

Fluid and Rock Characterization Using New NMR Diffusion-Editing Pulse Sequences and Two Dimensional Diffusivity- T_2 Maps

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1. Introduction

New down-hole nuclear magnetic resonance (NMR) measurement and interpretation techniques have substantially improved fluid and reservoir characterization. These techniques take advantage of the magnetic field gradient of the logging tools to make diffusion sensitive NMR measurements. In this work, new NMR pulse sequences called "diffusion-editing" (DE) are used to measure diffusivity and relaxation times for water, crude oil, refined oil, and a series of core samples fully and partially saturated with water and hydrocarbon. We use a new inversion technique to obtain two-dimensional maps of diffusivity and relaxation times, and propose new interpretation approaches for these maps.

It is well known that T_2 relaxation time distributions for water-saturated samples provide useful information about the pore-size distribution of the samples¹¹. A number of correlations relate aspects of these distributions to permeability. However, when a sample is partially saturated with oil and water, it is difficult to separate the oil and water relaxation time distributions from each other. Crude oil relaxation time distributions correlate with viscosity, so that oil distributions can also be used to estimate the viscosity of the oil provided that one can obtain separate water and oil distributions. Recent papers by Freedman^{12, 13} *et al* use a suite of Carr-Purcell-Meiboom-Gill (CPMG) measurements^{4, 33} in static external magnetic field gradients to exploit the diffusivity contrast between the water component of the signal and the crude oil component, providing accurate saturations and separated relaxation distributions for both fluids. The data suite consists of a suite of CPMGs including

measurements with very long echo spacings, which are required in order to robustly differentiate oil from water. For the sequences with very long echo spacings only a relatively few echoes have appreciable signal because the signal decays after only a small fraction of the echoes have occurred. This limits the long diffusion time information that is obtained using a suite of CPMGs and in some cases compromises the robustness of the estimated relaxation time distributions.

The CPMG-based DE (CPMG-DE) pulse sequences overcome this limitation by using only two echoes with long echo spacings to obtain diffusion information. Subsequent echoes are collected at the minimum echo spacing, providing diffusion-free relaxation information about the sample. Papers by Freedman¹⁴ *et al.* and Hurlimann^{22, 23} *et al.* discuss fluid and rock characterization using the DE sequence. The latter reference also introduces a different modification to the pulse sequence, where instead of merely modifying the spacing of the early pulses, the sequence begins with a stimulated echo. This version will be discussed briefly, but without great detail as it is not a viable technique for the laboratory apparatus used for these experiments. The second new pulse sequence discussed in full detail in this work modifies the stimulated echo DE sequence by removing it from the fixed magnetic field gradient and applying pulsed magnetic field gradients instead. This technique will be referred to as the PFG-SE DE

The PFG-SE DE sequence is particularly useful for investigating restricted diffusion³⁸, as it is capable of much longer diffusion times than the CPMG-DE

measurement, and can provide a more direct measurement of diffusivity as a function of diffusion time. Long diffusion-time measurements allow the investigation of more details of the pore geometry. Short diffusion times may allow only an average S/V determination. Longer times can yield S/V (or pore size) distributions, and pore-matrix information beyond the single pore. Restricted diffusion measurements that move beyond a single pore give a stronger indication of the permeability of the system. With long enough diffusion times, it should be possible to obtain measurements sensitive to the entire free path through the rock sample³⁵.

The D - T_2 maps provide a wealth of information not previously available with simple relaxation time distributions. The diffusion distribution of a water-saturated sample can give evidence of restricted diffusion, which could then be used to provide pore-size distribution information and permeability prediction independent of that provided by T_2 distributions. Oil relaxation times that do not correlate with viscosity may indicate the oil is wetting the rock surface, which would also be indicated by shifts in the water relaxation time distribution. Water diffusivities above that of bulk water can indicate the presence of internal gradients. The D - T_2 maps can be integrated to provide bulk distributions or windowed to provide more detailed information. This work will demonstrate that the D - T_2 map is a valuable new tool for the interpretation of NMR data, and that the DE measurements provide a very efficient way to obtain them.

2. Background

2.1 Relaxation Time Distributions

T_2 Relaxation time is an NMR parameter that describes the lifetime of a NMR signal in the transverse plane, related to fluid viscosity and therefore characteristic for a given fluid at a fixed temperature⁵. For mixtures such as crude oil, there is no single relaxation value but a distribution of relaxation times. This distribution can be used to estimate the viscosity of crude oils³⁷. Surface interactions can reduce fluid relaxation times, so a water wetting the surface of a rock pore would have a relaxation time shorter than that of bulk water, and in fact the value of the relaxation time in the pore wet and filled with water would be related to the surface-to-volume ratio of that pore. If that idea is extended to a core plug saturated with water, there would be a distribution of relaxation times corresponding to the distribution of pore sizes in the sample. This pore size measurement provides the connection between NMR measurements and sample permeability, which is the basis for a large number of NMR measurements in the oilfield. Also, in the presence of a magnetic field gradient, the relaxation time is sensitive to changes in position of the individual spins, and thus to the diffusivity of the sample.

$$\frac{1}{T_2} = \frac{1}{T_{2(bulk)}} + \frac{1}{T_{2(surface)}} + \frac{1}{T_{2(diffusion)}} \quad (1)$$

The basic measurement technique for determining T_2 relaxation time in a field with minor inhomogeneities is the CPMG sequence, shown in Fig. 1. The contributions to the relaxation time of a sample come from three terms¹¹: bulk fluid relaxation, surface relaxation, and relaxation due to diffusion. Eq. 1 lists the components of the relaxation time, while Eq. 2 expands those components. T_2 is the characteristic transverse relaxation time, γ is the gyro-magnetic ratio, D is the self-diffusion constant of the relaxing fluid, and g is the strength of the field gradient. ρ is the relaxivity, which describes the rate at which the particular surface relaxes or 'kills' the spins approaching the surface. It should be noted that surface relaxation only occurs in a surface-wetting fluid. When multiple fluids are present, a non-wetting fluid only undergoes bulk and diffusion-based relaxation.

$$\frac{1}{T_2} = \frac{1}{T_{2,bulk}} + \rho \frac{S}{V} + \frac{1}{12} \gamma^2 g^2 t_E^2 D \quad (2)$$

2.2 Multiple Fluids and Overlapping Distributions

The first technique developed for distinguishing multiple fluids present in a sample were based on exploiting T_1 contrast between the fluids present¹. By adding a measurement with a polarization time inadequate to fully polarize the complete sample, different fluids will experience different degrees of polarization. It is possible to separate the longest T_1 components by taking the difference between this and the fully polarized result. In the first technique for analyzing the data obtained through this technique, differences were taken between T_2

distributions, but in logging cases the signal-to-noise ratio of short polarization-time measurements is quite poor, and produces large errors in the results³⁹. In the time domain, results are only slightly improved and has found very limited success, and only for determination of gas. The T_1/T_2 ratio is much higher for gas in the presence of a field gradient, so gas signal that might overlap with other fluids in the T_2 distribution have much better separation in T_1 . This happens because the high diffusivity of gas causes more T_2 relaxation due to diffusion, but does not affect T_1 . For oil or brine contributions, the T_1 values correlate with T_2 , so T_1 contrast is not helpful.

The second technique for distinguishing fluids was the first step toward the methods used in this project: taking advantage of contrasts in the self-diffusion contrasts of different fluids¹¹. The parameter modified in this case is the echo spacing. The process was based on the contribution of diffusivity to relaxation time, and benefited from the inherent magnetic field gradients present in logging tools. Returning to Eq. 2, it is evident that the magnitude of the $T_{2(\text{diffusion})}$ term depends the value of the echo spacing. By repeating measurements with different echo spacings, the faster-diffusing components can be shifted to shorter apparent relaxation times.

The most advanced method using unmodified gradient CPMG measurements is the Magnetic Resonance Fluid characterization technique (MRF)^{12, 13}. This technique was not the first to propose large suites of gradient CPMG measurements, but was first to propose using those suites with a model to relate the distributions of relaxation and diffusivity of hydrocarbon fluids. This

model, called the Constituent Viscosity Model (CVM), proposes a constituent-by-constituent correlation between the two distributions, and allows the recovery of a complete T_2 distribution for the crude oil component, providing a prediction of oil viscosity.

There are two main hypotheses behind the CVM. The first is that the relaxation time of the k^{th} molecular constituent of a hydrocarbon correlates with viscosity in a way that is analogous to that in a bulk fluid. Eq. 3 shows the form of the macroscopic empirical correlation, with a as an empirical constant. Eq. 4 is the constituent form, where T is the temperature, and η_k is the constituent viscosity of the crude oil, which is not equal to the viscosity of any specific pure component present in the crude-oil mixture¹².

$$T_{2,lm} = \frac{aT}{\eta(T)} \quad (3)$$

$$T_{2,k} = \frac{aT}{\eta_k(T)} \quad (4)$$

The second is that the diffusion time of the k^{th} molecular constituent of a hydrocarbon also correlates with viscosity in a way that is analogous to that in a bulk fluid. In this case, Eq. 5 describes the correlation, where b is an empirically-determined constant. The major prediction of this model is that relaxation and diffusivity distributions are not independent. This is presented in equation form in Eq. 6¹².

$$D_k = \frac{bT}{\eta_k(T)} \quad (5)$$

$$\frac{D_k}{T_{2,k}} = \frac{b}{a} = \frac{D_{lm}}{T_{2,lm}} \quad (6)$$

The MRF technique has been successfully implemented for saturation determination, viscosity prediction, and in evaluating wettability changes in some samples. It is a very strong technique that can take full advantage of the benefits of DE measurements addressed in this work. However, the technique is dependent on two pieces of information: the correlation constants a (relating relaxation time to viscosity), and b (relating self-diffusion to viscosity). There is some literature available for both constants, but some samples have been observed to diverge from those values, and may provide misleading results. It would be convenient to have a direct model-independent determination of these values without requiring viscosity measurements, or perhaps a measurement only of the ratio a/b . The technique also assumes that wettability affects T_2 and diffusivity along the same correlation line as that in bulk fluids.

2.3 NMR Relaxation in Porous Media

Returning to Eq. 1, in the absence of a gradient, relaxation decay is often dominated by the transverse relaxation time constant $T_{2(\text{surface})}$. The value of $T_{2(\text{surface})}$ can be estimated according to what is called the ‘killing regime’, as characterized by Eq. 7.

$$T_{2(\text{surface})} \approx \begin{cases} \frac{a^2}{D}, \frac{\rho a}{D} \gg 1 \\ \frac{a}{\rho}, \frac{\rho a}{D} \ll 1 \end{cases} \quad (7)$$

Where a is the characteristic pore length (effectively the inverse of the surface to volume ratio for a given or assumed pore geometry). The surface relaxivity ρ is highly dependent on the chemical nature of the surface itself, and though it is very difficult to measure reliably, it is generally held to be constant according to the mineralogy of the solid matrix. In the strong killing regime, where $\frac{\rho a}{D} \gg 1$, relaxation is very fast once the surface is reached, so the surface relaxation is dominated by how quickly the proton moves in the pore, and how far it has to travel to reach the pore wall²⁸. This regime is also referred to as the slow diffusion regime. In most pores in the fast killing regime, relaxation is dominated by bulk relaxation ($T_{2(\text{bulk})}$), and interpretation of S/V from relaxation distributions is invalid because the relaxation time is independent of relaxivity. In the weak killing regime, where $\frac{\rho a}{D} \ll 1$, diffusion is fast enough to homogenize the spins in the pore, so the rate of relaxation at the surface dominates. This regime is also called the fast diffusion regime.

It would seem that measurements of the T_2 of a porous system could provide immediate assessment of the surface to volume ratio from a determination of diffusivity providing the porous medium fell into the strong killing regime. In the weak killing regime, S/V should be available from the T_2 alone. Unfortunately, the measurement is not as simple as it seems. In a real porous medium, there is not an easily defined single pore that can describe the entire

pore network. In fact, in the example of a clay-containing rock or a carbonate rock with vugs, the range of pore sizes in a single sample may vary of several orders of magnitude. Across that range, the contribution of strong-killing pores is generally very small. An analysis of the T_2 distribution, with the contribution of every pore included in a multiple exponential expression, provides a measurement of the pore size distribution¹¹. It can even be possible to determine a characteristic length scale, one that doesn't really describe any particular pore but gives a fair approximation of all pores. (Note: in carbonates, some studies use at least two length scales, one to describe inter-granular 'macro' pores, and another to describe intra-granular 'micro' pores.⁴⁰) Surface relaxation based methods fail to adequately estimate permeability in cases where the pore throats are not related to pore bodies, however. In those cases, it is necessary to explore beyond the single pore, through techniques such as the PFG-SE discussed below.

2.4 Permeability Prediction by NMR

Once hydrocarbon has been detected in a rock matrix, the key parameter of the porous system is the permeability, which describes the flow rate a given pressure drop will provide through the porous system. Essentially, permeability is the measure of how easy or difficult it will be to flow through the rock matrix. There is no static permeability measurement available today. A variety of empirical methods to obtain permeability from conventional logging measurements are in use, but they are often unreliable as they do not depend on

measurable physical parameters that directly affect permeability. NMR has shown the potential of providing a more direct measurement, because of its sensitivity to pore geometry¹¹.

In many samples, permeability can be estimated from the pore size distribution. One way to express the pore size is in terms of the ratio of its surface area to its volume (S/V). As shown in Eq. 2, NMR measurement can be used to derive S/V . However, S/V is not always a good indicator of permeability. The flow-limiting geometry in a porous system is actually the pore throat, or the narrowest pathway connecting two pores in a network. In most systems, there is a direct relationship between pore body and pore throat size, and S/V alone can provide the necessary information. In some cases of interest today, however, it is necessary to examine the detailed path through the entire pore network. This, finally, is the key to determining permeability in a pore network. Proposed techniques involved estimating the tortuosity of the system through NMR diffusion, and predicting pore connectivity and transport aided by that information⁴¹. At present, almost all NMR-based prediction of permeability arises from calculations based solely on S/V . The current techniques are discussed in section 2.5 (specifically with respect to carbonates), along with their limitations and proposed alternatives in systems of interest.

2.5 Carbonates

In well-logging, one situation in which permeability measurements become very important is in carbonate rocks. Carbonate reservoirs contain a large percentage of the world's hydrocarbon reserves. However, basic relaxation-

based NMR interpretation techniques are often invalid or misleading in carbonate samples⁴². The measurements presented in this work were developed to demonstrate the necessity of using diffusion to characterize permeability in many carbonate rocks.

Relaxation measurements alone are inadequate for a number of reasons. The main reason is that in some rocks, especially many carbonates, there is no strong correlation between pore body sizes and pore throat sizes⁴².

Another problem with relaxation-based permeability prediction in carbonates is diffusive coupling. The surface relaxivity of carbonates is significantly lower than that of sandstone samples, which means that single spins have more time to move from one pore to another before relaxing completely. The result of this diffusion is that there is a continuum of apparent relaxation times that obscure the true relaxation information that would correlate correctly with the pore information. To complicate the matter, carbonates have been shown to manifest varying relaxivities, so even two pores of the same size could have different relaxation properties².

An additional complication with NMR permeability prediction in carbonates is the presence of vugs¹⁹. The porosity of vugs is always visible to NMR measurements, but with low relaxivity and low S/V , a large vug will essentially relax as a bulk fluid, providing no pore-size information. In a sample with a large vug fraction, the vug contribution to the total porosity can be significant, but in many cases their contribution to the permeability of the sample can be quite low. In essence, unless the sample contains connected vugs, the vugular porosity can

often be completely ignored when estimating permeability. If the vugs are strongly connected, however, transport through the vugs tends to dominate the permeability of the sample.

There are two commonly used correlations for predicting permeability (k) from NMR relaxation data. The first is based on the Timur-Coates equation⁹ (Eq. 8), where the ratio between the free fluid index (FFI) and the bound volume irreducible (BVI) are defined by a cutoff time in the relaxation distribution. The equation itself was developed for sandstone samples, but can be extended to work for carbonates by using an appropriate cutoff value selected to take into account the different surface relaxivity of carbonates.

$$k = 10^4 \phi^4 \left(\frac{FFI}{BVI} \right)^2 \quad (8)$$

$$k = a(\phi)^4 (T_{2,lm})^2 \quad (9)$$

$$k = 4.75(\phi_{750})^4 (T_{2,lm,750})^2 \quad (10)$$

The second, the SDR equation²⁴ (Eq. 9) uses the log mean relaxation time to characterize the relaxation distribution, with a coefficient a which depends on the formation type. Chang⁶ presented a variation of the SDR equation (Eq. 10) for carbonates that does not include any porosity that relaxes slower than 750 milliseconds. This portion is assumed to be vugular porosity, and is assumed not to contribute to the permeability. This is not always a valid assumption. There are a number of other similar and related correlations, but those will not be addressed here.

Hidajat¹⁹ proposes a modification to the Chang equation⁶ that takes into account the tortuosity of the sample, effectively determining whether or not the vugular porosity should be expected to contribute to the permeability. This technique is based on using the formation factor or tortuosity measurements to

$$k = 4.75 \left(\left(\frac{\phi}{\phi_{750}} \right)^a \phi_{750} \right)^4 \left(\left(\frac{T_{2.lm}}{T_{2.lm,750}} \right)^a T_{2.lm,750} \right)^2 \quad (11)$$

$$a = 1 - \frac{1 - \frac{tort}{3}}{1 - \frac{tort_{max}}{3}} \quad (12)$$

determine to what degree the vugular porosity should be included in the permeability estimation. His equation is show in Eq. 11. The parameter a is shown in Eq. 12. The value of $tort_{max}$ is empirical and probably lithology-dependent. Hidajat proposes determining the tortuosity of the sample either through a model or through restricted diffusion measurements of the type described in section 2.9.

2.6 NMR and Diffusion

2.61 NMR in a Field Gradient

Diffusion has a major effect on NMR magnetization in the presence of a magnetic field gradient. When the magnetic field is not uniform, any spin (polarized proton) that diffuses from one field strength to another will no longer be coherent with the non-relaxed spins, and will therefore not be measured when

the total number of coherent spins is counted in a spin echo¹⁷. The spins are assumed to have displaced according to a Gaussian distribution due to molecular diffusion or Brownian motion.

The standard spin echo NMR diffusion measurement method involves rotating all polarized spins 90° out of the polarized direction, allow them to precess for a controlled amount of time (τ), then flip the spins 180°. The spins that have not relaxed back to polarization then precess back to their original position, where they achieve coherence called a 'spin echo'. The mechanism of gradient induced relaxation is different from the standard transverse relaxation, but both affect the attenuation of the magnetization. The echo attenuation in a gradient is shown in Eq. 13¹⁵.

$$M = M_0 e^{-2\tau/T_2} \exp\left\{-\frac{2}{3}\gamma^2 g^2 D \tau^3\right\} \quad (13)$$

Where M is magnetization as a function of time (M_0 at full polarization, time 0), and τ is half the time between the radio-frequency pulses, or half the TE. From this expression, the diffusion constant of the fluid can often be evaluated directly from the magnetization of a simple spin echo in a known field gradient.

For many systems, however, it is not possible to determine diffusion using a simple spin echo. For example, if the diffusivity or gradient strength is too high, the magnetization decay may be too fast to measure accurately. Also, if the diffusion constant is very small, or if the second term in the exponential is small compared to the first, decay due to diffusion in the field gradient may not be significant enough to measure directly. In porous systems the presence of

surface relaxation (due to paramagnetic materials in the matrix or similar mechanisms) tends to reduce T_2 to a far greater degree, leaving diffusion-based relaxation relatively minor¹⁶.

2.62 Pulsed Field Gradient Measurements

When a simple spin echo is no longer adequate for examining relaxation due to diffusion, it is possible to employ a different pulse sequence, called the Pulsed-Field Gradient (PFG) and shown in Fig. 2¹⁵. In this sequence, instead of allowing the entire experiment to take place in a field gradient, the gradient is applied in two short gradient pulses. The pulses are of time width δ and separation Δ . The sum of Δ and δ is referred to as the diffusion time t_D , as it determines the amount of time the spins are allowed to diffuse before the gradient encoding is removed. The first pulse labels the spins with different frequencies dependent on their positions where they are allowed to diffuse, effectively encoding the phase of the spins. Then, after the 180° pulse inverts the precession, the second gradient pulse returns the spins to their original phase for measurement, with the difference that now those spins that have diffused are not decoded to their original phase and are no longer measured in the spin echo. In this way, it is possible to separate the diffusion relaxation from transverse relaxation by comparing the magnetization with gradient pulses present to the magnetization with no gradient pulses according to Eq. 14¹⁵

$$\frac{M(g)}{M(g=0)} = \exp\left\{-\gamma^2 g^2 \delta^2 D \left(\Delta - \frac{\delta}{3}\right)\right\} \quad (14)$$

2.63 Pulsed Field Gradient – Stimulated Echo Measurements

In porous systems, however, it is still often not entirely effective to measure diffusivity with these methods due to the short transverse relaxation time. For this case, it is possible to take advantage of another NMR characteristic of porous media: the longitudinal relaxation time is often longer than the transverse relaxation time (that is: $T_1/T_2 > 1$). In this case, the spins can be rotated from the axis where they decay according to the transverse relaxation time to the axis where they experience longitudinal relaxation. This pulse sequence, called the Pulsed-Field Gradient Stimulated Echo (PFG-SE), is shown in Fig. 3⁴⁴. This sequence again begins with a 90° radio-frequency pulse, followed by a gradient pulse of width δ to encode the phase of the spins. In this case, however, another 90° radio-frequency pulse follows, moving the spins into the axis of longitudinal relaxation, where they by longitudinal relaxation instead of transverse (a major benefit in cases where $T_1 > T_2$). Immediately preceding the end of this diffusion time, another 90° pulse moves the spins back to the transverse plane so as to allow the development of an echo similar to the spin echo above, called the stimulated echo. Finally, a second gradient pulse undoes the spreading, again decoding the phase excluding those that have diffused out of coherence. This sequence is characterized by the same two timings as the PFG, δ and Δ . It should also be noted that δ is very small compared to the other times in the pulse sequence, so Δ is generally assumed to be equal to the diffusion time t_D . The equation for the magnetization of this system is shown in

Eq 15. Another benefit of the stimulated echo approach is that it allows the evaluation of apparent diffusivity as a function of t_D , which is necessary for restricted diffusion measurements discussed in section 3.3²².

$$\frac{M(g)}{M(g=0)} = \frac{1}{2} \exp \left\{ -\gamma^2 g^2 \delta^2 D \left(\Delta - \frac{\delta}{3} \right) \right\} \times \exp \left\{ -\frac{\Delta - \delta}{T_1} - 2\delta \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right\} \quad (15)$$

Diffusion-based measurement techniques have been employed for a number of applications, including probing surface-to-volume ratio^{26, 36}, detecting changes in saturation⁷, estimating irreducible fluid saturation³, pore length scales⁴¹, and pore-size distributions²⁵. Most of these techniques are based on restricted diffusion measurements, discussed at length the following sections.

2.7 NMR Diffusion in Porous Media

At short diffusion times, the porous medium has no effect on the measured diffusivity of the sample. As the diffusion time increases, however, the spins become more and more likely to encounter a pore wall, and the pore walls restrict the displacement of the spins. The actual displacement is less than the expected displacement, so the measured diffusivity begins to drop³⁵. The onset of this effect depends on the diffusivity and the diffusion time, usually combined into a term referred to as the diffusion length, shown in Eq. 16. The diffusion length gives the expected mean displacement of each spin over the duration of the diffusion measurement in the absence of pore walls. The most significant

$$l_d = \sqrt{Dt_D} \quad (16)$$

result of this effect is that the measured diffusivity now depends on the diffusion length. Since the diffusivity of the fluid is not changing, this effect is often referred to as time dependant diffusion.

The counterpart to the diffusion length might be the gradient pulse momentum, shown in Eq. 17³⁵. This term defines the resolution of the measurement, essentially indicating how much attenuation due to diffusion will occur in a given interval. As this term grows, more diffusion-based decay occurs in the same diffusion time. If q is too small, there is no resolution to the diffusivity, while if q is too large, fast-diffusing components will not be properly characterized, as they will decay too quickly.

$$q = \gamma g \delta \quad (17)$$

2.8 Time Dependant Diffusion: Short Diffusion Times

As stated above, the measured diffusivity in a porous medium can be dependent on the diffusion time t_D . In fact, this dependence also depends on the range of t_D under investigation. Fig. 4 shows cases in which the measured diffusivity will vary for a single pore. Subplot a. shows very short diffusion times, where the spins do not encounter the pore wall. Subplot b. shows short diffusion times, when spins begin to experience restriction from the pore walls. Subplot c. shows the same pore at very long diffusion time, where the spin can move outside the single pore and through the matrix. This case will be further discussed in Section 2.9.

Obviously, the self-diffusion constant of the fluid cannot be a function of time – a curve of diffusivity verses diffusion time should give a straight line for a

pure fluid, as show in Fig. 5 subplot a. Therefore, restricted diffusion is indicated by any deviation from that line³⁵. At very short t_D , the observed diffusion should behave exactly as the bulk-fluid diffusion, as very few spins diffuse long enough to encounter the pore walls. As the diffusion time increases, however, more and more spins will reach the wall and face restriction of its displacement, so the observed diffusivity will begin to diverge from the bulk-fluid diffusivity, shown in Fig. 5 subplot b. At the onset of this divergence, there will be a thin layer of spins close to the surface of the pore that diffuse under restriction, while those in the body of the pore still relax as bulk fluid. It should be apparent, then, that the deviation of the observed diffusion constant from the actual self-diffusion constant should be proportional to the surface to volume ratio. The equation to describe this deviation is shown in Eq. 18³⁵.

$$\frac{D_{obs}(t_D)}{D} = 1 - \frac{4\sqrt{Dt_D}}{3\sqrt{\pi}} \frac{S}{V} + O(Dt_D) \quad (18)$$

D_{obs} refers to the measured diffusivity, as opposed to the true diffusivity of the fluid, S is the surface area, and V is the pore volume. It should be noted that if the diffusion times are extremely short, the equation collapses down to free diffusion. It has also been speculated that the continued deviation over time should give some indication of the varying length scales throughout a system. The logic is this: if there are multiple distinct length scales in a sample, the development of each length scale should cause an inflection in a curve of D_{obs} vs. t_D representing each changing length scale. The smallest range of pore sizes would cause a deviation at short times, while the large pores will not show the

effects of restriction until longer diffusion times. As long as the pore size distribution consists of several distinct ranges, separated perhaps by one or two orders of magnitude, it should be possible to distinguish the contributions from the different pore-size ranges.

