



Original Paper

Numerical investigation on 2-D NMR response mechanisms and the frequency conversion of petrophysical parameters in shale oil reservoirs

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ABSTRACT

Characterizing the petrophysical properties holds significant importance in shale oil reservoirs. Two-dimensional (2-D) nuclear magnetic resonance (NMR), a nondestructive and noninvasive technique, has numerous applications in petrophysical characterization. However, the complex occurrence states of the fluids and the highly non-uniform distributions of minerals and organic matter pose challenges in the NMR-based petrophysical characterization. A novel T_1 - T_2 relaxation theory is introduced for the first time in this study. The transverse and longitudinal relaxivities of pore fluids are determined based on numerical investigation and experimental analysis. Additionally, an improved random walk algorithm is proposed to, on the basis of digital shale core, simulate the effects of the hydrogen index (HI) for the organic matter, echo spacing (T_E), pyrite content, clay mineral type, and clay content on T_1 - T_2 spectra at different NMR frequencies. Furthermore, the frequency conversion cross-plots for various petrophysical parameters influenced by the above factors are established. This study provides new insights into NMR-based petrophysical characterization and the frequency conversion of petrophysical parameters measured by laboratory NMR instruments and NMR logging in shale oil reservoirs. It is of great significance for the efficient exploration and environmentally friendly production of shale oil.

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1. Introduction

In recent years, the demand for energy has greatly increased. The development of renewable energy sources such as solar, geothermal energy, and wind, alongside conventional fossil fuels, cannot meet current energy needs (Esen and Yuksel, 2013; Van Erdeweghe et al., 2018; Sun et al., 2018a,b). The pressures of energy shortages have prompted exploration into shale oil and gas (Zhan et al., 2020; Liu et al., 2022), which has received great attention from scholars (Zamiri et al., 2022). Shale oil and gas can be economically recovered from shale through hydraulic fracturing, superheated steam injection, and pyrolysis exploitation technology (Osipov, 2017; Sun et al., 2017; Sun et al., 2018a,b; Xu et al., 2023; Jiang et al., 2023; Nie, 2023). Furthermore, shale can store large amounts of waste, such as CO₂, due to its low permeability. Thus, in shale oil reservoirs, investigating the petrophysical properties is

crucial (Liu et al., 2024a). However, the complex occurrence states of fluids and the high heterogeneity of minerals, as well as organic matter (OM), in shale pose challenges in petrophysical characterization (Dou and Wang, 2022; Liu et al., 2024b; Wang et al., 2023a). This, in turn, presents further challenges to environmentally friendly shale production and safe waste storage in shale (Wang et al., 2023b; Hu et al., 2018; Xu et al., 2023).

Two-dimensional nuclear magnetic resonance (2-D NMR), a nonintrusive and nondestructive technique, can be used to perform petrophysical characterization of reservoirs by detecting the signals of pore fluids (Washburn and Birdwell, 2013; Kausik et al., 2011). The petrophysical characterization of fluids can be acquired based on NMR T_1 - T_2 spectra (Zhang et al., 2020; Jiang et al., 2018, 2019; Silletta et al., 2022; Kausik et al., 2017), employing both experimental analysis and numerical simulations. Experimental analysis can directly determine the petrophysical properties, adapting to different magnetic field frequencies for precise petrophysical properties characterization (Fleury et al., 2013; Fleury and Romero-Sarmiento, 2016; Ma et al., 2020). However, experimental analysis does not consider the effects of the heterogeneity of minerals and

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OM across different shale samples (Zhu et al., 2021; Li et al., 2020). In addition, the frequency differences between NMR logging and laboratory NMR instruments can result in differences of petrophysical properties, posing difficulties in the petrophysical characterization of actual formations based on T_1 - T_2 spectra. Therefore, it is of great significance to characterize the complex heterogeneity of minerals and OM by NMR T_1 - T_2 responses.

In shale oil reservoirs, unlike experimental analysis, numerical simulation techniques can directly reflect their effects on the petrophysical properties. Moreover, numerical investigations can quantify the effects of different factors. However, very few scholars have conducted numerical simulation investigations of T_1 - T_2 due to the unclear T_1 - T_2 relaxation theory in shale oil reservoir. Currently, there are two main theories concerning the NMR T_1 - T_2 relaxation of pore fluids. One theory states that the dipole-dipole interactions caused by protons within and between hydrocarbon molecules are dominant (Bloembergen et al., 1948; Yang and Hirasaki, 2008; Kausik et al., 2018; Yang et al., 2012; Singer et al., 2018; Zhang and Daigle, 2017; Singer et al., 2020), while the other theory argues that the heteronuclear dipole-dipole interactions involving protons within hydrocarbon molecules and the paramagnetic sites from OM are dominant (Benamsili et al., 2014; Korb, 2018; Korb et al., 1996, 1997, 1999, 2014, 2015). Recently, Zhang and Daigle (2017) conducted experiments in which they mixed kerogen (without iron and manganese ions) with water, acetone, chloroform, and cyclohexane, then compared the T_2 values of the deuterated compounds of different fluids and their mixtures with kerogen. They confirmed that OM without iron or manganese ions has NMR response characteristics. They also pointed out that the intramolecular dipole-dipole interactions controlled the relaxation for oil, and it depends on the adsorption capacity of ^1H at surface layer, which depends on the adsorbate concentration at surface adsorption sites rather than the proton density of the surface layer, and that spin relaxation is controlled by molecular spins and the proton desorption process. They derived an expression for surface relaxivity according to proton dipole-dipole relaxation theory (the ZD model) (Zhang and Daigle, 2017). Tandon and Heidari (2019) developed an NMR relaxation theory for organic shale. Based on this theory, they determined the longitudinal surface relaxivity (ρ_1) and transverse surface relaxivity (ρ_2) of pore fluids and accurately quantified the transverse relaxation time (T_2) and longitudinal relaxation time (T_1) of protons in organic pores (Tandon and Heidari (2019)). The theories proposed by Zhang and Daigle (2017) and Tandon and Heidari (2019) are based on proton dipole-dipole interactions, but these theories have not been adequately verified by experiments on real pore fluids. Korb (2018) confirmed the reasonability of the theory supporting the dominance of heteronuclear dipole-dipole interactions by testing the frequency dependence from oil and experimentally verifying that the dipole-dipole interactions involving protons in pore fluids and VO^{2+} in bitumen control the NMR relaxation characteristics of organic pore fluids in shale oil reservoirs; consequently, the protons in organic pore fluids exhibit one-dimensional motion. The heteronuclear dipole-dipole interactions between protons in petrophysical properties and paramagnetic ions such as manganese and iron ions on mineral surfaces control the NMR relaxation for inorganic pore (IP) fluids in shale, due to which the protons in IP exhibit two-dimensional motion. While Korb (2018) improved the theories of the T_1 - T_2 relaxation for pore fluids in shale oil, they ignored the characteristics and effects of the NMR relaxation of OM. The plateau (P) model proposed by Singer et al. can be used to describe the strong frequency dependence of the T_1 of OM and the weak frequency dependence of the T_2 of OM (Singer et al., 2020).

Currently, numerical investigations of T_1 - T_2 conducted on shale oil reservoirs have mainly focused on the theoretical simulation of

simple equations. Another study explained the NMR relaxation of pore fluids in shale according to the homonuclear dipole-dipole relaxation theory. They simulated changes in relaxation dependence at different angles using rhombic pores with different aspect ratios, and established the Washburn-Mu-Tolke theory grounded in homonuclear dipole-dipole relaxation theory for both organic and inorganic pores (Washburn, 2014; Washburn et al., 2015). However, their theoretical modeling solely selected and used pore radius as a simulation parameter, leading to differences between the results of theoretical modeling and simulations of real shale samples. Chi et al. (2015) accounted for changes in wettability's impact on numerical simulation results, whereas Tandon et al. (2017) developed a finite volume-based inversion recovery-Carr-Purcell-Meiboom-Gill (IR-CPMG) simulation technique, employing pore-scale images of rock samples, topological structures of different fluids (phases), and bulk and surface properties of fluids. They verified the effectiveness of the simulation technique using digital sandstone and carbonate cores containing spherical pores (Tandon et al. (2017)). Building upon the aforementioned work, Tandon and Heidari (2019) simulated the T_1 - T_2 responses of hydrocarbons in ellipsoidal pores of organic-rich mudstone samples and the organic pores provided based on focused ion beam scanning electron microscope (FIB-SEM) images (Tandon and Heidari (2019)). However, in their study, the proton dipole-dipole relaxation theory was solely considered from NMR relaxation for oil rather than the OM and water. Meanwhile, the influences on T_1 - T_2 responses from the internal magnetic field gradient were not considered.

There are several deficiencies in the published articles on NMR T_1 - T_2 numerical simulations of shale oil reservoirs. (a) T_1 - T_2 relaxation theories are unclear, and few theories, describing the frequency dependence from pore fluids, OM, and the internal magnetic field gradient, are used for petrophysical properties characterization. (b) The effects from the complex occurrence states of pore fluids and the heterogeneity of minerals and OM on the 2-D NMR T_1 - T_2 response are not considered. (c) The effects from the complex occurrence states of pore fluids, the heterogeneous distributions of minerals and OM on petrophysical properties are not considered.

Herein, a T_1 - T_2 relaxation theory is proposed to characterize the frequency dependences for OM longitudinal and transverse bulk relaxation times ($T_{1B,K}$, $T_{2B,K}$), the longitudinal and transverse relaxivities for pore fluids ($\rho_{1S,O}$; $\rho_{1S,W}$; $\rho_{2S,O}$; $\rho_{2S,W}$), and internal magnetic field gradient. This theory was verified by the numerical simulations and experiments in this article. The $\rho_{1S,O}$, $\rho_{1S,W}$, $\rho_{2S,O}$, and $\rho_{2S,W}$ were determined based on the numerical simulations and experimental analysis, including extraction experiments, multi-frequency T_2 experiments, and 2-D T_1 - T_2 experiments conducted on parallel samples of digital shale cores. In addition, the improved random walk (IRW) algorithm was used for the first time to simulate the influences of parameters such as the hydrogen index (HI) of the organic matter, echo spacing (T_E), pyrite content, clay mineral type, and clay content on the T_1 - T_2 responses in shale oil reservoirs at different frequencies based on digital core technology. Frequency conversion cross-plots for various petrophysical properties derived from T_1 - T_2 spectra affected by the above factors were established.

2. Theory

2.1. T_1 - T_2 relaxation theory

For the first time, we have developed an improved Korb's theory for two-dimensional NMR T_1 - T_2 , premised on the assumption that water only exists in the IP and oil only exists in the OP. According to Korb's model of T_1 - T_2 relaxation theory, the longitudinal and

transverse bulk relaxation rates for pore fluids were determined due to intermolecular and intramolecular dipole-dipole interactions. Additionally, the longitudinal and transverse surface relaxation rates of pore fluids were determined, and the diffusion relaxation rates were determined based on the magnetic-dipole theory. The longitudinal and transverse relaxation rates of organic matter ($1/T_{1K}$, $1/T_{2K}$) are determined by longitudinal and transverse bulk relaxation rates ($1/T_{1B,K}$; $1/T_{2B,K}$). They can be expressed as

$$\begin{cases} \frac{1}{T_{1L}} = \frac{1}{T_{1RB,L}} + \frac{1}{T_{1TB,L}} + \frac{1}{T_{1S,L}} \\ \frac{1}{T_{1K}} = \frac{1}{T_{1B,K}} \\ \frac{1}{T_{2L}} = \frac{1}{T_{2RB,L}} + \frac{1}{T_{2TB,L}} + \frac{1}{T_{2S,L}} + \frac{1}{T_{2D,L}} \\ \frac{1}{T_{2K}} = \frac{1}{T_{2B,K}}, \end{cases} \quad (1)$$

where the subscript L represents water (W) or oil (O), while $T_{2TB,L}$ and $T_{2RB,L}$ denote the bulk relaxation times for pore fluids driven by intermolecular and intramolecular dipole-dipole interactions, and they may be described by the *L-S* and the *B-P-P* theories, respectively (Tandon and Heidari, 2019; Lipari and Szabo, 1982). $T_{2TB,L}$ and $T_{2RB,L}$ could be determined from numerical simulations in combination with extraction and gas chromatography (GC) experiments (Liu et al., 2024c). $T_{1TB,L}$ and $T_{1RB,L}$ could be determined by the same method. $T_{1B,K}$ and $T_{2B,K}$ are the longitudinal and transverse bulk relaxation times of organic matter (kerogen and bitumen)

