Geochemical Dynamics in Organic-Rich Mudstone Reservoirs: Interactions and Implications

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Abstract

This paper explores the intricate geochemical characteristics of organic-rich mudstone reservoirs, focusing on key factors such as thermal maturity, wettability, and adsorption properties. These reservoirs, often referred to as unconventional hydrocarbon systems, are composed of complex organic and inorganic phases that interact dynamically over geological timescales. Understanding these interactions is crucial for optimizing hydrocarbon recovery and developing effective reservoir management strategies.

One of the central themes of this study is **thermal maturity**, which governs the transformation of organic material into hydrocarbons. As mudstones undergo burial and increased temperature exposure, organic matter, primarily kerogen, is thermally degraded into oil and gas. The degree of thermal maturity affects the composition, phase behavior, and mobility of hydrocarbons within the reservoir. High-maturity shales tend to exhibit lower oil viscosity and increased gas content, which influence the overall fluid transport and production efficiency. Moreover, thermal maturity impacts the wettability of the rock, altering the interaction between hydrocarbons and the mineral matrix, which in turn affects fluid retention and migration pathways.

Another key factor considered is **wettability**, which plays a significant role in determining fluid distribution and flow behavior within mudstone reservoirs. Wettability refers to the preference of a solid surface to be in contact with either water or hydrocarbons. The organic-rich nature of these mudstones contributes to a highly heterogeneous wettability profile, with variations between oil-wet, water-wet, and mixed-wet conditions. These differences impact capillary pressures, relative permeability, and ultimately, the efficiency of hydrocarbon recovery. Experimental studies using contact angle measurements and nuclear magnetic resonance (NMR) techniques provide valuable insights into how wettability changes with thermal evolution and fluid exposure.

In addition to wettability, **adsorption properties** are critical in dictating hydrocarbon storage and transport mechanisms. Due to their high surface area and microporous nature, organic-rich mudstones can adsorb significant quantities of gas, particularly methane, through physical and chemical interactions. Adsorption is influenced by factors such as mineral composition, organic matter content, and pressure-temperature conditions. Computational approaches, including molecular dynamics (MD) simulations and density functional theory (DFT) calculations, have been instrumental in elucidating the fundamental mechanisms governing gas adsorption in these complex systems.

By integrating experimental findings with computational studies, this paper provides a comprehensive synthesis of the geochemical processes affecting organic-rich mudstone reservoirs. Insights from contemporary research are discussed, offering a nuanced understanding of the interplay between thermal maturity, wettability, and adsorption properties. These findings have important implications for optimizing hydrocarbon extraction strategies and improving reservoir management in unconventional energy resources.

Introduction

Organic-rich mudstones play a fundamental role in the global energy landscape due to their vast hydrocarbon potential. These unconventional reservoirs, including shale formations, have become crucial contributors to the world’s oil and gas supply, particularly with advancements in hydraulic fracturing and horizontal drilling. Unlike conventional reservoirs, where hydrocarbons migrate into porous rock formations, mudstones act as both the source rock and the reservoir, making their geochemical complexity an essential focus of study.

The composition of organic-rich mudstones is primarily defined by the interaction between organic matter (kerogen) and inorganic constituents such as quartz, pyrite, and various clays (Passey et al., 2010). Understanding these interactions and their evolution under different geological conditions is critical for optimizing hydrocarbon extraction, mitigating production challenges, and improving reservoir management strategies. This paper explores the geochemical properties of organic-rich mudstones, emphasizing thermal maturity, wettability, adsorption mechanisms, and the implications for hydrocarbon recovery.

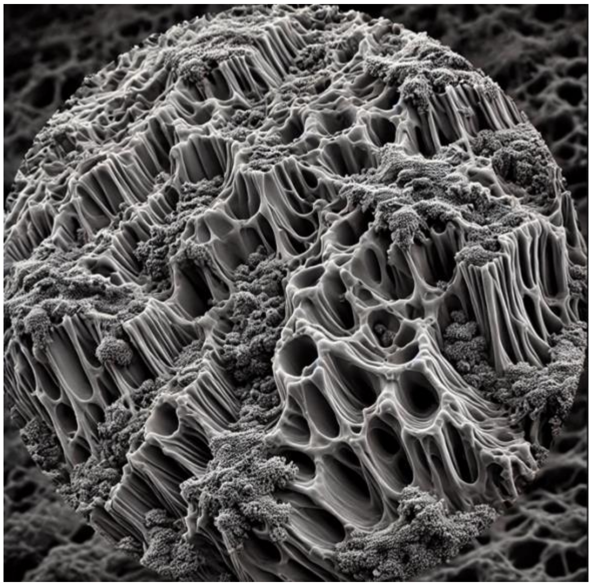

Fig 1: High resolution SEM of Kerogen pores

Composition and Thermal Maturity

The organic component of mudstones is dominated by **kerogen**, an insoluble macromolecular structure that serves as the precursor to hydrocarbons. Kerogen is classified into three primary types based on its hydrogen, carbon, and oxygen content:

- **Type I**: Algal-derived, rich in hydrogen, and primarily generates oil.
- **Type II**: Marine organic matter, generating a mix of oil and gas.
- **Type III**: Terrestrial plant material, rich in oxygen, and predominantly generating gas (Tissot & Welte, 1984).

