



## Original Paper

# Influence of sulfate on the generation of bitumen components from kerogen decomposition during catagenesis



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## ABSTRACT

High-quality source rocks in saline lacustrine or marine sedimentary environments often show early peak petroleum generation and enhanced hydrocarbon yields, which have conventionally been attributed to organosulfur-enhanced thermal decomposition of kerogen. However, there is increasing awareness that the coexisting inorganic salts, particularly sulfates, might also contribute to the acceleration of petroleum generation. In this study, we investigated the influence of sulfates on the thermal decomposition of kerogen sampled from the Pingliang Formation in the Ordos Basin. Our results demonstrate that the kerogen samples mixed with sulfate generate more hydrocarbons with a lower peak production temperature than their sulfate-free counterparts. Detailed chemical analysis revealed that the presence of sulfates significantly facilitated the generation of resins and asphaltenes at temperatures below 350 °C, corresponding in our simulations to the early stage of petroleum generation (Easy% $R_o < 1.0\%$ ). We hypothesize that sulfates can promote the fragmentation of kerogen via direct thermochemical oxidation into a complex mixture of bitumen components that consist mostly of compounds typically encountered in the classical resin and asphaltene fractions. The findings reveal a new reaction paradigm between sulfates and organic macromolecules that could offer useful guidance in the exploration for low-maturity oils.

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## 1. Introduction

The majority of proven oil and natural gas reserves are found in saline lacustrine or marine basins (Powell, 1986; Kelts, 1988; Carroll and Bohacs, 2001), where source rocks rich in organic matter contain or coexist with a variety of minerals such as carbonates, sulfates and chlorides (Fu et al., 1986; Orr, 1986; Ruble et al., 2001; Zhu et al., 2005; Wang et al., 2010; Hou et al., 2017; Liu et al., 2017). One of the notable petroleum geochemical features of source rocks in gypsum-bearing sedimentary basins is their ability to generate

hydrocarbons at a comparatively early stage, which has conventionally been attributed to the presence of sulfur-rich kerogen (Aizenshtat et al., 1986; Orr, 1986). Hunt et al. (1991) reported that the level of sulfur in type-II kerogen exhibited an inverse correlation with the modal activation energy of hydrocarbon generation. Furthermore, S-rich kerogen has been shown to generate organosulfur-bearing radicals at low thermal-stress levels, likely due to the low bond energy of S-C and S-S bonds, which leads to high concentrations of S-bearing free radical (Lewan, 1998).

However, there is increasing evidence that inorganic salts could also play an important role (Johns, 1979; Lewan et al., 2008; Hu et al. 2014, 2016; Rahman et al., 2018). Anhydrous open pyrolysis experiments suggest that carbonates, and particularly sulfates, are capable of accelerating the decomposition and condensation of kerogen, leading to earlier and sometimes enhanced hydrocarbon

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generation (Li et al., 1997; Luo et al., 2016; Huang et al., 2018; Chen et al., 2019). Conversely, chlorides were found to exert an inhibitory effect (Zhang et al., 2000; Li et al., 2002). Ma et al. (2013) observed similar effects in semi-open hydrous pyrolysis experiments on sulfate-bearing and sulfate-free Tertiary source rocks from the Dongpu Depression, where a strong correlation between hydrocarbon generation and the presence of sulfate was reported. Chen et al. (2019) found that the presence of gypsum minerals promoted the generation of light hydrocarbons and led to a decline in the dryness index of the gaseous products produced.

Despite the above findings, sulfates have not been widely regarded as a significant contributor to petroleum generation as organic sulfur in kerogen. It has been proposed that sulfates might play a catalytic role similar to clay materials in the decomposition of kerogen (Li et al., 1997; Ma et al., 2013). In this study, we separated and analyzed the S.A.R.A. (saturates, aromatics, resins and asphaltene) fractions generated from the pyrolysis of sulfate-bearing and sulfate-free kerogen samples in gold-tube simulation experiments. By comparing the differences in product profile, we identified a new reaction paradigm between sulfate and organic macromolecules under high *P-T* conditions, which could provide valuable insights into the geochemical behaviors of organic sediments in gypsum-bearing petroleum systems.

## 2. Experiments

### 2.1. Sample preparation

The kerogen used in this study was extracted from the Ordovician Pingliang Formation located along the western and southern margins of the Ordos Basin and processed at the Petroleum Exploration and Production Research Institute of Zhongyuan Oilfield Co., SINOPEC. The total organic carbon (TOC) and sulfur contents of the sample were 70.48% and 3.94%, respectively. The Rock-Eval Hydrogen Index (HI) of 482 mg/g TOC was consistent with the geochemical characteristics of type II kerogen. The  $T_{\max}$  value of 432 °C corresponds to a maturity at the onset of oil generation (oil window). The kerogen-sulfate mixture was prepared using sulfate-free kerogen and fine carbonate-free gypsum powder. Briefly, solid gypsum rocks from the Pingliang Formation, consisting of 65.5% anhydrite, 33.3% dolomite, 1.7% siderite and 0.5% quartz (based on XRD analysis), were ground to 100–200 mesh, mixed with 6 mol/L HCl solution, and stirred vigorously until no more CO<sub>2</sub> bubbles formed in the liquid. The reaction mixture was allowed to settle and the supernatant was decanted. The precipitate was then rinsed with deionized water five times to ensure the complete removal of carbonates, and dried in an oven at 80 °C to constant weight. Finally, 2.375 g of the dried, HCl-treated gypsum powder and 2.341 g of kerogen were thoroughly mixed and ground in a mortar with a pestle. The TOC of the resultant kerogen-sulfate mixture sample was determined to be 43.78%.