molecules, the $T_{1B,K}$ and $T_{2B,K}$ exhibited frequency dependence, which can be described by the *P* model (Singer et al., 2020) and expressed as

$$\begin{cases} \frac{1}{T_{1B,K}} \approx \frac{3}{20} \left(\frac{\mu_0}{4\pi} \right)^2 \gamma^4 \hbar^2 \frac{1}{N} \sum_{i=1}^N \sum_{j=i}^N \frac{k}{r_{ij}^6} \left[J_p(0, \tau_{R,L}, \tau_{1,L}) + 4J_p(2\omega, \tau_{R,L}, \tau_{1,L}) \right] \\ \frac{1}{T_{2B,K}} \approx \frac{3}{20} \left(\frac{\mu_0}{4\pi} \right)^2 \gamma^4 \hbar^2 \frac{1}{N} \sum_{i=1}^N \sum_{j=i}^N \frac{k}{r_{ij}^6} \left[3J_p(0, \tau_L, \tau_{1,L}) + \frac{5}{2}J_p(\omega, \tau_L, \tau_{1,L}) \right. \\ \left. + J_p(2\omega, \tau_L, \tau_{1,L}) \right] \\ \tau_K = \frac{4\pi}{3K_B} R_{R,K}^3 \frac{\eta_K}{T} \\ J_p(\omega, \tau_K, \tau_{1,K}) = \left((1 - s_K^2) \frac{2\tau_K}{1 + \omega\tau_K} + s_K^2 \frac{2\tau_{1,K}}{1 + \omega\tau_{1,K}} \right) \end{cases} \quad (2)$$

In addition, $1/T_{2D,L}$ in the modified Korb's model denotes the diffusion relaxation rate for pore fluids, which is related to the diffusion coefficient (D_L), gyromagnetic ratio (γ), internal magnetic field gradient (G_z), and T_E , can be expressed as

$$\frac{1}{T_{2D,L}} = \frac{D_L(\gamma G_z T_E)^2}{12} \quad (3)$$

The G_z exhibited frequency dependence, can be determined on the basis of the magnetic dipole theory (Liu et al., 2024c). In Eq. (1), $1/T_{1S,L}$ and $1/T_{2S,L}$ denote the longitudinal and transverse relaxation rates of water or oil, the $1/T_{1S,L}$, $1/T_{2S,L}$, $1/T_{1S,O}$, and $1/T_{2S,O}$ may be determined on the basis of the modified Korb's model and expressed as

$$\begin{cases} \frac{1}{T_{1S,W}} = \left(\frac{\mu_0}{4\pi} \right)^2 \pi / \left(30d\delta_W^2 \right) \cdot \sigma_{s,W} \rho_W S_{p,NMR,W} (\gamma_1 \gamma_S \hbar)^2 S(S+1) \tau_{m,W} \cdot \\ \left[3 \ln \left(\frac{1 + \omega_l^2 \tau_{m,W}^2}{\left(\frac{\tau_{m,W}}{\tau_{s,W}} \right)^2 + \omega_l^2 \tau_{m,W}^2} \right) + 7 \ln \left(\frac{1 + \omega_s^2 \tau_{m,W}^2}{\left(\frac{\tau_{m,W}}{\tau_{s,W}} \right)^2 + \omega_s^2 \tau_{m,W}^2} \right) \right] \\ \frac{1}{T_{2S,W}} = \left(\frac{\mu_0}{4\pi} \right)^2 2\pi / \left(30d\delta_W^2 \right) \cdot \sigma_{s,W} \rho_W S_{p,NMR,W} (\gamma_1 \gamma_S \hbar)^2 S(S+1) \tau_{m,W} \cdot \\ \left[2 \ln \left(\frac{\tau_{s,W}}{\tau_{m,W}} \right) + \frac{3}{4} \ln \left(\frac{1 + \omega_l^2 \tau_{m,W}^2}{\left(\frac{\tau_{m,W}}{\tau_{s,W}} \right)^2 + \omega_l^2 \tau_{m,W}^2} \right) + \frac{13}{4} \ln \left(\frac{1 + \omega_s^2 \tau_{m,W}^2}{\left(\frac{\tau_{m,W}}{\tau_{s,W}} \right)^2 + \omega_s^2 \tau_{m,W}^2} \right) \right] \\ \frac{1}{T_{1S,O}} = \left(\frac{\mu_0}{4\pi} \right)^2 \sqrt{2} / \left(15\pi R\delta_O^2 \right) \cdot \sigma_{s,O} \rho_O S_{p,NMR,O} (\gamma_1 \gamma_S \hbar)^2 S(S+1) \sqrt{\tau_{m,O} \cdot \tau_{s,O}} \cdot \\ \left[\frac{3\sqrt{1 + \sqrt{1 + \omega_l^2 \tau_{s,O}^2}}}{\sqrt{1 + \omega_l^2 \tau_{s,O}^2}} + \frac{7\sqrt{1 + \sqrt{1 + \omega_s^2 \tau_{s,O}^2}}}{\sqrt{1 + \omega_s^2 \tau_{s,O}^2}} \right] \\ \frac{1}{T_{2S,O}} = \left(\frac{\mu_0}{4\pi} \right)^2 \cdot 2 / \left(15\pi R\delta_O^2 \right) \cdot \sigma_{s,O} \rho_O S_{p,NMR,O} (\gamma_1 \gamma_S \hbar)^2 S(S+1) \sqrt{\tau_{m,O} \cdot \tau_{s,O}} \cdot \\ \left[1 + \frac{3\sqrt{2}}{8} \frac{\sqrt{1 + \sqrt{1 + \omega_l^2 \tau_{s,O}^2}}}{\sqrt{1 + \omega_l^2 \tau_{s,O}^2}} + \frac{13\sqrt{2}}{8} \frac{\sqrt{1 + \sqrt{1 + \omega_s^2 \tau_{s,O}^2}}}{\sqrt{1 + \omega_s^2 \tau_{s,O}^2}} \right] \end{cases} \quad (4)$$

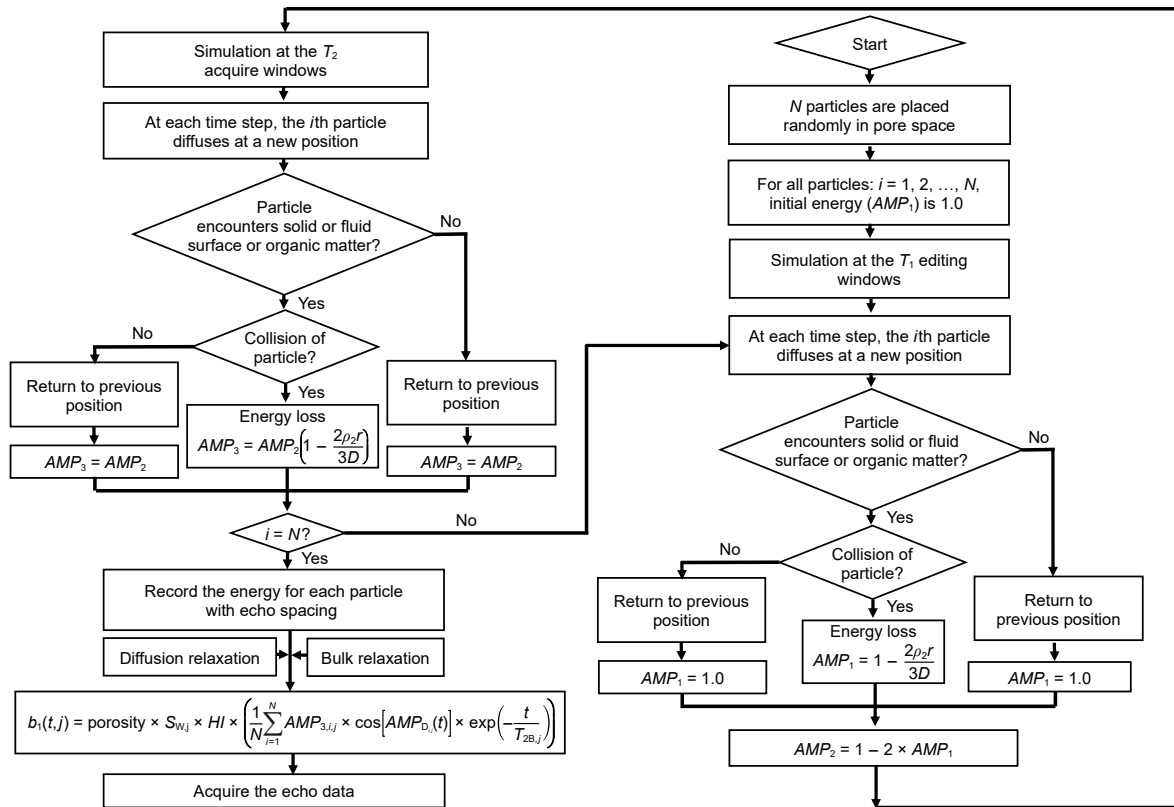


Fig. 2. Flow diagram for numerical simulation with the IRW algorithm.

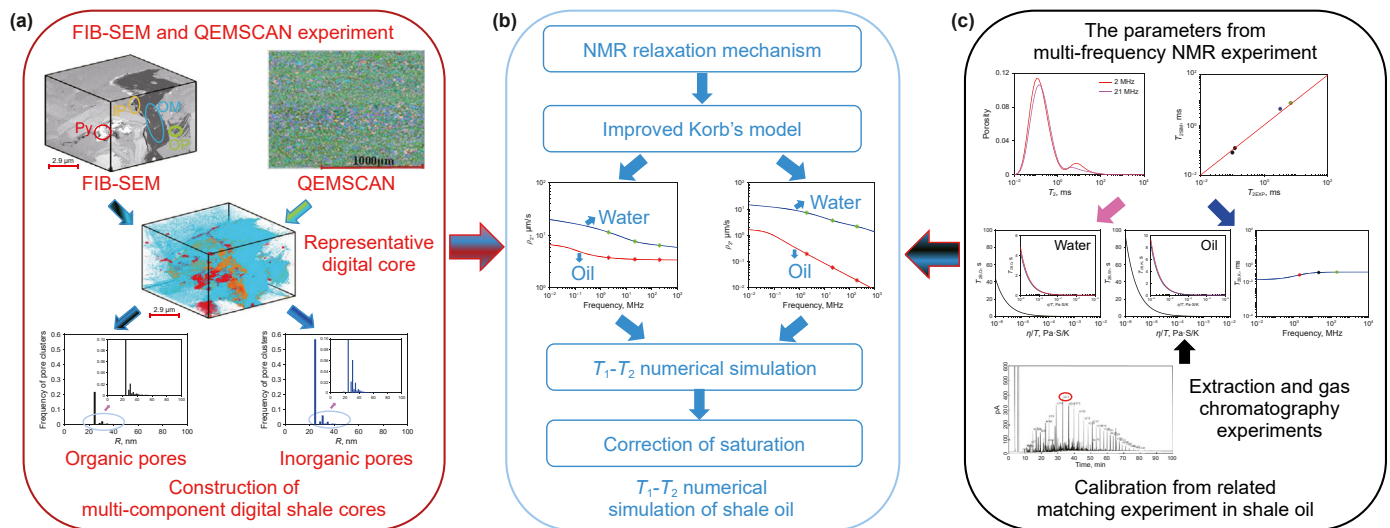


Fig. 3. Experimental processes and parameters determination.

Noise(T_w, t) is the noise in the measurement.

Random walk algorithms have been used in the numerical study for sandstones (Guo et al., 2020; Guo and Xie, 2019). Considering the uneven pore size distribution in shale oil reservoirs, the IRW algorithm was proposed on the basis of the previously constructed multi-component digital shale cores (Liu et al., 2023, 2024c) for the first time. Different from previous NMR numerical simulations in sandstone, in the T_1 editing window, the proposed method was used to simulate each hydrogen nucleus underwent a random walk

process, during which if the nucleus encountered OM or mineral, its energy decayed. Subsequently, the inversion recovery pulse was added. In the T_2 collection window, hydrogen nucleus continued its random walk. When it encountered OM or mineral, its energy decayed. Meanwhile, the energy of each hydrogen nucleus decayed due to diffusion relaxation, and it was counted statistically. Finally, the energy values of all hydrogen nuclei for each echo were added.