Thermal maturity is a crucial factor in hydrocarbon generation, as it determines the transformation of kerogen into liquid and gaseous hydrocarbons. This transformation occurs in stages:

1. **Diagenesis** (low temperature, shallow burial): Kerogen undergoes biochemical alterations with limited hydrocarbon generation.
2. **Catagenesis** (moderate temperature, deeper burial): Cracking of kerogen releases oil and gas.
3. **Metagenesis** (high temperature, deep burial): Further cracking produces methane and carbon residues.

The degree of thermal maturation directly influences hydrocarbon mobility, viscosity, and phase behavior within the reservoir. High-maturity shales, such as those in the Barnett and Marcellus formations, are known for their dry gas production due to advanced thermal degradation of kerogen (Jarvie et al., 2007).

Mineralogy and Wettability

The inorganic fraction of mudstones comprises **quartz, carbonates, feldspars, and clay minerals**, each playing a critical role in defining reservoir properties. Quartz and carbonate-rich formations tend to be more brittle, making them ideal candidates for hydraulic fracturing (Rickman et al., 2008). In contrast, clay-rich formations exhibit ductility, reducing their ability to sustain fracture networks.

Wettability, or the preference of a solid surface to be in contact with a particular fluid (oil or water), is a key parameter influencing hydrocarbon recovery. The wettability of mudstones is highly heterogeneous due to the coexistence of organic and mineral phases. Organic matter tends to be **oil-wet**, whereas mineral surfaces are typically **water-wet** (Chalmers & Bustin, 2007). This mixed-wettability behavior impacts capillary forces, relative permeability, and hydrocarbon expulsion efficiency.

Recent experimental studies using **X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM)** have confirmed that thermal maturity significantly alters wettability. Low-maturity shales often display more water-wet characteristics, whereas high-maturity shales become increasingly oil-wet due to the deposition of bitumen-like substances (Ho et al., 2016). Understanding wettability variations is crucial for designing effective fluid injection strategies in enhanced oil recovery (EOR) processes.

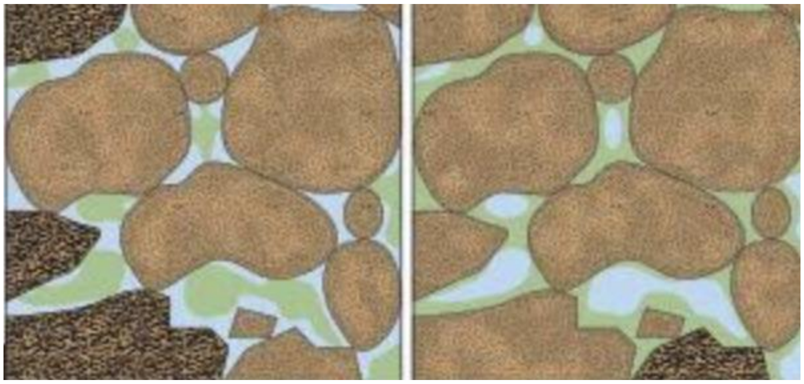

Fig 2: Oil-wet and water-wet

Adsorption Mechanisms and Hydrocarbon Storage

Unlike conventional reservoirs where hydrocarbons are stored in pore spaces, mudstones store gas through **adsorption onto organic matter surfaces, free gas in nanopores, and gas dissolved in liquids** (Zhang et al., 2012). The high surface area and microporous nature of kerogen provide numerous adsorption sites for methane, contributing significantly to gas-in-place estimates.

Gas adsorption capacity is influenced by several factors, including:

- **Kerogen Type and Maturity**: Type II and Type III kerogens exhibit higher adsorption capacities than Type I due to their greater aromaticity and microporosity (Tang et al., 2019).
- **Pore Structure**: Nano-scale pores in kerogen and clay minerals provide additional gas storage capacity.
- **Pressure and Temperature Conditions**: Higher pressures enhance adsorption, whereas elevated temperatures reduce it by increasing desorption rates.

