

Applying Solid-state NMR Methods to the Study of Organic Shale Rocks

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This dissertation is submitted for the degree of Doctor of Philosophy

Declaration

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Over the past twenty years, organic-rich shales have emerged as valuable systems for potential oil and gas production. Shale reservoirs are usually low in porosity, ultralow in permeability, and contain hydrogen-rich organic materials, making traditional low-field ^1H NMR relaxation methods difficult to apply. The mobilities of the different hydrocarbon components can differ dramatically, from producible methane to the solid kerogen (the biopolymer precursor to petroleum). These considerations imply a “paradigm shift” in petrophysical NMR, currently based on the knowledge that (i) NMR is lithology independent (responds only to the fluids, not the matrix) and (ii) the total signal amplitude is proportional to total “porosity”. Both statements are not valid for organic shales. An additional challenge is the presence of solid and highly viscous organic materials, such as kerogen and bitumen, which are usually not detectable with the standard Carr-Purcell-Meiboom-Gill (CPMG) method on low-field equipment, with the rapid T_2 signal decay of these components limiting access to decay information. The work presented within this thesis focusses on the development of NMR methods for improving the characterization of the various organic components in heterogeneous organic shales with potentially producible hydrocarbons. A combination of high-resolution solid-state ^1H and ^{13}C NMR spectroscopy methods and ^1H NMR relaxation measurements provided insights into the chemical and structural evolution of kerogen during thermal maturation. Part of the project is aimed at the optimization of pulse sequences which are appropriate for the investigation of shales under static (non-spinning) conditions and low magnetic fields. Various multiple-pulse sequences were explored and combined to develop new methods for identifying and quantifying both the immobile and mobile components in shales. A further study was focused on the application of double-quantum (DQ) ^1H NMR to shales for robust separation between solid and liquid signals, and results show that this technique offers a potential method for obtaining improved description of hydrogen-bearing components with limited mobility in shale rocks.

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List of publications

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Table of contents

Chapter 1:	Introduction	1
1.1	Organic shales.....	1
1.1.1	The “shale revolution”	2
1.1.2	Source rock properties	5
1.1.3	Shale porosity	5
1.1.4	Organic matter in shales.....	6
1.1.4.1	Kerogen.....	6
1.1.4.2	Bitumen	8
1.2	Basic principles of Solid-state NMR	9
1.2.1	The shielding interaction	10
1.2.2	The dipolar coupling interaction	12
1.2.3	Nuclear spin relaxation.....	14
1.2.3.1	Spin-lattice relaxation.....	14
1.2.3.2	Spin-spin relaxation	15
1.2.4	T_2 in solids.....	17
1.2.5	NMR relaxation theory	18
1.2.6	BPP theory	19
1.2.7	High-resolution techniques	20
1.2.7.1	Magic Angle Spinning	20
1.2.7.2	Cross polarization	21
1.3	NMR relaxation in shales.....	22
1.3.1	Porous media.....	22
1.3.2	Conventional reservoirs.....	22
1.3.3	Unconventionals.....	23
1.3.4	Relaxation via homonuclear dipolar coupling	26
1.3.4.1	Simple fluids	26
1.3.4.2	Heavy oils.....	27
1.3.4.3	Fluids under nanoconfinement	30
1.3.4.4	Kerogen.....	32
1.3.5	Surface relaxation in organic matter	33
1.4	Low-field ^1H NMR	39
1.4.1	Benchtop spectrometers	40
1.4.2	Well-logging tools	42
1.4.3	Limitations of low-field NMR for shale analysis	43
1.4.4	Data processing: numerical inversion	44

1.4.4.1	Kernel.....	46
1.4.4.2	Limitations of numerical inversion	46
1.4.5	Application of ^1H NMR relaxometry to shales.....	47
1.4.6	T_1 - T_2 correlation experiments.....	48
1.4.7	High-field NMR	51
1.5	Spin-echo refocusing pulse sequences.....	52
1.5.1	CPMG	52
1.5.2	Solid echo	53
1.5.3	Magic echo.....	53
1.5.4	Two-dimensional T_1 - T_2 correlation pulse sequence	55
1.6	Double-Quantum (DQ) ^1H NMR.....	55
1.6.1	The DQ experiment	56
1.6.2	The DQ build-up curve.....	57
1.7	Motivation and outline of the thesis.....	59
Chapter 2: Combined high-resolution solid-state $^1\text{H}/^{13}\text{C}$ NMR spectroscopy and ^1H NMR relaxometry for the characterization of kerogen thermal maturation		61
2.1	Abstract	61
2.2	Introduction.....	62
2.3	Experimental.....	65
2.3.1	Preparation of the kerogen isolates	65
2.3.2	Thermal maturity measures	65
2.3.3	^{13}C and ^1H MAS NMR	66
2.3.4	Static ^1H NMR relaxation	67
2.4	Results and discussion	67
2.4.1	^{13}C MAS NMR experiments.....	67
2.4.2	^1H MAS NMR experiments.....	71
2.4.3	Static ^1H NMR experiments	74
2.5	Conclusions.....	78
Chapter 3: Improved Description of Organic Matter in Shales by Enhanced Solid Fraction Detection with Low-Field ^1H NMR Relaxometry		80
3.1	Abstract	80
3.2	Introduction.....	81
3.3	Theory.....	82
3.4	Experimental.....	85

3.4.1	Sample preparation	85
3.4.2	Spin-echo refocusing pulse sequences	86
3.4.3	NMR experiments	87
3.4.4	Numerical inversion	88
3.5	Analysis protocol	88
3.5.1	Peak assignment in 2D T_1 - T_2 correlation maps	88
3.5.2	T_2 data segmentation	89
3.5.3	Analysis of T_2 signal amplitudes	91
3.6	Results and discussion	92
3.6.1	Relative effectiveness of the three pulse sequences with organic isolates	92
3.6.2	Oil- or brine-saturated shale powders	96
3.6.2.1	2D T_1 - T_2 correlation maps	96
3.6.2.2	1D T_2 distributions	99
3.6.2.3	T_2 signal amplitudes	102
3.6.2.4	Comparison between 1D T_2 analysis and 2D T_1 - T_2 maps	106
3.6.2.5	Summary oil- or brine-saturated shale powders	108
3.6.3	Thermally dehydrated, previously oil- or brine-saturated shale powders	110
3.7	Conclusions	113
Chapter 4:	Double-quantum ^1H NMR Methods and Applications for Shale Systems	115
4.1	Abstract	115
4.2	Introduction	115
4.3	The Double-quantum NMR Method	117
4.3.1	Double-quantum ^1H NMR pulse sequence	117
4.3.2	Double-quantum build-up curve analysis	119
4.4	Experimental	120
4.4.1	Materials and sample preparation	120
4.4.1.1	Thermally matured spent shales	120
4.4.1.2	Oil- or brine-saturated shales	121
4.4.2	NMR experiments	121
4.4.3	Numerical inversion	122
4.5	Results and discussion	122
4.5.1	Validation of the method	122
4.5.1.1	Homogeneous reference samples	123
4.5.1.2	Heterogeneous mixed samples	124
4.5.2	Thermally matured Green River shales	129

4.5.2.1	T_2 relaxation.....	129
4.5.2.2	Double-quantum build-ups	130
4.5.2.3	Summary: thermally matured shales	133
4.5.3	Oil- or brine-saturated shale powders	133
4.5.3.1	Organic isolates	133
4.5.3.2	Resaturated shales - T_2 relaxation	138
4.5.3.3	Resaturated shales - Double-quantum build-ups.....	139
4.5.3.4	Summary oil- or brine-saturated shales	142
4.5.3.5	Thermally dehydrated, previously oil- or brine-saturated shales	143
4.6	Conclusions.....	144
Chapter 5:	Conclusions and future work.....	146
Appendix 1:	Application of ^{129}Xe NMR to shale systems.....	150
A1.1	Introduction.....	150
A1.2	Experimental.....	150
A1.3	Preliminary results.....	151
References		155

Chapter 1: Introduction

1.1 Organic shales

Shales represent the most abundant of sedimentary rocks on the planet. According to the geological definition, shales are mud rocks mainly characterized by fine-grained laminated structures, consisting of silt- and clay-sized particles of biogenic-origin.^{1,2} In petrophysics, the term shale is applied more broadly to describe any system that requires hydraulic fracturing for the economic production of hydrocarbons.

Until recently, petroleum production exclusively involved conventional reservoirs, which are primarily composed of sandstones and carbonates, characterized by high porosity and permeability. The highly interconnected pore spaces of such rock formations allow oil and gas to flow out easily and to be extracted by the use of conventional wells.³ Unconventional shale reservoirs are extremely different from traditional petroleum systems in both composition and structure (Table 1.1). Unlike conventional reservoirs, shales are characterized by ultralow permeability and low porosity, and contain significant quantities of clays and organic matter, such as kerogen and bitumen.^{1,4,5} Kerogen is defined as the fraction of raw organic matter dispersed in sediments which is insoluble in usual organic solvents, such as dichloromethane and methanol. Bitumen refers to the organic matter fraction soluble in organic solvents. Under the influence of temperature and pressure, these organic materials are converted to oil and gas during the degradation process of catagenesis.^{3,5,6} Some of the produced oil and gas will migrate upward and be captured by conventional petroleum reservoirs, which act as a trap. However, considerable amounts of these resources are retained in the shale, due to the extremely low permeability.⁷ For this reason, shales are often self-sourced rocks, meaning the petroleum is formed and stored in place.³ Hydrocarbon species like oil and gas can be present in the organic pores of the shale (voids within kerogen), which are typically in the nanometer range, or within pores in the inorganic mineral matrix. Water is also present in shales, in either a bound phase adsorbed on clay structures, or in a mobile phase into mineral pores.

Conventional reservoirs	Unconventional reservoirs
Hydrocarbons migrate to the reservoir rock	Hydrocarbons are formed in place
Porosity: 10 % to 40 %	Porosity: 0.1 % to 20 %
Permeability: 10^{-13} to 10^{-11} m ² (unfractured)	Permeability: 10^{-23} to 10^{-19} m ² (unfractured)
Gas mainly exists as free gas	Gas in both adsorbed and free phase
Extraction: naturally flows to the surface	Extraction: special technologies are required

Table 1.1. Key differences between conventional and unconventional reservoirs.

1.1.1 The “shale revolution”

The shortage of conventional reservoirs, combined with a growing global demand for energy, has led to increased interest in unconventional resources. Over the past twenty years, organic-rich shales have emerged as valuable systems for potential oil and gas production.^{4,5,8,9} Such reservoirs were not considered to be significant oil and gas resources until new advanced technologies, the horizontal drilling and hydraulic fracturing, made the economic recovery from shales feasible.^{7,10,11} Horizontal drilling involves sinking a well a mile or more straight down vertically, and then out horizontally for another mile or more, providing greater access to the resource-bearing rocks (Figure 1.1). Hydraulic fracturing is a technique in which a mixture of water, sand and chemical additives (e.g., acids, sodium chloride, polyacrylamide) are injected into the well at high pressure to open small cracks in the rock and release the trapped hydrocarbons, which can flow out from the rocks into the well.¹² This technological breakthrough played a key role in the economics of the United States, where massive shale oil/gas resources that were previously inaccessible have been unlocked.^{13,14,15}

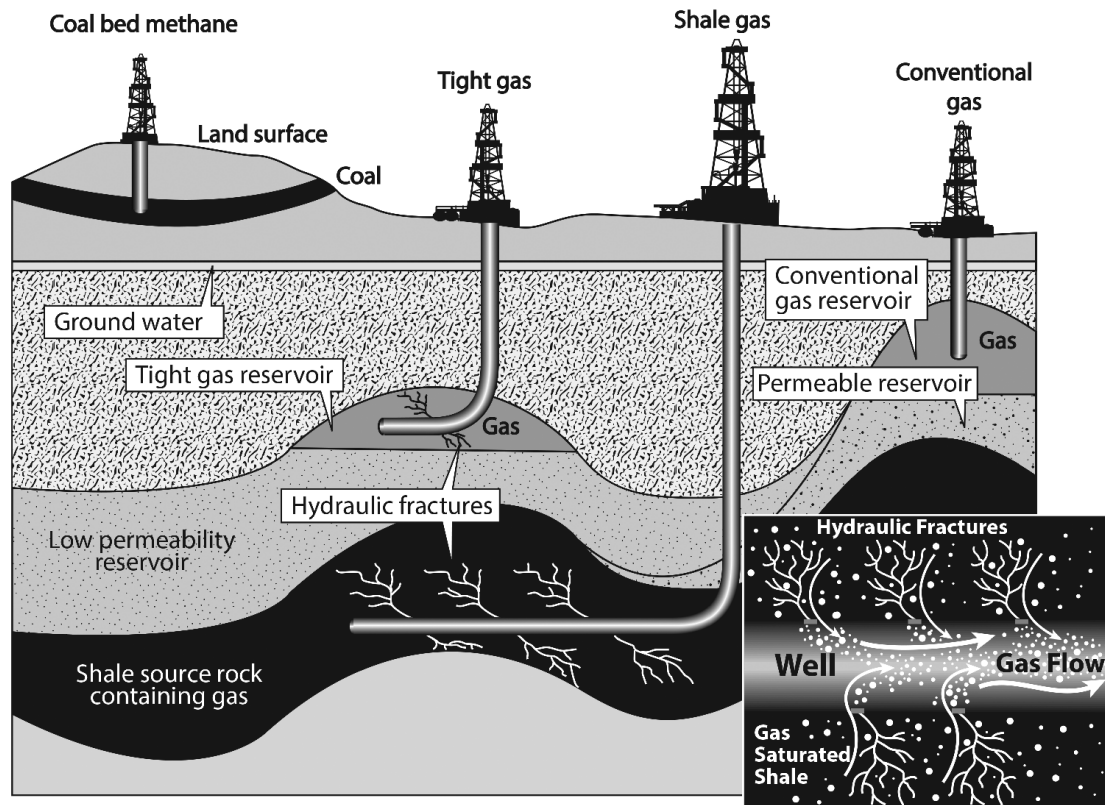


Figure 1.1. Comparison between geology, formation types and extraction methods for conventional and unconventional natural gas. Unconventional resources include tight gas, shale gas and coal bed methane. Tight gas refers to natural gas trapped in low porosity and low permeability clastic or carbonate reservoirs, shale gas is natural gas contained in the shale rocks, and coal bed methane refers to natural gas adsorbed into the solid matrix of the coal. Conventional gas resources are easily extracted with vertical wells. The recovery of hydrocarbons in low permeability tight gas and shale reservoirs requires horizontal drilling and hydraulic fracturing. The figure is adapted from reference [16].

Nowadays, shale gas and oil are resources of particular significance in the USA as a route to energy independence. These unconventional resources include tight gas, shale gas, coal bed methane and tight oil. Tight gas refers to natural gas trapped in low porosity and low permeability clastic or carbonate reservoirs, shale gas is natural gas contained in the shale rocks, and coal bed methane refers to natural gas adsorbed into the solid matrix of the coal. Tight oil (also known as shale oil) is light oil which is trapped in formations characterized by extremely low porosity and permeability. Before the advent of innovative technologies for extraction of shale resources, the US oil production fell ruinously from 9.6 million barrels per day (mb/d) in 1970, to only 5 mb/d in 2008. The “shale revolution” in the early 2000’s has led the oil industry to a substantial increase of production, reversing this declining trend (Figure 1.2a). Over the following years, recovery from shale oil reservoirs has led to the highest total annual average production of 12 mb/d in 2018, surpassing the level set in 1970 (9.6 mb/d). As illustrated in Figure 1.2a, the US Energy Information Administration (EIA) estimates that this trend is expected to continue to reach 14 mb/d by 2035, despite the

production decline of 2020 due to the COVID-19 pandemic. The great success in producing gas from shale reservoirs made the US become self-sufficient in gas resources for the next decades. In fact, shale gas production had a huge increment in the last ten years, leading the US to set annual natural gas production records of 34 trillion cubic feet (Tcf) in 2019. In 2020, dry shale gas production was about 26 Tcf, equal to approximately 78 % of total U.S. dry natural gas production that year. The EIA forecasts that annual natural gas production will average 40 Tcf in the early 2040 (Figure 1.2b).

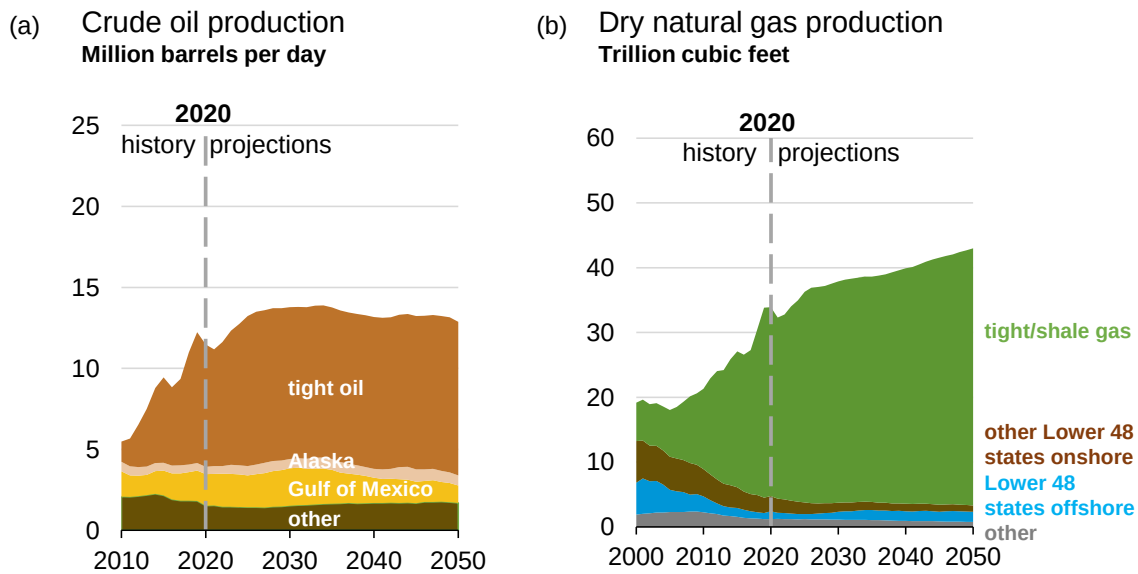


Figure 1.2. (a) US oil production in million barrels per day and (b) US natural gas production in trillion cubic feet (history and projections). Sources: EIA energy outlook 2021.

On the one hand, the shale boom is bringing the US closer to energy independence. On the other hand, the increased production of shale gas and oil has generated concerns over potential human health and environmental impacts. The main risks associated with the exploration and exploitation techniques are perceived as water resources contamination, air pollution (methane release), and the prospects for inducing seismic events.¹² Water contamination is principally induced by the mixture of water and chemicals injected underground during the process of drilling and hydraulic fracturing, which also contribute to release pollutants into the atmosphere.^{12,17} Migration of fugitive methane through induced and natural fractures could lead to an increase of greenhouse gases in the atmosphere. In fact, methane has high global warming potential (GWP = 25), which indicates the heat absorbed by any greenhouse gas in the atmosphere as a multiple of the heat that would be absorbed by the same mass of CO₂ (GWP = 1). Gas leakages are usually due to early-stage operations to find the optimal gas-flow rate in the extraction process.

While the best solution would be replacing high-carbon fossil fuels by renewable energy sources, the latter are still not available at reasonable amount and cost to meet industrial, social, and political needs. An advantage in using shale gas resources is that, in principle, if fully oxidized, methane is the cleanest form of fossil fuels in terms of carbon dioxide emissions. Shale natural gas may therefore represent a feasible compromise to replace high-carbon fossil fuels by not-so-high-carbon fossil fuels and provide a bridge until new energy sources are available.

1.1.2 Source rock properties

Understanding the properties of the solid matrix and fluids in shale reservoirs is critical for both resource evaluation and production. Information on shale reservoirs can be directly obtained from well logs, especially when information is combined from multiple sources, such as nuclear magnetic resonance (NMR), neutron spectroscopy, and dielectric dispersion.¹⁸ Many techniques have been applied to the study of unconventional formations. Shale mineral properties are typically evaluated by nuclear physics-based techniques, such as neutron scattering and X-ray spectroscopies, while fluid properties (oil and water) are usually investigated with resistivity and low-frequency electromagnetic measurements.¹⁹ Also, acoustic measurements are commonly used to estimate the mechanical properties of the rocks.

Quantitative evaluation and separation of kerogen, heavy oil (bitumen) and light oil is critical for determining the shale reservoir quality, which is a measure of the ability of the formation to produce hydrocarbons upon stimulation.^{18,20} In shale rocks containing gas resources, natural gas is more likely to be contained in organic pores in the kerogen matrix. Therefore, kerogen represents a positive reservoir quality indicator as it can be considered as a proxy for the organic porosity and, ultimately, for the natural gas fraction. However, if the shales contain tight oil, both kerogen and bitumen may produce negative effects on the reservoir quality, as they can trap the production fluids by adsorption, clogging pore throats and swelling, reducing the oil permeability.²¹

1.1.3 Shale porosity

The hydrocarbon storage capability of unconventional reservoirs depends critically on the pore structure of the shale. Over the last decades, many petrophysical models have been proposed to describe the shale pore structure.²² All these models are defined by two main components: a solid matrix and voids filled with fluids. The solid matrix in shales can be either mineral or organic, while

pores and fractures constitute voids. Various fluids can be found in these voids: bound and free water, light and heavy oil, and bitumen.

Different types of porosity in shales can be classified in interparticle porosity (pores between clay platelets or rock grains), intraparticle porosity (pores in clay platelets or minerals) and organic porosity (pores within organic matter).^{2,23} Intraparticle and interparticle pores may contain oil, gas, or water, depending on the wettability of the pore surfaces, while pores within organic matter are most likely to contain hydrocarbons. Although organic pores tend to be hydrophobic, some part may absorb water through hydrogen bonding.²⁴ Distinguishing the different pore environments in shales is a challenge. The conventional concept of porosity is not an appropriate model for shale formations, where much of the producible fluid is found within kerogen voids, and water tends to be present as an adsorbed layer on clays.²⁵ Organic porosity is formed during catagenesis as the organic matter is converted to oil and gas. The fraction of organic porosity will increase with increased thermal maturity, but may decrease above a certain level of maturity, possibly due to infill of less viscous forms of organic matter or by collapse of the organic structure.

1.1.4 Organic matter in shales

In contrast to conventional reservoirs, many shales contain significant quantities of organic matter. The type, amount, and thermal maturity of organic matter are key factors that control the petroleum generation within the shale. Other than light oil and gas, shales also contain solid and highly viscous organic materials, which are kerogen and bitumen.

1.1.4.1 Kerogen

The term “kerogen” refers to the fraction of organic matter in sedimentary rocks that generates petroleum and natural gas and is applicable to a wide range of solid fossil fuels.²⁶ These fuels can all be crudely described to have a complex macromolecular structure predominantly composed of carbon and hydrogen and also of small percentages of oxygen, nitrogen and sulfur.⁶ Kerogen is defined as the fraction of raw organic matter dispersed in sediments that is insoluble in common organic solvents.⁶ It can be further classified into different categories, depending on its source and location, on a Van Krevelen diagram based on the hydrogen to carbon (H/C) and oxygen to carbon (O/C) ratios, as illustrated in Figure 1.3.³ Type I kerogens derive from lacustrine environments and are, for the most part, aliphatic (H/C > 1.25); Type III kerogens come from terrestrial organic material

and tend to be predominantly aromatic ($H/C < 1$), while Type II kerogens represent an intermediate class that originate from marine environments.^{27,28}

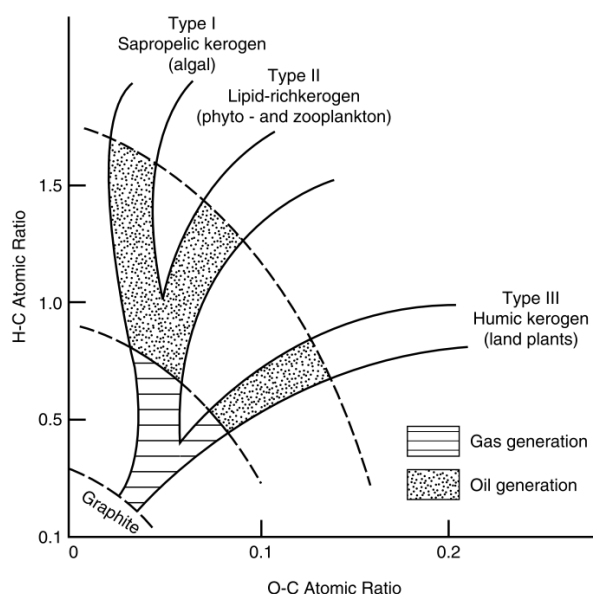


Figure 1.3. Van Krevelen diagram (H/C vs. O/C atomic element ratios) showing the kerogen hypothetical evolutionary pathways upon geological burial. Three main types are identified, from type I kerogen starting at low maturity with high H/C and low O/C, to type III kerogen starting at low maturity with low H/C and high O/C. The figure is adapted from ref. [29].

Kerogen is formed from biologically derived organic matter by diagenetic processes in the first few hundred meters of burial and it is converted to bitumen and then into oil and gas during the process of catagenesis, the thermal degradation stage of petroleum formation.^{3,5} Under high temperature and pressure conditions, the kerogen chemical structure is altered by condensation reactions, which lead to a gradual increase in the sp^2/sp^3 carbon hybridization ratio. At high thermal maturity, kerogen mainly consists of aromatic units in sp^2 hybridized graphitic structures.^{30,31,32,33} Figure 1.4 shows a simulated example of the evolution of a type II kerogen molecular structure over the maturation process.³⁴ The quality and amount of hydrocarbon generated is controlled by the concentration, type, and thermal maturity of the kerogen.^{35,36,37}

In unconventional reservoirs, kerogen characterization is of primary importance as much of the porosity in these rocks is present in this solid organic component. Furthermore, hydrocarbons can be potentially produced by cracking (thermal decomposition) of kerogen, which generates lower molecular weight products in a much faster way compared to natural maturation.

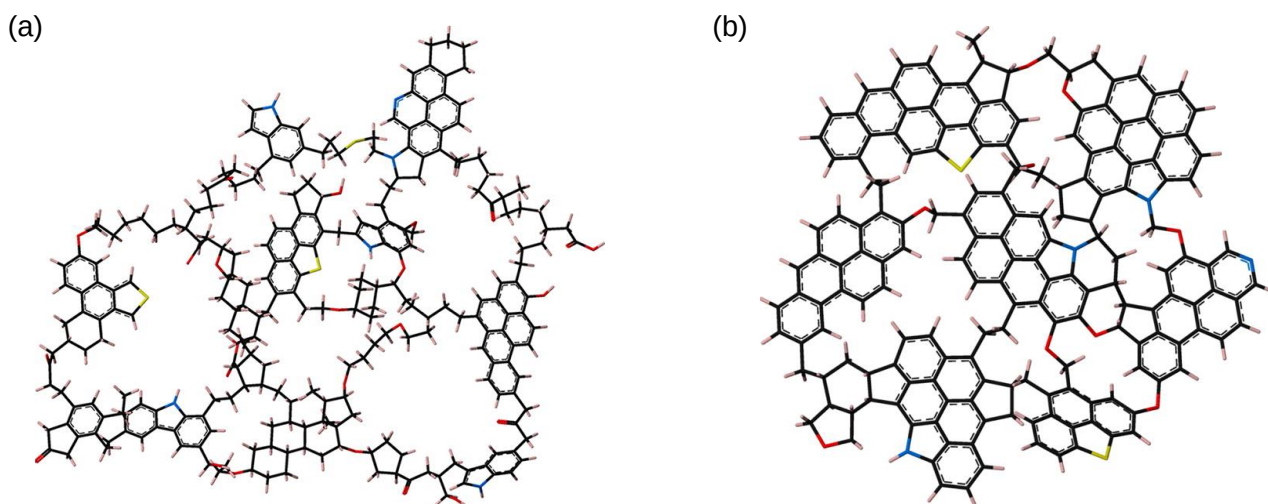


Figure 1.4. Molecular models of a type II kerogen in the immature stage (a), with chemical formula is $C_{252}H_{294}O_{24}N_6S_3$, and in the postmature stage (b), with chemical formula $C_{175}H_{102}O_9N_4S_2$. The colour code is the following: C (black), H (gray), O (red), N (blue), S (yellow). The figure is adapted from ref. [34].

1.1.4.2 Bitumen

Heavy crude oils, or bitumens, are viscous liquids that comprise a wide array of complex hydrocarbon compounds and are soluble in conventional organic solvents. Bitumen is traditionally considered as the intermediate phase during the transformation of kerogen to oil and gas. As such, it is characterized by a chemical structure and molecular weight that are intermediate between that of kerogen and petroleum. Bitumen contains large number of molecular species which vary widely in polarity and molecular weight. Elemental analysis of bitumen show that its composition is mainly determined by its crude oil source. A conventional characterization method separates the various crude oil species into saturates, aromatics, resins, and asphaltenes (SARA), depending on their solubility and polarity.³⁸ Saturates and aromatics are composed of various alkane isomers and small aromatic molecules, respectively, while asphaltenes consist of large polycyclic aromatic hydrocarbons with peripheral aliphatic side chains. Asphaltenes are insoluble in n-alkane solvents, but soluble in toluene. The asphaltene content in crude oils is often of considerable importance for several stages of processability, from oil recovery to refining.^{29,39}

1.2 Basic principles of Solid-state NMR

Nuclear magnetic resonance (NMR) spectroscopy involves the interaction between atomic nuclei with non-zero spin and magnetic fields. For a nucleus with a spin quantum number I there are $(2I + 1)$ spin states, with the magnetic quantum numbers $m_I = (-I, -I + 1, \dots + I)$. In the absence of a magnetic field these energy levels are degenerate. When an external magnetic field $\mathbf{B}_0$ is applied the spin states are split by the nuclear Zeeman interaction giving an energy separation:

$$\Delta E = -\hbar\gamma_I\mathbf{B}_0 \quad (1.1)$$

where γ_I is the gyromagnetic ratio of the nucleus and $\hbar$ is the reduced Planck's constant. The difference between the energies of two consecutive Zeeman states ($\Delta m_I = \pm 1$) is given by the Larmor frequency of the observed nucleus, ω_0 , defined as:

$$\omega_0 = -\gamma_I\mathbf{B}_0 \quad (1.2)$$

At thermal equilibrium the nuclear spins populate the Zeeman states following the Boltzmann distribution:

$$\frac{N_{m+1}}{N_m} = \exp\left(\frac{-\Delta E}{kT}\right) \quad (1.3)$$

where N_m is the population of the m spin state, ΔE is the energy difference between the spin states, k is the Boltzmann constant and T is the temperature in Kelvin. The population difference between the states leads to a net magnetization $\mathbf{M}$ parallel to the applied field $\mathbf{B}_0$, conventionally labelled as the z direction. In a generic NMR experiment, the equilibrium is perturbed by the application of a weak magnetic field ($\mathbf{B}_1$) perpendicular to the $\mathbf{B}_0$ field through the use radiofrequency (RF) pulses generated by a coil surrounding the sample. The RF pulse induces a “nutation” about the $\mathbf{B}_1$ field with the flip angle determined by the duration and field strength of the applied pulse. By controlling the duration (t_p) and the magnitude of the applied RF pulse, it is possible to define the degree of rotation (θ) of the magnetization:

$$\theta = \omega_1 t_p = -\gamma_I \mathbf{B}_1 t_p \quad (1.4)$$

Generally, the $\mathbf{B}_1$ field strength is fixed, and differing θ are selected by varying the duration of the pulse. In the simplest NMR experiment, a “ $\pi/2$ pulse” rotates the longitudinal magnetization $\mathbf{M}$ (along z) by 90° into the xy -plane. The magnetization then precesses in the xy -plane and gradually

relaxes to equilibrium, generating an oscillating electric current decaying over time, which is measured by the coil. This decay, called the free induction decay (*FID*), is usually Fourier transformed to obtain the NMR spectrum in the frequency domain.

1.2.1 The shielding interaction

Nuclear spins interact with the varying local magnetic field induced by the external magnetic fields in the electron clouds of the molecules. The local magnetic fields experienced by the nuclei in different chemical environments change with the local electron density. Hence, the chemical shift in NMR spectra reflects the local chemical environments of the observed nuclei. The shielding Hamiltonian is:

$$\hat{H}_{CS} = \gamma \hbar \vec{I} \cdot \underline{\sigma} \cdot \vec{B}_0 \quad (1.5)$$

where $\underline{\sigma}$ is the chemical shift tensor represented by a 3 x 3 matrix, and $\vec{B}_0$ itself is the external magnetic field vector. The secular part of $\hat{H}_{CS}$, which is the only part that commutes with the Zeeman Hamiltonian, contributes to the first-order corrections:

$$\hat{H}_{CS}^{sec} = \gamma \hbar \sigma_{zz} B_0 \hat{I}_z \quad (1.6)$$

where σ_{zz} is one of the elements of the $\underline{\sigma}$ matrix. The corresponding resonance frequency for the $|\alpha\rangle \rightarrow |\beta\rangle$ transition is:

$$\omega_{CS} = \omega_0 \sigma_{zz} \quad (1.7)$$

where $\omega_0 = \gamma B_0$ is the Larmor frequency and σ_{zz} is the zz component of the $\underline{\sigma}$ tensor, defined in the laboratory axes frame (where $\vec{B}_0$ is aligned along with the z axis), which depends on the molecular orientation. Figure 1.5 shows the relative orientation of the shift tensor $\underline{\sigma}$ in the laboratory frame.

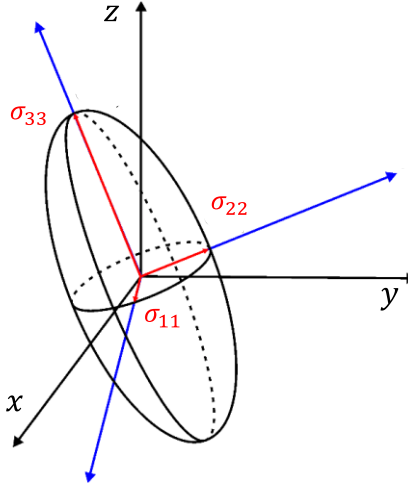


Figure 1.5. Relative orientation between the three independent components of the shielding interaction tensor $\underline{\sigma}$ and the laboratory axes frame (the z axis is the $\mathbf{B}_0$ direction). The Euler angles θ and ϕ define the orientation of $\mathbf{B}_0$ in the $(\sigma_{11}, \sigma_{22}, \sigma_{33})$ axis frame.

The laboratory axes frame component σ_{zz} can be expressed using the principal axes components $(\sigma_{11}, \sigma_{22}, \sigma_{33})$ of the $\underline{\sigma}$ tensor. The resonance frequency due to the chemical shift reported in equation (1.7) assumes the following form:

$$\begin{aligned}\omega_{CS} &= \omega_0 (\sigma_{11} \sin^2\theta \cos^2\phi + \sigma_{22} \sin^2\theta \sin^2\phi + \sigma_{33} \cos^2\theta) \\ &= \omega_0 \sigma_{iso} - \frac{1}{2} \omega_0 \Delta_{CS} ((3\cos^2\theta - 1) + \eta_{CS} \sin^2\theta \cos 2\phi)\end{aligned}\quad (1.8)$$

where σ_{iso} is the isotropic component, Δ_{CS} is the chemical shift anisotropy, and η_{CS} is the chemical shift asymmetry. These quantities are defined from the three principal axes values as follows:

$$\begin{aligned}\sigma_{iso} &= 1/3 (\sigma_{11} + \sigma_{22} + \sigma_{33}) \\ \Delta_{CS} &= (\sigma_{33} - \sigma_{iso}) \\ \eta_{CS} &= (\sigma_{11} - \sigma_{22})/(\sigma_{33} - \sigma_{iso})\end{aligned}$$

For a solid powder sample, where molecules can statistically assume all possible orientations with respect to the external field, the resonance signal is a powder pattern. This typical line shape is the result of the superimposition of the signals arising from different orientations of the molecules with respect to $\vec{\mathbf{B}}_0$ (inhomogeneous broadening) and represents the density distribution of $\omega(\theta, \phi)$ over all possible θ and ϕ angle values. In liquids, the molecules tumble rapidly through every conceivable molecular orientation, with equal probability for each orientation, averaging the anisotropic interaction to an isotropic value and, therefore, producing narrow NMR signals.

1.2.2 The dipolar coupling interaction

The magnetic moment related to a nuclear spin can interact through space with other nuclear spins in the local surrounding. In the classic model this interaction can be described as two bar magnets “feeling” each other. For two nuclear spins, I and S , the corresponding quantum mechanical operator is given by:

$$\hat{H}_D = \vec{I} \cdot \underline{D} \cdot \vec{S} \quad (1.9)$$

Where $\underline{D}$ is the dipolar coupling tensor, with principal values of $-d/2$, $-d/2$ and $+d$, where d is the dipolar coupling constant:

$$D = \frac{\mu_0 \gamma_I \gamma_S \hbar}{4\pi r^3} \quad (1.10)$$

where r is the spin-spin internuclear vector. The dipolar coupling constant D is therefore dependent on the involved spin types by their gyromagnetic ratios (γ) and on the distance between the two nuclear spins ($\propto 1/r^3$). For heteronuclear dipolar interaction ($\gamma_I \neq \gamma_S$), the secular part of the

$$\hat{H}_D^{IS} = \hbar \omega_D 2\hat{I}_{1z}\hat{I}_{2z} \quad (1.11)$$

where the coupling frequency ω_D represents the strength of the dipolar coupling between two spins:

$$\omega_D = \frac{\mu_0}{4\pi} \frac{\hbar \gamma^2}{r^3} \frac{1}{2} (3 \cos^2 \theta - 1) \quad (1.12)$$

The coupling frequency ω_D is inversely related to the cube of the through-space distance between the nuclei, r , and it depends on the angle θ between the internuclear vector and the static magnetic field B_0 .⁴⁰ The constant ω_D represents therefore a sensitive parameter for the measurement of interatomic distances, and the orientational dependence is expressed by the second Legendre polynomial $P_2 = \frac{1}{2} (3 \cos^2 \theta - 1)$. For powder samples, such orientational dependence (P_2) leads to a superposition of spectral lines at different frequencies resulting in a broad spectrum (a so-called Pake pattern for spin pairs) rather than a single line splitting (like a doublet in solution NMR).⁴¹ In fact, in rigid powders all possible orientations of spin-spin internuclear vectors are present, and these are associated with different coupling strengths. The angular dependence of the dipolar

coupling strength is illustrated in Figure 1.6. The cubic dependence on the distance between two nuclei causes a rapid decrease in ω_D for larger values of r and is the reason for the local nature of dipolar interaction (for proton-proton coupling and r in units of Å: $\omega_D/2\pi = 122 \text{ kHz}/r^3$).⁴² Sample regions with higher density will therefore exhibit stronger dipolar coupling than those with larger average distances between the nuclei. In addition, molecular motions may cause the change of orientation angle θ of different spin pairs and, as a result, fast molecular motions may completely average out the dipolar interaction.

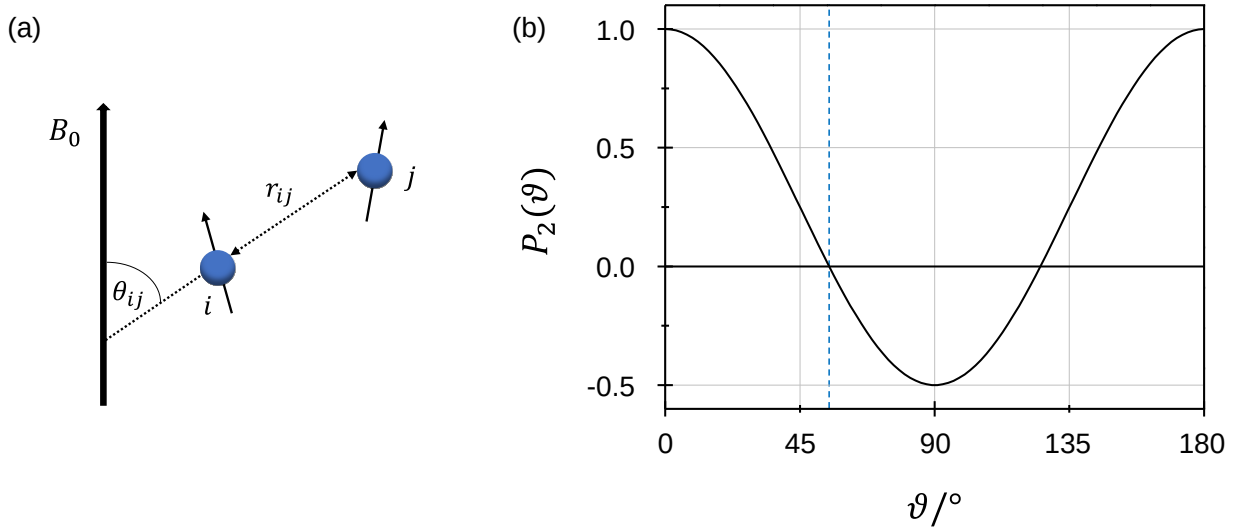


Figure 1.6. (a) Dipolar interactions between two spins. The angle θ_{ij} is the angle between the internuclear vector and the static magnetic field B_0 . (b) Angular dependence of the dipolar coupling strength, where P_2 is the second Legendre polynomial. The blue dashed line marks the magic angle $\theta = 54.74^\circ$, for which $P_2 = 0$.

For homonuclear dipolar coupling ($\gamma_I = \gamma_S$), the truncated Hamiltonian is given by:

$$\begin{aligned} \hat{H}_D^{II} &= -\frac{\mu_0 \gamma^2 \hbar^2}{4\pi r^3} \left((3 \cos^2 \theta - 1) \left(\hat{I}_{1z} \hat{I}_{2z} - \frac{1}{4} (\hat{I}_{1+} \hat{I}_{2-} + \hat{I}_{1-} \hat{I}_{2+}) \right) \right) \\ &= \hbar \omega_D (3 \hat{I}_{1z} \hat{I}_{2z} - \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2) \end{aligned} \quad (1.13)$$

where the θ angle defines the orientation of r in the laboratory frame and $\hat{I}_+$, $\hat{S}_+$ and $\hat{I}_-$, $\hat{S}_-$ are the ladder operators. The latter cause a continue energy exchange between the interacting spins. This mechanism, also known as *flip-flop* transition, is responsible for energy-conservative transitions which mix the Zeeman states.

1.2.3 Nuclear spin relaxation

A spin system in a magnetic field reaches a state of thermal equilibrium when the populations of the spin levels follow the Boltzmann distribution, and all the coherences are absent. After a perturbation, the system will return to the equilibrium state through a process known as relaxation. Two different types of relaxation are related to the movement of spin population back to their Boltzmann distribution and the decay of coherences: spin-lattice relaxation and spin-spin relaxation, respectively. Following the Bloch theory, the two relaxation processes can be treated independently.

1.2.3.1 Spin-lattice relaxation

The spin-lattice relaxation process describes the return to equilibrium of the longitudinal magnetization (M_z), which involves exchange of energy between the system and the environment (Figure 1.7). When the magnetization of a sample is taken away from its equilibrium position, for example by the application of a RF pulse, the net magnetization is no longer aligned with the static magnetic field B_0 . The spin system returns to equilibrium through a mechanism which implies transfer of energy to the surrounding environment. Such energy exchange is controlled by local fluctuations in the magnetic field, which are generally determined by molecular motions. The following Bloch equation describes the time dependence of the longitudinal magnetization $M_z(t)$:

$$\frac{dM_z(t)}{dt} = - \frac{M_z(t) - M_0}{T_1} \quad (1.14)$$

where M_0 is the magnetization value at equilibrium and T_1 is the spin-lattice relaxation time. The solution of the differential equation is an exponential function characterized by a time constant T_1 :

$$M_z(t) = M_0 \left(1 - e^{-\frac{t}{T_1}}\right) + M_z(0)e^{-\frac{t}{T_1}} \quad (1.15)$$

where $M_z(0)$ is the longitudinal magnetization amplitude immediately after the perturbation. The T_1 relaxation time can be measured by standard pulse sequences like the inversion recovery (IR) and saturation recovery (SR) experiments. The IR sequence consists of a 180° pulse, applied to invert the magnetization of the spin system, followed by a time delay τ , during which magnetization undergoes spin-lattice relaxation and recovers towards equilibrium. After the delay τ , a 90° pulse is used to flip the magnetization into the transverse plane for detection. The sequence is repeated many times with variable τ values to allow the measurement of the T_1 relaxation process as a function of time.

In practice, the magnetization is considered to have completely recovered along the z axis after a τ value about five times longer than T_1 . For the SR sequence, instead of a 180° pulse, we have an initial train of 90° pulses which saturates the longitudinal magnetization, so that, at the end of the train $M_z(0) = 0$ (Figure 1.7). The main advantage of the SR approach over the IR sequence is the possibility to use short recycle delays between two following scans.

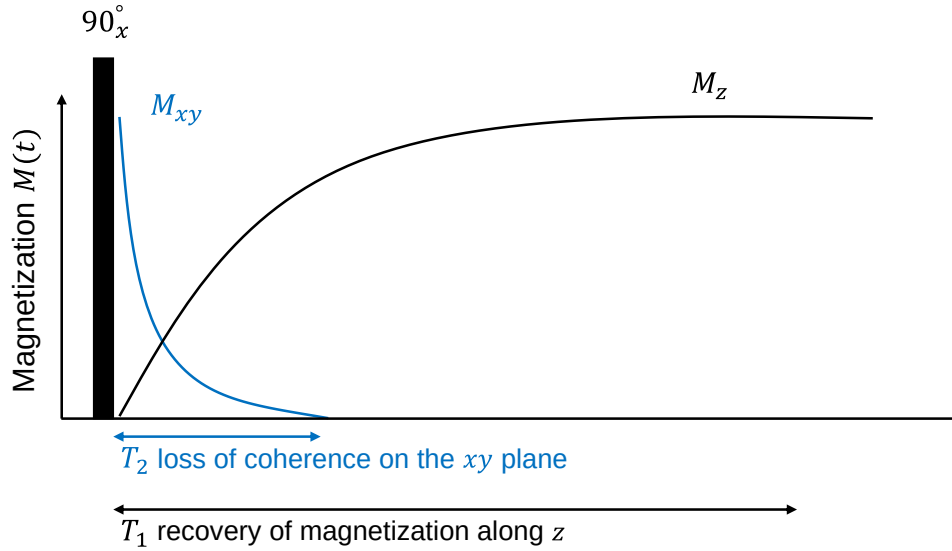


Figure 1.7. Schematic representation of the transverse magnetization (M_{xy}) decay, with time constant T_2 , and the longitudinal magnetization (M_z) recovery, with time constant T_1 . The T_2 decay is to loss of coherence on the $x'-y'$ plane. T_1 is a recovery of alignment of M along z' . The figure is adapted from ref. [43].

1.2.3.2 Spin-spin relaxation

The spin-spin relaxation describes the decay of the transverse magnetization (M_{xy}) formed after the application of the RF field, which occurs through energy exchanges among the spins. This process involves the loss of phase coherence in the xy plane (Figure 1.7), and it can be described by the following Bloch equation:

$$\frac{dM_{xy}(t)}{dt} = -\frac{M_{xy}(t)}{T_2} \quad (1.16)$$

which generally has the following solution:

$$M_{xy}(t) = M_{xy}(0) e^{-\frac{t}{T_2}} \quad (1.17)$$

where $M_{xy}(0)$ is the transverse magnetization amplitude immediately after the perturbation, and the characteristic time decay constant T_2 is the spin-spin relaxation time. The dephasing process is

due to variations in the precession frequencies of the spins caused by local magnetic field fluctuations. Such local variations of the magnetic field may be due to a variety of effects (inhomogeneities in the static B_0 field, susceptibility effects, dipole interactions). The “effective” spin-spin relaxation time T_2^* which governs the dephasing of the transverse magnetization can be expressed as a sum of two different contributions⁴⁴:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2'} \quad (1.18)$$

where T_2 is the spin-spin relaxation time determined by the fluctuations of nuclear interactions due to incoherent (time-variant) motional processes, while T_2' describes the transverse magnetization dephasing caused by coherent spin dynamics. The former cannot be reversed by a suitable pulse sequence. The coherent loss of transverse magnetization can be suppressed by appropriate pulse sequences, that extend the “lifetime” of the time-domain signal. In liquids, T_2' arises from interactions such as inhomogeneity of the external magnetic field or magnetic susceptibility, which can be refocused with the use of the standard Hahn-echo pulse sequence (Figure 1.8). In solids T_2' is largely represented by the anisotropic parts of the spin nuclear interactions. The Hahn-echo pulse sequence consists of a 90° excitation pulse and a 180° pulse separated by a time delay τ . During this time interval the spin ensemble loses phase coherence on the xy plane. The 180° pulse is then applied to invert the spins, reversing the rotation phase of all transverse magnetization components. The precession frequencies of each spin will be identical to those prior to inversion, but with opposite phase, and spin dephasing that has occurred via coherent effects, such as magnetic field inhomogeneity, is reversed. After a second delay of τ the magnetization components will refocus, leading to the formation of a spin echo at $TE = 2\tau$. The spin-spin relaxation T_2 can be measured repeating the spin-echo sequence for various echo times τ .

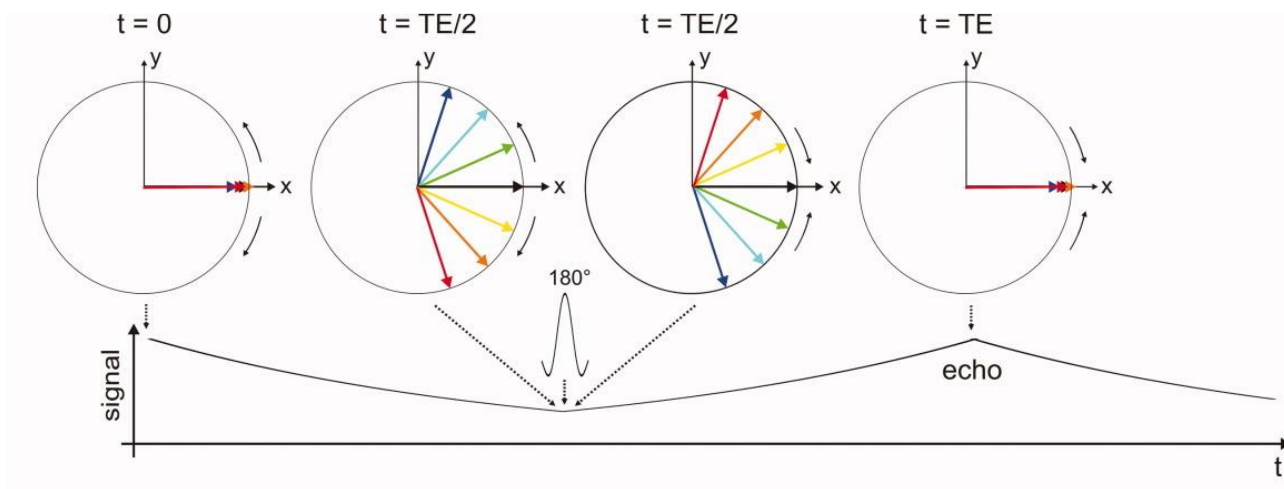


Figure 1.8. Schematic representation of the refocusing effect produced by a Hahn-echo pulse sequence. The coloured arrows represent the magnetization components with different precession frequencies.

1.2.4 T_2 in solids

Anisotropy of nuclear spin interactions (e.g., dipolar and chemical shift interactions) is the major source of NMR line broadening in solids. For a many-body system with spin-1/2 nuclei, such as protons in solid organic species, homonuclear dipolar couplings represent the dominant relaxation mechanism. These interactions lead to the observance of fast-decaying time-domain signals in solids, with effective T_2 times as short as 5-20 μs .⁴⁵ The origin of this effect lies in the dipolar interaction between hydrogen nuclei at a fixed distance r and oriented with respect to the static magnetic field B_0 in the absence of molecular motion. For rigid lattices with negligible diffusion, the dipole Hamiltonian (*Section 1.2.2*) exceeds the contribution of the Zeeman Hamiltonian, and the transverse magnetization decay depends on local fields of neighbouring dipoles. In solids, each i^{th} spin experiences a local field determined by its j^{th} neighbor, and temporal fluctuations in these local magnetic fields result in quick dephasing of the spin coherences (short T_2) and, consequently, in large NMR spectral line broadening.⁴⁶ In contrast, for fast isotropically tumbling molecules in liquids, the time-dependent dipolar frequency averages out on the NMR timescale, resulting in narrow NMR signals in the frequency domain.

