Water-soluble organic acids at deep-ultradeep depth in Chinese sedimentary basins: Experimental results and geological significances

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Abstract: Water-soluble organic acid anions (WSOAA) in subsurface water have been intensively studied during past several decades. They are used as natural gas precursor, tracer for the movement of underground fluid, indicator for porosity improvement, and

detecter of deep subsurface life on the Earth. However, little is known on the distributions and origins of organic acids at deep-ultradeep depth underground. Herein, we collected twenty-nine source rock samples covering wide maturity range from the Ordos, Qinshui, Junggar, Minhe, and Southern North China basins, as well as six subsurface water samples with depth between 6544 m and 8396 m from industrial gas producing wells in the Tarim Basin, China. We carried out pyrolysis experiments at various temperatures (250~450 ℃) to investigate the role of water on the generation of organic acids. Results show that there are considerable amounts of WSOAA detected in both high-over mature source rocks and deep-ultradeep subsurface water. WSOAA mainly consist of monocarboxylates, predominately formate and acetate. High-TOC oil-generating source rock has low production rate of organic acids due to lack of hydrogen. Different source rocks have distinct ratios of formate to acetate concentration, expressed as *c*(formate)/*c*(acetate), which is due to significant differences in both initial molecular structure and metabolite. This indicates that *c*(formate)/*c*(acetate) can be used to distinguish types of organic matters (OMs). Concentrations of WSOAA show a "sharp decrease-slight increase-slow decrease" evolution trend with progressive maturity. Moreover, there are higher production rates of organic acids under hydrous pyrolysis experiments at ⩾400 ℃. All geochemical signatures indicate that at both deep-ultradeep depth and high-over mature stages, the formation of organic acids is attributed to the thermochemical oxidation of organic components by mainly hydroxyl radicals, challenging the traditional model of organic acid evolution. This work suggests that petroleum exploration can be extended to great depths in sedimentary

basins, when formation temperatures are not exceeding 230 ℃.

Keywords: Water-soluble organic acids; High-over mature stages; Deep-ultradeep zone; Thermochemical oxidation of organic components; Hydroxyl radicals

1 Introduction

Water-soluble organic acid anions (WSOAA) in subsurface water have been paid sustained attention due to their huge implications in porosity improvement, natural gas precursor, tracing the movement of underground fluids, and understanding deep subsurface life on the Earth (Carother and Kharaka, 1978; Surdam et al., 1984, 1989; Workaman and Hanor, 1985; Yuan et al., 2019a, 2019b; Heuer et al., 2020; Sherwood Lollar et al., 2021; Li et al., 2023). In particular, the evolution of secondary porosity due to complex interactions between fluids and rocks during diagenetic processes, such as organic-inorganic interactions, is critical for commercial petroleum activities (Surdam et al., 1984, 1989; Surdam and Crossey, 1987; Surdam and MacGowan, 1987; Zhong and Zhu, 2008; Cao et al., 2018; Ivanova et al., 2019; Liu et al., 2019; Yuan et al., 2019a, 2019b, 2024; Chen et al., 2020; Helten et al., 2022; Li et al., 2023; Gong et al., 2023; Huang et al., 2024). Organic acids can dissolve carbonate and aluminosilicate minerals by providing proton and mainly complexing Al^{3+} and Si^{4+}, creating secondary pores and promoting reservoir porosity (Surdam et al., 1984; Eglinton et al., 1987; Surdam and MacGowan, 1987; Barth et al., 1988; Chen et al., 1994a; Zhang et al., 2009; Yuan et al., 2015, 2019a, 2019b; Li et al., 2018; Ivanova et al., 2019; Chen et al., 2020). Moreover, the extensive microscopic observations of numerous cores from petroleum-

bearing reservoirs with good physical properties have proven the presence of secondary pores (Zhong and Zhu, 2008; Cao et al., 2014; Yuan et al., 2015; Huang et al., 2016; Meng et al., 2017; Huang et al., 2024).

Statistical analysis of numerous subsurface water samples with depth >5 km from many petroleum-bearing basins worldwide indicate that concentrations of WSOAA range from dozens to thousands milligrams per liter, where acetate is of highest abundance (Carothers and Kharaka, 1978; Fisher, 1987; Barth and Riis, 1992; MacGowan and Surdam, 1990; Barth, 1991). Concentrations of WSOAA usually show good correlation with temperature. With increasing temperature at temperature not exceeding 140°C, maximum concentrations occur at approximately 90°C. Afterward, they decrease quickly (Fisher, 1978). However, data are absent at higher temperature intervals due to lack of drilling campaigns previously. Therefore, there is little information regarding the distributions of organic acids at both deep-ultradeep zones and at high-over mature stages. Nowadays, petroleum exploration and development have drilled to ~9000 m reservoirs below the surface, such as in the Shunbei and Fuman oil fields in China (Xu et al., 2022, 2024; Wang, 2023; Lu et al., 2024), and the presence of secondary pores are partly attributed to the dissolution of acidic fluids (Ma et al., 2019). Such conditions provide a window to look into the distributions and origins of organic acids.

Using heated ultrapure water to extract in-situ organic acids from sedimentary rocks is a very effective way. There are remarkable differences in the compositions and abundances of WSOAA in fluid extracts of coals and shales (Zhu et al., 2015; Li et al.,

2021a, 2021b). Besides acetate, fluid extracts of some coals and shales include high amount of formate. Concentrations of WSOAA are relatively high in immature source rocks, and correlate roughly positively with oxygen index (OI) as observed (Zhu et al., 2015; Li et al., 2021a, 2021b).

