The effect of biodegradation on adamantanes in reservoired crude oils from the Bohai Bay Basin, China

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ABSTRACT

The effect of biodegradation on adamantanes has been studied, based on a suite of genetically related crude oils with increasing degree of biodegradation, from the Miaoxi Depression, Bohai Bay Basin, China. Selectivity during biodegradation was observed for the adamantanes. The relative susceptibility to biodegradation of individual adamantane compounds was determined based on their compositional changes. Adamantanes with more alkyl substituents were generally more resistant to biodegradation, but exceptions also occurred. The position of alkylation had great control on the susceptibility to biodegradation. However, the more thermally stable compounds were not always more readily biodegraded, suggesting that the susceptibility of adamantanes is not directly controlled by thermodynamic stability. Selective biodegradation of adamantanes may be related to their stereochemical structures and demethylation could have occurred. Microbial alteration of adamantanes had negligible effects on the methyladmantane index, dimethyladamantane index 1, dimethyladamantane index 2, trimethyladamantane index 1 and trimethyladamantane index 2, suggesting that they could still be used to evaluate the thermal maturity of biodegraded crude oils. In contrast, the ethyladmantane index was significantly altered and thus is not valid for maturity assessment of biodegraded oils.

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1. Introduction

Diamondoid hydrocarbons are rigid and three-dimensionally fused ring alkanes with a diamond-like structure. They have been identified widely in crude oils (e.g., Petrov et al., 1974; Wingert, 1992; Chen et al., 1996; Dahl et al., 1999; Wei et al., 2007a), and in extracts of coals and sedimentary rocks with varying thermal maturity (Chen et al., 1996; Schulz et al., 2001; Wei et al., 2006b, 2007b). They have also been detected in pyrolysates of source rocks and kerogen (Wei et al., 2006a; Fang et al., 2015), crude oils and source rock extracts (Wei et al., 2007b; Fang et al., 2012, 2015), and component groups, such as saturated, aromatic, resin and asphaltene fractions (e.g., Berwick et al., 2011; Fang et al., 2013, and references therein). However, the origin of diamondoids is still unclear. They have been thought to be formed by: (1) rearrangements of polycyclic hydrocarbons under thermal stress with a strong Lewis acids acting as catalysts (Petrov et al., 1974;

Wingert, 1992; Lin and Wilk, 1995), (2) cracking of high molecular-mass fractions under high temperatures (Giruts et al., 2006; Giruts and Gordadze, 2007; Fang et al., 2013), (3) carbon surface reactions (Berwick et al., 2011), and (4) condensation reactions of lower diamondoids (Lin and Wilk, 1995; Dahl et al., 2010).

Extensive studies have focused on the application of diamondoids in petroleum geochemistry. Chen et al. (1996) and Zhang et al. (2005) proposed a series of diamondoid isomerization indices to ascertain the thermal maturity of source rocks and crude oils. Dahl et al. (1999) used the relative abundance of diamondoids to assess the extent of oil cracking. The distributions of diamondoids have also been observed to be related to source rock facies (Schulz et al., 2001; Wei et al., 2006c; Pytlak et al., 2017), and three ratios were introduced to distinguish source rock facies (Schulz et al., 2001). Grice et al. (2000) proposed that the ratio of methyladamantanes to adamantane can be used to assess petroleum biodegradation, and to identify mixtures of severely biodegraded and non-biodegraded oils.

Diamondoid hydrocarbons are generally considered to be more resistant to microbial alteration than other components, such as *n*-alkanes (Williams et al., 1986; Wingert, 1992; Pytlak et al., 2017). Grice et al. (2000) observed that the ratio of methyladamantanes

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to adamantane rises with increasing extent of biodegradation, suggesting that methyladamantanes are more resistant to biodegradation than adamantane. Wei et al. (2007a) further investigated the biodegradability of diamondoids. Their results showed that biodegradation of diamondoids is selective and stepwise; most diamondoids (with the exception of adamantane) are resistant to biodegradation and that the effect of microbial alteration of diamondoids on assessment of oil cracking using Dahl et al. (1999)'s method is negligible. They also reported a possible pathway for biodegradation of adamantane. Aerobic biodegradation of 1-methyl-, 1,3-dimethyl-, and 1,3,5-trimethyladamantanes under highly acidic conditions (pH 2.5) by *Mycobacterium* AGS10 showed that (1) aggregate state (solid versus liquid) may have a significant effect on bioavailability of these compounds, (2) adamantanes are generally more resistant to biodegradation than normal and isoprenoid alkanes, and (3) no evident preference during biodegradation of these alkyladamantanes (Ivanova et al., 2017). However, little is known about the effect of biodegradation on individual diamondoids. In the present study, the composition of adamantane and alkyladamantanes has been investigated in a suite of genetic related crude oils with increasing extent of biodegradation, reservoired in the Miaoxi Depression, Bohai Bay Basin, China. The objectives were to: (1) determine the susceptibility to biodegradation of individual adamantane compounds, (2) investigate the factors that influence the susceptibility to biodegradation, and (3) study the effect of biodegradation on adamantane-based thermal maturity indicators.

