Comparative Study on Thermodynamic and Geochemical Characteristics between Cemented and Clotted Parts of Thrombolite

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Abstract: Carbonate rocks are widely distributed in nature and are one of the main reservoir rocks for oil and gas. Microbes play an important role in the formation of carbonate rocks. Compared with the cemented part with fewer microorganisms (abiotic minerals), the nucleation and growth of the clotted part with more microorganisms (biotic minerals) are affected by the metabolic activities of microorganisms, so it has a unique morphology and crystal structure. However, there are still some confusing questions such as ones regarding the unique thermal decomposition characteristics and geochemical characteristics, which have rarely been studied. Here, X-ray diffraction (XRD) was used to determine the mineral composition of the cemented and clotted part in the same thrombolite. Then, thermal analysis and stable isotope geochemistry were used to explore the thermal stability and stable carbon isotope. The results of X-ray diffraction (XRD) show that the mineral components of the cemented and clotted part in the thrombolite are calcites, but their crystallinity is different. The crystallinity of the clotted part in the thrombolite is higher than that of the cemented part. Thermal analysis results show that the activation energy and the thermal stability of the clotted part in the thrombolite are relatively higher. In addition, the stable carbon isotope results show that, compared with the chemical precipitated calcite in the cemented part, the microorganisms in the clotted part absorb more 12C through photosynthesis, which results in more 13C in the clotted part, and the carbon isotope δ13C value is higher. This study helps to distinguish the crystallographic, thermodynamic and geochemical characteristics of cemented and clotted parts in thrombolite, and may be helpful to deepen our understanding of abiotic and biotic minerals.

Keywords: thrombolite; crystallinity; thermochemical technique; activation energy; carbon isotope

1. Introduction

Microbial carbonates are widely distributed in nature and are important storage locations for oil and gas resources [1–3]—carbonate rocks have high application potential and economic value. Microbes play an important role in the formation of microbial carbonate rocks. They not only provide a place for the nucleation of carbonate minerals, but also change the microenvironment of mineral precipitation through their unique metabolic activities, thus attracting many researchers to carry out research work [4–6]. There have been many studies of calcium- or phosphorus-containing minerals in the discovered biological minerals; microbial limestones have also become a research hot spot after microbial fossils were found in carbonate rocks. The research on the characteristics of microbial
limestone and how to effectively distinguish the abiotic minerals from biotic minerals has attracted widespread attention. The research of the characteristics of microbial limestone mainly includes rock section observation, mineral composition analysis and analysis of major or trace elements [7–9]; however, there has been a lack of a more accurate experimental method to distinguish microbial limestone and non-microbial limestone. Few studies have been conducted on other characteristics of microbial limestones, such as the crystallinity and thermal stability of the cemented and clotted parts in the same thrombolite. What is the difference between the cemented and clotted parts, and what are the characteristics that can distinguish the abiotic and biotic minerals?

Due to the long-term evolution of the earth, microbial carbonate rocks have undergone complex geological processes. In addition, coupled with a lack of microbial fossils, a large number of sedimentological and petrological studies have shown that their formation mechanism and the included geochemical information have been reorganized or modified [10–12]. In recent years, thermochemical analysis methods have provided a very effective for distinguishing biotic and abiotic minerals [13,14]. Han et al. investigated the unique thermal decomposition characteristics of microbial calcite and chemical calcite. The results show that microbial calcite exhibits higher thermal stability and activation energy, which is mainly due to the higher crystallinity of microbial calcite. Moreover, Zhuang et al. studied the biotic and abiotic calcite, which also suggests the thermal stability of biotic calcite was clearly higher. Therefore, we can use the thermochemical analysis method to further distinguish the thermal stability difference between the cemented and clotted parts in the same thrombolite.

In addition, Wang et al. (2006) showed that the change law of different carbon and oxygen isotopes can be combined with the geological environment, which can better reflect the formation environment of microbial limestone [15,16]. Liang et al. (2015) used laser microregion sampling technology to accurately sample, separate and analyze the organic matter in the dark laminar region and the light laminar region in the stromatolite. The research results show that the dark laminar area obviously contains organic matter and organic functional groups, but the test and analysis results of the light laminar area did not find organic matter or organic functional groups. The light laminar area is mostly debris or sediment formed by physicochemical action. The final results show that the dark lamellae are more likely to be enriched in $\delta^{18}O$ and $\delta^{13}C$ than the lighter lamellae [17]. Therefore, stable carbon isotopes are used to analyze the characteristics of microbial limestone and the formation environment, especially the stable carbon isotope analysis of the cemented and clotted parts in the same thrombolite. The formation environment and diagenetic information are of great significance in terms of identifying the early formation environment and diagenetic information of microbial rocks.

