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Investigating the effect of internal gradients on static gradient nuclear magnetic resonance diffusion measurements

Emily L. Fay¹, Denys J. Grombacher², and Rosemary J. Knight¹

ABSTRACT

Nuclear magnetic resonance (NMR) methods can be used to measure the diffusion coefficient D of fluids. In porous materials, diffusion of the pore fluid is restricted by pore boundaries, such that D may be smaller than the diffusion coefficient of the bulk fluid. This reduction in D provides information about the geometry of the pore space. Significant overestimates of D can, however, occur due to internal gradients caused by magnetic susceptibility contrasts between the pore fluid and the solid phase. We have investigated the way in which internal gradients can impact the measured diffusion coefficient and obscure the link to pore geometry in unconsolidated sediments. We focus on measurements of D obtained with a static gradient diffusion-

editing sequence, which can be used with NMR logging tools to measure D in subsurface sediments. Laboratory measurements of D measured with a diffusion-editing D - T_2 sequence indicate significant impacts from internal gradients, including D values several orders of magnitude larger than D of bulk water. The log-mean D values were found to be highly correlated with estimated internal gradient magnitudes and indicate no clear relationship to pore size. Samples with heterogeneous magnetic susceptibility of the solid phase indicate D distributions with multiple peaks, reflecting the nonuniform distribution of internal gradients in the sediment. We found evidence of high internal gradients impacting a majority of our samples, resulting in increased D values that do not reflect pore size even in samples with low magnetic susceptibility.

INTRODUCTION

Nuclear magnetic resonance (NMR) is a powerful technique for investigating porous materials. For environmental geophysics applications, NMR logging tools can be used to measure the response of the pore water in the geologic materials adjacent to a borehole and obtain information about the geometry of the pore space. This information can be used to estimate hydraulic conductivity (Dlubac et al., 2013; Knight et al., 2016) by using relationships originally developed for applications in the oil industry (Seevers, 1966; Timur, 1969; Kenyon et al., 1988). NMR logging applications in aquifer systems have, to date, relied on the measurement of NMR relaxation times to obtain information about pore-space geometry. We are interested in the potential for NMR diffusion measurements to contribute unique insight into pore size and pore connectivity. NMR relaxation times (T_1 and T_2) and the NMR-measured diffusion coefficient, referred to here as the apparent diffusion coefficient and denoted as D , are determined by the properties of the pore fluid and

the properties of the porous material; each measurement has different sensitivity to specific features.

Although the link between T_2 and pore size has been extensively studied, there has been relatively little focus on the controls on D measured with NMR logging tools. The results from previous studies suggest that D is sensitive to pore size (Woessner, 1963; Tanner and Stejskal, 1968; Sørland et al., 2007), and therefore it has the potential to provide complementary information to relaxation time measurements through the acquisition of D - T_2 data. There is however a complicating factor in the measurement of D in geologic materials. The measurement can be significantly impacted by pore-scale inhomogeneities in the magnetic field, referred to as internal gradients, caused by contrasting magnetic susceptibility between the solid phase and the fluid-filled pore space (Hürlimann, 1998; Sen and Axelrod, 1999). These internal gradients can cause erroneously high D values to be derived from the NMR measurement if not explicitly accounted for (Hürlimann et al., 2003, 2004; Leu et al., 2005). Models have been proposed to compensate for the

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effect of internal gradients in D - T_2 measurements for fluid-typing applications (Li and Chen, 2010); however, they require assumptions about pore size and geometry. Although measurement sequences have been designed to mitigate the impact of internal gradients on D measurements (Cotts et al., 1989; Latour et al., 1993), it is not possible to use these sequences with current NMR logging tools. The focus of this paper is determining under what conditions internal gradients are likely to obscure the link between measurements of D and pore size.

Figure 1a shows an example of a D log, acquired during a field study in Nebraska (described in Knight et al., 2012). The logged interval covered a section of the High Plains Aquifer, composed of a mix of sand, gravel, sandstone, silt, and siltstone. As can be seen in the figure, many of the reported D values were above D_{WATER} , the diffusion coefficient of bulk water, which is a clear indication that D was impacted by something other than diffusion. Figure 1b shows the magnetic susceptibility measurements of cuttings taken from the well, plotted with the mean-log D from Figure 1a. By scaling the axes in Figure 1b, we can see the strong correspondence between magnetic susceptibility and D . This

suggests that in these materials, magnetic susceptibility has a significant impact on D , due to the link between magnetic susceptibility and internal gradients. Note that the axis scales in Figure 1b were chosen to highlight this correspondence. Figure 1 motivates the need for a study to better understand the controls on D .

