

'Torturing' Crude Oils (until they confess)

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Search and Discovery Article #30686 (2025)**

Posted November 29, 2025

*Adapted from extended abstract based on oral presentation given at AAPG International Conference and Exhibition (ICE) Rio de Janeiro, 30 September - 3 October, 2025.

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Abstract

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, a large (> 1700 oils), non-exclusive geochemical database was assembled. Using a multi-parameter approach, compositionally distinct oil types or families can be recognized. Outliers with unique chemistries (e.g., Paleozoic source) or oils that experienced advanced maturity or extensive biodegradation, resulting in compromised biomarker distributions were excluded. Key geochemical indicators of source-rock paleo-environments and age developed in the South Atlantic Margin (Mello, et al., 1988; Schiefelbein et al., 1999, 2001, 2017) were then used to assign source ages 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 the West Africa Salt Basin 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 (abundant oleanane) 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.

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“Torturing Crude Oils Until They Confess”

An Ongoing (Geochemical) Crime Scene Investigation of the South Atlantic Margin

Craig Schiefelbein (Geochemical Solutions International)

William Dickson (Dickson International Geosciences)

John Zumberge (GeoMark Research)

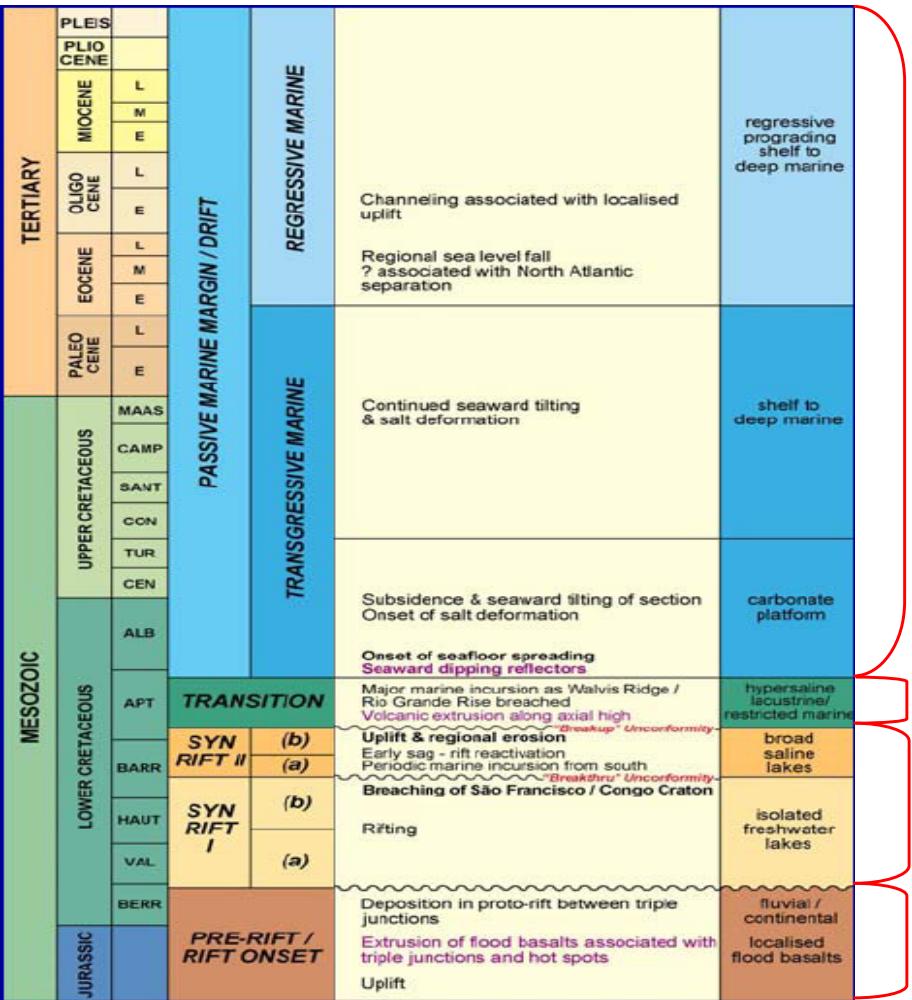
Introduction

Continuing research has clarified the tectono-structural history of the South Atlantic conjugate margins. This includes the creation and segmentation of source rock depocenters that correspond to paleogeographic reconstructions associated with five sedimentary mega-sequences: Continental, Transitional/Evaporitic, Carbonate Platform, Marine Transgressive and Marine Regressive with corresponding source rock depocenters (Gibbs et al., 2003). 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.

Petroleum geochemists have concurrently examined the nature and distribution of these associated source rocks by characterizing crude oils within a field, then a basin and across a series of basins. Crude oils possess important biological clues that can be used to unravel their genetic history from source to trap and beyond. Key geochemical indicators of source-rock paleo-environments and age in the South Atlantic Margin (Brice et al., 1980; Mello, et al., 1988; Schiefelbein et al., 1999; 2001; 2017) have developed along with increasing numbers of samples and a broadening range of data (i.e., deuterium isotopes, diamondoids) extracted from each sample. Geochemical data in this study are entirely non-exclusive and originated from Core Lab, Geochemical Solutions International, Geomark Research, and TDI Brooks International. These data have been integrated and interpreted within a multi-disciplinary framework as part of the MARIMBA project.

