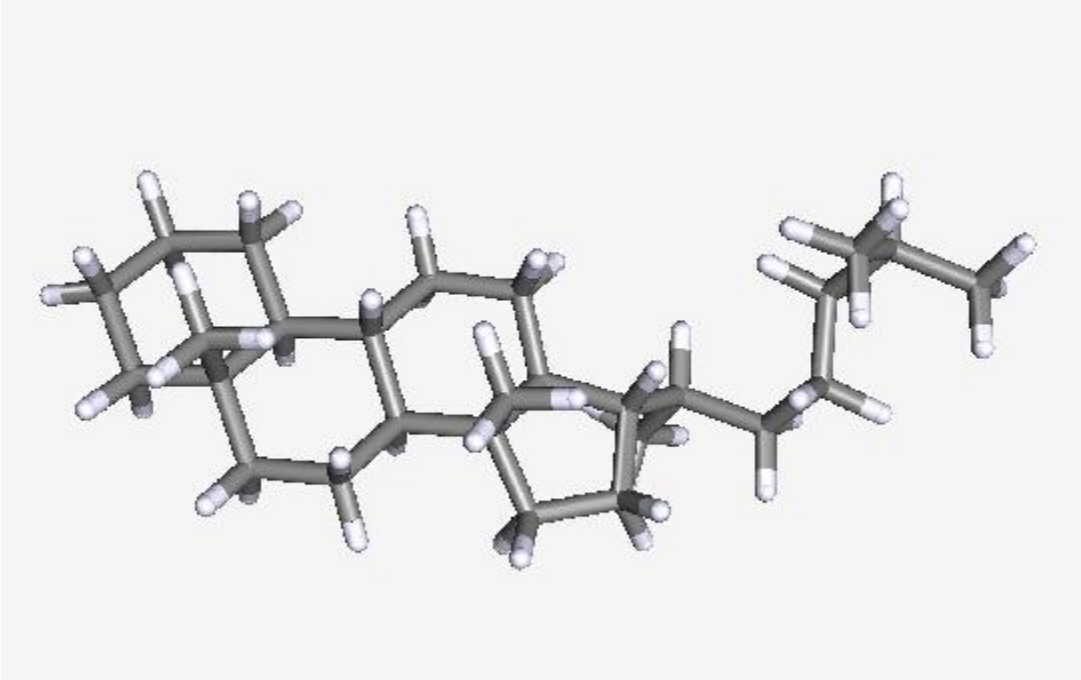
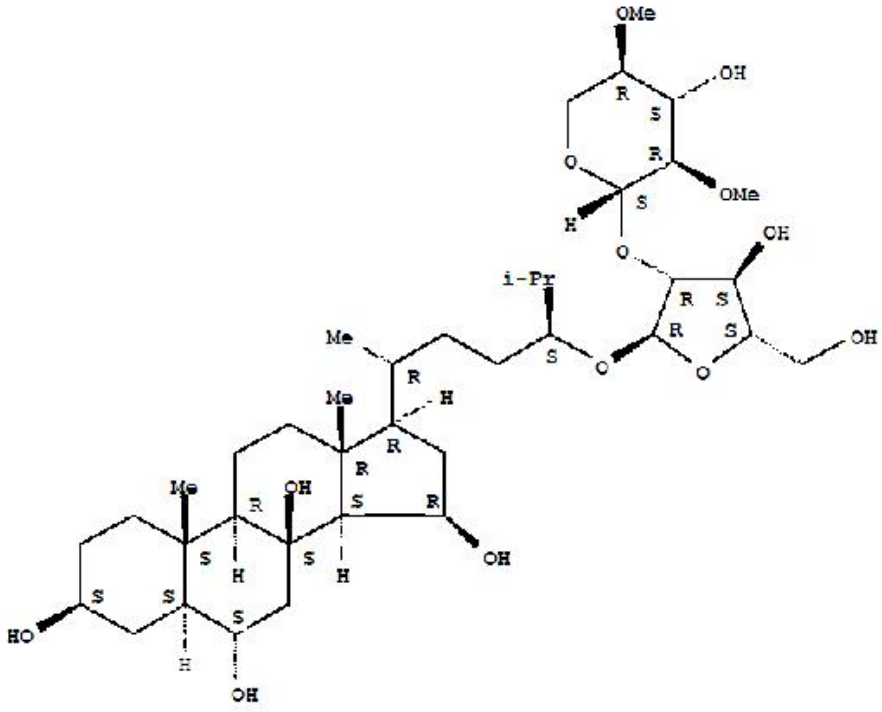
USING OIL BIOMARKERS IN PETROLEUM EXPLORATION

Biomarkers are a group of compounds, primarily hydrocarbons, found in oils, rock extracts, Recent sediment extracts, and soil extracts. Biomarkers consist of complex organic molecules whose chemical structures can remain largely unchanged during the processes of diagenesis and oil generation. This often allows them to be traced back to the original molecules in once living organisms. For this reason they are often called molecular fossils. They 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".