This paper has provided sufficient evidence to analyze the pyrolysis process of cemented and clotted parts by thermogravimetric (TG), derivative thermogravimetric (DTG) and differential scanning calorimeter (DSC) methods. In addition, a stable carbon isotope analysis was used to understand the formation environment of the thrombolite in Zhangxia formation, which indicating that the clotted parts with more microorganisms (biotic minerals) have a high $\delta^{13}C$ value. Its distribution rule not only reveals the mechanism of microbial action during the formation of microbialites, but also provides a reference for the next step in the study of induced microbial genesis mineral isotopes. In addition, a thermogravimetric analyzer was used to perform differential thermal analysis on cemented and clotted parts to explore the thermal stability of minerals, calculate the thermal weight loss and activation energy to analyze the different crystallinities of them. The results of the thermochemical analysis show that the thermal stability of the clotted part are higher, which provides more accurate data analysis for identifying microbial carbonate rocks in the field.
2. Materials and Methods

2.1. The Description of Sample

Microbial carbonate rocks are widely distributed in nature and are mainly bacterial aquatic sediments. The photosynthesis and sulfate reduction of algae and bacteria have led to the production of many sediments which promote the precipitation of calcium carbonate minerals such as calcite and calcite in the microenvironment surrounding cells, and captured some other sediment particles. The Cambrian is well-developed and well-exposed, and the microbial limestone is well-developed and complete in species in the Yishui area, Shandong Province. The lithology in the study area is mainly marine carbonate rocks and terrigenous clastic rocks. Figure 1a shows that the main sedimentary strata include the Liguan Formation, Zhushadong Formation, Mantou Formation, Zhangxia Formation, Gushan Formation, and Chaomidian Formation from bottom to top \cite{18,19}. In this study, the Cambrian chronostratigraphy, lithostratigraphy and biostratigraphy in western Shandong was shown in Figure 1a, and thrombolite (biotic limestone) was collected from the Zhangxia Formation of the Cambrian. The different thrombolites were numbered from ZX-1 to ZX-20. Moreover, the cemented and clotted parts were removed from the same thrombolite as shown in Figure 1b.

![Figure 1](image-url)

**Figure 1.** (a) Cambrian chronostratigraphy, lithostratigraphy in western Shandong; (b) sampling locations of cemented and clotted parts in thrombolite.

2.2. X-ray Diffraction (XRD) and Energy Dispersive Spectrometer (EDS) Methods

Different thrombolites were cut into small cube samples with a rock cutter, cleaned 3 to 4 times with an ultrasonic cleaning machine, and then polished. Then, the fresh surface of the cemented and clotted parts was blow-dried with an ultraquiet air compressor. Finally, a small amount of powder was drilled from the fresh surface by an electric engraving machine for a subsequent test. After being ground, the cemented and clotted parts were passed through a 200-mesh aperture lab standard test sieve, with an SI scale of 75 µm. An appropriate amount of mineral powder was taken out and tested.
by XRD (D/Max/2500PC, Neo Confucianism of Japanese Company, Tokyo, Japan) with Cu-Kα radiation to analyze the mineral components of the cemented and clotted parts. The sample was spread on the groove of the slide which was cleaned with absolute ethanol and dried in advance. During the measurement, the sample was placed in the sample tank without moving. Experimental conditions were set as a scanning angle of 10° to 90°, step size of 0.02, and scanning speed of 5°·min⁻¹.

In addition, the elemental compositions of the cemented and clotted parts were measured by EDS (Apollo XLT SDD, EDAX, New York, NY, USA) [13].

