



Original research paper

Advancement in application of diamondoids on organic geochemistry[☆]

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Received 19 July 2016; revised 10 August 2016

Available online ■■■

Abstract

Diamondoids occur in all kinds of fossil fuels. Due to peculiar cage molecular structures, diamondoids have been widely used in the maturity assessment of high mature to over-mature oils as well as source rocks since the 1990s. New advancements in maturity, oil-cracking, oil mixing, oil biodegradation, organic facies, TSR, gas washing, migration, and oil spill identification using diamondoids during the 21st century will be further discussed in this paper; the origin and possible forming mechanisms of diamondoids are also explained. Owing to the vagueness of the origin of diamondoid, the results of the maturity and oil cracking among researchers brought about great differences. It is suggested that the research of the evolution of diamondoid in different type oils and source rocks are beneficial when applied in organic geochemistry, especially for the depth limits for the deep reservoirs.

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Keywords: Diamondoids; Adamantane; Diamantane; Maturity; Oil-cracking; Biodegraded; Organic facies; Thermochemical sulfate reduction (TSR)

1. Introduction

Diamondoids, a cage hydrocarbon with a molecular formula of $C_{4n+6}H_{4n+12}$, widely occur in fossil fuels [1]. The basic repeated unit of diamondoids is adamantane [2,3] (Fig. 1), a four ring cage system containing 10 carbons. The scientific name of adamantane is tricyclo [3,3,1,1,(3,7)] decane, which can be regarded as composed by three rigidly fused cyclohexane rings in an all-chair configuration. The polyhomologous members of adamantanes include diamantanes, triamantanes, tetramantanes, pentamantanes, and hexamantanes, in which adamantanes, diamantane, and triamantanes belong to lower diamondoids, whereas repeated units reaching over 4 belong to higher diamondoids. Lower

diamondoids only contain one isomer, while polymantanes contain 4, 5, and 6 repeated units, the isomer numbers are 3, 6, and 17, respectively [3].

Diamondoids play a vital role by applying it in the field of petroleum geochemistry, medicine, chemistry, and nanometer new material [3] since Landa et al. [1] discovered adamantane in the oil from Hodonin oilfield within Czechoslovakia. Lin et al. [4] reported higher diamondoids namely tetramantane, pentamantane, and hexamantane in the condensate oil produced from the Jurassic Norphlet Formation sandstone in its depth of 6800 m within the U.S. Gulf of Mexico. Using reversed-phased high-performance liquid chromatography (HPLC), Dahl et al. [5,6] isolated the crystal of hexamantane or cyclohexamantane from distillate fractions from oil and determined the structure of $C_{26}H_{30}$ by means of X-ray diffraction, and GC-MS, 1H , ^{13}C NMR methods.

In fossil fuels, the abundance of adamantanes is the highest sequence. Assuming that the abundance of adamantanes is 100, the concentration of diamantanes, triadamantanes, tetramantanes, pentamantanes, and hexamantanes are 50, 15, 5, 1, and 0.1, respectively [4].

[☆] This is English translational work of an article originally published in *Natural Gas Geoscience* (in Chinese). The original article can be found at: [10.11764/j.issn.1672-1926.2016.05.0851](http://dx.doi.org/10.11764/j.issn.1672-1926.2016.05.0851).

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Peer review under responsibility of Editorial Office of *Journal of Natural Gas Geoscience*.

<http://dx.doi.org/10.1016/j.jnggs.2016.09.001>

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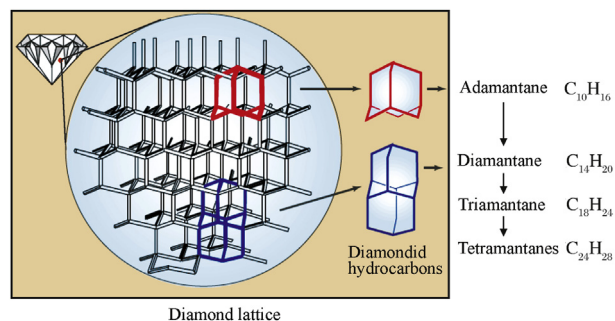


Fig. 1. Diamondoid structure (after Ref. [3]).