1.2.5 NMR relaxation theory

Spin relaxation is caused by time-dependent fluctuations of local magnetic fields, which are usually controlled by molecular motions through the orientation dependence of the NMR interactions. The latter represent incoherent processes that can be described by autocorrelation functions $G(\tau)$:

$$G(\tau) = \langle \mathbf{b}(t)\mathbf{b}(t + \tau) \rangle \quad (1.19)$$

where $\mathbf{b}(t)$ is a time-dependent local magnetic field and the angle brackets indicates an ensemble average. The $G(\tau)$ function defines the correlation of the values of the fluctuating field $\mathbf{b}$ between two time points separated by a delay of τ . This function is independent of the time t , but it only depends on τ . In particular, the higher the frequency of the fluctuations the more rapidly $G(\tau)$ will decay. The analogous function of $G(\tau)$ in the frequency domain, obtained through Fourier transformation, is the spectral density $J(\omega)$:

$$J(\omega) = \int_{-\infty}^{\infty} G(\tau) e^{-i\omega\tau} d\tau \quad (1.20)$$

The spectral density reflects a measure of the amount of motion available for the relaxation of a random motion at a specific frequency ω . Different models have been developed to provide analytical expression for the spectral densities, for which $G(\tau)$ and the corresponding $J(\omega)$ assumes different expressions. In the simplest case of isotropic rotational motion, the autocorrelation function $G(\tau)$ assumes the following exponential form:

$$G(\tau) = \langle b^2 \rangle e^{-\frac{\tau}{\tau_c}} \quad (1.21)$$

where $\langle b^2 \rangle$ is the mean square field fluctuating and τ_c is the correlation time of the molecular motion, which represents the characteristic time describing the decay of $G(\tau)$. The corresponding spectral density is a Lorentzian function:

$$J(\omega) = \langle b^2 \rangle \frac{2\tau_c}{1 + \omega_0^2 \tau_c^2} \quad (1.22)$$

Following the Redfield theory⁴⁷, the relaxation rates can be expressed as linear combinations of spectral densities:

$$R_k = \frac{1}{T_k(\omega)} = \sum_{i=0}^n a_i J(\omega_i) \quad (1.23)$$

where a_i is the coefficient relative to the spectral density at ω_i , and k indicates relaxation mechanisms ($k = 1, 2$).

1.2.6 BPP theory

BPP (Bloembergen, Purcell and Pound) theory⁴⁸ provides a model to correlate intramolecular dipolar coupling fluctuations induced by molecular motions to the experimentally measurable relaxation times. For pairs of spins that are within the same molecule, modulation of dipole interactions is caused by rotational motion of the molecule. The BPP model bases its description on isotropic rotational motions which are fast on the NMR timescale, i.e., for dipole-coupling induced relaxation the correlation time τ_c of the motion-induced fluctuating fields is fast compared to the static coupling frequency ω_D ($\omega_D \tau_c \ll 1$). According to this theory, the relaxation times for two spin-1/2 nuclei in an isotropic system, such as protons in water or oil molecules, are given by:

$$\frac{1}{T_1} = \frac{3}{20} D^2 [J(\omega_0) + 4J(2\omega_0)] \quad (1.24)$$

$$\frac{1}{T_2} = \frac{3}{40} D^2 [3J(0) + 5J(\omega_0) + 2J(2\omega_0)] \quad (1.25)$$

Where $J(\omega_0)$ is the spectral density at the Larmor frequency and D is the dipolar coupling constant defined in eq. (1.10). The dominant terms in the T_1 expression are the spectral densities at the single and double Larmor frequency. Consequently, T_1 results to be sensitive to the external magnetic field and motions in the Larmor frequency range. In the ultrafast motion limit (i.e., in liquids), $\omega_0 \tau_c \ll 1$, and the behavior of T_1 and T_2 is identical ($T_1/T_2 = 1$). As molecular mobility decreases, the T_1 value decreases to reach a minimum at $\omega_0 \tau_c \approx 1$ (Figure 1.9). Then, for samples exhibiting slower molecular dynamics (slow motion limit, $\omega_0 \tau_c \gg 1$), T_1 increases again whereas T_2 continues to decrease because it is dominated by the $J(0)$ term. Therefore, T_1 - T_2 maps can be used to investigate molecular mobility in fluids, both in their bulk state and under confinement, as they are sensitive to molecular motions in the frequency range between the Larmor frequency of the measurement and the low frequencies.

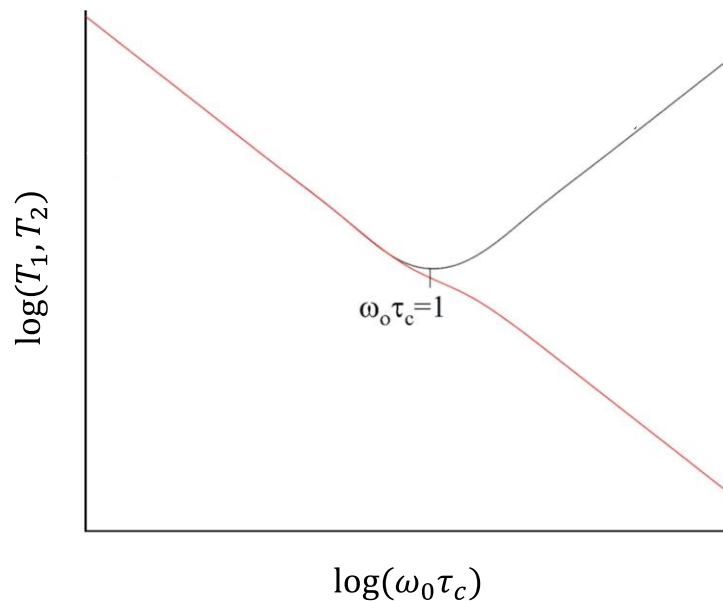


Figure 1.9. Dependence of relaxation times T_1 (black) and T_2 (red) on the correlation time τ_c , as predicted by the BPP relaxation theory.

1.2.7 High-resolution techniques

In solution NMR, most anisotropic NMR interactions are averaged out to an isotropic value by rapid molecular motion (tumbling). In a solid powder, where all orientations are assumed to be present, these interactions will depend on the relative orientation of each crystallite, which are not averaged out. Therefore, the NMR line shape of solid powders tends to be very broad, reducing the resolution compared to a liquid spectrum.

1.2.7.1 Magic Angle Spinning

Magic angle spinning technique enables averaging the anisotropy of those nuclear interactions which cause signal broadening for solid-state powder samples. Most NMR interactions are anisotropic and transform as a second-rank tensor under rotation. With an axially symmetric interaction, the orientation dependence of these anisotropic NMR interactions is typically given by the term $(3\cos^2\theta - 1)$, where θ is the angle between the spin interaction tensor and the B_0 field. When spinning the sample at an arbitrary angle of θ_R with respect to the applied B_0 field, provided the spinning frequency is fast enough compared to the interaction anisotropy, the time averaged orientation dependence is given by:

$$\overline{3 \cos^2 \theta - 1} = \frac{1}{2} (3 \cos^2 \theta_R - 1) (3 \cos^2 \beta - 1) \quad (1.26)$$

Where β describes the orientation of the spin interaction tensor with respect to the rotor axis (θ_R). This average value vanishes when the sample is rotated at the “magic” angle of $\theta_R = \arccos(1/\sqrt{3}) = 54.74^\circ$. Therefore, rotating the sample at a fast enough frequency around an axis which subtends an angle of 54.74° with respect to the static B_0 field will reduce the anisotropy to zero and produce narrow lines.

1.2.7.2 Cross polarization

Another important technique is the cross polarization (CP), which is used to enhance the signal sensitivity of lower γ like ^{13}C nuclei, whose natural abundance is low. The basic idea is a transfer of transverse magnetization (in the rotating frame) from the abundant ^1H to the dilute ^{13}C spin system, exploiting heteronuclear dipolar interactions. Experimentally, the magnetization transfer occurs during the simultaneous application of transverse RF fields to the ^1H and ^{13}C channels, under the Hartmann-Hann condition: $\gamma_C B_{1C} = \gamma_H B_{1H}$. The use of this basic technique provides two important advantages. Firstly, the CP enhances the polarization of the low γ nuclei, allowing a considerable increase in sensibility. Secondly, the recovery of the longitudinal magnetization is much faster, since it concerns the $^1\text{H } T_1$, which is generally much shorter than $^{13}\text{C } T_1$.

1.3 NMR relaxation in shales

1.3.1 Porous media

When a liquid is placed within a porous system, the observed relaxation rates are heavily influenced by the presence of the pore walls, which create heterogeneities within the sample. Relaxation of hydrogen nuclei in these systems will be the result of a combination of different processes, including dipolar coupling, interactions with paramagnetic ions, and diffusion in local magnetic field gradients. In the following sections, the main relaxation mechanisms occurring in conventional and unconventional porous media will be discussed.

1.3.2 Conventional reservoirs

NMR is a key technique for the characterization of fluid bearing porous materials.^{49,50,51} Under optimal conditions, NMR provides a lithology-independent measure of porosity in the wellbore, whereas all other logging tools produce a result that is formation-dependent.^{52,53} As lithology can vary largely along the length of a well, accurate rock type selection throughout the wellbore can represent a significant challenge. In conventional reservoirs, NMR measures only on the fluids present, so that porosity can be estimated directly from the NMR signal.⁵⁴ NMR relaxometry is widely used in the petroleum industry to provide a variety of information on both fluids present in the formations (water, oil)⁵⁵, and porosity^{56,57}/permeability.^{2,58} This technique relies largely on the measurements of spin-lattice (T_1) and spin-spin (T_2) relaxation times⁷, typically based on standard spin-echo measurements (Hahn-echo, Carr-Purcell-Meiboom-Gill [CPMG]). Relaxation experiments are usually performed in low-field benchtop spectrometers (≤ 2 MHz ^1H), for routine analysis of core samples recovered from the reservoir, or in well-logging tools, for direct measurements in a wellbore.⁵⁹

When low-viscosity fluids such as water and oil are placed in a porous material, the fluid molecules interact with the pore surface, leading to the enhancement of their NMR relaxation rates. The T_1 and T_2 relaxation times are influenced by three NMR relaxation mechanisms: bulk relaxation, surface relaxation, and diffuse relaxation. Assuming that protons in such fluids can diffuse in the entire pore before losing all their magnetization (fast diffusion limit), the measured T_1 and T_2 are given by the following equations⁶⁰:

$$\frac{1}{T_1} = \frac{1}{T_{1Bulk}} + \rho_1 \frac{S}{V} \quad (1.27)$$

$$\frac{1}{T_2} = \frac{1}{T_{2Bulk}} + \rho_2 \frac{S}{V} + \frac{D\gamma^2 G^2 T_E^2}{12} \quad (1.28)$$

Where T_{1Bulk} and T_{2Bulk} are the relaxation times of the bulk fluid, S is the pore surface area, and V the volume of the pores. Bulk relaxation is an intrinsic property of the fluid, and it is determined by its physical and chemical properties. Surface relaxation is predominantly caused by the interaction of fluid molecules with paramagnetic impurities on pore surfaces, and it describes how effective the material is at relaxing protons in the fluid. The parameters ρ_1 and ρ_2 are the surface relaxivities of the pore surface for T_1 and T_2 , respectively. The T_2 expression includes an additional diffusion term which does not affect T_1 relaxation, where D is the diffusion coefficient of the fluid, γ is the gyromagnetic ratio of the observed nucleus, G is the magnetic field gradient, and T_E is the echo spacing. Magnetic gradients in the sample may arise from magnetic susceptibility contrast between the pore matrix and the saturating fluid at the solid-liquid interface. Diffusion of molecules through these gradients causes additional dephasing of transverse magnetization, shortening the T_2 . In most measurements, low-field magnets and short echo spacings are used to avoid the influence of internal gradients on the NMR signal.⁶⁰ Therefore, ignoring the diffusivity term, the experimentally measured T_1 and T_2 values can be used directly to evaluate the pore-size distribution in porous media, using eqs. (1.27) or (1.28) in the following way:

$$\frac{S}{V} = \frac{1}{\rho_{1,2}} + \left(\frac{1}{T_{1,2}} - \frac{1}{T_{1,2Bulk}} \right) \quad (1.29)$$

However, the conversion of relaxation times into pore-size distributions requires an accurate measure of the surface relaxivity parameters, $\rho_{1,2}$.⁶¹ Estimates of $\rho_{1,2}$ for a specific rock lithology are commonly obtained from laboratory measurements of cored samples, but these may also be obtained directly from downhole measurements.

1.3.3 Unconventionals

Shale rocks are different from conventional reservoirs in both composition and structure. The non-invasive and non-destructive nature of NMR makes it a popular method for shale characterization

since other conventional methods of core analysis are hindered by the extremely low formation permeability. Among NMR techniques, low-field ^1H NMR relaxometry has emerged as the most common method for the characterization of organic matter in unconventional shale rocks.^{49,62,63,64,65} However, interpretation of NMR relaxation measurements in shale reservoirs is much more complex than for conventional ones. Shales have low porosity and pore sizes that are usually in the nanometer range, several orders of magnitude lower than in conventional reservoirs. The small size of the pores often results in extremely low permeability. In addition, shales contain significant amounts of hydrogen nuclei in solid and viscous organic materials (kerogen and bitumen) and clays, such that the resulting signal can no longer be assumed to be lithology independent. The composition diversity, the low porosity and ultra-low permeability of organic-rich shale formations, combined with the coexistence of multi-scale pores with complicated pore networks, make traditional NMR laboratory characterization methods difficult to apply. Interpretation of NMR signals from shale samples is usually challenged by low SNR, signal loss, and a signal overlapping.

Various type of interactions that may arise at the liquid/solid interface in the small size pores of shales are usually grouped together under the conventional view of surface relaxation.⁶⁶ However, grouping these interactions into a single value leads to a loss of information and potentially incorrect interpretation.⁵⁵ The usual model of surface relaxation via spin interactions with electrons of paramagnetic centers on the pore walls does not hold for shales, and standard equations (1.27) and (1.28) cannot be robustly applied for describing their relaxation behavior. In addition, the presence of solid and highly viscous organic materials (i.e., kerogen and bitumen) and surface-adsorbed hydroxyls (OH groups), are not encompassed by the conventional surface relaxivity model. These components exhibit strong ^1H - ^1H dipole interactions which are not averaged out by molecular motions, resulting in fast-decaying time-domain signal (short T_2).^{20,67,68} Low-field logging tools and benchtop spectrometers have a lower limit on spin-echo times, which is typically in the order of a few hundred microseconds, too long to be able to observe fast T_2 decays.⁵⁹ Moreover, for solid components, T_2 may be particularly difficult to interpret as the classic CPMG experiment may produce rapid, non-exponential T_2 decays.

The main relaxation mechanisms in shales are illustrated in a simple schematic in Figure 1.10. These include:

- (1) Dipolar coupling between hydrogen nuclei in the fluid (oil or water) and on the surface of the pore.

- (2) Intra- and inter-molecular dipole coupling among protons in fluid molecules.
- (3) Residual ^1H - ^1H dipole coupling in water molecules bound to the clay surface.
- (4) Residual ^1H - ^1H dipole coupling between gas molecules adsorbed in organic matter.
- (5) Multiple homonuclear dipolar coupling in the solid organic fraction.
- (6) Interactions between ^1H spins in fluid molecules and paramagnetic ions in the water phase or pore wall.

Due to the large variety of shale systems, which cover a broad range of structures and compositions, some of the relaxation mechanisms presented in this section may be relevant for certain samples and be negligible for others.

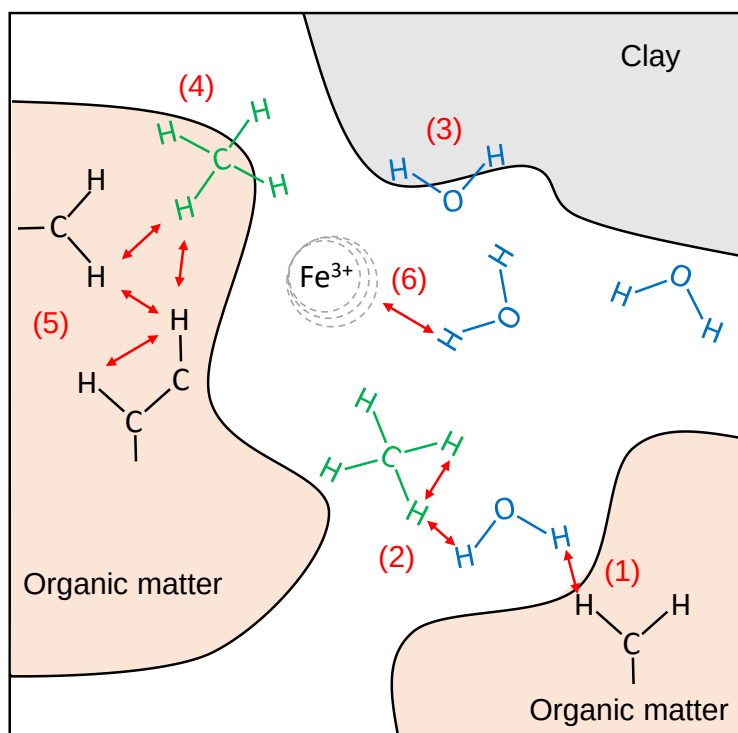


Figure 1.10. Schematic illustration of the main ^1H NMR relaxation mechanisms in shales: (1) dipolar coupling between hydrogen nuclei in the fluid and at the pore surface, (2) intra- and inter-molecular dipole coupling among protons in fluid molecules, (3) residual ^1H - ^1H dipole coupling in water molecules bound to the clay surface and (4) in gas molecules adsorbed in organic matter, (5) multiple homonuclear dipolar coupling in the solid organic fraction, (6) interactions between fluid molecules and paramagnetic ions in the water phase or pore wall.

In summary, while surface relaxation is assumed to be the main NMR relaxation mechanism in porous media, other relaxation mechanisms, such as homonuclear dipolar coupling, residual dipolar coupling, diffusional coupling between pores and transfer of magnetization between mobile and immobile phases, may have significant effect on measured T_2 relaxation signals in shales. In

particular, relaxation of highly viscous fluids and solids deviates significantly from the conventional behavior of low viscosity fluids in porous materials. For such species, instead of surface interactions with pores controlling relaxation, the relaxation rate is strongly influenced by intramolecular dipolar coupling within the solid. The next section focuses on the ^1H homonuclear dipolar coupling as this represents the dominant relaxation mechanism for the ^1H -bearing species in organic shales.

1.3.4 Relaxation via homonuclear dipolar coupling

Interpretation of NMR relaxation data in shales is challenging due to the presence of a wide variety of components in various environments, which undergo different dynamic regimes. The mobilities of these components differ dramatically, ranging from solid kerogen and highly viscous bitumen to mobile oil and water in intra- and interparticle pores. Light-hydrocarbon oil can be confined in kerogen nanopores or located in large inorganic pores, and water can exist in a clay-bound form, in small capillaries or as free water in the mineral pores. A review of the relaxation models used for the interpretation of relaxation measurement of the various components of a shale system is presented in the following sections.

1.3.4.1 Simple fluids

For simple liquids like oil and water in their bulk state, the overall relaxation behavior is dominated by rotation of the molecule. The spectral density function, which depends on the rotational correlation time of the molecules, τ_c , assumes the following Lorentzian form:

$$J(\omega_0) = \frac{2\tau_c}{1 + \omega_0^2\tau_c^2} \quad (1.30)$$

The relaxation rates for two spin-1/2 nuclei in water or oil molecules, are given by the BPP equations (eqs. (1.31)-(1.32)) and their relation to the correlation time τ_c is reported below:

$$\frac{1}{T_1} \propto 2J(\omega_0) + 8J(2\omega_0) \quad (1.31)$$

$$\frac{1}{T_2} \propto 3J(0) + 5J(\omega_0) + 2J(2\omega_0) \quad (1.32)$$

The BPP model is based on the Stokes–Einstein–Debye relation for hard spheres, where the rotational correlation time of any molecule can be estimated using the following equation:

$$\tau_c = \frac{4\pi R^3}{3k_B} \frac{\eta}{T} \quad (1.33)$$

Where η is the viscosity of the fluid, T is the temperature, k_B is the Boltzmann constant, and R is the Stokes radius. In the ultra-fast motion regime, which occurs in the limit of $\omega_0\tau_c \ll 1$, we have $T_1 = T_2 \propto (\tau_c)^{-1}$. Therefore, T_1 and T_2 are expected to be proportional to $(\eta/T)^{-1}$. This condition applies to many low-viscosity fluids at all typical magnetic field strengths and, within this limit, the measured T_1 and T_2 relaxation times can be directly related to molecular sizes and motional processes. For example, crude oils containing low amounts of asphaltenes or resins usually have a low-enough viscosity such that all saturate and aromatic oil components are in the fast-motion regime.⁶⁹ In the slow-motion regime ($\omega_0\tau_c \gg 1$), which apply for solid-like and highly viscous materials, T_1 can become much larger than T_2 , resulting in $T_1/T_2 > 1$. In this case, T_1 will be long due to the ineffective energy exchange with the surrounding environment resulting from the low frequency of fluctuations in solids, while T_2 will be short because of the strong dipolar couplings that quickly dephase the spins.

1.3.4.2 Heavy oils

For highly viscous heavy oils such as bitumen, the relaxation behavior is more complex due to the presence of large asphaltene molecules. Because of the restricted motions of these species, dipole interactions are not fully averaged, and the residual dipolar coupling leads to quick loss of signal.

For heavy oils, the relation between the relaxation times T_1 and T_2 and the correlation time τ_c deviates significantly from BPP model. In the slow-motion regime ($\omega_0\tau_c \gg 1$), the BPP theory predicts an increase of T_1 and a decrease of T_2 as a function of viscosity, respectively with $T_1 \propto (\eta/T)$ and $T_2 \propto (\eta/T)^{-1}$. However, several experiments^{70,71} on crude oils and bitumen have proved that instead of the anticipated increase, T_1 approaches a temperature plateau at high viscosities. Such T_1 temperature independence in (semi)solids is often explained in terms of ^1H - ^1H spin diffusion combined with paramagnetic centers acting as “relaxation sinks”. However, the same T_1 plateau, which has a value of 3 ms on a frequency-normalized scale for various viscosity samples (Figure 1.11), was also found for polydisperse polymers with negligible amounts of paramagnetic impurities^{70,72}, suggesting that the relaxation mechanism is independent of the paramagnetic concentration. Perhaps, local sites with high mobility, such as rotating methyl groups or encapsulated methane molecules, can act as relaxation sinks, as well.

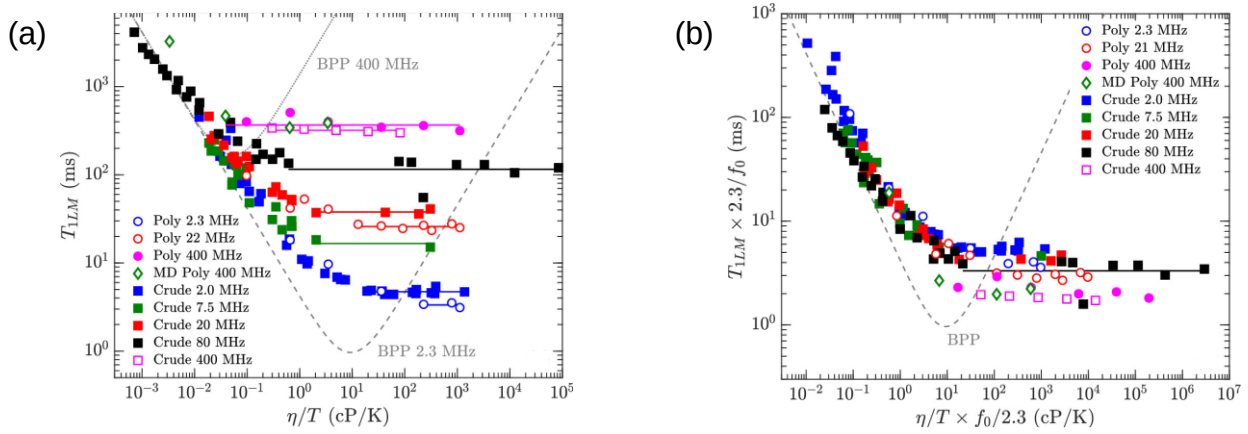


Figure 1.11. (a) Trend of the log-mean relaxation time T_{1LM} as a function of viscosity (η/T) for a series of polydisperse polymers with different viscosity and average molecular weight, measured at 2.3, 21, and 400 MHz, and for a series of crude oil and bitumen samples measured at 2 MHz, 7.5 and 20 MHz, 80 MHz and at 400 MHz. The solid horizontal lines show the log-average of T_{1LM} in the slow-motion regime. The same data are plotted on a frequency-normalized axes (normalized to $\nu_0 = 2.3$ MHz) in (b), with the average value $T_{1LM} \times 2.3/\nu_0 \approx 3$ ms (horizontal line). The BPP predictions at 400 MHz and 2.3 MHz are shown with the grey curved lines. The figure is adapted from ref. [71].

An anomalous behavior of T_2 was also experimentally proved for highly viscous systems, where the viscosity dependence of T_2 was found to be $T_2 \propto (\eta/T)^{-1/2}$, which again presents a significant deviation from the BPP prediction (Figure 1.12).

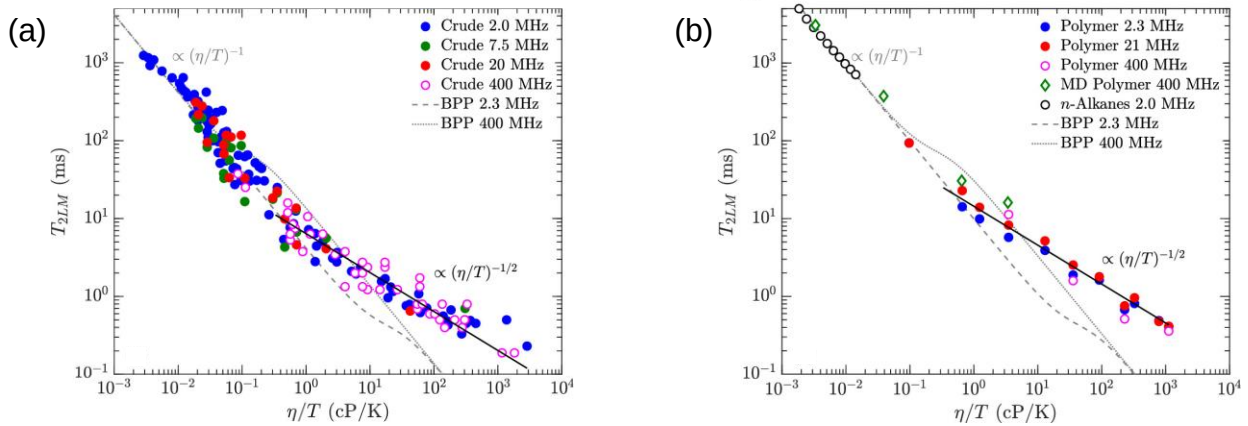


Figure 1.12. (a) Trend of the log-mean relaxation time T_{2LM} as a function of viscosity (η/T) for bitumen at 2.0 MHz^{73,74}, at 7.5 and 20 MHz⁷⁵, and at 400 MHz.⁷⁶ (b) The same plot for the polydisperse polymers shown in Figure 1.11 (a). Solid lines are fits using the model in eq. (1.37) for the high-viscosity region ($\eta/T \gtrsim 0.3$ cP/K). The BPP predictions at 400 MHz and 2.3 MHz are shown with the grey curved lines. The figure is adapted from ref. [71].

Singer et al.⁷¹ proposed a new phenomenological model to describe ^1H NMR relaxation in heavy oils, which accounts for the observed T_1 plateau and T_2 viscosity dependence. This theory is based on intramolecular dipole coupling, like BPP, but it also deals with internal motions of the non-rigid structures, and it includes distribution of correlation times. This model was developed experimentally by fitting relaxation data of various polydisperse polymers and polymer-heptane

mixes, which are commonly used for studying relaxation mechanisms in heavy oils. Internal motions of non-rigid polymer branches are described by the Lipari–Szabo (LS) model:^{77,78}

$$J_{LS}(\omega_0) = S^2 \frac{2\tau_R}{1 + (\omega_0\tau_R)^2} + (1 - S^2) \frac{2\tau_L}{1 + (\omega_0\tau_L)^2} \quad (1.34)$$

Where τ_R is the slow rotational correlation time of the polymer molecule, τ_L is the correlation time for local motion of the polymer branches, and the parameter S^2 is a measure of the rigidity of the polymer molecule, which describes the deviation of the long-chain molecule from the hard-sphere model by BPP. Rigid molecules with no internal motion of the polymer branches have $S^2 = 1$, while non-rigid molecules with fast isotropic internal motion of the polymer branches have $S^2 = 0$. In this case, $J_{LS}(\omega_0) = J_{BPP}(\omega_0)$.

The frequency exponent in eq. (1.34) is lowered from the BPP value $(\omega_0\tau_c)^2$ to $(\omega_0\tau_c)^1$ to account for the viscosity independence of T_1 in the slow-motion regime. As such, the η/T term is dropped out of the equation. Lowering the frequency exponent implies the introduction of a distribution of local rotational correlation times in the model. This leads to a significant difference from the BPP spectral densities, which account for single T_1 and T_2 values only. Woessner's theories^{79,80} show that for internal motions of less spherical molecules, which are more complex, the use of a distribution of correlation times is required. Therefore, in the new model, the exponent n in the term $1 + (\omega_0\tau_R)^n$ in the denominator of eq. (1.34) is set to 1, and the resulting spectral density is:

$$J_{LS}^{new}(\omega_0) = S^2 \frac{2\tau_R}{1 + \omega_0\tau_R} + (1 - S^2) \frac{2\tau_L}{1 + \omega_0\tau_L} \quad (1.35)$$

In the slow-motion regime ($\omega_0\tau_c \gg 1$), eq. (1.35) leads to the following leading-order terms for the relaxation rates:⁷¹

$$\frac{1}{T_1} \approx \frac{2D^2S^2}{\omega_0} \left(1 + \frac{5}{3} \frac{1 - S^2}{S^2} \omega_0\tau_L + \dots \right) \quad (1.36)$$

$$\frac{1}{T_2} \approx \frac{10}{3} D^2S^2\tau_R + \dots, \quad \text{where } \tau_R = (\tau_\eta\tau_0)^{1/2} \quad (1.37)$$

The experimental data obtained for polydisperse polymers and bitumen in the slow-motion regime are well described by these new model equations (Figures 1.11-1.12). In fact, according to this model, T_1 is proportional to frequency, $T_1 \propto \omega_0$, but it is independent of the viscosity. In eq. (1.37), the rotational correlation time is given by the phenomenological relation $\tau_R = (\tau_\eta\tau_0)^{1/2}$, which

shows the τ_R dependence on the Stokes–Einstein–Debye correlation time in eq. (1.33), i.e., $\tau_\eta \propto \eta/T$ at high viscosities. Therefore, T_2 relates to the viscosity according to the relation $T_2 \propto (\eta/T)^{-1/2}$, observed in the experimental results. Here, the term τ_0 refers to a constant which leads to the predicted behavior. The relation that describes the T_2 dependence on viscosity at high viscosities was already proposed by two different theories.^{76,81} Both theories describe relaxation in heavy oils driven by interaction between asphaltene aggregates and maltene molecules. The latter represents the lighter fraction of the oils and can relax by proton-electron interactions with paramagnetic centers in the asphaltenes⁸¹, or by ^1H intermolecular interactions modulated by slow motions due to their interactions with the asphaltenes.⁷⁶ Both type of interactions cause a reduction of the relaxation times. For example, in the study performed by Kausik et al.⁷⁶, τ_0 (which in the reference is referred to as τ_a) is defined as the sum of contributions from the rotational correlation time of the asphaltene aggregate (τ_{rot}), and the maltene's residence time (τ_m), on the asphaltene cluster. At high viscosities, the rotational motion of asphaltene aggregates becomes hindered, and τ_{rot} will be much longer. The correlation time τ_0 will be therefore dominated by τ_m , which is independent of viscosity.

1.3.4.3 Fluids under nanoconfinement

Hydrocarbon molecules confined within small pores relax more quickly than those in the bulk phase. The enhancement of the relaxation rate of these species is determined by surface relaxation. Various mechanisms of surface relaxation are analysed in *Section 1.3.4*, and these can all lead to further dephasing of the transverse magnetization. However, when small fluid molecules are strongly confined into nanopores, an additional effect may come into play. Such pores can be small enough to prevent molecules within them from making isotropic motion. As a result, these molecules will experience strong dipole coupling due to the lack of isotropic motional averaging.

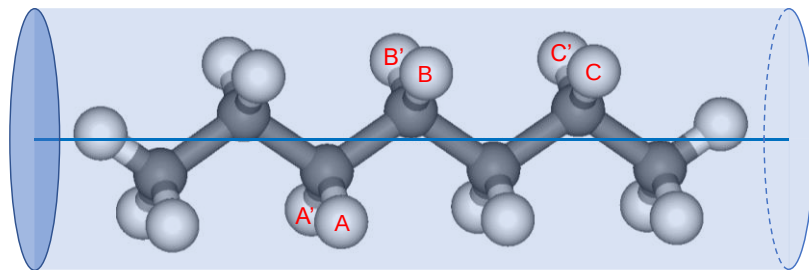


Figure 1.13. Schematic model representing a n-heptane molecule confined into a cylindrical nanopore.

Spin pair coupling	$r(i,j)$
A-B	2.53 Å
A'-B	3.10 Å
B'-B	1.80 Å
C-B	2.55 Å
C'-B	3.12 Å

$*D = (1\text{Å}/d) * 121 \text{ kHz}$

Table 1.2. Proton-proton distances $r(i,j)$ for the individual spin-pair couplings shown in the n-heptane molecule model in Figure 1.13.

As an example, the case of linear-alkane molecules that reside in tight nanopores is shown. Figure 1.13 shows a simplified representation of a n-heptane molecule located into a cylindrical pore channel with a diameter slightly larger than the Van-der-Waals diameter of a methane group (ca. 4.4 Å). In this example, we can assume that full rotation of the molecule is hindered, and only uniaxial rotation is allowed. In the case of fast anisotropic uniaxial dynamics, with correlation times much shorter than the inverse of the dipolar coupling strength, a motional-averaged residual dipolar coupling, $D_{res} = D\langle P_2 \cos(\theta) \rangle_t$, is measured. The effective dipole coupling will be scaled by the second Legendre polynomial $P_2 = (3 \cos^2 \theta_{ij} - 1)/2$, where θ_{ij} is the angle between the specific internuclear vector $r(i,j)$ and the local symmetry axis of rotation, which can be assumed to be along the molecule backbone. The distances between the different types of protons are reported in Table 1.2. The shortest distance is found for the methylene and methyl groups, with $r(B, B') = 1.8 \text{ Å}$, corresponding to a coupling of $\sim 21 \text{ kHz}$ in the absence of molecular motions. The neighbour protons B and C in the alkyl chain are 2.55 Å apart, which leads to a static coupling of $\sim 7.5 \text{ kHz}$. When the molecule undergoes fast uniaxial rotation, the BB' coupling will be scaled by a factor 1/2 ($\theta_{BB'} = 90^\circ$), while the BC coupling will not be averaged at all ($\theta_{BC} = 0$), as illustrated in Figure 1.14. Therefore, although small linear-alkane molecules are isotropic mobile components in the bulk phase ($D_{res} = 0$), they can undergo strong dipole couplings when confined to nanopore structures.

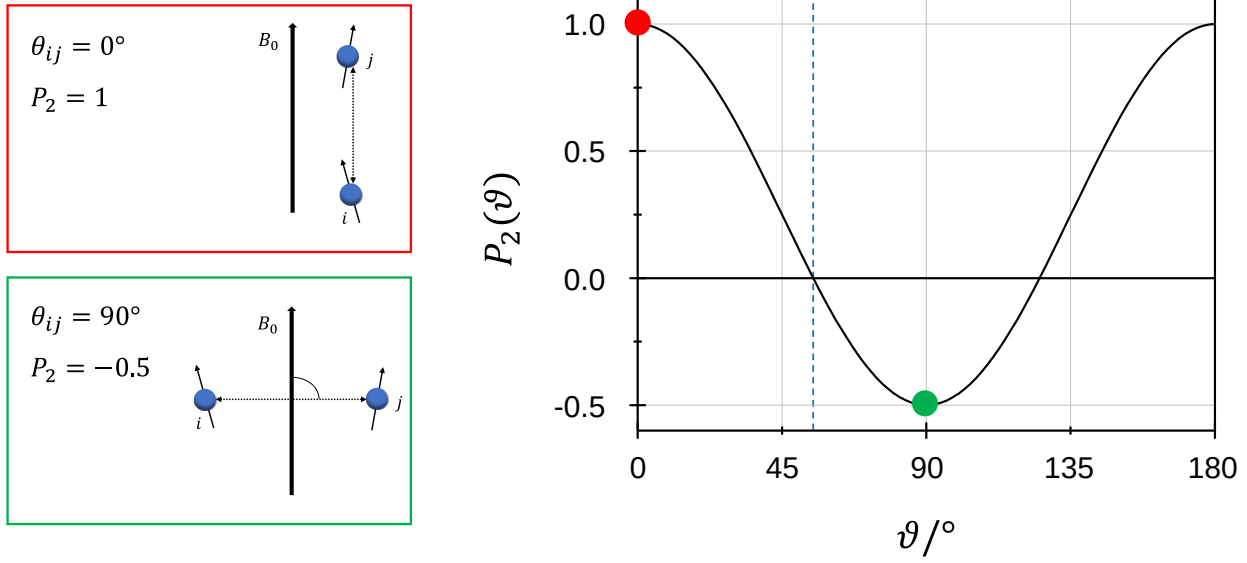


Figure 1.14. Simplified representation of the dipole coupling scaling factors for spin pairs oriented parallelly and perpendicularly to the symmetry axis of rotation (molecule backbone).

1.3.4.4 Kerogen

For solid systems like kerogen, the effective spin-spin relaxation time T_2^* reflects the coherent dephasing given by static dipolar interactions, and it cannot be interpreted in terms of BPP equations like eqs. (1.31)-(1.32). For two spins in the rigid lattice regime, i.e., in kerogen or in a fluid molecule adsorbed on the pore surface, the enhancement of the T_2 relaxation will be inversely proportional to the strenght of their coupling:^{82,83}

$$\frac{1}{T_{2D}} = |\omega_D| = \left| -\frac{\mu_0 \gamma^2 \hbar}{4\pi r_{ij}^3} \frac{1}{2} (3 \cos^2 \theta_{ij} - 1) \right| \quad (1.38)$$

where T_{2D} is the relaxation time of two hydrogen atoms which undergo dipole coupling, ω_D is the dipolar coupling frequency, γ is the gyromagnetic ratio of the nucleus of interest, $\hbar$ is the reduced Planck's constant, μ_0 is the vacuum permeability, r_{ij} is the distance between the two nuclei and θ_{ij} is the angle between the internuclear vector (r_{ij}) and the direction of the static magnetic field B_0 . Kerogen is a complex multi-spin system where multibody interactions between nearby protons at different distances and orientations lead to distributions in the dipolar couplings. Each i^{th} spin experiences a local field determined by its j^{th} neighbor, and temporal fluctuations in these local magnetic fields result in the observance of fast-relaxing time-domain signals, and consequently, of spectral line broadening. In fact, as discussed in *Section 1.2.4*, NMR signals from solid species tend to be short-lived as the strong dipole coupling quickly dephases the spins. Solid kerogen typically

exhibits short transverse relaxation times less than 50 μs , and results essentially invisible to conventional low-field (2 MHz) NMR methods as a consequence of such short signal lifetime.

1.3.5 Surface relaxation in organic matter

As described in eq. (1.28), the 1H T_2 relaxation rate of fluids in porous media can be expressed as:

$$\frac{1}{T_2} = \frac{1}{T_{2Bulk}} + \frac{1}{T_{2Surface}} + \frac{1}{T_{2Diffusion}} \quad (1.39)$$

Although shale rocks may contain significant amounts of paramagnetic impurities, these are generally extremely low in the organic matter components.⁸³ Due to the small pore sizes and the shortage of paramagnetic centers among organic pores, the effect of internal gradients on the signal appears often negligible, especially for measurements performed at low field. Consequently, the diffusion term ($T_{2Diffusion}$) can be removed in almost all situations. For small pore sizes, the bulk relaxation term (T_{2Bulk}) can be neglected as well. The relaxation time T_2 of fluids in shale pore structures is therefore dominated by surface relaxation:

$$\frac{1}{T_2} = \frac{1}{T_{2Surface}} = \rho_2 \frac{S}{V} \quad (1.40)$$

Many studies have investigated the interactions occurring in adsorbed-hydrocarbon phase trapped in kerogen pores, but the exact mechanism behind surface relaxivity remains unclear. Traditional models for quantifying surface relaxivity in conventional reservoirs are based on interactions between fluid molecules and paramagnetic impurities located on the surface of rock grains.^{66,84,85} In the context of paramagnetism, Korb et al.⁶⁴ proposed a model to describe heteronuclear coupling of protons with electrons in paramagnetic ions in asphaltenes in oil shales. However, the Korb-Nicot⁶⁴ theory cannot apply for surface-relaxivity in kerogen nanopores, as the quantity of paramagnetic species in the kerogen phase was found to be negligible.^{7,86,87} Therefore, relaxation caused by paramagnetic species in organic pores is considered minimal, leaving homonuclear dipole coupling interactions as the main responsible for surface relaxation.

Singer et al.⁸⁶ have shown the presence of intramolecular homonuclear dipolar coupling in fluid-filled organic matter. In their work, they performed T_2 experiments on kerogen isolates to avoid influence from inorganic pores. Kerogen samples were saturated with both normal distilled water and a mix of normal and deuterated water. If the presence of paramagnetic impurities was the main

cause of relaxation, the measured relaxation times of the two systems should be identical. However, for the partially deuterated system, an increase in the T_2 relaxation was observed (Figure 1.15), indicating a reduction of the intramolecular ^1H - ^1H dipole interactions. This method confirmed that homonuclear dipolar coupling among fluid protons in kerogen pores is the prevailing mechanism of surface relaxation.

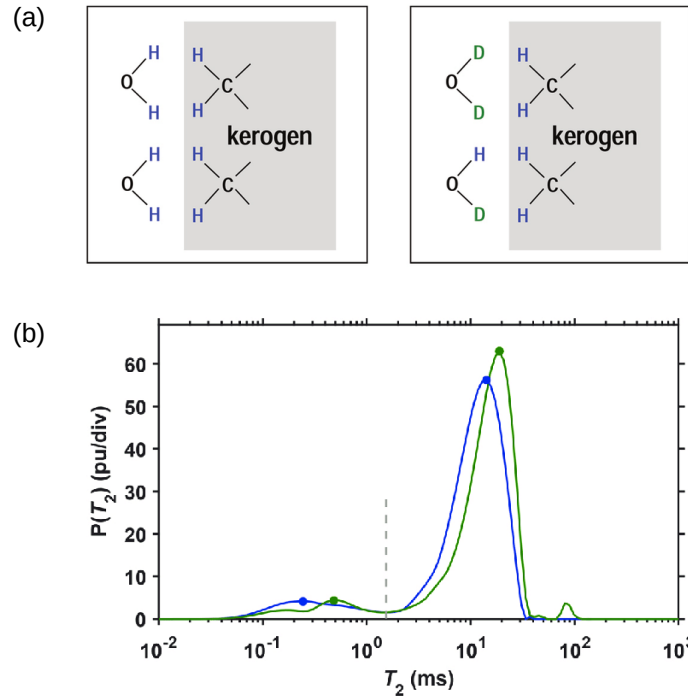


Figure 1.15. (a) Simplified schematic illustrating water molecules residing on the kerogen surface before (left-hand) and after (right-hand) partial deuteration. The partial deuteration reduces the dipole coupling between water molecules and kerogen. (b) Projected T_2 distributions from the 2D T_1 - T_2 correlation maps obtained from the two systems illustrated in (a): H₂O in kerogen (blue line) and a mix of 90 % D₂O – 10 % H₂O in kerogen (green line). The figure is adapted from ref. [86].

Zhang and Daigle⁸⁷ have confirmed that intramolecular dipole interactions are the dominant mechanism for proton surface relaxation in kerogen pores. The relaxivity model of Zhang and Daigle is readapted from the equation developed by Kleinberg et al.⁶⁶, which describes the behavior of paramagnetic surface relaxation in organic pores. While Kleinberg used this theory in the context of paramagnetism, Zhang and Daigle applied it in the context of ^1H dipole relaxation. According to their model, kerogen surface relaxivity is mainly determined by the number of adsorption sites on the pore surface, and the surface T_2 relaxation is given by:

$$\frac{1}{T_2} = \left(\frac{Sh}{V} \right) \left(\frac{m}{T_{2m}} \right) \quad (1.41)$$

Where h is the thickness of the surface layer through which relaxation occurs, and m is the relative fraction of hydrogen sites on the pore surface. T_{2m} is the transverse relaxation time for intramolecular dipole coupling in a two-spins system, which is given by the BPP equation. Therefore, the spectral densities in the T_{2m} expression assume a Lorentzian form like eq. (1.30), and they depend on a specific correlation time τ_c , which can be expressed as a combination of two different contributions:

$$\frac{1}{\tau_c} = \frac{1}{\tau_{des}} + \frac{1}{\tau_{rot}} \quad (1.42)$$

Where τ_{des} is the correlation time for molecular desorption, i.e., for how long a fluid molecule remains at the surface before exchanging with the bulk, and τ_{rot} is the rotational correlation time. It is clear from eq. (1.41) that surface relaxation due to intramolecular dipolar couplings depends on the adsorption capability of the pore surface. With a combination of theoretical analysis and experiment on kerogen isolates, Zhang and Daigle⁸⁷ concluded that oil surface relaxation in organic pores is controlled by intramolecular dipolar coupling, while water surface relaxation in kerogen probably derives from hydrogen bonding and intermolecular dipolar coupling.

Washburn et al.⁸³ reported a first direct evidence for intermolecular homonuclear dipolar coupling in organic porosity, suggesting that the dominant mechanism for surface relaxation in shales is the interaction between adsorbed hydrocarbon protons (liquid phase) and kerogen protons (solid phase). They used T_2 and T_1 - T_2 measurements on both as-received and re-saturated mudrock samples to identify liquid and solid constituents. They also performed transverse magnetization exchange measurements on re-saturated shales, demonstrating the existence of several cross peaks in the T_2 - T_2 maps which indicates an exchange of magnetization between the fluid molecules and the kerogen pore surface. Washburn et al.⁸³ proposed a new model to describe this type of surface transverse relaxation rate, which for a single pore in the fast diffusion limit is:

$$\frac{1}{T_2} = \left(\frac{Sh}{V} \right) \left(\frac{m}{T_{2D} + \tau_{des}} \right) \quad (1.43)$$

In addition to the model described in eq. (1.41), this equation contains the term T_{2D} , which is the relaxation rate for two spins in the rigid lattice regime introduced in eq. (1.38), and it is inversely proportional to the strenght of their coupling. Besides confirming a possible source of surface relaxation in shale organic matter, the results of this work⁸³ revealed the presence of coupling

between different magnetization environments, which is not encompassed by standard interpretation models of relaxation in porous media.

In their recent work, Tandon and Heidari⁸⁸ developed a new analytical method to quantify the relaxation mechanisms contributing to surface relaxation of light hydrocarbons in shale rocks. This new model is built on the generalized Langmuir adsorption (GLA) theory for the adsorption of hydrocarbons on kerogen pores, combined with the translational surface motion of fluid molecules, and considering their anisotropic rotation. The GLA theory has been successfully applied to quantify adsorption of small-chain hydrocarbon molecules onto organic/inorganic pore surfaces in shales and graphite,^{89,90,91,92,93,94} but it does not take into account surface translational motion, which has been documented for hydrocarbons in nanoporous media.^{95,96} A schematic of the new adsorption model is illustrated in Figure 1.16, and it is described in the following. The assumptions behind this theory are that (i) all adsorption sites can host only one molecule, (ii) they are energetically equivalent, and (iii) there is no interaction among molecules at adjacent sites. The hydrocarbon molecule in the free phase adsorbs onto specific sites in a single layer on the surfaces of solid grains. Then, it can leave that specific adsorption site to move to another one. During the migration to a different site, occurring in the proximity of the kerogen surface, the molecule is subject to hindered rotation, which is affected by the surface of the kerogen pore.⁹⁵ Finally, after several such interactions, the molecule detaches from the solid surface and is lost in the bulk phase.

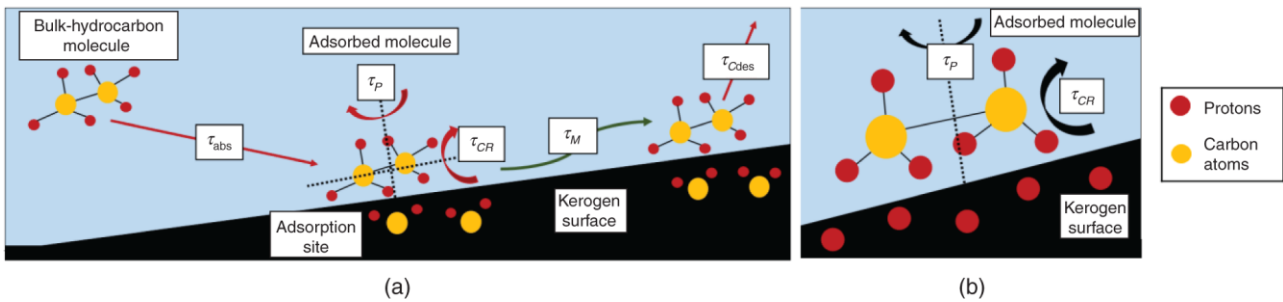


Figure 1.16. (a) Schematics of the adsorption model described by Tandon and Heidari⁸⁸ for the interaction between the hydrocarbon molecule and kerogen surface and (b) zoom in of the hydrocarbon molecule at the adsorption site. In the figure, τ_{abs} = correlation time for molecular adsorption, τ_p = correlation time in the axis normal to the plane of the kerogen surface, τ_{CR} = correlation times of hydrocarbons about axes parallel to the surface of the pore, τ_M = correlation time for the hydrocarbon molecule diffusing along the proton surface, τ_{des} = correlation time for molecular desorption. The figure is adapted from ref. [88].

As illustrated in Figure 1.16, the new surface-relaxivity model by Tandon and Heidari⁸⁸ is based on a combination of the interactions that take place at the liquid/solid interface, including both intermolecular and intramolecular dipole interactions among kerogen and hydrocarbon protons.

Therefore, the overall surface relaxivity can be expressed as a combination of individual coupling phenomena:

$$\rho_2 = \rho_{2R} + \rho_{2T} + \rho_{2RMTD} \quad (1.44)$$

Where ρ_{2R} is the intramolecular rotational surface relaxivity, ρ_{2T} is the intermolecular fluid/kerogen surface relaxivity, and ρ_{2RMTD} is the translational surface relaxivities of the adsorbed fluid molecule (RMTD meaning rotations mediated by translational displacements). The ρ_{2R} term reflects the relaxivity of the fluid molecule when adsorbed onto a specific site on the kerogen surface, and it can be estimated as:

$$\rho_{2R} = \frac{mh}{T_{2R} + \tau_{AS}} \quad (1.45)$$

where T_{2R} is time decay constant which accounts for the intramolecular rotational correlation time, and τ_{AS} is the time at the adsorption site. The value of τ_{AS} is often neglected as it is typically much lower than that of T_{2R} . The latter can be expressed as:

$$\frac{1}{T_{2R}} = \frac{3}{20} D^2 k \left[\frac{3}{2} J_{LS}(\omega_0, \tau_{CR}, \tau_I) + \frac{5}{2} J_{LS}(\omega_0, \tau_{CR}, \tau_I) + J_{LS}(2\omega_0, \tau_{CR}, \tau_I) \right] \quad (1.46)$$

Here, k represents the total number of nearest-neighbor protons in the molecule, d is the dipolar coupling constant, J_{LS} is the Lipari–Szabo spectral density function^{77,78} described in eq. (1.34), τ_{CR} is the correlation time of hydrocarbon molecule around the axes that is parallel to the surface of the pore (see Figure 1.16), and τ_I is the local interaction correlation time for internal interactions among protons undergoing intramolecular coupling. The Lipari–Szabo spectral densities were introduced to describe Internal motions of non-spherical hydrocarbon molecules. Similarly, the Intermolecular hydrocarbon/kerogen surface relaxivity at the adsorption site (ρ_{2T}) can be expressed in the following way:

$$\rho_{2R} = \frac{mh}{T_{2T} + \tau_{AS}} \quad (1.47)$$

In this case, T_{2T} is the time decay constant which accounts for intermolecular relaxation. In particular, considering the circular motion of the hydrocarbon molecule with respect to the kerogen surface illustrated in Figure 1.16b, T_{2T} is given by:

$$\frac{1}{T_{2T}} = \frac{k\pi}{60} \left(\frac{\mu_0}{4\pi} \right)^2 \gamma^4 \hbar^2 \left(\frac{\sigma_S}{d_{ij}^4} \right) \left[\frac{3}{2} J_{BPP}(\omega_0, \tau_P) + \frac{5}{2} J_{BPP}(\omega_0, \tau_P) + J_{BPP}(2\omega_0, \tau_P) \right] \quad (1.48)$$

where d_{ij} is the shortest proton distance between kerogen and the interacting hydrocarbon molecule, σ_s is the surface density of kerogen protons, and τ_p is the correlation time for conical motion of the molecule on the kerogen surface. In this expression, the spectral densities functions are those introduced by BPP theory in eq. (1.30).

Finally, the translational surface relaxivity term (ρ_{2RMTD}) was derived using the Lévy-walk statistics.⁹⁵ This model describes the effect of a molecule migration from one adsorption site to another. The underlying relaxation mechanism can be determined using the RMTD model described by Kimmich and Weber⁹⁵ and Zavada and Kimmich⁹⁷. According to this model, the main cause of relaxation is the intramolecular interaction of protons within the same molecule. However, this mechanism also accounts for restricted rotational motion of the molecule due to the kerogen surface. The translational surface relaxivity is:

$$\rho_{2RMTD} = \frac{h}{T_{2RMTD} + \tau_M} \quad (1.49)$$

where T_{2RMTD} is the time decay constant for intramolecular coupling during molecular diffusion, and τ_{AM} represents the residence time for the diffusion process. The time decay constant T_{2RMTD} can be expressed as:

$$\frac{1}{T_{2RMTD}} = \frac{3}{20} D^2 k \left[\frac{3}{2} J_{RMTD}(0, \tau_M) + \frac{5}{2} J_{RMTD}(\omega_0, \tau_M) + J_{RMTD}(2\omega_0, \tau_M) \right] \quad (1.50)$$

In this expression, J_{RMTD} is the spectral density function associated to the hindered molecular rotation.

