Selective chemical degradation of kerogen from Nenjiang Formation of the southern Songliao Basin

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A sequential selective chemical degradation has been performed on the kerogen from the Nenjiang Formation of the southern Songliao Basin by using a series of mild chemical degradations (alkaline hydrolysis, cleavage of ether-bonds and sulfur-bonds, and ruthenium tetroxide (RuO$_4$) oxidation). Subsequently, the GC-MS analyses are carried out on different degradation products. The results show that chemical degradations can release a great number of GC/MS-determinable biomarkers from insoluble kerogen, such as, alkaline hydrolysis products mainly comprise $n$-alkanes, fatty acids and alkanols; thiophene compounds are predominantly ether-bound to kerogen matrix; the products from the cleavage of sulfur-sulfur and sulfur-carbon bonds in the kerogen include fatty acids, alkanols and some $n$-alkanes with high carbon numbers; RuO$_4$ oxidation products are predominantly monocarboxylic acids and $\alpha,\omega$-dicarboxylic acids. The distributions of main degradation products indicate that organic matter in this kerogen is predominantly derived from algae and bacteria, and that small amounts of high plant-derived organic matter are possibly combined into kerogen matrix at the late stage by sulfur bonds and other means. This study will provide an important approach for further discussing sources of organic matter in source rocks and their depositional paleoenvironments.

1 Introduction

The Nenjiang and Qingshankou Formations of the Upper Cretaceous are considered as main source rocks in the Songliao Basin[1–3]. Our previous work[4] has revealed that the soluble organic matter in source rocks from the first member of Nenjiang Formation in the southern Songliao Basin has a large variation in hydrogen isotopic compositions of individual $n$-alkanes, the $\delta^D$ values ranging from $-140\%$ to $-300\%$ (remarkable differences of $\delta^D$ values occur not only in $n$-alkanes from one sample to another, even for $n$-alkane homologues taken within the same sample). In order to reveal the main reasons for the diversity of individual hydrogen isotopic compositions, we try to further investigate sources of organic matter in the source rocks from the first member of Nenjiang Formation and their depositional paleoenvironments.

Kerogen is the main form of organic matter in the geological body, comprising ca. 95% of the sedimentary organic matter in geosphere, and is considered as precursors of crude oils and natural gases. Many studies indicate that the bound biomarkers in kerogen can avoid the influences of various post-generation alterations so as to preserve the original information during the period of their formation. Therefore, the study on composition and structure of kerogen has always been an important part of organic geochemistry research. However, insolvency of kerogen and its complexity of composition and...
structure make it so difficult to study the kerogens by using conventional chemical methods. Selective chemical degradation is an important technique for investigating composition and structure of kerogen\(^{[5-7]}\). Large amounts of the GC-amenable biomarker compounds can be released by this approach from the insoluble macromolecular kerogen, and it has also been used to study composition and structure of asphaltene\(^{[8-10]}\). Combination of several selective chemical degradations will perform more elaborate identification and detailed discussion for the biomarkers bound to kerogen\(^{[5,7]}\). In this study, an immature source rock sample from the first member of Nenjiang Formation in the southern Songliao Basin was selected to carry out a sequential selective chemical degradation experiment, so as to obtain more abundant and accurate information on the origin of organic matter than that from free lipids. Alkaline hydrolysis\(^{[11]}\), BF\(_3\)-diethyl ether\(^{[12]}\), NiB\(^{[5,13]}\) and RuO\(_4\) oxidation\(^{[6,7]}\) were used to selectively cleave ester-, ether-, sulfide-bonds, and aromatic carbon and carbon-carbon double bonds respectively in this study. More information on sources of organic matter and depositional paleoenvironments were deciphered by GC, GC-MS analyses of degradation products, which would provide evidence for further revealing the generation conditions of good potential source rocks.

2 Experimental

The sample used in this study was taken from the first member of the Upper Cretaceous Nenjiang Formation in the well Hua37 (1288.5 m) of the Haituozi oilfield in the southern Songliao Basin. Basic data of the sample were as follows: TOC 1.20%, H/C 11.25, S\(_1\) 0.04 mg/g, S\(_2\) 3.0 mg/g, \(T_{\text{max}}\) 437°C, bitumen A 0.33 mg/g and \(R_o\) 0.40%. First, isolated kerogen was Soxhlet extracted with distilled chloroform for 72 h. The solvent-extracted kerogen was dried and then in turn treated by the following selective chemical degradations.

2.1 Alkaline hydrolysis

30 mL 1N KOH in methanol (MeOH) was added to 500 mg kerogen, refluxed for 6 h at 65°C under a nitrogen atmosphere, then centrifuged. The residue was washed with H\(_2\)O/MeOH (1:1, \(V/V\), 3\(\times\)) and with MeOH(3\(\times\)). The supernatant liquid and the washings were combined into a separatory funnel. The neutral and basic compounds were extracted with diethyl ether. The extracted water layer was acidified with HCl to pH 1, and then extracted again with diethyl ether to obtain the acidic fraction. The above steps were repeated once again. The two fractions were dried and weighed respectively.

2.2 Cleavage of ether-bonds

2 mL BF\(_3\)-diethyl ether was added to a suspension of alkaline hydrolysis residue in a mixture of 30 mL benzene/acetic anhydride (2:1 \(V/V\)). The mixture was stirred at room temperature for 1 h, and then centrifuged. The supernatant liquid was moved to cool water, neutralized with saturated NaHCO\(_3\) solution to pH 7, and extracted with dichloromethane. Similarly the above steps were repeated several times. The obtained organic component was dried and weighed.

2.3 Cleavage of sulfur-bonds

200 mg NiCl\(_2\) and 200 mg NaBH\(_4\) were added to a mixture of 10 mL MeOH/THF (1:1 \(V/V\)), then residue after the cleavage of ether-bonds was added. The mixture was refluxed in water bath for 1 h, and then centrifuged. The residue was rinsed with dichloromethane/MeOH (1:1 \(V/V\)) several times. The supernatant liquid and the filtrate were combined into a separatory funnel and were rinsed with the saturated NaCl solution. The organic layer was collected. The above steps were repeated several times. The obtained organic fraction was dried and weighed.

2.4 RuO\(_4\) oxidation

The desulfurized kerogen residue, ruthenium (III) chloride trihydrate (2 mg) and sodium periodate (1.5 g) were added to a mixture of carbon tetrachloride (10 mL), acetonitrile (10 mL) and water (10 mL). The mixture was stirred for 24 h at room temperature and separated by centrifugation. The lower organic layer and the upper aqueous layer were removed respectively. The residue was rinsed with dichloromethane and distilled water (3\(\times\)). The washings and the aqueous layer were combined, acidified with 6 mol/L HCl to pH 1, and extracted by dichloromethane. The extract and the above organic layer were combined, evaporated to dryness to obtain oxidation products. The same treatment was repeated. The results indicate that the total yield of products from four selective chemical degradations reaches to 8.4%, of which alkaline hydrolysis is 0.58%, ether-bond cleavage 0.80%, sulfur-bond cleavage 2.54% and RuO\(_4\) oxidation 4.52% (since there is loss of kerogen during each degradation, actual yields of degradation are pro-