Diamondoids: occurrence in fossil fuels, applications in petroleum exploration and fouling in petroleum production. A review paper

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Abstract: In this review paper, we report the molecular structure, origin, natural occurrence and variety of diamondoid hydrocarbons in petroleum fluids and other fossil fuels. In addition, we present the role of diamondoids as geochemical tools for petroleum characterisation, ways diamondoid molecules are used to play an important role in petroleum evaluation, and may be used to assess origin, extend of biodegradation and thermal maturity, as well as to identify the occurrence of petroleum. The diamondoid-based diagnostic ratios in environment science as well as diamondoid-based diagnostic ratios for petroleum maturity parameters are also presented and discussed. Such diamondoid-based parameters may be used to assess oil source, maturity and biodegrability, providing supporting information, especially when traditional evaluation data are not available or are difficult to interpret. We also report applications and problems associated with diamondoids in petroleum exploration and production. That is the role of diamondoids in petroleum and natural gas production fouling as well as separation, detection and measurements of petroleum diamondoids. We realise that the presence of diamondoids in petroleum has become much more than a chemical curiosity since it has advanced to be a resourceful instrument in petroleum science, biomedicine, materials science and an important family of molecular building blocks in nanotechnology. [Received: August 9, 2011; Accepted: November 23, 2011]
Keywords: adamantine; diamondoid; diamondoids genesis; fossil fuels; fouling; geochemical tool; petroleum characterisation; petroleum exploration; petroleum production.


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G. Ali Mansoori is a Professor of Bioengineering, Chemical Engineering and Physics at the University of Illinois at Chicago. He received his education and research trainings at Tehran University, University of Minnesota, University of Oklahoma, and Rice University. He has published extensively in the areas of thermodynamics, nanotechnology, molecular based study of disease diagnostic methods and therapeutic agents, nanobiоструктуры design (nanoclusters, nanoconjugates, nanoparticles), phase transitions, density functional theory, molecular dynamics simulations, statistical mechanics. He is the author of several books including Molecular-Based Study of Fluids, C7+, Fraction Characterization, Fluctuation Theory of Mixtures, Principles of Nanotechnology, and Molecular Building Blocks for Nanotechnology. He has been a consultant and lecturer to several organisations. For his research and educational achievements, he has received numerous recognitions and awards.

Elmo Silvano de Araujo joined the UFPE in 1996 and is currently a Full Professor at the Nuclear Energy Department. He received his PhD in Nuclear Science and Technology in 1993 from the University of São Paulo. He is active in the field of radiation effects on polymer materials for more than 20 years, his research interests have broadened to include mechanical and electrical behaviour of nano-filled polymer composites as well as polymer materials for energy technology. During his 2008 sabbatical leave, he worked as a Visiting Professor at UIC, developing studies on diamondoids as molecular building blocks for nanotechnology, with Professor G. Ali Mansoori.

1 Introduction

Underground fossil fuel reservoirs including natural gas, gas condensate, petroleum and coal are the natural resources of hydrocarbons including diamondoid hydrocarbons. The simplest representative of diamondoid hydrocarbons is the symmetrical tricyclodecane C_{10}H_{16}, which was isolated in 1933 from petroleum in the vicinity of Hodonin in Moravia, Czechoslovakia (Landa et al., 1933). This molecule was named adamantane,
a noun derived from the Greek word for diamond – αδαμαξ – ‘the invincible’ (Seiwerth, 1996). In this paper, we report the aspects of the origin of diamondoids (alkyladamantanes) in fossil fuels. In addition, we will present the state of the art in the technology of using diamondoids content of petroleum fluids as a geochemical tool in such reservoir fluids characterisation. We also report on the possible role of diamondoids in petroleum and natural gas production fouling.

In recent years diamondoids have found many other applications (Mansoori et al., 2012a), discussion of which is out of the scope of the present paper but we list such applications briefly here. Diamondoids are considered as one of the best molecular building blocks for nanotechnology (Mansoori et al., 2003; Mansoori, 2005; Ramezani and Mansoori, 2007). This is because diamondoids are almost entirely constituted by sp³ bonded carbons arranged in a three-dimensional network, these stiff, dense, covalent solids present many advantages over other types of nanotechnology molecular building blocks (Mansoori, 2007; Mansoori et al., 2007a, 2009). Diamondoid derivatives have found many applications in biomedicine (Mansoori et al., 2012a) including as drugs to slow down the progression of Alzheimer’s disease (Nazem and Mansoori, 2008, 2011). Nanomaterials and materials science is another branch of applications of diamondoids and derives and that includes diamondoids-DNA nanostructures (Ramezani et al., 2007a, 2007b), the role of diamondoids in crystal engineering (Mansoori, 2007); and their opto-electronic properties and applications in MEMS and NEMS (Xue and Mansoori, 2008; Marsusi et al., 2009, Mansoori et al., 2009). These new developments in applications of diamondoids are partly due to their stiff and symmetric structures and advances in understanding of their physics and chemistry (Zhang et al., 2007; Mansoori, 2007; Xue and Mansoori, 2010a, 2010b; Mansoori et al., 2012b). In this review paper, the occurrence of diamondoids in fossil fuels is presented in details. Then considering that the major source of diamondoids is petroleum fluids, their occurrence, identification and separation from petroleum fluids are presented along with their applications in petroleum exploration.

2 Diamondoids in petroleum reservoirs

Diamondoid molecules are cage-like, ultra stable, saturated hydrocarbons. The basic repetitive unit of diamondoids is a ten-carbon tetracyclic cage system called “adamantane” (Figure 1).

Figure 1 Three-dimensional molecular structures of diamondoid hydrocarbons, (a) adamantane (b) diamantane, (c) triamantane, and (d) anti-isomer of tetramantane, the smallest diamondoids, with chemical formulas C₁₀H₁₆, C₁₄H₂₀ and C₁₈H₃₄, respectively

Source: Ramezani et al. (2007b)
Diamondoids

They are called ‘diamondoid’ because they have at least one adamantane unit and their carbon-carbon framework is completely or largely superimposable on the diamond lattice (Balaban and Schleyer, 1978; Mansoori, 2007). The diamond lattices structure was first determined in 1913 by Bragg and Bragg (1913) using X-ray diffraction analysis.

Diamondoids show unique properties due to their exceptional atomic arrangements (Araujo et al., 2011). Adamantane consists of cyclohexane rings in ‘chair’ conformation. The name adamantane is derived from the Greek language word for diamond since its chemical structure is like the three-dimensional diamond subunit as shown in Figure 2.

Figure 2  The relation between lattice diamond structure and (a) adamantane, (b) diamantine, and (c) triamantane structures

Source: Mansoori (2007)

Most of the literature data on naturally occurring diamondoids are about petroleum diamondoids. Naturally, occurring adamantane present in petroleum is generally accompanied by small amounts of alkylated adamantane: 2-methyl-; 1-ethyl-; and probably 1-methyl-; 1,3-dimethyladamantane; and others (Katz et al., 2008; Nekhaev et al., 2011). Diamantane, triamantane and their alkyl-substituted compounds are also present in certain petroleum crude oils (Wingert, 1992). Wingert (1992) reported the formula, molar mass and structure for diamondoids found in petroleum as shown in Figure 3.

Concentration of adamantane in petroleum is the highest among all the petroleum diamondoids as reported in Table 1. Tetramantane, pentamantane and hexamantane were discovered for the first time in 1995 in a gas condensate (also known as NGL standing for natural gas liquid) produced from a very deep petroleum reservoir (~6,800 m below the earth’s surface) located in the US Gulf Coast, along with significant amounts of alkyl-substituted diamantanes and triamantanes (Lin and Wilk, 1995). A group of investigators reported isolation of crystals of [12312] hexamantane or cyclohexamantane (C26H30) as shown in Figure 4, from distilled Gulf of Mexico petroleum using reverse-phase high-performance liquid chromatography (HPLC).
### Figure 3  
Diamondoid molecules found in petroleum

<table>
<thead>
<tr>
<th>Formula, name, molecular wt</th>
<th>Structure</th>
<th>Formula, name, molecular wt</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{10}H_{16} Adamantane</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>C_{16}H_{24} 4,9-dimethyldiamantane</td>
<td><img src="image2.png" alt="Structure" /></td>
</tr>
<tr>
<td>mw = 136</td>
<td></td>
<td>mw = 216</td>
<td></td>
</tr>
<tr>
<td>C_{14}H_{14} 1,2,5,7-tetramethyladamantane</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>C_{13}H_{22} 1-methyldiamantane</td>
<td><img src="image4.png" alt="Structure" /></td>
</tr>
<tr>
<td>mw = 192</td>
<td></td>
<td>mw = 202</td>
<td></td>
</tr>
<tr>
<td>C_{12}H_{20} 1-ethyladamantane</td>
<td><img src="image5.png" alt="Structure" /></td>
<td>C_{16}H_{24} 1,4-dimethyldiamantane</td>
<td><img src="image6.png" alt="Structure" /></td>
</tr>
<tr>
<td>mw = 164</td>
<td></td>
<td>mw = 216</td>
<td></td>
</tr>
<tr>
<td>C_{13}H_{22} 1-ethyl-3-methyladamantane</td>
<td><img src="image7.png" alt="Structure" /></td>
<td>C_{16}H_{24} 2,4-dimethyldiamantane</td>
<td><img src="image8.png" alt="Structure" /></td>
</tr>
<tr>
<td>mw = 178</td>
<td></td>
<td>mw = 216</td>
<td></td>
</tr>
<tr>
<td>C_{14}H_{24} 1-ethyl-3,5-dimethyladamantane</td>
<td><img src="image9.png" alt="Structure" /></td>
<td>C_{16}H_{24} 4,8-dimethyldiamantane</td>
<td><img src="image10.png" alt="Structure" /></td>
</tr>
<tr>
<td>mw = 192</td>
<td></td>
<td>mw = 216</td>
<td></td>
</tr>
<tr>
<td>C_{12}H_{20} 1-ethyladamantane</td>
<td><img src="image11.png" alt="Structure" /></td>
<td>C_{17}H_{26} 1,3,4-trimethyldiamantane</td>
<td><img src="image12.png" alt="Structure" /></td>
</tr>
<tr>
<td>mw = 164</td>
<td></td>
<td>mw = 230</td>
<td></td>
</tr>
<tr>
<td>C_{14}H_{30} Diamantane</td>
<td><img src="image13.png" alt="Structure" /></td>
<td>C_{16}H_{22} 3-methylidiamantane</td>
<td><img src="image14.png" alt="Structure" /></td>
</tr>
<tr>
<td>mw = 188</td>
<td></td>
<td>mw = 202</td>
<td></td>
</tr>
<tr>
<td>C_{15}H_{22} 4-methylidiamantane</td>
<td><img src="image15.png" alt="Structure" /></td>
<td>C_{16}H_{24} 3,4-dimethylidiamantane</td>
<td><img src="image16.png" alt="Structure" /></td>
</tr>
<tr>
<td>mw = 202</td>
<td></td>
<td>mw = 216</td>
<td></td>
</tr>
</tbody>
</table>

*Source:* Modified from Wingert (1992)

### Figure 4  
Chemical structure of [12312] hexamantane or cyclohexamantane (C_{26}H_{50})

[![Chemical structure](image17.png)](image17.png)

*Source:* Modified from Dahl et al. (2003a)
Dahl et al. (2003a) determined the structure of C_{26}H_{30} using X-ray diffraction, mass spectroscopy, and ^1H, ^13C-NMR spectroscopy. They also used experimental Raman spectra of crystalline diamond, adamantane, and nanophase diamond to indirectly identify frequencies in the experimental Raman spectra of this peri-condensed hexamantane isomer.

Identification and isolation of crystals of many new medium-size and higher-order diamondoids from petroleum have been reported by Dahl et al. (2003b). These investigators reported the isolation of multiple families of higher diamondoid molecules containing four to 11 diamond-crystal cages from petroleum and supplied X-ray structures for three representative families. Separations of higher diamondoids from selected petroleum feedstock were performed by distillation, and the removal of non-diamondoids was achieved by pyrolysis at 400°C to 450°C. Aromatic and polar compounds were removed from pyrolysis products by argentie silica gel liquid chromatography. Higher diamondoids were then isolated by a combination of reversed-phase HPLC on octadecyl silane columns and highly shape-selective Hypercarb® HPLC columns. Individual higher diamondoids were re-crystallised to high purity (Dahl et al., 2003b). For some of the diamondoid molecules reported in Figure 3 their crystalline structures are determined by single-crystal X-ray. For example, [1(2,3)4] pentamantane forms pyramidal crystal that share some resemblance with macroscopic diamond (Figure 5).