South Atlantic Margin Tectono-Stratigraphy

Gibbs et al., PESGB/HGS
Africa Conference, 2003

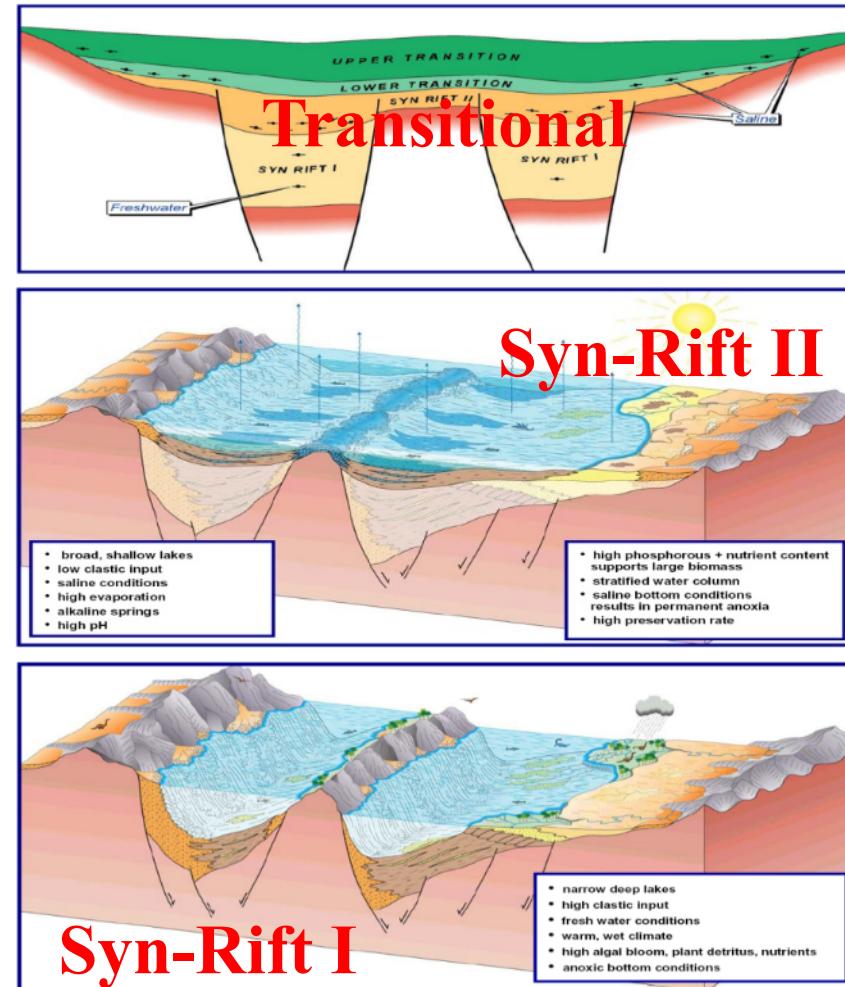


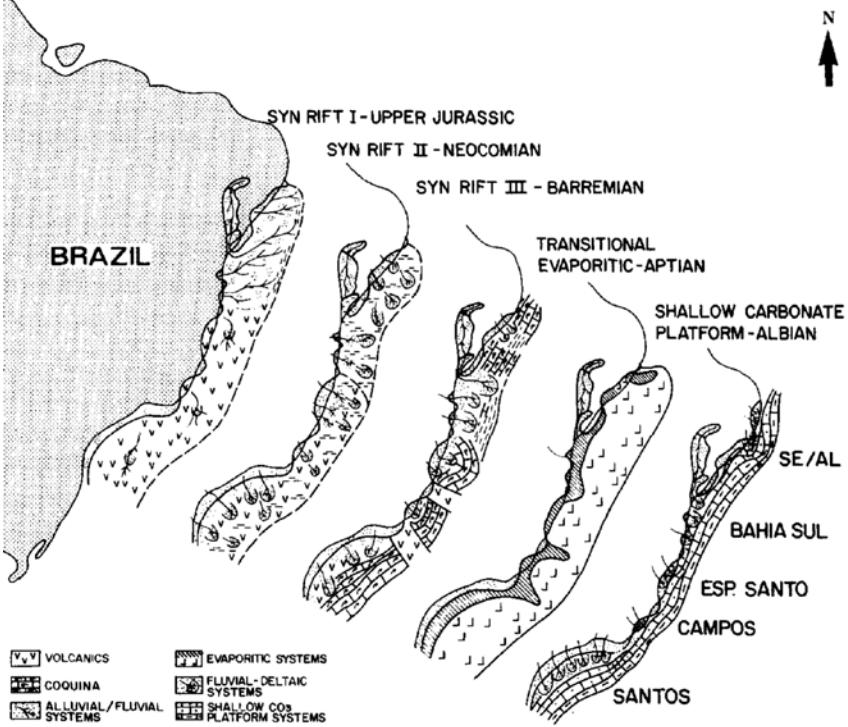
Drift

Transition

Syn-Rift

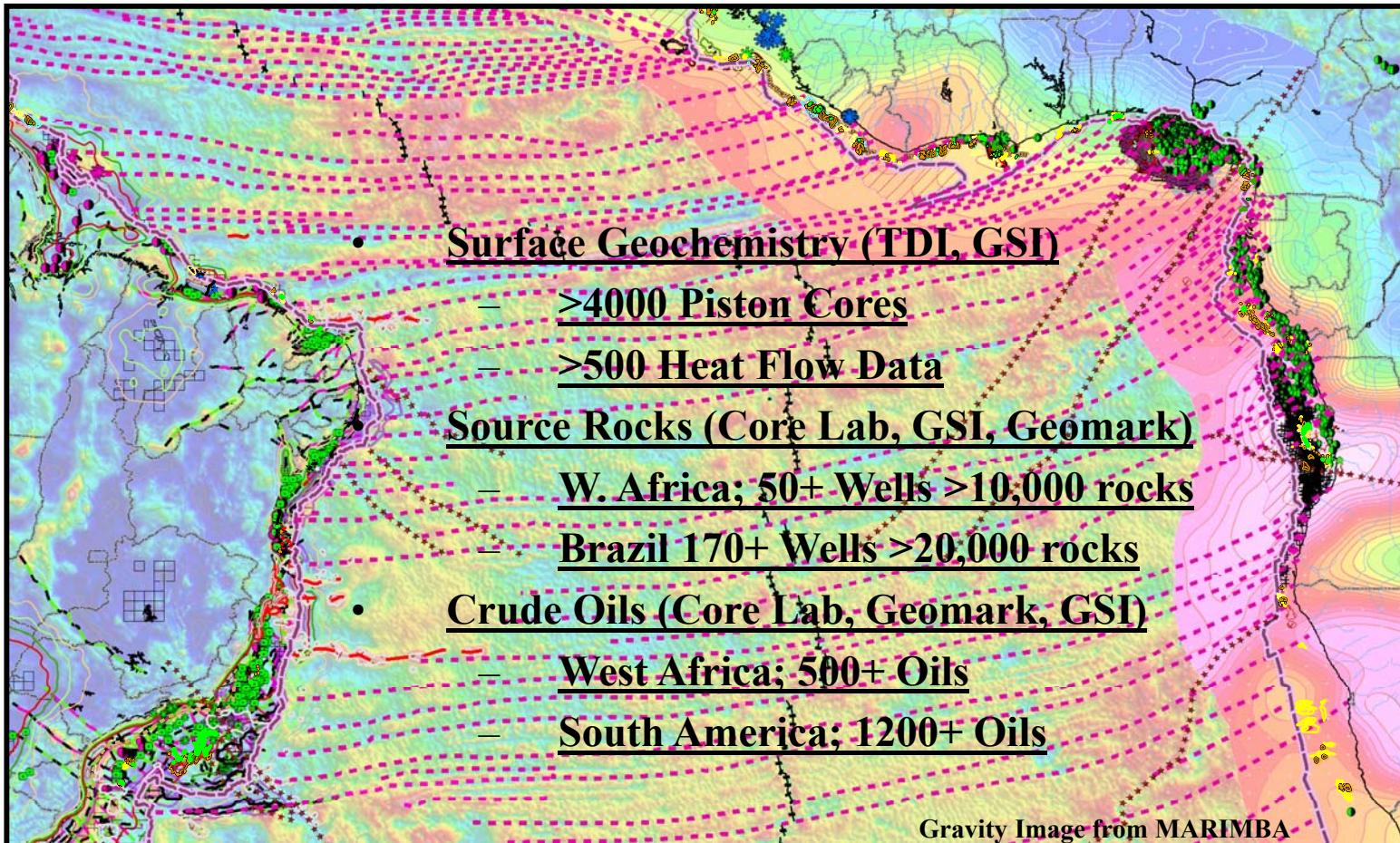
Pre-Rift





Paleogeographic Reconstructions from Chang, et al, 1992

South Atlantic Margin Data Set since the 1970's



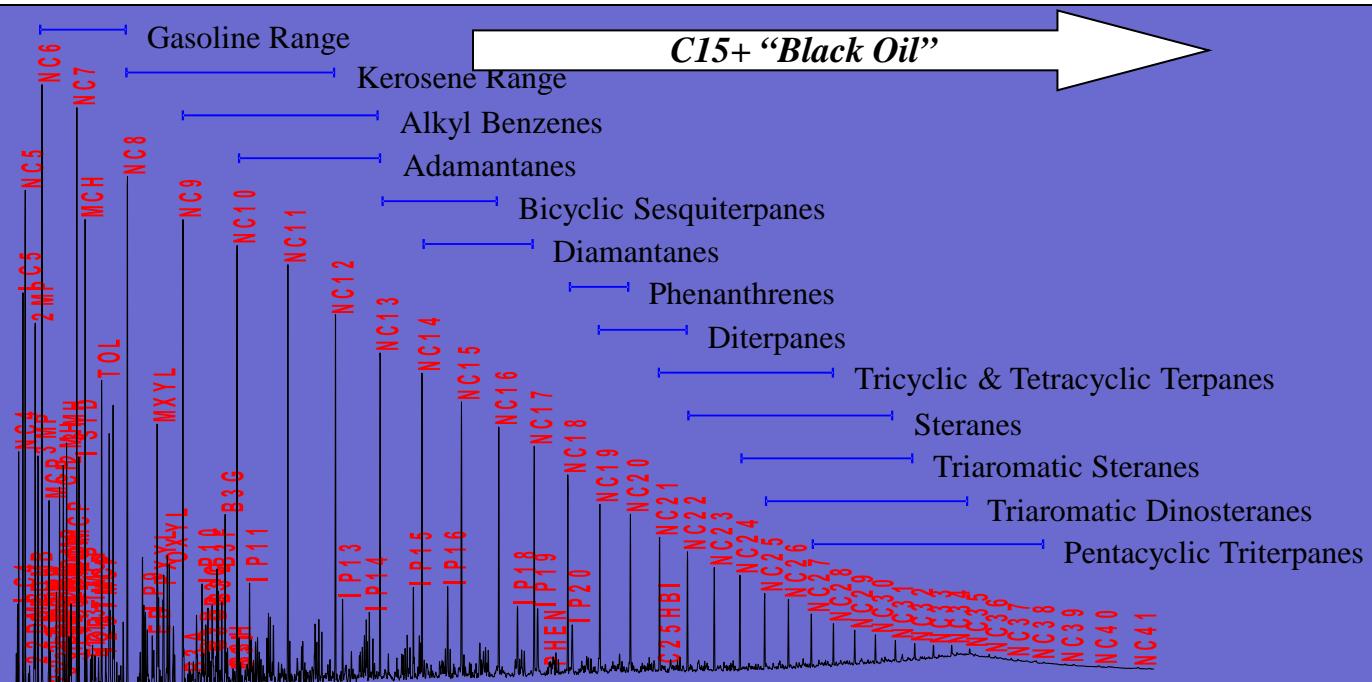
Analytical and Statistical Approach

Using a multi-parameter approach that relied on a combination of source dependent parameters corresponding to the ‘black oil’ ($>C_{15}$) component, compositionally distinct oil types or families can be recognized. Outliers with unique chemistries (e.g., Paleozoic source) or oils that experienced advanced maturity or extensive biodegradation, resulting in compromised biomarker distributions were identified and excluded.

Recognition and characterization of compositionally distinct oil types or families infers paleo-environmental conditions of source rock deposition and possible age. Source paleoenvironment and age are inferred, often using key biomarkers such as n-propyl C_{30} 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). Two key parameters useful in distinguishing lacustrine from marine oils are the proportion of C_{26} relative to C_{25} tricyclic terpanes (>1.2) and C_{30} Tetracyclic Terpanes (TTP) relative to C_{27} Diasteranes (from m/z 259; Holba et al., 2000; 2003). A lacustrine source is indicated when both ratios are elevated, and a marine source is suggested when either or both are low.

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.

Whole Oil Gas Chromatogram – Ideal World



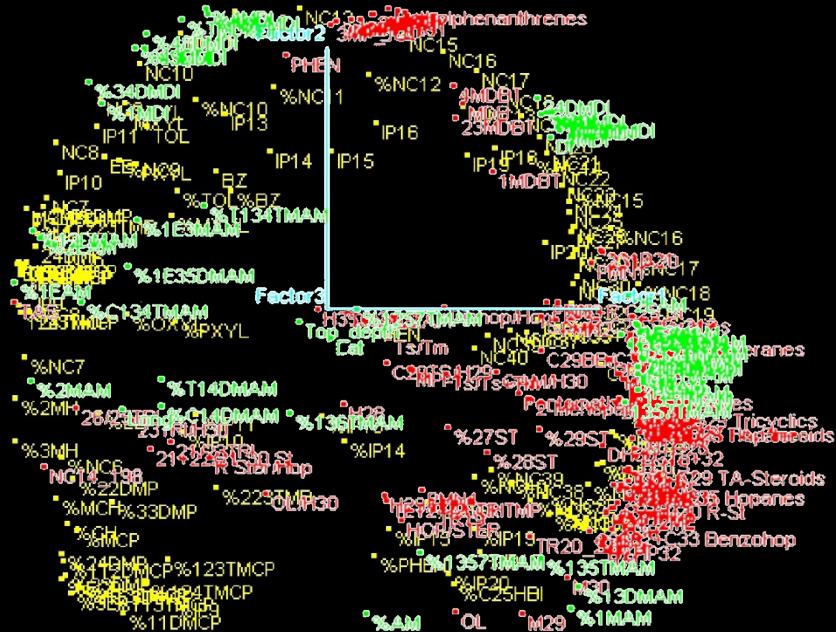
Analytical and Statistical Approach

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 are created (i.e., principal components) that 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 ‰) 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.

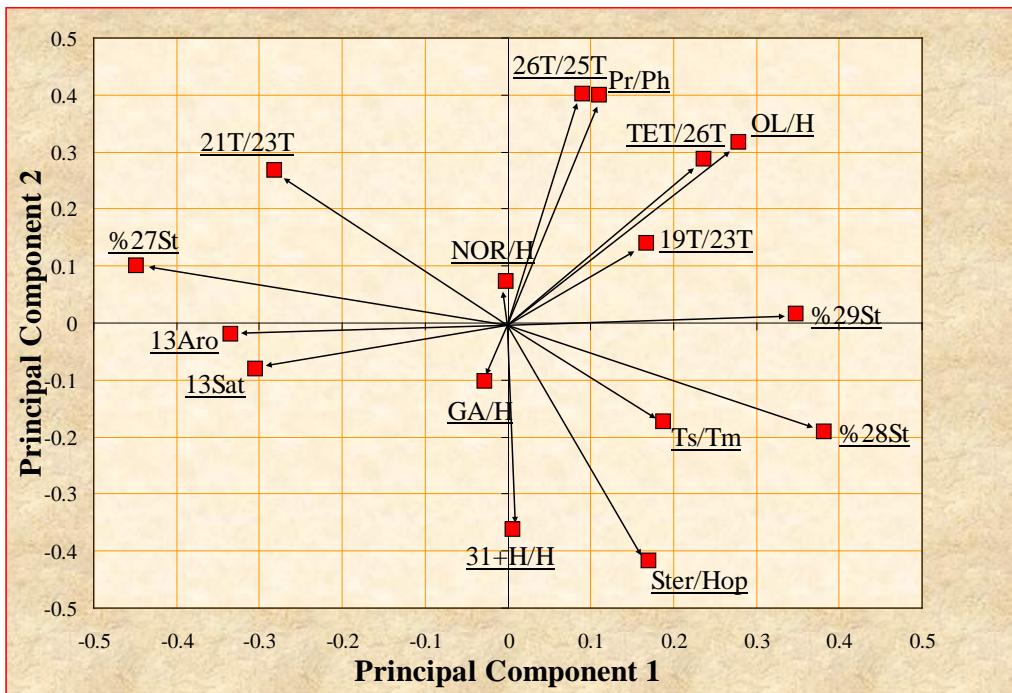
Statistical analysis of some 1700 oils allowed separation into five major families: Early SynRift; Late SynRift/Sag; Marine/Mixed; Marine; Tertiary Deltaic. Incorporation of additional geologic constraints from tectono-structural mapping suggest that oil family and sub-family distributions often relate 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.

Subsequent statistical analyses were performed using only oils derived from pre-salt lacustrine source rocks to better understand the genetic relationships established during the rifting event and only oils derived from postsalt (Aptian/Albian/Cenomanian/Turonian) marine source rocks.