The detailed simulation process was shown in Fig. 2.

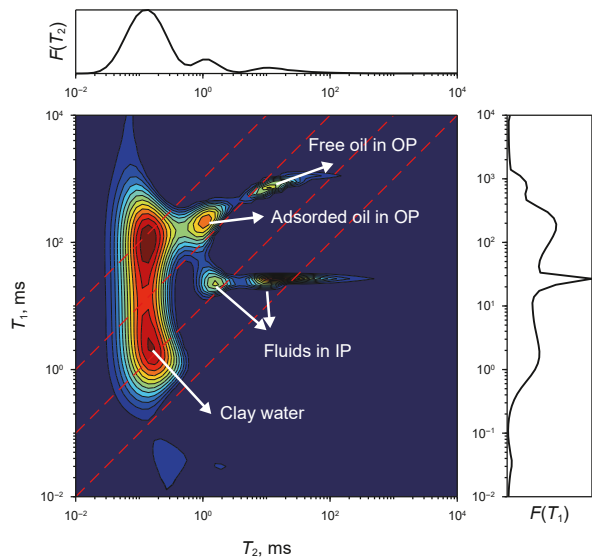


Fig. 4. Experimental results of the shale sample.

Table 1
Transverse and longitudinal relaxivities at different magnetic field frequencies.

Surface relaxivities, $\mu\text{m/s}$	Fluid types	Surface relaxivities at different frequencies, $\mu\text{m/s}$		
		2 MHz	21.36 MHz	200 MHz
ρ_{2S}	Oil	3.8	3.5	3.4
	Water	11.5	7.65	6.13
ρ_{1S}	Oil	0.2	0.06	0.02
	Water	9.8	3.7	2.9

3. Experimental

3.1. Research plans and ideas

The experimental part is the verification of this study. Fig. 3 shows the research ideas on the basis of experiments. We have created multi-component digital shale cores on the basis of FIB-SEM and quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN) (Liu et al., 2023) (Fig. 3(a)). Through different frequencies (2 MHz and 21.36 MHz) NMR, extraction and GC experiments (Fig. 3(c)), the $T_{2B,O}$, $T_{2B,W}$, and $T_{2B,K}$ of shale oil were determined (Liu et al., 2024c). Then one parallel sample can be conducted on IR-CPMG experiment in Section 3.1, and the T_1 - T_2 spectra can be acquired through inversion. In Section 3.2, the $\rho_{1S,O}$ and $\rho_{1S,W}$ would be determined through Eqs. (1)–(5) combined with IR-CPMG experiments. The accuracy of the T_1 - T_2 relaxation theory could be verified. These works provided foundations for subsequent numerical investigations on the basis of T_1 - T_2 relaxation theory and frequency conversion for the saturations of various components (Fig. 3(b)).

3.2. IR-CPMG experiment

A high-field NMR experiment was conducted on a shale sample (Sample #AA-2) using an NMR core analyzer (MesoMR23-060H-I, Niumag, China) with a 21.36 MHz frequency. The shale sample was measured by the IR-CPMG pulse sequence. During the measurement process, T_E is 0.08 ms, number of echoes (also known as echo train length) is 2000, and the ambient temperature is 25 °C. After the measurement was completed, the T_1 - T_2 spectra of sample #AA-

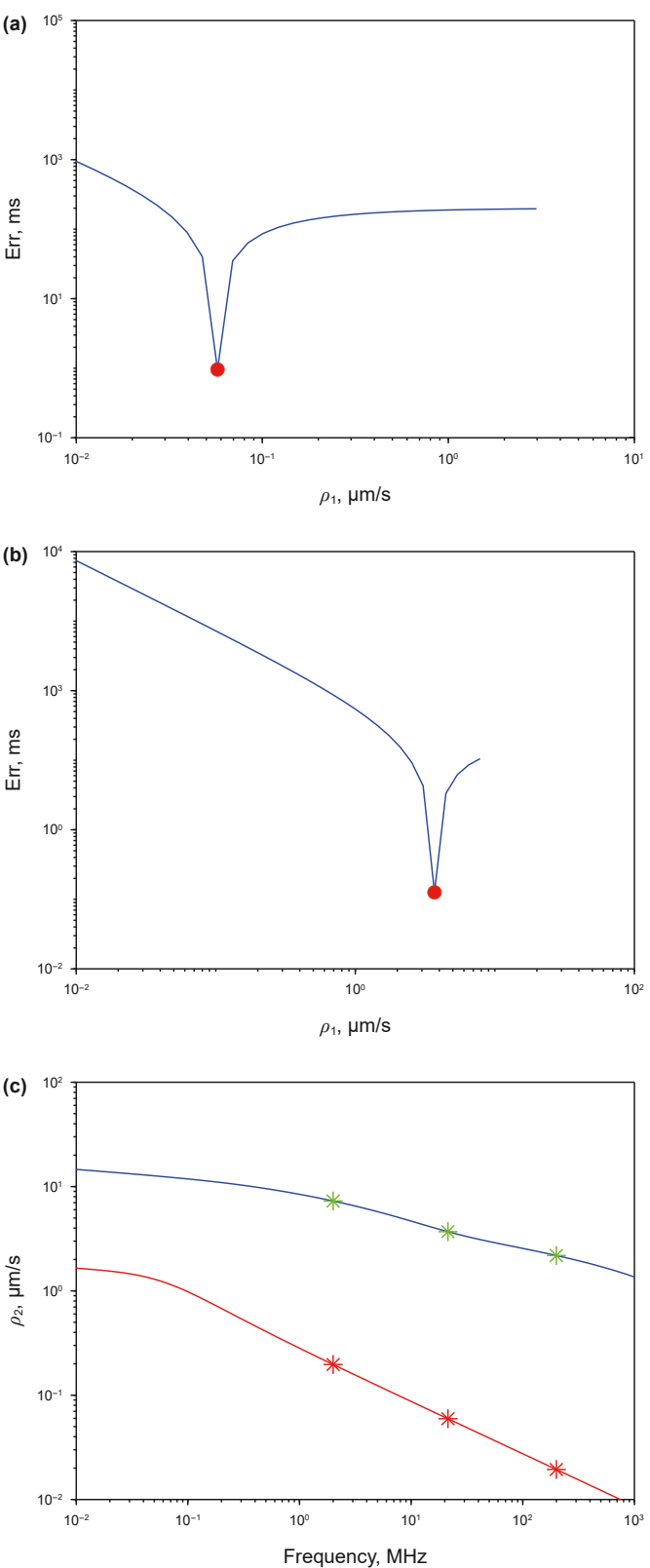


Fig. 5. Calibration of experimental parameters. In Fig. 5(a)–(b), the blue solid lines represent the variation of the error (Err) between the T_1 of numerical simulation and the experimental results as the function of $\rho_{1S,O}$ or $\rho_{1S,W}$ (ρ_1), and red solid dot are the optimal $\rho_{1S,O}$ or $\rho_{1S,W}$, respectively. In Fig. 5(c), the red and blue solid lines are the varying $\rho_{1S,O}$, $\rho_{1S,W}$.

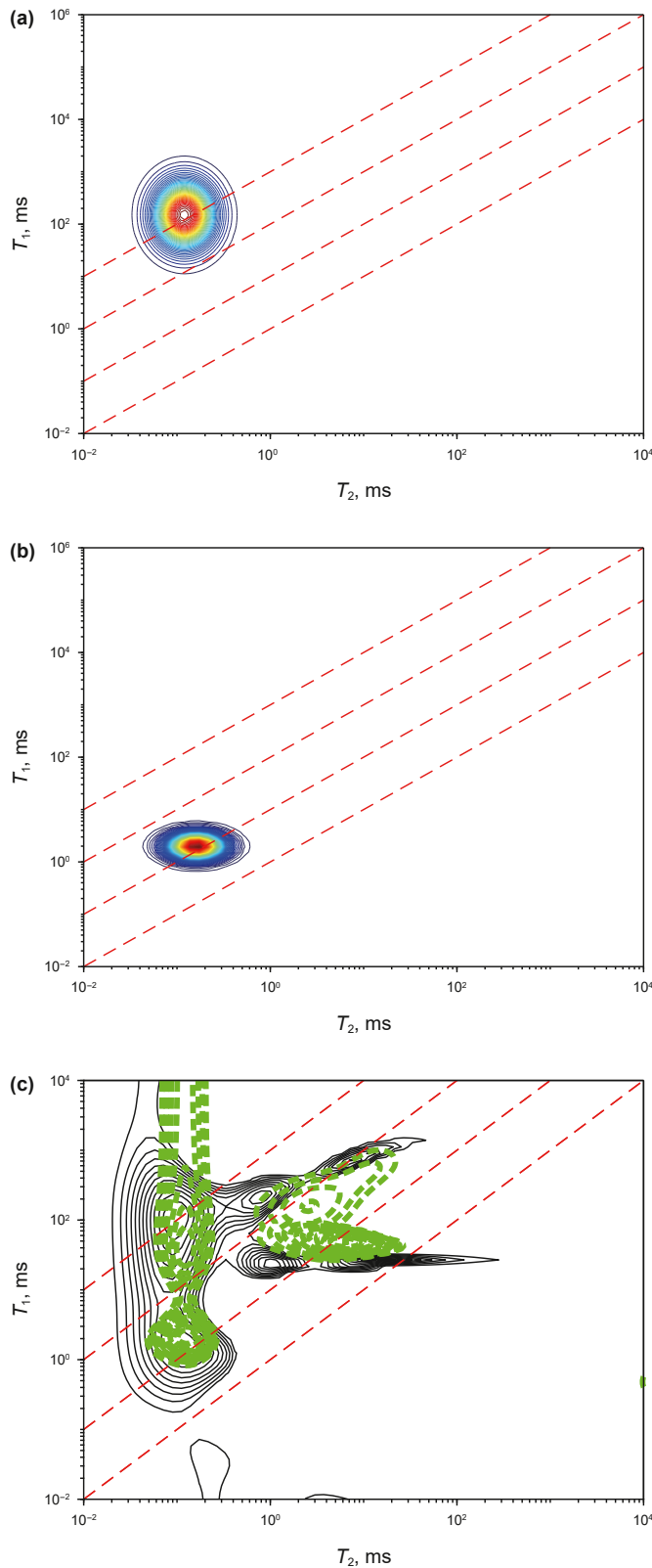


Fig. 6. Comparison of numerical investigations and experimental results. (a) T_1 - T_2 spectrum of organic matter; (b) T_1 - T_2 spectrum of clay-bound water; (c) comparison from the numerical and experimental T_1 - T_2 spectra. The black solid line is experimental T_1 - T_2 spectrum at the frequency of 21.36 MHz, and the green dotted line represents the T_1 - T_2 spectrum obtained from numerical simulations on the basis of digital core.

2 were obtained through Butler-Reeds-Dawson (BRD) inversion method (Butler et al., 1981). The distributions of the signals for various components on the T_1 - T_2 spectra were shown in Fig. 4. In Fig. 4, the signals for OM show a high T_1 value, a low T_2 value, and a high T_1/T_2 value, while the signals for adsorbed oil (OP oil during simulation) show a high T_1 value, a relatively low T_2 value, and a high T_1/T_2 value, and the signals for clay-bound water and IP water show low T_1 , T_2 and T_1/T_2 values. The results are consistent with the study from Li et al., which verifies the reasonability of the results (Li et al., 2020). It is noted that the #AA-2 has been previously used for NMR experiments with different frequencies. Therefore, the results of the high-field NMR experiment and the previous NMR experiments with different frequencies can be used to determine the $\rho_{1S,O}$, $\rho_{1S,W}$, $\rho_{2S,O}$, and $\rho_{2S,W}$.

3.3. Parameters determination and results verification

3.3.1. Parameters calibration

On the basis of improved Korb's theory, the $\rho_{1S,O}$, $\rho_{1S,W}$, $\rho_{2S,O}$, and $\rho_{2S,W}$ at 2, 21.36, and 200 MHz were determined. The results were given in Table 1. Since distributions of fluids and minerals in the shale sample remained unchanged, the determined parameters previously were unchanged.

