

Catalysis of Minerals in Pyrolysis Experiments

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Abstract: Recent research in the field of oil and gas geochemistry has focused on the catalytic role of minerals in geological history. Thermal simulation experiments are considered a valuable means of studying the formation and transformation of hydrocarbons. In this paper, we review the catalytic mechanisms, processes, and various arguments for different types of minerals in thermal simulation experiments from the perspective of mineral additives. We focus on two categories: (1) minerals that provide direct catalysis, such as clay minerals, alkali metals, carbonate rocks, and some transition metal elements, and (2) minerals, such as serpentine, that promote aqueous hydrogen and act as the material basis, as well as the radioactive element uranium. We also discuss existing disputes and prospects for the development direction of mineral catalytic thermal simulation experiments.

Keywords: pyrolysis; kerogen; catalysis; geological process



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1. Introduction

Since the discovery that oil and natural gas mainly derive from kerogen, organic geochemistry has investigated the composition, types, hydrocarbon (gas) generation law, and sedimentary environment of kerogen using pyrolysis, chromatography, and other methods [1–3]. The aim of this study is to discuss the types and transformation of organic matter [4], kerogen oil generation [5], gas from crude oil cracking [6], and the safe utilization of coal and oil shale [7]. To date, three types of pyrolysis experiments exist, namely closed, semi-open, and open pyrolysis methods. The gold tube closed-system pyrolysis experiment is the most widely used. Gold's good ductility and stability enables the pyrolysis experiment to consider higher temperatures and pressure environments and thus more geological conditions. The open pyrolysis test uses different gas atmospheres (such as nitrogen) to purge the pyrolysis products into the analytical instrument, which has the advantages of a simple experiment and high analysis efficiency. However, the process of hydrocarbon formation and transport is not carried out in such an open-system experiment. So open systems are limited in what they can simulate. In the semi-open system, a device for discharging pyrolysis products is added on the basis of the closed system. Due to the limitation of equipment and technology, the internal pressure of the hydrocarbon expulsion process will change and affect the liquid hydrocarbon expulsion. In the design of pyrolysis experiments, the controlled factors of experimental purposes and samples should be fully considered to avoid systematic errors of experimental results caused by different pyrolysis systems [8].

The simulation method has gradually started to consider the pore throat characteristics of different types of compounds in various reservoirs and the features of hydrocarbon generation and expulsion under pressure [9,10]. Coal, oil, kerogen, carbonaceous mudstone, carbonate rock, and other organic matters can be the subjects of simulation [11–13]. Please refer to the review article by Peng et al. [14] for more information on the status of thermal simulation experiments. However, the geological history of crude oil and natural

gas formation is much more complicated than previously thought, involving different surface interface behaviors and organic–inorganic interactions. Therefore, when designing experiments, geological factors, the selection of experimental equipment, and whether to add different minerals or water should be considered [15].

As far as current reports are concerned, different minerals provide varying catalytic effects in the process of thermal simulation experiments. The mechanism by which silicate clay minerals and carbonate minerals promote pyrolysis is still unclear, and the specific behavior of kerogen catalysis by some ions and minerals in geological processes is still controversial. Examples include coordinated metal ions in biomacromolecules from sedimentary environments, uranium captured during the formation of crude oil and natural gas, carbonate minerals such as calcite and dolomite, and potentially strongly catalytic metal ions. The catalytic mechanism of these metal ions during pyrolysis has not been thoroughly studied. This paper reviews the process of promoting kerogen to produce crude oil or natural gas from the perspectives of clay minerals, alkali metals, carbonate rocks, other metal minerals (mainly transition metals), uranium as thermal simulation additives, and serpentine olivine. This paper is mainly divided into two parts, one of which discusses how minerals directly play a catalytic role, while the other discusses how minerals and water coexist to generate hydrogen. The clear catalytic methods are summarized, while the controversial aspects are also reviewed.

2. Minerals Directly Promote Thermal Simulation Process

In modern crude oil and kerogen samples, a variety of minerals can be found. Prior to pyrolysis experiments, it is common practice to pretreat rocks with acidic fluids such as HCl and HF, which removes all minerals except kerogen. These minerals are influenced by the ancient environment during the earth's redox environment changes, and their unique characteristics can be used to infer sedimentary location environments, tectonic histories, and whether they have undergone epigenesis.

Moreover, these minerals can catalyze the formation of hydrocarbons in various forms. Typically, silico-aluminate dominated clay minerals promote the formation of petroleum in the form of unique solid acids, while various metallic elements enriched in other sedimentary environments are oxidation–reduction catalysts. In addition, contact between these minerals and liquids can result in secondary changes that promote the pyrolysis process.

2.1. Effect of Clay Minerals on Pyrolysis

The formation and structure of clay minerals in reservoirs are influenced by ancient water flow, environment, and provenance debris during the sedimentary period. Therefore, sedimentologists consider clay minerals as good indicators to reflect changes in sedimentary environments. Clay minerals are often used to divide sequences, construct and restore paleoenvironments, and judge major geo-historical events [16]. These silicate layered minerals contain metal elements such as potassium and aluminum, and their particle size is usually less than 3.9 μm . Researchers in the petroleum industry are highly interested in clay minerals [17].

The common types of clay minerals found in sedimentary environments are illite, montmorillonite, kaolinite, chlorite, and their mixed layers. Although clay minerals are not welcomed by reservoir engineers due to their special physical and chemical changes [18], such as water absorption and swelling, dispersed migration, and the release of metal ions including Fe and Al, they have gained attention in recent years among researchers exploring and developing unconventional reservoirs such as tight sandstone and shale. The nano-scale pores provided by clay minerals are excellent for preserving organic matter, and researchers are investigating this aspect [19].