Figure 5  Photomicrographs of [1(2,3)4] pentamantane crystallised from HPLC fractions of gas condensates and natural gas liquids from the Norphlet Formation, Gulf Coast USA and the Western Canada Basin

Notes: Crystals show visual similarities with macroscopic diamond but different physical properties (see Table 3). Field of view is approximately 3.5 mm. Photograph, Marilyn Olmstead, U.C. Davis (see also Dahl et al., 2003b, supplement information).

Nevertheless, weak van der Waals intermolecular interactions between the six molecules that constitute the orthorhombic unit cell and packing of crystalline [1(2,3)4] pentamantane, Figure 6(a), allow dissolution of this diamondoid substance in acetone (Dahl et al., 2003b). Also reported in Figure 6(b) is the 3-D structure of [1(2,3)4] pentamantane and its relation to diamond lattice structure.
Sulphur-containing diamondoid compounds, including thiadiamondoids and adamantaneethiols (Figure 7) occur naturally in petroleum, especially in oils and/or gas condensates subjected to thermochemical sulphate reduction (TSR) (Heydari and Moore, 1989; Hanin et al., 2002; Wei et al., 2007a). TSR is one of the most important organic-inorganic interactions in hot carbonate petroleum reservoirs and is characterised by the oxidation of petroleum by sulphate (generally anhydrite), with production of H₂S, CO₂, mercaptans, elemental sulfur and pirubitumen (Seewald, 2003). This phenomenon is well documented in numerous geological observations all around the world (Worden et al., 1996; Machel, 2001; Cai et al., 2003) and decreases commercial value of a crude
oil while increases its cost of production. TSR is responsible for substantial quantities of \( \text{H}_2\text{S} \) (between 10% to 80%) in some high-temperature natural underground petroleum reservoirs.

**Figure 7** Chemical structure of ten sulphur-containing adamantane molecules found in petroleum and/or gas condensates which have undergone TSR process

\[
\begin{align*}
\alpha - \text{SH} \\
\beta - \text{SH} \\
\alpha - \text{CH}_3 \\
\gamma - \text{CH}_3 \\
\alpha - \text{CH}_3 \\
\gamma - \text{CH}_3 \\
\beta - \text{CH}_3 \\
\gamma - \text{CH}_3 \\
\alpha - \text{CH}_3 \\
\beta - \text{CH}_3 \\
\gamma - \text{CH}_3 \\
\delta - \text{CH}_3
\end{align*}
\]

**Source:** Data from Wei et al. (2007a)

The presence of alkylated 2-thiadiamantane has also been suggested by gas chromatography-mass spectrometry (GC/MS) data (Hanin et al., 2002). Sulphur-containing diamondoids, particularly alkylthiaadamantanes may serve as molecular indicator of TSR occurring in deep petroleum reservoirs (Hanin et al., 2002) and can be used to detect the level of risk associated with the presence of \( \text{H}_2\text{S} \) in petroleum exploration and production operations.

In Table 1, we report concentration of adamantanes, diamantanes, 3-methyladamantane + 4-methyladamantane (3-,+4-MD) and total diamondoids determined through GC/MS experiments in several petroleum and two gas condensate samples.

Variations in concentration of (3-,+4-MD) are frequently reported as a model for diamondoids behavior in crude oils. Besides being relatively abundant, these two molecules possess low volatility and chemical behavior similar to other diamondoids. Thus, they satisfactorily represent most common diamondoid classes. (3-,+4-MD) concentrations in petroleum of different origins are reported in Table 1, along with concentrations of one-cage diamondoids (adamantane and derivatives), two-cage diamondoids (diamantane and derivatives), and total diamondoids determined through GC/MS measurements.
Table 1  A compilation of concentrations of diamondoids in various crude oils and condensates in [μg/g]

<table>
<thead>
<tr>
<th>Crude oil reservoir, location</th>
<th>[A]</th>
<th>[D]</th>
<th>[3-,+4-MD]</th>
<th>[TDs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orinoco, Venezuela</td>
<td>31.1</td>
<td>4.9</td>
<td>1.1</td>
<td>NA</td>
</tr>
<tr>
<td>Cold Lake, Canada</td>
<td>117.0</td>
<td>12.0</td>
<td>3.8</td>
<td>NA</td>
</tr>
<tr>
<td>Calgary, Canada</td>
<td>130.0</td>
<td>13.6</td>
<td>3.9</td>
<td>NA</td>
</tr>
<tr>
<td>Platform Elly, US West Coast</td>
<td>42.1</td>
<td>10.4</td>
<td>5.5</td>
<td>NA</td>
</tr>
<tr>
<td>Maya, Mexico</td>
<td>51.6</td>
<td>14.6</td>
<td>1.7</td>
<td>NA</td>
</tr>
<tr>
<td>Gulf of Mexico</td>
<td>121.0</td>
<td>12.3</td>
<td>3.3</td>
<td>NA</td>
</tr>
<tr>
<td>Saudi Arabia</td>
<td>87.8</td>
<td>22.8</td>
<td>6.7</td>
<td>NA</td>
</tr>
<tr>
<td>West Delta Canyon, Gulf of Mexico</td>
<td>126.0</td>
<td>17.2</td>
<td>4.8</td>
<td>NA</td>
</tr>
<tr>
<td>Alaska North Slope, Alaska</td>
<td>263.0</td>
<td>27.5</td>
<td>7.3</td>
<td>NA</td>
</tr>
<tr>
<td>Southern Alaska</td>
<td>209.0</td>
<td>9.1</td>
<td>2.1</td>
<td>NA</td>
</tr>
<tr>
<td>South Louisiana</td>
<td>1880.0</td>
<td>195.0</td>
<td>51.9</td>
<td>NA</td>
</tr>
<tr>
<td>Race Track, California</td>
<td>2285.2</td>
<td>53.6</td>
<td>14.2</td>
<td>2346</td>
</tr>
<tr>
<td>Buena Vista, California</td>
<td>212.6</td>
<td>5.1</td>
<td>1.2</td>
<td>221</td>
</tr>
<tr>
<td>Fruitvale, California</td>
<td>2091.7</td>
<td>38.6</td>
<td>9.6</td>
<td>2137</td>
</tr>
<tr>
<td>McKittrick, California</td>
<td>323.4</td>
<td>6.3</td>
<td>1.7</td>
<td>334</td>
</tr>
<tr>
<td>South Belridge, California</td>
<td>1188.6</td>
<td>18.5</td>
<td>4.6</td>
<td>1253</td>
</tr>
<tr>
<td>Kern River, California</td>
<td>453.2</td>
<td>11.0</td>
<td>2.96</td>
<td>465</td>
</tr>
<tr>
<td>Cymric, California</td>
<td>713.0</td>
<td>14.4</td>
<td>4.3</td>
<td>728</td>
</tr>
<tr>
<td>Prudhoe Bay, Alaska</td>
<td>273.0</td>
<td>38.9</td>
<td>10.1</td>
<td>312</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Gas condensate, location</th>
<th>[μg/g]</th>
<th>[μg/g]</th>
<th>[μg/g]</th>
<th>[μg/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hudson Canyon, US Atlantic</td>
<td>4,038; 4,266</td>
<td>704; 509</td>
<td>181; 148</td>
<td>NA</td>
</tr>
<tr>
<td>Tarin Basin, China</td>
<td>NA</td>
<td>NA</td>
<td>250</td>
<td>NA</td>
</tr>
</tbody>
</table>

Notes: [3-,+4-MD] = concentrations of 3-methyldiamantane + 4-methyldiamantane
[A] = concentrations of all one-cage diamondoids
[D] = concentrations of all two-cage diamondoids
[diamantane and its alkyl derivatives including (3-,+4-MD)]
NA = not available
[TDs] = concentration of total diamondoids
[μg/g] = microgram of diamondoids per gram of crude oil.

Source: From Yang et al. (2006), Wei et al. (2007c) and Wang et al. (2006a)

In Table 1, [A] represents concentration of all one-cage diamondoids (adamantane and its alkyl derivatives), [D] represents concentration of all two-cage diamondoids (diamantane and its alkyl derivatives including (3-,+4-MD)) and [TDs] represents concentration of all diamondoids (total diamondoids). In the case of crude oils data published by Yang et al. (2006), they only searched for one and two-cage diamondoids, thus, there is no [TDs] reported in their crude oils data. In some cases, when [A], [D], [3-,+4-MD] and [TDs] data are available, [TDs] is smaller than [A]+[D]+[3-,+4-MD]. This happens because many authors report [3-,+4-MD] and their variations as a model for diamondoids...
behavior in crude oils. As a result concentration of (3-,+4-MD) and possibly [D] and possibly [A] are counted twice, once as [D] and [A] and once in [3-,+4-MD].

Diamondoids are widespread in the bitumen of coals. In Table 2 we report a compilation of concentrations of (3-,+4-MD) diamondoids in various coals in microgram of diamondoids per gram of coal [μg/g] (Wang et al., 2006a; Sassen and Post, 2008; Zhang et al., 2005; Wei et al., 2006c). By comparing Tables 1 and 2 it becomes clear that generally petroleum fluids contain significantly more [3-,+4-MD] than coals. This is also the case for adamantane and diamantane in coals compared to petroleum fluids (Imuta and Ouchi, 1973; Aczel et al., 1975, 1979).

Table 2  A compilation of concentrations of (3-,+4-MD) diamondoids in various coals in [μg/g] = microgram of diamondoids per gram of coal

<table>
<thead>
<tr>
<th>Coal mine, location</th>
<th>[3-,+4-MD]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Richland, Montana</td>
<td>0.12</td>
</tr>
<tr>
<td>Campbell, Wyoming</td>
<td>0.02; 0.03</td>
</tr>
<tr>
<td>Mercer, North Dakota</td>
<td>0.11</td>
</tr>
<tr>
<td>Freestone, Texas</td>
<td>0.02</td>
</tr>
<tr>
<td>Bighorn, Montana</td>
<td>0.08</td>
</tr>
<tr>
<td>Rosebud mine, Montana</td>
<td>0.04</td>
</tr>
<tr>
<td>Jungar Basin, China</td>
<td>0.41; 0.58; 0.34</td>
</tr>
<tr>
<td>Colfax, Texas</td>
<td>0.54</td>
</tr>
<tr>
<td>Carbon, Utah</td>
<td>0.64</td>
</tr>
<tr>
<td>Kanawha, West Virginia</td>
<td>0.95</td>
</tr>
<tr>
<td>Dickenson, Virginia</td>
<td>1.23</td>
</tr>
<tr>
<td>Buchanan, Virginia</td>
<td>10.0</td>
</tr>
<tr>
<td>Greenbrier, West Virginia</td>
<td>23.0</td>
</tr>
<tr>
<td>Sommerset, Pennsylvania</td>
<td>47.0</td>
</tr>
<tr>
<td>Pennsylvania</td>
<td>70.0</td>
</tr>
<tr>
<td>Arkansas</td>
<td>206.0</td>
</tr>
<tr>
<td>Sullivan, Pennsylvania</td>
<td>341.0</td>
</tr>
<tr>
<td>Colombia, Pennsylvania</td>
<td>27.0</td>
</tr>
<tr>
<td>Luzcerne, Pennsylvania</td>
<td>3.18</td>
</tr>
<tr>
<td>Pappano Mine</td>
<td>2.64</td>
</tr>
</tbody>
</table>

*Source: From Wang et al. (2006a), Sassen and Post (2008), Zhang et al. (2005) and Wei et al. (2006c)*

3 Origin of petroleum and genesis of diamondoids

In order to answer the question ‘How could diamondoids be present in fossil fuels?’, it is important to discuss in some details about the origin of petroleum, the mechanisms involved in its maturation and degradation in the ground and then understand the mechanisms for diamondoids formation and concentration in petroleum. According to one hypothesis (Hunt, 1979), when living organisms die, their organic constituents
undergo physical, chemical, and biological transformations. Most of the resulting products are gaseous and water-soluble substances that are carried off by weathering agents. Subsequent oxidative processes in high-energy, oxygen-rich environments may ultimately transform organic carbon to carbon dioxide. Thus, carbon atoms present in the original organic matter would re-enter the earth’s carbon cycle. However, under appropriate conditions, organic matter is preserved and temporarily withdrawn from this geochemical cycle. This preserved matter would become fossil fuels including finely dispersed buried organic matter, coal and petroleum fluids.

A good example of such process occurs in sedimentary basins because water from these basins is rich in oxygen which makes it aerobic at the surface but sediments are exposed to anaerobic environment even at a few centimetres below surface. The organic matter in these sediments, especially humic material (humus), the major organic constituent of soil which may include resins, waxes and lipids stand a better chance of resisting degradation during long-term burial and thermal processes, becoming available for petroleum formation (Hunt, 1979; Andresen et al., 1994; Carpentier et al., 2007).

