Helping "Oddball Oils" Find their Nearest Neighbor(s)

By Craig Schiefelbein, *Geochemical Solutions International (craigs@geochemsol.com);*
William Dickson*, Dickson International Geosciences; and* ***John Zumberge****, Geomark Research*

Continuing research has clarified the tectono-structural history of the Atlantic conjugate margins. This includes the creation and segmentation of source rock depocenters. Since crude oils possess biological clues to their genetic history and evolution from source to trap and beyond, source ages could be assigned that correspond to paleogeographic reconstructions of the South Atlantic conjugate margins associated with five sedimentary mega-sequences: Continental, Transitional/Evaporitic, Carbonate Platform, Marine Transgressive and Marine Regressive with corresponding source rock depocenters. Within the Eastern Brazilian Rift Systems (EBRIS), these depocenters, as formed and segmented, correspond to Syn Rift I (Upper Jurassic), Syn Rift II (Neocomian), Syn Rift III (Barremian), Transitional/Evaporitic (Aptian) and Shallow Carbonate Platforms (Albian) (Chang et al., 1992). While present around the conjugate margins, these source types are supplemented locally by volumetrically dominant Upper Cretaceous Marine and Tertiary Deltaic intervals. The strongest genetic conjugate relationships are observed between oils from central Brazil and West Africa that originated from Barremian (Lower Rift/SynRift I) source rocks deposited in deep, freshwater lacustrine environments. Lacustrine oils in general showed strong correlations of age and location between conjugate salt basins although Great Campos (Southeast Brazil/Syn Rift III) oils stand apart with a unique chemistry.

Oils derived from Transitional/Evaporitic source rocks are limited to offshore northeast Brazil (Sergipe-Potiguar-Ceará). Most crude oils examined from the Niger Delta have unique chemistries associated with an origin from source rocks influenced by higher land plants (angiosperms; Tertiary Deltaic).

Marine oils often demonstrate age correlations related to global ocean anoxic events, independent of conjugate structuration. Several oils from Foz do Amazonas and Para Maranhão have chemistries that are unique relative to oils from all other Brazilian basins, but oils with similar chemistries can be identified when the sample coverage is expanded. Within the limited context of South America these Foz/Para oils are compositionally similar to oils from Suriname/Guyana to the west and Austral/Malvinas basins to the extreme south. When coverage is expanded to include the entire South Atlantic margin, these oils are broadly similar to oils from offshore Gabon, Angola, and the Kwanza Basin but have the strongest affinity to many oils from the conjugate Equatorial Margin (Cote d'Ivoire), where at least two different sources are active.

APPROACH

Our interpretive work began with the assembly of a data set and development of data intimacy through detailed inspection (e.g.,