2.9 Time Dependant Diffusion: Long Diffusion Times

If t_D is large enough to describe diffusion through the entire system, D_{obs} should approach a constant value representing the macroscopic diffusion coefficient³⁵. The macroscopic diffusion constant is essentially a measure of the path length through the pore network, as the proton is essentially allowed to diffuse long enough to navigate through all connected pores. At this point, the curve shown in Fig. 5 will reach the plateau show in subplot c., as the D_{obs} will cease to change, indicating it has reached the macroscopic diffusion constant. As a measure of connectivity, the macroscopic diffusion constant (called D_{eff}) can be used to determine the formation factor F , a fundamental parameter related to tortuosity. Formation factor is actually the ratio of conductivity through a porous system compared to conductivity through free fluid. The relationship between D_{eff} and F is show in Eq. 19, where ϕ is the porosity of the system.

$$D_{eff} = \frac{D_0}{F\phi} \quad (19)$$

D_{eff} is often referred to as the tortuosity limit or asymptote.

As a theoretical approach, long diffusion-time methods should give a strong indicator of tortuosity for any system, regardless of the correspondence between pore throats and pore bodies¹⁰. In practice, however, at times it is not possible to carry this measurement out due to the mechanisms of bulk and surface relaxation²⁷. Even in the longitudinal axis, a spin will relax in a finite amount of time, and if the measurable spins aren't diffusing fast enough to reach the tortuosity limit in that time, the observed diffusivity will attenuate to noise before it reach a state of time independence and equal the effective diffusivity. One situation in which it is possible to measure macroscopic diffusion is when the fluid in the pore space has a high diffusion constant, a long transverse relaxation time, and minimal surface relaxation.

Recently, developments in super-polarized Xenon NMR have made it possible to probe diffusion in porous media with Xe as the diffusing fluid^{30, 31, 32}. In this case the long relaxation time and high diffusivity of the Xe make it is possible to characterize the full range of time dependent diffusion down to a plateau that describes the macroscopic diffusion constant of the sample. In the experiment shown there, the emphasis was on long diffusion times, so it is not easy to determine the onset of deviation from the free diffusion (approximated by the short-time asymptote). For the long time limit, on the other hand, the establishment of a time independent diffusivity is very clear, shown by the tortuosity asymptote. Polarized gas NMR holds great promise for analyzing porous media. Today these methods are cumbersome and expensive, but as study continues in that field these obstacles are likely to be overcome. Our

proposal is to employ hydrocarbons in gas or supercritical fluid liquid state to perform the same form of experiment, without the complicated polarization process^{18, 43}. Dense supercritical ethane has a diffusion constant two orders of magnitude higher than water, and relaxes at a much slower rate as well⁴⁸. Dense ethane still falls an order of magnitude short of the diffusivity of xenon, but xenon-based measurements were actually performed with oxygen doping to reduce the relaxation time, and without doping the ethane sample, we believe we will be able to perform measurements at similar diffusion lengths.

3. Theory

3.0 Pulse Sequence Overview

Chapter 3 will introduce a trio of pulse sequences that can be used to perform diffusion editing measurements. The first pulse sequence, CPMG DE, is used primarily for separating oil and water signals, and obtaining the best available results for fast-relaxing components. The second is the SE DE, which is used primarily for long diffusion-time measurements in the presence of a fixed gradient. This sequence is not viable for laboratory experiments, but is very useful for field measurements. The third sequence is the PFG-SE DE, which is an adaptation of the SE DE for laboratory experiments. Table 1 provides a summary of pulse sequences listed in this chapter and in chapter 2, along with the measurements each provide and their limitations.

3.1 Modified CPMG DE Sequences

Most down-hole NMR measurements are based on the well-known Carr-Purcell-Meiboom-Gill (CPMG) sequence in a fixed magnetic field gradient¹⁶. This sequence provides T_2 relaxation information with sensitivity to pore surface-to-volume ratio and fluid diffusion. By combining multiple CPMG measurements on partially saturated rocks, it is possible to approach fluid saturation by taking advantage of the diffusivity contrast between oil and water¹². The measurements described in this section use a form of the CPMG sequence that has been modified to improve the robustness of the petrophysical data obtained through NMR measurements. This sequence is referred to as “diffusion editing” to describe the use of modified pulse timing to “edit” the amplitude of the echo data and provide diffusion information.

The sequence is displayed in Fig. 6. Like other CPMG-based techniques for obtaining saturation data, the CPMG-DE consists of a suite of similar NMR measurements. In this case, the independent variable that provides diffusion information is the echo spacing of the first two echoes of the sequence (called $T_{E,L}$). An increase in the spacing of these two echoes decreases the amplitude of subsequent echoes due to diffusion effects. The remaining echoes are at a fixed shorter echo spacing ($T_{E,S}$) selected to minimize further relaxation due to diffusion. The progressive amplitude loss over the first two echoes for a series of $T_{E,L}$ values provides information about the diffusivity of fluids in the sample, while the multi-exponential decay of subsequent data points provides T_2 relaxation distributions, as would an unmodified CPMG. Models that relate T_2 and

diffusivity distributions, such as the CVM, allow the separation of T_2 relaxation distributions for multiple fluids present in a sample. The technique used in this report, however, uses a method developed by Hurlimann^{22, 23} *et al* to obtain a model-independent simultaneous inversion for both relaxation and diffusion. This inversion provides the D - T_2 maps, which allow visual interpretation of multiple fluid systems. Like any fixed-gradient measurement, the CPMG DE only measures a thin slice of the total sample, corresponding to the bandwidth of the hardware.

The equation describing the magnetization decay of a CPMG DE sequence is shown in Eq. 20²². Note that the diffusion and relaxation terms

$$M(t_{E,L}, t) = \iint dD dT_2 f(D, T_2) e^{-t/T_2} \exp\left\{-\frac{1}{6} \gamma^2 g^2 D t_{E,L}^3\right\} \quad (20)$$

Distribution Function $\rightarrow f(D, T_2)$

Relaxation Term $\rightarrow e^{-t/T_2}$

Diffusion Term $\rightarrow \exp\left\{-\frac{1}{6} \gamma^2 g^2 D t_{E,L}^3\right\}$

are separable. This equation is useful for understanding the pulse sequence, but does not apply to a real data set, as it only account for the on-resonance terms, and does not included stimulated echoes from the off-resonance components. The stimulated echo contributions can be quite significant²¹ and the stimulated echoes decay under diffusion at twice the rate of the direct echo. The contribution from the off-resonance terms can be included as a second diffusion term, as in Eq 21. a and b are attenuation coefficients dependent on bandwidth.

a represents the contribution from the direct echo, and b represents the contribution from the stimulated echo.

$$M(t_{E,L}, t) = \iint dDdT_2 f(D, T_2) e^{-t/T_2} \left[a \exp\left\{-\frac{1}{6} \gamma^2 g^2 D t_{E,L}^3\right\} + b \exp\left\{-\frac{1}{3} \gamma^2 g^2 D t_{E,L}^3\right\} \right] \quad (21)$$

To best characterize the echoes collected for these experiments, a matched filter can be employed. In the matched filter technique, an average echo shape is obtained by average the 30th through 60th echoes of the shortest $T_{E,L}$, data set where $T_{E,L}$ is not equal to $T_{E,S}$. That average echo is then used as a windowing filter for all the subsequent echoes, using a dot product with the real echoes of all data sets to obtain a single value for each echo of each channel of all data sets.

3.2 Diffusion Editing with Stimulated Echoes

3.2.1 Stimulated Echo Diffusion Editing

The CPMG-DE measurements are difficult to interpret when restricted diffusion is taking place. Each data set in the suite has a different diffusion time, which provides the necessary diffusion sensitivity but makes it impossible to develop a D - T_2 map corresponding to a single diffusion length. The stimulated echo versions of the DE technique avoid that limitation by changing keeping the diffusion time constant, and changing instead the degree of phase encoding.

The basic Stimulated Echo Diffusion Editing (SE DE) sequence is shown in Fig. 7. δ is the time between the starting 90° pulse and the second 90° pulse, which moves the magnetization back to the longitudinal axis as in the basic PFG-

SE measurements. Δ is the spacing between the second and third 90° pulses, which makes up the bulk of the diffusion time in most cases. The stimulated echo occurs at time δ past the final 90° pulse, and it is followed by a series of 180° pulses to obtain a relaxation time measurement free of field inhomogeneity artifacts. The equation for the magnetization in this case Eq. 22

$$M(\delta, t) = \iint dDdT_2 f(D, T_2) e^{-t/T_2} \frac{1}{2} \exp\left\{-\gamma^2 g^2 \delta^2 D\left(\Delta - \frac{\delta}{3}\right)\right\} \times \exp\left\{-\frac{\Delta + \delta}{T_1} - 2\delta\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right\} \quad (22)$$

When Δ is much larger than δ , it is possible to eliminate the effect of T_2 relaxation on the system, resulting in equation Eq. 23

$$\frac{M(g)}{M(g=0)} = \frac{1}{2} \exp\left\{-\gamma^2 g^2 \delta^2 D\left(\Delta - \frac{\delta}{3}\right)\right\} \times \exp\left\{-\frac{\Delta + \delta}{T_1}\right\} \quad (23)$$

As with the CPMG DE measurement, the SE DE is only sensitive to a thin slice of the total sample, corresponding to the bandwidth of the hardware. Also, the timings required to carry out the two 90° pulses places a minimum on the diffusion times possible. The actual times depend on the dead times of the hardware at hand, but in any circumstance the SE DE technique will not be able to measure some fast-relaxing components.

The stimulated echo DE, though ideal for maintaining a logging tool analog, is not a viable technique in measurement systems that require a pseudo-static gradient, as the gradient pulse times are too high and generate too much heat. When the objective is long-time restricted diffusion, a limitation on the total diffusion time is not acceptable. Furthermore, the slice selection from a fixed-

gradient diffusion would limit the usefulness of long diffusion-length measurements. For that reason, it will be necessary to perform all measurements with a pulsed gradient version of the sequence.

3.22 Pulse Field Gradient Stimulated Echo Diffusion Editing

The PFG-SE DE sequence is shown in Fig. 8. The encoding portion of the sequence is now restricted to the duration of the gradient pulses, but otherwise the behavior is similar to the stimulated echo version. The equation for magnetization is the same, though δ now refers to the gradient pulse width instead of the 90° pulse spacing. A major benefit of the pulsed-gradient measurements is that the value of the gradient strength g can be changed conveniently to provide the necessary diffusion sensitivity without changing any of the time parameters of the experiment. Also, this technique is sensitive to the entire polarized sample, so no slice selection occurs. Like the SE DE, the PFG-SE DE technique suffers a minimum diffusion time. In this case, the timing has to include the dead times for the gradient pulses as well, which can be quite considerable if eddy currents are present.

The procedure for evaluating structure through restricted diffusion by DE involves several steps. The experiment consists of a series of data suites, each of which contain multiple data sets. Each data suite will have one fixed diffusion time, with each data set including a different value of g . The data suite can then be inverted to obtain a D - T_2 map for that given diffusion length. Further measurements are carried out on the same sample with larger diffusion lengths,

and as restriction sets in, the measured diffusivities will start to drop. This process is monitored either by watching diffusivity distribution curves shift to slower diffusivities or by monitoring an average diffusivity at different T_2 values.

Eventually, the drop in diffusivity will plateau, as the spins move outside the pore length scale and begin to navigate the entire pore matrix. This is the point where equation 19 can be employed to evaluate the formation factor of the system. It should be noted that this is not the only way of obtaining permeability information from the diffusivity data, and when enough data is collected it will be interesting and perhaps necessary to evaluate other diffusion-based permeability estimates.

3.3 Simulated Data D - T_2 Maps with CPMG-DE

A sample D - T_2 map based on CPMG-DE measurements is shown in Fig. 9. The map is a contour plot with diffusivity on the Y axis and relaxation on the X axis. This particular map shows the results for simulated data, with the actual values of D and T_2 marked with black circles (for simulated data only). There are several other details indicated on this map that will not be labeled on further examples, so it will be useful to discuss their necessity here. The horizontal dashed line indicated the self-diffusion constant of bulk water at the experimental conditions. In some figures, a solid vertical line will appear indicating the point (employing the X axis as real time, not relaxation time) where truncation occurs for results that did not include the pre-processing step. The solid diagonal line with a positive slope, on the right-hand side of the diagram, indicates the

correlation between diffusivity and T_2 for hydrocarbon mixtures according to Lo *et al*²⁹.

On the left-hand side, there are three other diagonal lines, each with the same negative slope. These lines indicate the region where diffusion information becomes progressively sparser. They are plotted using the X axis as real time in place of relaxation time, with the rightmost line indicating the time where the attenuation due to diffusion at that t_D will be 50% of the total signal, the middle line 20%, and the leftmost line showing where only 5% of the total signal will be attenuated due to diffusion. Considering that if the relaxation time was equal to the diffusion time, approximately 70% of the signal would have attenuated due to relaxation. It is clear that these lines indicate the limits of where diffusion measurements will be possible. Any component with a diffusion and relaxation pairing that falls to the left of these lines will have attenuated due to relaxation to the point where any attenuation due to diffusion would be negligible. These lines act as a guideline for the interpreter, showing that any information to the left of these lines is artifact, and any results falling on the lines is unreliable. These lines will be referred to later in this document as the diffusion limit lines.

There are some details involving D - T_2 maps that require extra care for interpretation. The list of $T_{E,L}$ s used for the measurement suite may need to be carefully tailored for some samples. For choosing the longest $T_{E,L}$, the diffusion time should be long enough to reduce the entire signal to the level of noise. If the list does not include long enough $T_{E,L}$ values to ensure that enough diffusion is measured to fully characterize the diffusivity of the system, the inversion will

treat lingering low-diffusivity signal as a non-diffusing fluid presence. This non-diffused signal will manifest as a peak that is narrow in relaxation space at approximately the correct value, but very broad in diffusion space and centered around the minimum end point of the inversion diffusivity range. For this reason, any diffusion contributions occurring at or near the inversion diffusivity minimum cannot be treated with confidence. An example with simulated data is shown in Fig. 10, where the diffusion information is not adequate to characterize the diffusivity present. In Fig. 11, the list has been expanded and the low-diffusivity information is recovered. For these examples, and all other maps generated for this report, the inversion diffusivity minimum was $1\text{e-}8\text{ cm}^2/\text{s}$. An approximation of the minimum reliable diffusivity can be obtained by determining the intercept between the diffusion limit lines and a vertical line crossing the X axis at the real time (as opposed to relaxation time) corresponding to the third echo of the data set. If any data seems to appear below the diffusivity of that intercept, it cannot be expected to resolve well, as inadequate diffusion has taken place during the diffusion time of the experiment to well characterize that diffusivity range.

Another issue is with the acquisition of high diffusivity data. To better characterize diffusivities above that of bulk water, it is necessary to collect data at values of $T_{E,L}$ that are relatively short (still longer than $T_{E,S}$). This data is not useful when no high-diffusing fluids are present, but is vital if internal gradients or gas are present. If short $T_{E,L}$ data is not collected, high diffusivity data will appear smeared and difficult to interpret. In this case, the focus is not in

having short enough $T_{E,L}$ values, but that there should be enough short- t_D values so more than 4 or 5 data sets contain signal above the noise level.

As with any regularized distribution, the signal-to-noise ratio can have a major effect on the inversion. Low signal-to-noise ratio will reduce the robustness of the distributions, causing artifacts or spreading the distributions very wide. This latter will also occur if not enough $T_{E,L}$ values are used in the suite. The relaxation distributions are usually robust unless the signal-to-noise ratio is very low, because it is easy to collect thousands of echoes for each relaxation measurement, and relaxation is measured with each diffusion measurement. For each diffusivity datum, however, it is necessary to perform an entire echo train. It is not practical to include as many diffusivity measurements as echoes, so the diffusivity measurements will remain less robust than the relaxation measurements.

Furthermore, the inversion algorithm used for these experiments⁴⁴ requires that the data exists as a complete matrix, with magnitude information at every echo time for every data set. As written it does not take into account any relaxation information from data points shorter than the third echo of the longest $T_{E,L}$ because each data set lacks equally-spaced echoes during the diffusion time. That means if $T_{E,L}$ must be long for correct diffusion characterization, short T_2 information will be lost. It is necessary to trade off low-diffusivity information for short relaxation information, or vice versa. To avoid this problem, it is necessary to work with data sets that have information for each data set at the echo times corresponding to the basic CPMG measurement. Since it is not

possible to acquire results during the diffusion time, these times must instead be filled with data extrapolated from the available information.

The extrapolation is performed in two steps. First, each data set in the suite is inverted through standard T_2 fitting algorithms to obtain relaxation time distributions. These distributions are then used to provide evenly spaced fitted echo data for the times missing from the data set. The extrapolated data should contain no relaxation or diffusion data that was not present in the measured data, but there is now echo information for each data set at each echo time, so the entire set can be inverted using the same basic algorithm without truncating the data at all. A simulated data set sample without preprocessing is shown in Fig. 12, with the extrapolated version of the same set shown in Fig. 11. Echoes to the left of the vertical line in Fig. 13 are not used by the original inversion.

Having presented this new extrapolation technique, it is necessary to demonstrate the effectiveness of the method. Fig. 14 shows a data set without preprocessing where all specified T_2 and D values lie on the right-hand side of the map, with Fig. 15 showing the same data set with preprocessing. On this plot, and those that follow, the vertical line indicates the time where echo truncation occurs. The two sets agree very well, with the preprocessed set showing slightly tighter results for the same regularization parameter, due to signal-to-noise differences. Fig. 16 shows a non-preprocessed set where one peak falls in the region between the truncation line and the diagonal lines indicating the diffusivity limits. Fig. 17 shows the same set with preprocessing, where the peak that was very broad without preprocessing becomes very clear.

While the first two examples show very positive results, neither involve signal in the region where interpretation becomes far more difficult, the area where diffusion information is unavailable. Fig. 18 shows a set where the data lies between the lines indicating limited diffusion information. According to Fig. 19, the results can be recovered through preprocessing, but the peak is broad and off-center. And finally Fig. 20 shows a set well to the left of the indicator lines, with the same relaxation time as the sample shown in Fig. 18 and a lower diffusivity. Fig. 21 shows that although a peak is still recovered, the diffusion constant indicated by the result is incorrect. Fig. 22 shows a relaxation time distribution comparison between projections onto the X axis of Figures 20 and 21, showing that the relaxation time distribution is essentially corrected by preprocessing, even when the diffusivity is not recovered. The total amplitude should be 1, and the preprocessed version overestimates slightly, but still provides a great improvement over the truncated version.

3.4 Simulated Data D-T2 maps with PFG-SE DE

The stimulated echo versions of the DE sequence produce maps quite similar to the modified CPMG version, with a different set of parameters that must be selected carefully. In the version of the sequence used in this work, the three key parameters are Δ , the diffusion time ($\Delta + \delta$), and the gradient strength g . For single suites, only the gradient strength will be changed, but in order to evaluate restricted diffusion, suites will have to be performed with progressively increasing diffusion time. It is important to ensure all three of these parameters

are selected to ensure full characterization of the range of diffusivities present in the sample.

The selection of ideal parameters is dependant on several factors. In general, the equipment will have certain limitations that will affect the experiment. Gradient pulses may have minimum acceptable widths (δ), and there will be a maximum available gradient strength (g). The diffusion time (t_D) will depend on the parameters of the experiment desired – for restricted diffusion measurements, t_D controls diffusion length. Δ has no major restrictions, but should be chosen to suit the desired t_D and δ . With poor choices for any of these parameters, artifacts may occur.

First of all, a wide range of values for g , the gradient strength, are necessary. These provide the diffusion sensitivity of the suite, similar to the $T_{E,L}$ for modified CPMG measurements. The results of three simulations indicate the effect of having an inadequate list of gradient strengths. Fig. 23 shows an ideal map, with g ranging from 2 to 28 g/cm. The peaks are clear, sharp, and round. If the gradient strength list doesn't include high enough values (2-18, for example), a result such as Fig. 24 may arise - the peaks are still correct, but the lower-diffusivity portion is poorly defined. As the maximum gradient decreases, the definition of lower-diffusing peaks will continue to get worse. On the other hand, if low enough values of g are not used, information about fast-diffusing peaks will be lost, as in Fig. 25. As with the CPMG DE measurements, it is desirable to choose a g list that includes high enough values to reduce the signal to the level of noise.

For δ , the effect is similar to that of g , though in this case only a single value is required, in place of a list. If the δ is too short, the range of g values must be much higher, as the q term will have been decreased a great deal. The same list of g values, with δ equal to 100 μs instead of 400, gives a results as shown in Fig 26, where the slower-diffusing peak appears as a poorly-defined streak. In the other direction, a longer δ can reduce the gradient strength required, but care must be taken to avoid losing information - as shown in Fig. 27, where δ is 1 ms. Also, some equipment may have eddies or residual gradient effects that limit the minimum value for δ , in which case the value of g must be adjusted to achieve the desired result within those limits.

The most significant parameter for the measurements discussed in this work is the diffusion time t_D . While it does not affect the sensitivity to diffusion of a measurement, it directly controls the diffusion length of that experiment, as Δ (in these experiments) is the difference between t_D and δ . The effects of diffusion time on measured diffusivity values are small, but the maximum t_D is limited by the relaxation time of the sample. Fig. 23 employed a diffusion time of 0.5 seconds, less than half of the relaxation time of the shortest component present. Fig. 28 uses half that t_D , and the results are still good, perhaps better. Clearly, as long there is time within t_D for the sequence to complete correctly, the shortest t_D will give the sharpest results, though it will give no benefit for restricted diffusion measurements. As the longer, the high-diffusivity peak becomes obscured and eventually becomes useless. Fig. 29 shows t_D of 2 seconds. The faster-diffusing peak suffers at lower values of t_D , as the amount of diffusion attenuation is

greater. Eventually, entire peaks would be lost, as they are attenuated to the level of noise before the echo collection begins, as in Fig. 30. This is the clearest indication that water-saturated rocks are not viable for long-Td restricted diffusion measurements, as even in the case of Fig. 30, the diffusion length was only .1 mm. That would not be adequate to approach the diffusivity limit of many samples. The diffusivity limit should be chosen to provide the desired diffusion length, but the relaxation time of the sample must be accounted for as well.

4. Experimental

4.1 Modified CPMG Measurements

4.1.1 Rock Samples

For these measurements, three distinctly different sandstone samples were measured. All were in the form of 1-inch long, 1-inch diameter cylinders. The first sandstone was a highly permeable and nearly clay-free Bentheim sample (BEN3). The second was a Berea sandstone (BER2 and BER3), known to contain kaolinite, illite, and some localized siderite crystals. Two samples of this type were measured. The final sandstone sample was a North Burbank (NBUR3), unusual due to the presence of chlorite flakes, which provide large magnetic susceptibility contrast and therefore large internal gradients. This last sample was only used in the second suite of experiments. All of these samples were included in the study by Zhang^{46, 47}. The carbonates used in this study were both dolomites from the Yates field in west Texas (Y1312, Y1573). These samples have a complex dual-porosity pore structure, vugs on the order of 100

microns, and exhibit mixed wettability. Rock properties for these samples are summarized in Table 2.

4.12 Bulk fluid experiments

The first suite of partially saturated core experiments was carried out using a North Sea crude oil (SCNS) with an API gravity of 33.2. This oil has no measurable asphaltenes (0.0 %) but a modest fraction of resins (7.9%). The bulk crude oil experiments employed a Gulf of Mexico crude (SMY), with an API gravity of 30.3. This oil has significantly more asphaltenes (5.5%) and more resins as well (12.5%). More details about these crude oils can be found in Table 3. The refined oil used in this study was a drilling fluid base oil referred to as Nova Plus, manufactured by Halliburton. The bulk water sample was tap water, and the hexane sample was not de-oxygenated. The NMR measurements for the water, hexane, Nova Plus, and SMY experiments were carried out in a Resonance Instruments MARAN Ultra spectrometer at 2.06 MHz with a static gradient of 13.2 G/cm. For the SCNS crude oil, the measurements were carried out in a fringe field apparatus at 1.76 MHz with a static field gradient of 13.2 G/cm. This fringe-field apparatus is located at Schlumberger-Doll Research in Ridgefield, CT. The $T_{E,L}$ list for the bulk fluid collection suites was 1.6, 5.6, 8.0, 10.4, 12.8, 17.6, 24.0, 32.0, 48, and 60 ms for the water, hexane, SMY, and Nova Plus. For the North Sea sample, the suite was 1.2, 2.4, 4.4, 8.4, 12.4, 16.4, 20.4, 24.4, 28.4, 32.4, and 36.4 ms. The $T_{E,S}$ was 0.4 ms for both suites.

4.12 Partially-saturated core experiments

The suite of partially-saturated core experiments include only the samples BEN3, BER2, Y1312, and Y1573. The samples were wrapped in heat shrinkable Teflon, water-saturated by vacuum, and then pressurized to remove any air. A set of diffusion editing NMR measurements was performed on these samples at 100% water saturation. The samples were then centrifuged submerged in SCNS crude at 3400 RPM for 11 hours for primary drainage. The samples were then inverted, and centrifuged for an additional hour. A second set of diffusion-editing measurements was performed. At this point, all the samples were submerged in water. For the sandstone samples, spontaneous imbibition was observed and no forced imbibition was performed. For the carbonates, no spontaneous imbibition was observed, so forced imbibition was performed by centrifuging the samples submerged in water at 3400 RPM for one hour. A final set of diffusion-editing experiments was carried out at this stage. The NMR measurements for this suite were carried out in a fringe field apparatus at 1.76 MHz with a static field gradient of 13.2 G/cm. For these measurements, the list of $T_{E,L}$ values used was 1.2, 2.4, 4.4, 8.4, 12.4, 16.4, 20.4, 24.4, 28.4, 32.4, and 36.4 ms, with a $T_{E,S}$ of 0.4 ms.