Numerous scholars have carried out a suite of hydrous pyrolysis experiment to explore the distributions, generation potential, dissolution capacity, and possible origin of organic acids during the thermal maturity of organic matter (OM) using natural samples such as crude oil, hydrocarbons, kerogen isolates, and organic matter-rich shale (e.g., Kawamura et al., 1986; Eglinton et al., 1987; Kawamura and Kaplan, 1987; Barth et al., 1988; Kharaka et al., 1993; Borgund and Barth; 1994; Chen et al., 1994a; Seewald, 2001; Dias et al., 2002; Zhang et al., 2009; Li et al., 2018; Yuan et al., 2019b). Source rocks with low thermal maturity and high OI tend to generate more organic acids (Chen et al., 1994a; Barth et al., 1998; Dias et al., 2002) because they have high oxygen content and more oxygen-containing functional groups, which demonstrates that organic acids can originate from the thermal degradation of OM. Whereas, it is challenging to interpret the development of secondary dissolution pores in deep-ultradeep reservoirs using the traditional knowledge of origin of organic acids, because source rocks have very low potential to generate organic acids due to their oxygen content at high-over mature stages. However, considerable levels of formate and acetate have been detected in coals at high-over mature stages (Li et al., 2021a, 2021b). Therefore, exploring the origin of organic acids at this stage is, although very difficult, extremely important.

This study aims to uncover the distributions of WSOAA in source rocks from immature to high-over mature stages, as well as in deep-ultradeep subsurface water samples, to analyze the major factors influencing the distributions of organic acids, and to discuss the origins of organic acids at high-over mature stages combined with pyrolysis experiments under different moisture contents conditions. This work can provide a deeper understanding of the origins of organic acids at high-over mature stages and the evolution of secondary porosity in deep-ultradeep strata.

2 Methods

2.1 Sample collection and pretreatment

In this study, twenty-nine source rock samples were collected from drill cores in several petroleum-bearing basins in China. They include five Shanxi Formation mudstones with various buried depths and almost same TOC content in Ordos Basin, seven Triassic Yanchang Formation shales with diverse TOC contents and almost same thermal maturity in Ordos Basin, and seventeen coals with different thermal maturities from Junggar Basin, Ordos Basin, Minhe Basin, Qinshui Basin and Southern North China Basin due to no a single basin containing samples with wide thermal maturity interval (Li et al., 2021a). In order to fully compare the effect of thermal maturity on the generation of organic acids, the vast majority of coal samples (thirteen out of seventeen) were chosen from the same stratigraphy in adjacent basins. Detailed information on all samples was presented in Table 1. Six subsurface water samples with depth between 6544 m and 8396 m from exploration wells in Tarim Basin were also collected, and their relevant information was presented in Table 2. These subsurface

water samples were preserved in Ordovician carbonate reservoirs that include good effective reservoir space (Jia et al. 2016; Chen et al., 2021).

Prior to Soxhlet extraction experiments and pyrolysis experiments, the surface of all source rocks must be removed due to surface oxidation or pollutions from drilling activities rather than cleaning by ultrapure water, because the latter can cause the loss of WSOAA. Then, powdered source rock samples (below 200 mesh) were freeze-dried for 48 h for eliminating the effect of moisture on the subsequent experiments.

2.2 Experiments

2.2.1 WSOAA analysis

In order to eliminate the pollutions from filter papers, filter papers were extracted using ultrapure water with the resistivity of 18.2 MΩ·cm for 72 h. Extracted filter papers were then freeze-dried for 48 h. Subsequently, 15 g of powdered samples packaged by treated filter paper was extracted using 250 mL of heated ultrapure water. Fluid extracts after filtering using a 0.22 um needle-tube filter were analyzed within 12 h using 930 Compact Flex Ion Chromatography System (Metrohm AG) for the compositions and abundances of WSSOA.

Measured WSOAA included monocarboxylate (formate, acetate, propionate and butyrate) and dicarboxylate (oxalate, malonate, succinate). Formate, acetate, propionate, butyrate, malonate and succinate in extracts were determined by Metrosep Organic Acids 250/7-8 column, with eluent of 2 mM H_2SO_4 plus 0.1 M LiCl, flow rate of 0.5 mL/min, and column temperature of 30 ℃. Oxalate in extracts was measured using Metrosep A Supp 17-250/4.0, with eluent of 5.0 mM Na_2CO_3 and 0.2 mM $NaHCO_3$

150 plus H_2SO_4 solution (1 L ultrapure water including 3 mL concentrated H_2SO_4), flow
151 rate of 0.9 mL/min, and column temperature of 40 ℃. The concentrations of WSOAA
152 were determined by external standard via a multiple-point standard calibration curve.
153 The correlation coefficients of standard curves for all WSOAA measurements was
154 above 0.995 (Figure 1).

155 **2.2.2 Analysis of geochemistry and infrared spectra**

156 TOC content was determined using a CS-920 High Frequency Infrared Ray
157 Carbon Sulphur Analyzer. Programmed pyrolysis was conducted using a Rock-Eval 6
158 Pyrolyser (VINCI Technologies). Detailed descriptions of test principle can be found
159 in Behar et al. (2001). Prior to TOC tests, powdered samples were soaked into the
160 solution with ten percent of hydrochloric acid to eliminate the effect of carbonate
161 minerals. Vritinite reflectance (R_o) was determined using Axio Scope A1 & JM
162 microscopic photometer (Zeiss) under ambient temperature (23 ℃) following SY/T
163 5214-2012.