Helping "Oddball Oils" Find their Nearest Neighbor(s) *continued on page 40*

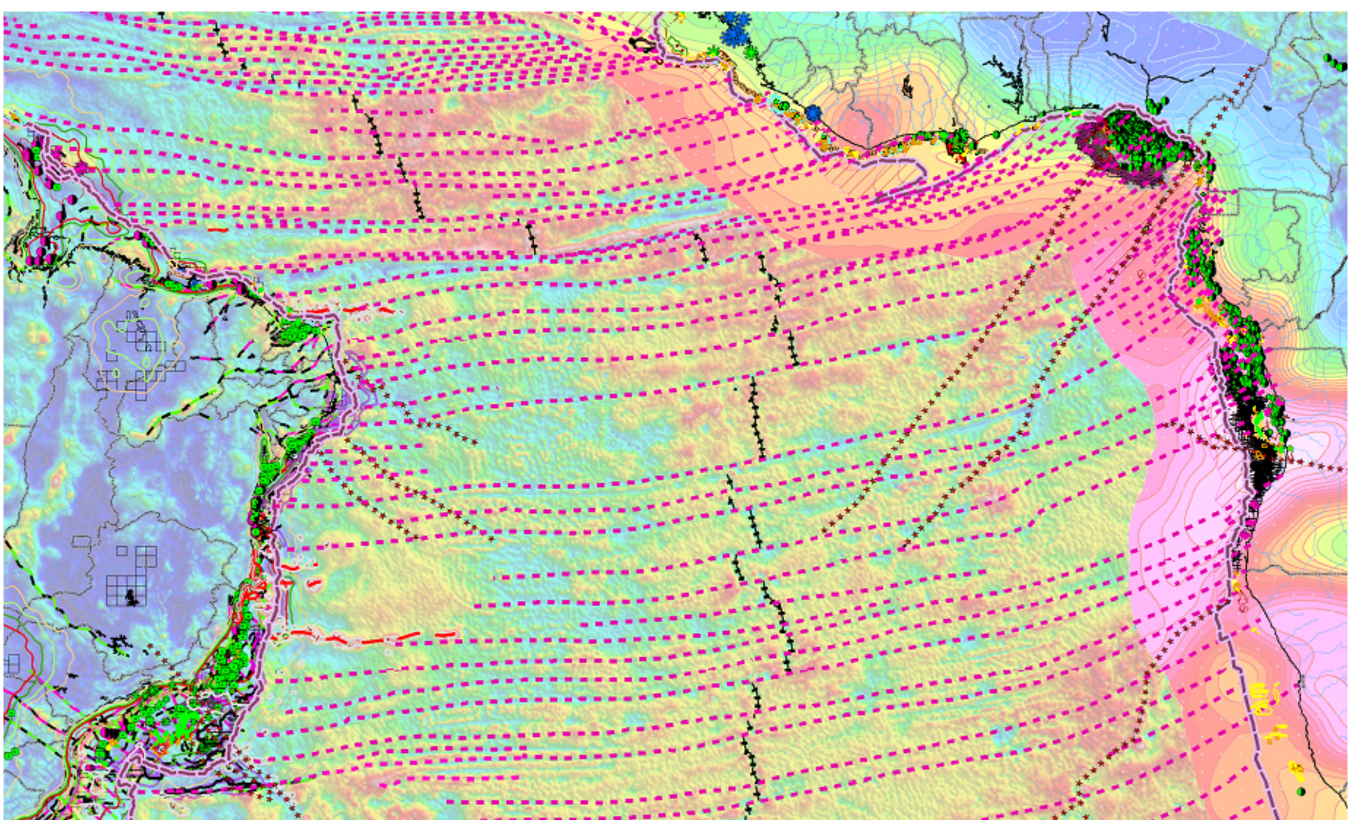

Figure 1. *Distribution of more than 1700 crude oils. (Gravity image compliments of GrizGeo)*

see Dickson et al., 2016). Values from different laboratories that employed different analytical schemes required determining which measurements were common to all samples (the Lowest Common Denominator). Missing parameters from specific samples were supplied from analogs, sample averaging, and standard relationships from other geochemical parameters based on the physical proximity of sample sites and the author's experience. First-pass cross-plotting of key oil constituents and ratios showed main "anchor" clusters within a broad scatter of points on two- and three-axis plots. Outliers were then examined for causes of scatter, typically unique chemistries (e.g., Paleozoic source) or oils that experienced advanced maturity or extensive bio-degradation, resulting in compromised biomarker distributions.

Recognition and characterization of compositionally distinct oil types or families infers paleo-environmental conditions of source rock deposition and possible age. The clearest results are obtained from pure end-member oils from a single lithology, single paleo-environment source, but this is uncommon to the South Atlantic margin with its compound basins, usually with drift-age marine fans overlying multi-stage rifts. Depositional environments may grade episodically from lacustrine to marine so that in late rift to sag phases, source rocks composed of mixed kerogens are deposited. Oils from such sources in similar phases of maturity may mimic mixed oils from discrete sources co-mingled in a common reservoir.

Key geochemical indicators of source-rock paleo-environments and age in the South Atlantic Margin (Mello, et al., 1988; Schiefelbein et al., 1999, 2001, 2017) have developed along with increasing numbers of samples and a broadening range of data (ie, deuterium isotopes, diamondoids) extracted from each sample. Our multi-parameter approach relied on a combination of parameters corresponding to the 'black oil' (>C15) component that are primarily influenced by source, but can also be affected by maturity and/or other alteration processes such as biodegradation. Genetic relationships are established based on compositional similarity.

Geochemical data utilized in this study are entirely non-exclusive and provided by Geochemical Solutions International and Geomark Research. Sample locations in **Figure 1**.

Multivariate statistical analyses [principal component analysis (PCA) and cluster analysis; PirouetteTM , Infometrix, Seattle, WA.] are used to more clearly distinguish the different types of oils present throughout the South Atlantic Margin. Briefly, in PCA, new independent variables (i.e., principal components) are created, which are linear combinations of the original variables (i.e., geochemical parameters). The primary objective of PCA is to reduce the dimensionality of the data to a few important components that best explain the variation in the data. Prior to PCA, the original geochemical variables are auto-scaled (the mean value for each variable is subtracted and divided by the standard deviation) so that stable carbon isotope values (e.g., -30 o/oo) can be meaningfully compared to sterane/hopane ratios, for example. The geochemical variables responsible for the PC axes can be viewed as a Loadings plot and the oil samples can be plotted in principal component space, PC1 versus PC2, as a Scores plot.

Hierarchal Cluster analysis (HCA) is an ancillary technique to PCA whereby a distance matrix is created from the scaled data; the distance between any two samples is a measure of their similarity (this distance is similar to a linear correlation coefficient; perfect correlation would have a value of 1.0 while poor correlation would have values < 0.5). The dendrogram is the output of a cluster analysis and shows groupings or clusters of oils.