2.3. The Thermal Decomposition Characteristics Analyzed by TG, DTG and DSC Methods

The effects of temperature changes and different heating rates on the mass loss, heat flow and phase transition of the sample were analyzed by thermal analysis. In the process of heating or cooling, different samples have different heat loss and heat flow changes. According to this feature, the composition and structure of different samples can be analyzed and distinguished by the thermal analyzer (TGA/DSC1/1600LF, METTLER TOLEDO Co., Schwerzenbach, Switzerland) at different temperature rates (5, 10, 20, and 30 K/min) from 323.15 to 1273.15 K. Recently, there are mainly three qualitative performance methods called TG, DTG and DSC, and a quantitative calculation method called thermal analysis kinetics for a comprehensive thermal analysis. After being ground, the cemented and clotted parts were uniformly passed through a 200-mesh aperture lab standard test sieve. In each experiment, the mass of the sample was 8 mg and all experimental procedures were repeated three times to ensure the accuracy of the results. Finally, all TG, DTG and DSC data were plotted by Origin Lab 9.0 software (Origin-Lab Corporation, Materials Data Ltd., Livermore, CA, USA).

2.4. Kinetic Analysis

The most direct calculation methods of thermal analysis kinetics is to calculate the three parameters of kinetics named activation energy (E), pre-exponential factor (lnA) and mechanism function G(α) by Flynn–Wall–Ozawa (FWO), Kissinger–Akahira–Sunose (KAS) and Popescu methods, which can fully understand the pyrolysis characteristics and thermal stability differences of samples during thermal decomposition [20,21].

It can be assumed that the initial mass of the sample is \(m_0\), the mass at any temperature and time is \(m_t\), and the final mass of the remaining sample is \(m_\infty\). Subsequently, the conversion rate \(\alpha\) is expressed as follows:

\[
\alpha = \frac{m_0 - m_t}{m_0 - m_\infty}
\]  
(1)

The decomposition rate can be also described as follows:

\[
\frac{d\alpha}{dt} = k(T)f(\alpha)
\]  
(2)

Here, the \(k(T)\) in Equation (2) according to Arrhenius equation can be described as follows:

\[
k(T) = Ae^{-E/RT}
\]  
(3)

The \(f(\alpha)\) can be confirmed by a mechanism function.

The heating rate \(\beta\) can be defined as \(\beta = \frac{dT}{dt}\), so Equation (2) can be changed as follows:

\[
\frac{d\alpha}{dT} = \frac{1}{\beta}k(T)f(\alpha)
\]  
(4)

Equation (4) can be changed as follows:

\[
\frac{da}{f(\alpha)} = \frac{1}{\beta}k(T)d(T)
\]  
(5)
The following result was obtained by integrating Equation (5)

\[ \int_{\alpha_n}^{\alpha_m} \frac{d\alpha}{f(\alpha)} = \frac{1}{\beta} \int_{T_n}^{T_m} k(T) dT \]  

(6)

Therefore, the left of Equation (6) can be expressed as follows:

\[ G(\alpha)_{mn} = \int_{\alpha_n}^{\alpha_m} \frac{d\alpha}{f(\alpha)} \]  

(7)

The right of Equation (6) was changed as follows:

\[ H(T)_{mn} = \int_{T_n}^{T_m} k(T) dT \]  

(8)

Therefore, Equation (9) was obtained from Equation (6).

\[ G(\alpha)_{mn} = \frac{1}{\beta} H(T)_{mn} = \int_{\alpha_n}^{\alpha_m} \frac{d\alpha}{f(\alpha)} = \frac{1}{\beta} \int_{T_n}^{T_m} k(T) dT \]  

(9)

Replace \( k(T) \) in Equation (8) by the form using in Equation (3):

\[ G(\alpha)_{mn} = \frac{1}{\beta} \int_{T_n}^{T_m} A e^{-E/RT} dT = \frac{A}{\beta} (T_m - T_n) \exp\left(\frac{-E}{RT_\xi}\right) \]  

(10)

where \( \alpha_m, \alpha_n \) were two different conversion rates and \( T_m, T_n \) were their corresponding temperature. Then,

\[ T_\xi = \frac{T_m + T_n}{2} \]  

(11)

\( G(\alpha)_{mn} \) was used as the y value, and \( 1/\beta \) was used as the x value for plotting. If the experimental data and the adopted \( G(\alpha)_{mn} \) can satisfy the \( G(\alpha)_{mn} - 1/\beta \) relationship as a straight line whose intercept tends to zero, then this \( G(\alpha)_{mn} \) can well-reflect the kinetic mechanism function of the thermal decomposition process.

