Llanos Basin: Unraveling Its Complex Petroleum Systems with Advanced Geochemical Technologies*

Mike Moldowan[1], Shaun Moldowan[1], Vladimir Blanco-Velandia[2], Yolima Blanco-Velandia[2], Claudia Orejuela-Parra[2], Geoffrey Bott[3], and Jeremy Dahl[4]

Search and Discovery Article #10776 (2015)**
Posted October 26, 2015

*Adapted from oral presentation given at AAPG Annual Convention & Exhibition, Denver, Colorado, May 31-June 3, 2015

[1]Biomarker Technologies, Inc., Rohnert Park, California, United States (jmmoldowan@biomarker-inc.com)
[2]Instituto Colombiano del Petróleo, Piedecuesta, Santander, Colombia
[3]GB Scientific, Inc., South Lake Tahoe, California, United States
[4]Laboratory for Materials & Energy Science, Stanford University, Stanford, California, United States

Abstract

Llanos Basin petroleum systems combine complex geology with complex petroleum geochemistry consisting of multiple source rocks and charges at different maturities. In addition, many of these charges were biodegraded to varying degrees. We have shown that all of these factors can converge in a single oil accumulation. Using advanced geochemical technologies (AGTs) we have determined that certain oilfields consist of multiple co-sourced accumulations with as many as four sources, thermally cracked light oil mixed together with normally-maturated black oil, and multiply-charged reservoirs culminating in a wide range of biodegradation severities in the same oil. AGTs were applied to see through biodegradation and maturity issues to determine source affinities and unravel mixtures.

The most critical AGTs are diamondoid-based, including compound specific isotope analysis (CSIA) and quantitative extended diamondoid analysis (QEDA), which are unaffected by biodegradation and high maturity. Through these diamondoid methods five oil sources and their mixtures were differentiated. By the addition of taxon-specific biomarker analysis and CSIA of biomarkers (CSIA-B), source rock age and depositional environment were constrained. The oils are of five source-types: (1) Early Cretaceous terrestrial-marine shale mix, (2) Cretaceous marine-terrestrial carbonate mix, (3) Tertiary terrestrial shale, and (4) and (5) both Cretaceous marine shale, but from distinct facies. Hydrous pyrolysis of asphaltenes introduced another dimension

to this study. Asphaltenes are both highly resistant to biodegradation and preferentially represent low-maturity oil charges. QEDA, CSIA and biomarker parameters applied to the pyrolysates revealed similarities and differences between sources for the maltenes and the asphaltenes, exposing and unraveling the co-sources with a high level of confidence. Biomarker Acids Analysis (BAA) was used to characterize oil biodegradation history and the relative importance of each charge pulse to the reservoirs. It was determined that most oil reservoirs have multiple charge-pulses with different levels of biodegradation. Losses of liquid oil due to biodegradation were estimated using High Temperature Simulated Distillation (HT-SimDis). Results were found to directly correlate to oil gravity. Since very little oil is necessary to run HT-SimDis it could be a useful tool for field development to estimate oil gravity from cores and oil shows.

Reference Cited

Dahl, J.E., J.M. Moldowan, K.E. Peters, G.E. Claypool, M.A. Rooney, G.E. Michael, M.R. Mello, and M.L. Kohnen, 1999, Diamondoid hydrocarbons as indicators of natural oil cracking: Nature, v. 399, p. 54-57.

Llanos Basin: Unraveling its complex petroleum systems with advanced geochemical technologies

CONTRIBUTORS:

Mike Moldowan Shaun Moldowan	*Biomarker Technologies, Inc. Rohnert Park, CA, USA*
Vladimir Blanco-Velandia, Yolima Blanco-Velandia, Claudia Orejuela-Parra	*Instituto Colombiano del Petróleo & Ecopetrol Colombia*
Geoff Bott	*GB Scientific, Inc. South Lake Tahoe, CA, USA*
Jeremy Dahl	*Stanford University Stanford, CA USA*

Llanos Basin: Unraveling its complex petroleum systems with advanced geochemical technologies

\- - -

COMPLICATING CIRCUMSTANCES

- Severe biodegradation
  - Post-mature/cracked oil
    - Multiple oil sources
      - Co-sourced oil mixtures

