

**KEROGEN-BOUND BIOMARKER PARAMETERS AT ELEVATED MATURITIES**Robert S. LOCKHART<sup>1</sup>, Will MEREDITH<sup>1</sup> and Colin E. SNAPE<sup>1</sup>*1. Nottingham Fuel and Energy Centre, SChEME, University of Nottingham, NG7 2RD, UK.*

Hydropyrolysis (hypy), is pyrolysis assisted by high hydrogen pressure (~15 MPa) and a dispersed sulphided Mo catalyst, has been proven to release extremely high yields (>65%) of hydrocarbons covalently bound into the kerogen of petroleum source rocks (Type I & II kerogens) and high volatile coals (Type III kerogens), with overall conversions of organic matter >85% (Love *et al.*, 1995). The hydrogen gas-sweep mechanism, crucially, allows hydropyrolysates, and associated biomarkers of the kerogen-bound phase, to retain their original stereochemistries, offering far superior skeletal preservation of biomarkers released from source rocks, compared to traditional pyrolysis techniques (Roberts *et al.*, 1995).

It has already been described, using isolated examples, that kerogen-bound hopanes and steranes undergo the same epimerisation reaction pathways as their solvent extractable, free counterparts within the bitumen, but are generally less mature in terms of isomerisation at both ring and side-chain chiral centres (Murray *et al.*, 1998), suggesting a much greater sensitivity to relatively small changes in maturity. These clathrated biomarkers display other characteristics of retarded thermal maturation thanks to the protection they have been afforded whilst bound within the macromolecular structure of the kerogen. Features of the bound phase include an absence of rearrangement products such as diasteranes and 18 $\alpha$ ,21 $\beta$ -22,29,30-trisnorneohopane (Ts) within  $m/z$  217 &  $m/z$  191 chromatograms respectively.

Using a variety of commonly accepted maturity parameters we present a comprehensive study of the retarded, but much higher resolution thermal maturity signal provided by kerogen-bound biomarkers, in comparison with those found in the solvent extractable phase. The covalently-bound biomarkers released via the hydropyrolysis of maturity sequences spanning the entire oil-generation window across three different suites of Type I, II and III kerogen are being examined, results presented here are representative of a suite of North Sea, Kimmeridge Clay Formation source rocks where HI reaches as low as 35 mg HC/g TOC. Importantly, this study presents a first insight into the behaviour of bound-biomarkers at elevated (late and post oil-window) maturities, where solvent extractable biomarkers have limited application. As described in Fig. 1(a) maturity parameters calculated for bound-biomarkers appear to react more sensitively than free-biomarkers to changes in thermal maturity at hydrogen indices (HI) greater than ~250 mg HC/g TOC, at which point

they appear to reach a thermodynamic equilibrium, with other factors including those source-related, becoming more important at elevated maturities.

It is well documented that many aliphatic biomarker maturity parameters obtained using the solvent extractable phase, reach equilibrium prior to the main part of the oil generation window (Zhang *et al.*, 2005). In some extreme cases aliphatic maturity parameters often show inversion at elevated maturities. Such trends are of course mirrored within aliphatic bound biomarkers profiles, albeit with a retarded rate of reaction, and larger variation in intensity. This study, the first to investigate the behaviour of covalently-bound aromatic biomarkers at elevated maturities, reports the first appearance of triaromatic steroids in bound-biomarker profiles, which interestingly only appear within samples of very high maturity,  $HI \geq 35$  mg HC/g TOC. Empirical ratios using methylhomologs of compounds like phenanthrene and dibenzothiophene have a limited application to bound biomarkers however, as indicated in Fig. 1 (b).

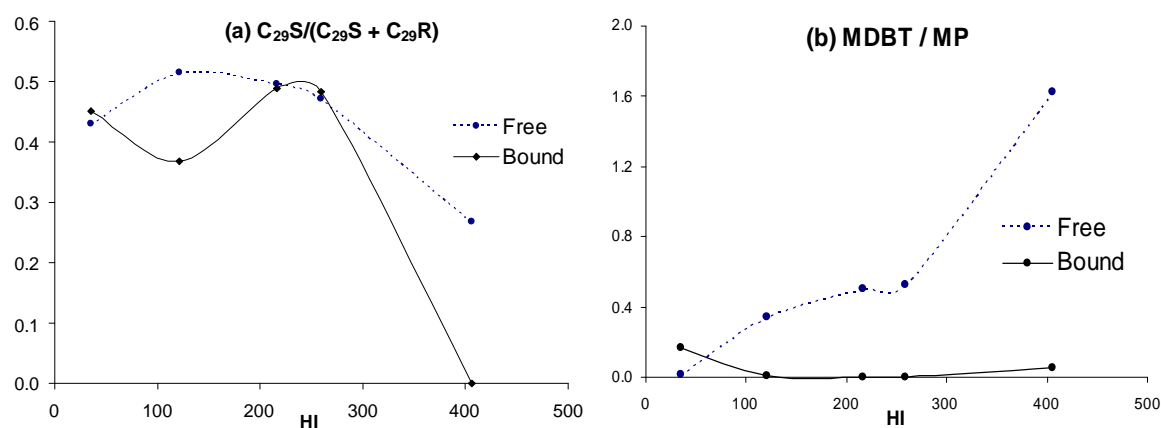


Figure 1 (a) Plot of  $C_{29}$  Steranes 20S/(20S+20R) against HI for a selection of Type II Kimmeridge Clay kerogens, showing much larger variations for bound steranes than for their solvent extractable (free) counterparts. (b) Relative abundance of 4 methyl dibenzothiophene isomers and the 4 methylphenanthrene isomers.

## REFERENCES

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