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Research paper

The effect of organic matter type on formation and evolution of diamondoids

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ABSTRACT

A series of anhydrous pyrolysis experiments, using sealed gold tubes, were performed on three types of kerogen to investigate the effect organic matter type has on the generation and evolution of thermogenic diamondoids. Based on the compositional variation of pyrolysis products, the cracking of kerogens can be divided into three stages: oil generation (0.6%–1.5% EasyRo), wet-gas generation (1.5%–2.1% EasyRo) and dry-gas generation (> 2.1% EasyRo). The experimental results indicate that diamondoids were mainly generated in the oil and wet-gas generation stages and decomposed in the dry-gas generation stage. In addition to thermal maturity, the formation of diamondoids is also influenced by the type of organic matter. Type I and II_A kerogens produced more diamondoids than Type III kerogen, and diamondoids generated from Type III kerogen were dominantly adamantanes. Therefore, the concentration and concentration ratios of diamondoids can be used to assess the maturity of source rocks (1.0%–1.5% EasyRo) and determine the type of organic matter (1.0%–2.0% EasyRo). Isomerization ratios of diamondoids depend mainly on thermal maturity and the type of organic matter has little effect. The use of isomerization ratios to determine thermal maturity is best for source rocks at higher maturity levels (1.5%–3.0% EasyRo). Therefore, bivariate diagrams of concentration versus isomerization indices of diamondoids (e.g., DMAs/MDs vs. DMAI-1 and DMAs/MDs vs. TMAI-1) can be used to evaluate the source rock maturity over a wider EasyRo range (1.0%–3.0% EasyRo) than single diamondoid parameters. As there are differences in the concentration and distribution of diamondoids in the extracts of three source rocks, the possibility exists to use diamondoid indices of immature rocks to determine the type of source rock.

1. Introduction

Diamondoids are rigid fused-ring alkanes with diamond-like structures. After adamantane was first recognized in crude oil from Czechoslovakia in 1933 (Landa and Machacek, 1933), diamondoids have been identified in crude oil from different basins (Williams et al., 1986; Wingert, 1992; Chen et al., 1996; Dahl et al., 1999), coal deposits, and sedimentary rocks (Schulz et al., 2001; Wei et al., 2006c). Diamondoids are more thermally stable than most other hydrocarbons (Dahl et al., 1999) and are significantly more resistant to biodegradation (Williams et al., 1986; Wingert, 1992; Grice et al., 2000). Therefore, diamondoids are commonly utilized to determine the thermal maturity of highly mature source rocks and crude oils (Chen et al., 1996; Li et al., 2000; Zhang et al., 2005), estimate the extent of oil cracking (Dahl et al., 1999), and evaluate biodegradation of crude oil (Grice et al., 2000; Wei et al., 2007a).

Although diamondoid indices are used routinely in different aspects of petroleum geochemistry, the formation and evolution of diamondoids in source rocks are not well understood. Diamondoids are derived from the pyrolysis of different source matters that include immature sedimentary rock (Wei et al., 2006c, 2007b), peat (Wei et al., 2007b), kerogens (Gordadze, 2002; Fang et al., 2015b), coal (Fang et al., 2015a), crude oil (Fang et al., 2012), different fractions of crude oil (Fang et al., 2013), and single *n*-alkanes (Gordadze and Giruts, 2008). These studies confirmed the importance of thermal maturation on the formation and evolution of diamondoids. And oil cracking experiments documented that diamondoids experience successive stages of generation, accumulation, and degradation with increasing thermal maturity (Fang et al., 2012). The catalytic effect of minerals on the formation of diamondoids has been studied using a series of simulation experiments and the results suggest that different types of minerals have distinct effects on the generation of diamondoids (Wei et al., 2006a, 2006c).

Organic matter in source rocks includes soluble (bitumen) and insoluble (kerogen) components (Burnham and Braun, 1990). The extractable

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bitumen in source rocks is the main component to create diamondoids during thermal maturation based on the results of simulation experiments (Fang et al., 2015b). Li et al. (2015) documented that lower diamondoids formed during the thermal maturation stage of source rocks are derived mainly from the secondary cracking of bitumen and not by the primary cracking of kerogens. However, bitumen is derived from kerogen during thermal maturation and the ability to generate bitumen is a function of the type of kerogen. Therefore, the type of a source rock can possibly be an important factor that determines its ability to generate diamondoids.

Studies on natural samples have documented the effect of different types of organic matters on the generation and distribution of diamondoids. Wei et al. (2006b) proposed that the abundance of diamondoids in organic-rich sedimentary rocks is greater, by an order of magnitude, compared with diamondoids in coal at the same maturity level. Differences are also noted in the distribution of diamondoids in other source rocks (Schulz et al., 2001).

The study of natural samples must account for differences in maturity, lithology, and depositional environment. It is also difficult to obtain a group of natural samples that have the same source, but represent a wide range in thermal maturity. Therefore, thermal simulation experiments are often conducted to study the potential effects of single parameters, meanwhile, exclude other factors. The present study conducted thermal simulation experiments on kerogens in three source rocks (e.g., Type I shale, Type II_A shale, and Type III coal) to investigate the effect of different organic matters on the generation and evolution of thermogenic diamondoids by comparing similarities and differences in diamondoid yields and diamondoid indices during thermal maturation of source rocks.