Clay minerals were first used in the petrochemical field in the mid-twentieth century, and montmorillonite clay was first used as the cracking catalyst for crude oil in the chemical industry [20]. Since then, geologists and geochemists have been interested in the promotion

of various mineral types in crude oil production. For instance, Eltantawy et al. [21] and Shimoyama [22] investigated the catalytic effects of clay minerals by heating natural fatty acids and alcohols in clay. The results showed that paraffin wax with a similar composition to crude oil and black carbonized residues attached to minerals was obtained, indicating that the catalysis of clay played a significant role in crude oil formation.

The catalytic effect of clay minerals, especially montmorillonite, in kerogen pyrolysis is widely recognized. However, the organic matter–water–rock reaction involved has not been fully explained. The catalytic effect of clay minerals in sedimentary layers mainly has the following two points: (1) the removal of heteroatoms from gum and asphaltene, promoting the formation of oil and the production of non-hydrocarbon substances such as CO_2 and H_2S , and (2) the condensation polymerization of kerogen, which forms C_1 – C_{15} short-chain alkanes through condensation polymerization (Figure 1):

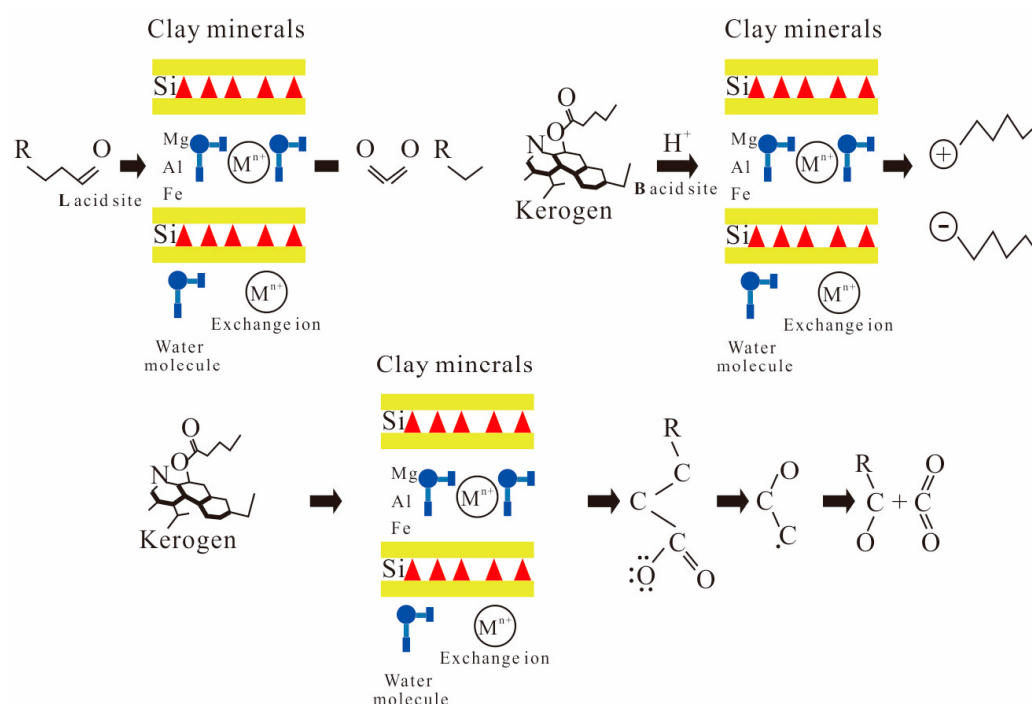


Figure 1. The main catalytic mechanism of clay minerals.

Currently, the accepted theory suggests that montmorillonite can promote the production of light hydrocarbons by facilitating the cracking of hydrocarbons and the isomerization of normal hydrocarbons via a mechanism involving carbocation intermediates [23]. The Brønsted acid sites in the interlayer space of montmorillonite are produced by interlayer dissociation water, which significantly promotes this process. In contrast, n-alkane isomerization and olefin-alkane conversion through hydrogenation lead to high saturated hydrocarbon/n-alkane and olefin/alkane ratios in pyrolysis products [24]. Brønsted acid sites can promote the pyrolysis of nitrogen-containing organic compounds through Hoffman elimination [25], while Lewis acid sites participate in the decarboxylation reaction of aliphatic compounds during pyrolysis and CO_2 is generated [26].

Ma et al. [27] have proposed that the primary catalytic mechanism of montmorillonite for low-maturity lignite pyrolysis is the free radical mechanism at low temperatures. Specifically, in the decarboxylation of organic matter, clay minerals may receive electrons from it during the decarboxylation of organic matter, which leads to the formation of free radicals. Free radicals cause rearrangement, resulting in the cleavage of the C single bond and the formation of short chain free hydrocarbons (Figure 1). However, the presence of water during the pyrolysis experiment has complicated results. Montmorillonite has different isomerization effects on alkanes in the presence or absence of water. Water

molecules are adsorbed on the surface of montmorillonite and in the interlayer space, providing an oxygen source for the generation of CO₂. It also inhibits the isomerization of n-alkanes in the pyrolysis process, leading to the dominant role of n-alkanes in the pyrolysis products. A lower interlayer water and surface adsorbed water content can greatly promote the isomerization of hydrocarbons and reduce the yield of CO₂ [28].

Due to the complexity of crude oil, we believe that the free radical mechanism and the carbocation intermediate mechanism will occur simultaneously in the transformation process of crude oil and kerogen. The clay minerals will also dehydrate and rearrange themselves when heated, resulting in a reduction in interlayer volume and the transformation to illite on a macro level. However, the addition of water will increase the solid acidity of minerals. During the pyrolysis process, the hydroxyl group in water is adsorbed on the surface of minerals and proton H is provided to the organic matter. Although the current report cannot distinguish the degree of contribution, future experiments could be designed to focus on this process.

