Fractionation of carbon and hydrogen isotopes of TSR-altered gas products under closed system pyrolysis

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Thermochemical sulfate reduction (TSR) is common in marine carbonate gas reservoirs, leading to complicated isotope characteristics of TSR-altered gas. This study aims to better understand how TSR affects the geochemical and isotopic compositions of alkanes in pyrolysis products. Pyrolysis of TSR were conducted with crude oil, nonane (C9) and methylnaphthalene (MN) in the presence of MgSO₄ solution at temperatures of 350 °C, 360 °C, and 370 °C for different durations of 4–219 h in a closed system. Results show that carbon and hydrogen isotope compositions of alkane gas resulting from TSR (pyrolysis with crude oil and MgSO₄) became heavier with increasing carbon number, i.e., δ¹³C₁ < δ¹³C₂ < δ¹³C₃ and δ²H–C₁ < δ²H–C₂ < δ²H–C₃. Compared with the δ¹³C₁, δ¹³C₂ and δ¹³C₃ increased in a much wider range as heating continued. Carbon and hydrogen isotopes of alkane gas produced by TSR became heavier with increasing gas souring index. Values for δ¹³C₁–δ¹³C₂ and δ²H–C₁–δ²H–C₂ typically decreased as oil and C₉ underwent thermal cracking. Comparative experiments using C₉ in the presence of MgSO₄ produced partially reversed carbon isotope series (δ¹³C₁ > δ¹³C₂), which, for the first time, confirmed the ability of TSR to cause isotopic reversal from pyrolysis. The residual heavy alkanes gradually became ¹³C-enriched during TSR, which increased δ¹³C values and changed the partially reversed isotope sequence to a positive sequence (δ¹³C₁ < δ¹³C₂). The discovery of a partial reversal of the carbon isotope series of alkane gases through pyrolysis will further deepen the understanding of TSR-altered natural gas.

H₂S is a harmful gas usually generated in deep marine carbonate gas reservoirs¹–⁶, which poses significant challenges for the safe production of natural gas. High concentrations of H₂S in gas reservoirs are mainly produced by thermochemical sulfate reduction (TSR)¹⁷–¹¹, during which sulfate is reduced by organic matters and/or hydrocarbons to H₂S and CO₂. In general, hydrocarbons with higher carbon number will react more readily with sulfate¹²–¹⁴. The reaction equations can be expressed as follows:

\[ \text{SO}_4^{2-} + \text{CH}_4 \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{S} + 2\text{H}_2\text{O} \]

\[ 3\text{SO}_4^{2-} + 4\text{C}_2\text{H}_6 \rightarrow \text{CO}_3^{2-} + 3\text{H}_2\text{S} + 4\text{CH}_4 + \text{CO}_2 + \text{H}_2\text{O} \]

\[ 3\text{SO}_4^{2-} + 2\text{C}_3\text{H}_8 \rightarrow 3\text{CO}_3^{2-} + 3\text{H}_2\text{S} + 2\text{CH}_4 + \text{CO}_2 + \text{H}_2\text{O} \]

\[ 3\text{SO}_4^{2-} + 4\text{C}_4\text{H}_{10} + \text{H}_2\text{O} \rightarrow 5\text{CO}_3^{2-} + 5\text{H}_2\text{S} + 8\text{CH}_4 + 3\text{CO}_2 \]

The effect of TSR has been studied extensively by characterising natural gas components, stable isotopes such as carbon, hydrogen, and sulfur, as well as inclusions and sulfur-bearing minerals⁹–¹⁰, Cai et al.²³–²⁴ concluded

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that CH$_4$ can be oxidised when the dryness coefficient is greater than 0.97 and presented fractionation equations for TSR in the presence of methane and ethane. Machel et al. proposed an initiation temperature of 100–140 °C for TSR, and Worden et al. thought that the initiation temperature for TSR was 140 °C. Amrani et al. and Meshoulam et al. systematically investigated the isotopic composition of sulfur compounds during TSR and proposed that the composition of sulfur isotopes may reflect the degree of TSR. Hao et al. Liu et al. and Cai et al. characterised geochemical properties of marine gas in the Sichuan Basin, China, and found that heavy hydrocarbons were preferentially involved in the TSR reaction compared with CH$_4$, which can increase the dryness coefficient of natural gas. TSR was also found to gradually cause partial carbon isotope reversal of the positive alkane gas series. Liu et al. discovered that hydrogen isotope fractionation for CH$_4$ generated by TSR via hydrogen isotope exchange between water and hydrocarbons was greater than that for CH$_4$ directly generated from kerogen. Although a carbon isotope fractionation model for alkane gas in H$_2$S-bearing gas reservoirs, such as the commonly observed pattern of the carbon isotope series of CH$_4$ and C$_2$H$_6$ that changes from positive to reversed and then back to positive, has been established, the hydrogen isotope fractionation of alkane gas has not been explored by laboratory pyrolysis. Liu et al. proposed that the rock salt and/or brine may play an important role for the occurrence of TSR based on the formation mechanism of H$_2$S-enriched gas reservoirs in the Sichuan Basin, China. Cross et al. reported, based on laboratory simulations, that temperature was the key factor for the occurrence of TSR, whereas pressure had a minor impact. Pan et al. conducted a high-temperature, long-time, step-by-step thermal cracking simulation with organic matter and Fe$_2$O$_3$, MgSO$_4$, and a mixture of both. They found that CH$_4$ was produced by TSR in the presence of heavy hydrocarbons and that isotope fractionation became more pronounced with increasing carbon number. Based on a thermal cracking simulation, Zhang et al. proposed that the initiation temperature for TSR was affected by the chemical composition of crude oil, and low molar ratios of water and MgSO$_4$ were favorable to the reaction. MgSO$_4$ affects pH, which in turn increases the concentration of the active sulfate species HSO$_4^{-}$.