### 2.2. Gold-tube hydrous pyrolysis experiments

All hydrous pyrolysis experiments were conducted using an ST-120-II gold-tube thermal simulation apparatus at the Thermal Simulating Lab for Generation and Expulsion of Petroleum, affiliated to the State Key Laboratory of Petroleum Resources and Prospecting. The length, inner diameter and wall thickness of the gold tube were 60 mm, 5.5 mm and 0.25 mm, respectively (Wu et al., 2020). Each tube was first heated to roughly 800 °C with a

butane-air torch for 3 min to remove all residual organic materials, then welded on one end using a PUK U4 microscope argon-arc welder (Lampert Werktechnik). The tubes were filled with 50–100 mg of sulfate-free kerogen or kerogen-sulfate mixture and 50 mg of distilled water. The exact amounts of the samples and water were determined by weighing the gold tube on an electrical balance (Shanghai Yoke Instruments) to a measurement precision of 1 mg (Table 1). The amount of water added to the experimental system was chosen such that a liquid water phase was present throughout the experiments. According to Lewan (1997)'s research the mass ratio of solid sample and (liquid) water does not affect the product yields.

The tube was flushed with argon for 5 min and the open end was crimped and welded. The sealed gold tube was subsequently placed in a stainless-steel autoclave. The temperature of each autoclave was raised from ambient to 250 °C in 30 min and then further increased linearly to one of the following pre-set targets (300 °C, 324 °C, 348 °C, 396 °C and 444 °C), at a rate of 2 °C/h. The temperature was kept constant for 24 h before being lowered back to the ambient level. The internal pressure of each autoclave was maintained at 30 MPa to prevent the gold tubes from rupturing due to the thermal expansion of the generated gaseous products. All thermal simulation experiments were performed in duplicate (represented by a and b in the Expt. IDs of Table 1), except for the one conducted at 324 °C with sulfate-free kerogen due to leakage of one of the gold tubes.

### 2.3. Extract recovery and S.A.R.A. Fractionation

After the end of each thermal simulation experiment, the reaction mixture inside the gold tube was transferred to a small, clean bottle, mixed with 4 mL of dichloromethane (DCM), and ultrasonicated in a water bath for 10 min. The extract was transferred to another clean bottle and concentrated as much as possible without causing precipitation of the extract. The asphaltene fraction was then precipitated by adding 50 mL of *n*-hexane and separated by filtration. The remaining filtrate was separated into three fractions by column chromatography with alumina-silica gel (2:3) as stationary phase. Saturated hydrocarbons were eluted with petroleum ether, aromatics with a solvent mixture of petroleum ether and DCM (1:2, v/v), and resins with DCM (Li et al. 2012, 2013).

### 2.4. Determination of gas compositions in three additional experiments

To analyze the chemical composition of the gaseous products, one additional experiment with sulfate-free kerogen at 300 °C (F-300c) and two experiments with a kerogen-sulfate mixture at 300 °C (B-300c) and 396 °C (B-396c) were performed. These three tubes were taken to the Power, Environmental and Energy Research Institute (PEERI), Covina, California, USA for analyses. Each gold tube was loaded into a custom-made glass apparatus equipped with a piercing unit and connected to a sample loop via a vacuum line. The internal pressure of the system was first reduced to 0.1 Pa. Then, the gold tube was pierced to release the gaseous products (i.e. C<sub>1</sub>–C<sub>5</sub>, CO<sub>2</sub>, H<sub>2</sub>S, and H<sub>2</sub>). Once the system pressure of the vacuum line had stabilized, the valve that separated the glass apparatus and the sample loop was closed, and the chemical composition of the gas mixture in the loop was analyzed on a two-channel Hewlett-Packard 6890 Series Gas Chromatograph custom-configured by Wasson ECE Instrumentation, following a method described by

**Table 1**

The quantities of sample components and soluble organic products (Extracts and the corresponding S.A.R.A. fractions, unit: mg).

