_2^*

CPMG

90$_x$ 180$_y$ 180$_y$ 180$_y$ 180$_y$ 180$_y$

0   τ 3τ 5τ 7τ 9τ time

T_2

Inversion Recovery

180$_x$ 90$_x$

0   τ time

T_1

| 1 | 2 | 3 | 4 | 5 | 6 |
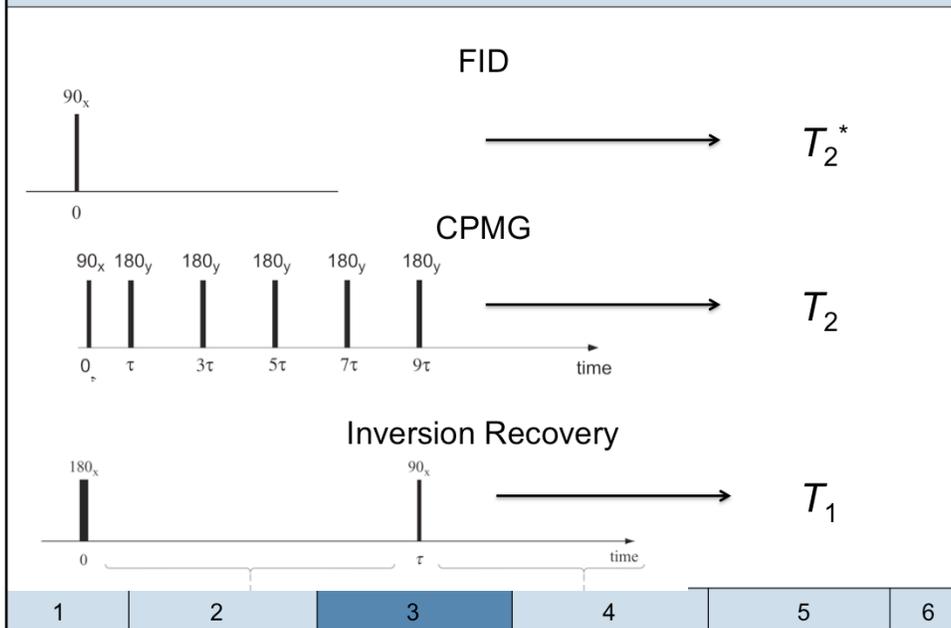
3. T_2^*, T_2, T_1 Relaxation

T_2^* relaxation in a single pore
Not typically measured in the laboratory

$$\frac{1}{T_2^*} = \frac{1}{T_{2B}} + \frac{1}{T_{2S}} + \frac{1}{T_{2IH}}$$

$\dfrac{1}{T_{2B}}$	$\dfrac{1}{T_{2S}} = \rho_2 \dfrac{\alpha}{r} = \rho_2 \dfrac{S}{V}$	$\dfrac{1}{T_{2IH}} \approx \dfrac{\gamma}{2\pi} \Delta B$
Bulk fluid relaxation Affected by: paramagnetic impurities (e.g. Fe^{3+}(aq)) Temperature Viscosity pH	Surface relaxation Affected by: paramagnetic impurities on the grain surface Pore size Surface area/roughness Pore volume	Inhomogeneous field dephase relaxation Affected by: Inhomogeneities in the magnetic field and diffusion. Above equation is a rough approximation.

1	2	3	4	5	6

Paramagnetic impurities indicates species with unpaired electrons and is not the same as a paramagnetic material, which indicates the structure of the magnetic domains. A common paramagnetic impurities is iron in the valence III state (Fe(III)).

The equation give for T2IH is a rough approximation. DeltaB is the total magnetic field inhomogeneities, but does not capture the statistics of the magnetic field inhomogeneities. Furthermore this equation does not account for diffusion through the magnetic field (i.e., as a spin diffuses it experiences multiple different field strengths)

For more information about the factors affecting T2* see Grunewald and Knight (2011).

3. T_2^*, T_2, T_1 Relaxation
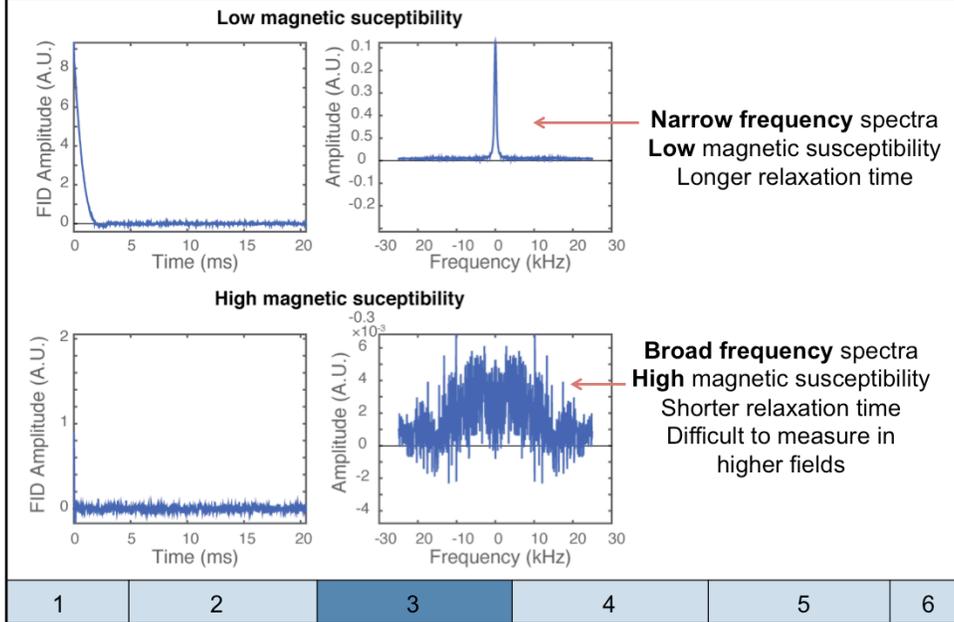
Unpublished data.

The top two plots represent the FID time domain and frequency spectra collected for a low magnetic susceptibility material; the bottom two plots represent the FID time domain and frequency spectra collected for a higher magnetic susceptibility material.

This data was collected using a 2 MHz system. The broadening of the frequency spectra will change depending on field strength used – at lower fields the frequency spectra will be narrower. This means that at lower frequencies the T2* decay will be lower.

3. T_2^*, T_2, T_1 Relaxation

T_2 relaxation in a single pore
Most common measurement
Spin-Spin Relaxation OR Transverse Relaxation

$$\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{1}{T_{2S}} + \frac{1}{T_{2D}}$$

$\dfrac{1}{T_{2B}}$	$\dfrac{1}{T_{2S}} = \rho_2 \dfrac{\alpha}{r} = \rho_2 \dfrac{S}{V}$	$T_{2D} = \dfrac{1}{12} D \left(G \gamma t_E \right)^2$
Bulk fluid relaxation Affected by: paramagnetic impurities (e.g. Fe^{3+}(aq)) Temperature Viscosity pH	Surface relaxation Affected by: paramagnetic impurities on the grain surface Pore size Surface area/roughness Pore volume	Diffusion relaxation or Dephasing relaxation Affected by: Inhomogeneities in the magnetic field and diffusion. Above equation is a one example of possible equations.

