

PS The Application of Tricyclic and Tetracyclic Biomarker Profiles to Infer the Organofacies of Source Rocks and Oils Using a Global Geochemistry Database*

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Abstract

Tricyclics and tetracyclic terpanes have previously been used for source facies evaluation and their use has been documented in the literature (see Zumberge, 1987 or Samuel et al., 2010). The tricyclic signature provides an excellent screening tool for source facies assessment from a limited molecular weight range that is highly resistant to alteration, thermally stable to elevated maturities and not susceptible to overprint by recent organic matter in seeps. Further evaluation using isotopic composition and full biomarker evaluation often provides only minor uplift, especially in larger regional or screening studies. Profiles of the C19 – C26 tricyclic compounds, including the C24 tetracyclic compounds, were created to classify the organofacies of source rocks and oils into 4 categories following the nomenclature of Pepper and Corvi (1995). Organofacies A constitutes a marine, sulfur-rich (>1%), clay-poor, carbonate to siliceous source rock that has relatively low C19 – C20, high C23 tricyclics and in some cases high C24 tetracyclic compounds. Organofacies B is a marine, low-sulfur (<1%), clay-rich, source rock that has relatively low C19 – C20, high C23 – C25 tricyclics and low C24 tetracyclic relative to C26 tricyclic. Organofacies C represents non-marine, lacustrine (freshwater to saline) source rocks that are differentiated from B by having higher C21 relative to C23 tricyclic and C26 tricyclic higher than C25 tricyclic. Organofacies D/E represents non-marine, fluvial to paralic, clay-rich, low sulfur source rocks characterized by high C19 – C20 tricyclics with high C24 tetracyclic compounds. This study demonstrates the utility of the method by applying it to a global geochemical database containing more than 14,500 gas chromatography/mass spectrometry (GC/MS) analyses of source rocks and oils ranging in age from Precambrian to Quaternary. A pattern recognition calculator was developed to allow for easy assignment of tricyclic-tetracyclic profiles to organofacies. The organofacies assignments were supported using multivariate statistical approaches of hierarchical cluster analysis (HCA) and principal component analysis (PCA) on a calibration dataset. Clusters differentiated by multivariate analysis are in good agreement with the visual analysis of tricyclic-tetracyclic profiles and support the organofacies model. Tricyclic-tetracyclic profiles that are not easily classified represent oils with a more complicated history of hydrocarbon generation from multiple source rocks and possible oil mixing. The analysis resulted in delineation of areas of major effective source rocks and their respective facies. Furthermore, through geologic time, the organofacies of source rocks deposited in different basins correlates with known global sea level cycles and oceanic anoxic events. Examples from basin-specific case studies illustrate the application of the methodology.

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Abstract

Tricyclic and tetracyclic terpanes have previously been used for source facies evaluation and their use has been documented in the literature (see Zumberge, 1987 or Samuel et al., 2010). The tricyclic signature provides an excellent screening tool for source facies assessment from a limited molecular weight range that is highly resistant to alteration, thermally stable to elevated maturities and not susceptible to overprint by recent organic matter in seeps. Further evaluation using isotopic composition and full biomarker evaluation often provides only minor uplift, especially in larger regional or screening studies.

Based on distinct, statistically significant tricyclic-tetracyclic terpane profiles of endmembers defined from a global dataset, a simple pattern recognition calculator was developed to allow for easy assignment of organofacies. The organofacies assignments were supported using multivariate statistical approaches of hierarchical cluster analysis (HCA) and principal component analysis (PCA) on a calibration dataset.

This study demonstrates the utility of the method by applying it to a global geochemical database containing more than 13,000 gas chromatography/mass spectrometry (GC/MS) analyses of oils ranging in age from Precambrian to Quaternary. The analysis resulted in delineation of areas of major effective source rocks and their respective facies. Furthermore, through geologic time, the organofacies of source rocks deposited in different basins correlates with known global sea level cycles and oceanic anoxic events.