2. Samples and methods

2.1. Samples

Sample descriptions and geochemical data are presented in Table 1. Sample A is an oil shale with total organic carbon (TOC) of 20.3 wt% from the Eocene–Oligocene Youganwo Formation in the Maoming Basin that contains high concentrations of Type I kerogen and has a low maturity (Table 1). Sample B is an immature shale with vitrinite reflectance (Ro) of 0.35% from the Oligocene Dongying Formation in the Bohai Bay Basin that contains Type II_A kerogen and has TOC = 2.2 wt% (Table 1). Type II_A organic matter type is a sapropel-humic mixed type (a subclass of type II) that the content of sapropel is more abundant than humic, which was suggested by Yang et al. (1982) based on the study of Chinese source rocks and was widely used in petroleum geology in China. Sample C is a semi-clarain of low-grade incoalation from the Paleocene Lijiaya Formation in the Bohai Bay Basin, and the Ro data indicate the coal is immature (Table 1).

2.2. Extraction of source rocks

Samples were cleaned using dichloromethane, ground, and sieved with a 100-mesh screen. A Soxhlet-extraction using mixed dichloromethane and methanol solvent (dichloromethane:methanol = 93:7, v/v) was performed on each aliquot of sample for 72 h. These extracts were rotary evaporated and placed in 2 mL sample vials for diamondoid analysis.

2.3. Pyrolysis experiments

The samples of ground shale and coal were demineralized using hydrochloric and hydrofluoric acids to isolate kerogen. The kerogen concentrates were ground and sieved with a 100-mesh screen. A Soxhlet-extraction using dichloromethane:methanol (93:7 v/v) was performed for 72 h to remove traces of free hydrocarbons potentially bound in the kerogen matrix. The extracted kerogens were then dried at 50 °C for 12 h.

Pyrolysis experiments involving three types of kerogen (e.g., Type I, II_A, and III; Table 1) were performed in sealed gold tubes after the method of Fang et al. (2012). The individual tubes were 40 mm long, with an inner diameter of 4.2 mm and 0.25 mm thick walls. Aliquots of each type of kerogen weighing 15–50 mg were loaded into the tubes and purged with argon for 10 min, before being sealed under an argon atmosphere. A pair of sealed tubes containing a specific type of kerogen was then placed in a stainless steel autoclave. Different series of samples were heated at two constant rates of 20 °C/h and 2 °C/h, respectively, under a constant pressure of 50 MPa. Samples were heated to a specific temperature and then removed from the autoclave to provide data between 330 °C and 595 °C. A total of 12 samples were analyzed for each heating rate. The thermal maturation of samples was calculated using the Easy%Ro method developed by Sweeney and Burnham (1990).

2.4. Analysis of pyrolytic products

Each pair of gold tubes for a specific type of kerogen and temperature point was analyzed using different methods to determine the composition of hydrocarbons and diamondoid. The method of Li et al. (2015) was used to identify gaseous hydrocarbons. Prior to analysis, individual gold tubes were weighed using a Sartorius CPA225D electronic balance accurate to 0.01 mg per 100 g. A tube was cleaned using dichloromethane and then placed in a glass vacuum system connected to the inlet of a gas chromatograph (GC). A steel needle was used to pierce the tube and the chemical compositions of gaseous hydrocarbons were determined by an Agilent 6890B GC modified by Wasson ECE Instrument, as described by Pan et al. (2006). Results were quantified using an external standard method.

Following GC analysis, the pierced gold tube was dried at 50 °C in an electric vacuum–drying oven to evaporate gasoline hydrocarbons. The drying continued until weights determined for the tube remained constant. The difference in weight of the tube after analysis is considered to be the total amount of inorganic gaseous compounds, gaseous hydrocarbons, and light hydrocarbons (LHs) generated from kerogen. Therefore, the yield of LHs is obtained by subtracting organic and inorganic gaseous compounds from the weight difference in the tube pre- and post-analysis.

After having determined the LHs mass, the gold tube was cut in half and placed in a 4 mL sample vial filled with dichloromethane. The vial was treated ultrasonically for 30 min to dissolve any heavy hydrocarbons (HHs) in the gold tube that formed from kerogen, and then the vial was left undisturbed for 12 h. The resulting solution was filtered and then evaporated using a stream of nitrogen gas to obtain a concentrate of HHs. This concentrate was weighed using the Sartorius

Table 1
Geochemical data of the samples used in the simulation experiments.

Sample	Lithology	Location	Formation	Age	TOC (wt %)	Ro (%)	Tmax (°C)	S_1 (mg/g)	S_2 (mg/g)	HI (mg/gTOC)	Type of kerogen
A	Shale	Maoming Basin, SouthChina	Youganwo	Eocene -Oligocene	20.3	0.41	423	2.3	97.54	480	I
B	Shale	Bohai Bay Basin, NorthChina	Dongying	Oligocene	2.2	0.35	427	4.18	10.86	503	II_A
C	Coal	Bohai Bay Basin, NorthChina	Lijiaya	Palaeocene	59.7	0.40	429	1.21	48.51	91	III

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