1	2	3	4	5	6

The first two terms are the same as the first two terms for the T2* equation. Despite the rephasing pulses in the CPMG pulse sequence, some component of the relaxation is irreversible dephased due to the diffusion of the spins through the fluid (in a solid with no diffusion full recovery would be possible). This leads to a faster relaxation due to the dephased spins. See Kleinberg and Horsfield (1990) for more information on the diffusion relaxation.

3. T_2^*, T_2, T_1 Relaxation

In Earth's field NMR it is typically assumed that $T_2 = T_2^*$.
However, in higher field laboratory measurements $T_2 > T_2^*$.

T_2^*	T_2
The spins are not rephased and are strongly affected by even weak magnetic field inhomogeneities.	Typically the spins are rephased and the
Relaxation is often too fast to measure in laboratory instruments.	In an strongly **inhomogeneous magnetic** field, dephased component can only be partially rephased.
The relaxation time distribution is not equivalent to pore-size distribution	In this case the relaxation time distribution not equivalent to the pore-size distribution.
Affect by the **dead time.**	Affected by the **echo time.**

1	2	3	4	5	6

In laboratory instruments it is rarely true that T2* = T2. It is often not possible to measure the FID in the laboratory as even small inhomogeneities in the magnetic field strongly affect relaxation.

References:
Grunewald and Knight (2011)

3. T_2^*, T_2, T_1 Relaxation

Low magnetic suceptibility

High magnetic suceptibility
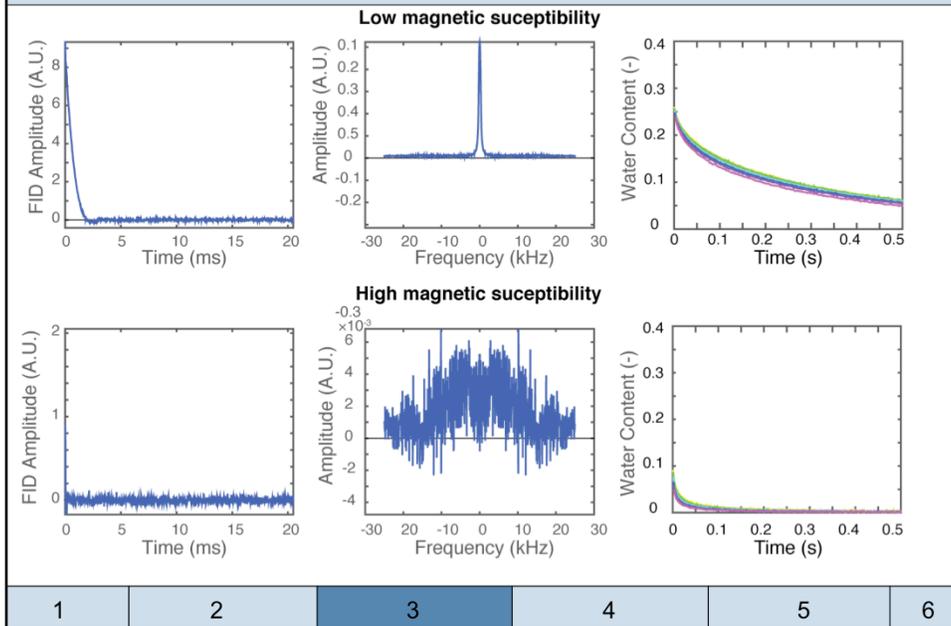
Unpublished data.

This data was collected using a 2 MHz system. The broadening of the frequency spectra will change depending on field strength used – at lower fields the frequency spectra will be narrower. Note that even in the case when the FID signal is difficult to measure, the CPMG pulse sequence can be detected (bottom figure).

3. T_2^*, T_2, T_1 Relaxation

T_1 relaxation in a single pore
Not affected by magnetic field inhomogeneities
Spin Lattice Relaxation OR Longitudinal Relaxation

$$\frac{1}{T_1} = \frac{1}{T_{1B}} + \frac{1}{T_{1S}}$$

$$\frac{1}{T_{1B}}$$

$$\frac{1}{T_{1S}} = \rho_2 \frac{\alpha}{r} = \rho_2 \frac{S}{V}$$

Bulk fluid relaxation	Surface relaxation
Affected by:	Affected by:
paramagnetic impurities	paramagnetic impurities
(e.g. Fe^{3+}(aq))	on the grain surface
Temperature	Pore size
Viscosity	Surface area/roughness
pH	Pore volume

1	2	3	4	5	6

3. T_2^*, T_2, T_1 Relaxation

Important consideration

$$T_2 < T_1$$

T_2	T_1
Spin-spin relaxation time	Spin-lattice relaxation time
Measures how long protons remain **coherent** (in phase)	Measures recovery towards **thermal equilibrium**
Magnetic interactions of spins	Energy exchange with lattice
Depends on temperature and only slightly on B_0	Depends on temperature and B_0

| 1 | 2 | 3 | 4 | 5 | 6 |

Similarly, rho2 is not equal to rho1, see for example Foley et al. (1996)

3. T_2^*, T_2, T_1 Relaxation

$1/T_1$, $1/T_2$, and $1/T_{2,sec} = 1/T_2 - 1/T_1$
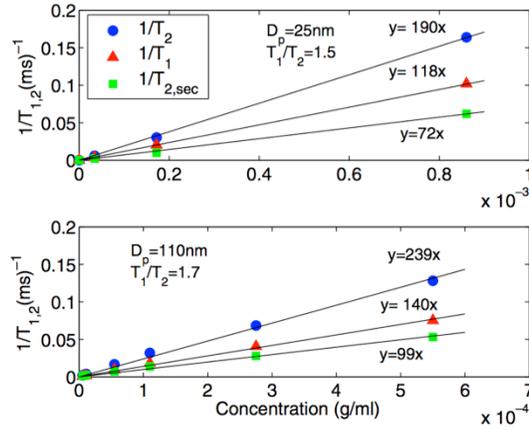
Plots of transverse, longitudinal and secular relaxation rates with the concentration of aqueous dispersions of magnetite nanoparticles. Dp is the diameter of the nanoparticles. The ratio of T1 to T2 is also given. Measurements were made at 2 MHz (@ 30 C). No echo spacing dependence observed.
Figure from Anand and Hirasaki (2008)

