Research Article

An Experimental Study of the Formation of Talc through CaMg(\(\text{CO}_3\))_2–SiO_2–H_2O Interaction at 100–200°C and Vapor-Saturation Pressures

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The metamorphic interaction between carbonate and silica-rich fluid is common in geological environments. The formation of talc from dolomite and silica-rich fluid occurs at low temperatures in the metamorphism of the CaO–MgO–SiO_2–H_2O system and plays important roles in the formation of economically viable talc deposits, the modification of dolomite reservoirs, and other geological processes. However, disagreement remains over the conditions of talc formation at low temperatures. In this study, in situ Raman spectroscopy, quenched scanning electron microscopy, micro-X-ray diffraction, and thermodynamic calculations were used to explore the interplay between dolomite and silica-rich fluids at relatively low temperatures in fused silica tubes. Results showed that talc formed at ≤200°C and low CO_2 partial pressures (\(P_{\text{CO}_2}\)). The reaction rate increased with increasing temperature and decreased with increasing \(P_{\text{CO}_2}\). The major contributions of this study are as follows: (1) we confirmed the formation mechanism of Mg-carbonate-hosted talc deposits and proved that talc can form at ≤200°C; (2) the presence of talc in carbonate reservoirs can indicate the activity of silica-rich hydrothermal fluids; and (3) the reactivity and solubility of silica require further consideration, when a fused silica tube is used as the reactor in high \(P–T\) experiments.

1. Introduction

The common metamorphic interaction between dolomite and silica-rich fluids plays important roles in many geological processes. For example, the interaction is closely associated with the formation of skarn ore deposits [1–3]. Talc was reported to form at low temperatures in the metamorphism of the CaO–MgO–SiO_2–H_2O–CO_2 system [4–6]. Talc is characterized by a trioctahedron structure [7] and is chemically inert, soft, white, and highly thermally conductive [8]. As a result, talc is used in various industrial applications [7, 9, 10]. Previous studies showed that talc mineralization can occur in various geological settings, such as the alteration of ultra-mafic rocks (e.g., [11–15]), the mixing of seafloor hydrothermal fluids and seawater [16], and the alteration of Mg-carbonate rocks [17–21]. However, it is most economical to extract from deposits associated with the hydrothermal alteration of dolostone/Mg-carbonate [17].

Hydrothermal dolomite and hydrothermally altered dolomite are important hydrocarbon reservoirs (e.g., [22–25]). Geologically pervasive silica-rich hydrothermal fluids derived from sources, such as deep formation brines or magma intrusions (e.g., [26–28]), can react with dolomite to form talc in carbonate reservoirs, influencing the reservoirs’ physical properties [29–31]. In addition, talc has
a low friction coefficient, so its formation along faults in carbonate rocks can promote the stable creep of a fault, releasing accumulated elastic strain and preventing strong earthquakes [32–35]. Therefore, thorough investigation of the CaMg(CO$_3$)$_2$–SiO$_2$–H$_2$O interaction can help elucidate many geological processes.

However, disagreements remained regarding the formation temperature of talc through the reaction between dolomite and a silica-rich fluid. The reaction has been theoretically calculated to occur at ≥150°C [5,35,36], but most geological studies have indicated that talc mainly forms at 250–400°C (e.g., [21, 37, 38]). For example, in the Saint-Barthélemy deposits in Switzerland, oxygen isotope thermometric calculations showed that talc mineralization occurred at about 300°C [21], which is consistent with fluid inclusion data (250–300°C) [39,40]. Experimental studies have sought to construct a phase diagram of the CaO–MgO–SiO$_2$–CO$_2$–H$_2$O system, but hydrothermal experimental studies have only been conducted above 250°C (e.g., [4,41–44]). Consequently, further experiments at lower temperatures are necessary to fully explore the formation temperature of talc.

In this study, the reactions for the CaMg(CO$_3$)$_2$–SiO$_2$–H$_2$O system were conducted in fused silica tubes at temperatures from 100 to 200°C. In situ Raman spectroscopy was used to characterize the vapor products. The quenched solid products were investigated with Raman spectroscopy, scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS), and micro-X-ray diffraction (micro-XRD). In addition, the Gibbs free energy of the reaction was also calculated using the geochemical modelling program.

