



geoconvention

Calgary • Canada • May 13-17 2019

## Interpreting classical molecular maturity parameters based on qualitative and quantitative data

Barry Bennett<sup>1</sup> and Steve Larter<sup>2</sup>

<sup>1</sup>Schlumberger Canada Ltd

<sup>2</sup>University of Calgary

### Summary

The application of molecular parameters for assessing the level of thermal maturity of oil during the time of petroleum expulsion from source rocks are based on presumed precursor – product relationships. For example, direct chiral isomerization at C-20 in the non-rearranged steranes measured by  $20S/(20R+20S)$ , conversion of  $C_{27}$  18 $\alpha$ (H)-22,29,30-trisnorhopane (Ts) relative to  $C_{27}$  17 $\alpha$ (H)-22,29,30-trisnorhopane (Tm) expressed as  $Ts/(Ts+Tm)$  and side chain cracking of the  $C_{28}$  to  $C_{20}$  triaromatic steroid hydrocarbons assessed by the ratio  $C20/(C20+C28)$  typically show increasing conversion in relation to increasing levels of thermal maturity. The interpretation based on ratios alone suggests the relationship between precursor and product may be represented by their interconversion. However, concentration data indicates these molecular parameters are not governed by conventional product reactant relationships, but by the competing processes of release/formation from macromolecular and/or functionalized moieties (hydrocarbon or non-hydrocarbon) followed by compound destruction and/or dilution.

### Introduction

Organic geochemists use essentially two types of quantitative molecular data, component concentration data and component ratio data. While environmental and inorganic geochemical analysis has been based on component abundance methods for decades, much of petroleum geochemistry remains based on component ratio data. Thus, component ratios formed the basis of geochemical interpretations in the 70's-90's and are still strongly relied upon today, even though more opportunities are available for geochemists to employ component concentration data which has advantages when process description, kinetic or thermodynamic studies are required. In the case of reservoir geochemical studies, absolute component concentration data is mandatory to allow oil mixing to be evaluated (Wilhelms and Larter, 2004). Li et al. (2007) using case studies from the Beaufort-Mackenzie and Pearl River Mouth basins showed that using the common fingerprint approach favored the source that contributed the relatively higher biomarker concentrations.

Here we consider the putative precursor-product relationship of the  $C_{29}$   $\alpha\alpha\alpha$  steranes through the isomerization reaction associated with the conversion of the biological configuration of  $C_{29}$   $\alpha\alpha\alpha$  20R sterane to the geological configuration of  $C_{29}$   $\alpha\alpha\alpha$  20S using the ratio of  $20S/(20R+20S)$ . In addition, other biomarker-based reactions are considered, such as the  $Ts/(Ts+Tm)$  and  $C20/(C20+C28)$  in the triaromatic steroid hydrocarbons. In this study we investigate the nature of these molecular parameters by considering qualitative and quantitative data.

## Method

Approximately 50-mg of oil was transferred, along with standard compounds (for quantitation), onto a polar solid-phase-extraction (SPE) column using a clean pipette. The total hydrocarbon fraction (THC) was eluted with hexane first and DCM later, and the collected eluate was combined in the same vial and solvent evaporated to a minimum volume. The saturated and aromatic hydrocarbon fractions were isolated from the THC by silica gel-pipette method. The saturated and aromatic hydrocarbon fractions were analysed by gas chromatography-mass spectrometry (GCMS). Peak area integration following GC-MS analysis was performed by using the Hewlett-Packard RTE integrator in ChemStation software. The relative response factors (RRF) between internal standards and related compounds were assumed to be one.

## Results

Figure 1a shows a cross plot of the biomarker parameter  $C_{27}$   $17\alpha(H)$ -22,29,30-trisnorhopane (Tm) relative to  $C_{27}$   $18\alpha(H)$ -22,29,30-trisnorneohopane (Ts) expressed as  $Ts/(Ts+Tm)$  versus level of maturity according to vitrinite reflectance equivalence (VRE) in a genetically related oil suite. The  $Ts/(Ts+Tm)$  correlates well with maturity providing support for the apparent inter-conversion of Tm to the more stable Ts. Figure 1b shows the plot of concentrations of Ts and Tm versus the level of VRE which shows both components are abundant during early oil window stage of thermal maturation. In general, biomarkers yields are highest in the oils representing the early oil window stage of petroleum generation. Meanwhile on progressing from the early oil window through to the middle and late oil window stage of maturation both Ts and Tm show rapid decreases in concentrations (Figure 1b). The relative abundance of Tm is slightly above Ts in the early oil window stage hence the low values of  $Ts/(Ts+Tm)$ , while in the middle and late oil window stages Ts is more abundant than Tm represented by the high  $Ts/(Ts+Tm)$  values. Therefore, the changes in the  $Ts/(Ts+Tm)$  in this case is due to the relative stability whereby Ts is more thermally stable and decreases slower than Tm thus changes in the ratio are governed by the rate of destruction or dilution due to mass balance due to generation of hydrocarbon products such as n-alkanes (Wilhelms and Larter, 2004).

