The use of 28,30-Bisnorhopane as a stratigraphic marker *by Laura Garner*

The demethylated hopane 17α , 21β (H)-28, 30-bisnorhopane (Figure 1) is a compound regularly used as a stratigraphic marker, particularly for Upper Jurassic source rocks and associated expelled oils within the North Sea and Norwegian Sea; however, there is still very little known of its origin.



Figure 1. Molecular structure of 28,30-Bisnorhopane and identification on m/z 191 GC-MS trace.

Seifert *et al.* (1978) proposed several fern constituent precursors such as adipedatol, adiantone and 21-hydroxyadiantone (Figure 2). The possibility of an enrichment in bisnorhopane due to a molecular sieve effect in nature (due to pore size of the inorganic matrix) was also suggested by these authors but is no longer considered. Grantham *et al.* (1980) identified small concentrations of bisnorhopane within pre-Devonian source rock extracts and related crude oils. Ferns are not thought to have existed prior to the Devonian, and therefore the formation of the hopane from such precursors is unlikely unless produced by an unknown organism active during the depositional environment of the source rocks.



Figure 2. Molecular structure of adipedatol and adiantone, potential precursors of 28,30-bisnorhopane.

©IGI Ltd., Hallsannery, Bideford, Devon EX39 5HE, UK. Tel. +44(0)1237 471749, Fax. +44(0)1237 421700, email. info@igiltd.com, web. www.igiltd.com A more widely accepted theory of a chemoautotrophic bacteria precursor has been proposed by numerous authors. Katz & Elrod (1983) identified an inverse correlation between the increasing abundance of bisnorhopane and decreasing pristane/phytane ratio, suggesting that bisnorhopane concentration is related to a strongly anoxic depositional environment. Schoell *et al.* (1992) used compound specific isotope analysis (CSIA) to determine the likely bacterial origin of 28,30-bisnorhopane. The isotopic signatures of the bisnorhopane stereoisomers within the immature Monterey-sourced oils are between 8-9‰ lighter than the whole oil, and around 6-8‰ lighter than other hopane compounds (Figure 3). This suggests that the precursor of bisnorhopane occupied a specific and different ecological niche compared to other hopane-synthesising organisms. The depletion in δ^{13} C within bisnorhopane requires biosynthesis by an organism that utilises δ^{13} C-depleted substrates, namely chemoautotrophic bacteria such as nitrifying and/or sulphur-oxidising species.



Figure 3. (Adapted from Schoell *et al.*, 1992) Stable carbon isotopic composition of 28,30-bisnorhopane and other hopane biomarkers in Monterey crude oil.

An unusual aspect of 28,30-bisnorhopane is that it is not found as part of the kerogen structure (as regular hopanes are) but is present only as a free (solvent-soluble) compound within the rock, as highlighted by Noble *et al.* (1985). Conducted pyrolysis experiments only yielded the common hopane and moretane series, indicating that the bisnorhopane (or its precursors) have not been part of the organic material incorporated into the kerogen matrix. At increasing levels of thermal maturity, the generation and release of hydrocarbons (containing regular hopanes) from the kerogen, results in the dilution of bisnorhopane, which explains why lower relative abundances of bisnorhopane are evident within crude oils compared to source rocks. Bisnorhopane/hopane ratios are therefore only a useful correlation parameter when samples have similar thermal maturities.

Both facies composition and thermal maturity therefore have important controls over the presence and abundance of bisnorhopane within oils and source rocks. Grantham *et al.* (1980) and Mackenzie *et al.* (1983) identified decreasing bisnorhopane content with decreasing organic sulphur content (the latter being shown to decrease as crudes are generated from increasingly more mature source rocks), indicating that potentially thermal maturity is the

biggest factor in bisnorhopane abundance in fluids. Conversely, Hughes *et al.* (1985) indicated the opposite trend to both Grantham and Mackenzie, in that relative bisnorhopane contents increased with decreasing sulphur contents (Figure 4), suggesting that concentrations are likely more facies controlled than due to thermal maturity.



Figure 4. (Adapted from Hughes *et al.*, 1985) Increasing bisnorhopane/hopane ratio to decreasing sulphur (wt.%) within greater Ekofisk crude oils.

It is important to note that although 28,30-bisnorhopane is typically associated with anoxic Upper Jurassic source rocks such as the Kimmeridge Clay Formation (KCF), this compound is not universally present in this stratigraphic interval. Dahl (2004) used 28,30-bisnorhopane as a stratigraphic marker in the North Viking Graben of the Norwegian North Sea, where higher relative amounts of bisnorhopane characterise the older "syn-rift" section of the Upper Jurassic Draupne Formation, with little to no bisnorhopane present within the younger "post-rift" Draupne section. Dahl & Speers (1985) and Schou *et al.* (1985) presented a marked absence of bisnorhopane in the KCF, with the former author highlighting the presence of the compound in the older Heather Formation. This supports that although bisnorhopane can be used as a stratigraphic marker, its absence does not exclude sourcing from the Upper Jurassic in the North and Norwegian Sea.

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