

Source Identification of Permian Basin Oils Using Higher Diamondoids

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Introduction

Like their larger cousins, macroscopic diamonds, diamondoids from petroleum exhibit unique properties derived from their interlocking carbon cage structure. This structure results in extreme strength, rigidity, high atomic density, low electron mean-free path, and low free energy. Fascinating properties unrelated to petroleum and environmental geochemistry include monochromatic photoemission and the ability to form a relatively stable cations enabling the drastic work-function lowering of higher diamondoid-coated metal surfaces. Due to the rigidity of the molecule, diamondoids have extremely strong Van der Waals attractions due to their low conformation entropy. This property has allowed for the creation of the longest stable alkane C-C bond ever recorded, 1.74 Å. The strange molecules are held together not by the long bond (which is extremely weak), but rather diamondoid Van der Waals forces on each side of the long bond. And because large diamondoids can be easily derivitized, they can be used to create exotic new moieties including a C-60 Buckeyball-diamondoid hybrid which was shown to be a molecular rectifier.

Many of these same unique properties make diamondoids valuable for geochemical applications related to the oil and environmental industries. For example, due to their extreme stability (for their size, they are the most stable molecules in petroleum) measurements of adamantane and diamantane ratios and absolute concentrations has allowed for assessment of petroleum thermal evolution and for fingerprinting oil-related pollution.

Results

Here we report on the relatively new technique of using the distributions and concentrations of higher diamondoids (tetramantane, pentamantane and hexamantane) isomers to distinguish oil source families. The study area is the Permian Basin, Andrews County, Texas. Effective source rocks in the region include the Ordovician Simpson, the Devonian Woodford and the Mississippian Barnett Shale. The predominant reservoir in this study is in the Devonian below the Woodford, although one of the oils is from the Ordovician Ellenberger and another, believed to be Barnett sourced, is in the Pennsylvanian. We show that each of these three end member sources can be distinguished by higher diamondoid relative concentrations and distributions (see Fig 1 below). In addition, mixed-source oils derived from multiple end members can be identified (most of the oils in this study are actually mixes) and the relative amount of charge from each qualitatively estimated.

We show that the application of tetramantane, pentamantane and hexamantane concentrations and ratios for oil correlations is almost identical to the use of biomarkers. For example, analogous to the sterane ternary diagrams so successfully used to correlate oils and distinguish oil families, we constructed ternary diagrams from diamondoid isomers including one consisting of the three tetramantane isomers, and also various combinations of the four pentamantane isomers analyzed, e.g. Figure 1 below. We have also have constructed

diagrams showing relative concentrations of tetramantanes, pentamantanes and hexamantanes in a very similar way to the typical graphical representation of relative homohopane concentrations. Although not shown here, this diamondoid diagram also differentiates the oil families and elucidates the mixtures in this study.

