RESEARCH

POSSIBLE ORIGIN OF HIGH MOLECULAR WEIGHT *n*-ALKAN-2-ONES
IN JURASSIC BITUMENS FROM THE SICHUAN BASIN
IN SOUTHWEST CHINA

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Lipid extracts from two Sichuan (China) bitumens have been systematically analyzed using gas chromatography—mass spectrometry (GC-MS). These extracts contain C_{25}-C_{35} n-alkan-2-ones with predominantly odd-carbon number homologs in the Yangba (YB) extracts and with exclusively odd-carbon number homologs in the Penglai (PL) extracts. We suggest that the n-alkan-2-ones with odd numbers of carbon atoms originated due to degradation (cleavage) of fatty acid salts containing one less carbon atom to form methyl and carbonyl radicals, followed by reaction between the latter. The distribution of n-alkan-2-ones with respect to number of carbon atoms can be used to identify the organic matter in sedimentary rocks from which the fatty acid salts were formed.

Key words: *n-alkan-2-ones, bitumen, origin, fatty acid salts, degradation, cleavage.*

The presence of *n*-alkan-2-ones has been confirmed in marine and lacustrine sediments, soils, peats, and bitumens [1-8]. However, the origin of these widely distributed compounds remains controversial because they have been observed in different rocks and consequently it is complicated to propose a single hypothesis for their formation. Generally compounds with an odd number of carbon atoms predominate among the observed *n*-alkan-2-ones. Most likely their source is microbial material [9-10]. *n*-Alkan-2-ones have also been observed in lipid fractions extracted from dispersed matter (aerosol particulates) [11]. *n*-Alkan-2-ones with more than 25 carbon atoms and predominantly odd-carbon number homologs are believed to have originated as a result of oxidation of vegetable wax, while *n*-alkan-2-ones with fewer than 25 carbon atoms and no preference for odd or even numbers of carbon atoms are believed to have originated from anthropogenic sources. Azevedo et al. [12] describe the

possible origin of aliphatic (linear and isoprenoid) and tricyclic terpane methyl ketones found in Tasmanian bitumens. It is believed that *n*-alkan-2-ones originated from β-oxidation of the corresponding hydrocarbons during sediment maturation.

Hernandez et al. [13] believed that the distribution of *n*-alkan-2-ones with respect to the number of carbon atoms can be used to identify marine organic matter in coastal regions. Baas et al. [14] proposed that long-chain *n*-alkan-2-ones be considered as biomarkers in sphagnous freshwater peatland systems. In addition, it has been observed that C_{27} and C_{29} *n*-alkane-2-ones predominate among the odd-carbon number homologs. The close resemblance of the distribution of *n*-alkan-2-ones to the distribution of terrigenous *n*-alkanes has led some authors to propose that microbial oxidation of *n*-alkanes is the source of *n*-alkan-2-ones while β-oxidation of fatty acids followed by decarboxylation is an alternate pathway for their formation [10, 15, 16].