Amrani et al. and Pan et al. conducted using a solution of crude oil, buffer, and MgSO$_4$ at temperatures of 350 °C and 370 °C. For each condition, the experiment was conducted for the pre-set reaction time. The gold capsules were then taken out of the autoclaves and quenched. Fluctuations in length, 6 mm in diameter) under argon gas. The gold capsules were placed in different autoclaves that were connected to each other. The pressure of the experimental system was maintained at 50 MPa to simulate the conditions under which most TSR occurs. After the reaction temperature was increased from room temperature (18 °C) to 200 °C at a rate of 20 °C/h, it was kept constant at 200 °C for half an hour to stabilise the system temperature. The temperature was then increased to the target temperature at a rate of 20 °C/h, and held constant for the pre-set reaction time. The gold capsules were then taken out of the autoclaves and quenched. Fluctuations of temperature and pressure in the autoclaves were 0.5 °C and 1 MPa, respectively. To compare and analyse the
effects of TSR, experiments were also conducted on nonane (C9) and methylnaphthalene (MN) at 360 °C following the same procedures. The amount of C9 and MN added in the experiments were both about 10 mg.

The chemical compositions of gas products were analysed using an Agilent 6890 N gas chromatograph equipped with a Poraplot Q column (30 mm × 0.25 mm × 0.25 μm). Helium was used as the carrier gas. The oven temperature was programmed as follows: an initial temperature of 50 °C for 2 min, raised to 180 °C at the rate of 4 °C/min, then held constant at 180 °C for 15 min. Deviation between replicate analyses was less than 1%. The stable carbon isotopic composition was analysed with an Isochrom II GC-IRMS isotope ratio mass spectrometer equipped with a Poraplot Q column. Helium was used as the carrier gas. The oven temperature program was started at 50 °C, held for 2 min, raised to 150 °C at a rate of 15 °C/min, and held at 150 °C for 8 min. Each sample was analysed twice with a deviation between the analyses of less than 0.3‰. Stable hydrogen isotope analyses were conducted with a Finnigan Delta Plus XL isotope ratio mass spectrometer equipped with a Dimythe column. The oven temperature was programmed as follows: an initial temperature of 40 °C held for 8 min, raised to 110 °C at a rate of 3 °C/min, then held at 110 °C for 2 min. Each analysis was conducted twice, with a deviation between the analyses of less than 4‰. Detailed results are listed in Tables 1 and 2.

### Results

**Yields of reaction products under different conditions.** The yields of all gaseous alkane produced from thermal cracking of crude oil at 360 °C increased with longer heating time, with CH4 exhibited the highest yields of 1.00–8.09 ml/g. The yields of H2S, CO2 and H2 also increased with increasing reaction time, but no H2S was detected in the first 40 h (Table 1). During thermal cracking of a mixture of crude oil, MgSO4 and buffer
at 360 °C (M15–M20), yields of CH₄ and C₂H₆ increased at first and then decreased as the reaction continued. The yield of CH₄ was in the range of 9.94–40.52 ml/g. The yields of C₃H₈, C₄H₁₀, and other heavy gaseous hydrocarbon products gradually decreased with longer heating time. The yield of H₂S increased at first and then decreased in the range of 47.92–378.63 ml/g. The CO₂ yield increased from 41.38 to 190.38 ml/g with time. The yield of H₂ decreased from 0.23 to 0.12 ml/g (Table 1) with increasing heating time. These results suggest that the presence of sulfate significantly increased the yields of H₂S and CO₂.

### Table 2. Carbon and hydrogen isotope compositions of the products of the thermal cracking simulation experiments. Note: n.d. no detection.