The $\rho_{1S,O}$ and $\rho_{1S,W}$ were calibrated by the IR-CPMG (Fig. 5). It can be seen from Fig. 5(a) that the $\rho_{1S,O}$ at 21.36 MHz is 0.06 $\mu\text{m/s}$, while the error of T_1 measurement is 6.9 ms, and the corresponding value of τ_s is 1.37 μs , which is just a bit above 0.78 μs determined by Korb et al (2014). As shown in Fig. 5(b), the determined $\rho_{1S,W}$ at 21.36 MHz is 3.7 $\mu\text{m/s}$, while the error of T_1 measurement is 0.13 ms, and the corresponding value of is 0.1 μs , which is close to 0.6 μs determined by Korb et al. The results above verify the reasonability of related parameters. In the meanwhile, the $\rho_{1S,O}$, $\rho_{1S,W}$, $\rho_{2S,O}$ and $\rho_{2S,W}$ were also determined (Table 1). Based on the results of Fig. 5(a) and (b) as well as Eqs. (4) and (5), Frequency conversion equations were determined (Fig. 5(c)). It can be utilized to lay the foundation for subsequent numerical investigations.

3.3.2. Results verification

The T_{1K} and T_{2K} can be determined according to the P model (Eq. (2)). The values for $T_{2B,K}$ at 2, 21.36, and 200 MHz determined on the basis of the P model were 80, 120, and 130 μs , respectively. The values for $T_{1B,K}$ at these frequencies were 17, 150, and 1355 ms. Fig. 6(a) shows the T_1 - T_2 spectra of OM at 21.36 MHz. Assuming that the signal of clay-bound water does not change with magnetic field frequency, the T_1 - T_2 spectra of clay-bound water were regarded as a Gaussian spectra with transverse bulk relaxation time ($T_{2B,CL}$) of 0.12 ms and longitudinal bulk relaxation time ($T_{1B,CL}$) of 1.5 ms. To verify the accuracy of T_1 - T_2 simulation, the T_1 - T_2 spectra of OM, clay-bound water, IP water, and OP oil obtained through the simulation of digital cores were compared with that from the experimental measurements at 21.36 MHz. The results show that the peaks of the T_1 - T_2 spectra of OM, clay-bound water, and OP oil, and IP water obtained from numerical simulations were highly consistent with those from experimental measurements, which verified the accuracy of NMR T_1 - T_2 relaxation theory. In addition, the $\rho_{1S,O}$, $\rho_{1S,W}$, $\rho_{2S,O}$, and $\rho_{2S,W}$ from experiments can be used for subsequent numerical investigations. It is noted that if the echo of OP oil and IP water were inverted together, the results of coupled inversion would be displayed, making it impossible to compare the peak positions of T_1 - T_2 spectra from experiment and numerical simulation. The reason is that the signal of oil was weaker than that of water. Therefore, the intensity of the signal of oil in the T_1 - T_2 spectrum obtained from numerical investigations was amplified 5 times.

The accuracy of the numerical simulations on the basis of an

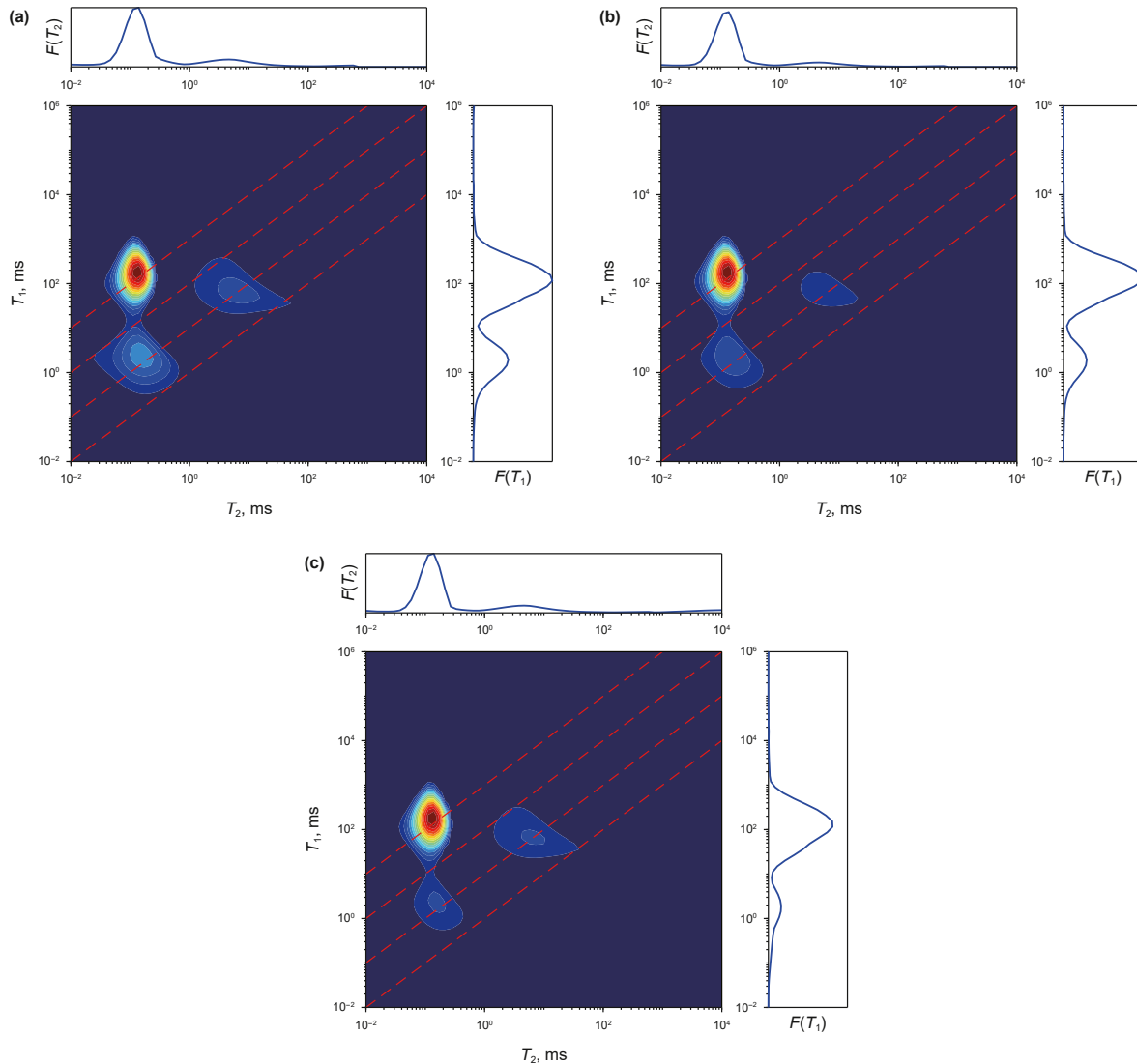


Fig. 7. Results for the T_1 - T_2 responses of organic matter with different HI values at the frequency of 21.36 MHz. Fig. 7(a), (b) and (c) show the T_1 - T_2 spectra of organic matter with HI values of 0.3, 0.5, and 0.7.

IRW algorithm and the NMR T_1 - T_2 relaxation theory has been verified in chapter 3.2. Since it is difficult to describe the effect of a single factor on T_1 - T_2 responses in shale oil reservoirs, the effect of each factor was quantified from numerical simulations to provide a foundation for the subsequent saturation frequency conversion for each component. The multi-component digital shale cores in this study are varying pyrite contents (0.55%, 1.77%, 2.68%, 3.94%, 5.3%, 6.9%), clay contents (0%, 1.03%, 3.39%, 5.12%, 10.49%, 20.14%) and types of clay mineral (Liu et al., 2024c).

4. Numerical simulation

4.1. Hydrogen index (HI) of OM

The HI of OM affects the determination of fluid component saturations for the T_1 - T_2 spectra. The T_1 - T_2 spectra for OM with varying HI were shown in Fig. 7. In Fig. 7, the signal intensity for OM increases with the increased HI of OM, while the signal intensities of clay-bound water, OP oil, and IP water decreases with the increased HI of OM.

4.2. Pyrite content

On the basis of the T_1 - T_2 relaxation theory and the previously constructed multi-component digital shale cores with varying pyrite contents (Liu et al., 2024c), the IR-CPMG was simulated using the IRW algorithm. The T_1 - T_2 spectra of all components (OM, clay-bound water, oil, and water) with varying frequencies, pyrite contents and T_E were obtained from BRD inversion (as shown in Fig. 8(a)–(i)). The results show that, as the magnetic field frequency enhances and other parameters are unchangeable, the peaks of the T_1 - T_2 spectra of OM shift toward the upper right corner because the $T_{1B,K}$ and $T_{2B,K}$ increased with the increased magnetic field frequency. $T_{1B,K}$ are more dependent on frequency than $T_{2B,K}$. Therefore, the peaks of the T_1 spectra of OM shift to a larger extent than the T_2 spectra. When pyrite content increases and other parameters are unchangeable, the peaks of the T_2 and T_1 spectra of OM and clay-bound water do not shift because pyrite content only have a minor impact on the $T_{2B,K}$ and $T_{2B,CL}$. The results show that, when magnetic field frequency is 2 MHz and pyrite content is low, T_2 and T_1 do not change with pyrite content (Fig. 8(a), (d) and (g)). When pyrite content is high, the peaks of the T_2 spectra shift toward the

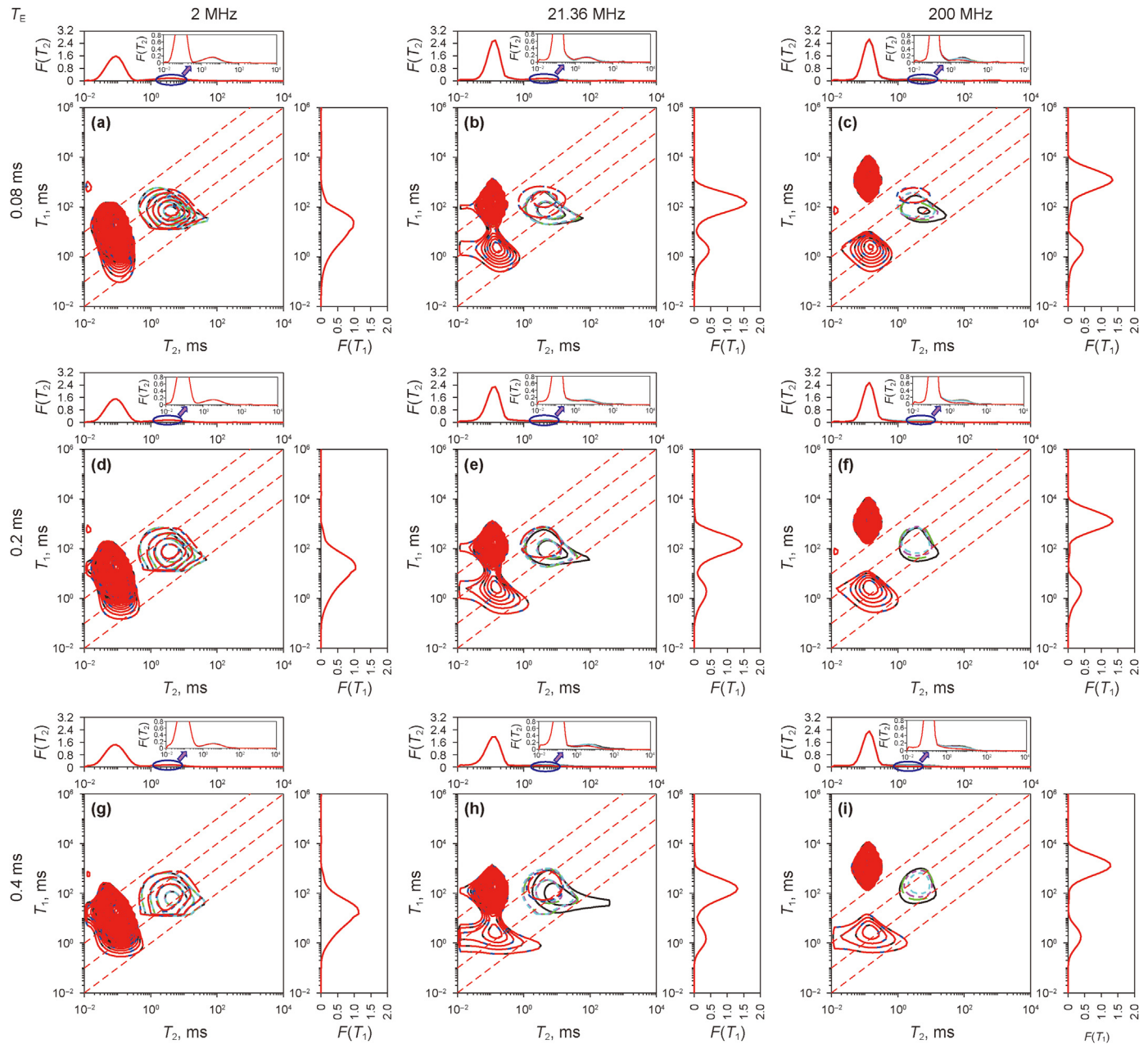


Fig. 8. T_1 - T_2 spectra of various fluids at different magnetic field frequencies with varying T_E and pyrite contents. The black, green, purple, cyan, blue and red lines are the T_1 - T_2 spectra for various fluids with varying pyrite contents (0.55%, 1.77%, 2.68%, 3.94%, 5.3%, and 6.9%).