The Popescu method was obtained from Equation (9) as follows:

\[ \ln\left(\frac{\beta}{T_n - T_m}\right) = \ln\left(\frac{A}{G(\alpha)}\right) - \frac{E}{RT_\xi} \]  

(12)

Then, according to Equation (12), taking \( \ln[\beta/(T_n - T_m)] \) as the ordinate and \( 1/T_\xi \) as the abscissa, the slope of the line was the activation energy value \( (E) \), \( \ln A \) can be obtained by the intercept of the line and \( R^2 \) was the correlation coefficient of the line fitting. In addition, the kinetic parameters \( E \) and \( \ln A \) can also be obtained by two other kinetic methods (FWO and KAS methods), and the equations were expressed as follows (Equations (13) and (14)):

\[ \ln \beta = \ln\left(\frac{AE}{RG(\alpha)}\right) - 5.331 - 1.052 \frac{E}{RT} \]  

(13)

\[ \ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{EG(\alpha)}\right) - \frac{E}{RT} \]  

(14)

According to Equations (13) and (14), \( \ln \beta \) and \( \ln[\beta/T^2] \) were taken as the abscissa, and \(-1.052/RT\) and \(-E/TR\) were taken as the ordinate, respectively. In the same way, the \( E \) and \( \ln A \) values can be obtained by slope and intercept, respectively [22,23]. The value of \( E \) was calculated by the FWO and KAS
methods, which can be obtained with the condition of uncertain mechanism function compared with the Popescu method. The three different methods can be compared and mutually verified to improve the accuracy of the results. The final $E$ value is the average of $E$ value obtained by different methods.

2.5. Stable Carbon Isotope Analysis

The treatment of inorganic carbon samples was as follows: the cemented and clotted parts were ground to 75-µm-sized grain and washed with deionized water. Then, the samples were dissolved with 5% sodium hypochlorite solution. After 48 h of reaction at room temperature, another 3 mL of sodium hypochlorite solution was added into the supernatant to observe whether the organic matter was completely removed. If bubbles appear after adding sodium hypochlorite solution, it means that the organic matter has not been completely removed, and so addition of sodium hypochlorite to the solution needs to continue, otherwise it means that the organic matter is completely removed. The samples were cleaned with distilled water repeatedly, and were bathed in ultrasonic water bath for 5 min. Finally, the dried powder samples were obtained after drying at 40 °C for 12 h. All inorganic carbon samples were analyzed by laser spectroscopic techniques using a Carbon Isotope Laser Spectrometer (Picarro G2121-i, Picarro Inc., Santa Clara, CA, USA) and used standards (NBS 18) for the carbon stable isotope measurements. In the experiment, carbon dioxide gas was collected after the sample reacted with phosphoric acid, and the $^{13}C/^{12}C$ of carbon dioxide was measured by an isotope analyzer. The $\delta^{13}C$ value relative to the Peedee Belemnite Standard (PDB) standard was calculated as follows:

$$\delta^{13}C = \left( \frac{^{13}C/^{12}C_{sample}}{^{13}C/^{12}C_{standard}} - 1 \right) \times 10000$$

(15)

3. Results and Discussions

3.1. XRD and EDS Analysis

The mineralogical analyses of the cemented and clotted parts of the same thrombolite are exhibited in Figure 2. It can be found that the mineralogical compositions of the cemented and clotted parts were all calcites according to the main diffraction peak position (Figure 2a). Furthermore, XRD analyses of the cemented and clotted parts also showed that the corresponding Full Width at Half Maximum (FWHM, unit: degree) value of the 104-crystal plane was different, which indicates that the crystallinity of the cemented and clotted parts was also completely different. It can be seen from Figure 2b that the FWHM value of cemented part was 0.243, while for the clotted part, the FWHM value was only 0.169. Therefore, it obviously showed that the FWHM value of the clotted part was lower than cemented part, which suggests that the crystallinity of the clotted part was higher.

Moreover, the cell density and cell volume were used to show the crystallinity index and special crystallographic information of the mentioned calcite minerals. The results of the changes in cell density and cell volume of different thrombolites were numbered from ZX-5, ZX-7, ZX-9, ZX-11, ZX-13, ZX-15, and ZX-17, which are shown in Figure 3a,b. The cell densities of the cemented parts were 2.688, 2.686, 2.684, 2.687, 2.691, 2.679 and 2.690. However, the cell densities of the clotted parts ranged from 2.701 to 2.716, which is higher than those of the cemented parts (Figure 3a). In addition, Figure 3b shows that the cell volumes of the cemented parts were 371.95, 371.15, 371.28, 370.98, 371.23 and 370.89. However, for the clotted parts, the cell volumes ranged from 368.58 to 369.54, indicating that the cell volumes were lower than cemented parts. In this study, the clotted parts exhibit a higher cell density and smaller cell volume because of their higher crystallinity.
The elemental compositions of cemented and clotted parts were carefully analyzed by EDS (Figure 4a,b). The elemental compositions of cemented and clotted parts were C, O, Ca, Al and Pt. Al came from the stage supporting the sample, and Pt arose from the spraying of gold during sample preparation. The C, O and Ca came from CaCO$_3$. Therefore, the chemical composition of the cemented and clotted parts were the same, and the mineral compositions were also the same combined with XRD analysis.