Our primary goal was to investigate under what conditions D might provide useful information on pore size. In this study, we focus specifically on effects from internal gradients that could complicate the link between D and pore size. We conducted a laboratory experiment to assess to what degree static gradient measurements of D are impacted by internal gradients in sediments. Measurements of D - T_2 , internal gradient magnitude, and magnetic susceptibility were collected for sediment samples with a range of grain sizes and magnetic susceptibilities.

BACKGROUND

NMR theory

To conduct an NMR experiment on a porous, water-saturated material, a tuned radio-frequency pulse is applied to excite the spins of hydrogen protons in the water in the sampled volume. Prior to excitation, the spins will be preferentially aligned with the background magnetic field, precessing about the direction of the field at the Larmor frequency f , given by

$$f = \frac{|\gamma B_0|}{2\pi}, \quad (1)$$

where γ is the gyromagnetic ratio of hydrogen and B_0 is the background magnetic field.

The preferential alignment leads to the formation of a net magnetization. Excitation at the Larmor frequency rotates the magnetization from this equilibrium state. Following excitation, the magnetization precesses about an axis aligned with the background field, generating a measurable signal that decays as the magnetization returns to equilibrium. The magnitude of this signal is determined by the total number of hydrogen atoms in the sampled volume. The T_1 relaxation time corresponds to longitudinal relaxation, the time required for the component of the magnetization parallel to B_0 to regrow to its equilibrium magnitude. In a single pore, T_1 is controlled by interactions between spins of the hydrogen protons in the fluid (characterized by the bulk relaxation time T_{1B}) and by interactions between the spins and the pore walls (characterized by the surface relaxation time T_{1S}), as shown in the following equation (Brownstein and Tarr, 1979):

$$T_1^{-1} = T_{1B}^{-1} + T_{1S}^{-1}. \quad (2)$$

The T_2 relaxation time corresponds to the decay of the signal measured in the transverse plane. As with T_1 , T_2 is impacted by bulk relaxation and surface relaxation; however, T_2 is also impacted by dephasing of the precessing spins. Immediately after the initial excitation pulse, the magnetization throughout the pore is coherent, producing maximum signal. Due to inhomogeneities in the local magnetic field, local magnetizations at different regions of the pore space may precess at different frequencies causing coherence loss that contributes to an accelerated decay. Refocusing pulses are applied to regain coherence, generating spin echoes whose amplitudes are representative of the relaxation time with minimal impact from

Figure 1. (a) The D log measured at a groundwater well in Nebraska with an MR scanner logging tool (Schlumberger). The color shows relative signal amplitude. The dashed line indicates $D_0 = 1.8 \times 10^{-9} \text{ m}^2/\text{s}$ (water at 16°C). (b) Magnetic susceptibility χ values measured on drill cuttings shown alongside mean-log D (D_m) values from (a) and D_0 .

this dephasing effect (Carr and Purcell, 1954; Meiboom and Gill, 1958). Diffusion causes a displacement of the spins; if spins move to a region with a different local magnetic field between refocusing pulses, the Larmor frequency of the spins changes, as can be seen in equation 1, and the ability of the refocusing pulses to regain maximum coherence is reduced. A term for decay due to diffusion in an inhomogeneous field, T_{2D} , is therefore included in the expression for T_2 :

$$T_2^{-1} = T_{2B}^{-1} + T_{2S}^{-1} + T_{2D}^{-1}, \quad (3)$$

where T_{2D}^{-1} is determined by the time between refocusing pulses t_E , the diffusion coefficient of the fluid D_0 , and the magnetic field gradient G (Kenyon, 1997):

$$T_{2D}^{-1} = \frac{1}{12} D_0 (\gamma G t_E)^2. \quad (4)$$

The surface relaxation time is related to the surface-area-to-volume ratio (S/V) of the pore space according to

$$T_{1,2S}^{-1} = \rho_{1,2} \frac{S}{V} \quad (5)$$

for relaxation occurring in the fast-diffusion regime (Senturia and Robinson, 1970; Brownstein and Tarr, 1979). The ρ term denotes the surface relaxivity, the property of the pore surface which quantifies the ability of the surface to enhance relaxation (Senturia and Robinson, 1970). Surface relaxivity is related to the abundance (Foley et al., 1996) and mineralogic form (Keating and Knight, 2010) of paramagnetic sites (such as iron and manganese ions) on pore surfaces. The relationship between relaxation time and S/V is thus impacted by the composition of the solid phase and not solely determined by the geometry of the pore space. In a porous material containing multiple pores, the decay rate will depend on the shape, size, and surface relaxivity of the different pores. The measured signal M will be a multiexponential decay of the form

$$M(t) = \sum_i P_i e^{-t/T_{2i}}, \quad (6)$$

where P_i is the proportion of pore fluid relaxing with the relaxation time T_{2i} .