3. T_2^*, T_2, T_1 Relaxation
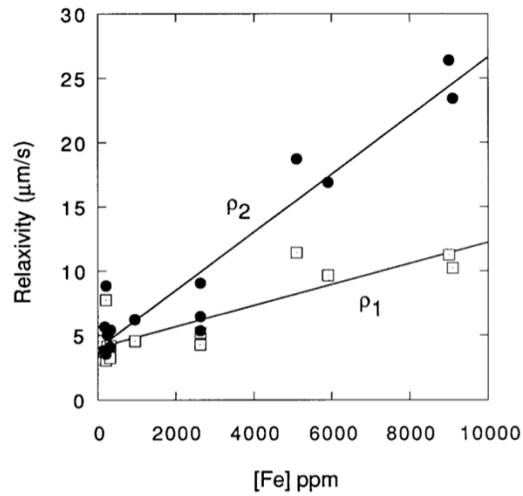
Surface relaxivity values for calcium silicates doped with
varying concentrations of iron(III)

| 1 | 2 | 3 | 4 | 5 | 6 |

As with T1 and T2, rho1 and rho2 for the same sample are not equal (rho1 < rho2). The above figure shows how both values vary with iron concentration. Figure from Foley et al. (1996)

3. T_2^*, T_2, T_1 Relaxation

Note that these equations come from the analytical solutions to the modified phenomenological Bloch Torrey equations.

An example of the set up for the Bloch-Torrey equations is given below. This equation neglects both bulk relaxation and diffusion relaxation. These equations can be used for pore-scale modeling

Transverse Magnetization	**Longitudinal Magnetization**
$$\frac{\partial M_{xy}(\mathbf{x},t)}{\partial t} = D\nabla^2 M_{xy}(\mathbf{x},t) - \frac{M_{xy}(\mathbf{x},t)}{T_{2B}}$$	$$\frac{\partial M_z(\mathbf{x},t)}{\partial t} = D\nabla^2 M_z(\mathbf{x},t) - \frac{M_0 - M_z(\mathbf{x},t)}{T_{1B}}$$

With the initial condition

$$M_{xy}(\mathbf{x},t) = 0 \qquad\qquad M_z(\mathbf{x},t) = M_0$$

And the boundary condition

$$D\hat{\mathbf{n}} \cdot \nabla M_{xy} - \rho_2 M_{xy} = 0 \qquad\qquad D\hat{\mathbf{n}} \cdot \nabla M_z - \rho_1 M_z = 0$$

1	2	3	4	5	6

Note that n^hat is the normal vector point perpendicular from the surface.

3. T_2^*, T_2, T_1 Relaxation
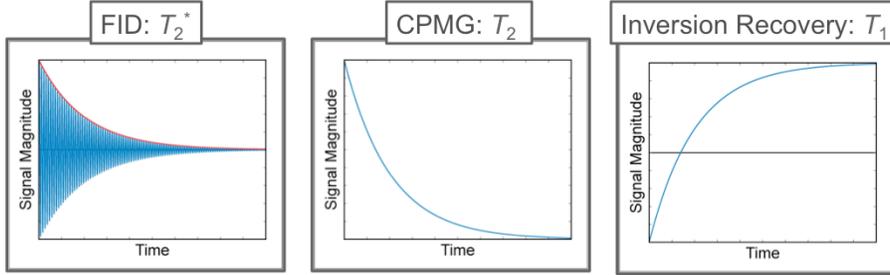
FID: T_2^*	CPMG: T_2	Inversion Recovery: T_1

Relaxation in bulk fluid or in a single pore

$$I_{xy}(t) = I_0\, e^{-t/T_2^*} \sin(2\pi f_0 t)$$

$$I_{xy}(t) = I_0\, e^{-t/T_2}$$

$$I_z(t) = I_0\left(1 - 2\,e^{-t/T_1}\right)$$

Relaxation in a porous system

$$I_{xy}(t) = I_0 \sum f_i\, e^{-t/T_{2i}^*} \sin(2\pi f_0 t)$$

$$I_{xy}(t) = I_0 \sum f_i\, e^{-t/T_{2i}}$$

$$I_z(t) = I_0\left(1 - 2\sum f_i\, e^{-t/T_{1i}}\right)$$

1	2	3	4	5	6

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3. T_2^*, T_2, T_1 Relaxation

Non-Negative Least Squares (NNLS) Fits

Determining the relaxation time distribution from the exponential decay is a non-unique problem and complex.

There are multiple different methods for determining a relaxation time distribution from a multiexponential decay:
- Stretched exponential
- Set number of exponential times (typically three)
- Non-negative least squares (NNLS) with Tikhonov regularization
  - Benefit: it does not assume a set shape or set number of exponentials
  - Drawback: strongly influenced by the degree of smoothing

Minimize: $$F(I) = \sum_j \left(\sum_i I_i \exp(-t_j / T_{2i}) - d_j \right)^2 + \lambda \sum_i I_i^2$$

Subject to $I_i > 0$

Where λ is the smoothing parameter and d_j is the data from the decay.

1	2	3	4	5	6

See Whittall et al. (1999) and Istratov and Vyenko (1999) for an overview.

3. T_2^*, T_2, T_1 Relaxation

Non-Negative Least Squares (NNLS) Fits
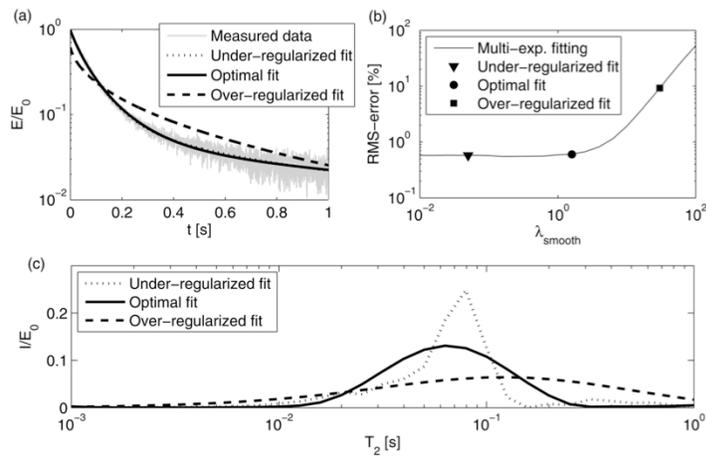
Figure from Costabel and Yaramanci (2007)

Method for choosing optimal fitting parameter. The drawbacks of over regularizing and under-regularization.
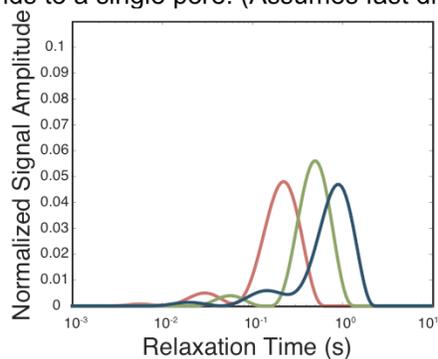
Figure adapted from Keating and Falzone (2013)