Groups	Expt. ID	T, °C	Easy%R <sub>o</sub> , %	m(samples)	m(H <sub>2</sub> O)	m(TOC)	m(Extracts)	m(Sat.)	m(Aro.)	m(Resin)	m(Asph.)	S.A.R.A Recover rate
Sulfate -free	F-300a	300	0.66	54	49	34	0.5	n.d.	n.d.	n.d.	n.d.	n.d.
	F-300b			48	49	38	1.5	0.1	0.0	0.6	1.2	127%
	F-324	324	0.77	100	201	70	6.8	1.4	1.8	1.5	2.4	104%
	F-348a	348	0.94	51	47	36	7.0	1.2	1.7	1.4	2.3	94%
	F-348b			51	48	36	6.0	0.7	1.5	1.2	2.4	97%
	F-396a	396	1.49	50	48	35	4.6	0.8	2.1	1.2	0.7	104%
	F-396b			50	50	35	4.7	1.0	2.2	0.9	0.9	105%
	F-444a	444	2.29	49	52	35	1.2	n.d.	n.d.	n.d.	n.d.	n.d.
	F-444b			52	49	37	1.7	0.0	0.0	0.4	0.9	76%
	Sulfate -bearing	B-300a	300	0.66	106	50	46	2.1	0.7	0.2	0.8	0.2
B-300b				98	51	48	2.1	0.6	0.4	0.0	1.3	110%
B-324a		324	0.77	98	47	43	5.9	1.3	1.0	1.6	2.0	100%
B-324b				96	50	42	7.6	0.4	0.5	2.7	3.1	88%
B-348a		348	0.94	104	50	46	7.2	0.9	1.3	1.6	3.2	97%
B-348b				96	48	42	8.7	1.2	2.3	2.3	2.1	91%
B-396a		396	1.49	110	51	48	1.2	n.d.	n.d.	n.d.	n.d.	n.d.
B-396b				97	51	42	3.0	0.2	0.6	0.0	2.3	103%
B-444a		444	2.29	68	39	30	n.d.	0.1	0.1	0.7	0.3	n.d.
B-444b				68	30	30	1.0	n.d.	n.d.	n.d.	n.d.	n.d.

Starting materials from sulfate-free (Expt. ID: F-Temperature) and sulfate-bearing groups (Expt. ID: B-Temperature) are kerogen and its sulfate-bearing source rock mixture, respectively. Their TOC of starting materials are 70.48% for sulfate-free group and 43.78% for sulfate-bearing group. Abbreviation: Sats: saturates; Aros: aromatics; Asph: asphaltene. n.d. indicates "not determined".

Zhang et al. (2007). The amount of each gas component in the gold tube was calculated based on the assumption of ideal gas behavior ( $pV = nRT$ ).

### 3. Results

#### 3.1. Soluble extracts and S.A.R.A. Fraction yields

The DCM extracts of the hydrous pyrolysis products of the kerogen-sulfate mixture and its sulfate-free counterpart both showed increasing yields of liquid products with temperatures increasing from 300 °C to 348 °C (Table 2). The presence of sulfates led to a significant boost in the hydrocarbon yield at 324 °C, but both samples produced nearly the same total amounts of DCM-soluble hydrocarbons at 348 °C (sulfate-free 181 ± 14 mg/g TOC and sulfate-bearing 183 ± 24 mg/g TOC). Upon further increase of the reaction temperature from 348 °C to 396 °C, the yield of recoverable hydrocarbons declined, with the decrease being significantly more pronounced for the kerogen-sulfate mixture than for the sulfate-free sample.

The amounts of saturated hydrocarbons obtained from the sulfate-free kerogen peaked at 348 °C (26 ± 7 mg/g TOC) and dropped slightly at 396 °C (25 ± 2 mg/g TOC). Similar trends were observed for resins and asphaltenes. The yields of aromatic

hydrocarbons, however, continued to increase until they reached a maximum value of 61 ± 1 mg/g TOC at 396 °C. On the other hand, the hydrous pyrolysis of the kerogen-sulfate mixture samples showed peak production of saturated and aromatic hydrocarbons at 348 °C, but the yields dropped precipitously at 396 °C as compared to the sulfate-free group. Furthermore, peak production of resins and asphaltenes from the kerogen-sulfate mixture occurred at lower temperatures compared to that from the sulfate-free sample. It should be emphasized that the standard errors for the quantitation of different hydrocarbon fractions from the kerogen-sulfate mixture sample were greater than those for the pyrolysis of the sulfate-free sample, particularly at 300 °C and 396 °C, where the hydrocarbon yields were too low to ensure accurate measurement. This was also indicated by the aberrant recovery rates shown in Table 1. Nevertheless, the low hydrocarbon yields at these temperatures were fully expected and had little impact on the interpretation of the results.

#### 3.2. Quantitation of volatile hydrocarbons generated in pyrolysis experiments at 300 °C and 396 °C

At 300 °C, the pyrolysis of the sulfate-free kerogen produced a greater amount of GC-detectable volatile hydrocarbons than the sulfate-free samples, with the sole exception of *n*-C<sub>5</sub>H<sub>12</sub>. However,

**Table 2**

Total extract yields of solid residues and proportions of S.A.R.A. fractions.

