



Differences in the thermal evolution of hopanes and steranes in free and bound fractions



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ARTICLE INFO

Article history:

Received 3 June 2016

Received in revised form 24 July 2016

Accepted 13 August 2016

Available online 17 August 2016

Keywords:

Thermal evolution

Bound fraction

Hopanes

Steranes

Catalytic hydrolysis

ABSTRACT

Hopanes and steranes are the two of the most commonly used biomarker classes in the application of organic geochemistry to petroleum exploration. The same carbon skeletons also occur as a bound fraction, and can be used in a relatively high maturity range compared to their extractable (free) counterparts as a result of protection by the kerogen macromolecular structure. The pools of free and bound biomarkers are expected to be thermally degraded over geological time. There has been little work to address the chemical stabilities of hopanes and steranes in both free and bound forms. This study uses anhydrous pyrolysis to simulate the thermal evolutions of biomarkers from two Type II kerogens. The bound biomarkers within the above thermally altered kerogen residues were also released by catalytic hydrolysis and discussed in this study. The anhydrous pyrolysis results show that source-related parameters based on hopanes are more stable than those based on steranes. The hydrolysis results show that the bound hopane distributions are quite stable even at 460 °C (Easy%Ro = 2.86), while the bound sterane distributions are changed beginning at 430 °C (Easy%Ro = 2.27). This indicates that the thermal stability of steranes is lower than that of hopanes in both free and bound fraction which can be explained by the different chemical structure and mode of incorporation of their precursors into kerogen.

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1. Introduction

Hopanes and steranes are among the two most abundant biomarker classes in that portion of most sedimentary rock samples that is soluble in organic solvents because their biogenic precursors, namely the hopanoids and steroids, occur ubiquitously in living organisms (Peters et al., 2005). They are widely used in thermal maturity assessment, organofacies studies and oil–oil/oil–source rock correlations (Peters et al., 2005 and references therein). Generally, the extract of source rocks (bitumen) or the crude oil which contains free biomarkers will be routinely analyzed in molecular geochemistry studies. The use of such solvent-soluble (free) biomarkers is limited to the immature through oil-generation window, because molecular indices based on relative thermal stability and stereochemical changes are completed in that range. Hopane and sterane biomarkers are seldom utilized where high levels of thermal stress have been attained (van Graas, 1990; Farrimond et al., 1998; Liang and Chen, 2005).

A great number of studies have reported that hopanes and steranes also can be released from kerogen and/or solid bitumen by thermal pyrolysis, chemical degradation and catalytic hydroly-

sis (Seifert, 1978; Tissot and Welte, 1978; Mackenzie et al., 1982a, 1982b; Mycke and Michaelis, 1986; Eglinton and Douglas, 1987; Mycke et al., 1987; de Leeuw et al., 1989; Abbott et al., 1990; Hoffman et al., 1992; Richnow et al., 1992; Adam et al., 1993; Love et al., 1995; Muhammad and Abbott, 2012). Various conditions (temperature and time) have been used for thermal pyrolysis. Generally, the temperature used for thermal pyrolysis is > 250 °C. Chemical degradation is a mild degradation method. Many kinds of chemical reagents were used for chemical degradation, such as Li/EtND₂ and Ni(0)cene/LiAlD₄ (Hoffman et al., 1992; Richnow et al., 1992), and BCl₃/LiAlH₄ (Michaelis et al., 1988; Jenisch et al., 1990). The nature of bonding inferred from the reagents used in chemical degradation processes (Mycke and Michaelis, 1986; Hoffman et al., 1992; Richnow et al., 1992) and the pyrolysis temperatures at which products are obtained (Seifert, 1978; Eglinton and Douglas, 1987) strongly indicated that such hopanes and steranes were covalently bound. The covalently bound hopanes and steranes are different from solvent soluble hopanes and steranes in composition and distribution characteristics (Tissot and Welte, 1978; Love et al., 1995, 2005; Lockhart et al., 2008; Liao et al., 2012; Wu et al., 2013). Because the steranes and hopanes obtained by the different methods (extraction and pyrolysis) are chemically distinct, previous workers have developed the idea of bound biomarkers and free biomarkers (e.g.,

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Abbott et al., 1990). Additionally, previous work also points out that the compounds released by various degradation processes were not covalently bonded to macromolecular structure but rather were occluded within it (Strausz et al., 1999a, 1999b; Liao and Geng, 2002; Russell et al., 2004; Gordadze et al., 2015; Snowdon et al., 2016). Thus, it is not clear that bound moieties released by pyrolysis and HyPy technique can be readily differentiated from occluded species (Snowdon et al., 2016). Therefore, most workers use the term bound biomarker (including both covalently bound and occluded biomarkers) to represent the products released from geological macromolecular structures.

The thermal evolution of bound biomarkers may be retarded to some extent compared to their free counterparts due to protection afforded by the macromolecular structure (Tissot and Welte, 1978; Love et al., 1995, 2005; Abbott et al., 2001; Lockhart et al., 2008; Muhammad and Abbott, 2012). This is especially apparent at low maturity stages (Love et al., 1995; Murray et al., 1998; Meredith et al., 2008; Wu et al., 2013). Maturity-related parameters based on bound biomarkers show constant values with increasing maturity in highly mature source rocks ($T_{\max} > 460\text{ }^{\circ}\text{C}$) (Lockhart et al., 2008; Wu et al., 2013; Liao et al., 2015) and artificially matured solid bitumen (simulation temperature $> 350\text{ }^{\circ}\text{C}$) (Liao et al., 2012). It therefore seemed that assessment of maturity based on the bound biomarkers at high- to over maturity stage was not possible. However, recently, Liao et al. (2012) reported that source-related biomarkers, including the distribution of regular steranes, are quite stable in hydrolysis (HyPy) products from laboratory heated bitumens of various maturities (Easy%Ro = 1.08–2.86). Wu et al. (2013) also found that the bound source-related biomarkers from the Permian Dalong Formation in the Sichuan Basin, China at the mature Guangyuan outcrop sections and overmature Wangcang outcrop sections are very similar. Those data indicate that biomarkers released from kerogen can be used in oil-source correlation studies in highly mature to over-mature areas. The bound biomarkers released by HyPy also were also used for oil-source correlation in the Majiang paleo-reservoir (Fang et al., 2014).

