

## Perspective

# Organic-inorganic interactions of clay minerals and organic matter: Action mechanism and analysis techniques

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### Abstract:

Elucidating the formation mechanism of organic-rich shale holds significant implications for hydrocarbon exploration, carbon sequestration, and carbon cycling. In recent years, the relationship between organic matter and clay minerals in shale has attracted widespread attention. This study aims to comprehensively overview the interactions between organic matter and clay minerals during deposition and diagenesis. Through sedimentation processes, climate and provenance control the composition of clay minerals in sediments jointly. Meanwhile, clay minerals exhibit selective adsorption of organic matter, thereby influencing the abundance and type of organic matter in sediments. In modern marine depositional environments, the interaction between clay minerals and organic matter significantly impacts the overall activity and burial efficiency of organic carbon. During the diagenesis stage, the presence of organic matter dramatically affects the transformation of smectite into illite. Conversely, the process of smectite illitization also exerts a significant influence on hydrocarbon generation. Furthermore, this study introduces state-of-the-art techniques to investigate the interactions between organic matter and clay minerals.

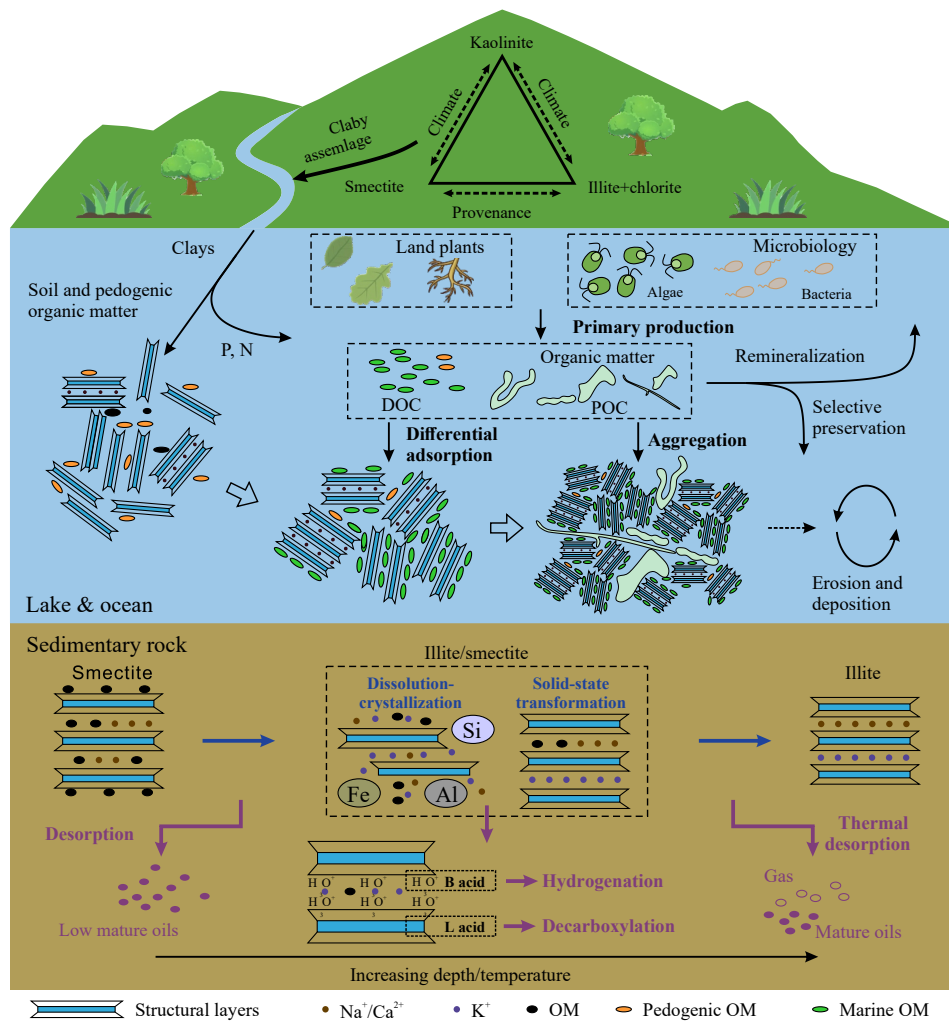
## 1. Introduction

Organic-rich shale serves as the material basis for hydrocarbon accumulation in sedimentary basins, making its development mechanism and diagenetic evolution key research fields in petroleum geology. While most current studies tend to focus on either organic matter or inorganic minerals, the interaction between organic matter and minerals in nature receives less attention. Nonetheless, their interactions are widespread and significant. Firstly, scanning electron microscopy (SEM) analyses of both modern sediments and ancient sedimentary rocks reveal that dispersed organic matter is often tightly bound to clay minerals (Zhao et al., 2023). Secondly, the specific surface area (SSA) of minerals and the content of organic carbon (OC) exhibit significant correlations in sediments from various environments (Cai et al., 2023). This association is also evident in ancient organic-rich shales. These above findings suggest that the interactions of clay minerals and

organic matter play a pivotal role in dictating the preservation of OC in surface sediments and sedimentary rocks. This paper aims to explore the interaction between organic matter and clay minerals during deposition and diagenesis and to review the latest research methods and progress in this field.