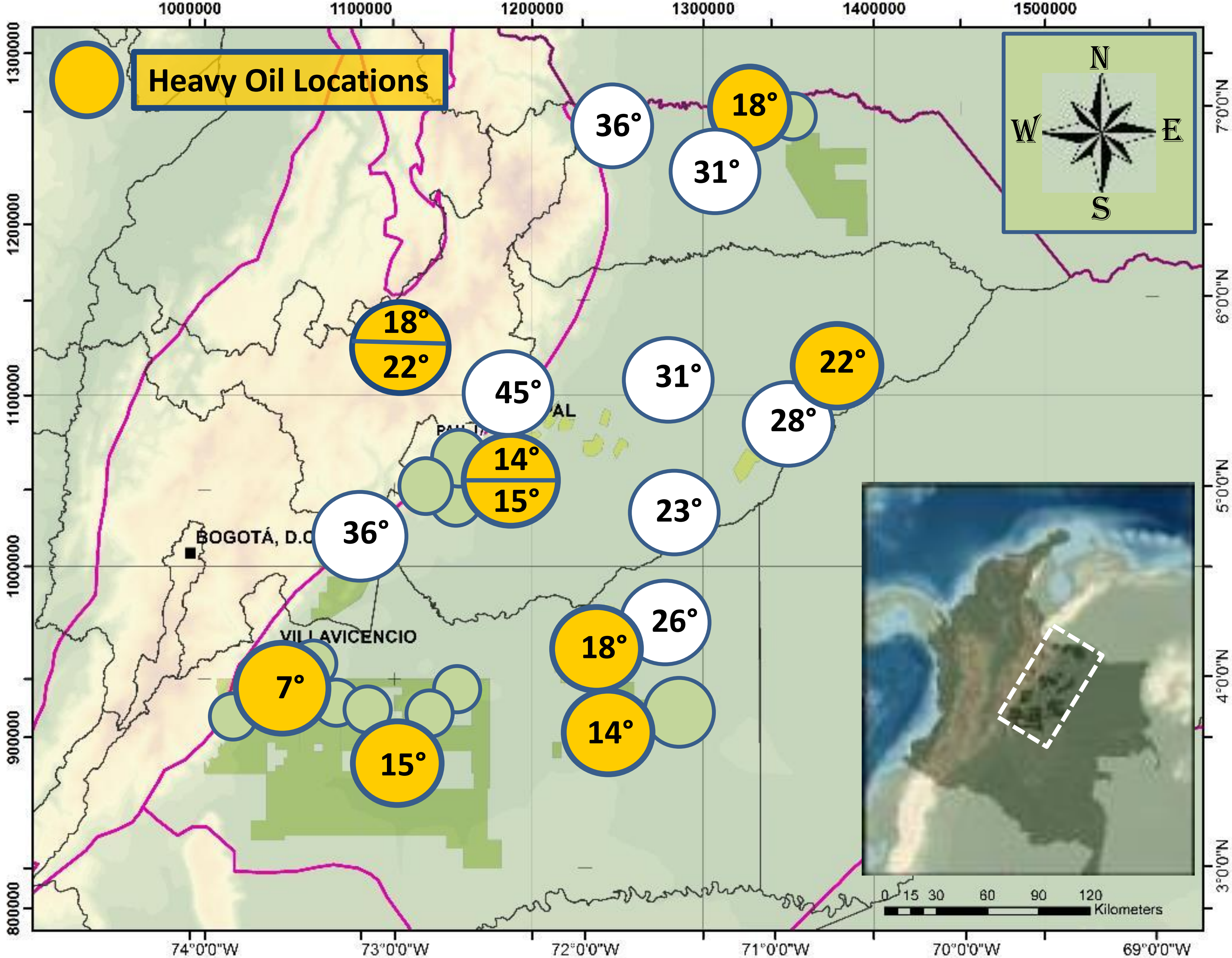
CONCLUSIONS – SOURCES

- **Five sources established by diamondoid correlations**
- **Biomarkers constrain depositional environment and age**
- **Most oils are co-sourced !!!**
- **Asphaltene analysis reveals the co-sources and identifies them**