Figure 2. XRD analysis of cemented and clotted parts in thrombolite. (a) the mineralogical compositions of the cemented and clotted parts; (b) the Full Width at Half Maximum (FWHM) of cemented and clotted parts.

Figure 3. (a) The results of the changes in cell density of cemented and clotted parts; (b) the results of the changes in cell volume of cemented and clotted parts.

The elemental compositions of cemented and clotted parts were carefully analyzed by EDS (Figure 4a,b). The elemental compositions of cemented and clotted parts were C, O, Ca, Al and Pt. Al came from the stage supporting the sample, and Pt arose from the spraying of gold during sample preparation. The C, O and Ca came from CaCO$_3$. Therefore, the chemical composition of the cemented and clotted parts were the same, and the mineral compositions were also the same combined with XRD analysis.
Cemented part

3.2. Thermal Analysis

Figure 5 shows TG and DTG curves with thermal decomposition characteristics of cemented and clotted parts at four different heating rates of 5, 10, 20 and 30 K/min, respectively. The results of Figure 5a,b show that the maximum heat loss of the sample increases significantly with the increase in temperature. In addition, for Figure 5c,d, which show the TG and DTG curves of cemented and clotted parts at a heating rate of 10 K/min, the thermogravimetric analysis showed the same results at other heating rates; therefore, it was not listed for the sake of brevity.

Figure 4. (a) The elemental compositions of the cemented part; (b) the elemental compositions of the clotted part.

Figure 5. Thermal decomposition characteristics of cemented and clotted parts; (a,b) the thermal decomposition characteristics of cemented and clotted parts; (c,d) the thermal decomposition characteristics of cemented and clotted parts at heating rate of 10 K/min.
The results of DTG curves could better reflect the temperature when the mass loss of the sample reaches the maximum, and it can be seen from Figure 5d that the whole pyrolysis process of the cemented and clotted parts can be clearly divided into three stages. The temperature range of the first stage was from the initial set temperature of 323.15 K to $T_1$, and the first stage of weight loss of the two samples was the evaporation of chemically bound water [24,25]. As the temperature continues to rise to $T_1$, the cause of mass loss was structural water loss. Moreover, it can be seen from the TG and DTG curves that the mass loss of two samples is similar. As the thermal decomposition temperature rose to $T_2$, the slope of the TG curve reached the maximum value, as seen in Figure 5c, which indicates that the thermal weight loss of the sample reached the maximum value. In addition, the temperature corresponding to the maximum thermal weight loss of the cemented part was 1035 K; however, the temperature corresponding to the clotted part was 1080 K, which is higher than that of the cemented part. At the same time, the Figure 5d curve shows that the main thermal decomposition of the two samples was the second stage ($T_1$ to $T_3$), and the main reason for mass loss in the second stage was the decomposition of calcium carbonate. The reaction equation is as follows:

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow$$  (16)

Finally, from $T_3$ to the final temperature (1273.15 K) was the third stage of thermal decomposition. It can be seen from the Figure 5d that the DTG curve at this stage basically maintains the level, which means the thermogravimetric process is over and the quality of the sample basically does not change.

In addition, the experimental results show that the final thermal weight loss of the cemented part was 45%, and the final thermal weight loss of the clotted part was 30%, which was lower than that of the cemented part (Figure 5c). Therefore, the thermal stability of the clotted part was higher. In this study, the clotted part of thrombolite contained more microorganisms and was generally considered to be the biotic mineral, and the cemented part of thrombolite contained fewer microorganisms and was generally considered to be the abiotic mineral. Under the action of more microorganisms, the crystallinity of calcite in the clotted part was higher. Therefore, only a part of calcite decomposes and the final mass loss of the clotted part was lower than the cemented part under the same temperature conditions.