### 2. Materials and Methods

#### 2.1. Sample Preparation

Dolomite powder was prepared from dolomite rocks of the Neoproterozoic Dengying Formation in the Sichuan Basin, Southwest China. Powder XRD analyses showed that the dolomite rock is comprised of >97% dolomite and <3% quartz. Calcite grains were prepared from colorless, transparent, rhombohedral calcite crystals. Distilled deionized water (18.2 KΩ cm) was used throughout. Amorphous SiO$_2$ originated from the fused silica tubes.

Chou et al. [46] have reported detailed procedures for constructing fused silica capillary capsules (FSCCs). The protective polyimide layer of the fused silica tube (0.5 mm in inner diameter and 0.65 mm in outer diameter) was burnt off in an oxyhydrogen flame, and one end of the tube was sealed. The dolomite/calcite powder and a 0.5-cm long water column were loaded into the tube and centrifuged to the sealed end. The open end was then connected to a pressure line. The air in the tube was evacuated, and the open end of the tube was sealed by fusion in the oxyhydrogen flame. As shown in Figure 1, the prepared FSCC is about 2 cm long and consists of the dolomite powder (≈0.5 cm in length), water (≈0.5 cm in length), and a vapor phase (≈1 cm in length).

High-pressure optical cells (HPOCs, Figure 2(a)) containing dolomite and water were also constructed for pressure measurements. The dolomite powder and deionized water were first loaded into a one-end-sealed fused silica tube (≈20 cm in length). Approximately 2 cm long mercury was then injected to separate the reaction system and the pressurization medium—water. The detailed procedures for preparing HPOCs are described in Chou et al. [47].

#### 2.2. Experimental Procedures

##### 2.2.1. In Situ Vapor-Phase Analyses

The reaction between dolomite and a silica-rich fluid to form talc involves decarbonation of dolomite and the generation of CO$_2$:

$$3\text{CaMg(CO}_3\text{)}_2 + 4\text{SiO}_2 + \text{H}_2\text{O} \rightarrow \text{Mg}_3\text{(Si}_4\text{O}_{10})\text{(OH)}_2 + 3\text{CaCO}_3 + 3\text{CO}_2$$  \(\text{(1)}\)

Raman spectroscopy is sensitive to CO$_2$ and can detect CO$_2$ at pressures lower than 0.6 bar [48,49]. Therefore, in situ Raman spectroscopy of the vapor phase was used to detect the reaction. FSCCs containing dolomite and water were heated in a heating stage (Linkam CAP500) calibrated with a K-type thermocouple, which had been previously calibrated with the triple point (0°C) and boiling point (100°C) of water at 0.1 MPa. The temperature difference along the 4 cm central line of the heating stage was less than 0.5°C at 300°C. The setup of in situ Raman spectroscopic analysis is shown in Figure 1. The target temperature was increased at increments of 10°C from an initial 60°C until a CO$_2$ signal was detected in the vapor phase after heating for ~24 h. To characterize the mechanism of CO$_2$ generation (metamorphic alteration or decomposition of dissolved CO$_2$$^2$−), Raman spectra of the vapor phase within FSCCs containing calcite and water were also acquired for comparison.

Raman spectra were collected in situ for the vapor phase within FSCCs containing dolomite and water at 200°C (higher than the reaction threshold) to investigate the kinetics of the reaction. The experimental duration was increased from 2 h to ~240 h.

##### 2.2.2. Pressure Measurements

The setup for the pressure measurement is shown in Figure 2(a). The HPOC containing dolomite and water was connected to a pressurization system. Pressures were monitored by a Setra 206D digital pressure transducer with Datum 2002 manometer (69 MPa full scale, accurate to ±0.14%). The HPOC containing dolomite and water was heated to 200°C using a Linkam CAP 500 heating stage. The position of mercury in the HPOC was fixed by adjusting the pressure with a pressure generator, and then the pressure of the whole system was recorded with experimental duration (Figure 2(a)).