Surface relaxation is often assumed to be the dominant relaxation mechanism in porous materials; the contribution of bulk relaxation is assumed to be negligible, and the contribution from T_{2D} is assumed to be small for short t_E , although this assumption may be violated in the case of large internal gradients (Grombacher et al., 2016). For most cases in which these assumptions are valid, the observed decay rate will be proportional to S/V . The NMR relaxation time is commonly taken to be an indicator of pore size, where pore size can be defined as the radius of the sphere that would fit into the pore space (Ehrlich et al., 1991). This is the (approximate) dimension that is expected to impact the diffusion of molecules in the pore fluid. The basis for using relaxation time in this way is the assumed link between S/V and pore size (e.g., $S/V = 3/r$ for spherical pores, where r is the pore radius).

We can only directly measure magnetization in the transverse plane, which means that to measure T_1 , the longitudinal signal must be rotated into the transverse plane. As a result, multiple excitation-relaxation steps are needed to measure T_1 (Vold, 1968). The T_2

decay can be measured with a single excitation by directly sampling the decay of the signal (via the spin echoes) in the transverse plane. Because T_1 takes significantly longer to measure than T_2 , the measurement of T_2 is often preferred, even though T_2 can be impacted by incomplete refocusing when the magnetic field is not uniform.

Diffusion in porous materials

The diffusion of fluid molecules in a porous material is impacted by the bulk diffusion coefficient of the fluid and by the restricting effect of the pore geometry. The bulk diffusion coefficient of a fluid, also referred to as the self-diffusion coefficient D_0 , is a measure of the average squared displacement of fluid molecules over a unit of time due to Brownian motion. The diffusion coefficient D_0 increases with decreasing fluid viscosity and with increasing temperature (Douglass and McCall, 1958).

The function $D(t)$ is a measure of the average displacement of the fluid molecules during time t . When there are no boundaries to restrict movement, $D(t) = D_0$ regardless of the diffusion time t . In a porous material, values of $D(t) < D_0$ may be observed due to the restricting effect of pore walls on diffusion. The degree to which diffusion is restricted depends on the pore size and diffusion time (Sen, 2004). Models have been developed to relate $D(t)$ to S/V , pore size, and surface relaxivity (Mitra et al., 1992, 1993; Mitra and Sen, 1992), enabling the estimation of these parameters by measuring $D(t)$ for a range of diffusion times (e.g., Latour et al., 1993; Hürlimann et al., 1994; Vogt et al., 2002; Fleury, 2007; Duschl et al., 2015; Luo et al., 2015). The D - T_2 distributions have also been used directly to obtain information about S/V , the distribution of pore sizes, and ρ (Callaghan et al., 2003; Zielinski et al., 2010; Liu et al., 2014).

NMR measurements of diffusion

The sensitivity of the NMR measurement to D arises from the diffusion of spins in an inhomogeneous magnetic field (Hahn, 1950), as shown by the T_{2D} term in equation 3. The measurement of D involves measuring the amplitude of the spin-echo following a set diffusion time in the presence of an applied magnetic field gradient. Comparing the attenuation of the signal for different diffusion times or different gradient magnitudes enables the calculation of D . The attenuation of the signal due to T_{2D} is determined by the variation in the background magnetic field experienced by the ensemble of spins during the time between refocusing pulses, which is referred to as the diffusion time. The change in background field that a spin experiences is controlled by the distance the spin travels during this time and by the change in the magnetic field over this distance, i.e., the magnetic field gradient. By applying a known constant magnetic field gradient, the average displacement of the spins between refocusing pulses (described by D) can be estimated from the signal attenuation for either different diffusion times or different gradient magnitudes. To obtain reliable estimates of D , the gradient must be precisely known. As seen in equation 4, the T_{2D} term is sensitive to DG^2 , and so any errors in the estimate of G will bias the calculated D value. An additional limitation on the measurement of D is T_2 relaxation, which contributes to signal attenuation. In the case of very fast T_2 relaxation, the signal may decay too quickly to provide information about D .