| Reaction condition | No | Time (h) | δ¹³C (‰, VPDB) | δ²H (‰, VSMOW) |
|--------------------|----|----------|----------------|----------------|
|                    |    |          | CO₂ | CH₄ | C₂H₆ | C₃H₈ | CH₄ | C₂H₆ | C₃H₈ |
| 360 °C oil         |    |          |     |     |      |      |     |      |      |
| M-9                | 10 | n.d      | -55.8 | -37.2 | -35.6 | -272 | -203 | -173 |
| M-10               | 24 | -22.6     | -51.3 | -35.9 | -34.5 | -274 | -204 | -174 |
| M-11               | 40 | -25.6     | -51.5 | -36.9 | -35.5 | -277 | -202 | -181 |
| M-12               | 72 | -24.4     | -49.1 | -35.7 | -34.7 | -278 | -209 | -184 |
| M-13               | 219 | -28.5    | -48.4 | -36.8 | -35.2 | -262 | -207 | -173 |
| 350 °C oil + MgSO₄ + buffer |    |          |     |     |      |      |     |      |      |
| M-32               | 19.5 | -20.7     | -42.7 | -35.9 | -33.5 | -237 | -169 | -141 |
| M-33               | 42 | -23.4     | -40.9 | -33.6 | -29.8 | -232 | -159 | -126 |
| M-34               | 79.5 | -24.6     | -39.2 | -31.3 | -24.9 | -242 | -140 | -129 |
| M-35               | 172 | -25.0     | -37.0 | -21.2 | n.d.  | -216 | -101 | n.d.  |
| 360 °C oil + MgSO₄ + buffer |    |          |     |     |      |      |     |      |      |
| M-37               | 10 | -15.7     | -41.3 | -34.3 | -33.1 | -226 | -174 | -136 |
| M-38               | 24 | -23.1     | -36.9 | -32.9 | -30.4 | -227 | -153 | -114 |
| M-39               | 40 | -25.1     | -36.7 | -31.8 | -26.5 | -224 | -134 | -105 |
| M-40               | 72 | -25.6     | -36.3 | -23.7 | n.d.  | -214 | -102 | n.d.  |
| 370 °C oil + MgSO₄ + buffer |    |          |     |     |      |      |     |      |      |
| M-42               | 5.5 | -19.0     | -38.8 | -34.1 | -32.8 | -228 | -173 | -130 |
| M-43               | 11 | -22.9     | -38.1 | -33.6 | -31.8 | -231 | -153 | -112 |
| M-44               | 21 | -25.0     | -35.0 | -29.8 | -23.4 | -216 | -122 | -102 |
| M-45               | 44 | -25.8     | -33.7 | -21.8 | n.d.  | -199 | -106 | n.d.  |
| 360 °C C₉ + MgSO₄ + buffer |    |          |     |     |      |      |     |      |      |
| M-46               | 4 | -2.1      | n.d  | n.d  | n.d  | n.d  | n.d  | n.d  |
| M-47               | 10 | -10.5     | n.d  | n.d  | n.d  | n.d  | n.d  | n.d  |
| M-48               | 24 | -23.3     | -29.2 | -31.6 | -30.1 | -216 | -184 | -158 |
| M-49               | 40 | -24.8     | -29.3 | -28.5 | -26.9 | -213 | -152 | -139 |
| M-50               | 72 | -25.8     | -29.1 | -27.6 | -26.2 | -211 | -132 | -123 |
| 360 °C MN + MgSO₄ + buffer |    |          |     |     |      |      |     |      |      |
| M-51               | 10 | -2.5      | n.d  | n.d  | n.d  | n.d  | n.d  | n.d  |
| M-52               | 24 | -5.7      | n.d  | n.d  | n.d  | n.d  | n.d  | n.d  |
| M-53               | 40 | -7.7      | n.d  | n.d  | n.d  | n.d  | n.d  | n.d  |
| M-54               | 72 | -11.8     | n.d  | n.d  | n.d  | n.d  | n.d  | n.d  |
| M-55               | 219 | -17.5    | n.d  | n.d  | n.d  | n.d  | n.d  | n.d  |

Compositions of main reaction products under different conditions. During thermal cracking of crude oil at 360 °C, the relative content of alkane gases generally increased with longer heating time, while some decreased as the heating time was increased to 219 h (Table 1). The relative content of CH₄ in the gaseous reaction products ranged from 39.84 to 48.02%, while that of CO₂ exhibited a decreasing trend with increasing heating time. Only trace amounts of H₂S were detected after a heating time of 72 h and 219 h (Table 1). Similarly, it was found that during thermal cracking of a mixture of crude oil, MgSO₄, and buffer at 360 °C (M15–M20), the relative content of CH₄ and C₂H₆ first increased and then decreased as the reaction continued. The relative content of CH₄ varied between 6.44% and 13.54%. Concentration of heavy hydrocarbon gases, including C₃H₈ and C₄H₁₀, decreased with longer heating time. The relative content of H₂S and CO₂ remained high during the entire reaction and increased with increased heating time. In all cases, the relative content of H₂S and CO₂ produced from thermal cracking of crude oil increased because of TSR. Thermal cracking (M46–M55) of C₉ and MN in the presence of sulfate also produced high amounts of CO₂ and low amounts of alkane gases (Table 1). To facilitate a comparison with other research and gas geochemical characteristics under actual geological conditions, we modelled the Easy%Ro (Table 1).

Isotopic composition of main reaction products produced under different conditions. Carbon and hydrogen isotopic compositions gaseous reaction products resulting from thermal cracking of various hydrocarbons under a range of experimental conditions are summarised in Table 2 above.
Discussion