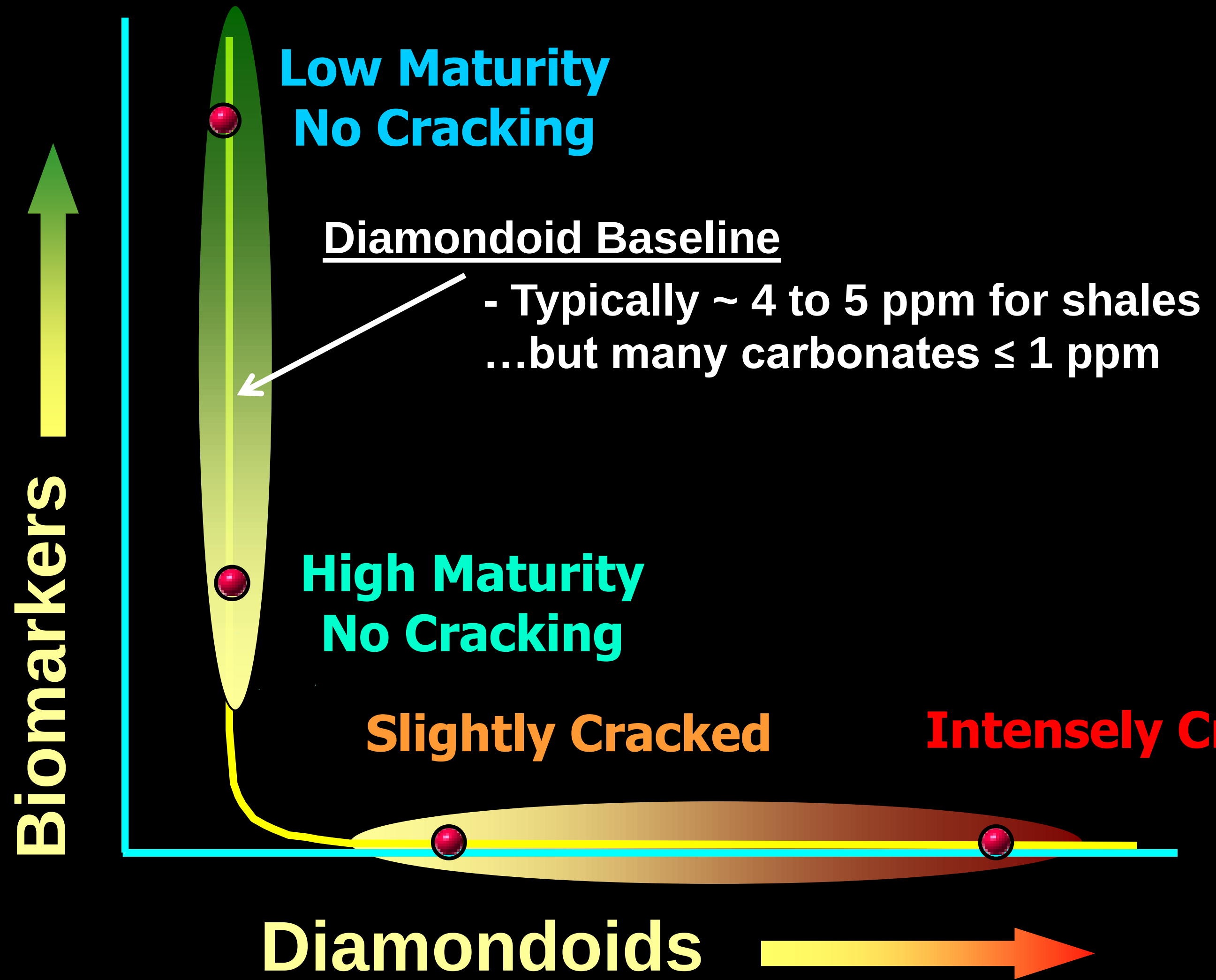
The most wide-spread major oil source in the Llanos Basin was missed in all previously published geochemical studies !!!

How is that possible?