direction of the short relaxation component as pyrite content increases (Fig. 8(a), (d) and (g)), while T_1 do not change significantly. When magnetic field frequency is 2 MHz and pyrite content is low, the fluid mainly undergoes surface relaxation, while bulk relaxation and diffusion relaxation are negligible. However, because diffusion relaxation cannot be neglected when pyrite content is high, the peaks of T_2 spectra shift toward the direction of the short relaxation component as pyrite content increases. The peaks of T_2 spectra shift toward the direction of the short relaxation component, and the spectral intensity decreases as pyrite content increases at 21.36 and 200 MHz frequencies (Fig. 8(b)–(c), (e)–(f), and (h)–(i)). Under the aforementioned conditions, the fluid is subject to the combined effects of surface relaxation and diffusion relaxation. As pyrite content increases, the magnetic susceptibility difference between the shale matrix and the fluid increases, and the

internal magnetic field gradient increases, relaxation rates accelerated due to the enhanced diffusion relaxation. Therefore, the peaks of the T_2 spectra shift to the left, and the spectral intensities decrease. When other conditions remain unchanged, an increased T_E would, on the one hand, reduce the instrument's ability to detect hydrogen signals and reduce the intensities of the signals of various components. On the other hand, it would enhance diffusion relaxation and accelerate echo, resulting in sparse signal contours and reduced spectral intensity (Fig. 8(a), (d), (g); Fig. 8(b), (e), (h); Fig. 8(c), (f), (i)). It should be noted that, when pyrite content is very high, enhanced diffusion relaxation can result in excessively low intensity of some T_1 - T_2 spectra, making it difficult to observe changes in contours in the T_1 - T_2 spectra (Fig. 8(e)–(f) and Fig. 8(h)–(i)).

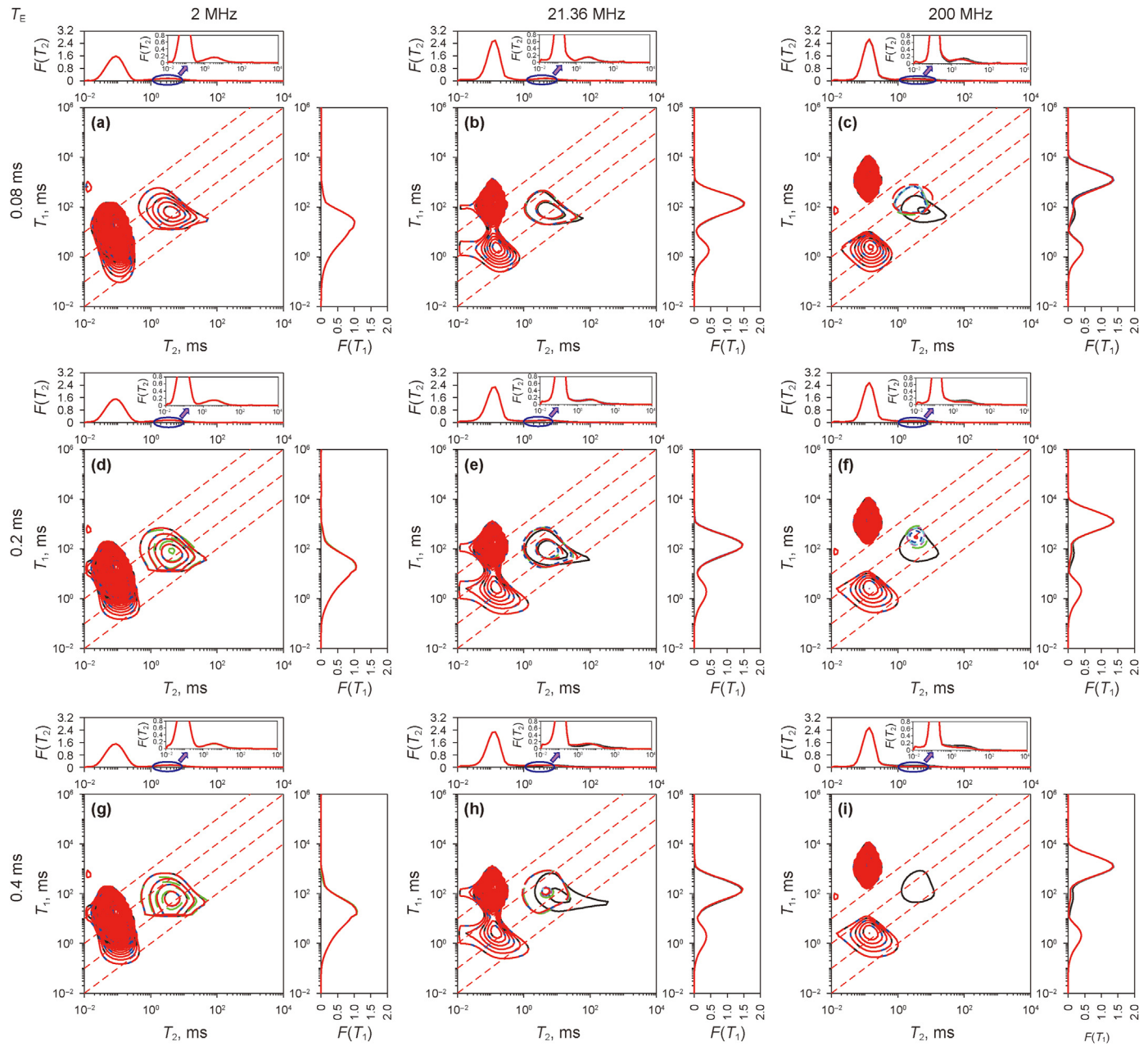


Fig. 9. T_1 - T_2 spectra of various fluids at different magnetic field frequencies with varying T_E and clay contents. The black line, green line, purple line, cyan line, blue line and red line represent the T_1 - T_2 spectra of various fluids under conditions of varying clay content (0%, 1.03%, 3.39%, 5.12%, 10.49%, and 20.14%).

4.3. Clay content

On the basis of the T_1 - T_2 relaxation theory and the previously constructed multi-component digital shale cores with varying clay content (Liu et al., 2024c), the IR-CPMG was simulated using the IRW algorithm. The T_1 - T_2 spectra of all components with varying frequency, T_E and clay content were obtained from BRD inversion (as shown in Fig. 9(a)–(i)). The results show that, as magnetic field frequency increases while other parameters are unchangeable, the peaks of the T_1 - T_2 spectra of OM shift toward the upper right corner. As clay content increases while other parameters are unchangeable, the peaks of the T_2 and T_1 spectra of OM and clay-bound water do not shift. We would not be explained repeatedly here because it has already been explained in the previous section. The results also show that, when magnetic field frequency is 2 MHz, T_2 and T_1 do

not change with clay content (Fig. 9(a), (d), (g)), and T_1 does not change significantly. When magnetic field frequency is 2 MHz, the fluid mainly undergoes surface relaxation, and bulk relaxation and diffusion relaxation are negligible. The T_2 spectra peak shift toward the direction of the short relaxation component, and the spectral intensity decreases as clay content increases at 21.36 and 200 MHz frequencies (Fig. 9(b)–(c), (e)–(f) and (h)–(i)), and T_1 does not change significantly. Because under the aforementioned conditions, the fluid was subject to the combined effects of surface relaxation and diffusion relaxation. As clay content increased, the magnetic susceptibility difference between the shale matrix and the fluid increased, and the internal magnetic field gradient increased, resulting in enhanced diffusion relaxation and accelerated echo. Therefore, the peaks of the T_2 spectra shifted to the left, and the spectral intensity decreased. When other conditions

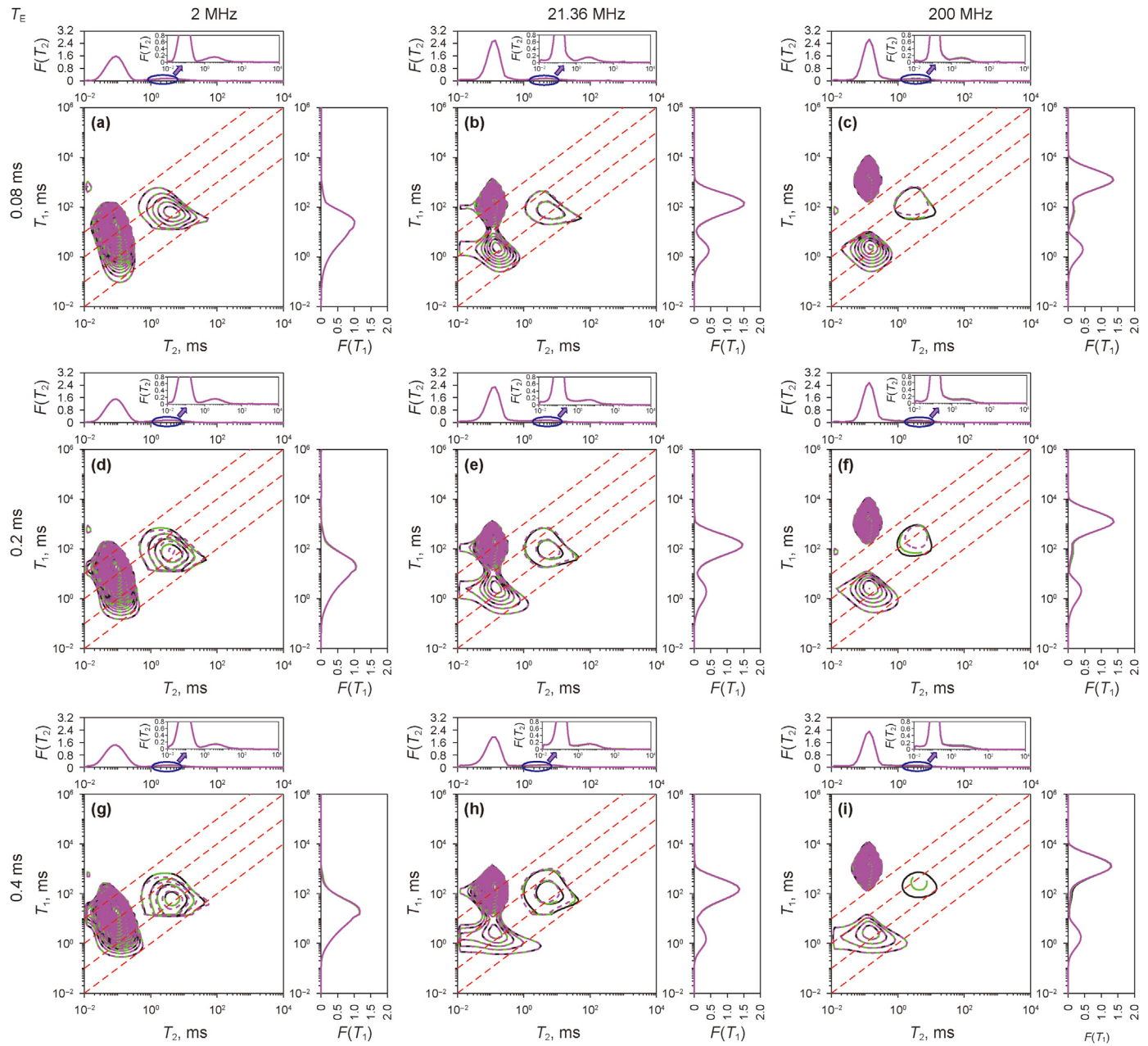


Fig. 10. T_1 - T_2 spectra of various fluids at different magnetic field frequencies with varying T_E and different types of clay mineral. The black, green and purple lines represent the T_1 - T_2 spectra of various fluids involving different types of clay mineral (M, ILL, CH).

remain unchanged, an increase in T_E would, on the one hand, reduce the instrument's ability to detect hydrogen signals and reduce the intensities of the signals of various components. On the other hand, it would enhance diffusion relaxation and accelerate relaxation rates, resulting in sparse signal contours and reduced spectral intensity (Fig. 9(a), (d), (g), (b), (e), (h), and (c), (f), (i)). It is to be noted that, when clay content is high and magnetic field frequency is very high, enhanced diffusion relaxation can result in excessively low intensities of some T_1 - T_2 spectra, making it difficult to observe changes in contours in the T_1 - T_2 spectra (Fig. 9(f) and (i)).