When it comes to illite, while it does exhibit catalytic effects, it is still slightly inferior to montmorillonite [29,30]. Due to illite lacking interlayer water, catalysis can only occur on its surface through solid acid sites. Hence, Lewis acid sites mainly occur on its outer surface [31]. The addition of illite slightly increased the relative cycloalkane content of kerogen-generated hydrocarbons in the experiment [32]. In contrast, the effect of kaolinite on the anhydrous pyrolysis of bituminous coal is not consistent with its effect in the pyrolysis with water. The addition of kaolinite inhibited the generation of light hydrocarbons but increased the yield when water was added [33].

In a study conducted by Espitalie [34], the effects of different clay minerals on the pyrolysis of type II kerogen were investigated. Results indicated that calcium montmorillonite showed better catalytic effects, promoting the formation of light hydrocarbons, and had better catalytic effects than sodium montmorillonite. On the other hand, kaolinite, illite, and attapulgite showed poor catalytic effects, but the residual products of attapulgite had a higher H/C ratio compared to the other two. The study also suggested that pyrolysis experiments in open systems at high temperatures and without water can enhance the interactions between minerals and hydrocarbons.

Roets et al. [35] found that kaolinite and quartz have little influence on the pyrolysis products of coal. Öztaş [36] showed that the treatment of coal with HF and HCl increased the pyrolysis efficiency of the treated samples, suggesting that clay minerals in coal may reduce the pyrolysis yield. He et al. [37] used the relative concentrations of C₇ compounds to evaluate the difference in the catalytic effect of different clay mineral contents, with toluene, 1,2-dimethylcyclopentane, and n-heptane showing the most significant differences. According to Cai et al. [38], the catalytic effect of clay minerals is ranked as montmorillonite > kaolinite > illite, with kaolinite dominating in the high-mature to over-mature stage due to its free radical mechanism and amphiphilic nature.

In summary, the catalytic effect of clay minerals on the pyrolysis of hydrocarbons varies depending on the type of clay mineral and the experimental conditions. Montmorillonite has been found to be the most effective due to its interlayer water and solid acid sites in the interlayer space, while illite and kaolinite have limitations in their catalytic effect.

2.2. Catalysis of Alkali Metals

The deposition of organic matter, especially type III kerogen, is influenced by the terrestrial environment and contains significant amounts of alkali metals and alkaline earth metals, such as Na, K, Mg, and Ca. Among these elements, Ca is considered the most active alkaline earth metal [39,40]. Alkali metals in low maturity coal can exist in the form of hydrogen ions in oxygen functional groups or can be freely present in reservoirs such as various crystalline or amorphous minerals [41]. When heated, these alkali metals and alkaline earth metals decompose and generate basic oxides, such as MgO, CaO, Na₂O, and K₂O [42]. The basic oxides in coal promote the cracking of oxygen-containing functional groups, leading to a more compact coal structure. This process strengthens the reaction

of tar macromolecules to form semi-coke, prevents tar macromolecules from escaping, and enhances the effect of demethanization and dehydrogenation [12]. For aromatic hydrocarbons, the catalysis of alkali metals can reduce the aromatic hydrocarbons with multi-side groups in pyrolysis products and increase the yield of small molecular aromatic hydrocarbons [43]. Generally speaking, alkali metals can accelerate the overall pyrolysis reaction rate, reduce the liquid yield, greatly improve the yield of gaseous hydrocarbons, and also reduce the contents of oxygen and sulfur in liquid products.

However, compared to marine carbonate reservoirs with vast storage capacity, the existing reports on the pyrolysis of kerogen III (coal) appear to be inconsistent with the reaction of crude oil, clay minerals, carbonate rocks, and kerogen. Karabakan and Yürüm [44] reported that carbonate minerals promote the pyrolysis of kerogen, and the total activation energy of kerogen decreases without HF treatment. They believe that alkaline earth metal oxides produced by carbonate minerals after heating promote the pyrolysis process. The reason why silicate minerals inhibit pyrolysis is not clear. Ballice et al. [45] came to a similar conclusion, stating that the inhibition of silicate minerals is greater than the promotion of carbonate in shale, which is attributed to the strong adsorption of clay minerals on hydrocarbons.

2.3. Influence of Carbonate Rock on Pyrolysis

Most carbonate rocks have a marine sedimentary environment and were formed during the early sedimentary period. Common carbonate minerals found in these rocks include aragonite (CaCO_3), calcite (CaCO_3), and dolomite ($\text{CaMg}(\text{CO}_3)_2$). Giant carbonate oil and gas reservoirs located in the Middle East have played a significant role in contributing to the world's energy reserves [46]. The secondary changes that carbonate rocks undergo during sedimentation and diagenesis greatly influence their reservoir properties. For example, the process of dolomitization causes a reduction in the volume of limestone, which has the potential to increase the reservoir area [47]. Furthermore, sedimentary processes and secondary changes contribute to the creation of various types of pores, providing carbonate reservoirs with ample storage space [48]. However, the uneven development of carbonate reservoirs and the high sulfur content in some of these reservoirs limit further exploration and development [49]. As such, carbonate reservoirs have been a focal point of research for petroleum geologists.

Petroleum geologists have always been interested in carbonate rocks, which they believe can serve as source rocks due to the discovery of both reservoirs and source rocks in these formations [50–52]. Scientists have also studied the oil generation process of carbonate rocks. Unfortunately, the content of organic carbon in modern carbonate reservoirs is often very low. Currently, there are several explanations for this phenomenon: (1) Diagenesis and dissolution during the formation of carbonate rocks can cause the loss of organic matter, leading to a loss of 15%–50% of organic carbon in clastic rocks and 80%–90% of organic carbon in carbonate rocks [53]. (2) Organic matter may not deposit with carbonate rocks during the deposition process [54]. (3) The organic matter may have reached the threshold of hydrocarbon generation and been expelled. After hydrocarbon expulsion, the total organic carbon (TOC) of type I, type II, and type III kerogen decreased by 80%, 50%, and 20% [55], respectively, and carbonate rocks with high organic carbon content are not conducive to organic matter preservation after hydrocarbon expulsion [56]. (4) Organic matter may transform during carbonate rock deposition processes (e.g., running water, oxidation, and recrystallization), but this process appears to have little effect on organic carbon [57]. Reservoir geochemists find it challenging to understand carbonate reservoirs with conventional petroleum geology methods, and the indicators used to evaluate source rocks (e.g., vitrinite reflectance, organic matter deterioration degree) seem to have no effect on carbonate rocks [58]. This has prevented the development of a deep understanding of carbonate oil generation.