Expt. Group	T, °C	Easy%R <sub>o</sub> , %	Yields, mg/g TOC				
			Extracts	Sats	Aros	Resin	Asph
Sulfate-free kerogen	300	0.66	27(12)	2.6	0	16	32
	324	0.77	96	20	26	21	34
	348	0.94	181(14)	26(7)	43(4)	36(3)	65(1)
	396	1.49	132(1)	25(2)	61(1)	30(4)	23(3)
	444	2.29	41(6)	0	0	13	25
Kerogen-sulfate mixture	300	0.66	45(1)	14(1)	6.3(2.0)	8.6(8.6)	16(11)
	324	0.77	159(22)	20(10)	18(6)	51(13)	60(14)
	348	0.94	183(24)	24(4)	42(13)	45(10)	60(10)
	396	1.49	48(23)	7.1	14	0	54
	444	2.29	34	3.4	3.4	24	10

Standard errors given in parentheses apply to the last digit cited. Values without error indicate that only one valid measurement was available for this fraction. Abbreviation: Sats: saturates; Aros: aromatics; Asph: asphaltene.

**Table 3**

Comparison of gas compositions produced in additional pyrolysis experiments with sulfate-free kerogens and kerogen-sulfate mixtures at 300 °C and 396 °C.

Expt. ID		F-300c (300 °C)	B-300c (300 °C)	B-396c (396 °C)
Sample type		Sulfate-free kerogen	Kerogen-sulfate mixture	
m(sample), mg		99.9	200.1	199.8
TOC, mg		70.4	87.6	87.5
Yields of gas compositions, mL/g TOC				
	CH <sub>4</sub>	6.8	5.3	28.8
	C <sub>2</sub> H <sub>6</sub>	0.25	0.069	0.0
	C <sub>3</sub> H <sub>8</sub>	0.13	0.043	0.0
	<i>i</i> -C <sub>4</sub> H <sub>10</sub>	0.065	0.023	0.0
	<i>n</i> -C <sub>4</sub> H <sub>10</sub>	0.075	0.046	0.0
	<i>i</i> -C <sub>5</sub> H <sub>12</sub>	0.043	0.032	0.0
	<i>n</i> -C <sub>5</sub> H <sub>12</sub>	0.054	0.066	0.0
	CO <sub>2</sub>	16.6	14.9	31.7
	H <sub>2</sub> S	0.0	0.032	32.7

the yield differences between the two groups were lesser for larger hydrocarbon molecules. No significant difference in the yields of CO<sub>2</sub> was observed (Table 3).

At 300 °C the kerogen-sulfate mixtures produced measurable amounts of H<sub>2</sub>S (0.032 mL/g TOC), whereas the H<sub>2</sub>S yields of the sulfate-free experiments were below the detection limit. These data indicate a clear correlation between the presence of sulfates in the kerogen samples and the amount of H<sub>2</sub>S generated. The production of CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>S all increased considerably at 396 °C compared to the results obtained at 300 °C, implying significant contributions from thermochemical sulfate reduction (TSR) reaction (Table 3).

## 4. Discussion

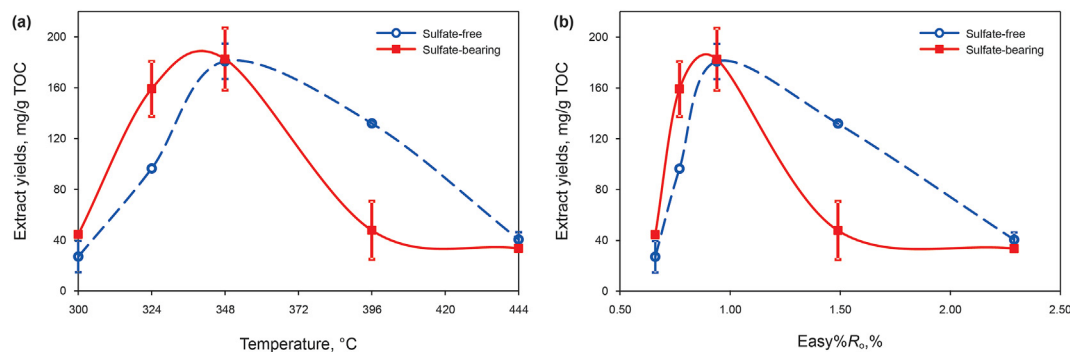
### 4.1. Influence of sulfate on the yields of soluble extracts

In order to understand the extent of thermal evolution during the experiments, we estimated the thermal maturity in each experiment using the Easy%*R*<sub>0</sub> model (Sweeney and Burnham, 1990). The corresponding Easy%*R*<sub>0</sub> values for each experimental temperature are listed in Table 2.

