

UNEXPECTED DEMETHYLATED HOPANES AND HOMOHO PANES IN OILS AND ROCK EXTRACTS FROM A BRAZILIAN MARGINAL BASIN

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The formation of 25-norhopanes by the microbial removal of the methyl group at C-10 in the hopanes nucleus during petroleum biodegradation is well documented in the literature (Peters *et al.*, 2005). On the other hand, the presence of 25-norhopanes in apparently non-biodegraded or slightly biodegraded oils is also observed. Is the presence of 25-norhopanes in this case suggesting an intense biodegradation event in the initial phases of reservoir filling? Or is there a possible source component of 25-norhopanes which was present since petroleum expulsion?

To investigate these hypotheses, quantitative analyses have been performed to evaluate the presence and abundance of the series of 25-norhopanes ranging from C₂₆ to C₃₄ in a set of oil samples with an increasing level of biodegradation, as well as in related immature source rocks from a Brazilian marginal basin.

The series of demethylated hopanes has been identified by MRM-GC-MS analyses in all oil samples, regardless of the aspect of the GC trace and the API gravity. Hence, even samples in which the GC trace showed no or slight biodegradation contained all the series of demethylated compounds, although the series from C₃₀-C₃₄ is present in very low amounts (< 5ppm in the saturated fraction). Two hypotheses can be advanced for the generalized presence of demethylated hopanes. On the one hand, it is possible that a certain background amount was present in the original oil since the onset of reservoir filling. In this case, the varying abundance of 25-norhopanes could be interpreted as the result of their relative enrichment due to different extents of biodegradation on a pristine oil already containing demethylated hopanes. On the other hand, reservoir filling can be envisaged as a continuous process in which alternate discrete events of charging and biodegradation follow in close succession. In the more intense biodegradation events, 25-norhopanes would be formed by demethylation of their hopane precursors. The formation of demethylated hopanes would be related only to bacterial activity on the hopanes compounds after the depletion of normal and branched alkanes.

Quantitative results of 25-norhopanes in extracts of potential source rocks in an immature stage demonstrate that in most extracts this compound series is present in very low concentrations. Hence, one can admit that a background amount of demethylated hopanes is

source-derived and inherited from the originally expelled oils, being present in oils submitted to no or slight biodegradation. Thereafter, with increasing biodegradation, their concentrations in the oil would relatively increase due to the greater susceptibility of other compounds to bacterial attack. However, our results indicate that the concentrations of 25-norhopanes increase by almost two orders of magnitude in the most biodegraded oils, and this increase cannot be explained solely by the enrichment related to the estimated maximum oil mass loss due to biodegradation, which is around 50-60% (Larter *et al.* 2005). Therefore, neoformation of 25-norhopanes by demethylation of their hopane precursors must be invoked to explain the increase of their concentrations in the studied oils. Our quantitative results established that there is an inverse relation between the hopane precursor (C₃₀ hopane) and its demethylated product (C₂₉ 25-norhopane) with increasing biodegradation. Furthermore, it is worth noticing that the decrease of C₃₀ hopane is not completely compensated by the formation of C₂₉ 25-norhopane, as also indicated by Bennett *et al.* (2005).

According to the new data obtained on Brazilian oils and their related source-rock extracts, the presence of the 25-norhopane series in oils can be interpreted as the combined result of processes previously considered under two independent hypotheses. The fact that apparently non-biodegraded oils contain 25-norhopanes can be explained by a source component of these compounds since petroleum expulsion. Therefore, the presence of these compounds in small amounts (< 5 ppm) cannot serve as a definitive indication that a paleobiodegradation event has occurred. From this point on, with the progress of biodegradation, source-derived 25-norhopanes will be relatively enriched in the oils. Concomitantly, as saturates are severely affected by biodegradation, neoformation of 25-norhopanes from their hopane precursors will occur. Nevertheless, not all hopanes are transformed into 25-norhopanes, and the extent of conversion of one into the other is quite variable. Hence, a unique scale relating extent of biodegradation and amounts of 25-norhopanes seems not to exist.

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