Input variables are primarily source dependent and based on information obtained from the detailed analysis of the C15+ saturate and aromatic hydrocarbon fractions ('black oil'). The fifteen (15) source dependent variables used in the multivariate statistical analyses describe 75% of the variance and include the pristane/phytane ratio, the stable carbon isotopic compositions of the C15+ saturate and aromatic hydrocarbon fractions, and thirteen biomarker ratios, including the distribution of the 14β, 17β-C27, -C28 and –C29 steranes (from m/z 218), C27 Ts/Tm hopanes, C31-35 hopanes/C30 hopane, gammacerane/C30-hopane, C29-demethylated norhopane/C30-hopane, and oleanane/C30-hopane. Ratios based on the distribution of tricyclic and tetracyclic terpanes were also used: C21-Tri/C23-Tri, C26-Tri/C25-Tri, and C24-Tetra/C26-Tri.

RESULTS AND DISCUSSION: STATISTICAL ANALYSES

Starting from a collection of 1740 samples, 329 oils were excluded due to either high maturity, biodegradation, contamination, and /or other post-generative processes. The remaining 1411 samples were statistically separated into five major families: Early SynRift; Late SynRift/Sag; Marine/Mixed; Marine; Tertiary Deltaic (**Figure 2**). Incorporation of additional geologic constraints from tectono-structural mapping suggest that oil family and sub-family distributions often relate to sediment thickness and basin to sub-basin structure; lacustrine oils show strong correlations of age and location between conjugate salt basins; and marine oils demonstrate age correlations related to global ocean anoxic events. Source paleoenvironment and age are inferred, often using key biomarkers such as n-propyl C30 steranes that only have marine precursors (Moldowan, et al., 1990) or oleanane, a specific biomarker associated with higher land plants and, in this study, a Tertiary source (Moldowan, et al., 1994). The relative abundance of nuclear demethylated hopanes or the C27 Ts/Tm ratio help identify areas where extensive paleodegradation or advanced

Helping "Oddball Oils" Find their Nearest Neighbor(s) *continued on page 41*

Helping "Oddball Oils" Find their Nearest Neighbor(s)