During and after sedimentation, organic matter could be submitted to three distinct transformation processes: diagenesis, catagenesis and metagenesis (Tissot and Welte, 1984):

- **Diagenesis** is the earliest stage of transformation of sedimentary organic matter. During this process, biological, physical and chemical alterations occur before extensive thermal degradation, usually in depths where temperature ranges from ambient to 50°C (Tissot and Welte, 1984). Typical biomacromolecules, such as polysaccharides, proteins and lignins along with other biocompounds (e.g., lipids and pigments) may be consumed by burrowing (fossorial) organisms or may enter into complex formation with mineral components. Alternatively, microbial enzymatic attack is possible to convert the biomacromolecules into simpler molecules, such as amino acids, monosaccharides, fatty acids, and phenols. Part of these low molecular weight substances may react to form geopolymers that are precursors of kerogen.

The term ‘kerogen’ is generally referred to the organic matter (oil) in oil shale released upon heating (Hunt, 1979). A more recent definition states that kerogen is a type of particulate organic matter insoluble in organic solvents that consists of various macerals originated from components of plants, animals, and bacteria, preserved in sedimentary rocks.

Macerals are microscopically recognisable constituents of a fossil fuel that can be differentiated by their physical and chemical properties. Macerals can be seen as analogs of minerals of inorganic rocks with less uniform chemical composition and a larger variety of physical characteristics (Hunt, 1979). The three main maceral groups are liptinite, vitrinite and inertinite (Hunt, 1979; Scott, 2002).

Studies on kerogen’s three main maceral groups compositions revealed that kerogen contains practically the same diversity of organic compounds as found in living organisms, including terpenoids, steroids, porphyrins, amino acids, carbohydrates, carboxylic acids, ketones, alcohols and ether bridges (Hunt, 1979). During early burial and diagenesis, many complex organic compounds originating from former living organisms are preserved. These molecular fossils are called biomarkers or biological markers and show only slight or no alterations in structure when compared with their parent biological molecules. Biomarkers occur not only in sediments and
rocks but in crude oils as well, evidencing their resistance to thermal stress and biodegradation (Peters et al., 2005).

- **Catagenesis** is the process within which thermal cracking of kerogen produces petroleum hydrocarbons (Durand, 1980; Pepper and Corvi, 1995; Behar et al., 1997). Catagenesis is characterised by thermocatalytic alterations in buried organic material subjected to temperatures in the range of 50°C to about 150°C. This process lasts millions of years during which main chain scissions, decarboxilation and hydrogen disproportionation are some of the predominant chemical reactions that occur (Hunt, 1979). During catagenesis, biomarkers undergo some structural changes that are indicative of the extent of thermal stress imposed on (or suffered by) source rocks or expelled oil. As a result, biomarker occurrence can be used as an indication of the origin of expelled oil that have migrated miles away from its original formation site by comparing the key structural features and distribution of biomarkers both in migrated oil and source rocks (Peters et al., 2005).

- **Metagenesis** is the transformation stage when an organic material is exposed to temperatures in the range of 150°C to 200°C; it undergoes extensive thermal cracking, leading to final conversion into methane and/or graphite (Landes, 1967). During this final stage, biomarkers undergo dramatic decrease in concentration or complete destruction (Peters et al., 2005).

It is important to point out that the limits for the onset of each of the three processes are not rigid. In addition, many factors other than time and temperature are important in oil formation, maturation and destruction. For example, the presence of water, high fluid pressures and retention of products in closed systems could inhibit thermal cracking of oil, typical of metagenesis process in laboratory experiments. The absence of water, low fluid pressures, and open systems conditions appear to promote oil thermal cracking (Price, 1993). Bacteria may also play important roles in the formation of crude oil and natural gas. In well-oxygenated sedimentary environments, oxidation of organic matter by aerobic bacteria may result in its poor preservation. Conversely, lower oxygen levels may contribute to preservation of oil-prone organic matter. Biodegradation is another aspect of petroleum lifecycle that can interfere in its accumulation processes. Sometimes, such alterations are so extensive that makes geochemical evaluation of thermal maturity and source correlation almost impossible (Clayton, 1992).

The ideas of what chemical processes are involved in the formation of petroleum have evolved since 1970s into a modern vision of the ‘petroleum system’, in which four geological components are necessary for hydrocarbon accumulation:

1. a source rock, where petroleum is or could be generated
2. a reservoir rock which is a body of rock having sufficient porosity and permeability to store and transmit fluids
3. a cap rock or seal, an impermeable rock that acts as a barrier to further migration of hydrocarbon liquids
4. a trap, a configuration of rocks suitable for containing hydrocarbons and sealed by a relatively impermeable formation through which hydrocarbons will not migrate (Magoon, 1992).
Moreover, these four geological components must be properly placed in a dynamic scenario where the source rock plays the major role as its thermal history gives the guidelines for organic matter transformations in the basin (Huc, 2003).

3.1 Diamondoids genesis in petroleum

Diamond is believed to be an abiogenic matter (not produced by the action of living organisms) since in nature it is formed from abiogenic source. However, the carbon framework for diamondoids in oil are believed to be biogenic. Diamondoids in petroleum are believed to be formed by hydrocarbon rearrangement reactions under acidic conditions, compatible with those found in clay minerals in petroleum source rocks (Katz et al., 2008).

In 1964, Fort and von Schleyer (1964) suggested that adamantane could have been formed during petroleum genesis from cyclic hydrocarbon precursors by Lewis acid-catalysed isomerisation and rearrangement, through a mechanism similar to that observed during the synthesis of adamantane from endo-tricyclocdecane (Figure 8).

Laboratory experimental data available at the time also pointed to the same conclusion. For example, when adamantane-free samples from Hodonin oil were subjected to fractioning and treatment with various catalysts, additional amounts of adamantane were formed in the fractions having boiling points in the 170°C to 190°C range after treatment with aluminium chloride.

Likewise, diamantane and triamantane can be synthesised by superacid-catalysed isomerisation of suitable polycycloalkane precursors (McKervey, 1980; Olah, 1990) and might have their geochemical formation related to the same mechanism.

Nevertheless, higher diamondoids are unlike to be formed the same way, primarily because it is difficult to find large (> 22 carbons) polycyclic hydrocarbons with chemical formula C_{4n+6}H_{4n+12} in petroleum. As higher polycyclic hydrocarbons are not reported to occur in living organisms, they cannot be structurally related biological molecules.

It is proposed that tetramantane, pentamantane and hexamantane may be generated via homologation of the lower alkyl-substituted diamondoids at high pressures and temperatures in the natural underground fossil fuel reservoirs (Lin and Wilk, 1995).

Alkylated diamondoids are frequently found in petroleum, as discussed above in Section 2 of this paper. These substituted diamondoids may be formed by reactions between abundant methane and polymantyl cations catalytically generated from polymantanes in acidic sites. Of course, direct reaction between methane and diamondoid molecules is difficult. It is believed the presence of clays in the underground oil reservoirs may have provided the acid sites necessary to catalytically convert...
polymantanes into polymantyl cations. The resulting alkyl-substituted diamondoid molecules can then be converted into higher members of the diamondoid family (Lin and Wilk, 1995). A scheme of the homologation of triamantane into anti-tetramantane is shown in Figure 9.

**Figure 9** Homologation of triamantane into anti-tetramantane, (a) ethyl-dimethylation of triamantane that may occur in clay sites of rock sources (b) homologation of ethyl-dimethyltriamantane into anti-tetramantane ([121]tetramantane) under high pressure and temperature

![Diagram](image)

Triamantane → Ethyl-dimethyltriamantane → Anti-tetramantane

Note: New alkyl groups are shown in bold lines, dashed lines represent forming bonds

Source: Replotted from Lin and Wilk (1995)

More recently efforts have been made to investigate the formation of diamondoids during thermal maturation of preserved organic matter and clarify the influence of minerals on the generation of diamondoid molecules.

Experiments involving artificial hydrothermal maturation of different types of immature sediments (sediments that have seen little migration and erosion) from organic-rich modern mud samples and carbonate sediment (Wei et al., 2006a) and immature sedimentary rocks and peats (Wei et al., 2007b) indicated that diamondoids could not be found in extracts of organic-rich modern sediment or immature peats prior to artificial maturation. Conversely, they were present in immature sedimentary rocks which had gone through a certain level of natural thermal maturation. These findings suggest that diamondoid generation is not related to biosynthetic pathways and has its onset during diagenesis. Diagenesis is any change in sediment, after its initial deposition and during and after its hardening.

The presence of artificially-added minerals such as montmorillonite K10 clay or acidic aluminosilicate during artificial maturation of modern mud samples and carbonate sediment revealed that they exhibit strong catalytic effect on diamondoid genesis, while CaCO₃ (an alkaline salt) has an inhibiting action. These minerals showed similar effects when kerogen samples of various types were subjected to artificial thermal maturation (Wei et al., 2006b). When CaCO₃ is mixed with montmorillonite K10 clay, it tends to neutralise the catalytic activity of montmorillonite K10 clay even if only a small amount of CaCO₃ is present in the mixture. Catalytic effect of such Lewis acids suggests that the natural formation of diamondoids follows a carbonium rearrangement. Carbocation rearrangement is seen for chemical synthesis of diamondoid molecules (Mansoori et al., 2012b). Experimental results are detailed below in the later paragraphs.

Table 3 shows a comparison of (3-,+4-MD) yields after hydrous pyrolysis treatment of sediments and kerogen types I, II, II-S and III (Mansoori et al., 2012a). The combined (3-,+4-MD) group diamondoid molecules are chosen to represent all diamondoid classes because they are less volatile and relatively abundant.
Table 3  Yields of 3-methyldiamantane + 4-methyldiamantane (3-,+4-MD) before and after artificial maturation pyrolysis experiments, in sediments and kerogen from various locations

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Location (environment or lithology)</th>
<th>TOC [wt%]</th>
<th>[3-,+4-MD] yield [ng/g]</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mud</td>
<td>Calif., San Francisco Bay (salt marsh)</td>
<td>8.0</td>
<td>0.09 1.84 0.55 24.07 26.63</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mud</td>
<td>Elkhorn Slough (marsh)</td>
<td>5.0</td>
<td>0.02 5.80 0.48 36.17 36.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mud</td>
<td>Calif., Santa Barbara Basin (continental margin)</td>
<td>7.0</td>
<td>0.07 1.12 0.86 10.00 3.89</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonate</td>
<td>Mexico, Celestun Lagoon (mangrove)</td>
<td>6.0</td>
<td>NA 0.14 0.11 0.44 1.47</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rock</td>
<td>Brazil, Irati formation (limestone)</td>
<td>2.4</td>
<td>0.34 0.93 NT NT NT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rock</td>
<td>Brazil, Irati formation (shale)</td>
<td>7.0</td>
<td>0.79 1.12 NT NT NT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rock</td>
<td>Nevada, Vinini Creek (limestone)</td>
<td>1.7</td>
<td>1.58 3.70 NT NT NT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peat</td>
<td>Germany, Outcrop (fen peat)</td>
<td>37.9</td>
<td>NA 1.13 NT NT NT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peat</td>
<td>Germany, Outcrop (bog peat)</td>
<td>34.4</td>
<td>NA 1.53 NT NT NT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type I</td>
<td>Brazil, Irati formation (limestone)</td>
<td>2.4</td>
<td>NT 1.09 1.04 22.14 10.81</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type I</td>
<td>Brazil, Irati formation (shale)</td>
<td>7.0</td>
<td>NT 0.99 0.41 26.70 18.36</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type II</td>
<td>Calif., San Joaquin Basin (shale)</td>
<td>2.0</td>
<td>NT 2.68 1.81 33.92 23.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type II-S</td>
<td>Calif., Naples Beach (siliceous shale)</td>
<td>3.8</td>
<td>NT 0.46 0.23 32.72 13.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type II-S</td>
<td>Calif., Naples Beach (shale)</td>
<td>16.5</td>
<td>NT 0.23 0.14 25.04 13.53</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type III</td>
<td>New Mex., Raton Basin (coal)</td>
<td>15.0</td>
<td>NT 9.68 3.28 46.15 37.49</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: (a) Extract by a solvent made of 1:1 (methanol:dichloromethane).
(b) After sample hydrous pyrolysis.
(c) After (sample + CaCO₃) mixture hydrous pyrolysis.
(d) After (sample + montmorillonite K10) mixture hydrous pyrolysis.
(e) After (sample + acidic aluminosilicate (MS-25)) mixture hydrous pyrolysis.
The mass ratios for the three (sample + mineral) mixtures are 6:1 for sediments and 1:20 for kerogen. For sediments: [ng/g] is defined as ‘nanogram of diamondoid per gram of dry sediment’. For kerogens: [ng/g] is defined as ‘nanogram of diamondoid per gram of dry extracted pyrolysate’. NA = not available. NT = not tested. TOC = total organic carbon.

