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The effect of evaporation on the concentration and distribution of diamondoids in oils

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ABSTRACT

Diamondoids are commonly found in petroleum and sediments and have an inherent resistance to thermal and biological destruction, which means they can provide useful information in situations where conventional biomarkers cannot. Here, we present the results of an investigation of the effects of atmospheric evaporation on the concentration and distribution of low molecular weight diamondoids in four petroleum fractions (gasoline, condensate, diesel and fuel oil). These experiments indicate that both adamantanes and diamantanes evaporate with the other light hydrocarbons from oils and that variations in the concentrations of these compounds during evaporation are controlled by the type of petroleum fraction, the extent of evaporation and the boiling point of the diamondoid compounds within the oil. Evaporation has a significant effect on adamantane concentration ratios, whereas no changes in diamantane concentration ratios occur, suggesting that diamantane-based concentration and distribution indices can be used for the correlation of oils and determination of maturity even if oils have undergone evaporation. Some diamondoid concentration ratios, such as adamantane/1-methyladamantane, 1-methyladamantane/2-methyladamantane, 1-methyladamantane/1-ethyladamantane, 1-methyladamantane/4-methyldiamantane, adamantane/diamantane and 1,3-dimethyladamantane/4,9-dimentyldiamantane, progressively decrease with ongoing evaporation and are independent of petroleum fraction type, indicating that given the original unaltered index value, these indices can be used to deduce the relative extent of oil evaporation. The study also indicates that slight to moderate evaporation of oils leads to an increase in diamantane concentrations that is nearly proportional to the extent of oil evaporation, indicating that these compounds can be used as indices to estimate the extent of oil evaporation.

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1. Introduction

Diamondoids are a series of diamond-like cage hydrocarbons that are present in a wide range of crude oils and source rock extracts (Wingert, 1992; Schulz et al., 2001; Wei et al., 2006). They are resistant to both thermal and biological destruction and the concentration and distribution of diamondoids form the basis of a number of indices that are used to distinguish petroleum source facies (Schulz et al., 2001), determine the thermal maturity of highly mature oils and source rocks (Chen et al., 1996), and estimate the extent of oil cracking and biodegradation (Dahl et al., 1999; Grice et al., 2000). Diamondoids can also provide useful information to identify the origin of spill oils (Stout and Douglas, 2004; Wang et al., 2006).

Identifying the effects of thermal maturation on the abundance and distribution of diamondoids in oils and source rock extracts not only requires knowledge of diamondoid formation and destruction (Wei et al., 2006), but also identification of other labile components within oils and source rock extracts that can thermally degrade and cause increased diamondoid concentrations. Other controls on the distribution of diamondoids, such as evaporation and biodegradation, have also been quantitatively investigated by analyzing various naturally biodegraded oils (Grice et al., 2000; Wei et al., 2007) and oils that were altered during artificial evaporation and biodegradation experiments (Wang et al., 2006). The low concentrations of diamondoid compounds and complex compositions of these oils meant that these studies generally required a number of sample preparation steps (e.g., extraction, column separation and concentration) prior to gas chromatography–mass spectrometry (GC–MS) analysis of such compounds. Adamantanes elute mainly between C_{10} and C_{13} normal alkanes in gas chromatograms, whereas diamantanes generally elute between n-C_{15} and n-C_{16} (Wingert, 1992), indicating that adamantanes are somewhat more volatile and susceptible to evaporation than diamantanes. This indicates that the sample preparation steps used in previous research

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may have had a significant effect on the abundance and distribution of diamondoids prior to analysis.

Evaporation is a ubiquitous natural process that can cause petroleum hydrocarbon mass loss, a process that particularly affects light, low molecular weight components of oils. Evaporation can occur in a wide variety of settings, including during sample collection, transportation and storage. The different evaporation behavior of individual diamondoids and other components in oils can cause changes in the concentrations and distribution of hydrocarbons, further affecting diamondoid parameter based interpretations. This indicates that it is essential to clarify the possible effects of evaporation on the molecular compositions of diamondoids in oils before the interpretation of any diamondoid data, for example as maturity indices. The majority of previous research on the effects of evaporation merely identified the general volatility of diamondoids, rather than the exact evaporation behavior of these compounds.

Our previous work demonstrated that gas chromatography–triple quadrupole mass spectrometry (GC–MS–MS) is a promising method for the quantitative determination of diamondoids in oils, especially where diamondoids are present in low concentrations (Liang et al., 2012). This method has allowed the origin and evolution of diamondoids in petroleum to be quantitatively investigated by pyrolysis analysis of an oil sample and associated components (Fang et al., 2012, 2013). Here, we present the results of an investigation of the effect of evaporation on diamondoid concentrations and compositions in oils during laboratory evaporation experiments and quantitative GC–MS–MS analysis of diamondoids in evaporated oils. This study focuses on the results of laboratory evaporation experiments that were conducted on four different petroleum fractions from light gasoline to heavy fuel oil. The findings of the study have significant implications for the use of diamondoid parameters during the evaluation of natural hydrocarbons and source rocks.

2. Experiments

2.1. Evaporation experiments

Progressive evaporation experiments were conducted on four petroleum fraction samples: a Tarim condensate, a diesel fuel, a gasoline (octane number = 93, primarily comprised of alkanes in the range n-$C_{4–12}$), and a fuel oil (kinematic viscosity = 180 cst, primarily comprised of alkanes in the range n-$C_{10–23}$). Analysis began with the delivery of an aliquot (approximately 40 mg of condensate and diesel and 400 mg of gasoline and fuel oil) of each petroleum fraction sample into a series of 4 ml glass vials where each aliquot was weighed. These vials were then placed in a fume cupboard to allow open evaporation at room temperature over durations that varied from 20 min to 1 week according to petroleum fraction type. After evaporation, each vial was removed, reweighed and rapidly filled with n-pentane before being tightly capped with aluminium–rubber seals, shaken in an ultrasonator for 10 min to increase the dissolution of the residual hydrocarbons into the n-pentane solvent and stored in a freezer prior to analysis.

The use of a simple dilution without any other sample preparation minimized the amount of diamondoid evaporation outside of the controlled evaporation described above. GC–MS–MS was used to quantify diamondoid abundance and type within the petroleum fractions described above and the extent of evaporation of these different petroleum fractions was calculated based on weight loss after evaporation.

2.2. Diamondoid quantification

GC–MS–MS analysis was performed using a TSQ Quantum XLS system (Thermo Fisher Scientific, USA) and details of the procedure used are provided in Liang et al. (2012). In brief, 1 µl aliquots of each sample were injected into the GC system using an AS 3000 autosampler. The GC was equipped with a programmed temperature vaporization (PTV) injector and a DB-1 fused silica capillary column (50 m × 0.32 mm × 0.52 µm film thickness) and the PTV was used in splitless mode with the inlet temperature set at 300 °C, and the split flow set at 15 ml/min following 1 min of splitless flow. High purity helium (99.999%) was used as a carrier gas in constant flow mode at a rate of 1.5 ml/min. The GC oven temperature was initially set at 50 °C for 2 min, then programmed at 15 °C/min to 80 °C and at 2.5 °C/min to 250 °C, before a final change at 15 °C/min to 300 °C, where the temperature was held for 10 min. Diamondoid compound quantification involved comparing peak areas of target analyte in the selective reaction monitoring (SRM) mode to corresponding n-dodecane-d_{26} internal standards. In SRM–MS–MS assay, the parent ions are selected by the first quadrupole and then collide with argon molecules in the second quadrupole. The fragment ions of the collision are selected by the third quadrupole and be detected.

3. Results and discussion

3.1. Evaporation of diamondoids in oils

Adamantane and diamantane mass chromatograms for the four initial petroleum fraction samples prior to evaporation are shown in Fig. 1 and the concentrations of 32 individual diamondoid compounds (listed in Table 1) in pre-evaporation and evaporated petroleum fractions obtained during this study are given in Table 2. Initial diamondoid concentrations are relatively high in both the condensate and diesel, but the light gasoline contains low concentrations of adamantanes and no diamantanes, and the fuel oil contains only trace amounts of both diamondoids. The high diamondoid concentration and high methyladamantane index (MAI) and methyldiamantane index (MDI) values of the Tarim condensate indicate that this is a cracked oil of high thermal maturity. In addition, the distribution of diamondoids in the other petroleum fractions is consistent with their respective oil types (Wang et al., 2006).

