The role of exogenous oxygen in organic acid generation in deep reservoirs of petroleum-producing basins: Progress and prospects

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Abstract. The source, yield, and distribution of organic acids in oilfield waters in petroleum-producing basins have not been satisfactorily explained by previous studies that have focused on oxygen-containing functional groups in kerogen as the major source of such acids. This study reviews four possible mechanisms by which exogenous oxygen can participate in petroleum or organic acid generation. Biodegradation and mineral oxidation generate organic acids in oilfield waters, leading to an increase in the oxygen content of altered oils, which then have greater potential for producing organic acids. Hydrolytic disproportionation reaction and thermochemical sulfate reduction reactions at high temperatures lead to the in situ generation and accumulation of organic acids in deep reservoirs. The incorporation of exogenous oxygen increases the yield and expands the distribution of organic acids in reservoirs at various depths. The acids derived from exogenous oxygen play critical roles in the development and preservation of deep reservoirs. Further research is required to determine the volumes and compositions of organic acids produced by these reactions, and to further understand the role of organic acids in the alteration of deep reservoirs under more realistic conditions.

1. Introduction
Since their widespread occurrence in waters of petroleum-producing basins was first documented in 1978 [1], the origin, distribution, and geochemical significance of low-molecular-weight (LMW) organic acid anions (C₁−C₃) have become a popular field of study in geochemistry. Laboratory simulations have indicated that multiple geological processes, such as kerogen maturation, petroleum cracking, and mineral oxidation on reservoir hydrocarbon, can generate organic acids with variable yields [2–4]. However, the source and distribution of organic acids in oilfield waters is still difficult to explain from these simulation results.

In oilfield waters, organic acids act as sources of protons, and as pH and Eh buffering agents [1,2,5]; therefore, they can change the kinematics and mechanisms of mineral dissolution reactions through surface complexation with metal ions [6,7]. Previous experimental studies have shown that organic acids play key roles in mineral dissolution, development of secondary porosity, and reservoir alteration [8–10]; however, it is difficult to determine the role of organic acids in reservoir alteration. One problem is the source of organic acids is difficult to explain as mentioned above. Other problem is the composition...
and concentration of these acids was intensively altered by geological processes such as water mixing, thermal destruction [11], and thus very different to those of acids when they participated in reservoir alteration.

Recent exploration in western China discovered several oil- and gas- fields accumulated in deep strata (> 6000 m), along with vertically developed fault systems [12,13]. These reservoirs commonly exhibit cavernous spaces, possibly resulting from intensive dissolution by acidic fluids, with organic acids being considered potential candidate fluids. It is therefore necessary to investigate the sources and formation mechanisms of organic acids in deep reservoirs.

In this study, we (1) review models of organic acid generation from kerogen maturation, (2) consider the role of exogenous oxygen in organic acid generation under various geological conditions, and (3) describe potential organic acid generation pathways in deep reservoirs and their influence on reservoir characteristics, leading to suggestions for further study.

2. Generation of organic acids from oxygen-containing functional groups in kerogen
Previous studies have focused mainly on the role of oxygen-containing functional groups in kerogen in the generation of organic acids. The maximum total organic acid yields recorded during maturation of different kerogen types in hydrus pyrolysis simulations are in the range of 5.0–67.7 mg g\(^{-1}\) total organic carbon (TOC) [14–16]. Such acids include mainly formate, acetate, propionate, and oxalate species with minor butyrate, valerate, and succinate. Acetate has always been the major component, with modal proportions of >80%. This distribution of organic acids is consistent with that collected from oilfield waters, and oxygen-containing functional groups in kerogen have therefore been suggested as a major source of organic acids in these waters (Figure 1a–c), with further studies indicating that large amounts of organic acid are generated from kerogen that has a high oxygen content [17]. However, data indicate that acid yields are not simply attributable to kerogen oxygen content. For example, immature brown coal with an oxygen index (OI) value of 30 mg CO\(_2\) g\(^{-1}\) TOC, yielded a maximum of 67.7 mg organic acid g\(^{-1}\) TOC [14], more than five times that from immature clay (Type II kerogen) with the same OI value (13.8 mg g\(^{-1}\) TOC) [18]. The composition and distribution of oxygen bonds (e.g., carboxyl, carbonyl) in different kerogen types may therefore play a critical role in acid generation.

Previous studies have provided no common view on the generation mechanism of organic acids, with some suggesting that organic acid production occurs mainly during maturation before the oil window [8,19], whereas others observed that acid yields increase with simulation temperature, with most being generated near the end-point of hydrocarbon generation [20] (Figure 1a, b). It appears that organic acids sourced from kerogen influenced the quality of reservoirs when they were charged with hydrocarbons. In deep strata, the acids began to decarboxylate in high-temperature environments, with the oxygen content in kerogen being insufficient to generate organic acids. The in situ alteration of deep reservoirs could not relate with organic acids from source rocks.

3. Exogenous oxygen in organic acid generation
Compared with the oxygen content of kerogen itself, inorganic oxygen is extremely abundant in geological repositories as, for example, O\(_2\), H\(_2\)O, and CaSO\(_4\), and could participate in various reactions at different reservoir depths in different stages. In the last century, the aerobic biodegradation at surface and mineral oxidation when oil charges into reservoirs have been noticed as two ways of inorganic oxygen adding into organic acids [24,25]. Hydrolytic disproportionation and thermochemical sulfate reduction (TSR) reactions have recently shown potential for generating organic acids in deep reservoirs [21,26]. The participation of exogenous oxygen could thus increase the yield and broaden the distribution of organic acids in sedimentary basins, and it is necessary to investigate its role in the formation of organic acids and the role of these acids in deep reservoirs.