Yields and relative contents of TRS reaction products. Yield of CH$_4$, CO$_2$, and H$_2$S from direct thermal cracking of crude oil are significantly lower than those resulting from cracking of a crude oil and MgSO$_4$ solution under similar experimental conditions (Table 1). Increased yields of gaseous products might be attributed to the involvement of sulfur in the reaction, which may also trigger TSR$^{37,38}$, converting heavier hydrocarbons into CH$_4$, CO$_2$, and H$_2$S$^{12}$. Since the activity energy for alteration of hydrocarbons TSR is lower than that for thermal cracking$^{38}$, gas yields from the crude oil and MgSO$_4$ solution is higher than those for thermal cracking of crude oil alone under the same pyrolysis conditions (temperature and time). Compared to the increase of CH$_4$ yield during thermal cracking of crude oil, the CH$_4$ yield during thermal cracking of crude oil and MgSO$_4$ rapidly increased in the first 72 h at 360 °C, and then slightly decreased (Fig. 1a), which may be related to the oxidation of methane to H$_2$S and CO$_2$ during TSR$^{12,27}$. The H$_2$ yield from thermal cracking of crude oil gradually increased with time up to 219 h, but the H$_2$ yield from crude oil and MgSO$_4$ decreased from 0.23 ml/g to 0.15 ml/g until 72 h, and remained almost constant at less than 0.15 ml/g as the reaction continued (Fig. 1b). This observation suggests that TSR may have a very limited effect on H$_2$ formation during pyrolysis. During the reaction of crude oil and MgSO$_4$, the yield of H$_2$S and CO$_2$ increased rapidly before until 72 h (Fig. 1c, d), after which the CO$_2$ yield remained almost constant as the H$_2$S yield decreased slightly. Because the presence of a MgSO$_4$ solution introduces sulfur and oxygen into the pyrolysis system, the yield of H$_2$S and CO$_2$ increased$^{37,27}$. After 72 h, the yield of CH$_4$ and H$_2$S slightly decreased (Fig. 1a, d), indicating that the TSR process consumed...
these components to some extent and led to the production of CO$_2$ and sulfur$^{27,40,43}$. The dryness coefficient (C$_1$/C$_{1–5}$) of the gas formed by thermal cracking of crude oil is low, while the dryness coefficient of gas formed during pyrolysis with TSR is higher, accompanied by an increased CH$_4$ content (Table 1), which further indicates that oxidation of heavy hydrocarbons by TSR will generate CH$_4$^{12,40,43}.

Because the source gas of CO$_2$ and H$_2$S is produced during the TSR process, the ratios of CH$_4$/CO$_2$ and (CO$_2$ + H$_2$S)/(CO$_2$ + H$_2$S + ∑C$_{1–5}$) were used to investigate variations of the chemical composition of gas altered by TSR. As shown in Fig. 2, ratios of (CO$_2$ + H$_2$S)/(CO$_2$ + H$_2$S + ∑C$_{1–5}$) sharply decrease with increasing CH$_4$/CO$_2$ ratios. The ratio of CH$_4$/CO$_2$ for crude oil, C$_9$, and MN with MgSO$_4$ is less than 1.0, while the ratio of CH$_4$/CO$_2$ for thermal cracking of crude oil is above 1.0 (Fig. 2a). In contrast to the ratios of CH$_4$/CO$_2$ and (CO$_2$ + H$_2$S)/(CO$_2$ + H$_2$S + ∑C$_{1–5}$) for crude oil, the same ratios for C$_9$ and MN with MgSO$_4$ are less than 1.0, and the ratio of (CO$_2$ + H$_2$S)/(CO$_2$ + H$_2$S + ∑C$_{1–5}$) decreases as the CH$_4$/CO$_2$ ratio increases. Compared to the wide range of ratios for pyrolysis of crude oil and MgSO$_4$, the ratio of CH$_4$/CO$_2$ and (CO$_2$ + H$_2$S)/(CO$_2$ + H$_2$S + ∑C$_{1–5}$) for C$_9$ or MN with MgSO$_4$ shows a smaller range (Fig. 2b). These variations of CH$_4$/CO$_2$ and (CO$_2$ + H$_2$S)/(CO$_2$ + H$_2$S + ∑C$_{1–5}$) caused by thermal cracking of crude oil and different degrees of TSR alteration during pyrolysis are similar to those caused by thermal cracking and TSR alteration of natural gas in gas reservoirs$^{1,20,21}$. Thermal cracking of crude oil produced more CH$_4$, while TSR increased the yield of CO$_2$ and H$_2$S. The content of CH$_4$ in alkane gas further increased with increased thermal cracking. In contrast, the CO$_2$ and H$_2$S contents varied at different stages of TSR. Based on the properties of H$_2$S-bearing natural gas and previous simulation results$^{1,6,12,23,40}$, variations in gas produced by TSR pyrolysis are similar to those of H$_2$S-bearing natural gas altered by TSR.

Fractionation characteristics of carbon and hydrogen isotopes during TSR. The carbon isotopic composition of produced CO$_2$ from crude oil, C$_9$, and MN with MgSO$_4$ at different temperature is negatively correlated with heating time. The δ$^{13}$C$_{CO_2}$ value gradually decreased from −2.1‰ (C$_9$, 360 °C, 4 h) to −28.5‰ (crude oil, 360 °C, 219 h) (Table 2, Fig. 3). The carbon isotopic composition of CO$_2$ from crude oil, C$_9$, and MN with MgSO$_4$ became significantly lighter over time until about 20 h heating time. After that, the δ$^{13}$C$_{CO_2}$ value for crude oil and C$_9$ with MgSO$_4$ remained mostly constant, which is similar to what happens during thermal cracking of crude oil. The decrease of δ$^{13}$C$_{CO_2}$ values during the first 20 h can be attributed to a greater fractionation of carbon isotopes at the onset of TSR$^{12}$. After 20 h, the carbon isotope fractionation gradually reached a balance between CO$_2$ and CH$_4$. Although the δ$^{13}$C$_{CO_2}$ value for CO$_2$ produced from MN with MgSO$_4$ decreased with heating time, CO$_2$ was relatively more enriched in $^{13}$C when compared to crude oil, C$_9$, and MgSO$_4$. In addition to having a heavy carbon isotopic composition, MN was also the most easily oxidised component during TSR. Due to the addition of MgSO$_4$ to MN, MN was quickly oxidised by TSR and converted to gas with CO$_2$ as the main component. Concentrations of heavy hydrocarbon gases were below the detection limit of the instruments. In summary, the transformation of crude oil, C$_9$, and MN by TSR converts $^{12}$C-rich hydrocarbons to $^{12}$C-enriched CO$_2$, which might be converted to $^{12}$C-rich calcite and precipitated in gas reservoirs$^{8,21}$.