4.4. Clay mineral type

On the basis of the NMR relaxation theory and the previously constructed multi-component digital shale cores with different clay

minerals (Liu et al., 2024c), the IR-CPMG was simulated using the IRW algorithm. The T_1 - T_2 spectra of all components for different clay minerals were obtained from BRD inversion with varying frequencies and T_E (as shown in Fig. 10(a)–(i)). The results show that, as magnetic field frequency increases while other parameters are unchangeable, the peaks of the T_1 - T_2 spectra of OM shift toward the upper right corner. As clay mineral type changes (the magnetic susceptibility increased) while other parameters are unchangeable, the peaks of the T_2 and T_1 spectra of OM and clay-bound water do not shift. The reason would not be explained repeatedly here because it has already been explained in the previous section. The results also showed that, when magnetic field frequency is 2 MHz, T_2 and T_1 do not change with clay mineral type (Fig. 10(a), (d), (g)), and T_1 do not change significantly. When magnetic field frequency is 2 MHz, the fluid mainly underwent surface relaxation, and bulk

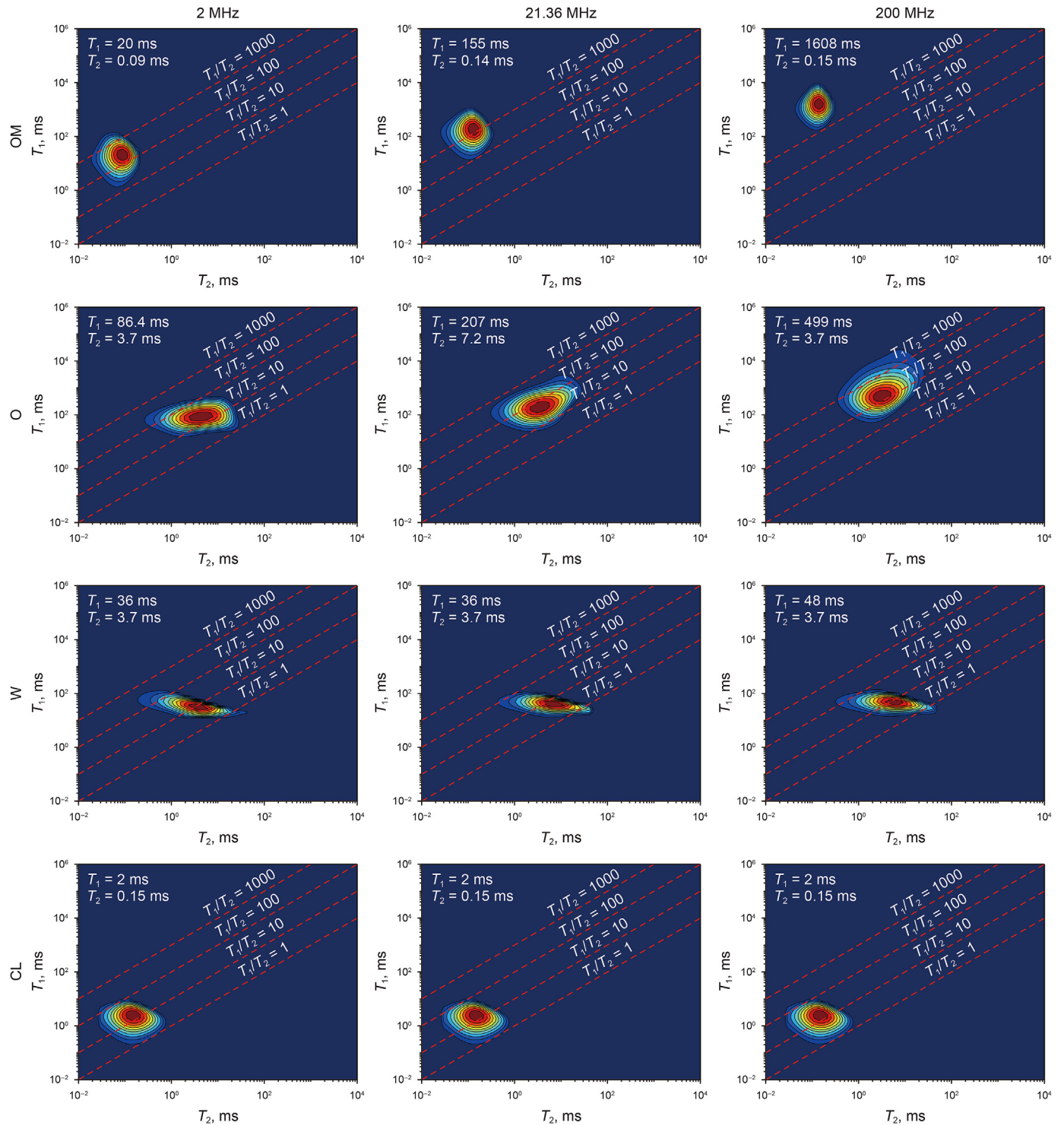


Fig. 11. T_1 - T_2 spectra of original digital cores containing pyrite of 0.55% obtained at different frequencies. In Fig. 11, magnetic field frequency, OM, O, W, and CL denote magnetic field frequency, OM, oil, water, and clay-bound water, respectively.

relaxation and diffusion relaxation were negligible. For frequencies of 21.36 and 200 MHz, the T_2 spectra peaks shift toward the direction of the short relaxation component as clay mineral type changed (the magnetic susceptibility increases), and the spectral intensity decreases (Fig. 10(b)–(c), (e)–(f) and 10(h)–(i)), and T_1 does not change significantly. The reason is that, under the

aforementioned conditions, the fluid is subject to the combined effects of surface relaxation and diffusion relaxation. The magnetic susceptibility difference between the shale matrix and the fluid increased, and the internal magnetic field gradient increase as clay mineral type changes (the magnetic susceptibility increases), the relaxation rates accelerated due to the enhanced diffusion

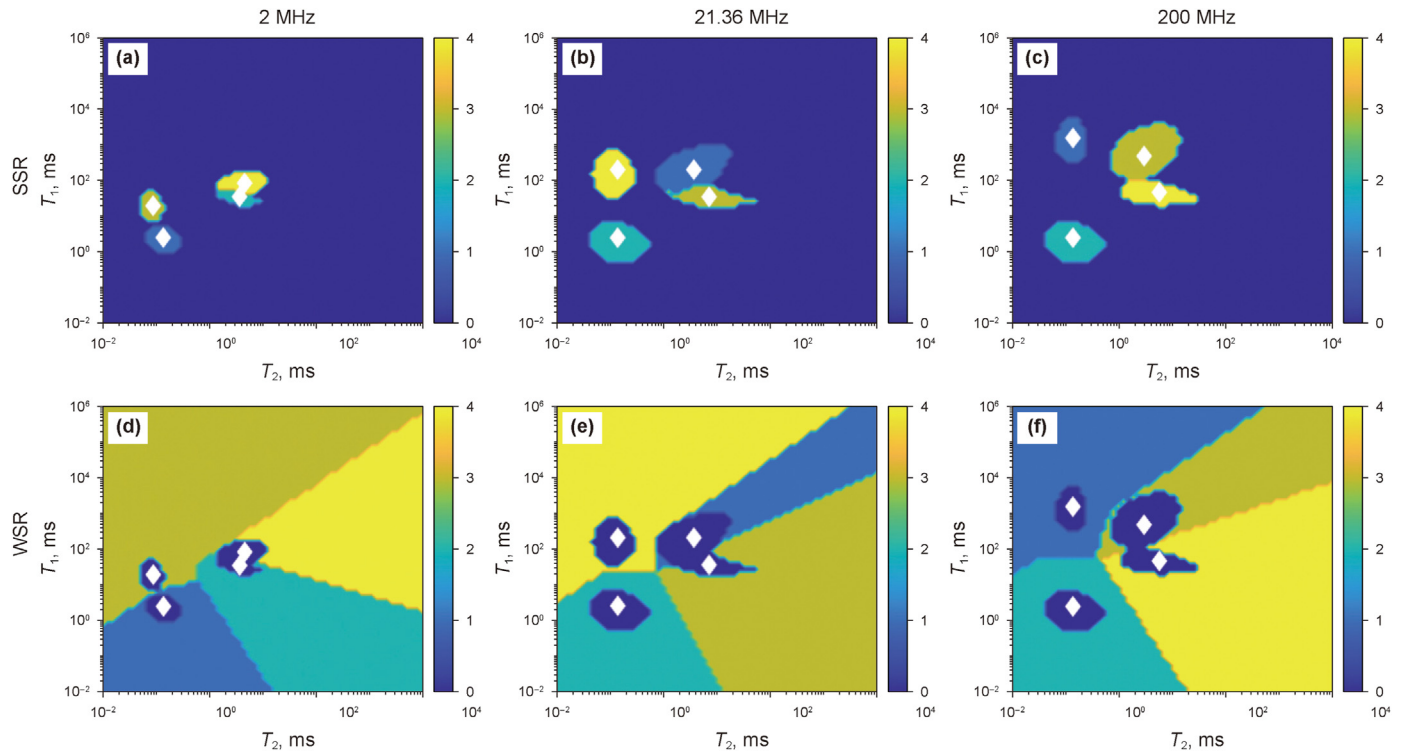


Fig. 12. T_1 - T_2 spectra of original digital cores containing pyrite of 0.55% obtained at different frequencies. For the frequency of 2 MHz, the strong signal diagram (a) corresponds to the weak signal diagram (d); the dark yellow, yellow, green and blue zones represent OM, oil, water, and clay-bound water, respectively. For the frequency of 21.36 MHz, the strong signal diagram (b) corresponds to the weak signal diagram (e); the yellow, blue, dark yellow and green zones represent OM, oil, water, and clay-bound water, respectively. For the frequency of 200 MHz, the strong signal diagram (c) corresponds to the weak signal diagram (f); the blue, dark yellow, yellow and green zones represent OM, oil, water, and clay-bound water, respectively. SSR represents strong signal area and WSR represents weak signal area.

relaxation. Therefore, the peaks of the T_2 spectra shift to the left, and the spectral intensity decreases. When other conditions remain unchanged, an increase in T_E would, on the one hand, reduce the instrument's ability to detect hydrogen signals and reduce the intensities of the signals of various components. On the other hand, it would enhance diffusion relaxation and accelerate relaxation rates, resulting in sparse signal contours and reduced spectral intensity (Fig. 10(a), (d), (g), (b), (e), (h), and (c), (f), (i)). When the magnetic susceptibility of clay is high and magnetic field frequency is very high, enhanced diffusion relaxation can result in excessively low intensities of some T_1 - T_2 spectra, making it difficult to observe changes in contours in the T_1 - T_2 spectra (Fig. 10(f) and (i)).

5. Frequency conversion of petrophysical parameters

The effects of pyrite content, clay mineral type, and clay content on T_1 - T_2 responses in shale oil reservoirs were analyzed from numerical simulations at 2, 21.36, and 200 MHz. Next step, we tried to accurately quantize the effects of various factors on petrophysical parameters such as saturation of each component.

