Petroleum Biomarker in Oil Exploration

Biomarkers

Biomarkers are a group of compounds, primarily hydrocarbons, found in oils, rock extracts, Recent sediment extracts, and soil extracts. What distinguishes biomarkers from other compounds in oil is that biomarkers can reasonably be called "molecular fossils". Biomarkers are structurally similar to, and are diagenetic alteration products of, specific natural products (compounds produced by living organisms). Typically, biomarkers retain all or most of the original carbon skeleton of the original natural product, and this structural similarity is what leads to the term "molecular fossils".

Biomarkers have a variety of applications in petroleum exploration. For example:

1. When samples of oil and candidate source rocks are available, biomarkers can be used to make oil-source rock correlations, or
2. When samples of candidate source rocks are NOT available, the biomarker distribution in an oil can be used to infer characteristics of the source rock that generated the oil WITHOUT examining the source rock itself. Specifically, biomarkers in an oil can reveal (1) the relative amount of oil-prone vs. gas-prone organic matter in the source kerogen, (2) the age of the source rock, (3) the environment of deposition as marine, lacustrine, fluvio-deltaic or hypersaline, (4) the lithology of the source rock (carbonate vs. shale), and (5) the thermal maturity of the source rock during generation (e.g., Peters and Moldowan, 1993). Such data may be key inputs to effective basin modeling of a prospect or block.

Petroleum Biomarkers Indicative of Source Rock Organic Matter Input and Depositional Conditions (Table 1)
Below are a few examples of oil biomarker parameters that provide information about the depositional environment of the source rock and the origin of the organic matter in the source rock.

<table>
<thead>
<tr>
<th>Source Information</th>
<th>Biomarker Parameter</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marine Source Rock</td>
<td>24-(n)-propylcholestanes</td>
<td>Ubiquitous in oils derived from marine source rocks. (Moldowan et al., 1990)</td>
</tr>
<tr>
<td>(C_{42-46}) Cyclopentylalkanes with odd/even carbon preference</td>
<td>(Carlson et al. 1993; Hsieh and Philp, 2001)</td>
<td></td>
</tr>
<tr>
<td>Lacustrine Source Rock</td>
<td>Botryococcane</td>
<td>Presence = lacustrine source. Absence = meaningless. (e.g., Moldowan et al., 1980, Metzger and Laegeau 1999)</td>
</tr>
<tr>
<td>Sterane/Hopanes</td>
<td>Low in oils derived from lacustrine source rocks. (Moldowan et al., 1985)</td>
<td></td>
</tr>
<tr>
<td>(C_{26}/C_{25}) tricyclic terpanes</td>
<td>&gt; 1 in many lacustrine-shale-sourced oils. (Zumberge, 1987)</td>
<td></td>
</tr>
</tbody>
</table>
Tetracyclic
Polyrenoids
High in oils from lacustrine sources.
Cyclopentylalkanes (Holba et al., 2000)
with even/odd carbon preference
or with no preference