The δ$^{13}$C$_1$ of gaseous products from simulation experiments of different mixtures at various temperatures is shown in Fig. 3. With increasing carbon numbers, the carbon isotopes of alkane gas from thermal cracking of crude oil at a pyrolysis temperature of 360 °C became heavier in the order of δ$^{13}$C$_1$ < δ$^{13}$C$_2$ < δ$^{13}$C$_3$. The δ$^{13}$C$_1$ values gradually increased over a relatively large range, while both δ$^{13}$C$_2$ and δ$^{13}$C$_3$ increased in a more narrow range as heating time increased (Fig. 4a). The carbon isotopic composition of alkane gas produced from crude oil and MN with MgSO$_4$ at different temperature and heating times is shown in Fig. 4. With increasing carbon numbers, the carbon isotopes of alkane gas from thermal cracking of crude oil at a pyrolysis temperature of 360 °C became heavier in the order of δ$^{13}$C$_1$ < δ$^{13}$C$_2$ < δ$^{13}$C$_3$. The δ$^{13}$C$_1$ values gradually increased over a relatively large range, while both δ$^{13}$C$_2$ and δ$^{13}$C$_3$ showed larger increase as the reaction proceeded (Fig. 4b–d). It is obvious that the δ$^{13}$C$_1$ of alkane gas produced in the presence of a MgSO$_4$ solution is higher than that produced during comparative experiments without MgSO$_4$. In a single thermal system, the δ$^{13}$C$_1$ of alkane gas from thermal cracking of crude oil gradually becomes higher with increasing carbon number, and is linearly correlated with the reciprocal of the carbon number (1/n)$^{44}$. The reduction in the variation of δ$^{13}$C$_1$...
values produced by TSR alteration indicates that these hydrocarbons are rapidly oxidised to \( \text{CH}_4 \) with a \( \delta^{13}\text{C}_1 \) value similar to the source material. The TSR process leads to a \( ^{13}\text{C} \) increase in \( \text{CH}_4 \), producing a carbon isotopic composition more similar to that of crude oil \( (\sim -32.8\%o) \). In contrast, \( \text{CO}_2 \) becomes gradually enriched in \( ^{12}\text{C} \) due to equilibrium fractionation of carbon isotopes between \( \text{CO}_2 \) and \( \text{CH}_4 \). Overall, the variation of \( \delta^{13}\text{C}_1 \) is significantly smaller in the presence of \( \text{MgSO}_4 \), during TSR of crude oil, similar to that of \( \text{H}_2\text{S} \)-bearing alkane gas in the Sichuan Basin, where natural gas shows a heavy carbon isotopic composition of \( \text{CH}_4 \). The carbon isotope composition of \( \text{CO}_2 \) formed in the presence of TSR is lighter than that formed in the absence of TSR, because TSR will oxidise a large portion of the hydrocarbons, leading to more intense \( \delta^{13}\text{C}_{\text{CO}_2} \) fractionation. Therefore, \( \delta^{13}\text{C}_{\text{CO}_2} \) values related to crude oil cracking are relatively heavier, while \( \delta^{13}\text{C}_{\text{CO}_2} \) will be relatively enriched in \( ^{12}\text{C} \) during pyrolysis (with TSR) in the presence of a \( \text{MgSO}_4 \) solution (Table 2).

Our experiments show for the first time that the carbon isotopic composition of gas produced from \( \text{C}_9 \) with \( \text{MgSO}_4 \) became partially reversed to \( \delta^{13}\text{C}_1 > \delta^{13}\text{C}_2 < \delta^{13}\text{C}_3 \) after a heating time of 24 h. The \( \text{CH}_4 \) produced from \( \text{C}_9 \) with \( \text{MgSO}_4 \) shows an extremely small variation in \( \delta^{13}\text{C}_1 \) values. The variation of \( \delta^{13}\text{C}_2 \) became larger than that of \( \delta^{13}\text{C}_3 \) with longer reaction time (Fig. 4e). This partial reversal of the carbon isotope series of alkane gas is similar to that of \( \text{H}_2\text{S} \)-bearing alkane gas in the Sichuan Basin, Ordos Basin, and other locations. Therefore, it is likely that the partial reversal of the carbon isotope series of alkane gas in \( \text{H}_2\text{S} \)-bearing natural gas reservoirs happens when light hydrocarbons are altered by TSR. The isotopic composition of reaction products of pyrolysis with \( \text{MN} \) could not be detected due to the low content of alkane gases.