Introduction & Motivation

The **standard geochemical workflow** at Hess for source facies determination of oils, extract and seep samples involves comparison to a well characterized global data set of 60 oils derived from different source facies. **Distinct trends that are evident** from working with the 60 oil sample dataset suggest characteristic **tricyclic-tetracyclic terpane profiles** (Figure 1) for each facies group. Similar trends have been described previously by Zumberge (1987), Peters and Moldovan (1993), Samuel et al. (2010), Tao et al. (2015) and many others. Since tricyclic-tetracyclic components are relatively resistant to the effects of maturation, biodegradation or overprint by recent organic material, their fingerprints are easy to identify when working with larger sample sets or under time constraints. To take advantage of this, these fingerprints were used to **develop a simple organofacies calculator tool** for rapid identification of source facies.

Figure 1. Peak identification for tricyclic (red), tetracyclic (blue) and pentacyclic (black) terpanes on m/z 191.

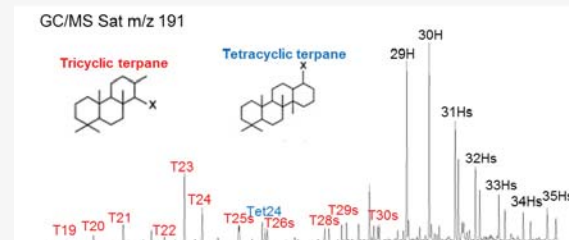


Figure 1. Peak identification for tricyclic (red), tetracyclic (blue) and pentacyclic (black) terpanes on m/z 191.

Figure 2. map showing distribution of global training set.

Methodology

The 60 oil sample training set (see Figure 2 for sample locations) shows distinct geochemical signatures and can be classified into 6 groups based on statistical evaluation of 19

predominantly source facies related molecular biomarker parameters in a Principal Component Analysis (Figure 3) as well as Hierarchical Cluster Analysis (Figure 4). These groups correspond to **6 organofacies which can be classified** following a scheme modified from Pepper and Corvi (1991):

- A1: a marine carbonate family;
- A2: a more marly variant of A1;

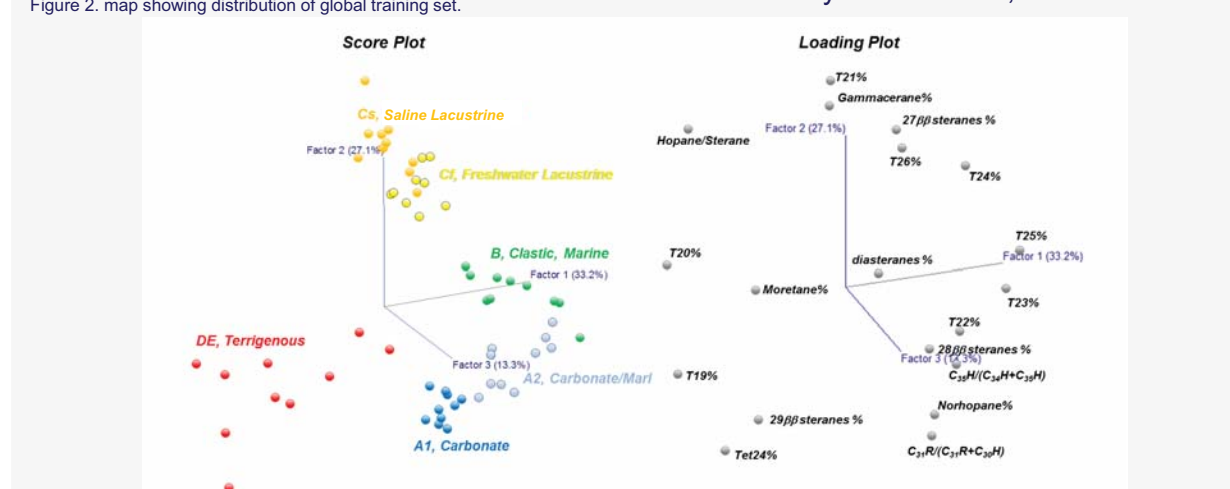


Figure 3. Score and loading plots for principal component analysis of the 60 oil comparison training set. A total of 19 molecular parameters (see loading plot) was used. The statistical analysis allows clear identification of 6 facies groups. Two carbonate families, one terrigenous, a clastic marine as well as a saline and freshwater lacustrine family can be distinguished.