The thermal simulation experiments of the sulfate-free samples exhibited no appreciable generation hydrocarbons at 300 °C (Easy%*R*<sub>0</sub> = 0.66%) and no extractable products until 444 °C (Easy%*R*<sub>0</sub> = 2.29%), whereas the kerogen pyrolysis in the presence of sulfates already reached roughly 20% of the peak hydrocarbon yield at 300 °C. No significant difference in the total amount of DCM-soluble hydrocarbon products was observed between the two experiment groups at 444 °C, suggesting that the reaction end-

points were almost reached. These temperature-dependent trends are in line with the conventional theory on the origin and thermal evolution of kerogen described by Tissot and Welte (1984). However, the pyrolysis of the kerogen-sulfate mixture showed significantly accelerated and increased hydrocarbon generation at lower temperatures compared to that of the sulfate-free sample (Fig. 1a, b). The hydrocarbon yield of the kerogen-sulfate mixture declined sharply at *T* > 350 °C, likely because the products or their precursors, were consumed by TSR reactions. In fact, GC-MS analysis indicated that only CO<sub>2</sub>, H<sub>2</sub>S and CH<sub>4</sub> remained in the gold tubes at the end of the experiments with kerogen-sulfate mixtures at 396 °C (Easy%*R*<sub>0</sub> = 1.49%).

Although the water-soluble salts and insoluble carbonates in the source rocks were removed by HCl treatment, quartz and most of the anhydrite were not affected and remained in our experimental system. Quartz is widely considered chemically inert even under the experimental conditions employed in this study, and therefore was unlikely to affect hydrocarbon generation. Furthermore, the same kerogen was used in both sets of experiments. Therefore, the effects of carbonates and quartz, if any, would apply similarly to both groups. Based on these considerations, we tentatively conclude that the alterations in the time course and maximum yield of hydrocarbon generation that we observed in this study are due primarily to sulfate-driven reactions. Overall, the presence of sulfates caused the peak hydrocarbon production to occur at a lower temperature and significantly increased the yield of hydrocarbons generated during the early phase of kerogen decomposition. These findings are consistent with the conclusions of a number of previous studies (Li et al., 1997; Ma et al., 2013).



**Fig. 1.** Total extract yields of the kerogen-sulfate mixture (red solid square) and the sulfate-free kerogen (blue open circles) with increasing (a) experimental temperature and (b) calculated thermal maturity Easy%*R*<sub>0</sub>. Standard errors of the yields are indicated by error bars, except for the sulfate-free experiment at 324 °C and the sulfate-bearing one at 444 °C (Table 2). Some of the error bars are too short to be exhibited.

## 4.2. Sulfate oxidation is responsible for increased yields of resins and asphaltenes

The yield of *saturated hydrocarbons* from the kerogen-sulfate mixture was significantly greater than from the sulfate-free sample at Easy% $R_o$  of 0.66%, but the opposite was observed from Easy% $R_o$  of 0.94%–2.29% (Fig. 2a). Pyrolysis of the kerogen-sulfate mixture produced almost the same yields of *aromatic hydrocarbons* as that of the sulfate-free sample below Easy% $R_o$  of 0.94% (Fig. 2b). In comparison, the presence of sulfates more than doubled the yields of *resins* and *asphaltenes* at Easy% $R_o$  of 0.77% (Fig. 2c, d). Furthermore, peak production of both fractions from the sulfate-bearing group occurred already at Easy% $R_o$  of roughly 0.8%, i.e. at approximately 0.2% maturity index units lower than that for the sulfate-free sample. Therefore, the accelerated generation of hydrocarbons and other components from kerogen during the early stage of catagenesis (Easy% $R_o$  between 0.66% and 0.94%) in the presence of sulfates is linked with the elevated yields of resins and asphaltenes. On the other hand, the yields of different S.A.R.A. fractions all declined at temperatures above 350 °C, likely due to the onset of TSR, with asphaltenes being less affected than the others as a result of their higher molecular weights and chemical resiliency.

