



# Comparative study of conventional maturity proxies with the methyl-diamantane ratio: Examples from West Texas, the Middle East, and northern South America

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## ABSTRACT

Diamantanes are a class of cage-like hydrocarbons that are structurally similar to small pieces of diamonds. Their formation from polycyclic precursors parallels their dynamic stability. Diamantanes occur naturally in virtually every oil and condensate as well as in source-rock extracts. Their ubiquitous nature in oils and extracts of any thermal maturity level, along with their proven stability with increasing maturity, makes them useful as thermal maturity proxies past peak oil window and in the identification of mixtures of low- and high-maturity fluids. Two relationships in particular, methyl-diamantane index (or MDI) and 3- + 4-methyl-diamantane concentration vs. Stigmastane [5 $\alpha$ , 14 $\alpha$ , 17 $\alpha$ (H)-24-ethylcholestane 20R C29 sterane] concentration, are repeatedly used to establish thermal maturity relationships between oils and between oils and extracts and to identify mixtures of fluids with different thermal maturities.

The present comparative study shows how methyl-diamantane proxies from West Texas oils and extracts (sourced from the Woodford Shale) and in oil samples from northern South America (Colombia) and the Middle East show overall a very good agreement with classic maturity proxies, such as T<sub>max</sub> values from Rock-Eval pyrolysis and vitrinite reflectance (V<sub>ro</sub>). However, caution is advised when using methyl-diamantane-derived proxies in the presence of drilling additives and contaminants (e.g., oil-based mud or OBM) and of oils and extracts that have experienced biodegradation. The latter is probably a highly unrecognized issue when using methyl-diamantanes, which can result in erroneous interpretations of thermal maturity and mixing. Based on the results of this study we recommend the necessity of a holistic, multi-proxy approach, based on the integration of geochemical screening, organic petrography, and molecular geochemistry techniques as the best possible solution when dealing with such geochemical conundrums.

## 1. Introduction

Diamantanes are a class of rigid fused-ring alkanes that were first recognized in crude oils from Czechoslovakia in 1933. Diamantanes is a class of compounds reported to be resistant to biodegradation (Dahl et al. 1999; Grice et al. 2000; Schulz et al. 2001). They possess a cage-like structure and have been used to predict the extent of oil cracking, distinguish mixtures of oils, or compare biodegraded oils (Dahl et al. 1999; Grice et al. 2000; Schulz et al. 2001). They occur naturally in every oil, condensate, and source rock extract and are thermally more stable than most hydrocarbons. They are thought to be formed from polycyclic hydrocarbons under thermal stress with a strong Lewis acid acting as a catalyst (Chen et al., 1996). Diamantanes are resistant to thermal cracking and biodegradation (Wingert, 1992) with the possible exception of adamantane (Wei et al., 2007), which makes them ideal

compounds to study petroleum geochemistry. Diamantanes can be used to estimate the extent of oil cracking (conversion of liquid HCs to gas and pyrobitumen) and evaluate the degree of biodegradation of crude oil. Diamantanes can be used as an alternative - and novel - thermal maturity proxy, especially in high thermal maturity settings where other maturity indicators cannot be applied to evaluate thermal maturity. These include cases when biomarker compounds, such as steranes and terpanes, are absent or unreliable, when their isomerization ratios have reached equilibrium, or when studying severely biodegraded oils in which hopanes are absent and 25-norhopanes are ubiquitous.

The smallest diamantane structures are the tricyclic adamantanes, the cage structure of which contains C<sub>10</sub>H<sub>16</sub>. On the other hand, pentacyclic diamantane possess two-cage structure (C<sub>14</sub>H<sub>20</sub>) that provides greater resistance to evaporative losses. Sulfur-incorporating

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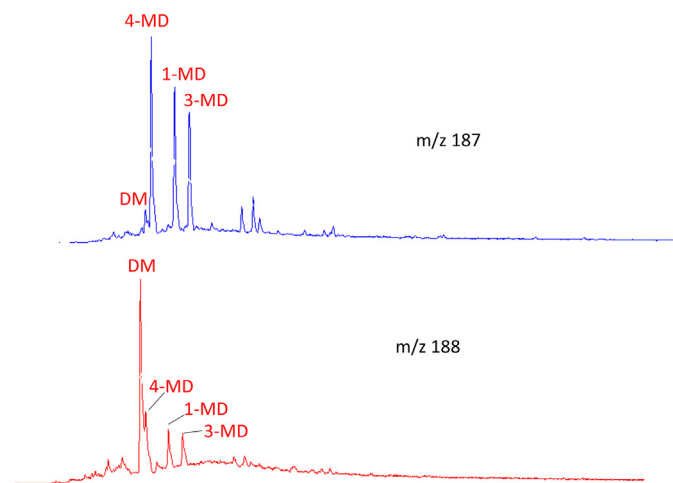
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**Table 1**  
Description of the type and number of samples used in this study.