4. NMR Petrophysics

In this section we will consider the properties that can be estimated with NMR parameters

Water Volume, Saturation, Water Content, and Porosity
S/V , r, and Pore-size distributions
Mobile/Immobile water content
Permeability

1	2	3	4	5	6

4. NMR Petrophysics

I_0 → Water volume, V_w

T_{2B} = 2.27665 s

R^2 = 0.998

Water Volume (ml)

Initial Signal Amplitude, (a.u.)
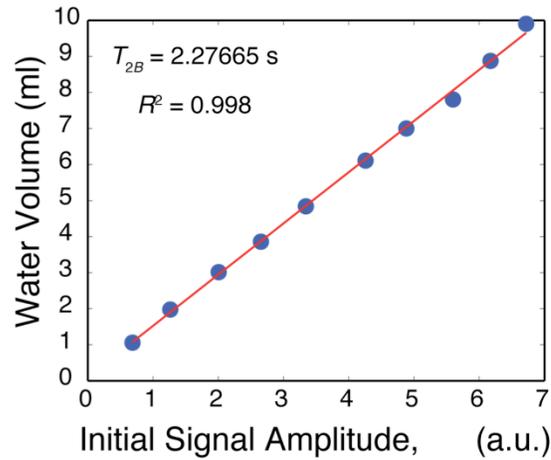
| 1 | 2 | 3 | 4 | 5 | 6 |

It is well known that the NMR initial signal amplitude it proportional to the water content. We can develop a calibration curve that can be used to estimate the water volume from the NMR initial signal magnitude.

4. NMR Petrophysics

Saturated
$I_0 \rightarrow$ Porosity, ϕ

Unsaturated
$I_0 \rightarrow$ Saturation, S_w
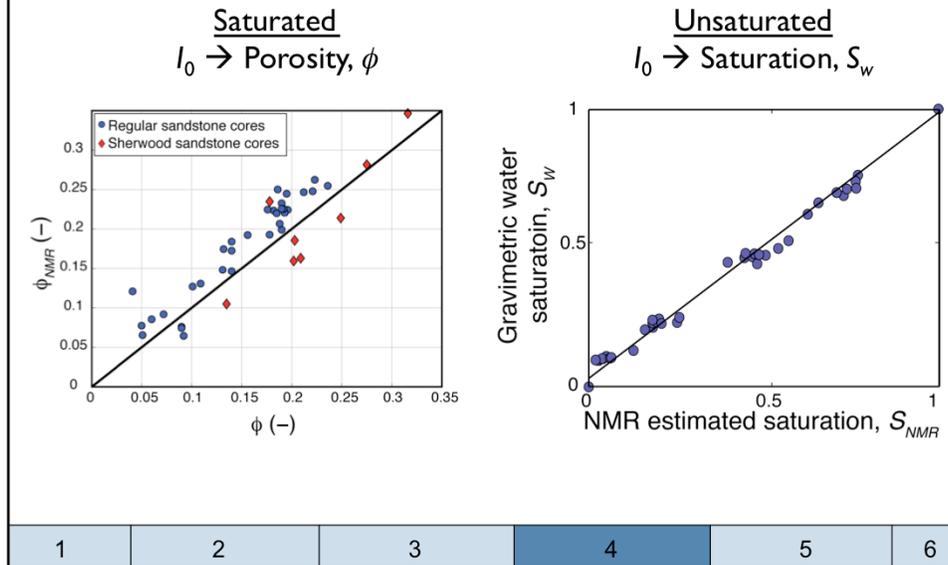
We can use the NMR estimated water volume to determine the porosity, in a saturated system; this calculation requires that the volume of the sample is known. Similarly, we can determine the water content and/or saturation in an unsaturated system. These data tend to be noisier than data from a sample of water because of the faster relaxation that occurs in porous media.

4. NMR Petrophysics

Assumption in NMR Relaxation time Interpretation

$$\frac{1}{T_{2S}} >> \frac{1}{T_{2B}} \;\; \text{and} \;\; \frac{1}{T_{2S}} >> \frac{1}{T_{2D}}$$

In a single pore

$$\frac{1}{T_2} \sim \frac{1}{T_{2S}} = \rho_2 \frac{\alpha}{r} = \rho_2 \frac{S}{V}$$

In a system of pores

$$\frac{1}{T_{2i}} \sim \frac{1}{T_{2Si}} = \rho_2 \frac{\alpha}{r_i} = \rho_2 \left(\frac{S}{V} \right)_i$$

| 1 | 2 | 3 | 4 | 5 | 6 |

Note that in laboratory data if the above assumption is not true, then we can measure T_{2B} by extracting the pore fluid. We can also measure T_{2D} by collecting measurements at multiple echo times; however, it is not that straight forward to account for diffusion relaxation in the distribution.

From Keating and Falzone (2013)

From Keating and Falzone (2013); the surface relaxivity values were calculated from the mean log relaxation time and the surface area to volume ratio determined using Nitrogen BET.

4. NMR Petrophysics
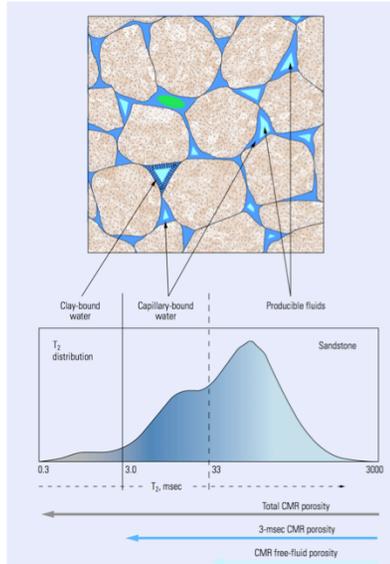
Mobile/Immobile Water Content

Also called bound/producible porosity. Qualitative boundaries, defined to distinguish "producible" porosity in the petroleum industry.

$$\text{Immobile Water Content} = \phi_{NMR} \sum_{T_2 \leq T_{cutoff}} f_i$$

$$BFI = \sum_{T_2 \leq T_{cutoff}} f_i$$

$$\text{Mobile Water Content} = \phi_{NMR} \sum_{T_2 > T_{cutoff}} f_i$$

$$FFI = \sum_{T_2 \leq T_{cutoff}} f_i$$

| 1 | 2 | 3 | 4 | 5 | 6 |

The mobile and immobile water contents are a qualitative assessment of the capillary bound water versus the free water. Theoretically, three different porosity regions can be distinguished from the NMR relaxation time distribution. The smallest pore sizes correspond to the clay-bound water, slightly larger pore sizes correspond to capillary bound water, and the largest pore sizes correspond to the mobile or producible water. Figure from (Allen et al., 2000)

The FFI = the free fluid index, which corresponds to the fraction of the porosity corresponding to the mobile water content.