Several NMR methods exist for measuring D (e.g., Stejskal and Tanner, 1965; Cotts et al., 1989); here, we focus on a static gradient

sequence that can be used with NMR logging tools, the diffusion-editing sequence, as described by Hürlimann et al. (2002). This sequence, illustrated in Figure 2, encodes diffusion by varying the diffusion time δ between the first two echoes, then records the T_2 relaxation of the remaining signal using a standard Carr-Purcell-Meiboom-Gill (CPMG) sequence (a train of closely spaced refocusing pulses). The resulting data set, $M(\delta, t)$, consists of the measured signal amplitudes at echo time t for each diffusion encoding time step δ . As δ is increased, decay due to diffusion will increase the signal attenuation, reducing the amplitude of the signal at time t_0 .

In porous materials, $M(\delta, t)$ will be a multiexponential decay due to the differences in pore sizes, surface relaxivities, and if multiple fluid phases are present. From $M(\delta, t)$, we can calculate a D - T_2 distribution that reflects the distribution of D and T_2 values in a sampled volume, $f(D, T_2)$. To calculate $f(D, T_2)$, $M(\delta, t)$ is expressed as a function of two separable kernels:

$$M(\delta, t) = M_0 \iint f(D, T_2) k_D(D, \delta) k_{T_2}(T_2, t) dD dT_2, \quad (7)$$

where M_0 is the initial magnetization, determined by the number of hydrogen spins in the sampled volume. The kernel $k_D(D, \delta)$ describes the model that is used to calculate D from $M(\delta, t)$. For the diffusion-editing sequence, it is given by (Leu et al., 2005)

$$k_D = \exp\left(-\frac{4}{3}\gamma^2 G^2 D \delta^3\right). \quad (8)$$

The accuracy of D estimates derived from this model is limited by how well G is known. Typically, G is assumed to be equal to the known tool gradient. However, when internal gradients are present, spins will experience an effective G that is the sum of the tool gradient and the internal gradients.

Diffusion-editing D - T_2 sequence

Figure 2. The diffusion editing sequence for measuring D - T_2 . The diffusion time δ is varied to encode D and additional echoes with constant spacing t_E are collected starting at t_0 to measure T_2 . The applied gradient G is constant throughout the sequence.

Table 1. Magnetic susceptibilities of some common minerals. Values are taken from Blum (1997) and Sharma (1997).

	Magnetic susceptibility (10^{-6} SI)
Water	-9
Quartz, feldspar	-13 to -17
Kaolinite	-50
Hematite	500-40,000
Magnetite	>1,000,000

Sequences that measure diffusion by varying the magnitude of the applied gradient are less sensitive to internal gradients because the contribution of the internal gradients to the total signal attenuation will be the same at each diffusion-encoding step (Leu et al., 2005). Sequences that use static gradients of fixed amplitude encode diffusion by varying the diffusion time, which causes the signal attenuation due to internal gradients to be coupled with the signal attenuation due to the applied gradient. This coupling results in higher sensitivity to internal gradients. NMR logging measurements of D rely on the static gradient caused by the decreasing strength of the magnetic field with increasing distance from the permanent magnets in the logging tool. In the diffusion-editing sequence described above, the magnitude of the internal gradients relative to the applied gradient determines how much D will differ from the expected (i.e., internal gradient-free) value.

Internal gradients

In geologic materials, magnetic susceptibility contrasts between the pore fluid and the solid matrix can lead to significant pore-scale background magnetic field inhomogeneity. Previous work has found that large internal gradients exist in many natural sediments due to the presence of ferromagnetic materials (Walbrecker et al., 2014) and paramagnetic materials (Sun and Dunn, 2002; Washburn et al., 2008; Fay et al. 2015), both of which have magnetic susceptibility values very different from that of water. A list of magnetic susceptibility values of some common minerals is given in Table 1. In addition to magnetic susceptibility contrasts, pore geometry also impacts the magnitude of the internal gradients; gradients increase as pore size decreases (Song, 2001). Internal gradients also vary with their proximity to the pore walls (Cho et al., 2009), with the highest localized gradients occurring near inflection points (such as sharp corners) on a pore surface (Brown and Fantazzini, 1993; Zhang et al., 2003; Grombacher et al., 2016). The background field strength controls the magnitude of internal gradients, such that measurements conducted at lower fields will be less impacted by internal gradients (Mitchell et al., 2010; see also Figure 11 in Fay et al. 2015). This is relevant because different logging tools operate at different frequencies (e.g., 2 MHz, Prammer et al. [2001] versus 2 kHz, Walsh et al., 2013).

The magnitude of the internal gradients in a sample can be estimated from CPMG measurements made with variable echo spacing (Zhang et al., 2003). The measurement relies on the dependence of the T_{2D} term on echo spacing (as seen in equation 4) to encode information about the gradients, which, in the absence of an applied gradient, will reflect internal gradient magnitudes. The slope of the estimated mean-log T_2 value versus echo time squared can provide an approximation of the average magnitude of the internal gradients impacting the measurements.