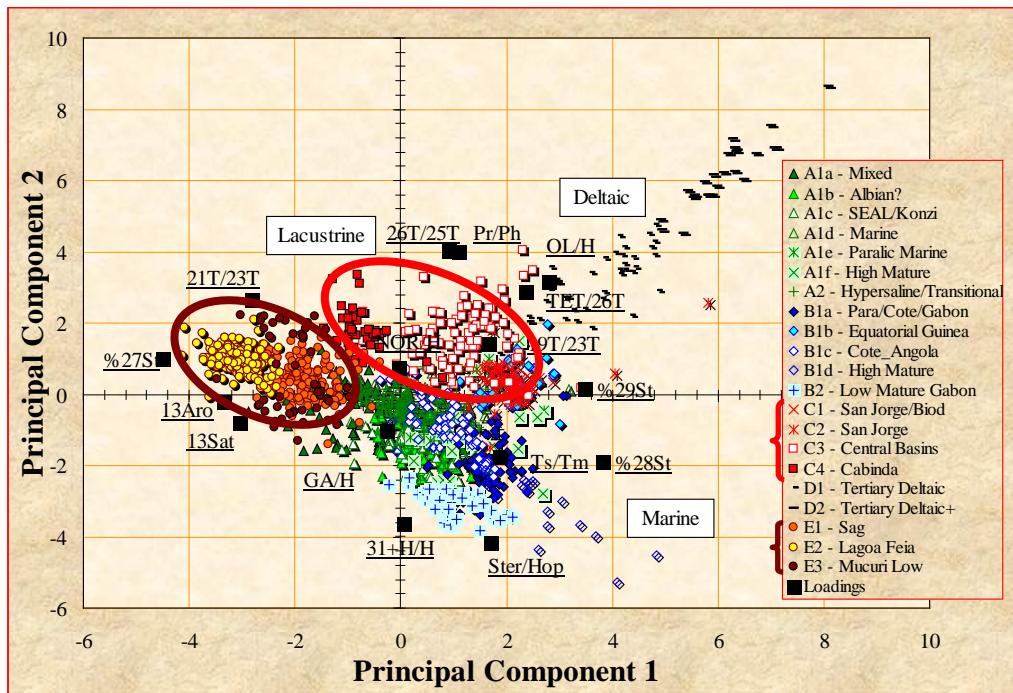
PCA Loadings – GC, GCMS, 13C Data



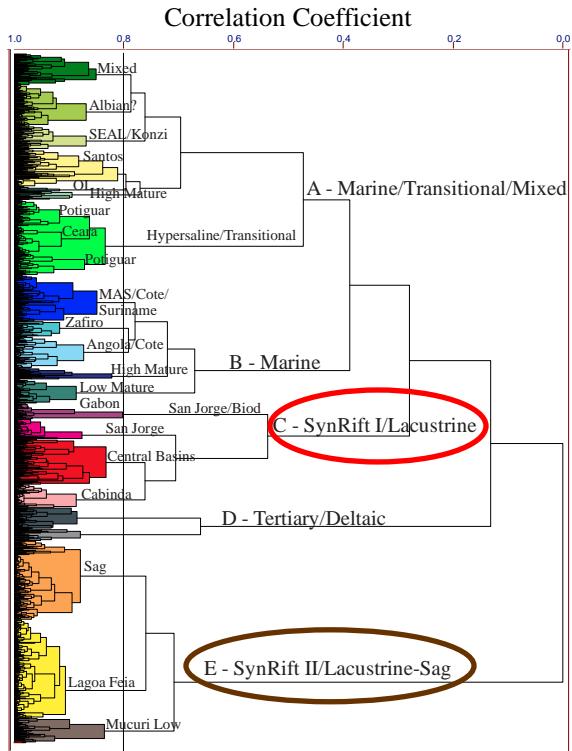
PCA Loads – All SAM Oils



PCA Loads/Scores – All SAM Oils



S. Atlantic 2020: HCA Dendrogram



- of 1651 oils, 255 excluded, 1396 oils tortured (again)
- 16 source dependent parameters
- 56.5% of variance described by 3 PCs (principal components)
- 5 Families A-E @ 0.47 correlation; 21 subfamilies @ 0.80 correlation
- 621 oils from Families C & E analyzed separately

Results and Discussion

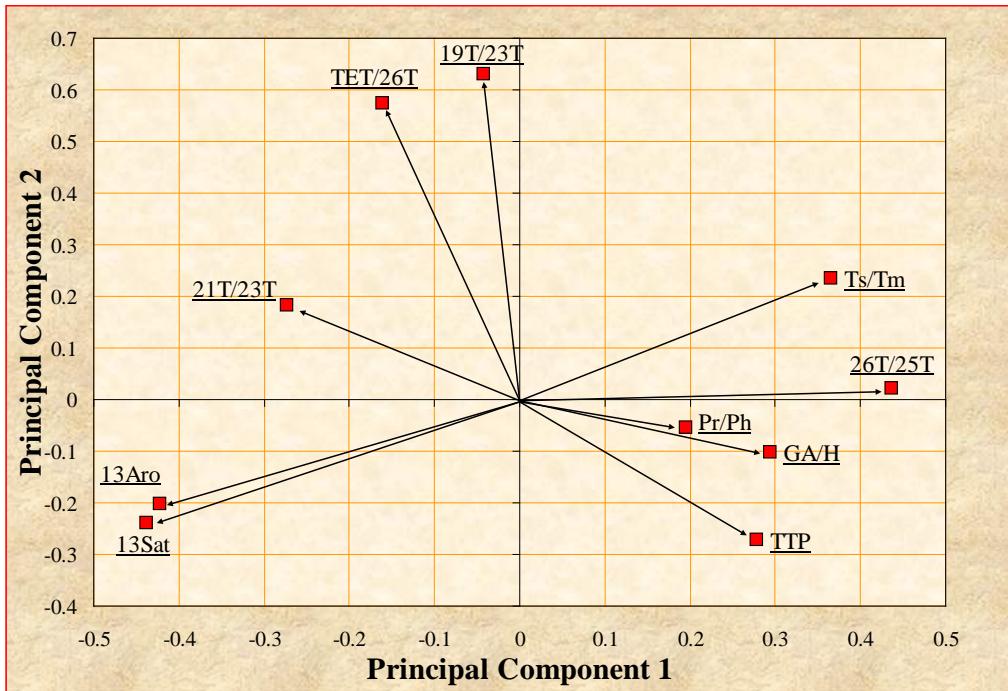
Genetic relationships are established based on compositional similarity. The strongest genetic conjugate relationships are observed between oils from central Brazil and the West Africa Salt Basin that originated from Barremian (Lower Rift/SynRift I) source rocks deposited in deep, freshwater lacustrine 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).

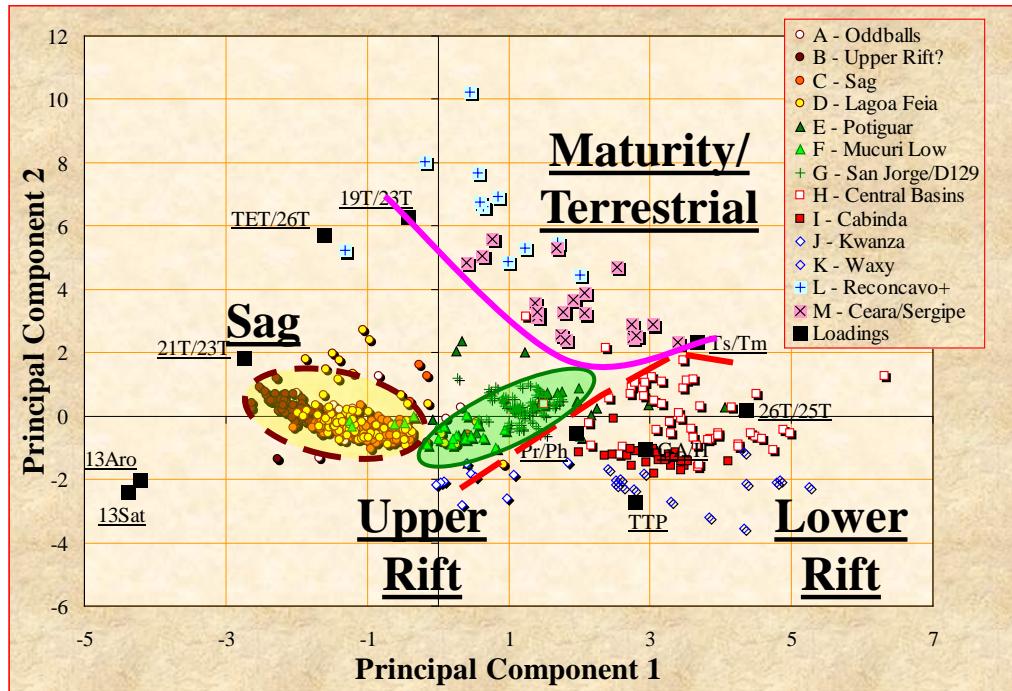
Most crude oils examined from the Niger Delta have unique chemistries (abundant oleanane) associated with an origin from source rocks influenced by higher land plants (angiosperms; Tertiary Deltaic).

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.

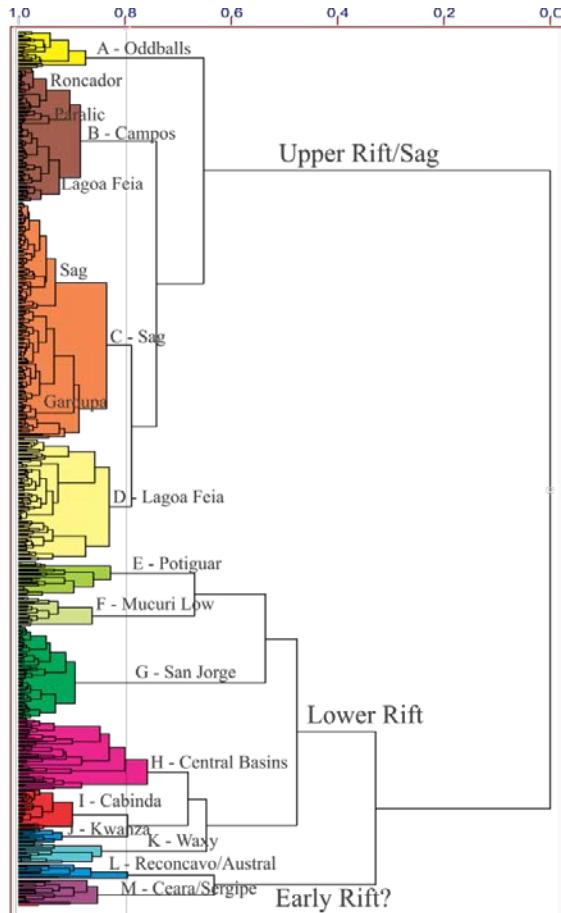
PCA Loads – Only PreSalt/Lacustrine Oils



PCA Loads/Scores – Only PreSalt/Lacustrine Oils



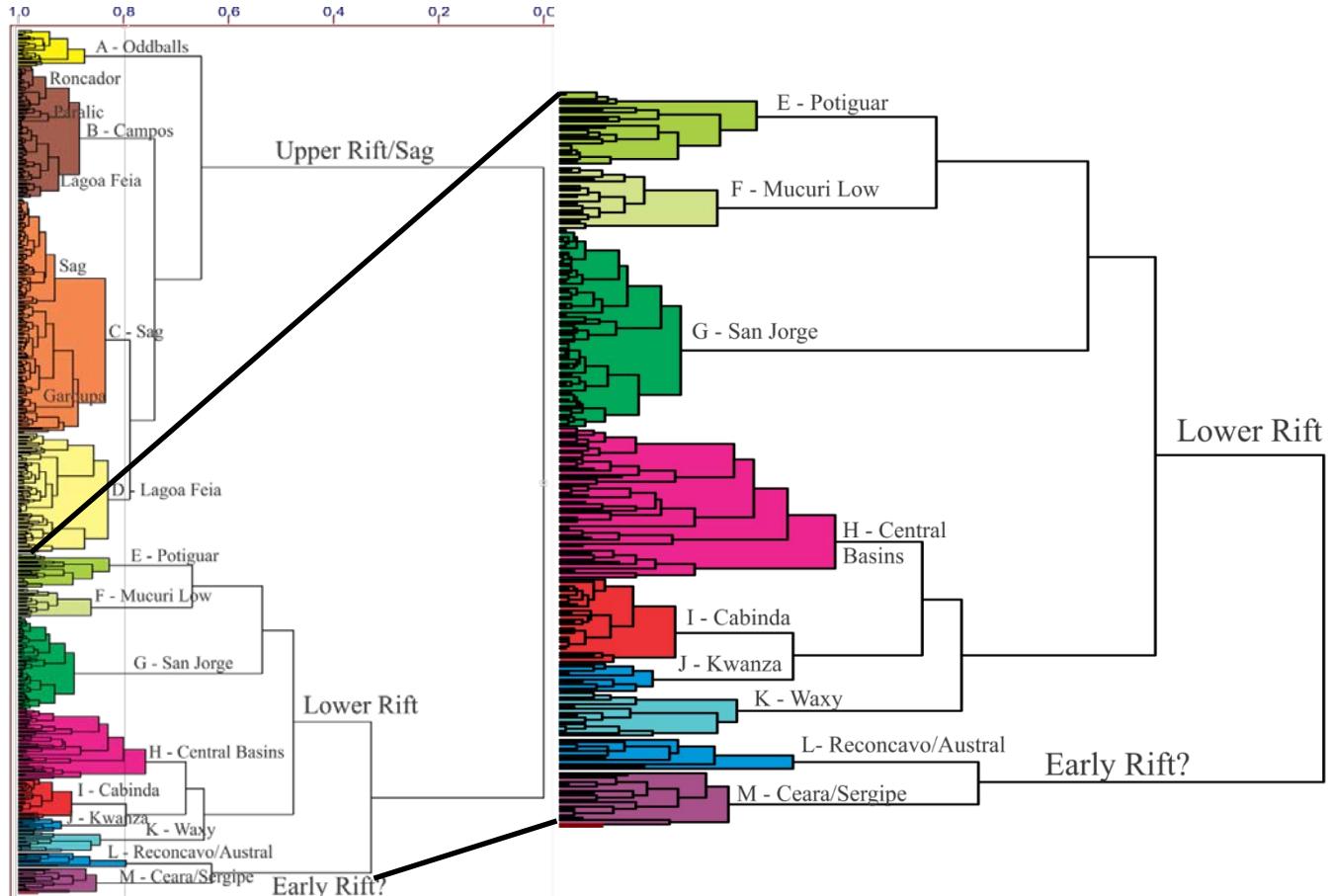
Correlation coefficient



PreSalt 2020: HCA Dendrogram

- 621 oils from Groups C & E analyzed separately
- 10 parameters focused on lacustrine oils (minor marine influence)
- 65% of variance in 3 pc (principal components)
- 2 major groups, 3 subgroups; 13 subfamilies @ 0.80 correlation
- Oils in upper cluster are restricted to Brazil
- Oils in the bottom cluster are related to early rifting events