The BFI = the bound fluid index, which corresponds to the fraction of the porosity corresponding to the immobile water content.

4. NMR Petrophysics

A sandstone core was measured saturated then centrifuged to desaturate the sample and determine the bound volume of water.

sandstones
$T_{2cutoff} \sim 33$ ms

carbonates
$T_{2cutoff} \sim 100$ ms

| 1 | 2 | 3 | 4 | 5 | 6 |
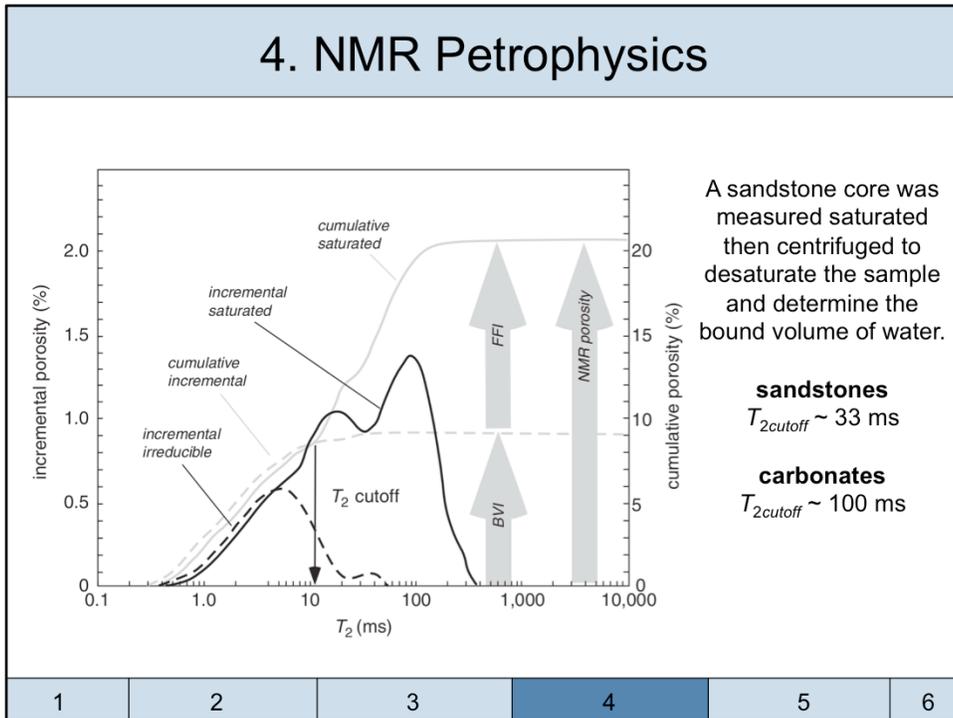
In the oil industry, the cutoff times between bound and mobile fluid volumes are determined from a core sample. This cutoff time is then used to distinguish the mobile from producible pore volumes. In general, sandstone cores have a cutoff time of 33 ms; carbonates cores have cutoff times that range from 80 to 120 ms. No research has been done to determine a cutoff time specific for near surface materials.

Figure from Callaghan (2011)

In the figure BVI = BFI;

4. NMR Petrophysics

Permeability Estimation (from pore geometry)
Kozeny–Carman equation

$$k = \frac{\phi}{T\left(S/V\right)}$$

Estimate ϕ from ϕ_{NMR}
Estimate S/V from T_{2ml}
No NMR parameter to estimate T

$$K = \frac{\rho g}{\mu}k$$

Converting permeability to
hydraulic conductivity
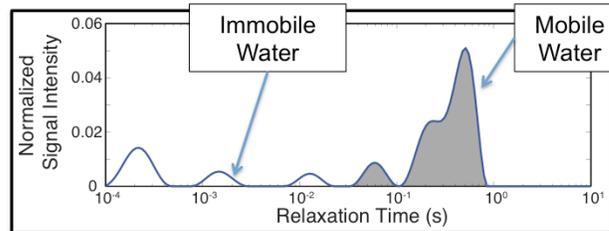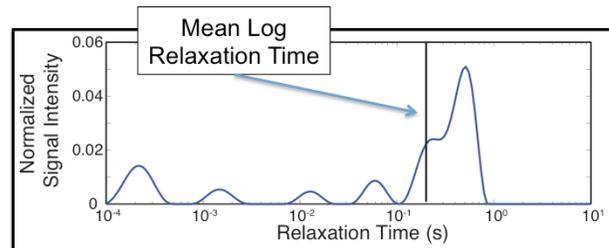
1	2	3	4	5	6

These equations were developed for applications in the petroleum industry. Typically, for a given reservoir, cores are collected for each lithology and the empirical constants *a, b,* and *c*, are through laboratory measurements comparing the permeability to the NMR data. *a* accounts for the tortousity and the lithology. *b* is often set to 2 and *c* is often set to 4

4. NMR Petrophysics

Permeability versus $aT_2{}^b\phi^c$ for sandstones.

$$a = 0.214$$
$$b = 2.163$$
$$c = 3.424$$
$$r^2 = 0.778$$
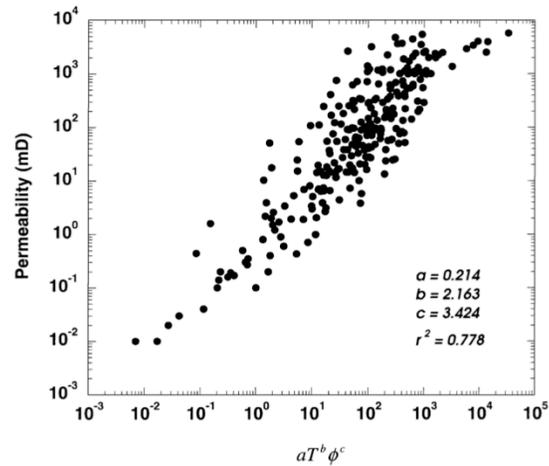
1	2	3	4	5	6

In the oil industry, core from a well are often used to determine the fitting parameters *a, b,* and *c* for each lithological layer. These values are then used to estimate the permeability in the log. The figure shows an example curve and the fitting parameters determined from a set of sandstones. Figure from: Dunn et al. (1999).