Calcite in carbonate rocks was first observed by Shimoyama and Johns [59] and has very close contact with organic matter during the pyrolysis of calcite fatty acids. They

suggest that calcite provides catalysis in the pyrolysis process. However, it can be seen from the surface/interface relationship that the interface between calcite and polar macromolecules in crude oil [60] is more easily adsorbed. Therefore, this phenomenon is not enough to conclude that calcite has catalytic effect. Tannenbaum and Aizenshtat et al. [61] suggested that the heteroatoms present in carbonate rocks provide the essential catalysis for hydrocarbon generation from organic matter and kerogen. Jones et al. [62] concluded that there is no significant difference in the oil production process between carbonate rocks and shale, whereas Huizinga et al. [23] pointed out that CaCO_3 has little impact on the thermal evolution and petroleum cracking behavior of kerogen. Pan et al. [63] further observed that the addition of calcite during crude oil cracking experiments had little effect on the cracking of main components in crude oil, but the formation rate of methane and total hydrocarbon gas was relatively low compared to other experimental groups. They postulated that calcite inhibits the secondary cracking of moisture ($\text{C}_2\text{--C}_5$) into methane.

Chen et al. [64] combined Rock–Eval pyrolysis data and hydrocarbon generation kinetics to conduct pyrolysis experiments on middle-upper Ordovician argillaceous carbonate rocks in Tarim Basin, China. The kerogen conversion rate reached 90%, indicating a high original potential. The argillaceous component has a relatively strong ability to preserve organic matter [65], but on the whole, carbonate rocks contain few argillaceous components. Therefore, whether well-preserved argillaceous carbonate rock experiments can accurately represent the hydrocarbon generation process in geological processes remains to be discussed.

Dolomite, unlike calcite, is currently regarded as a cheap and excellent catalyst for biomass gasification in the industry. Islam et al. [66] suggested that its catalytic effect comes from decomposition products, such as MgO and CaO , that form when the temperature exceeds 600°C . However, the temperature of pyrolysis typically does not reach this limit. Thus, the catalytic mechanism of dolomite pyrolysis remains unclear.

Wu et al. [67] studied the effect of dolomite and calcite on the pyrolysis of crude oil using closed flexible gold capsules. They found that the presence of dolomite slightly reduced the yield of $\text{C}_1\text{--C}_5$ but significantly increased the yield of $\text{C}_6\text{--C}_{13}$. Moreover, they conducted pyrolysis experiments of MgCO_3 and $\text{MgCO}_3 + \text{CaCO}_3$, which produced similar results to those of petroleum and dolomite. Thus, it is evident that the influence of dolomite on petroleum pyrolysis is closely related to the content of Mg in dolomite. In addition, the lower content of dolomite can promote the TSR (Thermochemical Sulfate Reduction) of crude oil. Specifically, dolomite- MgCO_3 promotes the formation of SO_4^{2-} . The coexistence of SO_4^{2-} , water, and H_2S then initiates the sulfate thermochemical reduction (TSR) reaction, which destroys hydrocarbons and produces CO_2 and H_2S [68]. However, the high content of dolomite can absorb or convert some H_2S into other forms [69]. Moreover, the reaction of MgCO_3 with water can generate $\text{Mg}(\text{OH})_2$ (R2), which further reduces the amount of H_2S generated.



Maimaiti et al. [70] conducted a pyrolysis study using the same method as Wu et al. [67] to investigate the effect of carbonate rocks on crude oil cracking. They observed that different mineral types, such as calcite and dolomite, had varying degrees of inhibition on methane production at high maturity stages ($\text{EasyRo} > 3.5\%$), but had no effect on $\text{C}_2\text{--C}_5$ hydrocarbons, while simultaneously inhibiting C_{14+} . Additionally, the yield of CO_2 in the pyrolysis products with carbonate minerals increased significantly, and unique changes in carbon isotopes were observed. Unlike typical thermally driven isotope fractionation, the addition of dolomite promoted the shift of carbon isotopes of methane, whereas calcite inhibited it. In crude oil + dolomite, crude oil + calcite, and simple crude oil pyrolysis experiments, $\delta^{13}\text{C}_1$ was -49.89 , -54.08 , and -51.77% , respectively ($\text{EasyRo} = 0.96\%$). However, the carbon isotope fractionation process of ethane and propane remained unaffected by minerals. They speculate that this phenomenon may be due to dolomite increasing the diversity of methane sources during pyrolysis and the differential adsorption of various

organic gases by different minerals. Nevertheless, there is still insufficient evidence to support this claim.

Furthermore, Wang et al. [71] observed that increasing the carbonate concentration in source rocks led to a corresponding increase in the yield of CO₂ and heavier carbon isotopes in CO₂. They believe that carbonate rocks significantly contribute to CO₂ in pyrolysis products, which is derived from the dissolution of carbonate minerals by organic acids during pyrolysis, despite the lower pyrolysis temperature compared to the decomposition temperature of carbonate rocks.