Simultaneously, the results in Figure 6a,b show the heat flow changes of the cemented and clotted parts at different heating rates. The peak area in the DSC curve corresponded to the heat absorbed or released (i.e., enthalpy change) [26,27]. Although the mass of the sample was slightly different each time during the experiment, the heat flow per unit mass can be used to reflect the heat absorbed or released by the sample. In this study, Figure 6a,b show that the heat flow changes of cemented and clotted parts at heating rates of 5 and 10 K/min, respectively. Figure 6a shows the change in heat flow of the sample at a heating rate of 5 K/min. The DSC curve in Figure 6a shows that the first stage is an endothermic process and this stage corresponds to the dehydration process that requires heat to be absorbed from the external environment. Moreover, the second stage was also an endothermic process, because the mass loss of the sample in the second stage needed to absorb heat from the external environment. In the third stage, the mass of the sample did not change, and the temperature range was relatively narrow from $T_3$ to 1273.15 K. This stage was accompanied by a small endothermic peak, which was mainly due to the release of carbon dioxide from the sample. It can be seen from Figure 6a that the $\Delta H$ values of the cemented and clotted parts were 95.3 and 140.5 kJ/mol at a heating rate of 5 K/min, meanwhile, the corresponding peak temperatures were 975 and 1010 K. Similarly, the $\Delta H$ values of the cemented and clotted parts calculated from the peak area were 123.2 and 165.9 kJ/mol at a heating rate of 10 K/min accompanied by peak temperatures of 1023 and 1045 K (Figure 6b).
were higher than those of the cemented part. Prepared calculation process to show that the activation energy and crystallinity of the clotted part were higher than that of cemented part. Moreover, combined with the results of the previous XRD research, the crystallinity of the clotted part was also higher than that of the cemented part, showing that the results were consistent.

2020 344.6 kJ

It can be seen that the heat absorbed by the clotted part during the whole pyrolysis process was always higher than the cemented part at heating rates of 5 and 10 K/min, and the corresponding peak temperature of the clotted part was also higher, which fully shows that the thermal stability of the clotted part was higher than that of cemented part. Moreover, combined with the results of the previous XRD research, the crystallinity of the clotted part was also higher than that of the cemented part, showing that the results were consistent.

3.3. Kinetic Analysis

In the second stage of thermal decomposition, selecting different conversion rates and their corresponding temperatures under the conditions of known heating rates, and then the conversion rates and corresponding temperatures at other heating rates, were obtained [28,29]. The results of the mechanism functions are shown in Table 1. The conversion rates of the cemented and clotted parts were selected in the range of 0.3 to 0.5 and 0.6 to 0.8. Therefore, the optimal mechanism functions of the clotted part were $G(\alpha) = (1 - \alpha)^{-1}$ and $G(\alpha) = \alpha^{1/2}$; in addition, the optimal mechanism functions of the clotted part were $G(\alpha) = -\ln(1 - \alpha)$ and $G(\alpha) = 1 - (1 - \alpha)^{1/2}$. The higher correlation coefficient ($R = 0.95$–$0.99$) indicates the reliability of the experimental results.

![Figure 6](image-url) Heat flow changes of cemented and clotted parts. (a) The heat flow changes of cemented and clotted parts at heating rate of 5 K/min; (b) the heat flow changes of cemented and clotted parts at heating rate of 10 K/min.

Table 1. The optimal mechanism functions of cemented and clotted parts.

| Sample          | Conversion Rate/\(\alpha\) | Integral Form \(G(\alpha)\)         | \(R\)  |
|-----------------|---------------------------|------------------------------------|-------|
| Cemented part   | 0.3–0.5                   | \(G(\alpha) = (1 - \alpha)^{-1}\) | 0.96  |
|                 | 0.6–0.8                   | \(G(\alpha) = \alpha^{1/2}\)        | 0.98  |
| Clotted part    | 0.3–0.5                   | \(G(\alpha) = -\ln(1 - \alpha)\)  | 0.99  |
|                 | 0.6–0.8                   | \(G(\alpha) = 1 - (1 - \alpha)^{1/2}\) | 0.95  |