Correlation coefficient

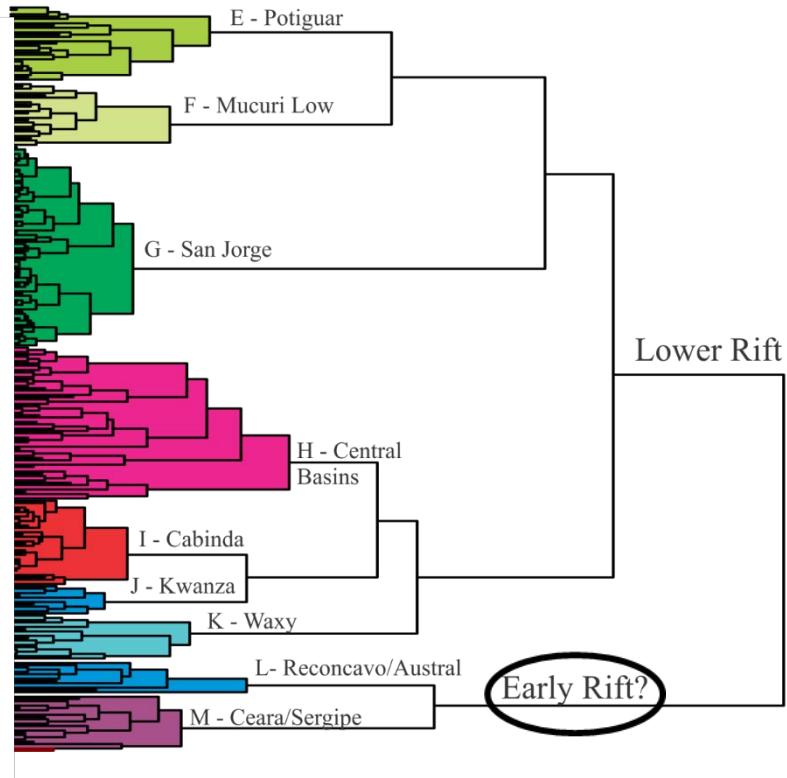


Paleogeography

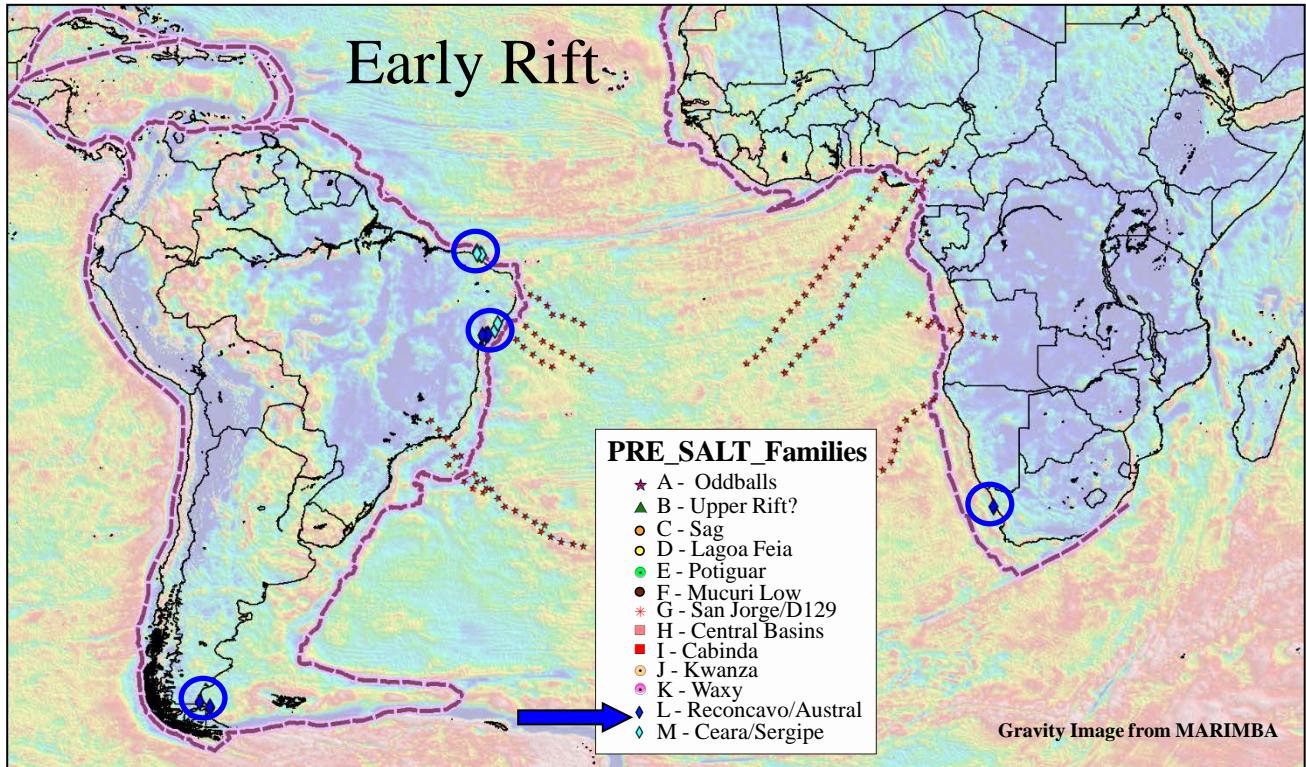


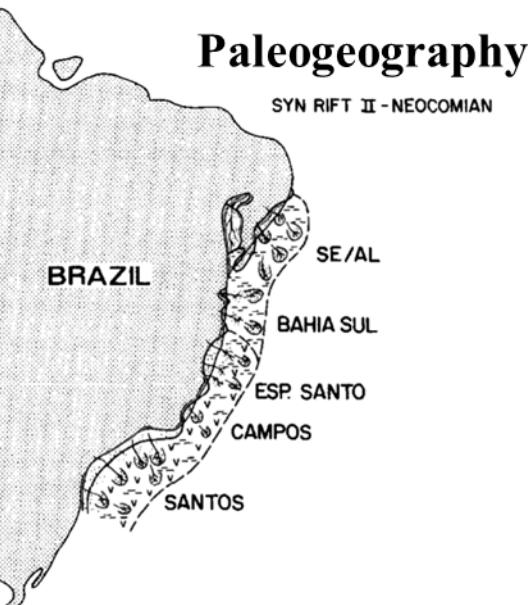
Chang, et al, 1992

VOLCANICS	EVAPORITIC SYSTEMS
COQUINA	FLUVIAL- DELTAIC SYSTEMS
ALLUVIAL/FLUVIAL SYSTEMS	SHALLOW CO ₂ PLATFORM SYSTEMS



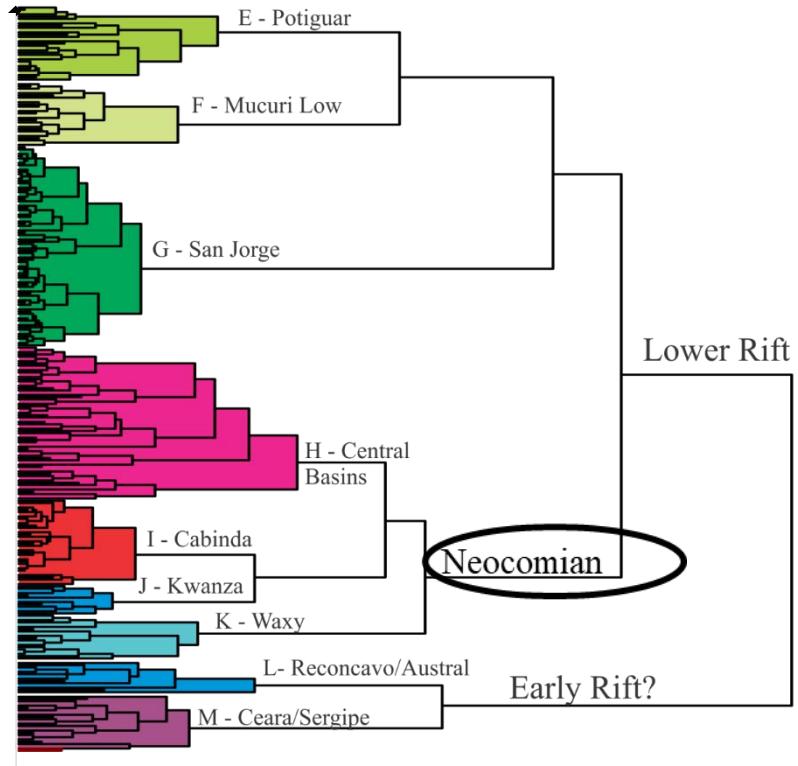
Early Rift



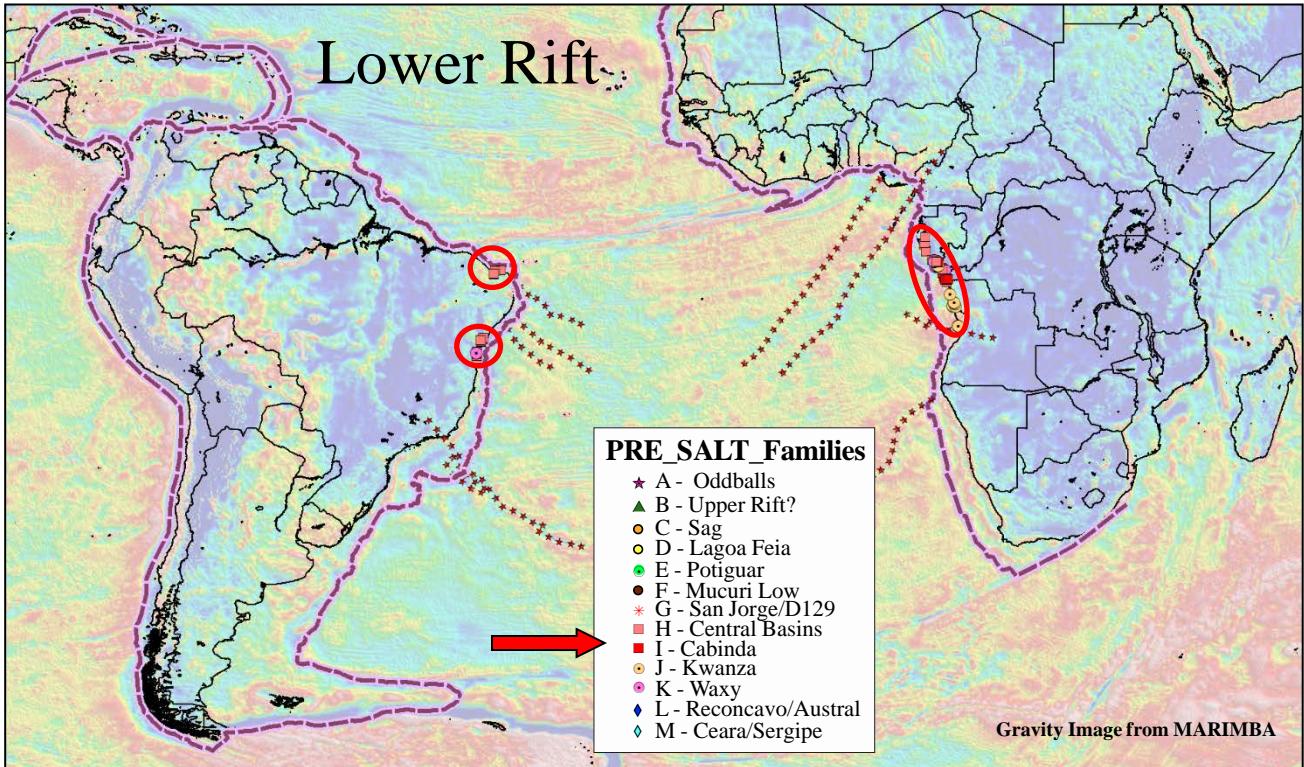