Although some studies have established a correlation between the distributions of *n*-alkan-2-ones, *n*-alkanes, and fatty acids, this correlation is not always obvious enough to establish precursor → product sequences between these compounds [17]. Various diagenetic processes may be the reason for the similar distribution of the indicated compounds. It has also been suggested that when *n*-alkanes were formed as a result of microbial oxidation of matter before its accumulation in the bed of sedimentary rocks, they had a distribution close to the distribution of *n*-alkane-2-ones which is usually observed when algal and higher plant matter are
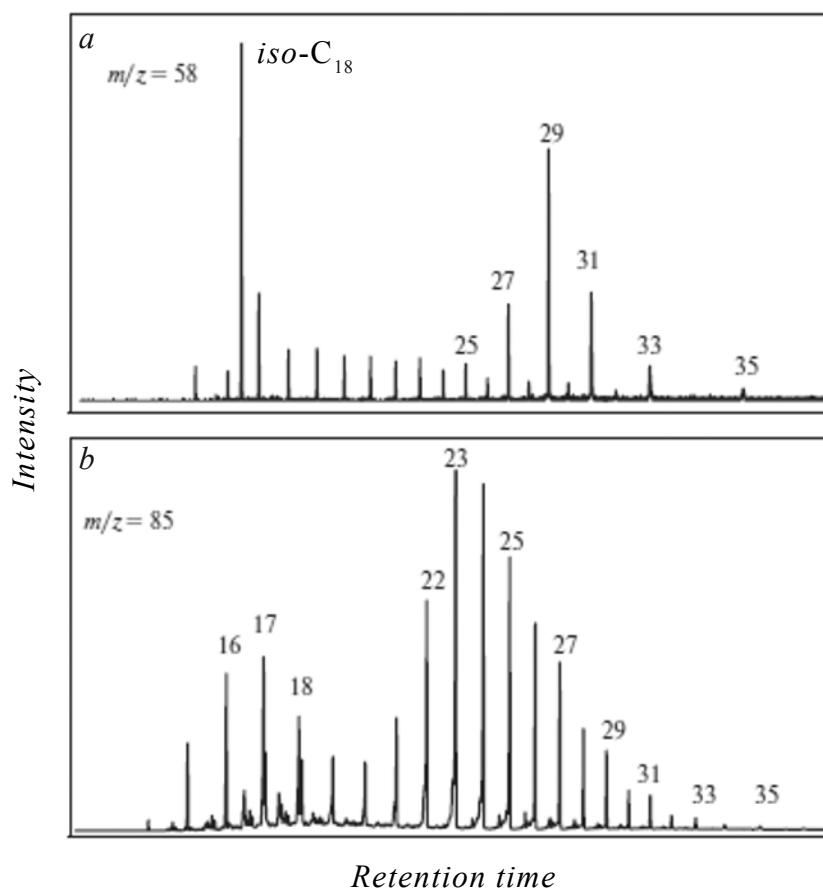

Fig. 1 Chromatogram for *n*-alkan-2-ones (*a*) and *n*-alkanes (*b*) in the YB sample (the numbers on the chromatogram indicate the number of carbon atoms; *iso*-C_{18} = 6,10,14-trimethylpentadecan-2-one).

simultaneously present in the sedimentary rocks [17]. More recently [18, 19], it has been reported that *n*-alkan-2-ones have been detected in higher plant and phytoplankton biomass.

Regardless of origin, *n*-alkan-2-ones are ubiquitous in aquatic environments. A similar distribution of carbon-number homologs is typical for sedimentary rocks formed by higher plant or microbial matter. The aim of this study has been to investigate C_{25}-C_{35} *n*-alkane-2-ones with predominantly C_{29} homologs observed in bitumens from Sichuan Basin, Southwest China and to identify the sources and mechanisms for their formation.

The Sichuan Basin is located in southwestern China and developed on top of pre-Cambrian metamorphic rocks. Sichuan Basin is a rhomboid-shaped sedimentary basin on the Yangtze Platform. The basin has an area of 190 000 km² and is filled down to 8000-12 000 meters with Sinian to Middle Triassic marine carbonates and also Upper Triassic to Eocene non-marine clastic rocks. Two bitumen samples (YB and PL) were obtained from two wells located in the Triassic marine carbonate reservoir in Sichuan Basin. The characteristics of the Sichuan Basin were studied for decades when two sampling campaigns were carried out in the center of the basin [20-22].

Sample preparation. The silica gel and cotton wool were washed for 24 h on a Soxhlet apparatus with a methanol/acetone mixture (9:1) and then twice with dichloromethane before the experiments. All glassware was washed successively with detergent, water, chromic acid, and twice-distilled water and then baked at 500°C for 24 h. The quartz filters were baked at 500°C for 6 h before use in order to remove adsorbed organic compounds. The filters were stored in aluminum foil packages. Organic solvents were twice-distilled before use. Filter paper was washed in a Soxhlet apparatus with dichloromethane before use.

The analyte bitumen samples were extracted on a Soxhlet apparatus with a mixture of chloroform and methanol (93:7) for 76 h, then the extracts were separated into hydrocarbon, ketone/ester/aromatic, polar, and acid fractions using an established procedure [7]. Components of the extracts were identified by gas chromatography-mass spectrometry (GC-MS). The spectra of the methyl ketones were assigned by comparison with literature data and from the presence of the McLafferty rearrangement at *m/z* = 58 [16].