Due to the known increase in internal gradient magnitudes with decreasing pore size, there is the potential for internal gradients to cause the apparent diffusion coefficient measured with NMR to increase with decreasing pore size, opposite to the expected behavior due to restricted diffusion. This obviously adds complexity to interpreting the measurement of D . We want to use D to estimate pore size yet internal gradients, which impact D , are also related to pore size.

Figure 3 shows the results from a simulation that we conducted to compare the effect of pore size versus the effect of sediment magnetic susceptibility on D measurements. We simulated the

diffusion-editing experiment for a model pore with internal gradients. The distribution of internal gradients was calculated using COMSOL Multiphysics software for a 2D pore, in which we specified the magnetic susceptibility for the solid phase and the pore fluid ($\chi_{\text{WATER}} = -9\text{e} - 6$). Simulations were run over a range of pore sizes and χ values for the solid phase. Specifics about the algorithm used to simulate the diffusion-editing sequence are given by Grombacher and Nordin (2015). Parameters for the simulated pulse sequence were selected to match those used in our laboratory study. To isolate the effect of internal gradients from that of surface relaxation, we used a low ρ value in the simulations ($\rho = 1\text{e} - 6$). From the simulated experiments, the mean-log D value (D_{ml}) was calculated by applying the same inversion as we use with our laboratory D - T_2 measurements (Song et al., 2002; Venkataramanan et al., 2002).

From Figure 3, it is clear that our choice of χ for the solid phase has a significant impact on the relationship between D_{ml} and pore size. Low values of χ enable us to see the effect of restricted diffusion on D , with D_{ml} decreasing as pore size decreases. For higher χ values, we see D_{ml} increase as pore size decreases, reflecting the increasing internal gradient magnitudes, which are impacting the measurement of D . For the highest χ value, the signal decayed too rapidly to estimate D in the smaller pores.

The simulation result suggests that it may be possible to estimate pore size from D measurements in sediments with low magnetic susceptibility. However, the degree to which these results can be applied to 3D systems of interconnected pores, where χ is expected to be nonuniform, is highly uncertain. This motivates the need for a laboratory study to explore the relative importance of the effects from internal gradients and restricted diffusion in real sediments.

MATERIALS AND METHODS

We designed a laboratory experiment to assess the impact of internal gradients on static gradient measurements of D in unconsolidated sediments of varying grain size and varying magnetic susceptibility. The laboratory study comprised a total of 46 samples, including native sediments from six sites (ranging from coarse sand to clay) and samples prepared in the laboratory (including materials such as quartz sand, clay, hematite, and magnetite). The volume susceptibility of each dry sediment sample was measured using a susceptibility meter (Model MS3, Bartington Instruments). A suite of NMR measurements was collected for each sample with a 2 MHz Rock Core Analyzer (Magritek, Wellington, New Zealand). The NMR samples were prepared in 40 mL Teflon holders and saturated with tap water ($T_2 = 2.6$ s, $D_0 = 2.2\text{e} - 9$ m²/s at 23°C). Samples were held at approximately 23°C during the NMR measurements.

The T_1 data were collected with the inversion recovery method (Vold et al., 1968), using 30 inversion recovery delays ranging from 150 μ s to 10 s. The T_2 data were collected with a standard CPMG sequence (Carr and Purcell, 1954; Meiboom and Gill, 1958) and 200 μ s echo spacing. The D - T_2 data were collected using a diffusion-editing CPMG sequence (Hürlimann et al., 2002) and a static gradient of 15 G/cm (0.15 T/m). Eight diffusion encoding steps were measured, with δ ranging from 200 μ s to 10 ms. Data were averaged for 20 repeated measurements, yielding a noise level of approximately 0.5% (with reference to maximum signal for a water sample). The signal-to-noise ratio (S/N) of the D - T_2 measurements ranged from 12 to 40, where samples with shorter relaxation times tended to have lower S/N.

Inversion of the data was performed using a nonnegative least-squares algorithm with Tikhonov regularization. The regularization parameters were selected to balance goodness of fit and solution smoothness. The T_1 and T_2 data were inverted according to the method described by Whittall et al. (1991). Data were fit to 100 logarithmically spaced values between 0.001 and 5 s. The inversion of the D - T_2 data used a 2D fast Laplace inversion algorithm (Song et al., 2002; Venkataramanan et al., 2002; Godefroy and Callaghan, 2003). Data were fit to 100 logarithmically spaced values, ranging from 10^{-11} to 10^{-6} m²/s for D and 0.005 to 5 s for T_2 . Mean-log T_1 and T_2 values were calculated from the 1D distributions, whereas mean-log values of D were calculated from the D - T_2 distributions.