Overall, the Tandon and Heidari⁸⁸ model explains surface relaxivity in shale organic pores, grouping together the effects of different surface interactions that take place when hydrocarbon molecules adsorb onto the kerogen surface. Experimental data and simulation analysis on shales with the new surface-relaxivity model revealed that the dominant coupling mechanism varies with the proton-surface correlation times and the applied NMR frequency. Other parameters, such as the kerogen type and hydrocarbon properties, also affect the surface relaxation in kerogen pores.

In summary, several authors have described the surface relaxation mechanism occurring in kerogen pores, and this may be attributed to the combination of several magnetic interactions, which are mainly intramolecular and intermolecular homonuclear dipolar couplings. However, the assumptions and approximations behind these models cannot be taken for granted. T_2 relaxation

mechanisms in shale can be highly complex, and only apparent T_2 values can be measured, making interpretation of NMR signals challenging.

1.4 Low-field ^1H NMR

Low-field NMR refers to the range of magnetic field strengths corresponding to $B_0 = 10 \text{ mT}$ to 1 T , equivalent to ^1H Larmor frequencies from 425 kHz to 42.5 MHz , respectively. Such magnetic fields correspond to typical bench-top and portable NMR devices based on permanent magnet technology, which are widely used in many applications involving food and agriculture industry, petrophysics analysis and biomedical studies. A summary of the most common experiments and applications performed with low-field NMR is presented in Figure 1.17.

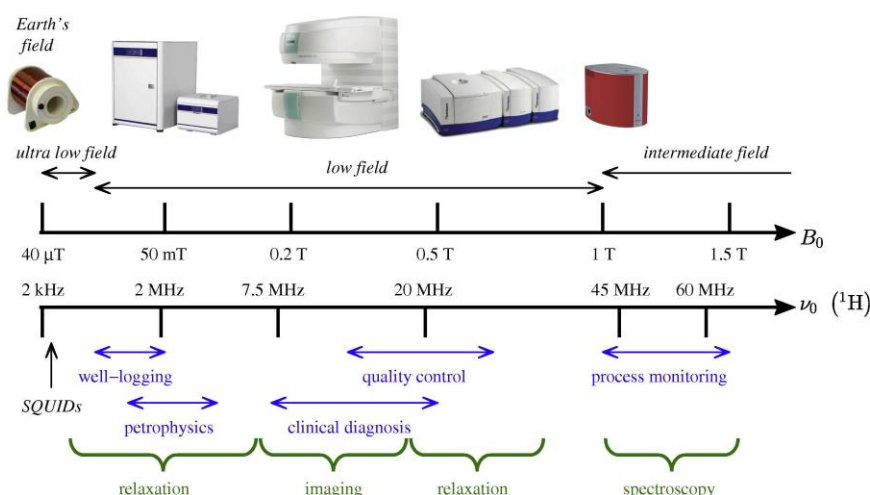


Figure 1. 17. Summary of the main applications and type of measurements for permanent magnets at various magnetic field strenghts (from $B_0 = 40 \mu\text{T}$ to $B_0 = 1.5 \text{ T}$). Permanent magnets can be used for a wide range of applications, including oil reservoir well-logging, clinical diagnosis, quality control and process (chemical reaction) monitoring. Different possible types of measurements that can be performed with such low-field devices are relaxation, diffusion and imaging. Images of several low-field NMR magnets designed for different purposes are illustrated at the top (from left to right): a Magritek Earth's field NMR system ($B_0 \sim 40 \mu\text{T}$), an Oxford Instruments bench-top rock core analyzer ($B_0 = 50 \text{ mT}$), a Siemens C-shaped whole body MRI system ($B_0 = 0.35 \text{ T}$), a Bruker bench-top analyzer ($B_0 = 0.5 \text{ T}$), and a Magritek bench-top spectroscopy magnet ($B_0 = 1 \text{ T}$). Permanent magnet designs are often tailored to specific applications and can be open-access or single-sided. The figure is adapted from ref. [59].

The weak magnetic field and poor magnetic field homogeneity of low-field NMR magnets prevent the acquisition of information on the chemical shifts of the resonance species. The free induction decay (FID) is generally dominated by B_0 inhomogeneity (liquids) or dipolar coupling (solids), resulting in intrinsic line broadening of the NMR spectra, which are largely considered unhelpful. Therefore, low-field NMR mainly relies on relaxometry, diffusion or imaging applications. Despite

the low chemical resolution, low-field NMR offers the opportunity to investigate proton dipolar coupling interactions, the intensity of which does not depend on the applied magnetic field strength.

A main disadvantage of low-field NMR is the reduced sensitivity, i.e., the signal to noise ratio will be lower due to the reduced Boltzmann factor compared to higher fields. Moreover, low-field permanent magnets are usually characterized by poor field stability. Thermal fluctuations in the magnet poles cause variation in the B_0 field which produces a shift in the Larmor frequency of the observed nuclei. Temperature stability can be improved by the presence of a large thermal mass, such as an iron yoke, which improves the temperature regulation. Also, shim coils can be placed on both sides of the NMR probe and generate appropriate magnetic field gradients to continuously compensate for the inhomogeneities of the permanent magnetic field.

Nevertheless, permanent magnets present several advantages over high-field NMR spectrometers. The high cost and immobility of high-field superconducting magnets make them inappropriate for routine analysis. Low-field permanent magnets are extremely cheap, do not require cryogenic cooling and relevant safety considerations, and provide experimental versatility for installation in various industrial environments. Beyond the practical limitations of installing high-field superconducting magnets, strong magnetic fields result inappropriate for the study of fluids in porous media. The magnetic susceptibility contrast between the solid and fluid phases at the interface gives rise to large magnetic field gradients which distort the NMR signal.⁹⁸ Such “internal gradients” are known to scale with magnetic field strength, and the application of low-field spectrometers is one method for reducing sample-induced magnetic field inhomogeneities.⁶⁰ Therefore, the evaluation of heterogeneous, fluid-saturated materials, such as oil-field reservoir rocks, is typically performed with low-field instruments to mitigate “internal gradient” effects on the observed T_2 relaxation times.

1.4.1 Benchtop spectrometers

The schematic of a basic NMR benchtop spectrometer is illustrated in Figure 1.18. The transmitter, detector and computer constitute the electronic part (the spectrometer), which can be used with different magnet configurations. A common and simple permanent magnet design (parallel plate magnet) consists of two magnetic pole pieces made of a ferromagnetic material, such as a neodymium-iron-boron alloy, which has been permanently magnetized to a constant field.⁵⁹ The

static magnetic field B_0 is generated along the z -axis between the two pole pieces. The sample is placed in a solenoid RF coil which generates a B_1 field.

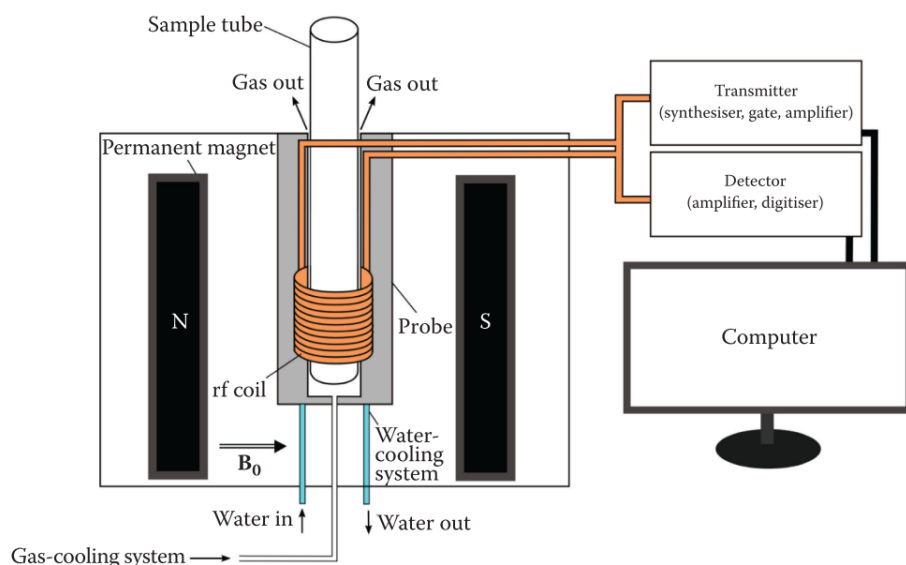


Figure 1.18. Schematic of a basic NMR benchtop instrument showing the primary components. The spectrometer is formed by primary electronic components (transmitter, detector, and computer) which can be used with a wide variety of magnet configurations. The figure is adapted from ref. [43].

A second popular magnet design for benchtop NMR is the cylindrical Halbach permanent magnet.⁹⁹ This magnet consists of a series of polarized magnetic pole pieces arranged in a circular pattern, where the direction of polarization of each piece is slightly rotated with respect to its immediate neighbors. A uniform B_0 field with zero stray field is generated across the rotating pattern of magnetic blocks in the ideal limit of an infinite number of blocks.⁵⁹ Both types of magnet configurations can be made with a broad range of magnetic field strengths for many laboratory applications. Parallel plate and Halbach magnets are currently available at magnetic field strengths ranging from $B_0 = 0.05$ T ($\nu_0 \sim 2$ MHz) for rock core analysis¹⁰⁰ to $B_0 = 1$ T ($\nu_0 \sim 42.5$ MHz) for NMR spectroscopy.^{101,102}

In this thesis, all low-field NMR experiments were performed with two Oxford Instruments benchtop Rock Core Analyzers working at 2 MHz and 12 MHz for ^1H . This type of benchtop instrument comprises a vertical-bore permanent magnet thermostated to 35°C. The B_0 field (z axis) is horizontal in the benchtop configuration, providing a solenoid RF resonator to generate a B_1 field along the vertical y -axis.

1.4.2 Well-logging tools

Unlike standard NMR spectrometers, where the sample is placed into the NMR instrument, a well-logging device is placed itself in a wellbore, at the center of the formation to be analyzed. NMR well-logging tools can measure an external sample by using a weak magnetic field while moving along the borehole. An antenna surrounding this magnet is used to transmit RF pulses to excite and acquire signal from hydrogen nuclei in a defined volume of the formation surrounding the borehole. Well-logging tools usually operate at a ^1H NMR frequency of 2 MHz, generating relatively weak and inhomogeneous magnetic fields. Due to the total absence of chemical resolution, wellbore investigations are limited to the use of ^1H relaxation data only. Figure 1.19a shows the Combinable Magnetic Resonance (CMR) tool,¹⁰³ which was designed to combine NMR measurements with a multitude of other logging techniques on a single device. The CMR tool contains permanent magnets generating a standard resonant frequency of $\nu_0 = 2$ MHz. These poles are arranged in such a way as to generate a defined “sweet spot” of known volume from which the NMR signal is detected.

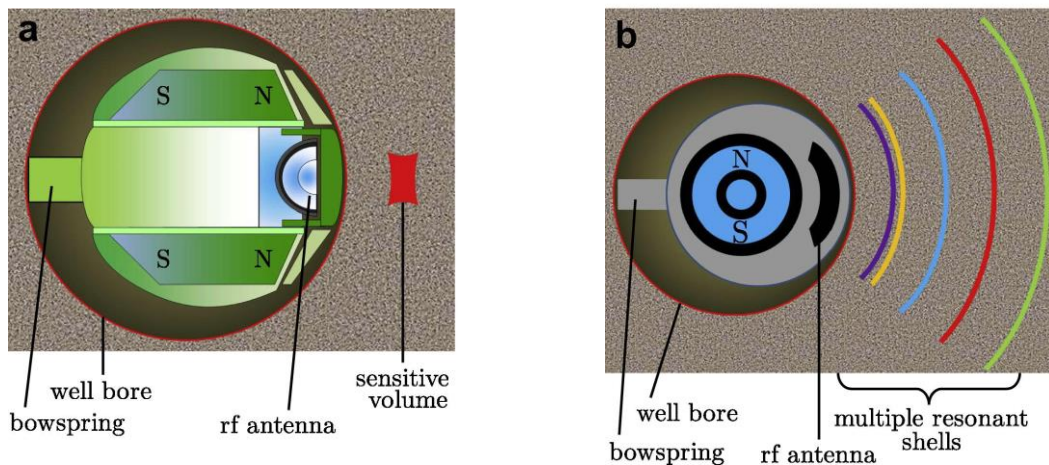


Figure 1.19. Cross-sectional diagrams of NMR logging tool sensors: (a) the Combinable Magnetic Resonance (CMR) tool, based on a sweet-spot design and (b) the Magnetic Resonance Scanner (MRScanner), based on a gradient tool design. The CMR tool has permanent magnets arranged in such a way that provide a defined sensitive volume, while the MRScanner can detect signal from multiple resonant “shells”. The figure is adapted from ref. [59].

A different tool is the Magnetic Resonance Imaging Logging (MRIL), introduced by NUMAR in 1991,¹⁰⁴ illustrated in Figure 1.19b. This device consists of a permanent magnet that generates a magnetic gradient over the formation, permitting to measure proton signal from multiple sample volumes. In fact, in the presence of a gradient magnetic field, different resonant “shells” are generated by pulses with varying frequencies, and protons in different regions of space can be excited and measured.

The most common applications of well logging tools are exploration and monitoring of a formation of interest. Exploration implies running a tool in a new well to determine the formation type, physical properties (porosity and permeability), and fluid content (oil, gas, or brine) as a function of depth. These parameters will be used for the evaluation of the commercial feasibility of a reservoir and predictions on oil or gas production volumes. Monitoring operations are employed to control the recovery of oil or gas through the formation, to estimate the lifespan of a reservoir, and to regulate injection protocols such as the enhanced oil recovery (EOR) pilot which serves for quick, cost-efficient trials of new recovery methods.

1.4.3 Limitations of low-field NMR for shale analysis

Although low-field NMR magnets operating at 2 MHz for ^1H are widely used for routine characterization of rock core samples, there are several limitations when used for analysing unconventional shales:

- The signal-to-noise ratio (SNR) is inherently poor due to the weak magnetic field, which ensures measurements on low porosity samples like shales are challenging.
- The low frequency results in long recovery delays on the RF probe so that minimum echo times are typically on the order of 100 μs , preventing the acquisition of short relaxation time components.
- The RF probe is typically optimised for standard cylindrical core plugs as in ref. [105]. However, in a commercial service it is more common to receive shale fragments for analysis. The poor probe filling factor further reduces SNR.

Together, these factors complicate the detection of solid organics and surface hydroxyls (typically characterized by $T_2 < 100 \mu\text{s}$) in most of the shale samples. Besides the loss of signal, interpretation of NMR signal may result extremely challenging because of the low SNR and the overlapping response of several components.

Fleury suggested intermediate-field NMR as the optimal tool for probing shale samples, demonstrating that at 23 MHz for ^1H ($B_0 = 0.55 \text{ T}$) it is possible to detect and identify all the protonated species present.^{55,106} As diffusion is heavily restricted in low permeability shale systems, the magnetic susceptibility contrast does not degrade CPMG data at the higher magnetic field strength. The NMR experiment inherently returns more signal due to the enhanced Zeeman splitting as the field strength is increased, and the higher frequency enables the application of shorter RF

pulses without significant deformation of the pulse shape. Short RF pulses permit short echo spacings to capture the rapidly decaying T_2 signals of the solid-like components. The higher field also simplifies some experimental aspects, such as suppression of ^{19}F signal contamination without the need for a ceramic RF coil former or digital filters with excessively long dead times.

1.4.4 Data processing: numerical inversion

When the spins in the sample have varying physical and chemical environment, they may be characterized by a range of relaxation times (longitudinal T_1 and transverse T_2) values. In this case, a multiexponential decay is observed, instead of the monoexponential decay. The signal is described by various components that can be measured by a multiexponential fitting model, based on T_1 and T_2 Bloch equations (1.14) and (1.16). When relaxation time data are expected to contain only a few components (maximum 3), the most reliable way to fit these data is through a nonlinear least-squares fit to the expected exponential function. For example, in the analysis of transverse relaxation decays, the experimental signal can be reproduced by a linear combination of exponential functions:

$$s(t) = \sum I_k \exp\left(-\frac{t}{T_{2k}}\right) \quad (1.51)$$

The least-squares fitting can be performed via an iterative algorithm, which minimizes the sum of the squared difference between data points and the function describing the data. This method allows T_{2k} parameters, as well as the relative weight (I_k) of each k component, to be obtained. However, this method is dependent on *a priori* knowledge of the number of components in the system, implying the need of several trials to find the solution and, therefore, it is not well-suited to materials characterized by a distribution of relaxation time constants. In that case, it is necessary to establish the distributions of these parameters to interpret the measured NMR data. A common approach is the use of numerical inversion operations to generate probability distribution functions of relaxation times. This procedure involves the transformation from a time domain to a domain of exponential parameters with a known range. Such transformation is achieved by fitting the distribution of the exponential parameters to the data, and it is an example of an inverse problem. The signal is decomposed into a summation of discrete exponential components, each with a unique time constant and amplitude. All NMR relaxation data can be described by a Fredholm integral equation of the first kind with the general form:

$$s(t) = \int K(x, t)f(x)du \quad (1.52)$$

Where $s(t)$ is the normalized noiseless signal, f is the probability density distribution governed by the time constants in x , and K is the kernel, i.e., the model function describing the signal. Given the NMR data $s(t)$, the aim in solving eq. (1.52) is the determination of the function $f(x)$. The inverse problem in eq. (1.52) is typically presented with the following matrix equation:

$$\mathbf{s} = \mathbf{K}\mathbf{f} + \mathbf{e} \quad (1.53)$$

where lowercase letters represent vectors, and uppercase letters represent matrices. The numerical inversion represents an “ill-posed” problem, because there is not enough information available in the data to allow the determination of a unique solution that is stable in the presence of noise. This means that large number of solutions that provide a reasonable fit to the data exist. However, a stable inversion in the presence of noise can be achieved using a regularization procedure, which is applied to estimate the most likely distribution of amplitudes for a set of predefined exponential components. Regularization is achieved by imposing constraints on the estimated solution: the distribution is always smooth, positive, and limited in range. Direct fitting of the data without regularization will result in distributions which are extremely sensitive to the noise, and not just the signal. For example, the Tikhonov regularization involves fit to the data through the following minimization problem:

$$\hat{\mathbf{f}} = \arg \min_{\mathbf{f} \geq 0} \|\mathbf{s} - \mathbf{K}\mathbf{f}\|_2^2 + \alpha \|\mathbf{L}\mathbf{f}\|_2^2 \quad (1.54)$$

Where $\|\dots\|_2$ is the Euclidean norm of the vector. The first term ($\|\mathbf{s} - \mathbf{K}\mathbf{f}\|_2^2$) is referred to as the fidelity term, and it measures the difference between the data and the fit. The second term ($\alpha \|\mathbf{L}\mathbf{f}\|_2^2$) is referred to as the penalty term, and it regulates the degree of smoothing applied to the solution. The amplitude of the penalty term is controlled by the regularization parameter, α . The operator $\mathbf{L}$ represents the choice of smoothness criterion, such as the 2nd derivative. The effect of the regularization is to search for solutions that have minimal penalty term, narrowing down the number of potential solutions. Proper selection of the parameter α is critical for the final solution. For example, a large value of α will cause smaller values of the penalty term in eq. (1.54), resulting in a smoother distribution, and larger values of the fidelity term, reducing the fit quality to the experimental data. The bias between the fidelity and penalty terms can be minimized by choosing α such that the two terms are comparable. Therefore, the regularization parameter α must be

optimized (α_{opt}) to provide the best trade-off between smoothness and accuracy in the solution. Several approaches for determining α_{opt} have been developed, and these include the L-curve method¹⁰⁷, the generalized cross-validation (GCV) method¹⁰⁸, the Butler-Reed-Dawson (BRD) method¹⁰⁹, and a uniform penalty (UPEN) function.¹¹⁰ In this thesis, the parameter α is chosen by using GCV. This method was proposed by Golub et al. and it operates through a GCV score, $\Phi_{GCV}(\alpha)$, which is determined in a way that the minimum score corresponds to α_{opt} . GCV is a cross-one out technique, where each point of the NMR signal is omitted in turn, and the accuracy of the solution at predicting the removed data points is determined. For a defined value of α , a GCV score is the average of the discrepancies between the removed points and the respective predicted values. A GCV score is therefore calculated for a range of values of α , and α_{opt} is chosen as the one that minimizes that score.

1.4.4.1 Kernel

The kernel is the model function that describes the expected form of the signal, which depends on the type of experiment (i.e., the pulse sequence). Typically, for NMR T_1 and T_2 relaxation measurements, the kernel function assumes an exponential form. For the standard CPMG experiment, the kernel function will be:

$$K = \exp(-\tau/T_2) \quad (1.55)$$

The CPMG experiment produces a list of echo times τ and a list of T_2 values, and the kernel matrix K is generated by imputing all combinations of τ and T_2 into the appropriate function. For an inversion recovery experiment to measure T_1 , the kernel function is also exponential:

$$K = 1 - 2\exp(-\tau/T_1) \quad (1.56)$$

Here, τ is the experimental recovery time after the inversion pulse. The kernel matrix therefore gives the expected form of the data for any set of experimental and fit parameters. These expected values are compared with the measured signal amplitudes in the fitting procedure to establish the most likely distributions of these parameters that reproduce the experimental signal.

1.4.4.2 Limitations of numerical inversion

When performing numerical inversion of NMR relaxation data, the resulting distribution of relaxation times is sensitive to the mathematics of the method applied. The SNR of the NMR data can be a critical factor in determining the smoothness of the final solution.¹¹¹ For example, noisy data can be excessively smoothed, while high SNR can lead to under-smoothing and instabilities in

the solution. The fit may therefore be sensitive to imperfections in the spin dynamics, such as non-ideal RF pulses, which may lead to artifacts in the distribution. Selecting the fitting parameters, in particular the choice of range and number of relaxation time coefficients being fitted, represents an important step for the determination of the distribution. It is common to see unphysical peaks appearing at the limits of the fitting range, resulting from fitting non-exponential behavior in the first few points of the NMR data. In this case, the nature of these peaks can be determined by repeating the fit with a larger fitting range: artifact peaks will move and remain at the extremities of the range. Also, repeating the experiment with slightly different experimental parameters may provide an additional way to distinguish between true peaks and artifacts. Another parameter that must be set properly is the number of data points for the acquisition of the signal. An insufficient number of data points will produce a bad fit, while too many points will overload the computation without improving the quality of the fit. A general rule of thumb in low-field NMR is to acquire 32 points, appropriately spaced on the time axis.¹¹² When fitting a multiexponential decay, for instance, the temporal separation between the points should increase logarithmically. For single-shot signal acquisitions, like for the CPMG train, large number of echoes are quickly collected and can significantly increase the computation required for the fitting. In such cases, the number of data may be reduced to 32 points through window averaging (data compression) without influencing the result.

Understanding the limitations of the numerical inversion is therefore essential for avoiding over-interpretations of the obtained fitting results. However, when NMR data are acquired with proper SNR, reasonable experimental parameters, and sufficient number of data points, the resulting distributions result stable and reliable.

1.4.5 Application of ^1H NMR relaxometry to shales

The first NMR applications for the characterization of organic-rich shales were performed with low-field NMR (2 MHz) T_2 measurements.^{105,113,114,115} These works showed fast NMR signal decays revealing that the measured NMR signals of hydrocarbons in shales are dominated by the presence of kerogen and by surface interactions. Additional NMR T_2 measurements on re-saturated shale rock samples proved that the hydrocarbon phase is mostly trapped in the kerogen pores^{113,115}, while most of the water phase was found to be and in mineral intergranular pores, or in clay micropores (clay-bound water). Several approaches have been proposed for classifying NMR signals from shales.

Rylander et al.¹⁰⁵ presented a T_2 -based classification scheme of NMR signals from Eagle Ford shale samples at different temperatures, which is reported in Table 1.3. Identification of shale components depends on specific T_2 cut-offs in the T_2 distributions obtained at low magnetic field. In general, mobile components such as water and oil will reveal relatively slow T_2 relaxation, on the order of $T_2 \sim 10 - 100$ ms, while solid-like kerogen and bitumen will show faster transverse relaxation, on the order of $T_2 \sim 100 \mu\text{s} - 10$ ms.^{55,116,117} Hydroxyl groups in clay structures or at the edge of clay platelets have extremely short $T_2 \sim 10 \mu\text{s}$.⁵⁵

Fluid	T_2/ms	Temperature dependent
Effective porosity	> 3.5-5.5	Yes
Clay bound water and bitumen	< 3.5-5.5	Yes
Free fluid (oil) in organic matter	> 10	Yes
Bound oil, residual oil	< 10	Yes
Free fluid in inter/intra particle pores	> 100	No
Capillary bound water	< 100	No

Table 1.3. Classification of NMR signals from Eagle Ford shale based on T_2 cut-offs and temperature dependence, after Rylander et al.¹⁰⁵

However, accurate quantification of oil and water saturations was limited by the overlapping magnetization decays from clay-bound water and hydrocarbons in kerogen pores. A combination of low- and high-field NMR T_1 - T_2 measurements was applied to distinguish between water and hydrocarbons in pores.^{5,116,118,119,120} Several studies performed on as-received mudrock samples revealed that hydrocarbons confined in organic pores yield $T_1/T_2 \approx 4$ or higher^{86,116,119,120}, while clay-bound and interparticle water gives rise to a signal with $T_1/T_2 \approx 2$.¹¹⁶ Hence, T_1/T_2 maps can be used to define empirical T_1/T_2 and T_2 cutoff values for estimating hydrocarbon and water-saturation values.

1.4.6 T_1 - T_2 correlation experiments

Two-dimensional T_1 - T_2 correlation experiments provide a method to identify shale components, as they can be used to separate contributions from different proton chemical environments. As described in Section 1.2.6, the behavior of the spin-lattice relaxation time T_1 depends on proton mobility and the sources of local magnetic fields: it is Larmor-frequency-dependent and has a maximum at $\omega_0\tau_c \approx 1$, where τ_c is the rotation correlation time of molecular moieties. For correlation times either larger or smaller, the rate of this relaxation process decreases. Therefore,

T_1 tends to be long both for mobile liquids or gas, where the molecular mobility is high, and solids, where molecular mobility is low.¹⁹ The T_1/T_2 ratio provides sensitivity to surface interactions and molecular mobility, while the T_2 dimension retains some sensitivity to pore size, even if limited by diffusive coupling between neighbouring pores. Fleury et al.¹¹⁶ introduced an efficient typing scheme for protons in shale samples based on the T_1 - T_2 correlation measurements performed at a Larmor frequency of 23 MHz. Figure 1.20 shows a universal T_1 - T_2 map for all different constituents of shale at a Larmor frequency of 2 MHz, proposed by Kausik et al.⁶² The different protons in the T_1/T_2 map can be assigned as follows:

- Surface hydroxyls: OH groups which are part of clay structures or located at the edge of clay platelets. This signal is always at the limit of detection for benchtop spectrometers, at $T_2 < 100 \mu s$, while T_1 can range over several orders of magnitude.
- Organic matter: the signal from solid-like organic matter can vary with maturity and overlap with that of the surface hydroxyls. The viscous bitumen typically has $T_2 < 1 ms$, and T_1/T_2 ratios ranging from 4 to 15 or even higher. Solid kerogen has extremely short T_2 and therefore it is not detectable with 2 MHz benchtop spectrometers.
- Water: this signal is typically located at $T_1/T_2 \approx 2$ even in small interparticle pores in clay structures.
- Methane: this signal overlaps with the water signal in the T_2 dimension, but it has a high $T_1/T_2 \approx 10$.¹¹⁵ The signal from methane confined in pores has no specific signature because it is in fast exchange with free methane.
- Oil: the light oil region is generally located at $T_1/T_2 \approx 2$, and as such can be difficult to distinguish from water on the T_2 axis depending on the surface wettability. Heavier oils like bitumen exhibit larger T_1/T_2 ratios depending on molecular mobility.¹⁰⁵

The same T_1 - T_2 scheme-based approach performed at a resonance frequency of 400 MHz was presented by Yang and Kausik¹¹⁷ and it shows the frequency dependence of the various shale components (see Figure 1.21). Increasing the detection frequency results in a greater dispersion, and hence easier assignment, of the T_1 - T_2 components of the immobile fractions (kerogen, bitumen, bound water) plus mobile oil in the organic pores. For example, the increased Larmor frequency allows to separate bitumen from bound water, since the respective T_1 values have a different frequency dependence. Mobile fluids (oil, water, gas) have $T_1/T_2 \approx 1$ at any frequency.

Moreover, because the higher frequency enables short echo times to be applied, kerogen is also visible in the T_1 - T_2 map.

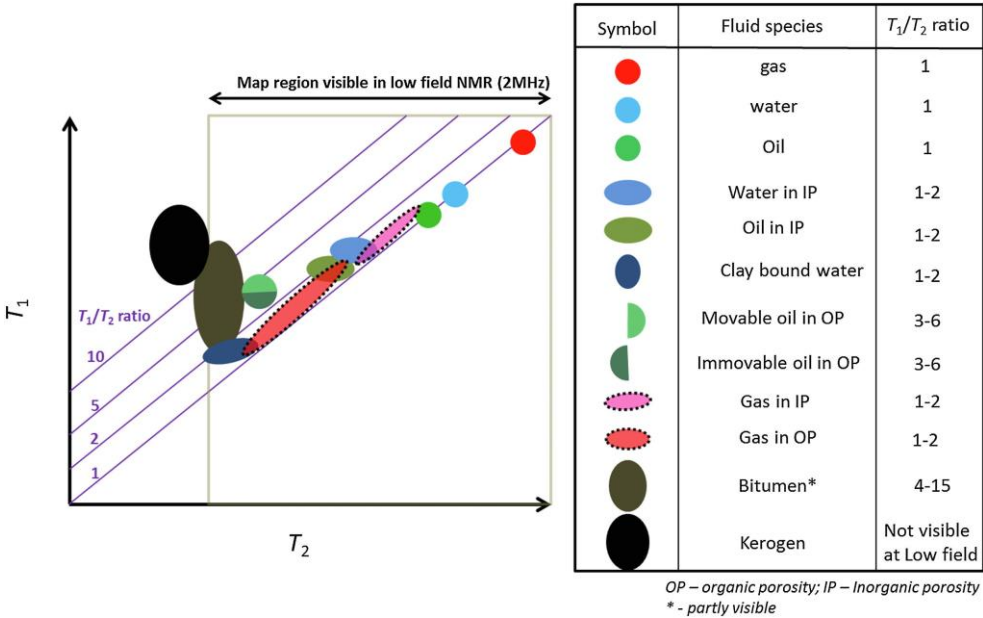


Figure 1.20. Universal T_1 - T_2 map for all the components in unconventional shales at a Larmor frequency of 2 MHz. The figure is adapted from ref. [62].

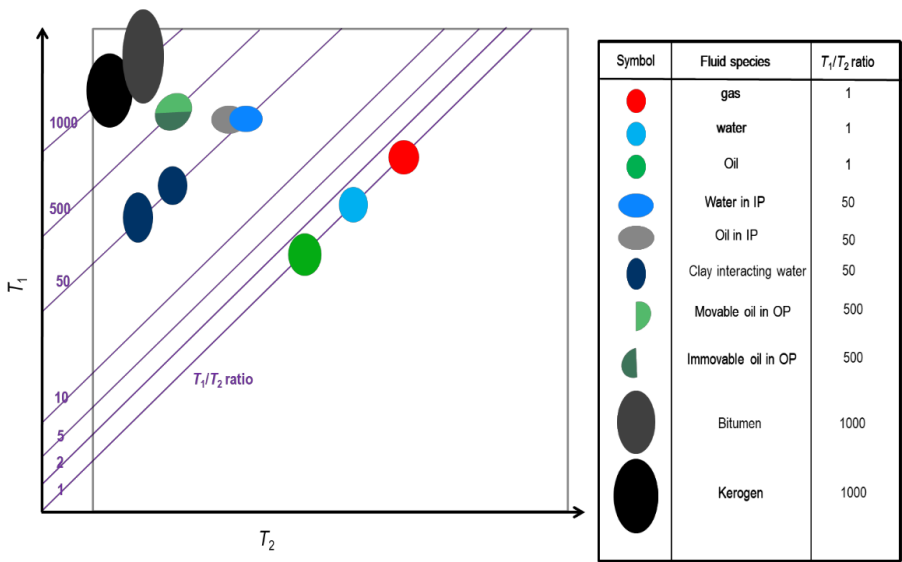


Figure 1.21. Universal T_1 - T_2 map for all the components in unconventional shales at a Larmor frequency of 400 MHz. IP = inorganic porosity, OP = organic porosity. The figure is adapted from ref. [117].

1.4.7 High-field NMR

NMR Measurements of shale at high field (e.g., $B_0 = 9\text{ T}$, $\nu_0 = 400\text{ MHz}$ for ^1H or 100 MHz for ^{13}C) have focused on specific applications such as identification of solid hydrocarbons^{121,122,123,124,125} or monitoring of fracturing under pressurized methane gas injection.¹²⁶ Compared to low-field measurements, the use of high-field NMR provides higher NMR signal to noise ratio, i.e., better sensitivity. The high frequency also enables short RF pulses to be applied, permitting short echo time spacings to be achieved. Therefore, fast-decaying signals from solid-like components can be detected.^{21,127}

Most of these high-field experiments on shales have largely relied on ^{13}C solid state magic angle spinning. This is an extremely specialised technique, requiring superconducting magnets that are prohibitively costly, and present significant HSE issues for use in a commercial core analysis laboratory. It is not practical to implement such analysis with current benchtop permanent magnet technology, even if using intermediate-field spectroscopy systems (e.g., $B_0 = 1.5\text{ T}$, $\nu_0 = 60\text{ MHz}$ for ^1H or 15 MHz for ^{13}C). It is unlikely that this class of experiments will gain widespread application in core analysis until they can be implemented robustly on benchtop spectrometers.

1.5 Spin-echo refocusing pulse sequences

Detection of fast decaying signals of organic species with limited mobility, such as kerogen and bitumen, is a challenge in ^1H NMR relaxometry of shale rocks. These components exhibit strong ^1H - ^1H dipole interactions which are not averaged out by molecular motions, resulting in short transverse relaxation times T_2 .^{20,67,68} Low-field logging tools and current laboratory benchtop spectrometers have a lower limit on spin-echo times which are typically in the order of a few hundred microseconds, too long to be able to observe fast T_2 decays.⁵⁹ One way to extend the time-domain signal and narrow the spectral lines, typically in high field solid-state NMR spectroscopy, is magic angle spinning (MAS), which averages out static field inhomogeneity, susceptibility effects, chemical shift anisotropy and dipolar interactions.⁴⁴ However, the high cost and immobility of such equipment make these inappropriate for routine analysis.⁵⁹ On a benchtop spectrometer, these challenges can be addressed through the application of spin-echo pulse sequences that refocus the coherence dephasing due to static dipolar interactions, overcoming instrumental effects (such as probe ring down) and allowing for detection of fast-decaying signals.

1.5.1 CPMG

The Carr-Purcell-Meiboom-Gill (CPMG) is the archetypal experiment for acquisition of transverse relaxation decay in well-logging measurements. This pulse sequence (Figure 1.22) is used to refocus dephasing effects due to magnetic field inhomogeneity, chemical shift and susceptibility effects.^{128,129} The CPMG pulse sequence consists of a 90° pulse followed by an echo train induced by repeatedly applying 180° pulses, and the signal is recorded at each echo maximum (every 2τ , where τ is the inter-pulse spacing). For the CPMG train to be effective, the inter-pulse spacing must be short enough to ensure slow that translational and rotational diffusion of molecules does not play a role on the loss of coherence phase. The CPMG sequence is not able to refocus signal losses due to dipolar interactions as the signs of all bilinear operators (e.g., $I_{xi}I_{xj}$, $I_{yi}I_{yj}$, $I_{zi}I_{zj}$) are not reversed by a 180° pulse.

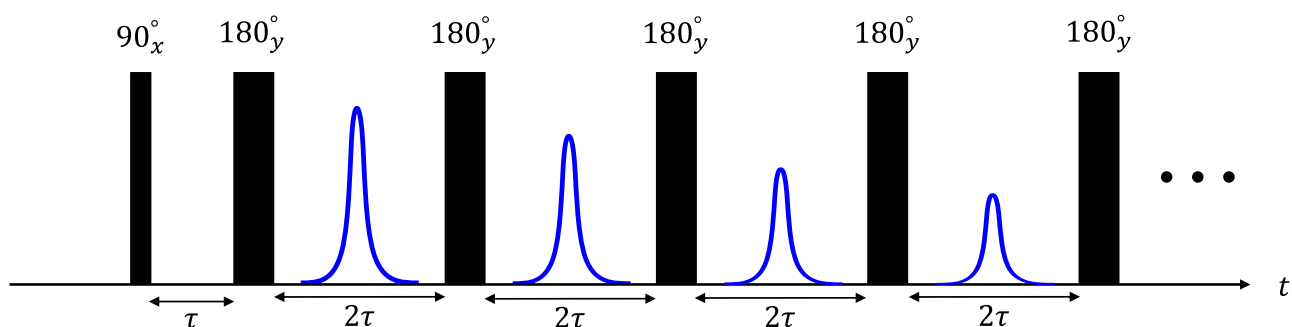


Figure 1.22. The CPMG pulse sequence.

1.5.2 Solid echo

The solid-echo pulse sequence (Figure 1.23) was developed as a method for obtaining zero-time information in the *FID* experiment for solids.¹³⁰ This method involves the application of two phase shifted 90° pulses that refocus the static homonuclear dipolar interactions, and also provides some refocusing of any I_z interactions (e.g. static field inhomogeneity), though less efficiently than CPMG. However, this technique only completely refocuses the homonuclear dipolar coupling for isolated pairs of coupled spin.^{5,68,21} For a given τ , the solid-echo pulse sequence has the lowest RF duty cycle among the sequences presented in this thesis. Consequently, within the limitation of the NMR hardware (maximum RF power, shortest dead time), the solid echo has the minimal sampling time.

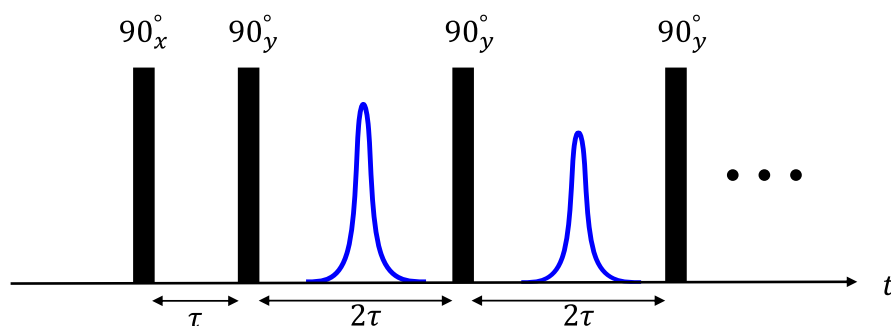


Figure 1.23. The solid-echo pulse sequence.

1.5.3 Magic echo

The magic-echo pulse sequence is another method for reversing homonuclear dipole coupling typical of solid components and, in contrast to the solid echo, is highly efficient even when nuclei undergo multiple homonuclear dipolar interactions^{21,131,132} (e.g., in a dipolar network made by more than two spins). The refocusing effect of the ME sequence is based on the averaging of dipole Hamiltonian to zero during the sequence. In Figure 1.24, the 90°_x excitation pulse flips the

magnetization on the x - y plane, and the spin system evolves under the effect of the dipolar Hamiltonian $\hat{H}_D$ during the free-evolution of duration τ . The following part comprises two time-reversal spin locking pulses (α) sandwiched between two 90° pulses of the same phase. The first 90_y° pulse excites the spins along the burst-pulse field, and the application of the pulse α induces the time reversal of $\hat{H}_D$, so that the magnetization evolves under $-0.5 \hat{H}_D$ over a time interval of 2τ . Therefore, the dipolar dephasing of the coherences during the free-evolution time τ is completely refocused after a period of 3τ , as $(\hat{H}_D) \tau + (-0.5 \hat{H}_D) 2\tau = 0$. The magnetization evolves again inversely $(-0.5 \hat{H}_D)$ in the second half of the magic sandwich. In the last free-evolution period of τ , the coherences dephase under conventional $\hat{H}_D$, so that the average dipolar Hamiltonian vanishes, and a magic echo appears at a time $t = 6\tau$.

The phase of the second 90° sandwich pulse (φ_5) can be changed to the same phase of the first 90° pulse (φ_2) obtaining the “mixed” echo version of the magic echo. The latter effectively adds another 180° refocusing pulse which acts as in the CPMG sequence without affecting refocusing of dephasing caused by dipole coupling.¹³¹ The mixed-echo sequence is therefore able to rewind static homonuclear dipolar couplings, as well as any inhomogeneous dephasing effects, such as static field inhomogeneity, chemical shift anisotropy and susceptibility effects.^{68,21} The change of the pulse phase of the second burst pulse α does not play any role in refocusing the signal, but it is necessary for the compensation of possible phase imperfections.⁴⁵

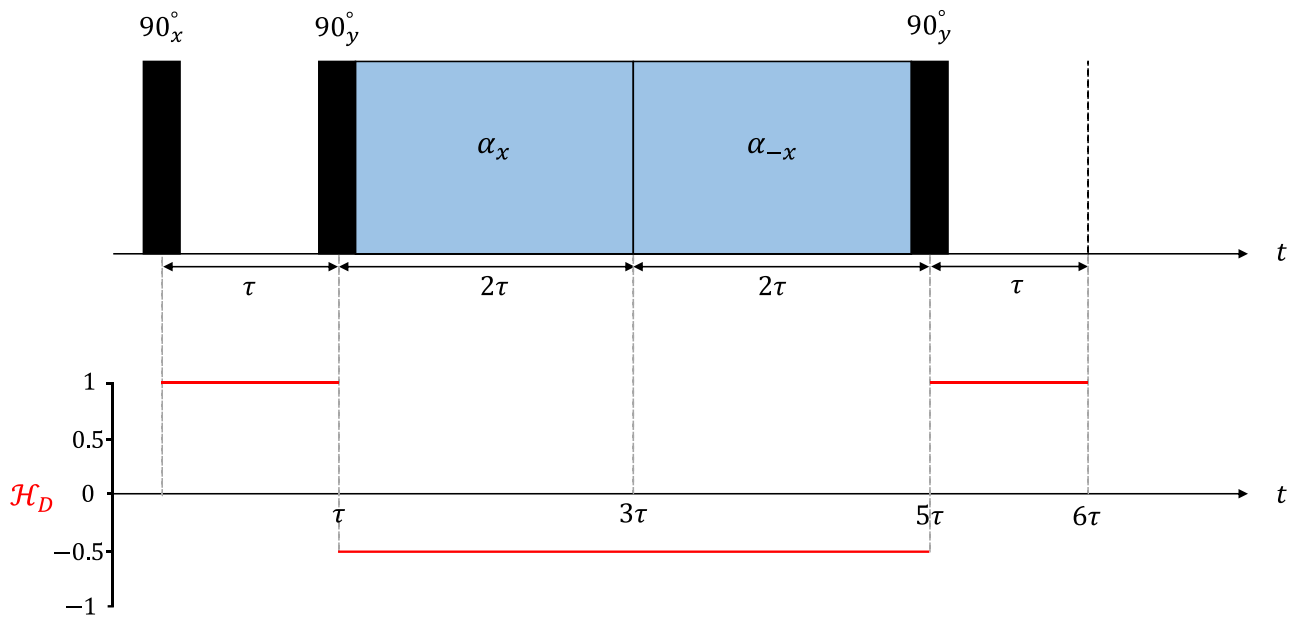


Figure 1.24. The magic-echo pulse sequence with a schematic representation of the dipolar Hamiltonian acting during the pulse sequence.

1.5.4 Two-dimensional T_1 - T_2 correlation pulse sequence

Robust separation of the shale components can be achieved with two-dimensional relaxation time correlations, although the interpretation (based on T_1/T_2 ratios) depends on the Larmor frequency which is determined by the chosen hardware. The pulse sequence for 2D T_1 - T_2 acquisitions is shown in Figure 1.25, with T_1 encoded using inversion recovery and T_2 using CPMG. The initial inversion pulse may be replaced with any suitable alternative sequence for measuring T_1 . The CPMG portion of the T_1 - T_2 correlation may likewise be replaced with a different pulse sequence, like for example the solid echo (180° refocusing pulse is replaced with a 90° pulse). The NMR data are obtained by repeating the sequence at different inversion recovery delays and acquiring a train of echoes for each delay.

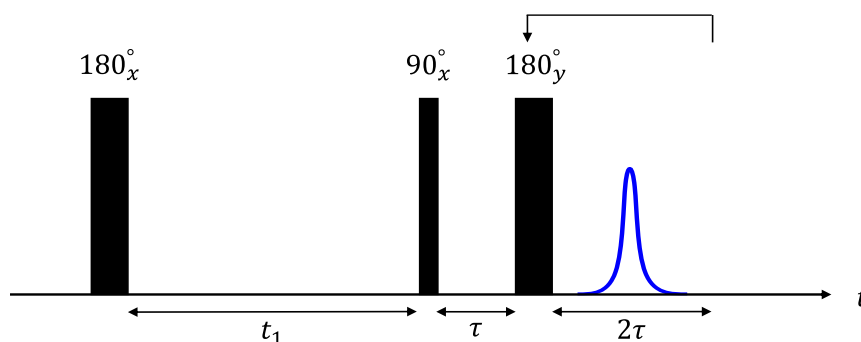


Figure 1.25. T_1 - T_2 pulse sequence for measuring correlations between T_1 and T_2 . The first portion of the pulse sequence is inversion recovery, where T_1 is encoded by incrementing t_1 over successive experiments. The second portion of the pulse sequence is CPMG. This part may be replaced by a different pulse sequence.

1.6 Double-Quantum (DQ) ^1H NMR

According to the NMR selection rules, only single-quantum (SQ) transitions ($\Delta m = \pm 1$) are allowed. A SQ coherence corresponds to an observable transverse magnetization. However, the presence of two or more interacting spins lead to multiple-quantum transitions, for which $\Delta m \neq \pm 1$. Multiple-quantum coherences cannot be directly detected, but only via manipulation of the observable SQ coherences. By applying a series of RF pulses, it is possible to track magnetization that has evolved coherently between strongly coupled spins. Double-quantum (DQ) experiments can be exploited to measure dipole couplings between the spins in dipolar-coupled systems, as the efficiency of excitation of DQ coherences is directly related to their dipolar coupling. In fact, DQ coherences

cannot be excited in the limit of fast isotopic motion, where dipolar couplings are completely averaged out. The main advantage of DQ NMR is that it can be used for direct measurements of proton residual dipolar couplings which are partially averaged by anisotropic molecular motion. The way of measuring such residual dipolar coupling generally relies on spin-echo experiments, but transverse relaxation decays tend to be contaminated by incoherent relaxation effects. In contrast to ^1H NMR T_2 relaxometry, DQ NMR methods can provide reliable separation between the coherent build-up of DQ coherences, and the incoherent loss of transverse magnetization, yielding information on dynamics and local order of the investigated material.^{133,134} In addition, due to the strong dependence of the dipolar coupling with the distance, DQ NMR represents a powerful tool to probe internuclear distances. DQ ^1H NMR techniques are widely used in polymer science for the study of polymer chain dynamics and structural constraints in a variety of systems, as extensively described by Saalwächter.¹³⁵ For these materials, the DQ signal reflects the residual proton dipole coupling resulting from restrictions of the polymer-chain mobility, posed by topological constraints such as crosslinks and entanglements.^{133,136,137,138} Over the last few years, DQ NMR has emerged as one of the most powerful methods for the study of anisotropic chain motion in a variety of systems, such as polymers and large organic molecules, as these are readily applicable to unlabeled materials, and can also be easily implemented and performed on standard low-field devices.

1.6.1 The DQ experiment

The general scheme of a pulse sequence for selectively converting the double-quantum coherence into detectable magnetization is illustrated in Figure 1.26. The sequence consists of an excitation and a reconversion part. During the excitation time, longitudinal spin polarization is converted into DQ coherences, which are generated for coupled protons for which dipolar coherent effects are stronger than incoherent relaxation processes. Since DQ coherences cannot be directly detected, the DQ signal is converted back into SQ coherence during the reconversion time. The excitation and reconversion periods have equal time duration τ , which is varied over consecutive experiments to obtain a DQ build-up curve.

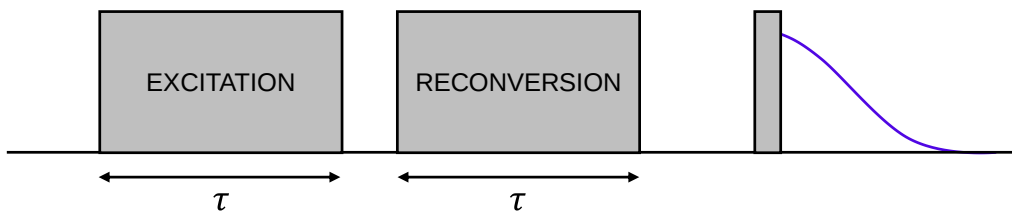


Figure 1.26. General scheme for excitation and reconversion of the DQ coherences.

1.6.2 The DQ build-up curve

The DQ build-up curve of a poly(methyl methacrylate) (PMMA) sample is shown in Figure 1.27a as an example. This curve was obtained by repeating the DQ experiment with increasing τ values.

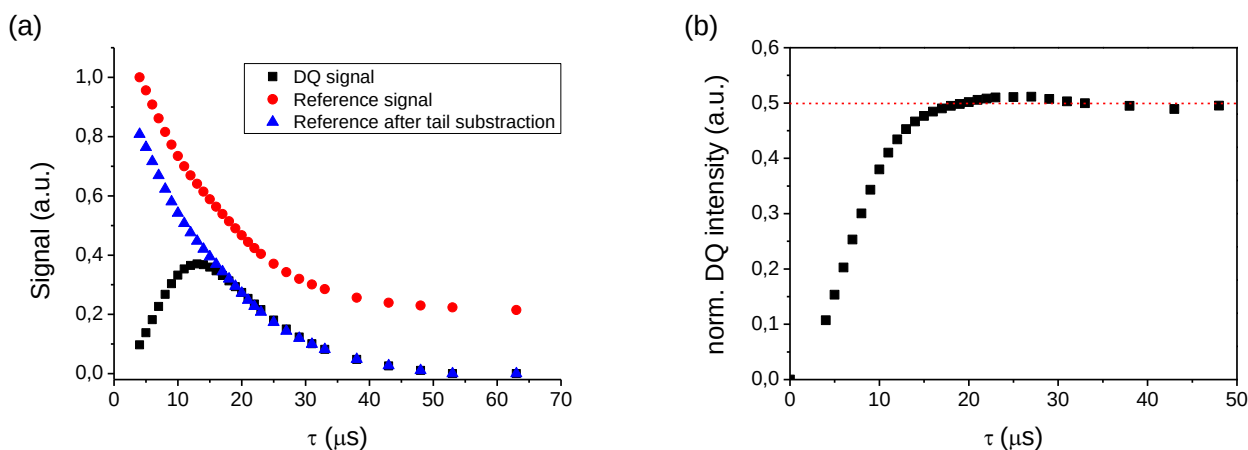


Figure 1.27. (a) Double-quantum build-up (black), reference signal (red), and reference signal after tail subtraction (blue) for a poly(methyl methacrylate) (PMMA) sample. (b) Normalized DQ build-up obtained after point-by-point normalization.

A main advantage of the DQ technique is that two complementary signal functions can be recorded with a simple change in the phase cycle of the receiver.^{139,140} In addition to the DQ build-up, which contains the desired information on the residual dipolar coupling, a reference signal can also be measured. This represents all magnetization that has not evolved into DQ, and that is subject to the same relaxation effects. The sum of the two experimental data ($I_{ref} + I_{DQ}$) reflects the full magnetization of the sample, which includes signal from strongly dipolar-coupled phases, as well as from dipolar uncoupled (mobile) protons. Note from figure 1.27a that the reference signal may also contain additional contributions from mobile species characterized by a long effective T_2 relaxation, for which the build-up of DQ coherences is slower than the overall loss of coherence phase. Such components give rise to long-time tails in the reference signal, which can be fitted and removed. For polymer systems, the relaxation contribution to the DQ and the reference signals is typically

almost equal, and it can be removed from the DQ build-up by a point-by-point normalization. This operation yields normalized DQ build-ups which carry structural information only,^{141,142} as illustrated in Figure 1.27b. The initial curvature of the normalized DQ signal underlies the relation between DQ build-ups and dipole couplings. Therefore, direct information on the residual dipolar couplings can be obtained by fitting these data to appropriate model functions. A complete account on the analysis of double-quantum build-up curves is reported in Chapter 4.

1.7 Motivation and outline of the thesis

Recovery from shale reservoirs in the present economic climate demands more efficient production with significant cost reductions. Costs and environmental impacts can be reduced through targeted drilling and fracturing, which relies on improved descriptions of the reservoir and identification of producible resources. Consequently, there remains a drive to implement new technologies for improved evaluation of shale reservoirs and better estimates of production.