2.4. Effect of Metal Minerals on Pyrolysis Experiments

The precursors of crude oil and kerogen contain many metal elements that exist in organisms in the form of metalloenzymes, playing an important role in the evolution of life and the maintenance of biological functions [72]. These metal elements can be captured at any stage of deposition, hydrocarbon generation, and migration, and are relatively enriched in macromolecules such as colloid and asphaltene, and even complexed or bonded into kerogen [73]. For instance, porphyrin, which is widely found in chlorophyll and heme, is also present in petroleum and kerogen, with the metal elements coordinated being different depending on the living body and its environmental conditions [74]. The proportions of vanadoporphyrin and nickel porphyrin in kerogen, crude oil, and rock represent marine and continental sedimentary environments, respectively. Additionally, these bio-lipids are also considered important catalysts for transforming into rearranged alkanes in crude oil, and the relative content of rearranged alkanes in crude oil produced in some geological periods lacking chlorophyll is lower [75]. Furthermore, these metals and their oxides are important catalysts for the transformation of the Earth's environment from simple to complex [76]. Based on chemical principles, active intermediates are formed by the coordination between ligands and receptors due to the d orbitals around the metal elements not being fully occupied. This reduces the activation energy of the reaction and promotes the formation of organic matter [77]. Moreover, the larger internal pores generated after the organic–inorganic interaction between minerals and organic matter also promote this process [78]. However, Lewan et al. [79] presented different opinions, reporting no obvious difference in gas type, yield, dryness, and formation rate of low-cooked kerogen after 72 h of aqueous pyrolysis at 330 and 355 °C. They argued that various transition metals with catalytic properties were not in an active state during the geological maturation of kerogen and exhibited suitable catalytic activity.

Gao and colleagues [80] conducted anhydrous pyrolysis experiments on low-rank coal with the transition metal Ni. The addition of the transition metal Ni catalyzed the decomposition of organic matter and the synthesis of abiogenic methane during the maturity of source rocks. With the addition of Ni, the content of CH₄ in pyrolysis products increased, and the yields of ethane and propane decreased. They concluded that Ni played a catalytic role in the whole process of kerogen, crude oil, and heavy hydrocarbon gas cracking, and Fischer–Tropsch Type (FTT) reaction occurred in the pyrolysis experiment, which catalyzed together with heavy hydrocarbon gas cracking, significantly improving methane yield and greatly improving CH₄ yield at all temperatures (see Figure 2). In all the experimental groups, δD became smaller, but $\delta^{13}C$ gradually became positive with the increase in temperature.

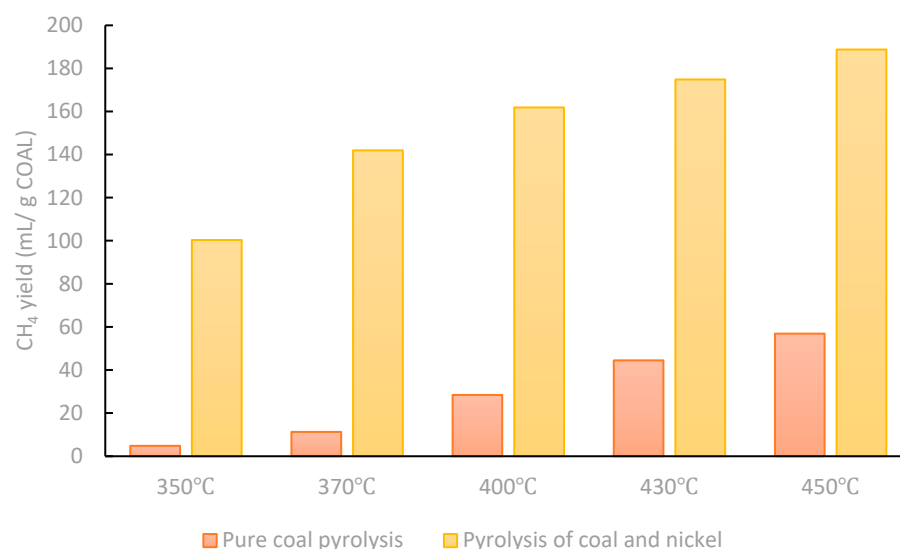


Figure 2. Variation diagram of pyrolysis yield of increasing Ni (Adapted from [80]).

He et al. [81] investigated the impact of iron-containing minerals, specifically FeCO_3 , FeS_2 , and Fe_2O_3 , on the pyrolysis of 1-methylnaphthalene under high pressure. They explored different catalytic mechanisms by utilizing isotope differences at different temperature ranges. The coexistence of water and minerals greatly increased the ratio of i-C₄/n-C₄ isomers, which is consistent with the pyrolysis trend observed in water-bearing minerals by Cai et al. [82]. The reactions at different mineral interfaces also varied. The presence of FeS_2 and Fe_2O_3 minerals promoted the reaction between water and hydrocarbons, leading to a significant increase in CH_4 yield. In contrast, the experimental group containing FeCO_3 showed little difference in CH_4 yield but exhibited positive carbon isotope. The authors hypothesized that the FTT reaction occurs at the interface between minerals and hydrocarbons at higher temperatures (400–450 °C), contributing to abiotic CH_4 production.

The catalytic action of transition metals in the pyrolysis process is related to their chemical forms. For instance, in the low-temperature stage, Fe^{3+} combines with oxygen-containing functional groups in coal or π bonds in unsaturated hydrocarbons using its own d empty orbital, resulting in chemical adsorption. The cations in coal have a positive effect on the organic structure of coal, making the coal molecules more polar and increasing their pyrolysis activity. As the temperature increases, the form of iron changes into crystalline oxide, which can catalyze the transformation of heavy components into primary pyrolysis products, reducing tar yield and increasing the gaseous yield [82]. However, He et al. [83] argued that transition metals, including iron, have a catalytic effect only in the elemental state, which can explain the differences observed in the experiment by Lewan et al. [79]. Guan et al. [84] reported that the different occurrence states of the same element have a significant influence on the results of thermal simulation experiments. In thermal simulation experiments conducted at low temperatures for an extended period (150 °C, 30 days), the Mn solution promoted crude oil yield, whereas Mn elemental substance showed obvious inhibition. Interestingly, the final crude oil yield of low-concentration Mn solution was 18.19 kg/t TOC, much lower than that of high-concentration Mn solution, which yielded 5.4 kg/t TOC (Figure 3).