Figure 5 shows the variation of \( \delta^{13}\text{C} \) in alkane gases produced from crude oil at 360 °C, from a mix of crude oil and \( \text{MgSO}_4 \) at 350, 360, and 370 °C, as well as from a mix of \( \text{C}_9 \) and \( \text{MgSO}_4 \) at 360 °C. Similar to the \( \delta^{13}\text{C} \) values, the hydrogen isotopic composition of alkane products from crude oil and a mixture of crude oil and \( \text{MgSO}_4 \) became heavier with increasing carbon number under all conditions, i.e. \( \delta^{13}\text{H}–\text{C}_1 < \delta^{13}\text{H}–\text{C}_2 < \delta^{13}\text{H}–\text{C}_3 \). The \( \delta^{13}\text{H}–\text{C}_1 \) values gradually increased in a relatively large range, and both \( \delta^{13}\text{H}–\text{C}_2 \) and \( \delta^{13}\text{H}–\text{C}_3 \) increased in a narrower range as heating time increased (Fig. 5a). The \( \delta^{13}\text{H}–\text{C}_1 \) value for a mix of crude oil and \( \text{MgSO}_4 \) gradually increased over time, but in a relatively small range for each temperature. The \( \delta^{13}\text{H}–\text{C}_2 \) and \( \delta^{13}\text{H}–\text{C}_3 \) values also

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**Figure 4.** The \( \delta^{13}\text{C} \) values of products from simulation experiments with crude oil at 360 °C (a), a mixture of crude oil and \( \text{MgSO}_4 \) at temperatures of 350 °C (b), 360 °C (c), 370 °C (d), and a mixture of \( \text{C}_9 \) and \( \text{MgSO}_4 \) at 360 °C (e).
increased with heating time, but in a much larger range compared with that of δ²H–C₁ (Fig. 5b–d). The variation of δ²H–C₂ is slightly larger than that of δ²H–C₃. The δ²H–C₁ values remained almost constant during the TSR alteration of C₉, while the δ²H–C₂ values show much larger variations. The δ²H–C₃ show the largest variations, but a reversed trend of the hydrogen isotopic composition of alkane gas was not observed during pyrolysis (Fig. 5e). These results indicate that the TSR can reduce the variation of δ²H–C₁, possibly due to the similar hydrogen isotopic composition of the reaction product (C₁ gas) and that of the precursor and/or the involvement of hydrogen derived from water. The δ²H–Cₙ fractionation could not be accurately calculated because of a lack of the hydrogen isotopic composition of H₂ and H₂S. However, TSR of crude oil in the presence of MgSO₄ greatly reduced the variation of δ²H–C₁, which is consistent with the characteristics of H₂S-bearing alkane gas in the reservoirs of the Sichuan Basin, China. In general, hydrogen isotope fractionation during pyrolysis system may be more complicated than fractionation of carbon isotopes, because hydrogen contributes both to formation of alkane gas and H₂, while also providing hydrogen for the formation of H₂S. More importantly, the presence of water may provide an important hydrogen during pyrolysis.

These results suggest that TSR can alter both the carbon and hydrogen isotopic composition of gaseous alkane products, and even lead to a reversed trend of the carbon isotope series of CH₄ and C₂H₆ for a mix of C₉ and Mn with a MgSO₄ solution, which lead to production of mainly H₂S and CO₂. TSR is more sensitive to Mn, which makes it possible that Mn can be completely oxidised into CO₂ and H₂S (Table 1). The smallest variation of both carbon and hydrogen isotopic compositions was observed for CH₄, and was closest to that of the precursor. The heavier carbon isotopic composition of the precursor and C₂H₆ produced from thermal cracking initially led to a reversed

Figure 5. The δ²H–Cₙ of gaseous products from simulation experiments with crude oil at 360 °C (a), a mixture of crude oil and MgSO₄ at the temperature 350 °C (b), 360 °C (c), and 370 °C (d), as well as a mixture of C₉ and MgSO₄ at 360 °C (e).
Figure 6. The plot of \( \frac{H_2S}{H_2S + \Sigma C_{1-5}} \) versus \( CO_2 \) of simulation products.

Figure 7. The plot of \( \frac{H_2S}{H_2S + \Sigma C_{1-5}} \) versus \( \delta^{13}C_{CO_2} \) of simulation products.

Figure 8. The plot of \( \frac{H_2S}{H_2S + \Sigma C_{1-5}} \) versus \( \delta^{13}C_1 \) (a), \( \delta^{13}C_2 \) (b), \( \delta^{13}C_3 \) (c), \( \delta^{13}C_1 - \delta^{13}C_2 \) (d) of alkane gas products from simulation experiments under different conditions.
carbon isotope series of the alkane gas (Table 2, M-48). However, the temperature of our experiments (360 °C) was much higher than that in natural geological environments. Therefore, heavy hydrocarbons enriched in $^{12}$C tended to become unstable, and were subject to thermal cracking, which led to isotope fractionation. $^{13}$C was enriched in the residual heavy hydrocarbons, and the effect of fractionation was larger than that for CH$_4$ during TSR, changing the carbon isotope sequence back to positive.