##### 2.2.3. Analyses of Solid Products

Several one-end-open fused silica tubes containing dolomite and water were placed in a 10 mL batch stainless steel reactor equipped with a Teflon (PTFE) internal cup (Figure 2(b)). The reactor was then heated at 150 and 200°C for 20–90 days in an oven with a temperature accuracy of ±5°C. During the reaction, the reactor was opened and the product CO$_2$ was released several
times to promote the reaction. After heating, micro-XRD and Raman spectroscopy were used to characterize the composition of the quenched solid product at room temperature. Then, the SEM was used to observe the morphology of the product. The chemical composition was analyzed using EDS.

2.3. Analytical Methods. Raman spectra were collected with a high-resolution Raman spectrometer (LabRAM HR800, JY/Horiba) using a 532 nm laser from an air-cooled, frequency-doubled Nd:YAG laser excitation, a 50x objective (Olympus), and a 1800 groove/mm grating with a spectral resolution of about 1 cm$^{-1}$. An approximate 9.5 mW laser was focused on the central level of the horizontal tube for vapor spectra acquisition and on the surface of the solid phase for solid spectra acquisition. Spectra were collected from 100 to 1600 cm$^{-1}$. To obtain a high signal-to-noise ratio spectrum, three accumulations were collected in denoise mode (120 s for the vapor phase and 30 s for the solid phase), and averaged for each spectrum. Before collection, the Raman spectrometer was calibrated with the $v_1$ band of silicon at 520.2 cm$^{-1}$. Labspec 5 software was used for Raman spectral analyses.

Micro-XRD investigations of the quenched reacted dolomite were carried out with a diffractometer (D/Max Rapid II, Rigaku) equipped with a Mo tube and a 300-μm diameter collimator. The diffractometer was operated at 50 kV and 90 mA with an angular velocity of 6°/s and an exposure time of 15 min. Jade 6 software was used to characterize the compositions of the solid phase.

The morphology of the quenched reacted dolomite was observed using a field emission (FE) SEM (Supra55, Zeiss) with an accelerating voltage of 15 kV. The approximate chemical composition of the solid phase was analyzed by an EDS (Oxford Instruments, Inca X-Max 150 mm$^2$). All experiments were performed at the Institute of Energy Sciences and the State Key Laboratory for Mineral Deposits Research hosted in School of Earth Sciences and Engineering, Nanjing University.

In addition, we calculated the Gibbs free energy of talc formation from the CaMg(CO$_3$)$_2$–SiO$_2$($aq$)–H$_2$O system for the $P$–$T$ conditions covered in these experiments, using the Hch program (version 4.4) and its incorporated Unitherm database [51].

3. Results

3.1. Vapor-Phase Characterization. The linear CO$_2$ molecule has four vibrational modes: a symmetric stretching mode ($v_1$), two bending modes ($2v_2$: $v_2a$ and $v_2b$), and an antisymmetric stretching mode ($v_3$) (e.g., [48, 52, 53]). The modes $v_1$ and $2v_2$ are both Raman active and have a similar energy (~1335 cm$^{-1}$) and the same symmetry species, resulting in a Fermi resonance [48]. Fermi resonance causes the excited admixed states to split into two prominent peaks: an upper band at ~1388 cm$^{-1}$ and a lower band at ~1285 cm$^{-1}$ [48, 54]. Weak hot bands flanking the Fermi diads may also appear in the spectrum [48]. Raman spectroscopy has very low detection limits for CO$_2$ and thus is used frequently for CO$_2$ characterization in fluid inclusions [53, 55–58].

Figure 3(a) shows the Raman spectra of the vapor phase in FSCCs containing CaMg(CO$_3$)$_2$–H$_2$O and CaCO$_3$–H$_2$O after heating at 90–150 °C for 24 h. For the FSCCs containing dolomite and water, no CO$_2$ signal was observed after heating at ≤90 °C. Weak but clear CO$_2$ Fermi bands at ~1285 and 1384 cm$^{-1}$ were observed after heating at 100 °C. The Raman intensity of CO$_2$ was much stronger after heating at 150 °C than that at 100 °C (Figure 3(a)). That is to say, CO$_2$ was generated in the CaMg(CO$_3$)$_2$–SiO$_2$–H$_2$O system when heated at ≥100 °C with an experimental duration of 24 h. However, the signals of CO$_2$ were not observed in FSCCs containing calcite and water after heating at 100–200 °C for 24 h. Considering that a greater concentration of CO$_2^{2−}$ dissolved from calcite than from dolomite in pure water at temperatures of 100–150 °C [59, 60], we suggest that the CO$_2$ from the dolomite-bearing system was generated by decarbonation via metamorphic reaction (1) instead of the decomposition of dissolved CO$_3^{2−}$.