4.14 High internal gradient experiments

These experiments were carried out on the North Burbank (NBUR3) sample. The sample was wrapped in heat-shrinkable Teflon, water saturated by vacuum, and then pressurized to remove air. It was then spun at 5000 rpm in SMY crude oil for one hour, aged at 80° C for seven days, submerged in water

and centrifuged at 5000 rpm for one hour. Measurements were taken at each stage of this process. Unfortunately the NMR equipment malfunctioned, and was only possible to obtain usable DE data for the final stage of saturation, where the rock showed approximately 95% water saturation. The NMR measurements for these data sets were carried out in a Resonance Instruments MARAN Ultra spectrometer at 2.06 MHz with a static gradient of 13.2 G/cm. The $T_{E,L}$ list for this suite was 0.8, 1.6, 2.4, 4.0, 5.6, 6.4, 8.0, 10.4, 12.8, and 17.6 ms, with a $T_{E,S}$ of 0.4 ms.

4.15 Air de-saturation experiments

These experiments were performed on the BER3 sample. This sample was water saturated by vacuum, and a suite of DE measurements was collected. The sample was then centrifuged at 9500 RPM (100 PSI) for 17 hours, and a second suite of DE measurements was collected. The final S_w achieved was 0.43. The NMR measurements for these data sets were carried out in a Resonance Instruments MARAN Ultra spectrometer at 2.06 MHz with a static gradient of 13.2 G/cm. The $T_{E,L}$ list for this suite was 1.6, 5.6, 8.0, 10.4, 12.8, 17.6, 24.0, 32.0, 48, and 60 ms with a $T_{E,S}$ of 0.4 ms.

5. Results

5.1 Modified CPMG Measurements.

5.11 The D - T_2 Maps

The D - T_2 maps presented here were all prepared using the preprocessing described in the theory section. The regularization parameter for the bulk fluid plots is 1.0, while for the rock measurements, a values of 5.6 was used.

Fig. 31 shows the D - T_2 map for bulk water at 27°C. The log mean values of the diffusivity and relaxation time correspond to known values for bulk tap water. The log mean T_2 value for that sample is 2.95 seconds, and the log mean diffusivity of the sample is $2.49\text{e-}5 \text{ cm}^2/\text{s}$, very close to the literature value of $2.50\text{e-}5 \text{ cm}^2/\text{s}$ ⁶. Fig. 32 shows the T_2 distribution developed by summing the map bins across all diffusivities, plotted alongside the distribution obtained from the standard Rice T_2 relaxation time inversion⁸, applied to the first data set of the DE suite, where $T_{E,L} = T_{E,S}$. The agreement is very good.

Fig. 33 shows the map for a hexane sample. The diffusivity is higher than that of water, while the relaxation time appears slightly shorter. The T_2 values agree very well with published results by Y. Zhang⁴⁸ for non-deoxygenated hexane. Data from Y. Zhang also suggest that if the sample was de-oxygenated, it is expected that the T_2 would increase till the distribution lay on the correlation line. The T_2 distribution, shown in Fig. 34, again agrees very well with the result obtained by a standard inversion.

The distribution for the refined oil mixture, Nova Plus, is shown in Fig. 35. The peak is narrow, and centered exactly on the line indicating the correlation between relaxation and diffusion. Fig. 36 shows the T_2 distribution comparison, and the agreement is very good.

Fig. 37 shows the D - T_2 map of the SMY crude oil. This oil sample seems to contain components that fall to the left of the diffusion limit lines, creating some artifacts along the length of the limit lines. The bulk of the major peak seems to fall above the correlation line. The distribution comparison in Fig. 38 still shows a close fit.

Fig. 39 shows the D - T_2 map of the North Sea crude oil sample. This is the oil sample that will be used to partially saturate the core samples. The distributions for both diffusivity and relaxation time are quite broad. The distribution itself is centered on the correlation line, indicating that this oil follows the correlation described by Lo *et al*²⁹. Agreement between the T_2 distributions shown in Fig. 40 is very good.

5.12 BEN3

Fig. 41 shows the D - T_2 map of sample BEN3 fully saturated with water. There is a single peak visible in the plot, with a diffusivity distribution centered at $2.00\text{e-}5 \text{ cm}^2/\text{s}$ and a T_2 range between 200 milliseconds and 1.2 seconds. The diffusivity value indicated suggests that all of the water in the sample diffuses similar to bulk, with little restricted diffusion occurring. The relaxation time distribution agrees well with the same distribution obtained from a single CPMG measurement, as shown in Fig. 42. The BEN3 sample is highly permeable, highly porous, and known to have very low clay content, all of which would agree with the results obtained from the D - T_2 map.

Fig. 43 shows the same BEN3 sample, now at very high oil saturation (approximately 95%). The position of the only strong peak corresponds well to the bulk North Sea oil shown in Fig. 39. The conclusion that can be drawn is that the oil in this rock sample does not wet the surface, as it relaxes and diffuses as the bulk fluid.

Fig. 44 is again the BEN3 sample, this time with an oil saturation of approximately 57%. Here, one peak corresponding to the water content is clearly visible, as well as another representing the oil. The oil peak is very much the same as it appeared at higher saturations, again behaving as bulk oil. The water peak still diffuses as it did in the fully water-saturated measurement, but the T_2 distribution has lost all amplitude above 1 second. This indicates that the largest pores, formerly occupied by water, have been filled with oil instead, and the water is now contained in smaller, faster relaxing pores. The water still lines the walls of the larger pores (otherwise the oil T_2 distribution would be affected by oil wetting) but the reduced volume of water present increases the surface/volume ration, and thus decreases relaxation time.

5.13 BER2

Fig. 45 shows the D - T_2 map for the water BER2 sample. The T_2 distribution covers shorter times than the BEN2, indicating stronger surface relaxation, probably due to smaller pores and the presence of clays. The diffusion distribution remains close to that of bulk water, though a fair portion of the signal occurs well above the line. This indicates the possible presence of

internal gradients, which will be discussed further later in this document. In the relaxation distribution comparison, shown in Fig. 46, the agreement between the map-generated distribution and the standard inversion is good.

The BER2 sample at high oil saturation is shown in Fig. 47. The oil does not appear to undergo any surface relaxation, suggesting the surface remains water-wet. The oil portion compares very well to Fig. 39 at lower diffusivities, but at high diffusivities the oil peak seems to merge with the water distribution, suggesting some restricted diffusion may be occurring in the water-filled pores relaxing at a T_2 close to the bulk oil. This would occur when a pore is nearly completely filled with oil, and the water present undergoes restriction between the pore walls and the oil interface. The water relaxation distribution for this sample appears to separate into several distinct peaks, suggesting that diffusive coupling has been broken off between the larger pores and the microporosity. Some of the data falls on the diffusion limit lines, and cannot be interpreted with confidence, while another peak occurs at the very top of the map, indicating again that internal gradients might be present. There is also a foot on the oil peak that wasn't present in the bulk oil, possibly indicating restricted diffusion of water in small pores that do not contain internal gradients.

At lower oil saturation, the BER2 sample provides a more complicated picture, shown in Fig. 48. To begin with, the water portion relaxing faster than 200 milliseconds manifests both lower diffusivity values, while the longer-relaxing components show diffusivities higher than that of bulk water. Our interpretation for this wide range of diffusivity values is that the elimination of diffusive coupling

increases the contribution of internal gradients and restricted diffusion. In small pores where internal gradients are large, spins that are not coupled to larger pores spend more time in regions of high gradient, appearing to diffuse faster than they would if coupled. In small pores without large internal gradients, the spins are instead heavily restricted. The diffusivities measured in those pores are lower than that of free-diffusing water. This situation is possible in the BER2 sample, as this sample is known to contain illite, and kaolinite clays⁸ as well as siderite deposits. The siderite deposits are usually present as isolated crystals rather than pore coating, but may serve as an iron source for the illites. The illite clays have been shown to have internal gradients in some circumstances, in particular when iron is present at the surface of the clay. So iron-bearing illites could account for the portion of the small pores that experience internal gradients. The kaolinites, though, do not create internal gradients, and so water bound to kaolinite clays would only experience restricted diffusion. The diffusivity of clay-bound water can be so low that it appears near the correlation line for hydrocarbons. The signal below $10\text{e-}6 \text{ cm}^2/\text{s}$, and relaxing faster than 100 milliseconds must be water, as none of the oil shown in Fig. 39 would be found in that region. The peak position and broadness seen in the map may also been an artifact, as discussed in the Theory section. Due to the low diffusivities indicated here, it is not clear that adequate diffusion information took place to correctly characterize the slow-diffusing components of this system. The data set was inverted for a diffusion range of $1\text{e-}4$ to $1\text{e-}7 \text{ cm}^2/\text{s}$, and information this close to the minimum of the inversion range is not reliable.

5.13 Carbonate results

The fully water-saturated Y1312 sample, shown in Fig. 49, diffuses as bulk, and relaxes as might be typical of vuggy carbonates with broad pore-size distributions, ranging from 200 milliseconds to 1.5 seconds. There is some slight skewing towards lower values in the diffusivity distribution, indicating the possibility of restricted diffusion. The agreement between map-generated and standard inversion-generated T_2 distributions is very good, shown in Fig. 50.

At high oil saturations, there is overlap developing between the oil distribution and severely restricted water diffusion. The D - T_2 map is shown in Fig. 51. Around half of the water distribution lies beneath the line indicating the diffusivity of water, and at short relaxation times, the diffusivity starts to drop off even further. This indicates that all the water present experiences severe restriction, either in small pores or between the pore wall and the oil in the pore body, but the smallest pores experience the greatest restriction. The severely restricted water appears near the hydrocarbon correlation line, as observed with the BER2 sample shown in Fig. 48. Again, the peak position and broadness seen in the map may also been an artifact, as discussed in the Theory section.

When this carbonate sample undergoes forced imbibition, little new information is revealed. The D - T_2 map is shown in Fig. 52. The water again behaves largely as bulk, with short components alone indicating restricted diffusion. The water in the larger pores relaxes at higher values than in the fully water-saturated sample in Fig. 49, indicating that the effective surface area for

water in large pores has been decreased. This would occur either if some of the water exists as droplets in the oil phase, or if some of the large pore surface is oil-wet. As an emulsion does not seem probable under the circumstances, the sample has probably entered a mixed-wet state, a conjecture supported by the observation that this sample experienced no spontaneous imbibition.

The Y1573 sample shows several features hinted at by the previous sample, but much clearer in this example. Firstly, in the fully water-saturated case shown in Fig. 53, restricted diffusion is clearly visible at shorter T_2 s. In the T_2 distribution, shown in Fig. 54, the agreement between the map-produced version and the standard inversion is good. These distributions also suggest that there are more small pores in this sample than in the Y1312.

After primary drainage, much of the water present in the Y1573 sample experiences severe restriction. The map is shown in Fig. 55. Signal relaxing faster than 100 milliseconds appears below the diffusivity of bulk water. As in the cases of BER2 (Fig. 48) and Y1312 (Fig. 51), a tail into low diffusivity values appears that may be an artifact.

After forced imbibition, the restricted water remains restricted, and most of the oil signal disappears. The D - T_2 map is shown in Fig. 56. The center of the oil distribution has slightly shifted to lower T_2 values, and the amplitude of water above the maximum T_2 of the fully water-saturated sample is higher. This again presents evidence of some mixed-wet surfaces in this sample.

5.14 Internal Gradient: NBUR 3

The diffusion time list for this sample was different from the other samples to provide greater information about the higher diffusivity information in the sample. Though the true diffusivity of water does not change regardless of the sample, the measured or effective diffusivity depends upon the static gradient present. In the presence of an internal gradient, the static gradient experienced will differ from the applied gradient. It has been shown⁴⁷ that in a clay-lined rock, there is not a single internal gradient present but in fact a distribution of gradients depending on pore geometry and the nature of the clay present. A diffusion-editing measurement in an internal gradient should provide a diffusivity distribution that corresponds to the distribution of gradients, with some coupling of the peaks to account for spins moving through areas with different static gradients. In any case, this result should be extremely useful in developing a better understanding of how internal gradients exist inside a rock sample.

Fig. 57 shows the D - T_2 map for the NBUR3 sample, fully water-saturated. Most of the signal occurs above the line indicating the diffusivity of water, indicating that the internal gradients are indeed very strong. The lower, higher amplitude peak shows that the gradients increase as the pore size decreases. This is to be expected, as the smaller pores might occur between or around the clay flakes that provide the internal gradients. There is also a peak at high gradients and very fast relaxation time, which appears to contribute a great deal to the relaxation distribution shown in Fig. 58. It is not clear how this peak should be interpreted, but one possibility is proposed considering results obtained by Zhang⁸. This peak might correspond to the spins near the corner of the clay

flakes, where the internal field gradients reach very high values in a small area. More measurements would be necessary to better understand this phenomenon, including some measurements where the larger pores would be filled with crude or refined oil, eliminating communication between small and large pores.

5.15 Air De-saturation: BER3

The D - T_2 map for the fully water-saturated BER3 sample is shown in Fig. 59. The D - T_2 for the air de-saturated sample is shown in Fig. 60. In this case, prominent internal gradients and strong restricted diffusion are visible for short relaxation times. The interpretation here is as for the previous Berea sandstone, but without interference from the presence of oil. Restricted diffusion is probably occurring in the kaolinite clay-filled pores, while internal gradients dominate illite clay-filled pores. The effect for both is increased due to the absence of diffusive coupling with larger pores, as those pores no longer contain water. In the air de-saturated system, the non-wetting fluid does not have any NMR signal, so all the measured signal is clearly due to water. This provides confirmation for the interpretation of BER2 above.

6. Conclusions

The data sets presented in this report present some of the first experiments involving the DE sequence and core samples saturated with real crude oils. In water-saturated samples as well as bulk fluids, the T_2 information obtained from the D - T_2 map agrees well with standard T_2 inversions, while the

diffusion information was previously unavailable in any form. In mixed-saturated experiments, the DE measurement allows separate examination of the diffusion and relaxation of fluids with contrasting diffusivities. In single-fluid saturated samples, aspects of the pore geometry that are difficult or impossible to interpret from relaxation alone measurements can be approached.

7. Future Work

The benefit of clear, easily interpreted D - T_2 maps for partially saturated rocks should be obvious – saturation, oil viscosity, and wettability changes can all be successfully evaluated. In single fluid-saturated sample, there are other petrophysical details that can be interpreted – restricted diffusion and internal gradient effects. As consistent interpretation for the D - T_2 continues to develop, a new, more comprehensive interpretation for NMR well logging data will become available.

DE measurements have opened up new areas of analysis in two major areas of NMR investigations of porous media: restricted diffusion and wettability change monitoring. The restricted diffusion measurements require long relaxation times and faster diffusion, in order to extend the probing distance of a single spin. In order to pursue this goal, we intend to perform experiments with samples saturated with light hydrocarbons such as methane or ethane. Wettability change investigations will require further measurements with partially-saturated samples with crude oils, base oils and additives.

The primary focus of further work, though, will be in employing the techniques developed here to extend our understanding of vug connectivity in carbonates, with the final goal of obtaining an effective NMR based permeability estimation technique in vuggy carbonates. By employing the PFG-SE DE measurements to evaluate restricted diffusion and relaxation simultaneously, we believe we have access to a new interpretation tool that will provide insight to this problem not available from other means. Measurements will be performed on a set of carbonate samples from the Yates oilfield in west Texas, where a wide range of permeability values have been observed.

By obtaining PFG-SE DE diffusion maps for a series of vuggy carbonate samples at a range of diffusion times, we expect to determine features and aspects of the two-dimensional distributions that indicate the presence of connected vugs in the sample. The primary indicator we expect to observe will be a plateau in the value of the observed diffusion constant with the increase of diffusion time, in particular for the slow-relaxing components of the distribution corresponding to the vugular porosity. The onset of this plateau will be interpreted as a characteristic length-scale for the sample, which will then be correlated with the sample permeability measured through external means. We will also investigate the correspondence between this characteristic length and the tortuosity required by the Hidajat modification to the Chang equation (Eq. 9).

A secondary topic of great interest is the use of diffusion editing and D - T_2 maps to monitor wettability changes in rock samples. This scope of this study will be to study a series of Berea sandstone samples at a range of water, oil, and

base oil saturations, including in some cases base oil additives that will change the wettability of the samples. The changes in the D - T_2 map at these different saturation states will allow us to observe changes in wettability and also to predict in what pore size range the wettability might be changing.

Other aspects of the technique and interpretation of DE measurements will also be considered in this work. Detailed methods for applying a matched filter for improving the signal-to-noise ratio of data with narrow echoes will be presented. The possibility of obtaining accurate quantitative saturation estimates will be investigated. Methods for selecting optimal parameters and parameter lists, as well as techniques for estimating the direct echo and stimulated echo contributions to a CPMG-DE result, will be developed.

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9. References

1. Akkurt, R., Vinegar, H. J., Tutunjian, P. N., Guillory, A. J.: "NMR Logging of Natural Gas Reservoirs", *Log Analyst*, **37**, No. 33 (1996)
2. Allen, D. F. et al: "The Practical Application of NMR Logging in Carbonates: 3 Case Studies", paper presented at the 2001 Annual Meeting of the Society of Professional Well Log Analysts.
3. Appel, M., Stallmach, F., Thomann, H.: "Irreducible Fluid Saturation Determined by Pulsed Field Gradient NMR", *Journal of Petroleum Science and Engineering*, **19**(1998)
4. Brownstein, K. R., Tarr, C. E.: "Importance of Classical Diffusion in NMR Studies of Water in Biological Cells", *Physical Review A*, **19**, No. 6 (1979)
5. Carr, H. Y., Purcell, E. M.: "Effects of Diffusion on Free Precession in Nuclear Magnetic Resonance Experiments", *Physical Review*, **94** (1954)
6. Chang, D., Vinegar, H., Morriss, C., Straley, C.: "Effective Porosity, Producing Fluid, and Permeability in Carbonates from NMR Logging" *Log Analyst*, **38**, No. 2 (1997)
7. Chen, S., Qiao, J., Liaw, H.-K., Watson, A. T.: "Studies of Rock Structures Using NMR Restricted Diffusion Measurements and Analyses", SCA Conference Paper Number 9313 (1993)
8. Chuah, T-L.: "Estimation of Relaxation Time Distributions for NMR CPMG Measurements" Masters dissertation, Rice University, Houston (1996)
9. Coates G. R., and Dumanoir J. R.: "A New Approach to Improved Log-Derived Permeability," *The Log Analyst*, **15**, No. 1 (1974)
10. Coates, G. R., Vinegar, H. J., Tutunjian, P. N., Gardner, J. S.: "Restrictive Diffusion from Uniform Gradient NMR Well Logging", paper presented at the 1993 Annual Technical Conference and Exhibition of the Society of Petroleum Well Engineers, Houston, TX.
11. Dunn, K.-J., Bergman, D. J., Latorraca, G. A.: Nuclear Magnetic Resonance Petrophysical and Logging Applications, Pergamon Books, (2002)

12. Freedman, R. *et al.*: "A New Method of Fluid Characterization in Reservoir Rocks: Experimental Confirmation and Simulation Results" *SPE Journal* (December 2001)
13. Freedman, R., Heaton, N., and Flaum, M.: "Field Applications of a New Nuclear Magnetic Resonance Fluid Characterization Method" SPE paper 71713, presented at 2001 SPE Annual Technical Conference and Exhibition.
14. Freedman, R. *et al.*: "Wettability, Saturation, and Viscosity Using the Magnetic Resonance Fluid Characterization Method and New Diffusion-Editing Pulse Sequences" SPE paper 77397, presented at 2002 SPE Annual Technical Conference and Exhibition.
15. Fukushima, E., Roeder, S.B.W.: Experimental Pulse NMR, Perseus Books (1981)
16. Goelman, G., Prammer, M. G.: "The CPMG Pulse Sequence in Strong Magnetic Field Gradients with Applications to Oil-Well Logging" *Journal of Magnetic Resonance*, **113**, (1995)
17. Hahn, E. L.: "Spin Echoes", *Physical Review*, **80** (1950)
18. Hari, P. *et al.*: "NMR Characterization of Hydrocarbon Gas in Porous Media", *Magnetic Resonance Imaging*, **16** (1998)
19. Hidajat, I.: "Stochastic porous media reconstruction, NMR response simulation and study of carbonate structure using NMR and CT scanner," PhD dissertation, University of Houston, Houston (2002)
20. Hurlimann, M. D., Helmer, K. G., Latour, L. L., Sotak, C. H.: "Restricted Diffusion in Sedimentary Rocks. Determination of Surface-Area-to-Volume Ratio and Surface Relaxivity" *Journal of Magnetic Resonance*, **111** (1994)
21. Hurlimann, M. D.: "Diffusion and Relaxation in General Stray Field NMR Experiments" *Journal of Magnetic Resonance*, **148**, (2001)
22. Hurlimann, M. D., and Venkataramanan, L.: "Quantitative Measurement of Two-Dimensional Distribution Functions of Diffusion and Relaxation in Grossly Inhomogeneous Fields," *Journal of Magnetic Resonance*, **157**, (2002)
23. Hurlimann M. D. *et al.*: "Diffusion-Editing: New NMR Measurement of Saturation and Pore Geometry," paper presented at the 2002 Annual

- Meeting of the Society of Professional Well Log Analysts, Oiso, Japan, June 2-5 2002.
24. Kenyon, W. E., Day, P. I., Straley, C., Willemsen, J. F.: "A Three-Part Study of NMR Longitudinal Relaxation Properties of Water-Saturated Sandstones", *SPE Formation Evaluation* **3** (1988). An erratum to this article was published in *SPE Formation Evaluation* **4** (1989).
 25. Kenyon, W. E., Allen, D. F., Lisitza, N. V., Song, Y.-Q.: "Better Pore-Size Distributions from Stimulated-Echo NMR Lab Measurements Using Magnetic Susceptibility Contrast and Small Encoding Angles", paper presented at the 2002 Annual Meeting of the Society of Professional Well Log Analysts, Oiso, Japan, June 2-5 2002.
 26. Latour, L. L., Mitra, P. P., Kleinberg, R. L., Sotak, C. H.: "Time- Dependent Diffusion Coefficient of Fluids in Porous Media as a Pribe of Surface-to-Volume Ratio", *Journal of Magnetic Resonance, Series A* **101**, (1993)
 27. Latour, L. L., Kleinberg, R. L., Mitra, P. P., Sotak, C. H.: "Pore-Size Distributions and Tortuosity in Heterogeneous Porous Media", *Journal of Magnetic Resonance, Series A* **112**, (1995)
 28. Lipsicas, M., Banavar, J. R., Willemsen, J.: "Surface Relaxation and Pore Sizes in Rocks- A Nuclear Magnetic Resonance Analysis", *Applied Physics Letters* , **48**, 1554 (1986)
 29. Lo, S.-W. et al: "Mixing Rules and Correlations of NMR Relaxation Time with Viscosity, Diffusivity, and Gas/Oil Ratio of Methane/Hydrocarbon Mixtures," *SPE Journal* (March 2002)
 30. Mair, R. W. et al: "Pulsed-Field-Gradient Measurements of Time-Dependent Gas Diffusion", *Journal of Magnetic Resonance*, **135** (1998)
 31. Mair, R. W. et al: "Probing Porous Media with Gas Diffusion NMR", *Physical Review Letters*, **83**, No. 16 (1999)
 32. Mair, R. W. et al: "Tortuosity Measurement and the Effects of Finite Pulse Widths on Xenon Gas Diffusion NMR Studies of Porous Media", *Magnetic Resonance Imaging*, **19** (2001)
 33. Meiboom, S., Gill, D.: "Modified Spin-Echo Method for Measuring Nuclear Relaxation Times", *Review of Scientific Instruments*, **29** (1958)
 34. Mills, R.: "Self-diffusion in Normal and Heavy Water in the Range 1-45°," *Journal of Physical Chemistry*, **77**, No. 5, 1973

35. Mitra, P., Sen, P.: "Effects of Microgeometry and Surface Relaxation on NMR Pulsed-Field-Gradient Experiments: Simple Pore Geometries", *Physical Review B*, **45**, 1 (1992)
36. Mitra, P. P., Sen, P. N., Schwartz, L. M.: "Short Time Behavior of the Diffusion Coefficient as a Geometrical Probe of Porous Media", *Physical Review B*, **47**, No. 14 (1993)
37. Morris, C. E., et al: "Hydrocarbon Saturation and Viscosity Estimation from NMR Logging in the Belridge Diatomite: *The Log Analyst*, v. 38, p. (1997)
38. Peled, S., Cory, D. C., Raymond, S. A. Kirschner, D. A., Jolesz, F. A.: "Water Diffusion, T2, and Compartmentation in Frog Sciatic Nerve", *Magnetic Resonance in Medicine*, **42**, (1999)
39. Prammer, M.G., Mardon, D., Coates, G.R., and Miller, M.N.: "Lithology-independent gas detection by gradient-NMR logging", SPE-30562, paper presented at the 1995 Annual Technical Conference and Exhibition of the Society of Petroleum Well Engineers, Richardson, TX.
40. Ramakrishna, T.S., et al: "Forward Models for Nuclear Magnetic Resonance in Carbonate Rocks", paper presented at the 2002 Annual Meeting of the Society of Professional Well Log Analysts, 1998.
41. Song, Y.-Q., Ryu, S., Sen, P.: "Determining Multiple Length Scales in Rocks" *Nature*, **406**, (2000)
42. Song, Y.-Q., Lisitza, N. V., Allen, D., F., Kenyon, W. E.: "Pore Geometry and its Geological Evolution in Carbonate Rocks" *Petrophysics*, **43**, No. 5 (2002)
43. Straley, C.: "An Experimental Investigation of Methane in Rock Materials", paper presented at the 2002 Annual Meeting of the Society of Professional Well Log Analysts, Houston, TX, 1997.
44. Tanner, J. E.: "Use of the Stimulated Echo in NMR Diffusion Studies", *Journal of Chemical Physics*, **52**, No. 5 (1970)
45. Venkataramanan, L., Song, Y.Q., Hurlimann, M. D.: "Solving Fredholm Integrals of the First Kind With Tensor Product Structure in 2 and 2.5 Dimensions," *IEEE Transactions on Signal Processing*, **50**, No. 5 (2002)
46. Zhang, Q., Huang, C. C., Hirasaki, G. J.: "Interpretation of Wettability in Sandstones," *Petrophysics*, Vol. **41** No 3 (May-June 2000)

47. Zhang, Q., Hirasaki, G.J., House, W. V.: "Effect of Internal Field Gradients on Porous Media," *Petrophysics*, **42**, No. 1 (Jan-Feb 2001)
48. Zhang, Y.: "NMR Relaxation and Diffusion Characterization of Hydrocarbon Gases and Liquids," PhD dissertation, Rice University, Houston (2002)

10. Tables

Table 1: Pulse Sequence Summary

	Figure	Measures Relaxation?	Measures Diffusion?	Captures Fast Relaxation	Measures Restricted Diffusion	Measures Full Sample
CPMG	1	Yes	No	Yes	No	Yes
PFG	2	No	Yes	No	Yes	Yes
PFG-SE	3	No	Yes	No	Yes	Yes
CPMG DE	6	Yes	Yes	Yes	No	No
SE DE	7	Yes	Yes	No	Yes	No
PFG-SE DE	8	Yes	Yes	No	Yes	Yes

Table 2: Rock Properties

Sample	Porosity	Permeability (md)
BEN3	23.4	2960
BER2	19.6	205
BER3	19.4	205
NBUR3	24.6	290
Y1312	20.8	137
Y1572	14.2	57

Table 3: Oil Properties

Oil	API Grav	Density	% asph	% resin	% arom	% sat	Visc.
North Sea	33.2	.856	0.0	7.9	24.9	67.1	9.4
SMY	30.3	.892	5.5	12.5	51.5	30.6	20.9
Nova Plus	-		-	-	-	-	3.20
Hexane	-	0.66	-	-	-	-	0.31

11. Figures

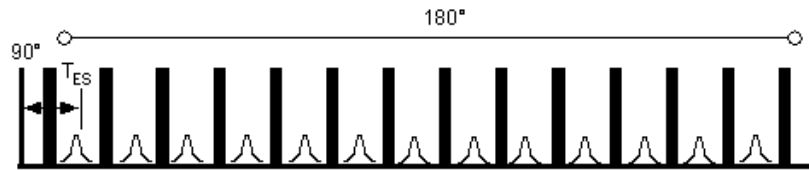


Figure 1: Diagram of a Standard CPMG Pulse Sequence. $T_{E,s}$ represents the short echo spacing selected to minimize the gradient effects on T_2 .