4. NMR Petrophysics

Permeability versus $9.289 \times 10^{-8}\ T_2^2 \phi^4$ for isotropic and anisotropic sandstones.
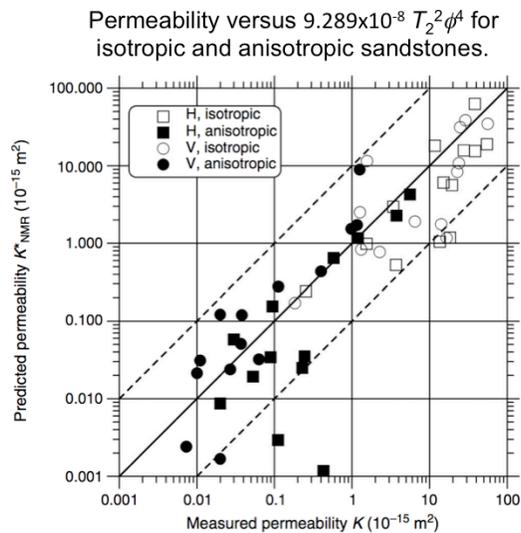
| 1 | 2 | 3 | 4 | 5 | 6 |

One well known problem with the use of NMR parameters to estimate permeability is that NMR measurements only give the bulk sample properties and are not sensitive to directionality. This means that NMR measurements cannot be used to detect anisotropy in the permeability.

Figure shows Permeability calculated from NMR mean relaxation time and porosity plotted versus permeability measured on Bahariya sandstones samples. The dashed lines indicate a distance of one de- cade to both sides of the measured permeability. Figure from Weller et al. (2010)

5. Uncertainty in NMR Petrophysics

<u>Factors that make the interpretation of</u>
<u>NMR data uncertain</u>

surface relaxivity
Fast/slow diffusion

| 1	2	3	4	5	6

5. Uncertainty in NMR Petrophysics
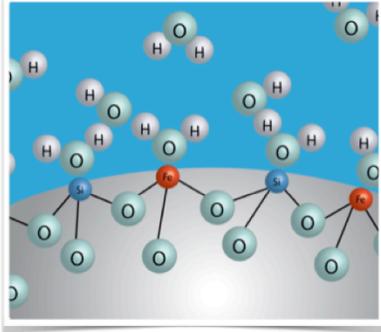
Surface relaxation due to:
- coupling of spins (paramagnetics on pore surface)

Surface relaxivity depends on:
- iron content/distribution
- mineral type/morphology

$$\rho_2 \propto \frac{\sigma_S}{\delta^4}\left(\gamma_I \gamma_S \hbar\right)^2 S\left(S+1\right) f\left(\tau_m, \tau_s\right)$$

Where (variables not in table):

σ_s is the surface density of paramagnetic species (Fe(III))

S is the spin number of the paramagnetic species

δ is the distance of closest approach from the nuclear spin to the paramagnetic species

γ is the gyromagnetic ratio for electrons (I) or magnetic spins (S)

τ_m is the correlation time of a surface diffusion event

τ_s is the finite residence time of the protons on the pore surface

| 1 | 2 | 3 | 4 | 5 | 6 |

From Godefroy et al. (2001)

5. Uncertainty in NMR Petrophysics

ρ_2 small
r_{grain} medium
r_{grain} ~ 0.2 mm

ρ_2 medium
r_{grain} medium
r_{grain} ~ 0.2 mm

$S_s = 0.12$ m^2/g

~99.9% Silica (SiO_2)
<0.03% Fe

$S_s = 0.20$ m^2/g

~99.5% Silica (SiO_2)
~0.1% Hematite (Fe_2O_3)
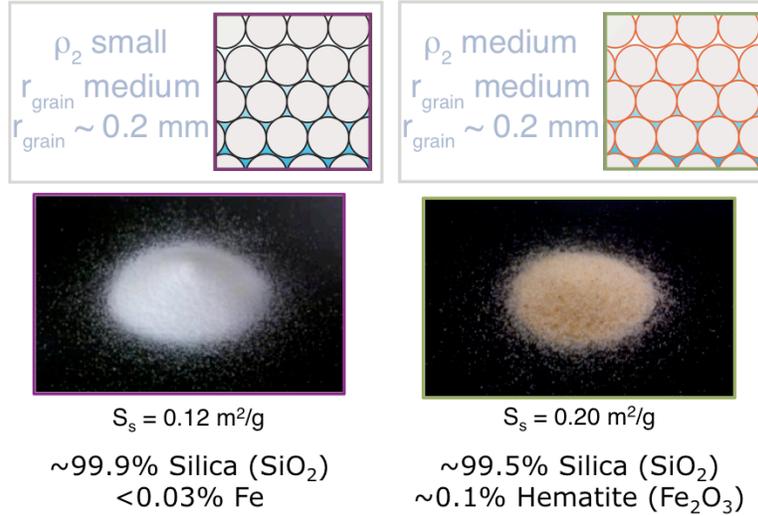
| 1 | 2 | 3 | 4 | 5 | 6 |

Unpublished data and data from Keating and Falzone (2013)