Some biomarkers are prolific in many organisms while others are only found in specific types of organisms and hence these can be used as markers of source input. Additionally, some biomarkers do not appear until their parent organism has evolved, and therefore the presence of these compounds can be used as an age diagnostic marker. Similarly, some biomarker structures are more stable in certain depositional environments than others and hence their abundance can be used to infer depositional environments. Also, subtle chemical transformation from one chemical structure into another can occur due to thermal stress and hence the ratio of these biomarkers can be used as a maturity marker.

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

- When samples of oil and candidate source rocks are available, biomarkers can be used to make oil-source rock correlations, or
- 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

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.

Source Information	Biomarker Parameter	Comments
Marine Source Rock	24-n-propylcholestanes	Ubiquitous in oils derived from marine source rocks. (Moldowan et al., 1990)
	C42-46 Cyclopentylalkanes with odd/even carbon preference	(Carlson et al. 1993; Hsieh and Philp, 2001)
Lacustrine Source Rock	Botryococcane	Presence = lacustrine source. Absence = meaningless. (Moldowan et al., 1980, Metzger and Laegeau 1999)
	b-Carotane	Presence = lacustrine source. Absence = meaningless. (Hall and Douglas, 1983; Jiang and Fowler, 1986)
	Sterane/Hopanes	Low in oils derived from lacustrine source rocks. (Moldowan et al., 1985)
	C26/C25 tricyclic terpanes	> 1 in many lacustrine-shale-sourced oils. (Zumberge, 1987)
	Tetracyclic Polyprenoids	High in oils from lacustrine sources. (Holba et al., 2000)
	C42-46 Cyclopentylalkanes 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. (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)
	C29 steranes	High relative to total C27-C29 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)
	C31 homohopanes	High relative to total C31-C35 in some coal-sourced oils
Hypersaline Depositional Environment	Gammacerane	High relative to C31 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	C35 homohopanes	High relative to total hopanes in oils derived from source rocks deposited under anoxic conditions (Peters and Moldowan, 1991). Abundance of C35 homohopanes in oils (Relative to C31-C34 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., C29/C30 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/phenanthrene	> 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)
	C29 Monoaromatic Steroids	High in oils derived from sources older than 350 mybp. (Moldowan et al., 1985)
	C11-C19 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 processes that occur during source rock maturation:

- ***Cracking***--large molecules break into smaller molecules
- ***Isomerization***--changes in the 3-dimentional arrangements of atoms in molecules.
- ***Aromatization***--formation of aromatic rings (loss of hydrogen from naphthenes)

Petroleum Biomarkers Indicative of Source Rock Maturity

Petroleum Fraction (Compound Class)	Biomarker Parameter Measured in Petroleum Fraction	Effect of Increasing Maturity	Comments
Saturated Hydrocarbons	C29 Steranes [20S/(20S+20R)]	Increase	Useful in early to mid oil window. Decreases at very high maturity levels.
	C29 Steranes [*abb*/(*abb*+*aaa*)]	Increase	Useful in early to mid oil window.
	Moretane/Hopane	Decrease	Useful in early oil window.
	C31 Hopane [22S/(22S+22R)]	Increase	Useful in immature rocks to onset of early oil window.
	Ts/(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: (C21+C22)/[C21+C22+C27+C28+C29]	Increase	Useful in early to late oil window; resistant to effects of biodegradation.
	Triaromatic Steroids: (C20+C21)/[C20+C21+C26+C27+C28]	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.

Various 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 [Triaromatic/(Monaromatic +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 are generally minor components of a crude oil or rock extract, and highly selective and sensitive methods of analysis employing gas chromatography – mass spectrometry (GC-MS) are necessary for their measurement. Typically a crude petroleum sample is separated into a saturate and aromatic fraction prior to biomarker analysis and then both fractions are analyzed independently. This provides greater resolution with less interference and allows for the determination of biomarker concentrations down to the low ppm and ppb levels. It is typical for a single analysis to monitor several hundred biomarkers. If additional selectivity is needed to resolve more complex biomarker distributions a tandem mass spectrometry technique (GC-MSMS) is used to analyze and distinguish biomarkers further.

For more information on the techniques described here, or to discuss a specific project, e-mail us at oiltracers@weatherfordlabs.com, or call us at U.S. **(214) 584-9169.**

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