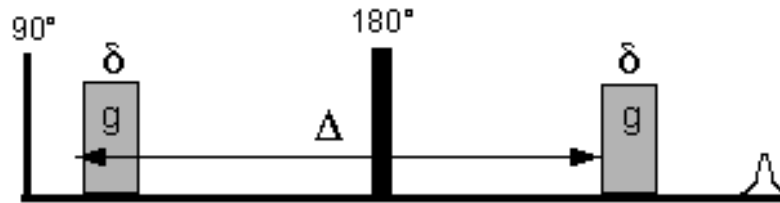


Figure 2: Diagram of the PFG Pulse Sequence.



Figure 3: Diagram of the PFG-SE Pulse Sequence.

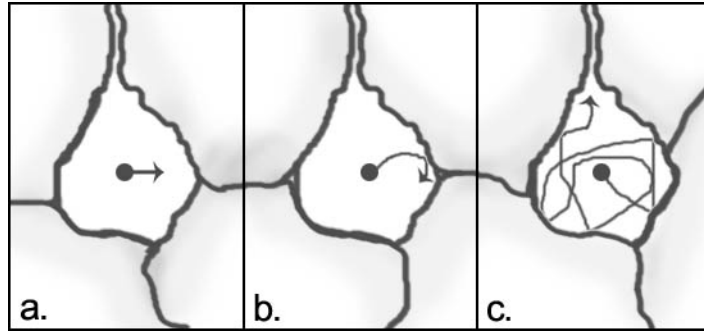


Figure 4: Diffusions of a water molecule in a pore space. Subplot a. shows free diffusion. Subplot b. shows the onset of restricted diffusion. Subplot c. shows restricted diffusion at long diffusion times.

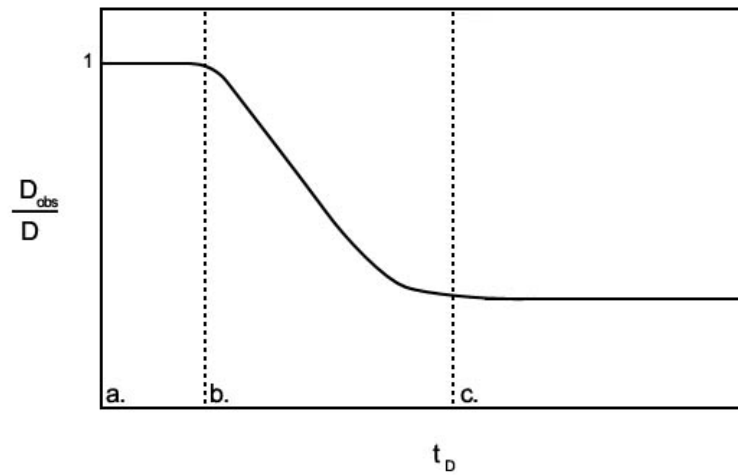


Figure 5: Reduced diffusivity as a function of diffusion time. Section a. shows free diffusion. Section b. shows the onset of restricted diffusion. Section c. shows restricted diffusion at long diffusion times.

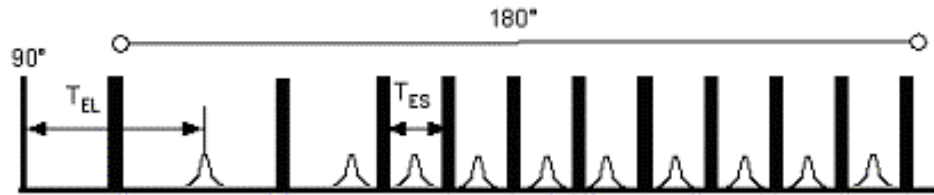


Figure 6: Diagram of the Modified CPMG DE Pulse Sequence. $T_{E,l}$ represents the long echo spacing varied to provide diffusion sensitivity, $T_{E,s}$ represents the short echo spacing selected to minimize the gradient effects on T_2 . This sequence is used in the presence of a static magnetic field gradient.

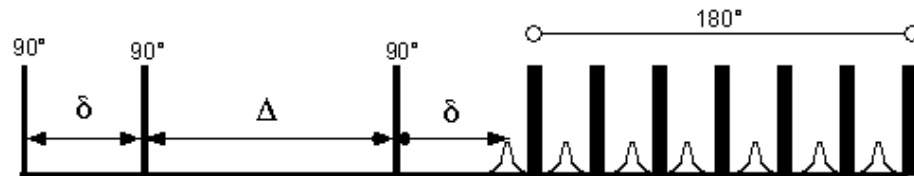


Figure 7: Diagram of the Stimulated Echo DE Pulse Sequence. This sequence is used in the presence of a static magnetic field gradient.

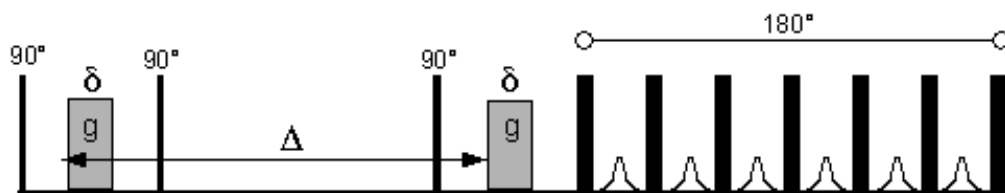


Figure 8: Diagram of the PFG-SE DE Pulse Sequence

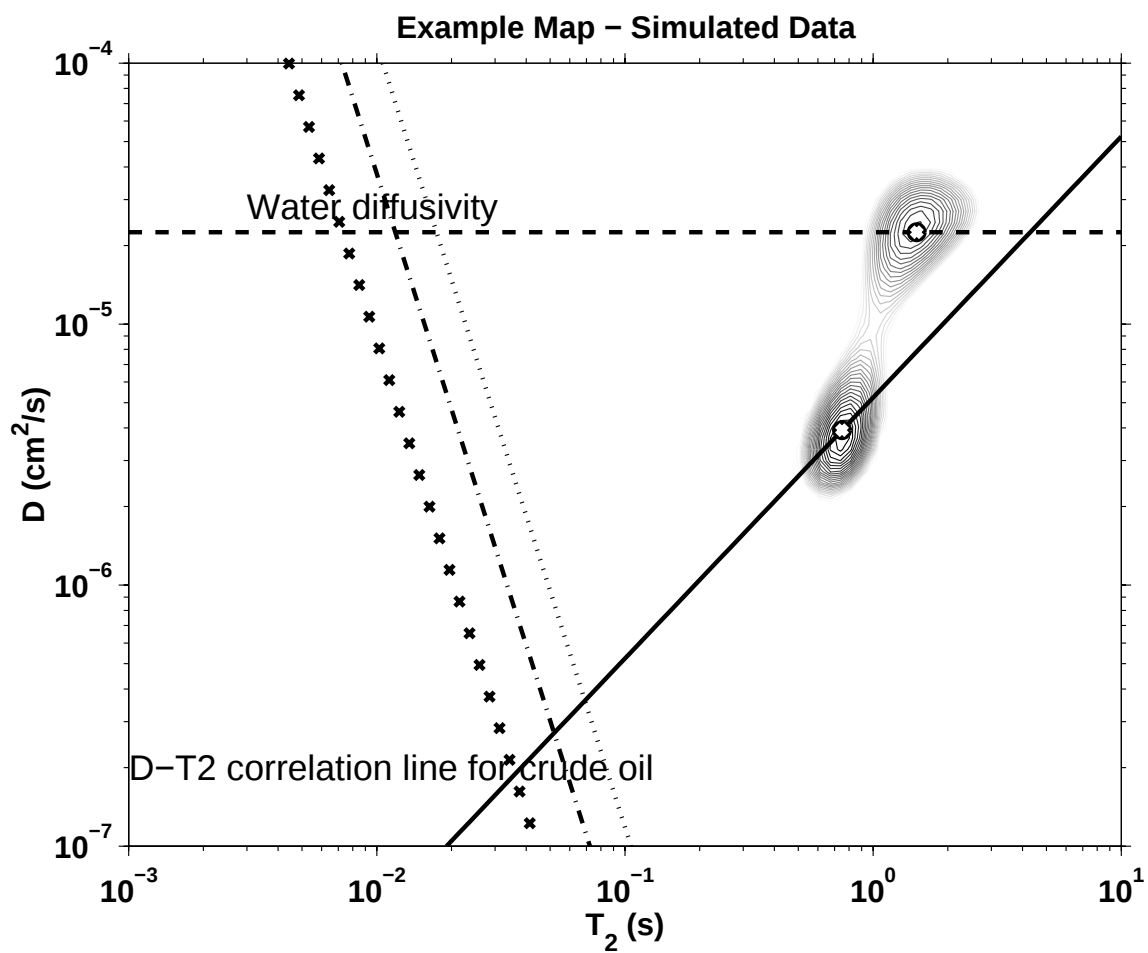


Figure 9: Example D - T_2 Map

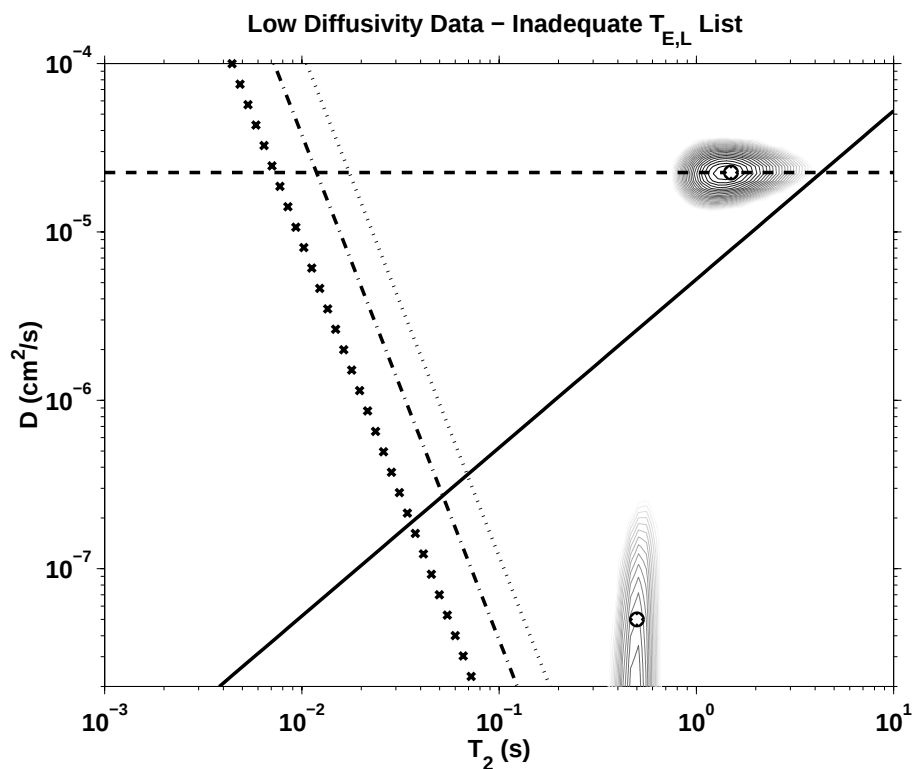


Figure 10: Broad diffusivity distribution due to inadequate diffusion time list. Max $T_{E,L}$ was 48 milliseconds

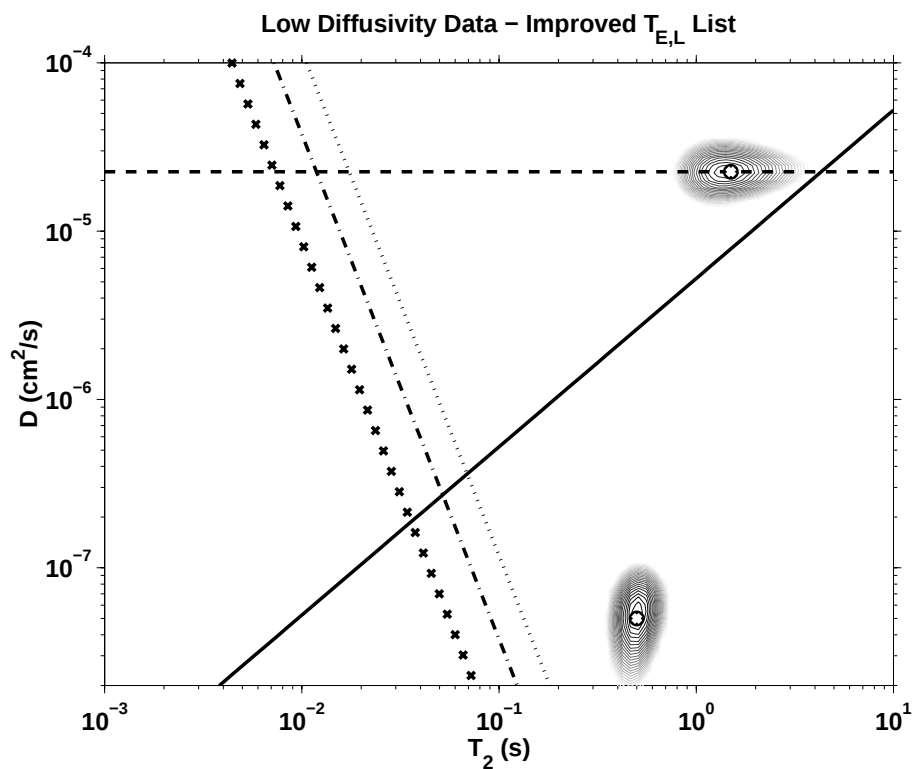


Figure 11: Improved diffusivity distribution due to extended diffusion time list. Max $T_{E,L}$ was 200 milliseconds.

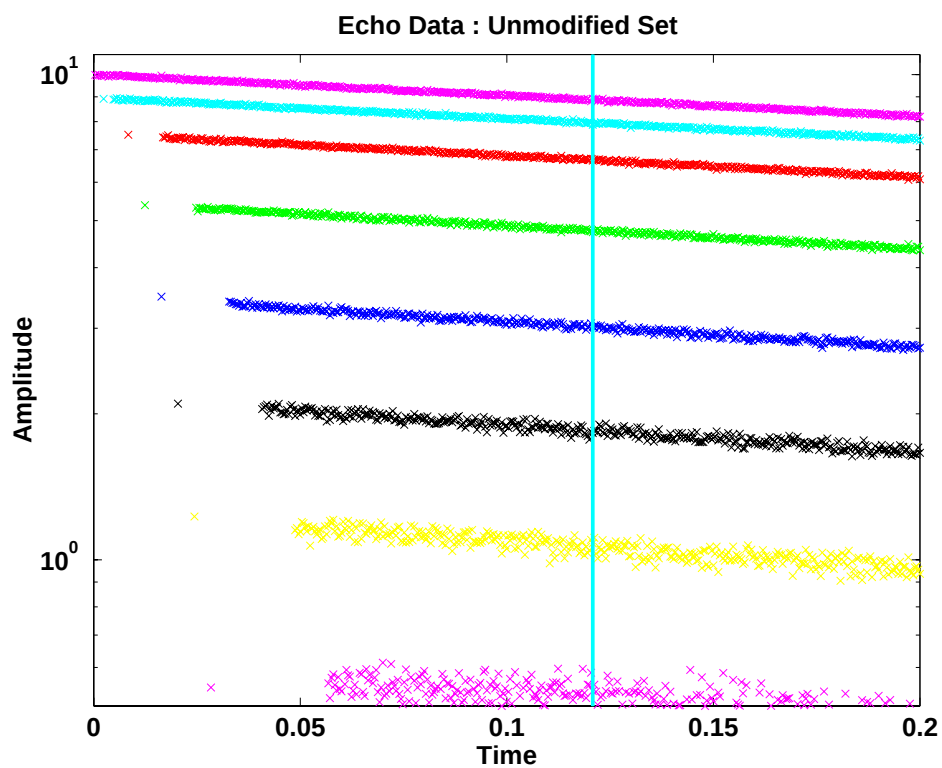


Figure 12: Data suite without preprocessing.

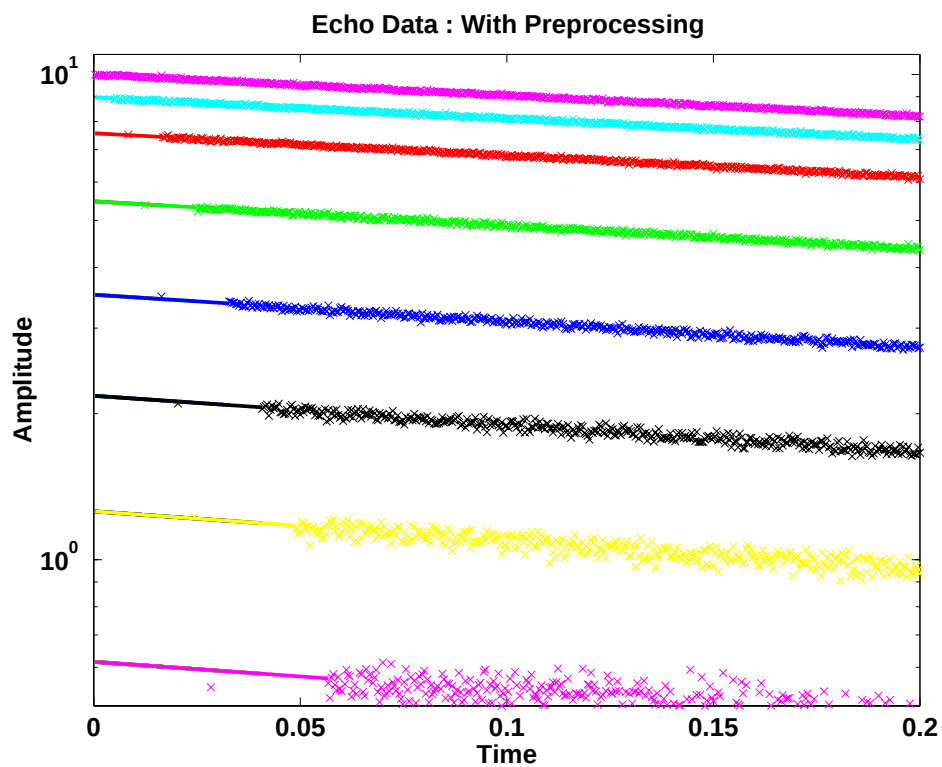


Figure 13: Data suite after preprocessing.

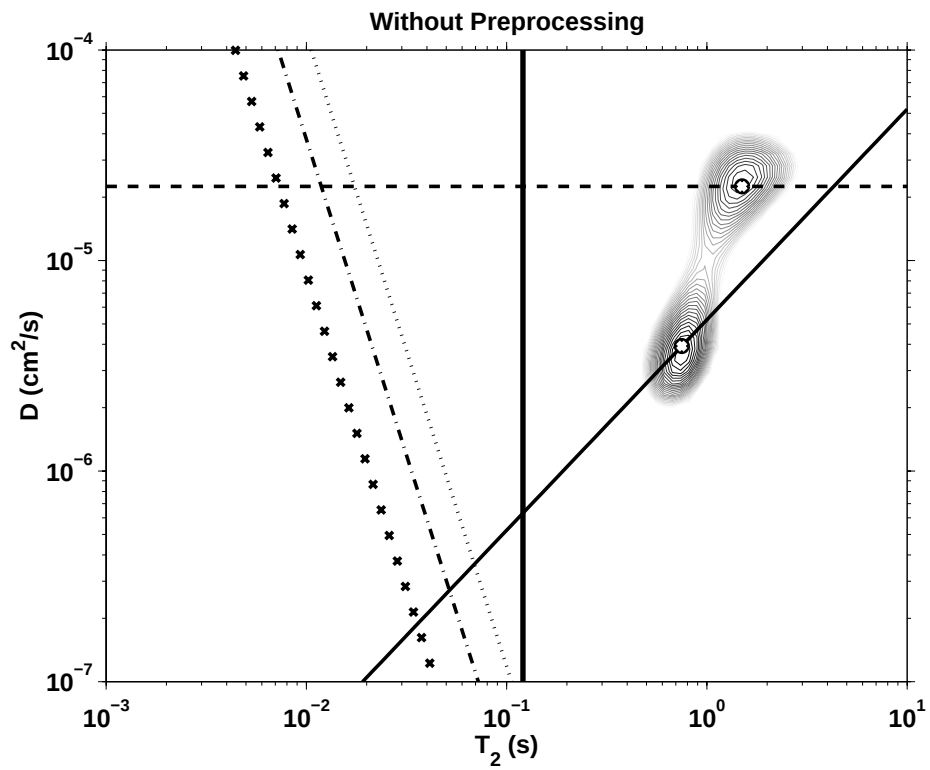


Figure 14: D - T_2 map of first simulated data suite without preprocessing.

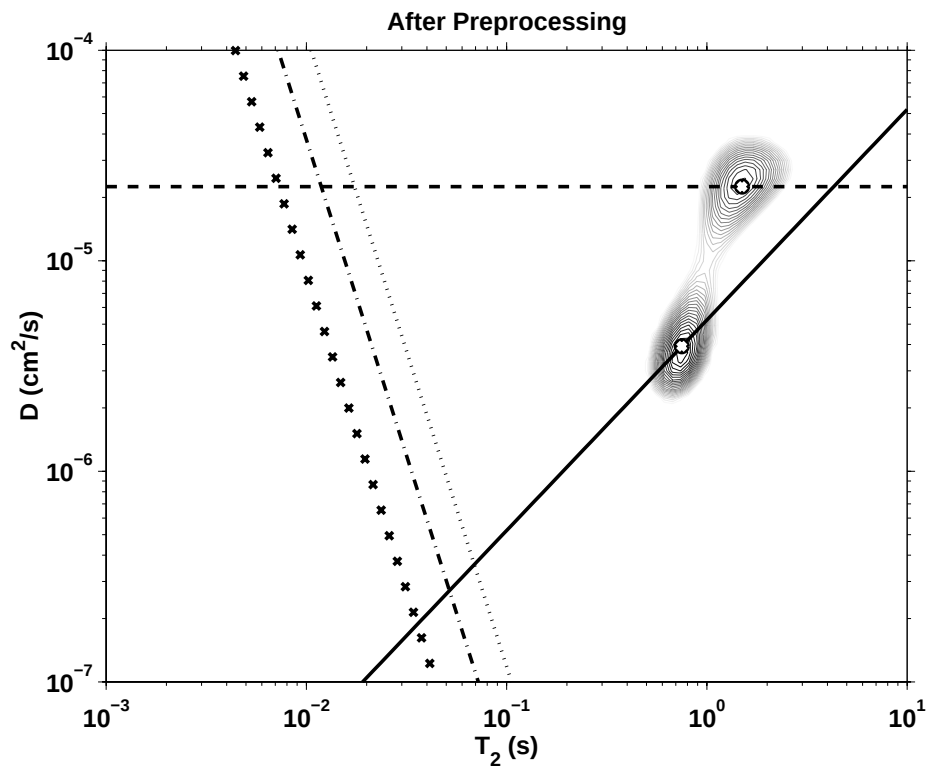


Figure 15: D - T_2 map of first simulated data suite after preprocessing.