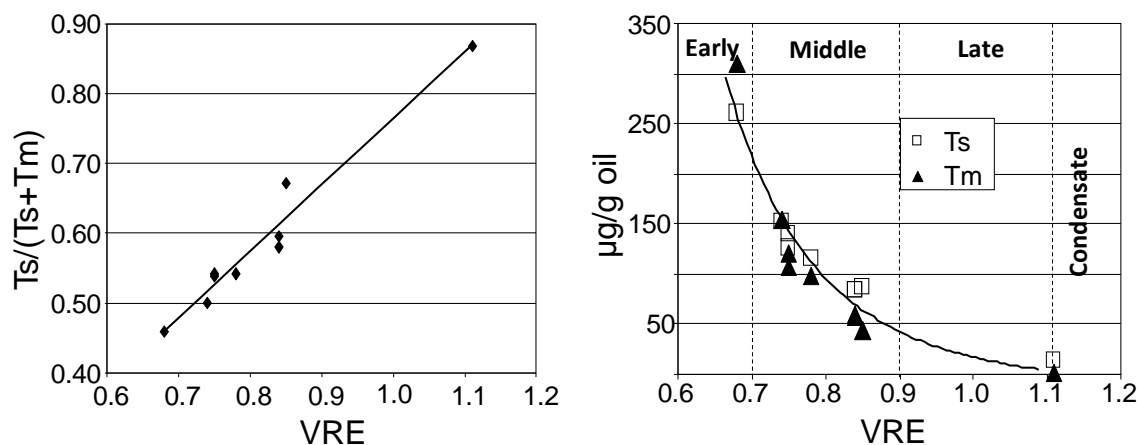


Figure 1. Cross plots of (a)  $Ts/(Ts+Tm)$  and (b) concentrations of Ts and Tm versus level of maturity according to the vitrinite reflectance equivalent (VRE).



# geoconvention

Calgary • Canada • May 13-17 2019

The impact of concentration data on understanding the behavior of the C<sub>29</sub> sterane isomerization parameter 20S/(20S+20R) was previously investigated during studies on the hydrous pyrolysis of Messel kerogen (Abbott et al., 1990) and the impact of contact metamorphism (Bishop and Abbott, 1993). Although the molecular parameters display strong correlation relative to thermal maturity, the concentration data revealed that both 20S and 20R are released during thermal decomposition of the kerogen. Meanwhile at higher maturity levels the concentrations of both compounds decrease, therefore the control on the behavior of the steranes is generation followed by destruction, whereby 20S isomer is more stable and is consumed at a slower rate than 20R sterane thereby accounting for the relative increase in 20S sterane. The reaction appears to be controlled by the net generation and destruction/dilution rather than simple interconversion.

The side chain cracking parameters in the triaromatic steroids is based on the conversion of C<sub>28</sub> triaromatic (20S and 20R) steroid hydrocarbons to the C<sub>20</sub> triaromatic steroid (TAS) expressed as C<sub>20</sub>/(C<sub>20</sub>+C<sub>28</sub>). Again, the concentration data shows the C<sub>20</sub> TAS decreases slowly with increasing maturity, while there is a dramatic reduction in C<sub>28</sub> TAS concentrations. The consequence of the decreasing concentrations of both C<sub>20</sub> and C<sub>28</sub> TAS, albeit C<sub>20</sub> at a much slower rate than C<sub>28</sub> according to the C<sub>20</sub>/(C<sub>20</sub>+C<sub>28</sub>)-TAS is mainly attributed to their relative rates of decrease of both compounds rather than inter-conversion.

## Conclusions

Detailed quantitative investigation into the behavior of molecular maturity parameters based on isomerization and carbon-carbon bond cracking reactions indicates the ratios appear to be controlled by the relative interplay of component generation and subsequent destruction and/or dilution. Concentration data provides a means to investigate petroleum generation and accumulation processes and when considered along with a spectrum of hydrocarbon components representing different stages of petroleum generation, may be used to unravel mixed accumulations.

## Acknowledgements

The authors acknowledge Fuqing Song and Kimberley Noke for GCMS and integration. Geoff Abbott and Maowen Li are thanked for useful discussions.

## References

- Abbott, G.D., Wang, G.Y., Eglinton, T.I., Home, A.K., Petch, G.S., 1990. The kinetics of sterane biological marker release and degradation processes during the hydrous pyrolysis of vitrinite kerogen. *Geochimica et Cosmochimica Acta* 54, pp. 2451-2461.
- Bishop, A.N. and Abbott, G.D., 1993. The interrelationship of biological marker maturity parameters and molecular yields during contact metamorphism. *Geochimica et Cosmochimica Acta* 57, pp. 3661-3668.
- Li, M., Zhang, S., Snowdon, L., Issler, D., 2007. Oil-source correlation in Tertiary deltaic petroleum systems: A comparative study of the Beaufort-Mackenzie Basin in Canada and the Pearl River Mouth Basin in China. *Organic Geochemistry* 39, 1170-1175.



Wilhelms, A., Larter, S.R., 2004. Shaken but not always stirred. Impact of petroleum charge mixing on reservoir geochemistry. From: Cubitt, J.M., England, W.A. & Larter, S. (eds) 2004. Understanding Petroleum Reservoirs: towards an Integrated Reservoir Engineering and Geochemical Approach. Geological Society, London, Special Publications 237, 27-35.