



## Geochemical Implication of some Chemical Fossils as Indicators of Petroleum Source Rocks

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**ABSTRACT:** Chemical fossils (biomarkers) are molecules in crude oils, source rocks and sediments whose carbon structures or skeletons can be traced back to living organisms. Three of such diagnostic fossils have been typically reviewed with respect to maturation changes, precursor-product relationship, utility for source rock/crude oil, crude oil/crude oil correlations and role in basin development. Fingerprints (composition and distribution) of hopanes, oleananes and steranes have been highlighted. Defunctionalization and breakage of double bonds which occur during diagenesis as well as stereochemical changes which occur during catagenesis have also been highlighted. Napthenic hydrocarbons, such as steranes (C<sub>27</sub> - C<sub>29</sub>) and triterpanes (C<sub>29</sub> - C<sub>32</sub>), are useful in geochemical correlations because of their unique compound distributions and the fact that they are not seriously affected by migration, thermal alteration and biodegradation. Although individual biomarkers are in concentrations of only 10 to 200 ppm in crude oils, they can be accurately measured in spite of their unusual complexity and variety which find use in source rock correlation and maturation studies. Correlations using chemical fossil technology can be applied in real cases by recognizing the source chromatogram (GC) or fragmentogram of the hydrocarbon molecules in the oils to know whether they have the same biomarkers or similar geohistory of origin and migration. Therefore, genetically related oils are differentiated from unrelated oils on the assumption that the same source material and environment of deposition produce the same oil. Thus, a chemical fossil compound in a particular source rock would be expected to appear in the oils it generated. @JASEM

The determination of the origin and fate of past life has traditionally been the preserve of paleontologists, palynologists and sedimentologists. They have relied on the morphology of macro, micro and trace fossils to identify possible biotic precursors and infer the origin, and age of the rocks in which the remnants of erstwhile living organisms are found (Tissot and Welte, 1984; Kruger, 1986; Lo, 1992; Magoon and Dow, 1994). Regrettably, some sedimentary rocks, for example, those containing mainly amorphous organic matter (Types 1 and 11 kerogen) often contain few or no fossils, and besides, these traditional methods cannot be applied to petroleum which being a fluid, possesses neither macro- nor micro-fossils for visual or microscopic examination. Hence, paleoreconstruction of cases such as these can only be effectively undertaken at the molecular level by means of biomarkers, otherwise called chemical-fossils (Pym, 1975; Petters, 1980; Philp and Gilbert, 1986; Ekweozor and Telnaes, 1989; Moldowan et al., 1992; ).

Chemical fossils are molecules in crude oils, source rocks and sediments whose carbon skeletons can be traced back to living organisms (Hunt, 1996). These organic compounds which are unequivocally related to their natural product precursors originated from chemical and geological transformation of biomolecules of organisms that were deposited during sedimentary processes. Within the stable carbon-carbon skeleton of such compounds are embodied essential information on the habitat, nature and fate of the ancestral flora and fauna which can

facilitate the reconstruction of environment of deposition of ancient sediments and petroleum. Such compounds may also provide information on the thermal history of a basin or parts of a basin (Ekweozor and Strauz, 1983; Kleme, 1989; Peters and Moldowan, 1993; Peters and Cassa, 1994). The composition and distribution (fingerprint) of certain diagnostic chemical fossil can therefore indicate the dominant source of sedimentary organic matter (marine or non-marine), the physicochemical conditions prevalent and the paleoenvironment (oxicity/anoxicity and salinity status) as well as the maximum thermal stress experienced by the rocks or petroleum in which the compounds are found (Staplin, 1979; Ekweozor

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and Strauz, 1982). Since petroleum is generated from the organic matter in fine-grained rocks, it is possible to relate oil accumulations in a stratigraphic column with specific source-rock intervals by biomarker fingerprinting. Crude oils having a common source, but reservoired at different horizons in a field or basin can likewise be correlated with one another (Idowu and Ekweozor, 1989; Idowu et al., 1993; Hunt, 1996; Osuji and Antia, 2002).

Typical chemical fossils include the terpenoids (e.g., pristane, phytane, sterane, hopane); the porphyrins (e.g., chlorophyll), the odd-numbered n-paraffin carbon chains (e.g., C<sub>25</sub> to C<sub>37</sub>) the iso- and anteiso- branched carbon chains (e.g., 2-Methyldecane and 3-Methyldecane respectively)

(Ekweozor, 1978; Ekweozor et al., 1979a and b; Noble, 1991; Hunt, 1996).