Grain Size Distribution

Data collected by: Sam Falzone

T_2 Distribution
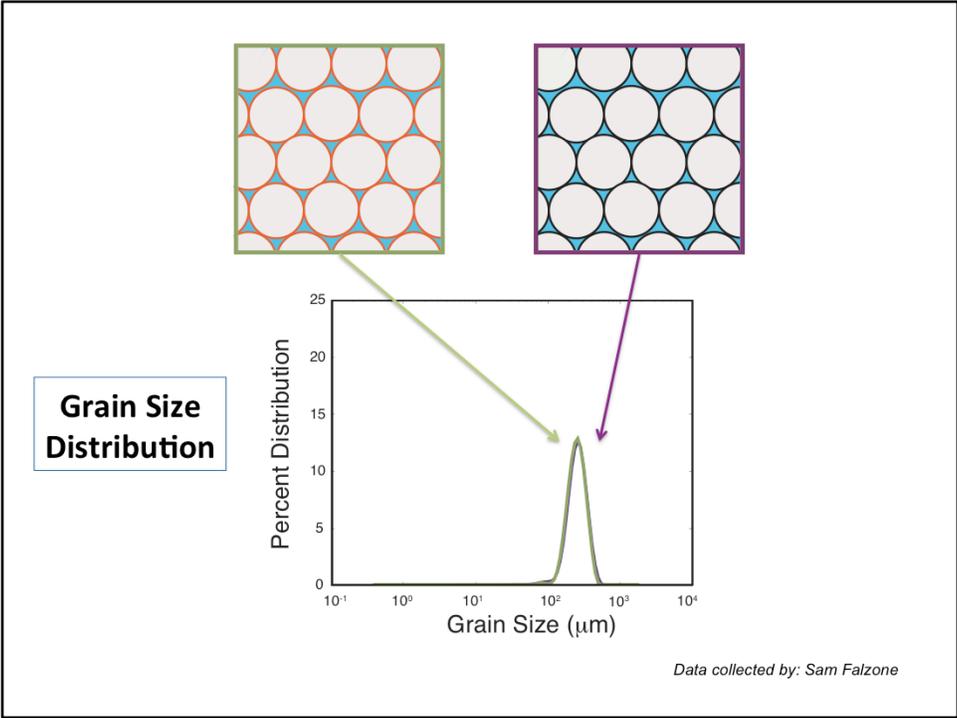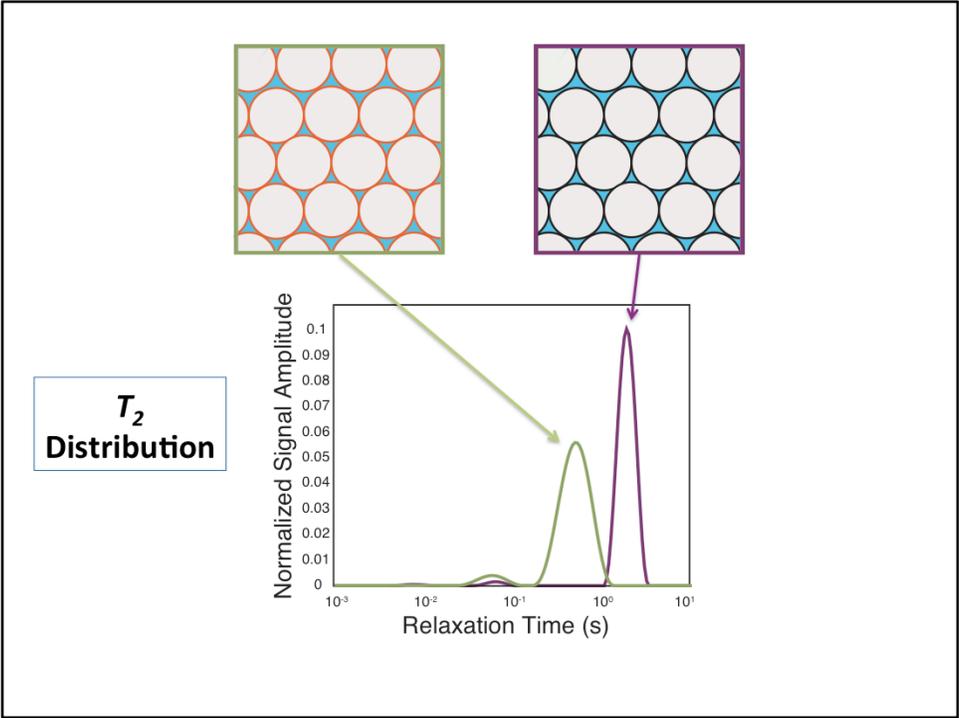
data from Keating and Falzone (2013)

5. Uncertainty in NMR Petrophysics

Note that, as previously mentioned, the equations we have described for T_2 and T_1 come from the analytical solutions for the Bloch Torrey equations.

Brownstein and Tarr determined an eigenvalue solution to these equations. In the **fast diffusion regime** or **surface limited regime**, this simplifies to the equations we have been discussing.

Transverse Magnetization	**Longitudinal Magnetization**

$$\frac{\partial M_{xy}(\mathbf{x},t)}{\partial t} = D\nabla^2 M_{xy}(\mathbf{x},t) - \frac{M_{xy}(\mathbf{x},t)}{T_{2B}}$$

$$\frac{\partial M_z(\mathbf{x},t)}{\partial t} = D\nabla^2 M_z(\mathbf{x},t) - \frac{M_0 - M_z(\mathbf{x},t)}{T_{1B}}$$

With the initial condition

$$M_{xy}(\mathbf{x},t) = 0$$

$$M_z(\mathbf{x},t) = M_0$$

And the boundary condition

$$D\hat{\mathbf{n}} \cdot \nabla M_{xy} - \rho_2 M_{xy} = 0$$

$$D\hat{\mathbf{n}} \cdot \nabla M_z - \rho_1 M_z = 0$$

1	2	3	4	5	6

5. Uncertainty in NMR Petrophysics

<u>Fast Diffusion assumption*</u>

For this to be true $\kappa \ll 1$; $\kappa < 0.1$ considered sufficient

$$T_{2i} = \frac{1}{\rho_2}\frac{r_i}{\alpha}, \quad \kappa = \frac{\rho_2 r}{D}$$

In this case each pore in the distribution has one associated relaxation time and the above equation for T_{2i} holds (neglecting T_{2B} and T_{2D}).

This means we have a linear relationship between pore size and relaxation time.

1	2	3	4	5	6

Brownstein and Tarr (1979) ; Godefroy et al. (2001)

*Note the name "fast diffusion" is misleading. It does not imply that diffusion is faster in this regime.
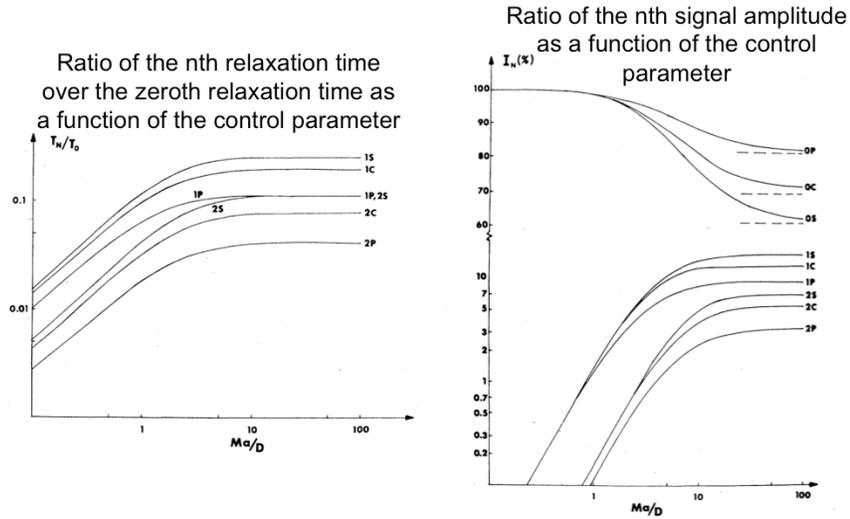
Figure from Brownstein and Tarr (1979). In this "M" signifies the surface relaxivity and "a" signifies the average distance a proton must travel to reach a paramagnetic site. 1S = the first mode for spherical pores; 1C = the first mode for cylindrical pores; 1P = the first mode for planar pores; 2S = the second mode for spherical pores etc.

5. Uncertainty in NMR Petrophysics

Two additional regimes the intermediate and slow diffusion regimes.