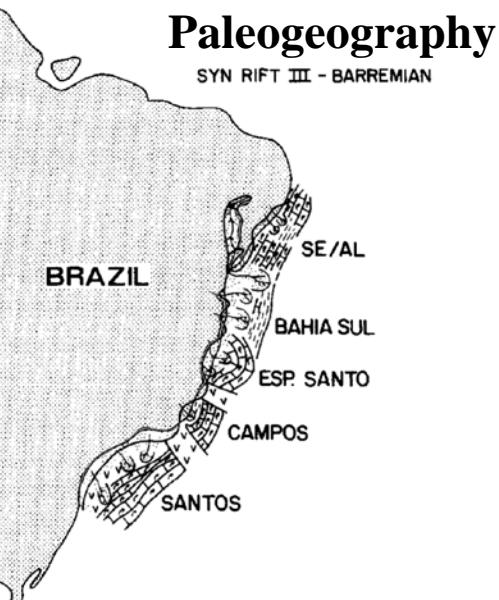
Chang, et al, 1992

VOLCANICS	EVAPORITIC SYSTEMS
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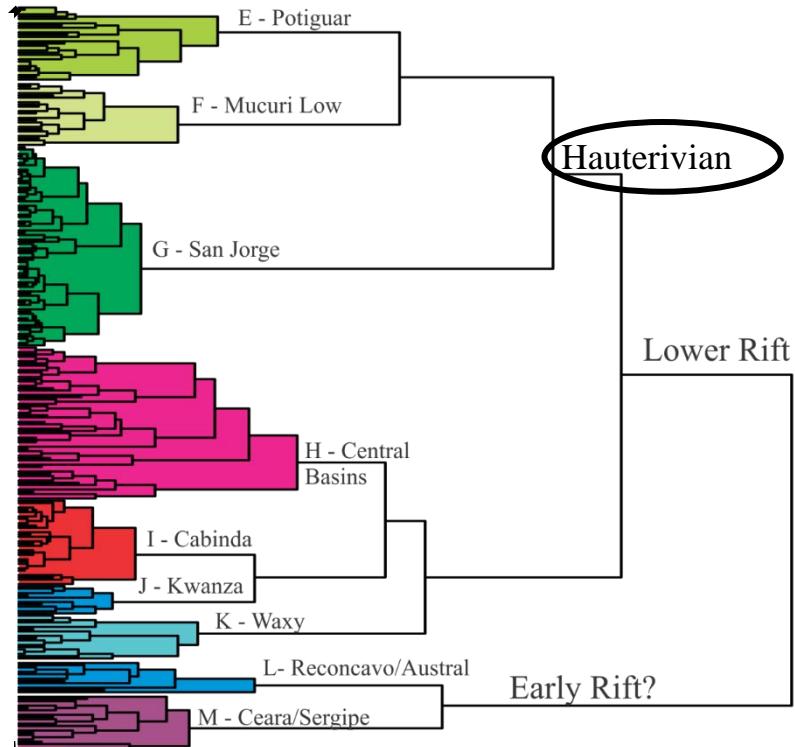
Lower Rift



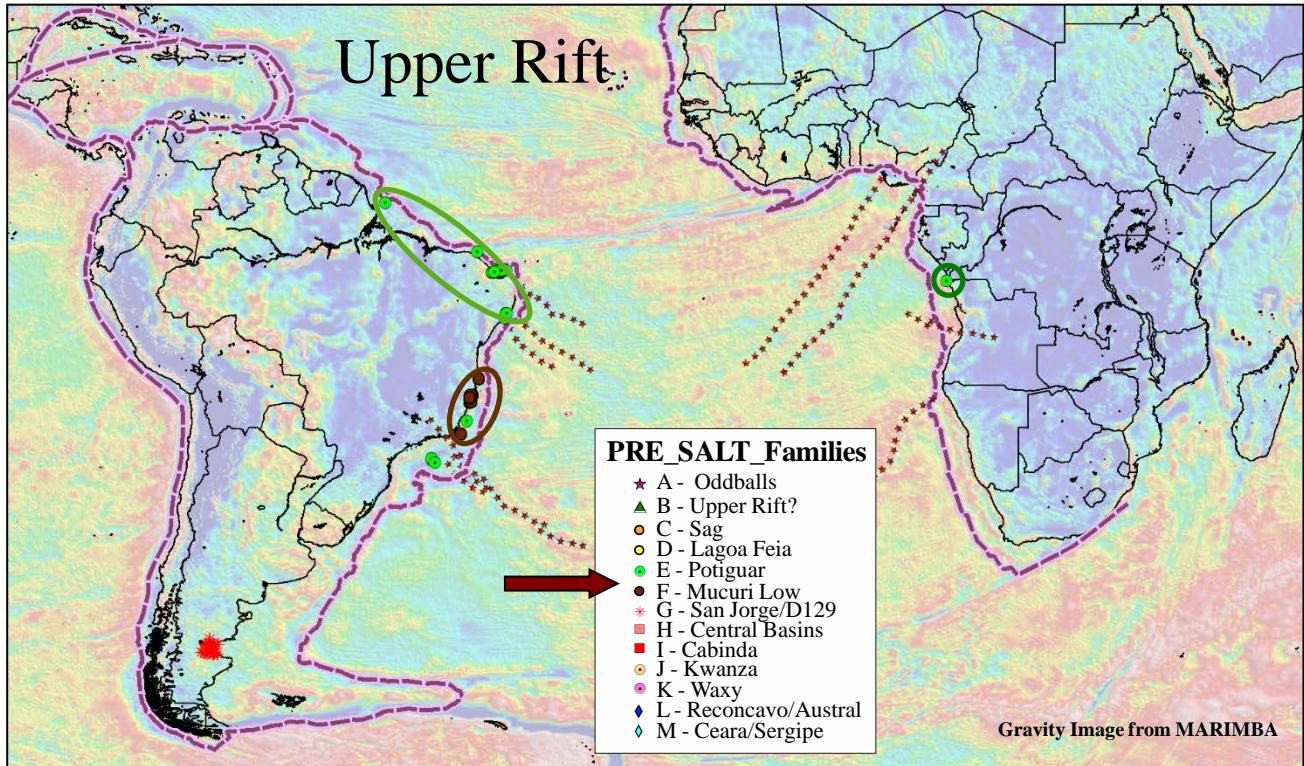


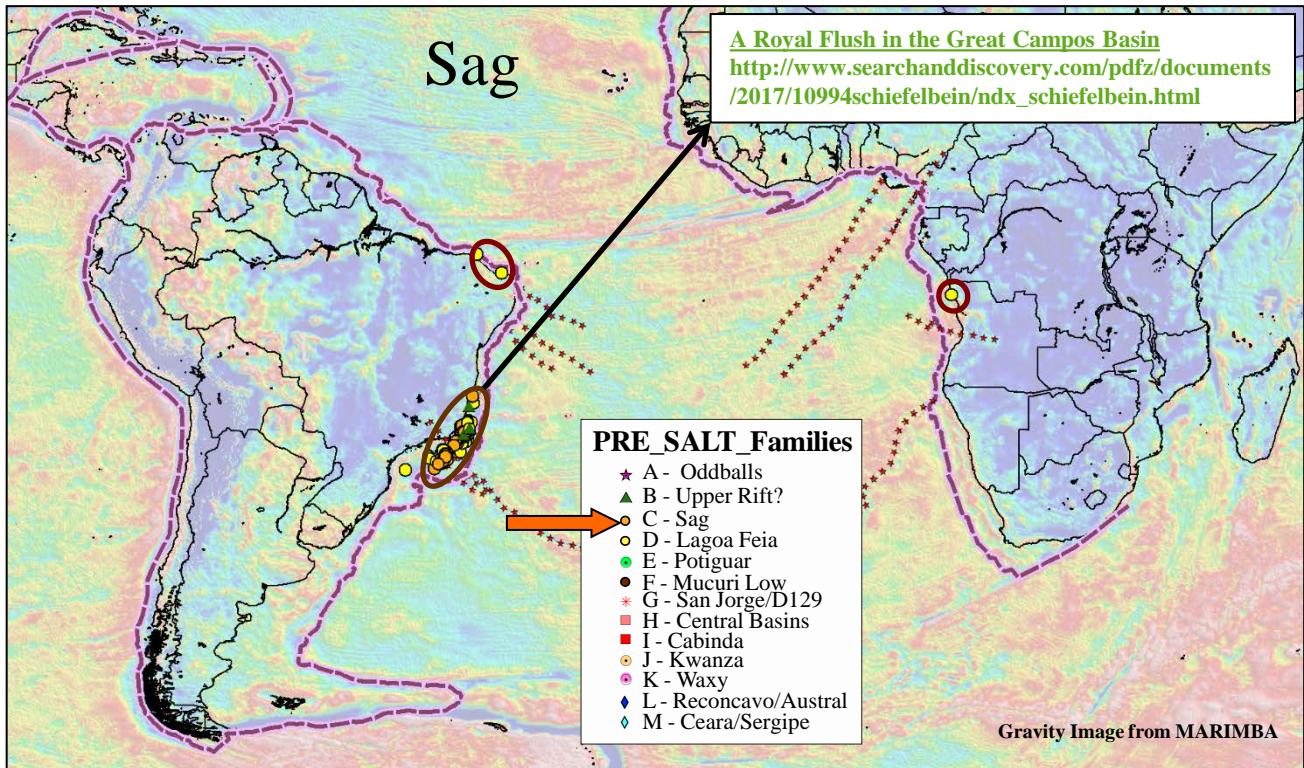
Chang, et al, 1992

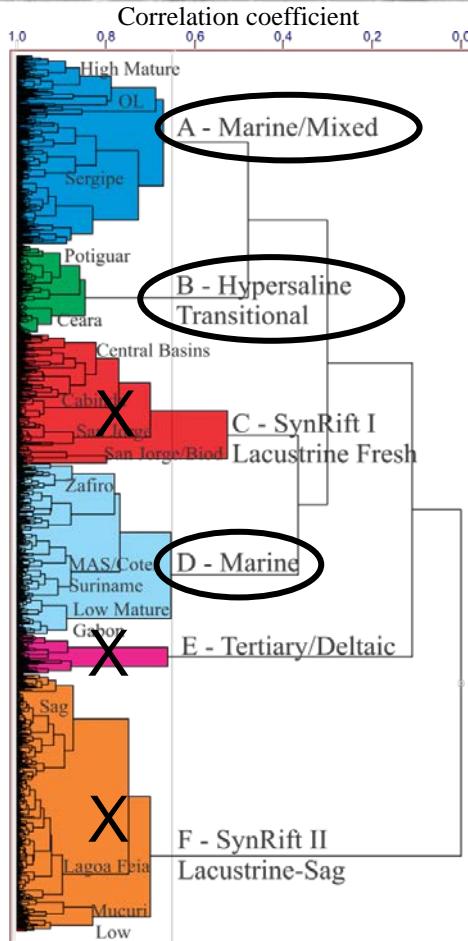
VOLCANICS	EVAPORITIC SYSTEMS
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Upper Rift