Gas chromatography/mass spectrometry (GC-MS) was performed using a Hewlett-Packard 6890 gas chromatograph (GC) coupled to a Hewlett-Packard 5973 mass selective detector (MSD). An HP-5 capillary column
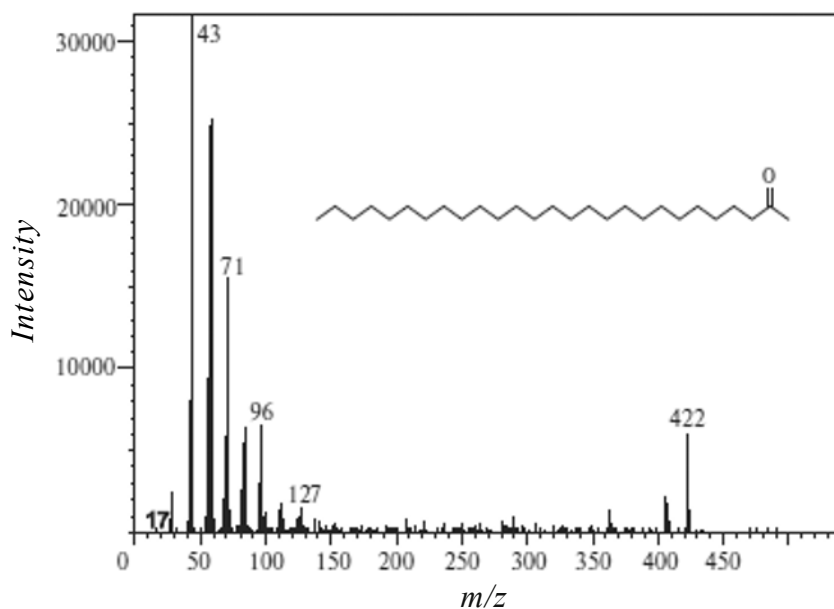

Fig. 2 Mass spectrum of the *n*-alkan-2-one $C_{29}H_{58}O$

was used (length 30 m; inner diameter 0.25 mm; film thickness 0.25 µm). Temperature programming: temperature increase from 80°C to 280° at a rate of 3 degrees per minute, initial and final hold times 1 minute and 30 minutes respectively. Helium was used as the carrier gas, fed at a linear velocity of 28 cm/sec. The injector operated at constant flow rate of 0.9 mL/min. Operating parameters of the mass-selective detector: ionization energy 70 eV, ion source temperature 230°C, and electron multiplier voltage 1800 V, mass range 35-550 daltons.

Occurrence and distribution of n-alkan-2-ones. The distribution of *n*-alkan-2-ones was studied by analyzing *m/z* 58 fragment ions (Fig. 1*a*). The *n*-alkan-2-ones were identified by comparison of the mass spectra (Fig. 2) and retention indices with literature data [23-24]. In the YB sample, C_{15} to C_{35} *n*-alkan-2-ones are present. This sample has a bimodal distribution of *n*-alkan-2-ones with respect to number of carbon atoms (Fig. 1a and Fig. 3b). The short chain compounds are represented by C_{15}-C_{24} homologs, dominated by C_{17}, and no significant odd-carbon number preference is observed. However, the long chain C_{25}-C_{35} homologs show appreciable odd-carbon number preference, dominated by the C_{29} homolog.