164 Mineral compositions for Triassic Yangchang Formation shale from Ordos Basin
165 were obtained using Rigaku Ultima IV X-ray diffractometer at 40 kV and 40 mA with
166 a CuKα radiation of λ=1.5406. Shale samples were scanned stepwise at a rate of 4°/min,
167 scanning range is 3°-75° (2θ).

168 Infrared spectra for coals with various maturities were measured by an Infrared
169 spectrometer (Bruker)using the most used KBr pellet method. Data was collected
170 within scan range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1} for 100 s. Detailed
171 procedures were described in Li et al. (2021a).

2.2.3 Pyrolysis experiments

20 g of powdered shale samples from Triassic Yanchang Formation of Ordos Basin were placed into the high-temperature and high-pressure stainless-steel reactor, and then pyrolysis experiments were conducted for 72 h. 2 mL ultrapure water was added into reactor as hydrous pyrolysis system for comparison with anhydrous pyrolysis system. Creating an inert condition in sealed stainless-steel reactor is via six-time displace of high purity of N_2 and subsequent evacuation. Pyrolysis experiments were conducted at 250 ℃, 300 ℃, 350 ℃, 400 ℃ and 450 ℃ respectively. The tightness of pyrolysis system was checked through applying soapy water at the exhaust port during the pyrolysis experiments. After pyrolysis experiments, 5 g of powdered shale samples were extracted using heated ultrapure water for 72 h to obtain WSOAA. Results of Rock-Eval pyrolysis parameters for pyrolysis shale residues could be found in Li et al. (2023).

3 Results

3.1 WSOAA in source rocks and deep-ultradeep subsurface water

The concentrations of WSOAA in source rocks are shown in Figure 2a. They range from 0.244 mg/L to 83.192 mg/L. Mudstones from Permian Shanxi Formation have relatively low concentrations of WSOAA, ranging between 3.409 mg/L~13.201 mg/L. Concentrations of WSOAA in the shales from Triassic Yanchang Formation are in the range of 8.108 mg/L~39.943 mg/L. Concentrations of WSOAA in coals with very wide maturity intervals (T_{max} from 420 ℃ to 618 ℃) are between 0.244 mg/L and 83.192 mg/L. Concentrations of WSOAA in deep-ultradeep subsurface water samples from the

Tarim Basin are in the range of 3.693 mg/L~394.486 mg/L (Figure 2a). In addition, with increasing pH value of subsurface water, the concentrations of WSOAA in the samples show a dramatic decrease when pH<7 (from 394.486 ppm to 61.257 ppm) and then a gradual reduction (Figure 2b).

For both source rocks and deep-ultradeep subsurface water samples, the percentages of monocarboxylates are significantly greater than those of dicarboxylates (Figure 2c), which is similar to what was documented in previous literatures (Carothers and Kharaka, 1978; Fisher, 1987; Barth and Rill, 1992; MacGowan and Surdam, 1990; Barth, 1991). Monocarboxylates are dominated by formate and acetate, and dicarboxylates are mainly composed of oxalate and succinate (Figure 2c).

Formate concentrations in all samples are significantly different from the values reported in previous studies. Formate concentrations have rarely been reported in previous works (i.e., Carothers and Kharaka, 1978; Fisher, 1987). In this study, formate has relatively high abundance. For some samples with mainly type-III OM, such as coals from Permian Shanxi Formation, it even outnumbers acetate concentration. In addition, some recent literatures also have reported elevated level of formate from sedimentary rocks (Zhu et al., 2015; Li et al., 2018; Li et al., 2021a, 2021b, 2023), ancient fracture fluids (Lollar et al., 2021), products of hydrous pyrolysis (Li et al., 2018; Yuan et al., 2019b), hydrothermal fields (Lang et al., 2010; MaDermott et al., 2015), and flowback water (Faksness et al., 2004; Luek and Gonsior, 2017; Orem et al., 2014). McCollom and Seewald (2003) have demonstrated that formate is thermodynamically stable under strongly reducing and moderately alkaline pH

conditions. Therefore, the most possible reason for formate not being detected in subsurface water may be attributed to low analytical techniques at that time.

3.2 Production rate of organic acids

Production rate of organic acids for shales under different pyrolysis conditions at different temperatures are shown in Figure 2d. At ≤350 ℃ pyrolysis temperature, the production rate of organic acids is almost equivalent under both anhydrous and hydrous pyrolysis, which is determined by the natural maturity of the shale used in this work. However, at ⩾400 ℃ pyrolysis temperature, the production rate of organic acids is significantly higher under hydrous than anhydrous pyrolysis, and the difference between two pyrolysis series increases from 400 ℃ to 450 ℃ pyrolysis temperature. This indicates that the presence of water promotes the generation of organic acids.

4 Discussion

4.1 Factors affecting the distributions of WSOAAs in source rocks

4.1.1 TOC content

According to the fluid products from the hydrous pyrolysis of OM/kerogen (Eglinton et al., 1987; Barth et al., 1988; Chen et al., 1994a; Zhang et al., 2009; Helten et al., 2022) and crude oil (Curiale et al., 1992; Kharaka et al., 1993; Borgund and Barth; 1994), and liquid extracts from shales and coals using heated ultrapure water (Zhu et al., 2015; Li et al., 2021a, 2021b), source rocks can generate and release organic acids under thermal stress.