### 3.1 Biodegradation
Biodegradation is one of the most common secondary oil-alteration mechanisms, occurring in shallow strata (depth < 1800 m) at temperatures of 20°C–75°C. Significant amounts of organic acid, including
aliphatic and benzene-ring structures, are produced during this process [24] (Figure 2a), but may be consumed during further bacterial activity. The overall process of organic acid generation and biodegradation is still not well understood, although it is clear that biodegradation alters the composition of oils and leads to an increase in their heteroatom (e.g., oxygen) content [27,28].

![Figure 1. Summary plot describing models and stages of organic acid generation. (a) Generation model based on hydrocarbons [19]; (b) generation models of low-molecular-weight organic acids [8,12,21,22]; (c) structural model of immature kerogen [23]; (d) hydrolytic disproportionation reaction pathway [21].](image)

### 3.2 Mineral oxidation
Field observations have indicated that significant bleaching occurs when hydrocarbons invade red sandstone [25], due to the oxidation of hematite and magnetite by hydrocarbons (Figure 2b) [25,29]. Such oxidative interaction has been confirmed in laboratory studies, with a 10-fold increase in organic acid yield being reported when oxidizing agents are involved [3]. It is possible that the oxygen content of oils increases during mineral oxidation, as in biodegradation, although there are currently no data to support this.

### 3.3 Hydrolytic disproportionation
Hydrocarbons dissolved in liquid water are highly reactive at the higher temperatures and pressures found in deep strata [30,31], and undergo hydrolytic disproportionation reactions to produce shorter-chain compounds incorporating water-derived hydrogen and oxygen. These reactions eventually lead to the conversion of long-chain alkanes in oil to short-chain hydrocarbons in natural gas (Figures 1d and 2c). As an intermediate, organic acids were demonstrated to generate and accumulate to a certain concentration in the simulation [32,33].

### 3.4 Thermochemical sulphate reduction
Thermochemical sulphate reduction occurs widely in deep reservoirs with temperatures > 100°C and supplies largely sulfate dissolved [34,35]. This process involves a series of sequential reactions involving oxygen-containing intermediates (e.g., alcohols, ketones, and carboxylic acids), ultimately generating altered hydrocarbons, pyrobitumen, H₂S, and CO₂ (Figure 2c) [35–37]. Molecular analyses by Fourier transform ion cyclotron resonance mass spectrometry (FT ICR-MS) indicate that oils in Smackover carbonates (USA) are gradually oxidized and enriched in carboxyl groups [38]. Another simulation detected acetate as an intermediate in TSR when labile sulfur species were chosen as starting materials [26]. Inorganic oxygen in dissolved SO₄²⁻ is thus incorporated into either the macromolecular structures of oils or LMW organic acids.

**Figure 2.** Possible roles of exogenous oxygen in the generation of low-molecular-weight organic acids and oxygen-rich oils with increasing reservoir depth: (a) aerobic biodegradation; (b) mineral oxidation; and (c) TSR plus hydrolytic disproportionation.

4. **Role of organic acids in the preservation and development of deep reservoirs**

Organic acids generated through biodegradation and mineral oxidation dissolve minerals and improve the quality of reservoirs. When occupied by hydrocarbons, the newly generated reservoir spaces are well preserved, even if strata experience significant subsidence, forming deeply buried reservoirs. Furthermore, altered oils from both processes acquire increased oxygen contents, and may generate further organic acids during deep burial process. Previous studies have shown that the yield of organic acids cracked from oil with an oxygen content of 0.60 wt.% reach ~250 mg g⁻¹ TOC [2]. The generation of oxygen-enriched oils after geologic alteration should be given more attention, especially in superimposed basins that have undergone complex tectonic movement.

Hydrolytic disproportionation, TSR, and cracking of oxygen-enriched oils directly generate organic acids in deep strata, and these acids dissolve minerals at the hydrocarbon-water interface. As more gas accumulates at the top of reservoirs, the interface moves downward, with gradual reservoir quality improvement in strata formerly occupied by water, thus developing deep reservoirs. Organic acids generated from kerogen would lose a part of dissolution capacity in source rocks and conduits, whereas acids generated *in situ* in deep reservoirs would retain full alteration capabilities in reservoir spaces.
5. Summary and conclusions

Exogenous oxygen sources increase organic acid yields and broaden their distribution in petroleum-producing basins. However, understanding is limited on the acid-generation process, or factors controlling the conversion of inorganic oxygen in geological repositories to organic in hydrocarbons and acids, although four types of mechanism have been suggested: biodegradation, mineral oxidation, hydrolytic disproportionation, and TSR. The evaluation of relationships between acid decarboxylation at high temperatures and production of organic acids in deep reservoirs is difficult. Further qualitative and quantitative analyses are necessary, particularly to characterize the amounts and compositions of organic acids involved in these processes.

The generated organic acids dissolve reservoir minerals to form secondary porosity, and cause precipitation of dissolved ions in other areas, although whether there are sufficient acids and fluid activities to cause large-scale reservoir alteration in deep strata is open to question. Further simulation of the role of organic acids on deeply buried reservoirs under realistic conditions is therefore required.

Acknowledgements
This study was supported by the National Science and Technology Major Project of China (Grant No. 2017ZX05008-003-022; 2017ZX05008-002-010), and State Key Laboratory of Organic Geochemistry (Grant No. SKLOG2020-1).

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