continued from page 40

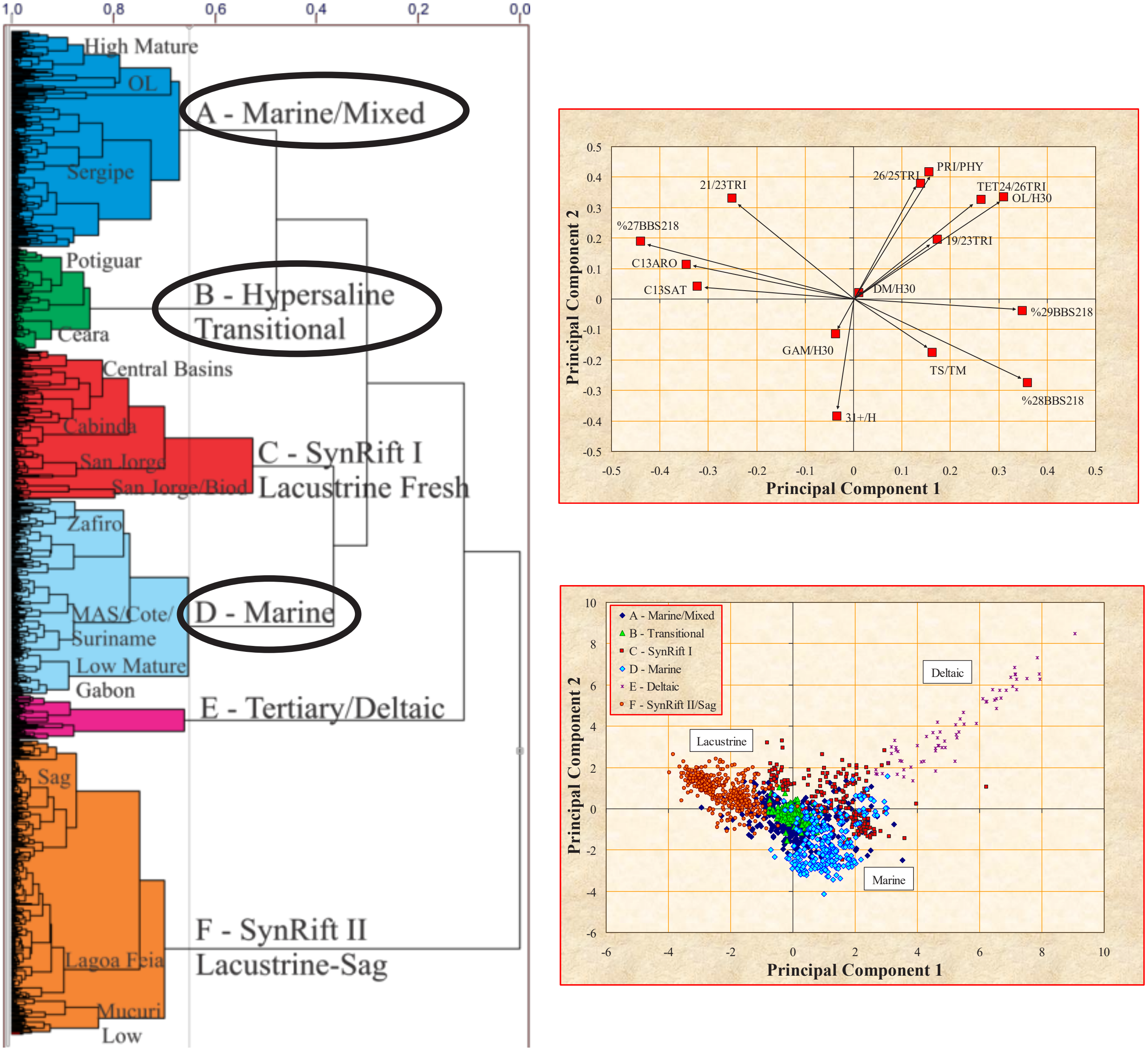

Figure 2. *Hierarchal Cluster Analysis (HCA) Dendrogram (left) and Principal Cluster Analysis (PCA) loadings and scores for all South Atlantic Margin oils.*

maturity has occurred. In other words, chemical composition data and multivariate were utilized to separate oils into compositionally similar groups according to source depositional environment and likely age/rifting event.

The strongest genetic relationships are observed between oils from central Brazil and West Africa that originated from Barremian source rocks deposited in similar deep, freshwater lacustrine environments (Family C; Lower Rift/SynRift I). Family F oils have a unique source chemistry related to SynRift II and/or sag depositional environments and are mainly from the Great Campos sub-basins. Family E oils are all from the Niger Delta area and are distinguished by the presence of oleanane, a specific biomarker associated with deltaic environments and a probable Tertiary origin.

To better understand the origin and distribution of oils derived from middle to upper Cretaceous source rocks deposited in different marine environments (Families A, B and D), a second statistical analysis was performed. Oils from Families C, E and F were excluded and PCA loadings were modified to include the proportion of C30 tetracyclic terpanes relative to C27 diasteranes (TTP Index; from m/z 259; Holba et al., 2000; 2003). Two other parameters (C29-demethylated norhopane/C30-hopane, and oleanane/C30-hopane) were omitted. Two major groups and

Helping "Oddball Oils" Find their Nearest Neighbor(s) *continued on page 42*

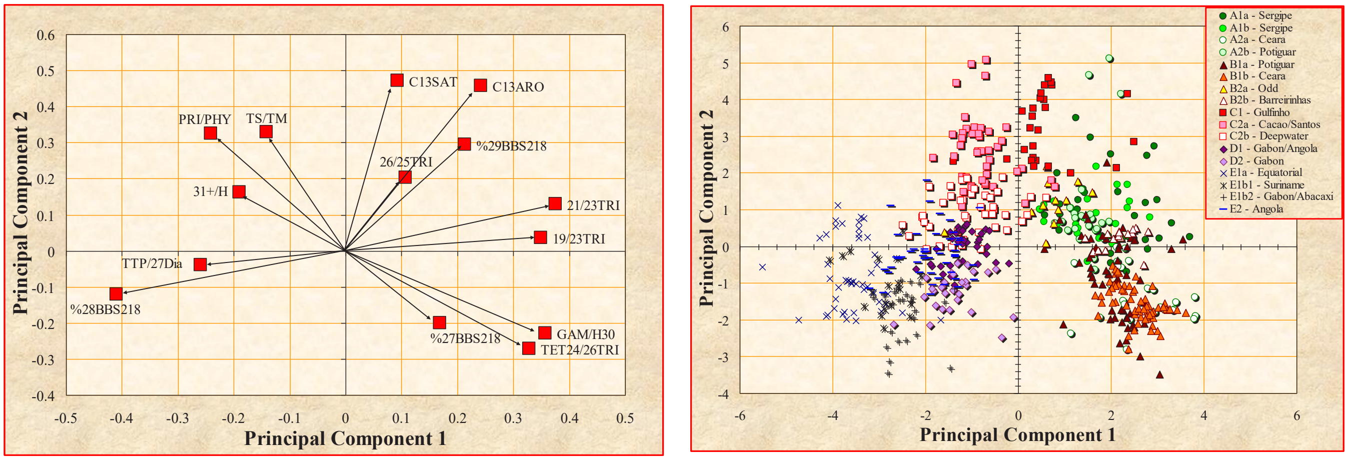

Figure 3a. *Principal Cluster Analysis (PCA) loadings and scores for marine oils from the South Atlantic Margin.*