Source: From Wei et al. (2006a, 2006b)

Moreover, it is possible to observe similar features between (3-,+4-MD) and other diamondoid yields concerning catalytic effects of minerals, as shown in Figures 10(a) to 10(f). Results presented on Figures 10(c) to 10(e) are related to experiments in which montmorillonite K10 clay (43.77% SiO₂, 18.57% Al₂O₃, 36.09% H₂O and minor oxide components), acidic aluminosilicate MS-25 (76.40% SiO₂, 23.20% Al₂O₃ and minor oxide components) or CaCO₃ (99.99% purity) were used, respectively. This figure is very enlightening, since it is an experimental evidence to support the hypothesis of natural diamondoid formation in the very source rock bed through Lewis acid catalysis. Moreover, the negative interference of alkaline minerals is also demonstrated.
Figure 10  Demonstration of variations of yields (in ng per g of sediment) of various diamondoids in different modern sediments as a result of 72 hours hydrous pyrolysis of sediments at 340°C in the presence and absence of various minerals

Notes: When a mineral is used the w/w ratio of sediment to mineral is 6/1.

The various minerals used include CaCO₃, montmorillonite K10 clay, and acidic aluminosilicate (known as MS-25). EOM = extractable organic matter without any hydrous pyrolysis; HP = hydrous pyrolysis of sediments without minerals; CaCO₃ = hydrous pyrolysis of sediments + CaCO₃ mixture; K10 = hydrous pyrolysis of sediments + K10 mixture; MS-25 = hydrous pyrolysis of sediments + MS-25 mixture.

Source: Wei et al. (2006a)

According to Table 3 under ‘extract’, column (a), various amounts of (3,+4-MD) were detected in all non-pyrolysed extractable organic matter of mud and rock sediments. Carbonate, peat and kerogen samples showed no detectable extract quantities of (3,+4-MD) as also reported in Table 3. The traces of (3,+4-MD) found in mud samples were attributed to contaminations from oil spills or oil seeps.

Notes: When a mineral is used the w/w ratio of sediment to mineral is 6/1.
In addition, the presence of biomarkers, normally absent in modern sediments, served as a confirmation of the sample contamination. Mexico’s Celestun Lagoon carbonate sample, nevertheless, lacked biomarkers typical of oil contaminants. German peat samples presented bulky geochemical and biomarker profiles consistent with immature modern organic-rich sediment. These results suggest that diamondoid formation is associated with processes of maturation, which these modern sediments had not gone through yet. Overall, according to Figure 10 and Table 3, higher concentrations of diamondoids are expected to be found in samples that present lower concentrations of alkaline minerals. This conclusion is also supported by the data collected from natural mature sediment samples. For example, according to column (a) of Table 3, extracts from Brazil’s Irati shale rocks contained twice as much (3,4-MD) as Irati limestone extracts from the same location.

Factors other than the presence of alkaline minerals, such as differences in mineralogy and thermal maturity, may interfere in the generation of diamondoids. As an example, according to column (a) of Table 3, extracts from Nevada’s Vinini Creek limestone contained higher amounts of (3,4-MD) than extracts of both Brazil’s Irati limestone and Brazil’s Irati shale rocks.

Calcite plus dolomite carbonate minerals represented almost 55%, 10% and 80% of total mineral content of the Irati limestone, Irati shale and Vinini Creek limestone samples, respectively. Clay minerals fractions of these three samples, in their turn, were approximately 6%, 31%, and 8%, respectively. Nevertheless, optical and chemical maturity assessments showed that Vinini Creek limestone is a marginally mature source rock, whereas Irati shale and limestone samples are thermally immature. Thus, the presence of twice as much diamondoids in the Vinini creek samples as in Irati shale samples might be attributed to its higher levels of thermal stress in spite of its higher concentration of alkaline carbonates and low acidic clay minerals content.

Other factors, such as differences in organic source input (type and origin of buried organic matter), cannot be neglect when samples from distinct origins are compared, because possible organic diamondoid precursors may be more abundant in some rock samples than in others. In this particular study, isoprenoids and cycloalkanes were present in higher amounts in Vinini Creek limestone than in Irati limestone. This may have contributed to observed differences as well, since these compounds might somehow act as diamondoid precursors.

Higher acidity of a source rock appears to be a more important factor in samples with similar levels of maturity, as can be seen from a direct comparison of (3,4-MD) concentration in samples of Irati limestone (0.34 ng/g) and shale (0.79 ng/g) according to Table 3, column (a). Thus, lower acidity caused by larger amounts of carbonate minerals and lower concentration of clay minerals might be responsible for such discrepancy in diamondoid content on extractable organic matter (EOM) of these samples. The presence of diamondoids in all three immature or marginally mature source rocks,

- Brazil, Irati formation (limestone)
- Brazil, Irati formation (shale)
- Nevada, Vinini Creek (limestone),
as reported in Table 3 is an indication that thermal maturity equivalent to diagenic process offers minimum physicochemical conditions to diamondoid formation. Thus, diamondoids appear in preserved organic matter prior to oil generation. Non-pyrolysed kerogen samples cannot be evaluated since there are not EOM in these materials.

Table 3 column (b) shows results obtained by artificial maturation of the organic matter present in sediments and kerogen through hydrous pyrolysis of the samples at 340°C for 72 h. These conditions simulate the thermal stress associated with peak oil generation and provide a favourable environment for the creation of diamondoid cages, compatible to what is found during geological maturation. Added acidic minerals are expected to act as catalysts for the related chemical reactions. Results for hydrous pyrolysis experiments in the presence of added minerals are shown in column (c) through (e) of Table 3.

All organic sediments and kerogen released (3,4-MD) after hydrothermal treatment according to column (b) of Table 3. High quantities of biomarkers released during artificial maturation process were also detected (Wei et al., 2006a). Pyrolysates of sediment samples exhibited increased amounts of (3,4-MD) when compared to amounts found in EOM. Artificial maturation of Elkhorn Slough mud yielded larger amounts of (3,4-MD) than the other sediment samples. Celestun carbonate, in its turn, produced very small quantities of these diamondoids (0.14 ng/g), probably due to its poor natural acidity. Yields for San Francisco Bay and Santa Barbara Basin mud samples and German peats exhibited minor differences. Among source rocks increases from 1.4 up to 2.7 times in (3,4-MD) concentration in pyrolysates were observed.

Additional hydrous pyrolysis experiments for source rocks and peats were performed at temperatures from 230°C to 450°C in order to verify alterations in diamondoid release with increase in thermal maturity. For comparison, a biomarker (C_{29} \alpha\alpha\alpha\alpha stigmastane 20R) was also dosed at the same temperature range. Total pyrolysate yields were maximised at 340°C for peats, at 350°C for Irati shale and at 360°C for both limestone samples (Wei et al., 2007b). Figure 11 shows concentration (in ng/g) of (3,4-MD) (left Y-axis) and biomarker (right Y-axis) in various pyrolysates of Irati limestone, shale, Vinini Creek limestone [Figure 11(a)], and peats [Figure 11(b)].

Concentration of (3,4-MD) show little alteration in pyrolysates below 340°C (solid lines). Conversely, intense biomarker release was detected in all samples (dashed lines). In a first analysis, this may appear contradictory, because diamondoid generation is expected to increase with thermal stress. In fact, absolute diamondoid formation increased with temperature, but other petroleum hydrocarbons were simultaneously formed from kerogen cracking. Hence, the net effect results in minor variations in concentration of (3,4-MD). The relative abundance of (3,4-MD) markedly increases above 360°C for rocks and above 340°C for peats. This range corresponds to the beginning of oil cracking, with degradation of less stable hydrocarbons. Diamondoids, nevertheless, resist thermal stress and become more concentrated in pyrolysates obtained at higher temperatures, although intensity of diamondoid formation decreases due to loss in catalytic activity of clay minerals under such conditions. This evidence suggests that diamondoids formation and release happens not only during diagenesis but proceeds throughout catagenesis along with the liberation of other oil hydrocarbons and biomarkers.
Figure 11  (a) Concentration of (3,+4-MD) (left vertical-axis) in pyrolysates of Irati limestone (■), Irati shale (●), and Vinini Creek (▲) versus temperature* (b) concentration of (3,+4-MD) (left vertical-axis) in pyrolysates of Bog peats (+) and Fen peats (♦) versus temperature**

Notes: *Concentration of C_{29} \alpha\alpha\alpha stigmastane 20R biomarkers (right vertical-axis) in pyrolysis, Irati limestone (○), Irati shale (○), and Vinini Creek (△) versus temperature.
**Concentration of C_{29} \alpha\alpha\alpha stigmastane 20R biomarkers (right vertical-axis) in pyrolysis Bog peats (+) and Fen peats (○) versus temperature.

Source: Wei et al. (2007b)
Hydrous pyrolysis of kerogen samples produced different amounts of (3,4-MD) depending on the type of kerogen. Naturally mature gas-prone type III kerogen, extracted from Raton Basin coal, presented the highest yield (9.68%) while type II-S kerogens produced small amounts of diamondoids (0.46 and 0.23% for Naples Beach siliceous shales and shales, respectively). Results for type III kerogen may be explained by the thermal stability of diamondoids that allows them to be preserved in higher temperatures while hydrocarbons are being cracked. Since this kerogen sample had already undergone geothermal maturation, it was diamondoid-enriched prior to hydrous pyrolysis process. Additional heating treatment promoted bond cleavage and diamondoid releasing.

Type II-S kerogen is rich in sulphur, thermal decomposition of this material releases sulphur species, which may act as an inhibitor for diamondoid formation.

Figure 12 shows a model for adamantanes and diamantanes releasing from kerogen, after pyrolysis (Wei et al., 2006b).

Figure 12  Possible schemes for the releasing of diamondoids from kerogen pyrolysis without catalysts

Note: Adamantanes or diamantanes bound to the kerogen skeleton with polysulfide ether or ester groups.

Source: Adapted from Wei et al. (2006b)

In this model, it is assumed diamondoid moieties are linked to kerogen macromolecules through polysulfide, ether or ester groups, in a similar fashion as what is observed for biomarkers (Richnow et al., 1992; Schaeffer et al., 1995; Hold et al., 1998; Khaddor et al., 2002). Thus, during kerogen thermalolysis, C-O and C-S bonds are cleaved and diamondoids are released along with other hydrocarbons, biomarkers, and organic sulphur compounds. Such model may be helpful in explaining differences in yields obtained from type I and type II kerogens: type II kerogens are known to bear many C-heteroatom bonds (Tissot and Welte, 1984). These weaker bonds would easily undergo scissions for diamondoid liberation. Conversely, type I kerogen present fewer ester, ether or polysulfide bonds, and thus fewer sites for diamondoid release.

The yields of (3,4-MD) increased in pyrolysates about three to 14 times and about four to almost 110 times in kerogen samples when acidic minerals were added to sediments. CaCO₃ had an inhibitory effect on diamondoid yields this was particularly high on Elkhorn Slough mud sample, in which yields reduced from 5.80 ng/g to 0.48 ng/g after CaCO₃ addition. However, in Celestun Lagoon carbonate and type I kerogen from Brazilian limestone, very little inhibiting effect could be noticed.

An explanation of such results may be related to catalytic effects of minerals on total hydrocarbon yields and diamondoids in particular during kerogen pyrolysis experiments. Montmorillonite clays are capable of adsorbing hydrocarbons and catalyse a number of reactions under pyrolysis condition (Tannenbaum and Kaplan, 1985; Tannenbaum et al.,...
1986; Huizinga et al., 1987a, 1987b; Saxby et al., 1992). For example, the presence of bentonite (a mineral which has montmorillonite as its main component) in pyrolysis experiments changed distribution of hydrocarbon classes in coal pyrolysates due to increasing aromatic content in comparison with aliphatic hydrocarbons and decreasing the overall oil yield (Saxby et al., 1992). Tannenbaum and Kaplan (1985) reported a significant catalytic effect on production of C1 to C6 hydrocarbons for kerogen after montmorillonite addition, with yields up to five times higher than those observed for kerogen alone. The dominance of branched hydrocarbons in the C4 to C6 range of hydrocarbons was also detected. Small or no similar effects were observed with illite (an aluminosilicate) and calcite (Tannenbaum and Kaplan, 1985). Catalytic effect of montmorillonite is generally attributed to cracking via a carbonium-ion (carbocation) intermediate which forms on the acidic sites of the clay (Tannenbaum and Kaplan, 1985). Montmorillonite promotes degradation of kerogen and decreases the activation energies of the generation of gas and light oil; thus, it increases yield of low molecular weight products (Li et al., 1998).

A similar carbocation mechanism is proposed for diamondoids formation during pyrolysis according to the following steps:

1. Montmorillonite adsorbs possible organic precursors released from kerogen.
2. As Lewis acid sites (mainly associated with octahedral \( \text{Al}^{3+} \) ions) become available with increase in temperature (Johns, 1979), protons are transferred from montmorillonite to various unsaturated organic compounds to produce carbocations.
3. Carbocations undergo rearrangements, deprotonations, isomerisations and subsequent reactions at Lewis acid sites to yield diamondoids (Wei et al., 2006a).