- B: marine clastic facies;
- Cf and Cs: freshwater and saline lacustrine facies, respectively;
- DE: terrigenous, non-marine facies

Each group shows a characteristic tricyclic-tetracyclic terpane fingerprint (Figure 4). Organofacies A has relatively low $C_{19} - C_{20}$, high C_{23} tricyclics and in some cases high C_{24} tetracyclic compounds (variant A1). Organofacies B is characterized by relatively low $C_{19} - C_{20}$, high $C_{23} - C_{25}$ tricyclics and low C_{24} tetracyclic relative to C_{25} tricyclic. Organofacies C shows higher C_{21} relative to C_{23} tricyclic and C_{26} tricyclic higher than C_{25} tricyclic with small but distinct differences between the freshwater and saline variety. Organofacies DE is characterized by high $C_{19} - C_{20}$ tricyclics with elevated C_{24} tetracyclic compounds. Based on these distinct signatures, one oil from each group was chosen as an endmember (see Figure 5) for comparison in a **spreadsheet-based organofacies calculator tool** which uses a correlation function to determine the best match of a given sample to a particular endmember. **Input for the calculator tool are the tricyclic-tetracyclic terpane fingerprint** (Figure 5) as well as a **correlation factor cut-off** designed to chose the level of correlation required. The calculator tool's output was able to identify nearly all samples in the training set. At a correlation factor (CF) of 0.9, only few samples were unidentifiable (Figure 6a).

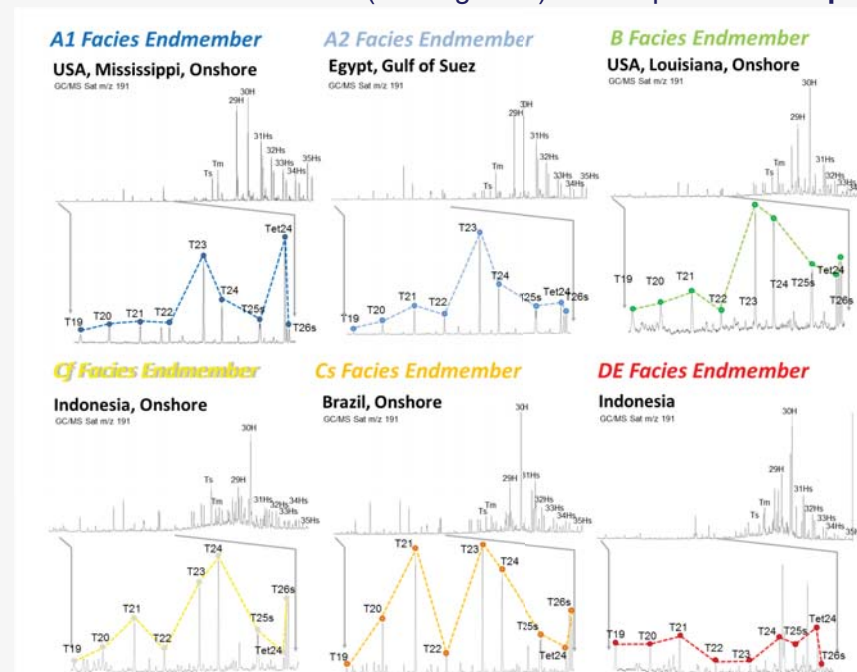


Figure 5. Tricyclic and pentacyclic terpane signature (full m/z 191 as well as enlarged C_{19} to C_{29} molecular weight range) for endmembers representing each of the 6 organofacies groups.

When decreasing the correlation factor, the number of predicted samples increases and reaches 100% at CF of 0.7 (Figure 6b).

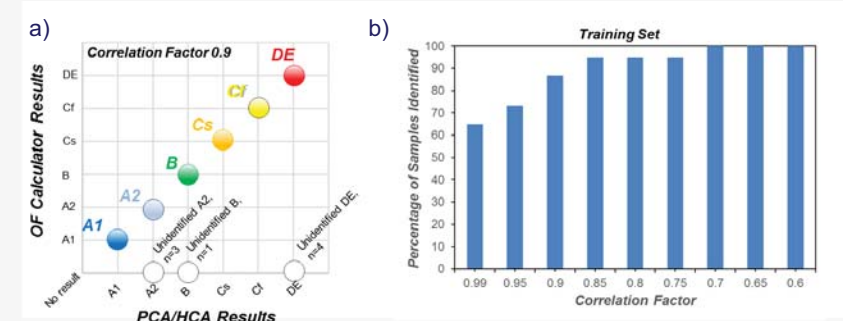


Figure 6. a) The organofacies calculator returns similar results compared to the PCA/HCA approach. Using a correlation factor of 0.9, only 8 of the 60 samples in the training set cannot be classified. All others are classified as per the PCA/HCA analysis. b) Changing the correlation factor setting allows classification of additional samples. At a correlation factor of 0.7, all samples can be classified.