## 2. Adsorption of clay minerals and organic matter enrichment

The distribution of different clay mineral types in global marine sediments matches tightly with climate zones: kaolinite and smectite are predominant in warm and humid low-latitude regions, whereas chlorite and illite tend to accumulate in cold and dry high-latitude areas (Fagel, 2007). Clay minerals in sediments originate primarily from detrital minerals formed through the weathering of continental rocks. Key factors influencing rock weathering include climate, provenance, and the time extension of weathering. Among these factors, cli-



**Fig. 1.** Schematic of organic-inorganic interactions in the sedimentation and diagenesis of clay minerals, modified from Cai et al. (2023) and Zhao et al. (2023).

matic conditions play a pivotal role in governing clay mineral formation (Galán, 2006). Illite and chlorite predominantly form through physical weathering processes. The formation of kaolinite is strongly associated with warm and humid tropical or subtropical climates, whereas conditions for smectite formation are more diverse, typically favoring environments with alternating wet and dry seasonal climates. Furthermore, the composition of parent rocks also influences the weathering products. Smectite dominates mafic provenance areas, whereas kaolinite is predominant in felsic and mixed provenance areas (Zhao et al., 2023). In summary, climate and provenance jointly dictate the composition of clay minerals in sediments (Fig. 1).

The interaction between clay minerals and organic matter is controlled by the properties of both components as well as hydrochemical conditions. As layered silicates, clay minerals possess large SSA due to their structural characteristics. The amount of cations adsorbed onto the surface of clay minerals is termed the cation exchange capacity (CEC). The SSA and CEC determine the amount and type of organic matter adsorbed by clay minerals. The interaction of clay minerals

and organic matter involves multiple binding mechanisms, including ligand exchange, ion exchange, cation bridging, hydrophobic interactions, van der Waals forces, and hydrogen bonding (Keil and Mayer, 2014). Organic matter adsorbs onto mineral surfaces through the above mechanisms and forms zonal structures. Over time, adsorbed organic-clay mineral complexes can evolve into more complex organic matter-mineral aggregates. Furthermore, the adsorption of organic matter by clay minerals is significantly influenced by hydrochemical conditions. Specifically, acidic environments and high ionic concentrations can enhance the adsorption of organic matter by clay minerals (Feng et al., 2005). Additionally, clay minerals adsorb organic matter more effectively in environments with high-valent cations than in those with low-valent cations (Feng et al., 2005).