Limestone and other carbonate rocks are frequently reported as petroleum source rocks (Brosse et al., 1990; Pepper and Corvi, 1995; Abdullah and Connan, 2002; Lu et al., 2007; Konyukhov, 2008). Oils associated with carbonates frequently present higher amounts of heavy hydrocarbons than oils derived from deposits containing active surface minerals. This fact indicates the role of clay minerals as effective hydrocarbon cracking acid catalysts in the ground (Brooks, 1948). Moreover, there are indications of a possible role of \( \text{CaCO}_3 \) as a catalyst in petroleum formation, especially in the presence of ammonia, during artificial maturation of organic matter (Evans and Felbeck, 1983). Nevertheless, montmorillonite clay demonstrates little or no catalytic activity at the temperature of maximum hydrocarbon yields (Evans and Felbeck, 1983), particularly with regards to heavy hydrocarbons formation (Li et al., 1998).

The results discussed so far clearly indicate that both clays and carbonate minerals have strong interference in either natural or artificial thermal maturation of organic matter. Their presence can alter the course of oil generation and destruction. Results presented in Table 3 also confirm clays and carbonate minerals interference in diamondoids formation. In the case of hydrous pyrolysis of dried natural Celestun Lagoon carbonate and type I kerogen from Brazilian limestone, experiments indicated little difference with the addition of \( \text{CaCO}_3 \) since this mineral was naturally present in the samples. For the Brazilian limestone sample, despite carbonate removal prior to artificial maturation, \( \text{CaCO}_3 \) presence during burial may have altered organic diamondoid precursor’s distribution, hampering subsequent transformation that could have ultimately created diamondoids. Thus, in the presence of added \( \text{CaCO}_3 \) (and absence of acidic catalysts) yields remained practically unchanged.
As discussed previously, evidence of diamondoid generation in the presence of Lewis acid sites in clay minerals has been presented over the years, but this is still a controversial subject. Hence, the role of minerals in the formation of diamondoids from modern organic-rich sediments, kerogen or petroleum remains unsettled.

The experiments reported so far depict the complexity of diamondoid generation in petroleum. Pyrolysis data are useful for understanding of oil formation in general and diamondoid formation in particular. However, the large number of variables involved in the process makes it difficult to model geological generation of diamondoid based on controlled laboratory experiments. For example, Wei et al. (2006a, 2006b) suggested that almost every organic compound could create diamondoids in the presence of suitable catalysts, but nature and distribution of the products is dependent on the original organic matter composition.

Lithology of the source rock can alter diamondoid formation process in unexpected ways, such as in condensates from Hudson Canyon, US Atlantic (Sassen and Post 2008) reported in Table 1, where extremely high concentration of diamondoids could be found in oils from sandstones. The authors suggested that the similarities between condensates from Hudson Canyon and Smakover Formation of the US Golf Cost (Wingert, 1992) indicate that laminated lime mudstones is a favorable environment to diamondoid formation because carbonate rocks may form complex natural systems containing siliciclastic minerals, including clay catalysts. Other factors, such as level of maturity of the source rock and the presence of water or inorganic gases presence in the generation and/or accumulation sites are believed to interfere with creation and releasing of diamondoids, making the understanding of diamondoid formation even more difficult. In fact, much work remains to be done in order to understand diamondoid genesis in fossil fuels.

4 Diamondoids as geochemical tools for petroleum characterisation

Diamondoid research has many implications in petroleum geochemistry. Used solely or in conjunction with biomarkers investigation (Chen et al., 1996; Dahl et al., 1999; Grice et al., 2000; Schulz et al., 2001; Peters et al., 2005; Azevedo et al., 2008; Springer et al., 2010), diamondoid molecules can be an important tool for advanced geochemical analysis, after initial screening for selection of sediments, rock and crude oil samples made through well-known geochemical methods, such as Rock-Eval pyrolysis, vitrinite reflectance, scanning fluorescence, gas chromatography, mass spectrometry and stable isotope analysis (Carr, 2000; Garcia-Valles et al., 2000; Peters et al., 2005).

The isolation and identification of biomarkers is very helpful in petroleum exploration technology. The most important investigated biomarkers are hydrocarbons possessing intact steroid, terpenoid or isoprenoid carbon skeleton (Seifert and Moldovan, 1986). Many biomarkers are used in petroleum exploration for correlation, biodegradation and maturity assessments (Mackenzie et al., 1980; Seifert and Moldovan, 1986; vanGraaas, 1990; Ekweozor and Telnae, 1990; Requejo, 1994; Farrimond et al., 1998; Obermajer et al., 2000; Bennett and Olsen, 2007; Azevedo et al., 2008; George et al., 2008). Similarly, diamondoid molecules are proposed to play an important role in petroleum evaluation, and may be used to assess origin, extend of biodegradation and thermal maturity, as well as to identify the occurrence of petroleum. It is important to
point out that, in spite of their biogenic origin, diamondoids are not biomarkers, because they do not share structural similarities with their putative biomolecular precursors.

Petroleum hydrocarbons are degradable by certain microorganisms (Atlas, 1975; Ahsan et al., 1997; Trolio et al., 1999). In this process, hydrocarbons are transformed into CO2 and partially oxidised organic compounds, such as carboxylic acids. Petroleum volume and its commercial value decrease with increasing of biodegradation. Thus, information on the extent of biological alterations is important in petroleum prospects. Since diamondoids present high thermal stability and are resistant to biodegradation, they may be used to characterise heavily biodegraded (William et al., 1986; Grice et al., 2000; Schulz et al., 2001; Wei et al., 2007c) or highly mature oils (Chen et al., 1996; Jinggui et al., 2000; Sassen and Post, 2008), which frequently lack or have few biomarkers.

The use of diamondoid identification and quantification in petroleum geochemistry is mainly based on GC/MS data as presented in Section 5 of this paper. Analyses are more conveniently performed on isolated fractions of saturated hydrocarbons (known as saturates) rather than on the whole oil, because of aromatic compounds interference (Wingert, 1992; Vazquez et al., 1998; Vakili-Nezhaad et al., 2005). Saturates samples are spiked with known amounts of deuterated diamondoids or other suitable substances as internal standards for quantification of diamondoids by peak areas comparisons. Reconstructed ion chromatograms of the base-peak of adamantane (with mass to charge ratio, m/z, equal to 136 and alkyl-substituted CnH(2n–5) series); diamantane (base-peak m/z = 188 and CnH(2n–9) series) and triamantane (base-peak m/z = 240 and CnH(2n–13) series) are obtained by selective ion-recording (SIR), or selective ion monitoring (SIM) modes, as reported in several related literature. Peak assignments are based on elution order and confirmed by full mass spectral data acquisition (Wang et al., 2006a; Yang et al., 2006; Azevedo et al., 2008; Schulz et al., 2001; Chen et al., 1996; Zhang et al., 2005, Jinggui et al., 2000). Figure 13 shows a reconstructed ion chromatogram for the base-peak m/z = 187 obtained from GC/MS/SIR analysis of a coal extract sample. This peak belongs to the alkylated CnH(2n–9) series of diamantane. Two deuterated diamondoids were used as internal standards in this particular coal extract sample (Wei et al., 2006c).

**Figure 13** Reconstructed ion chromatogram for the base-peak m/z = 187 (C14H19) of diamondoids showing distribution of methyl-diamantanes and ethyl-diamantanes in coal extracts

Notes: I.S.-1 = D3-1-methyl-diamantane; I.S.-2 = D5-2-ethyl-diamantane. I.S.-1 and I.S.-2 are synthetic internal standards.

Source: Wei et al. (2006c)
4.1 Diamondoid-based geological correlations for petroleum characterisation

In petroleum geology, it is customary to look for correlations which could be based on geochemical comparisons among crude oils, refined products and/or extracts from prospective source rocks. From these comparisons, it may be possible to determine whether a relationship of origin exists (Peters and Moldowan, 1993, 2005; Waples and Curiale, 1999). Frequently referred correlations are:

a. *oil-source rock correlation* which is based on similarities between compositions of migrated oils and the remained bitumen in the source rocks

b. *oil-oil correlation* which is a comparison of chemical composition to describe relations between oils origins without necessarily identifying rock sources (Peters et al., 2005).

Availability of correlations is a valuable tool in locating new petroleum sites and extending existing productions.

Among all the correlations there are a number of diamondoid-based correlation ratios (such as facies parameter, biodegradation and oil-source correlation and differentiation assessment) which were suggested by various investigators as maturity parameter. These diamondoid-based correlation ratios are reported in Tables 4 and 5.

**Table 4** Some diamondoid-based diagnostic correlation ratios used for petroleum evaluation

<table>
<thead>
<tr>
<th>Diamondoid-based ratios</th>
<th>Mathematical expression and main features</th>
<th>Applications</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyladamantane index (MAI)</td>
<td>MAI = [\frac{[1-MA]}{[1-MA]+[2-MA]}]</td>
<td>Maturity parameter</td>
<td>Chen et al. (1996), Grice et al. (2000), Sassen and Post (2008), Wei et al. (2007b), and Zhang et al. (2005)</td>
</tr>
<tr>
<td>Methyladamantane index (MDI)</td>
<td>MDI = [\frac{[4-MD]}{[1+3+4-MD]}]</td>
<td>This may be affected by source rock lithology</td>
<td>Chen et al. (1996), Grice et al. (2000), Jinggui et al. (2000), Sassen and Post (2008), Schulz et al. (2001), Wei et al. (2007b), and Zhang et al. (2005)</td>
</tr>
<tr>
<td>Ethyladamantane index (EAI-1)</td>
<td>EAI-1 = [\frac{[1-EA]}{[1+2-EA]}]</td>
<td>Maturity parameter</td>
<td>Zhang et al. (2005) and Wei et al. (2007b)</td>
</tr>
<tr>
<td>Ethyladamantane index (EAI-2)</td>
<td>EAI-2 = [\frac{[2-EA]}{[1+2-EA]}]</td>
<td>Facies parameter</td>
<td>Schulz et al. (2001)</td>
</tr>
</tbody>
</table>

Note: All maturity parameters are suggested for thermal maturity assessment.
### Table 4  Some diamondoid-based diagnostic correlation ratios used for petroleum evaluation
(continued)

<table>
<thead>
<tr>
<th>Diamondoid-based ratios</th>
<th>Mathematical expression and main features</th>
<th>Applications</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyladamantane index (DMAI-1)</td>
<td>$\text{DMAI-1} = \frac{[1,3\text{-DMA}]}{[1,2 + 1,3\text{-DMA}]}$</td>
<td>Maturity parameter</td>
<td>Zhang et al. (2005) and Wei et al. (2007b)</td>
</tr>
<tr>
<td>Dimethyladamantane index (DMAI-2)</td>
<td>$\text{DMAI-2} = \frac{[1,3\text{-DMA}]}{[1,3 + 1,4\text{-DMA}]}$</td>
<td></td>
<td>Zhang et al. (2005)</td>
</tr>
<tr>
<td>Trimethyladamantane indices (TMAI)</td>
<td>$\text{TMAI-1} = \frac{[1,3,5\text{-TMA}]}{[1,3,5\text{-TMA} + 1,3,6\text{-TMA}]}$</td>
<td></td>
<td>Zhang et al. (2005)</td>
</tr>
<tr>
<td></td>
<td>$\text{TMAI-1} = \frac{[1,3,5\text{-TMA}]}{[1,3,5\text{-TMA} + 1,3,4\text{-TMA}]}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethyldiamantane indices (DMDI)</td>
<td>$\text{DMDI-1} = \frac{[4,9\text{-DMD}]}{[4,9\text{-DMD} + 3,4\text{-DMD}]}$</td>
<td></td>
<td>Zhang et al. (2005) and Wei et al. (2007b)</td>
</tr>
<tr>
<td></td>
<td>$\text{DMDI-2} = \frac{[4,9\text{-DMD}]}{[4,9\text{-DMD} + 4,8\text{-DMD}]}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyltriamantane index (MTI)</td>
<td>$\text{MTI} = \frac{[9\text{-MT}]}{[5 + 8 + 9 + 16\text{-MT}]}$</td>
<td>Maturity parameter</td>
<td>Wei et al. (2007b)</td>
</tr>
</tbody>
</table>

Note: All maturity parameters are suggested for thermal maturity assessment.