(Carlson et al.)
1993; Hsieh and Philp, 2001)
Higher plant input
to Source Rock
Oleananes,
Lupanes,
Taraxeranes
Biomarkers indicating flowering plant input to source. (e.g., Ekweozor and Udo, 1988)
Bicadinanes
Derived from
Dipterocarpaceae
tree resins. (Cox et
al., 1986)
Retene, Cadalene
Biomarkers indicating conifer input to source.
(Noble et al., 1985)
Tetracyclic
diterpanes
Biomarkers indicating conifer input to source.
(Noble et al., 1985)
C_{29} steranes
High relative to total C\textsubscript{27}-C\textsubscript{29} steranes. (Huang and Meinschein, 1979; Moldowan et al., 1985)
Coal Source Rock
Pristane/phytane
Very high in coal-sourced oils; e.g., > 3.0 (Hughes et al., 1995)
C_{31} homohopanes
High relative to total C\textsubscript{31}-C\textsubscript{35} in some coal-sourced oils
Hypersaline
Depositional
Environment
Gammacerane
High relative to $C_{31}$ hopanes in oils derived from sources deposited under hypersaline depositional conditions. High values indicate stratified water column during source deposition. (Sinninghe Damste et al., 1995)
Pristane/phytane
Very low values (e.g., < 0.5) in oils derived from source rocks deposited under hypersaline conditions (due to contribution of phytane from halophilic bacteria). (ten Haven et al., 1987; 1988)
Anoxic Depositional Environment of Source Rock
C$_{35}$ homohopanes
High relative to total hopanes in oils derived from source rocks deposited under anoxic conditions (Peters and Moldowan, 1991). Abundance of C\textsubscript{35} homohopanes in oils (Relative to C\textsubscript{31} - C\textsubscript{34} homohopanes) is correlated with source rock Hydrogen Index (Dahl et al., 1994).
Pristane/phytane
1.0 can indicate anoxic conditions, but the ratio is affected by many other factors.
Isorenieratane & related compounds
(2,3,6 and 2,3,4 - Trimethylaryl isoprenoids), Chlorobacteria
Presence in oil indicates anoxic photic zone during source rock deposition, since these compounds are biomarkers for green sulfur bacteria. (Summons and Powell, 1987; Grice et al., 1998; Koopmans et al., 1996)
V/(V+Ni) Porphyrins
High = reducing conditions. (Lewan, 1984)
28,30-bisnorhopane
High in certain reducing environments. (Schoell et al., 1992; Moldowan et al., 1984)
Carbonate Source
Rock
30-norhopanes
High in carbonate-sourced oils; e.g., $C_{29}/C_{30}$ hopanes ~ 1 (Fan Pu et al., 1987; ten Haven et al., 1988; Subroto et al., 1991)
Diasteranes/steranes
Low in carbonate-sourced oils. (Rubinstein et al., 1975; Hughes, 1984)
Dibenzothiophene/p henanthrene
> 1.0 in oils derived from high-sulfur carbonates. (Hughes et al., 1995)
2a-methylhopanes
High in carbonate derived oils
(Summons et al., 1999)
Age of Source Rock
Deposition
Oleanane
Present in oils derived from Late Cretaceous or younger sources (Moldowan et al., 1994)
(24-norcholestanes) / (26-norcholestanes)
High in many Tertiary sources. Low values are not age-diagnostic. (Holba et al., 1998A; 1998B)
Dinosteranes,
triaromatic
dinosteroids
Absence always means Pre-Mesozoic, while presence USUALLY means Mesozoic or younger. (Moldowan et al., 1996)
\text{C}_{29} \text{ Monoaromatic Steroids}
High in oils derived from sources older than 350 mybp. (Moldowan et al., 1985)
C_{11}-C_{19} Paraffins
Odd-carbon-number predominance in oil from many Ordovician sources. (Douglas et al., 1991; Fowler, 1992)
(24-isopropylcholestanes)/(24-n-propylcholestanes)
High in oils from pre-Ordovician sources. (McCaffrey et al., 1994B)

To characterize charge risk, these biomarker parameters can be used in a variety of innovative ways. For example, specific biomarker parameters can be calibrated against specific kerogen quality parameters in a given basin. Then, the biomarker ratios are measured in an oil sample from the basin, and the values are projected onto calibration curves to quantitatively predict characteristics of the source rock.

This approach, pioneered by the founders of OilTracers, allows explorationists to assess whether an oil was generated primarily from an oil-prone or gas-prone organic facies (Dahl et al., 1994; McCaffrey et al., 1994). The information gained from oil biomarkers (source type, age, maturity, kerogen quality) when integrated
into a basin model has substantial economic impact because it provides early estimates of oil quantity and GOR for exploration targets in the area of interest.

**Using Biomarkers in Oil to Assess Source Thermal Maturity**
The relative abundances of certain biomarkers in petroleum change as a function of source rock maturity. As a result, a variety of biomarker parameters have been identified that are very useful for characterizing the source rock maturity simply from analysis of the migrated oil (e.g., Peters and Moldowan, 1993).