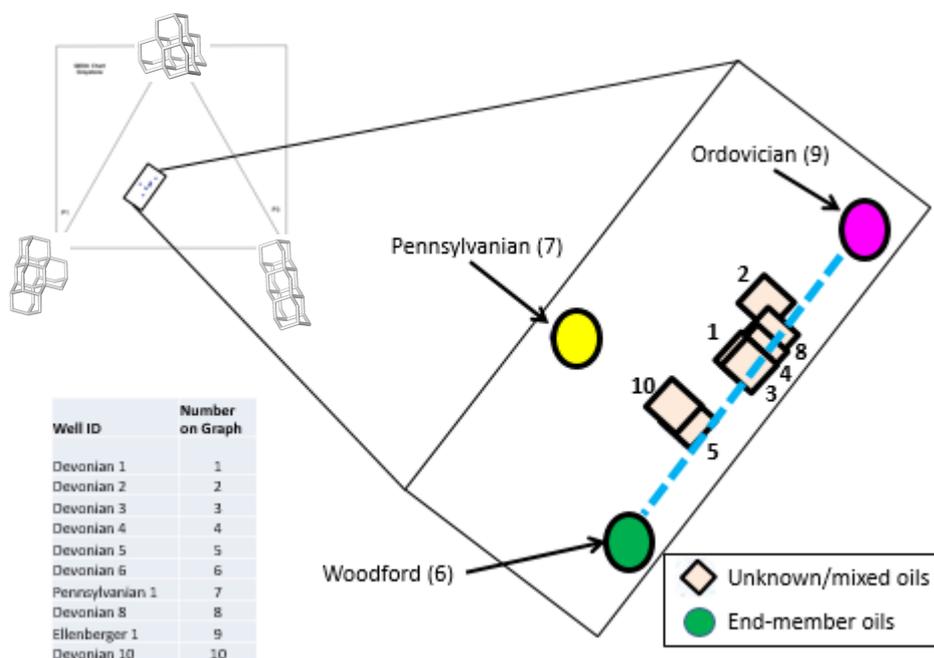


Figure 1. Example pentamantane ternary diagram (structures shown) used to distinguish genetic families and to recognize oil mixes in the Permian Basin.

Although higher diamondoids can be used to correlate oil families in way almost exactly analogous to biomarkers, diamondoids have advantages due to their extreme thermal stability. Whereas biomarker concentration tend to disappear in the Late-Oil to Wet-Gas maturity window, diamondoids remain (they are actually concentrated). Therefore, it is possible to correlate any fluid to its source no matter the maturity provided the diamondoid fingerprints are different. Even condensates from “dry gas” wells can be correlated to their source or to related lower-maturity black oils without having to worry about contamination in carrier beds during migration due to low concentrations.

Another advantage of using tetramantane, pentamantane and hexamantanes to correlate oils is that mixtures of oils derived from two source rocks of different maturities can be recognized and the sources determined. An excellent example is shown in this study. The Devonian Woodford Shale is in the Middle of the Oil Window and oils derived from it have plentiful biomarkers. On the other hand, the underlying Ordovician Simpson is in the Wet-Gas Window and oils from it contain no almost no biomarkers. Oils from the principle target Devonian reservoir have Woodford biomarkers, and therefore, based on biomarkers, one would conclude that they were sourced only from the Woodford. However, as seen in Figure 1, using the diamondoid method, it is clear that these oils are actually mixes, derived from both the Woodford and the underlying Simpson. This conclusion is supported by both the carbon isotopes of the mixed oils and the fact that the *n*-alkanes of mixed oils have a *G. Prisca* signature indicative of the Ordovician.

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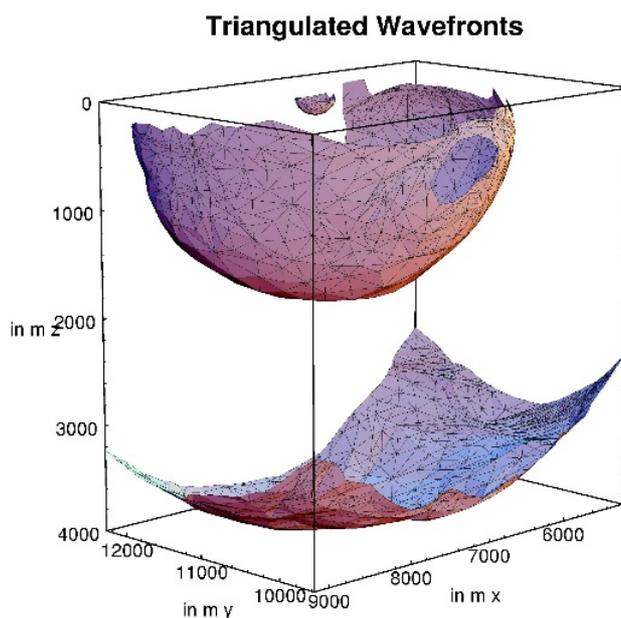


Figure 1 This is an example of a figure imported from jpeg (courtesy of Gilles Lambaré). Left click on Insert on the menu bar and then select Picture. Supply a **short caption (in Italics)** for the figure; more detailed discussion of the figure can be reserved for the text.

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