The identification of hydrocarbon phases in shales represents a main challenge to the oil industry, which relies on NMR-based characterization methods. Current shale methods are based on ^1H NMR relaxation measurements performed at low magnetic fields (^1H NMR frequency ≤ 2 MHz). However, shale reservoirs are usually low in porosity and ultralow in permeability, and contain hydrogen-rich organic materials, making traditional laboratory characterization methods difficult to apply. These considerations imply a “paradigm shift” in petrophysical NMR, currently based on the knowledge that (i) NMR is lithology independent (responds only to the fluids, not the matrix), and (ii) the total signal amplitude (as measured in logging tools) is proportional to total “porosity”. Both statements are not valid for organic shales.

The main challenge in ^1H NMR relaxometry of shale rocks is the detection of fast-decaying signals of organic species with restricted mobility. Considerable advances have been made in recent years with modern digital spectrometers and with the use of multiple-pulse sequences to remove proton-proton homonuclear dipolar coupling. Some of the known refocusing methods (solid echo, magic-sandwich echo) and magnetization transfer methods (double-quantum filters) have already appeared in the petrophysical literature, with plausible but unquantified interpretations in organic shales.

The main objective of the thesis is to develop NMR methods for improving the characterization of the various organic components in heterogeneous organic shales with potentially producible hydrocarbons. The project is therefore aimed at optimization of known pulse sequences, or at the identification of new ones, which are appropriate for use under static (non-spinning) conditions and low magnetic fields, for the investigation of immobile as well as mobile hydrocarbons in shales. The aims of this project can be summarized in five main points:

- (1) to explore and optimize relevant NMR pulse sequences that remove or suppress the proton-proton dipole coupling in solid or solid-like hydrocarbons.
- (2) to identify NMR sequences that are appropriate for use under static conditions to examine heterogeneous mixtures (immobile/mobile hydrocarbons).
- (3) to implement these pulse sequence in low-field benchtop spectrometers, where magic angle spinning (MAS) is unavailable as a method for high resolution spectra.
- (4) to compare the low-field behavior with that on high-field NMR instruments to map the frequency-dependence of relaxation rates.
- (5) to develop quantitative models for the relaxation of nuclear spins under the chosen sequences, for the various component classes of organic shales.

Chapter 2 presents a study based on a combination of high-resolution solid-state ^1H and ^{13}C NMR spectroscopy methods and ^1H NMR relaxation measurements on kerogen to provide insights into the chemical and structural evolution of kerogen during thermal maturation.

In Chapter 3, various multiple-pulse sequences were explored and combined to develop new methods for identifying and quantifying both the immobile and mobile components in shales. Such pulse sequences are appropriate for the investigation of shales under static conditions and low magnetic fields.

In Chapter 4, double-quantum (DQ) ^1H NMR is applied to shale systems as a potential method for obtaining improved description of hydrogen-bearing components with limited mobility.

Chapter 5 summarises the main conclusions of the work presented within this thesis and suggests the direction for future works.

Chapter 2: Combined high-resolution solid-state $^1\text{H}/^{13}\text{C}$ NMR spectroscopy and ^1H NMR relaxometry for the characterization of kerogen thermal maturation

2.1 Abstract

A key factor for the petroleum potential of source rock is the degree of chemical and physical structure evolution of its kerogen fraction through a range of maturation processes. In this chapter, various high-field, solid-state NMR methods have been applied to a series of kerogen isolates (type I) over a defined maturity range (vitrinite reflectance R_0 from 0.98 to 1.86%). Results obtained from ^{13}C MAS NMR show that the sp^2/sp^3 -hybridized carbon ratio of kerogen, here defined as the aromatic/aliphatic ratio, increases with increasing maturity. ^1H MAS NMR spectra contain partly overlapping aliphatic and aromatic resonances with distinct transverse relaxation behavior. In Hahn-echo experiments, the aromatic signal decays more slowly than the aliphatic signal, indicating that for these systems, transverse ^1H relaxation is rather controlled by local distances between hydrogen atoms than by molecular mobility. Similar relaxation differences are also found in static (non-spinning) ^1H Hahn-echo NMR experiments, here used to discriminate between phases with different proton mobilities and/or densities in the kerogen samples and, ultimately, between aromatic and aliphatic fractions. The distributions of the static transverse relaxation time (T_2), extracted from the Hahn-echo decays, are characterized by a short- T_2 peak ($\sim 10\ \mu\text{s}$) and a long- T_2 peak ($\sim 100\ \mu\text{s}$). The ratio between these two peaks correlates well with the aliphatic-to-aromatic signal intensity ratios in MAS NMR spectra of the corresponding kerogen samples, suggesting that a net decrease in kerogen proton density—occurring during maturation—is also reflected by ^1H NMR relaxation. For the investigated kerogen isolates, the long- T_2 peak in the T_2 distribution can be considered an indicator of aromatic content, which can be directly detected by measuring ^1H T_2 relaxation.

2.2 Introduction

Kerogen is defined as the solid, insoluble organic fraction of shale rocks that generates petroleum and natural gas. Kerogen is formed from biologically derived organic matter by diagenetic processes in the first few hundred meters of burial and it is converted to bitumen and then into oil and gas during the thermal degradation process of catagenesis.^{3,5} During this stage, the increase in temperature and pressure results in a progressive alteration of its chemical structure, which undergoes successive condensation reactions leading to a gradual increase in the sp^2/sp^3 carbon hybridization ratio.^{30,31,32,33} At high thermal maturity, the kerogen structure condenses to mainly aromatic units in sp^2 hybridized graphitic structures. The quality and amount of hydrocarbon generated is controlled by the concentration, type, and thermal maturity of the kerogen.^{35,36,37} In this respect, many efforts have been devoted to the kerogen isolation and to the characterization of its chemical structure and evolution during thermal maturation, aiming at a better prediction of the potential oil and gas production.

The most commonly used parameter for thermal maturity assessment in petroleum exploration is vitrinite reflectance.³ Vitrinite is the term applied to a group of macerals (i.e., organics) with different physical and chemical properties, which change through the course of coalification.^{143,144} Vitrinite reflectance values are generally used to indicate whether a source rock is in the oil, gas, or condensate-producing windows.²⁶ Source rocks with % R_0 values less than 0.8 % are considered immature while the oil zone is between 0.8 and 1.0 %. The condensate/mixed zone is between 1.0 % and 1.4 %, and the dry gas window is for values larger than 1.4 %.¹⁴⁵

However, vitrinite materials are of terrestrial origin, and therefore, are generally rare or absent in Type I and Type II kerogens being present as a major maceral only in Type III kerogen.³⁷ Errors are involved in measuring reflectance on vitrinite, as this sub-component may not be present in kerogen. Accurate predictions of oil potential rely upon a consistent quantification of thermal maturity, which is essential for the effective assessment of source rock data. The most common analytical techniques used for detailed analysis of hydrocarbons present in source rocks and recognition of kerogen chemical structure, which may provide insights into the thermal evolution of organic matter, are destructive in nature (e.g., pyrolysis). For this reason, spectroscopic methods such as Raman spectroscopy (RS),¹⁴⁶ Fourier transform infrared (FT-IR),¹⁴⁷ X-ray photoelectron spectroscopy (XPS),¹⁴⁸ X-ray absorption near edge structure (XANES)¹⁴⁹ and solid-state nuclear magnetic resonance (ssNMR)^{150,151} have been successfully applied to study solid-like materials such

as kerogen.¹⁵² These techniques may be used to analyze the whole solid sample without the need to alter its structure (during the sample work-up for the measurements), the obtained information representing an averaged composition for the bulk sample. FT-IR may be used to investigate the structures of organic heteroatoms in kerogen and to estimate qualitatively their changes as a function of thermal maturity. The use of XPS and XANES methods offer a way to quantify organic oxygen functional groups but also to investigate organic nitrogen and sulfur species in complex carbonaceous materials. Among these techniques, magic angle spinning (MAS) ^{13}C NMR is the most reliable method for quantification of fractions of molecular components of kerogen and can be used to evaluate the aromatic/aliphatic ratio, which is considered an excellent thermal maturity indicator.^{122,153} Over the last decades, different solid-state NMR techniques have been applied to the study of structural changes in kerogen during thermal maturation, and several authors have found a correlation between NMR-derived aromaticity and vitrinite reflectance.^{121, 148,154,155,156,157,158} Most of these investigations have used the ^{13}C cross polarization (CP) MAS NMR technique, which is not able to determine the fractions of non-protonated carbons and mobile groups. Contrarily, ^{13}C direct excitation (DE) NMR can provide quantitative spectra, but this technique requires the recycle delay between scans to be five times longer than the longest ^{13}C spin-lattice relaxation time, which are often forbiddingly long. Previous studies have shown that the aromatic carbon content increased significantly in a narrow vitrinite reflectance window during petroleum generation.^{122,147,159,160} Nevertheless, the corresponding specific R_0 interval and the cause are still not clear. The aromatic carbon rate calculated by ^{13}C NMR has different relations with the vitrinite reflectance depending on the different kerogen types (I type, II type and III type).¹⁶¹ In particular, for kerogen type I, a dramatic change in the kerogen structure was observed at ca. Easy % R_0 0.80–0.90, corresponding to the peak oil window.¹⁶² Other studies have used ^{13}C NMR to track the evolution of the various carbon-containing functional groups with increasing maturity^{163,164}, revealing that the kerogen structural changes over maturation involves defunctionalization of heteroatom functional groups, the increase of total aromatic and bridgehead aromatic fraction, and shortening of the aliphatic chain length.

A limitation of using solid-state NMR spectroscopy to study kerogen thermal maturation is that it is difficult to get a detectable signal directly from shale rocks as they contain small amounts of organic materials. High resolution MAS NMR experiments are generally performed using costly, high-field superconducting magnets, their high cost making these high-field NMR spectrometers often impractical for routine analysis. Furthermore, they cannot be readily moved to different locations

in the field (or wellbore). The energy industry needs a fast, simple, and reliable method of maturity determination, which must also be cost-effective. Here, the potential of ^1H NMR relaxometry as an inexpensive and rapid alternative method to assess the maturity level of kerogen isolates is explored. The main advantage of using these measurements is that they can also be performed on simple low-field permanent magnets, which are already used for routine analysis of core samples recovered from the reservoir or directly in a wellbore.^{21,59}

In polymer systems, ^1H NMR relaxometry has been used to investigate different dynamic environments in the sample, as the ^1H transverse magnetization relaxation is essentially determined by the averaging of ^1H – ^1H dipolar interactions by molecular motions.¹⁶⁵ Proton spin-spin (T_2) relaxation experiments are generally used to investigate different dynamic environments in the polymer, such as the local chain mobility and the cross-link and entanglement densities.^{137,165,166,167,168} The analogy with polymer systems can help to understand relaxation for hydrocarbons confined in organic matter such as the bitumen and kerogen found in organic-rich shales. A key assumption of this analogy in both systems is that the NMR relaxation mechanism is not dominated by paramagnetism but by the ^1H – ^1H dipole-dipole interactions instead.^{7,70} Kerogen can be considered, essentially, to be composed of cross-linked polymers where cross-linking turns the liquid polymers into solid kerogen.⁷⁰ A second assumption is that protons are homogeneously distributed in the sample. In the presence of phases characterized by different ^1H density, ^1H T_2 relaxation measurements will also be affected by the ^1H – ^1H distances. Since the dipolar coupling strength varies with $(1/r^3)$, where r is the distance between the nuclei, sample regions of higher density will exhibit stronger couplings than those with larger average distances of the hydrogen nuclei.

In this study, several high-field, solid-state NMR techniques are applied to five kerogen samples at different maturities to investigate the structural evolution undergone by kerogen over the thermal maturation. The investigated kerogen isolates are extracted from oil shales thermally matured to various extents through a pyrolysis process performed under controlled conditions.

The primary focus is on applying ^{13}C MAS NMR to determine the aliphatic/aromatic contrast of the samples, which can be considered a thermal maturity indicator. The carbon aromatic fraction (f_{Ar}) is used as a starting point to explore whether the static ^1H T_2 measurements exhibit observable effects caused by the increased maturity and so, by the alteration of the kerogen structure. With increasing maturity, condensation and aromatization reactions lead to a progressive increase in the proportion of sp^2 bonds and a corresponding decrease of sp^3 . These molecular changes are reflected

by variations in kerogen ^1H relaxation properties. The main objective is to perform a preliminary study to assess a new possibility to use ^1H T_2 relaxation measurements as a thermal maturity test, which can be also easily implemented and performed on standard low-field devices.

2.3 Experimental

2.3.1 Preparation of the kerogen isolates

A series of staged maturity kerogen isolates prepared as part of a previous project¹⁶⁰ involving the pyrolysis of Green River shale under semi-open laboratory pyrolysis conditions carried out over a range of pressures (1–5 MPa), heating rates (2–120 °C/h), plateau temperatures (300–425 °C), and plateau times (5–12.5 h) were used for the study (Table 2.1). The spent shale remaining after pyrolysis of the shale was dispersed in a 9:1 mix of dichloromethane/methanol to extract bitumen, and subsequently demineralized by removing silicates and carbonates with hydrochloric acid and hydrofluoric acid, followed by boric acid to remove precipitated fluoride (Figure 2.1).

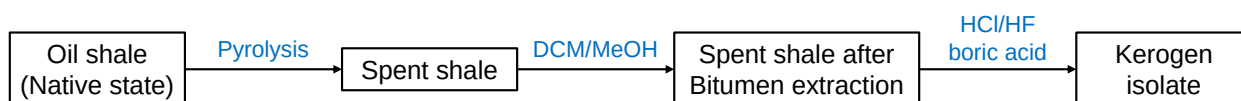


Figure 2.1. Preparation of kerogen isolates.

2.3.2 Thermal maturity measures

The thermal maturity of the kerogen isolates is often expressed in terms of vitrinite reflectance. Green River kerogen is algal in origin (type I kerogen) and thus devoid of vitrinite. For the studied kerogen isolates in this study a synthetic vitrinite reflectance, Easy % R_0 , has therefore been determined as extensively described in the Supporting Information to ref. [160]. In short, the empirical relation between vitrinite reflectance and the so-called Time-Temperature Index (TTI_{ARR}) was used to calculate Easy % R_0 as:^{169,170}

$$\begin{aligned}
 EASY\% R_0 = & 0.9412 + 0.2668 \cdot \log(TTI_{ARR}) + 0.08577 \cdot \log(TTI_{ARR})^2 \\
 & + 0.01828 \cdot \log(TTI_{ARR})^3
 \end{aligned}
 \tag{2.1}$$

TTI_{ARR} , in turn, is derived from the pyrolysis procedure: (1) linear ramp with slope $\propto$ from initial temperature $T_1 = 180$ °C to varied temperature T_2 followed by (2) constant temperature T_2 during time Δt . For a first-order rate conversion and Arrhenius dependent rate constants governed by a distribution p_i of activation energies E_i this yields: ^{171,172}

$$TTI_{ARR} = \sum_i p_i \left\{ \frac{A}{\propto} \left[\frac{RT_2^2}{E_i + 2RT_2} \exp\left(-\frac{E_i}{RT_2}\right) - \frac{RT_1^2}{E_i + 2RT_1} \exp\left(-\frac{E_i}{RT_1}\right) \right] + \Delta t A \exp\left(-\frac{E_i}{RT_2}\right) \right\} \quad (2.2)$$

The weights p_i , activation energies E_i , and pre-exponential factor A were derived from Rock-Eval kinetic measurements of the native state kerogen isolates performed in the previous project.¹⁶⁰ For the kerogen isolates in our study, the TTI_{ARR} values are mainly (> 99%) determined by the plateau temperature T_2 and duration Δt .

Sample ID	Heating rate $\propto$ (°C/h)	Temperature (°C)	Pressure (atm)	Duration time (h)	Maturity log(TTI_{ARR})	Maturity (Easy % R_0)
A	63	333	20	7.5	0.138	0.98
B	63	332	40	12.5	0.318	1.04
C	20	359	30	10	1.017	1.32
D	20	359	30	15	1.182	1.41
E	6	393	20	7.5	1.875	1.86

Table 2.1. Pyrolysis conditions and maturity measures Time-Temperature Index (TTI_{ARR}) and synthetic vitrinite reflection Easy % R_0 for the kerogen isolates.

2.3.3 ^{13}C and ^1H MAS NMR

^{13}C and ^1H MAS NMR experiments were performed on a Bruker Avance 9.4 T spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C , and equipped with a 2.5 mm Bruker HX MAS probe. ^{13}C NMR spectra were recorded either by use of cross-polarisation (CP) or Hahn-echo (HE) pulse sequences with 10 kHz MAS and under high-power two-pulse, phase-modulated (TPPM) proton decoupling. Recycle delays of 3 s and 10 s were used for CP and HE acquisitions, respectively. A contact time of 1 ms was chosen for all CP acquisitions. The 90° pulse lengths for ^1H and ^{13}C were of 5 μs and 3.5 μs , respectively.

^1H NMR rotor-synchronized Hahn-echo experiments were acquired at 20 kHz MAS, with echo time 2τ equal to an even number of the rotor period (50 μs). Evaluation of the peak-area fractions of the ^1H NMR spectra through deconvolution analysis, and estimation of relative standard errors, were performed using the origin software program. The T_2 values were measured by discrete fitting analysis of the Hahn-echo decays performed with the nonlinear least-squares method in Origin. Both ^1H and ^{13}C NMR spectra were referenced relative to adamantane, at 1.81 ppm for ^1H and at 38.56 ppm for the ^{13}C , and were acquired at room temperature. About 6-10 mg of kerogen sample were used for each experiment. Error bars for the NMR peak areas were obtained from statistical analysis of integrals over equally long baseline stretches.

2.3.4 Static ^1H NMR relaxation

Static ^1H NMR experiments were performed on a Bruker Avance 9.4 T spectrometer working at 400 MHz using the Hahn-echo pulse sequence. The first echo time was set to 10 μs , and it was gradually increased up to a maximum of 6 ms, over a total of 32 discrete τ values spaced logarithmically. A recycle delay of 3 s was used. Smooth distributions of relaxation time T_2 , constrained to be always positive and bound by set limits in the relaxation time dimension, were generated from the NMR data using the inversion method of Venkataramanan *et al.*¹⁷³ with generalized cross validation (GCV) method for optimisation of smoothing parameter. A 90° pulse length was of 3 μs was used for all experiments, and the spectrometer dead time was of 4.5 μs .

2.4 Results and discussion

2.4.1 ^{13}C MAS NMR experiments

Figure 2.2 shows a comparison of the ^{13}C NMR spectra of the staged maturity kerogen samples acquired using cross polarization (CP) and direct excitation (DE) at 10 kHz MAS. The simplest DE technique is single-pulse excitation (SPE), but the spectra are generally affected by probe ringing and pulse “leakage,” which can lead to baseline distortions. For this reason, the DE spectra were acquired by inserting a Hahn echo before detection,¹⁷⁴ obtaining a good baseline for all the spectra. The ^{13}C MAS NMR spectra consist of two distinct bands assigned to sp^3 hybridized (0–90 ppm) and to sp^2 hybridized (90–240 ppm) carbon atoms. For simplicity, these two bands are labeled “aliphatic”

and “aromatic”, respectively. Actually, the “aliphatic” band also includes sp^3 carbon connected to oxygen (e.g., ether moieties). The “aromatic” band also comprises olefin and carboxyl signals. While the two bands are clearly separated, the spectral resolution of functional groups within these bands is rather poor. Four main regions were integrated to obtain higher chemical resolution of the thermal maturation, corresponding to alkyl (0-45 ppm), alkyl ether (45-90 ppm), aromatic/olefins (90-160 ppm) and carboxyl/carbonyl groups (160-240 ppm) in the ^{13}C NMR DE spectra of the five kerogen isolates (Table 2.2).

Kerogen sample	Vitrinite reflectance (Easy % R_0)	Alkyl	Alkyl ether	aromatic/olefins	carboxyl/carbonyl
		0 – 45 ppm (%)	45 – 90 ppm (%)	90 – 160 ppm (%)	160 – 240 ppm (%)
A	0.98	67.5	14.2	18.3	< 0.1
B	1.04	70.6	11.0	18.4	< 0.1
C	1.32	46.6	12.2	41.2	< 0.1
D	1.41	14.6	6.8	78.6	< 0.1
E	1.86	14.7	5.6	79.7	< 0.1

Table 2.2. Fractions of different structural groups calculated from ^{13}C NMR DE spectra.

Both CP and DE spectra of the thermally immature kerogens (% R_0 0.98 and 1.04) are dominated by a resonance in the aliphatic region. The aromatic band increases progressively from a small fraction at R_0 0.98 % to become the dominant feature at R_0 1.41 %. Both the alkyl and ether fractions decrease with increasing maturity, but the alkyl fraction decreases relatively more than the other one. Magic angle spinning sidebands of the aromatic peak start to be observable in the spectra of kerogen at % R_0 of 1.41 and 1.86. The left-hand spinning sideband is centered at around 210 ppm, while the right-hand sideband overlaps with the aliphatic signal. All DE spectra have a relatively small sharp peak at around 110 ppm, which is not present in the corresponding CP spectra, indicating that it arises from either non-protonated carbons or carbons in mobile molecules or moieties. This small peak can be attributed to substituted alkene groups cyanides. This feature appears to stay constant as the aromatic fraction of the kerogen samples increases.

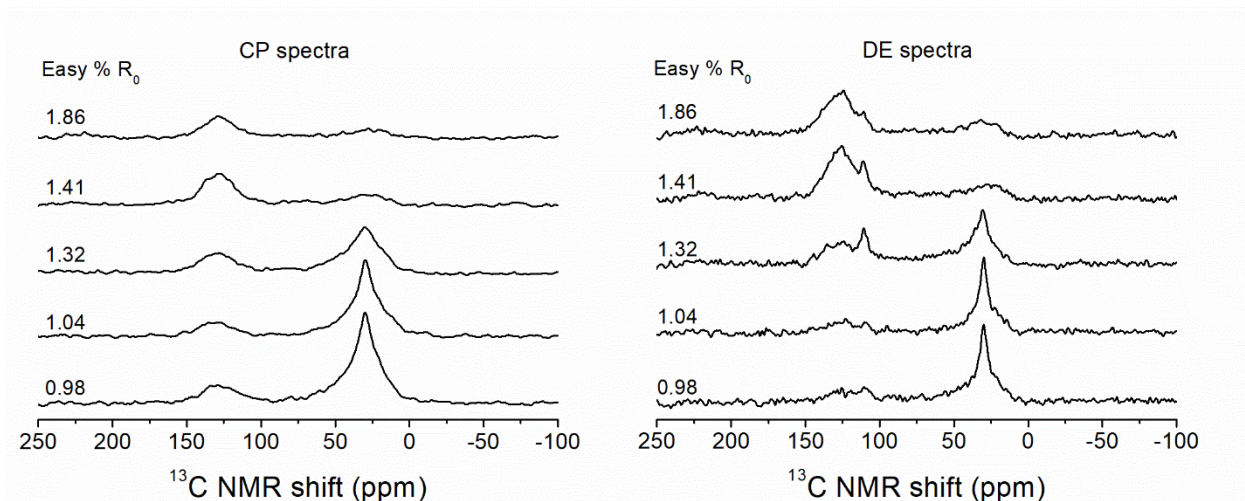


Figure 2.2. Comparison of the proton decoupled CP (left-hand side) and DE (right-hand side) ^{13}C NMR spectra of the staged maturity kerogen samples, recorded at 10 kHz MAS. The CP spectra were recorded with a contact time of 1 ms. All spectra are shown in absolute intensity mode.

The aromatic fraction (f_{Ar}) is defined as the ratio of the integrated signal of the aromatic band (90–240 ppm), to the total integrated signal.¹⁷⁵ For kerogens with % R_0 of 1.41 and 1.86, the integral of the spinning sidebands (SSBs) has been taken into account for the evaluation of f_{Ar} , assuming that both SSBs were of equal intensity (since one of these overlaps with the aliphatic signal). The values of f_{Ar} derived from both CP and DE spectra are reported in Table 2.3.

Kerogen sample	Vitrinite reflectance (Easy % R_0)	^{13}C Cross Polarization	^{13}C Direct Excitation	^1H Hahn echo
		f_{Ar} (%)	f_{Ar} (%)	f_{Ar} (%)
A	0.98	19.9	18.3	20.8
B	1.04	19.2	18.4	21.0
C	1.32	25.9	41.2	22.4
D	1.41	78.3	78.6	54.0
E	1.86	77.1	79.7	50.2

Table 2.3. Comparison of the fractions (%) of the aromatic (f_{Ar}) component calculated from CP and DE ^{13}C NMR spectra and from deconvolution of the ^1H NMR Hahn-echo spectra of the kerogen samples, and the vitrinite reflectance. The aliphatic fraction is $f_{Al} = 100 - f_{Ar}$.

Figure 2.3 shows the relative aromatic fraction f_{Ar} of the staged maturity kerogens derived from CP and DE ^{13}C NMR spectra. The relationship between aromaticity and maturity is positive but not linear. Considering CP spectra, kerogens with % R_0 0.98 and 1.04 have a similar f_{Ar} around 20%, which increases to around 26% at the vitrinite reflectance value of % R_0 1.32. Then, a large jump occurs between % R_0 of 1.32 and 1.41 where f_{Ar} increases significantly from 26% to 78%. Thereafter, the value of f_{Ar} remains constant despite a jump in the maturity window from % R_0 1.41 to 1.86. This result suggests that a significant change in structure takes place within a narrow vitrinite reflectance interval. Figure 2.3 indicates that vitrinite reflectance is not linearly correlated with the

chemical composition of the samples. The non-linearity of the trend is probably related to the way samples are prepared. The investigated kerogen isolates are what remain after the thermally matured shales are dissolved in organic solvents to remove bitumen. The extraction procedure may represent a selective step for the final chemical composition of kerogen, as soluble organics are easily removed while cross-linkages present in the organic fraction are hardly dissolved. Therefore, the extraction may alter the sp^2/sp^3 carbon hybridization ratio of the kerogen residuals.

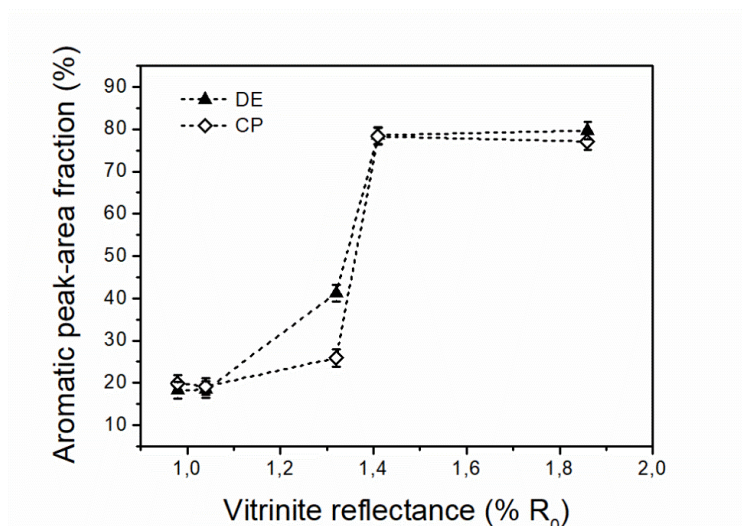


Figure 2.3. Aromatic peak-area fraction (f_{Ar}) of the kerogen samples derived from CP and DE ^{13}C NMR spectra as a function of increasing vitrinite reflectance. Error bars show standard errors.

Some inherent drawbacks related to the cross polarization technique such as low efficiency for non-protonated carbons and mobile groups¹²⁴ prevent a quantitative description of these results. Moreover, the relative intensities of the aliphatic and aromatic signals depend on the fixed CP contact time. Nevertheless, CP and DE spectra are similar, indicating that the measurements were carried out in a quasi-quantitative regime. In fact, the f_{Ar} values derived from corresponding CP and DE spectra differed by only less than 3% in all cases except for the kerogen with % R_0 1.32. In this case, f_{Ar} calculated from the DE spectrum was found to be 41.2 %, instead of the 25.9 % obtained from CP.

2.4.2 ^1H MAS NMR experiments

The ^1H NMR Hahn-echo spectra of the staged maturity kerogen samples recorded at 20 kHz MAS are reported and compared in Figure 2.4. The MAS NMR experiments were performed to resolve the aliphatic and the aromatic signals in the ^1H NMR spectra. As expected, a significant improvement in resolution is observed with respect to the same ^1H NMR spectra obtained in static conditions. This is due to the time averaging of the ^1H - ^1H dipole couplings caused by MAS. The figure shows the center band signal only, situated in the range of 0-10 ppm. The corresponding spinning sidebands are separated by the center band by 50 ppm (20 kHz) and are not present in the figure (out of range). The aromatic structures resonate at higher chemical shifts with the center of the peak around 7-8 ppm, while the aliphatic peak is centered at around 1-2 ppm. The aromatic and aliphatic peaks are partially resolved, allowing deconvolution analysis to be performed with good accuracy. The spectra in Figure 2.4 are height normalized to show how the relative aromatic/aliphatic ratio changes over the increased maturation of the kerogen. An abrupt change in the proton spectrum is observable between % R_0 1.32 and 1.41, where the aromatic signal becomes considerably larger. The aromatic fractions obtained from deconvolution analysis of the spectra are reported in Table 2.3.

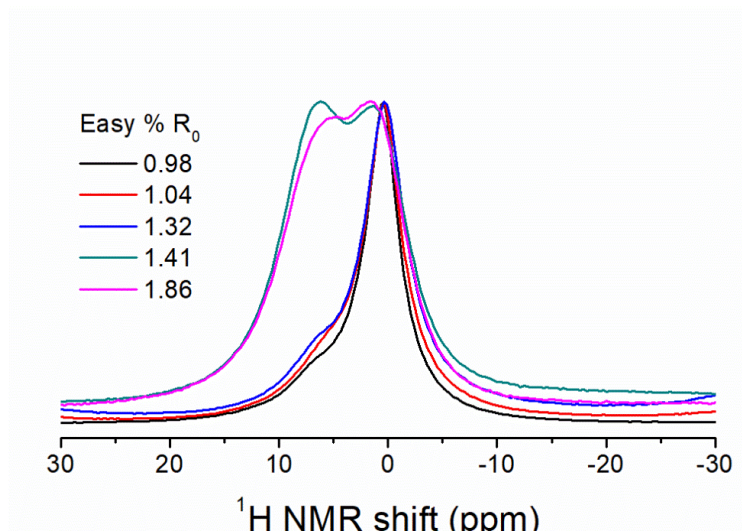


Figure 2.4. Hahn-echo ^1H NMR spectra of the staged maturity kerogen samples recorded with echo time of 100 μs and with a 20 kHz MAS.

The portion of aromatic protons stays constant at around 21-22% from % R_0 0.98 to 1.32, as shown in Table 2.3. Again, a sudden increase in f_{Ar} is observed between % R_0 of 1.32 and 1.41, where f_{Ar} rises significantly from 22.4 % to 54.0 %. Then, f_{Ar} falls slightly to 50.2 % at % R_0 of 1.86. Kerogen D and kerogen E (with % R_0 of 1.41 and 1.86, respectively) have a considerably larger aromatic content. A comparison between f_{Ar} derived from ^{13}C and ^1H NMR is illustrated in Figure 2.5. Figure 2.5a

shows that f_{Ar} obtained by ^1H NMR are always lower than those measured by ^{13}C NMR, except for the immature samples (% R_0 0.98 and 1.04), where the aromatic fractions are similar. The correlation between these two values depends on the hydrogen to carbon ratio (H/C) characteristic of the hydrocarbon compounds present in the samples. The difference may be due to the presence of fewer protonated carbons in the molecular structure of the high-maturity systems. As the maturity increases, a gradual rise in the sp^2/sp^3 carbon hybridization ratio takes place and at high thermal maturities, the kerogen structure transforms into mainly aromatic units in sp^2 hybridized graphitic structures. The H/C ratio is therefore expected to decrease with increasing maturity. However, the aromatic fractions of the staged maturity kerogen estimated by these two methods have similar trends. Figure 2.5b shows that the correlation between the aromatic fraction derived from ^1H NMR and from CP ^{13}C NMR spectra reveals a linear trend with correlation coefficient $R^2=0.99$. The correlation between ^1H NMR and DE ^{13}C NMR aromatic fraction exhibits an identical trend, except for the 1.32 % R_0 kerogen, which is found to be an outlier.

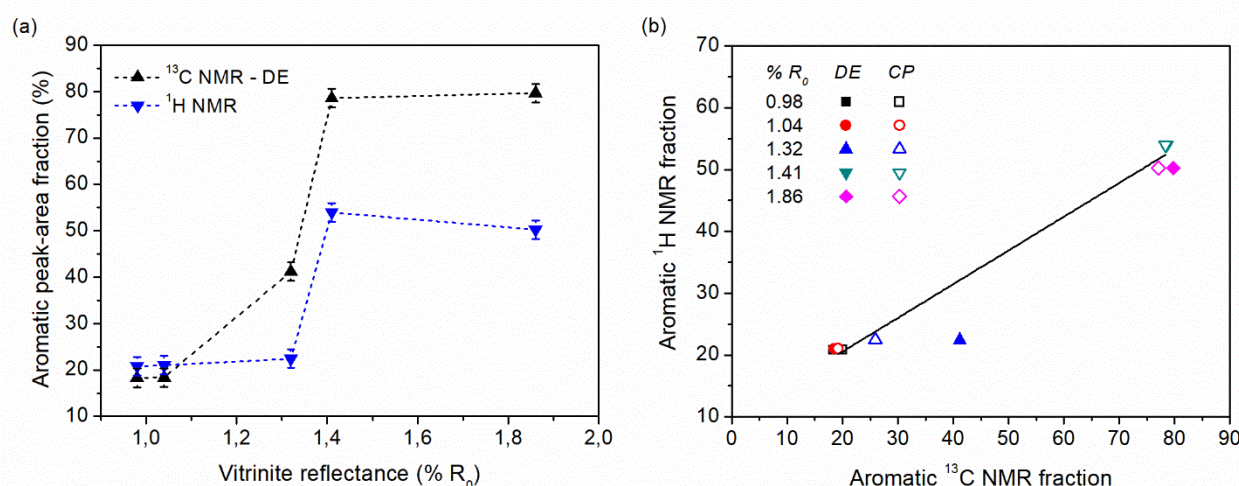


Figure 2.5. (a) Comparison between the aromatic peak-area fraction (%) of the staged maturity kerogen samples obtained from deconvolution of the 20 kHz MAS ^1H NMR Hahn-echo spectra, and from ^{13}C DE NMR spectra. (b) Correlation between the aromatic fraction measured from ^1H NMR spectra and from CP and DE ^{13}C NMR spectra, for the staged maturity kerogens. Error bars show standard errors.

Figure 2.6 shows the Hahn-echo ^1H NMR spectra filtered at different echo times (2τ) acquired for kerogen A (% R_0 0.98) and kerogen E (% R_0 1.86) to investigate the relaxation dynamics of the aliphatic and aromatic components. These two samples were chosen because they represent the two extremes of the maturity window. The ^1H NMR spectra of the two kerogen samples taken at different echo times were deconvolved with a peak-fitting analysis, as shown in Figure 2.7. As a result, the ^1H transverse relaxation decays of the aromatic and aliphatic signals were determined for both the immature (% R_0 0.98) and the mature (% R_0 1.86) kerogen. The graphs on the bottom

side of Figure 2.7 show the relative intensities of the deconvolved peaks obtained at different echo times. This type of data analysis reveals a slightly different trend for the ^1H transverse relaxation decays of the aromatic and aliphatic components. In both kerogen samples, the aliphatic and aromatic decays are monoexponential. Fitting of the data reveals that the aromatic component has a relatively slower decay, with a $T_2 \sim 250 \mu\text{s}$, while the aliphatic component is characterized by a $T_2 \sim 170 \mu\text{s}$. Therefore, ^1H MAS NMR allows the aliphatic and aromatic structures to be distinguished between, but only small differences between the two components are observed.

However, the obtained Hahn-echo decays are affected by MAS averaging. As expected, at least for a rigid solid, the exponential decays are much slower than those obtained in static conditions. Like molecular mobility, MAS also reduces/averages the dipole interactions causing the effective T_2 relaxation (T_2^*) to become slower. Unfortunately, it was not possible to perform the same type of peak-resolved analysis with the ^1H spectra obtained in static conditions, as the signal was too broad to distinguish between the aliphatic and the aromatic components.

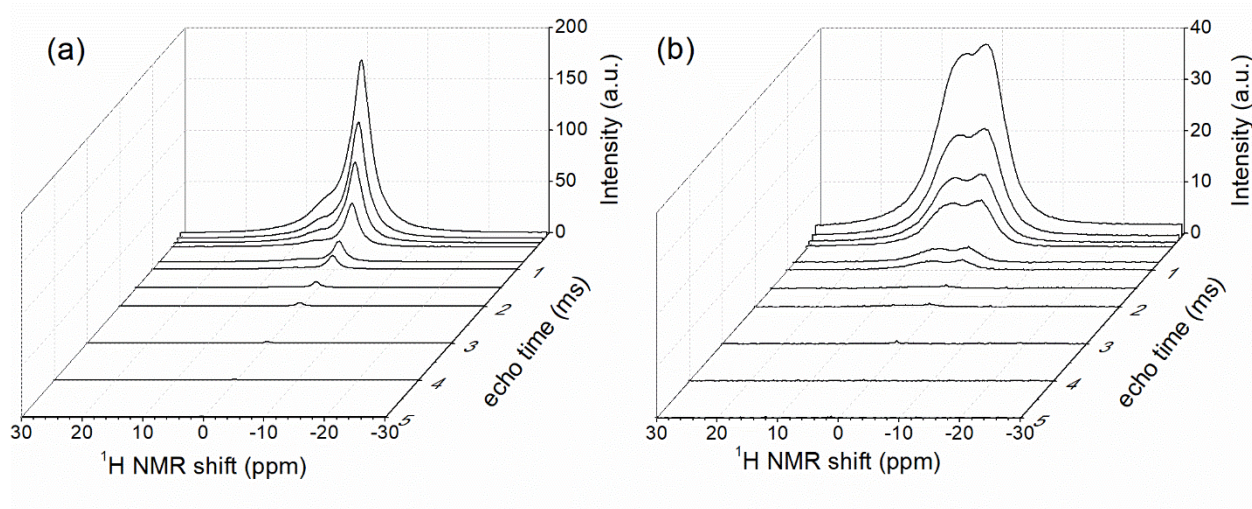


Figure 2.6. ^1H NMR Hahn-echo spectra recorded at various echo time and with 20 kHz MAS of (a) kerogen A (% R_0 0.98) and (b) kerogen E (% R_0 1.86).

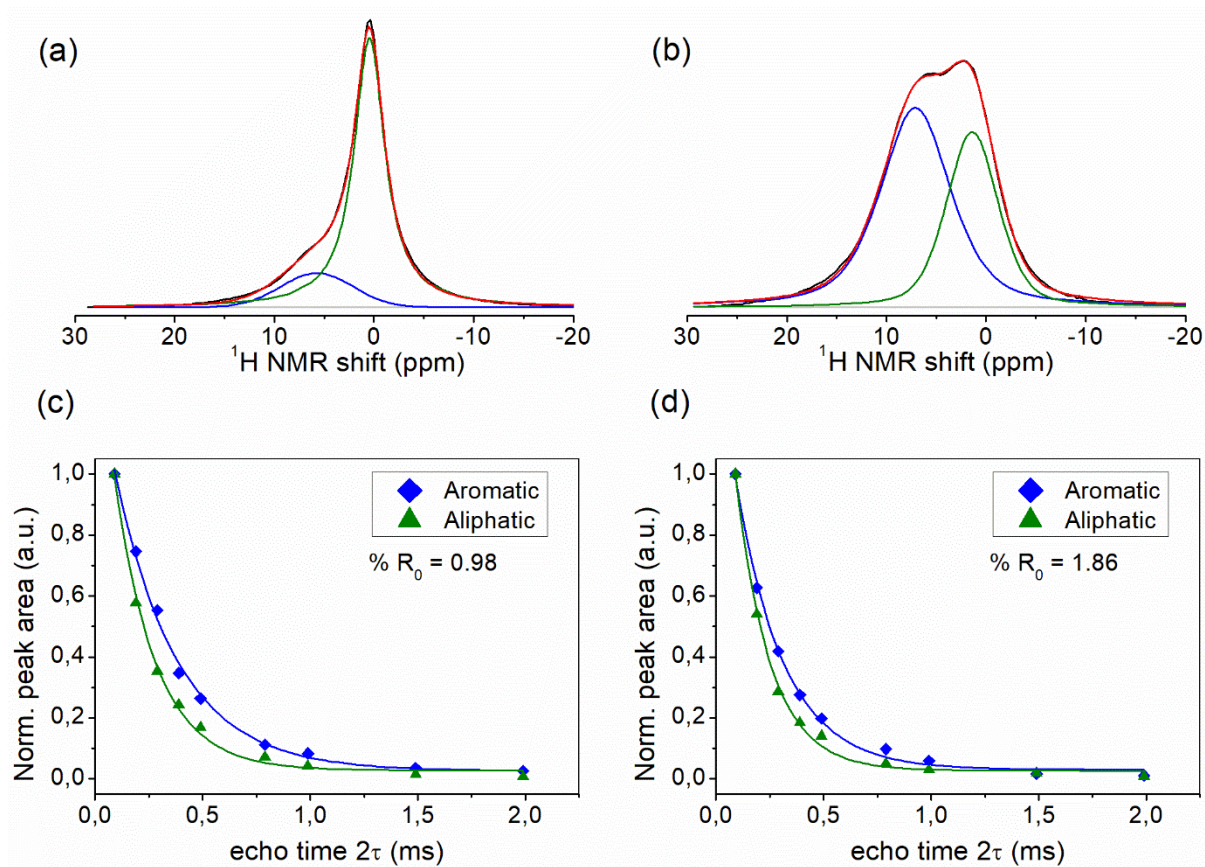


Figure 2.7. Deconvolution analysis of the ^1H NMR Hahn-echo spectrum recorded at 20 kHz MAS of (a) kerogen A (% R_0 0.98) and (b) kerogen E (% R_0 1.86). The plot shows the experimental spectrum, the deconvolved peaks and their sum (red line). The graphs on the bottom report the normalized intensities of the deconvolved peaks obtained at different echo times for (c) kerogen A (% R_0 0.98) and (d) kerogen E (% R_0 1.86), and the best fits to the data yielding T_2 s of about 250 μs for the aromatic component and of about 170 μs for the aliphatic component.

2.4.3 Static ^1H NMR experiments

Figure 2.8 shows the ^1H Hahn-echo decays of the kerogen samples at different thermal maturities obtained in static conditions and the corresponding T_2 distributions obtained using the numerical inversion method of Venkataramanan *et al.*¹⁷³ All signals exhibit a fast T_2 decay with an additional slower-decaying component, which become more significant for the more mature kerogen samples. The kerogen T_2 distributions are characterized by two well separated peaks: one centered at $T_2 \sim 10 \mu\text{s}$ and one at $T_2 \sim 100 \mu\text{s}$. The cut-off value used to separate the two signals is $T_2 = 40 \mu\text{s}$. In principle, the short- T_2 peak can be associated to protons located in rigid solid-like environments, while the long- T_2 peak is characteristic of intermediate-mobile components. Overall, the relatively short T_2 components suggest that kerogen samples are mostly made up by rigid-like domains.

Evaluation of the area under the T_2 distribution curve signals from each kerogen allows estimation of the relative intensities of the short- and long- T_2 components (Table 2.4).

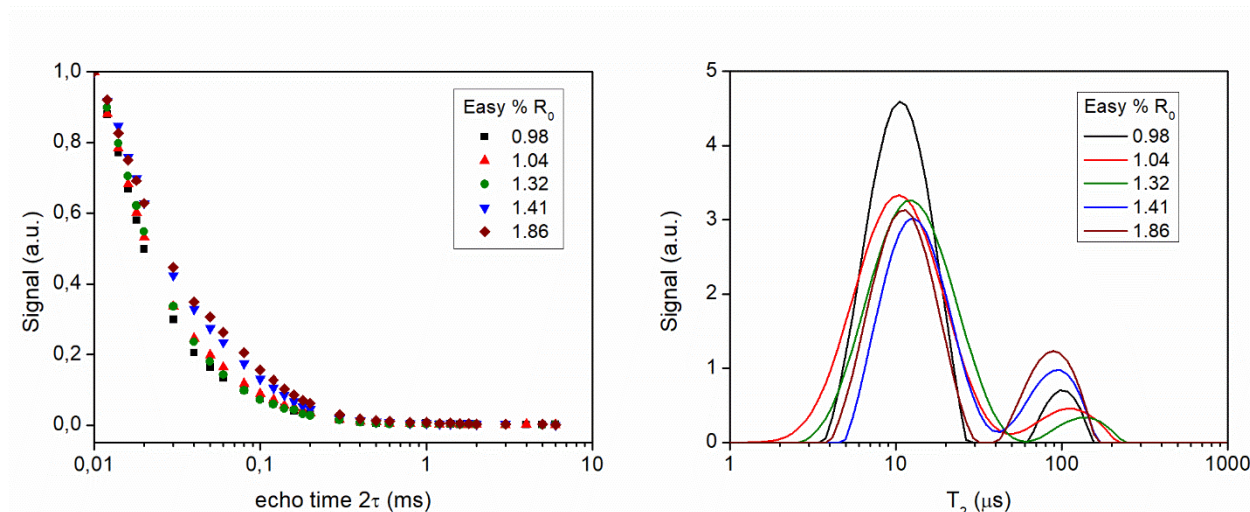


Figure 2.8. The left-hand panel shows the ^1H transverse magnetization decays of the staged maturity kerogens acquired using the Hahn-echo pulse sequence in static conditions. The right-hand panel shows the corresponding T_2 distributions obtained from numerical inversion of the Hahn-echo decays.

Kerogen sample	Vitrinite reflectance (Easy % R_0)	Peak intensity (%)	
		<i>short-T_2</i>	<i>long-T_2</i>
A	0.98	92.6	7.4
B	1.04	91.9	8.1
C	1.32	94.6	5.4
D	1.41	80.6	19.4
E	1.86	76.9	23.1

Table 2.4. Fractions of the short- ($\sim 10 \mu\text{s}$) and longer- T_2 ($\sim 100 \mu\text{s}$) signals calculated by integration of the T_2 distribution curves of the staged maturity kerogen samples.

The fraction of the long- T_2 component in the T_2 distributions is plotted against R_0 in Figure 2.9. The trend reported in Figure 2.9 indicates that the relative intensity of the long- T_2 peak becomes larger as the aromaticity (f_{Ar}) of kerogen increases. The long- T_2 peak intensity remains at a constant low fraction of 5.4 – 8.1 % for low maturity kerogen samples (% R_0 0.98-1.32). Then, it increases considerably up to 19.4% at % R_0 1.41, and after that, it stays nearly constant. This trend is similar to that of f_{Ar} measured from ^{13}C NMR (Figure 2.3), indicating that the structural jump observed at % R_0 1.32 is also reflected by the long- T_2 component in the T_2 distributions. This outcome reveals the presence of a correlation between the ^1H T_2 relaxation and the fraction of aromatic compounds present in the kerogen.

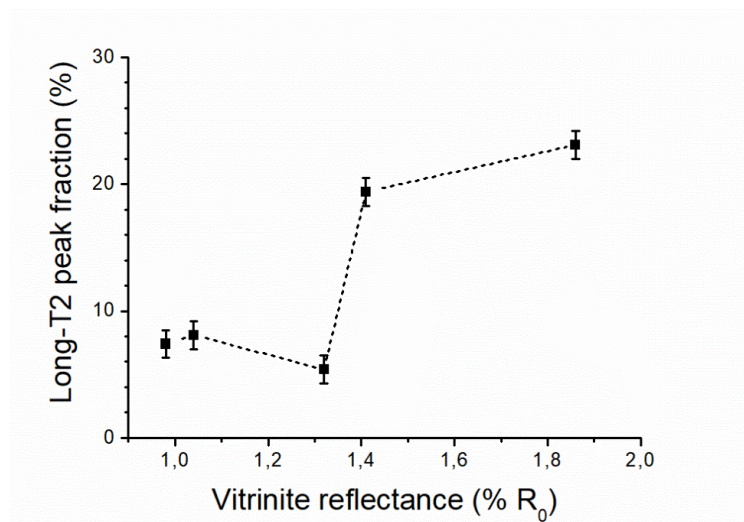


Figure 2.9. Changes in fraction of the area under the T_2 distribution curves of the long- T_2 component in relation to increasing vitrinite reflectance (Easy % R_0). Error bars show standard errors.

In polymer NMR, the decay of the proton transverse magnetization is essentially determined by the averaging of ^1H – ^1H dipolar magnetic interactions by molecular motions.¹⁶⁵ Proton T_2 relaxation is therefore a useful probe to investigate several dynamic parameters of polymer networks (e.g. local chain mobility and cross-link density). In principle, the ^1H NMR relaxation mechanisms of solid-like organic matter such as kerogen can be compared to those of polymer networks, as the main cause of relaxation for both systems is the ^1H dipolar coupling.^{70,7} An assumption behind this analogy is that protons are homogeneously distributed in the kerogen sample, like they generally are in polymer networks. If this were the case, we would expect the aromatic component to give larger contribution to the short- T_2 peak due to the restricted molecular motions characteristic of such structures. The restriction of molecular reorientations can be induced by local constraints that increase during maturation such as the shortening of the aliphatic chain length and the formation of bi-aryl zero mass bridges.¹⁶² The existence of such bridges and the short aliphatic segments between aromatic clusters in the kerogen structure generates a high degree of reticulation, which makes the anisotropic chain motions, and thus, dipolar spin interactions, not averaged to zero. Against our initial expectation, however, the long- T_2 peak becomes larger in intensity as the kerogen becomes richer in aromatic content. The observed effect on the T_2 distributions may be due to a drastic decrease of proton density of the sample that takes place over the thermal maturation. With increasing maturity, the breakdown of aliphatic moieties and the formation of aromatic units in sp^2 hybridized graphitic structures alter the chemical composition of kerogen, leading to a net loss of hydrogen molecules in the system. The larger distance between ^1H nuclei causes a more rapid decrease in their average dipolar coupling interactions, *the dipolar coupling constant being inversely*

related to the cube of the distance between the nuclei ($\Delta\omega \propto 1/r^3$).⁴⁰ Thus, the lower proton density of the aromatic fractions results in longer ^1H - ^1H distances, which in turn, are reflected by a longer- T_2 peak in the T_2 distribution.

These results are consistent with the trend observed in the Hahn-echo ^1H NMR spectra of the different maturity kerogens. The long- T_2 peak in the ^1H T_2 distributions may arise from the slow-decaying relaxation component observed through peak-fitting analysis of the ^1H NMR spectra of kerogen (Figure 2.7). This component is assigned to the ^1H transverse relaxation decay of the aromatic peak, which is found to decay more slowly than the aliphatic signal. This hypothesis is supported by the increase in the long- T_2 peak intensity in T_2 distributions observed for samples with higher aromatic fraction. Therefore, the slow decay (long- T_2 peak in T_2 distribution) can be considered as an indicator of aromatic content, which can be directly detected by measuring the ^1H T_2 relaxation decays of the kerogen samples. Nevertheless, the aliphatic/aromatic split cannot be achieved robustly on the basis of T_2 relaxation measurements alone.

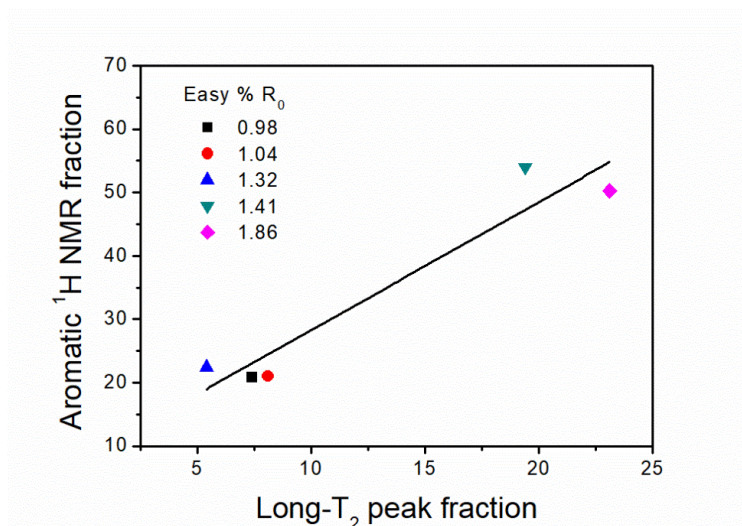


Figure 2.10. Correlation between the aromatic fraction measured from ^1H NMR spectra and the fraction of the long- T_2 component in the T_2 distributions for the staged maturity kerogens.

Figure 2.10 shows the correlation of the aromatic fraction calculated from ^1H MAS NMR with the long- T_2 fraction obtained from the T_2 distributions, for the staged maturity kerogens. The outcome is the same as the one observed by comparing f_{Ar} derived from the ^1H and ^{13}C NMR spectra (Figure 2.5b), except for the 1.32 % R_0 kerogen, which is found to be out of the maturation sequence. However, the fractions obtained integrating the long- T_2 peak in the T_2 distributions are considerably lower than those obtained by integrating the aromatic peak in the ^{13}C DE spectra. A possible explanation is that the long- T_2 peak do not reflect exclusively the pure aromatic fraction of kerogen. Both aliphatic and aromatic components contribute to both T_2 peaks to different extents, where

the aromatic molecules give a larger contribution to the long- T_2 signal. However, for this series of samples, low- and high-maturity kerogens can be identified by ^1H T_2 relaxation measurements.