The intensity and wavenumber of the CO$_2$ Fermi diad bands vary with changes in the CO$_2$ pressure and temperature [48, 53, 56]. Previous studies have suggested that the Fermi diad splits increase with increasing CO$_2$ pressure at a constant temperature (e.g., [61]). Accordingly, several equations were constructed for quantitative measurements of the CO$_2$ density based on the Fermi diad splits by using reference samples with P$_{CO_2}$ > 0.6 bar ([49] and references therein). In this study, the Fermi diad peak positions and splits of CO$_2$ produced from CaMg(CO$_3$)$_2$–SiO$_2$–H$_2$O interaction were also obtained (Table 1). However, negative density values were obtained when applying these calibration curves to quantitatively measure the CO$_2$ content in the FSCC. This result indicates that only a small amount of CO$_2$ was produced in the FSCC and that the CO$_2$ pressure was lower than 0.6 bar. Table 2 shows the variation of the internal pressure of a HPOC containing dolomite and water with experimental duration. Results showed that the internal pressure fluctuated with reaction time. Consequently, the exact partial pressure of CO$_2$ generated from the metamorphic reaction (1) cannot be obtained; this should also result from the very low P$_{CO_2}$.

The variation in the Raman intensity of CO$_2$ as a function of the experimental duration can reflect the kinetics of reactions yielding CO$_2$ [57]. Increasing the experimental duration could increase the CO$_2$ intensity (Figure 3(b)). The peak areas...
Figure 2: (a) The setup for measurements of the internal pressures within a HPOC containing dolomite and water; (b) the batch stainless reactor in the oven. The left schematic diagram showing the structure of the reactor. SCR represents the stainless cup of the reactor, RC represents the reactor cover, IC represents internal cup, and CIC represents cover of the internal cup.

Figure 3: Raman spectra of the vapor phase in FSCCs containing (a) CaCO$_3$–H$_2$O and CaMg(CO$_3$)$_2$–H$_2$O after heating at 90–150°C for 24 h and (b) CaMg(CO$_3$)$_2$–H$_2$O after heating at 200°C from 2 to 41 h.

The intensity of the CO$_2$ Fermi diad bands increased with experimental duration up to about 120 h (200°C) before eventually leveling off (Figure 4, Table 1). Solid-phase characterization (see Section 3.2) indicated that the dolomite was unlikely to run out over the length of the experiment. Consequently, the reaction reached an equilibrium state after reaction for ~120 h. The degree of the reaction ($R$) can be calculated using the ratio between the total Raman peak area of CO$_2$ at time $t$ ($A$) and that at equilibrium state ($A^*$):

$$R (%) = \frac{A}{A^*} \times 100\%.$$  

As shown in Figure 4 (diamonds), the slope of $R$ decreases with the increase of reaction time, indicating that the
Table 1: Fermi diad bands, splits, and peak areas of CO\textsubscript{2} generated in the FSCC containing dolomite and water at 200°C, and the calculated degree of reaction.

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<tr>
<th>Reaction time (h)</th>
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\textsuperscript{a}The total Raman peak area of CO\textsubscript{2} at equilibrium state is an average of those after reaction for \(\sim 120\) h. Then, the degree of reaction can be regarded as 100% when the reaction time exceeds 120 h.

reaction rates decrease with the increase of experimental duration/\(P_{CO_2}\). The results also showed that the reaction rate increased with increasing temperature. For example, the Raman intensity of CO\textsubscript{2} was stronger at higher temperature within a given period of time (Figure 3(a)).

3.2. Solid-Phase Characterization. Figure 5 shows XRD patterns of the quenched solid relicts in the fused silica tubes. After heating at 200°C for \(\sim 20\) days, the talc signals were weak. However, heating for 80 days produced calcite and talc as the main phases in the solid relicts, whereas dolomite signals were hardly visible in the XRD pattern (Figure 5).