### Table 5  Some diamondoid-based diagnostic correlation ratios used for petroleum evaluation

<table>
<thead>
<tr>
<th>Diamondoid-based ratios</th>
<th>Mathematical expression and main features</th>
<th>Applications</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyladamantane/ adamantane</td>
<td>$\frac{[1 + 2\text{-MA}]}{[\text{Ada}]}$</td>
<td>Biodegradation assessment</td>
<td>Grice et al. (2000)</td>
</tr>
<tr>
<td>Methyladamantane/ diamantane</td>
<td>$\frac{[1 + 3\text{-MD}]}{[\text{Dia}]}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyladamantane/ ethyladamantane</td>
<td>$\frac{[1\text{-MA}]}{[\text{2-EA}]}$</td>
<td>Oil-source correlation and differentiation</td>
<td>Yang et al. (2006)</td>
</tr>
<tr>
<td>Methyladamantane/ dimethyladamantane</td>
<td>$\frac{[1\text{-MA}]}{[\text{1,2-DMA}]}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyladamantane/ trimethyladamantane</td>
<td>$\frac{[1\text{-MA}]}{[\text{1,3,4-TMA}]}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyladamantane/ tetramethyladamantane</td>
<td>$\frac{[1\text{-MA}]}{[\text{1,2,5,7-TeMA}]}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5  Some diamondoid-based diagnostic correlation ratios used for petroleum evaluation
(continued)

<table>
<thead>
<tr>
<th>Diamondoid-based ratios</th>
<th>Mathematical expression and main features</th>
<th>Applications</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyladamantane/trimethyladamantane</td>
<td>[1,4-DMA]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[1,3,4-TMA]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trimethyladamantane/trimethyladamantane</td>
<td>[1,3,5-TA]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[1,2,5,7-TeMA]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trimethyladamantane/tetramethyladamantane</td>
<td>[1,3,5-TMA]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[1,3,6-TMA]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetramethyladamantane/tetramethyladamantane</td>
<td>[1,3,5,7-TeMA]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[1,2,5,7-TeMA]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As an example of the use of these correlations Figure 14 is reported by Schulz et al. (2001).

Figure 14  DMDI-1, DMDI-2 and EAI parameters (%) versus the temperature at which the maximum release of hydrocarbons from cracking of organic matter occurs during pyrolysis (Tmax), for five different rock sources

Source:  Schulz et al. (2001)

In Figure 14, there are no clear correlations between Tmax (the temperature at which the maximum release of hydrocarbons from cracking of organic matter occurs during pyrolysis) and the three parameters (DMDI-1, DMDI-2 and EAI) reported in Table 4. Observed lack of significant correlation indicates that these parameters are practically unaffected by thermal maturity of source rock which is a good thing. This is because Tmax is an indication of the stage of maturation of the preserved organic matter, in rock sources and sediments. A lack of correlation suggests little or no influence of source rock thermal maturity on the measured values of these parameters. Thus, DMDI-1 DMDI-2 and EAI
are able to show oil-source rock correlation in a broad range of source rock thermal maturity levels.

As another example of the use of correlations Figure 15 is reported by Schulz et al. (2001). In this figure, DMDI-1, DMDI-2; and EAI were used to distinguish oils from marine and terrigenous organic facies. Facies are a set of rocks with distinct features, regarding any chemical, mineralogical, morphological or structural features, that make it possible to determine where and when the rock was formed.

Figure 15 exhibits a correlation of percentage of DMDI-1 versus percentage of EAI values for Norwegian Continental shelf oil samples.

**Figure 15**  The EAI and DMDI-1 for the Norwegian Continental shelf oil samples

Note: Suggested boundary lines for type II (Spekk formation) and type III (are formation) organic facies were taken from Figure 14.

*Source:* Schulz et al. (2001)

Most of the samples showed DMDI-1 values in the range of 60% to 75%. These values are in the range of the type II marine source rock from the Spekk formation (compare with DMDI-1 values in Figure 14). Furthermore, these samples had EAI values (65% to ~80%) in the range of the same source rock, as well (as seen in Figure 15). A few oil samples showed DMDI-1 and EAI in the range of type III terrestrial 'are formation' (see upper right rectangle in Figure 15). Several other oils had values consistent with mixed oils from both formations. These findings are in good agreement with the current knowledge about the studied petroleum system. No differences between oil and condensate samples from the same field were observed, indicating that DMDI-1 and EAI parameters are not affected by oil natural fractioning (Schulz et al., 2001).
Indices DMDI-1, DMDI-2 and EAI are determined by diamondoid concentration in petroleum. These concentrations, far from being random, keep close relation with the very important petroleum characteristics. These indices are useful to determine the source where the oil is from. In doing so, they are even ‘aging proof’ of the oil. In addition, DMDI-1 and EAI are able to tell in which environment the source rock was formed – marine or terrestrial, for oils coming from the same shelf! Not even fractioning got in their way, and mixed oils were ‘denounced’, as well.

Figure 16 GC/FID signal (saturated hydrocarbons) and mass chromatograms m/z = 191 from hopane biomarkers and m/z = 201 from DMDs of two oils from the same field on the Norwegian Continental shelf

<table>
<thead>
<tr>
<th>Saturated Hydrocarbons, FID</th>
<th>Hopanes, m/z 191</th>
<th>Dimethyl diamantanes, m/z 201</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oil A</strong> (non-degraded)</td>
<td>30H</td>
<td>1,4-DMD, 2,4-DMD, 4,8-DMD, 3,4-DMD</td>
</tr>
<tr>
<td>S</td>
<td>30H</td>
<td>4,9-DMD</td>
</tr>
<tr>
<td>Pr</td>
<td>30H</td>
<td>1,4-2,4-DMD, 4,9-DMD</td>
</tr>
<tr>
<td>Ph</td>
<td>30H</td>
<td>1,4-2,4-DMD</td>
</tr>
<tr>
<td><strong>Oil B</strong> (heavily biodegraded)</td>
<td>30H</td>
<td>4,8-DMD, 3,4-DMD</td>
</tr>
<tr>
<td>S</td>
<td>30H</td>
<td>4,9-DMD</td>
</tr>
<tr>
<td>S</td>
<td>30H</td>
<td>4,9-DMD</td>
</tr>
</tbody>
</table>

Notes: S = saturated hydrocarbons (internal standard – GC tracer); Pr = pristane; Ph = phytane (both Pr and Ph are branched acyclic isoprenoid biomarkers); 30H = (C30-hopane); 4,9-DMD = (4,9-dimethyldiamantane); 1,4-2,4-DMD = (1,4-dimethyldiamantane) + (2,4-dimethyldiamantane); 4,8-DMD = (4,8-dimethyldiamantane); 3,4-DMD = (3,4-dimethyldiamantane).

Heavily biodegraded oil B is depleted in hopane biomarkers while DMD peaks appear unaffected by biodegradation, allowing (oil a)-(oil b) correlation.

Source: Schulz et al. (2001)

Schulz et al. (2001) also used DMDI-1 and DMDI-2 to assess correlations of biodegraded and non-biodegraded oils. Figure 16 shows a comparison between two well-known correlation methods:

- gas chromatography with flame ionisation detector (GC/FID) signals for saturated hydrocarbons
- gas chromatography-mass spectrometry with selected ion monitoring (GC/MS/SIM) for m/z = 191 of hopane biomarkers, and the values for DMDI-1 and DMDI-2 (GC/MS/SIM for m/z = 201 DMDs peak) obtained for oil sample A (non-biodegraded) and oil sample B (heavily biodegraded), both from the same field.
While chromatographic patterns of saturated hydrocarbons and hopanes were severely altered by biodegradation in oil sample B, DMDI-1 values remained unchanged (65%) and DMDI-2 values slightly increased (from 70% to 72%). Besides, overall DMDs peak quantities and relative intensities are virtually the same in both oils A and B, regardless of differences in their biodegradations. These results, once more, demonstrate the utility of diamondoid-based geological correlations for petroleum characterisation in investigating the source of degraded oils. While no correlation could be verified from saturated hydrocarbons or biomarkers data, DMDI-1 and DMDI-2 enabled correlation between oils A and B. Such correlation is also supported by models of oil migration established for the same field of the Norwegian Continental shelf (Schulz et al., 2001).

Table 6  Concentrations of diamondoids in crude oils of different maturity levels

<table>
<thead>
<tr>
<th>Crude oil field</th>
<th>Bio-degradation rank</th>
<th>Diamondoids [μg/g]</th>
<th>Total Diam’s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Adamantane</td>
<td>Diamantane</td>
</tr>
<tr>
<td>Race Track</td>
<td>0</td>
<td>2285.2</td>
<td>53.6</td>
</tr>
<tr>
<td>Buena Vista</td>
<td>0–1</td>
<td>212.6</td>
<td>5.1</td>
</tr>
<tr>
<td>Fruitvale</td>
<td>2</td>
<td>2,091.7</td>
<td>38.6</td>
</tr>
<tr>
<td>McKittrick</td>
<td>2–3</td>
<td>323.4</td>
<td>6.3</td>
</tr>
<tr>
<td>South Belridge</td>
<td>3</td>
<td>1,188.6</td>
<td>18.5</td>
</tr>
<tr>
<td>South Belridge</td>
<td>3.5^</td>
<td>1,310.8 to 1,648.5</td>
<td>17.3 to 23.0</td>
</tr>
<tr>
<td>South Belridge</td>
<td>4^</td>
<td>899.0 to 1,544.8</td>
<td>15.7 to 22.6</td>
</tr>
<tr>
<td>South Belridge</td>
<td>4.5</td>
<td>655.4</td>
<td>15.9</td>
</tr>
<tr>
<td>South Belridge</td>
<td>5^</td>
<td>580.3 to 689.9</td>
<td>14.0 to 36.7</td>
</tr>
<tr>
<td>South Belridge</td>
<td>5.5^</td>
<td>917.4; 935.7</td>
<td>13.1; 15.5</td>
</tr>
<tr>
<td>South Belridge</td>
<td>6</td>
<td>747.1</td>
<td>19.2</td>
</tr>
<tr>
<td>South Belridge</td>
<td>8</td>
<td>680.9</td>
<td>16.0</td>
</tr>
<tr>
<td>Kern River</td>
<td>7</td>
<td>453.2</td>
<td>11.0</td>
</tr>
<tr>
<td>Cymric</td>
<td>8</td>
<td>713.0</td>
<td>14.4</td>
</tr>
</tbody>
</table>

Notes: The eight South Belridge samples reported in this table are from various parts of the South Belridge Field at different levels of maturation. [μg/g]: micrograms of diamondoid per gram of crude oil. ‘Biodegradation rank’ is defined based on the extent of destruction of compound class (Peters and Moldovan, 1993): (0–1) = non-biodegraded, (1–2) = slightly or moderately biodegraded, (2–4) = heavily biodegraded, (4 or more) = severely biodegraded.

Source: From Peters and Moldovan (1993)

4.2 Susceptibility of diamondoids biodegradation by microorganisms

In spite of their resistance to biodegradation, diamondoids may be attacked by microorganisms. Wei et al. (2007c) investigated diamondoid molecules present in non-biodegraded and biodegraded oil of similar thermal maturities from San Joaquin Valley, California. Their work showed that these cage compounds are susceptible to
biodegradation in the reservoir, but the process is selective and appears to evolve step-wise. The biodegradation ranking reported in Table 6 was developed by Peters and Moldowan (1993) and it is based on the extent of destruction of compound classes. According to Table 6, biodegradation ranking is closely related with the total diamondoids contents of the crude oils.

Figure 17 shows variations of adamantanes, diamantanes and biomarkers concentrations relative to concentration of the sample having the lower rank 3, with biodegradation rank increase, in samples from South Belridge oils. (3,4-MD) are also plotted in separate and exhibit close resemblance with total diamantanes behaviour (Dahl et al., 1999).

Figure 17 Change in concentration of adamantanes shown by (●) [which include adamantane, 1-methyl, 2-methyl-1-ethyl-, 2-ethyl-, 1,3-dimethyl-, 1,4-dimethyl-, and 1,2-dimethyl-adamantanes]; diamantanes shown by (○) [which include diamantane, 1-methyl-, 3-methyl-, 4-methyl-, 1-ethyl-, 2-ethyl-, 4,9-dimethyl-, 4,8-dimethyl-, 1,4+2,4-dimethyl and 3,4-dimethyl-diamantanes]; 3+4-methyldiamantanes shown by (*), and biomarkers shown by (□) \( C_{30} \) \( \alpha \alpha \beta \) - hopane + \( C_{29} \) \( \alpha \alpha \alpha \) stigmastane 20R, a sterane; relative to concentration in sample presenting biodegradation rank equal to 3, from South Belridge oil samples with increasing biodegradation.

Note: Lines show general trends of data.