Figure 2.11 shows a summary of the kerogen aromatic fractions measured from ^1H and ^{13}C MAS NMR spectroscopy and ^1H NMR relaxometry. Overall, a large structural change of kerogen within a narrow vitrinite reflectance window (Easy % R_0 1.32–1.41) is reflected in a sudden increase of the aromatic fraction (f_{Ar}) measured from either ^{13}C and ^1H NMR spectra and in a considerable rise of the long- T_2 peak intensity in the T_2 distribution. The latter may result from a net decrease of the kerogen proton density—occurring during maturation—because of the progressive increase in sp^2/sp^3 carbon hybridization ratio.

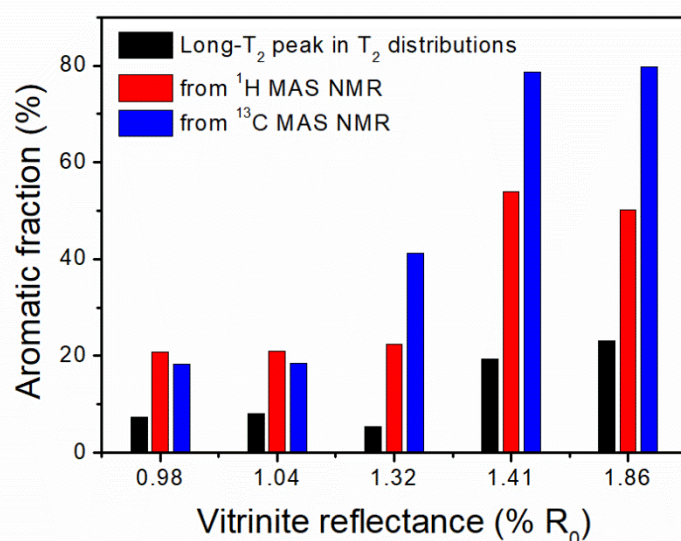


Figure 2.11. Summary bar graph reporting the relative abundances (%) of aromaticity measured from ^1H and ^{13}C MAS NMR, and of the long- T_2 peak intensity in T_2 distributions obtained from static Hahn-echo measurements, for the staged maturity kerogen samples.

2.5 Conclusions

The aim of the study presented in this chapter was to assess a new possibility to use ^1H NMR T_2 relaxometry as a thermal maturity test, which can also be easily performed on standard low-field devices. Results obtained from the staged maturity kerogen isolates show a correlation between the sp^2/sp^3 hybridized carbon ratio in the kerogen, estimated from ^{13}C MAS NMR spectroscopy, and the ratio between short and long T_2 components in static ^1H NMR relaxometry. The long T_2 component represents a kerogen phase characterized by lower proton density and can therefore be considered as an indicator for the aromatic content. The step change in the aromatic fraction

over a narrow vitrinite reflectance window (Easy % R_0 1.32–1.41) indicates that the vitrinite reflectance calculated from the pyrolysis conditions is not a reliable indicator for the sp^2/sp^3 carbon hybridization ratio in the kerogen isolates. This may be caused by the selectivity of the extraction procedure, which leaves the more insoluble fraction in the isolates behind. Further method development will be necessary to evaluate or characterize the aromatic fraction of kerogen samples from 1H NMR T_2 relaxometry at low fields.

Chapter 3: Improved Description of Organic Matter in Shales by Enhanced Solid Fraction Detection with Low-Field ^1H NMR Relaxometry

3.1 Abstract

Nuclear magnetic resonance (NMR) relaxometry is routinely used to characterize the oil fraction in unconventional shale formations with low-field benchtop NMR hardware. However, organic phases with restricted mobility like kerogen and bitumen are typically not detectable with the standard Carr-Purcell-Meiboom-Gill (CPMG) method on such equipment, with the rapid spin-spin (T_2) signal decay of these solid/viscous components not visible to the measurement. The solid-echo (SE) and mixed-echo (ME) pulse sequences offer an alternative to the CPMG, extending the lifetime of the time-domain signal and allowing the capture of solid hydrogen-containing species. Accordingly, NMR relaxation data generated from the application of the CPMG, SE, and ME experiments to a set of powdered oil- and brine-saturated Eagle Ford shale samples, are combined with the aim of identifying and quantifying both the immobile (kerogen/bitumen) and mobile (oil/brine) components. Two-dimensional relaxometry correlating spin-lattice relaxation times T_1 to the effective decay times T_2 obtained using CPMG and SE techniques provides more complete information on the immobile phases in the shales, such as solid organic matter and clay-bound water. The three spin-echo techniques have similar efficiencies when detecting signal from mobile and low-viscosity fluids, while significant differences are seen in shale samples containing immobile organics. Overall, the combination of the three spin echo techniques provides an improved description of the solid, viscous, and liquid components in the investigated shales at low magnetic field.

3.2 Introduction

Over the last 20 years, unconventional organic-rich shales have emerged as valuable systems for potential oil and gas production.⁴ Despite the prolonged downturn in the oil and gas industry, interest in shale resources is expected to continue, with some research focusing on new applications in their use to synthesize chemical products. Recovery from shale reservoirs will depend on more efficient production with significant cost reductions, which can be achieved through targeted drilling and fracturing. Consequently, improved technologies for better evaluation of shale reservoirs and predictions on production are required.^{10,11}

One- and two-dimensional ^1H NMR relaxometry is widely used for the characterization of organic matter in unconventional shale rocks.^{49,62,63,64,65} This technique relies largely on the measurements of spin-lattice (T_1) and spin-spin (T_2) relaxation times⁷, typically based on spin-echo measurements (Hahn-echo, CPMG), which can provide a variety of information on both fluids present in the formations (water, oil)⁵⁵, and porosity^{56,57} or permeability.^{2,58} Such experiments are generally performed in low-field benchtop spectrometers (^1H NMR frequency ≤ 2 MHz), for routine analysis of core samples recovered from the reservoir or in well-logging tools, for direct measurements in a wellbore.⁵⁹ Detection of fast decaying signals of organic species with restricted mobility, such as kerogen and bitumen, is a challenge in ^1H NMR relaxometry of shale rocks. These components exhibit strong ^1H - ^1H dipolar interactions, which are not properly refocused in standard Hahn-echo and CPMG methods and therefore lead to a fast loss of the NMR signal.^{20,67,68} Low-field logging tools and benchtop spectrometers (resonance frequency for ^1H of 2 MHz) have a lower limit on spin-echo times, which are typically on the order of a few hundred microseconds, too long to be able to observe fast T_2 decays.⁵⁹ One way to extend the time-domain signal and narrow the spectral lines, typically in high-field solid-state NMR spectroscopy, is magic angle spinning (MAS), which averages out static field inhomogeneity, susceptibility effects, chemical shift anisotropy, and dipolar interactions.⁴⁴ However, the high cost and complexity of such equipment make them inappropriate for routine analysis.⁵⁹ As an alternative remedy, a number of groups have applied solid-echo (SE)^{67,68} or magic-echo (ME)⁶⁸ pulse sequences that, unlike CPMG, do refocus the coherence dephasing due to homonuclear dipolar interactions and, in this way, enhance the detectability on a benchtop spectrometer.

Similarly to ref. [68], in this chapter, a combination of the CPMG, SE, and ME sequences that refocus ^1H - ^1H dipolar couplings to different extents, was used. In standard low-field (2 MHz) spectrometers, the long probe ringing times complicate detection of components with relaxation times $< 100 \mu\text{s}$.⁹⁸ By going to higher field (13 MHz) and using a spectrometer design with reduced probe ringing and receiver dead time, relaxation data with higher sensitivity and better time resolution are obtained (minimal half-echo time $20 \mu\text{s}$). In principle, the higher field comes with increased susceptibility gradients, but their effect on T_2 relaxation is minor, because diffusion is heavily restricted in low-permeability shale systems.^{7,65,100} The goal of the proposed method is to identify the fractions of solid kerogen, semisolid bitumen, and mobile oil/water in shale samples, by comparing differences in signal amplitudes and relaxation times under the different pulse sequences. This approach was first tested with extracted components of the shale, such as kerogen, bitumen, and light oil. Then, it was applied to oil- and brine-resaturated shales recovered from various depths in the Eagle Ford area. Resaturation of shale is applied to address one of the major drawbacks of the NMR core-analysis methodologies, which is the loss of mobile oil during core retrieval to the surface.⁶² The resaturation approach involves reinjecting fluids at high pressure into tight-oil shale core plugs, to make them reasonably representative of down-hole reservoir conditions. Because these samples contain both solid and liquid components, they are excellent samples to test our methodology for the organic content characterization of shales. Additional 2D T_1 - T_2 NMR relaxometry separates relaxation components from immobile organic matter and bound water, which overlap in 1D T_2 relaxometry. The proposed approach enables detailed differentiation between immobile and mobile hydrocarbon components in these heterogeneous systems.

3.3 Theory

The decay of the NMR signal in the time domain is determined by coherent and incoherent processes. Accordingly, the “effective” decay time T_2^* can phenomenologically be expressed as a sum of two contributions⁴⁴:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2'} \quad (3.1)$$

where T_2 is the spin-spin relaxation time determined by incoherent fluctuations of nuclear interactions due to random molecular motion, while T_2' characterizes the loss of transverse magnetization by coherent spin dynamics. The T_2 contribution is irreversible, but the T_2' decay can

be reversed by the application of appropriate pulse sequences. This increases the lifetime of the NMR signal and improves the detectability. Here, the case of hydrogen atom-bearing species in organic shales, for which ^1H - ^1H dipolar interactions represent the dominant relaxation mechanism, is considered.

In strong magnetic fields the Hamiltonian for the dipole interaction between two ^1H spins i and j , is approximately given by⁴⁰:

$$H_D^Z = \sum_{i < j} \omega_D(\theta_{ij}) (3I_{zi}I_{zj} - \mathbf{I}_i \cdot \mathbf{I}_j) \quad (3.2)$$

where

$$\omega_D(\theta_{ij}) = -\frac{\mu_0 \gamma^2 \hbar}{4\pi r_{ij}^3} \frac{1}{2} (3 \cos^2 \theta_{ij} - 1) = D \frac{1}{2} (3 \cos^2 \theta_{ij} - 1) \quad (3.3)$$

with γ is the gyromagnetic ratio of the nuclei, $\hbar$ is the reduced Planck's constant, μ_0 is the vacuum permeability, and D is the dipole coupling constant. The dipolar coupling frequency $\omega_D(\theta_{ij})$ is inversely proportional to the cube distance between the nuclei r_{ij} and depends on the orientation of the internuclear vector θ_{ij} with respect to the magnetic field. In most solids, there is an isotropic distribution of orientations, which causes spectral line broadening of the NMR signal or, equivalently, a reversible decay of the NMR signal, symbolized by T_2' in eq. (3.1). For comparison, in fluids with fast isotropically tumbling molecules, the now time-dependent dipolar frequency averages out on the NMR time scale, $\overline{\omega_D(\theta_{ij}(t))} = 0$, resulting in narrow NMR signals in the frequency domain. Then, the NMR decay time is mainly determined by T_2 and T_2' arising from magnetic field inhomogeneity. For viscous and semisolid systems, the dipolar interaction is somewhere in between.

BPP (Bloembergen, Purcell, and Pound) theory⁴⁸ provides a useful model to correlate dipolar coupling fluctuations induced by random molecular motions to the experimentally measurable irreversible spin-lattice and spin-spin relaxation times T_1 and T_2 . For the archetypical case of isotropic reorientation (typically small molecules in fluids), the ensemble of dipolar coupling fluctuations is characterized by a monoexponential autocorrelation function:

$$G(\tau) = \frac{5}{2 D^2} \langle \omega_D(t) \omega_D(t + \tau) \rangle = e^{-\tau/\tau_c} \quad (3.4)$$

with τ_c is the rotational correlation time. In BPP theory, τ_c is assumed to be short on the dipolar time scale ($D\tau_c \ll 1$). Fourier transformation yields the corresponding Lorentzian spectral density function:

$$J(\omega) = \frac{\tau_c}{1 + \omega^2 \tau_c^2} \quad (3.5)$$

BPP theory relates the longitudinal and transversal relaxation rates for two spin-1/2 nuclei, such as protons in water or oil molecules, to the value of $J(\omega)$ at the zero-, single- and double-quantum Larmor frequency 0, ω_0 , and $2\omega_0$, as:

$$\frac{1}{T_1} = \frac{3}{20} D^2 [J(\omega_0) + 4J(2\omega_0)] \quad (3.6a)$$

$$\frac{1}{T_2} = \frac{3}{40} D^2 [3J(0) + 5J(\omega_0) + 2J(2\omega_0)] \quad (3.6b)$$

The trend of T_1 and T_2 with increasing motion time scale τ_c follows from eqs. (3.6a)-(3.6b). In the ultrafast motion limit, $\omega_0 \tau_c \ll 1$, T_1 and T_2 are identical and inversely proportional to τ_c . This is the typical situation for small molecules in solution. As molecular mobility decreases, both relaxation times decrease until T_1 reaches a minimum around $\omega_0 \tau_c \approx 1$. Then, for samples exhibiting even slower molecular dynamics, $\omega_0 \tau_c \gg 1$, T_1 increases again proportional to τ_c whereas T_2 continues to decrease as it is dominated by the $J(0)$ term. This is typically the case for molecular motion in viscous media. Combined measurement of T_1 and T_2 relaxation, especially in the form of 2D T_1 - T_2 maps, can be used to distinguish between components with different mobility in heterogeneous mixtures like oil and water in porous media.

T_1 and T_2 expressions such as eqs. (3.6a)-(3.6b) are frequently referred to in the petrophysical literature. However, it should be stressed that the underlying assumptions are not valid for highly viscous and solid systems, in which isotropic motion is slow or absent. Consequently, the spin-spin relaxation time T_2 cannot be quantitatively interpreted in terms of eq. (3.6b). In such systems, dipole interactions are only partially averaged by restricted (anisotropic) motions, and the residual dipolar coupling leads to a quick loss of single-quantum coherence. The resulting short NMR signals can be difficult to detect on benchtop spectrometers. It is therefore advantageous to use pulse sequences to suppress the dipolar Hamiltonian, hence extending the lifetime of the time-domain signal, by canceling the $(3I_{zi}I_{zj} - \mathbf{I}_i \cdot \mathbf{I}_j)$ contribution in eq. (3.2) through careful manipulation of the spin ensemble.

3.4 Experimental

3.4.1 Sample preparation

A series of twin core plug shales extracted from various depths in the Eagle Ford area, resaturated with either oil (Isopar-M, paraffin oil) or brine solution (6 wt % NaCl brine), were used for this study (Table 3.1). These samples were prepared as part of a previous project using the high-pressure core resaturation setup described in ref. [62]. The resaturation setup consists of a polyether ether ketone (PEEK) sample holder located within a fiberglass unit connected to both a high-pressure pump, supplied with either paraffin oil or brine solution, and a vacuum pump, through a three-way valve system. Each shale core plug was cut in half, one part saturated with oil (labeled as set A) and the other one with brine (labeled as set B), forming a set of twin samples. After saturation, the shale core plugs (38 mm diameter) were crushed into powders for NMR measurements in the small-bore probe (18 mm internal diameter). The powder samples were placed in 5 mm diameter NMR tubes, which were filled to a height of ~ 5 cm.

Sample ID	Core depth (ft)	Bulk volume (cm ³)		Mass (g)	
		<i>Oil saturated (A)</i>	<i>Brine saturated (B)</i>	<i>Oil saturated (A)</i>	<i>Brine saturated (B)</i>
1	7042.28	27.4	22.8	70.4	59.0
2	7048.40	25.7	27.1	64.2	67.9
3	7179.45	25.7	26.8	66.5	69.8
4	7338.45	32.3	26.5	83.4	68.5
5	7371.20	22.1	33.0	55.2	83.5
6	7429.30	18.0	17.5	45.4	44.0
7	7465.70	25.0	26.4	62.7	66.9
8	7603.50	29.8	30.4	77.1	79.0
9	7656.90	31.1	27.7	77.7	69.8
10	7668.25	29.6	30.2	76.1	78.3

Table 3.1. Description of the oil-saturated (labelled as A) and brine-saturated (labelled as B) shale core plug samples. Bulk volume and mass values refer to the core shale sample prior to crushing.

3.4.2 Spin-echo refocusing pulse sequences

The standard CPMG pulse sequence (Figure 3.1a) is used to refocus dephasing effects due to magnetic field inhomogeneity, chemical shift, and susceptibility effects.^{128,129} However, the CPMG sequence is not able to refocus signal losses due to dipolar interactions. The solid-echo and magic (mixed)-echo sequences (Figure 3.1b and 3.1c, respectively) are well known methods to refocus dipolar interactions of solid components. While the solid-echo pulse sequence only completely refocuses the homonuclear dipolar coupling for isolated pairs of coupled spins, the magic-echo pulse sequence is highly efficient even when nuclei undergo homonuclear dipolar interactions with more than one other spin.^{21,131,132}

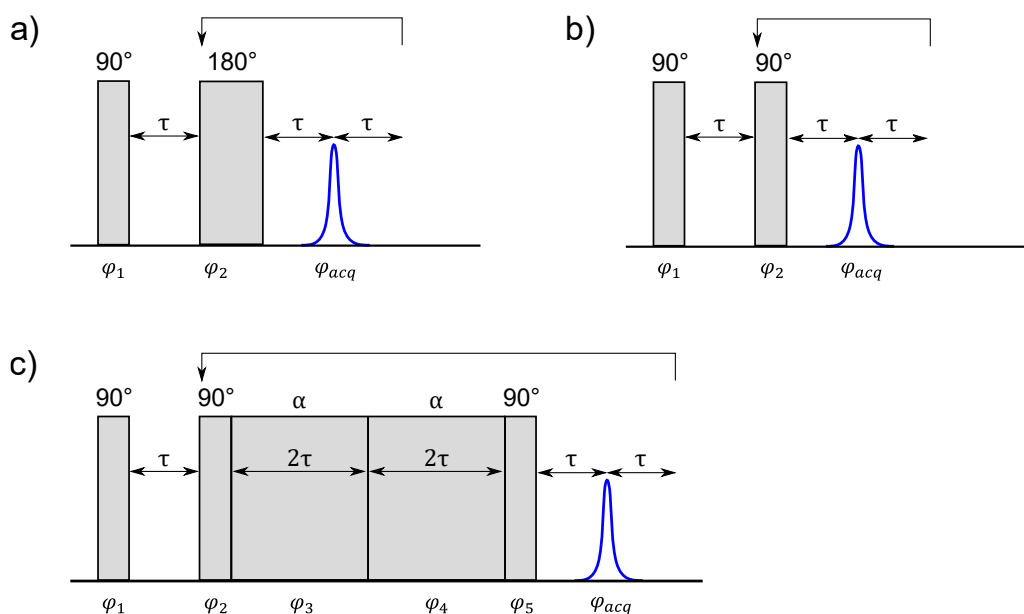


Figure 3.1. (a) CPMG, (b) solid-echo, and (c) and magic(mixed)-echo pulse sequences. The echo maximum is at $t=2\tau$ for the CPMG and SE and at $t=6\tau$ for the ME. The phase cycle of the CPMG and SE is given in Table 3.2, the phase cycle of the ME is given in Table 3.3.

Cycle	A	B	C	D	E	F	G	H
φ_1	x	y	-x	-y	x	y	-x	-y
φ_2	y	-x	-y	x	-y	x	y	-x
φ_{acq}	x	y	-x	-y	x	y	-x	-y

Table 3.2. Phase cycle for the CPMG and solid-echo pulse sequences.

The magic-echo pulse sequence (Figure 3.1c) makes use of spin-locking pulses (α) applied to spins on the z-axis, which are sandwiched between 90° pulses. While the combination of 90° pulses provides a net 180° refocusing pulse, the spin lock prevents the sustained evolution of dipolar couplings. The phase of the second 90° sandwich pulse (φ_5) can be changed to the same phase of

the first 90° sandwich pulse (φ_2) obtaining the “mixed” echo version of the magic echo, effectively adding another 180° refocusing pulse, similar to the CPMG sequence, while the dephasing caused by dipolar coupling is still refocused.¹³¹ The mixed-echo sequence is therefore able to rewind static homonuclear dipolar interactions, as well as any inhomogeneous dephasing effects, such as static field inhomogeneity, chemical shift anisotropy, and susceptibility effects.^{68,21}

Cycle	A	B	C	D	E	F	G	H
φ_1	x	y	-x	-y	-x	-y	x	y
φ_2	y	-x	-y	x	y	-x	-y	x
φ_3	x	y	-x	-y	x	y	-x	-y
φ_4	-x	-y	x	y	-x	-y	x	y
φ_5	y	-x	-y	x	y	-x	-y	x
φ_{acq}	x	y	-x	-y	-x	-y	x	y

Table 3.3. Phase cycle for the mixed-echo pulse sequence.

The mixed echo has a minimum echo time of 6τ due to the inclusion of the spin-locking moiety and, as such, benefits greatly from the reduced delay required by the RF electronics at the higher field of 13 MHz for ^1H . While the longer echo duration of the mixed echo compared to the CPMG and solid-echo experiments means a delay in the acquisition of the first data point, the lifetimes of short T_2 components are extended through the aforementioned processes enabling their more reliable acquisition. Components with $T_1 < 100 \mu\text{s}$ are not refocused and lost, which, in the present work, confers an additional benefit that is discussed in detail below.

3.4.3 NMR experiments

The spin-echo pulse sequences were implemented on an Oxford Instruments benchtop spectrometer working at $B_0 = 0.3 \text{ T}$, operating at a ^1H NMR frequency of $\omega_0/2\pi = 12.93 \text{ MHz}$. The spectrometer is equipped with a narrow-bore (18 mm internal diameter) probe and an active damping feedback preamplifier for rapid probe response times (probe dead time $< 10 \mu\text{s}$). This is combined with careful digital filter design for ^{19}F suppression (arising from the PTFE coil support), permitting half-echo times of $\tau \leq 20 \mu\text{s}$. A 90° pulse length of $3 \mu\text{s}$ was used for all experiments.

Transverse magnetization decays of the shale powders have been acquired using the CPMG, SE, and ME pulse sequences (Figure 3.1). For all experiments, the half-echo time was $\tau = 20 \mu\text{s}$, and the probe dead time was $10 \mu\text{s}$. A total of 11 data points were acquired symmetrically about the top of

each spin echo with a dwell time of $t_{dw} = 1 \mu\text{s}$. The time duration of each T_2 decay was 2 s, and 20000 echoes were recorded. A recycle delay of $t_{RD} = 3 \text{ s}$ was included between each scan. T_1 - T_2 correlation data were obtained by means of an inversion recovery (IR) followed either by a CPMG (IR-CPMG) or by a solid echo (IR-SE). The T_1 dimension was encoded using the inversion recovery sequence while the T_2 dimension can be encoded by either the CPMG or the SE pulse sequence. The NMR data were obtained by repeating the sequence at different inversion recovery delays and acquiring a train of echoes for each delay. The T_1 recovery interval was varied logarithmically from $\tau_1 = 100 \mu\text{s}$ to 1 s over 32 increments. For the CPMG and SE, the echo time was fixed at $t_e = 40 \mu\text{s}$. A total of 11 data points was acquired at the top of each spin echo, and a dwell time of $t_{dw} = 1 \mu\text{s}$ and a recycle delay of $t_{RD} = 3 \text{ s}$ were used.

3.4.4 Numerical inversion

Smooth distributions of relaxation time T_2 ,—constrained to be always positive and bound by set limits in the relaxation time dimension—were generated from the NMR data using the inversion method of Venkataramanan *et al.*¹⁷³. The generalized cross validation (GCV) method was used to optimize the value of the regularization parameter for each data set, to provide suitable balance between smoothness and accuracy in the solution. All T_2 distributions were obtained using an exponential kernel in the numerical inversion, where the kernel is the model function that describes the expected form of the data. Distributions of relaxation time in 2D were generated simultaneously using two appropriately different parts of the kernel representing the T_1 (exponential recovery) and T_2 (exponential decay) encoding parts.

3.5 Analysis protocol

3.5.1 Peak assignment in 2D T_1 - T_2 correlation maps

T_1 - T_2 correlation experiments were used to discriminate between different chemical environments of protons in the investigated shales. The proton signals in these T_1 - T_2 maps are assigned to different components of the shale samples according to the classification schemes of Fleury *et al.*¹¹⁶, Kausik *et al.*⁶², and Mitchell⁹⁸ (see *Section 1.4.6*). The peak assignment is also based on 2D correlation experiments performed on kerogen and bitumen isolates (*Section 3.6.1*), as

schematically illustrated in Figure 3.2. The green lines in Figure 3.2 separate signals from immobile organic matter (kerogen and bitumen), clay-interacting water and mobile fluids.

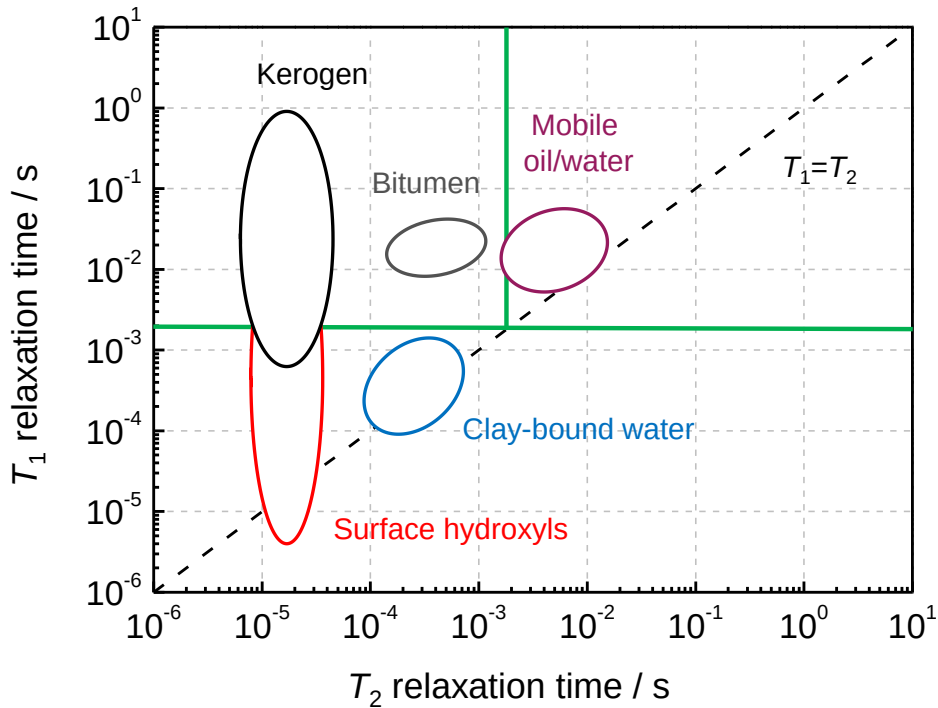


Figure 3.2. Typing scheme for assignment of regions in T_1 - T_2 correlation maps acquired at 13 MHz on various shale components. The green lines are used to separate immobile organic matter (kerogen and bitumen) from clay-interacting water and from mobile fluids. The green horizontal line is drawn at a $T_1 \sim 2$ ms, and the green vertical line is drawn at $T_2 \sim 2$ ms. The diagonal dashed line indicates $T_1 = T_2$.

3.5.2 T_2 data segmentation

T_2 data were first generated from the application of the CPMG, SE, and ME experiments to the powdered oil- and brine-saturated shale samples (Table 3.1). The results were then compared with the aim of identifying and separating immobile (kerogen, bitumen, and oil in nanopores) and mobile (oil) organic components. Mobile components such as water and oil in larger intra- and interparticle pores typically have slow T_2 relaxation, on the order of $T_2 \sim 10 - 100$ ms, while solid-like kerogen and bitumen have faster T_2 relaxation, on the order of $T_2 \sim 10 \mu\text{s} - 10$ ms.^{55,116,117} Hydroxyl groups in clay structures or at the edge of clay platelets have an extremely short T_2 of $\sim 10 \mu\text{s}$.⁵⁵

Example CPMG, SE, and ME T_2 distributions of the powdered shale samples 1A and 1B are presented in Figure 3.3. These were generated using an exponential kernel in the numerical inversion, as the Gaussian model does not provide better representation of the system and produces more

components (see *Section 3.6.2.2*, Figure 3.11). All distributions are divided into three T_2 regions (1, 2 and 3) determined by selected T_2 cut-offs (vertical green lines). The segmentation of the T_2 distributions is based on literature data (specifically on a technique described by Kausik et al.⁶², where native-state and resaturated Eagle Ford shale samples are compared) and on the interpretation of T_1 - T_2 plots, described in *Section 3.5.1*. T_2 cut-offs were also estimated by matching the T_2 distributions of the oil- and brine-saturated shale samples.

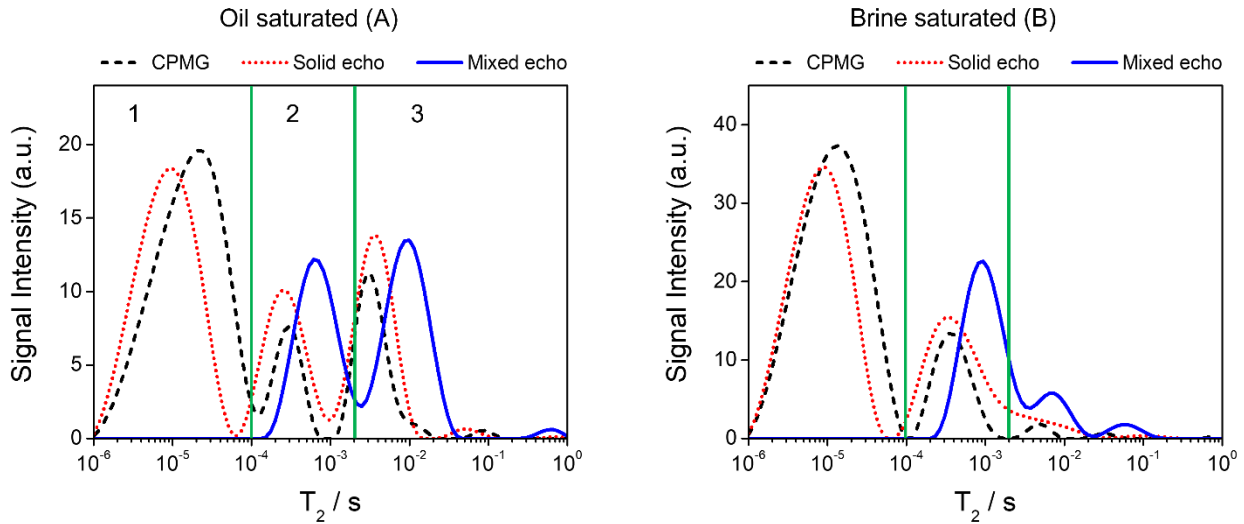


Figure 3.3. T_2 distributions obtained from the shale powders 1A and 1B. The CPMG (black), SE (red), and ME (blue) signals are the output of the numerical inversion described above (*Section 3.4.4*). The green lines represent T_2 cut-offs defined to separate immobile organic matter plus bound water (region 2) from mobile oil and water (region 3). Region 1 is associated with no components, because it is defined by only two sampling points.

Region 1. CPMG and SE distributions contain a short T_2 peak, centered at $T_2 \sim 10 \mu\text{s}$, which corresponds to region 1. This signal likely arises from short- T_2 components (kerogen, structural hydroxyls, and (potentially) organics in nanopores) that are represented only by the first and most unstable two to three points (100 μs) of the CPMG and SE decays. Because of the low number and poor quality of these data points, quantitation of this component is fraught with instability. In the case of the ME, region 1 does not contain signal as the first data point is acquired at 120 μs .

Region 2. For CPMG, SE and ME data the second T_2 region ($100 \mu\text{s} < T_2 < 2 \text{ ms}$) includes signal from semimobile organic matter, bitumen and bound water present in the clay pores. Importantly, however, the efficient extension of the kerogen signal lifetime by the ME sequence shifts this component to the higher T_2 values of region 2, resulting in a stark increase in the ME signal amplitude in region 2 relative to the CPMG and SE. This effect is validated and explored in greater detail in *Section 3.6*.

Region 3. The last T_2 region ($T_2 > 2$ ms) is attributed to mobile oil and water in micro / macropores and within interparticle space. Signals in this area are found to be larger for shales saturated with oil than for those saturated with brine. This may indicate that a part of the matrix porosity, presumably hydrophobic organic porosity, is accessible to oil species only, and that this porosity fraction is located at $T_2 > 2$ ms.

This segmentation of the T_2 distributions was used to determine the immobile organics plus bound water separately from the mobile fluids.

3.5.3 Analysis of T_2 signal amplitudes

T_2 signal amplitudes obtained from CPMG, SE, and ME were compared as follows. Normalization of the T_2 decay data was performed by integrating the area under the respective T_2 distribution, which is equivalent to projecting the measured relaxation decay back to time zero. The resulting integrated intensities from the three pulse sequences are compared per individual sample separately. The heterogeneity of shale rocks with respect to pore structure and mineralogy, even within a single core plug, causes variations in the fluid-filled volume. This complicates a meaningful comparison of absolute peak intensities between these small powder samples. Furthermore, during the crushing process, much of the macroporosity and some of the microporosity are disrupted, resulting in a loss of fluids from these regions and introducing greater uncertainty in the bulk density. For each sample, the largest signal intensity obtained among the three sequences was set to 1 (in almost all cases the ME signal), and the other intensities were scaled accordingly to allow for ease of comparison.

These sequences refocus dipolar coupling interactions to different extents, and their relative ratio can potentially be used to measure the contributions of the various shale components. To quantify this effect, two parameters named R_{se} and R_{cpmg} were defined in the following way:

$$R_{se} = \frac{I_{se}}{I_{me}} \quad (3.7)$$

$$R_{cpmg} = \frac{I_{cpmg}}{I_{me}} \quad (3.8)$$

where R_{se} and R_{cpmg} , respectively, are the SE- and CPMG-signal amplitude relative to the ME amplitude.

3.6 Results and discussion

3.6.1 Relative effectiveness of the three pulse sequences with organic isolates

A kerogen isolate (solid), a bitumen isolate (viscous), and a paraffinic oil (liquid) were used as model samples to compare the T_2 responses of the CPMG, SE, and ME to the more dilute organic phases in the investigated shale samples. The T_2 decays of these standard samples were acquired with the three pulse sequences, and the corresponding T_2 distributions were compared.

CPMG, SE, and ME T_2 distributions are presented in Figure 3.4 for the kerogen (a) and bitumen (b) isolates. For kerogen, part of the T_2 signal in the CPMG and SE distributions is located at $T_2 < 100 \mu\text{s}$. The ME signal for the kerogen isolate is larger and shifted to longer- T_2 values (centered at about $T_2 \sim 1 \text{ ms}$), confirming the improved efficacy of the ME sequence in preventing rapid signal decay due to homonuclear dipolar coupling. The T_2 distributions obtained from bitumen show a peak at $100 \mu\text{s} < T_2 < 2 \text{ ms}$ for all sequences, with an additional high-intensity signal at long $T_2 \sim 10\text{-}100 \text{ ms}$, associated with a mobile component, possibly oil or residual solvent from the extraction procedure. Importantly, here, an increased signal amplitude can be observed for the shorter- T_2 signal from the more solid-like components in the ME data, relative to the CPMG and SE traces, with little-to-no effect observable on the mobile components.

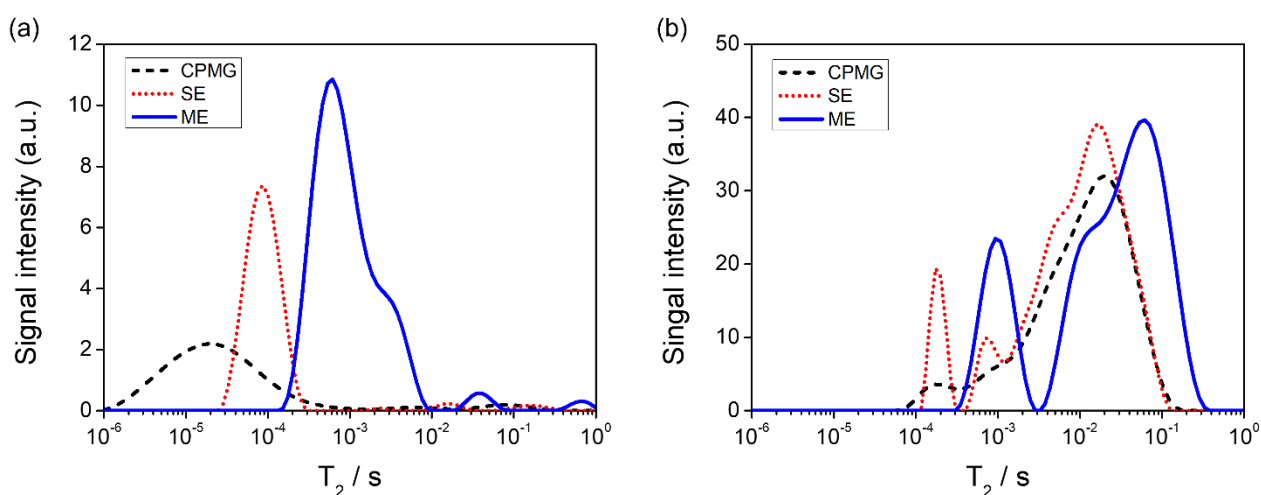


Figure 3.4. CPMG, SE, and ME T_2 distributions obtained from (a) kerogen and (b) bitumen isolates.

Figure 3.5 shows the T_1 - T_2 correlation maps of the kerogen isolate obtained with (a) inverse-recovery CPMG (IR-CPMG) and (b) and the inverse-recovery solid-echo (IR-SE) pulse sequences.

Both T_1 - T_2 maps of kerogen are characterized by a broad peak centered at $T_2 \sim 50 \mu\text{s}$, which extends across several orders of magnitude in T_1 . The improved sensitivity of the SE train partially shifts this peak to a region at $T_2 \sim 150 \mu\text{s}$, and with $T_1 \sim 200 \text{ ms}$. The shift of this signal is consistent with the modest improvement in signal amplitude returned by the SE over the CPMG, observed in the isolate kerogen T_2 data.

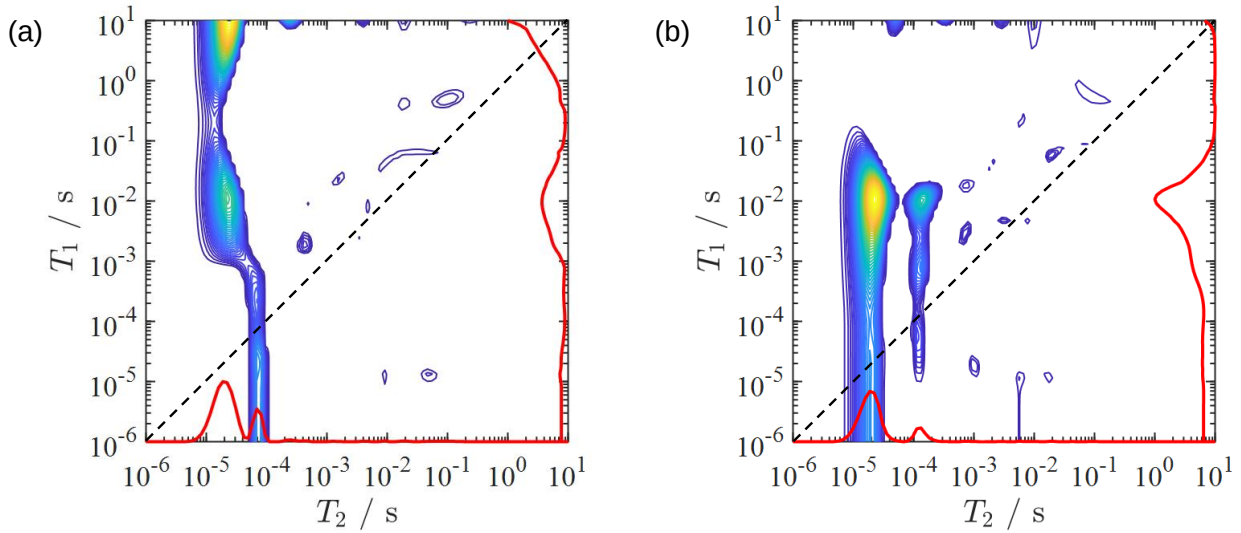


Figure 3.5. T_1 - T_2 correlation maps obtained from a kerogen isolate with T_2 encoded using (a) CPMG and (b) SE. The diagonal line indicates $T_1 = T_2$. Marginal projections of T_2 and T_1 are included for clarity. Signal below the $T_1 = T_2$ diagonal line is artifactual, resulting from a deviation from the exponential behavior assumed by the applied numerical inversion.

Figure 3.6 presents the T_1 - T_2 correlation maps of the bitumen isolate obtained with (a) inverse-recovery CPMG (IR-CPMG) and (b) and the inverse-recovery solid-echo (IR-SE) pulse sequences. The T_1 - T_2 maps of bitumen appear to be considerably different from that of kerogen. All signals have relatively high T_1 values between 10 and 100 ms and range over a wide spectrum of T_2 values. The signal observed at short T_2 , that extends from $T_2 \sim 50 \mu\text{s}$ to 1 ms, corresponds to highly viscous bitumen and it appears to be lower in intensity compared to the signal at longer T_2 . The latter has a $T_1/T_2 \sim 1$, and it represents a more mobile oil fraction present in the sample.

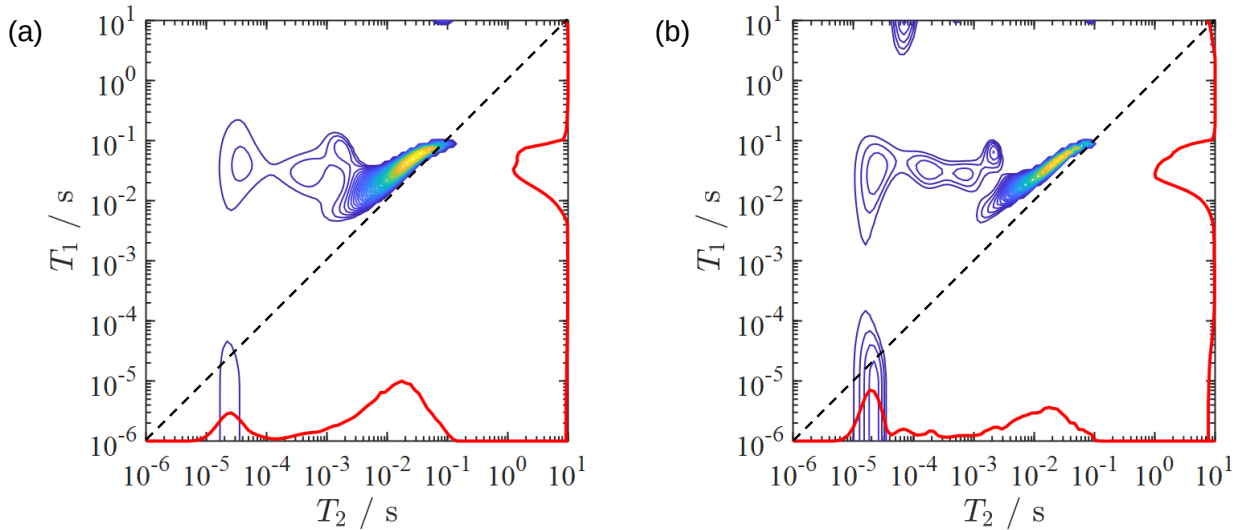


Figure 3.6. T_1 - T_2 correlation maps obtained from a bitumen isolate with T_2 encoded using (a) CPMG and (b) SE. The diagonal line indicates $T_1 = T_2$. Marginal projections of T_2 and T_1 are included for clarity. Signal below the $T_1 = T_2$ diagonal line is artifactual, resulting from a deviation from the exponential behavior assumed by the applied numerical inversion.

The area under the T_2 distributions of the kerogen, bitumen, and oil samples (Figure 3.4) were integrated, which is equivalent to projecting the relaxation decay back to time zero. For each sample, the intensities of the CPMG and SE signals were then scaled to the ME signal amplitude, which was set to 1 for ease of comparison. Figure 3.7 shows the relative integrated intensities of the CPMG, SE, and ME T_2 signals, for each of the investigated organic isolates.

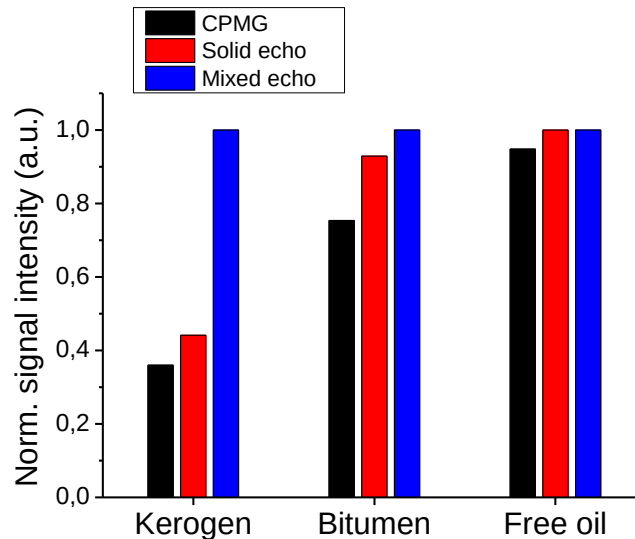


Figure 3.7. Integrated intensities of the CPMG and SE T_2 distributions relative to the ME, obtained from a kerogen isolate, a bitumen isolate, and a paraffinic oil sample. For each sample, the integral area of the ME signal was set to 1, and the CPMG and SE signal intensities were scaled accordingly.

The fraction of the integrated signal intensity of the SE and CPMG relative to the ME (R_{se} and R_{cpmg}) for these organic isolates is given in Table 3.4. The intensities of the CPMG, SE, and ME T_2 signals of a paraffinic oil sample are nearly equal ($R_{se} = 100\%$ and $R_{cpmg} = 94.8\%$). For this mobile species, the three methods provide almost identical results, indicating that the signal decay under these sequences is caused by magnetic field inhomogeneity, chemical shift, and susceptibility effects. For the highly viscous bitumen isolate, a small difference between the SE and ME signal amplitudes was observed, with the CPMG returning around 80% of the ME signal. The SE and ME techniques have similar efficiency at refocusing magnetization for this component while, as expected, the CPMG appears to be unable to recover signal dephasing caused by dipolar coupling. For a kerogen isolate, the CPMG and SE return ~ 35 and 45% of the ME signal, respectively. Kerogen can be considered as a dipolar-coupled network of hydrocarbons, where the cross-linking turns the liquid polymers into an amorphous solid. For such coupled systems, the transverse magnetization decay is almost exclusively determined by the local dipolar interactions between neighboring spins, and the large difference observed between the SE and the ME signal intensities likely results from the SE inefficiency at refocusing dipolar interactions for spins that undergo multiple homonuclear dipolar couplings.

Sample	$R_{se} (\%)$	$R_{cpmg} (\%)$
Kerogen	44.1	36.1
Bitumen	92.9	75.3
Free oil	100	94.8

Table 3.4. Difference in intensity between the ME and the SE/CPMG signals (R_{se} and R_{cpmg}) calculated from the 1D T_2 distributions of the three organic isolates.

As this example shows, the three sequences have different efficiencies when refocusing transverse magnetization dephasing for materials with different molecular mobility and proton density. In particular, the ME method increases the detection level of immobile components like kerogen. It is likely that when the same measurements are performed on shale samples containing kerogen, bitumen and oil, the NMR response will not be a simple superposition of individual relaxation contributions from the various components, but it will also depend on possible interactions between these species and with the shale pore walls.

3.6.2 Oil- or brine-saturated shale powders

3.6.2.1 2D T_1 - T_2 correlation maps

T_1 - T_2 correlation plots of a crushed shale sample resaturated with oil (sample 1A) and one resaturated with brine (sample 1B), with the T_2 dimension acquired using CPMG and solid echoes, are illustrated in Figure 3.8. Peaks in the T_1 - T_2 plot of sample 1A, obtained using the CPMG to acquire the T_2 dimension, are assigned to different components according to the classification scheme presented in *Section 3.5.1*. The peak centered at $T_2 \sim 20$ -50 μ s—which extends across several orders of magnitude in T_1 —arises from the solid phases of the shale, which include hydroxyl groups in clay structures (red circle) and solid-like organic matter, i.e., kerogen (black circle). The signal with a slightly longer T_2 , between 100 μ s and 1 ms, and characterized by $T_1/T_2 \sim 2$, is typical of brine that can enter smaller size pores in clays and form bound water (blue circle). Oil species cannot access many of these hydrophilic clay pores, which are generally considered water-saturated because of their wettability and capillarity. This peak has larger intensity for the brine-saturated shale powder than for the oil-saturated one. The latter has a high-intensity peak at $T_2 > 1$ ms assigned to oil in both organic and inorganic pores (purple circle). The same peak is found to have much lower intensity for the brine-saturated shale samples, and it corresponds to mobile water.

T_1 - T_2 correlation maps recorded with the inverse-recovery solid-echo (IR-SE) pulse sequence from the same oil- and brine-saturated samples are substantially different. The key difference between the IR-CPMG and IR-SE T_1 - T_2 maps is the sensitivity to components with $T_2 < 1$ ms, located on the left-hand side of the plots (region 1 and region 2). A short T_2 peak characterized by a broad T_1 distribution is still present in the IR-SE plots, again associated with structural hydroxyls. The improved sensitivity of the SE train partially resolves another peak centered at $T_2 \sim 150$ μ s, and with $T_1 \sim 200$ ms, which is assigned to immobile organic matter components (kerogen, bitumen), allowing more robust separation of the signals. This immobile organic signal overlaps with that of bound water in the T_2 dimension. This reinforces that the modest improvements in signal amplitude returned by the SE over the CPMG, observed in the isolate T_2 data, also occur in the shale samples, and specifically to the region known to contain solid-like organic matter. The shift of this signal in the IR-SE T_1 - T_2 map is also observed in the 2D correlation experiments performed on a kerogen isolate (Figure 3.5). IR-SE T_1 - T_2 correlation maps provide a greater number of resolved peaks and better signal-to-noise ratio in these shale samples containing solid species than conventional T_1 - T_2

correlations based on CPMG. These results indicate that the use of the SE improves the quality of fit in the numerical inversion and returns narrower distributions that are easier to assign to specific hydrocarbon fractions.

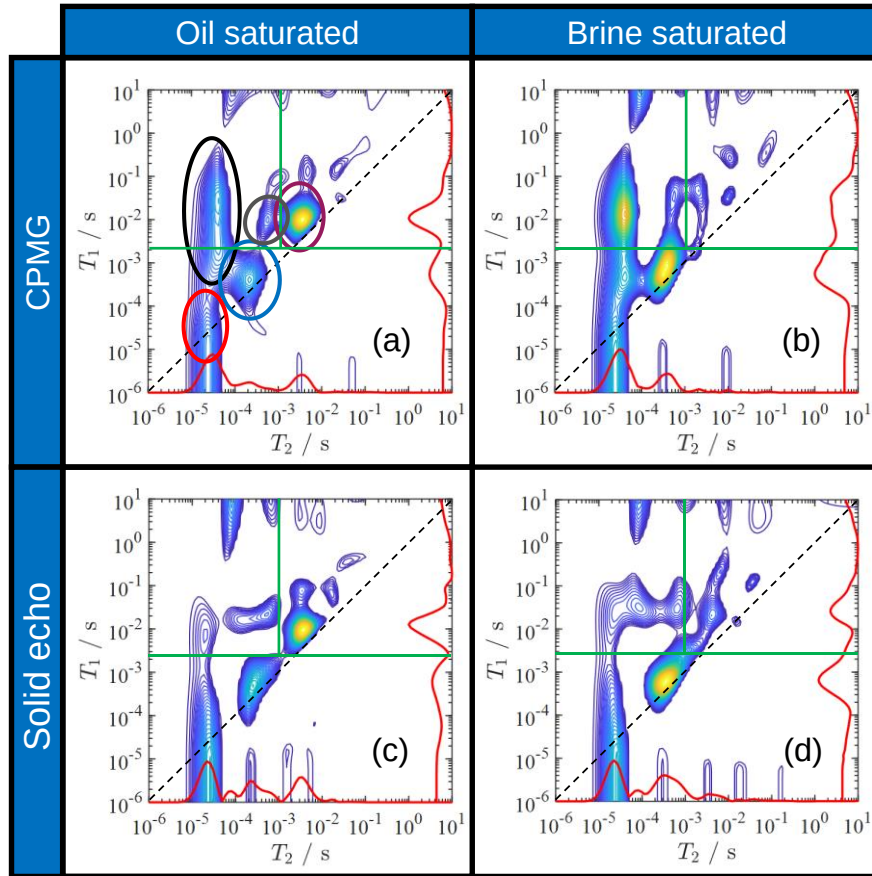


Figure 3.8. T_1 - T_2 correlation maps obtained from shale powders 1A and 1B with T_2 encoded using CPMG (a-b) and SE (c-d). The diagonal line indicates $T_1 = T_2$. Marginal projections of T_2 and T_1 are included for comparison with the T_2 distributions in Figs. 8 and 9. Classification of peaks as described in Section 3.5.1 (colored ovals) with red: surface hydroxyls, black: kerogen, blue: clay-bound water, dark gray: bitumen, and purple: mobile oil. The green lines are used to separate immobile organic matter (kerogen and bitumen) from clay-interacting water and from mobile fluids. Signal below the $T_1 = T_2$ diagonal line is artifactual, resulting from a deviation from the exponential behavior assumed by the applied numerical inversion.