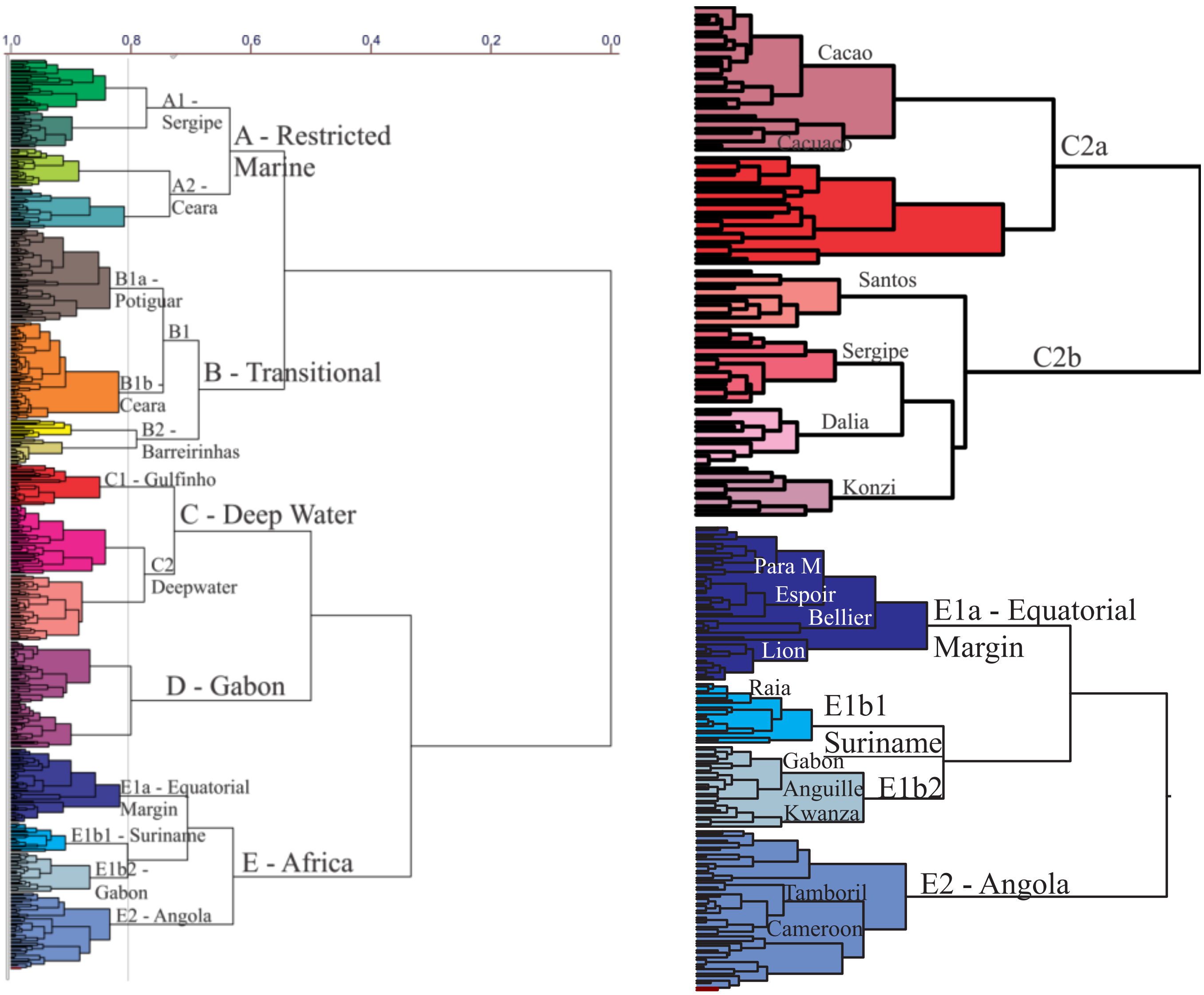

Figure 3b. *Hierarchal Cluster Analysis (HCA) Dendrograms for marine oils from the South Atlantic Margin.*

Helping “Oddball Oils” Find their Nearest Neighbor(s) *continued on page 43* continued from page 42

five sub-families of oils are distinguished and can be associated with different environments including Transitional/Evaporitic, Carbonate Platform, Marine Transgressive and Marine Regressive (**Figure 3**). Correlations between oils in the seventeen marine oil sub-families may be considered as age correlations possibly related to global ocean anoxic events.

Oils in Families A and B originated from Aptian source rocks deposited in restricted marine or hypersaline transitional environments. These oils mainly occur in the Barreirinhas, Ceará, Potiguar and Sergipe-Alagoas basins located in northeastern Brazil. Oils in Family D originated from Albian to Senonian source rocks deposited in a different marine environments. These oils are limited in distribution and are from mainly onshore and offshore northern Gabon. Oils in Families C and E are more widely distributed and therefore considered as 'odd' in the sense that they are found on both sides of the margin.

The strongest genetic relationships are observed between oils from central Brazil and West Africa that originated from Barremian source rocks deposited in similar deep, freshwater lacustrine environments (Family C; Lower Rift/SynRift I). Family F oils have a unique source chemistry related to SynRift II and/or sag depositional environments and are mainly from the Great Campos sub-basins. Family E oils are all from the Niger Delta area and are distinguished by the presence of oleanane, a specific biomarker associated with deltaic environments and a probable Tertiary origin.