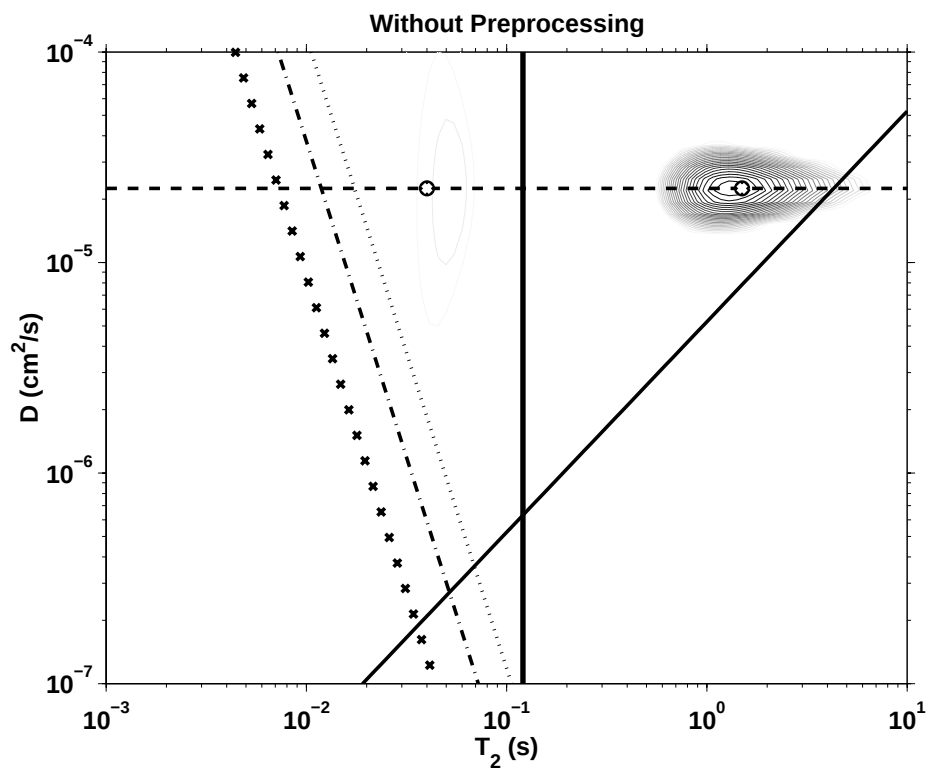


Figure 16: D - T_2 map of second simulated data suite without preprocessing.

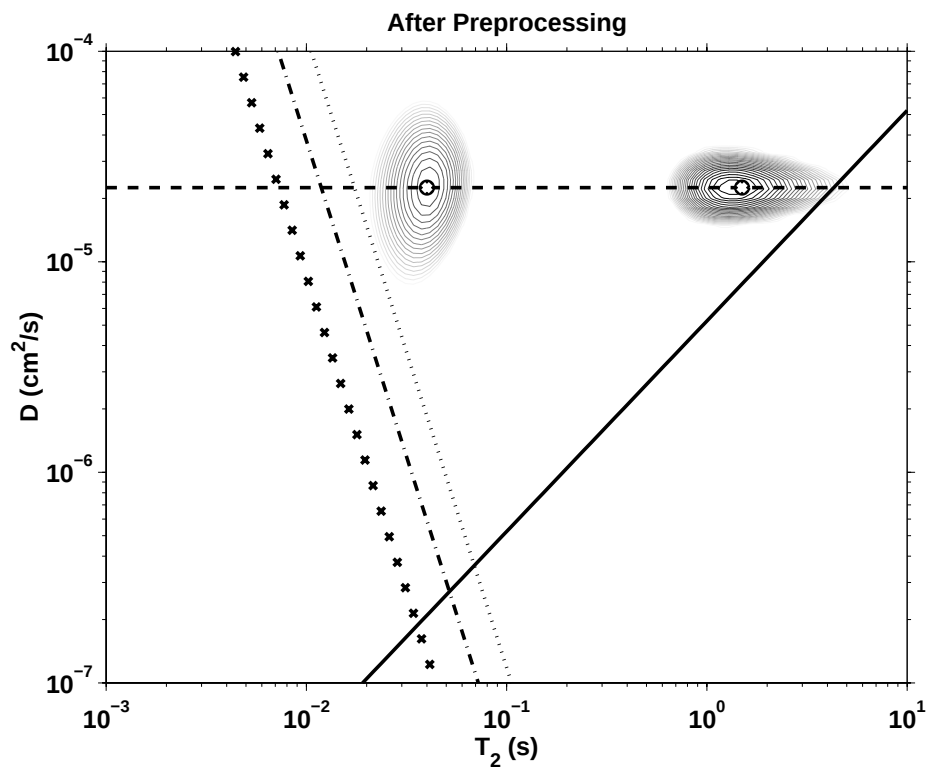


Figure 17: D - T_2 map of second simulated data suite after preprocessing.

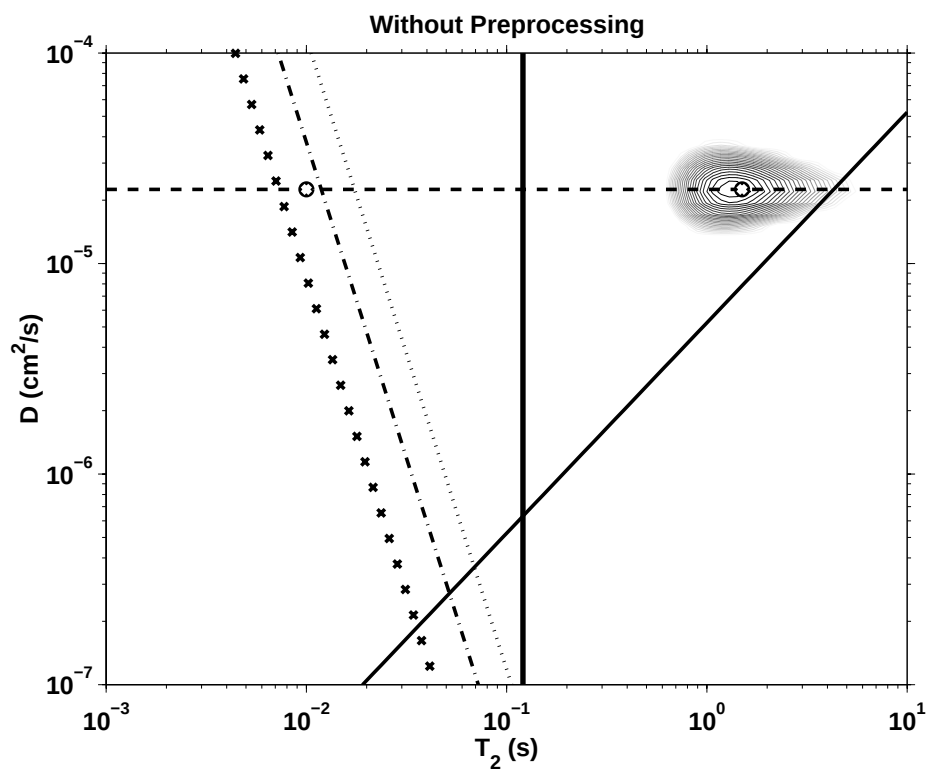


Figure 18: D - T_2 map of third simulated data suite without preprocessing.

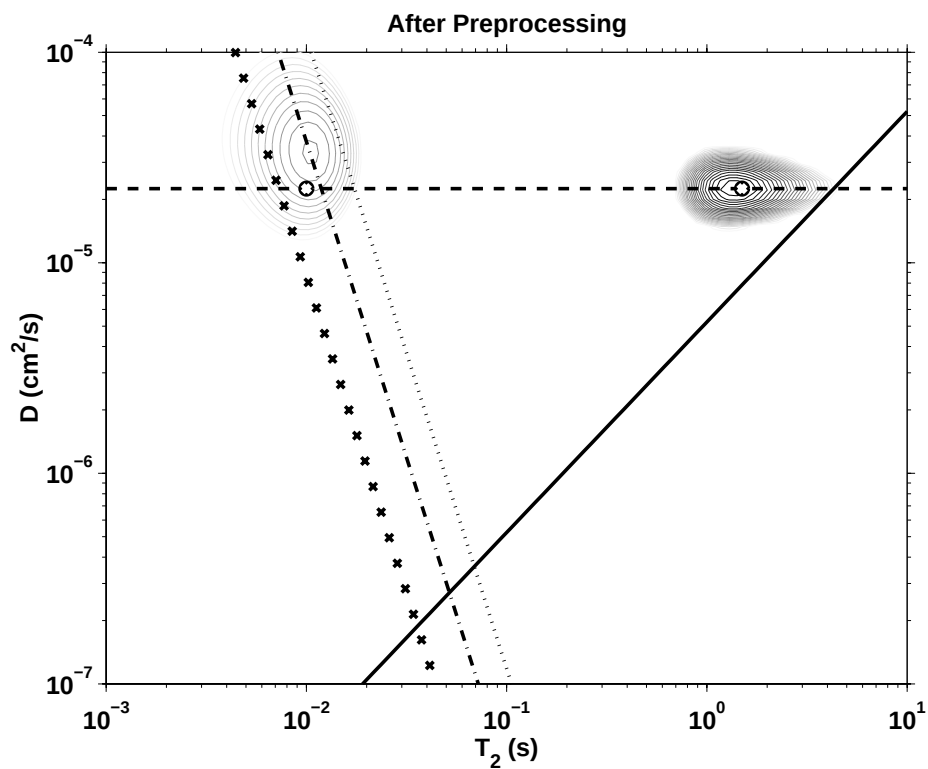


Figure 19: D - T_2 map of third simulated data suite after preprocessing.

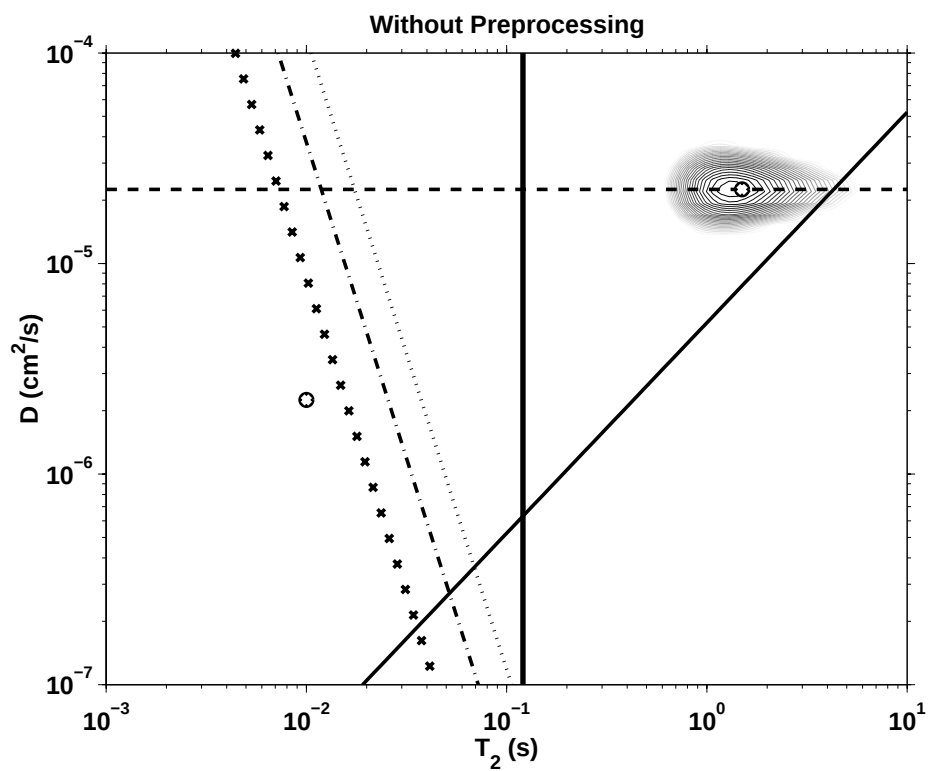


Figure 20: D - T_2 map of fourth simulated data suite without preprocessing.

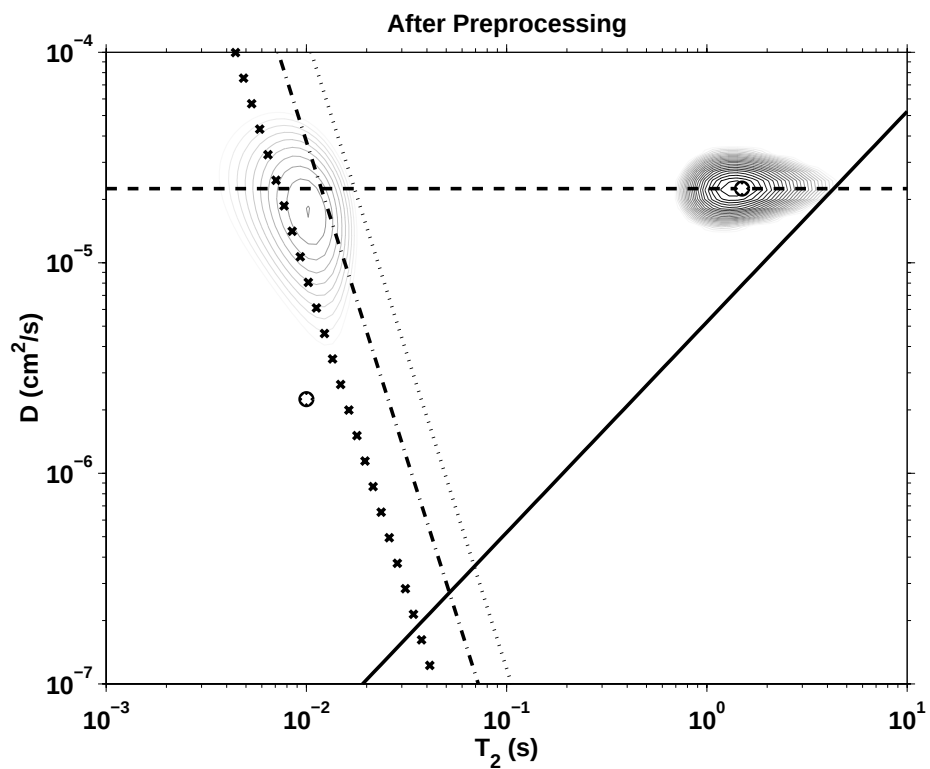


Figure 21: D - T_2 map of fourth simulated data suite without preprocessing.

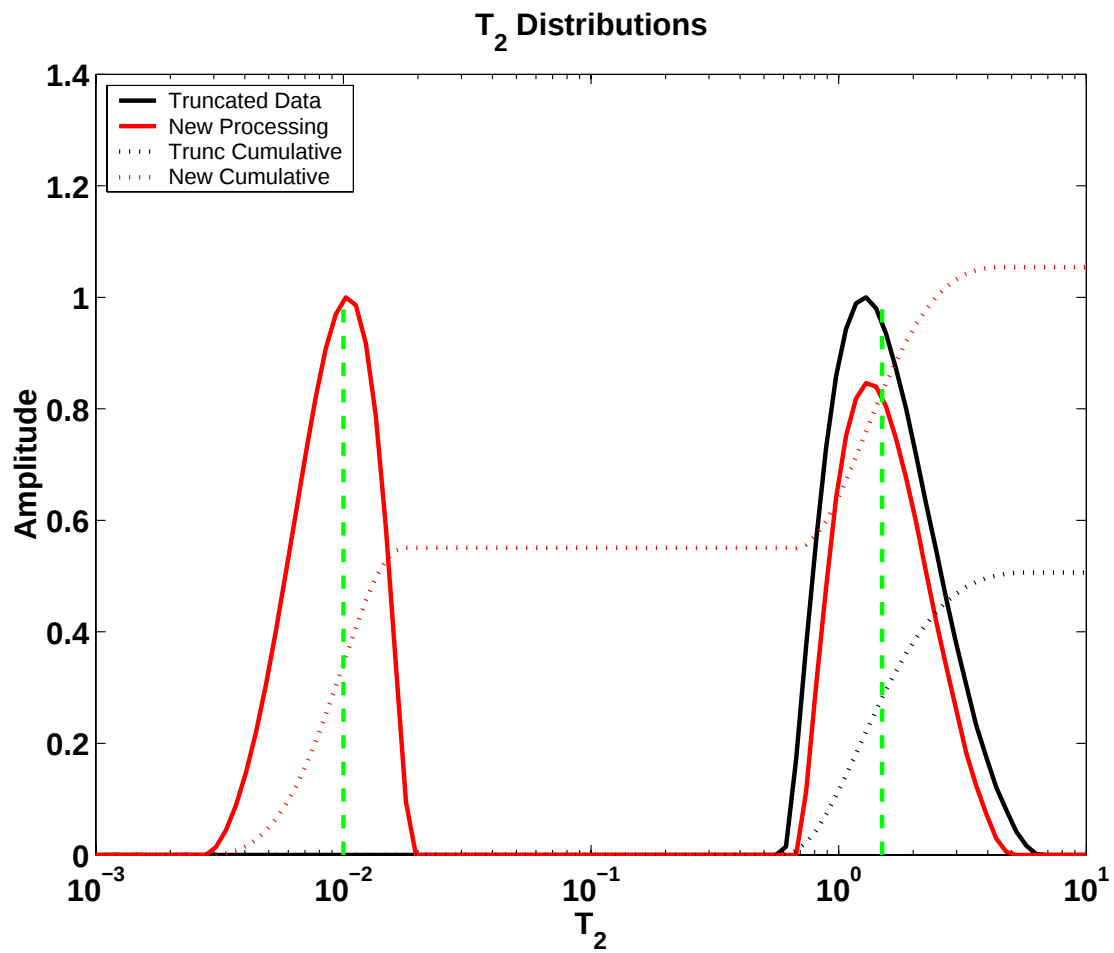


Figure 22: T_2 distribution comparison for fourth simulated data suite with and without preprocessing.

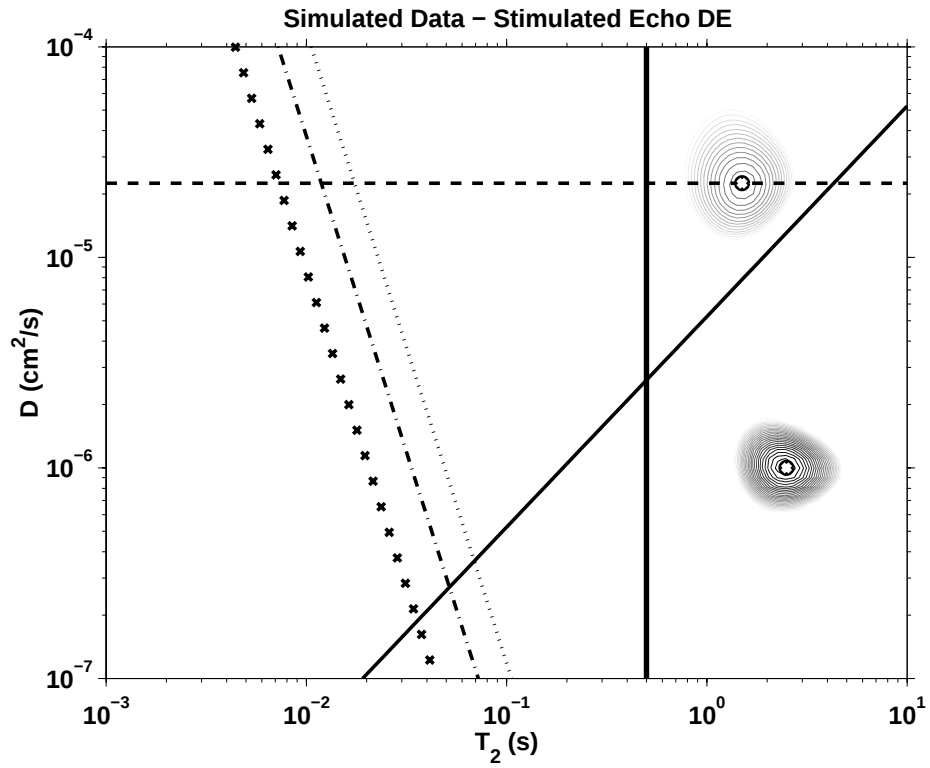


Figure 23: D - T_2 map from PFG-SE. δ of 400 μ s, t_D of 0.5 seconds.

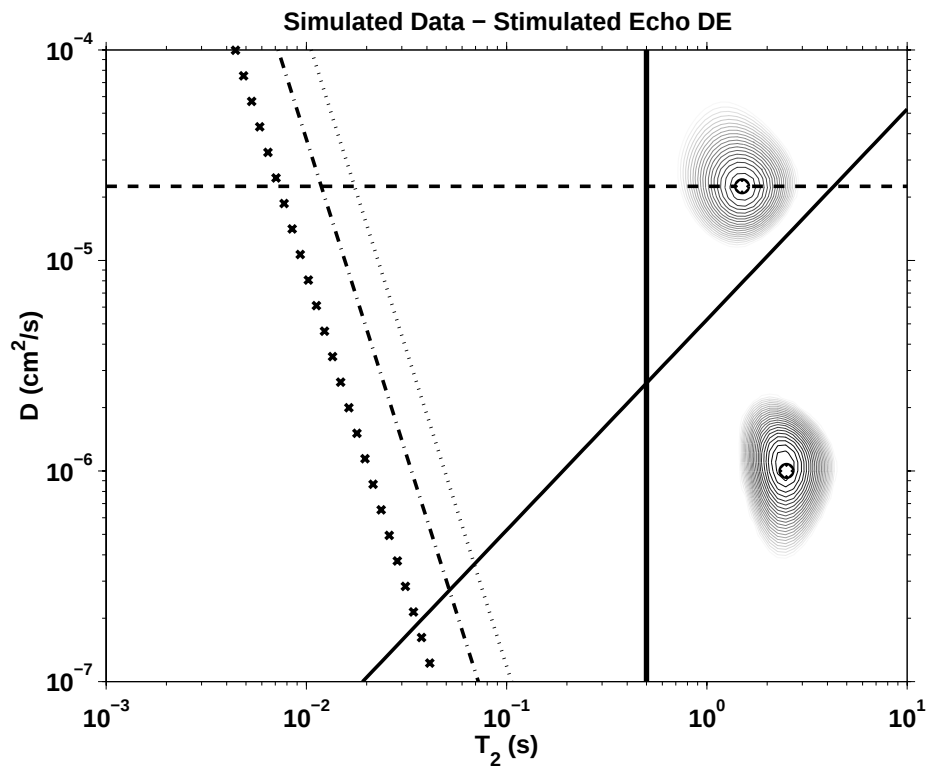


Figure 24: D - T_2 map from PFG-SE. δ of 400 μ s, t_D of 0.5 seconds. The grade list for this file included no higher values.

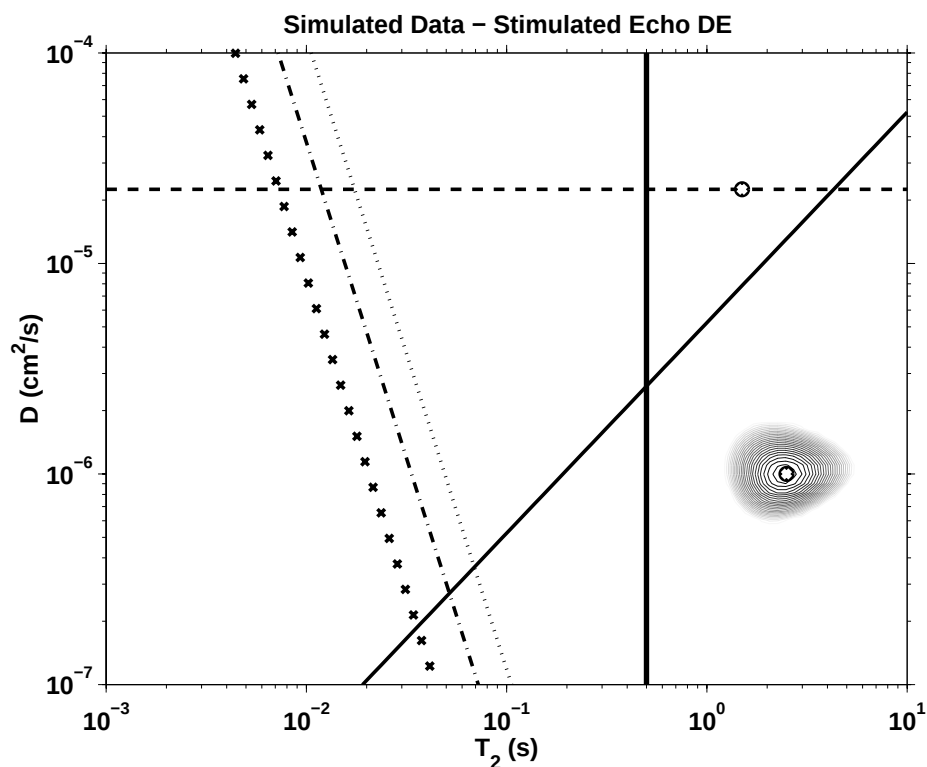


Figure 25: D - T_2 map from PFG-SE. δ of 400 μ s, t_D of 0.5 seconds. The grade list for this file included no lower values.

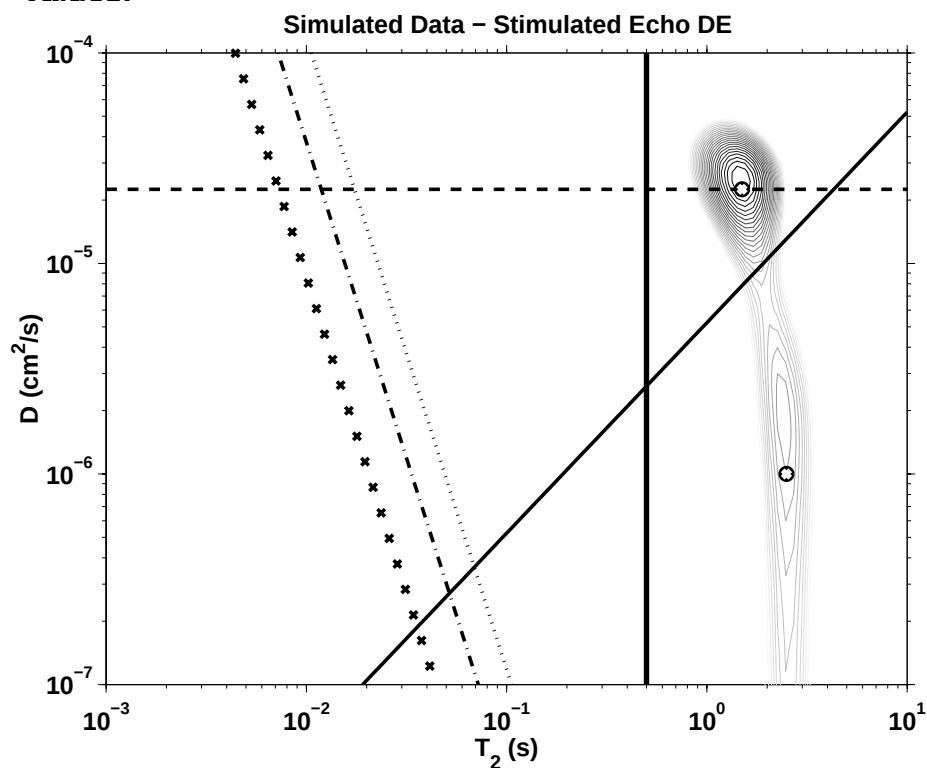


Figure 26: D - T_2 map from PFG-SE. δ of 100 μ s, t_D of 0.5 seconds.