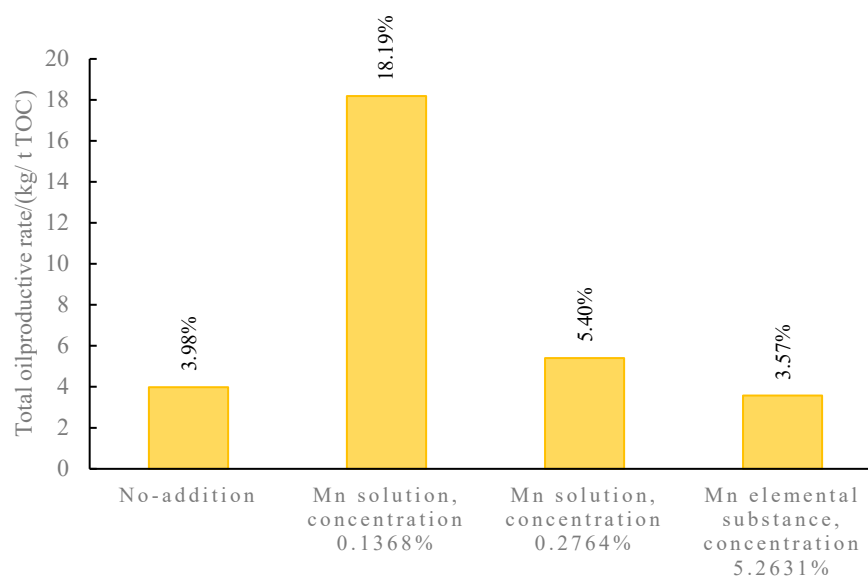


Figure 3. Comparison diagram of different forms of Mn element addition on oil production rate in thermal simulation experiment (adapted from [84]).

3. Thermal Simulation Process Promoted by Catalytic Hydrogenation of Minerals

Hydrogen plays a crucial role in the transformation of organic matter, as it not only provides the material basis for kerogen but also enhances the hydrogenation reaction during oil and gas generation and promotes the thermal evolution of source rocks. Specifically, hydrogen atoms can combine with carbon free radicals during the thermal simulation process, leading to the formation of smaller molecular hydrocarbons and ultimately increasing the final hydrocarbon yield [85,86]. Surprisingly, even a highly evolved solid pitch can generate hydrocarbons again under the influence of hydrogen [87].

Several sources of exogenous hydrogen are present in sedimentary basins, including water in sedimentary environments, hydrogen-containing fluids resulting from volcanic hydrothermal activity in the mantle, serpentine in ultrabasic volcanic rocks, and enrichment and radiation of radioactive minerals.

3.1. Water Is an Important Source of Hydrogen for Hydrocarbon in Natural Basins

Water has been reported to increase the production of gaseous hydrocarbons in pyrolysis experiments [88,89]. This is because water undergoes a disproportionation reaction during pyrolysis reaction, releasing hydrogen that promotes the cracking of kerogen oil or crude oil. This reduces cross-linking reactions and promotes thermal cracking, thereby altering the original pyrolysis law [90].

Water is transported to the deep part of the earth in the subduction zone of the subducting plate [91], where it reacts with iron under different temperature and pressure conditions to form a unique high-magnesium iron hydride [92,93]. Finally, dehydrogenation takes place and hydrogen-rich fluids in the mantle return to the surface through volcanic hydrothermal activity [94,95]. Meanwhile, hydrogen plays various roles in the Earth's C cycle [96–99]. Mantle-derived gas also has a profound impact on the transformation of organic matter and the formation of hydrocarbons. The hydrocarbons that may be affected by mantle-derived gas can be determined by the difference in hydrogen isotopes [95,100–103].

3.2. The Role of Hydrogen Generation from Serpentine in Pyrolysis

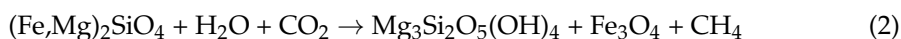
During the early stages of Earth's evolution, catalytic metals carried up from the mantle by volcanic activity were believed to play a significant role in the formation of primitive life and small organic molecules (Table 1). Transition metals such as iron, manganese, cobalt, zinc, and vanadium were transported into the ancient ocean via hydrothermal vents. Similar to their modern-day counterparts, the hydrothermal vents in the deep sea support

a variety of complex biological and chemical processes, including sulfate reduction, iron oxidation and reduction, serpentine formation, and methane production, which contribute to the largest primary productivity in the deep ocean [104–108].

Table 1. Primary metabolic reactions of various microorganisms near hydrothermal solution (cited from Martin et al. [76]).

Metabolism	Reaction	Examples in Vent Environments
Anaerobic	$4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ $\text{CH}_3\text{CO}_2^- + \text{H}_2\text{O} \rightarrow \text{CH}_4 + \text{HCO}_3^-$ $4\text{HCOO}^- + \text{H}^+ \rightarrow 3\text{HCO}_3^- + \text{CH}_4$	<i>Methanococcus</i> spp. common in magma-hosted vents; Methanosarcinales at Lost City
	$\text{S}^0 + \text{H}_2 \rightarrow \text{H}_2\text{S}$	Lithotrophic and heterotrophic; hyperthermophilic archaea
	$\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HS}^- + \text{HCO}_3^- + 2\text{H}_2\text{O}$	<i>Methanosarcina</i> spp. and epsilonproteobacteria at mudvolcanoes and methane seeps
	$\text{SO}_4^{2-} + \text{H}^+ + 4\text{H}_2 \rightarrow \text{HS}^- + 4\text{H}_2\text{O}$	Deltaproteobacteria
	$8\text{Fe}^{3+} + \text{CH}_3\text{CO}_2^- + 4\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + 8\text{Fe}^{2+} + 9\text{H}^+$	Epsilonproteobacteria, thermophilic bacteria and hyperthermophilic Crenarchaeota
	$\text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 2\text{C}_6\text{H}_6\text{O} + 2\text{CO}_2$	Many genera of bacteria and archaea
Aerobic	$\text{HS}^- + 2\text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{H}^+$	Many genera of bacteria; common vent animal symbionts
	$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{HCO}_3^- + \text{H}^+ + \text{H}_2\text{O}$	Common in hydrothermal systems; vent animal symbionts
	$\text{H}_2 + 0.5\text{O}_2 \rightarrow \text{H}_2\text{O}$	Common in hydrothermal systems; vent animal symbionts
	$\text{Fe}^{2+} + 0.5\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + 0.5\text{H}_2\text{O}$	Common in low-temperature vent fluids; rock-hosted microbial mats
	$\text{Mn}^{2+} + 0.5\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{MnO}_2 + 2\text{H}^+$	Common in low-temperature vent fluids; rock-hosted microbial mats; hydrothermal plumes
	$\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$	Many genera of bacteria