Molecular dynamics (MD) simulations and **density functional theory (DFT)** calculations have provided critical insights into gas adsorption behavior at the atomic scale. Studies have demonstrated that methane molecules preferentially adsorb onto kerogen surfaces through van der Waals interactions, with adsorption energies varying depending on kerogen maturity and surface chemistry (Chen et al., 2020). These findings have significant implications for predicting shale gas recovery and optimizing production strategies.

Implications for Hydrocarbon Recovery and Reservoir Management

The unique geochemical characteristics of organic-rich mudstones present both opportunities and challenges for hydrocarbon extraction. Understanding the interplay between **thermal maturity, wettability, and adsorption** is essential for optimizing **fracturing fluid selection, production forecasting, and reservoir stimulation techniques**.

1. **Fracturing Fluid Design**: Wettability alterations with maturity necessitate tailored fracturing fluids to maximize hydrocarbon flow. Surfactants and wettability modifiers are increasingly being tested to enhance oil recovery in organic-rich shales (Wang et al., 2019).
2. **Gas Desorption Models**: Advanced gas desorption models integrating molecular simulations and laboratory data can improve production estimates for shale gas reservoirs (Javadpour et al., 2007).
3. **Thermal Stimulation Strategies**: High-maturity shales with strong adsorption capacities may benefit from thermal stimulation techniques, such as CO_2 injection, to enhance gas recovery (Liu et al., 2021).

Recent advancements in **machine learning and artificial intelligence (AI) applications** are further improving reservoir characterization and production optimization. AI-driven models integrating **geochemical, petrophysical, and production data** are enhancing predictive capabilities for hydrocarbon recovery in unconventional reservoirs (Ma et al., 2022).

The geochemical complexity of organic-rich mudstones underscores the need for a **multidisciplinary approach** that combines experimental techniques, computational modeling, and advanced analytical methods. By understanding the **thermal evolution, wettability variations, and adsorption mechanisms** of these reservoirs, researchers and industry professionals can develop more efficient strategies for hydrocarbon extraction and reservoir management.

As global energy demand continues to grow, **unconventional reservoirs will remain a key component of the energy transition**, necessitating continued research into their geochemical behavior and production optimization techniques.

Thermal Maturity and Kerogen Properties

Thermal maturity is a key driver of geochemical transformations in organic-rich mudstones, influencing the physicochemical properties of **kerogen**, the primary organic component responsible for hydrocarbon generation and retention. As mudstones undergo **progressive burial and heating**, kerogen evolves through different stages of maturity, impacting **wettability, adsorption behavior, and hydrocarbon mobility** (Tissot & Welte, 1984).

Recent studies (Jagadisan & Heidari, 2019; 2022) have provided valuable insights into how these changes influence **fluid-rock interactions**, demonstrating that increasing thermal maturity enhances **aromaticity**, thereby shifting the behavior of kerogen from **hydrophilic to hydrophobic**. This transformation significantly affects **fluid distribution, capillary forces, and gas storage capacity**, which are crucial for understanding **hydrocarbon recovery** in unconventional reservoirs.

Wettability Dynamics

Wettability is a fundamental property that dictates the interaction between fluids and reservoir surfaces, ultimately controlling fluid distribution, capillary pressure, and hydrocarbon recovery efficiency. In organic-rich mudstones, the wettability of kerogen, the primary organic component, evolves due to geochemical transformations induced by thermal maturation and diagenetic processes. Recent molecular simulation studies (de Araujo, Jagadisan, and Heidari, 2023) have provided insights into how these transformations modify kerogen's affinity for water and hydrocarbons, demonstrating that increasing maturity leads to a shift from hydrophilic to hydrophobic behavior. These findings align with experimental investigations (Garcia et al., 2020), which reveal the critical role of functional groups in altering surface properties.

The wettability of kerogen is primarily determined by its molecular structure, including the presence of oxygen-, nitrogen-, and sulfur-containing functional groups. At lower thermal maturity, kerogen retains a significant proportion of polar functional groups, such as hydroxyl (-OH), carboxyl (-COOH), and carbonyl (C=O) moieties, which impart a hydrophilic character. This allows water to preferentially adhere to organic surfaces, increasing the water-wet nature of the reservoir. However, as kerogen undergoes thermal maturation, these functional groups are progressively lost due to decarboxylation and dehydrogenation reactions. Simultaneously, aromaticity increases, resulting in a more nonpolar surface with a higher affinity for hydrocarbons. De Araujo, Jagadisan, and Heidari (2023) used molecular dynamics (MD) simulations to demonstrate that as kerogen becomes more graphitic, water contact angles increase, confirming the transition to a more oil-wet state.