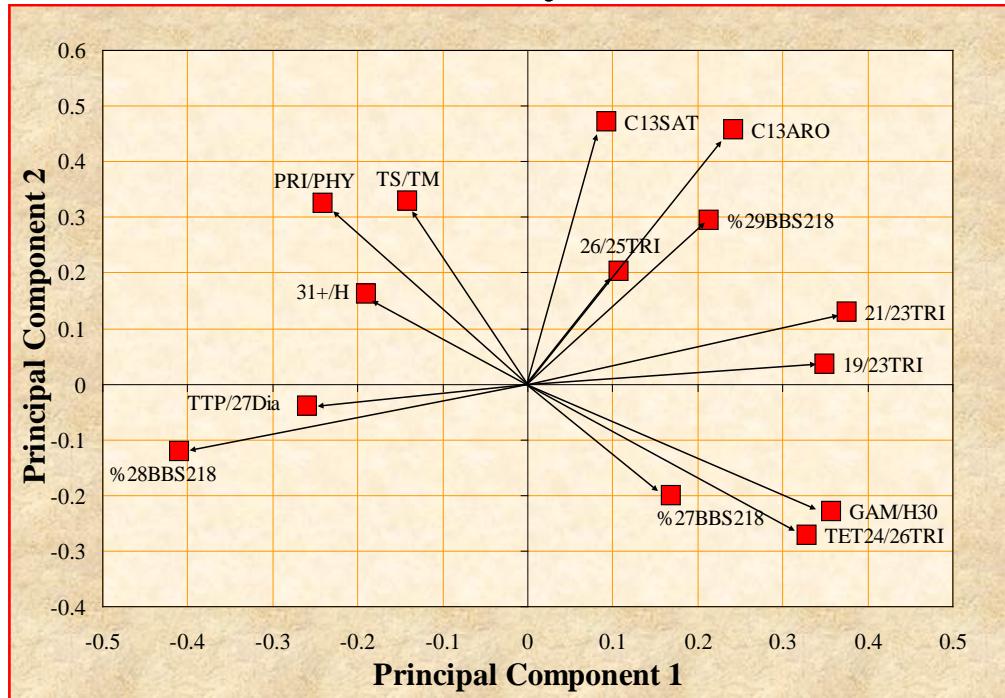




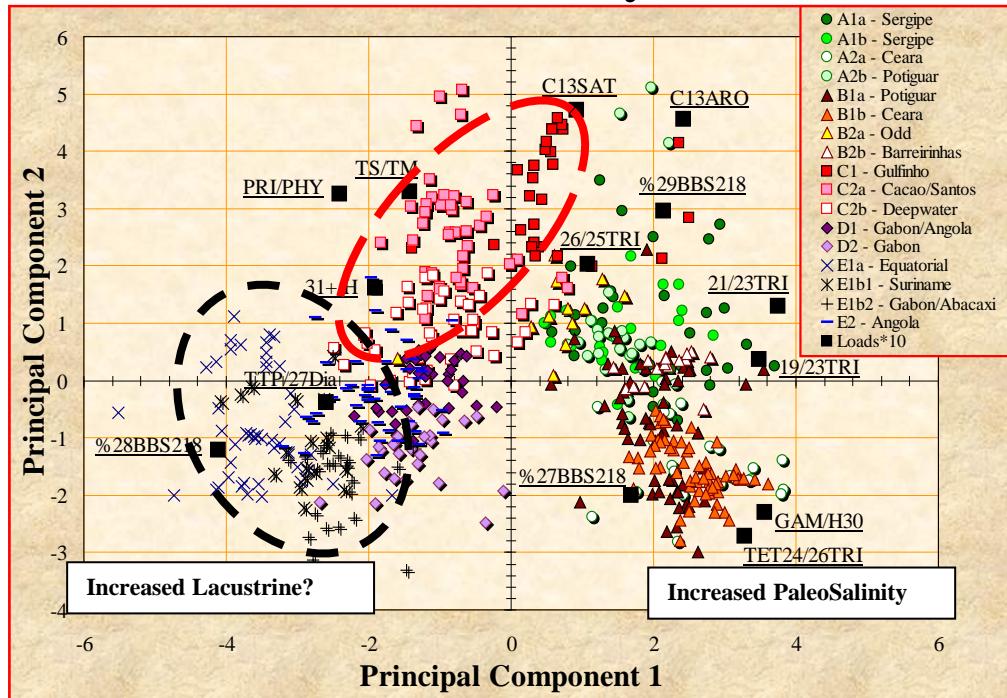
S. Atlantic 2022: HCA Dendrogram

- of 1740 oils, 329 excluded, 1411 oils tortured (again)
- 15 source dependent parameters
- 75% of variance described by 5 PCs (principal components)
- 6 families A-F @ 0.5 correlation; 19 subfamilies @ 0.80 correlation
- Oils in families A, B, D are primarily marine-derived and were analyzed separately

PCA Loads – Only PostSalt Oils

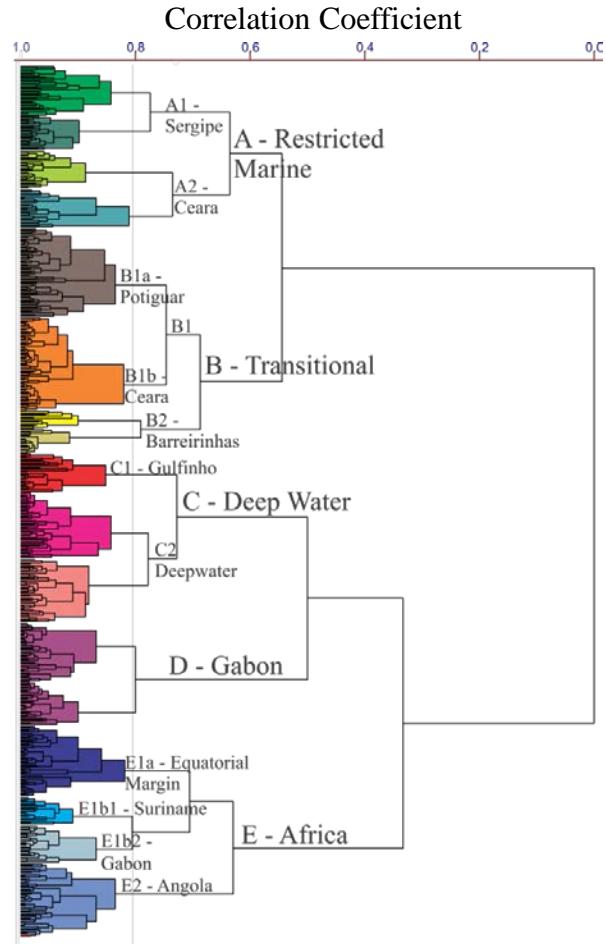


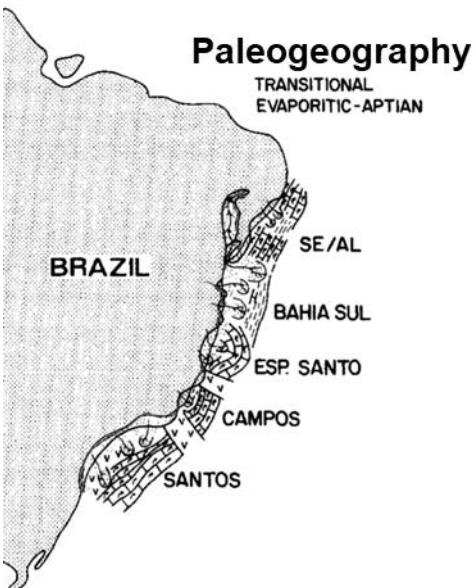
PCA Loads/Scores – Only PostSalt Oils



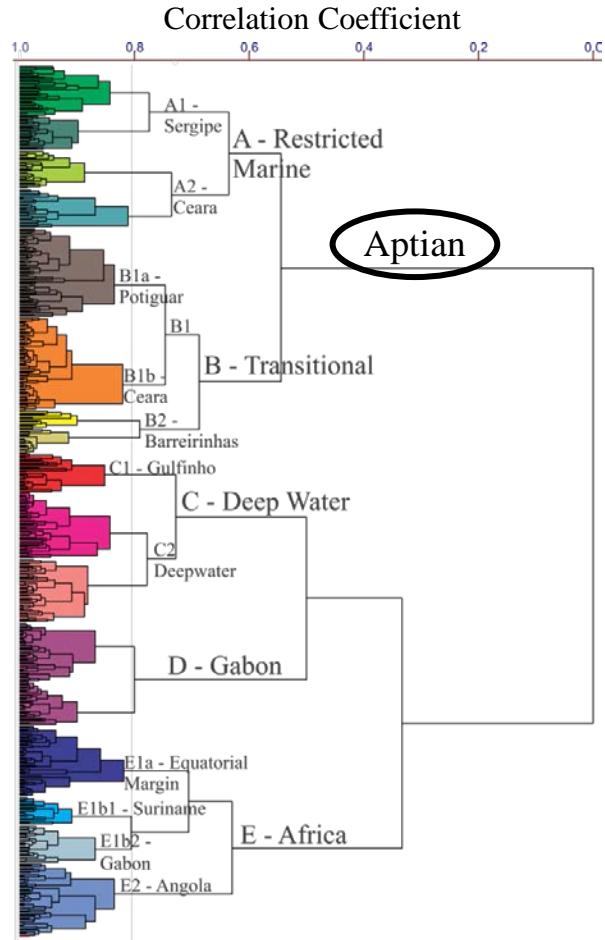
PostSalt Oils 2022: HCA Dendrogram

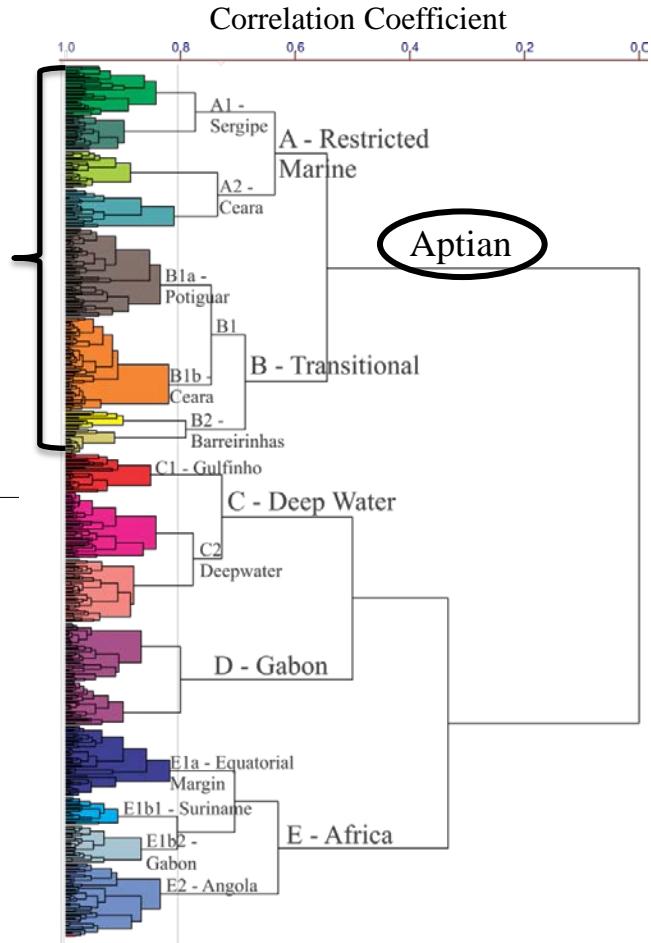
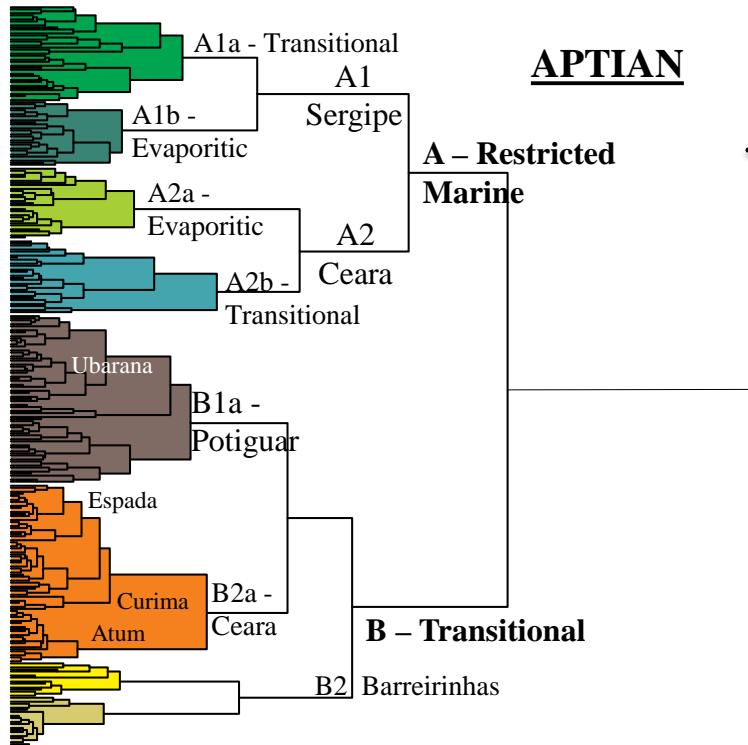
- 576 oils from Groups A, B & D
- 14 source dependent parameters
- 62% of variance in 3 pc (principal components)
- 2 major groups, 5 subgroups; 17 subfamilies @ 0.80 correlation
- Oils in top cluster originated from Aptian source rocks deposited in transitional environments
- Oils in bottom cluster originated from Middle Cretaceous marine source rocks