The data in Table 2 indicate that variation in diamondoid concentrations between petroleum fractions is largely dependent on the type of petroleum fraction, the extent of evaporation that the petroleum fraction has undergone and the volatility of individual diamondoid compounds. The concentrations of diamondoids in different petroleum fractions from light gasoline to heavy fuel oil have distinctly different trends during evaporation, with the high evaporation rate of the gasoline sample analyzed during this study yielding a whole oil mass loss of > 90% after 20 h of evaporation and a remarkable increase in the concentration of all adamantane compounds (no diamantanes were detected). In comparison, the Tarim condensate has a relatively moderate evaporation rate, losing about one third of the original weight of the sample after 168 h of evaporation. The concentration of adamantanes within the condensate significantly decreased with ongoing evaporation, indicating that these compounds are relatively susceptible to volatilization after 168 h of evaporation compared to the majority of other components in this oil. In contrast, diamantanes have higher boiling points that yield a slight increase in diamantane compound concentrations after the same amount of evaporation. This also means that the condensate has a very low evaporation rate after 168 h. The diesel is slower to evaporate than the condensate and the two have similar adamantane concentration trends although distinctly different diamantane concentration trends. In addition, the variations in diamantane concentrations within the diesel are relatively complicated, with concentrations initially increasing
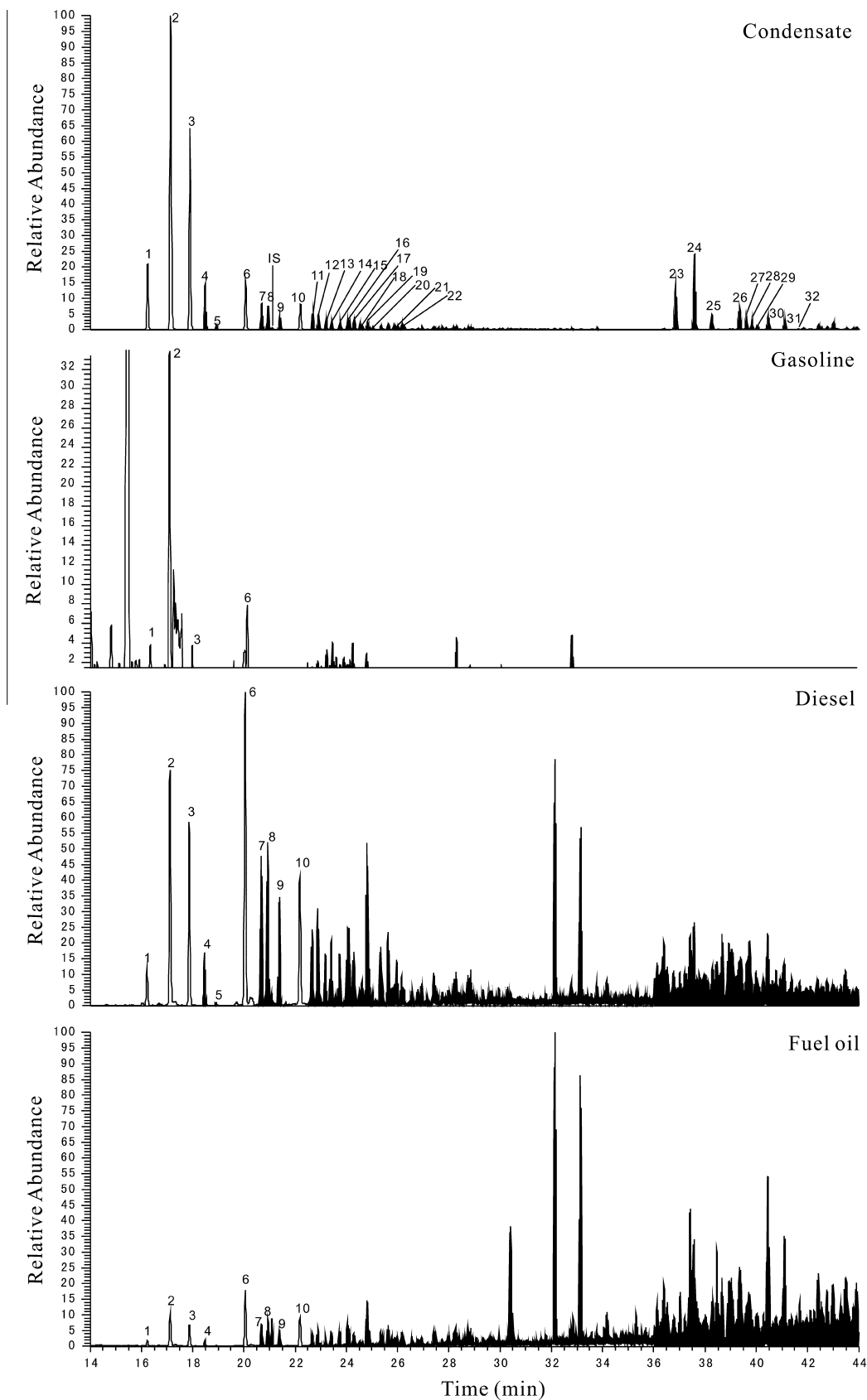
Fig. 1. Mass chromatograms of diamondoids in the four pre-evaporation petroleum fractions. Peak identifications are given in Table 1.

before then decreasing. The fuel oil sample is less volatile and has almost invariant concentrations of individual diamondoids throughout the evaporation period.

Individual diamondoid compound mass losses (in %) during evaporation were calculated to better understand the evaporation behavior of diamondoids in oils; these losses were determined by

Table 1
Diamondoid compounds detected in this study.

Peak number	Molecular formula	Assignment	Abbreviation
1	$C_{10}H_{16}$	Adamantane	A
2	$C_{11}H_{18}$	1-Methyladamantane	1-MA
3	$C_{12}H_{20}$	1,3-Dimethyladamantane	1,3-DMA
4	$C_{13}H_{22}$	1,3,5-Trimethyladamantane	1,3,5-TMA
5	$C_{14}H_{24}$	1,3,5,7-Tetramethyladamantane	1,3,5,7-TeMA
6	$C_{11}H_{18}$	2-Methyladamantane	2-MA
7	$C_{12}H_{20}$	1,4-Dimethyladamantane(cis)	1,4-DMA(*cis*)
8	$C_{12}H_{20}$	1,4-Dimethyladamantane(trans)	1,4-DMA(*trans*)
9	$C_{13}H_{22}$	1,3,6-Trimethyladamantane	1,3,6-TMA
10	$C_{12}H_{20}$	1,2-Dimethyladamantane	1,2-DMA
11	$C_{13}H_{22}$	1,3,4-Trimethyladamantane(cis)	1,3,4-TMA(*cis*)
12	$C_{13}H_{22}$	1,3,4-Trimethyladamantane(trans)	1,3,4-TMA(*trans*)
13	$C_{14}H_{24}$	1,2,5,7-Tetramethyladamantane	1,2,5,7-TeMA
14	$C_{12}H_{20}$	1-Ethyladamantane	1-EA
15	$C_{12}H_{20}$	2,6-+2,4-Dimethyladamantane	2,6-+2,4-DMA
16	$C_{13}H_{22}$	1-Ethyl-3-methyladamantane	1-E-3-MA
17	$C_{13}H_{22}$	1,2,3-Trimethyladamantane	1,2,3-TMA
18	$C_{14}H_{24}$	1-Ethyl-3,5-dimethyladamantane	1-E-3,5-DMA
19	$C_{12}H_{20}$	2-Ethyladamantane	2-EA
20	$C_{14}H_{24}$	1,3,5,6-Tetramethyladamantane	1,3,5,6-TeMA
21	$C_{14}H_{24}$	1,2,3,5-Tetramethyladamantane	1,2,3,5-TeMA
22	$C_{15}H_{26}$	1-Ethyl-3,5,7-trimethyladamantane	1-E-3,5,7-TMA
IS	$C_{12}D_{26}$	*n*-Dodecane-d$_{26}$	nC_{12}-d$_{26}$
23	$C_{14}H_{20}$	Diamantane	D
24	$C_{15}H_{22}$	4-Methyldiamantane	4-MD
25	$C_{16}H_{24}$	4,9-Dimethyldiamantane	4,9-DMD
26	$C_{15}H_{22}$	1-Methyldiamantane	1-MD
27	$C_{16}H_{24}$	1,4-+2,4-Dimethyldiamantane	1,4-+2,4-DMD
28	$C_{16}H_{24}$	4,8-Dimethyldiamantane	4,8-DMD
29	$C_{17}H_{26}$	1,4,9-Trimethyldiamantane	1,4,9-TMD
30	$C_{15}H_{22}$	3-Methyldiamantane	3-MD
31	$C_{16}H_{24}$	3,4-Dimethyldiamantane	3,4-DMD
32	$C_{17}H_{26}$	3,4,9-Trimethyldiamantane	3,4,9-TMD