Each pore exhibits multiple-exponential relaxation.
T_{2i} is the slowest mode but accounts for the most of the relaxation and is described by:

$$T_{2i} = \frac{1}{\rho_2}\frac{r_i}{\alpha} + \frac{r_i^2}{2\alpha D}$$

| 1 | Brownstein and Tarr 1979 Physical Review A & Godefroy et al., 2001 Physical Review E | 6 |

Brownstein and Tarr (1979); Godefroy et al., (2001)

6. Advanced Laboratory NMR

Pulsed gradient spin-echo (PGSE) sequence
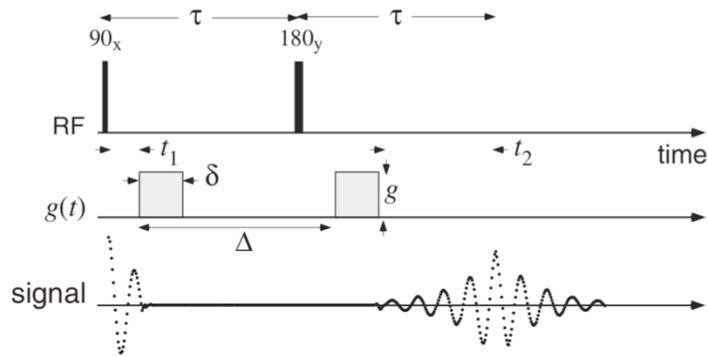
Pulsed gradient spin-echo (PGSE) sequence, with gradient amplitude g, pulse duration, δ, and gradient pulse spacing Δ.τ is the time between the 90 and 180 RF pulses and corresponds to half the spin-echo formation time, TE. From Callaghan (2011)

6. Advanced Laboratory NMR
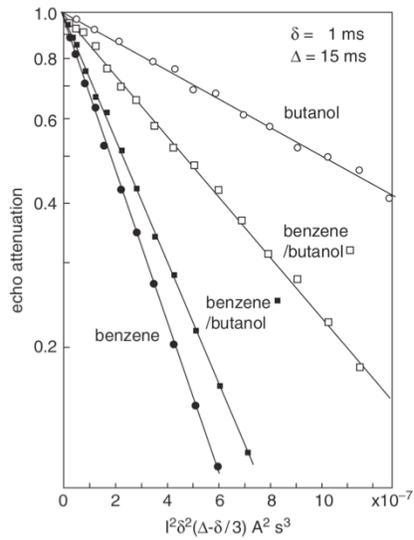
The negative slope of the plot is the effective self diffusion coefficient of the saturating fluid.

| 1 | 2 | 3 | 4 | 5 | 6 |

From Callaghan (2011)

From Callaghan (2011)

6. Advanced Laboratory NMR

T1-T2 Correlation plot: limestone sample

The solid thick line is the theoretical behavior of the
Figure from Callaghan (2011)

A limestone rock sample saturated with brine, in which the distribution of pore sizes covers a wide range, and have broad T1 and T2 distributions. The major peak at long T1 and T2 approaches the line of T1 = T2 expected for bulk water. By contrast the peak at shorter relaxation times is close to the line T1
= 4T2, typical for water in pores, where surface relaxation effects dominate. The behaviour is consistent with the rock structure indicated from optical microscopy, where grains containing small pores are close-packed with large inter-grain void spaces of around 100μm in size. The solid line in is obtained from a simple model in which the relaxation rate is assumed to be a sum of surface and bulk rates, under the condition that the ratio of the surface T1 and T2 relaxation times is 4.5. (Callaghan, 2011)

The map is created from the data using a 2D-Laplace transform inversion algorithm.

6. Advanced Laboratory NMR

Pulse sequence used for D-T2 maps
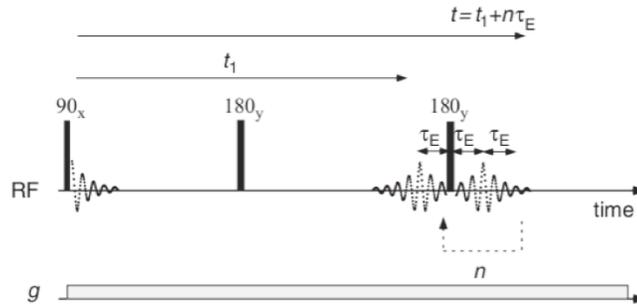
A pulse sequence used to create a D-T2 correlation map. It is a modified CPMG pulse sequence where the first echo time (t_1) is varied, and then an echo train with echo spacing of τ_E, typically set to the smallest echo spacing of the instrument. A constant gradient is applied. These maps can also be constructed using a pulse sequence similar to the PGSE.

1	2	3	4	5	6

From Callaghan (2011)

6. Advanced Laboratory NMR

D–T$_2$ Map – Bentheim Sample after Spontaneous Imbibition

Diffusion coefficient line for water

Diffusion coefficient line for oil

| 1 | 2 | 3 | 4 | 5 | 6 |
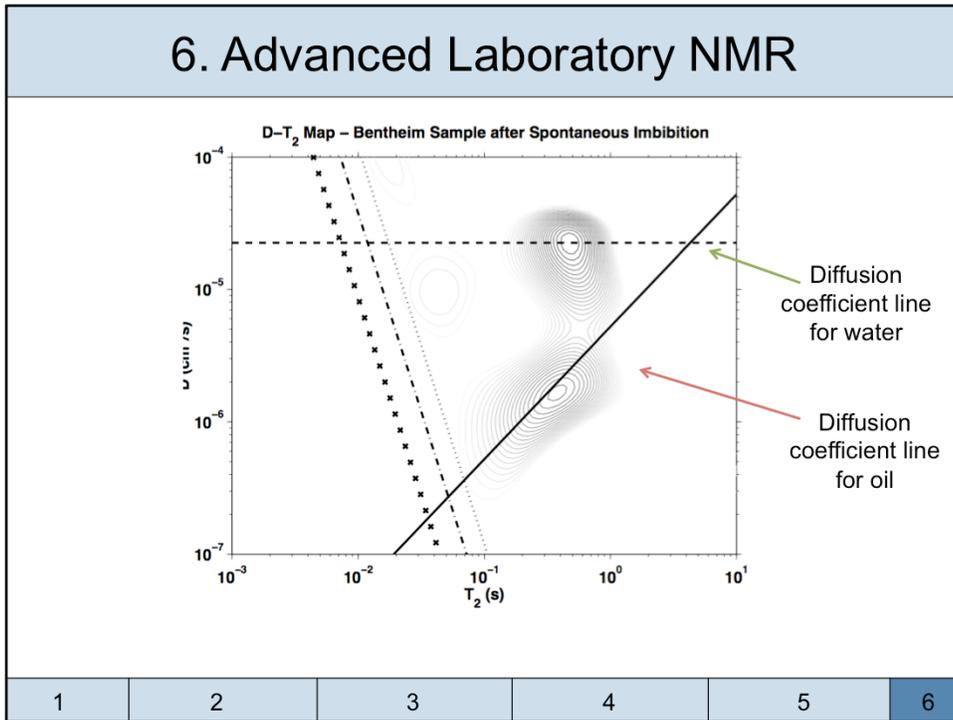
Bentheim Sandstone D - T2 Map, Partially Oil-Saturated. Figure from Flaum et al. (2004)

Notice that in T2-direction the oil and the water peak over lap so it would not be possible to distinguish these two peaks from a T2 relaxation time distribution.