The interplay between wettability and hydrocarbon mobility is a crucial factor in unconventional resource development. In low-maturity formations, strong water affinity can lead to higher water saturation in nanopores, inhibiting hydrocarbon migration. Conversely, in high-maturity formations, where kerogen becomes predominantly hydrophobic, hydrocarbons are more easily expelled, improving recovery potential. Garcia et al. (2020) conducted core flooding experiments on shales with varying maturity and observed a direct correlation between wettability and hydrocarbon recovery factors. Their results demonstrated that at higher maturity levels, spontaneous imbibition of oil increased while water retention decreased, further confirming the molecular simulation predictions.

Apart from thermal maturity, mineral-kerogen interactions and brine composition also play critical roles in modifying wettability. Clay minerals, such as illite and smectite, often coexist with kerogen and contribute to mixed-wet conditions due to their inherent hydrophilicity. Additionally, the presence of divalent cations (Ca^{2+}, Mg^{2+}) in formation water can influence electrostatic interactions, altering adhesion forces between fluids and solid surfaces. Advanced spectroscopic techniques, such as X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), have been employed to analyze these effects at the nanoscale, further validating computational models.

Understanding the evolution of wettability in organic-rich reservoirs is essential for optimizing extraction strategies, including hydraulic fracturing fluid design and enhanced oil recovery (EOR) methods. Wettability modification techniques, such as surfactant treatments and CO_2 flooding, have been proposed to enhance hydrocarbon displacement efficiency in mixed-wet and oil-wet systems. By integrating molecular simulations, experimental observations, and geochemical analyses, researchers can develop more effective approaches to managing fluid flow in complex unconventional reservoirs.

Conclusion

Wettability plays a crucial role in determining fluid distribution, capillary behavior, and hydrocarbon recovery efficiency in organic-rich mudstone reservoirs. As an essential property governing fluid-rock interactions, it evolves in response to geochemical transformations, particularly thermal maturation. Understanding these changes is vital for optimizing resource extraction strategies in unconventional reservoirs. Through a combination of molecular simulations and experimental investigations, researchers have gained significant insights into how kerogen's affinity for water and hydrocarbons is altered over geological time scales. These findings have profound implications for reservoir engineering, fluid flow dynamics, and enhanced oil recovery techniques.

One of the most striking findings from recent studies is the clear correlation between thermal maturity and wettability. At lower maturity levels, kerogen retains a substantial proportion of polar functional groups such as hydroxyl, carbonyl, and carboxyl moieties, which promote hydrophilicity. This results in stronger water adhesion and reduced hydrocarbon mobility. As thermal maturation progresses, these functional groups undergo degradation, leading to increased aromaticity and a transition toward a more hydrophobic, oil-wet state. Molecular dynamics (MD) simulations, such as those conducted by de Araujo, Jagadisan, and Heidari (2023), provide a detailed mechanistic understanding of this transformation, demonstrating how the loss of polar groups leads to an increase in water contact angles and enhanced hydrocarbon adhesion. Experimental studies, such as those by Garcia et al. (2020), further validate these computational findings, showing that highly mature shales exhibit greater oil imbibition and reduced water retention.

This transition in wettability has significant implications for hydrocarbon recovery. In low-maturity formations, where kerogen surfaces are predominantly water-wet, hydrocarbon migration is often restricted due to high water saturation in nanopores. This can lead to inefficient hydrocarbon displacement during production. In contrast, in high-maturity reservoirs where kerogen surfaces become oil-wet, hydrocarbons are more easily expelled, facilitating improved recovery. However, oil-wet conditions can also pose challenges, particularly in water-based hydraulic fracturing operations, where water penetration into nanopores may be hindered, reducing overall stimulation effectiveness. Understanding the wettability evolution helps in tailoring fracturing fluid formulations to maximize hydrocarbon extraction while minimizing formation damage.

Beyond thermal maturity, factors such as mineral composition, brine chemistry, and surface roughness contribute to the wettability of organic-rich mudstones. The presence of clay minerals, which tend to be hydrophilic, can create heterogeneous wetting conditions, complicating fluid transport dynamics. Additionally, formation water composition, including salinity and divalent cation concentration, influences electrostatic interactions at the fluid-rock interface. Studies using advanced surface characterization techniques, such as X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), have provided further evidence of these complex interfacial processes.

Given the critical role of wettability in unconventional reservoir development, modifying this property to enhance hydrocarbon recovery remains an area of active research. Techniques such as surfactant-based wettability alteration and CO_2 flooding are being explored to optimize fluid mobility in organic-rich mudstones. By integrating computational models, laboratory experiments, and field-scale observations, future studies can develop more effective strategies for managing fluid flow in these complex systems. As unconventional resource exploitation continues to expand, a comprehensive understanding of wettability evolution will be essential for maximizing recovery while minimizing environmental and operational challenges.

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