The Raman spectrum of the solid phase before heating (Figure 6) showed only dolomite peaks (\(\sim 177, 300.5, 1098\) cm\textsuperscript{-1}; [62]), indicating that the dolostone was of high purity, consistent with the XRD analysis. However, in addition to dolomite, characteristic calcite signals (\(\sim 282\) and 1086 cm\textsuperscript{-1}; [63]) and talc signals (190.5, 360.5, and 675 cm\textsuperscript{-1}; [64]) appeared after heating at 200°C for 60 days.

Figure 7 shows the morphology of the solid phase after heating at 200°C for 60 days. The solid phase has a honeycomb-like texture and was widely distributed in the relicts (Figures 7(a)–7(d)). It was identified by EDS as talc (Figure 7(c)). The talc exhibited unoriented textures because it formed under strain-free conditions [21]. Some cylindrical talc also occurred along the inner surface of the FSCC (Figure 7(d)). The dolomite grains had smooth edges (Figure 7(c)), indicating dissolution during heating. Some products of rhombohedral calcite (Figure 7(d)) were also present in the solid phase, which formed along with the talc via reaction (1).

The amount of Mg-silicate mineral produced at 150°C for 40 days was below the detection limit of the micro-XRD equipment. Only dolomite and a small amount of calcite were observed in the XRD pattern after heating at 150°C for 40 days (Figure 5). This further supports the view that the metamorphic reaction rate is largely dependent on temperature. Some researchers view talc as the initial metamorphic mineral for the CaMg(CO\textsubscript{3})\textsubscript{2}–SiO\textsubscript{2}–H\textsubscript{2}O system.
Figure 4: Raman peak areas of CO$_2$ and the degree of reaction versus reaction time at 200°C. Black rectangles and red circles denote the peak areas of the lower band at $\sim$1285 cm$^{-1}$ and the upper band at $\sim$1385 cm$^{-1}$, respectively. Blue triangles represent the total peak areas of both bands. The green diamonds represent the degree of the reaction. Data plotted are from Table 1.

Figure 5: X-ray patterns of the solid relicts in FSCCs containing dolomite and water after heating at 150°C for $\sim$40 days (lower blue line) and at 200°C for $\sim$20 days (middle orange line) and $\sim$80 days (upper black line).

(e.g., [4–6]). However, serpentine minerals, like lizardite and chrysotile, are also likely to form at low temperatures during metamorphism of the CaO–MgO–SiO$_2$–H$_2$O–CO$_2$ system, especially in contact or regional metamorphic settings [65–67]. Some researchers have even pointed out that serpentine forms at lower temperatures than talc during metamorphism of the MgO–SiO$_2$–H$_2$O–CO$_2$ system [68, 69]. In fact, while serpentine is likely to form in a low-silica environment,
further introduction of SiO$_2$ will make talc stable relative to serpentine [70–73]. Considering the fact that talc was characterized as the product of Mg-silicate mineral in the 200°C experiment via reaction (1), we speculate that, while not detected by XRD, talc also formed below 200°C since CO$_2$ was generated during the experiment (see above).

3.3. Thermodynamic Calculations. Due to the limits of the Unitherm database, we used aqueous silica as the SiO$_2$ species that participated in the reaction. Considering that the solubility of amorphous silica was high at elevated temperatures [74], the calculated results should approximate the conditions of the experiments. The Gibbs free energy ($\Delta G$) of formation for talc from CaMg(CO$_3$)$_2$, aqueous SiO$_2$, and H$_2$O at the pressure and temperature of interest are given in Table 3. The $\Delta G$ of reaction decreases with increasing temperature at the saturation pressure. This indicates that the reaction is more favorable at higher temperatures. The $\Delta G$ becomes negative at $T \geq 80^\circ$C, which implies that the formation of product talc from dolomite and a silica-rich fluid is thermodynamically favored. However, this reaction may not commence until even higher temperatures are reached due to the probable initial kinetic barrier to the reaction. These thermodynamic calculations support the implication from the experimental results that talc formation can occur at temperatures above 100°C.