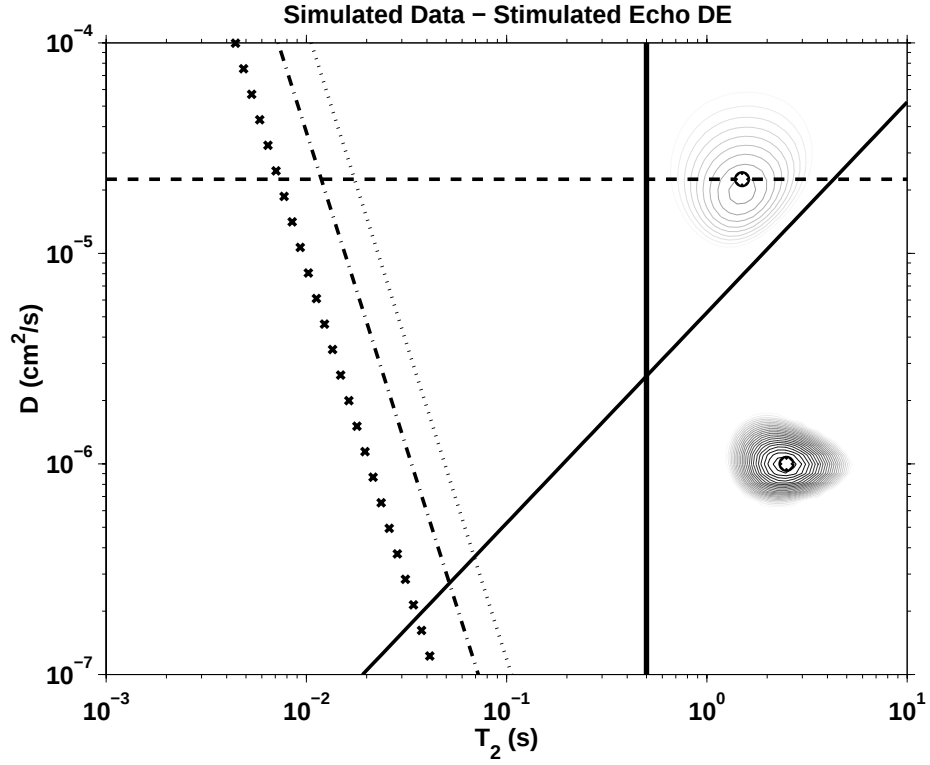


Figure 27: D - T_2 map from PFG-SE. δ of 1000 μs , t_D of 0.5 seconds.

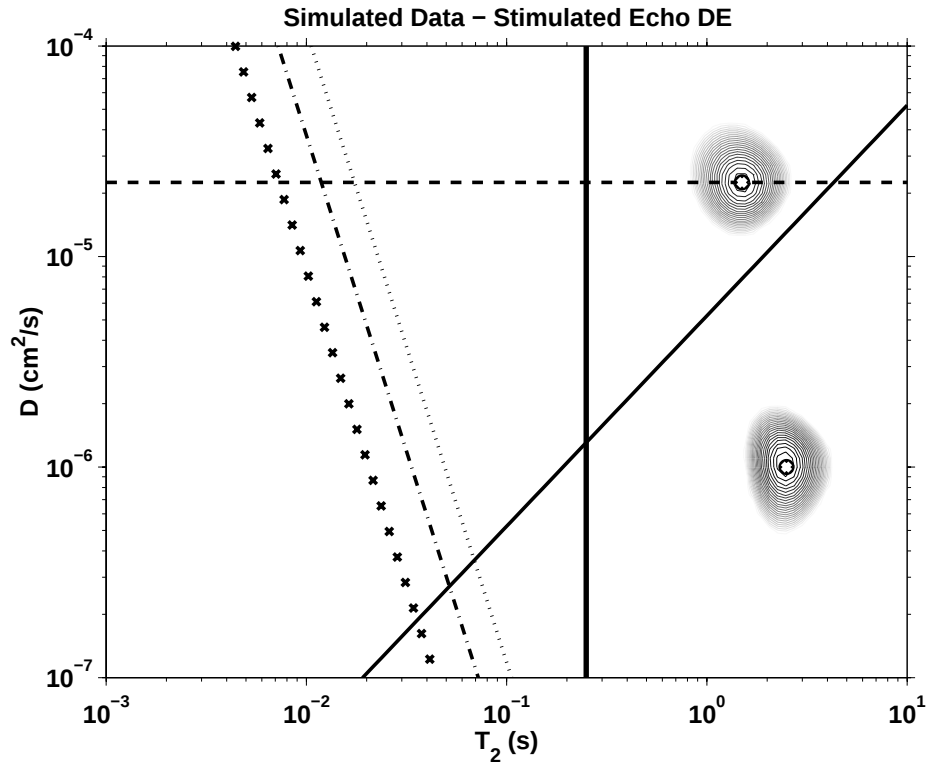


Figure 28: D - T_2 map from PFG-SE. δ of 400 μs , t_D of 0.25 seconds.

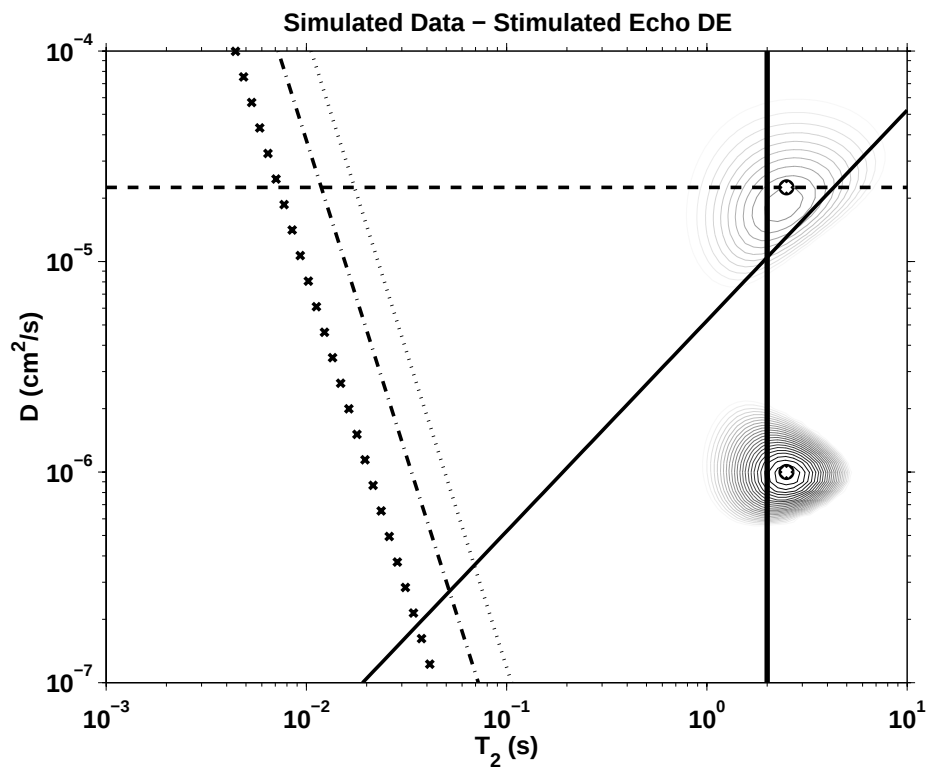


Figure 29: D - T_2 map from PFG-SE. δ of 400 μ s, t_D of 2.0 seconds.

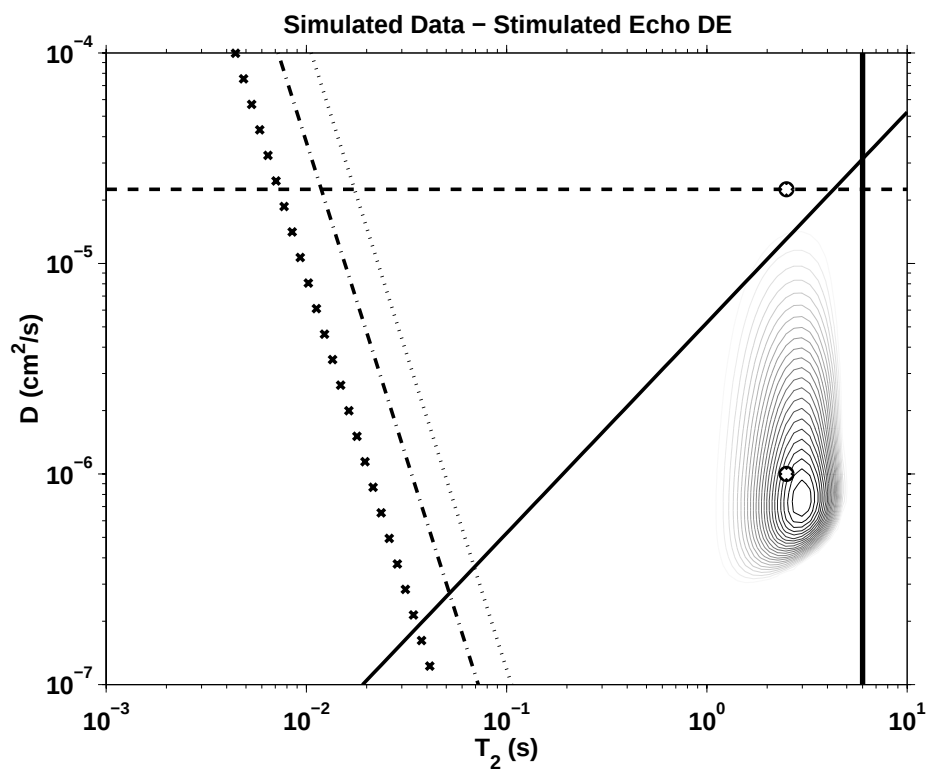


Figure 30: D - T_2 map from PFG-SE. δ of 400 μ s, t_D of 6.0 seconds.

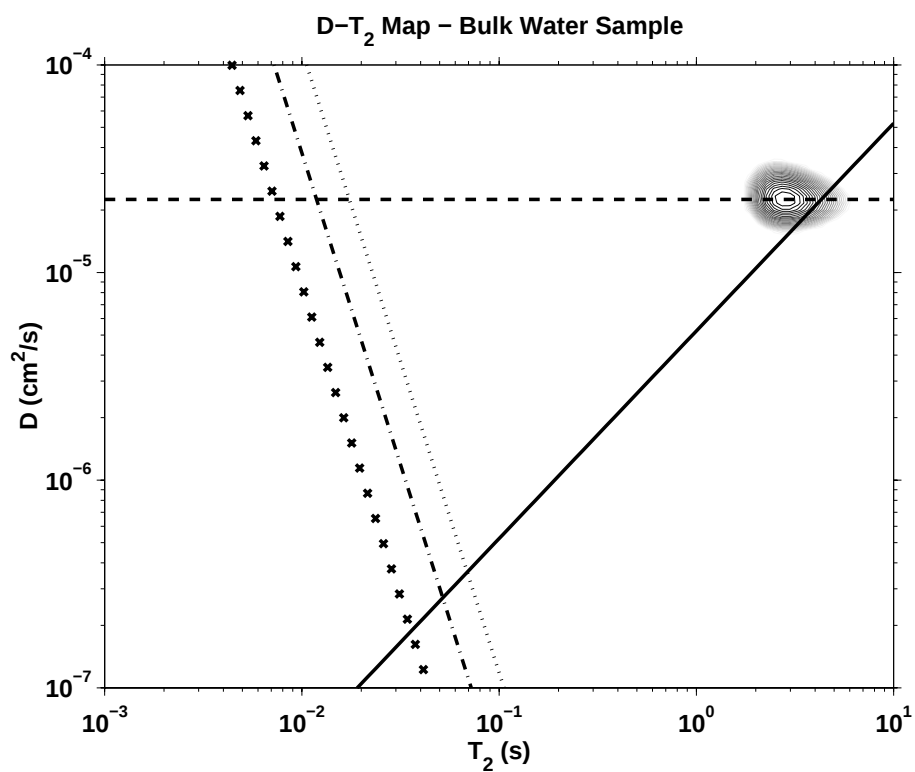


Figure 31: D - T_2 map of bulk water sample.

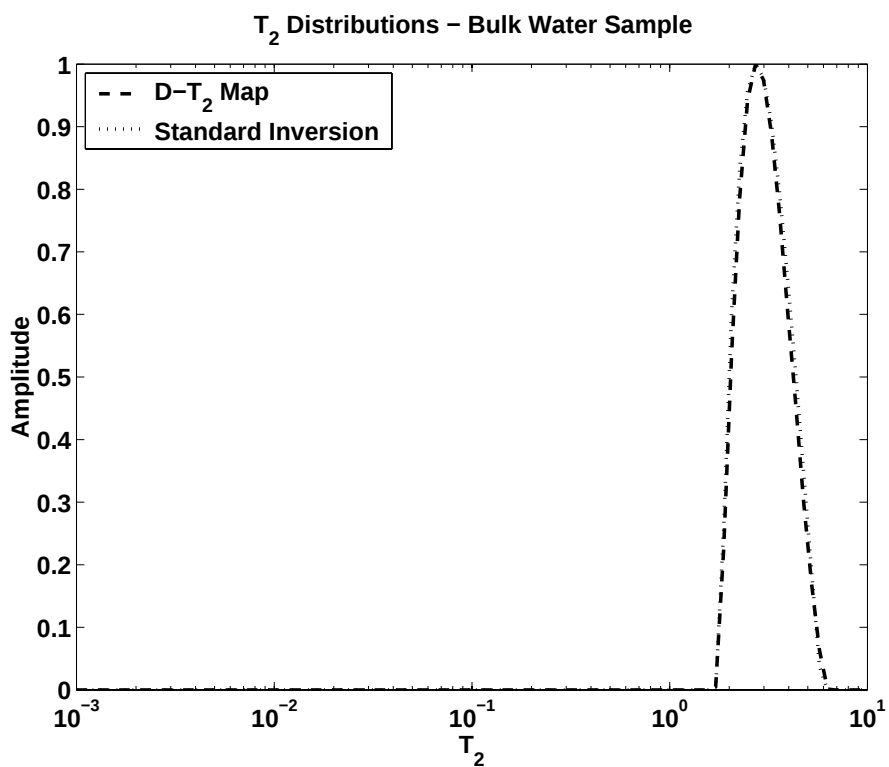


Figure 32: T_2 distributions of bulk water sample.

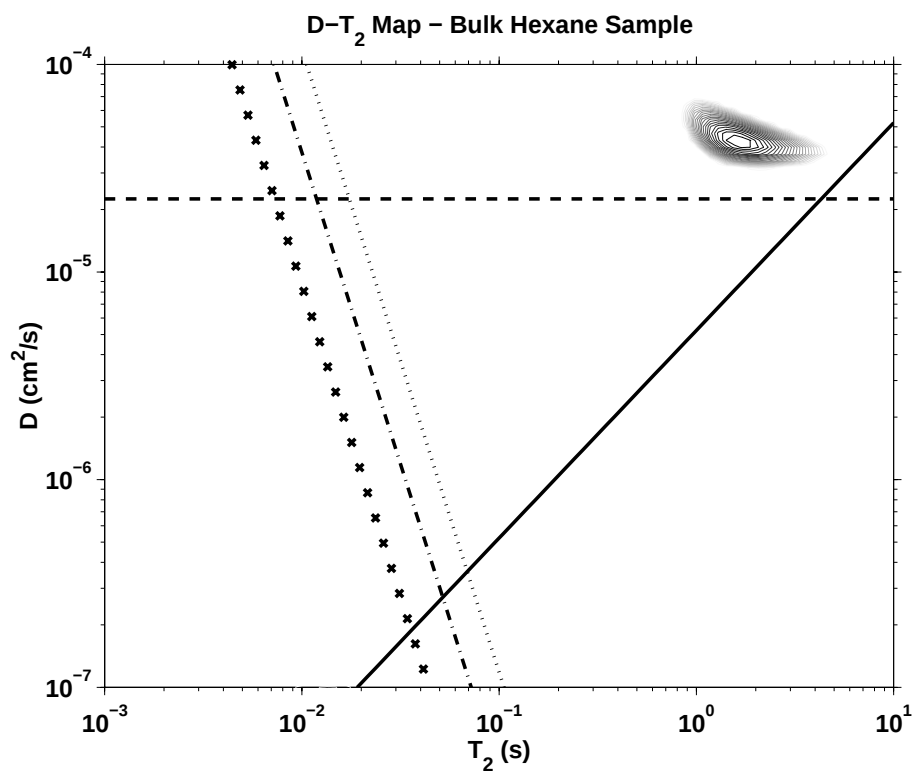


Figure 33: D - T_2 map of bulk hexane.

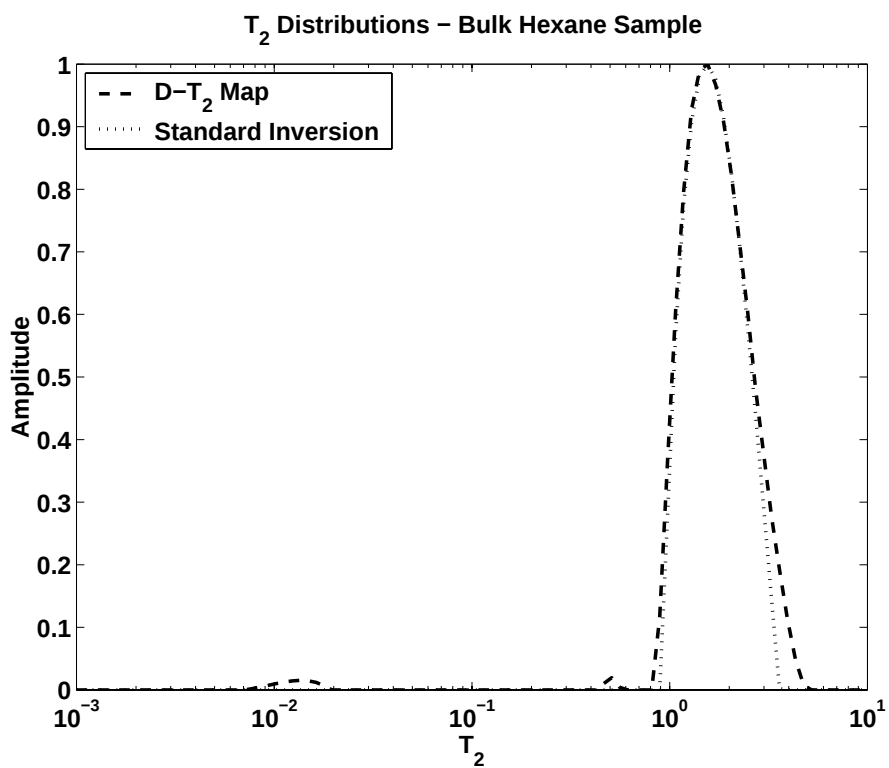


Figure 34: T_2 distributions of bulk hexane sample.

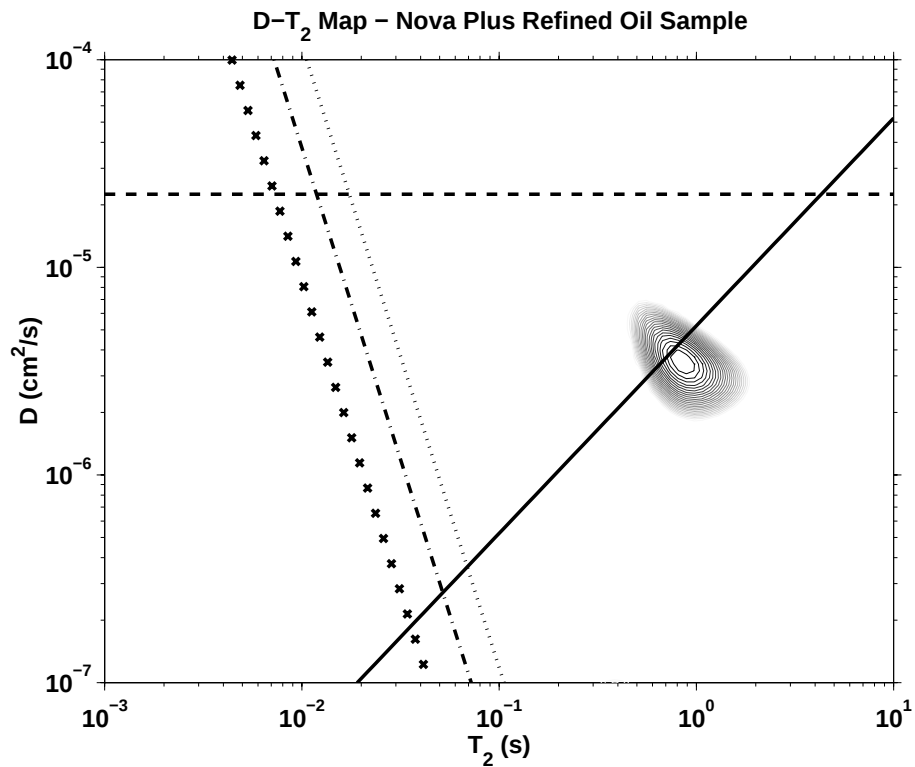


Figure 35: D - T_2 map of bulk Nova Plus refined oil sample.

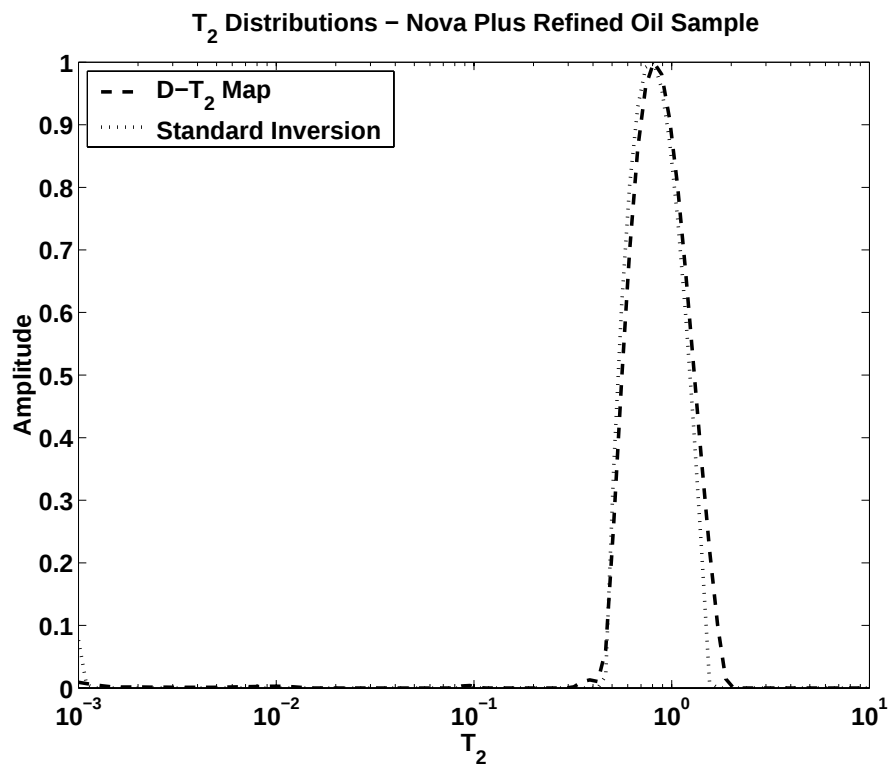


Figure 36: T_2 distributions of bulk Nova Plus refined oil sample.

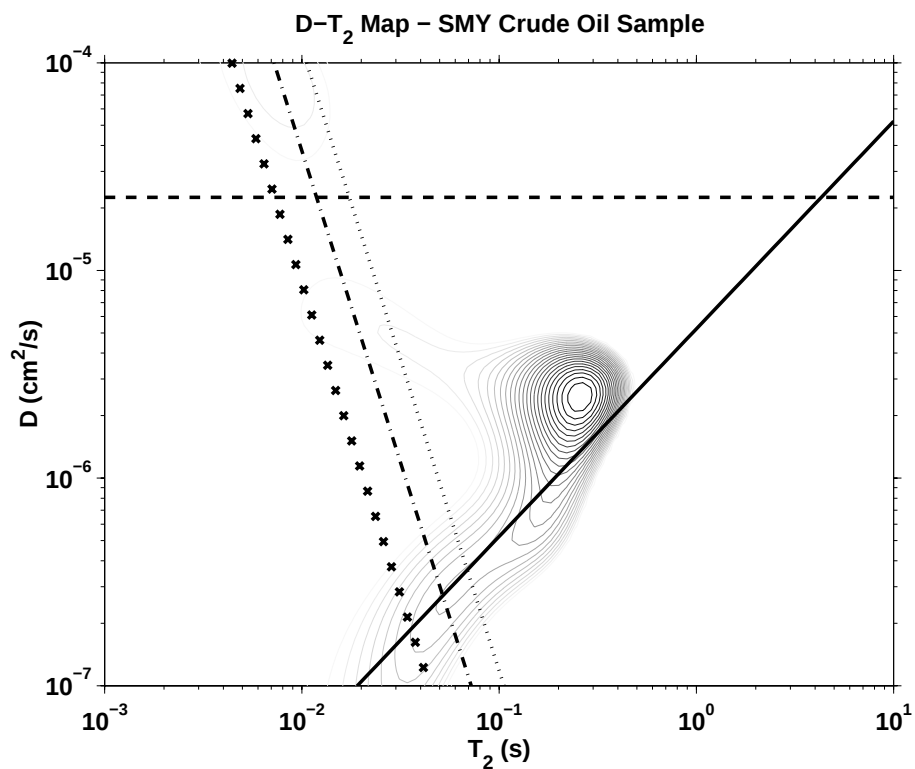


Figure 37: D - T_2 map of bulk SMY crude oil sample.

