What are age-diagnostic biomarkers? by Paul Farrimond

Biomarkers (<u>bio</u>logical <u>marker</u> compounds), in a petroleum geochemical context, are molecules found in oils and source rocks that have a chemical structure that can be unambiguously linked to a known natural product in living organisms. They can be considered as "chemical fossils" (Eglinton & Calvin, 1967) left behind by ancient organisms. The best-known groups of biomarkers are the hopanes and steranes which have long been used in oils to determine the environment of deposition, lithology and maturity of the source rock, and in correlations between different oils and their potential source rocks.

Significantly, biomarkers also have the potential to provide information about geological age. This is due to the evolution and extinction of organisms over geological time, and their changing biochemistry; changes that resulted in changes to the biomarkers preserved in the rock record.

Oleanane is an example of an age-diagnostic biomarker associated with the evolution of land plants, specifically the angiosperms (flowering plants). Although angiosperms originated earlier, they became widespread during the Cretaceous, leaving oleanane (and other related compounds) as chemical fossils in many Cretaceous and younger sedimentary rocks (Moldowan *et al.*, 1994). The Oleanane Index (oleanane relative to $C_{30} \alpha\beta$ hopane; see Figure) is thus a very useful age-diagnostic geochemical parameter to recognise Cretaceous and Tertiary aged samples.



Figure: Three age-diagnostic biomarker parameters driven by: (1) the evolution of land plants (Oleanane Index), (2) the evolution of marine phytoplankton (Norcholestane Ratio) and (3) the Triassic-Jurassic extinction event (Extended Tricyclic Ratio).

The steranes in marine source rocks and oils are mostly derived from phytoplankton, and their composition has changed through geological time due to the evolution of the dominant phytoplankton groups. One of the most reliable age-diagnostic parameters based on these changes is a ratio of two groups of C₂₆ steranes (norcholestanes; Holba *et al.*, 1998). The ratio of 24-nor/27-norcholestanes (see Figure; or nordiacholestanes) expressed as an index (Norcholestane Ratio [NCR] and Nordiacholestane Ratio [NDR] respectively) increases progressively in marine-sourced oils through the Jurassic, Cretaceous and Tertiary due to the evolution and diversification of the dinoflagellates, coccolithophores and diatoms. Higher values of this parameter are typically found in oils with the youngest source rock.

Drastic changes to primary producers of sedimentary organic matter due to Earth's major extinction events can also cause a change in the biomarker record. The Triassic-Jurassic extinction event (~200 Ma ago), thought to have resulted from huge volcanic eruptions associated with the rifting of Pangea and the emplacement of the Central Atlantic Magmatic Province, apparently caused a reduction in the amounts of extended (C_{28} +) tricyclic terpanes in Jurassic oils compared to Triassic-sourced oils (Holba

et al., 2001). The Extended Tricyclic terpane Ratio (ETR; see Figure) is the ratio of $C_{28} + C_{29}$ tricyclic terpanes to the rearranged C_{27} hopane Ts, and generally falls significantly across the Triassic-Jurassic boundary because of the loss of many unidentified organisms that produced the precursors of the extended tricyclic terpanes.

There are other age-diagnostic biomarker parameters than those mentioned here, but almost all can only be used for oils of Triassic age or younger. C_{30} sterane isomers can be used to recognize Late Proterozoic to Early Cambrian-sourced oils (McCaffrey *et al.*, 1994), and particularly prominent C_{17} & C_{19} *n*-alkanes are associated with some Ordovician oils with abundant *Gloeocapsomorpha prisca* input, but at the present time there are very few age markers that can be applied in the Paleozoic. This gap has attracted some research (e.g. Schwark *et al.*, 2006), and continues to do so.

References

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