4. Discussion

4.1. Implications for the Formation of Mg-Carbonate-Hosted Talc. Geologically, Prochaska [18] grouped the talc deposits into five types: (1) talc related to ultramafics (e.g., [13–15]); (2) Mg-carbonate-hosted talc (e.g., [20, 37]); (3) metamorphic talc (e.g., [75, 76]); (4) talc related to banded iron formations (mostly minnesotaite; [77, 78]); and (5) secondary talc deposits [18]. The most economically viable of these deposits are usually related to the metamorphic reaction between an Mg-carbonate infiltrated by a silica-rich hydrothermal fluid [18, 20, 21, 37]. Intense fractures that increase the permeability of geological fluid flow generally develop near such deposits [18, 20, 21, 37, 38].

Investigating the formation temperature of talc can improve our understanding of its mineralization process. This has previously been done using several methods. These include microthermometric measurements of relevant fluid inclusions (e.g., [39, 40, 79]) and calculations using talc–dolomite oxygen isotope thermometry, assuming that the mineral pairs achieve oxygen isotope equilibrium [21, 36]. In addition, the phase diagram of the CaO–MgO–SiO$_2$–CO$_2$–H$_2$O system has often been referred to for evaluating the formation temperature of talc [5, 35]. The diagram was established based on hydrothermal experiments, geological case studies, and thermodynamic calculations [4, 5, 43, 44]. However, the
temperatures of interest and their corresponding saturation pressures. (cf. reaction (1)). However, large-scale talc mineralization is temperature (200 < 200 °C). As shown here, dolomite could react at temperatures below 200 °C, because CO₂ is a product of the metamorphic reaction (1) and its presence greatly decreases the solubility of SiO₂ in the fluid [80]. CO₂ is a common component in geological fluids and can be either released from magmas (e.g., [81–84]) or generated from the hydrothermal alteration of carbonate (e.g., [85–87]). The oxidation (e.g., [88]) and hydrothermal maturation of organic matter are also natural sources of CO₂ [89, 90]. Therefore, talc mineralization should occur at relatively high temperatures in the presence of CO₂. Secondly, as our results have shown, the reaction rate for reaction (1) increases sharply with increasing temperature, facilitating talc deposits to form at higher temperatures. This study can also contribute to understanding the fault weakening mechanism in the upper crust. The elastic strain accumulation along a fault can be released through a sudden seismic slip (earthquake) or aseismic creep slip [32]. A lower frictional coefficient for a fault will facilitate stable creep, weakening the fault and suppressing the occurrence of strong earthquakes [35]. The frictional coefficient of a fault generally decreases with increasing temperature [35]. Therefore, faults are likely to be weakened due to high temperatures in the deep crust, but not in the cool shallow crust. The pervasive distribution of clay minerals along faults has also been thought to weaken faults [33–35, 91–94], because layered clay minerals exhibit much lower frictional coefficients than other minerals [95]. For example, talc discovered along the San Andreas fault zone is responsible for helping in aiding slippage along the fault [35, 95]. As shown here, dolomite could react at <200 °C with silica-rich fluids traveling along fault planes to form talc and hence might be an important mechanism of fault weakening in carbonate sequences in the upper crust.

4.2. Implications for Hydrothermal Dolomite Reservoir Research. Carbonate rock is the main type of hydrocarbon reservoir worldwide, hosting over 60% of petroleum reserves [31]. Dolomite hydrocarbon reservoirs are important, comprising about half of the carbonate hydrocarbon reservoirs worldwide [96]. Recent research has suggested that hydrothermal alteration can increase the porosity and permeability of dolomite reservoirs substantially and is an important factor affecting the development and distribution of dolomite reservoirs [24, 25, 97–101]. The Tarim basin is one of the most important petroliferous basins in China and contains a lower Palaeozoic carbonate series, which is also an important hydrocarbon reservoir. Recent exploration has shown that silica-rich hydrothermal fluids have infiltrated these carbonate series, improving the physical properties of the reservoirs considerably (e.g., the Shunnan area of the Tarim Basin; [102, 103]). It has been proposed that silica-rich hydrothermal fluids were transported through extensional faults from the deep strata to the shallow carbonate sequence, where they migrated laterally through porous and permeable carbonate formations (~6670 m in the Shunnan area; [104]). Hydrothermal fluids originating in deep basins are generally hot. Microthermometric measurements have indicated that the silica-rich hydrothermal fluids in the Tarim basin reach over 200 °C [101, 103]. Given that the lower part of the lower Palaeozoic sequence is mainly composed of dolomite, silica-rich hydrothermal fluids could react with the dolomite to form talc and thus change the physical properties of the reservoir. Recently, petrologic and diagenetic research have revealed pervasive silicification in Early Cretaceous ultra-deep water carbonate reservoirs in the Atlantic Ocean, offshore from Brazil [105]. The presence of talc, calcite, quartz, and dolomite on the thin-section scale may indicate that the dolomite was strongly corroded by a silica-rich hydrothermal fluid.