Although it was widely accepted that source-related biomarkers within kerogen (bound fraction) are more stable than their free counterparts, we still know little about the thermal stability and thermal evolution of different kinds of biomarkers. The Dalong Formation was deposited under very similar conditions, but shows quite different maturity at different locations. Biomarkers obtained by both Soxhlet extraction and HyPy from these rocks have been well investigated (Wu et al., 2013). In the present study, two early mature Type II kerogens from the Dalong Formation were selected for artificial thermal alteration followed by HyPy experiments on the kerogen residues. The aim of this study is to compare the effects of thermal maturation on source-related biomarker parameters based on free biomarkers and bound biomarkers. This is very important for the interpretation of bound biomarkers released from high to over-mature samples.

2. Experimental

2.1. Samples and preparation

The investigated samples are siliceous rock (GY-8) and mudstone (GY-17) selected from the fresh outcrop of the Permian

Dalong Formation in Sichuan Basin, China (Lat. $32^{\circ}19'11''\text{N}$, Long. $105^{\circ}27'18''\text{E}$). None of the selected samples were strongly weathered. The Dalong Formation contains interbedded marine dark siliceous rock and mudstones, and mainly occurs in the Guangyuan-Wangcang trough and Western Hubei-Chengkou trough (Wang et al., 2006; Tenger et al., 2008; Li et al., 2009). The basic geochemical characteristics of the samples have already been presented by Wu et al. (2012, 2013) and are summarized in Table 1. The TOC (total organic carbon) content is 8.76% for GY-8 and is 3.67% for GY-17. Their measured vitrinite reflectance are in the range of 0.58–0.68 %Ro. They also have very similar values of T_{\max} (438 °C) and hydrogen Index (343–357 mg/g TOC). The investigated samples are classified as early mature Type II kerogens.

The source rock samples were crushed to ≤ 80 mesh powders. Then, kerogen isolation was performed by acid treatment. First the ground samples were treated with 3 M HCl (80 °C for 4 h), and washed with distilled water and separated by centrifugation. Then a mixture of 1 M HCl and HF (1:1, v:v) was used (80 °C for 4 h) and recovered by additional water washing and centrifugation. Before the artificial thermal alteration experiment was conducted, the isolated kerogen from GY-8 was Soxhlet extracted using an azeotropic ternary solvent system (benzene/acetone/methanol, 5:5:2, v:v:v) for 2 weeks to remove the residual bitumen, while the GY-17 kerogen was not Soxhlet extracted with the ternary solvent (Fig. 1). The aim of different kerogen preparations was to study the influence of free bitumen on the thermal evolution of bound biomarkers within kerogen.

2.2. Artificial thermal alteration experiments

Tubes were loaded with about 0.6 g of the prepared kerogen (GY-8 and GY-17) and sealed under an inert nitrogen atmosphere. Isothermal pyrolysis was then performed for 72 h at 350, 380, 400, 430 and 460 °C, and each sample was heated from room temperature to the final temperature. The calculated vitrinite reflectance (% Ro) by the Easy%Ro method (Sweeney and Burnham, 1990) for the kerogens heated at 350 °C, 380 °C, 400 °C, 430 °C and 460 °C were 1.08, 1.49, 1.74, 2.27 and 2.86, respectively (Table 2). After thermal pyrolysis, the pyrolysate (pyrolysis product) was recovered by repeated dichloromethane (DCM) sonication. Prior to HyPy, kerogen residues were further Soxhlet extracted for two weeks using the ternary solvent azeotrope to remove soluble organic matter (Fig. 1).

2.3. Hydrolysis experiments

Catalytic hydrolysis (HyPy) of the samples was conducted using the apparatus and procedure described in detail elsewhere (Snape et al., 1989; Love et al., 1995; Wu et al., 2013). The solvent-extracted kerogen was impregnated with an aqueous solution of ammonium dioxodithiomolybdate $[(\text{NH}_4)_2\text{MoO}_2\text{S}_2]$ to give a nominal loading of 5 wt% molybdenum as catalyst. Then, the catalyst loaded kerogen was put into the HyPy reactor tube. The HyPy experiment involves two steps at the same hydrogen pressure (15.0 MPa) and hydrogen flow (4 L/min). The first step was heating from ambient temperature to 300 °C (5 min) at 250 °C/min. The aim of the first step is to remove the weaker covalent bonds

Table 1
Basic information on the investigated source rocks.

Sample ID	Lithology	$\delta^{13}\text{C}$ (‰)	%Ro	TOC (%)	S1	S2	T_{\max} (°C)	HI
GY-8	Silicalite	−27.6	0.58	8.75	1.22	30.1	438	343
GY-17	Mudstone	−27.8	0.68	3.67	0.61	13.3	438	357

Data from Wu et al. (2013).

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