Blind source separation (BSS) algorithms have been usually used for saturation calculation of fluid components in T_1 - T_2 spectra (Gu et al., 2021). On the basis of the results of numerical simulations for original digital cores, the peak positions of various components in the T_1 - T_2 spectra were determined. Blind source separation algorithms were performed for fluid signals in the T_1 - T_2 spectra from 100 different porosity data, and the signals of OM, oil, water, and clay-bound water at 2, 21.36, and 200 MHz were obtained (Fig. 11). The results showed that the signals of various components were clear.

The signals shown in Fig. 11 were classified into strong and weak signals, and their distributions for various components were identified (as shown in Fig. 12). The results showed the strong and weak signals were clear (Fig. 12(a), (d), 12(b), (e), and 12(c), (f)). The BSS results obtained at different frequencies can be used to determine the saturation of various components with varying pyrite content, types of clay mineral, and clay content.

5.1. Petrophysical parameters frequency conversion for different pyrite contents

On the basis of the T_1 - T_2 spectra shown in Fig. 12, the changes in OM saturation, Oil saturation (S_O), IP water saturation (S_W), and clay-bound water saturation (S_{CL}) with varying magnetic field frequencies, T_E and pyrite contents were identified (Fig. 13(a)–(d)). As shown in Fig. 13(a), OM saturation increases and other parameters are unchangeable as magnetic field frequency increases. Due to the frequency dependence from OM, the $T_{2B, K}$ and $T_{1B, K}$ increased with the increased frequency. As T_E increases and other parameters are unchangeable, OM saturation decreases with low pyrite content and increases with high pyrite content (Fig. 13(a)). For formations with high pyrite content, the significantly enhanced diffusion relaxation of pore fluids would cause the fluid signals to move to the position around OM in T_1 - T_2 spectra. For formations with low pyrite content, the movement extents of fluid signals in T_1 - T_2 spectra are low, and the increased T_E would reduce intensities of the detected fluid signals. As shown in Fig. 13(b) and (c), S_O and S_W decrease as magnetic field frequency increases and other parameters are unchangeable. When magnetic field frequency increases, the significantly enhanced diffusion relaxation of pore fluids would

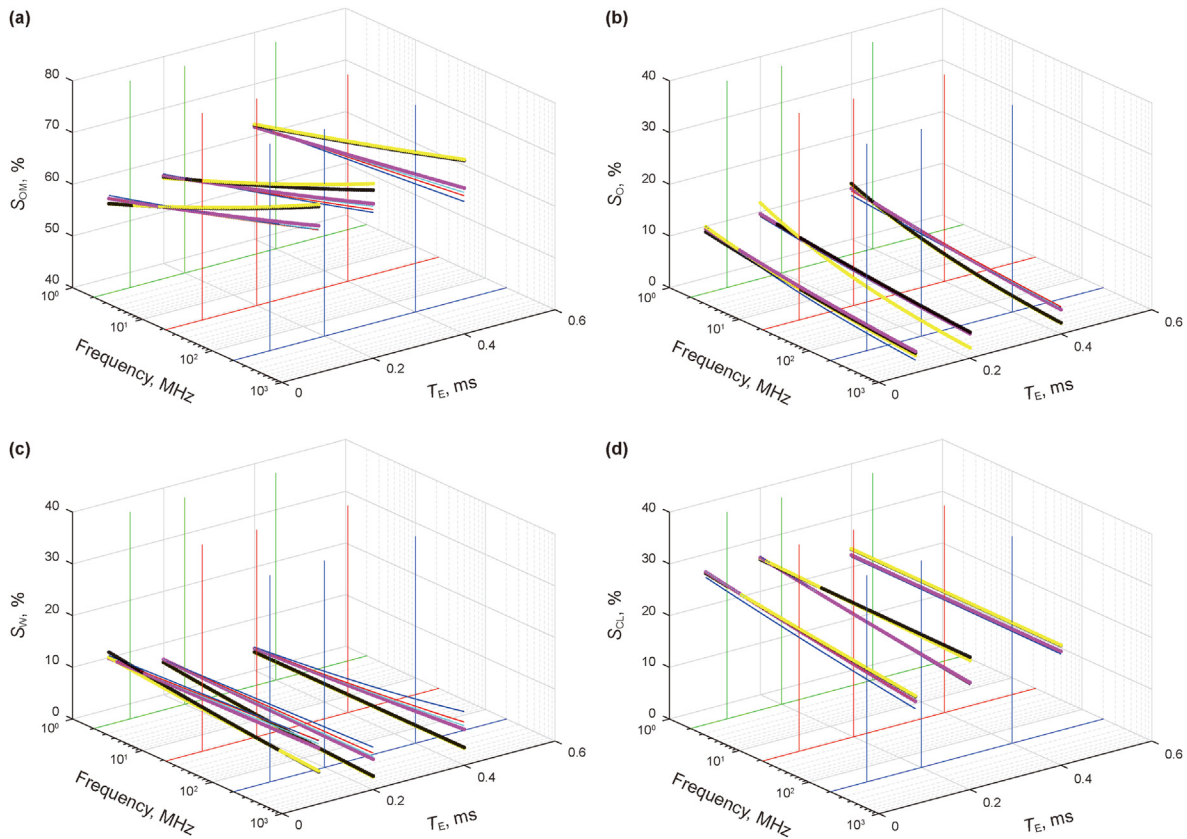


Fig. 13. Changes in OM saturation (S_{OM}), S_O , S_W , and S_{CL} with magnetic field frequency with varying pyrite contents. The blue solid line, red solid line, cyan dotted line, magenta dash-dotted line, black dotted-line, and yellow dotted-line represent the changes in the saturation of each component with varying pyrite contents (0.55%, 1.77%, 2.68%, 3.94%, 5.3%, and 6.9%). (a), (b), (c) and (d) represent OM, oil, water, and clay-bound water, respectively. The blue, red, and green dashed lines are the boundary lines for 2, 21.36, and 200 MHz.

lead to accelerated echo decay, and the peaks of the T_1 - T_2 spectra of oil and water would shift toward the upper left corner, due to which the determined S_O and S_W would be lower. As pyrite content increases and other parameters are unchangeable, the peaks of the T_1 - T_2 spectra of oil and water would shift toward the upper left corner more obviously, and S_O and S_W would therefore decrease more rapidly. As shown in Fig. 13(d), S_{CL} decreases slightly as magnetic field frequency increases and other parameters are unchangeable. Because when magnetic field frequency increases, the clay-bound water content remains unchanged, but the contents of OM, oil, and water would change. When the changes in OM content are greater than that in oil and water, S_{CL} would decrease. When the changes in OM content are close to that from oil and water, S_{CL} would be a fixed value. Therefore, for formations with high pyrite content, the changes in oil and IP water contents are close to the changes in OM contents, and the clay-bound water contents are close to a fixed value. When pyrite content is 5.3%, T_E is 0.4 ms, and magnetic field frequency are 2, 21.36, and 200 MHz, respectively, the OM saturation are 63.1%, 66.9%, and 70.7%, which are 112.8%, 120.0%, and 126.4% of the OM saturation from the original shale cores. The S_O are 8.18%, 6.11%, and 4.64%, which are 112.2%, 86.7%, and 67.9% of the S_O from the original shale cores. The S_W are 3.56%, 3.52%, and 3.48%, which are 34.1%, 41.0%, and 48.7% of the S_W from the original shale cores. The S_{CL} are 25.7%, 23.7%, and 22.0%, which are 91.3%, 98.4%, and 105.8% of the S_{WC} from the original shale cores.

5.2. Petrophysical parameters frequency conversion for different clay contents

The changes in OM saturation, S_O , S_W , and S_{CL} with magnetic field frequency under conditions of varying T_E and clay contents were identified on the basis of the saturation results (Fig. 14(a)–(d)). As shown in Fig. 14(a), OM saturation increases as magnetic field frequency increases and other parameters are unchangeable. As T_E increases and other parameters are unchangeable, OM saturation decreases with low clay content and increases with high clay content (Fig. 14(a)). These results are not interpreted because they have been interpreted in previous section. As shown in Fig. 14(b) and (c), S_O and S_W decrease as magnetic field frequency increases and other parameters are unchangeable. When magnetic field frequency increases, the significantly enhanced diffusion relaxation of pore fluids would lead to accelerated echo decay, and the peaks of the T_1 - T_2 spectra of oil and water would shift toward the upper left corner, due to which the determined S_O and S_W would be lower. As clay content increases and other parameters are unchangeable, the peaks of the T_1 - T_2 spectra of Oil and IP water would shift toward the upper left corner more obviously, and S_O and S_W would therefore decrease more rapidly. As shown in Fig. 14(d), S_{CL} decreases slightly as magnetic field frequency increases and other parameters are unchangeable. These results are not interpreted because they have been interpreted in previous section. When clay content is 10.49%, T_E is 0.4 ms, and magnetic field frequency is 2,

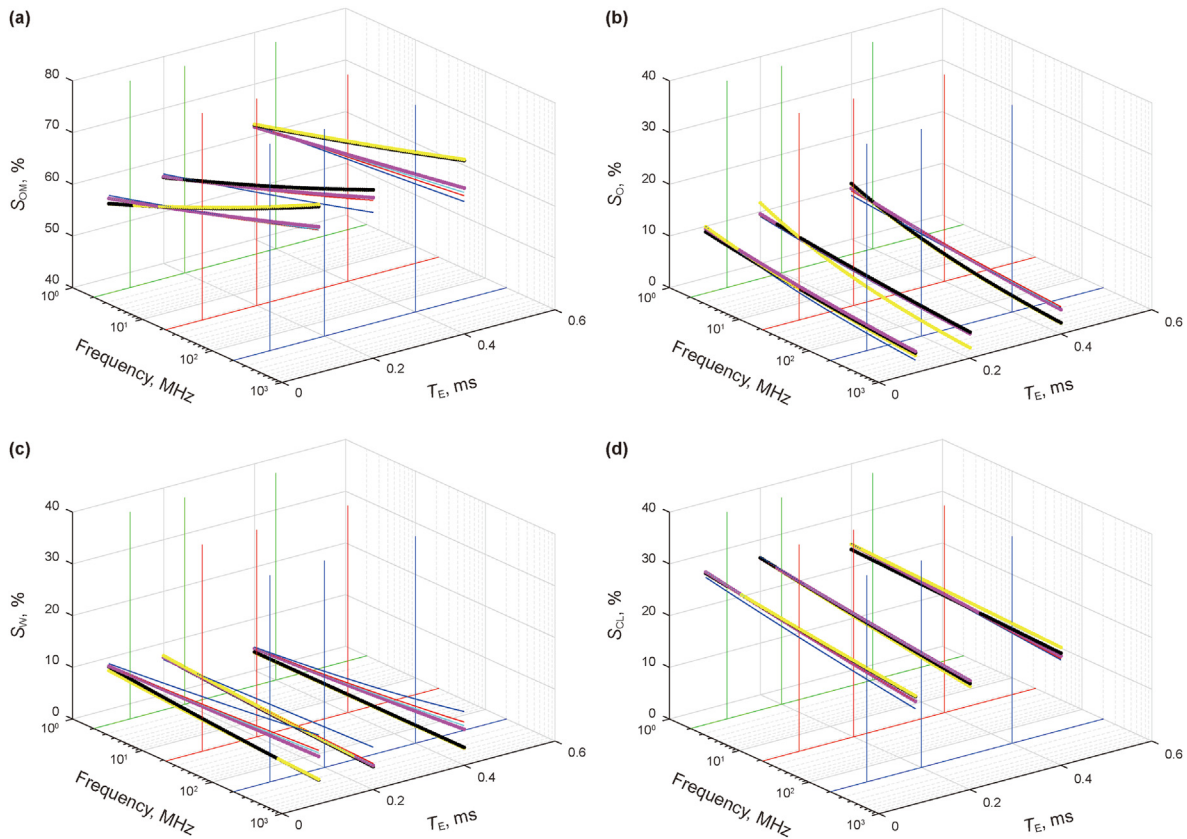


Fig. 14. Changes in S_{OM} , S_O , S_W , and S_{CL} with magnetic field frequency with varying clay contents. The blue solid, red solid, cyan dotted, magenta dash-dotted, black dotted, and yellow lines are the saturation variations from each component with varying pyrite contents (0%, 1.03%, 3.39%, 5.12%, 10.49%, and 20.14%). (a), (b), (c) and (d) represent OM, oil, water, and clay-bound water, respectively. The blue, red and green dashed lines are the boundary lines for 2, 21.36, and 200 MHz.