**Gas souring index (GSI) and carbon and hydrogen isotope fractionation of alkane gas.** Because H$_2$S can be produced during TSR, the gas souring index (GSI), i.e., $\frac{H_2S}{(H_2S+\sum C_{1-5})}$, has been used as an indicator for the occurrence and degree of TSR$^{46}$. The variation of the GSI at different stages of TSR can be established by statistical analysis of H$_2$S-bearing natural gas samples$^{45}$. To reproduce the variation of molecular and isotopic compositions of H$_2$S-bearing natural gas during TSR, the GSI and carbon and hydrogen isotope fractionation mechanism of alkane gas were studied during pyrolysis at different temperatures with various heating times.

During thermal cracking of crude oil, a very small amount of H$_2$S with minor CO$_2$ was produced, indicating that no TSR occurred during direct thermal cracking of crude oil. In contrast, the CO$_2$ yield gradually increased with a larger GSI (> 0.6) for TSR involving a mixture of crude oil and MgSO$_4$ solution, and increased rapidly with further increasing GSI (Fig. 6), which is similar to the relationship between GSI and CO$_2$ content of H$_2$S-bearing natural gas$^{20}$. The $\delta^{13}$CO$_2$ values remained nearly constant but gradually decreased with increasing GSI during thermal cracking due to the presence of TSR (Fig. 7). This phenomenon can be attributed to TSR,

**Figure 9.** The plot of $\frac{H_2S}{(H_2S+\sum C_{1-5})}$ versus $\delta^2$H–C$_1$ (a), $\delta^2$H–C$_2$ (b), $\delta^2$H–C$_3$ (c) and $\delta^2$H–C$_1$–$\delta^2$H–C$_2$ (d) of alkane gas products from simulation experiments under different conditions.

**Figure 10.** The plot of $\delta^{13}$C$_1$–$\delta^{13}$C$_2$ versus $\delta^2$H–C$_1$–$\delta^2$H–C$_2$ of alkane gas products from simulation experiments under different conditions.
which preferentially incorporates $^{12}$C from hydrocarbons into CO$_2$ leading to $^{12}$C-enrichment with increasing TSR intensity 44.

Figure 8 shows the relationship between the gas souring index and δ$^{13}$C$_1$, δ$^{13}$C$_2$, and δ$^{13}$C$_3$. The direct thermal cracking of crude oil produced only a small amount of H$_2$S due to low sulfur content of the crude oil, resulting in a GSI of less than 0.1. The GSI significantly increased with the addition of MgSO$_4$ solution to the crude oil to above 0.6 under different conditions. Meanwhile, the carbon isotopic composition of alkane gas became larger with increasing TSR intensity, i.e., longer reaction time (Fig. 8). The carbon isotopic composition of the alkane gas revealed that the δ$^{13}$C$_1$ variation of CH$_4$ produced in the presence of MgSO$_4$ was much lower than that of C$_2$H$_6$. The carbon isotope composition changed more significantly with the increasing GSI and longer heating time. Therefore, during TSR, the variation of δ$^{13}$C$_1$ became smaller, compared with that of δ$^{13}$C$_2$ and δ$^{13}$C$_3$. The δ$^{13}$C$_1$–δ$^{13}$C$_2$ difference became higher with increasing GSI, which is completely different from that of natural gas formed by direct thermal cracking of crude oil. During thermal cracking of crude oil, the carbon isotope composition of gaseous products gradually becomes more similar with increasing carbon number 45.

The δ$^{2}$H–C$_n$ values of alkane gas show a variation similar to the δ$^{13}$C$_n$ values, with increasing GSI during the TSR process. The range of δ$^{2}$H–C$_1$ values is fairly low, while that of δ$^{2}$H–C$_2$ is higher, especially for the TSR of C$_6$ whose δ$^{2}$H–C$_1$ remained almost constant (Fig. 9). Similar to the carbon isotopic composition, the δ$^{2}$H–C$_1$–δ$^{2}$H–C$_2$ difference increased as the gas souring index became larger, indicating that TSR can lower δ$^{2}$H–C$_1$ values and increase those of δ$^{2}$H–C$_2$, producing an abnormal hydrogen isotope composition of alkane gas, which is only characteristic of thermal cracking of crude oil. Both δ$^{13}$C$_1$–δ$^{13}$C$_2$ and δ$^{2}$H–C$_1$–δ$^{2}$H–C$_2$ became lower with increasing TSR intensity. However, in the case of oil cracking, δ$^{13}$C$_1$–δ$^{13}$C$_2$ and δ$^{2}$H–C$_1$–δ$^{2}$H–C$_2$ show the opposite trend with increasing TSR (Fig. 10). This observation may be caused by the small variation of the
\( \delta^{13}C_1 \) and \( \delta^{2H}–C_1 \) produced by TSR, which is similar to the isotopic composition of the precursor. The carbon and hydrogen isotopic composition of \( C_2H_6 \) was more heavily affected by the thermal cracking than oxidation by TSR. Therefore, the variation of its carbon and hydrogen isotope compositions is higher. In addition, the difference in the carbon and hydrogen isotopic composition between \( CH_4 \) and \( C_2H_6 \) gradually increased with a larger GSI.