Alteration of dolomite to talc will also modify the porosity and permeability of carbonate hydrocarbon reservoirs [29–31]. The silica required for the minor alteration can be provided by either silica-rich hydrothermal fluids or silica (e.g., quartz, chert, and opal) within the carbonate reservoirs [106]. If SiO₂ derives from quartz/chert in the dolomite sequences.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>ΔG² (kJ/mol)</th>
<th>P_sat^b (bar)</th>
<th>Temperature (°C)</th>
<th>ΔG (kJ/mol)</th>
<th>P_sat (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>7.709</td>
<td>0.032</td>
<td>100</td>
<td>−7.083</td>
<td>1.434</td>
</tr>
<tr>
<td>50</td>
<td>4.663</td>
<td>0.124</td>
<td>110</td>
<td>−9.951</td>
<td>1.434</td>
</tr>
<tr>
<td>60</td>
<td>2.771</td>
<td>0.199</td>
<td>120</td>
<td>−12.938</td>
<td>1.987</td>
</tr>
<tr>
<td>70</td>
<td>0.609</td>
<td>0.312</td>
<td>130</td>
<td>−16.032</td>
<td>2.703</td>
</tr>
<tr>
<td>80</td>
<td>−1.778</td>
<td>0.474</td>
<td>140</td>
<td>−19.223</td>
<td>3.615</td>
</tr>
<tr>
<td>90</td>
<td>−4.351</td>
<td>0.702</td>
<td>150</td>
<td>−22.502</td>
<td>4.761</td>
</tr>
</tbody>
</table>

^aΔG refers to the Gibbs free energy of the reaction; ^bP_sat represents the corresponding saturation pressures, which are calculated based on the thermodynamic model proposed by Zhang and Duan [45].
the hydrothermal alteration would increase the porosity of the dolomite reservoirs. McKinley et al. [29] reported that the total volume of minerals within a dolomite reservoir can be reduced by 13% to 17% through the reaction between dolomite and quartz in reaction (1). In addition, the reaction between dolomite and silica-rich hydrothermal fluids can act as an important source of CO$_2$ in hydrocarbon reservoirs. The presence of CO$_2$ can lower the pH of the formation water and thus promote the dissolution of carbonate minerals [60, 107, 108], increasing the porosity of the reservoirs [109–111]. However, the pore throats may be blocked by the formation of talc or other clay minerals [29, 112]. Therefore, more detailed factors should be considered in order to unequivocally evaluate the effects of silica-rich hydrothermal fluids in dolomite reservoirs.

Although talc can form from the interaction between dolomite and silica-rich fluids at low temperatures, it is seldom observed in hydrocarbon reservoirs [29, 31] for the following two reasons. (1) A large amount of CO$_2$ can be produced by the maturation of organic matter and the reaction between carbonate minerals and organic acid [98, 101]. The presence of CO$_2$ decreases the lower thermal stability field of talc [113]. (2) The reaction path is dependent on the composition of the hydrothermal fluid. For example, K$^+$ and A$^{3+}$ are also important components of geological fluids. Montmorillonite instead of talc is more likely to form in the presence of only a small quantity of A$^{3+}$ [41], and the formation of talc can also be inhibited by K$^+$ [29].

4.3. Implications for High P–T Experiment Using Fused Silica Capillary Tubes as Reactors. FSCCs are used to construct synthetic fluid inclusions containing organic and inorganic components [46]. They offer advantages such as being inert to many components, especially acids and S, allowing for the convenient synthesis of fluid inclusions, and facilitating in situ optical and Raman spectroscopic observations (e.g., [57, 114–117]). Fused silica tubes can tolerate relatively high temperatures up to 600°C and pressures up to 300 MPa. As a result, FSCCs are used in many research fields. For example, in addition to construction of synthetic fluid inclusions [46, 53, 118], FSCCs were used in studying the properties of hydrothermal fluids as optical and Raman spectroscopic cells [115–117, 119–121]. FSCCs were also used as reactors in investigating the mechanism of thermochemical sulfate reduction [114] and the decomposition of organic matter [57].