To better understand the origin and distribution of oils derived from middle to upper Cretaceous source rocks deposited in different marine environments (Families A, B and D), a second statistical analysis was performed. Oils from Families C, E and F were excluded and PCA loadings were modified to include the proportion of C30 tetracyclic terpanes relative to C27 diasteranes (TTP Index; from m/z 259; Holba et al., 2000; 2003). Two other parameters (C29-demethylated norhopane/C30-hopane, and oleanane/C30-hopane) were omitted. Two major groups and five sub-families of oils are distinguished and can be associated with different environments including Transitional/Evaporitic, Carbonate Platform, Marine Transgressive and Marine Regressive (Figure 3). Correlations between oils in the seventeen marine oil sub-families may be considered as age correlations possibly related to global ocean anoxic events.

Oils in Families A and B originated from Aptian source rocks deposited in restricted marine or hypersaline transitional environments. These oils mainly occur in the Barreirinhas, Ceará, Potiguar and Sergipe-Alagoas basins located in northeastern Brazil. Oils in Family D originated from Albian to Senonian source rocks deposited in a different marine environments. These

Helping "Oddball Oils" Find their Nearest Neighbor(s) continued on page 44

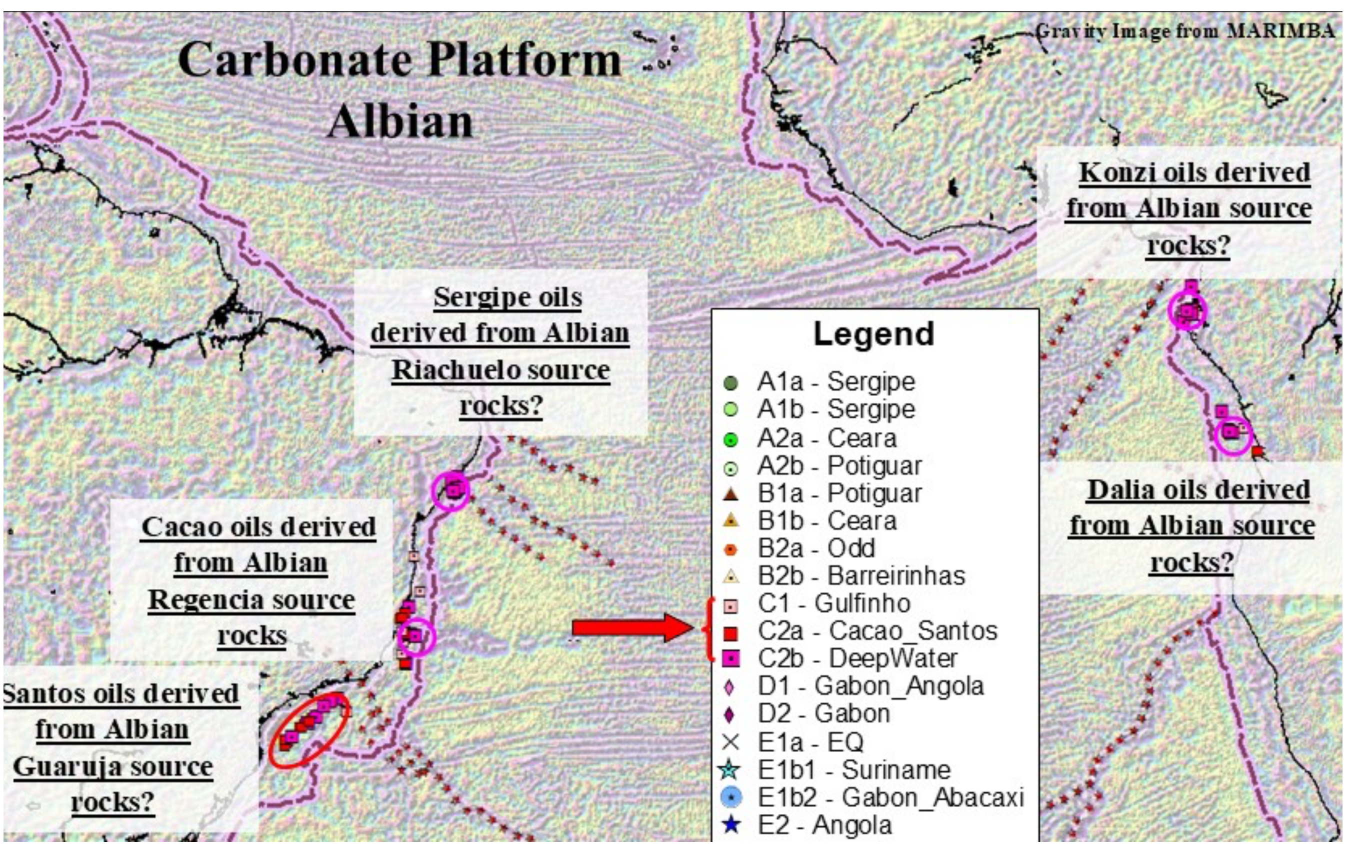