21.36, and 200 MHz, respectively, the OM saturation are 63.1%, 66.9%, and 70.7%, which are 112.8%, 108.6%, and 104.7% of OM saturation from the original shale cores. The S_O are 9.17%, 5.29%, and 3.15%, which are 198.0%, 76.5%, and 60.4% of the S_O from the original shale cores. The S_W are 3.57%, 3.57%, and 3.56%, which are 46.1%, 55.9%, and 67.0% of the S_W from the original shale cores. The S_{CL} are 24.2%, 23.6%, and 23.0%, which are 94.3%, 99.5%, and 104.8% of the S_{CL} from the original shale cores. It is to be noted that S_{CL} changes with frequency, but it is not a fixed value, indicating that the effect of clay content on S_{CL} is smaller than that of pyrite content. However, these effects are neglected for formations with high clay content.

5.3. Petrophysical parameters frequency conversion for different clay mineral types

The changes in OM saturation, S_O , S_W , and S_{CL} with frequency under conditions of varying T_E and clay mineral type were identified on the basis of the saturation results (Fig. 15(a)–(d)). As shown in Fig. 15(a), OM saturation increases as magnetic field frequency increases and other parameters are unchangeable. As T_E increases and other parameters are unchangeable, OM saturation decreases for clay minerals with low MS and increases for clay minerals with high MS (Fig. 15(a)). These results are not interpreted because they have been interpreted in previous section. As shown in Fig. 15(b) and (c), S_O and S_W decrease as magnetic field frequency increases and other parameters are unchangeable. When magnetic field frequency increases, the significantly enhanced diffusion relaxation of pore fluids would lead to accelerated echo decay, and the peaks

of the T_1 – T_2 spectra of oil and water would shift toward the upper left corner, due to which the determined S_O and S_W would be lower. As the MS of clay minerals increases and other parameters are unchangeable, the peaks of the T_1 – T_2 spectra of oil and water would shift toward the upper left corner more obviously, and S_O and S_W would therefore decrease more rapidly. As shown in Fig. 15(d), S_{CL} decreases slightly as magnetic field frequency increases while other parameters are unchangeable. These results are not interpreted because they have been interpreted in previous section. It should be noted that S_{CL} changes with frequency, but it is not close to a fixed value, indicating that the effect of clay mineral type on S_{CL} is smaller than that of pyrite content.

6. Discussion

In this work, according to the hypothesis that water only exists in the IP and oil only exists in the OP, we developed the T_1 – T_2 numerical simulation methods in shale oil reservoirs with complex minerals, and the accuracy of numerical simulation was verified from NMR T_1 – T_2 experiments from the parallel samples. The samples selected for the experiments showed heterogeneity. To minimize this variability, the parallel samples that closely matched the core used for the FIB-SEM experiment were selected. Meanwhile, the OM content, oil, and the water in the digital shale core from the FIB-SEM experiment were determined to be 22.36%, 0.55%, and 1.39% respectively. Due to the significant difference between the OM content and pore fluids, the simulation results showed strong signal intensity for OM, while the signal intensities of water and oil were comparatively weak. In actual shale formations, where the

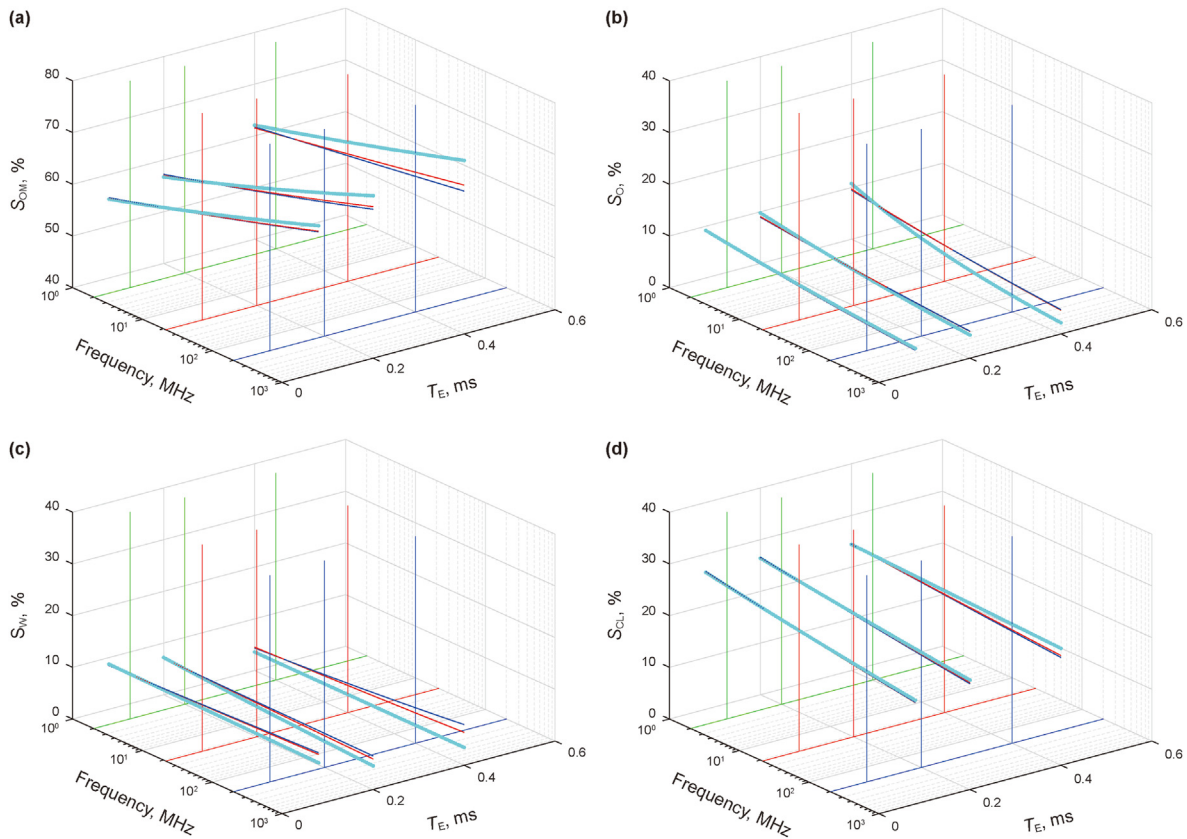


Fig. 15. Changes in S_{OM} , S_O , S_W , and S_{CL} with magnetic field frequency with varying clay mineral types. The dark blue solid, red dash-dotted, and cyan dotted lines represent the changes in the saturation of each component with varying clay mineral types. (a), (b), (c), and (d) represent OM, oil, water, and clay-bound water, respectively. The blue, red, and green dashed lines are the boundary lines for 2, 21.36, and 200 MHz.

OM content is typically lower, the signal intensity of OM in the T_1 - T_2 spectra remained low, particularly when T_E is set to 0.4 ms or 0.2 ms. Actually, the occurrence state of fluids is also a key factor influencing the NMR responses of shale oil. Nevertheless, despite these challenges, this study still provides new insights into the 2-D T_1 - T_2 responses in shale oil reservoirs across different frequencies. In the future, we will continue to explore the effects from occurrence state of fluids.

7. Conclusions

In shale oil reservoirs, T_1 - T_2 spectra are of great significance in characterizing the petrophysical properties. However, factors such as the highly non-uniform distributions of minerals and OM in shale affect NMR-based petrophysical properties characterization. Numerical simulations can effectively quantify these effects on the petrophysical properties. In addition, differences in frequency and acquisition parameters between laboratory NMR instruments and NMR logging also affect the NMR-based the petrophysical properties characterization.

In this study, for the first time, the NMR T_1 - T_2 relaxation theory was developed on the basis of modified Korb's theory. The transverse and longitudinal relaxivities of pore fluids were determined from numerical simulations and experimental analysis (extraction, GC, multi-frequency NMR, and NMR 2-D T_1 - T_2 experiments) conducted on digital shale cores. Based on digital core technology, the IRW algorithm was developed and used for the first time to simulate the effects of the HI of OM, T_E , pyrite content, clay mineral type, and clay content on T_1 - T_2 spectra at different magnetic field

frequencies. Frequency conversion cross-plots for various petrophysical properties were established for the first time. The conclusions are as follows:

- (1) The modified Korb's theory describes the frequency dependences for $T_{1B,K}$, $T_{2B,K}$, $\rho_{1S,O}$, $\rho_{1S,W}$, $\rho_{2S,O}$, $\rho_{2S,W}$, and the internal magnetic field gradient. This provides new ideas for the quantitative evaluation of the pore fluids in shale oil reservoirs, petrophysical characterization of shale oil, and frequency conversion for petrophysical parameters such as fluid saturation on the basis of T_1 - T_2 spectra obtained from laboratory NMR instruments and field NMR logging.
- (2) The results of the T_1 - T_2 numerical simulations performed with the developed Korb's theory show the HI of OM affects qualitative analysis of the pore fluids, and the T_E should be minimized to reduce the impact of the diffusion relaxation. Factors such as magnetic field frequency, pyrite content, clay mineral type, and clay content affect the T_1 - T_2 responses. The pyrite content has the greatest impact on the T_1 - T_2 responses. When the pyrite content is 5.3%, the T_E is 0.4 ms, and the magnetic field frequency are 2, 21.36, and 200 MHz, the OM saturation values are 63.1%, 66.9%, and 70.7%, which are 112.8%, 120.0%, and 126.4% of the OM saturation values from the original shale cores, respectively. Similarly, the oil saturation values are 8.18%, 6.11%, and 4.64%, respectively, which correspond to 112.2%, 86.7%, and 67.9% of the oil saturation values from the original shale cores. In addition, the IP water saturation values are 3.56%, 3.52%, and 3.48%, respectively, which correspond to 34.1%, 41.0%, and 48.7% of the IP S_W

from the original shale cores. The S_{CL} are 25.7%, 23.7%, and 22.0%, respectively, representing 91.3%, 98.4%, and 105.8% of the S_{CL} from the original shale cores. Furthermore, when the magnetic susceptibility and content of clay increase, OM saturation increases, S_O , S_W , and S_{CL} decrease. In summary, compared with clay content and clay mineral type, pyrite content has a greater impact on the T_1 - T_2 responses.

- (3) Petrophysical parameters such as OM saturation, the S_O , S_W , and S_{CL} are affected by the pyrite contents and clay minerals under conditions of varying NMR frequencies and T_E . Based on the results of numerical simulations, the frequency-conversion of petrophysical parameters including fluids saturation can be achieved to accurately determine S_O , S_W , and S_{CL} .

This study could be of great significance for quantitatively evaluating the saturation for fluids, the petrophysical characterization, and frequency conversion for petrophysical parameters using both laboratory NMR instruments and field NMR logging in shale oil reservoirs. It could play an important role in enhancing the recovery rate of fluids. In this paper, the NMR T_1 - T_2 relaxation theory proposed could serve as a foundation for understanding how NMR responses may be altered during the displacement of other fluids by CO_2 injection into shale reservoirs. Therefore, NMR technology could be used to monitor the sequestration of CO_2 .

CRediT authorship contribution statement

Ji-Long Liu: Writing – original draft, Software, Resources, Methodology, Investigation, Formal analysis, Data curation. **Ran-Hong Xie:** Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition. **Jiang-Feng Guo:** Writing – review & editing, Visualization, Validation. **Guo-Wen Jin:** Visualization, Validation, Supervision, Software.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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List of abbreviation

HI	Hydrogen index
OM	Organic matter
IP	Inorganic pore
OP	Organic pore
IR-CPMG	Inversion recovery-Carr-Purcell-Meiboom-Gill
FIB-SEM	Focused ion beam scanning electron microscope
GC	Extraction and gas chromatography experiments
IRW	Improved random walk
HI	Hydrogen index
T_E	Echo spacing
S_O	Saturation of oil
S_W	Saturation of water
S_{CL}	Saturation of clay bound water
S_{OM}	Saturation of organic matter

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