Sample Locations Showing API Gravities

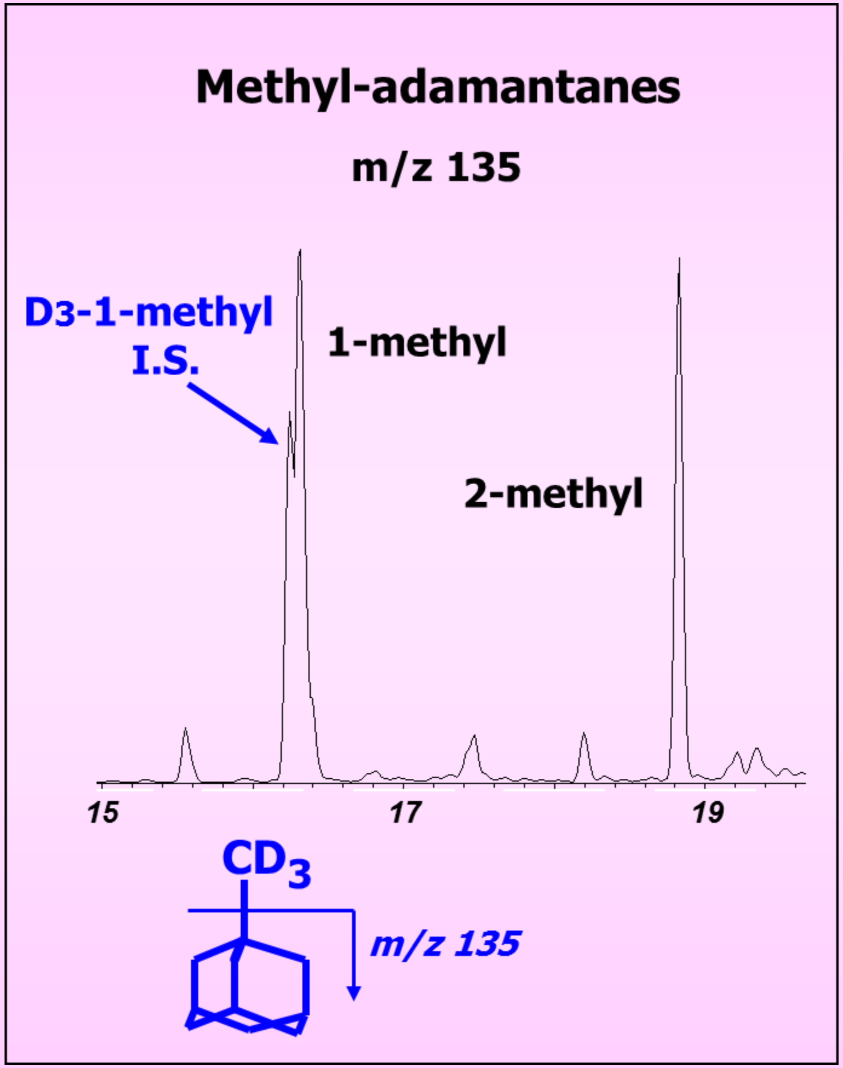


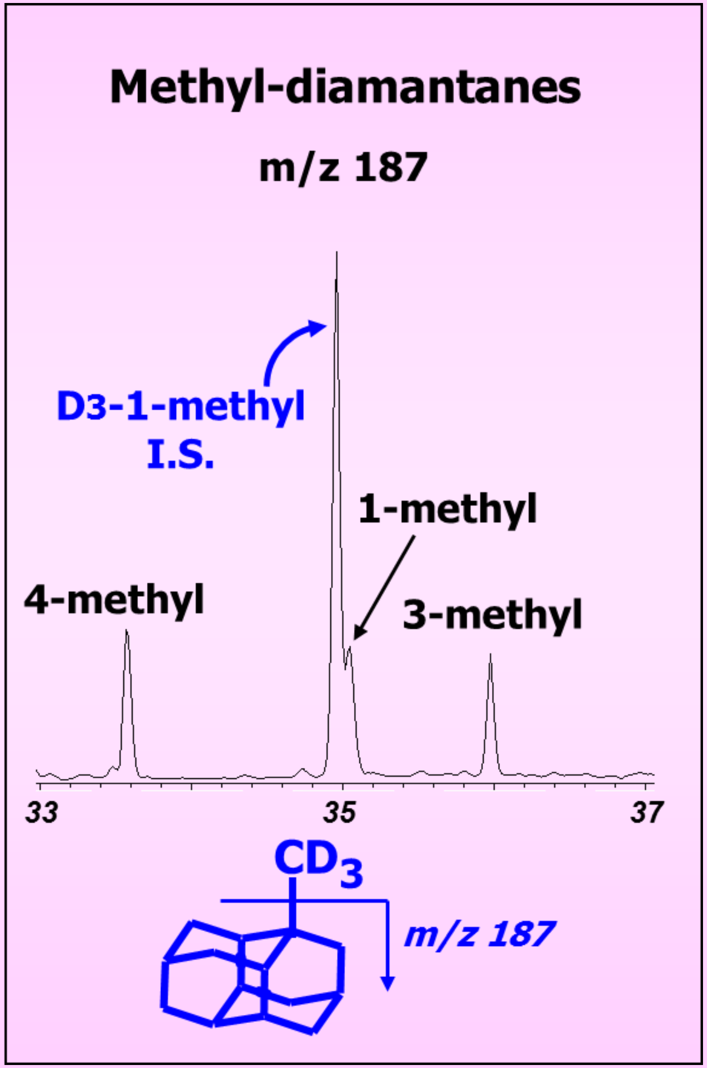
Diamondoid-biomarker cracking method provides a means to recognize thermally cracked oil