The process of igneous oxidation of olivine and pyroxene in the lower oceanic crust and upper mantle of the earth is referred to as serpentinization. In the presence of water, the Fe(II) present in these minerals is oxidized by Fe(III), leading to the precipitation of Fe_3O_4 and the release of diatomic H_2 , which can react with carbon to produce methane (as shown in Formula (2)). This process generates a substantial amount of heat and significantly affects the pH around the minerals, resulting in the deposition of carbonate rocks that are widespread in the hydrothermal vents of modern mid-ocean ridges.



Hydrocarbons, primarily C_1 – C_4 and formic acid, are the most commonly detected compounds in modern hydrothermal activities on the ocean floor. Although only a small portion of these compounds are believed to be produced by the thermal cracking of other hydrocarbons, recent studies have detected some macromolecular hydrocarbons and lipid compounds with the participation of microorganisms near the deep sea [109,110]. However, the source of macromolecular compounds near hydrothermal solutions in the marine environment is still controversial [111], and man-made organic pollution is one possible factor. It is also challenging to distinguish the contribution of organic and inorganic actions

to hydrocarbons. Therefore, only a small portion of CH_4 is currently considered to be generated by the cracking of other hydrocarbons [112].

When organic matter is affected by volcanoes, it can also be impacted [113–115]. Different stages of volcanic hydrothermal activity in sedimentary basins have different catalytic behaviors on hydrocarbon behavior. The upward movement of magma is selective, and without other favorable channels, sedimentary basins that lack rigidity are more susceptible to invasion [116]. Once organic matter accumulates, the heat brought by the magmatic hydrothermal solution accelerates its maturity, promotes the thermal metamorphism of mudstone and sandstone, squeezes clastic material, and produces structural cracks. If this effect occurs during the sedimentary period, it can change the original sedimentary environment [117]. Metal minerals and other inorganic gases with catalytic properties brought by hydrothermal solutions will provide all the necessary elements for primary productivity, resulting in explosive growth of aquatic organisms. The addition of volcanic ash leads to water stratification, which enhances the reduction and preservation conditions of organic matter in the basin, improves the primary biological productivity of the basin, and easily forms high-quality source rocks, as shown in Figure 4 [84].

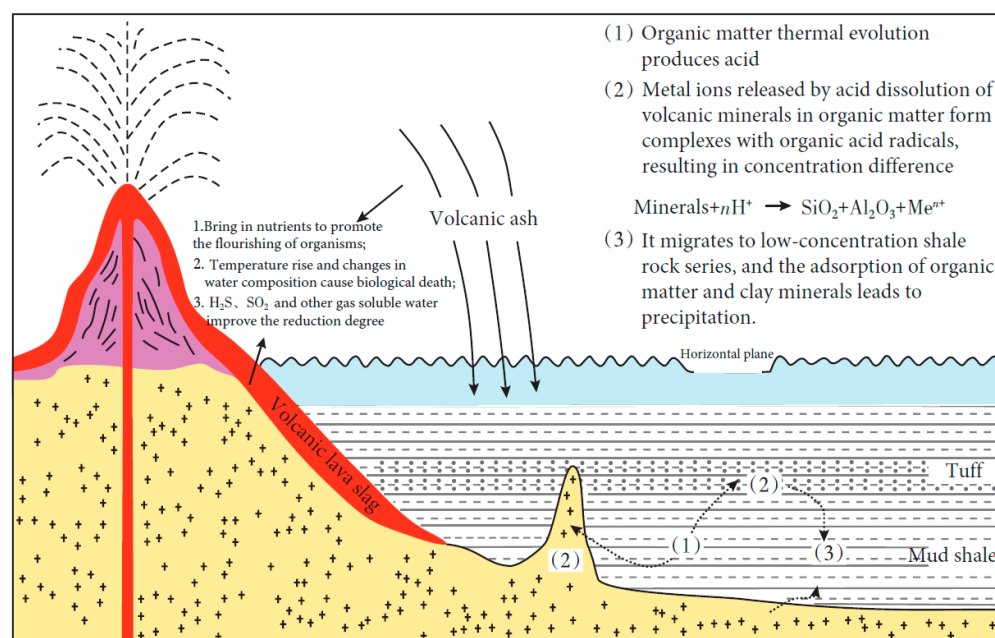
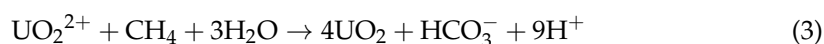


Figure 4. Influence model of volcanic activity on sedimentary basins (Ref. [85]).

3.3. The Role of Radioactive Hydrogen Production from Uranium in Pyrolysis

Uranium, a special transition metal element, is the cornerstone of the nuclear industry and has garnered significant attention for its potential in energy transformation [118]. Geologists are particularly interested in the unique sandstone-type pitchblende and its associated relationships and formation mechanisms. This phenomenon has been reported in most sedimentary basins worldwide [119–124].