Figure 4. *Distribution of Marine-Derived oils from Family C.*

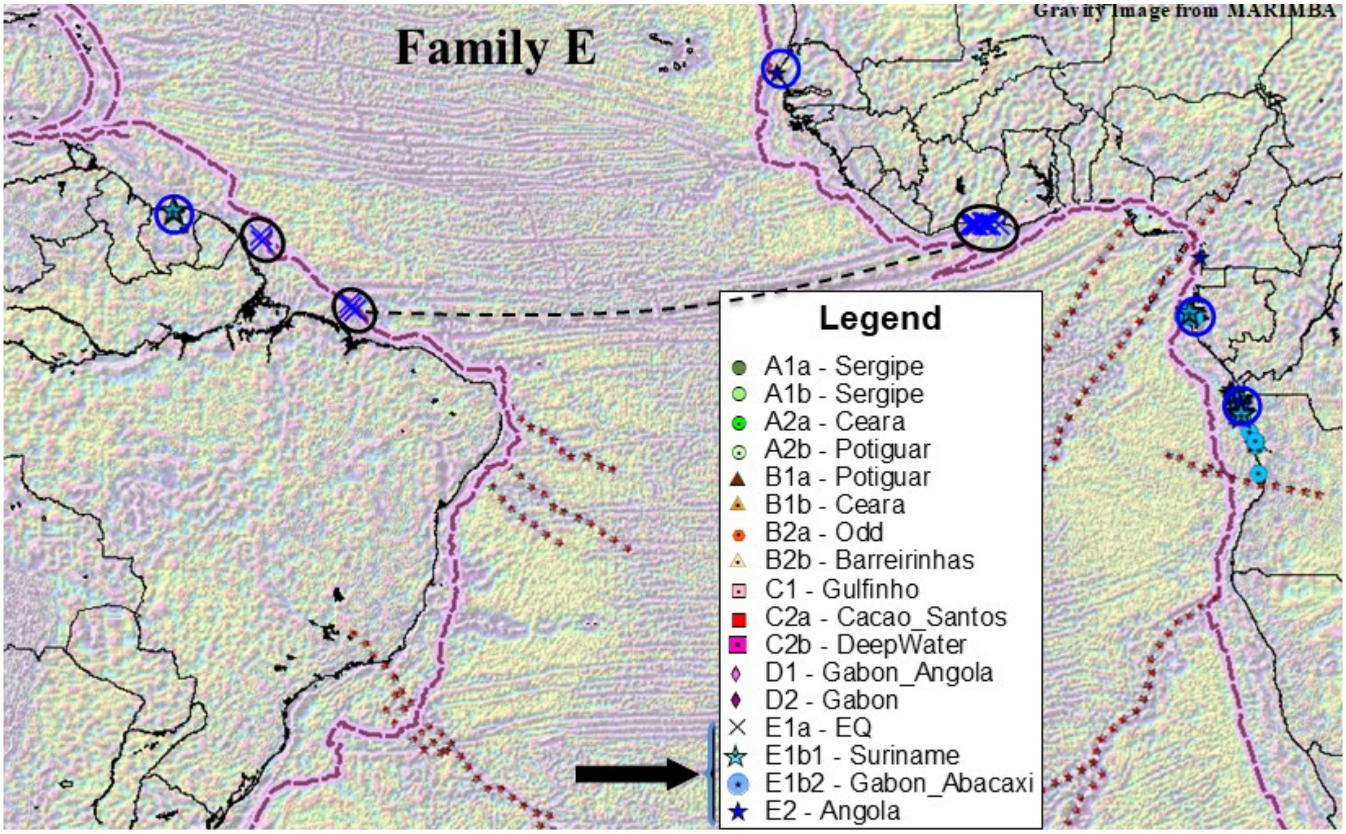

Figure 5. *Distribution of Marine-Derived oils from Family E.*

oils are limited in distribution and are from mainly onshore and offshore northern Gabon. Oils in Families C and E are more widely distributed and therefore considered as 'odd' in the sense that they are found on both sides of the margin.

Family C oils can be separated into six subgroups and many of these oils have been positively correlated to Albian source rocks in multiple different basins (GSI and Core Lab non-exclusive studies). As can be seen from **Figure 4**, these oils are located in Santos (Itajai Acu and Guaruja formations), Espírito Santo (Regencia Formation) and Sergipe (Riachuelo and Continguiba formations?) basins offshore Brazil and offshore northern Gabon (Konzie Field) and central Angola on the African side. Previous investigations (Dickson, et. al. 2012) utilizing piston core and remote sensing data suggest that several oils from the Dalia/Girassol area offshore central Angola have a complex history and may also contain a pre-salt oil component. Similar observations can be made for Espírito Santo oils from the Gulfinho area. Two oils from offshore Sergipe contain anonymously high concentrations of oleanane that may be related to a local Eocene thermal volcanic event (Schiefelbein, et. al., 2016) which is supported by source rock maturity data.