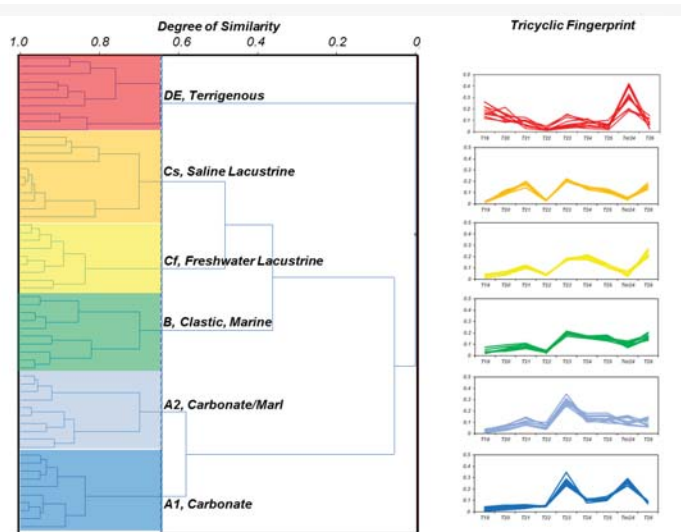


Figure 4. Hierarchical cluster analysis of 60 oils based on 19 molecular parameters (see corresponding PCA in Figure 3) also allows clear differentiation of 6 organofacies groups. These organofacies groups appear to have characteristic tricyclic and tetracyclic terpane signatures (see right-hand side plots).

Results

After development of the **organofacies calculator tool**, the Hess global geochemistry database containing 13,260 samples (with complete entries; total # of samples is 14,977) was processed. Using a correlation factor of 0.85, 80% (or 10,260) of all samples are interpreted and are shown on the map below. Changing the correlation factor (see Figure 7) to a lower value will increase the number of interpreted samples at the expense of the quality of interpretation.

The screening exercise visualizes known global trends and highlights the key source rocks in many of the worlds most important petroleum provinces. A few examples are:

- Middle East: Jurassic Hanifa marine carbonate
- West Siberia: Jurassic Bazhenov marine shales
- South East Asia/Australia: Tertiary coaly shales
- South Atlantic: Cretaceous Bucomazi (Congo basin) and Lagoa Feia (Brazil) lacustrine shales

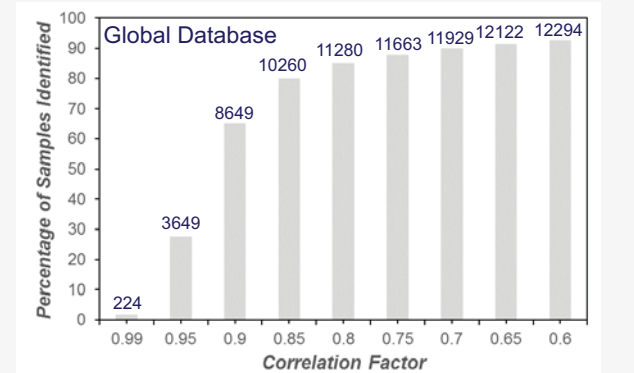


Figure 7. The organofacies calculator tool was applied to the Hess global oil database (with 13,260 complete entries). At a correlation factor of 0.85, ~80% of the entries can be interpreted. The results are shown on the map in Figure 8.