The impact of clay minerals on the enrichment of organic matter is primarily manifested in three aspects. Firstly, nutrient supply during clay mineral deposition significantly influences organic matter production. The weathering of continental igneous rocks, particularly mafic rocks, serves as a primary source of phosphorus for sedimentary and biological systems.

Smectite exhibits strong adsorption capacity, and binds abundant organic matter generated under eutrophic conditions, thus favoring the enrichment of organic matter in sediments (Zhao et al., 2023). Secondly, the selective adsorption of organic compounds by clay minerals significantly affects the type of sedimentary organic matter. Studies have shown that mineral surfaces tend to preferentially adsorb high molecular weight compounds, aromatic compounds, and aliphatic compounds (Ahmat et al., 2017). Lastly, the adsorption by clay minerals plays a crucial role in the preservation of organic matter. Compared with other mechanisms of organic matter preservation, mechanisms of mineral protection facilitate the deposition of fresh, unstable, and diverse organic matter, significantly enhancing the preservation of intact material (Hemingway et al., 2019). However, it is noteworthy that, under aerobic exposure, adsorbed organic matter can still undergo degradation over a long time (Keil and Mayer, 2014).

### 3. Organic-inorganic interactions in modern marine environments

Continental margins serve as “hot spots” of OC burial in modern marine environments. Numerous studies are examining modern OC from various perspectives, including its sources, degradation processes, and quantification (Hedges and Keil, 1995; Blair and Aller, 2012). Among these, the interaction between OC and minerals significantly impacts the efficiency of OC preservation, yet exhibits distinct differences across various marine systems. The following paragraphs explore the interaction between organic matter and minerals in semi-enclosed fjords and expansive continental margins.

As a semi-enclosed marginal sea estuary system, fjords are a classic example of glacially-formed estuaries. A previous study shows that fjord systems account for 11-12% of annual OC burial in modern oceans (Smith et al., 2015). However, there is limited research on carbon cycling processes in fjords over glacial-interglacial timescales. Based on this, Cui et al. (2022) conduct RPO-<sup>14</sup>C analysis on organic matter in representative fjords worldwide. When both OC content and OC loading are low, OC exhibits higher stability; conversely, the overall stability of OC is relatively low when both parameters exhibit high values. This could be due to the coexistence of stable rock-derived carbon and newly added fresh carbon in sediments. OC-rich samples consist primarily of reactive OC with lower activation energies (Hemingway et al., 2019). Thus, increased proportions of fresh carbon not only raise the OC content in sediments but also lower the overall activation energy of OC. Significant amounts of degradable OC are buried in interglacial fjords, which may undergo rapid mineralization due to glacial migration during glacial periods. Thus, fjords serve as temporary reservoirs for sedimentary OC.

The passive continental margin system, with its complex organic matter sources and intensified OC degradation processes, provides an ideal setting for investigating OC preservation and degradation. In the estuarine zone, the relatively high stability of OC is attributed to the prolonged aging of terrestrial organic matter (Blair and Aller, 2012). However, the overall stability of OC diminishes towards the ocean or continental

shelf due to the inclusion of fresh marine-derived organic matter. Additionally, organic matter abundance and sources dictate proportions of labile, intermediate and recalcitrant carbon components (Huang et al., 2023). Specifically, proportions of labile and intermediate carbon components elevate under high mineral SSA and abundant OC content, whereas the fraction of recalcitrant carbon decreases proportionally. This phenomenon is attributed to the sufficient mineral SSA of sediments, which offers numerous mineral adsorption sites for OC. As particles enter the ocean, suspended sediments with high mineral SSA adsorb more labile and moderate OC to mineral surfaces (Sun et al., 2022), thereby reducing the overall reactivity of sedimentary OC.

### 4. Organic-inorganic interactions during diagenesis

There exists a close interaction between clay minerals and organic matter in sediments, therefore, the evolution of clay minerals and organic matter during burial are not isolated processes. The subsequent sections will delve into how organic matter impacts the diagenetic evolution of clay minerals and the role of clay minerals in the hydrocarbon generation from organic matter.