comparing masses in each vial before and after evaporation. The quantitative data in Table 3 clearly indicate that both adamantanes and diamantanes can volatilize, with both compounds having mass losses in all petroleum fractions (except the fuel oil) that progressively increase with increasing evaporation. In addition, adamantanes are generally more susceptible to evaporation than diamantanes. However, the mass loss of diamantanes in diesel is highly variable, with some negative values that may result from the low concentrations of diamantanes within diesel and interference from other compounds (Fig. 1) that affect the absolute quantification of diamantane concentrations. This indicates that diamondoid concentration variations during evaporation actually reflect the volatility of diamondoids relative to other components within the oils. For example, a diamondoid compound evaporation rate that is lower than the evaporation rate of the host oil will cause an increase in the concentration of diamondoids within the evaporated oil. Conversely, diamondoid concentrations decrease as the extent of oil evaporation increases. Table 3 shows that the volatility of diamondoid compounds is related to their boiling point and molecular structure, with lower boiling point diamondoid compounds generally being more susceptible to evaporation.

Diamantanes are more resistant to evaporation than adamantanes, as reflected by negligible mass losses until around 20–25% of the condensate oil has evaporated. In addition, non-evaporated oils have generally higher concentrations of adamantanes than diamantanes. This indicates that the higher concentrations of diamantanes compared with adamantanes in evaporated oils can be explained by preferential loss of the latter.

3.2. Effect of evaporation on diamondoid concentration ratios

The concentrations of individual diamondoids in residual oils (i.e., the ratio of individual diamondoid mass to the entire oil mass)

are affected by evaporative losses of both diamondoids and other components within the oil. One approach that eliminates the effect of this dual evaporation is to calculate adamantane and diamantane concentration ratios (Table 4).

Adamantane concentration ratios in gasoline are generally uniform until 85% of the oil has been evaporated (after 12 h). In addition, no obvious change is detected in either adamantane or diamantane concentration ratios in both pre-evaporation and evaporated fuel oil after 120 h of evaporation. The concentration ratios of alkyl adamantane compound pairs, such as A/MAs, MAs/DMAs, A/1-MA, and 1-MA/1,3-DMA, in both condensate and diesel decrease significantly with ongoing evaporation (Table 4), producing a strong linear trend in A/MAs vs. MAs/DMAs and A/1-MA vs. 1-MA/1,3-DMA diagrams (Fig. 2). Thus, we can determine the relative extent of evaporation by using a plot that is constructed by the related ratios of original, unaltered samples and some evaporated samples from same source. In contrast, no obvious variation is present in alkyl diamantane concentration ratios, such as D/MDs, MDs/DMDs, D/4-MD, and 4-MD/4,9-DMD (Table 4), indicating that the relationships between the concentrations of diamantane pairs are not altered by evaporation, although their concentrations may change to some extent.

3.3. Effect of evaporation on diamondoid isomerization indices

A number of common diamondoid isomerization indices were also calculated and are presented in Table 4. Adamantane parameters, such as MAI, MEI, DMAI-1, DMAI-2, TMAI-1 and TMAI-2, progressively decrease with ongoing evaporation of condensate and diesel oils, indicating that evaporation has a significant effect on these adamantane indices. In comparison, all diamantane ratios, such as MDI, DMDI-1 and DMDI-2 are relatively constant during evaporation, indicating that these ratios are not affected. This

Table 2
Concentrations of individual diamondoids within pre-evaporation and evaporated petroleum fractions determined in this study.