Internal gradient magnitudes were estimated using repeated CPMG measurements with variable echo spacing, using 14 t_E steps from 200 μ s to 1 ms. The average internal gradient magnitude G_{int} was calculated from the slope of $1/T_{2\text{ML}}$ versus t_{E2} following the method described in Fay et al. (2015).

RESULTS

The samples used in this study were selected to cover a range of unconsolidated sediments, including well-sorted and poorly sorted sediments with grain sizes ranging from clay to coarse sand, and χ ranging from $-1.1\text{e} - 5$ to $2.4\text{e} - 2$ (diamagnetic materials exhibit negative magnetic susceptibility, see Table 1). It was not possible to measure D - T_2 in 12 of the samples because the signal decayed too rapidly; all of these samples had $T_2 < 10$ ms.

We observed a strong correlation between our estimates of G_{int} and the distribution of D values. Figure 4a shows the D distributions measured in the 34 samples with $T_2 > 10$ ms, ordered by G_{int} . The expected value for D_{WATER} is shown for comparison. The samples with low G_{int} exhibit fairly consistent D distributions, with peak values slightly above D_{WATER} . In Figure 4b, we see that values of G_{int} less than approximately 20 G/cm correspond to the D distributions with minimal effects from internal gradients. As G_{int} increases greater than 20 G/cm, we see increasing D values in the distributions in Figure 4a. For G_{int} greater than approximately 75 G/cm, we see D values extending up to the upper limit allowed

Figure 3. Simulated relationship between mean-log D and pore size for different magnetic susceptibilities. The D_{ml} values were calculated from simulated diffusion-editing experiments for 2D model pores with a range of different χ values for the solid phase. Data points are missing for $\chi = 1\text{e} - 2$ where the signal levels were too low to estimate D . The value for D_{WATER} is indicated for reference.

by our inversion, multiple orders of magnitude larger than D_{WATER} . Figure 4c shows the corresponding T_2 distributions for each sample. There does not appear to be a strong relationship between the T_2 distributions and either G_{int} or D .

Controls on D_{ml}

To further investigate the relationship between D and internal gradients, we take the simplified approach of using D_{ml} to represent the D distribution. We first consider the relationship between D_{ml} and $T_{1\text{ml}}$, plotted in Figure 5a. We use $T_{1\text{ml}}$ as a qualitative indicator of pore size. In the absence of internal gradients, we would expect to see evidence of decreasing D_{ml} with decreasing pore size due to restricted diffusion. The color scale indicates $\Delta\chi$, the contrast in

magnetic susceptibility between the sediment and the pore fluid ($\chi_{\text{WATER}} = -9 \times 10^{-6}$). We use $\Delta\chi$ instead of χ (which includes negative values), so that we can plot magnetic susceptibility on a logarithmic scale. In Figure 5a, we see no clear relationship between D_{ml} and $T_{1\text{ml}}$. Instead, we see that samples with low $\Delta\chi$ exhibit low D_{ml} values, whereas higher $\Delta\chi$ values correspond to increased D_{ml} values. The only relationship between D_{ml} and pore size that we observe is a possible increase in D_{ml} due to decreasing pore size, which is known to increase internal gradient magnitudes. This suggests that the impact of internal gradients on D_{ml} overwhelms any effects we might expect to observe from restricted diffusion in small pores. This is supported in Figure 5b, where D_{ml} is plotted versus G_{int} with the color scale again indicating $\Delta\chi$. For values of G_{int} greater than 10–20 G/cm, we see a steep increase in measured D_{ml} with increasing G_{int} . We also observe the expected relationship between $\Delta\chi$ and G_{int} , with increasing susceptibility contrast leading to higher internal gradient magnitudes.

From these plots, we conclude that the D_{ml} value that we measure in sediments is largely controlled by internal gradients. We see no evidence of decreasing D_{ml} due to restricted diffusion, even though several of our samples have very low χ values in which we expect restricted diffusion might be observed. We believe this could be due to heterogeneous χ , such that D_{ml} is biased by regions of the pore space where χ is high. We can look at the D - T_2 distributions to further investigate the effects of heterogeneous χ on D .

The impact of internal gradients on D - T_2

Although we estimate internal gradient magnitudes with a single value (G_{int}), each sediment will in reality have a distribution of internal gradient magnitudes that impact the distribution of D values that we measure. This is for several reasons. The magnitude of internal gradients depends on the susceptibility contrast between the solid phase and the pore fluid, and so variability in χ of the solid phase will result in different gradient magnitudes. Pore size, pore geometry, and proximity to pore walls also impact internal gradient magnitudes (Cho et al., 2009; Grombacher et al., 2016), such that even sediments with uniform χ will exhibit a distribution of internal gradient magnitudes.