In order to accurately determine the effect of OM abundance on the distributions of WSOAA, and minimize the effect of other factors, such as sedimentary environment,

thermal maturity history, OM provenance and burial depth, seven representative shales from Triassic Yanchang Formation with diverse TOC contents (from 0.84 to 23.90 %) from well YK1 located in Ordos Basin are selected.

Results show that TOC content correlates positively with concentrations of WSOAA (Figure. 3a). This indicates that shales with high TOC contents generate more organic acids. Moreover, concentrations of WSOAA are positively proportional to the percentage of dicarboxylate (Figure. 3b). Organic acids can dissolve carbonate, aluminosilicate and quartz as demonstrated through a suite of acid fluid-minerals/rocks dissolution simulation experiments, which is consistent with the negative correlations observed between concentrations of WSOAA and the amounts of carbonate, clay minerals and quartz respectively (Figures. 3c, 3e and 3f).

Note that feldspar content does not correlate with the concentrations of WSOAA (Figure 3d), which is due to that strong volcanism inputting pyroclasts alters the relationship between them. Jones et al. (2022) have demonstrated that pyroclasts include multiple forms of plagioclase via microscope observations, such as phenocryst, microphenocryst, and xenocryst. Additionally, previous studies have demonstrated that there are multiply episodes of volcanism during the Triassic period, causing the enrichment of organic matter and abnormally high TOC content in shale from the Yanchang Formation (Liu et al., 2024; Zhang et al., 2020). To sum up, in this study, we observed the unique occurrence that some shale from Yanchang Formation had both high feldspar content and concentrations of WSOAA.

Commonly, soluble minerals have greater solubility in dicarboxylate than in

monocarboxylate buffer system (Surdam et al., 1984; Knauss and Copenhaver, 1995; Chen et al., 2008; Bennett, 1991; Welch and Ullman, 1996; Blake and Walter, 1999; Gama and Ganor, 2006; Chen et al., 2020). Taking hydrargillite as an example, the content of aqueous Al^{3+} is three orders of magnitude higher in oxalic than in acetic acid buffer system (Surdam et al., 1984). Chen et al. (2008) also have demonstrated stronger complexing capacity of difunctional carboxylic acid buffer system. According to the findings from Chen et al. (1994b), oxalate can combine quartz to form ring-like compounds to prevent silica from agglomerating. However, Manning et al. (1994) have documented that only the rate of albite dissolution is promoted, but its solubility cannot be essentially enhanced under acetic acid buffer system, which challenges the complexing potential of acetate. Although there are some controversies over the dissolution mechanisms on complexing ability of monofunctional carboxylic anions, the complexing ability of difunctional carboxylic anions is beyond doubt.

Al and Si released by the dissolution of organic acids generated can react with dicarboxylate to form stable organic complex (Cama and Ganor, 2006; Welch and Ullan, 1996; Prasad and Sulaxna, 2005). Moreover, the seventh member of shale from Triassic Yanchang Formation undergoing progressive generation of hydrocarbon caused overpressure of fluid (Li et al., 2010). When the pressure of fluid was above pore pressure, stable organic complex would migrate up or down during the expulsion of liquid hydrocarbons generated. Without required elements such as Al and Si, the growth of clay minerals and quartz would be inhibited, which is significant for reservoir space.

TOC-normalized concentration of WSOAA, which can be used to evaluate the

organic acid production rate per gram of TOC, is negatively proportional to TOC as shown in Figure 3e. This indicates that shale with high TOC has low organic acid production rate, although it can generate great levels of organic acids. This is consistent with the work by Lundegard and Senftle (1987), who carried out a suite hydrous pyrolysis experiments at temperature interval of 250~350 ℃ for 72 h using carbonaceous shale. At the same pyrolysis temperature, lower organic acid production rate always is found for shale with 7.71 % TOC than shale with 4.05 % TOC (Lundegard and Senftle, 1987). Low organic acid production rate possibly depends on limited ability of hydrogen supply.

Hydrogen source is vital for the generation of hydrocarbon. H_2O and H_2 are important hydrogen sources, participating in thermal degradation and cracking and promoting hydrocarbon production rate (Hawkes, 1972; Lewan, 1997; Jin et al., 2004; Liu et al., 2019; Gao et al., 2020; Huang et al., 2022; Liang et al., 2021). Lewan (1997) demonstrated that OM could evolve into an insoluble bitumen-pyrobitumen under anhydrous pyrolysis condition due to the absence of hydrogen, and cross linking was the dominant reaction pathway. The experimental results from Yuan et al. (2019b) also supported the generation of pyrobitumen under an anhydrous pyrolysis system. On the contrary, OM generates saturate-enriched oil with enough hydrogen provided by H_2O under hydrous pyrolysis condition, during which thermal cracking is the major reaction pathway (Lewan, 1997). In summary, during the thermal evolution of OM, the higher the initial TOC content, the more serious deficiency of hydrogen source, therefore, the lower hydrocarbon conversion rate.