Although TSR alteration decreased the variation of both carbon and hydrogen isotope compositions of \( CH_4 \), as compared with products from direct thermal cracking of crude oil, \( \delta^{13}C_2 \) became larger with increasing \( \delta^{13}C_1 \). The \( \delta^{13}C_2 \) versus \( \delta^{13}C_1 \) plot (Fig. 11a), showed positive correlations, with the latter having a higher correlation. The \( \delta^{13}C_1 \) and \( \delta^{13}C_{CO_2} \) values are negatively correlated (Fig. 11c), possibly because the carbon isotopic composition of \( CO_2 \) produced by TSR is enriched in \( ^{12}C \). For \( CH_4, C_2H_6, \) and \( C_3H_8, \) the \( \delta^{13}C_2 \) and \( \delta^{13}C_3 \) are positively correlated with temperature and heating time. \( \delta^{2H}–C_3 \) values increase with increasing \( \delta^{2H}–C_1 \) values. The positive correlation between \( \delta^{2H}–C_1 \) and \( \delta^{2H}–C_3 \) is even more significant (Fig. 12). Based on these results, it can be concluded that the oxidation of hydrocarbons by TSR is accompanied by thermal cracking of crude oil, resulting in distinct patterns among the \( \delta^{13}C_2 \) values of alkane gases. Although TSR effect can lead to smaller variations of carbon and hydrogen isotope compositions of \( CH_4 \) compared with \( C_2H_6 \) and \( C_3H_8 \), \( \delta^{13}C_2 \) values increased with increasing \( \delta^{13}C_1 \) values (Fig. 13), suggesting that direct thermal cracking of crude oil also produced \( CH_4 \). However, the \( CH_4 \) produced during pyrolysis of \( C_9 \) should be primarily produced by TSR.

All TSR simulation experiments of crude oil, \( C_9 \) and MN under different conditions suggest that the TSR alteration produces \( CH_4 \) with similar carbon and hydrogen isotopic compositions to those of its precursor and reduced variations of isotopic compositions. The difference between \( CH_4 \) and \( C_2H_6 \) in carbon isotope and hydrogen isotopic composition increases with increasing TSR intensity, while the carbon and hydrogen isotopic composition of \( C_2H_6 \) and \( C_3H_8 \) became heavier and shows smaller differences with increasing temperature, similar to the results from thermal cracking of crude oil. The production of alkane gas with similar chemical and isotopic compositions to \( H_2S \)-bearing natural gas during these experiments, suggest that TSR can alter the carbon and hydrogen isotopic composition of alkane gas\(^{20,21} \). In addition, a partially reversed carbon isotope series of alkane gas (\( \delta^{13}C_1 > \delta^{13}C_2 < \delta^{13}C_3 \)) was observed, which further confirms the above conclusion. \( ^{12}C \)-enriched \( CO_2 \) was mainly produced from the oxidation of hydrocarbons by TSR. However, dissolution of \( CO_2 \) and precipitation of carbonate minerals in aqueous fluids can complicate the carbon isotopic composition in the marine carbonate reservoir\(^{45} \).

Conclusions

Pyrolysis of TSR was carried out using different organic matter (crude oil, nonane and methylnaphthalene), and the characteristics of carbon and hydrogen isotopes, as well as the composition and yields of the reaction products were analysed. The following main conclusions can be drawn:

1. The carbon and hydrogen isotopic composition of alkane gas generally becomes heavier with increasing carbon number, i.e., \( \delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 \) and \( \delta^{2H}–C_1 < \delta^{2H}–C_2 < \delta^{2H}–C_3 \). At the same temperature, the carbon and hydrogen isotopic composition of \( CH_4 \) gradually became larger with longer reaction time. The carbon and hydrogen isotopic composition of \( C_2H_6 \) and \( C_3H_8 \) also became heavier as the reaction continued, but the variation was significantly larger than that for \( CH_4 \). The variation of the carbon and hydrogen isotopic composition of \( C_2H_6 \) is higher than that of \( C_3H_8 \). Rapid oxidation of source material by TSR produced \( CH_4 \) with a small variation in carbon and hydrogen isotopic values, revealing that this process can alter the carbon and hydrogen isotopic composition of \( CH_4 \), making it similar to those of the original precursor material.

2. The partially reversed carbon isotope series observed in alkane gas produced from a mixture of \( C_9 \) and \( MgSO_4 \) indicates that TSR can cause abnormal isotope series of alkane gas in natural gas. As the reaction continued, \(^{13}C \) became enriched in residual heavy hydrocarbon gas, which altered the commonly observed
order of $\delta^{13}C_1 > \delta^{13}C_2$ to a positive carbon isotope series ($\delta^{13}C_1 < \delta^{13}C_2$). For the first time, we confirmed the ability of TSR to alter the isotopic composition of alkane, causing isotope reversal during TSR pyrolysis. (3) Under conditions of TSR, hydrogen isotopes of alkane gases form a positive isotope series ($\delta^2H–C_1 < \delta^2H–C_2$). Isotope fractionation is large, especially for ethane and propane, presumably due to the low molecular weight of hydrogen.

4) During pyrolysis, oil cracking and TSR result in different $\delta^{13}C_1–\delta^{13}C_2$ and $\delta^2H–C_1–\delta^2H–C_2$ evolutionary trends. While $\delta^{13}C_1–\delta^{13}C_2$ and $\delta^2H–C_1–\delta^2H–C_2$ became smaller with increasing intensity of TSR, $\delta^{13}C_1–\delta^{13}C_2$ and $\delta^2H–C_1–\delta^2H–C_2$ became larger with increasing intensity of oil cracking.
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Competing interests
The authors declare no competing interests.

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