The illitization of smectite represents a pivotal mineral transformation process during diagenesis. Simulation experiments show that the participation of organic matter significantly modifies the rate of smectite illitization compared to that with pure smectite minerals. Pure smectite minerals evolve rapidly in the early stage of diagenesis, but the presence of organic matter accelerates the rate of smectite evolution in the later stage. Consistently, the study on red and dark mudstones in sedimentary basins supports these findings (Li et al., 2016). The mechanisms of smectite illitization can be classified into two categories: solid-state transformation and dissolution-crystallization. Under the solid-state transformation mechanism, the mineral structure remains relatively stable, with changes primarily occurring to interlayer ions (Fig. 1). In contrast, the dissolution-crystallization mechanism involves abrupt changes of mineral structures. Specifically, organic acids generated in the presence of organic matter promote mineral dissolution, resulting in the formation of silica tetrahedra and aluminum octahedra (Fig. 1). These structural units subsequently reassemble into 2:1 type minerals, which bind with potassium ions to form a stable illite structure. Furthermore, the type of adsorbed organic matter influences the mechanism of smectite illitization considerably (Du et al., 2019).

In turn, clay minerals also exert a significant influence on the hydrocarbon generation process of organic matter: smectite illitization releases organic matter their adsorbed initially (Fig. 1), hydrogen ions provided by clay minerals are critical in the hydrogenation processes of organic matter during hydrocarbon generation, and clay minerals possess on their surfaces two types of solid acids -Brønsted acid (B acid) and Lewis acid (L acid). The former supplies inorganic hydrogen, whereas the latter promotes the decarboxylation of organic matter (Fig. 1). Thus, clay minerals function both as catalysts and

reactants in the hydrocarbon generation process of organic matter, with mineral transformations being closely linked to organic matter maturation (Cai et al., 2023). During the early diagenetic stage, organic matter weakly bound to clay minerals is released, mainly non-hydrocarbon organics. With increasing burial depth, pressure and time, organic matter tightly bound to minerals is progressively released. Clay mineral transformation alters the functionalities of B acid and L acid. Specifically, the enhancement of L acids intensifies the decarboxylation reaction, leading to an increase in the organic content of saturated and aromatic hydrocarbons and a corresponding decrease in non-hydrocarbon organics.

## 5. Analysis techniques for the interaction between organic matter and clay minerals

Organic matter interacts with minerals through mechanisms such as chemical adsorption, physical encapsulation, and coprecipitation. Various techniques are employed to study these coupling relationships, including micro-imaging, particle size/density fractionation, and, more recently, ramped-temperature pyrolysis/oxidation (RPO) (Hemingway et al., 2019; Cui et al., 2022). RPO techniques are instrumental in elucidating the thermal stability of OC and its interaction with minerals. In general, lower temperatures correspond to younger  $^{14}\text{C}$  ages of carbon dioxide, indicating weaker binding with minerals, thus lower thermal stability and activation energy. Conversely, higher temperatures yield older  $^{14}\text{C}$  ages, signifying strong organic-mineral binding, greater thermal stability, and higher activation energy.

Hydrothermal simulation experiments are pivotal for investigating organic-inorganic interactions during diagenetic evolution. These experiments involve sample preparation with variable clay minerals and organic matter, followed by systematic observation of their properties and evolution across various temperature conditions. This approach elucidates how organic matter influences mineral evolution and reciprocally, how mineral evolution impacts the hydrocarbon generation process of organic matter. The status of organic matter holds particular information of organic-inorganic interactions. Presently, methods such as SSA analysis, infrared spectroscopy, and rock pyrolysis are predominantly utilized to analyze the occurrence states of organic matter and their respective proportions.

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## Conflict of interest

The authors declare no competing interest.

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