Figure 4 shows different evolution pathways of oxygen-containing functional groups at diverse levels of hydrogen systems. In a system lacking of hydrogen, the dehydration reactions of diverse oxygen-containing functional groups or multiple carboxyl groups are important pathways to form H_2O. Meanwhile the cyclization and aromatization of hydrocarbons are important pathways to form H_2. These H_2O and H_2 are vital for the generation of hydrocarbons (Liu et al., 2019). However, the decrease of oxygen-including functional groups due to dehydration reactions results in low organic acid production rate. In a system with sufficient hydrogen, the direct fall-off of oxygen-including functional groups such as carboxyl, and the hydrolysis of ester tend to form organic acids. Moreover, under favorable conditions, the dissociation of water produces hydroxyl radicals, oxidizing hydrocarbon to alcohol to aldehyde/ketone to final carboxylic acid (Seewald, 2001, 2003). Overall, shales with low TOC contents, corresponding to sufficient hydrogen system, has high production rate of organic acids due to either more initial carboxylic acids directly falling off from OM or other organic components oxidized by hydroxyl radical, such as oxygen-containing functional groups and hydrocarbons.

4.1.2 Maturity

Figure 5 shows that concentrations of WSOAA change with T_{max}. As T_{max} rises, concentrations of WSOAA first present a quick downtick, followed by a slight uptick and an ongoing downtick to trace afterward (Figure 5a). Concentrations of major WSOAA, such as formate, acetate and oxalate, show almost same evolution trend over T_{max} (Figures. 5b, 5c, and 5d). Moreover, there are positive correlations among

326 concentrations of formate, acetate and oxalate as observed (Figures. 5e, 5f, and 5g),
327 suggesting the same origin and occurrence of organic acids.

328 Thermal evolution of OM is a process during which the contents of hydrogen and
329 oxygen decrease gradually but carbon becomes enriched, leading to gradually increased
330 degree of aromatization (He et al., 2017). At immature stage, oxygen-containing
331 functional groups such as carboxylic-acid, ester and carbonyl groups, fall off
332 substantially. Robin and Rouxhet (1978) demonstrated that there were huge differences
333 in the stability of oxygen-containing functional groups. Carboxylic-acid groups were
334 less thermally stable, followed by ester groups and carbonyl groups. Relative to the
335 atomic ratio of H/C, atomic ratio of O/C has shown significantly decreased rate
336 according to the generalized van Krevlan diagram (Surdam et al., 1987). Element
337 analysis of coal from Li et al. (2021a) and infrared spectrum (Figure 6) also support the
338 dramatic decrease of oxygen contents. Moreover, the product from kerogen is mainly
339 water-soluble organic components at immature stage. Overall, the concentrations of
340 WSOAA are relatively high, and present remarkable downtick over maturity.

341 During mature stage, OM converts into large amounts of liquid hydrocarbons and
342 bitumen under thermal stress. These components consist of certain amount of oxygen-
343 containing functional groups, which is well substantiated by fourier transform infrared
344 spectroscopy and column chromatography (Craddock et al., 2015; Zhang et al., 2006).
345 Moreover, thermal stress at this stage is insufficient to cause thermal cracking of these
346 liquid hydrocarbons and bitumen. Therefore, concentrations of WSOAA at this stage is
347 relatively low.

With progressive maturity, the increase of thermal stress results in the thermal cracking of liquid hydrocarbon and bitumen to generate certain concentrations of organic acids. In addition, at high-over mature stages, gaseous hydrocarbons, especially CH_4 as the byproducts of these liquid hydrocarbons and bitumen, possibly are oxidized thermochemically by hydroxyl radical to form organic acids, which seem to be well consistent with the experimental results of this study (Figure 2d). Lewan (1997) used numerous hydrous pyrolysis experiments to explore the interactions between water and OM, and demonstrated that water oxidizing organic components to form organic acids was thermodynamically practicable. This suggests that concentrations of organic acids after mature stage is not limited to the protal oxygen content of OM/kerogen. Overall, concentrations of WSOAA at high-over mature stages present a slight uptick due to thermal cracking of liquid hydrocarbons and thermochemical oxidation of organic components.

As maturity increases, the content of oxygen in coal becomes extremely low. For instance, coal with 618 ℃ T_{max} only has 2% oxygen content (Li et al., 2021a), which is consistent with almost no responses to oxygen-containing functional groups with 1500-1800 cm^{-1} wavenumber (Figure 6). Moreover, this is well substantiated by the low extraction rate and low amounts of bitumen plus non-hydrocarbon compositions (Zhang et al., 2006). Coal is almost completely of aromatization. Therefore, concentrations of WSOAA are trace at this stage.

4.1.3 Type of OM

Coal, typical type-III OM, has high oxygen content at immature stage in particular.

Li et al. (2021a) documented that lignites with T_{max} less than 425 ℃ in Ordos Basin and Junggar Basin in China has over 20 % oxygen content. Mangi et al. (2020) reported that coals with 0.4 % R_o in Lower Indus Basin in Pakistan contained oxygen content from 39.38 % to 50.84 %. Such high oxygen content in coal is very conductive to generate great levels of organic acids (Cooles et al., 1987). As expected, concentrations of WSOAA in coal are significantly greater than those in shales (type-I or -II OM) at immature stage as shown in Figure 7. With progressive maturity, concentrations of WSOAA in diverse types of OMs are roughly comparable. This is due to little differences of oxygen content. It coincides with the chemical model of kerogen proposed by Behar and Vandenbroucke (1987). The huge difference in O/C atomic ratio is at the beginning of diagenesis, O/C atomic ratios in type-I, -II and -III kerogens are 0.060, 0.196 and 0.281 respectively, but O/C atomic ratios are 0.013, 0.026 and 0.059 respectively at the end of catagenesis (Behar and Vandenbroucke, 1987).