In Figure 6, D - T_2 distributions are shown for six of the sediment samples. We chose these samples from the 46 samples included in the laboratory study as examples of natural sediments (left column) and artificial samples (right column) with a range of χ and G_{int} values (increasing from the top row to the bottom row). The χ and G_{int} values for each sample are listed on the plots in Figure 6.

The artificial samples were prepared to control for the distribution of χ . They include a sample in

Figure 4. (a) The D distributions measured for 34 unconsolidated sediment samples, ordered by increasing G_{int} . (b) Internal gradient magnitudes estimated with variable echo-spacing CPMG measurements. (c) The T_2 distributions for 34 unconsolidated sediment samples, ordered by increasing G_{int} .

Figure 5. The D_{ml} is plotted versus (a) $T_{1\text{ml}}$ and (b) G_{int} , with color indicating $\Delta\chi$.

which all of the grains were coated with hematite as well as two samples containing distributed magnetite grains. To characterize the distribution of χ in the three natural sediment samples, we sieved each sample with a 0.05 mm sieve to separate the sand fraction from the silt and clay fraction and measured the magnetic susceptibility of each fraction. We also used a magnet to detect grains with very high χ (i.e., magnetic grains).

The two samples whose D - T_2 distributions are plotted in the top row of Figure 6 have relatively low magnetic susceptibility and moderate G_{int} . The D - T_2 distributions show no obvious evidence of internal gradients. Sample A (Figure 6a) is a poorly sorted clayey sand; magnetic separation revealed negligible magnetic mineral content. The T_2 distribution exhibits a single broad peak, with maximum amplitude at approximately 50 ms. The D distribution is centered around D_{WATER} , with no evidence of significant effects from internal gradients. Sample B (Figure 6b) is 250–350 μm quartz sand coated with hematite (Dlubac, 2013). The T_2 distribution peaks at approximately 200 ms but extends down to 10 ms. The D distribution is centered slightly above D_{WATER} and is nearly uniform across all T_2 values. The hematite coating appears to be enhancing T_2 relaxation while not noticeably impacting D .

In the middle row of Figure 6, the D - T_2 distributions clearly show effects from internal gradients. Sample C (Figure 6c) is a medium to fine sand with moderate magnetic susceptibility (9.6×10^{-4}) and a small fraction of fines. Magnetic separation indicated a small fraction of fine sand sized magnetic grains. This sample exhibits a broad T_2 distribution, ranging from approximately 1 s to 5 ms; this is consistent with a range of pore sizes. It is possible that the higher magnetic susceptibility of the sample is impacting the observed relaxation — this could be due to higher ρ and/or due to contributions from T_{2D} . The signal with longer T_2 exhibits D values just above D_{WATER} . For the signal with shorter T_2 , we observe very high D values, indicative of high internal gradients, and $D < D_{\text{WATER}}$, evidence of restricted diffusion. Sample D (Figure 6d) is 350–500 μm quartz sand with a small fraction of coarse magnetite grains distributed throughout the sample. In the D - T_2 plot, we see two distinct peaks at approximately the same T_2 values; one exhibits D slightly above D_{WATER} , whereas the other exhibits D values an order of magnitude higher. For samples C and D, we expect that the presence of multiple D values over a single range of T_2 values is caused by heterogeneous χ : pores adjacent to high χ grains contribute signal with high D values, whereas pores with only low χ grains contribute lower D values.

The bottom row in Figure 6 shows the D - T_2 distributions for two samples with very high G_{int} values. In both plots, we observe D values extending up to the maximum D value included in the inversion, nearly three orders of magnitude higher than D_{WATER} . Sample E (Figure 6e) is a sandy silt with moderate susceptibility; we found that the fine-grained fraction had a somewhat higher χ value than the sand fraction. Magnetic separation revealed many silt-sized high χ grains. This sample exhibits short T_2 relaxation, as expected for silt, with $T_2 < 20$ ms. We suspect that the high internal gradients measured in this sample are the combined effect of high χ of the fine-grained fraction and the small pore size. The D distribution is clearly impacted by high internal gradients, extending from just above D_{WATER} to the upper bound of the plot. Sample F (Figure 6f) is 125–250 μm quartz sand with coarse magnetite grains added. Compared with sample D, it exhibits shorter T_2 relaxation, as expected based on the smaller grain size. Although

samples D and F have similar χ , G_{int} was found to be higher in sample F, likely due to smaller pores. This difference is reflected in the D distributions: The two distinct D peaks in Figure 6f are at higher D values than the peaks in Figure 6d.

