Chapter 3
Geochemical Fossils in Crude Oils and Sediments as Indicators of Depositional Environment and Geological History

3.1 Significance of Fossil Molecules
Geochemical fossils are biological markers that can convey information about the types of organisms contributing to the organic matter incorporated in sediments. Thus, they can be used for characterization, correlation, and/or reconstitution of the depositional environment, in the same manner as macro- or microfossils are commonly used by geologists. However, it should be remembered that aside from geochemical fossils, also other molecules may be used for correlation, provided they are characteristic enough.

In addition, a comparison between the original biogenic molecule and the molecule found in source rocks or crude oils may give valuable information about the history experienced by the molecule: microbial activity or chemical rearrangement at the time of deposition, and subsequent chemical reactions during catagenesis.

The most common uses of geochemical fossils may be listed as follows:

a) as correlation parameters (oil–oil and oil–source rock);

b) for reconstitution of depositional environment;

c) for elucidation of chemical transformations during diagenesis and catagenesis;

d) for detection of contamination with foreign material in marine or freshwater Recent sediments.

The problem of oil–oil and oil–source rock correlations will be treated separately (Chap. V.2), as it is not specifically related to geochemical fossils but includes other markers.

The quality of information provided by geochemical fossils in terms of depositional environment depends on three factors:

– their state of conservation, which may or may not allow one to link them to their biochemical precursor molecule;

– the distribution of this biochemical precursor (parent molecule) in the present animal and/or plant kingdom;

– the assumption that the distribution was comparable in ancient organisms.

Conservation of the original characteristics depends mostly on the structure of the original biogenic molecule. Relatively inert molecules, such as \( n \)-alkanes, suffer little chemical alteration, and their relative abundances are affected especially by dilution, when new alkanes are generated during catagenesis. On the contrary, acids, alcohols, ketones, etc. may suffer several alterations, depending on diagenetic and catagenetic conditions: loss of functional groups, alkylation, dealkylation, reduction, aromatization, etc. As a result, the molecules found in ancient sediments may range from unchanged biogenic molecules, for example
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*n*-alkanes, and less frequently acids or alcohols, through compounds very close to the original molecule, such as steranes and triterpanes, to molecules keeping only the cyclic skeleton, like aromatic steroids.

Generally, one can expect geochemical fossils to be useful for correlation. For reconstitution of paleo-environments, however, the original structural details have to be preserved. For instance, the carbon skeleton of steroids may be derived from a wide range of specific steroids, known from a large number of animals or plants, so that the occurrence of molecules retaining only the tetracyclic nucleus cannot be linked to a particular environment of deposition.

The information deduced from the occurrence of fossil molecules is also a function of the distribution of the precursor in living organisms. On one hand, biogenic molecules, typical for certain organisms or for a class of organisms, provide information on the fossil biological association. For instance, odd-carbon-numbered high molecular weight *n*-alkanes and related waxes found in sediments are typical products of terrestrial higher plants. On the other hand, very common molecules occurring in many kinds of organisms provide little or no information on the paleogeography, facies, and environmental conditions. For example, C\textsubscript{15}–C\textsubscript{20} *n*-alkanes without odd-carbon-number predominance may be generated by all types of kerogen during catagenesis.

Therefore, the interest in geochemical fossils depends on the distribution of biochemical precursors in presently living organisms. It should be emphasized, however, that the distribution of different precursors in contemporaneous organisms is still insufficiently known. Most structural determinations of biogenic molecules carried out until now have been made for the needs of the food or drug industries.

Thus, only the organisms, or even certain parts or organisms used in industrial processes have been analyzed: tobacco leaves, grains of cereals, essential oils of higher plants, whilst the rest of the plant is practically unknown. Furthermore, the lipids, hydrocarbons, etc. synthesized or accumulated by prokaryotic organisms, and particularly bacteria, are almost unknown with regard to the numerous existing species. Nevertheless, the bacterial biomass can in some cases be very significant compared to the total organic input. An example of the still incomplete knowledge on the occurrence of biochemical precursors of geochemical fossils in living organisms is pentacyclic triterpenoids of the hopane series. They were first considered as characteristic of lower terrestrial plants, as they were mostly known from ferns, mosses, and other plants. Later they were discovered in one anaerobic bacteria, then in several other prokaryotic organisms stemming from many different environments (Ensminger et al., 1974, van Dorsselaer, 1975). In fact, since then they have been found in many ancient sediments including petroleum source rocks, oil shales, coals, and also in crude oils, proving that they are very wide-spread in geological conditions (van Dorsselaer, 1975).

A new tool for relating fossil molecules to existing biogenic compounds is stereochemistry. Ackman et al. (1972), Cox et al. (1972) and Maxwell et al. (1973) demonstrated the interest of stereochemistry of acyclic isoprenoids to clarify this relationship. Along the same line, Ensminger et al. (1974) distinguished the importance of the genetic heritage and the subsequent evolution in the stereochemistry of pentacyclic molecules of the hopane type.