Considering previous works and this work, formate and acetate are dominant components, especially in deep-ultradeep zone and at high-over mature stages. In order to uncover the differences in distributions between formate and acetate in different types of OMs, the ratio of formate concentration to acetate concentration, expressed as *c*(formate)/*c*(acetate), are plotted vs. T_{max} as shown in Figure 8. For type-III OM, such as most of the Permian coals from the Shanxi Formation in the Northern North China Basin and Qinshui Basin, *c*(formate)/*c*(acetate) ratios are close to or above 1, while they are below 1 for type-I and -II OMs, such as shales from Triassic Yanchang Formation, Jurassic Posidonia Formation, Mississippian Bakken Formation, Late Devonian

392 Duvernay Formation (Figure 8). Moreover, as T_{max} increases, for type-III OM
393 *c*(formate)/*c*(acetate) ratios increase while they decrease for type-I and -II OMs (Figure
394 8). This suggests that type-III OM is enriched in formic acid but type-I and -II OMs are
395 enriched in acetic acid. Note that some coal samples collected from the Ordos Basin
396 have *c*(formate)/*c*(acetate) ratios close to or below 1. This is due to that besides type-
397 III OM, these coals include some type-II or -I OMs formed in a marine-terrestrial
398 transitional environment. Insights from sedimentology, detrital zircon U-Pb
399 geochronology, and organic geochemistry, the Ordos Basin experienced a transition
400 from marine to terrestrial conditions during the Carboniferous–Permian period (Zhao
401 et al., 2021; Li et al., 2024).

402 The differences in the abundances of organic acids in different types of OMs are
403 closely related to macromolecular structure and their metabolites. According to the
404 chemical model proposed by Behar and Vandenbroucke (1987), at the beginning of
405 diagenesis, relative to type-I and -II kerogens, type-III kerogen has a number of shorter
406 oxygen-containing side chains, such as methoxy and methyl ester, the fall-off of these
407 functional groups tends to generate high level of formic acid. Herein, generated formic
408 acid comes from the fall-off of oxygen-containing functional groups before mature
409 stage.

410 At high-over mature stages, type-III OM mainly generates significant amount of
411 light gaseous hydrocarbons via thermal cracking, especially CH_4. Zhang et al. (2019)
412 reported that CH_4 in No.3 coal seam in Qinshui Basin reaching up to 96.22 % (vol.). It
413 can be deduced that formic acid is generated via thermochemical oxidation of CH_4,

414 which will be discussed below in Section 4.2.

415 For type-I and -II OMs, liquid hydrocarbon and bitumen mainly evolve into light
416 condensate at high-over mature stages, lacking of CH_4 relatively. Although acetic
417 acid/acetate can occur decarboxylation to form CH_4, the kinetic barrier of acetic
418 acid/acetate decomposition is very high (Wang et al., 2021). The decomposition rate for
419 acetic acid/acetate reactive system is extremely low at 180 °C, only 2.48×10^{-9} s^{-1} at 60
420 MPa of fluid pressure and 90 MPa of lithostatic pressure (Li et al., 2017; Li et al.,
421 2021c). Therefore, acetate acid is commonly the most abundant component in type-I
422 and -II OMs.

423 **4.2 Origin of organic acids at high-over mature stages**

424 Combining the results of extraction experiments and hydrous pyrolysis
425 experiments in this study, and the simulation experiments of thermal stability of organic
426 acid buffer system (Li et al., 2017; Li et al., 2021c), it is reasonably inferred that organic
427 acids can be formed via thermochemical oxidation of organic components at high-over
428 mature stages. The requirements for thermochemical oxidation of organic components
429 including temperature and oxidant, along with isotope fractionation evidences, are
430 analyzed in detail.

431 The thermochemical oxidation of organic components commonly takes place at
432 temperature above 100 °C (Machel, 2001; Kiyosu and Imaizumi, 1996). Hu et al. (2018)
433 demonstrated that CH_4 can be oxidized by high-valence Mn within 90-135 °C in natural
434 system (Triassic Baikouquan Formation mudstone in Junggar Basin, China) based on
435 the evidences from the carbon isotope of calcite and the thermometry of fluid inclusions.

436 The lower temperature (below 65 ℃) could meet the conditions of CH_4 oxidized by
437 high-valence Mn, which had been demonstrated by Cai et al. (2021) according to the
438 clumped isotope of calcite. Wan et al. (2021) documented via a suite of pyrolysis
439 experiments that CH_3OH and CH_4 could be oxidized by MnO_2 and Fe_2O_3 at the
440 temperature of approximately 100 ℃ and 200 ℃ respectively. Yuan et al. (2019b)
441 demonstrated the interrelated changes of minerals, gaseous byproducts and organic
442 acids in heated oil-water-feldspar systems via a suite of thermal simulation experiments
443 at the temperature of 360 ℃. They observed considerable levels of organic acids in the
444 $C_{20}H_{42}$ (2 g) plus H_2O (5 g) pyrolysis system, and the concentration of oxalic acid in
445 the liquid residues reached up to 50 mg/L. In summary, high-over mature stages
446 corresponding to geological temperature could meet the requirement for the
447 thermochemical oxidation of organic components.