Only C_{25}-C_{35} *n*-alkan-2-ones are present in the PL sample; shorter chain homologs are not detected. This sample has a unimodal distribution of homologs with respect to number of carbon atoms (Fig. 3*d*). The C_{29} homolog predominates among the C_{25}-C_{35} *n*-alkan-2-ones in this sample. The C_{25}-C_{35} *n*-alkan-2-ones in the PL sample show
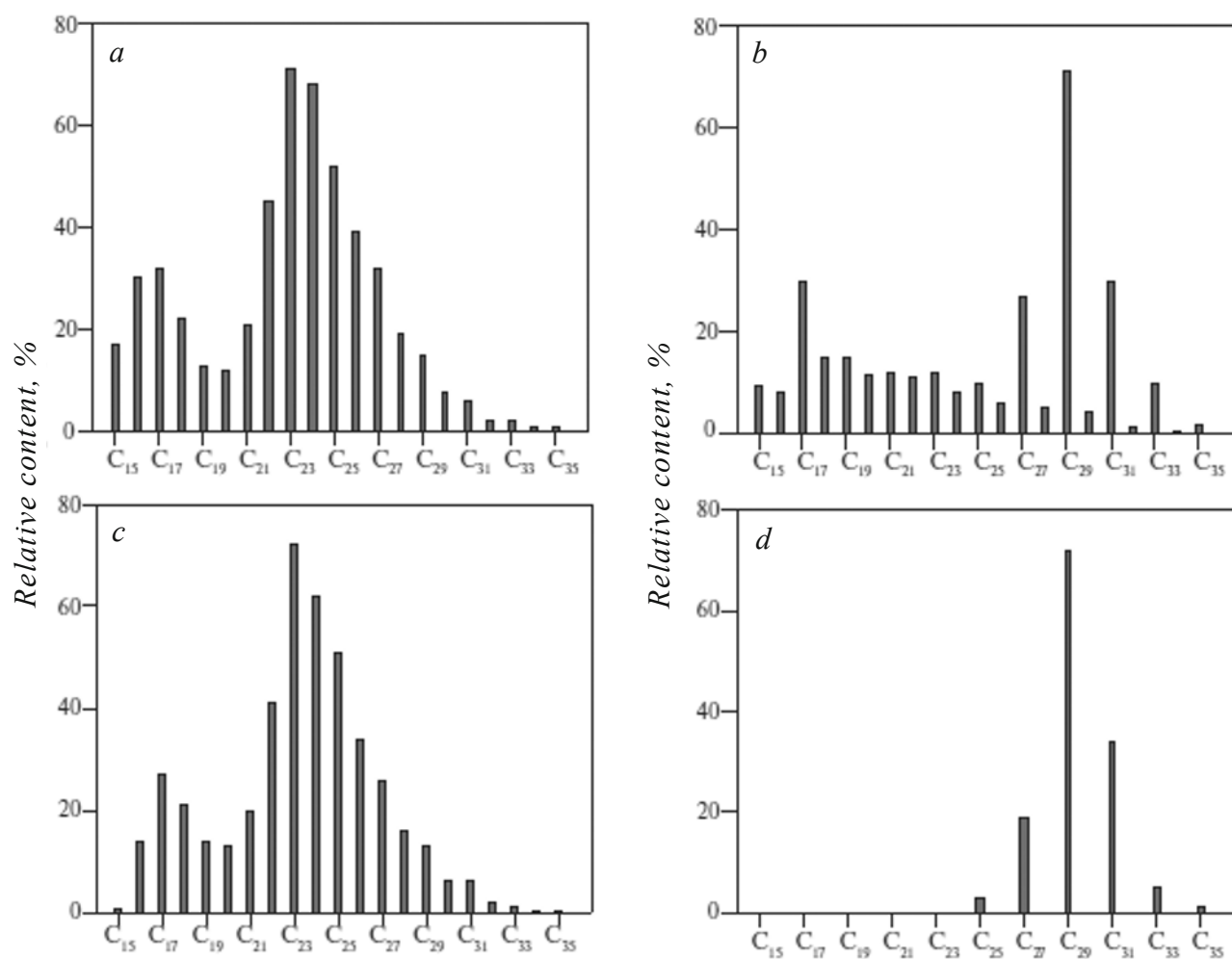

Fig. 3 Distribution of *n*-alkanes [(*a*) YB sample, (*c*) PL sample] and *n*-alkan-2-ones [(*b*) YB sample, (*d*) PL sample] with respect to number of carbon atoms.

an odd-carbon number preference while the C_{15}-C_{35} *n*-alkan-2-ones in the YB sample do not show a preference for homologs with an odd number of carbon atoms.

n-Alkan-2-ones: reaction products of organic acid salts. It is believed that *n*-alkan-2-ones play a crucial role in biogeochemical cycling of dissolved organic matter. However, the sources of *n*-alkan-2-one formation and the mechanism for these processes have been poorly studied. In recent years, homologous series of *n*-alkan-2-ones have been isolated from many compounds in sedimentary rocks, including marine and lacustrine sediments, soils and peats [25, 26]. Methyl ketones are present in plants, but none of the *n*-alkan-2-ones with more than 13 carbon atoms have been observed in plants [27]. Many insects produce methyl ketones with fewer than 13 carbon atoms in scent glands as cuticular wax, but long-chain ketones are not present in the cuticular wax [27]. Many taxa of bacteria also produce methyl ketones during metabolism of fatty acids [28], fatty alcohols [29], and alkanes [27]. Similarly, many taxa of fungi produce methyl ketones during sequential biooxidation [27]. However, no methyl ketones with more than 13 carbons have been observed in products of fungal or bacterial metabolism in experiments using alkanes or fatty acids as substrates [27, 30, 31].