2. Diamondoid detection method, internal standards, and pretreatment

Wingert [7] used MID–GC–MS to identify the diamondoids in petroleum. In mainland China, Zhao et al. [8] adapted MID–GC–MS to detect diamondoids in marginal mature source rock, in which it can reach the triamantane series. Both the GC–MS and GC–MS–MS methods were applied to detect the diamondoids in the Molecular Organic Geochemistry Laboratory at Stanford University [9]. Liang et al. [10,11] proposed that the sensitivity of the GC–MS–MS is about 4–66 times higher than that of the GC–MS, considering that the former has a better recovery. Through the development of technology, the comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry, this was adapted to assess the diamondoids in crude oil. Using GC/GC-TOFMS, over 100 compounds of adamantane, diamantane, and triamantane can be identified [12,13].

The Molecular Organic Geochemistry Laboratory supervised by K. E. Moldowan at the Stanford University has the most advanced technology of determining diamondoid concentrations by using six internal standards including D_4 -adamantane, D_3 -1-methyladamantane, D_3 -1-methyldiamantane, D_4 -diamantane, D_4 -ethyladamantane, and D_4 -triamantane. Quantitation of alkyl-adamantanes, diamantanes, and triamantanes were achieved by integrating peak heights with respect to corresponding standards: D_3 -1-methyladamantane, D_3 -1-methyldiamantane, and D_4 -triamantane, respectively. D_4 -adamantane, D_4 -diamantane, and D_4 -triamantane were used to quantify adamantane, diamantane, triamantane, and tetramantane, respectively. Meanwhile, D_5 -1-ethyladamantane was used to quantify ethyl diamantanes. Their standard deviation was less than 8% [9]. Inland, Ma et al. [14] used two internal standards (D_{16} -adamantane and D_3 -1-methyldiamantane) to quantify the concentration of diamondoids in oils. Azevode et al. [15], Spriner et al. [16], and Liang et al. [10,11] adapted the diamondoid kits from the Chrion AS Company of Norway as the calibration solution and used the n - $C_{12}D_{26}$, n - $C_{16}D_{34}$ as the internal standards to quantify the adamantanes and diamantanes, respectively.

In the pretreatment of compound-specific isotope analysis of diamondoids, Huang et al. [17] used the β -cyclodextrin (β -

CD) to enrich diamondoids. This method has a high recovery of the diamondoids in the oils and can satisfy the compound-specific isotope analysis (CSIA).

3. Application of diamondoids in organic geochemistry

3.1. Maturity determination of high mature to overmature oils and source rocks

The stability of diamondoids relies on the methyl substitution position. For the reason that methyl substitution attached to a bridgehead position, 1-methyl adamantane, and 4-methyl diamantane showed more stability than that of diamondoids with methyl substitution positioned at the quaternary carbon. Based on the aforementioned mechanism, Chen et al. [18–20] proposed two diamondoid maturity ratios:

Methyl adamantane index I, $MAI = 1-MA/(1-MA + 2-MA)$

Methyl diamantane index II, $MDI = 4-MD/(1-MD + 3-MD + 4-MD)$

Both MAI and MDI, showing good correlation with vitrinite reflectance (Table 1), were widely used as maturity indicators for high mature oils and condensate in China [20–29]. In addition, Fu et al. [30] made use of the preceding ratios to determine the maturity of gas from the southern Qiongdong Basin in China. The determined result is consistent to that of the maturity obtained by carbon isotope of methane from the gas.

Some other diamondoids maturity ratios are as follows [31–35]:

$DMDI-1$ (dimethyldiamantane index 1) = $4,9-DMD/(4,9-DMD + 3,4-DMD)$

$DMDI-2$ (dimethyldiamantane index 2) = $4,9-DMD/(4,9-DMD + 4,8-DMD)$

EAI (ethyladamantane index) = $1-EA/(1-EA + 2-EA)$

$DMAI-1$ (dimethyladamantane index 1) = $1,3-DMA/(1,3-DMA + 1,2-DMA)$

$DMAI-2$ (dimethyladamantane index 2) = $1,3-DMA/(1,3-DMA + 1,4-DMA)$

$TMAI-1$ (trimethyladamantane index 1) = $1,3,5-TMA/(1,3,5-TMA + 1,2,4-TMA)$

$TMAI-2$ (trimethyladamantane index 2) = $1,3,5-TMA/(1,3,5-TMA + 1,3,6-TMA)$

Table 1
Relationship between the diamondoids' parameters and vitrinite reflectance (after Ref. [18]).

Index I: MAI/%	Index II:MDI/%	R_o /%
50–70	30–40	1.1–1.3
70–80	40–50	1.3–1.6
80–90	40–60	1.6–1.9
>90	>60	>1.9

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