According to Equations (12)–(14), the kinetic parameters \(E\) and \(\ln A\) were calculated by different non-isothermal integration methods (Popescu, FWO and KAS methods). All the results are shown in Tables 2 and 3. The results show that the \(E\) values of the cemented part were 243.7, 238.5 and 243.1 kJ/mol accompanied by an average value of 241.7 kJ/mol at different heating rates. While, for the clotted part, the \(E\) values were 342.3, 341.3 and 350.3 kJ/mol, accompanied by an average value of 344.6 kJ/mol, which was higher than the cemented part. Therefore, thermal analysis kinetics provide a prepared calculation process to show that the activation energy and crystallinity of the clotted part were higher than those of the cemented part.
Table 2. The results of $R$, $E$, and $\ln A$ of cemented part.

| Conversion Rate/a | FWO Conversion Rate/α | KAS | Popescu | FWO Conversion Rate/α | KAS | Popescu |
|------------------|-----------------------|-----|---------|-----------------------|-----|---------|
|                  | $R$ | $E$ | $\ln A$ | $R$ | $E$ | $\ln A$ | $R$ | $E$ | $\ln A$ |
| 0.1              | 0.97 | 343.3 | 31.1 | 0.93 | 334.6 | 17.9 | 0.93 | 341.4 | 22.5 |
| 0.2              | 0.99 | 356.1 | 37.4 | 0.91 | 354.9 | 21.4 | 0.92 | 365.2 | 28.3 |
| 0.3              | 0.92 | 342.9 | 32.7 | 0.92 | 323.3 | 18.6 | 0.90 | 352.6 | 20.7 |
| 0.4              | 0.95 | 367.6 | 30.2 | 0.94 | 356.5 | 23.3 | 0.95 | 357.2 | 26.2 |
| 0.5              | 0.92 | 342.8 | 29.8 | 0.97 | 321.5 | 28.8 | 0.99 | 325.5 | 22.8 |
| 0.6              | 0.98 | 341.2 | 32.6 | 0.92 | 342.1 | 22.7 | 0.94 | 364.7 | 26.7 |
| 0.7              | 0.91 | 324.5 | 29.2 | 0.98 | 362.6 | 27.6 | 0.97 | 335.2 | 22.2 |
| 0.8              | 0.92 | 320.2 | 33.2 | 0.99 | 351.3 | 21.5 | 0.92 | 360.6 | 26.5 |
| 0.9              | 0.93 | 342.3 | 38.2 | 0.92 | 324.9 | 29.5 | 0.93 | 341.3 | 14.9 |
| Average          | 342.3 ± 13.5 | 341.3 ± 14.9 | 350.3 ± 13.7 |

Table 3. The results of $R$, $E$, and $\ln A$ of clotted part.

| Conversion Rate/a | FWO Conversion Rate/α | KAS | Popescu | FWO Conversion Rate/α | KAS | Popescu |
|------------------|-----------------------|-----|---------|-----------------------|-----|---------|
|                  | $R$ | $E$ | $\ln A$ | $R$ | $E$ | $\ln A$ | $R$ | $E$ | $\ln A$ |
| 0.1              | 0.92 | 252.3 | 30.2 | 0.96 | 229.6 | 16.9 | 0.94 | 242.7 | 23.4 |
| 0.2              | 0.93 | 242.1 | 34.4 | 0.98 | 236.9 | 23.4 | 0.97 | 237.1 | 21.5 |
| 0.3              | 0.98 | 238.9 | 35.7 | 0.99 | 252.9 | 19.6 | 0.99 | 252.3 | 25.9 |
| 0.4              | 0.97 | 243.6 | 39.2 | 0.96 | 236.2 | 20.3 | 0.92 | 260.5 | 22.5 |
| 0.5              | 0.98 | 252.9 | 32.8 | 0.98 | 228.5 | 19.8 | 0.91 | 231.3 | 21.9 |
| 0.6              | 0.99 | 245.5 | 34.6 | 0.93 | 231.1 | 20.7 | 0.93 | 252.9 | 22.4 |
| 0.7              | 0.93 | 257.2 | 38.2 | 0.99 | 254.6 | 23.6 | 0.94 | 228.5 | 25.6 |
| 0.8              | 0.91 | 228.6 | 36.2 | 0.91 | 242.3 | 27.5 | 0.88 | 237.4 | 20.7 |
| 0.9              | 0.94 | 232.6 | 37.2 | 0.93 | 234.9 | 19.5 | 0.94 | 231.4 | 23.4 |
| Average          | 243.7 ± 8.9 | 238.5 ± 9.1 | 243.1 ± 10.3 |

In addition, the FWHM and activation energy results of different thrombolites numbered from ZX-5, ZX-7, ZX-9, ZX-11, ZX-13, ZX-15, and ZX-17 are shown in Figure 7. XRD results show that the FWHM values of the cemented part in thrombolite range from 0.219 to 0.243, and the FWHM values of the clotted part range from 0.169 to 0.193 (Figure 7a). The thermogravimetric analysis results show that the activation energy of the cemented parts range from 251.8 to 274.3 kJ/mol, and the activation energy of the clotted parts range from 338.7 to 369.2 kJ/mol (Figure 7b). In summary, at different sampling levels, the crystallinity and thermal stability of the clotted part are higher than that of the cemented part.