Samples	Evaporation time (h)	Mass loss (%)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
Condensate	Original	0	1206	2828	2130	796.7	82.8	276.6	198.6	185.9	266.6	205.8	314.4	291.0	204.1	131.9	63.7	236.2	221.9	84.6	62.5	68.8	116.6	138.9	1176	1099	197.4	325.8	126.4	103.4	48.0	196.1	113.4	11.0
	1	3.2	1198	2893	2180	826.2	85.4	276.5	206.3	192.2	281.8	215.0	318.4	307.3	215.8	135.5	67.5	251.5	235.1	89.3	65.7	74.7	122.4	146.4	1229	1165	207.9	340.9	133.7	112.9	49.8	208.2	121.9	12.8
	2.5	5.6	1130	2773	2097	797.1	84.9	276.0	202.0	188.7	275.3	209.8	312.8	300.1	211.7	135.3	64.4	239.6	231.3	88.4	65.0	73.9	119.3	143.3	1213	1150	205.4	339.6	131.4	110.4	49.5	205.8	120.0	12.9
	9	9.2	1053	2669	2004	784.3	83.8	271.7	206.3	193.3	284.1	217.8	326.1	312.6	220.8	141.1	67.4	255.4	242.2	92.8	67.8	77.1	126.6	151.7	1271	1193	211.8	353.4	136.7	114.5	53.2	214.7	122.7	12.8
	16	13.4	868.1	2358	1852	739.0	81.0	257.9	199.5	188.0	278.5	213.6	320.4	312.8	222.0	141.7	66.7	255.7	239.7	92.4	67.9	75.4	124.9	153.2	1324	1249	222.1	370.9	143.7	119.2	53.4	223.1	129.6	13.2
	24	17.6	563.6	1761	1493	640.7	73.6	226.1	177.3	168.1	257.0	189.4	297.8	284.7	204.8	128.9	61.9	238.7	224.6	87.8	62.5	71.2	122.0	148.7	1320	1280	227.1	376.0	147.5	121.2	54.5	222.4	131.8	13.5
	40.5	20.4	360.0	1285	1219	558.8	68.4	198.4	163.1	156.3	239.6	181.4	285.4	282.1	207.6	130.6	61.0	240.7	229.0	91.7	64.2	77.0	126.3	153.6	1427	1334	238.2	400.8	154.6	129.2	58.4	240.7	138.2	13.7
	65.5	25.1	141.2	681.5	726	402.7	53.6	142.8	120.5	122.4	201.5	147.2	251.1	249.2	187.9	110.7	55.0	217.4	205.9	84.5	58.7	70.1	114.7	140.0	1364	1291	230.9	384.8	150.0	124.8	56.0	232.6	133.2	13.7
	120.5	29.3	19.5	133.9	156.2	156.1	27.5	59.7	64.8	65.6	123.7	93.9	173.8	176.6	146.6	79.3	39.1	166.2	159.1	70.0	45.6	58.3	103.7	129.7	1419	1330	239.8	378.6	158.1	132.7	59.6	246.1	140.9	14.2
	132	30.1	12.5	98.9	119.0	127.5	23.8	48.6	53.4	53.0	104.9	78.7	149.2	152.1	127.9	66.2	33.8	147.8	140.1	64.6	40.4	52.1	94.3	117.5	1420	1379	250.0	423.3	168.5	140.6	63.4	261.5	153.0	15.7
	168	33.6	3.27	35.2	58.2	74.5	16.2	29.0	35.4	36.5	77.7	58.2	116.4	122.3	107.0	55.3	26.8	124.2	122.0	56.8	33.6	46.4	88.1	109.4	1422	1351	246.8	391.8	161.2	138.8	60.8	251.0	149.6	15.4
Gasoline	Original	0	–	37.1	2.56	1.19	0.23	2.61	0.99	1.31	0.76	0.71	0.43	0.58	0.31	7.59	0.55	1.19	0.49	0.32	2.16	0.06	0.26	0.26	–	–	–	–	–	–	–	–	–	–
	0.33	13.6	–	39.5	2.86	1.26	0.24	2.82	1.09	1.41	0.82	0.64	0.52	0.63	0.32	8.39	0.54	1.34	0.55	0.29	2.42	0.07	0.29	0.32	–	–	–	–	–	–	–	–	–	–
	1	24.7	–	43.4	3.00	1.37	0.26	3.05	1.09	1.48	0.9	0.69	0.56	0.74	0.35	9.16	0.64	1.38	0.57	0.37	2.66	0.07	0.32	0.33	–	–	–	–	–	–	–	–	–	–
	2	34.7	–	49.4	3.45	1.57	0.3	3.47	1.26	1.72	1.03	0.82	0.61	0.78	0.41	10.5	0.69	1.73	0.76	0.37	2.98	0.11	0.38	0.36	–	–	–	–	–	–	–	–	–	–
	3	46.7	–	58.7	4.05	1.88	0.37	4.21	1.57	2.1	1.15	0.95	0.70	0.98	0.49	12.7	0.87	2.06	0.75	0.45	3.56	0.1	0.48	0.51	–	–	–	–	–	–	–	–	–	–
	4	56.1	–	65.2	4.46	2.13	0.40	4.70	1.79	2.37	1.36	1.13	0.86	1.08	0.52	14.3	0.92	2.22	0.91	0.48	3.96	0.1	0.61	0.54	–	–	–	–	–	–	–	–	–	–
	6	65.1	–	80.6	5.71	2.62	0.52	5.59	2.18	2.93	1.69	1.31	0.97	1.27	0.70	17.0	1.24	3.01	1.12	0.75	4.86	0.15	0.68	0.62	–	–	–	–	–	–	–	–	–	–
	8	74.3	–	95.8	8.05	3.60	0.68	6.46	2.16	3.11	1.57	1.26	0.92	1.27	0.71	16.6	0.85	2.77	1.02	0.67	4.41	0.16	0.77	0.79	–	–	–	–	–	–	–	–	–	–
	12	85.5	–	144.1	12.1	5.53	1.10	12.2	4.26	5.87	3.22	2.52	2.02	2.60	1.26	32.1	2.00	5.66	2.34	1.30	8.70	0.47	1.24	1.30	–	–	–	–	–	–	–	–	–	–
	20.2	92.7	–	208.7	16.8	8.13	1.56	18.0	6.21	8.91	4.85	3.68	3.09	4.01	2.01	47.7	2.87	7.71	3.29	2.10	12.6	0.43	1.82	2.01	–	–	–	–	–	–	–	–	–	–
	46	98.4	–	418.6	38.3	20.2	4.38	42.9	17.5	24.1	14.5	15.2	9.23	11.84	6.56	156.3	11.3	25.12	11.32	5.84	49.9	1.46	7.08	8.16	–	–	–	–	–	–	–	–	–	–
Diesel	Original	0	75.9	203.3	125.8	83.6	7.40	175.2	111.3	122.9	183.6	103.1	138.4	176.4	128.6	111.9	43.0	209.6	125.3	62.2	111.5	26.4	120.3	78.8	95.2	95.1	21.6	111.2	27.6	31.6	10.0	105.3	46.6	4.04
	3	3.3	74.2	193.8	120.6	81.1	7.30	172.6	108.4	119.8	177.8	101.4	136.8	173.4	124.9	111.6	42.7	208.2	122.4	61.7	111.1	25.6	119.2	76.4	110.2	94.1	19.7	107.9	26.5	30.5	9.40	104.5	44.8	3.77
	10	5.95	65.0	178.4	115.4	79.7	7.10	168.6	108.3	119	181.9	103.1	139.2	177	129.9	115.9	42.7	216.3	127.8	64.9	115.1	27.1	123.4	81.4	117.4	105.5	21.2	128.5	29.4	32.7	10.6	100.7	52.1	3.86
	22.3	9.10	48.7	147.1	100.5	73.2	6.70	153.3	100.8	112	174	98.2	135.7	173.0	127.3	110.5	42.3	216.4	126.7	64.3	111.9	26.4	125.9	83.2	121.2	102.3	23.2	130.5	32.0	33.9	10.9	115.7	50.9	5.05
	62	15.7	15.4	70.1	59.9	51.9	5.50	109.7	79.5	90.6	152.5	85.2	124.3	162.1	125.6	103.2	40.9	208.8	125.9	66.0	109.6	28.2	133.9	85.7	132.4	119.5	27.8	148.7	33.2	40.9	12.7	118.8	60.8	4.78
	94.5	18.7	5.91	33.3	35.1	35.6	4.00	73.8	58.9	68.4	119.6	67.5	104.1	136.0	111.1	84.5	34.3	169.9	108.3	58.9	98.7	24.7	122.9	79.5	127.8	122	26.9	141.9	37.5	42.3	12.7	120.8	60.0	5.17
	120	21.6	2.37	17.1	20.8	23.8	2.80	50.3	42.1	49.9	93.1	51.0	83.4	109.5	90.9	70.5	27.3	141.7	90.8	50.0	80.4	21.9	108.7	70.3	117.5	113.1	24.7	132.1	36.4	38.8	12.5	114.6	56.3	4.81
	133	25.9	0.87	7.00	10.6	13.8	2.00	30.6	27.4	32.6	64.4	35.3	60.6	80.1	71.4	53.5	20.7	111.2	70.0	39.9	63.4	16.8	87.6	57.9	136.7	101.1	21.5	127.3	31.2	33.4	10.3	103.4	52.0	4.09
Fuel oil	Original	0	0.001	0.21	0.12	0.07	0.004	0.26	0.14	0.17	0.22	0.19	0.22	0.29	0.16	0.23	0.10	0.36	0.27	0.11	0.31	0.05	0.26	0.22	0.93	1.19	0.28	1.50	0.39	0.40	0.16	1.78	1.01	0.002
	120	0	0.001	0.25	0.14	0.08	0.004	0.29	0.15	0.19	0.23	0.20	0.23	0.31	0.17	0.24	0.10	0.40	0.28	0.11	0.32	0.06	0.27	0.22	0.89	1.14	0.28	1.47	0.42	0.46	0.15	2.20	1.21	0.002

[a] Peak number is the same as that listed in Table 1.

Table 3
Mass loss (%) for individual diamondoids from petroleum fractions evaporation.