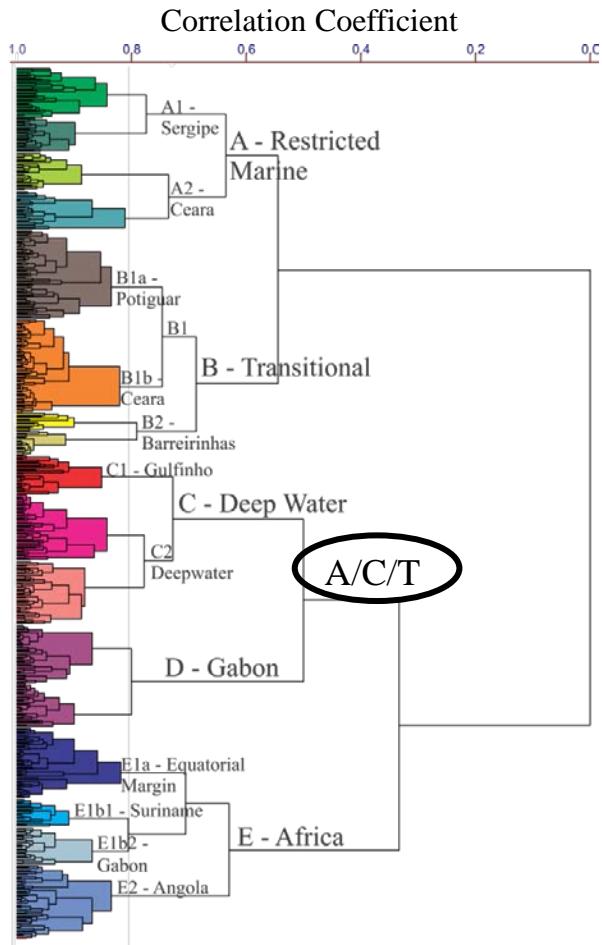
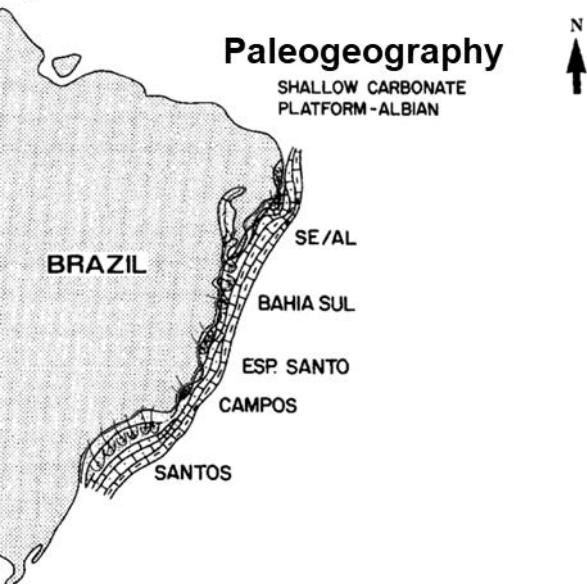


