## Comparison between free and bound biomarkers in petroleum source rocks

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For petroleum exploration, aliphatic biomarkers which are useful in oil-source correlation, maturity assessment, and palaeoenvironment reconstruction frequently suffer from drilling mud contamination or microbial degradation. In addition, the source-related biomarkers are systematically altered by increasing maturity. To attenduate these distractions, we developed a new method, namely MSSV-Hy, to release the covalently bound biomarkers from the petroleum source rock sample, which utilises PtO2 and tetralin as catalyst and hydrogen donator, respectively.

Free and bound biomarkers of 21 samples, from six productive shales, were systematically investigated. The major difference between those two types of biomarkers lies in the absence of rearranged biomarkers, e.g., diasterane and trisnorneohopane, in the bound fraction. When Ro is lower than 0.85%, diagnostic parameters between free and bound biomarkers are highly comparable. For example, gammacerane index, homohopane index,  $C_{30}$  sterane index, and the  $C_{27}$ - $C_{28}$ - $C_{29}$  sterane ratio, which are indicators of palaeosalinity, redox condition, and precursor input, are proportional to each other in these two fractions. Importantly, the bound biomarkers are much less susceptible to contamination. When Ro is between 0.85-1.00%, most free normal steranes are transformed to diasteranes in response to the thermal stress but bound sterane biomarkers continue to provide key information on the source of the organic matter. Since the isomerisation of biomarkers is heating rate dependent (Strachan et al., 1989), the maturity indicators in the free and bound fractions are not identical but still generally proportional to each other.

Releasing bound biomarkers by the MSSV-Hy method not only provides practical solutions for problems traditional biomarkers may encounter in petroleum exploration, but also offers a new window to investigate the incorporation, the release and the evolution of biomarkers in sedimentary rocks.