Biomarker maturity parameters (e.g., parameters such as those in Table 2) make use of several processes that occur during source rock maturation:
1. Cracking--large molecules break into smaller molecules

2. Isomerization--changes in the 3-dimentional arrangements of atoms in molecules.

3. Aromatization--formation of aromatic rings (loss of hydrogen from naphthenes)

**Petroleum Biomarkers Indicative of Source Rock Maturity (Table 2)**

<table>
<thead>
<tr>
<th>Petroleum Fraction (Compound Class)</th>
<th>Biomarker Parameter Measured in Petroleum Fraction</th>
<th>Effect of Increasing Maturity</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated Hydrocarbons</td>
<td>C_{29} Steranes [20S/(20S+20R)]</td>
<td>Increase</td>
<td>Useful in early to mid oil window. Decreases at very high maturity levels.</td>
</tr>
<tr>
<td>C_{29} Steranes [abb/(abb+aaa)]</td>
<td>Increase</td>
<td></td>
<td>Useful in early to mid oil window.</td>
</tr>
<tr>
<td>Moretane/Hopane</td>
<td>Decrease</td>
<td></td>
<td>Useful in early oil window.</td>
</tr>
<tr>
<td>$C_{31}$ Hopane</td>
<td>Increase</td>
<td>Useful in immature</td>
<td></td>
</tr>
</tbody>
</table>
\[ \frac{[22S]}{[22S+22R]} \] rocks to onset of early oil window.
\frac{\text{Ts}}{\text{Ts+Tm}}
Increase
Also influenced by source lithology.
Tricyclic
Terpanes/Hopanes
Increase
Useful in late oil window; also increases at high levels of biodegradation.
Diasteranes/Steranes
Increase
Useful in late oil window; also affected by source lithology (low in carbonates, high in shales); also increases at high levels of biodegradation.
Aromatic Hydrocarbons
Monoaromatic Steroids: \((C_{21}+C_{22})/\)
\([C_{21}+C_{22}+C_{27}+C_{28}+C_{29}]\)
Increase
Useful in early to late oil window; resistant to effects of biodegradation.
Triaromatic
Steroids: \((C_{20} + C_{21})/\n\[C_{20} + C_{21} + C_{26} + C_{27} + C_{28}\]
Increase
Useful in early to late oil window; resistant to effects of biodegradation.
Triaromatic
/(Monoaromatic +
Triaromatic
Steroids)
Increase
Useful in early to late oil window; resistant to effects of biodegradation.

Several considerations must be kept in mind when using petroleum biomarkers to assess source rock thermal maturity. For example:

1. The exact relationship between a biomarker parameter and the source maturity is a function of heating rate, source lithofacies, and source organic facies (kerogen type). As a result, the exact maturity (i.e., vitrinite reflectance equivalent) associated with a given value for a biomarker parameter can change from basin to basin. Furthermore, the relationship between a
biomarker maturity indicator and source rock maturity is generally non-linear.

2. With increasing maturity, many biomarker maturity indicators reach terminal values; hence, a given biomarker parameter is applicable only over a specific maturity range.

3. The concentrations of biomarkers in petroleum decrease with thermal maturity.

Despite these limitations, biomarker indicators of source maturity can be extremely useful. For example, biomarker maturity parameters can be used to determine what
the API gravity of a biodegraded oil was *prior to biodegradation*. This is accomplished by collecting a suite of *non-degraded* oils from the same petroleum system as the degraded oils. Using the non-degraded oils, the geochemist develops a correlation or "transform" between a biomarker maturity parameter and API gravity. The same biomarker parameter is then measured on a degraded oil, and the original gravity is determined using the transform developed from the non-degraded oil suite. Moldowan, et al. (1992) provide an excellent example of this approach in which they determine the original gravity of degraded Adriatic oils. For this application, the most effective biomarker parameters are those based on compounds that are highly resistant to biodegradation, such as 

\[ \text{Triaromatic}/(\text{Monaromatic} + \text{Triaromatic steroids}) \].
Source Rock descriptions and source rock maturity information derived from oil biomarkers are often key input data for basin modeling of a prospect or block.

Biomarkers in Petroleum are analyzed by gas chromatography mass spectrometry (GC-MS) or gas chromatography - tandem mass spectrometry (GC-MS-MS). Analyses are typically performed on the saturated hydrocarbon fraction or the aromatic hydrocarbon fractions. The oil fractions are prepared by liquid chromatography.
source: Weatherford Laboratories Service