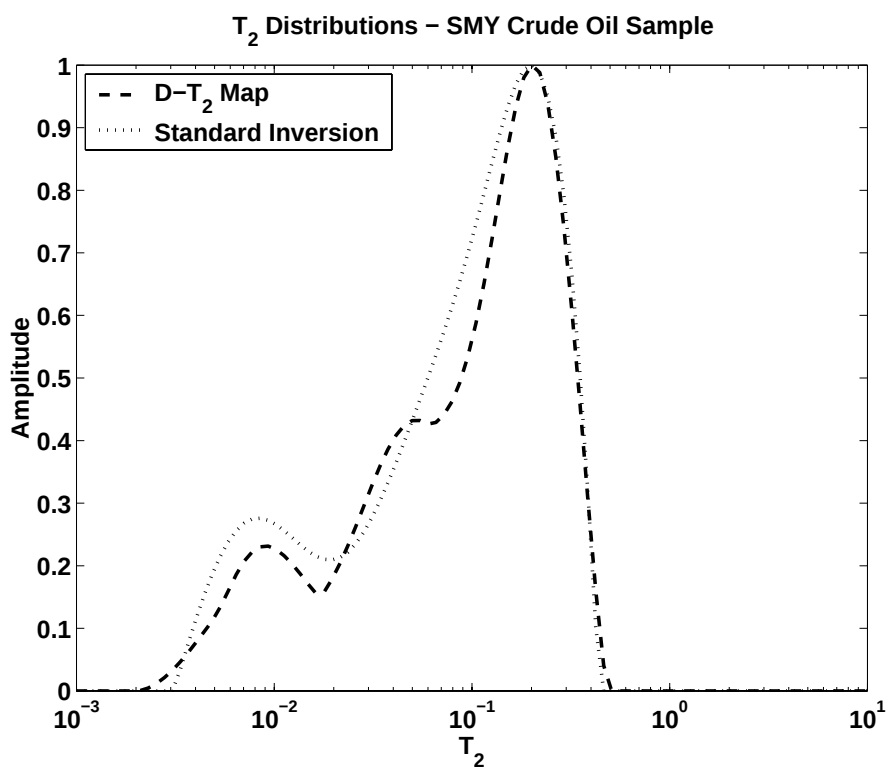


Figure 38: T_2 distributions of bulk SMY crude oil sample.

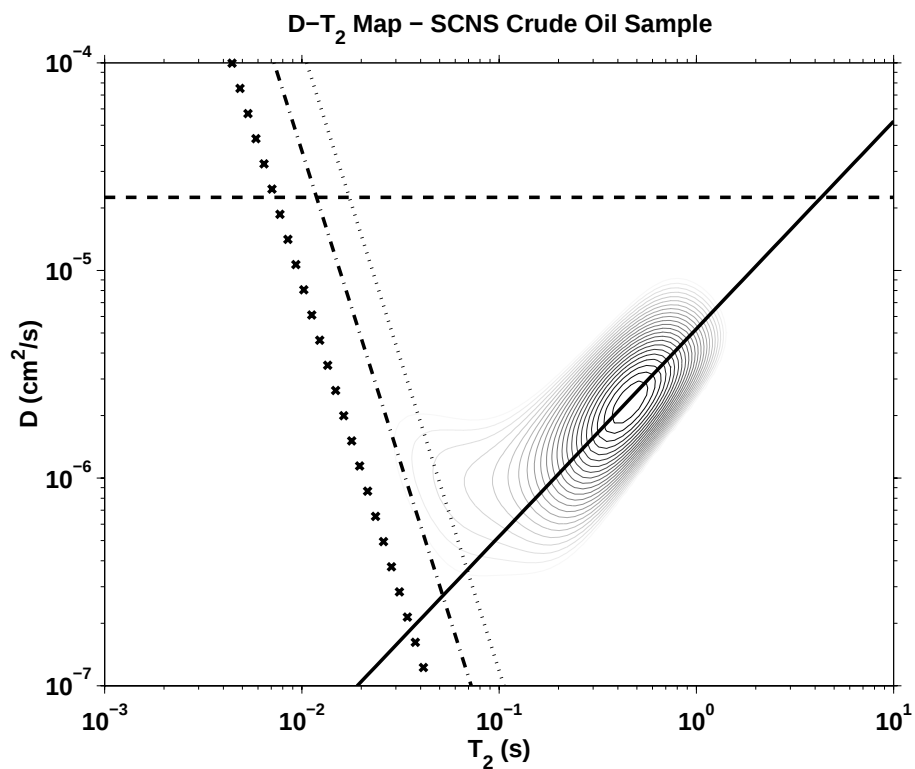


Figure 39: D - T_2 map of bulk SCNS crude oil sample.

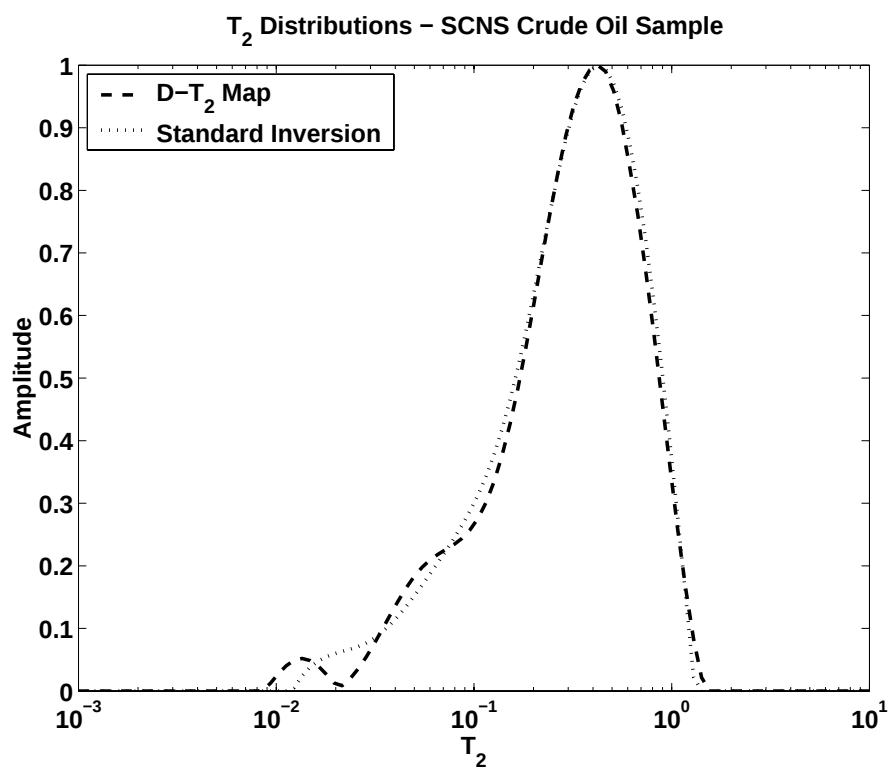


Figure 40: T_2 distributions of bulk SCNS crude oil sample.

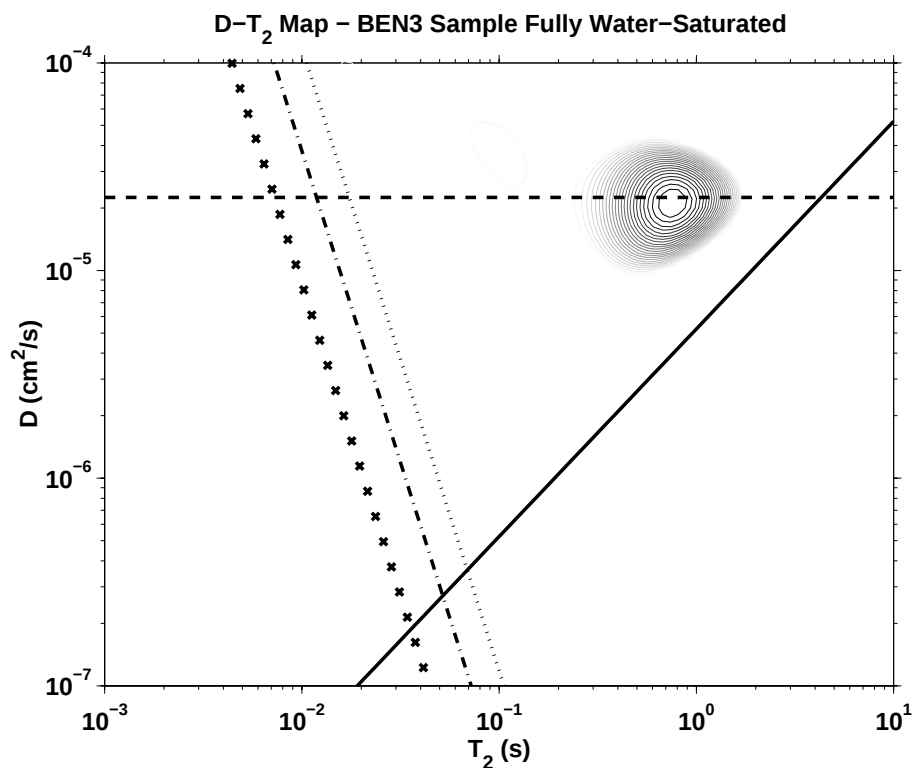


Figure 41: D - T_2 map of BEN 3 sample, fully water-saturated.

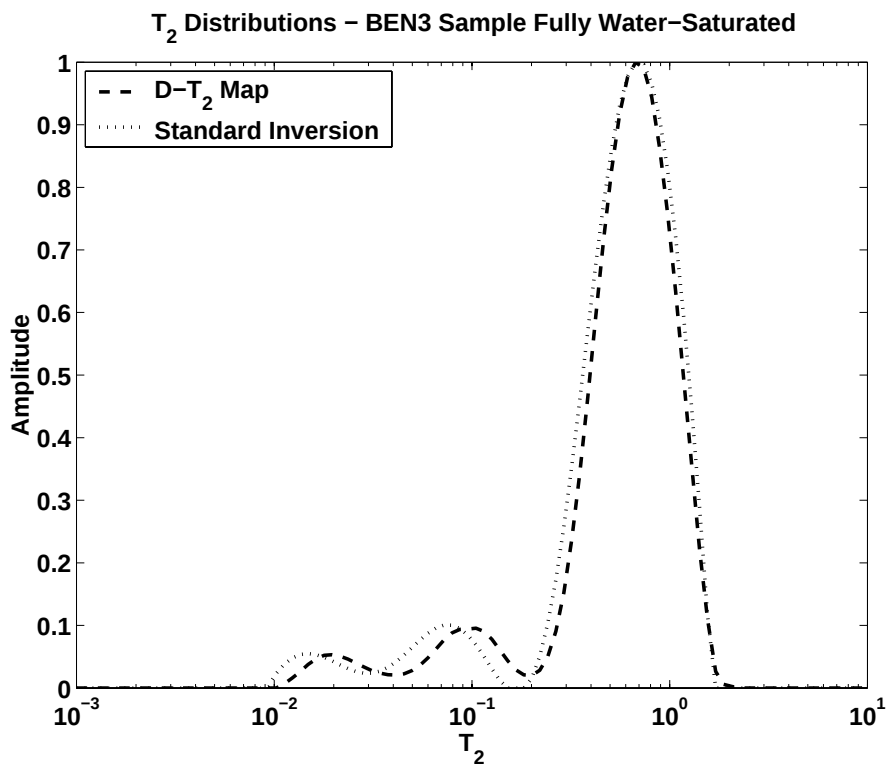


Figure 42: T_2 distributions of BEN 3 sample, fully water-saturated.

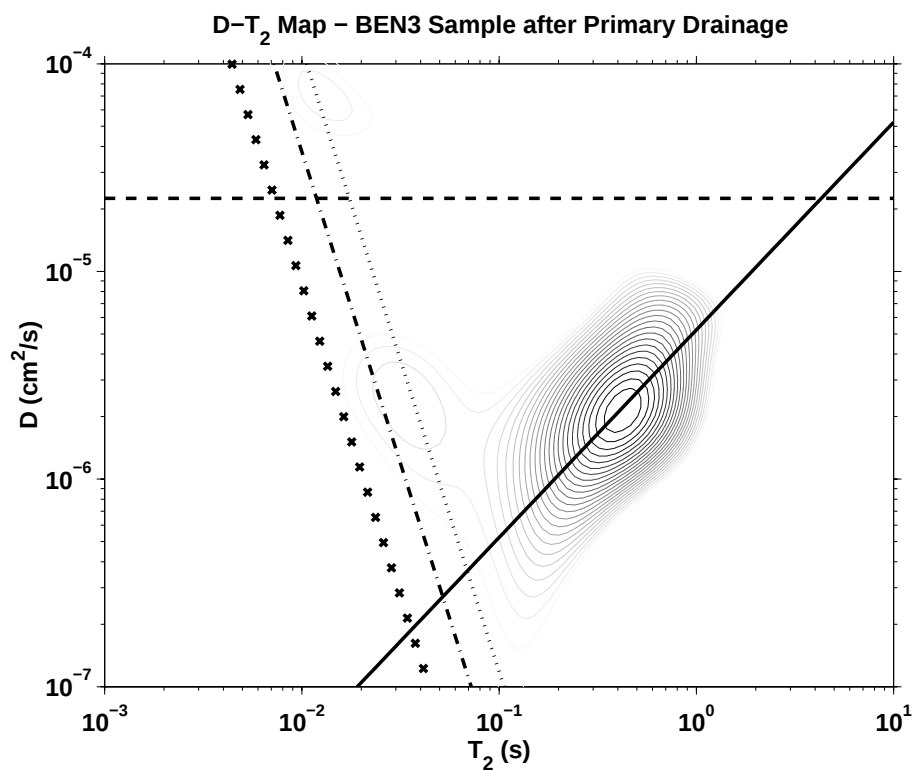


Figure 43: D - T_2 map of BEN 3 sample, after primary drainage. S_o is approximately 0.95.

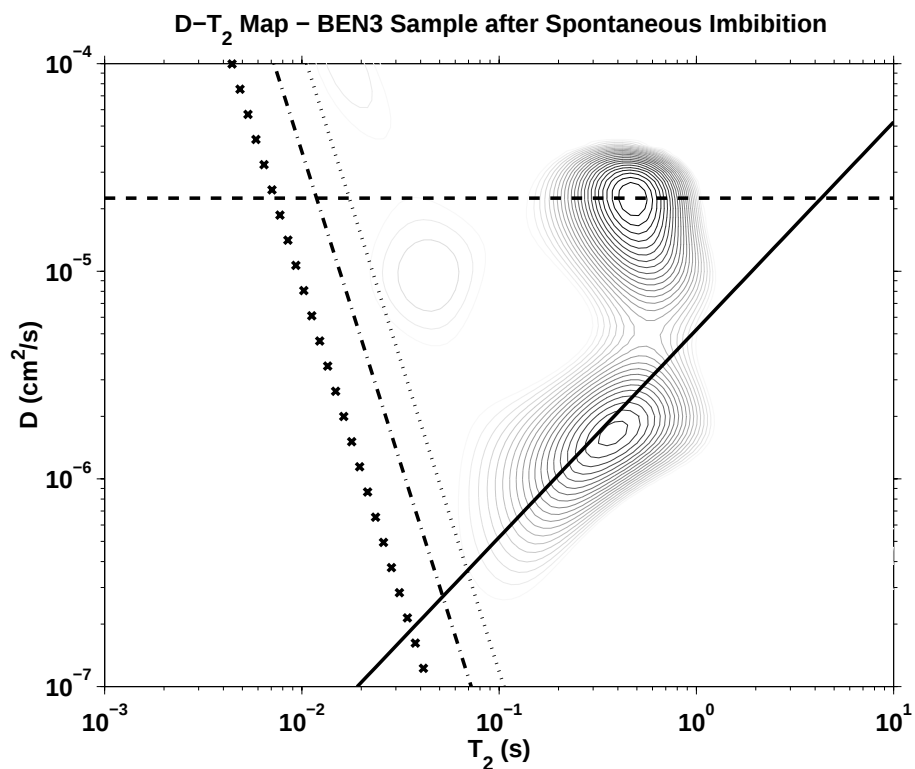


Figure 44: D - T_2 map of BEN 3 sample, after spontaneous imbibition. S_o is approximately 0.57.

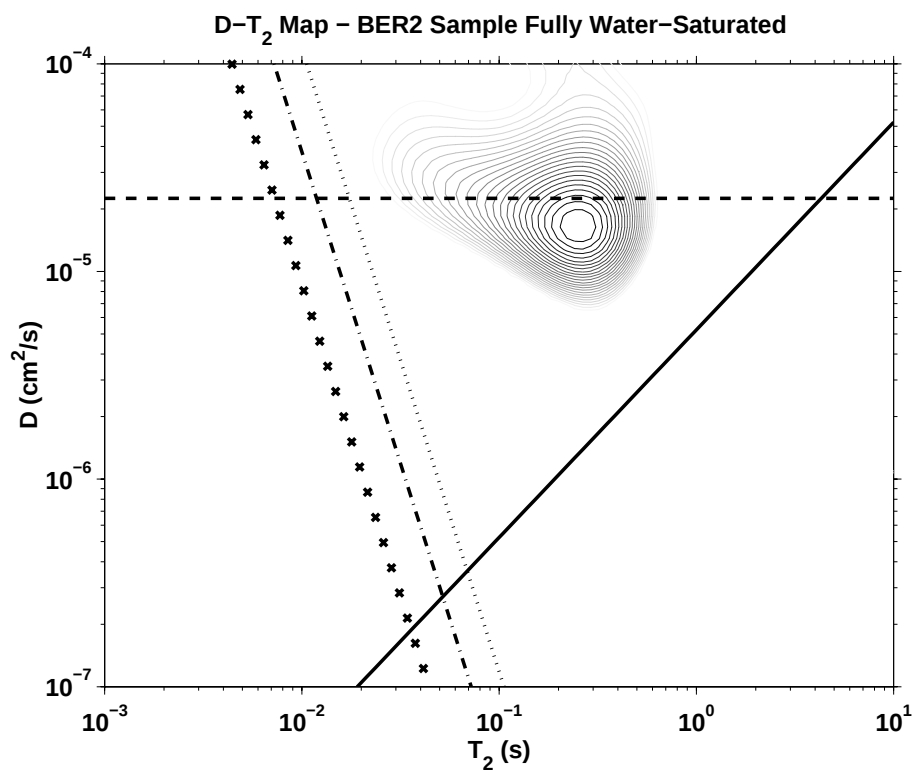


Figure 45: D - T_2 map of BER 2 sample, fully water-saturated.

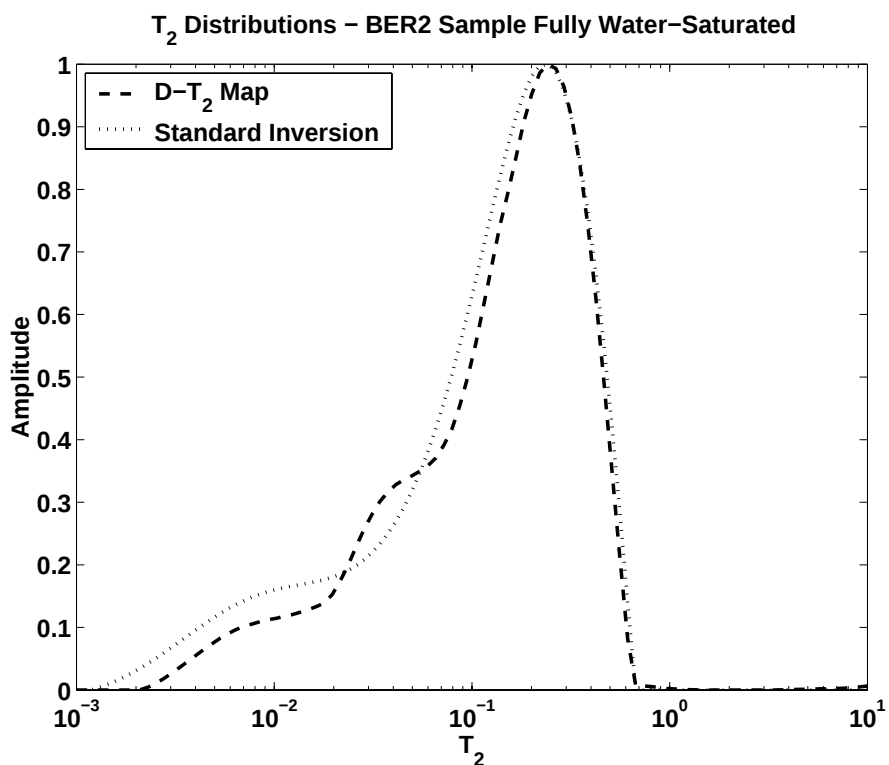


Figure 46: T_2 distributions of BER 2 sample, fully water-saturated.

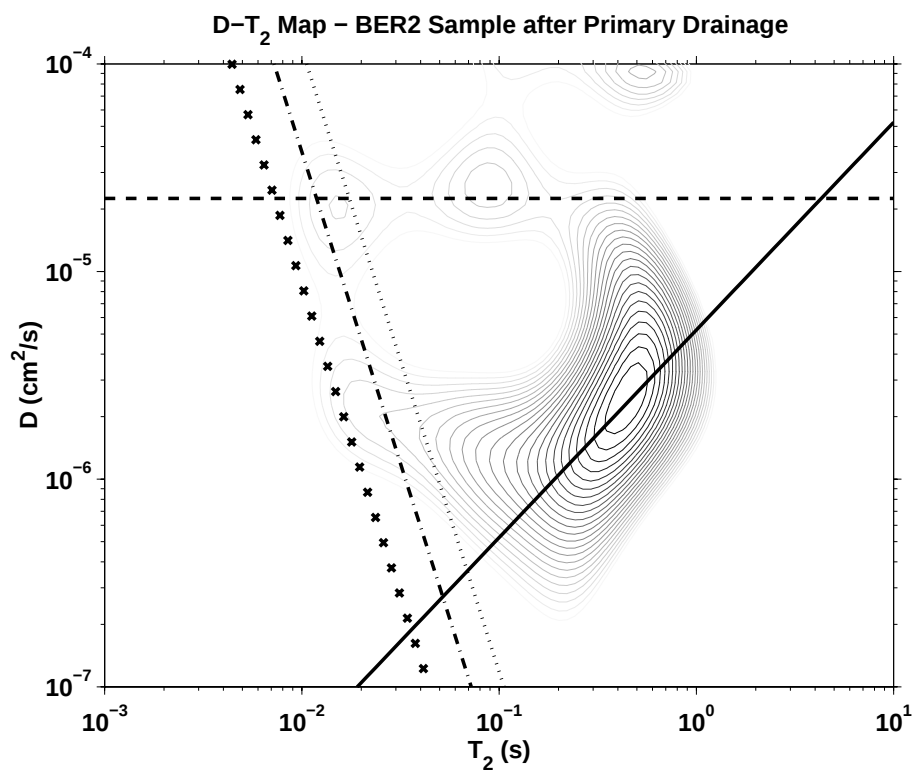


Figure 47: D - T_2 map of BER 2 sample, after primary drainage. S_o is approximately 0.79.

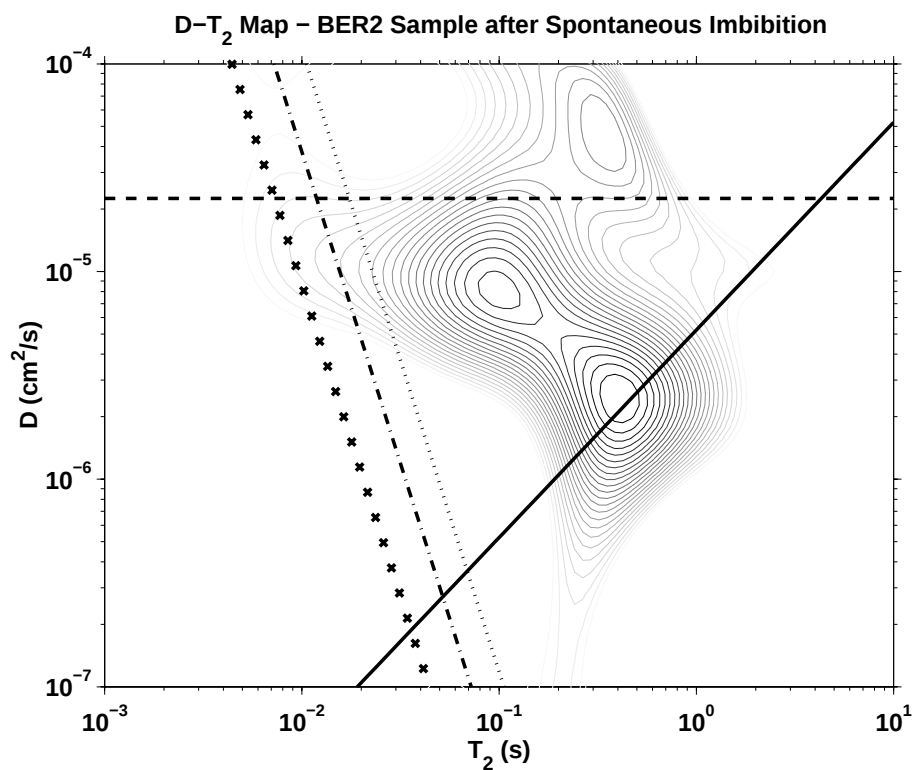


Figure 48: D - T_2 map of BER 2 sample, after spontaneous imbibition. S_o is approximately 0.46.

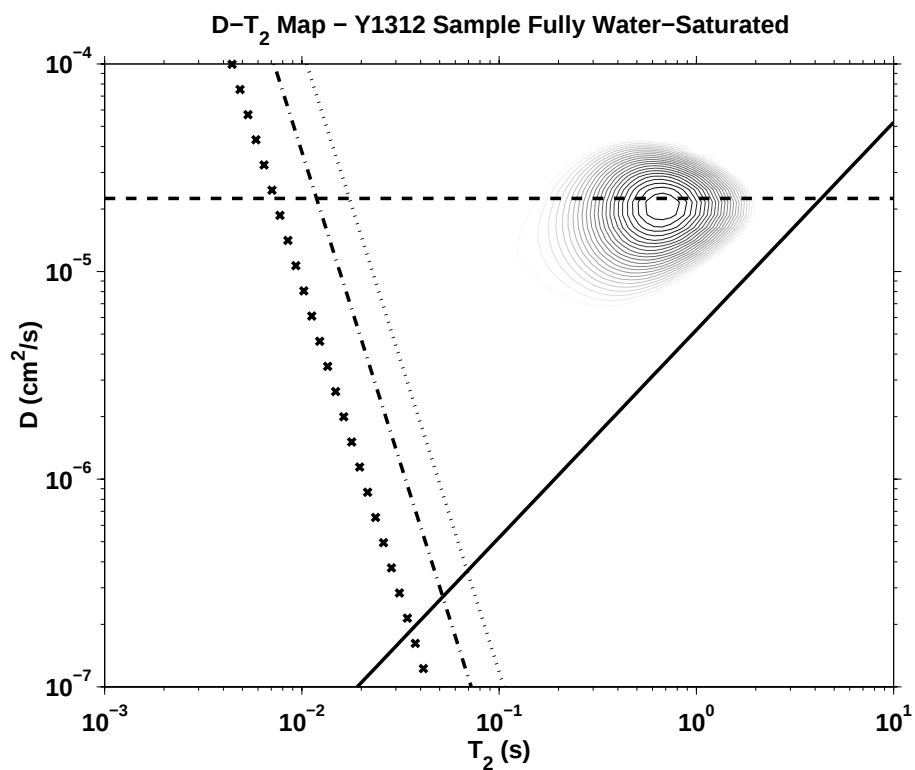


Figure 49: D - T_2 map of Y1312 sample, fully water-saturated.