Samples	Evaporation time (h)	Mass loss (%)	Mass loss (%) of diamondoid compounds[a]																															
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
Condensate	Original	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	1	3.2	3.8	1.0	0.9	−0.4	0.2	3.2	−0.6	−0.1	−2.3	−1.1	2.0	−2.2	−2.3	0.6	−2.6	−3.1	−2.6	−2.2	−1.8	−5.1	−1.6	−2	−1.2	−2.6	−1.9	−1.3	−2.4	−5.7	−0.4	−2.8	−4.1	−12.6
	2.5	5.6	11.5	7.4	7.1	5.6	3.2	5.8	4.0	4.2	2.5	3.8	6.1	2.6	2.1	3.2	4.6	4.2	1.6	1.4	1.8	−1.4	3.4	2.6	2.6	1.2	1.8	1.6	1.9	−0.8	2.7	0.9	0.1	−10.7
	9	9.2	20.7	14.3	14.6	10.6	8.1	10.8	5.7	5.6	3.2	3.9	5.8	2.5	1.8	2.9	3.9	1.8	0.9	0.4	1.5	−1.8	1.4	0.8	1.9	1.4	2.6	1.5	1.8	−0.5	−0.6	0.6	1.8	−5.7
	16	13.4	37.7	27.8	24.7	19.7	15.3	19.3	13.0	12.4	9.5	10.1	11.7	6.9	5.8	7.0	9.3	6.3	6.5	5.4	5.9	5.1	7.2	4.5	2.5	1.6	2.6	1.4	1.5	0.2	3.7	1.5	1.0	−3.9
	24	17.6	61.5	48.7	42.2	33.7	26.8	32.6	26.4	25.5	20.6	24.2	22.0	19.4	17.3	19.5	19.9	16.7	16.6	14.5	17.6	14.7	13.8	11.8	7.5	4.0	5.2	4.9	3.8	3.4	6.4	6.5	4.2	−1.1
	40.5	20.4	76.2	63.8	54.4	44.2	34.2	42.9	34.6	33.1	28.5	29.8	27.7	22.8	19.0	21.2	23.8	18.9	17.9	13.7	18.2	10.9	13.8	12.0	3.4	3.4	3.9	2.1	2.6	0.5	3.2	2.3	3.0	0.9
	65.5	25.1	91.2	82.0	74.5	62.1	51.5	61.3	54.6	50.7	43.4	46.4	40.2	35.9	31.0	37.1	35.3	31.1	30.5	25.2	29.7	23.7	26.3	24.5	13.1	12.0	12.4	11.5	11.1	9.6	12.6	11.2	12.0	6.7
	120.5	29.3	98.9	96.7	94.8	86.1	76.5	84.7	76.9	75.1	67.2	67.7	60.9	57.1	49.2	57.5	56.6	50.3	49.3	41.5	48.4	40.1	37.1	34.0	14.7	14.4	14.1	17.8	11.6	9.3	12.2	11.3	12.2	8.7
	132	30.1	99.3	97.6	96.1	88.8	79.9	87.7	81.2	80.1	72.5	73.3	66.8	63.5	56.2	64.9	62.9	56.3	55.9	46.6	54.8	47.1	43.5	40.9	15.6	12.3	11.5	9.2	6.8	5.0	7.7	6.8	5.7	0.2
	168	33.6	99.8	99.2	98.2	93.8	87.0	93.0	88.2	87.0	80.6	81.2	75.4	72.1	65.2	72.2	72.1	65.1	63.5	55.4	64.3	55.2	49.8	47.7	19.7	18.4	17.0	20.1	15.3	10.9	15.9	15.0	12.4	7.0
Gasoline	Original	0	–	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–
	0.33	13.6	–	8.0	3.5	8.5	9.8	6.6	4.9	7.0	6.8	22.1	−4.5	6.2	10.8	4.5	15.2	2.7	3.0	21.7	3.2	−0.8	3.6	−6.3	–	–	–	–	–	–	–	–	–	–
	1	24.7	–	11.9	11.8	13.3	14.9	12.0	17.1	14.9	10.8	26.8	1.9	3.9	15.0	9.1	12.4	12.7	12.4	12.9	7.3	12.2	7.3	4.4	–	–	–	–	–	–	–	–	–	–
	2	34.7	–	13.1	12.0	13.8	14.8	13.2	16.9	14.3	11.5	24.6	7.4	12.2	13.6	9.7	18.1	5.1	−1.3	24.5	9.9	−19.7	4.6	9.6	–	–	–	–	–	–	–	–	–	–
	3	46.7	–	15.7	15.7	15.8	14.3	14.0	15.5	14.6	19.3	28.7	13.2	9.9	15.8	10.8	15.7	7.7	18.4	25.0	12.2	11.2	1.6	−4.6	–	–	–	–	–	–	–	–	–	–
	4	56.1	–	22.8	23.5	21.4	23.7	20.9	20.6	20.6	21.4	30.1	12.2	18.3	26.4	17.3	26.6	18.1	18.5	34.2	19.5	26.8	−3.0	8.8	–	–	–	–	–	–	–	–	–	–
	6	65.1	–	24.2	22.2	23.2	21.1	25.3	23.1	21.9	22.4	35.6	21.3	23.6	21.2	21.8	21.3	11.7	20.2	18.2	21.5	12.8	8.7	16.8	–	–	–	–	–	–	–	–	–	–
	8	74.3	–	33.6	19.2	22.3	24.0	36.4	43.9	39.0	46.9	54.4	45.0	43.7	41.1	43.8	60.3	40.2	46.5	46.2	47.5	31.5	23.9	21.9	–	–	–	–	–	–	–	–	–	–
	12	85.5	–	43.7	31.5	32.6	30.7	32.2	37.6	35.0	38.6	48.5	31.9	35.0	41.1	38.7	47.3	31.0	30.8	41.1	41.6	−13.6	30.8	27.5	–	–	–	–	–	–	–	–	–	–
	20.2	92.7	–	58.9	52.1	50.1	50.5	49.7	54.2	50.3	53.4	62.2	47.5	49.5	52.7	54.1	61.9	52.7	51.0	52.1	57.4	47.7	48.9	43.6	–	–	–	–	–	–	–	–	–	–
	46	98.4	–	81.9	76.1	72.8	69.5	73.7	71.7	70.6	69.5	65.7	65.7	67.3	66.1	67.1	67.1	66.2	63.0	70.8	63.0	61.1	56.4	49.8	–	–	–	–	–	–	–	–	–	–
Diesel	Original	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	3	3.3	5.5	7.8	7.3	6.2	4.6	4.7	5.8	5.7	6.4	4.9	4.4	4.9	6.1	3.6	4.0	3.9	5.5	4.1	3.6	6.2	4.2	6.2	−11.9	4.3	11.8	6.2	7.2	6.7	9.1	4.0	7.0	9.8
	10	5.95	19.5	17.5	13.7	10.3	9.8	9.5	8.5	8.9	6.8	6.0	5.4	5.6	5.0	2.6	6.6	2.9	4.1	1.9	2.9	3.5	3.5	2.8	−16.0	−4.3	7.7	−8.7	−0.2	2.7	0.3	10.1	−5.2	10.1
	22.3	9.10	41.7	34.2	27.4	20.4	17.7	20.5	17.7	17.2	13.9	13.4	10.9	10.9	10.0	10.2	10.6	6.2	8.1	6.0	8.8	9.1	4.9	4.0	−15.7	2.2	2.4	−6.7	−5.4	2.5	0.9	0.1	0.7	−13.6
	62	15.7	82.9	70.9	59.9	47.7	37.3	47.2	39.8	37.9	30.0	30.3	24.3	22.5	17.7	22.3	19.8	16.0	15.3	10.5	17.1	10.0	6.2	8.3	−17.2	−5.9	−8.5	−12.7	−1.4	−9.1	−7.1	4.9	−10.0	0.3
	94.5	18.7	93.7	86.7	77.3	65.4	56.1	65.8	57.0	54.8	47.0	46.8	38.8	37.3	29.8	38.6	35.1	34.1	29.7	23.0	28.0	23.9	16.9	18.0	−9.1	−4.3	−1.2	−3.7	−10.5	−8.8	−3.3	6.7	−4.7	−4.0
	120	21.6	97.6	93.4	87.0	77.7	70.3	77.5	70.3	68.2	60.2	61.2	52.8	51.3	44.6	50.6	50.2	47.0	43.2	37.0	43.5	35.0	29.2	30.1	3.2	6.8	10.3	6.9	−3.4	3.7	2.0	14.7	5.3	6.7
	133	25.9	99.2	97.4	93.8	87.8	80.0	87.1	81.8	80.3	74.0	74.6	67.6	66.4	58.9	64.6	64.3	60.7	58.6	52.5	57.9	52.8	46.0	45.6	−6.4	21.2	26.2	15.2	16.2	21.7	23.7	27.2	17.3	25.0
Fuel oil	Original	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	120	0.0	0.0	−0.2	−0.2	−0.1	0.0	−0.1	−0.1	−0.1	−0.1	−0.1	−0.1	0.0	−0.1	0.0	−0.1	−0.1	0.0	0.0	0.0	−0.2	0.0	0.0	0.0	0.0	0.0	0.0	−0.1	−0.1	0.0	−0.2	−0.2	0.0

[a] Peak number is the same as that listed in Table 1.

Table 4
Diamondoid parameters for petroleum fractions during evaporation determined in this study.