For comparison to the results obtained for the shale powders, IR-CPMG T_1 - T_2 maps measured at 2 MHz and 13 MHz from shale core plugs 1A and 1B are shown in Figure 3.9. These experiments were performed using a standard cylindrical RF probe (51 mm internal diameter) that can accommodate standard core plugs (38 mm internal diameter). Given the limit on the echo spacing for the standard cylindrical probe, these experiments were performed with $\tau = 50 \mu\text{s}$. At the low frequency of 2 MHz, short relaxation time components associated with surface hydroxyl groups and solid organic matter ($T_2 < 100 \mu\text{s}$) cannot be detected. Signals located at $T_2 < 1 \text{ ms}$ are assigned to bitumen and bound water, while those at $T_2 > 1 \text{ ms}$ reflect free fluids in inter/intra particle pores. Part of these signals

may also be fluids on the surface of the shale cores. At a higher Larmor frequency of 13 MHz, the higher sensitivity enables not only better separation of the oil and bound water peaks, but also improves the detection limit of short- T_2 components. The signal associated with solid organic matter (short T_2) is of low intensity compared to the other components, especially for the brine-saturated core plug. The relative intensity of this peak increases when a narrow-bore probe is used instead of the larger probe (Figure 3.8), providing an improved description of the solid components in the samples. The narrower bore probe enables the application of shorter RF pulses, improving the time resolution of the experiment and providing better excitation of the broad line shale samples. Some information is lost because of the crushing of the samples, as indicated by the absence of the long- T_2 peaks in the T_1 - T_2 plots obtained from the shale powders, which may be due to the loss of surface fluids. However, the long- T_2 peaks may not be visible in shale powders because of diffusional coupling between fluids on the powder grain surface and the grain porosity, where diffusion is rapid enough to average the relaxation time.

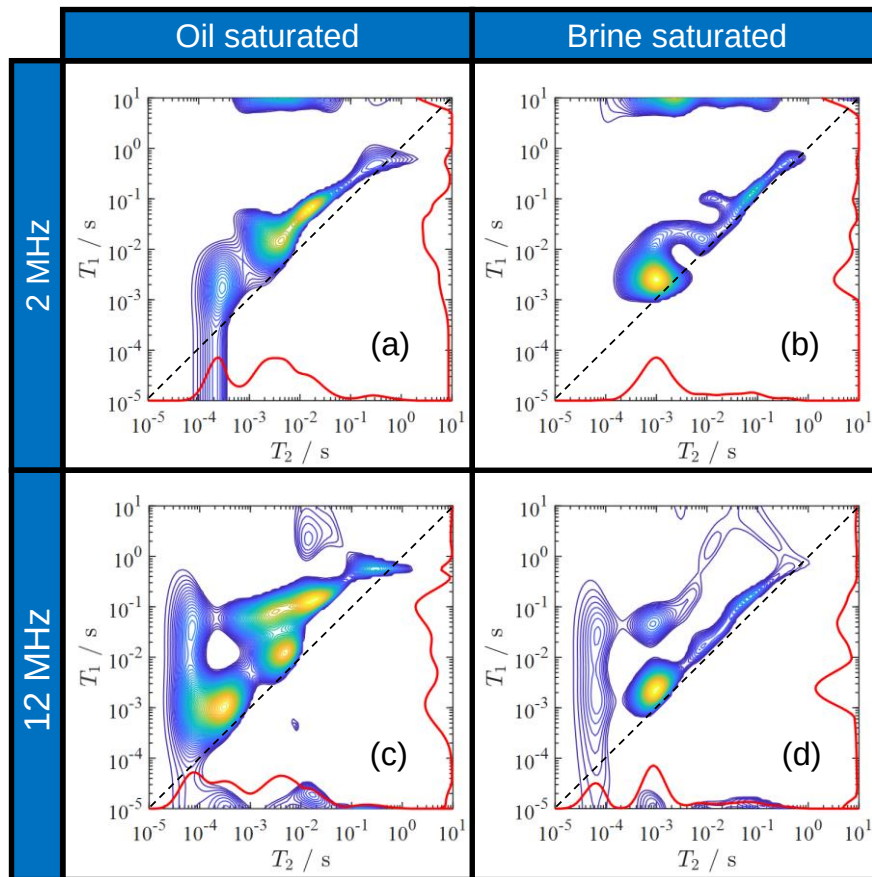


Figure 3.9. IR-CPMG T_1 - T_2 correlation maps obtained at 2 MHz (a-b) and 13 MHz (c-d) with a standard cylindrical RF probe from shale core plugs 1A and 1B. The diagonal line indicates $T_1/T_2 = 1$. Marginal projections of T_2 and T_1 are included for comparison with Fig. 6. Signal below the $T_1 = T_2$ diagonal line is artifactual, resulting from a deviation from the exponential behavior assumed by the applied numerical inversion.

3.6.2.2 1D T_2 distributions

In this section, the CPMG, SE and ME T_2 signals of the powdered shale samples are compared and analyzed directly in the T_2 domain. To robustly analyze these T_2 distributions, their respective time-domain data were previously examined. Figure 3.10a shows the T_2 decays obtained with the three pulse sequences and the corresponding T_2 distributions for shale 1A.

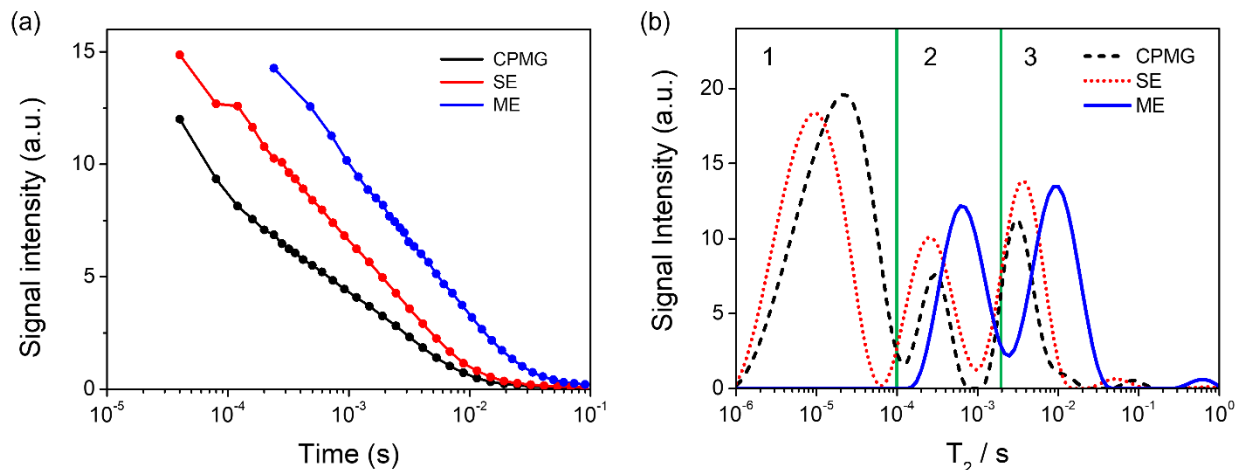


Figure 3.10. (a) CPMG, SE, and ME Time-domain signals and (b) corresponding T_2 distributions obtained from oil-saturated shale 1A.

As expected, for a given echo time, the ME sequence always gives higher signal intensity in the time domain, but the multiple-pulse nature of each ME cycle restricts the shortest measurable echo time to ~ 120 μ s. Figure 3.10b shows that the short T_2 component in region 1 of CPMG and SE T_2 distributions seem to be the dominant fraction. However, as described in *Section 3.5.2*, this peak is unlikely to be reliable for further quantitative analysis. In this respect, a few more qualitative considerations can be made by comparing the T_2 decays obtained with the three sequences.

Although the ME is better at refocusing coherent interactions, it cannot restore the incoherent loss of magnetization ultimately limited by the spin-lattice relaxation time T_1 (always $> T_2$). Therefore, the ME sequence extends the lifetime of the T_2 signal only for components with long-enough T_1 to survive over the sequence (sampling time > 100 μ s). This makes the ME technique inefficient to clay-bound water / surface hydroxyls with $T_1 < 100$ μ s, but highly efficient to the long- T_1 kerogen signal, providing an additional benefit for the present work, which is aimed at improving detection of solid organic components in the shale.

This is consistent with results obtained from the kerogen isolate (Figure 3.4a), where the intensity of the peak in region 1 is much lower than that observed for the shale powders. For shales (Figure

3.10), a large part of the signal in region 1 may therefore arise from surface hydroxyls, as observed in the corresponding T_1 - T_2 correlation maps. As expected, a significant fraction of the short- T_2 signal (region 1), associated with surface hydroxyls, is lost in the ME, and the ratio of intensities between the ME and SE/CPMG signals in region 2 is much lower compared to that observed for pure kerogen.

In addition, the large-intensity peak in region 1 may result from a deviation from the exponential behavior assumed by the applied numerical inversion, considering that for echo times $< 100 \mu\text{s}$, coherent solid-state ^1H dipolar coupling may produce Gaussian-like behavior. The exponential kernel in the inversion analysis tends to exaggerate the intensity of the extrapolated time decay back to time zero or, equivalently, the peak area of the short- T_2 component in the T_2 distribution. However, the CPMG, SE, and ME T_2 decays in Figure 3.10a do not show a clear sign of initial Gaussian behavior. The CPMG, SE, and ME T_2 data were also generated using a Gaussian kernel in the numerical inversion to compare results with those obtained with an exponential kernel (Figure 3.11, shale 1A is shown as an example). The Gaussian analysis do not give a better representation and, in general, it produces more components. Therefore, the model with the least number of components, which is the exponential kernel, was chosen.

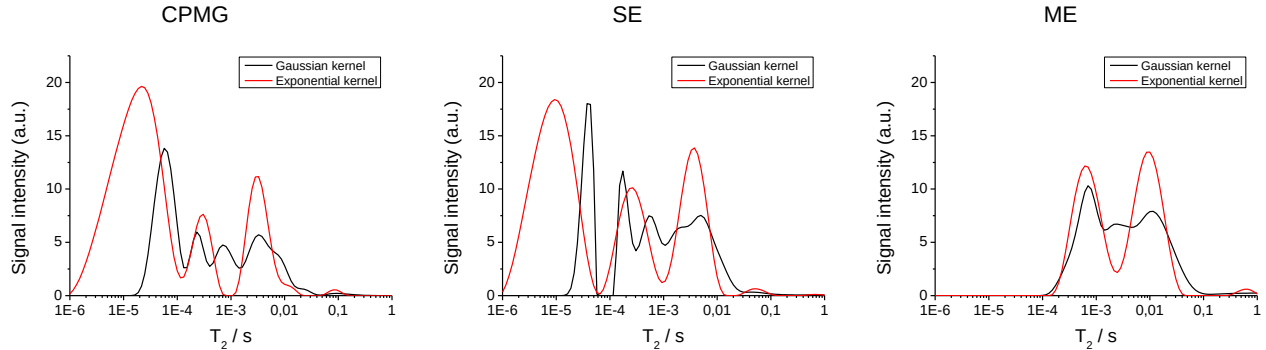


Figure 3.11. T_2 distributions obtained using an exponential (red) or Gaussian (black) kernel in the numerical inversion of the CPMG, SE, and ME time-domain signals obtained for oil-saturated shale 1A.

Together, these factors support our choice of excluding region 1 from the following T_2 signal amplitude analysis. With the aim of making a fair comparison between the three T_2 distributions, the inversion of the CPMG and SE data (results for sample 1A are shown in Figure 3.12) was repeated without the first two to three data points of the decay at time $< 100 \mu\text{s}$. However, the obtained T_2 distribution reveals a drastic change in the shape of the two remaining peaks with $T_2 > 100 \mu\text{s}$, making comparison with ME T_2 distributions more complicated.

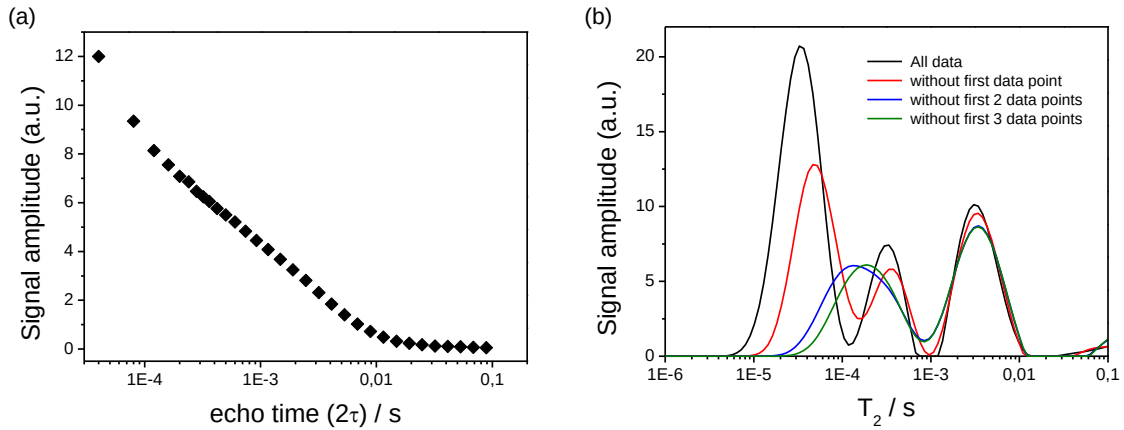


Figure 3.12. (a) CPMG T_2 decay obtained from shale 1A and (b) corresponding T_2 distributions obtained by removing the first 2-3 data points in the time-domain signal.

CPMG, SE, and ME T_2 distributions of all powdered shale samples from different depths are presented in Figure 3.13. All distributions are divided into three T_2 regions (1, 2, and 3) as described in Section 3.5.2. The green lines are used as guidelines for the eyes, and integration of each region is performed following the peak shape. Region 1 is shaded in the figure, because it is neglected in the quantitative analysis.

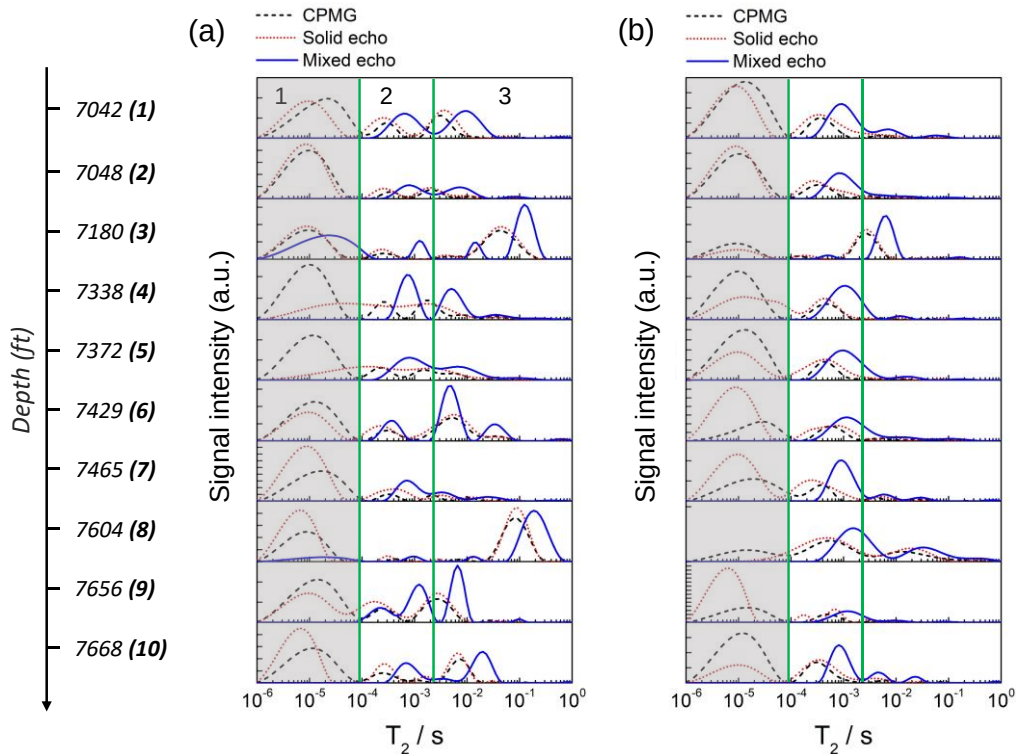


Figure 3.13. T_2 distributions obtained from the oil-saturated (a) and brine-saturated (b) shale powders from various depths. The CPMG (black), SE (red), and ME (blue) signals are the output of the numerical inversion described above (Section 3.4.4). The green lines represent T_2 cut-offs defined to separate immobile organic matter plus bound water (region 2) from mobile oil and water (region 3). Region 1 is shaded in the figure because it is excluded from the subsequent T_2 signal analysis.

All T_2 distributions include signal from immobile (region 2) as well as from mobile components (region 3). For ME data, region 2 also contains kerogen signal, the lifetime of which is efficiently extended by the ME sequence, while this component sits in the not-reliable region 1 ($T_2 < 100 \mu\text{s}$) in CPMG and SE T_2 distributions. For all sequences, the shape and number of peaks is the same in region 2 and region 3, suggesting that these signals have real physical meaning and that the applied T_2 segmentation is reliable.

3.6.2.3 T_2 signal amplitudes

The area under the CPMG, SE, and ME T_2 distributions of each shale powder in Figure 3.13 were integrated and compared to assess the suitability of the combination of the three pulse sequences to evaluate the fraction of immobile and mobile components. Figure 3.14 shows the resulting normalized signal intensities obtained from each of the two T_2 peaks representing immobile organic matter plus bound water (region 2) and mobile fluids (region 3). For each sample, the largest intensity among the three signals was set to 1, and the other intensities were scaled accordingly to allow for ease of comparison. The intensity ratio between ME and SE/CPMG signals (R_{se} , R_{cpmg}) was calculated separately for region 2 ($R_{se,2}$, $R_{cpmg,2}$) and for region 3 ($R_{se,3}$, $R_{cpmg,3}$) (Table 3.5). The short- T_2 peaks with $T_2 < 100 \mu\text{s}$ (region 1) observed in the CPMG and SE distributions was not considered in this analysis and in the rest of the manuscript (see *Section 3.5.2*). This region is probably not reliable, because it is strongly affected by the few data points for times $< 100 \mu\text{s}$, which cause artifacts in the inversion procedure.

The CPMG, SE, and ME T_2 signal intensities for the immobile organic matter plus bound water component in oil-saturated shales are compared in Figure 3.14a. The SE and CPMG returns on average about 78 % and 45% of the ME signal, respectively. On the contrary, for the mobile component (Figure 3.14b) the three sequences provide more equal refocusing (average $R_{se,3} \sim 90$ % and $R_{cpmg,3} \sim 70$ %). Notably, for samples 3A and 8A similar results to those obtained for a free oil sample were found (Figure 3.7), with almost no difference between the SE and ME signals. The T_2 distributions of these two samples present only a particularly long T_2 signal at $T_2 \sim 100\text{-}200$ ms, typical of bulk solution, which may reflect mobile oil in large pores, which are often inorganic.^{2,23}

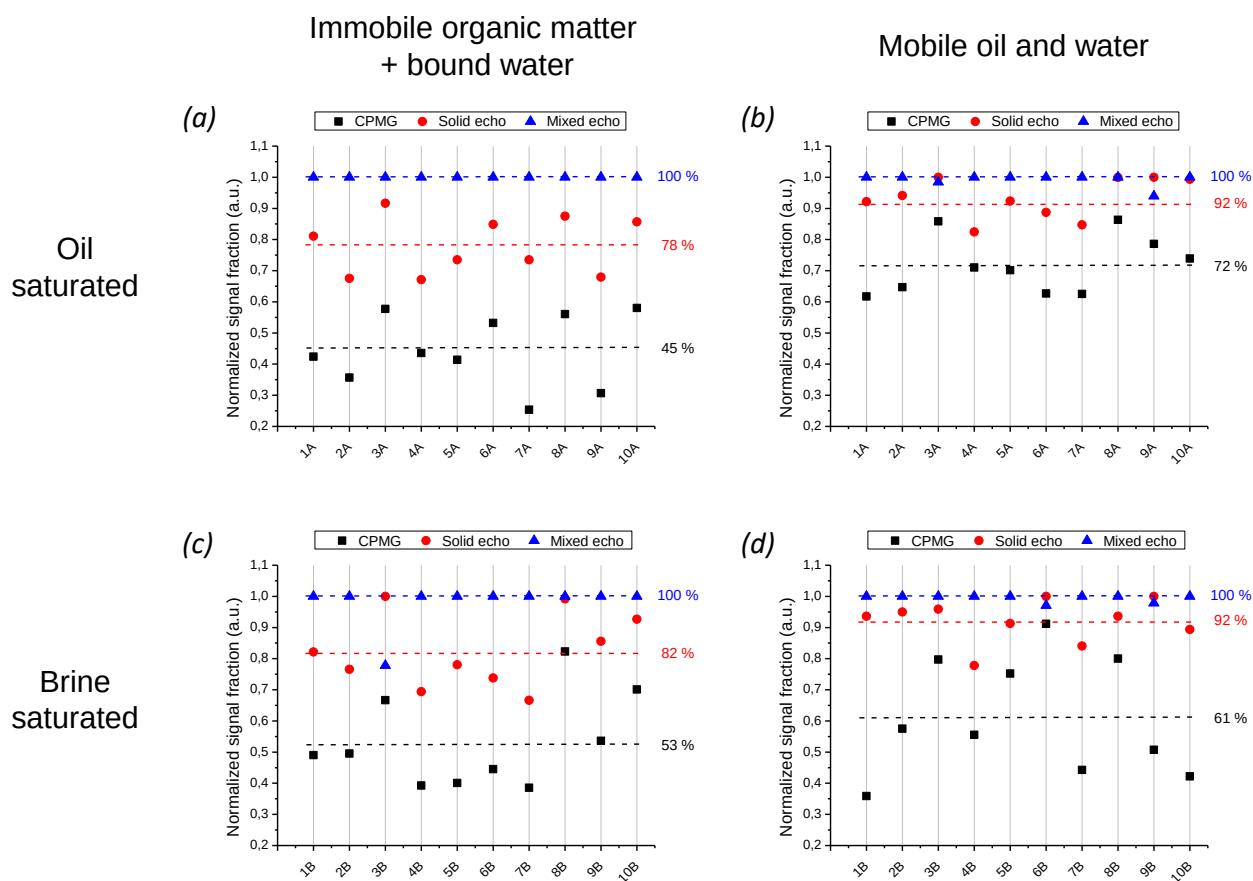


Figure 3.14. Relative integrated intensities obtained from the CPMG, SE, and ME T_2 distributions of the oil-saturated (a-b) and brine-saturated samples (c-d), for the two defined T_2 regions representing immobile organic matter plus bound water (a-c, region 2) and mobile fluids (b-d, region 3). For each sample, the largest signal intensity obtained from the three sequences was set to 1, and the others were scaled accordingly. The dashed lines represent the average percentage value of the ratio of intensities between the CPMG, SE, and ME signals.

Similar results were obtained for the brine-saturated shale samples. Figure 3.14c shows the differences between the CPMG, SE, and ME signals for the immobile component, which are on average slightly lower than those obtained for their oil-saturated counterparts. As expected, there is a much smaller difference in the integrated signal intensity between the ME and SE for the mobile water component (Figure 3.14d). However, unlike results obtained for mobile oil, the contrast between the ME and CPMG signals remains considerably large for mobile water (average $R_{cpmg,3} \sim 60\%$), with significant variation from sample to sample. It should be noted that T_2 peaks in this area have a much smaller intensity compared to those found in the same T_2 region for the oil-saturated shales.

Sample ID	Oil saturated (A)				Brine saturated (B)			
	$R_{se,2}$	$R_{cpmg,2}$	$R_{se,3}$	$R_{cpmg,3}$	$R_{se,2}$	$R_{cpmg,2}$	$R_{se,3}$	$R_{cpmg,3}$
1	81.1	42.4	92.2	61.7	82.2	49.0	93.6	35.9
2	67.5	35.7	94.1	64.7	76.6	49.5	95.0	57.5
3	91.6	57.7	100	85.8	100	66.7	95.9	79.7
4	67.1	43.5	82.4	71.0	69.4	39.3	77.8	55.6
5	73.5	41.4	92.3	70.2	78.0	40.1	91.3	75.2
6	84.9	53.2	88.7	62.7	73.8	44.5	100	91.2
7	73.5	25.4	84.7	62.5	66.6	38.5	84.1	44.2
8	87.5	56.1	99.9	86.3	99.2	82.3	93.6	80.0
9	67.9	30.7	100	78.6	85.6	53.6	100	50.7
10	85.7	58.0	99.3	73.9	92.6	70.1	89.4	42.2

Table 3.5. Difference in intensity between the ME and the SE/CPMG signals calculated for region 2 ($R_{se,2}$, $R_{cpmg,2}$) and for region 3 ($R_{se,3}$, $R_{cpmg,3}$) from the 1D T_2 distributions of the oil- and brine-saturated shale samples. Region 2 represents immobile organic matter plus bound water while region 3 represents mobile fluids.

Results obtained for the powdered oil- and brine-saturated shales exhibit similar trends, where larger differences between the integrated signal intensity of the T_2 distributions acquired with the CPMG, SE, and ME sequences are observed for immobile organic matter and bound water. The three techniques generate similar responses from mobile species but considerable discrepancies from solid components. The same behavior was observed for measurements made on isolates of solid kerogen, semisolid bitumen, and mobile oil (Figure 3.7). As expected, the CPMG gives the lowest signal amplitudes, proving that this standard technique is inappropriate for T_2 measurements of kerogen and bitumen in shale samples. The contrast between the SE and ME performances may result from the SE inefficiency at refocusing multiple dipole couplings in strongly dipolar-coupled phases. Therefore, R_{se} may reflect the presence of coupled multiple-spin networks as opposed to isolated spin pairs and ultimately, it may reveal information on the underlying chemical structure of the solid organic fractions in shales. Also, the ME cycle has the additional feature of providing better refocusing of any I_z interactions (e.g., static field inhomogeneity, chemical shift), which may contribute to the difference between the two signal intensities. Among the species that feature short T_2 , kerogen exhibits the strongest ^1H dipolar interactions as it is a solid complex multispin system, where multibody interactions between nearby protons at different distances and orientations lead to distributions in the dipolar couplings. Bitumen generally features comparatively lower residual dipolar couplings, having a molecular structure that is intermediate between that of kerogen and petroleum and being more liquid-like than kerogen. In principle, these species are

better refocused by the ME technique. However, not only kerogen and bitumen but also highly confined small molecules (i.e., linear-alkane molecules residing in tight nanopores) can undergo strong dipole coupling. Hydrocarbon molecules in the bulk phase are subjected to isotropic motional averaging, and the CPMG, SE, and ME T_2 responses are identical (see free oil in Figure 3.7). Nevertheless, when confined into nanopore structures, these species will experience strong dipole coupling due to the lack of isotropic motional averaging. This means that the ME sequence may also enhance the signal from small oil molecules in tightly fitting nanopores.

The bound water signal arises from water molecules with restricted mobility located in small-size clay pores. In contrast to immobile organic matter, this component is in principle refocused to the same extent by the ME and the SE cycles, as the coupled spin pairs are more likely to be isolated rather than distributed in a dipolar-coupled network.

Distinct differences between the standard CPMG and the ME/SE methods are also observed for mobile components. These may be due to residual dipolar coupling resulting from oil and water species that undergo hindered motion because they are confined in small-pore structures or located at the interface with the pore surface in larger pores. In particular, the ratio of intensities between the ME and CPMG signals for the mobile component ($R_{cpmg,3}$) was found to be considerably larger for brine-saturated samples than for the oil-saturated ones, indicating that different types of interactions take place between the fluids present in the pores (oil or water) and the pore surface (organic or inorganic pores), probably due to the wettability.

Overall, this type of analysis shows that immobile species in the shale samples are characterized by large signal differences between the ME and the CPMG/SE techniques, while mobile components have more equal refocusing by the three pulse sequences. Specifically, the large increase in the ME signal amplitude in region 2 relative to the CPMG and SE results from kerogen signal, which is efficiently refocused by the ME, while hydroxyl components with $T_1 < 100 \mu\text{s}$ are filtered out.

The combination of the techniques described can potentially be used to evaluate the fraction of immobile and mobile components in the shales. However, separation of the immobile organic matter from the bound water contribution is not possible from just the 1D T_2 analysis, as the respective T_2 signals overlap. For that reason, the obtained results are compared with 2D T_1 - T_2 correlation plots obtained from the powdered shales.

3.6.2.4 Comparison between 1D T_2 analysis and 2D T_1 - T_2 maps

2D T_1 - T_2 correlation maps enable discrimination between the immobile organic matter and bound water components due to their different T_1 values. 2D IR-SE T_1 - T_2 correlation plots of the powdered shale samples were compared with results obtained from the 1D T_2 analysis to evaluate the contribution of immobile organic species like kerogen to the intensity ratio between the three sequences. To make this comparison, the total intensity of the normalized 1D T_2 distributions (region 2 + region 3) was used to calculate R_{se} and R_{cpmg} , and not the intensities of two separated T_2 regions ($R_{cpmg,se,2}$, $R_{cpmg,se,3}$) (Table 3.6).

Sample ID	Oil saturated (A)		Brine saturated (B)	
	R_{se} (%)	R_{cpmg} (%)	R_{se} (%)	R_{cpmg} (%)
1	87.0	52.7	83.7	47.2
2	80.8	50.2	79.4	50.8
3	100	82.5	98.1	80.1
4	74.5	56.9	70.0	40.5
5	81.6	53.8	79.2	43.2
6	87.7	60.3	77.5	50.8
7	77.5	38.7	69.6	39.5
8	99.3	84.8	97.2	81.5
9	84.8	53.9	87.6	53.4
10	94.1	67.8	91.9	64.1

Table 3.6. Difference in intensity between the ME and the SE/CPMG signals (R_{se} and R_{cpmg}) calculated from the total intensity of the 1D T_2 distributions (region 2 + region 3) of the oil- and brine-saturated shale samples.

The ratio of intensities between the ME and CPMG/SE signals (R_{se} and R_{cpmg}) is expected to be large for samples with high amounts of immobile organics. Figure 3.15 shows the IR-SE T_1 - T_2 maps obtained from the oil-saturated shales presented in ascending order of R_{se} . The green lines in the figure help distinguishing between immobile organic matter and clay-interacting water. From low signal differences between the three methods ($R_{se} \sim 100$ % and $R_{cpmg} \sim 80$ -85 %) of samples 3A and 8A, T_1 - T_2 plots presenting a single long- T_2 peak, typical of low-viscous oil located in large pores, were obtained. For a slightly lower $R_{se} \sim 95$ % of sample 10A, the T_1 - T_2 map shows a dominant mobile oil peak ($T_2 \sim 10$ ms, $T_1 \sim 200$ ms) with an additional weak bound water signal ($T_2 \sim 0.2$ ms, $T_1/T_2 \sim 2$). A weak immobile organic matter signal starts to be observable in the 2D distribution

of samples 6A and 1A, for which the ratio of the SE/ME integrated signals is larger than 85 %. Although this peak overlaps with that of bound water in the T_2 dimension, it can be separated, because it is characterized by a longer T_1 ($T_1/T_2 \sim 100$). For larger contrast between ME and SE signals (R_{se} ranging between 75 and 85 %) of the rest of the samples, the T_1 - T_2 maps exhibit high-intensity peaks in the short- T_2 area of the plot representing the immobile organics of the system.

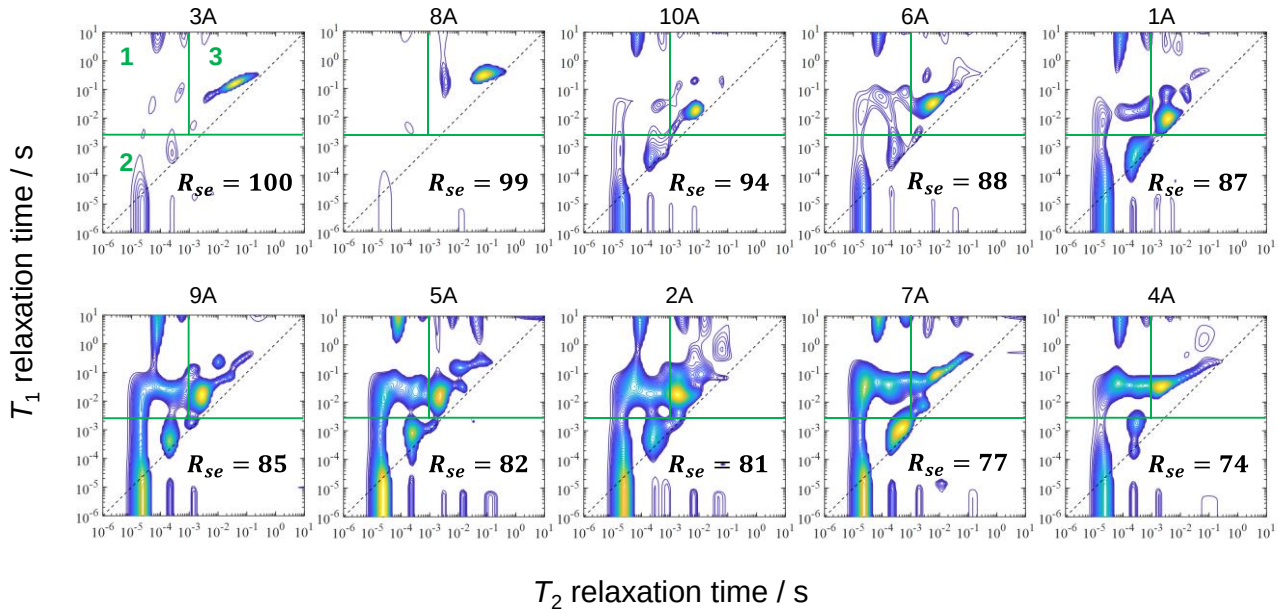


Figure 3.15. T_1 - T_2 correlation maps of the oil-saturated shale powders obtained with the IR-SE pulse sequence. The intensity ratio between the ME and SE signals (R_{se} %) calculated from the 1D T_2 distributions is shown for each sample, and plots are presented in ascending order of R_{se} . The green lines separate the three regions: 1 = immobile organic matter, 2 = clay-interacting water, 3 = mobile fluids.

Figure 3.16 shows the same 2D plots obtained from the brine-saturated shales. Again, from small differences in the integrated signal intensity between the ME and SE/CPMG of samples 3B and 8B, T_1 - T_2 maps with a main peak centered at a relatively long $T_2 \sim 3$ ms, attributed to a mobile water component, were obtained. For all the other samples, the T_1 - T_2 maps present additional bound water and immobile organic matter peaks. For a relatively lower ratio of intensities between ME and SE measurements (R_{se} about 85-92 %) of samples 10B, 9B, and 1B, the intensity of the immobile organic matter peak results to be low compared to the bound water signal. As we scan through samples with decreasing R_{se} , the relative intensity of the immobile organic matter peak in the T_1 - T_2 maps increases accordingly. Samples 4B and 7B have high-intensity immobile organic matter signals, and they are characterized by the smallest R_{se} and R_{cpmg} values, of about 70 and 40%, respectively.

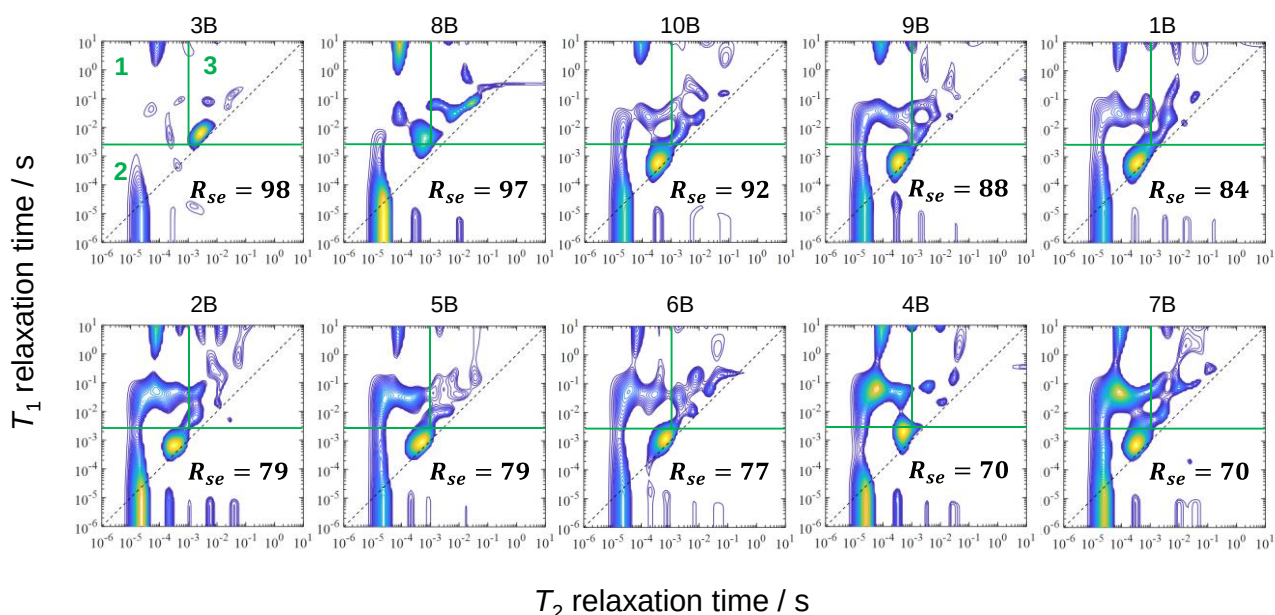


Figure 3.16. T_1 - T_2 correlation maps of the brine-saturated shale powders obtained with the IR-SE pulse sequence. The intensity ratio between the ME and SE signals (R_{se} %) calculated from the 1D T_2 distributions is shown for each sample, and plots are presented in ascending order of R_{se} . The green lines separate the three regions: 1 = immobile organic matter, 2 = clay-interacting water, 3 = mobile fluids.

These results show that the contrast between the ME and SE signal amplitudes (R_{se}) is well-correlated to the peak intensity of the short- T_2 components in the T_1 - T_2 correlation maps and, therefore, to the fraction of immobile phases in the shale. While shale samples containing solely mobile species have nearly equal refocusing by the three pulse sequences, major differences are observed for shales with strong contributions from components with limited mobility, indicating that these signals are better refocused by the ME technique. In particular, the ratio between the ME and SE signals decreases with increasing intensity of the immobile organic matter peak in the T_1 - T_2 plots, supporting the hypothesis that R_{se} indicates the presence of highly dipolar-coupled phases undergoing multiple homonuclear dipolar couplings. This promotes greater confidence in the idea that the additional signal obtained with the ME technique comes from immobile organics such as kerogen, bitumen, and small molecules in tightly fitting nanopores.

3.6.2.5 Summary oil- or brine-saturated shale powders

Results presented for this series of powdered shale samples indicate that the combination of standard CMPG with the alternative SE and ME methods show the potential to identify and quantify both the highly-viscous/solid organics and mobile oil in shale rocks. Table 3.7 reports a summary of the three pulse sequences' efficiency to refocus the various shale components. Among the three

techniques, the ME sequence gives the best performance in terms of detection of the organic content of the shales. When performed on shale samples containing solid species, the ME sequence extends the lifetime of the short- T_2 components and provides more signal than the SE and CPMG in the reliable T_2 regions ($T_2 > 100 \mu\text{s}$). An additional benefit of the ME sequence is that surface hydroxyls / bound water components with $T_1 < 100 \mu\text{s}$ are not refocused and lost, promoting enhanced detection of immobile organic components like kerogen. Lastly, in addition to kerogen and bitumen, the ME may also enhance signals from small hydrocarbon molecules under nanoconfinement.

From the 1D T_2 analysis, large differences in signal intensity between the three T_2 methods were obtained only for species with limited mobility. A comparison with 2D T_1 - T_2 maps confirmed the presence of a correlation between the ME and SE/CPMG signal ratio (R_{se} , R_{cpmg}) and the amount of immobile organic matter present in the shale. Therefore, the ratio of intensities between the three signals can potentially be used as a proxy for the fraction of immobile hydrocarbon in the shale. However, the differences between the three T_2 measurements methods cannot be attributed to specific components in the shales. Several types of interactions may occur between solid and liquid species, such as spin diffusion and homonuclear dipolar coupling between organic pores and fluid molecules, which can affect the T_2 measurements.

Fluid/solid components	CPMG		SE		ME	
	Refocusing	T_2 (ms)	Refocusing	T_2 (ms)	Refocusing	T_2 (ms)
Kerogen	-	< 0.1*	+/-	< 0.1*	+	0.6 – 1
Hydroxyls	-	< 0.1*	-	< 0.1*	-	0.6 – 1
Bitumen	+/-	0.1 – 0.4	+	0.1 – 0.4	+	0.6 – 1
Bound water	+/-	0.1 – 0.4	+	0.1 – 0.4	+	0.6 – 1
Mobile oil/water	+	2 – 4	+	2 – 4	+	2 – 10

Table 3.7. CPMG, SE and ME efficiency to refocus shale components. Typical T_2 values obtained with the three pulse sequences are also shown. The symbols state for: (-) not refocused, (+) refocused, and (+/-) partially refocused. *) detected but quantitation unreliable due to the poor quality of the data points.

3.6.3 Thermally dehydrated, previously oil- or brine-saturated shale powders

In an attempt to remove bound water, the same 2D T_1 - T_2 and 1D T_2 experiments were repeated for four oven-dried shale powders. Samples 6A-B and 10A-B were dried under vacuum at 80°C for 24 hours. Figure 3.17 shows a comparison between the IR-SE T_1 - T_2 correlation maps obtained from these samples, before and after they were dried. As described in *Section 4.2.3*, the T_1 - T_2 maps of the oil-saturated samples 6A and 10A present a dominant oil peak, as well as two weak signals of immobile organic matter and bound water. The T_1 - T_2 maps of the dry samples are substantially different. Instead of a single oil peak at $T_2 \sim 5$ ms, more peaks with lower intensity are observed between $T_2 \sim 1$ ms and $T_2 \sim 10$ ms. Part of the oil peak has moved to a shorter- T_2 region, while the location of the immobile organic matter and bound water peaks remained unchanged. The shift of the oil peak implies a rearrangement of the oil phase from a more mobile state to an immobile state. Such a transition may be caused by migration of oil species into smaller pores, induced by the drying procedure, or by the removal of a water fraction in the interparticle pores that was preventing oil from aggregating and forming an immobile phase.

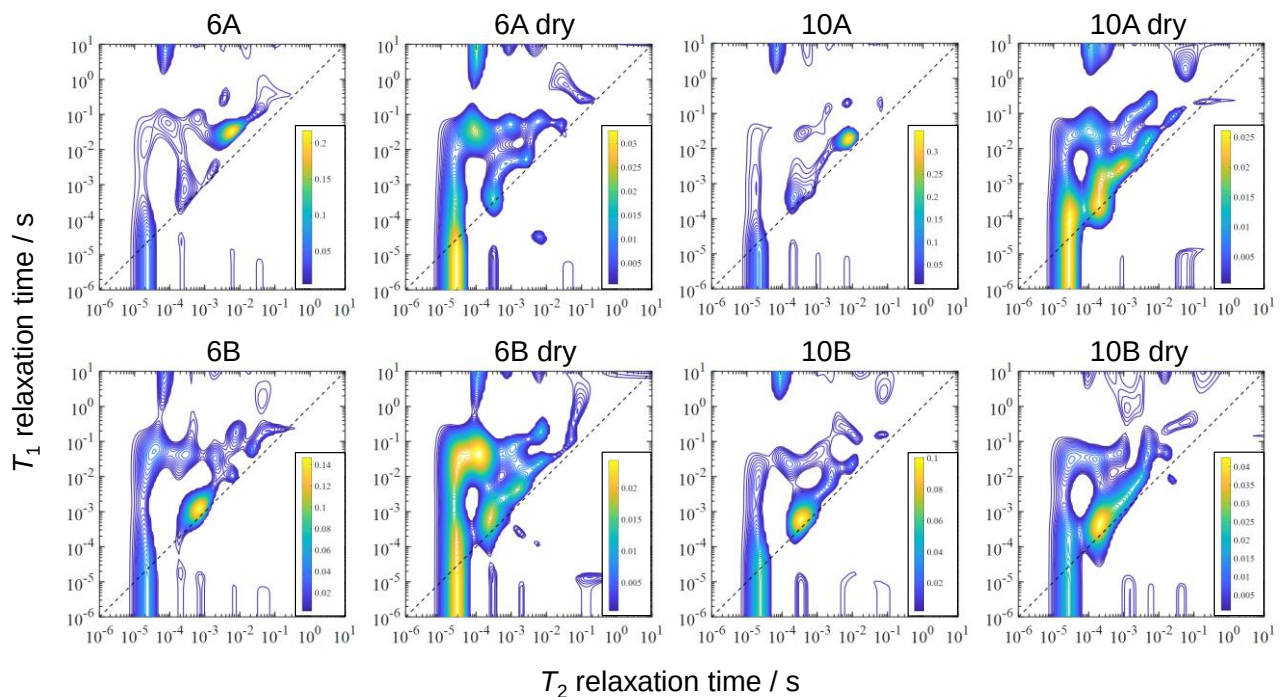


Figure 3.17. IR-SE T_1 - T_2 correlation maps of shales 6A-B and 10A-B obtained before and after the samples were dried.

The T_1 - T_2 distribution of the dry shale 6B shows an increase in the relative intensity of the immobile organic matter and bound water signals, indicating that part of the mobile water and light oil has been removed. The same behavior is observed also for shale 10B, to a lesser extent.

CPMG, SE and ME T_2 distributions of the powdered shale samples 6A-B and 10A-B, obtained before and after the samples were oven-dried, are presented in Figure 3.18 and 3.19, respectively. The short T_2 peak in CPMG and SE distributions (region 1, with $T_2 < 100 \mu s$) is excluded from the T_2 signal amplitude analysis because it is defined by only two sampling points. All T_2 distributions contain signal from immobile organic matter plus bound water (region 2, with $100 \mu s < T_2 < 2 ms$) as well as from mobile fluids (region 3, with $T_2 > 2 ms$). The signal intensity of the long- T_2 peak associated with mobile fluids (region 3) is much lower in all distributions obtained from the dry shales, and this effect is enhanced in oil-saturated shales. The intensity of the immobile organic matter plus bound water signal (region 2) also slightly decreases in the dry shales.

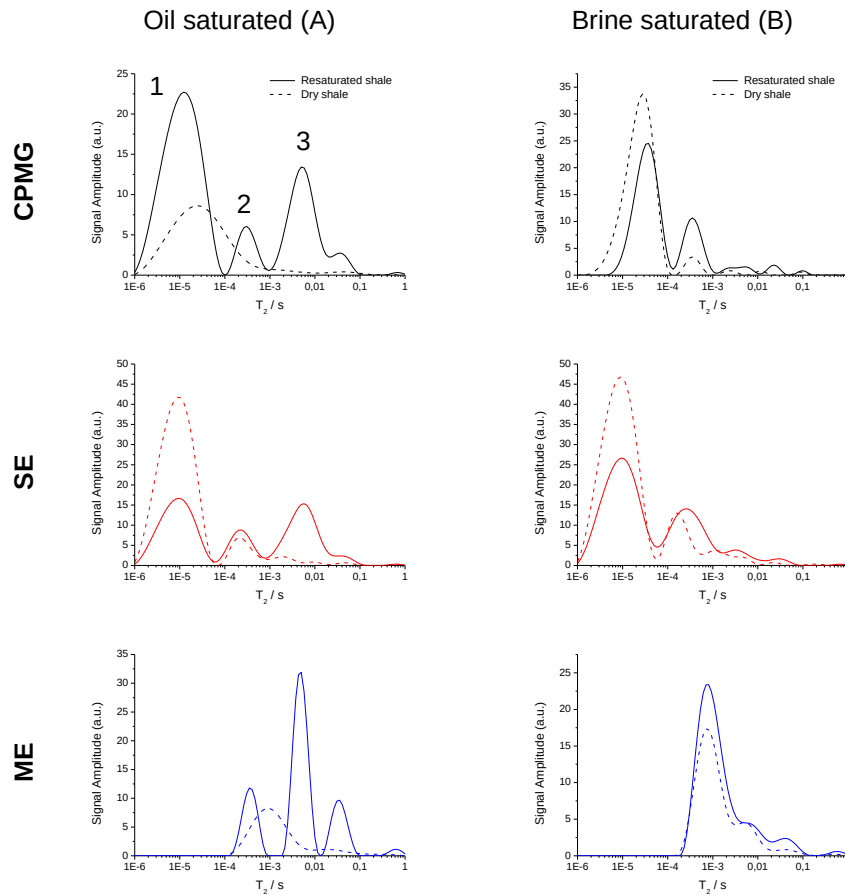


Figure 3.18. CPMG, SE and ME T_2 distributions obtained from shale powders 6A and 6B before (solid line) and after (dashed line) the samples were dried. The peaks correspond to immobile organic matter plus bound water (region 2) and mobile oil and water (region 3). Region 1 is associated with no components because defined by only two sampling points.

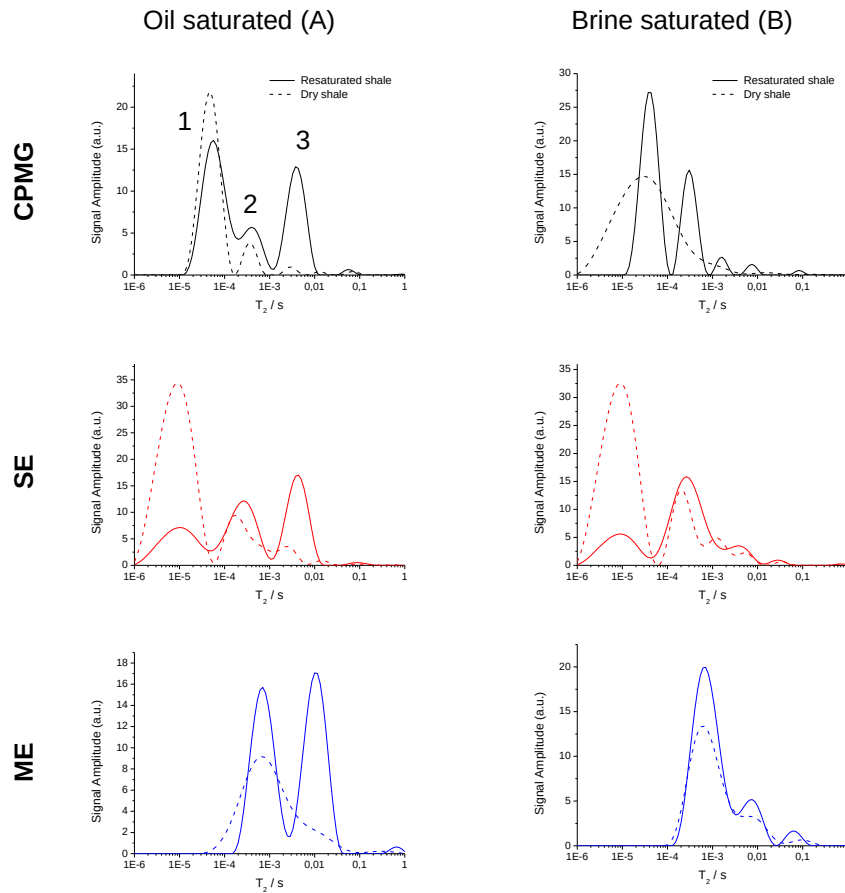


Figure 3.19. CPMG, SE and ME T_2 distributions obtained from shale powders 10A and 10B before (solid line) and after (dashed line) the samples were dried. The peaks correspond to immobile organic matter plus bound water (region 2) and mobile oil and water (region 3). Region 1 is associated with no components because defined by only two sampling points.

Relative signal intensities obtained from the CPMG, SE and ME 1D T_2 distributions of the dry shale samples are illustrated in Figure 3.20, and the respective signal differences are given in Table 3.8.

Sample ID	<i>Oil saturated (A)</i>		<i>Brine saturated (B)</i>	
	R_{se} (%)	R_{cpmg} (%)	R_{se} (%)	R_{cpmg} (%)
6 dry	66.0	12.7	72.5	13.4
10 dry	72.9	15.2	79.3	19.4

Table 3.8. Fractions of the SE and CPMG signals relative to the ME signal (R_{se} and R_{cpmg}) calculated from the 1D T_2 distributions of the dry shale samples 6A-B and 10A-B.

Both the CPMG and SE signal amplitudes, relative to the ME intensity, decrease considerably in the dry shales. The CPMG fraction of sample 6A is about 60% of the ME signal, and it drops down to only about 10% after the sample is dried, while the SE fraction is reduced by about 20%. The same trend is observed for the brine-saturated sample 6B, but the signal decrease is much less than that of its oil-saturated counterpart. Similar results are obtained for samples 10A and 10B. The significant

reduction of the CPMG and SE signal fractions, for the oil-saturated shales, is consistent with the formation of an oil phase with limited mobility, observed in the T_1 - T_2 maps. This immobile phase may reflect oil species strongly confined in small pores, which are not efficiently refocused by the CPMG and SE sequences. These results demonstrate that for a more coupled system the SE cycle becomes less efficient at refocusing the coherence dephasing. Not only kerogen and bitumen but also oil species under nanoconfinement may represent highly dipolar-coupled phases, which contribute to the signal difference between the ME and the SE methods. However, the large difference between signal intensities obtained with the three sequences (low values of R_{se} and R_{cpmg}) are also due to the increased relative intensity of the immobile organic matter and bound water peaks, which results from a partial removal of light oil and mobile water components during the drying procedure.