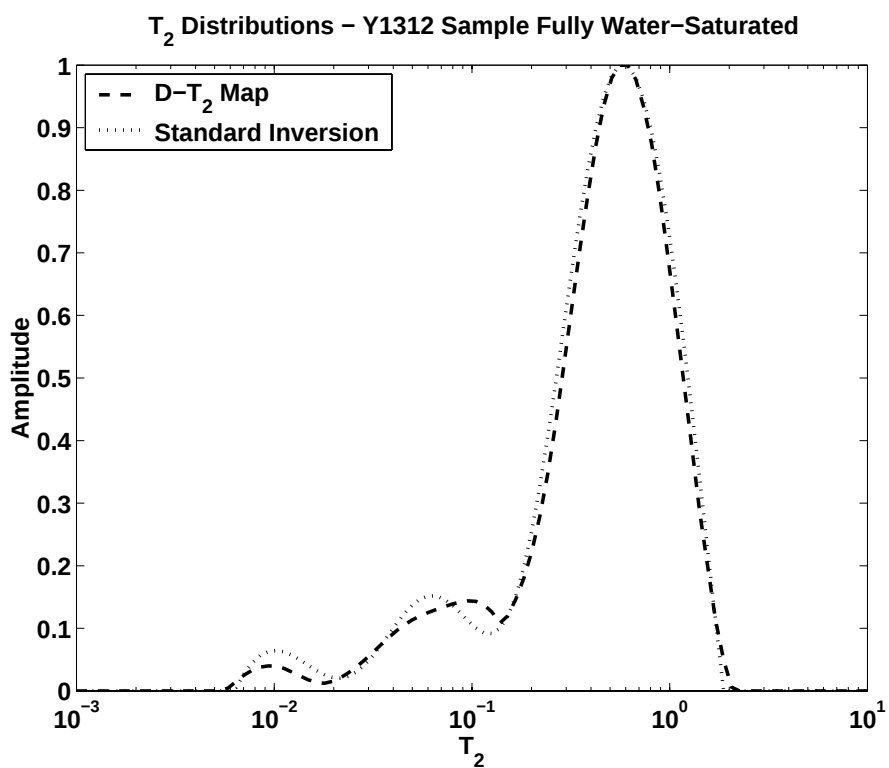


Figure 50: T_2 distributions of Y1312 sample, fully water-saturated.

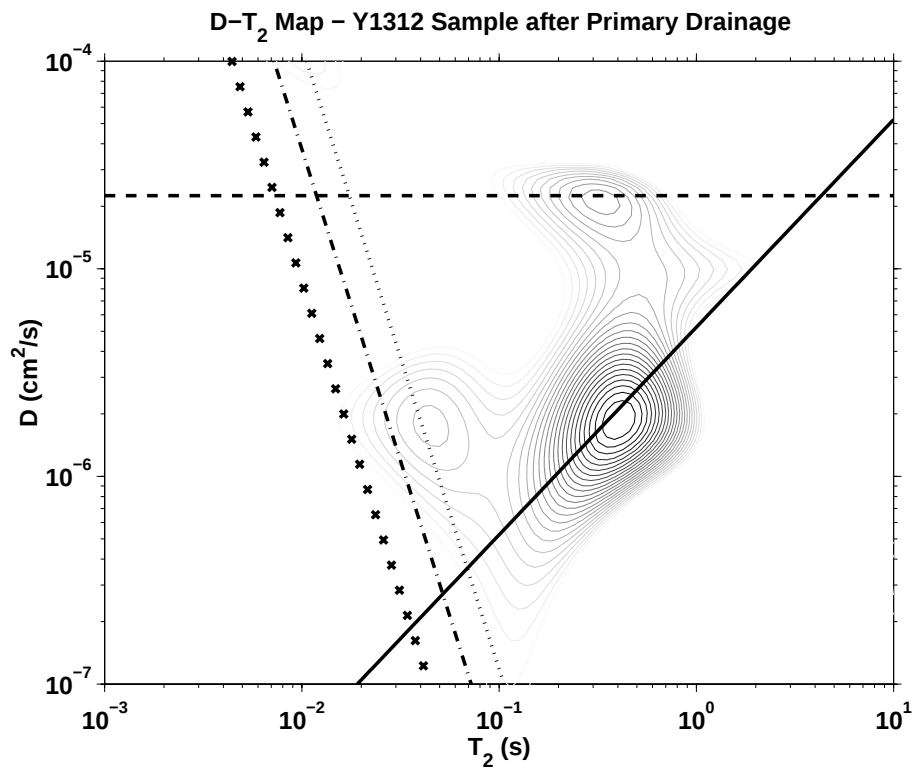


Figure 51: D - T_2 map of Y1312 sample, after primary drainage. S_o is approximately 0.86.

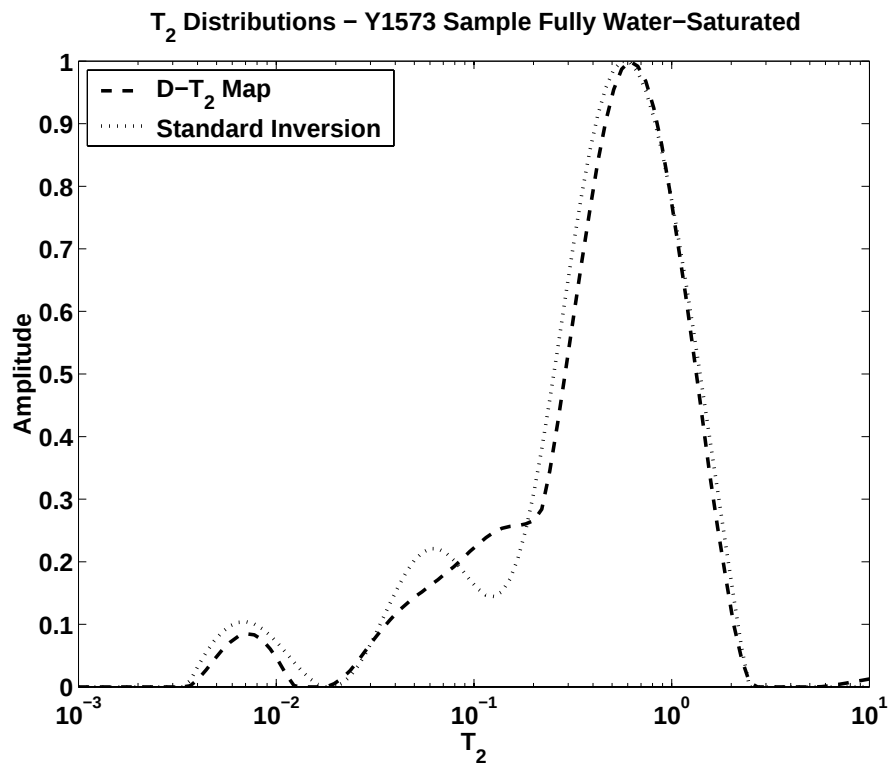


Figure 52: D - T_2 map of Y1312 sample, after forced imbibition. S_o is approximately 0.37.

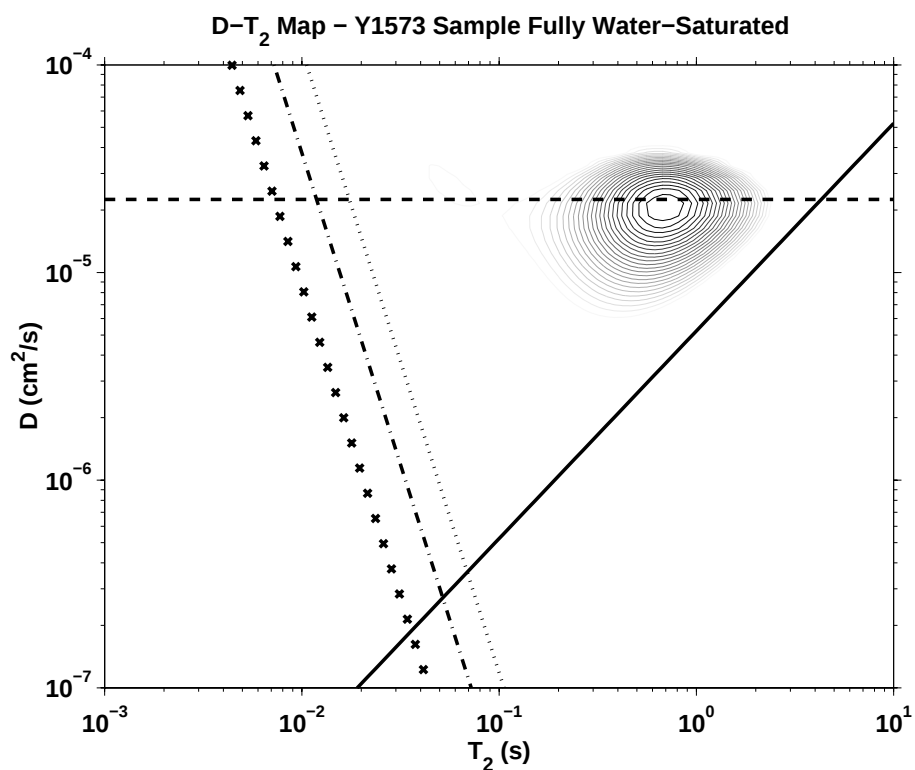


Figure 53: D - T_2 map of Y1573 sample, fully water-saturated.

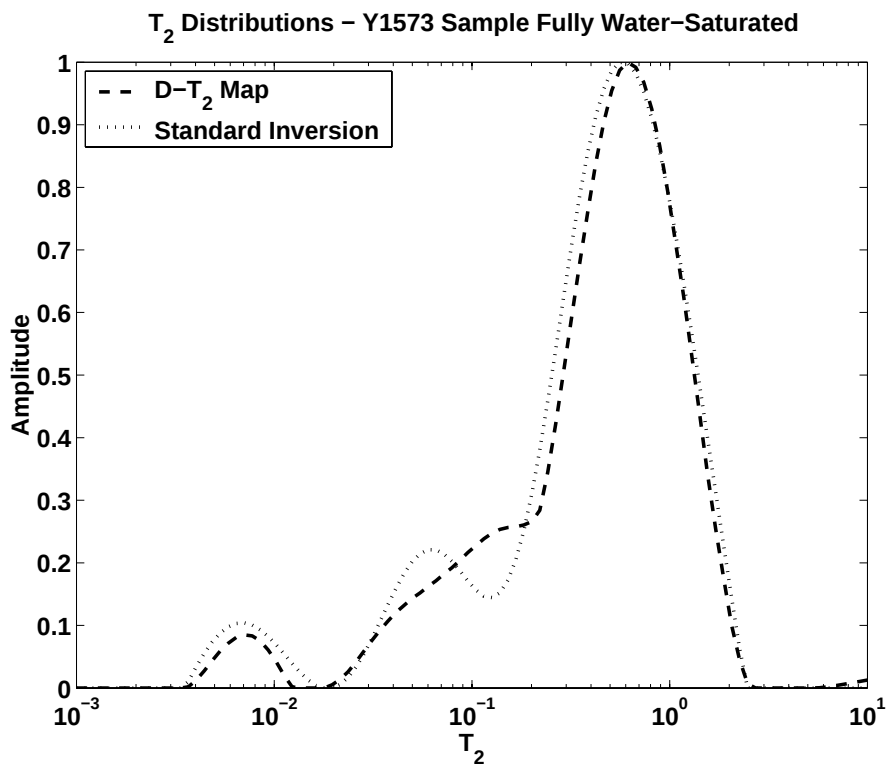


Figure 54: T_2 distributions of Y1573 sample, fully water-saturated.

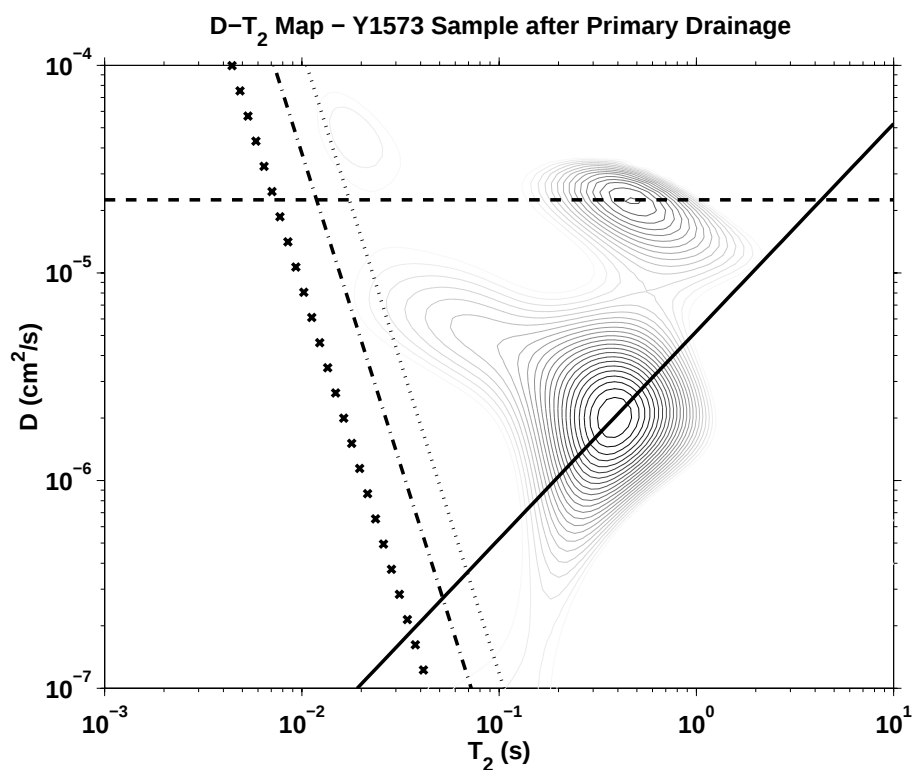


Figure 55: D - T_2 map of Y1573 sample, after primary drainage. S_o is approximately 0.81.

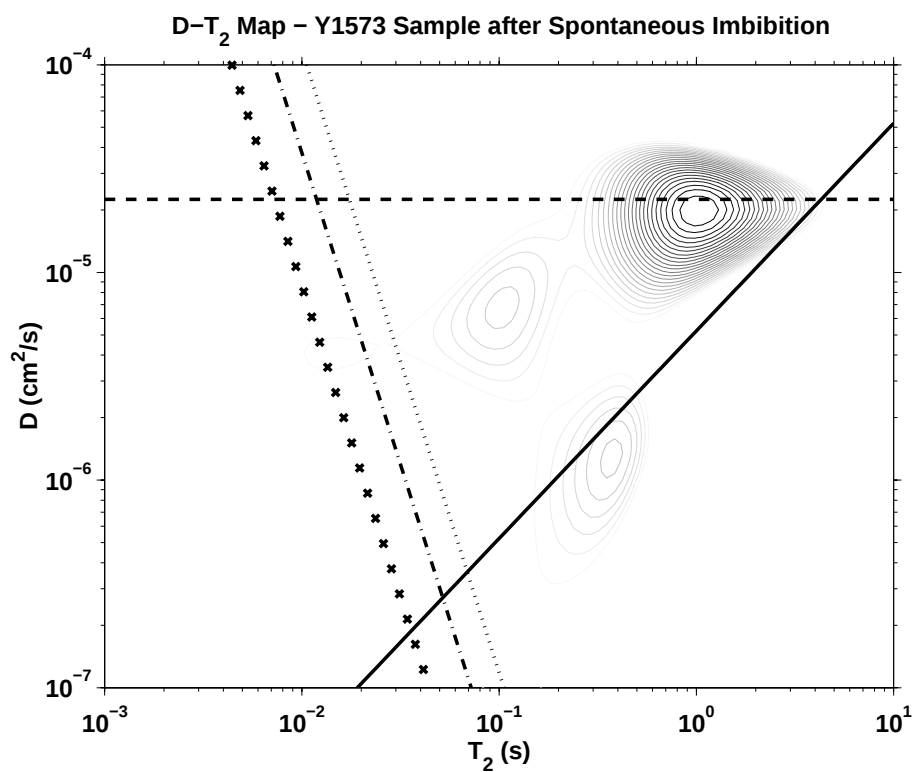


Figure 56: D - T_2 map of Y1573 sample, after forced imbibition. S_o is approximately 0.33.

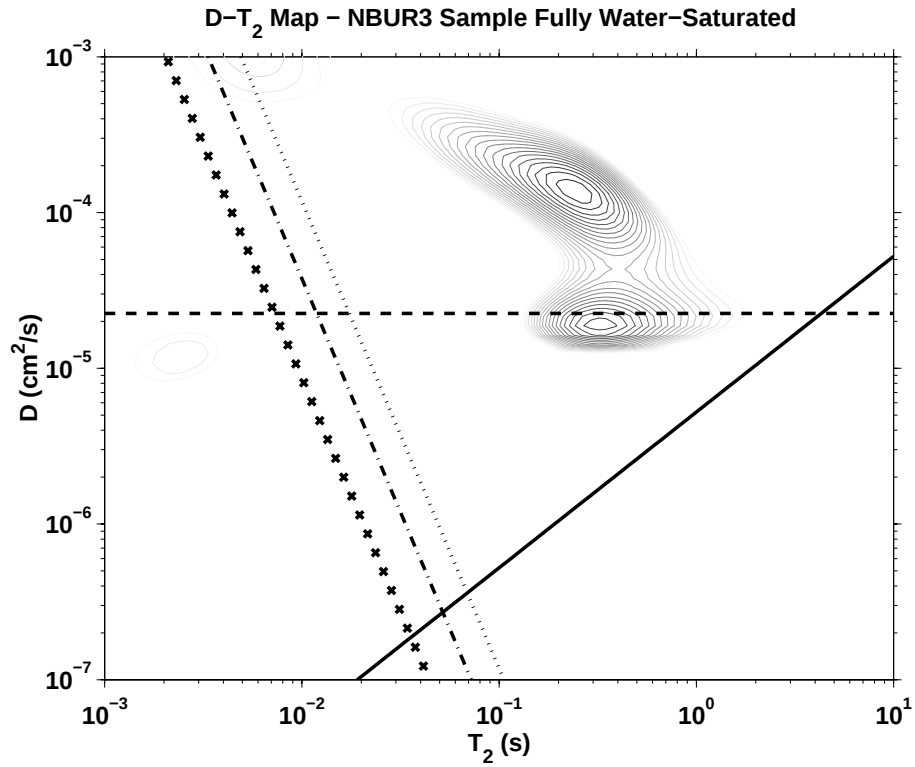


Figure 57: D - T_2 map of N BUR3 sample.

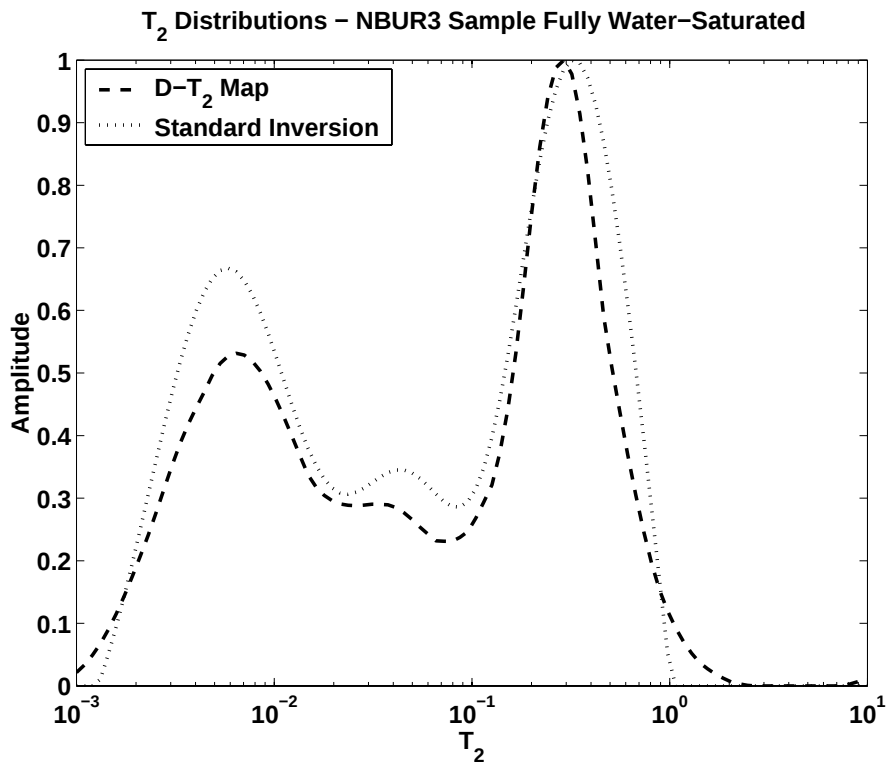


Figure 58: T_2 distributions of N BUR3 sample.

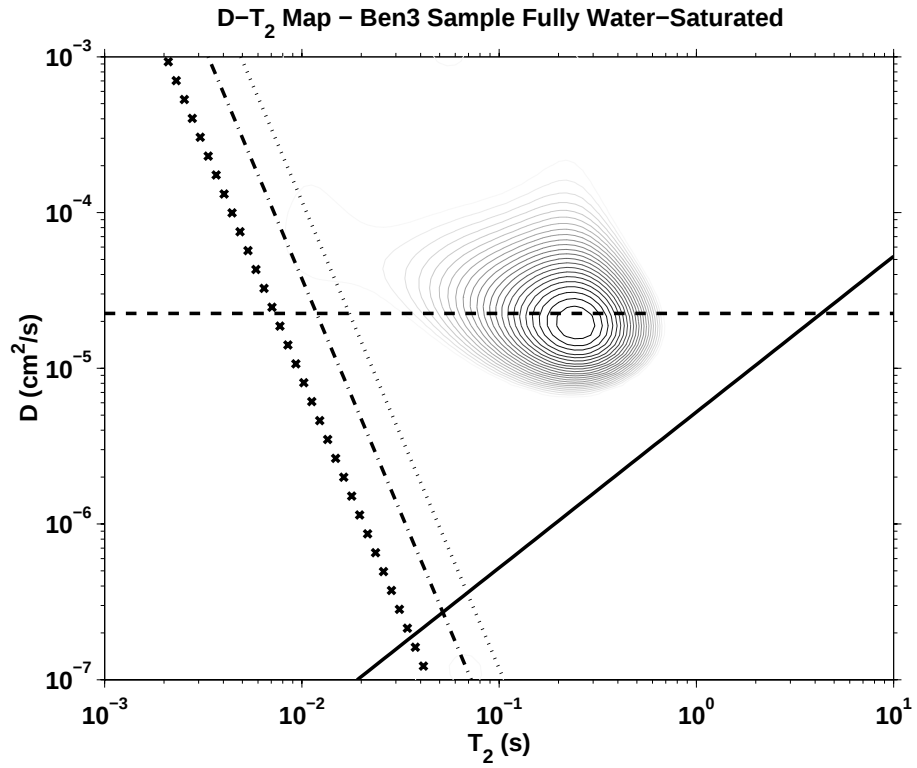


Figure 59: D - T_2 map of BER3 sample.

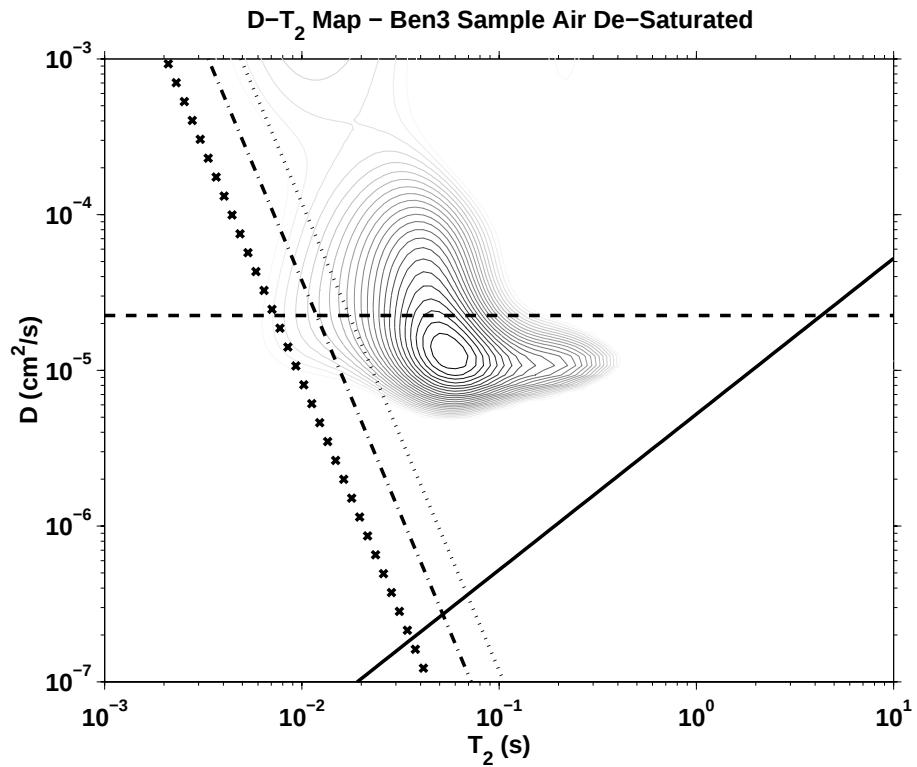


Figure 60: D - T_2 map of BER3 sample, after air de-saturation. S_w is approximately 0.43.