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Occurrence and distribution of long-chain acyclic ketones in immature coals

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Abstract

Seven coal and carbonaceous mudstone samples were collected from outcropping Jurassic coal beds, on the margin of the Dingxi Basin, Northwestern China. The *n*-alkane distributions in all of the samples are characterised by high concentrations of the C_{19}–C_{29} homologues, and very much lower amounts outside of this range. C_{23} or C_{24} are usually the most abundant *n*-alkanes. Straight chain *n*-alkanes from C_{23} to C_{29} show moderate odd-to-even C number predominances (CPI range: 1.26–2.70). Long-chain acyclic *n*-alkan-2-ones, *n*-alkan-3-ones and *n*-alkan-4-ones ranging from C_{15} to C_{33} with moderate odd-to-even C number predominances, were detected together with one isoprenoid methyl ketone (6,10,14-trimethylpentadecan-2-one) in all of the samples. The C number distributions of the three series of alkanones show a similar distribution to that of the *n*-alkanes, but the correspondence is not sufficient to substantiate a product–precursor relationship. It can be concluded that the *n*-alkan-2-ones are a mixture of the products of microbially-mediated β-oxidation of corresponding *n*-alkanes in the sediments and from the microbial oxidation of higher plant-derived *n*-alkanes prior to incorporation in the sediments. The *n*-alkan-3-ones and *n*-alkan-4-ones were formed from microbially mediated oxidation of the corresponding *n*-alkanes in the γ and δ positions, respectively. Generation of the ketones from higher plant *n*-fatty alcohols and *n*-alkanoic acids could be a possible way to form some of the ketones observed, but it can only play a minor role in the samples analysed.

1. Introduction

There has been considerable interest in a series of long straight-chain acyclic ketones and a C_{18}-isoprenoid ketone which occur widely in ancient rocks, oil shales, peats, young sediments and living organisms (Ikan et al., 1973; Simoneit, 1973; Cranwell, 1977; Volkman et al., 1980a, 1981; Cranwell et al., 1987; Lehtonen and Ketola, 1990; Rieley et al., 1991; Rontani et al., 1992). Just as the *n*-alkane distributions occur in a variety of oils and sediments, long-chain acyclic ketones are also detected as homologous series and usually show similar distributions to those of *n*-alkanes. The homologous series of *n*-alkan-2-ones are commonly found with an odd C number predominance and their source is most likely microbial (Cranwell, 1977; Brassell et al., 1980; Albaigés et al., 1984). Significant amounts of *n*-alkan-2-ones have been detected in the oil-pyrolysates of lignites

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and may be derived from *n*-alkanoic acids by β-oxidation during microbial action, followed by pyrolysis (Teerman and Hwang, 1991). The *n*-alkan-2-ones, *n*-alkan-3-ones and *n*-alkan-4-ones have also been detected in lipid fractions extracted from aerosol particulate matter (Simoneit et al., 1988, 1991) and hydrothermal petroleums and sediment extracts from Guaymas Basin (Leif and Simoneit, 1995). The $>C_{25}$ homologs, with a high odd C number predominance, were interpreted to originate from vegetation wax by oxidation and those $<C_{25}$, with no odd or even C number predominance, from anthropogenic sources by combustion or exposure to high temperatures (Leif and Simoneit, 1995). This paper deals with some immature coal and carbonaceous mudstone samples in which three series of long-chain acyclic ketones (*n*-alkan-2-ones, *n*-alkan-3-ones and *n*-alkan-4-ones) were detected. The distribution characteristics of these alkanone series and the mechanisms by which they may have formed are discussed here.

2. Materials and experimental methods

2.1. Geologic setting and materials

The Mesozoic–Neozoic Dingxi Basin in NW China is one of the basins belonging to the Qilian fault basin area (Fig. 1). It covers an area of 17000 km^2. The Jurassic bed of the Dingxi basin is a coal-bearing sequence which has a probable petroleum potential not yet been identified. No wells have been drilled in the Dingxi Basin, so the 7 coal and mudstone samples used in this study were selected from the outcropping Jurassic coal beds, on the NE margin of the Dingxi Basin (Fig. 1). The sedimentary environments were fresh water bog and flood plain facies.

2.2. Experimental methods

The coal and carbonaceous mudstone samples were collected from outcrops (30–50 cm depth into the outcrop depending on the weathering condition). Exterior organic matter was removed from the samples by washing the bulk sample with chloroform three times. The exterior laminae were removed mechanically and the remaining samples were crushed to less than 120 mesh. The rock powders were then subjected to Soxhlet extraction with chloroform for 72 h. The extracted organic matter was concentrated by evaporation and deasphaltened by addition of excess hexane. Aromatic fractions (which included aromatic and ketone compounds), saturated hydrocarbon fractions and nonhydrocarbon fractions were separated by column chromatography on neutral alumina over silica gel (about 4 g of each resulting in a column length/with a ratio of 50/1). Separation was achieved by elution with hexane (150 ml for saturated fractions), methylene chloride/methanol (9:1 V/V) (200 ml for aromatic and ketone fractions), and methanol (30 ml for nonhydrocarbon fractions), respectively.

GC-MS analyses of the saturated and aromatic hydrocarbon fractions were carried out on a Hewlett–Packard 5890II gas chromatograph interfaced to a Hewlett–Packard 5989A mass spectrometer. The gas chromatograph was equipped with a HP-5 fused silica capillary column (50 m × 0.2 mm). The carrier gas was He. The oven temperature was isothermal for 1min at 80 °C and then programmed from 80 to 300 °C at 4 °C/min. The mass spectrometer was operated at a electron energy of 70 eV, and the ion source temperature was 250 °C.

All compounds were identified from interpretation of their mass spectra or by comparison of the mass spectra with previously published data (Eadon et al., 1971;

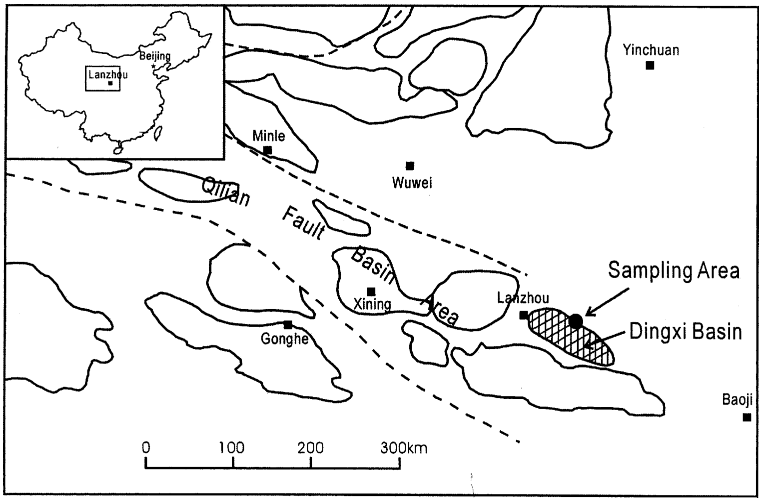

Fig. 1. Location of the Dingxi Basin, NW China and the sampling area.