Figure 7. Full Width at Half Maximum (FWHM) (a) and activation energy (b) of cemented and clotted parts in thrombolite.
3.4. Stable Carbon Isotope Analysis of Cemented and Clotted Parts in Thrombolite

In order to further explore the relationship between the cemented and clotted parts in thrombolite, the C-isotope values of the inorganic carbon were detected and presented in Table 4. These values for cemented parts in thrombolite ranged from $-1.21$ to $-1.48\%$, and the results showed that the $\delta^{13}C$ values of the clotted parts ranged from $-0.3$ to $-1.89\%$. Moreover, in the same thrombolite numbered from ZX-1 to ZX-20, the $\delta^{13}C$ values also became more positive.

| Location | Sample | Sample Number | Cemented Parts $\delta^{13}C_{PDB}$ (%) | Clotted Parts $\delta^{13}C_{PDB}$ (%) |
|----------|--------|---------------|----------------------------------------|----------------------------------------|
| Zhangxia Formation | Thrombolite | ZX-20 | $-1.21$ | $-0.3$ |
|            |        | ZX-19 | $-0.89$ | $-0.2$ |
|            |        | ZX-18 | $-0.16$ | $0.06$ |
|            |        | ZX-17 | $-0.06$ | $0.02$ |
|            |        | ZX-16 | $-0.3$ | $0.05$ |
|            |        | ZX-15 | $-0.08$ | $0.2$ |
|            |        | ZX-14 | $-0.02$ | $-0.01$ |
|            |        | ZX-13 | $-0.24$ | $-0.15$ |
|            |        | ZX-12 | $-0.09$ | $-0.2$ |
|            |        | ZX-11 | $-0.16$ | $-0.1$ |
|            |        | ZX-10 | $0.5$ | $0.01$ |
|            |        | ZX-9  | $-0.24$ | $0.56$ |
|            |        | ZX-8  | $-0.42$ | $0.84$ |
|            |        | ZX-7  | $-0.47$ | $1.32$ |
|            |        | ZX-6  | $0.28$ | $1.12$ |
|            |        | ZX-5  | $0.87$ | $1.05$ |
|            |        | ZX-4  | $1.25$ | $1.8$ |
|            |        | ZX-3  | $0.89$ | $1.52$ |
|            |        | ZX-2  | $1.48$ | $1.74$ |
|            |        | ZX-1  | $1.35$ | $1.89$ |

The clotted part of thrombolite contains more microorganisms and is generally considered to be the biotic mineral. The cemented part of thrombolite contains fewer microorganisms and is generally considered to be the abiotic mineral, and this part is mainly composed of calcite, dolomite, quartz and clay minerals [30]. The stable carbon isotope results show that, compared with the chemical precipitated sparry calcite in the cemented part, the clotted part contains more microorganisms, which can absorb more $^{12}C$ through photosynthesis and results in more $^{13}C$ in the clotted part. Therefore, the carbon isotope $\delta^{13}C$ value is higher.

4. Conclusions

The purpose of this paper is to explore the mineralogical characteristics, thermal decomposition unique characteristics and geochemical characteristics of cemented and clotted parts in the same thrombolite. In this study, the cemented and clotted parts were pyrolyzed in a thermogravimetric analyzer at different heating rates. It can be concluded that the thermal stability and crystallinity of the clotted part were higher than the cemented part. In addition, the stable carbon isotope results show that the microorganisms in the clotted part absorb more $^{12}C$ through photosynthesis, which results in more $^{13}C$ in the clotted part, and the carbon isotope $\delta^{13}C$ value is higher. Therefore, this study not only provides a reference for distinguishing abiotic and biotic minerals, but also provides a basis for exploring the formation mechanism and geological significance of microbial rocks in the field.

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