Source: Wei et al. (2007c)

According to Figure 17 at rank 3.5, adamantanes relative concentrations appear to slightly increase, probably due to the loss of other components of higher biodegradability, such as \( n \)-alkanes and isoprenoids. Diamantanes and biomarker values are around 1, showing no indication of significant variation with increase in rank. At rank 4, all compounds present larger variation in relative concentration, but without a clear indication of significant alteration. Relatively stable behavior of diamondoids regarding biodegradation starts to exhibit alteration at the 4.5–8.0 rank intervals, with a drop in relative concentration of adamantanes and diamantanes to about 0.60 and 0.85,
respectively. These results show that adamantanes are more affected by biodegradation than diamantanes, but relatively high amounts of both diamondoids can still be detected in severely biodegraded samples. Biomarkers concentration present some fluctuation after rank 4.0, nevertheless, their overall relative concentration seems to remain unchanged, as it would be expected for hopanes and steranes, which do not undergo major biodegradation in ranks lower than 6 (Peters and Moldowan, 1993). In higher biodegradation rank, a substantial depletion of biomarkers is observed, with concentration at the rank 8 sample been equivalent to c.a. 16% of the concentration in the rank 3 sample. Hence, some decrease in the relative concentration of diamondoids could be noticed in less biodegraded oils, while biomarkers degradation occurs in higher rank levels. As rank increases, adamantanes and diamantanes are preserved while biomarkers are degraded.

In order to evaluate and compare the influence of biodegradation rank on diamondoid-based diagnostic ratios among samples from the same oil field, some diamondoid ratios normalised by values found to the less biodegraded sample (rank 3) for South Belridge oils are reported in Figure 18.

**Figure 18** Effect of biodegradation on diamondoid-based parameters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>△</td>
<td>1-α2-MA adamantane</td>
</tr>
<tr>
<td>□</td>
<td>dimethyl-adamantane adamantane</td>
</tr>
<tr>
<td>○</td>
<td>alkyl-adamantane adamantane</td>
</tr>
<tr>
<td>◯</td>
<td>methyl - diamantane z diamantane</td>
</tr>
<tr>
<td>■</td>
<td>dimethyl - diamantane z diamantane</td>
</tr>
<tr>
<td>×</td>
<td>alkyl-diamantane z diamantane</td>
</tr>
</tbody>
</table>

Note: Relative parameter values were calculated by dividing the value of the biodegradation parameter for the oil sample by the same value observed for oil samples presenting biodegradation rank equal to 3, from South Belridge field.

**Source:** Wei et al. (2007c)

General trends for diamantane/adamantane (Dia/Ad, solid line), adamantanes-based (dashed line), and diamantanes-based (dotted line) ratios indicate that these ratios are influenced by biodegradation level in different ways. All samples show no significant alteration in biodegradation ranks 3.5. After this point, Dia/Ada ratio presented the highest variation in relative parameter values, with a dramatic increase of 4.5 times in rank 8 sample. A particularly high concentration of diamantane (9.02 ng/g) in the rank 6 sample is partially responsible for an extreme relative value of 6.5. Such increase in Dia/Ada values is a reflection of the difference in the biodegradability of these two caged hydrocarbons, as adamantane is attacked in a greater extent than diamantane. The three calculated adamantanes-based ratios,
Diamondoids

- $[1\text{-}+2\text{-}methyladamantanes/adamantane]$
- $[1,2\text{-}+1,3\text{-}+1,4\text{-}dimethyladamantanes/adamantane]$
- $[\text{alkyladamantanes/adamantane}]$

... show similarities in relative values and exhibit minor elevation at higher ranks, while three diamantanes-based ratios,

- $[1\text{-}+3\text{-}+4\text{-}methyldiamantanes/diamantane]$
- $[3,4\text{-}+4,8\text{-}+4,9\text{-}dimethyldiamantanes/diamantane]$
- $[\text{alkyldiamantanes/diamantane}]$

... show slight decrease with increase in biodegradation rank. Such results may indicate that alkyl-substitutions have opposite effects on biodegradability of diamondoid cages, making alkyladamantanes less susceptible than adamantane while they make alkyldiamantanes more readily biodegradable than diamantane.

An earlier report on $(1\text{-}+2\text{-}MA)/A\text{da}$ and $(1\text{-}+3\text{-}+4\text{-}MD)/D\text{ia}$ ratios calculated for oils from two Australian sedimentary basins (the Gippsland and the Carnarvon Basins) suggested their use as indicators of oil biodegradation and oil mixing (Grice et al., 2000). As can be seen in Figure 19, for the Gippsland Basin, very little alteration in $(1\text{-}+2\text{-}MA)/A\text{d}$ ratio could be noticed in non-biodegraded to moderate biodegraded oils (levels 0 to 3), with ratio values around 6.0. The first important change in this ratio occurs at biodegradation level range 3–4, and the increase in ratio value proceeds to reach 14.5 in the level range 4–5, and 10.2 in level 7.

Figure 19: Effect of biodegradation level on $1\text{-}+2\text{-}methyladamantanes/adamantane$ $(1\text{-}+2\text{-}MA/A\text{d})$ and $1\text{-}+3\text{-}+4\text{-}methyldiamantanes/diamantane$ $(1\text{-}+3\text{-}+4\text{-}MD/D\text{ia})$ ratios for Australian oils from (a) the Gippsland basin and (b) the Carnarvon Basin

Source: Grice et al. (2000)
These results exhibit similarities with variations found in South Belridge oils, in which \((1+2\text{-MA})/\text{Ada}\) increases \textit{c}.\textit{a.} 55\% in the level range of 3–8 as shown in Figure 17.

\textbf{Figure 20} Some possible aerobic biological pathways for adamantane degradation

\textit{Source:} From Wei et al. (2007c) with corrections
In samples from the Carnarvon Basin, the (1-+2-MA)/Ada ratio (grey bars in Figure 19) is almost three times lower in non-biodegraded samples (biodegradation level 0) than in the severely biodegraded ones (biodegradation level 8). Such fact points out to the importance of differences in microbial attack on alkyl-substituted adamantanes when compared with adamantane.

(1-+3-+4-MD)/Dia ratio showed initial decrease until biodegradation level 3, appearing to reach equilibrium value around 2.0 in severely biodegraded oils from the Gippsland basin (Figure 19, dotted white bars). Very severely biodegraded Carnarvon oils (level 8) showed an elevation of c.a. 66% in (1-+3-+4-MD)/Dia ratio in comparison to non-biodegraded samples from the same basin (dotted grey bars). These results indicate that significant changes in (1-+3-+4-MD)/Dia ratio only occur in extreme biodegradation levels, possibly caused by concomitant degradation of less resistant hydrocarbons and increased concentration of the more resistant diamantanes. Based on the previous discussion, (1-+2-MA)/Ada appears to have a more predictable behaviour than (1-+3-+4-MD)/Dia and can be more useful as an indicator of biodegradation extension, particularly in extreme biodegradation levels, in which little information can be retrieved from biomarkers data due to their biological destruction in such oil samples. These findings reinforce the idea of using diamondoid-based ratios for petroleum characterisation (Grice et al., 2000).

Wei et al. (2007c) suggested a mechanism for biological degradation of adamantane in petroleum, based on the data published for in vitro enzymatic aerobic hydroxylation of adamantane (White et al., 1984) and microbial oxidation of adamantanone (Selifonov, 1992). Their suggested aerobic biological pathway for adamantane degradation is reported in Figure 20.

According to Figure 20 the main biosynthetic intermediates are 4-oxahomo-adamantane-5-1 and 5-hydroxyadamantan-2–1, obtained through the action of camphor 1,2-monooxygenase and camphor 5-monooxygenase enzymes from a gram-negative saprotrophic bacterium named Pseudomonas putida, respectively. Nevertheless, geological conditions in petroleum sites are primarily anaerobic, making any aerobic biochemical pathway less probable to occur.

4.3 Diamondoid-based diagnostic ratios in environment science

Some techniques for correlating relationships between ‘source rock’ and ‘crude oil’ have been applied for the study of environmental pollution. Environmental fingerprinting of biomarkers is used in the assessment of fuel pollutants to characterise the type of the fuel contaminants, to determine their source, and to understand their fate in the environment (Alimi et al., 2003; Christensen et al., 2004; Wang et al., 2006b). Selected diamondoid ratios, distribution or relative abundance, by their turn, may be useful for oil spill source identification (Wang et al., 2006a) and distinguishing sources of refined products as well (Stout and Douglas, 2004; Yang et al., 2006).

All crude oils contain a wide range of hydrocarbons such as light gaseous hydrocarbons, liquid hydrocarbons and heavy ends which may include heavy hydrocarbons, resins and asphaltenes. Crude oils also may contain smaller amounts of sulphur, oxygen, nitrogen and metals (nickel, vanadium and iron). On the other hand, refined petroleum products are fractions derived by distillation and upgrading of crude oil. Thus, they have differences in their chemical compositions due to the dissimilarities
in characteristics of crude oil feed stocks as well as variations in refinery industrial processes.

Variations in chemical compositions of crude oils may result in unique chemical ‘fingerprints’ for each oil, providing a basis for identifying the source(s) of spilled oil. GC/MS is the standard analytical method for oil chemical fingerprinting, since it could identify a broad range of polycyclic aromatic hydrocarbons (PAHs) and petroleum markers. In fact, the identification of individual diamondoids is based on the full mass spectral data for structural elucidation and comparison with the literature and MS library data, as well as comparison of GC retention data with authentic standards, determination of refractive index (RI) (Kovats, 1965), and comparison with the literature RI values. GC/MS chromatograms analyses have shown distinct distribution patterns of diamondoids in crude oils and refined products of different origins. Nevertheless, oils of the same origin or from the same area exhibit similar diamondoid signatures (Stout and Douglas, 2004; Yang et al., 2006).

4.4 Diamondoid-based diagnostic ratios for petroleum maturity parameters

The thermal maturation of sedimentary organic matter is one of the important aspects of petroleum formation and occurrence. The determination of maturity is the keystone for determining of the boundary conditions of petroleum generation, coke stability prediction in coals, identification of many geological phenomena (faulting, thrusting, intrusion, unconformity, etc.) and temperature history in the basin evolution (Karlsen et al., 1993; Mango, 1997; Rodriguez and Littke, 2001). There exist a large number of optical, pyrolytic and chemical methods which can be used to assess thermal maturity (Farrimond et al., 1998; Durand, 1980; Tissot and Welte, 1984; Mukhopadhyay, 1994, Peters et al., 2005). These methods differ in approach and in effectiveness to assess various stages of maturation.

The presence of diamondoids is considered to be closely related to the geological maturity of an oil field (Chen et al., 1996; Gao et al., 2001; Shimoyama and Yabuta, 2002). Some investigators have used relative abundances of diamondoids to estimate the degree of geological thermal maturity of source rocks and crude oil, especially in mature and post-mature samples (Fang et al., 1996, Chen et al., 1996, Dahl et al., 1999).

The first reported diamondoid-based maturity parameters were MAI and MDI as defined by the following expressions (Chen et al., 1996):

\[
\text{MAI}(%) = 1 - \frac{100 \cdot \text{MA}}{\text{1MA} + 2\text{MA}} \quad \text{MDI}(%) = 4 - \frac{100 \cdot \text{MD}}{\text{1MD} + 3\text{MA} + 4\text{MA}}
\]

where

\[
1\text{MA} = 1\text{-methyl-adamantane} \\
2\text{MA} = 2\text{-methyl-adamantane} \\
1\text{MD} = 1\text{-methyl-diamantane} \\
3\text{MD} = 3\text{-methyl-diamantane} \\
4\text{MD} = 4\text{-methyl-diamantane}.
\]
These two indices, MAI and MDI, were proposed and used to evaluate the maturation and evolution of petroleum from Chinese Basins, through GC/MS investigation of diamondoid and biomarkers content of crude oils, condensates and source rocks from more than five different basins (Chen et al., 1996). At least thirty diamondoids could be identified from these samples: 17 adamantanes, ten diamantanes and three triamantanes. 1MA was the most abundant diamondoid and 4MD was the most abundant within the diamantane series. Both molecules are substituted at the bridgehead position (top-CH-location of adamantane molecule). Bridgehead-substituted diamondoids experience less steric interactions than diamondoids substituted at secondary carbons such as 2-methyl-adamantane and 3-methyl-diamantane (Engler et al., 1972); thus, they are expected to possess higher thermal stability and higher concentration in more mature oils.

MAI and MDI were found to increase in source rocks with the increase in vitrinite reflectance ($R_0$) of the rocks. This was observed in several samples of different lithology that included mudstones in the Tarim Basin and dolomites and coals in the Erdos Basin, bearing quite different types of organic matter (Chen et al., 1996).

Vitrinite reflectance ($R_0$), the major maturity parameter, accurately establishes the effective maximum paleotemperature (the ancient temperature of a geologic process) and its duration at any stage in geological timescale (Robert, 1980; Mukhopadhyay, 1994). Practical applications of $R_0$ are frequent in various geological activities including fossil fuel exploration, mining, beneficiation, utilisation, energy prospecting, etc. Simplicity, precision and affordability make this method of particular importance for commercial use especially in petroleum, coal, and other industries (Gray, 1991; DeVanney and Stanton, 1994). The vitrinite reflectance ($R_0$) measurement method is based on irreversible chemical reactions (as a response to increasing temperature and pressure through geological eras) that take place in vitrinite macerals present as dispersed organic particles of sedimentary rocks (Rimmer, 1991; Mukhopadhyay, 1994). The level of maturation or coalification attained is a function of temperature and the duration of heating.