Family E can be separated into four broad sub-groups that include oils from Suriname, Senegal, Cameroon, Gabon, Angola and both sides of the equatorial margin (**Figure 5**). Observations based on the strong correlation between oils along Equatorial Margin Basins (Dickson et. al., 2016) suggest that the Equatorial Atlantic opening was structurally asymmetric with deep monoclinal basins forming along the African margin between the St Paul and Chain Fracture Zones (FZ) while the Brazilian-Guyanan conjugate margin appears to have retained much or all of the early syn-rift architecture. This opening asymmetry a) biased the location of lacustrine (early to mid-Cretaceous pre-rift to early syn-rift) source rocks and b) locally narrowed the width of the optimal marine (well-known Mid to Late Cretaceous post-rift) source kitchens. The latter, where rapidly buried offshore Ivory Coast and Ghana, contribute to a risk of late charge from light (condensate and gas) hydrocarbons. Although multiple lacustrine-sourced oil families are seen all along the NE Brazil margin, none have been identified along the West African Transform (WAT) Margin.

CONCLUSIONS

Marine oils often demonstrate age correlations related to global ocean anoxic events, independent of conjugate structuration. Several oils from Foz do Amazonas and Para Maranhão have chemistries that are unique relative to oils from all other Brazilian basins, but oils with similar chemistries can be identified when the sample coverage is expanded. Within the limited context of South America these Foz/Para oils are compositionally similar to oils from Suriname/Guyana to the west and Austral/Malvinas basins to the extreme south. When coverage is expanded to

Helping "Oddball Oils" Find their Nearest Neighbor(s) *continued on page 45*

Helping "Oddball Oils" Find their Nearest Neighbor(s)

continued from page 44

include the entire South Atlantic margin these oils are broadly similar to oils from offshore Gabon, Angola (Dalia/Girassol) and the Kwanza Basin but have the strongest affinity to many oils from the conjugate Equatorial Margin (Cote d'Ivoire) where at least two different sources are active.

REFERENCES

Chang, K.C, R.O. Kowsmann, A.M. Fereira Figueredo and A.A, Bender, 1992. Tectonics and stratigraphy of the east Brazil Rift System: an overview. Teconophysics, October 1992, p97-138.

Dickson, W.G., C.F. Schiefelbein, C.F., J.E. Zumberge and J. Brooks, 2012. Girassol? Angola's First deepwater pre-salt discovery? PESGB-HGS Africa Conference, Sept. 2012.

Dickson, W.G., C.F. Schiefelbein, C.F., M.E. Odegard and J.E. Zumberge, 2016. Petroleum Systems Asymmetry across the South Atlantic Equatorial Margins. Geological Society, London, Special Publications, 431, 3 March 2016.

Holba, A.G., Tegelaar, E., Ellis, L., Singletary, M.S., and Albrecht, P. 2000. Tetracyclic polyterprenoids: indicators of freshwater (lacustrine) algal input. Geology 28, p251-254.

Holba, A.G., L.I. Dzou, G.D. Wood, L. Ellis, P. Adam, P. Schaeffer, P. Albrecht, T. Greene, and W.B. Hughes, 2003. Application of tetracyclic polyprenoids as indicators of input from fresh-brackish water environments. Org. Geochemistry 34, no. 3: p441-469.

Mello, M.R., N.Telnaes, P.C. Gaglianone, M.I. Chicarelli, S.C. Brassell, and J.R. Maxwell, 1988. Organic geochemical characterization of depositional paleoenvironments of source rocks and oils in Brazilian marginal basins. Organic Geochemistry, v.13, p31-45.

Moldowan J.M., Fago F.J., Lee C.Y., Jacobson S.R., Watt D.S., Slougui N.E., Jeganathan A., and Young D.C., 1990. Sedimentary 24-n-propylcholestanes, molecular fossils diagnostic of marine algae. Science 247, p309-312.

Moldowan J.M., Dahl J., Huizinga B.J., Fago F.J., Hickey L.J., Peakman T.M., and Taylor D.W., 1994. The molecular fossil record of oleanane and its relation to angiosperms. Science 265, p768-771.

Schiefelbein, C.F., J.E. Zumberge, N.R. Cameron and S.W. Brown, 1999. Petroleum systems in the South Atlantic margins in Geological Society, London, Special Publication 153, p69-179.

Schiefelbein, C.F., J.E. Zumberge, N.C. Cameron, and S.W. Brown, 2001. Geochemical comparison of crude oil, South Atlantic Margins. in: M.R. Mello & B.J. Katz (eds.), Petroleum Systems of the South Atlantic Margin. AAPG Memoir 73, p15-26.

Schiefelbein, C.F., W.G. Dickson, C.M. Urien and J.E. Zumberge, 2017. Genetic comparison of crude oils from West Africa and South American Conjugate Basins. in: 5th Atlantic Conjugate Margins Conference, Porto de Galinhas, Pernambuco, Brazil, August 22-25, 2017.

Schiefelbein, C.F. and W.G. Dickson, 2018. To deep water Sergipe-Alagoas Basin and Beyond. Projections and Cautions from recent drilling and geochemical analyses. Rio Oil and Gas Conference 2018 Proceedings (IBP1918_18).