#### Maturation Changes And Precursor-Product Relationship

The thermal break-down of kerogen to form oil during catagenesis results in significant changes in the biomarkers that enable them to be used for source-rock evaluation. The predominance of the odd-carbon normal-paraffin chains formed biologically is destroyed through the break-down of larger equal amounts of even and odd chains generated thermally. Such changes as defunctionalization and breakage of double bonds are common during diagenesis (Fig. 1). In the hopane family (hopanoids) for example, the hydroxyl groups are lost forming olefins; there is also breaking of double bonds, but the ring system remains intact. Other prominent features of hopane maturation include stereochemical changes at C-27, C-24 and C-29 and the possibility of carbon-carbon cleavage. As seen in Fig. 2, these features occur during catagenesis of the hopanoids where A (22R) is the least stable and C (22R + S) the most stable. The abundance of R and S tells how close the geological material is to the oil threshold (TIHG). Another typical example of maturation changes is seen in the conformational transformation of the oleananes (Unomah, 1989). The oleananes have a biological conformation of a major 18 $\beta$ (H) and minor 18 $\alpha$ (H), and a geological conformational inversion shows the precursor-product relationship in the oleanoids, as seen in the schematic in Fig. 3. Apart from the hopanoids and oleanoids, there are other typical examples of maturation changes in chemical fossils, all of which show precursor-product relationship. These include 2,6,10,4-tetramethylpentadecane which has an original configuration of 6 (R), 10 (S) in the biosphere, but isomerizes into the 6 (S), 10 (S) and 6 (R), 10 (R) isomers in the geosphere giving a final mixture of the three configurations in the ratios 2: 1: 1 for the 6 (S), 10 (R); 6 (S), 10 (S) and 6 (R) configurations. For Steranes, transformations occur from 14 $\alpha$  (H), 17 $\alpha$  (H): 20 (R) conformation to 14 $\beta$  (H), 17 $\beta$  (H): 20 (R+S) as final conformation. These molecular or configurational transformations give an insight into the degree of maturation, thermal stress that sediments have passed through and other vital information necessary for paleoreconstruction. (Simoneit, 1986; Ekweozor and Udo, 1987; Mango, 1990; Magoon and Dow, 1994; Hunt, 1996).

Utility And Problems Of Chemical Fossils  
n- Alkane Distribution

The evaluation of the n-alkane distribution is a standard method of classifying oils and rocks according to whether terrestrially or marine-derived organic matter predominates in the source rock. Terrigenous organic matter contributes to the high molecular weight usually with odd-even carbon number predominance (OEP) in the range C<sub>25</sub> to C<sub>35</sub> and with maximization at C<sub>27</sub>, C<sub>29</sub> or C<sub>31</sub> alkanes. The Carbon Preference Index (CPI) and the Odd/Even Carbon Ratio (OER) are both commonly used as a measure of maturity of organic matter and are defined as follows:

$$CPI = \frac{C_{17} + C_{19} + \dots + C_{29} + C_{31}}{C_{17} + C_{19} + \dots + C_{29} + C_{31}} \quad (1)$$

$$C_{16} + C_{18} + \dots + C_{28} + C_{30} \quad C_{18} + C_{20} + \dots + C_{30} + C_{32}$$

$$OER = \frac{2 \times C_{30}}{C_{28} + C_{30}} \quad (2)$$

Both the CPI and OER in terrestrial organic matter decreases from over 5.0 in recent sediments to 1.0 in mature sediments and oils as well as in mature marine organic matter (Brassel et al., 1978)

Pristane/n-C<sub>17</sub> vs. Phytane /n-C<sub>18</sub> plot and Pristane/Phytane Ratio

The nature of the organic matter and the redox potential in the depositional environment during early diagenesis of the main precursor of phytane and pristane, i.e., chlorophyll, or specifically its phytol chain, is generally reflected by the ratio of Pristane (Pr) to Phytane (Ph). Marine organic matter usually have Pr/Ph ratio < 1.5 while terrestrial O.M. have ratios 3.0. Pr/Ph ratio therefore increases with increasing maturity. The ratio Pr/n-C<sub>17</sub> has been used to differentiate O.M. from swamp environment (>1.0) from those formed under marine environment (<0.5), but this ratio is affected by maturity, as well as biodegradation, hence the use of a crossplot of Pr/n-C<sub>17</sub> against Ph/n-C<sub>18</sub>. (Seifert, 1977; Ekweozor, 1978; Ekweozor et al., 1981; Philp et al., 1983; Unomah, 1989; Moldowan et al., 1992).