In Table 7, we report the relation between ‘stage of maturation’, ‘level of maturity’ and vitrinite reflectance ($R_0$). Figure 21 shows the relations between MAI and MDI with $R_0$ found for source rocks from Erdos and Tarim Basins.

### Table 7

<table>
<thead>
<tr>
<th>Stage of maturation</th>
<th>Level of maturity</th>
<th>$R_0$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diagenesis</td>
<td>Immature</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Early</td>
<td>0.65–0.90</td>
</tr>
<tr>
<td></td>
<td>Peak</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Late</td>
<td>0.90–1.35</td>
</tr>
<tr>
<td>Catagenesis</td>
<td>Mature</td>
<td>1.35–2.0</td>
</tr>
<tr>
<td></td>
<td>Post-mature</td>
<td>2.0–4.0</td>
</tr>
<tr>
<td>Metagenesis</td>
<td>Post-mature</td>
<td>4.0–5.0</td>
</tr>
</tbody>
</table>

Note: *Mukhopadhyay (1994); †Peters and Cassa (1994)
As it is shown in Figure 21, MDI presents good correlation with $R_0$, with its value slightly higher in the Tarim Basin as compared with Erdos Basin values, probably due to the presence of acid catalyst clay mineral in mudstones in higher amounts than in the dolomites and coals from the Erdos Basin. MAI possess higher values than MDI in both basins, with some fluctuations in the 1.35–1.70 range of $R_0$. Part of the inconsistencies in MAI values may be attributed to losses of adamantanes by sublimation during transportation and processing of samples. It is important to note that both MAI and MDI parameters could be measured at various vitrinite reflectance ($R_0$) values corresponding to late mature (0.9–1.35) and postmature ($> 1.35$) samples (Tables 7 and 8), in which either biomarkers parameters have already reached equilibrium values or could not be calculated due to total depletion of biomarker molecules. Hence, diamondoid-based parameters, especially MDI, may be useful instruments for evaluation of thermally mature and postmature petroleums.

The applicability of MDI as a maturity parameter was tested in mature and postmature carbonate source rocks from Majiagou Formations, Shanganning Basin, China (Jinggui et al., 2000) and in crude oils (within the oil window and late mature) of several basins from the continental margin of Brazil (Jesuino, 2005). As shown in Figure 22, no clear correlation between MDI and $R_0$ (%) was observed in these basins. These results indicate that diamondoid parameters are affected by a number of factors, as are diamondoid concentrations, making the extended use of such parameters in different petroleum sites less reliable.
Figure 22  Comparison between MDI (%) versus $R_0$ (vitrinite reflectance, %) values calculated for: bitumens from over-mature gas-prone carbonate source rocks, Shanganning Basin, China (●) (Jinggui et al., 2000); and crude oils from three sedimentary basins in Brazilian continental margins: LSC (●), LSS (○) and LSS (△).

Note: $R_0$ was determined as the reflectance of solid bitumen in the whole rock thin section of Shanganning samples and based on ααα-C29 steranes from Brazilian crude oils according to Sofer et al. (1993).

Source: Jesuino (2005)

Figure 23  Changes in MAI and MDI ratios as a function of mineralogy in hydrous pyrolysis of modern sediments

Notes: HP = hydrous pyrolysis of modern sediments; CaCO3 = hydrous pyrolysis of sediments mixed with CaCO3 (6:1 w/w); K10 = hydrous pyrolysis of sediments mixed with montmorillonite K10 (6:1 w/w); MS-25 = hydrous pyrolysis of sediments mixed with MS-25 (6:1 w/w).

Source: Wei et al. (2006a)

An example of the influence of mineral content on MAI and MDI can be seen in experiments of artificial maturation through hydrous pyrolysis of modern sediments [Table 3, Figures 23(a) and 23(b)]. MDI appears to be affected by mineral content and it
is suppressed by the presence of CaCO$_3$. In contrast, the presence of montmorillonite (K10 or MS-25) tends to elevate MDI value. Similar behavior is observed to MAI values. In another example, CaCO$_3$ had little influence on yields of (3,+4-MD) and total diamondoids after dry pyrolysis in Celestun Lagoon (see columns b and c of Table 3 for Celestun Lagoon and Figure 10 for CaCO$_3$), but severely reduced MDI values of this sample from 26% to 11%. This may be an indication of the distinct action of minerals on generation and release of diamondoids, depending on the type of isomer formed.

5 The role of diamondoids in petroleum and natural gas production fouling

The relatively high melting points of diamondoids may cause their precipitation in oil wells, transport pipelines and processing equipment during production, transportation and refining of diamondoids-containing petroleum crude oil and natural gas (Escobedo, 1999; Vazquez et al., 1998; Vazquez and Mansoori, 2000; Mansoori, 1997, 2009, 2010; Mansoori et al., 2007b). This may then cause fouling of pipelines and other oil processing facilities. Diamondoids deposition and possible fouling problems are usually associated with deep natural underground petroleum reservoirs that are rather hot and at high pressure. Other hydrocarbons with molecular weights in the same range as diamondoids generally have much lower melting points and do not precipitate at high temperatures (Vazquez et al., 1998).

The practice of petroleum production may lead to an environment that favours the reduction of diamondoid solubility in petroleum, their separation from petroleum fluid phase, and their precipitation. Deposition of diamondoids from petroleum streams is associated with phase transitions resulting from changes in temperature, pressure, and/or composition of reservoir fluid. Generally, these phase transitions are solid-gas or solid-liquid transitions. Deposition problems are particularly cumbersome when the fluid stream is, so called, ‘dry’ (i.e., low LPG content in the stream which includes propane C$_3$H$_6$ and butane C$_4$H$_{10}$). Phase segregation of solids takes place when the fluid is cooled and/or depressurised. In a, so called, ‘wet reservoir fluid’ (i.e., high LPG content in the stream) the diamondoids partition into the LPG-rich phase and the gas phase. Deposition of diamondoids from a wet reservoir fluid is not as problematic as in the case of dry streams (Vazquez et al., 1998; Vazquez and Mansoori, 2000; Mansoori, 1997). As a result, diamondoids may nucleate out of solution upon drastic changes of pressure and/or temperature. Instabilities of this sort in petroleum fluids may potentially initiate deposition of other heavy organic compounds (including asphaltenes, paraffins, and resins) on such nucleation sites (Vazquez et al., 1998; Vazquez and Mansoori, 2000; Mansoori, 1997). Therefore, knowledge about the solubility behaviour of diamondoids in organic solvents and dense gases, as reported by Mansoori (2007) becomes important.

Adamantane and diamantane are usually the dominant diamondoids found in petroleum and natural gas pipeline deposits (Vazquez et al., 1998; Vazquez and Mansoori, 2000). This is because diamondoids are soluble in light hydrocarbons at high pressures and temperatures. Upon expansion of the petroleum fluid coming out of the underground reservoir and a drop in its temperature and pressure, diamondoids could deposit.

Deposition of diamondoids can be particularly problematic during production and transportation of natural gas, gas condensates, and light crude oils. However, their
Diamondoids in petroleum fluids is usually ignored due to their low concentration in these fluids. Nevertheless, in certain cases existence of these molecules in natural gas and gas condensate sources could lead to severe complex system problems of deposition and eventual plugging of flow paths. These nucleation sites may promote interactions among other heavy organic species and serve as their flocculation sites. Thus, it is important to determine whether or not diamondoids are present in a reservoir fluid at a harmful level. For this purpose the separation, detection and measurements discussed in the next section are used.

6 Detection, measurement and separation of diamondoids in petroleum

Petroleum crude oil, gas condensate and natural gas are generally complex mixtures of various hydrocarbons and non-hydrocarbons with diverse molecular weights. In order to analyse the contents of a petroleum fluid it is a general practice to separate it first into six separate components (known as fractions) which include volatiles, inorganic materials, saturates, aromatics, resins and asphaltenes as shown in Figure (24) (Vazquez et al., 1998; Vazquez and Mansoori, 2000; Mansoori, 1997; Mansoori et al., 2008).

Volatiles consist of the low-boiling fraction of crude oil separated at room temperature and under vacuum (~27°C and 10 mmHg) from crude oil. The contents of the volatiles fraction can be further analysed using gas chromatography (GC). Inorganic materials are separated by adding toluene to the vacuum residuum. All the organic materials in the oil will dissolve in toluene and the inorganic materials are filtered out. The remaining five families of components (fractions) are separated from the vacuum residue with the use of a column liquid chromatography [i.e., SARA separation (Jewell et al. 1974)]. Initially, the asphaltenes – fraction of the sample is removed by the ASTM D3279-90 separation method (ASTM, 2005). Then the saturates-fraction is extracted with n-hexane solvent by passing the sample through a liquid chromatography column that is packed with silica gel and alumina powder. Since diamondoids are saturated hydrocarbons the analysis to determine their presence and composition in a crude oil must be performed on the saturates-fraction. Mass spectrometry analyses must then be performed on the low-boiling part of the saturates-fraction to determine whether diamondoids are present in it. To achieve this, the saturates-fraction is analysed through GC/MS (Wingert, 1992; Lin and Wilk, 1995; Escobedo, 1999; Vazquez et al., 1998; Vazquez and Mansoori, 2000; Mansoori et al., 2007) according to Figure 25.
Figure 25  Gas chromatography plus mass spectrometry for identification and measurement of
diamondoids content of saturates fraction of petroleum fluids

Source:  Escobedo (1999)

Some representative chromatograms of petroleum fluids containing diamondoids
obtained through GC/MS by various investigators are reported in Figures 26–30.
Adamantane, if present in the sample, will elute between nC_{10} and nC_{11}; diamantane will
elute between nC_{15} and nC_{16}; triamantane will elute between nC_{19} and nC_{20}, etc. (Stout
and Douglas, 2004). There are a number of other methods for the separation of
diamondoids from petroleum fluids or natural gas streams which include the following:

- a gradient thermal diffusion process (Alexander et al., 1990a) is proposed for
  separation of diamondoids

- a number of extraction and absorption methods (Alexander et al., 1991; Henderson
  and Sitzman, 1993) have been recommended for removing diamondoid compounds
  from natural gas streams

- separation of certain diamondoids from petroleum fluids has been achieved using
  zeolites (Alexander et al., 1990b; Rollmann et al., 1996) and a number of other solid
  adsorbents.

Figure 26  Standard molecular fragmentation spectrum of adamantane (136 = m/z)

Source:  Mansoori (2007)
**Figure 27**  Gas chromatogram of a gas condensate (NGL = natural-gas liquid) sample

![Gas chromatogram](image)

Note: The peak with retention time of 5.70 eluted between nC\textsubscript{15} and nC\textsubscript{16} is indicative of the probable existence of diamantane in the sample.

*Source:* Vazquez et al. (1998)

**Figure 28**  Gas chromatogram of a crude oil sample showing the possible existence of adamantane and diamantane in the sample

![Gas chromatogram](image)

*Source:* Mansoori (2007)
Figure 29  Gas chromatogram of a diamondoid-rich gas-condensate (NGL) sample showing clusters of peaks representing adamantanes, diamantanes, triamantanes and tetramantanes


Figure 30  Gas chromatogram from the full-scan CC/MS analysis of a high temperature distillation fraction (343°C) containing diamondoids

In this review paper, we present the natural occurrence of diamondoids in petroleum fluids and other fossil fuels. In order to clarify the origin of diamondoids in petroleum we discuss the origin of petroleum and genesis of diamondoids. Then we discuss the role of diamondoids as geochemical tools for petroleum characterisation. We also discuss the ways diamondoid molecules are used to play an important role in petroleum evaluation, and may be used to assess origin, extend of biodegradation and thermal maturity, as well as to identify the occurrence of petroleum. Another aspect of diamondoids presented in this paper is diamondoid-based diagnostic ratios in environmental science as well as diamondoid-based diagnostic ratios as petroleum maturity parameters. Then we present the role of diamondoids in petroleum and natural gas production fouling as well as separation, detection and measurement of petroleum diamondoids. Diamondoid-based parameters may be used to assess oil source, maturity and biodegradability, providing supporting information, especially when traditional evaluation data are not available or are difficult to interpret.

Throughout this review paper, it is possible to realise that the presence of diamondoids in petroleum has become much more than a chemical curiosity since Landa et al.’s (1933) initial findings in Czechoslovakian crude oils and has advanced to be a resourceful instrument in petroleum science and engineering, biomedicine, materials science and an important family of molecular building blocks in nanotechnology (Mansoori et al., 2012a).

References


Diamondoids


Diamondoids


Diamondoids