In general, the deposition of uranium in sedimentary basins is closely related to the transportation, reduction, enrichment, and preservation of organic matter (Figure 5) [119,125,126]. Uranium is highly reactive and can react with most elements, especially in terms of its strong reduction ability. Under reduction conditions, U(VI) is converted to an immobile tetravalent state, U(IV) (see Formula (3)), which predominantly occurs in shale that is rich in organic matter [127]. The reduction and mineralization of uranium may occur simultaneously with the bacterial sulfate reduction in crude oil [128,129].



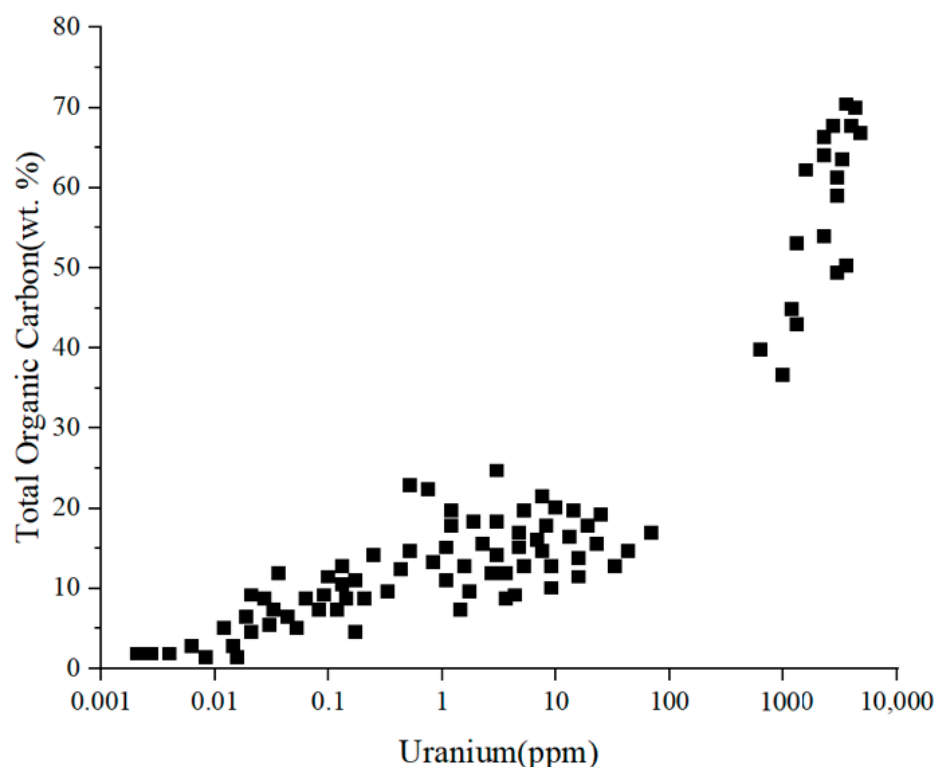


Figure 5. Correlation between uranium and TOC (quoted from Schulz et al. [125]).

When uranium is enriched to a certain extent, high radioactive anomalies can also be found in the formation. The decay of uranium can release α , β , and γ rays, and the particles in these rays can decompose water to provide 3_1H_4 for hydrogen and oxygen, resulting in the generation of active hydrogen. The radioactive decay and the provision of hydrogen are also considered to promote the pyrolysis process of organic matter in natural strata. The reaction process is as follows:



Uranium enrichment can result in high radioactive anomalies in formations, releasing α , β , and γ rays that can decompose water to generate foreign hydrogen and promote the pyrolysis process of organic matter in natural strata. This foreign hydrogen compensates for the hydrogen required for the thermal degradation of organic matter and enhances the methane yield and total hydrocarbon yield [86]. In sedimentary basins, compounds can reach metastable thermodynamic equilibrium during hydrocarbon generation, leading to the formation of olefin-alkane equilibrium when the H concentration is sufficient [130]. Uranium ore can catalyze the pyrolysis of immature kerogen II, as discussed by Cai et al. [131], with liquid and gas products increasing significantly during gold tube closed-system pyrolysis. Deuterium in hydrocarbon gas was consumed, indicating that water and uranium ore can participate in the thermal evolution of organic matter and provide a hydrogen source for hydrocarbon generation. However, under this condition, the carbocation mechanism

is inhibited to some extent, as the i-C₄/n-C₄ ratio in the experimental group containing uranium ore and water is low.

According to Yang et al. [132], the catalysis of uranium can cause an exponential change in kerogen structure. With an increase in uranium content in kerogen, the gas/oil ratio and aromatic hydrocarbon content of pyrolysis products continuously increase compared to the hydrocarbon generation law of conventional marine shale. FT-ICR-MS results show that macromolecular compounds in uranium-rich samples are more alkylated and oxygenated compounds are more abundant, which can be attributed to free radicals generated by the in situ reaction of highly active OH produced by the radioactive cracking of water with organic matter during diagenesis. However, the more complex cross-linked structure of uranium-rich samples can hinder further cracking.

4. Conclusions and Outlook

Previous studies have shown that different minerals exhibit different forms of catalysis in laboratory-scale experiments. However, detailed consideration of the geological background and the corresponding design of thermal simulation experiments remain a primary concern, particularly with respect to shale and deep carbonate rocks that are currently the focus of research in China. Future research should focus on the development and application of combined measuring equipment, such as TG-IR, TG-MS, and TG-XRD, which can more accurately reflect the catalytic process and mechanism by monitoring changes in molecular markers, minerals, and parameters during the experimental process. Furthermore, with the continuous development of computational chemistry, there is a need to explore more accurate and precise modeling of thermal simulation experiments on computers. Numerical simulations can easily change experimental parameters and provide a more intuitive molecular reaction mechanism. They are also more environmentally friendly and faster than thermal simulation experiments.

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