448 Hydroxyl radical is one of the most powerful oxidizing agents (Gligorovski, et al.,
449 2015; Nosaka and Nosaka, 2017; Pei et al., 2020). Its oxidation potential is up to 2.8 V,
450 only second to Fluorine oxidizer (3.05 V). It can be yielded in the aqueous phase at
451 certain conditions such as radiolysis (Gilles et al., 2018; Smith et al., 2021), electric
452 field (Xiong et al., 2020). Yuan et al. (2024) carried out diverse pyrolysis experiments
453 using a transparent silica capillary thermal experimental system that was equipped with
454 the high-temperature, high pressure Hastelloy reactors. They observed the formation of
455 large amounts of microdroplets near the water-oil interface without surfactants since
456 the pyrolysis temperature exceeded 150~165 ℃; moreover, hydroxyl radicals occurred
457 simultaneously with microdroplet formation through electron paramagnetic resonance

458 tests (Yuan et al., 2024). In this work, we observed higher concentrations of WSOAA
459 at 400 ℃ and 450 ℃ under hydrous pyrolysis, which was attributed to the hydroxyl
460 radicals oxidizing organic components. With the exception of hydroxyl radical, coal
461 itself and its roof and floor generally contain diverse key metals, such as iron,
462 manganese, gallium, titanium, vanadium, germanium, uranium and rare earth elements
463 (Seredin and Finkelman, 2008; Seredin et al., 2013; Dai et al., 2020), these high-valence
464 metals also possibly have certain capacity of oxidizing organic components, resulting
465 in the formation of organic acids. In summary, the presence of abundant oxidants in
466 geological conditions can meet the requirements for the thermochemical oxidation of
467 organic components.

468 From isotope evidence, Dias et al. (2002) demonstrated that $\delta^{13}C$ values of acetic
469 acid showed an uptick trend at pyrolysis temperature higher 260 ℃, which
470 demonstrated the preferential oxidization of ^{12}C, subsequently resulting in the
471 enrichment of ^{13}C in acetic acid with the increase of pyrolysis temperature. Overall, the
472 thermochemical oxidation of organic components is an important mechanism to form
473 organic acids at high-over mature stages.

474 **5 Geological implications**

475 The role of organic acids as acid fluid, and as metastable intermediates due to the
476 thermochemical oxidation of organic components, have important geochemical
477 implications in sedimentary basins. The first implication centers on the phenomena that
478 different OMs have remarkable differences in *c*(formate)/*c*(acetate) ratios. They show
479 reverse trends with T_{max} for different types of OMs (Figure 8). Therefore

480 *c*(formate)/*c*(acetate) ratio can be used as an index distinguishing the type of OM and
481 evaluating the thermal maturity of OM. These findings can provide constraint on the
482 identification of OM type and the evaluation of thermal maturity.

483 The second implication is related to both the uptick of concentrations of WSOAA
484 at high-over mature stages and considerable concentrations of organic acids at deep-
485 ultradeep depth. Anomalous concentrations of organic acids are largely attributed to the
486 thermochemical oxidation of organic components by mainly hydroxyl radicals. Within
487 the crust of the Earth, water is ubiquitous in rock pores, fractures and hydrated minerals
488 (Lewan, 1997). With continuous subsidence of strata, hydroxyl radicals are generated
489 at the water-hydrocarbon interfaces, which initiates the extensive thermochemical
490 oxidation of organic components, resulting in the ongoing generation of organic acids
491 and simultaneously creating new secondary pores. Well-developed corroded cavities in
492 No. 3 or No. 15 coals (Ro$\geqslant$2.0 %) in Qinshui Basin, China (Figure 9) are visible
493 evidence with regard to the dissolution of acidic fluids. Moreover, we observed higher
494 pore volume via low-pressure N_2 adsorption under hydrous than anhydrous pyrolysis
495 at $\geqslant$400 ℃, which is partly due to the dissolution of organic acids (Li et al., 2023).
496 Consequently, petroleum exploration can be extended to great depths in sedimentary
497 basins, when formation temperatures are not exceeding 230 ℃, because organic acids
498 occur to decompose extensively at temperature above 230 ℃ (Li et al., 2017).

499 These evidence mentioned above challenge the organic acid model proposed by
500 Surdam et al. (1989), where high concentration interval of organic acids occurred at
501 temperature between 80-120 ℃. Beside the temperature interval proposed by Surdam

et al. (1989), there is at least another one at deep-ultradeep zone. However, it is difficult to capture this temperature interval so far due to the compilation of limited dataset. It still requires extensive further studies.

6 Conclusions

(1) Percentage of monocarboxylate is significantly higher than that of dicarboxylate in both source rocks and deep-ultradeep subsurface water samples. Monocarboxylate is mainly dominated by formate and acetate, and dicarboxylate is mainly composed of oxalate and succinate.

(2) TOC content, maturity and OM type jointly affect the distributions of WSOAA. Although high-TOC oil-generating source rocks generate elevated level of organic acids, it has low organic acid production rate possibly due to lack of hydrogen. Concentrations of WSOAA show a "sharp decrease-slight increase-slow decrease" evolution trend with progressive maturity. At immature stage, gas-generating source rock contains higher concentrations of WSOAA, due to the presence of abundant oxygen-bearing function groups. Gas-generating source rock is rich in formic acid while oil-generated source rock is rich in acetic acid, which relates closely to macromolecular structure and their metabolites.