2. Samples and methods

2.1. Sample descriptions

Six crude oils selected from a suite of thirteen biodegraded crude oils from the Miaoxi Depression of Bohai Bay Basin, China were used in this study (Table 1) as well as in a previous study on biodegradation of polycyclic aromatic hydrocarbons (Cheng et al., 2018). The crude oils were generated from the Eocene Shahejie Formation source rock in the middle oil window (Cheng et al., 2016, 2018). They comprise a reference oil (PL15-1B) and five severely biodegraded oils (PL15-1A, PL91A, PL15-8A, PL15-8B, and PL15-8C) with increasing extents of biodegradation (Table 1).

The oils were carefully collected at the wellhead from wells and stored in 100 ml amber colored glass containers with a screw-on cap lined with Teflon. The oils were refrigerated at 4 °C in the laboratory. Additionally, the loss of volatile components, specifically adamantanes, during work up was minimized by taking some precautions (as outlined in the next section). Hence, the potential for evaporative losses of oil components (e.g., diamandoids) prior to and during work up was minimal.

The presence of alkylbenzenes and naphthalenes in the PL15-1B oil and varying amounts of naphthalenes in the other samples, suggested that water washing was not a significant factor controlling the chemical composition of the oils; in contrast, varying extents of biodegradation are more likely to be the primary controlling factor.

Although the PL15-1B oil is slightly biodegraded (PM level 2) and contains some severely biodegraded residues, the relatively intact nature shows that the mixing of initial biodegraded residues and the later slight biodegradation did not affect the validity of the PL15-1B as a reference oil to assess the alteration of diamondoids in the other oils (Cheng et al., 2018). The remainder of the selected samples has not been subjected to recharge, based on geochemical compositions of aliphatic and aromatic fractions.

The more biodegraded oils in the Miaoxi Depression, Bohai Bay Basin, occur at shallower depths, and the degree of biodegradation increases with increasing depth toward the oil–water contact. These observations suggest that the in reservoir biodegradation is very likely aerobic. However, the possibility of anaerobic biodegradation cannot be precluded. The effect of biodegradation of biomarkers and polycyclic aromatic hydrocarbons in the crude oils is documented in Cheng et al. (2016, 2018).

2.2. Separation of petroleum fractions

The asphaltenes in crude oils were precipitated using excess *n*-hexane over night in a freezer. After filtration and blow down using nitrogen, the maltenes were separated into aliphatic and aromatic fractions and resins by column chromatography over activated silica gel and alumina with different solvents (Cheng et al., 2016). To minimize the loss of volatile diamondoids, fractionations were performed at a laboratory temperature of ca 15 °C with no heating and relatively low nitrogen flows (empirical, not quantified) applied during blow down of the solvents. The eluted

Table 1
Normalized abundance of adamantane and alkyladamantanes in the crude oils.

Peak number	Compound	Abbreviation	Normalized abundance of adamantanes in samples with increasing biodegradation (%)					
			PL15-1B	PL15-1A	PL91A	PL15-8B	PL15-8B	PL15-8C
		PM level[a]	2	7	7	8	8	8
1	Adamantane	A	6.27	5.64	5.33	5.27	5.26	4.98
2	1-Methyladamantane	1-MA	13.78	14.09	13.29	13.72	13.66	13.29
3	2-Methyladamantane	2-MA	7.37	7.56	7.50	7.55	7.70	7.76
4	1-Ethyladamantane	1-EA	3.22	3.53	3.67	3.61	3.63	3.69
5	2-Ethyladamantane	2-EA	9.43	8.24	7.84	6.54	6.06	5.75
6	1,3-Dimethyladamantane	1,3-DMA	10.46	10.51	10.18	10.73	10.88	10.76
7	1,4-Dimethyladamantane (*cis*)	1,4-DMA (*cis*)	7.17	6.92	7.05	7.05	7.04	7.29
8	1,4-Dimethyladamantane (*trans*)	1,4-DMA (*trans*)	7.42	6.64	6.65	6.76	6.75	6.94
9	1,2-Dimethyladamantane	1,2-DMA	8.56	8.27	8.54	8.43	8.50	8.61
10	1-Ethyl,3-methyladamantane	1-E, 3-MA	2.46	2.61	2.66	2.68	2.71	2.81
11	1,3,5-Trimethyladamantane	1,3,5-TMA	3.00	3.32	3.32	3.46	3.50	3.49
12	1,3,6-Trimethyladamantane	1,3,6-TMA	4.48	4.43	4.64	4.70	4.76	4.77
13	1,3,4-Trimethyladamantane (*cis*)	1,3,4-TMA (*cis*)	4.24	4.85	5.16	5.13	5.16	5.23
14	1,3,4-Trimethyladamantane (*trans*)	1,3,4-TMA (*trans*)	4.78	5.39	5.59	5.55	5.58	5.62
15	1-Ethyl, 3,5-dimethyladamantane	1-E,3,5-DMA	4.35	4.74	5.06	5.34	5.30	5.46
16	1,3,5,7-Tetramethyladamantane	1,3,5,7-TeMA	0.45	0.49	0.52	0.51	0.52	0.53
17	1,2,5,7-Tetramethyladamantane	1,2,5,8-TeMA	2.55	2.77	3.02	2.98	2.99	3.04

[a] Biodegradation level based on the scale in Peters and Moldowan (1993).