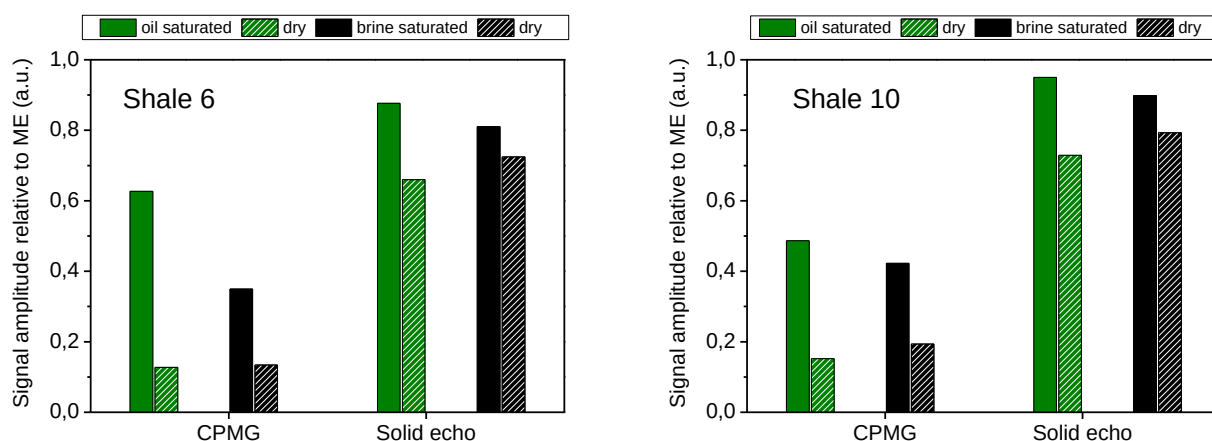


Figure 3.20. Normalized T_2 signal intensities of the CPMG and SE T_2 distributions, relative to the ME intensity, obtained from the oil-saturated samples 6A and 10A (green bars) and from the brine-saturated samples 6B and 10B (black bars), before and after the samples were dried. For each sample, the integral area of the ME signal was set to 1 and the CPMG and SE signal intensities were scaled accordingly.

3.7 Conclusions

In this work, a shales characterization approach based on a combined analysis of ^1H NMR relaxation CPMG, solid-echo (SE), and mixed-echo (ME) pulse sequences was proposed. Solid-state pulse-sequences that can suppress ^1H - ^1H dipolar coupling, applied at a 13 MHz (^1H) frequency on a benchtop spectrometer, enable signals from organic fractions with restricted mobility, including kerogen and bitumen, in several oil- and brine-saturated shales to be captured. These experiments were interpreted with a typing scheme based on T_1 - T_2 correlation experiments that provides a more

complete description of the solid/highly viscous and mobile phases in the shale. Specifically, this approach resolves signal contributions from immobile organic matter and the clay-bound water, which generally overlap in 1D T_2 distributions. Results show that the three spin-echo techniques perform similarly for mobile/low-viscosity fluids, and substantially differently for shale systems containing high amounts of immobile organic materials. In particular, the intensity ratio between the ME and SE signals reflects the presence of strongly dipolar-coupled phases, such as kerogen, bitumen, and small hydrocarbon molecules under nanoconfinement. Further work will be required to broaden the understanding of the multifarious NMR responses of the materials resident in the shale, and to develop further methods for their gravimetric quantification.

Chapter 4: Double-quantum ^1H NMR Methods and Applications for Shale Systems

4.1 Abstract

Quantitative characterization of the solid organic matrix and fluids in shale reservoirs is critical for both resource evaluation and production. This chapter reports on the application of double-quantum (DQ) ^1H NMR methods for the quantitative evaluation of solid and viscous organic phases in unconventional shale rocks. It is shown that this technique is able to selectively excite the immobile organic components of shales, namely kerogen and bitumen, which exhibit strong ^1H dipole interactions, not averaged out by molecular motions. Here, DQ NMR is applied to (i) a series of artificially matured Green River shales, to investigate the chemical and physical structure evolution of the solid organic fraction during the maturation process, and (ii) a set of powdered oil- or brine-saturated Eagle Ford shales, to identify and quantitatively separate the immobile components. An innovative approach for the analysis of ^1H DQ build-ups, involving the numerical inversion of DQ data, yields distributions of residual dipolar coupling (RDC) constants, that underlie structural information on the immobile hydrocarbon phases of the investigated shales. In contrast to traditional ^1H T_2 Hahn-echo measurements, for which information on RDC are typically masked by effects of intermediate motions, DQ NMR is shown to provide reliable separation between strongly dipolar-coupled phases, such as kerogen, and more weakly-coupled species, such as oil molecules under nanoconfinement. Results show that DQ NMR offers a potential method for obtaining improved description of hydrogen-bearing components with limited mobility in shale rocks.

4.2 Introduction

Quantitative evaluation and separation of kerogen, bitumen and light oil is critical for determining the shale reservoir quality, which is a measure of the ability of the formation to produce hydrocarbons upon stimulation.^{18,20} In shale rocks containing gas resources, natural gas is more

likely to be contained within organic pores in the kerogen matrix. Therefore, kerogen represents a positive reservoir quality indicator because it can be considered as a proxy for the organic porosity and, ultimately, for the natural gas fraction. However, if the shales contain light oil (tight-oil shales), both kerogen and bitumen may produce negative effects on the reservoir quality. These components can trap the production fluids by adsorption, clogging pore throats and swelling, reducing the oil permeability.²¹

¹H NMR relaxometry has emerged as one of the key methods for characterizing the organic content in shale formations, but quantitative detection of solid and highly viscous materials in shale rocks remains a main challenge. As a result of the restricted (anisotropic) character of molecule motions in these systems, dipole interactions are not fully averaged, and the residual dipolar coupling (RDC) leads to quick loss of signal in CPMG experiments (short transverse relaxation times T_2).^{67,68} Such fast-decaying time-domain signals are not detectable by current low-field NMR spectrometers due to their lower limit on the spin-echo time.⁵⁹ The same residual dipolar coupling that underlie the short T_2 relaxation of these components can also be used to generate double-quantum coherences in hydrogen spin pairs. Double-quantum (DQ) experiments can be exploited to measure dipole couplings between the spins in dipolar-coupled systems, as the efficiency of excitation of DQ coherences is directly related to their dipolar coupling.⁴⁴ Compared to the traditional CPMG or Hahn-echo sequences, which are limited by their minimal echo sampling time, the DQ sequence can measure signals immediately after the receiver dead time, enabling acquisition of the short T_2 components. In addition, in contrast to ¹H NMR T_2 relaxometry, DQ NMR methods can provide reliable separation between the coherent build-up of DQ coherences and the incoherent loss of transverse magnetization, yielding direct information on the proton-proton dipole coupling.^{133,134} Therefore, this technique can be used as an alternative method to standard T_2 relaxometry to measure kerogen and bitumen in the shale. DQ ¹H NMR is widely used in polymer science to investigate polymer chain dynamics and structural constraints in a variety of systems.¹³⁵ For these materials, the DQ signal reflects the residual proton dipole coupling resulting from restrictions of the polymer-chain mobility, posed by topological constraints such as crosslinks and entanglements.^{133,136,137,138}

In this chapter, the potential of DQ ¹H NMR methods for the quantitative characterization of organic phases with limited mobility in various shale systems, is explored. In previous work, Washburn⁷ has performed some preliminary experiments using basic DQ filter spin-diffusion measurements to

monitor exchange of magnetization between solids and saturating fluids in shales. However, to the authors' knowledge, the study in this chapter represents a novel DQ NMR approach for petrophysical applications, where DQ build-up curves obtained from shale samples are shown for the first time. This technique is able to selectively excite only the solid and highly viscous fractions of the shale and it could provide a route to robust kerogen/bitumen discrimination. Results obtained for two different case studies of DQ ^1H NMR applications to shale systems are reported. In the first case study, a series of thermally matured Green River shales is analyzed to investigate the evolution of the chemical composition and structure of the solid organic fraction over the maturation process. The second case involves the study of a set of powdered oil- and brine-saturated shales, recovered from various depths in the Eagle Ford area, to quantitatively separate the various organic components. Re-saturation of these samples was performed to address the loss of producible fluids during core retrieval to the surface, with the aim to make them reasonably representative of the formation in-situ state.

In both studies, the DQ build-up curves are analyzed using numerical inversion with a Gaussian kernel to generate RDC distributions, which help identifying and quantifying solid and viscous components present in the shale. This work demonstrates that DQ NMR can be used to measure RDC constants of distinct material phases, which can be directly related to the immobile organic species in the investigated shales.

4.3 The Double-quantum NMR Method

4.3.1 Double-quantum ^1H NMR pulse sequence

The pulse sequence for selectively generating and converting the double quantum coherence into detectable single quantum coherence (SQ) is illustrated in Figure 4.1, and the used phase cycle is reported in Table 4.1. During the first interval (excitation time), longitudinal spin polarization is converted into double-quantum coherences, which are generated for coupled protons for which dipolar coherent effects are faster than incoherent NMR relaxation processes. Since DQ coherences cannot be directly detected, the DQ signal is converted back into SQ coherence during the reconversion time. The excitation and reconversion periods have equal time duration τ , which is varied over consecutive experiments to obtain a DQ build-up curve. The evolution time interval t_1 ,

between the excitation and reconversion time, is kept constant at short time ($3\ \mu\text{s}$) to prevent signal decay. A z-filter delay (t_f), typically on the order of 1 ms, is inserted before the acquisition to remove undesired coherences arising from pulse imperfections. Selection of multiple quantum coherences is realized by incrementing the pulse phase by $\Delta\varphi$ over successive step of the phase cycle and, at the same time, by incrementing the receiver phase by $n\Delta\varphi$, where n is the coherence order to be selected. With $n = \pm 2$, this phase cycle selects DQ coherences and cancels all unwanted coherences. A reference measurement, which represents all signal that has not evolved into DQ, is obtained by suitable adjustment of the phase cycle of the receiver.

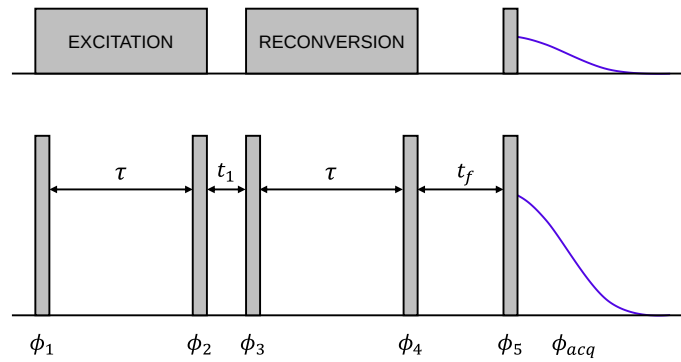


Figure 4.1. The 5-pulse double-quantum (DQ) NMR pulse sequence. The DQ build-up curves are obtained by varying τ while keeping t_1 and t_f fixed. The grey bars represent the 90° pulses.

Cycle	A	B	C	D	E	F	G	H
φ_1	x	y	x	y	x	y	x	y
φ_2	-x	-y	-x	-y	-x	-y	-x	-y
φ_3	y	y	y	y	y	y	y	y
φ_4	-y	-y	-y	-y	-y	-y	-y	-y
φ_5	x	x	y	y	-x	-x	-y	-y
$\varphi_{acq} (DQ)$	x	-x	y	-y	-x	x	-y	y
$\varphi_{acq} (ref)$	x	x	y	y	-x	-x	-y	-y

Table 4.1. Phase cycling used for the DQ pulse sequence. The phase cycle of the acquisition pulse can be changed to acquire either the DQ signal or the reference signal.

4.3.2 Double-quantum build-up curve analysis

The DQ experiment generates DQ coherence, which is only sustained by the strongly coupled spins in a solid.⁴⁰ In this context, "*solid*" means any material, including viscous fluids, for which the dipole interactions are only partially averaged by restricted anisotropic motions. In principle, the DQ experiment returns a signal from rigid and soft solids, but not from mobile species, for which dipolar couplings are completely averaged out by fast isotropic motions.

DQ build-up curves are obtained by incrementing the excitation and reconversion time (τ) over consecutive experiments. Two complementary signal functions can be recorded with a simple change in the phase cycle of the receiver.^{139,140} The first signal is the DQ build-up, I_{DQ} , which contains the desired information on the RDC. The second signal is the reference intensity, I_{ref} , which represents all coherences that have not evolved into DQ and that is subjected to the same relaxation effects as I_{DQ} . The I_{DQ} and I_{ref} signals have, respectively, a sine and cosine dependence on $\omega_D \tau$ ¹³⁶, where ω_D is the dipolar coupling frequency (eq. 1.12):

$$I_{DQ}(\tau) \propto \langle \sin^2(\omega_D \tau) \rangle \quad (4.1a)$$

$$I_{ref}(\tau) \propto \langle \cos^2(\omega_D \tau) \rangle \quad (4.1b)$$

where $\langle \dots \rangle$ represents the ensemble average over all possible orientations. The sum of the two experimental data ($I_{ref} + I_{DQ}$) reflects the full coherence of the system, which includes signal from strongly dipolar-coupled phases as well as from dipolar uncoupled (liquidlike) protons. Generally, for a proton network (e.g., in polymer systems), the effect of incoherent molecular motions on the DQ and the reference signals is nearly equal. Therefore, the relaxation contribution to I_{DQ} can be removed by a point-by-point normalization of the DQ build-up curve, generating normalized DQ build-ups (I_{DQ}^N), which carry structural information only.^{141,142} However, I_{ref} may contain additional contributions from mobile species characterized by a long effective T_2 relaxation, for which the overall loss of coherence phase is faster than the build-up of DQ coherences. These components may give rise to long-time tails in the reference signal, which needs to be fitted and subtracted. For example, considering a monoexponential signal tail decaying with T_{2a} , the corrected normalized DQ intensity will be expressed as:

$$I_{DQ}^N = \frac{I_{DQ}}{I_{ref} + I_{DQ} - a \exp(-\tau/T_{2a})} \quad (4.2)$$

The success of an appropriate tail subtraction is confirmed by the observation of an intensity plateau of I_{DQ}^N at 0.5, reflecting the equal partitioning of all quantum orders between I_{DQ} and I_{ref} (see eq. (4.1), I_{DQ} and I_{ref} tend to 0.5 in the long-time limit).^{140,176} The initial curvature of the signal underlies the relation between DQ build-ups and the dipole coupling constants. Therefore, direct information on the RDC can be obtained by fitting these data to appropriate model functions. In the simplest second-moment approximation^{138,176}, the parabolic start of the build-up from time zero reflects the sum of all squared ^1H - ^1H dipole coupling constants. According to this phenomenological model, I_{DQ}^N is given by eq. (4.3), where D_{res} represents the apparent RDC arising from the averaged action of many spin-pair couplings:

$$I_{DQ}^N(\tau, D_{res}) \approx 0.5\{1 - \exp(-0.4D_{res}^2\tau^2)\} \quad (4.3)$$

However, when DQ build-ups reflect a non-monomodal RDC distribution, like the case of heterogeneous materials, eq. (4.3) will not provide a good description of the DQ curves because it only considers a single D_{res} value.¹⁷⁷ In this case, the distribution parameters, i.e., the D_{res} components and their relative weights, can be evaluated by numerical inversion procedures, using eq. (4.3) as the kernel function:

$$s(\tau) \approx \int_0^\infty I_{DQ}^N(\tau, D_{res}) p(D_{res}) dD_{res} \quad (4.4)$$

Where $s(\tau)$ is the measured signal, and $p(D_{res})$ represents the distribution of residual dipolar coupling. Therefore, $p(D_{res})$ can be obtained by inverting eq. (4.4) with the use of a proper regularization method that provides a suitable balance between smoothness and accuracy in the solution.

4.4 Experimental

4.4.1 Materials and sample preparation

4.4.1.1 Thermally matured spent shales

A series of spent shales prepared as part of a previous project¹⁶⁰ involving the artificial maturation of Green River shale by pyrolysis using semi-open laboratory conditions were investigated. The kerogen isolates characterized in Chapter 2 were extracted from the here investigated spent shales.

The spent shale is the granular solid matter remaining after pyrolysis, and it contains inorganic as well as organic matter fractions, which are kerogen and bitumen. The pyrolysis procedure was carried out over a range of pressure (1–5 MPa), heating rate (2–120 °C/h), plateau temperature (300–425 °C), and plateau time (5–12.5 h) conditions, which are shown in Table 4.2. The maturation scale of the shales was determined using a synthetic vitrinite reflectance, Easy % R_0 . Details on the maturity measures are reported in *Section 2.3.2*.

Sample ID	Heating rate α (°C/h)	Temperature (°C)	Pressure (atm)	Duration time (h)	Maturity (Easy % R_0)
A	63	333	20	7.5	0.98
B	63	332	40	12.5	1.04
C	20	359	30	10	1.32
D	20	359	30	15	1.41
E	6	393	20	7.5	1.86

Table 4.2. Pyrolysis conditions and maturity measure (Easy % R_0) for the spent shale samples.

4.4.1.2 Oil- or brine-saturated shales

The same series of twin core plug shales extracted from various depths in the Eagle Ford formation, investigated in Chapter 3, was also used in this chapter (Table 3.1). Each shale core plug (38 mm internal diameter) was cut in half, one part saturated with oil (labeled as set A) and the other one with brine (labeled as set B), forming a set of twin samples. Before the NMR experiments, the shale core plugs were crushed into powders for fitting in a 4 mm sample holder.

4.4.2 NMR experiments

Static ^1H NMR experiments were performed on a Bruker Avance III spectrometer working at 200 MHz, equipped with a 4 mm MAS coil at the magic angle with respect to the magnetic field. All the experiments were implemented under static (non-spinning) conditions, at room temperature and with a 90° pulse length of 3 μs . The recycle delay was set to 3 s and dead time of the spectrometer was 5 μs . In Hahn-echo experiments, the first echo time was set to 10 μs , and it was gradually increased up to a maximum of 6 ms, over a total of 32 discrete values spaced logarithmically. In DQ ^1H NMR experiments, the excitation and reconversion time τ was gradually increased from 1 μs to 100 μs , with a total of 32 discrete points. Discrete fitting analysis of the normalized DQ build-up signals was performed using the nonlinear least-squares method in the Origin software program (OriginLab).

4.4.3 Numerical inversion

Distributions of relaxation time T_2 , constrained to be always positive and bound by set limits in the relaxation time dimension, were generated from the Hahn-echo NMR data using the an exponential kernel in the inversion method of Venkataramanan *et al.*¹⁷³ with generalized cross validation (GCV) method for optimisation of smoothing parameter. The same method was used to generate RDC distributions from the DQ NMR data, using a Gaussian kernel in the numerical inversion.

4.5 Results and discussion

Results obtained for two different case studies of DQ ^1H NMR applications to shale systems are presented here. In the first case study (*Section 4.5.2*), the DQ NMR approach is applied to a series of thermally matured Green River shales containing solid organics, i.e., kerogen and bitumen, plus inorganic materials. In this study, DQ NMR is used to probe the evolution of the chemical composition and structure of these solid organic fractions over the maturation process, by tracking the relative proton density changes.

The ^1H DQ NMR method was also applied to a set of powdered oil- or brine-saturated shales, recovered from various depths in the Eagle Ford area, which contain various hydrogen-bearing components (*Section 4.5.3*). The molecular mobility of these components differs dramatically, ranging from solid kerogen and highly viscous bitumen to light oil, which can be present in the organic nanopores or in large inorganic pores, and to bound or free water. In this case, DQ NMR is used as a method to quantitatively separate the immobile components in the shales.

4.5.1 Validation of the method

The applicability of the DQ pulse sequence is demonstrated on (1) standard homogeneous samples with different proton mobility and (2) mixed samples that feature bimodal behavior. These proof-of-concept experiments were performed to test whether the DQ pulse sequence can be used to distinguish between components with different molecular mobility and proton density in complex heterogeneous shale systems.

4.5.1.1 Homogeneous reference samples

In principle, the DQ experiment returns a signal from rigid and soft solids but not from mobile species, for which dipolar couplings are completely averaged out by fast isotropic motions. The DQ pulse sequence was tested with three homogeneous reference samples with different molecular mobility: polyether ether ketone (PEEK) (solid), adamantane (plastic crystal) and olive oil (liquid). DQ build-up and reference signals obtained from the three model samples are shown in Figure 4.2. These DQ build-up curves were obtained by repeating the experiment with increasing τ . The DQ build-up curve of PEEK exhibits a steep initial slope with a maximum at around 18 μs , while the DQ signal measured from adamantane appears to have a slower rise, and its maximum is found at 40 μs . For the solid PEEK, the RDC constants are considerably strong, and give rise to a rapid increase in the DQ build-up at short τ values. Adamantane is a plastic crystal in which the nearly spherical molecules can tumble isotropically in the solid phase. At room temperature, the isotropic rotation of the molecules is fast enough to average all intramolecular couplings to zero, leaving weak intermolecular couplings.^{178,179,180} As a result, the average dipolar coupling strength in adamantane is weaker than in PEEK, and this effect is reflected by a slower build-up of DQ coherences. As expected, no DQ signal is observed for mobile olive oil due to the fast isotropic molecular motions that average out the dipolar Hamiltonian.

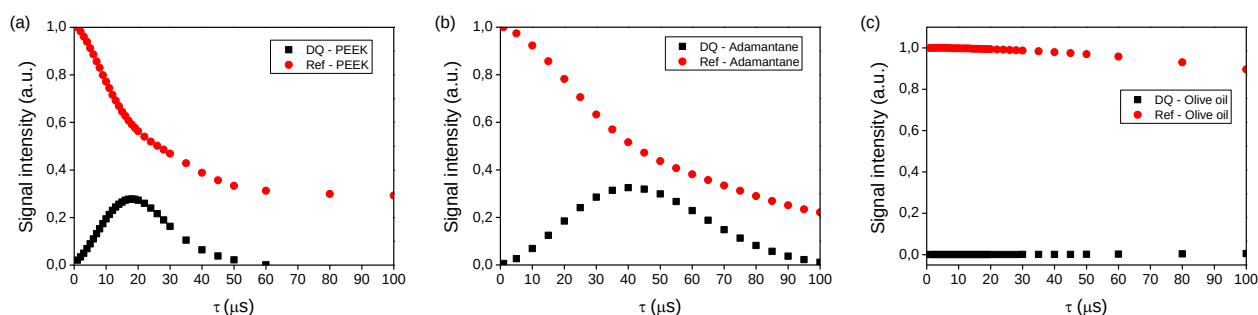


Figure 4.2. Double-quantum build-up (black) and reference (red) signals obtained from the three homogeneous reference samples: (a) PEEK, (b) adamantane and (c) olive oil.

This first test demonstrates that the DQ technique can be used to discriminate between homogenous phases with different molecular mobility.

4.5.1.2 Heterogeneous mixed samples

DQ and reference signals from mixed samples of adamantane and poly(methyl methacrylate) (PMMA) were measured to test the applicability of this technique for the identification and quantification of different components in multi-phase networks. The two components were physically mixed, leaving their structures unaltered. The mixed samples (Table 4.4) were prepared with the following concentration of adamantane (expressed in weight fraction %): 0 %, 25 %, 45 %, 75 % and 100 %. The sample number indicates the weight fraction of adamantane in percent, so that sample ada0 refers to pure PMMA, and sample ada100 refers to pure adamantane.

Sample ID	Adamantane	Adamantane
	weight fraction wt (%)	¹ H fraction wt (%)
ada0	0	0
ada25	0.25	0.33
ada45	0.45	0.55
ada75	0.75	0.82
ada100	100	1

Table 4.3. Mixed samples of adamantane and PMMA. The sample number indicates the weight fraction of adamantane in percent.

The ¹H NMR spectra of the mixed samples obtained in static conditions are illustrated in Figure 4.3. As expected, the spectrum of ada100 (pure adamantane) is to be much narrower than that of ada0 (pure PMMA). The peak becomes broader with increasing fraction of the more rigid PMMA phase in the mixed samples. The observed NMR line-broadening is due to the higher content of PMMA in the sample, for which restricted anisotropic chain motions are responsible for incomplete averaging of ¹H dipolar couplings.

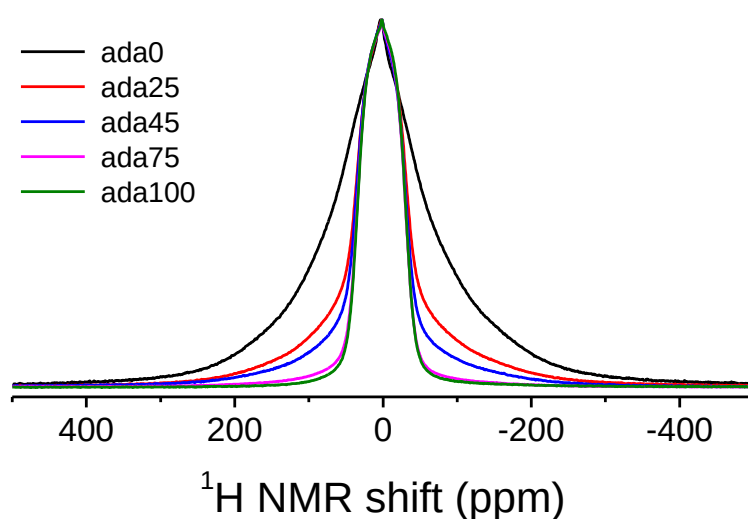


Figure 4.3. Static ^1H NMR spectra obtained from the mixed samples of adamantane and PMMA.

Figure 4.4 shows the DQ and reference signals obtained from the adamantane-PMMA mixed samples. The DQ build-up curves of samples ada0 (pure PMMA, in black) and ada100 (pure adamantane, in green) exhibit a single maximum located at $10\ \mu\text{s}$ and $40\ \mu\text{s}$, respectively. The PMMA build-up is characterized by a steep slope that indicates stronger RDC, while for the more mobile adamantane the DQ signal reveals a slower build-up. As the adamantane fraction in the mixed sample increases, the initial slope of the DQ build-up becomes less steep and two distinct maxima appear, indicating the presence of a two-components mixture.

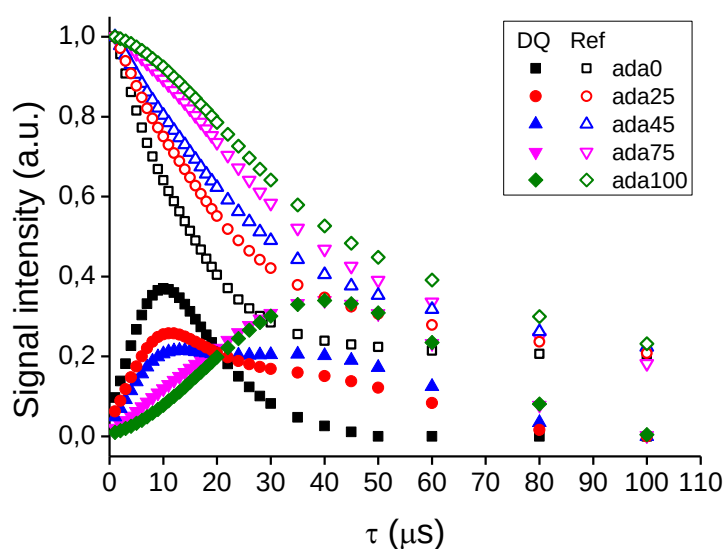


Figure 4.4. Double-quantum and reference signals obtained from the mixed samples of adamantane and PMMA.

The DQ signals were normalized and fitted with a non-linear least-square fitting program, where the standard χ^2 analysis was used to estimate the quality of the fits. The DQ build-ups of pure PMMA and adamantane (samples ada0 and ada100, respectively) were well reproduced by the Gaussian function (second-moment approximation) of eq. (4.3). In this respect, information on the averaged dipolar coupling constant (D_{res}) of homogeneous single-phase materials can be directly obtained by fitting the Gaussian model to the normalized DQ build-ups. Figure 4.5a shows the normalized DQ build-ups of the mixed samples with the corresponding fitting curves, and fitting results are shown in Table 4.5. The single-Gaussian build-up function of eq. (4.3) provides good fits to the DQ build-up curves obtained from the single-component systems, but it does not reproduce the curve signals obtained for the mixed materials. Because of the chemical heterogeneity, these systems are characterized by more than one RDC constant. Therefore, these curves were fitted with a linear combination of two Gaussian components:

$$S_{DQ}(\tau, D_{res}) = a S_{DQ}(D_{res,1}) + (1 - a) S_{DQ}(D_{res,2}) \quad (4.5)$$

where $D_{res,1}$ and $D_{res,2}$ refer to the RDC constants of the PMMA and adamantane phases, respectively, and the parameter a represents the PMMA relative weight. Fitting results (Table 4.5) show that pure PMMA (sample ada0) and pure adamantane (ada100) are characterized by a single component with $D_{res,1} \sim 20$ kHz and $D_{res,2} \sim 6$ kHz, respectively. For adamantane, this value is consistent with earlier estimates of the average residual dipolar coupling strength (6.1 kHz).¹⁸¹ Build-up curves of samples ada25, ada45 and ada75 were fitted as binary mixtures, with $D_{res,1}$ and $D_{res,2}$ fixed to the values obtained for the pure components (Table 4.5). Although results show a good agreement between the known proton content of adamantane (^1H wt (%)) and that extracted from the fitting analysis, $(1 - a)$, the fit quality is not good (large χ^2). For this reason, the fitting procedure for the DQ build-up curves of mixed materials was repeated allowing parameters $D_{res,1}$ and $D_{res,2}$ to vary. The higher number of free parameters provides better fit quality (lower χ^2), but worse predictions of the adamantane proton fraction. Fit results (last three rows in Table 4.5) show slightly different values of the RDC constants from those obtained for the pure components, where larger deviations of $D_{res,1}$ and $D_{res,2}$ are observed for mixtures with lower content of PMMA and adamantane, respectively.

The measured RDC constants also depend on how the model compounds are mixed. These results suggest that the two components are not mixed at local level, but DQ build-up curves are heterogeneous superpositions of individual contributions from the pure components. As such, the

analysis of DQ build-up curves can be used to identify and quantify the two components in these bi-modal networks.

Overall, as illustrated in Table 4.5 and Figure 4.5b, fit results show a small discrepancy between the theoretical and estimated fractions of adamantane. These positive deviations from linearity are probably related to error analysis of the method, which can occur during the sample preparation, or during the normalization and fitting processes.

Sample	Adamantane ^1H wt (%)	$D_{res,1}$ (kHz)	$D_{res,2}$ (kHz)	$(1 - a)$	$\chi^2 \times 10^3$
ada0	0	19.0	-	-	0.028
ada25	0.33	19.0*	5.5*	0.36	0.174
ada45	0.55	19.0*	5.5*	0.58	0.224
ada75	0.82	19.0*	5.5*	0.93	0.063
ada100	1	-	5.5	1	0.053
ada25	0.33	20.1	3.6	0.42	0.049
ada45	0.55	21.4	4.6	0.59	0.044
ada75	0.82	27.9	5.6	0.93	0.063

Table 4.4. Fitting results obtained by reproducing the normalized build-up curves with a linear combination of Gaussian functions. The asterisk indicates fit parameters that are fixed during the fitting procedure. The last three rows show results for the mixed materials, when parameters $D_{res,1}$ and $D_{res,2}$ are free to vary.

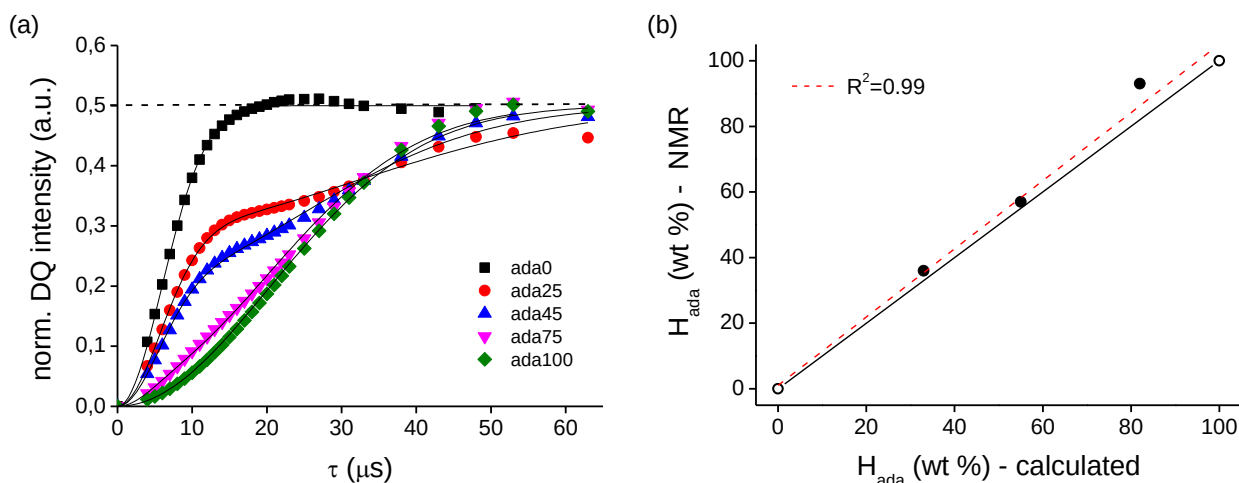


Figure 4.5. (a) Normalized DQ build-ups of the PMMA-adamantane mixed samples. The black lines correspond to the best-fit simulation results and the sample number indicates the weight fraction of adamantane in percent. (b) Correlation between the adamantane proton fraction determined from fitting analysis of DQ build-ups and the theoretical one.

A different approach to fit DQ build-ups to the Gaussian formula, eq. (4.3), or a superposition of Gaussian components, consists of analyzing the DQ build-up curves in terms of *continuous*

distributions of residual dipolar couplings. In this respect, the same Gaussian model is entered as the kernel function in a numerical inversion algorithm that makes use of the generalized cross validation (GCV) regularization method to obtain RDC distributions.

Figure 4.6 shows the D_{res} distributions obtained from the adamantane-PMMA mixed samples. As expected, the distribution of sample ada0 (pure PMMA) presents a single peak with a large D_{res} centered at about 20 kHz, while sample ada100 is characterized by a single peak located at a lower D_{res} of about 5-6 kHz. The two distinct D_{res} peaks in the D_{res} distributions of the mixed materials represent the fraction of adamantane and PMMA. As the adamantane/PMMA ratio of the sample increases, the intensity of the large- D_{res} peak decreases accordingly, and the lower- D_{res} component becomes more prominent. The signal amplitudes obtained by integrating the area under the distribution curves are essentially identical to the fractions obtained with the discrete fitting analysis, indicating that the two methods produce same results for these mixed materials. However, the numerical inversion method provides some advantages compared to the nonlinear least-squares fit method. The least-squares fitting is dependent on *a priori* knowledge of the number of components in the system, implying the need of several trials to find the solution. Therefore, this method is not well-suited for systems characterized by continuous distribution of residual dipolar couplings. The numerical inversion approach represents a more convenient way of analyzing DQ build-ups obtained from these materials as it enables to directly determine the number of components with different RDC, and their relative weight.

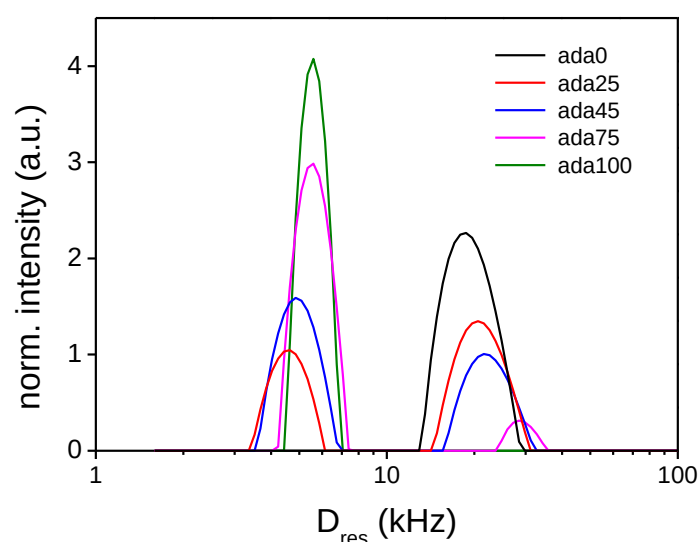


Figure 4.6. Distribution of residual dipolar couplings of the PMMA-adamantane mixtures obtained by processing the DQ NMR data using a Gaussian kernel in the numerical inversion.

4.5.2 Thermally matured Green River shales

4.5.2.1 T_2 relaxation

The spent shales investigated in this section are residual materials remaining after pyrolysis, containing inorganic material and solid organic fractions (kerogen and bitumen only). ^1H Hahn-echo decays obtained from the spent shales at different thermal maturities and the corresponding T_2 distributions are illustrated in Figure 4.7. All signals exhibit a fast T_2 decay with an additional slower-decaying component, which becomes more significant for the more mature spent shales.

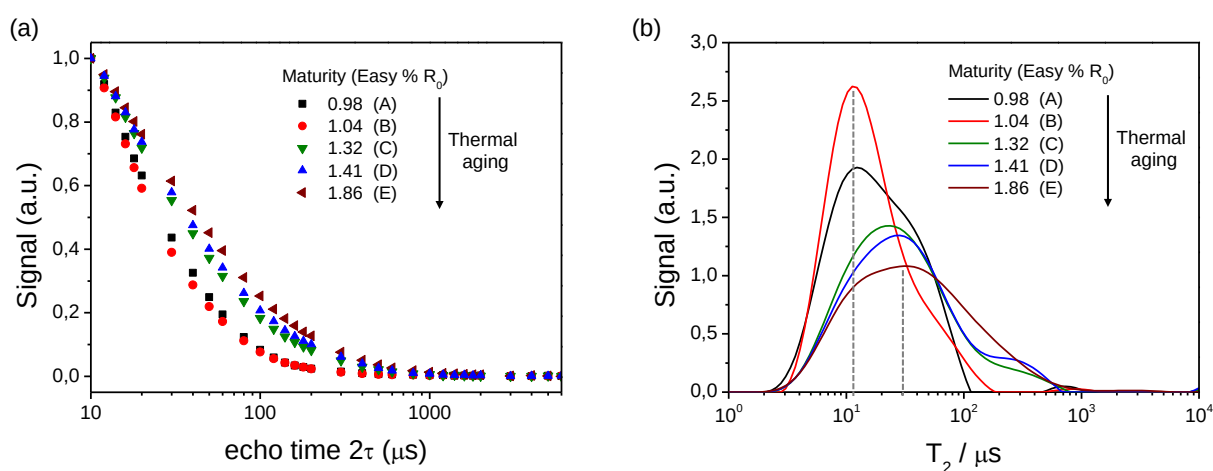


Figure 4.7. (a) ^1H transverse magnetization decays of the staged maturity spent shales acquired using the Hahn-echo pulse sequence in static conditions and (b) corresponding T_2 distributions obtained using an exponential kernel in the numerical inversion.

Numerical inversion of T_2 data obtained from the low-maturity shales A and B generates broad bimodal T_2 distributions with a dominant peak centered at $T_2 \sim 10 \mu\text{s}$, and a second peak located at about $T_2 \sim 40 \mu\text{s}$. The relative intensity of the short- T_2 peak appears to become smaller as the maturity level of the spent shale increases, with the position of this peak shifting to longer T_2 values. The short- T_2 peak is located at $T_2 \sim 30 \mu\text{s}$ in the T_2 distributions of the more mature shales C, D and E, which also present an additional smaller T_2 peak at a longer $T_2 \sim 300 \mu\text{s}$. Overall, a large part of these broad T_2 signals is observed at short T_2 values, indicating that the organic components of these spent shales, i.e., kerogen and bitumen, are mostly made up of rigid domains. However, because of the overlapping of the two peaks in the T_2 distributions, quantitative evaluation of the respective integral area is not possible.

These results are consistent with those shown in Chapter 2, which involved kerogen isolates extracted from the here investigated spent shales¹⁸², where a correlation between the long- T_2 peak in the T_2 distributions and the kerogen aromatic content is shown. This effect may be due to a drastic decrease in proton density of the sample that takes place during the thermal maturation. With increasing maturity, some carbon aliphatic moieties break down and aromatic units in sp^2 -hybridized graphitic structures form, altering the chemical composition of the organic compounds in the shale and leading to a net loss of hydrogen molecules in the system. The larger distance between hydrogen nuclei in the aromatic fraction (lower proton density) results in relatively weaker average dipole coupling interactions, which are reflected by a longer- T_2 peak in the T_2 distribution. This hypothesis is supported by ^{13}C NMR spectra obtained from the staged maturity kerogen extracted from the spent shales (see Chapter 2) which reveals that the sp^2/sp^3 -hybridized carbon ratio of the organic fraction in the kerogen, also defined as the aromatic/aliphatic ratio, increases with increasing maturity.

4.5.2.2 Double-quantum build-ups

Figure 4.8a shows the normalized ^1H DQ build-up curves obtained from the spent shales at different maturities. These build-up curves were fitted by a bi-Gaussian model, and results are reported in Table 4.6. Standard χ^2 analysis was used to estimate the quality of the fits. The DQ curves of the low maturity spent shales A and B (Easy % R_0 of 0.98 and 1.04) were well reproduced by the Gaussian build-up function described by eq. (4.3). Adding a second Gaussian component did not change the fit outcome or improve the fit quality. In this respect, shales A and B behave as a single homogeneous phase characterized by a strong RDC constant value of ~ 20 kHz. In contrast, eq. (4.3) does not provide a good fitting to the DQ signals obtained from the highly mature spent shales C, D, and E, as can be seen from the high χ^2 values in Table 4.6. With increasing maturity, considerable deviations from the single-Gaussian build-up function were observed, suggesting the presence of multiple RDC components. Figure 4.8a shows that the initial slope of the normalized DQ build-ups of the spent shales decreases with increasing thermal maturation. The DQ curves of shales C, D, and E exhibit considerably less steep initial slopes, indicating the presence of an additional weakly-coupled component. These curves were well described by the bi-Gaussian model of eq. (4.5) (much lower χ^2 values), where $D_{res,1}$ and $D_{res,2}$ are the average RDC constants of two distinct phases, and the parameter a represents the weight of the component with stronger RDC. Adding a third Gaussian component did not improve the fit quality. Fit results (Table 4.6) show that samples A and

B are characterized by a single component with $D_{res,1} \sim 20$ kHz, which is also observed for the other shales. This value is consistent with static dipolar coupling typically encountered for protons in methylene and methyl groups, having proton-proton distances of 1.8 Å. Samples C, D, and E present an additional small fraction ($\sim 20\%$) with a lower RDC constant, $D_{res,2} \sim 5$ kHz, which is compatible with proton dipole coupling in benzene or olefinic structures, where proton-proton distances are longer.

Samples ID	Maturity (Easy % R_0)	Eq. (4.3) – Gaussian		Eq. (4.5) – bi-Gaussian model			
		D_{res} (kHz)	$\chi^2 \times 10^3$	$D_{res,1}$ (kHz)	$D_{res,2}$ (kHz)	a	$\chi^2 \times 10^3$
A	0.98	19.5	0.051	19.5	3.2	1	0.098
B	1.04	19.6	0.056	19.6	3.4	1	0.095
C	1.32	17.4	0.213	18.9	4.5	0.82	0.021
D	1.41	16.8	0.145	18.1	4.9	0.84	0.007
E	1.86	15.8	0.247	17.6	4.4	0.77	0.014

Table 4.5. Results of fits of the normalized DQ build-ups of the staged maturity shale samples to the single-Gaussian build-up function of eq. (4.3) and to the bi-Gaussian model of eq. (4.5).

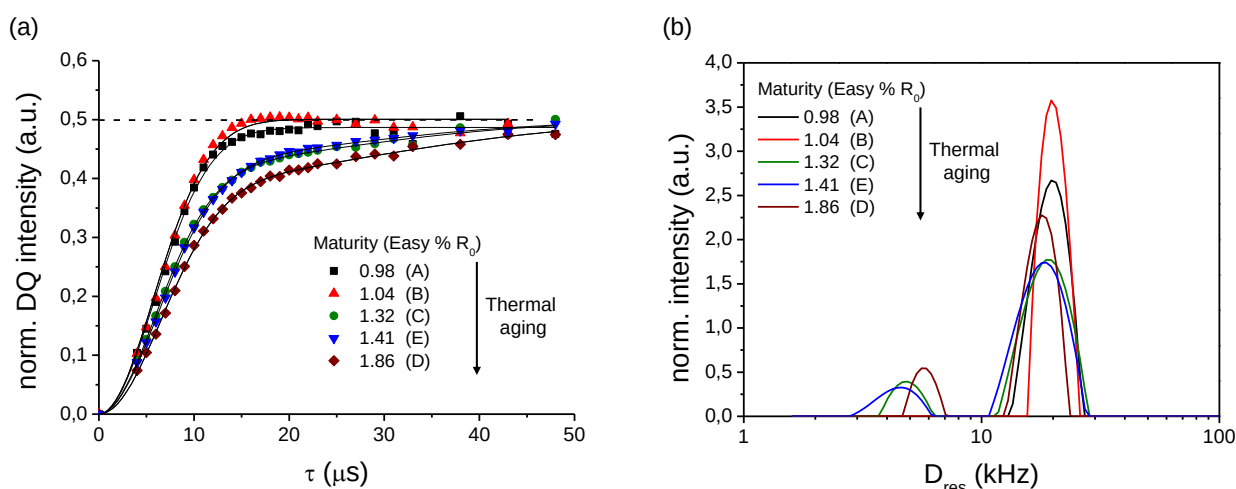


Figure 4.8. (a) Normalized DQ build-up signals obtained from the staged maturity shales. The black lines represent the best bi-Gaussian fits to the curves. (b) Corresponding distributions of residual dipolar coupling obtained by processing the NMR data with a Gaussian kernel in the numerical inversion.

The DQ build-up curves were also analyzed in terms of a *continuous* RDC distribution, using the Gaussian model of eq. (4.3) as the kernel function in the numerical inversion. The D_{res} distributions obtained from the staged maturity spent shales are illustrated in Figure 4.8b. In contrast to T_2 distributions (Figure 4.7b), the D_{res} distributions present two well separated peaks, permitting a more reliable distinction of two different proton environments. The D_{res} distributions of the low-

maturity shales A and B exhibit a single peak centered at $D_{res,1} \sim 20$ kHz, representing a highly dipolar-coupled phase. As the maturity of the shales increases, a second peak characterized by smaller D_{res} appears in the distribution ($D_{res,2} \sim 3-6$ kHz). This component, which represents a weaker residual dipolar coupling, is only present in the D_{res} distributions of the high-maturity samples, and it may reflect a phase characterized by lower ^1H density. Because the dipole coupling strength varies with $(1/r^3)$, with r being the distance between the nuclei, sample regions of lower density will exhibit weaker couplings than those with smaller average distances of the hydrogen nuclei. Therefore, the observed effect on the D_{res} distributions may be due to a drastic decrease in proton density of the organic component of the spent shale, which takes place during thermal maturation. Figure 4.9a shows the weighted average D_{res} and T_2 values of the shale samples as a function of thermal maturity. These results show an apparent inconsistency from the expected monotonous trend between the obtained D_{res} values and the maturity level of the shale (Easy % R_0), where sample B seems to be more proton-rich (larger D_{res}) than sample A. However, the same deviation is also observed for T_2 values, which are consistent with D_{res} values extracted from the analysis of the DQ build-up curves (Figure 4.9b). This provides greater confidence that DQ NMR can be used to track proton density changes of solid organic species in shales during the thermal aging and, therefore, to probe their chemical and physical structure evolution.

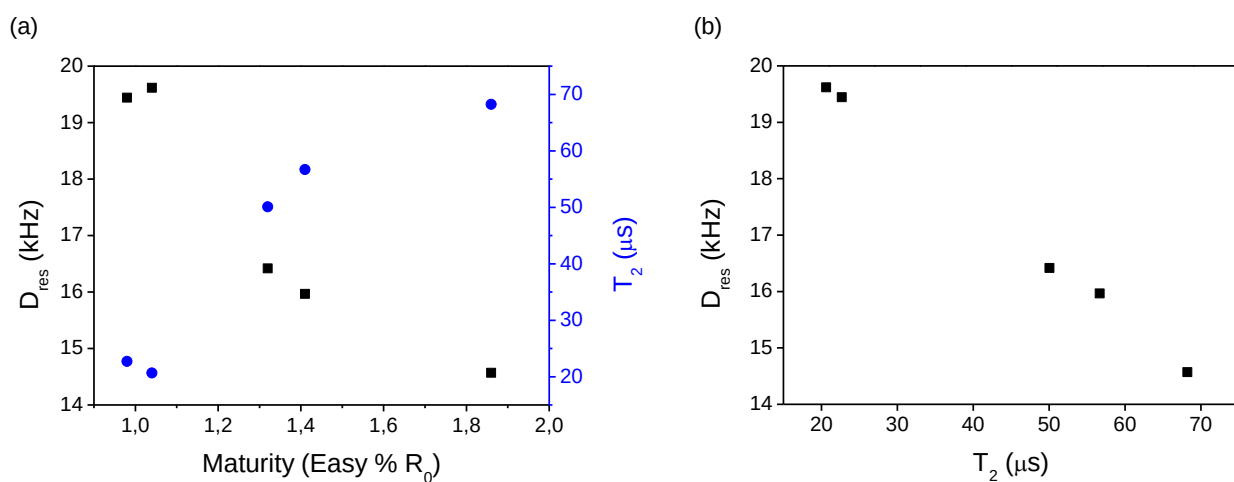


Figure 4.9. (a) Weighted average D_{res} and T_2 values measured for the Green River shales as a function of thermal maturity (Easy % R_0) and (b) correlation between D_{res} and T_2 values.

4.5.2.3 Summary: thermally matured shales

This first study shows that DQ NMR helps to identify and discriminate between sample regions with different proton density in the staged maturity spent shales. The main advantage of this technique over T_2 Hahn-echo measurements is the reliable separability of coherent build-up of DQ coherences from incoherent NMR relaxation. Consequently, this method gives access to RDC distributions which contain structural information only, while for Hahn-echo T_2 distributions, information on RDC is always masked by effects of intermediate motions. For this series of samples, DQ NMR provides more complete information on the immobile organic components in the shales.

The discrete fitting model and the numerical inversion give consistent results for the investigated artificially matured Green River shales. However, the numerical inversion analysis provides an improved description of DQ build-ups obtained from shales characterized by a continuous RDC distribution. This approach represents an alternative and convenient method of analyzing DQ build-ups. Instead of trying various models with an arbitrary few discrete RDC components to fit the initial part of the DQ build-ups, the numerical inversion procedure enables direct determination of the bimodal character and the estimated composition of the shale systems.

4.5.3 Oil- or brine-saturated shale powders

In this study, the ^1H DQ NMR approach was also applied to a set of powdered oil- or brine-saturated shales recovered from various depths in the Eagle Ford area. These samples contain solid, viscous, and liquid components, representing therefore excellent systems to test the proposed methodology for the characterization of solid species in the shale. Before showing results obtained from these re-saturated shales, DQ experiments performed on organic isolates analogous to the more dilute hydrocarbon phases in the investigated shales are presented.

4.5.3.1 Organic isolates

Kerogen and bitumen

A kerogen and a bitumen isolate, extracted from Green River shales, were used as standard samples for evaluating the DQ responses on solid and highly viscous organic matter phases comparable to those in the investigated shales. Initially, the T_2 decays of the two organic isolates were acquired with Hahn-echo measurements under static conditions, and the corresponding T_2 distributions are compared in Figure 4.10. The T_2 distribution obtained from the kerogen isolate is characterized by

a main peak centered at $T_2 \sim 10 \mu\text{s}$, with a second small peak at $T_2 \sim 100 \mu\text{s}$. The T_2 distribution obtained from bitumen shows the same short- T_2 peak observed for kerogen, in addition to a signal at long $T_2 \sim 0.1 - 1 \text{ ms}$, associated to a more mobile bitumen portion.

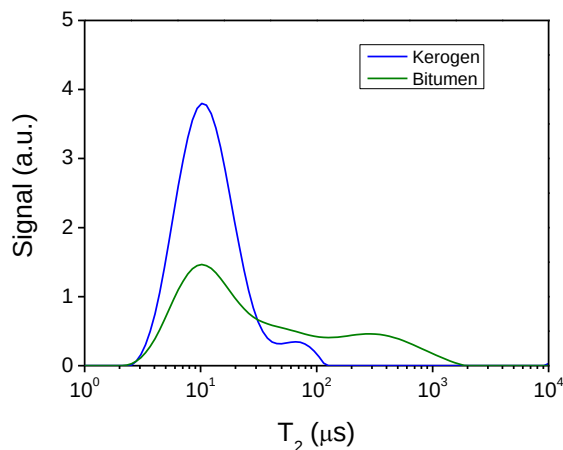


Figure 4.10. T_2 distributions obtained from the kerogen and bitumen isolates with Hahn-echo measurements under static conditions.

DQ build-ups of the kerogen and bitumen isolates were measured and normalized according to the procedure described in *Section 4.3.2*. Figure 4.11a shows that the two normalized build-up signals have similar initial curvature, but slightly steeper for kerogen. Numerical inversion of these DQ data produces the D_{res} distributions illustrated in Figure 4.11b. The distribution obtained from kerogen is defined by a single peak ranging from 10 to 30 kHz. The bitumen distribution has the same large- D_{res} peak found for the kerogen, and an additional relatively lower- D_{res} peak at 7-10 kHz.