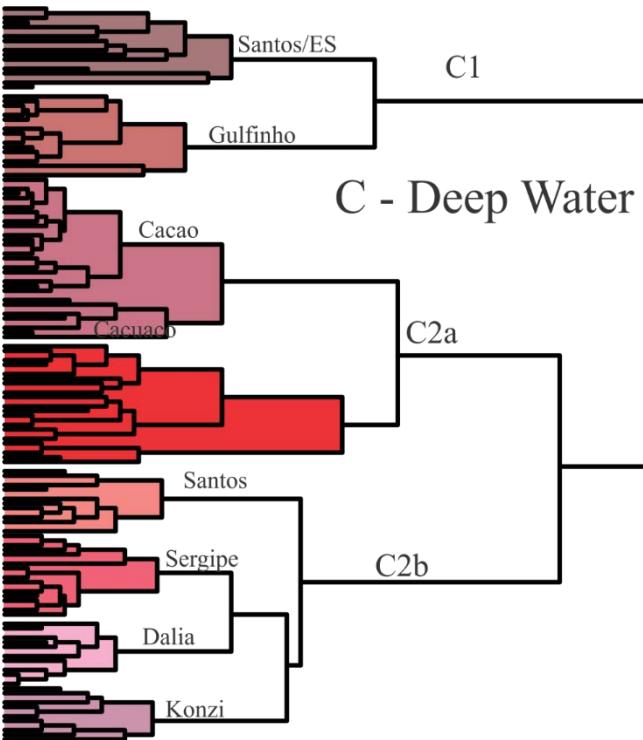


Chang, et al, 1992

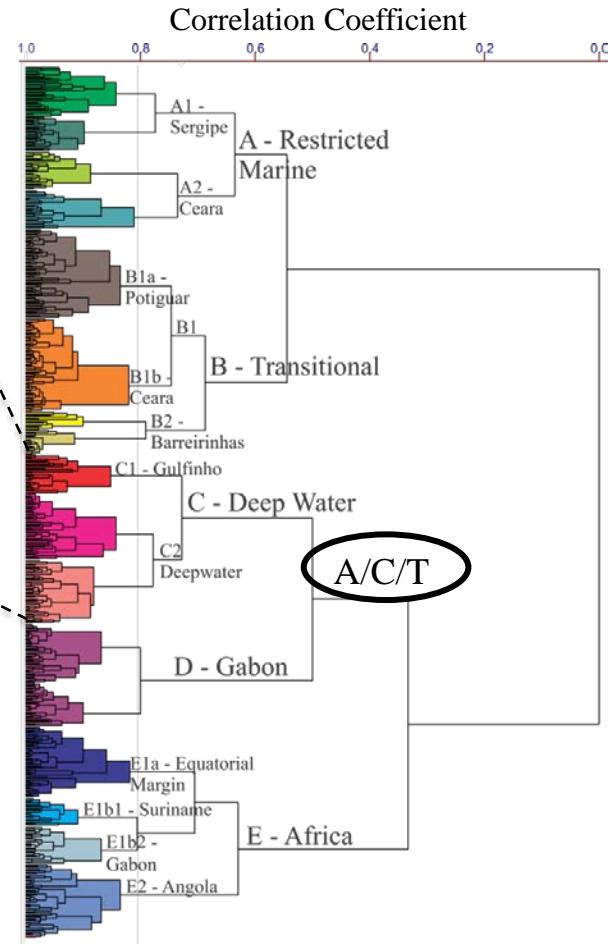




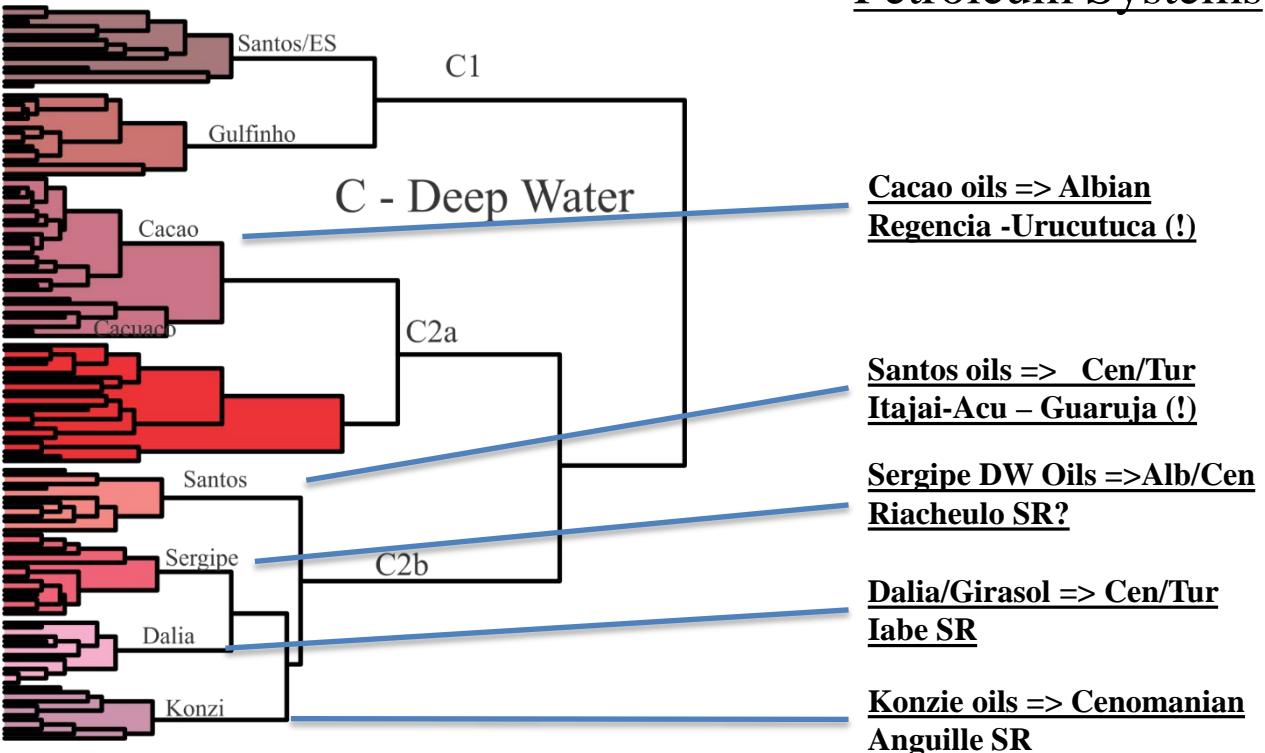




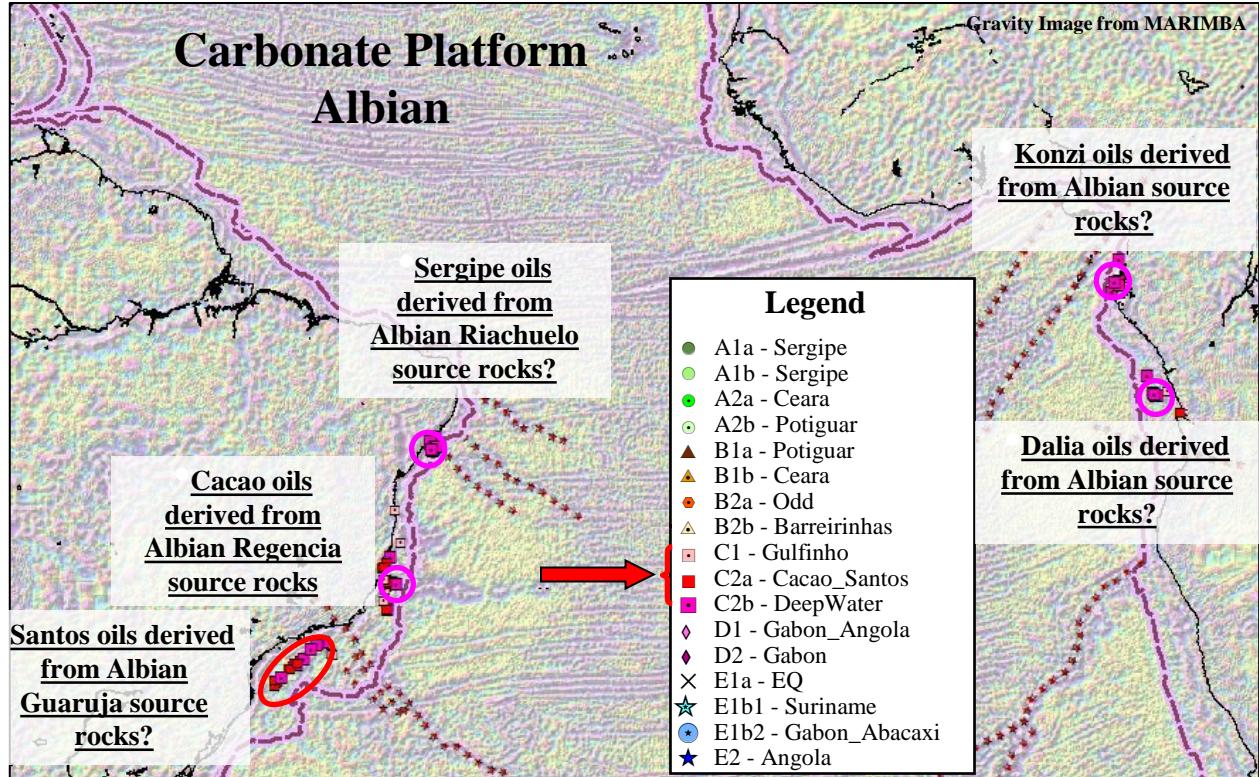
C - Deep Water

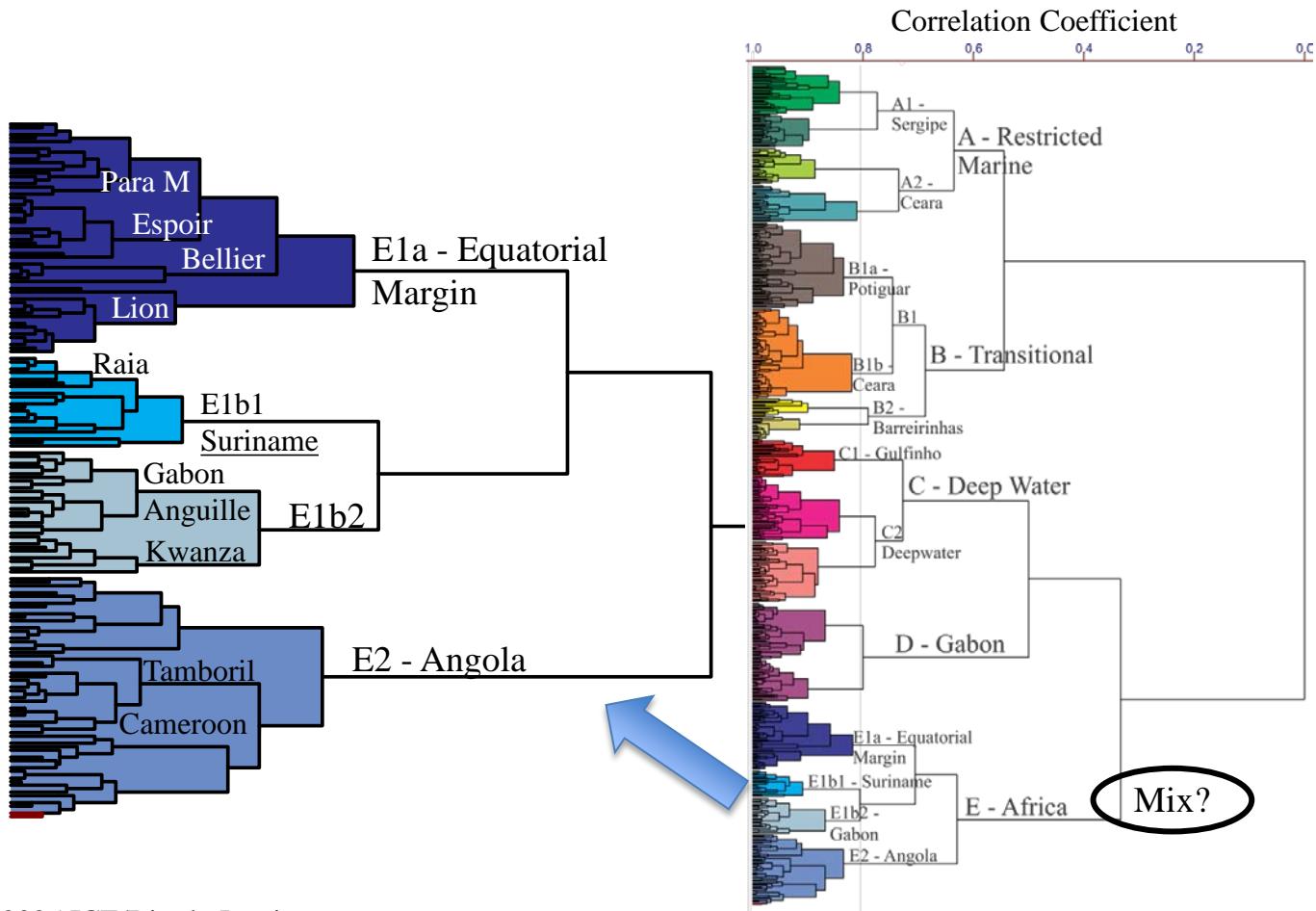


Petroleum Systems

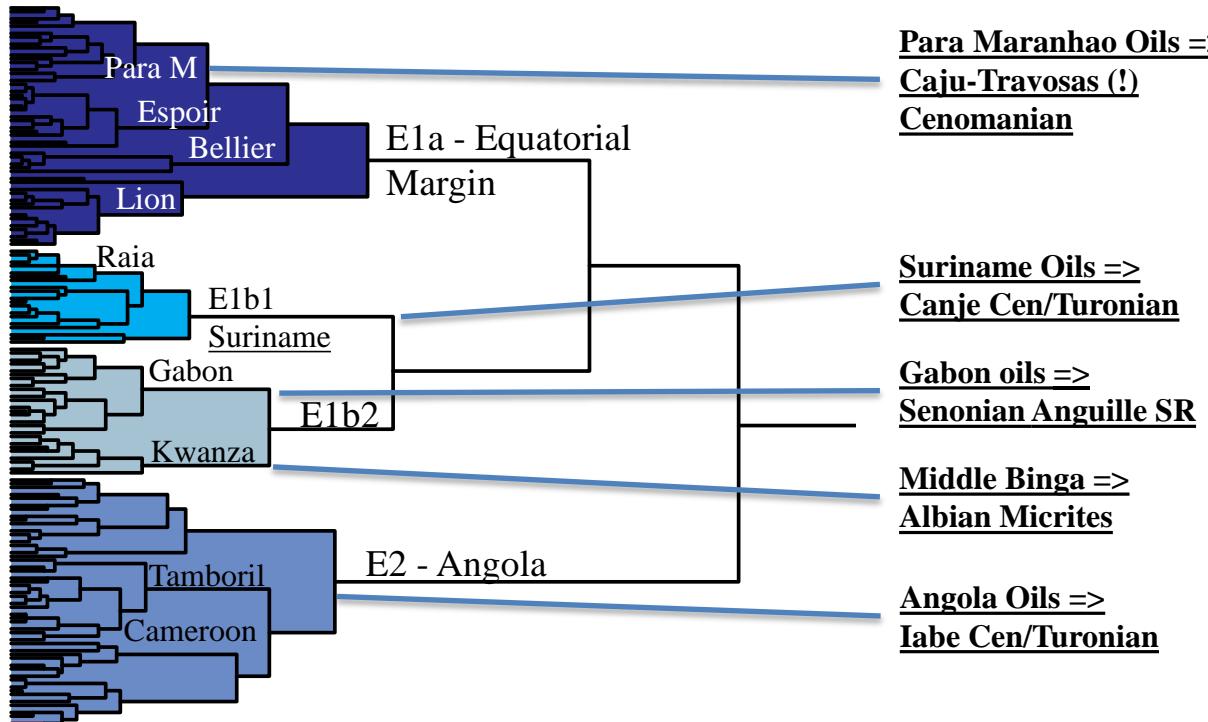


Carbonate Platform Albian



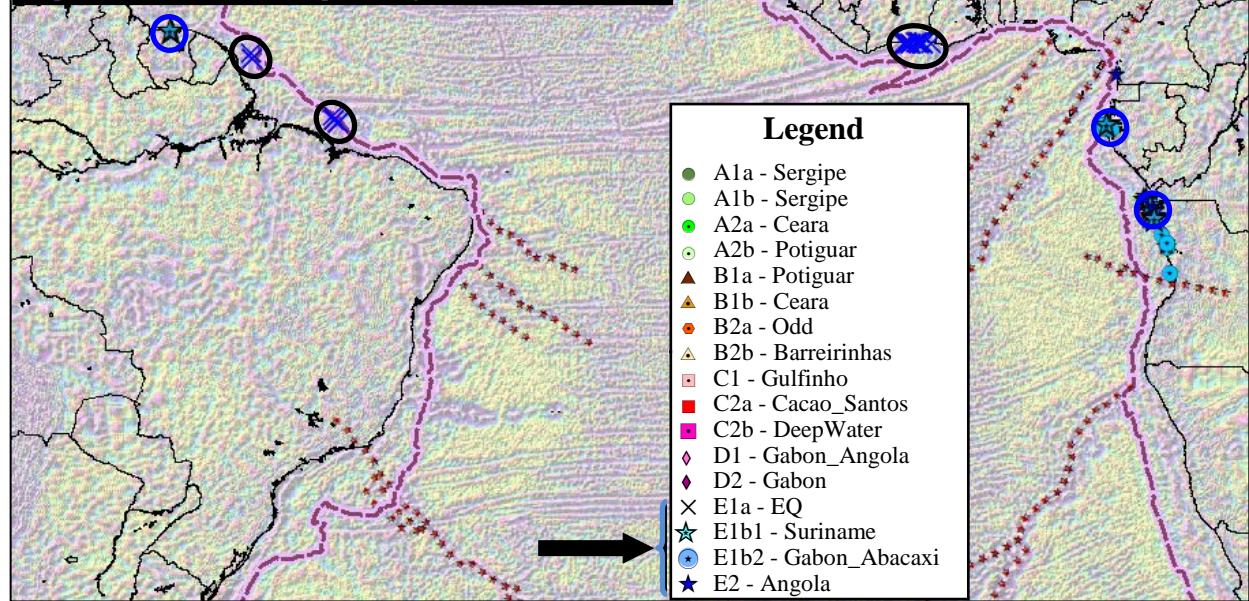


Petroleum Systems



Petroleum Systems Asymmetry across the South Atlantic Equatorial Margins

- Transform Margins: Development, Controls and Petroleum Systems. Geological Society, London, 2016
- Special Publications, 431, <http://doi.org/10.1144/SP431.13>



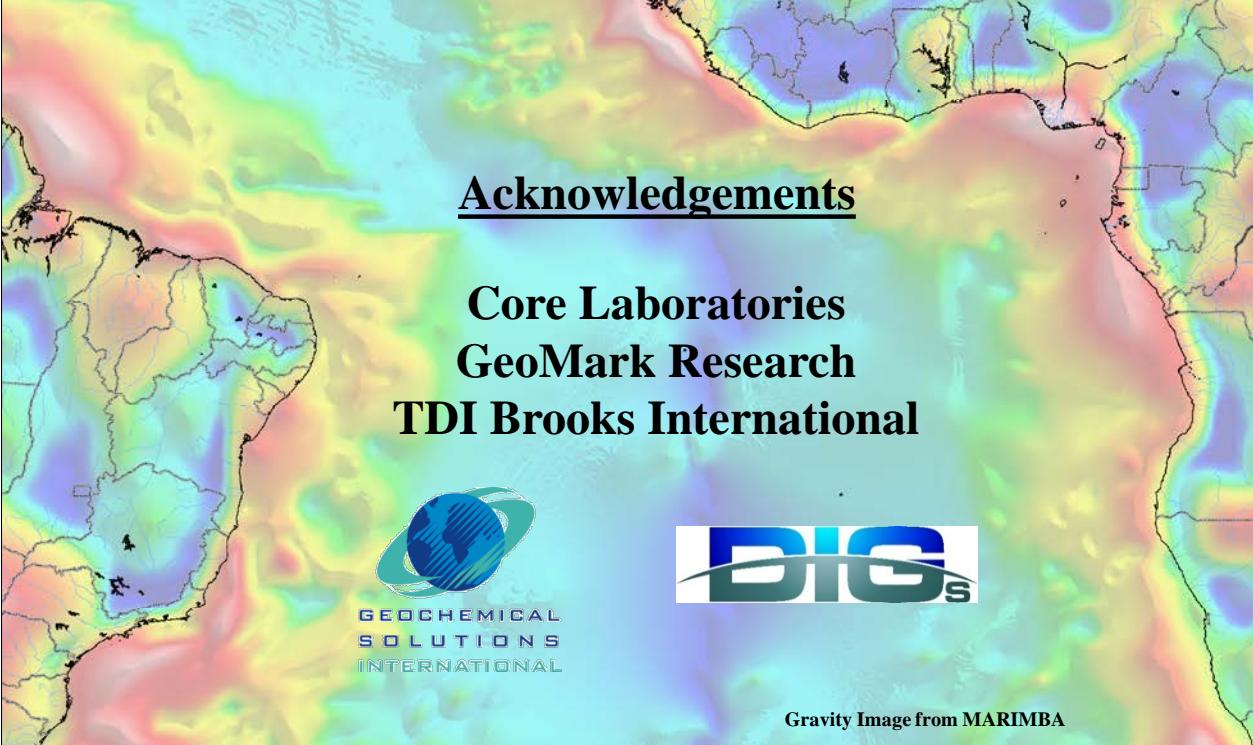
Observations

Statistical analysis of some 1700 oils allowed separation into five major families: Early SynRift; Late SynRift/Sag; Marine/Mixed; Marine; Tertiary Deltaic. 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. Best conjugate basin correlation extends from central Brazil to central West Africa (Lower Rift/SynRift I).

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 (abundant oleanane) 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.



Acknowledgements

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Gravity Image from MARIMBA