As shown in Table 1, common minerals such as quartz, feldspar, and kaolinite all have very low χ . Small amounts of minerals with very high χ , namely, hematite and magnetite, are likely to be the main cause of increased bulk χ values. Chlorite is another mineral that is known to contribute to increased bulk χ and high internal gradients (Hürlimann et al., 2004). High internal gradients will be present in pores that are adjacent to high χ grains, whereas other pores may have negligible internal gradients. Due to the heterogeneous distribution of χ within a sample, the bulk χ value will not necessarily tell us whether our measurement of D will be impacted by internal gradients. It is perhaps more useful to think of the bulk χ value as a measure of the fraction of high χ grains in a sample, and therefore an indicator of the fraction of the pore space likely to exhibit high D . This distinction between uniformly distributed χ and heterogeneous χ will affect our assumption that the impact of internal gradients on D will scale with the background field strength. Although it is true that internal gradient magnitudes will

Figure 6. (a) The D - T_2 distributions for a clayey sand, (b) hematite-coated medium quartz sand, (c) fine to medium sand, (d) medium quartz sand with magnetite grains, (e) sandy silt, and (f) fine quartz sand with magnetite grains. The dashed line indicates D_{WATER} at 23°C.

decrease at lower fields, and would thus be lower for logging tools operating at lower frequencies, gradients that are due to very high χ grains (such as magnetite) will still be very large at 200 kHz. We expect that in sediments containing even a small fraction of grains with high χ , the D - T_2 distributions will be noticeably impacted by internal gradients even at 200 kHz. The lower fields used by logging tools are therefore unlikely to improve our ability to estimate pore size from D in many real sediments, even when the bulk χ value is relatively low.

The results of this laboratory study show that internal gradients significantly impact static gradient measurements of D in a wide range of unconsolidated sediments. Estimates of D_{ml} were found to be highly correlated with estimates of G_{int} and largely unrelated to pore size. The D - T_2 distributions showed complex distributions of D , which we attribute to heterogeneous χ . Some D - T_2 distributions did exhibit D values below D_{WATER} , evidence of restricted diffusion in some regions of the pore space. Although values of $D < D_{\text{WATER}}$ are indicative of smaller pores, the estimation of pore size from the D distributions is expected to be highly unreliable due to effects from internal gradients.

CONCLUSION

Measurements of the apparent diffusion coefficient D of pore fluids are sensitive to pore size due to the restricting effect of pore walls on diffusion. In geologic materials, complications in the estimation of pore size from D arise due to internal gradients caused by susceptibility contrasts between the solid phase and the fluid phase. Although the effects from internal gradients can be minimized when D is measured by varying the magnitude of the applied gradient, measurements of D obtained with static gradient sequences, such as those used in NMR logging, are more likely to be impacted by internal gradients. The purpose of this study was to assess the potential to use measurements of D obtained with NMR logging tools to estimate pore size in subsurface sediments.

Our study focused on D measured with a static gradient diffusion-editing sequence. Laboratory measurements of D in sediments, conducted at 2 MHz using a static gradient diffusion-encoding sequence, showed increasingly high distributions of D values for samples with average internal gradient magnitudes greater than approximately 20 G/cm. Mean-log D values were primarily controlled by the magnitude of the internal gradients and could not be used to indicate pore size. Internal gradient magnitudes increase with increasing χ and with decreasing pore size, further complicating the relationship between D and pore size. We were unable to measure D for samples with T_2 shorter than 10 ms due to the rapid decay of the signal.

Although internal gradients are known to increase with increasing magnetic susceptibility of the solid phase, we found that the average χ of a sample was not a reliable indicator of the impact of internal gradients on the D distribution. A small number of high χ grains can cause high internal gradients in a portion of the pore space, which in turn cause high D values in the D - T_2 distribution. The assumption that the impact of internal gradients will be negligible below a certain χ value therefore should not be applied to sediments with heterogeneously distributed χ , which is very likely the case for most sediments. We expect high internal gradients to be present in sediments containing even a small fraction of high χ grains, such that even D - T_2 measurements conducted at lower fields

are likely to exhibit some high D values due to internal gradients, complicating the interpretation of pore size from D .

Although previous studies have shown a link between laboratory measurements of D and pore size, we conclude that NMR logging measurements of D will be limited in their ability to indicate pore size due to the significant impact from internal gradients in natural sediments on static gradient measurements of D .

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