Samples	Evaporation time (h)	A/MAs	MAs/DMAs	A/1-MA	1-MA/1,3-DMA	D/MDs	MDs/DMDs	D/4-MD	4-MD/4,9-DMD	A/D	MAs/MDs	DMAs/DMDs	1-MA/4-MD	1,3-DMA/4,9-DMD	MAI	EAI	DMAI-1	DMAI-2	TMAI-1	TMAI-2	MDI	DMDI-1	DMDI-2
		Concentration ratios of diamondoids													Isomerization ratios of diamondoids								
Condensate	Original	0.39	1.12	0.43	1.33	0.73	3.00	1.07	5.57	1.03	1.92	5.15	2.57	10.79	0.91	0.68	0.91	0.85	0.57	0.75	0.68	0.64	0.66
	1	0.38	1.11	0.41	1.33	0.72	2.97	1.05	5.60	0.97	1.85	4.96	2.48	10.49	0.91	0.67	0.91	0.85	0.57	0.75	0.68	0.63	0.65
	2.5	0.37	1.10	0.41	1.32	0.72	2.99	1.05	5.60	0.93	1.80	4.87	2.41	10.21	0.91	0.68	0.91	0.84	0.57	0.74	0.68	0.63	0.65
	9	0.36	1.09	0.39	1.33	0.72	3.01	1.07	5.63	0.83	1.67	4.59	2.24	9.46	0.91	0.68	0.90	0.83	0.55	0.73	0.68	0.63	0.65
	16	0.33	1.04	0.37	1.27	0.72	3.00	1.06	5.62	0.66	1.42	4.10	1.89	8.34	0.90	0.68	0.90	0.83	0.54	0.73	0.68	0.63	0.65
	24	0.28	0.95	0.32	1.18	0.70	2.99	1.03	5.64	0.43	1.06	3.33	1.38	6.57	0.89	0.67	0.89	0.81	0.52	0.71	0.68	0.63	0.65
	40.5	0.24	0.83	0.28	1.05	0.72	2.99	1.07	5.60	0.25	0.75	2.70	0.96	5.12	0.87	0.67	0.87	0.79	0.50	0.70	0.68	0.63	0.65
	65.5	0.17	0.70	0.21	0.94	0.71	2.99	1.06	5.59	0.10	0.43	1.83	0.53	3.14	0.83	0.65	0.83	0.75	0.45	0.67	0.68	0.63	0.65
	120.5	0.10	0.46	0.15	0.86	0.73	2.91	1.07	5.55	0.01	0.10	0.62	0.10	0.65	0.69	0.63	0.62	0.55	0.31	0.56	0.68	0.63	0.64
	132	0.08	0.44	0.13	0.83	0.69	2.90	1.03	5.52	0.01	0.07	0.47	0.07	0.48	0.67	0.62	0.60	0.53	0.30	0.55	0.67	0.62	0.64
	168	0.05	0.30	0.09	0.60	0.71	2.86	1.05	5.47	0.00	0.03	0.31	0.03	0.24	0.55	0.62	0.50	0.45	0.24	0.49	0.68	0.62	0.64
Gasoline	Original	–	6.49	–	14.49	–	–	–	–	–	–	–	–	–	0.93	0.78	0.78	0.53	0.54	0.61	–	–	–
	0.33	–	6.47	–	13.81	–	–	–	–	–	–	–	–	–	0.93	0.78	0.82	0.53	0.52	0.61	–	–	–
	1	–	6.73	–	14.47	–	–	–	–	–	–	–	–	–	0.93	0.77	0.81	0.54	0.51	0.60	–	–	–
	2	–	6.66	–	14.32	–	–	–	–	–	–	–	–	–	0.93	0.78	0.81	0.54	0.53	0.60	–	–	–
	3	–	6.59	–	14.49	–	–	–	–	–	–	–	–	–	0.93	0.78	0.81	0.52	0.53	0.62	–	–	–
	4	–	6.55	–	14.62	–	–	–	–	–	–	–	–	–	0.93	0.78	0.80	0.52	0.52	0.61	–	–	–
	6	–	6.45	–	14.12	–	–	–	–	–	–	–	–	–	0.94	0.78	0.81	0.53	0.54	0.61	–	–	–
	8	–	6.63	–	11.90	–	–	–	–	–	–	–	–	–	0.94	0.79	0.86	0.60	0.62	0.70	–	–	–
	12	–	5.84	–	11.91	–	–	–	–	–	–	–	–	–	0.92	0.79	0.83	0.54	0.54	0.63	–	–	–
	20.2	–	5.89	–	12.42	–	–	–	–	–	–	–	–	–	0.92	0.79	0.82	0.53	0.53	0.63	–	–	–
	46	–	4.34	–	10.93	–	–	–	–	–	–	–	–	–	0.91	0.76	0.72	0.48	0.49	0.58	–	–	–
Diesel	Original	0.20	0.75	0.37	1.62	0.31	2.45	1.00	4.40	0.80	1.21	3.97	2.14	5.82	0.54	0.50	0.55	0.35	0.21	0.31	0.31	0.32	0.41
	3	0.20	0.74	0.38	1.61	0.36	2.52	1.17	4.78	0.67	1.20	4.06	2.06	6.12	0.53	0.50	0.54	0.35	0.21	0.31	0.31	0.31	0.39
	10	0.19	0.71	0.36	1.55	0.35	2.47	1.11	4.98	0.55	1.04	3.61	1.69	5.44	0.51	0.50	0.53	0.34	0.20	0.30	0.32	0.29	0.39
	22.3	0.16	0.66	0.33	1.46	0.35	2.49	1.18	4.41	0.40	0.86	3.24	1.44	4.33	0.49	0.50	0.51	0.32	0.19	0.30	0.29	0.31	0.41
	62	0.09	0.50	0.22	1.17	0.34	2.38	1.11	4.30	0.12	0.46	2.19	0.59	2.15	0.39	0.48	0.41	0.26	0.15	0.25	0.31	0.31	0.40
	94.5	0.06	0.41	0.18	0.95	0.33	2.31	1.05	4.54	0.05	0.28	1.58	0.27	1.30	0.31	0.46	0.34	0.22	0.13	0.23	0.32	0.31	0.39
	120	0.04	0.35	0.14	0.82	0.33	2.30	1.04	4.58	0.02	0.19	1.22	0.15	0.84	0.25	0.47	0.29	0.18	0.11	0.20	0.31	0.30	0.39
	133	0.02	0.30	0.12	0.66	0.41	2.40	1.35	4.70	0.01	0.11	0.92	0.07	0.49	0.19	0.46	0.23	0.15	0.09	0.18	0.30	0.29	0.39
Fuel oil	Original	0.00	0.65	0.00	1.75	0.21	2.15	0.78	4.25	0.00	0.11	0.35	0.18	0.43	0.45	0.43	0.39	0.28	0.12	0.24	0.27	0.22	0.41
	120	0.00	0.69	0.00	1.79	0.19	2.03	0.78	4.07	0.00	0.11	0.33	0.22	0.50	0.46	0.43	0.41	0.29	0.13	0.26	0.24	0.19	0.38

As, MAs, and DMAs are sum of concentrations of adamantanes, methyl adamantanes, and dimethyl adamantanes listed in Table 1, respectively; Ds, MDs, and DMDs are sum of concentrations of diamantanes, methyl diamantanes, and dimethyl diamantanes listed in Table 1, respectively. MAI = 1-MA/(1-MA + 2-MA), EAI = 1-EA/(1-EA + 2-EA), DMAI-1 = 1,3-DMA/(1,2-DMA + 1,3-DMA), DMAI-2 = 1,3-DMA/(1,3-DMA + 1,4-DMA), TMAI-1 = 1,3,5-TMA/(1,3,5-TMA + 1,3,4-TMA), TMAI-2 = 1,3,5-TMA/(1,3,5-TMA + 1,3,6-TMA), MDI = 4-MD/(4-MD + 1-MD + 3-MD), DMDI-1 = 4,9-DMD/(4,9-DMD + 3,4-DMD), DMDI-2 = 4,9-DMD/(4,8-DMD + 4,9-DMD).
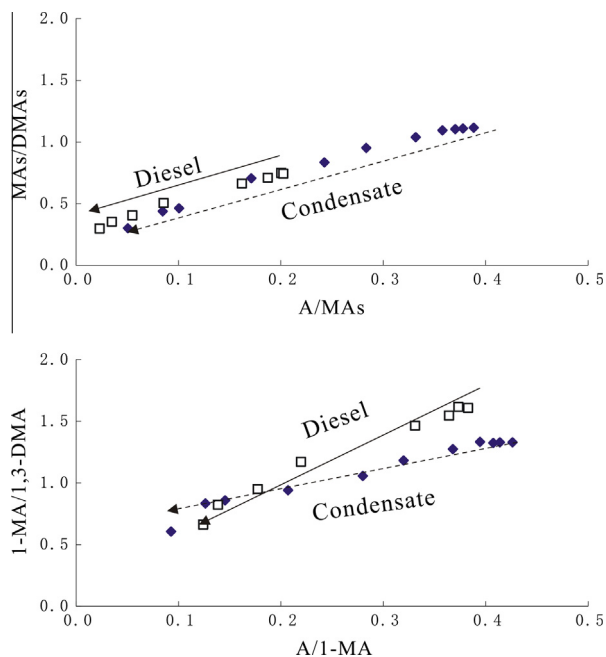
Fig. 2. Adamantane concentration ratio cross plots for the Tarim condensate and diesel oil samples used in this study.