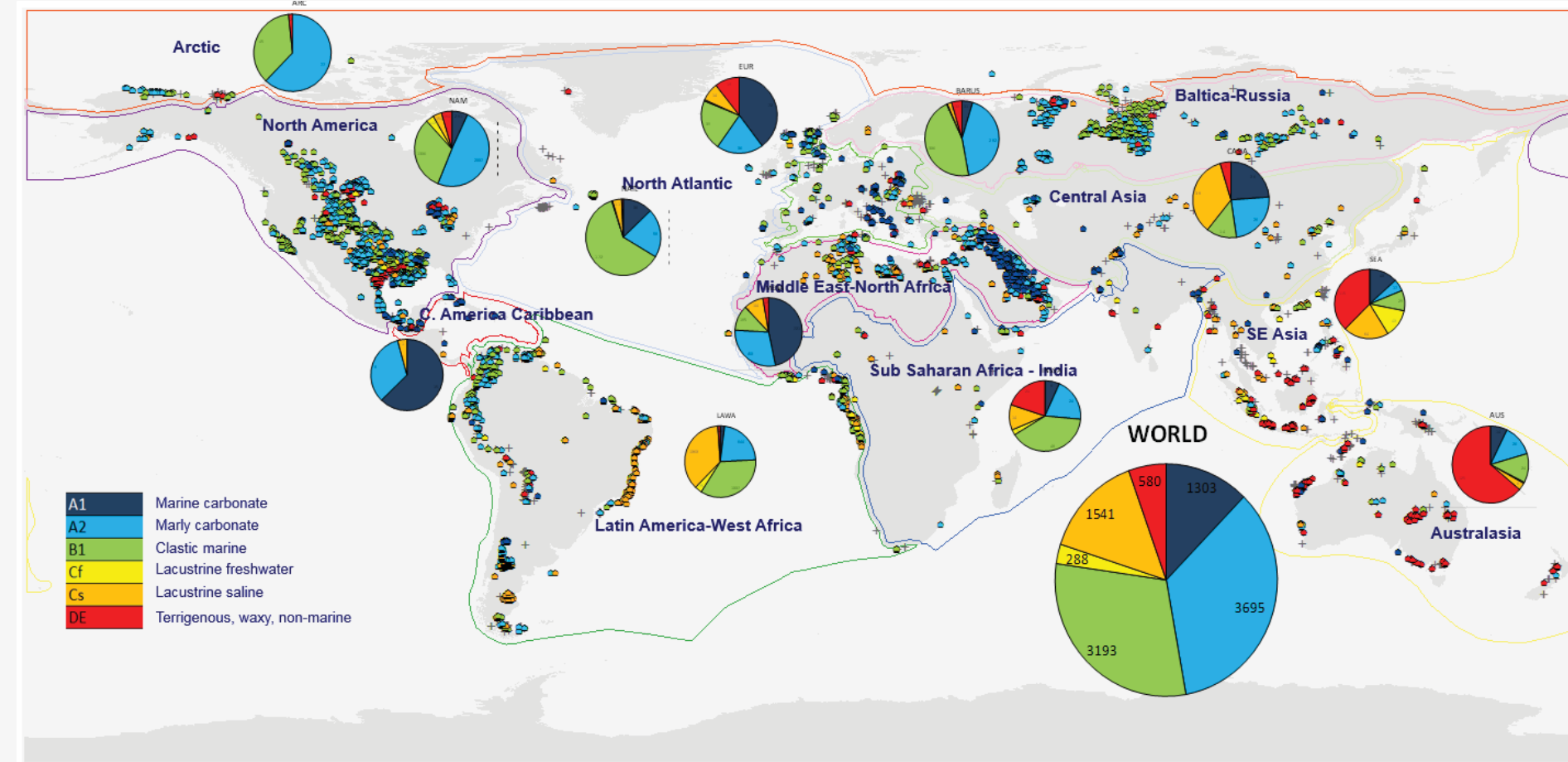


Figure 8. Worldmap showing the results of the organofacies interpretation using the newly developed organofacies calculator applied to all samples in the Hess global geochemistry database as well as a summary breakdown of the organofacies distribution by region. Note that unidentified samples (shown in black crosses) are excluded from the pie charts.

Conclusions

A simple screening tool has been developed that utilizes tricyclic-tetracyclic terpane profiles to allow for easy and consistent assignment of organofacies. Application to the Hess global database reveals organofacies distributions consistent with well-understood source rock distributions. Outliers are likely related to fluid mixtures derived from separate organofacies, data quality issues, etc. While the screening tool provides an easy first-pass interpretation of organofacies origin, the tool does not preclude the need for more complete data analysis in basin-specific studies.

Acknowledgements and References

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