Example	# of samples	Sample type	Location	Basin
Woodford	3	Condensate	West TX	Delaware
Woodford	34	Source Rock Extracts	West TX	Delaware
Woodford	2	Condensate	West TX	Midland
Woodford	12	Source Rock Extracts	West TX	Midland
Cambrian Source Rocks	4	Condensate	Middle East	NA
La Luna	1	Biodegraded Oil	Colombia	MMB
Mirador	1	Biodegraded Oil	Colombia	Llanos Basin

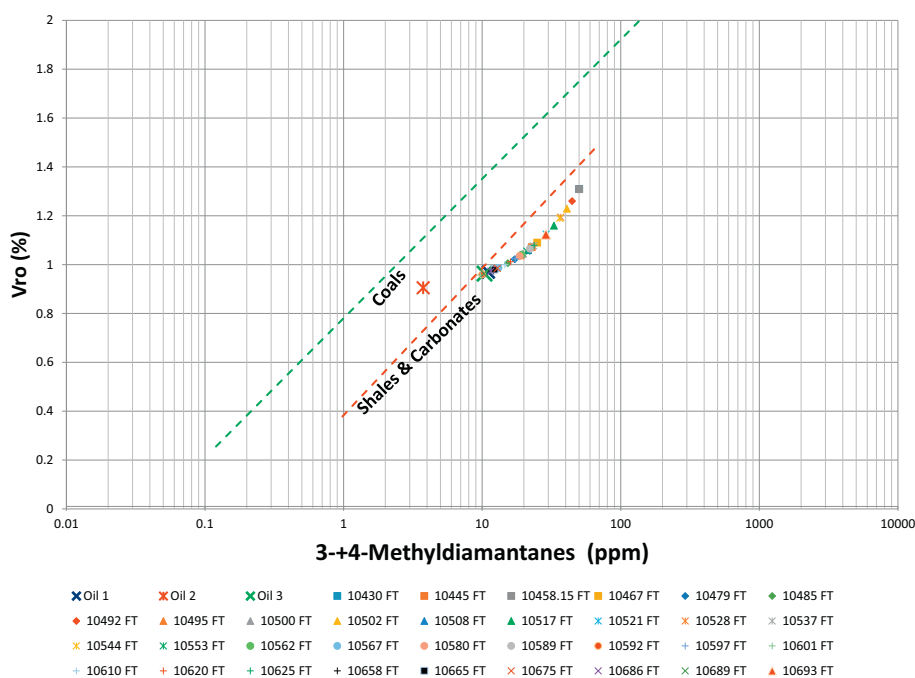


**Fig. 1.** Partial mass chromatograms of a Woodford-sourced oil sample for the m/z 187 (upper panel) and 188 (lower panel) fragment ions of diamantane and methyladamantanes. Dm = Diamantane; 1-MD = 1-methyldiamantane; 3-MD = 3-methyldiamantane; 4-MD = 4-methyldiamantane.

diamantoids (e.g., thiadamantanes) are believed to be indicative of thermochemical sulfate-reducing reactions between hydrocarbons and sulfates under high temperature conditions at depth (Wei et al., 2012). The most stable diamondoid structures possess a methyl group in the bridgehead position because those that contain a greater degree of substitution by bridgehead carbons (C that connects different rings within the same molecule) are more stable. This results in the following order in stability: 1-methyladamantane (1-MAAd) > 2-MAAd and 4-methyldiamantane (4-MDdia) > 3-MDdia and 1-MDdia. Chen et al. (1996) introduced two indices, namely the methyladamantane index [(MAI = 1-MAAd/(1-MAAd + 2-MAAd)] and the methyldiamantane index [MDI = 4-MDdia/(4-MDdia + 1-MDdia + 3-MDdia)], which showed to increase with increasing vitrinite reflectance in source rocks from China.

Both adamantanes and diamantanes are created during the oil window (0.6–1.5%Vro) and the wet gas stage (1.5–2.1%Vro), and start to decompose in the dry gas (> 2.1%Vro). Li et al. (2000) stated that MDI cannot be used to determine thermal maturity in carbonate-rich rocks at Vro > 2.0%. Diamondoids from Type I and IIA kerogen are derived from the cracking of bitumen whereas those generated from Type III kerogen are derived from the cracking of kerogen (Jiang et al. 2018). Using pyrolysis of the above kerogen types, these authors concluded that diamondoids derived from Type I and IIA kerogen are 4–5 × greater compared to those derived from Type III kerogen concentrations. Type III kerogen produces mainly adamantanes. Concentration ratios (CRs), such as MAs/MDs, DMAs/MDs, DMAs/DMDs, and As/Ds all show similar evolutionary trends (i.e., a sharp increase at 0.60%Vro; peak at 1.5%Vro in the wet gas stage; a sharp drop at ~2.0%Vro, followed by flattening at ~2.5%Vro in the dry gas stage) (Jiang et al. 2018).

Using pyrolysis experiments up to 600 °C, Wei et al. (2006) studied the fate of diamondoids in source rocks and coals from low to very high maturities and concluded that they are cracked into aromatic hydrocarbons, pyrobitumen, and gases. They proposed three phases of diamondoid evolution (birth: < 1.1%Vro, growth and enrichment: 1.1–4.0%Vro, and destruction or death: > 4.0%Vro). The greatest application though of an analysis called QEDA (Quantitative Extended Diamondoid Analysis) is in being able to determine the source rock of any hydrocarbon fluid regardless of its maturity (from the early oil window to the dry gas window), correlating one oil to another, and



**Fig. 2.** Relationship between vitrinite reflectance in oil (Vro%) vs. the concentration of 3- + 4-methyldiamantane for three (3) oils (named Oil 1, Oil 2, and Oil 3) and thirty-four (34) extracts sourced from the Mississippian-age Woodford Shale in the Texas Panhandle. Also shown are the two trend lines for coals (green dashed line,  $Vro = 0.0151 * 3 - + 4 - MD + 0.5361$ ) and for shales and carbonate rocks (red dashed line,  $Vro = eq = 0.0087 * 3 - + 4 - MD + 0.8726$ ; modified from Wei et al., 2006, 2007). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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