The authors of [15, 16, 32] connect the close resemblance of the distribution of *n*-alkan-2-ones and *n*-alkanes to formation of *n*-alkan-2-ones as a result of microbial oxidation of *n*-alkanes and β-oxidation of fatty acids, followed by decarboxylation. However, the distribution of *n*-alkanes (Fig. 1*b*, Fig. 3*a*, and Fig. 3*c*) in our samples (where the C_{23} *n*-alkane predominates) does not match the distribution of *n*-alkan-2-ones. No odd-carbon number preference is observed in the homologous series of *n*-alkanes, suggesting that *n*-alkanes are not the precursors of the *n*-alkan-2-ones [13]. Furthermore, biodegradation of *n*-alkanes is inhibited by high temperature, low salinity of the medium, and anoxia [16]. The factors listed occur in the basin from which our samples came, and consequently we can ignore microbial conversion of *n*-alkanes to *n*-alkan-2-ones. Thus conversion reactions of linear fatty acids and linear fatty alcohols may be one possible pathway for the formation of the ketones present in our samples, but the role of these reactions is not significant.

The authors of [15] propose that *n*-alkan-2-ones were formed in microbial degradation of the corresponding *n*-alkanes. Other researchers [1] believe that *n*-alkan-2-ones are the products of rapid thermal maturation of organic matter [1]. The *n*-alkan-2-ones in marine sediments could be formed from β-oxidation of hydrocarbons during sediment maturation.

Based on the results of experiments done in [33], we suggested that *n*-alkan-2-ones could be formed from organic acid salts. In [33], we studied the characteristics of the thermal evolution of organic acid salts by means of a simulation experiment. We showed that thermal evolution of organic acid salts leads to formation of *n*-alkan-2-ones. In the YB and PL samples, we found a large amount of *n*-alkan-2-ones but did not detect ketones with the oxygen atom at the 3, 4, 5, and other carbon atoms. Accordingly, we can conclude that the *n*-alkan-2-ones in Jurassic bitumen could be formed from organic acid salts.

The mechanism for the formation of n-alkan-2-ones from organic acid salts. We can hypothesize that the most important step in conversion of organic acid salts to *n*-alkan-2-ones is formation of carbonyl and methyl radicals. This hypothesis is confirmed by the results of the experiments in [33]. In the first step, the organic acid salt decomposes to form in particular methyl and carbonyl radicals:

$$\left(CH_3COO \right)_2 Ca \rightarrow CH_3CO \cdot + CH_3 \cdot$$

$$\left(RCOO \right)_2 Ca \rightarrow RCO \cdot + R \cdot$$
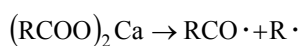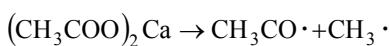
Then the alkyl radicals react with the carbonyl radicals:

$$CH_3\cdot + RCO\cdot \rightarrow RCOCH_3$$

$$R\cdot + CH_3CO\cdot \rightarrow RCOCH_3$$
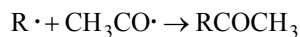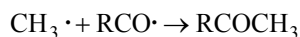
The methyl and carbonyl radicals are the chain transfer agents, and as a result of their reaction the primary reaction products are formed: *n*-alkan-2-ones. In other words, the key step in the process of *n*-alkan-2-one formation is formation of carbonyl radicals from organic acid salts.

Although organic acid salts represented only a small portion of the dissolved organic matter, they were quite active in geochemical transformations of sedimentary rocks and therefore we cannot ignore their presence in these rocks. Further investigations of the processes involved in evolution of organic acid salts would be helpful in studying biogeochemical cycling of dissolved organic matter. In addition, new studies of *n*-alkan-2-ones present in different rocks are needed, as well as study of the transformations of the sources from which they are formed.

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