Fig. 3. Diamantane concentration ratio DMAI-1 vs. DMAs/MDs cross plot for the diesel, condensate and fuel oil samples used in this study.

indicates that diamantane indices can be used for oil correlation and maturity determination of oils that have undergone evaporation. Interestingly, adamantanes can be detected in gasoline even after up to 90% evaporation, yielding essentially unaltered adamantane indices, suggesting that these indices can be used with highly volatile oils.

A DMAI-1 vs. DMAs/MDs cross plot has been suggested as a possible tool to assess oil maturity (Fang et al., 2013). However, differences in evaporation loss means that less volatile diamondoids will gradually increase in relative abundance compared to more volatile diamondoids with increasing evaporation. This indicates that the concentration ratio of a more volatile compound to a less volatile component, for example DMAs/MDs, will decrease with ongoing evaporation. Fig. 3 shows that both DMAI-1 and DMAs/MDs ratios progressively decrease with increasing evaporation. Thus, the experimental result suggests that evaporation prior to pyrolysis causes the difference between measured and calculated data in the plot of DMAI-1 vs. DMAs/MDs (Fang et al., 2013). This suggests that evaporation probably interferes with the interpretation of some diamondoid indices, a factor that needs to be considered when these indices are applied to natural examples.

3.4. Estimating oil evaporation extent

The ratio of a more to a less volatile compound can be used to determine the extent of evaporation of a spilled fuel or oil (Snape et al., 2005; McIntyre et al., 2007). Thus, some diamondoid indices, such as A/1-MA, 1-MA/2-MA, 1-MA/1-EA, A/D, 1-MA/4-MD and 1,3-DMA/4,9-DMD, can be used to assess the extent of diamondoid evaporation. These concentration ratios were calculated using the data in Table 2 before being normalized to their original ratios in non-evaporated oils. All of these normalized ratios gradually decrease with increasing evaporation, with trends being nearly independent of variations in the type of petroleum fraction (Fig. 4, Table 5). This means that it is possible to estimate the extent of evaporation that an oil has undergone using diamondoid indices for both non-evaporated and evaporated oils as shown in Fig. 4.

The evaporation percentage of an oil (EP_{oil}), defined as the ratio of the mass loss of oil after evaporation compared to the non-evap-
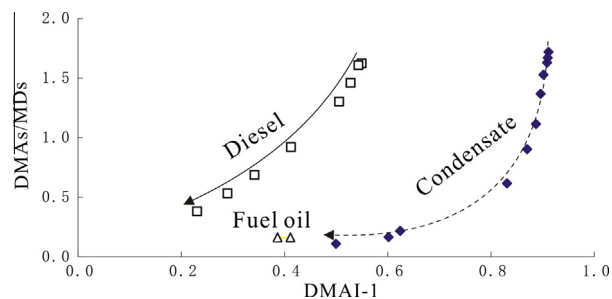
orated oil, a value that is equal to the mass loss percentage, can also be used to assess the extent of evaporation. Table 2 lists EP_{oil} (mass loss in %) values for the four petroleum fractions analyzed in this study at different stages of evaporation. Here, we propose a diamondoid based approach to estimate EP_{oil} (%) values and verify the range of values by comparing estimated and determined values.

The extent of evaporation of salt water can be determined by the variation of salinity before and after evaporation, with a doubling of salinity implying 50% evaporation (Dahl et al., 1999). Here, we used the same principle to assess the extent of oil evaporation by comparing diamondoid concentrations in evaporated and non-evaporated oils using the following equation:

$$EP_{oil}\ (\%) = (1 - C_{dia}(o)/C_{dia}(t)) \times 100 \qquad (1)$$

where $C_{dia}(o)$ is the concentration of diamondoids (an individual compound, a group of compounds, or all diamondoid compounds) in the original oil and $C_{dia}(t)$ is the concentration of the corresponding diamondoid compounds in an evaporated oil from the same source.

The selected diamondoid compounds used in Eq. (1) should be non-volatile or have low volatility in order to obtain accurate estimates of EP_{oil} (%). The analyses discussed above demonstrate that diamantanes are less volatile than adamantanes, indicating that diamantane compounds can be used to estimate EP_{oil} (%) using Eq. (1), with measured and calculated EP_{oil} (%) for condensate oil compared in Fig. 5. These data correlate well at low to moderate stages of evaporation, indicating that this approach is viable for oils that have undergone relatively little evaporation. However, significant errors occur for oils that have undergone substantial evaporation (e.g., > 50 h of evaporation), most probably due to evaporative loss of diamantanes.

4. Conclusions

The effect of evaporation on the concentration and distribution of diamondoids in petroleum fractions was investigated by laboratory evaporation experiments and quantitative determination of diamondoid compounds. The results obtained from these analyses indicate the following. Both adamantanes and diamantanes evaporated with other light hydrocarbons from petroleum fractions, and the concentrations of both types of compound are controlled by petroleum fraction type, extent of evaporation and the boiling point of individual diamondoid compounds.

Evaporation has a significant effect on adamantane concentration ratios, indicating that any influence of evaporation has adverse effect on adamantane indices. In contrast, no obvious change is observed for diamantane ratios, indicating that diamantane concentration and distribution indices can be used to assess oil correlations and the maturity of evaporated oils.
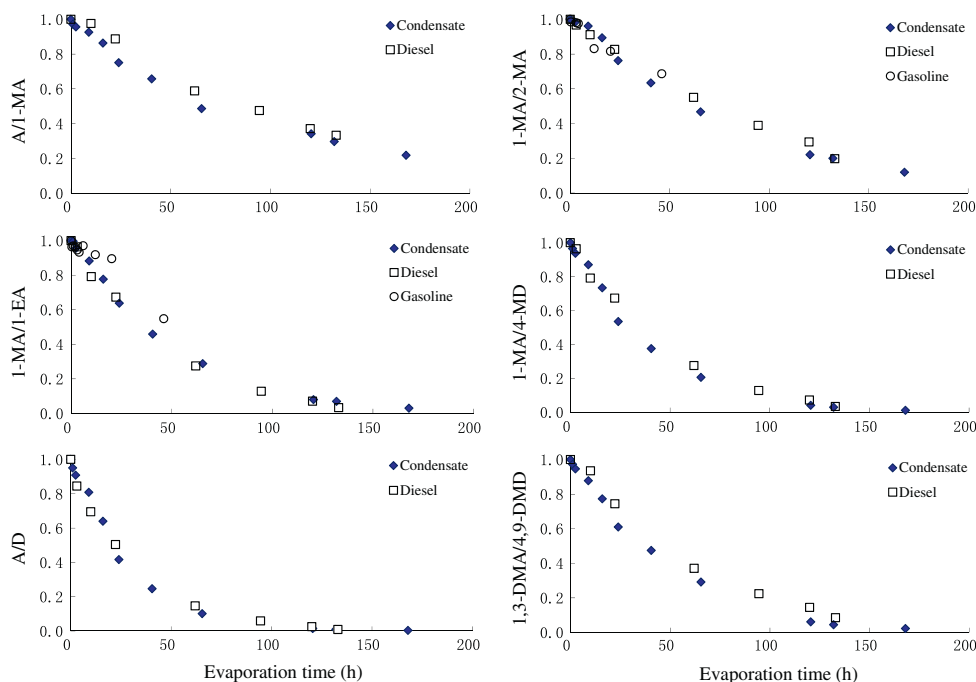
Fig. 4. Diagram showing variations in adamantane and diamantane concentration ratios in petroleum fraction samples used in this study with ongoing evaporation.

Table 5
Initial and normalized values of A/1-MA, 1-MA/2-MA, 1-MA/1-EA, 1-MA/4-MD, A/D, 1,3-DMA/4,9-DMD during evaporation referring to Fig. 4.