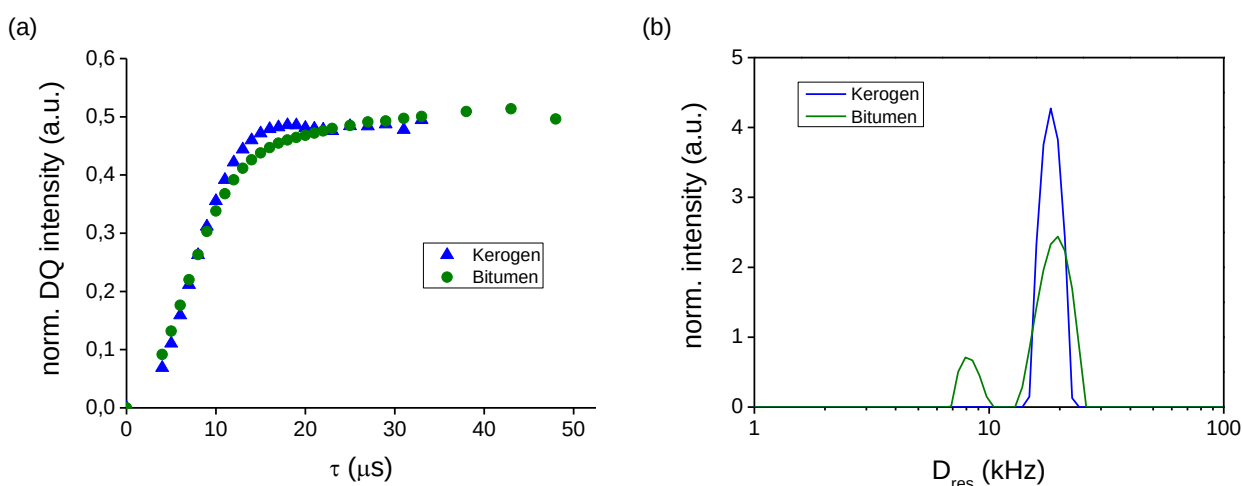


Figure 4.11. (a) Normalized DQ build-up signals obtained from kerogen and bitumen isolates and (b) corresponding distributions of residual dipolar coupling obtained by processing the NMR data with a Gaussian kernel in the numerical inversion.

The high- D_{res} peak observed in the kerogen and bitumen D_{res} distribution represents a strongly dipolar-coupled phase, which is consistent with the immobile state of these organic components. Kerogen is a solid material made of coupled multiple spin networks, where multibody interactions between nearby protons at different distances and orientations lead to a distribution of the dipolar couplings. Bitumen is a viscous organic material, which is formed as an intermediate state of the transformation of kerogen to oil and gas. Therefore, it is more mobile than kerogen, and it is typically expected to feature comparatively lower residual dipolar couplings. The lower- D_{res} peak in the bitumen D_{res} distribution may therefore represents a more mobile fraction of bitumen. In order to test this hypothesis, DQ experiments at variable temperature were performed on the bitumen isolate. The effect of temperature on bitumen can be deduced from Figure 4.12, which shows the static ^1H NMR spectra obtained from bitumen at variable temperature of 293 K, 333 K and 343 K. At the low temperature of 293 K, the NMR spectrum of bitumen presents a broad unresolved peak with a full width at half maximum (FWHM) of about 30 kHz, and a narrower component on top of that. The broad signal results from strong dipolar couplings experienced by the coupled protons in this highly viscous material. With increasing temperature, the linewidth of the NMR spectrum narrows as a result of the increased mobility of a bitumen fraction, presumably the aliphatic chain structures, which leads to motional averaging of the dipolar coupling. At a temperature of 343 K, the bitumen spectrum reveals a distinct narrow line, which arise from this mobile portion of the material, and it still presents a broad unresolved resonance, which is associated with a more rigid phase.

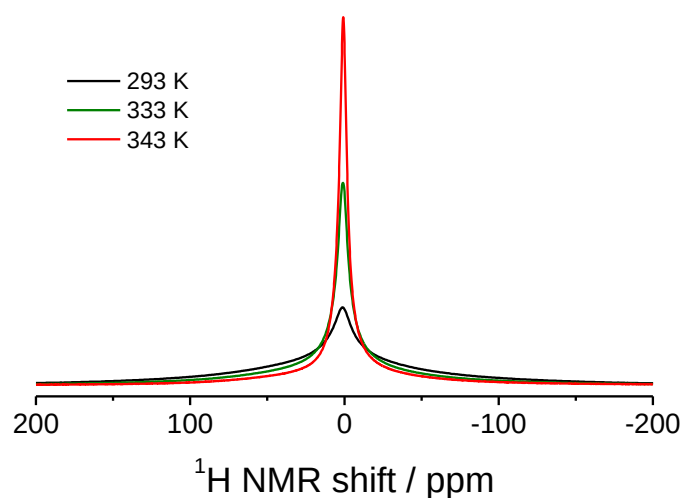


Figure 4.12. Comparison of static ^1H NMR spectra for the bitumen isolate measured as a function of temperature.

The normalized DQ build-up curves of bitumen at different temperature and relative RDC distributions are shown in Figure 4.13. As the temperature increases, the initial curvature of the DQ signal decreases considerably, reflecting the enhanced motional averaging of the dipolar coupling due to the increased mobility. Also, a second component which build-ups with slower rate becomes more prominent in the DQ curve. Consequently, the D_{res} distributions show two distinct peaks. The large- D_{res} signal at $D_{res,1} \sim 10\text{-}30\text{ kHz}$ was measured at all temperatures, and it is consistent with a more rigid phase of the sample, which exhibits strong RDC. With increasing temperature, the fraction of the phase characterized by a strong coupling ($D_{res,1}$ peak) decreases, and the distribution reveals an additional signal centered at a lower $D_{res,2} \sim 1\text{-}4\text{ kHz}$. These results suggest that part of the bitumen network, presumably a fraction composed of long aliphatic chains, undergoes different and faster dynamics. For this component, the dipole coupling is partly averaged by faster and larger amplitude chain motions at increased temperature.

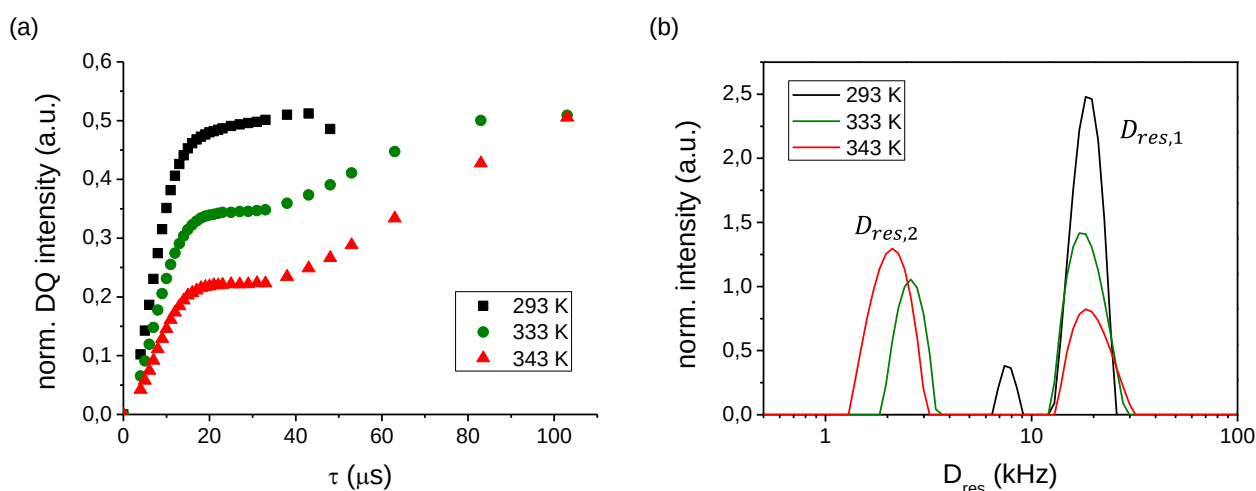


Figure 4.13. (a) Normalized DQ build-up signals and (b) corresponding distributions of residual dipolar coupling obtained from a bitumen isolate at variable temperature. The distributions are generated by processing the DQ NMR data with numerical inversion using a Gaussian kernel.

Free and absorbed oil

Tight-oil shale formations contain light-hydrocarbon oil, which can exist in either the bulk unconfined state in large inorganic pores or in a confined state in nanometer pores within kerogen. Here, olive oil absorbed in porous materials was used as a model system to simulate the state of small hydrocarbon molecules confined within small organic pores in shales. Two different “absorbed” oil phases were prepared by soaking sand or porous carbon in olive oil. A bulk olive oil sample was measured for reference. Figure 4.14a shows an overlay of the ^1H NMR spectra obtained from the bulk oil and the two absorbed oil phases, i.e., oil absorbed in sand, and oil absorbed in

porous carbon. Comparing the general features of these spectra, the bulk olive oil spectrum exhibits narrow lines typical of mobile oil species, while the two absorbed oil phases reveal single broad unresolved peaks, which appear to have similar line widths. For these species, the observed NMR line-broadening is consistent with an increased immobilization of the oil phase. In this confined state, the coupled protons will experience strong RDC due to reduced motional averaging.

DQ build-up and reference curves obtained from the free oil, oil absorbed in sand, and oil absorbed in porous carbon are illustrated in Figure 4.14b. As expected, no DQ signal is observed for free olive oil, as the rapid molecular reorientations average out the dipolar Hamiltonian. On the contrary, a slow DQ build-up is observed for the oil-soaked sand and oil-soaked porous carbon samples. The two signals have similar initial slopes, and reach a maximum at about 80 μs (oil in porous carbon) and at about 110 μs (oil in sand).

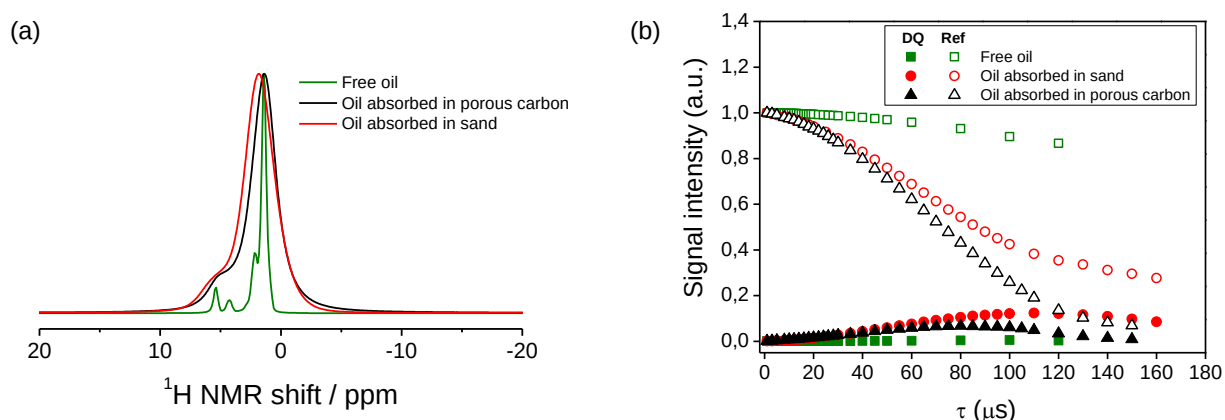


Figure 4.14. (a) Comparison of static ^1H NMR spectra obtained from free oil, oil absorbed in porous carbon, and oil absorbed in sand. (b) DQ build-up curves and reference signals obtained from the three samples in (a).

Detection of multiple-quantum transitions from the absorbed-oil materials indicates that these species experience significant dipolar couplings. The DQ signals obtained from the oil in sand and oil in porous carbon samples were normalized, and the obtained data were processed with numerical inversion to generate RDC distributions. The normalized DQ build-ups and corresponding D_{res} distributions are presented in Figure 4.15. Both distributions show a single peak located at $D_{res} \sim 1\text{--}3$ kHz, with the sand-absorbed oil phase that seems to have slightly larger D_{res} values. As expected, the amplitude of the RDC constant obtained for these confined oil species is considerably lower than that observed for immobile hydrocarbons like kerogen and bitumen.

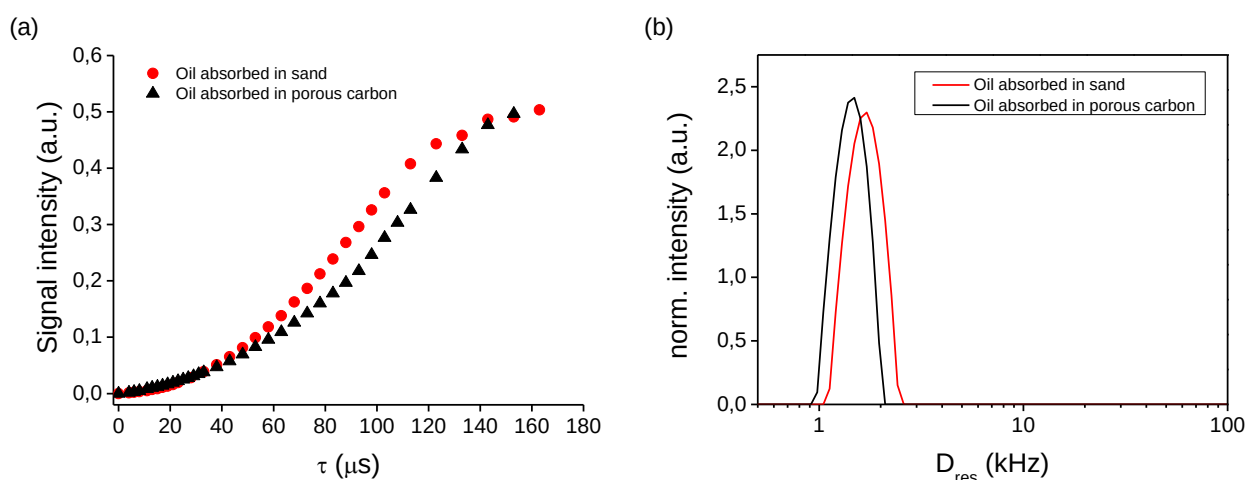


Figure 4.15. (a) Normalized DQ build-up signals obtained from oil absorbed either in sand or in porous carbon and (b) corresponding distributions of residual dipolar coupling obtained by processing the NMR data with a Gaussian kernel in the numerical inversion.

These results demonstrate that oil species may experience relatively large dipolar couplings when confined within small-pore structures. Such pores can be small enough to prevent oil molecules within them from rotating freely and undergoing isotropic motion. As a result, these molecules will experience strong residual dipole coupling due to the lack of isotropic motional averaging. This example may reflect the condition of small hydrocarbon molecules (i.e., linear-alkane molecules) confined within organic nanopores in shales.

4.5.3.2 Resaturated shales - T_2 relaxation

T_2 decays of the oil- or brine-saturated shale powders from different depths were obtained with static Hahn-echo measurements. The corresponding T_2 distributions are shown in Figure 4.16. These shales contain solid and viscous organic matter (kerogen and bitumen) and clay-bound water, in addition to mobile oil and water, as confirmed by low-field T_1 - T_2 correlation maps presented in Chapter 3. All T_2 distributions are mainly characterized by two broad peaks centered at about $T_2 \sim 20 - 50 \mu\text{s}$ and $T_2 \sim 200 - 500 \mu\text{s}$. The first T_2 signal ($10 \mu\text{s} < T_2 < 100 \mu\text{s}$) is associated to solid-like organic matter, i.e., kerogen/bitumen, and clay-bound water. The second T_2 peak ($T_2 > 100 \mu\text{s}$) is assigned to mobile oil and water in the inter/intra particle pores. Signals in this area are larger for shales saturated with oil than for those saturated with brine, suggesting the presence of a fraction of organic pores that is accessible to oil species only. In particular, the T_2 distributions of shales 3A and 8A present a signal at considerably long $T_2 \sim 1 - 2 \text{ ms}$, which may reflect mobile oil in large pores. However, the broad T_2 peaks overlap for most of these resaturated shales, making separation between different components challenging.

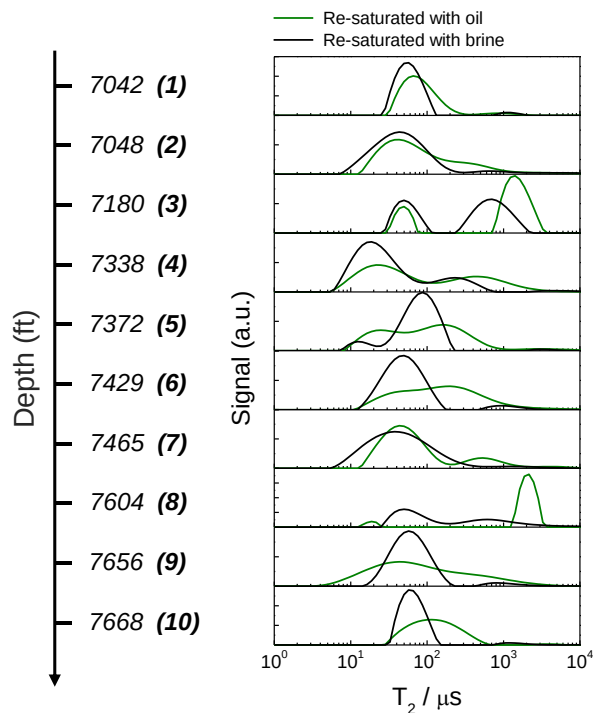


Figure 4.16. T_2 distributions obtained from the oil-saturated (green) and brine-saturated (black) shale powders at various depths with Hahn-echo measurements under static conditions.

4.5.3.3 Resaturated shales - Double-quantum build-ups

Figure 4.17a shows the ^1H NMR DQ signals obtained from the powdered oil- and brine-saturated shales at different depths. The detection of DQ coherences indicates the presence of solid-like components in the shale, which correspond to immobile organic matter and bound water. The raw experimental DQ build-ups of the brine-saturated shales (black squares in Figure 4.17a) exhibit a steeper slope compared to their oil-saturated counterparts. The latter present a slightly slower initial rise (weaker RDC), followed by a slower decay, which reveals faster molecular motion. In particular, the DQ build-ups of almost all oil-saturated shales feature two distinct maxima, indicating the presence of two distinct phases characterized by different averaged dipolar coupling. Consequently, the corresponding normalized DQ curves (Figure 4.17b) show a two-step build-up that can be analysed to extract information on the two D_{res} components and their relative fractions. Interestingly, no DQ signal is obtained for samples 3B and 8B (brine saturated), while a considerably slow DQ build-up is observed for samples 3A and 8A (oil saturated). The corresponding T_2 distributions (Figure 4.16) show that these shales contain mobile species only, i.e., oil and water in

large inter/intra particle pores. The normalized DQ signals were transformed into D_{res} distributions (Figure 4.17c) using a Gaussian kernel in the numerical inversion procedure.

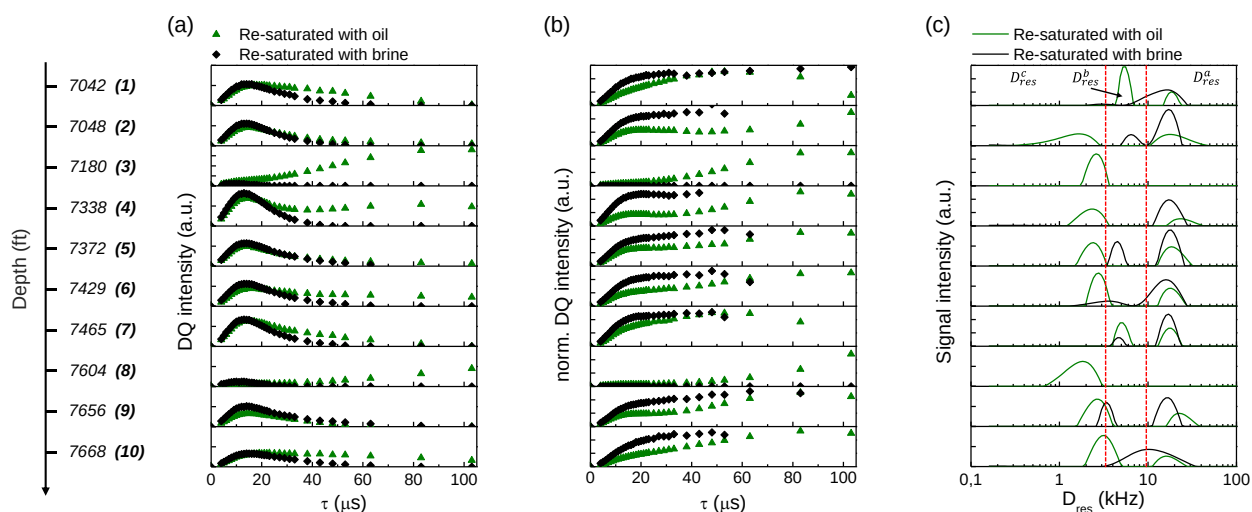


Figure 4.17. (a) Raw and (b) normalized ^1H NMR DQ build-up curves of the oil-saturated (green) and brine-saturated (black) shales at various depths. (c) Distributions of residual dipolar couplings of the oil- and brine-saturated shales obtained by processing the NMR data with a Gaussian kernel in the numerical inversion procedure.

The D_{res} distributions obtained from the oil- and brine-saturated shales are substantially different. Almost all D_{res} distributions show two distinct peaks which reflect sample regions characterized by different molecular mobility and/or proton density. The detected D_{res} components represent an average over different intra- and intermolecular ^1H dipole interactions resulting from different types of chemical environments in the shale. In an attempt to interpret results obtained from the analysis of the DQ build-up curves, the D_{res} distributions were divided into three different regions, as illustrated in Figure 4.17c. The segmentation of the D_{res} distributions was performed by matching D_{res} distributions obtained from the oil- and brine-saturated shales, and it was also based on results obtained from DQ experiments on organic isolates (see *Section 4.5.3.1*).

A broad distribution (D_{res}^a) at a large D_{res} ranging from about 10 to 40 kHz, is observed for all samples except for shales 3A-B and 8A-B, which contain mobile species only. This range of RDC constants may correspond to kerogen, bitumen, and the bound water, which are common between the oil- and brine-saturated shales. In fact, this component describes a phase characterized by strong dipolar couplings and therefore it reflects a sample region with restricted mobility, which is consistent with the highly dipolar-coupled state of the solid organic matter. Similar D_{res} values were observed for the kerogen and bitumen isolates (*Section 4.5.3.1*), suggesting that part of the D_{res}^a signal arises from such immobile organic species. In particular, the largest- D_{res} components of the

D_{res}^a peak may reflect the kerogen in the shale, which is known to exhibit the strongest ^1H - ^1H dipolar interactions. Another contribution to this DQ signal may also come from water molecules that tend to be present as an adsorbed layer on clays (clay-bound water). Compared to mobile water in pores, these bound water species may experience strong residual dipole coupling resulting from reduced motional averaging.

A second peak with lower D_{res} values of about 3-10 kHz (D_{res}^b) is observed for some of the oil- and brine-saturated shales. The D_{res}^b fraction may arise from heavy oil species which feature comparatively lower RDC than those found for kerogen. This D_{res} component may therefore reflect a bitumen portion which is not in a solid state like kerogen, or in a highly viscous phase. Bitumen is expected to be more liquid-like than kerogen as its molecular structure is typically intermediate between that of kerogen and petroleum. However, distinction between these immobile hydrocarbon species is not straightforward. Organic phases in shale rocks present a wide variation of viscosity and can exhibit a large distribution of dipole interactions as nearby hydrogens may undergo different dynamics regimes. For example, bitumen molecular mobility may be reduced when this is confined to the solid kerogen matrix, and the DQ signal from this highly viscous bitumen phase probably contributes to the higher D_{res}^a component.

The D_{res} distributions obtained from the oil-saturated shales present an additional smaller- D_{res} peak ($D_{res}^c \sim 1\text{-}3$ kHz). This lower- D_{res} fraction (D_{res}^c) represents a less coupled phase which appears to be characteristic of oil-saturated shales. The fact that a proton environment with D_{res}^c is observed only for oil-saturated shales suggests that this signal arises from constrained oil species, for which orientational averaging of the dipolar coupling is incomplete. Part of this signal may be due to hydrocarbon molecules residing in small-pore structures, such as tight nanopores. Although these molecules have isotropic mobility in the bulk phase (i.e., $D_{res} = 0$), their RDC can still be significant when they are confined in nanopore structures, which prevent them from rotating freely. Similar D_{res} values were also found for oil absorbed in sand and oil absorbed in porous carbon (Section 4.5.3.1), promoting greater confidence in the idea that the D_{res}^c signal comes from small oil molecules in tightly fitting pores.

The area under the higher- D_{res}^a (10-40 kHz) and the lower- $D_{res}^{b,c}$ (1-10 kHz) peaks in the D_{res} distributions presented in Figure 4.17c were integrated and compared. A comparison between the fraction of the D_{res}^a and $D_{res}^{b,c}$ signals for the oil- and brine-saturated shales is illustrated in Figure 4.18. The weakly-coupled component (lower $D_{res}^{b,c}$) prevails in all D_{res} distributions obtained from

oil-saturated shale powders, while it represents only a small fraction of the DQ signal measured from the brine-saturated shales. D_{res} distributions of the brine-saturated shales are dominated by the D_{res}^a coupling population, which is always larger than 70 %. The D_{res}^a fraction is lower than 50 % for all shales saturated with oil, and it is absent for the two samples containing mobile species only (samples 3A and 8A). The hydrogen-bearing components in shales 3B and 8B are too mobile to generate DQ coherences. These two shales are known to have little-to-no content of kerogen/bitumen, so that the corresponding ^1H NMR signal consists of the saturation fluids only.

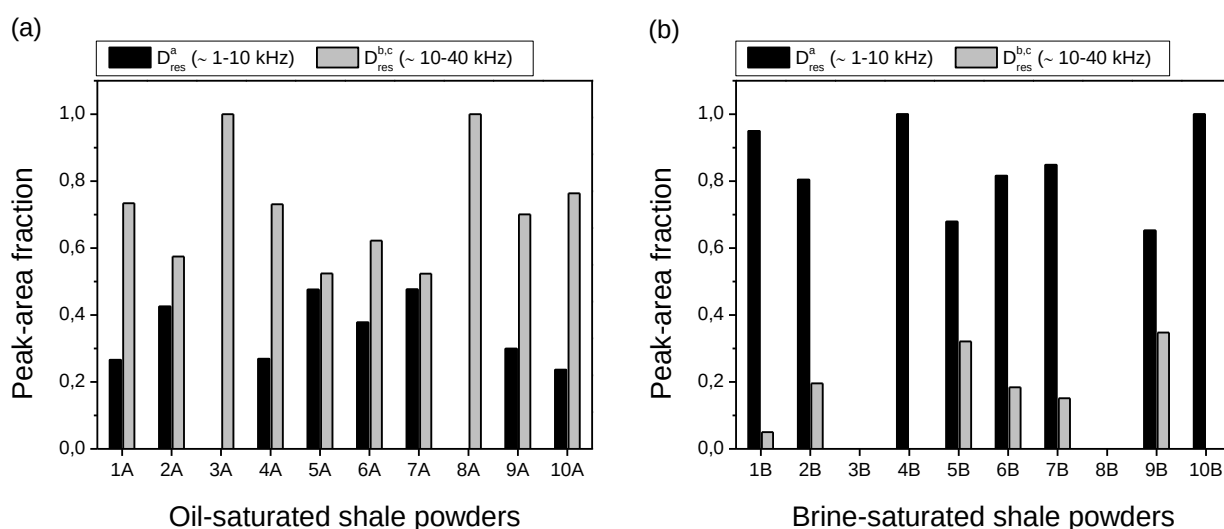


Figure 4.18. Normalized fractions of the high D_{res}^a and low $D_{res}^{b,c}$ peaks obtained from the D_{res} distributions of the oil-saturated (a) and brine-saturated (b) shale powders.

4.5.3.4 Summary oil- or brine-saturated shales

In summary, results obtained from the powdered re-saturated shales show that, compared to T_2 distributions, the D_{res} distributions present distinct peaks that can be attributed to components with limited mobility in the shale. This study demonstrates that the DQ sequence offers a potential method for discriminating between solid/highly viscous components (with a large DQ signal) and isotropic liquid species (no DQ signal) in shales. While quantitative separation of kerogen and bitumen remains a main challenge, DQ NMR helps identifying different solid and viscous organic phases characterized by a wide range of RDC, providing improved description of immobile hydrocarbons in shales. For the investigated shale samples, this technique enables reliable separation between a strongly dipolar-coupled phase, attributed to kerogen and highly viscous

bitumen, and a more weakly-coupled phase which reflects small oil molecules in tightly fitting nanopores.

4.5.3.5 Thermally dehydrated, previously oil- or brine-saturated shales

Shales 6A-B and 10A-B were dried under vacuum at 80 °C for 24 hours, in an attempt to remove bound/mobile water and to measure DQ responses from just the hydrocarbon components of the shale. DQ experiments were repeated for these oven-dried shale powders. Figure 4.19a shows the ^1H NMR spectra of samples 6A and 6B, before and after they were dried. Both spectra of sample 6A and 6B feature a broad peak ranging over 400 ppm, which can be attributed to solid and viscous components in the shale, i.e., kerogen and bitumen. The spectrum of the oil-saturated shale (6A) shows an additional narrow peak, arising from a more mobile oil component. When shale 6A is dried (green dashed line in Figure 4.19a), the narrow component disappears leaving the broad signal, revealing a transition of the oil phase to a less mobile state. The immobilization of the oil component may be caused by migration of oil species into smaller pores, induced by the thermal dehydration, or by the removal of a water fraction in the interparticle pores that was preventing oil from aggregating and forming an immobile phase. These results are consistent with those found in *Section 3.6.3*.

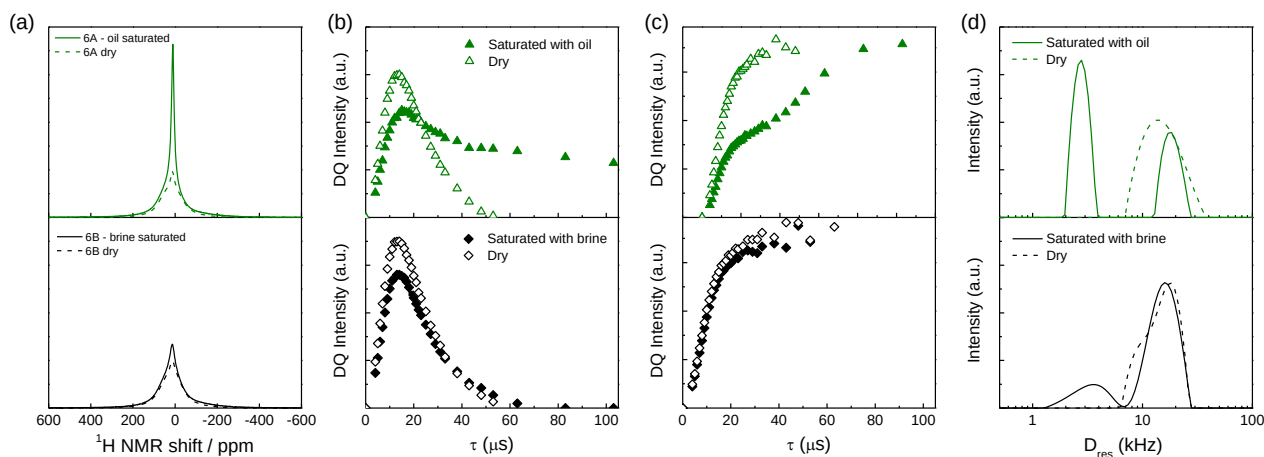


Figure 4.19. (a) Static ^1H NMR spectra, (b) raw and (c) normalized ^1H NMR DQ build-up curves, and (d) D_{res} distributions of the oil- and brine-saturated samples 6A and 6B, before and after the samples were dried.

The phase rearrangement of the oil component is also reflected by the DQ signals of the dry shales. Raw and normalized DQ build-ups obtained from the dry shales are illustrated in Figure 4.19b and 4.19c, respectively. The initial rise of the DQ curves of shale 6A increases remarkably when the shale is dried, reflecting a drastic change in the dipolar coupling, which indicates reduced mobility of the

oil component. Consequently, in the D_{res} distribution of the dry shale (green dashed line in Figure 4.19d), the weaker component at $D_{res} \sim 2-4$ kHz collapses into the broad, large D_{res} distribution ranging over 10-40 kHz. This shift is consistent with the formation of immobilized oil species, experiencing stronger dipole couplings. The effect of thermal dehydration on the measured DQ build-ups of brine-saturated sample 6B is much lower. After drying the sample, only small changes are observed in the DQ build-up curve, and the main peak in the D_{res} distribution remains unchanged. Nevertheless, the lower D_{res} component is not present in the distribution of the dried shale 6B, suggesting that part of the bound water has been removed. Similar results were obtained from shales 10A-B and are shown in Figure 4.20.

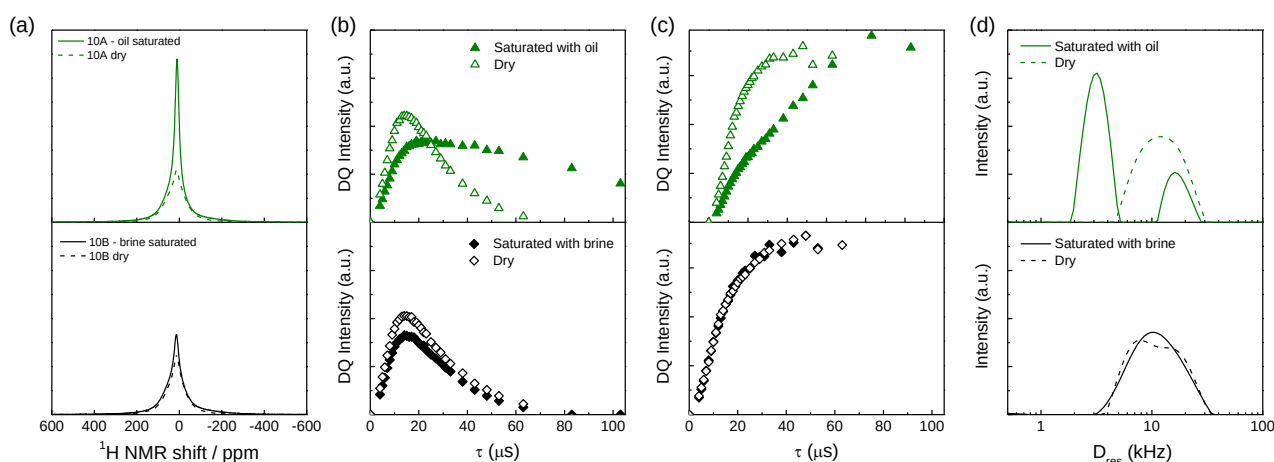


Figure 4.20. (a) Static ^1H NMR spectra, (b) raw and (c) normalized ^1H NMR DQ build-up curves, and (d) D_{res} distributions of the oil- and brine-saturated samples 10A and 10B, before and after the samples were dried.

Overall, these results confirm that the high D_{res} component observed in the D_{res} distributions of the investigated shales contain contributions not only from kerogen, but also from other components, such as heavy oil with limited mobility or bound water.

4.6 Conclusions

This chapter presents the first instance of a DQ NMR approach used for petrophysical applications. As demonstrated, DQ ^1H NMR can be used as a powerful tool for characterizing solid and highly viscous hydrogen-bearing components in organic shales. Compared to standard spin-echo sequences like the CPMG, which are limited by their minimal echo sampling time, the DQ sequence can measure signals immediately after the receiver dead time, enabling reliable acquisition of the

strongly dipolar coupled components with short T_2 times, such as kerogen and bitumen. A second advantage of this technique over traditional ^1H T_2 Hahn-echo measurements, for which information on RDC is typically masked by effects of intermediate motions, is that DQ build-up data can be normalized to remove any influences of relaxation processes, enabling absolute values for RDC constants to be determined.

DQ NMR is shown to provide insight into the complex network structures of immobile organics in (i) a series of artificially matured Green River shales and (ii) a set of powdered oil- or brine-saturated Eagle Ford shales recovered from various depths. The analysis of DQ build-up curves involves a numerical inversion approach to generate distributions of residual dipolar coupling constants, which underlie structural information on the immobile species in the shale. This approach helps identifying and separating phases characterized by different molecular mobility and/or proton density in the investigated materials. For example, DQ NMR can be used to track proton density changes in shale solid organics during thermal maturation, providing useful information on the degree of their chemical and physical structure evolution, which is ultimately related to petroleum potential of these source rocks. Compared to the overlapping T_2 peaks observed in the T_2 distributions, which are difficult to quantify and interpret, the D_{res} distributions reveal well separated peaks, more easily attributed to the immobile components of the shale. Although further work is needed for quantitative separation of kerogen, bitumen and clay-bound water, the study presented in this chapter demonstrates that DQ NMR can be used to detect highly dipolar-coupled phases, such as kerogen and highly viscous bitumen, as well as oil species under nanoconfinement, providing improved description of the immobile hydrocarbon phases in shale systems.

Chapter 5: Conclusions and future work

The principal objective of this thesis was to develop NMR methods that can be applied to characterize heterogeneous organic shales with potentially producible hydrocarbons. Costs and environmental impacts for recovery from shale reservoirs can be reduced through targeted drilling and fracturing, which relies on improved descriptions of the shale formation and identification of producible resources. Consequently, effort was focused on devising new techniques for improved evaluation of shale reservoirs and better estimates of production.

Identification and quantification of solid and viscous organic components (kerogen and bitumen) is fundamental to determine the reservoir quality (RQ) of unconventional formations, which represents their ability to produce hydrocarbons upon stimulation. A combination of several NMR techniques, which are appropriate for use under static (non-spinning) conditions and low magnetic fields, were explored and used for the investigation of these immobile hydrocarbons in shales. The methods presented within this thesis can potentially be combined and integrated into NMR workflows for the exploration and characterization of organic-rich shale reservoirs. With further development, such multi-measurement approach may be implemented in routine core and cutting analysis to evaluate the shale petrophysical properties, to quantify solid and liquid components, and to determine productivity. The studies in this thesis focus on separation of signals from immobile and mobile hydrocarbon components, detection of the kerogen-bitumen ratio and detection of the thermal maturity, which all represent possible answer-products for NMR in shales. Although the presented techniques and methodologies are used to investigate shale systems, they can be applied to a wider range of materials that contain NMR nuclei in highly heterogeneous environments. A more detailed summary of the main results will now be presented.

A combination of high-resolution solid-state $^1\text{H}/^{13}\text{C}$ NMR spectroscopy methods and ^1H NMR relaxation measurements was used in Chapter 2 to investigate the chemical and physical structure evolution of kerogen isolates during thermal maturation. Thermal aging controls the quality and amount of hydrocarbons produced from kerogen, making it a critical parameter for understanding the process of oil and gas generation and, therefore, for productivity predictions. Results obtained from this study showed a correlation between the content of carbon aromatic structures in the kerogen isolates, evaluated from ^{13}C MAS NMR spectroscopy, and the long- T_2 component in the T_2 distributions, obtained with static ^1H NMR relaxometry. The long- T_2 component represents a

kerogen phase characterized by lower proton density and can therefore be considered as an indicator for the aromatic content. ^1H NMR T_2 relaxation measurements, which can also be easily implemented on standard low-field devices, have shown to be successful to track compositional changes of kerogen during the maturation process. Such T_2 relaxometry approach can be used as a potential thermal maturity test for kerogen. However, further work is required to develop methodologies for the evaluation of the kerogen maturity level based on ^1H NMR T_2 relaxometry only.

Although ^1H low-field NMR is well-suited for investigations of conventional formations, the complexity of shale rocks presents significant challenges to the traditional approaches. The main limitations with low-field spectrometers for the analysis of unconventional low-porosity shales arise from (i) the inherently poor signal-to-noise ratio (SNR), and (ii) the long probe ringing times ($\sim 100\ \mu\text{s}$ in well-logging tools). Together, these factors complicate the detection of solid organics and surface hydroxyls (typically characterized by $T_2 < 100\ \mu\text{s}$) in shales with typically low organic content. In this respect, effort was focused on devising pulse sequences to attempt to extend the lifetime of the time-domain signal of these immobile species, through careful manipulation of the spin ensemble. In Chapter 3, an experimental method based on the combination of CPMG, solid-echo (SE), and magic(mixed)-echo (ME) pulse sequences, is presented as a composite approach to deal with the challenging issue of characterising the different forms of organic matter in shales. These multiple-pulse sequences were implemented on a low-field benchtop NMR spectrometer working at 13 MHz, and the proposed approach was used to measure the relative contributions of immobile and mobile organic fractions in several oil- or brine-saturated shales from the Eagle Ford area. Immobile species (kerogen/bitumen) were found to be characterized by large signal differences between the ME and the CPMG/SE techniques, while mobile components (oil/brine) have more equal refocusing by the three pulse sequences. Specifically, the large increase in the ME signal relative to the CPMG and SE results from organic species with limited mobility, such as kerogen, bitumen, and also small hydrocarbon molecules under nanoconfinement, which are more efficiently refocused by the ME pulse sequence. Therefore, the ratio of intensities between the three signals may be used as a proxy for the fraction of immobile hydrocarbon in the shale. Overall, the relatively high time-resolved 13 MHz relaxometry, and the combined analysis of amplitudes and rates of the relaxation components under the three pulse sequences presented, have the potential to inform the petrophysicist in a more complete manner about the different forms of organic matter in shales. Inevitably, more work is required to develop a practicable workflow for the quantitative

measurement solid kerogen, semisolid bitumen, and mobile oil/water. In addition, extending this approach to NMR logging may provide a valuable service on wells, where characterization of shale formations with quick measurements is needed.

An entirely different technique to selectively excite only the solid fraction of the shale is double-quantum (DQ) NMR. The DQ NMR study presented in Chapter 4 of this thesis introduces a novel approach into the petrophysical research field. Here, this technique is applied for the quantitative characterization of hydrogen-bearing components with limited mobility in the shale, and DQ ^1H NMR build-up curves obtained from shale systems are shown for the first time. There are two main advantages of using DQ NMR as opposed to ^1H NMR T_2 relaxometry for the detection of viscous and solid components in shales: (a) the DQ sequence can measure signals immediately after the receiver dead time, compared to the standard CPMG or Hahn-echo sequences, which are limited by their minimal echo sampling time, and (b) DQ NMR methods can provide reliable separation between the coherent build-up of DQ coherences and the incoherent loss of transverse magnetization, yielding direct information on the proton-proton dipole coupling. These factors enable robust detection of solid components with fast-decaying time-domain signals, promoting the DQ technique as a potential answer-product candidate for improved kerogen and bitumen detection.

The DQ NMR approach was applied to various shale systems for the identification and separation of organic matter phases characterized by different molecular mobility and/or proton density. In a first study, DQ NMR was used to probe the degree of chemical and physical structure evolution of kerogen and bitumen during thermal maturation of Green River shales, providing useful information on the petroleum potential of these source rocks. The same method was applied to a series of oil- or brine-saturated Eagle Ford shales containing solid and liquid components. In this case, the DQ sequence offers a potential method for discriminating between solid/highly viscous components (large DQ signal) and isotropic liquid species (no DQ signal) in shales. In addition, it enables quantitative separation between highly dipolar-coupled phases, such as kerogen and bitumen, and more weakly-coupled species, such as oil molecules under nanoconfinement, providing improved description of the immobile hydrocarbon phases in shale systems. A natural extension to this work would be the implementation of the DQ sequence in low-field benchtop spectrometers. In this case, the main challenge arises from the longer probe ringing times of low-field spectrometers compared to that of their high-field counterparts. However, as shown in Chapter 3, commercial 2 MHz or 13

MHz bench-top spectrometers can be optimized to reduce the dead time, for example with the use of narrow bore probes.

To take any of the sequences proposed in this thesis forward as commercial answer-products will require improved understanding of the spin physics. In a following step, spin dynamics simulations can be used to better understand and optimise the CPMG, SE, and ME pulse sequences, particularly under imperfect pulse conditions. Combining the optimization of experimental parameters (e.g., pulse length, pulse power) of these multiple-pulse sequences with spin dynamics simulations, would represent an important step forward in terms of interpreting the shale relaxation time data. This approach can help explore how well the investigated pulse sequences work at different fields and different T_2 times, for spin systems that closely mimic those found in the shale components. Spin dynamics simulations could also be helpful to better understand the effect of pulse imperfection and low-field (inhomogeneous static and RF field) effects on DQ NMR.

A different extension to the work presented in this thesis would be to study the mobility of methane in the shales by use of pulsed field gradient ^1H NMR. This would be of interest for (a) measures of pore size, using the physics of restricted diffusion, and (b) measures of pore connectivity, which still represents a controversial issue for the organic nanopores within kerogen, that are believed to be the principal host material for the free methane in shale reservoirs. In this respect, another NMR technique that can be used to investigate shale systems is Xenon nuclear magnetic resonance (^{129}Xe NMR) spectroscopy. Preliminary results (presented in appendix 1) show that ^{129}Xe NMR spectroscopy can be applied to the study of the porous network of shale rocks. This is also of particular interest for investigating the dynamics of gas within the shale, the xenon being a useful analogue of methane (similar molecular size and wettability). Therefore, there is a great scope to extend the study of organic shale with ^{129}Xe NMR.

Appendix 1: Application of ^{129}Xe NMR to shale systems

A1.1 Introduction

Xenon nuclear magnetic resonance (^{129}Xe NMR) spectroscopy represents a potential tool to better understand the porous structure of shale systems. Because of their small Van der Waals diameter of 4.4 Å, non-polarity, and chemical inertness, xenon atoms are excellent molecular probes for porous materials.^{183,184,185} Xenon gas can be easily absorbed into the void spaces of many solid materials and, due to the large and polarizable electron cloud, its chemical shift results extremely sensitive to the local environment. The chemical shift of the absorbed xenon strongly depends on the composition of the material, the shape and size of the pores, and the nature of the interaction between xenon atoms and the pore surface. Consequently, ^{129}Xe NMR spectra can be used to extract useful information about the local structure of the pores. In addition, the observed ^{129}Xe isotope is a spin-1/2 nucleus, with a relatively high natural abundance (26%), making NMR experiments easy to apply. ^{129}Xe NMR spectroscopy has proven to be a valuable technique for studying a variety of porous materials^{184,185}, such as zeolites^{183,186}, soils¹⁸⁷, clays¹⁸⁸, and coal.¹⁸⁹ A ^{129}Xe NMR study of shale samples from different geographical areas has been carried out in previous works.^{190,191} The authors found micropores and mesopores with the pore sizes ranging from 1 to 10 nm in shales from USA, while for shale samples from China they observed broad ^{129}Xe resonances with both positive and negative chemical shifts, attributed to strong interactions between the atomic nuclei of the adsorbed xenon and paramagnetic impurities.

Here, we present the ^{129}Xe NMR spectrum of powdered shale rock. These preliminary results shows that ^{129}Xe NMR spectroscopy potentially reveals information about pore size distributions in shale rocks.

A1.2 Experimental

A schematic of the xenon gas filling setup is illustrated in Figure A.1. This consists of a NMR tube connected to both a xenon gas cylinder and a vacuum pump, through a three-way valve system. One of the oil-saturated shale samples investigated in Chapter 3, shale 6A, was used for these

experiments. The powdered shale sample was placed in 5 mm diameter heavy-wall NMR tube, which was filled to a height of ~ 5 cm. The sample was subsequently evacuated for 24 hours at 80 °C in a vacuum line. Thereafter, ^{129}Xe isotope-enriched (91%) xenon gas was condensed in the sample using liquid N_2 , and the final xenon pressure inside the glass tube was controlled by a regulator. The NMR experiments were carried out with a solution-state 500 MHz AVIII spectrometer operating at a magnetic field of 11.7 T. The ^{129}Xe NMR spectra were acquired with single pulse measurements at room temperature, using a 90° pulse length of 8 μs and a recycle delay of 1 s.

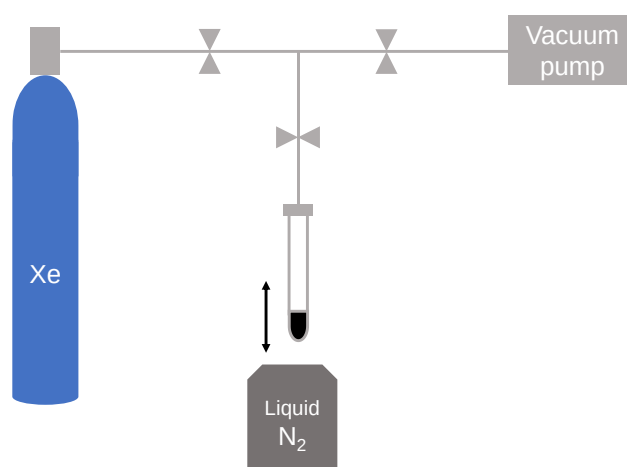


Figure A.1. Schematic illustration of the homemade setup for filling NMR tubes with xenon gas.

A1.3 Preliminary results

^{129}Xe NMR spectra of a powdered shale (sample 6A) prepared with xenon pressures of 1 and 3 bar are illustrated in Figure A.2a. Both spectra present three broad peaks, which are due to probe background (probably acoustic probe ringing). These signals are also present when a spectrum is acquired from the same shale sample without xenon (blue line). The spectra were also measured with the Hahn-echo pulse sequence to avoid background distortions, but no signal was obtained. The two spectra show an additional intense narrow signal, centered at about 0-20 ppm. A zoom-in on this signal, shown in Figure A.2b, reveals small differences between the line shapes of the two spectra obtained with 1 and 3 bar of xenon, which seem to be superposition of two different peaks. A signal centered at about 0 ppm prevails in the NMR spectrum of the shale sample loaded with 1 bar of xenon. This resonance is attributed to xenon gas in large pore structures or interparticle

pores, and it is named “free gas” signal. At the higher pressure of 3 bar, the main peak is shifted downfield, at about 5 ppm. This peak probably belongs to xenon adsorbed at the surface of the particles, given its position is close to that of xenon in the free gas phase at 0 ppm. In summary, it is possible that xenon atoms only enter the interparticle space and “(sub-)surface” particle pores in the powder. The observed NMR lineshape possibly result from fast exchange of xenon atoms in interparticle pores and (sub-)surface sites. Xenon atoms may exchange quickly between different adsorption sites and the gas phase during the NMR experiment, resulting in a single resonance with a weighted-average chemical shift between that of the xenon in the adsorbed state and in the free gas phase. The absence of broad peaks reflecting xenon atoms absorbed in the inner-particle pores is probably due to incomplete removal of moisture during the sample thermal dehydration, blocking access to the pores, or because the void spaces are already largely filled with kerogen/bitumen. Alternatively, the absence of the expected ^{129}Xe signal may also result from the presence of paramagnetic impurities in the rocks, with the T_2 of xenon atoms within the inner-particle pores being too short and preventing the signal to survive the Hahn-echo sequence. In principle, single pulse excitation could be used to detect short- T_2 components, but the probe background signal will also accumulate.

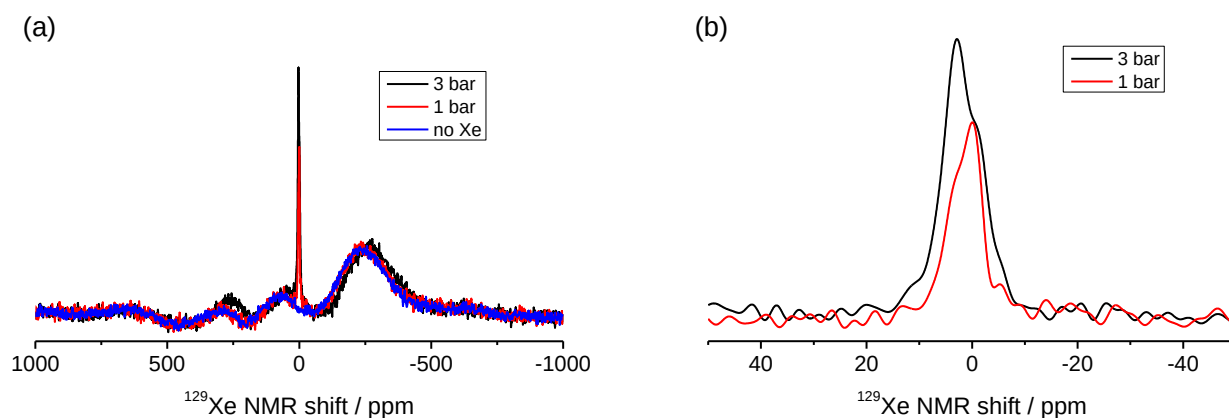


Figure A.2. (a) ^{129}Xe NMR spectra of a powdered shale sample at xenon pressures of 1 and 3 bar. The background signal is also shown in blue. (b) Zoom-in on the narrow signal at 0-20 ppm.

The observed chemical shifts of xenon in the shale powder can be quantitatively interpreted in terms of pore size distribution using models based on fast exchange between adsorbed xenon and the gas phase.^{187,192,193} However, determination of the pore size will require more xenon sorption measurements as a function of pressure. Future work will also focus on the optimization of the experimental setting, and specifically on suppressing the accumulation of unwanted probe background signal during acquisition in single-pulse excitation experiments. This can be achieved by

preceding the pulse sequence by a “blinking 180° pulse” (on/off in subsequent scans), or, equivalently, a composite “ 90_+° - $90_\pm^\circ$ ” pulse with alternating phase.

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