However, SiO$_2$ in the FSCC acted as a reagent in this study and was partially dissolved, as indicated by the pits on the inner surface of the tube (Figures 8(a)–8(d)). The dissolution of silica from FSCCs containing alkali sulfate solutions was also observed after quenching from ≥350°C (Figures 8(e) and 8(f)). The severe dissolution of fused silica can be ascribed to three factors. (1) Amorphous silica is more soluble than quartz, especially at high temperatures. In neutral solutions, its solubility increases sharply with temperature from 100 ppm at 20°C to 1500 ppm at 310°C [74, 122, 123]. (2) Under basic conditions, the solubility of amorphous silica is greatly enhanced by the ionization of silicic acid (H$_4$SiO$_4$ + OH$^-$ → H$_2$SiO$_4$$^-$ + H$_2$O; [124]). (3) SiO$_2$ may act as a reagent as it did in this experiment. The presence of dissolution pits will weaken the mechanical strength of the silica tube. In addition, the presence of dissolved silica can make the system more complicated than expected. Therefore, the solubility and reactivity of silica under hydrothermal conditions should be evaluated before FSCCs are used as reactors.

5. Conclusion

The reactions in the CaMg(CO$_3$)$_2$–SiO$_2$–H$_2$O system at low temperatures were investigated using fused silica tubes as reactors. Results showed that dolomite reacted with a silica-rich fluid to form talc, calcite, and CO$_2$ at ≤200°C and low P$_{CO_2}$. The reaction rate increased with increasing temperature and decreased with rising P$_{CO_2}$. Therefore, high temperature and the presence of a conduit to release CO$_2$ will promote the formation of talc. This experiment has important geological and geochemical implications.

(1) The results confirmed the mechanism of talc mineralization in Mg-carbonate hosted talc deposits. Dolomite reacted with silica-rich hydrothermal fluids to form talc, calcite, and CO$_2$. Talc could form at ≤200°C, whereas previous hydrothermal experiments examining the CaO–MgO–SiO$_2$–CO$_2$–H$_2$O system were mainly conducted at >250°C. However, considering the effect of temperature on the reaction rate, and other geological conditions, massive talc deposits are still more likely to form at higher temperatures. The formation of talc along a fault in a Mg-carbonate formation will also weaken the fault, thus preventing strong earthquakes.

(2) Talc in carbonate reservoirs can indicate the activity of silica-rich hydrothermal fluids. Fluid-aided alteration of dolomite can change the physical properties of dolomite reservoirs substantially. The reaction between dolomite and quartz within the carbonate can decrease the total volume of minerals by 13%–17%. The generation of CO$_2$ can promote the dissolution of carbonate minerals elsewhere under the appropriate conditions, increasing the porosity and permeability of carbonate reservoirs. However, talc minerals may block pore throats in the reservoirs. Therefore, additional factors need to be considered when evaluating the effects of CaMg(CO$_3$)$_2$–SiO$_2$–H$_2$O interactions on the physical properties of carbonate reservoirs.

(3) The solubility and reactivity of silica should be considered when using fused silica tubes as reactors in high P–T experiments. The dissolution of silica will increase the complexity of the system and weaken the mechanical strength of the tube.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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**References**


R.G.EggertandD.M.Kerrick,”Metamorphic equilibrium in the


H. M. Lamadrid, Geochemistry of fluid-rock processes [Doctoral dissertation], Virginia Polytechnic Institute and State University, Blacksburg, VA, USA, 2016.


Z. Duan and D. Li, “Coupled phase and aqueous species equilibrium of the H₂O–CO₂–NaCl–CaCO₃ system from 0 to 250°C, 1 to 1000 bar with NaCl concentrations up to saturation of halite,” Geochimica et Cosmochimica Acta, vol. 72, no. 20, pp. 5128–5145, 2008.