Samples	Evaporation time (h)	Initial values						Normalized values					
		A/1-MA	1-MA/2-MA	1-MA/1-EA	1-MA/4-MD	A/D	1,3-DMA/4,9-DMD	A/1-MA	1-MA/2-MA	1-MA/1-EA	1-MA/4-MD	A/D	1,3-DMA/4,9-DMD
Condensate	0	0.43	10.22	21.44	2.57	1.03	10.79	1.00	1.00	1.00	1.00	1.00	1.00
	1	0.41	10.46	21.35	2.48	0.97	10.49	0.97	1.02	1.00	0.97	0.95	0.97
	2.5	0.41	10.05	20.50	2.41	0.93	10.21	0.96	0.98	0.96	0.94	0.91	0.95
	9	0.39	9.82	18.92	2.24	0.83	9.46	0.93	0.96	0.88	0.87	0.81	0.77
	16	0.37	9.14	16.64	1.89	0.66	8.34	0.86	0.89	0.78	0.73	0.64	0.77
	24	0.32	7.79	13.66	1.38	0.43	6.57	0.75	0.76	0.64	0.53	0.42	0.61
	40.5	0.28	6.48	9.84	0.96	0.25	5.12	0.66	0.63	0.46	0.37	0.25	0.47
	65.5	0.21	4.77	6.16	0.53	0.10	3.14	0.49	0.47	0.29	0.21	0.10	0.29
	120.5	0.15	2.24	1.69	0.10	0.01	0.65	0.34	0.22	0.08	0.04	0.01	0.06
	132	0.13	2.03	1.49	0.07	0.01	0.48	0.30	0.20	0.07	0.03	0.01	0.04
	168	0.09	1.21	0.64	0.03	0.00	0.24	0.22	0.12	0.03	0.01	0.00	0.02
Gasoline	0	–	14.21	4.89	–	–	–	–	1.00	1.00	–	–	–
	0.33	–	14.01	4.71	–	–	–	–	0.99	0.96	–	–	–
	1	–	14.23	4.74	–	–	–	–	1.00	0.97	–	–	–
	2	–	14.24	4.70	–	–	–	–	1.00	0.96	–	–	–
	3	–	13.94	4.62	–	–	–	–	0.98	0.95	–	–	–
	4	–	13.87	4.56	–	–	–	–	0.98	0.93	–	–	–
	6	–	14.42	4.74	–	–	–	–	1.01	0.97	–	–	–
	8	–	14.83	5.77	–	–	–	–	1.04	1.18	–	–	–
	12	–	11.81	4.49	–	–	–	–	0.83	0.92	–	–	–
	20.2	–	11.59	4.38	–	–	–	–	0.82	0.90	–	–	–
	46	–	9.76	2.68	–	–	–	–	0.69	0.55	–	–	–
Diesel	0	0.37	1.16	1.82	2.14	0.80	5.82	1.00	1.00	1.00	1.00	1.00	1.00
	3	0.38	1.12	1.74	2.06	0.67	6.12	1.03	0.97	0.96	0.96	0.84	1.05
	10	0.36	1.06	1.54	1.69	0.55	5.44	0.98	0.91	0.85	0.79	0.69	0.93
	22.3	0.33	0.96	1.33	1.44	0.40	4.33	0.89	0.83	0.73	0.67	0.50	0.74
	62	0.22	0.64	0.68	0.59	0.12	2.15	0.59	0.55	0.37	0.27	0.15	0.37
	94.5	0.18	0.45	0.39	0.27	0.05	1.30	0.48	0.39	0.22	0.13	0.06	0.22
	120	0.14	0.34	0.24	0.15	0.02	0.84	0.37	0.29	0.13	0.07	0.03	0.14
	133	0.12	0.23	0.13	0.07	0.01	0.49	0.33	0.20	0.07	0.03	0.01	0.08

Some diamondoid ratios, such as A/1-MA, 1-MA/2-MA, 1-MA/1-EA, 1-MA/4-MD, A/D and 1,3-DMA/4,9-DMD, progressively decrease with ongoing evaporation independent of petroleum fraction type, indicating that these indices can be used to deduce the extent of evaporation. In addition, the extent of evaporation experienced by slightly to moderately evaporated oils can be estimated using diamantane concentrations, because these concentrations increase nearly in proportion with the extent of evaporation.
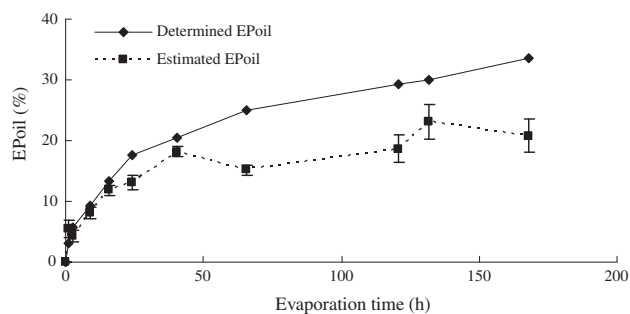
Fig. 5. Diagram showing the determined and estimated oil evaporation percentages for the Tarim condensate used in this study. [*] The short line segments on the estimated EP$_{oil}$ curve represent the error bars.

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References

Chen, J., Fu, J., Sheng, G., Liu, D., Zhang, J., 1996. Diamondoid hydrocarbon ratios: novel maturity indices for highly mature crude oils. Organic Geochemistry 25, 179–190.

Dahl, J.E., Moldowan, J.M., Peters, K.E., Claypool, G.E., Rooney, M.A., Michael, G.E., Mello, M.R., Kohnen, M.L., 1999. Diamondoid hydrocarbons as indicators of natural oil cracking. Nature 399, 54–57.

Grice, K., Alexander, R., Kagi, R.I., 2000. Diamondoid hydrocarbon ratios as indicators of biodegradation in Australian crude oils. Organic Geochemistry 31, 61–73.

Fang, C.C., Xiong, Y.Q., Liang, Q.Y., Li, Y., 2012. Variation in abundance and distribution of diamondoids during oil cracking. Organic Geochemistry 47, 1–8.

Fang, C.C., Xiong, Y.Q., Li, Y., Chen, Y., Liu, J.Z., Zhang, H.Z., Adedosu, T.A., Peng, P.A., 2013. The origin and evolution of adamantanes and diamantanes in petroleum. Geochimica et Cosmochimica Acta 120, 109–120.

Liang, Q.Y., Xiong, Y.Q., Fang, C.C., Li, Y., 2012. Quantitative analysis of diamondoids in crude oils using gas chromatography–triple quadrupole mass spectrometry. Organic Geochemistry 43, 83–91.

McIntyre, C.P., Harvey, P.Mc.A., Ferguson, S., Wressnig, A.M., Snape, I., George, S.C., 2007. Determining the extent of weathering of spilled fuel in contaminated soil using the diastereomers of pristane and phytane. Organic Geochemistry 38, 2131–2134.

Schulz, L.K., Wilhelms, A., Rein, E., Steen, A.S., 2001. Application of diamondoids to distinguish source rock facies. Organic Geochemistry 32, 365–375.

Snape, I., Harvey, P.Mc.A., Ferguson, S.H., Rayner, J.L., Revill, A.T., 2005. Investigation of evaporation and biodegradation of fuel spills in Antarctica I. A chemical approach using GC-FID. Chemosphere 61, 1485–1494.

Stout, S.A., Douglas, G.S., 2004. Diamondoid hydrocarbons—application in the chemical fingerprinting of natural gas condensate and gasoline. Environmental Forensics 5, 225–235.

Wang, Z.D., Yang, C., Hollebone, B., Fingas, M., 2006. Forensic fingerprinting of diamondoids for correlation and differentiation of spilled oil and petroleum products. Environmental Science and Technology 40, 5636–5646.

Wei, Z.B., Moldowan, J.M., Jarvie, D.M., Hill, R., 2006. The fate of diamondoids in coals and sedimentary rocks. Geology 34, 1013–1016.

Wei, Z.B., Moldowan, J.M., Peters, K.E., Wang, Y., Xiang, W., 2007. The abundance and distribution of diamondoids in biodegraded oils from the San Joaquin Valley: implications for biodegradation of diamondoids in petroleum reservoirs. Organic Geochemistry 38, 1910–1926.

Wingert, W.S., 1992. GC–MS analysis of diamondoid hydrocarbons in Smackover petroleums. Fuel 71, 37–43.