(3) Both an uptick of concentrations of WSOAA at high-over mature stages and the presence of high level of organic acids in deep-ultradeep subsurface water are due to thermochemical oxidation of organic components by mainly hydroxyl radicals. These geochemical signatures provide new insight into the origins of organic acids and the evolution of secondary porosity at deep-ultradeep depth. It indicates that

524 petroleum exploration can be extended to great depths (formation temperature not
525 exceeding 230 ℃) in sedimentary basins.

526 **Conflict of Interest**

527 The authors declare that they have no conflict of Interest.

528 **Date availability**

529 Data will be made available on request.

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867 **Table 1** Information on sedimentary rock samples

ID	Lithology/ Subsurface water	Basin	Stratum	TOC (%)	Depth (m)	T_{max} (℃)	Ro (%)	S_3 (mg/g)	Type of OM
YK46	Shale	Ordos Basin	Triassic Yanchang Formation	5.82	182.2	433		0.01	I or II
YK55				0.84	198.1	442		0	
YK78				13.40	223.4	435		0.01	
YK81				14.40	228.9	436		0.45	
YK83				16.60	231.5	436		0.38	
YK93				23.90	237.8	442		0.48	
YK107				12.80	256.8	442		0.38	
L30-1	Mudstone		Permian Shanxi Formation	0.92	3797.7	n.d.	1.68	n.d.	III
L30-2				1.37	3849.7		1.41		
Q44				0.91	2861.4		1.24		
S16				1.08	2201.3		1.61		
S202				0.99	2704.3		1.38		
JZMY	Coal		Jurassic Yan'an Formation	58.25	138.6	420		10.8	III
JXD				57.07	140.3	424		9.4	
S27			Permian Shanxi Formation	66.32	2060.0	481		0.80	
S394				60.49	2932.4	502		0.89	
S13				69.84	2148.5	456		1.28	
E82				76.80	3760.6	500		0.95	
E27				55.62	3891.7	473		0.97	
JJ-GB		Junggar Basin	Jurassic Xishanyao Formation	64.36	99.5	425		8.99	
YJ		Minhe Basin	Jurassic Yaojie Formation	75.52	362.4	450		0.49	
PSD		Southern North China Basin	Permian Shanxi Formation	74.91	605.1	452		0.78	
ZJZ				68.73	455.2	522		0.23	
LG				46.12	350.5	594		0.12	
ZGX				63.21	742.3	618		0.06	
SL		Qinshui Basin		53.48	451.1	460		0.36	
YX				74.92	608.1	477		0.59	
ZZ				67.12	695.4	540		0.94	
HD				60.60	355.6	604		0.22	

868 **Table 2** Information on deep-ultradeep subsurface water samples in the Tarim Basin

ID	Depth (m)	pH	Salinity (g/L)	Concentrations of WSOAA (ppm)
TH12214CH	6890~7135	6	253	109.929

TH12328	6279~6544	7.4	206	61.257
SB53-2H	7749~8847	7	119	62.625
SB5-15H	7632~8211	6.4	107	3.693
SB42X	7385~7996	4.7	no data	394.486
SB8X	7738~8396	8.9	159	16.149

869

870 **Figure captions and Explanation plates**

871 **Figure 1.** Fitting curves of peak area vs. concentrations of WSOAA

872 **Figure 2.** WSOAA in various sedimentary basins in China. (a) Concentrations of
873 WSOAA in source rocks and deep-ultradeep subsurface water. (b) Plot of pH and
874 concentration of WSOAA for subsurface water samples in the Tarim Basin, China. (c)
875 Percentages of diverse WSOAA in source rocks and deep-ultradeep subsurface water,
876 Solid and blank bars represent dicarboxylates, and monocarboxylates respectively. (d)
877 Production rate of organic acids for shales after pyrolysis experiments at different
878 temperatures.

879 **Figure 3.** Distributions of WSOAA in shales with different TOC contents. Plots of TOC
880 content vs. concentrations of WSOAA (a), concentrations of WSOAA vs. percentage
881 of dicarboxylates (b), concentrations of WSOAA vs. carbonate content (c),
882 concentrations of WSOAA vs. feldspar contents (d), concentrations of WSOAA vs. clay
883 mineral content (e), concentrations of WSOAA vs. quartz contents (f), TOC content vs.
884 TOC-normalized concentrations of WSOAA (g).

885 **Figure 4.** Diverse evolution pathways associated with oxygen-containing functional

886 groups in systems with different levels of hydrogen. R-, R_1, R_2, R_3, R_4, R_5, and R_6 all
887 represent alkyl groups.

888 **Figure 5.** Distributions of WSOAA in coals with various maturities. Plots of T_{max} versus
889 concentrations of WSOAA (a), formate (b), acetate (c) and oxalate (d), correlations
890 among concentrations of formate (e), acetate (f) and oxalate (g).

891 **Figure 6.** Infrared spectrum for coals with different maturities

892 **Figure 7.** Plots of T_{max} vs. concentrations of WSOAA in diverse types of OMs

893 **Figure 8.** Plot of T_{max} versus *c*(formate)/*c*(acetate) ratio for different types of OMs,
894 including Duvernay shale, Posidonia shale, Bakken shale and New Zealand coal (date
895 from Zhu et al., 2015).

896 **Figure 9.** Corroded cavities in No.3 and No. 15 high-rank coals in Qinshui Basin, China.
897 Corroded cavities are area defined by red lines.