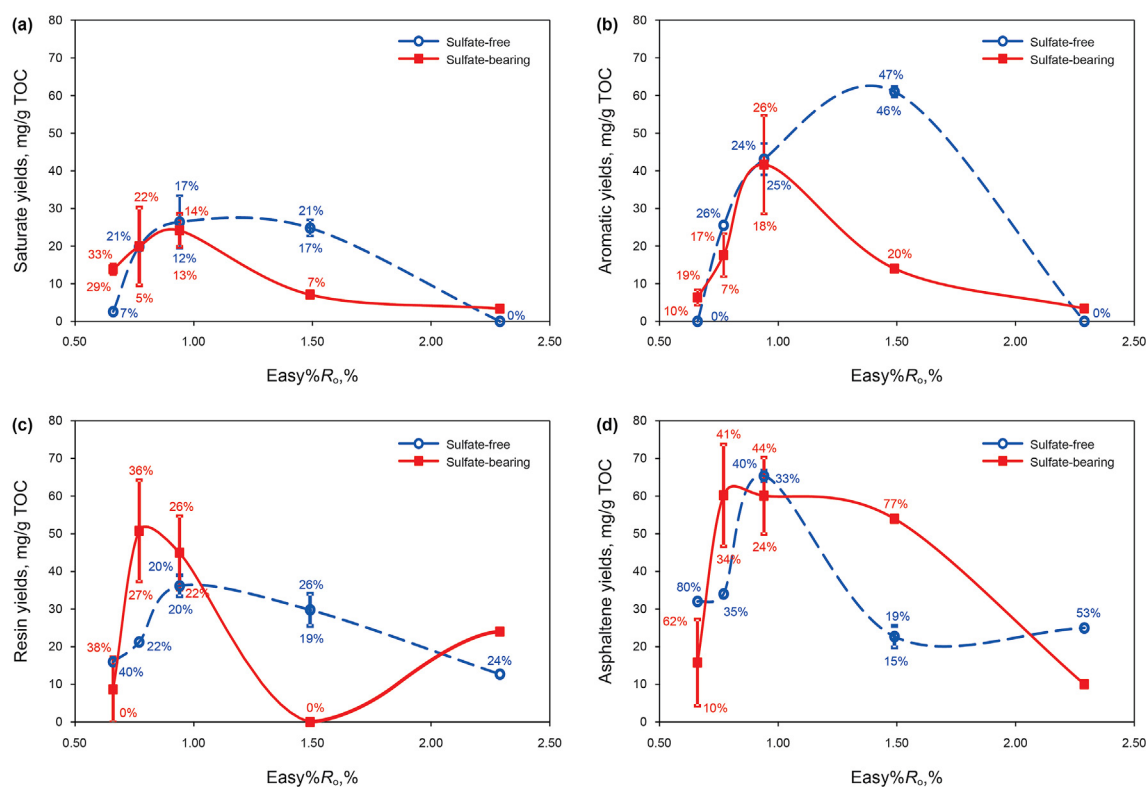
Although earlier hydrocarbon generation and increased component yields in the pyrolysis of kerogen-sulfate mixtures has been previously reported, the exact geochemical mechanisms are not well understood. Both Li et al. (2002) and Ma et al. (2013) contended that the stimulatory effects of sulfates are likely to be catalytic in nature. Alternatively, Chen et al. (2019) argued that there is insufficient evidence to determine whether sulfates act as catalysts or reactants during the early stage of hydrocarbon

generation. However, by definition, catalysts only alter the rate of chemical reactions but not the (thermodynamically controlled) final composition (Hanefeld and Lefferts, 2018), which contrasts with our findings that the two groups of samples produced significantly different peak levels of resins and asphaltenes after pyrolysis. This suggests that the sulfate in the kerogen-sulfate mixtures participated in the generation of hydrocarbons and polar compound as reactant.

Consistent with our speculation, Lewan (1985) reported that the hydrous pyrolysis of kerogen occurs in two stages starting with the conversion of kerogen to bitumen around 330 °C, followed by the onset of hydrocarbon generation around 350 °C (Lewan, 1985). As further evidence, the results of subsequent chemical analysis indicated that the bitumen extracted after the first reaction stage contained a larger proportion of polar compounds (Lewan, 1997). Therefore, we speculate that sulfates promote hydrocarbon generation by facilitating the thermal decomposition of kerogen into resins and asphaltenes.

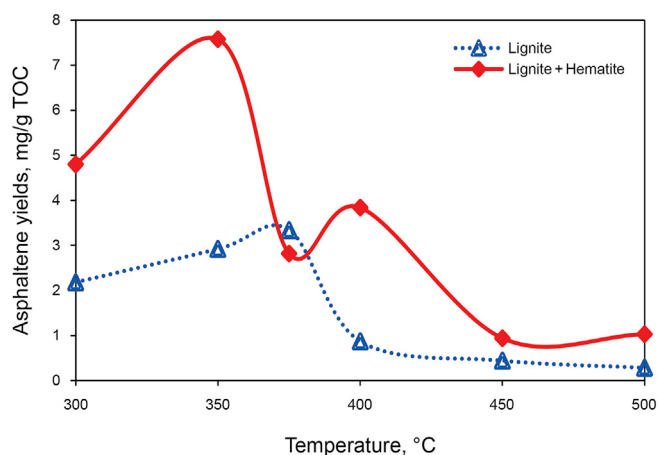
A previous pyrolysis study conducted by Ma et al. (2014) demonstrated that the presence of hematite in lignite resulted in a two-fold increase in asphaltene yield and a downward shift in peak generation temperature from 375 °C to 350 °C (Fig. 3). Particularly of note is the detection of magnetite by Mössbauer spectroscopic analysis, likely resulting from the reduction of hematite, in the pyrolysis products at 375 °C. Therefore, the results of Ma et al.'s study are supportive of our above hypothesis that sulfates could promote the decomposition of kerogen and the generation of polar fractions by oxidation reaction.