*Steranes and Hopanes*

The isomeric distribution of the steranes and diasteranes have been used for assessing the maturity of source rocks. Naturally occurring steroids and steranes from recent sediments have exclusively 5 $\alpha$ (H) or 5 $\beta$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H) conformation while an increased proportion of the 20S isomer is generated with maturity. Hence, the ratio, 20S / 20S

+ 20R - C<sub>29</sub> sterane, has a starting value of 0.0 in recent sediments, but progresses to an equilibrium mixture achieved well into the oil window (TOGW). The onset of oil generation starts at 0.4. Similarly, hopanes can be used for assessing the maturity of source rocks. Thus, the ratio:

$$C_{31} \text{ homolopane,} = \frac{22S}{22 + 22R}$$

has a starting value of 0.0 and an equilibrium value of 0.6, the complex isomerization at C-22 being achieved before the threshold of intense hydrocarbon generation (TIHG).

#### Tricyclic and Pentacyclic Terpanes

Abundant tricyclic terpanes have been detected in crude oil and source rock extracts. Philp and Gilbert (1986) indicated that extended tricyclic terpanes were abundant in marine sourced oils but generally absent in terrigenous oils. Ekweozor et al (1979a and b) also reported that some tricyclic terpanes were present in the Niger Delta oils and were derived from sequential cleavage of the bonds of pentacyclic terpanes. Ekweozor and Strauz (1982) identified some C<sub>19</sub> - C<sub>30</sub> tricyclic alkanes from a hexaisoprenoid precursor. The distribution of pentacyclic triterpanes alone have been very useful in source rock/crude oil correlations. Triterpane mass chromatograms such as that of m/e 191 have been used to compare various crude oils (Pym et al 1975; Hunt, 1996)

#### Chemical Fossils in Basin Development

The most relevant geochemical criteria are those, which reflect the genetic relationship between organic matter at different levels in the stratigraphic column as well as provide information about migration of the mobile fluids. The data which they provide are useful for source rock/crude oil, and crude oil/crude oil correlations which are usually based on the recognition of compositional similarities. (Ekweozor et al., 1976b; Tissot et al; 1974 Brassel et al; 1978). Correlation of crude oil accumulations at different stratigraphic depths (horizons) in a well or in oil fields located at different positions of a basin, is useful in determining the importance of vertical and lateral migration in the area. This information, when complemented with other geological criteria that indicate locations of structures such as traps and faults, is useful in elucidating the most likely migration patterns and hence would facilitate a more accurate siting of future wells during basin development. (Brassel et al., 1978; Staplin, 1979; Ekweozor et al, 1979a;

Yukler, 1987; Hunt, 1996). Each family of oils represents one element of a distinct petroleum system. Consequently, identifying the number of oil families is equivalent to defining the number of petroleum systems. By identifying the source rocks of each family, the drilling can focus on prospects within the drainage areas of those sources (Cooper, 1990).

#### Application of Biomarker Fingerprints in Real Cases

Gas chromatograms or fragmentograms have been widely used for correlating oils and source rocks since the pioneering work of Seifert (1977) who differentiated oils produced from San Joaquin Basin of California on the basis of sterane and terpane fingerprints. Recognizing such source fingerprints of the hydrocarbon molecule enables us to know whether they have the same biomarkers or similar geohistory of origin and migration. Thus, genetically related oils can be differentiated from unrelated oils on the assumption that the same source material and environment of deposition produce the same oils in which case a chemical fossil compound in the source rock would be expected to appear in the oils it generated. Obtaining a whole oil GC fingerprint requires analyzing an entire oil for the C<sub>2</sub> - C<sub>45</sub> hydrocarbon range on a gas chromatograph with a fused silica capillary column.

#### Conclusion

The field of chemical fossil (biomarker) geochemistry is fast growing with new discoveries invalidating or drastically modifying old concepts. Chemical fossils have been found useful for both basin evaluation and development. They constitute the most widely used correlation parameters for comparing crude oils of different source, migration, and biodegradation, for both crude oil - crude oil and crude oil - source rock correlations. They also constitute the most useful method for comparing conventional oils with very heavy oils, asphalts, and pyrobitumens. A more successful correlation, however, is a multi-parameter approach using biomarkers (fingerprint and ratio), isotopes, gas chromatograms, and the content of heavy metals, nitrogen, sulphur, and the like. The study has opened new vistas in Earth Science namely "Molecular Paleontology" and "Molecular Stratigraphy", which are increasingly being put to good use in geochemical exploration.

#### Nomenclature

C<sub>22</sub>= Hydrocarbon with 22 carbon atoms.

C-22 = Carbon No.22.

CPI = Carbon Preference Index.

OER = Odd/Even Ratio.  
 OEP = Odd/Even Predominance.  
 OM = Organic Matter.  
 Ph = Phytane.  
 Pr = Pristane.  
 TIHG = Threshold of Intense Hydrocarbon Generation.  
 TOGW = Top of Oil Generation Window

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