We further reason that sulfates exert an oxidative effect on kerogen based on the fact that the hydrous pyrolysis of the kerogen-sulfate mixture produced more H<sub>2</sub>S than the sulfate-free



**Fig. 2.** The S.A.R.A. fraction yields of the sulfate-bearing mixture (red solid squares) and the sulfate-free kerogen (blue open circles) with increasing thermal maturity. Standard errors of the yields are expressed by error bars, except for the sulfate-free experiment at 324 °C (Table 2). The proportions of S.A.R.A. fractions are shown next to the error bars in matching colors. a) saturated hydrocarbons; b) aromatic hydrocarbons; c) resins; d) asphaltenes.





**Fig. 3.** Influence hematite on asphaltene yields during isothermal pyrolysis of lignite. Experiments were performed at varying temperatures for 48 h (modified after Ma et al., 2014).

experiments. Sulfate-dependent oxidation is not a new geological concept; in fact, TSR is one of the best-known sulfate-induced oxidation processes that occur under geological conditions, as verified in a number of previous studies (Zhang et al. 2007, 2008b; Amrani et al., 2008; Walters et al., 2015). However, we argue that what occurred in our pyrolysis experiments cannot be explained satisfactorily by TSR, which tends to favor the complete oxidation of hydrocarbon molecules into  $\text{CO}_2$ . This is at odds with our observation that the yields of saturated and aromatic hydrocarbons did not show any significant decline when sulfate reduction to  $\text{H}_2\text{S}$  was observed during the early stage of catagenesis ( $T < 350$  °C, Easy%  $R_o < 1.0\%$ , Table 3). Overall, our data strongly suggested that sulfates directly oxidize kerogen to form resins and asphaltenes under high  $P$ - $T$  conditions.

#### 4.3. Potential mechanism for sulfate-assisted thermal degradation of kerogen

Zhang et al. (2008a) analyzed the product mixture derived from the TSR of sulfates with saturated hydrocarbons, and found that the generated  $\text{H}_2\text{S}$  can react with hydrocarbon compounds to form S-bearing resins. In fact, the S-bearing resins proved to be chemically labile and could be readily oxidized by sulfates in a similar manner as saturated hydrocarbons. These findings were corroborated by computational analysis (Ma et al., 2008), which showed that redox reactions between contact ion-pairs (CIP) of sulfates and C-C single bonds, can lead to the formation of sulfites and C=C double bonds. Based on these findings, it is not far-fetched to hypothesize that contact ion-pairs of sulfates should also be able to oxidize C-C bonds in organic macromolecules such as kerogen and asphaltenes. From a mechanistic standpoint, the generated C=C double bonds are more reactive and can be further converted to carbocations or radicals, thereby facilitating the cleavage of the C-C bond between  $\alpha$ -C and  $\beta$ -C of the corresponding C=C double bonds. Notably, the experiments with kerogen-sulfate mixtures in our current study exhibited greater variability in product composition than those without sulfates, providing some tentative evidence for a biphasic reaction between solubilized sulfates and solid kerogen.

Taken together, there are two possible mechanisms by which sulfates may react with kerogen and asphaltenes. Our experimental results and previously described theoretical data (Ma et al., 2008) indicate that sulfates can directly oxidize certain covalent bonds in kerogen and asphaltenes, possibly through the formation of a cyclic

diester intermediate similar to those involved in  $\text{MnO}_4^-$  or  $\text{OsO}_4$ -based oxidation. This is consistent with mechanisms for the formation of TSR intermediates proposed in a number of earlier studies. For example, Walters et al. (2015) reported that the levels of carboxylic acids derived from polycyclic aromatic hydrocarbons and their derivatives showed a positive correlation with the extent of TSR in crude oils generated from Oxfordian lower Smackover Formation carbonates, suggesting that these oxygenated compounds were likely to be the oxidation intermediates formed from the ring-opening of aromatic polycycles. A similar mechanistic hypothesis was proposed by Püttmann et al. (1989) in their study on the variable compositions of organic matter from the Kupferschiefer zone in the Konrad and Rudna mines, southwest Poland. In this study, the oxidized products, which normally contain O-bearing functional groups, were separated into resin and asphaltene fractions. As the level of residual kerogen was significantly greater than that of resins and asphaltenes combined at the end of the experiments, more polar components were generated by the reaction of sulfates with kerogen than were consumed by further oxidation with sulfates. Therefore, the presence of sulfates showed a net positive contribution to the generation of resins and asphaltenes, which was consistent with their yields in sulfate-bearing experiments. On the other hand, the results of Zhang et al. demonstrate that  $\text{H}_2\text{S}$  may accelerate the TSR of hydrocarbons by promoting the formation of chemically labile organosulfur compounds (Zhang et al., 2008a; Amrani et al., 2019). Thus, it is reasonable to speculate that sulfate-dependent thermal decomposition of kerogen can be stimulated by the  $\text{H}_2\text{S}$  that it generates. However, we argue that direct oxidation is likely to be the main mechanistic pathway because i) kerogen already contains a large number of sulfur heterocycles and thus requires no further activation by  $\text{H}_2\text{S}$ , and ii) enhanced hydrocarbon production from kerogen-sulfate mixtures has previously been observed in open systems, where  $\text{H}_2\text{S}$  tends to escape rapidly. Of course, the possible involvement of  $\text{H}_2\text{S}$  cannot be ruled out completely.

#### 4.4. Geological implications

As elucidated earlier, the accumulation of high-level  $\text{H}_2\text{S}$  in natural gas reservoirs has conventionally been attributed to TSR between sulfates and small organic molecules. Our current study, however, suggests that sulfates can directly oxidize structurally complex organic macromolecules such as kerogen and asphaltenes in homogenous or biphasic systems. These results thus greatly expanded our understanding of organic-inorganic interactions in gypsum or anhydrite bearing source rocks or reservoirs in sedimentary basins. On the one hand, there is compelling evidence that the reaction of sulfates with kerogen likely involves the formation of oxygen- and sulfur-bearing resins as key intermediates, which are then more susceptible to oxidation by sulfate than their hydrocarbon precursors (Walters et al., 2015). For this reason, the yields of resins were found to decline more rapidly than saturated and aromatic hydrocarbons in simulation experiments above 348 °C (Easy% $R_o > 0.94\%$ , Fig. 2c). On the other hand, sulfate-stimulated oxidative fragmentation of kerogen and asphaltenes could also alter the chemical distribution and the geochemical behavior of trace elements trapped in the cross-linked macromolecular network. One example is the Re-Os chronometer, as both trace elements are enriched in asphaltenes. It has been previously reported that TSR-altered oils from the Permian Phosphoria Formation of the Bighorn Basin showed a younger average Re-Os isotopic age than the normal oils in the same region (Lillis and Selby, 2013). Taken together, we hypothesize that heteroatoms could weaken adjacent C-C bonds by an inductive effect, thereby rendering them more susceptible to TSR.

Sulfates are the most abundant form of sulfur in gypsum-bearing sedimentary basins, which are commonly characterized by hydrocarbon generation at earlier maturity levels, high hydrocarbon yields, and a tendency to produce low-maturity crude oils (Fu et al., 1986). In general, immature or low-maturity oils show much earlier peak hydrocarbon generation than regular petroleum. Based on a compilation by Huang et al. (2003), among 180 immature or low-maturity oil samples collected from sedimentary environments across China (including the Songliao Basin, Dongpu Sag, Raoyang Sag, Jinxian Sag, Jiangnan Basin, Qaidam Basin and Subei Basin), 91 showed a S content above 1%, and 22 above 5%. All of the 22 samples were derived from gypsum-bearing sedimentary strata located in the Jiangnan Basin and the Jinxian Sag. Another supporting evidence is that immature oil has been discovered in the 3rd member of Qianjiang Formation from well Ban 1, Xiaoban Sag, Jiangnan Basin, which is sandwiched between two gypsum-bearing strata (Jiang et al., 1988). The oil is low in saturated hydrocarbons (13.3%) but rich in resins and asphaltenes (74.8% in total). Importantly, the fact that the oil shows a normal *n*-alkane distribution eliminates microbial degradation as a possible cause, and thus strongly suggests the involvement of sulfates.

The presence of sulfates, as confirmed by our current study, may further expedite petroleum generation by lowering the activation energy barrier for kerogen decomposition. As a consequence, the temperature of peak hydrocarbon generation from a kerogen-sulfate mixture was significantly lower than that for its sulfate-free counterpart. The presence of sulfate promotes the yields of polar components and therefore may promote the primary migration of petroleum (Espitalie et al., 1980; Pelet et al., 1986). These results suggest that adding sulfates to the source rock matrix might facilitate petroleum expulsion.

Our current study provides strong experimental evidence that sulfates and other inorganic sulfur species may play as significant a role in petroleum generation as endogenous organosulfur sources in kerogen-hosted systems. Thus, we argue that the evaluation of sulfate-bearing source rocks should include the measurement of additional parameters, such as the occurrence of sulfate in the matrix and the kinetics of hydrocarbon generation in whole rocks, which have not been sufficiently addressed in conventional assessment methods. As a start, the thermal simulation experiments and kinetic characterizations detailed in this study could provide a framework to help researchers better understand the high level of petroleum production in sulfate-bearing saline lacustrine or marine source rocks, and offer useful guidance for the exploration of lower-maturity oils.

## 5. Conclusions

The results of our study suggest that inorganic sulfates may play as important a role as the presence of a S-rich kerogen in promoting early hydrocarbon generation from source rocks in gypsum-bearing sedimentary basins. Importantly, we showed that sulfates can directly oxidize C-C bonding in kerogen and that sulfates are consumed as reactants rather than serving as catalysts. This represents a new reaction paradigm between sulfates and solid-phase organic macromolecules in petroleum systems during maturation. Our data also provide convincing experimental evidence that TSR may also occur in source rocks and not just in reservoir settings. The results of our current study provide important insights into the mechanisms responsible for the generation of low-maturity oils and the impact of oxidation by sulfate on the geochemical behavior of trace elements sequestered in sedimentary organic macromolecules.

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