Dahl et al., 1999

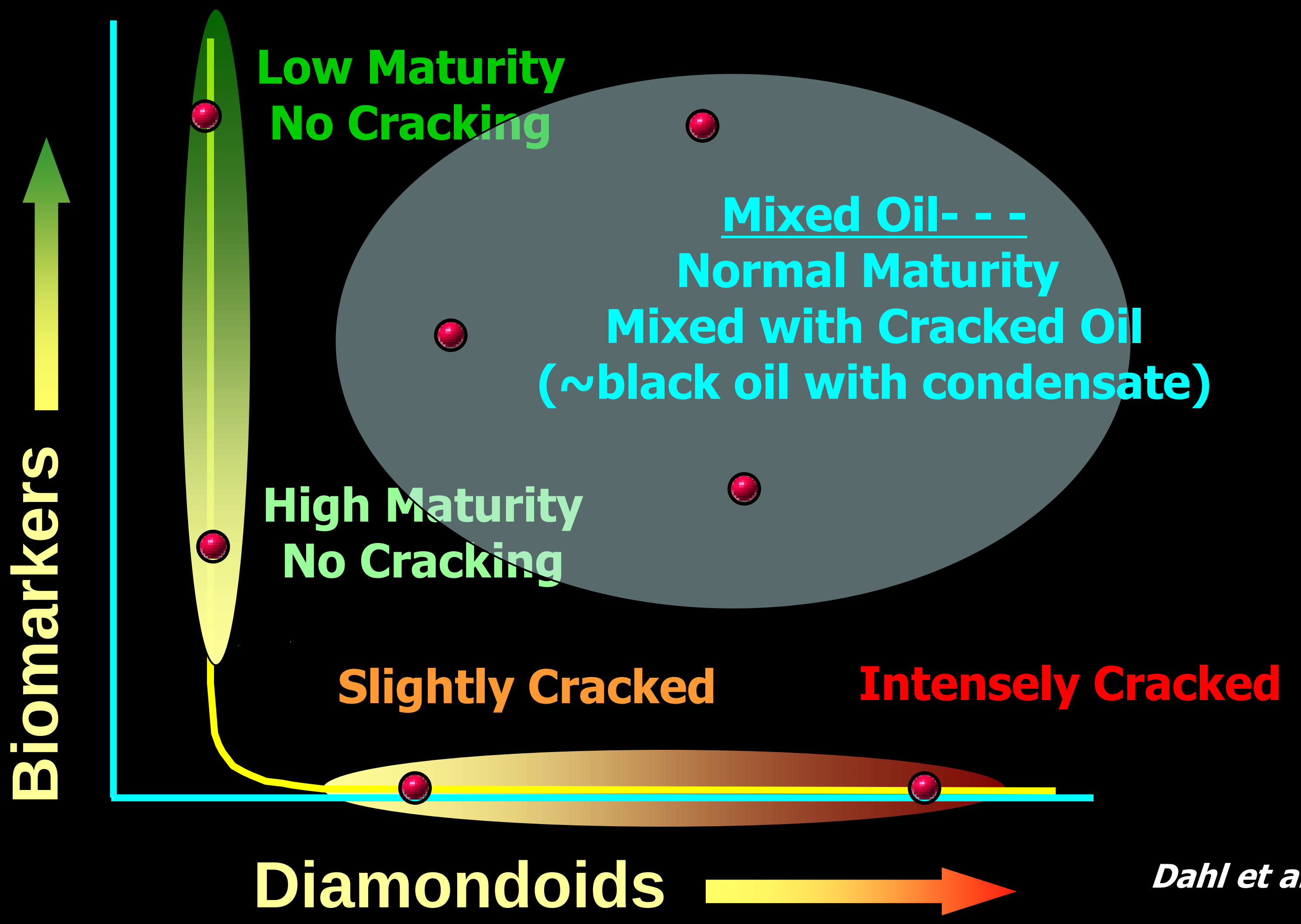
Accuracy of Diamondoid Quantification Depends on Internal Standards





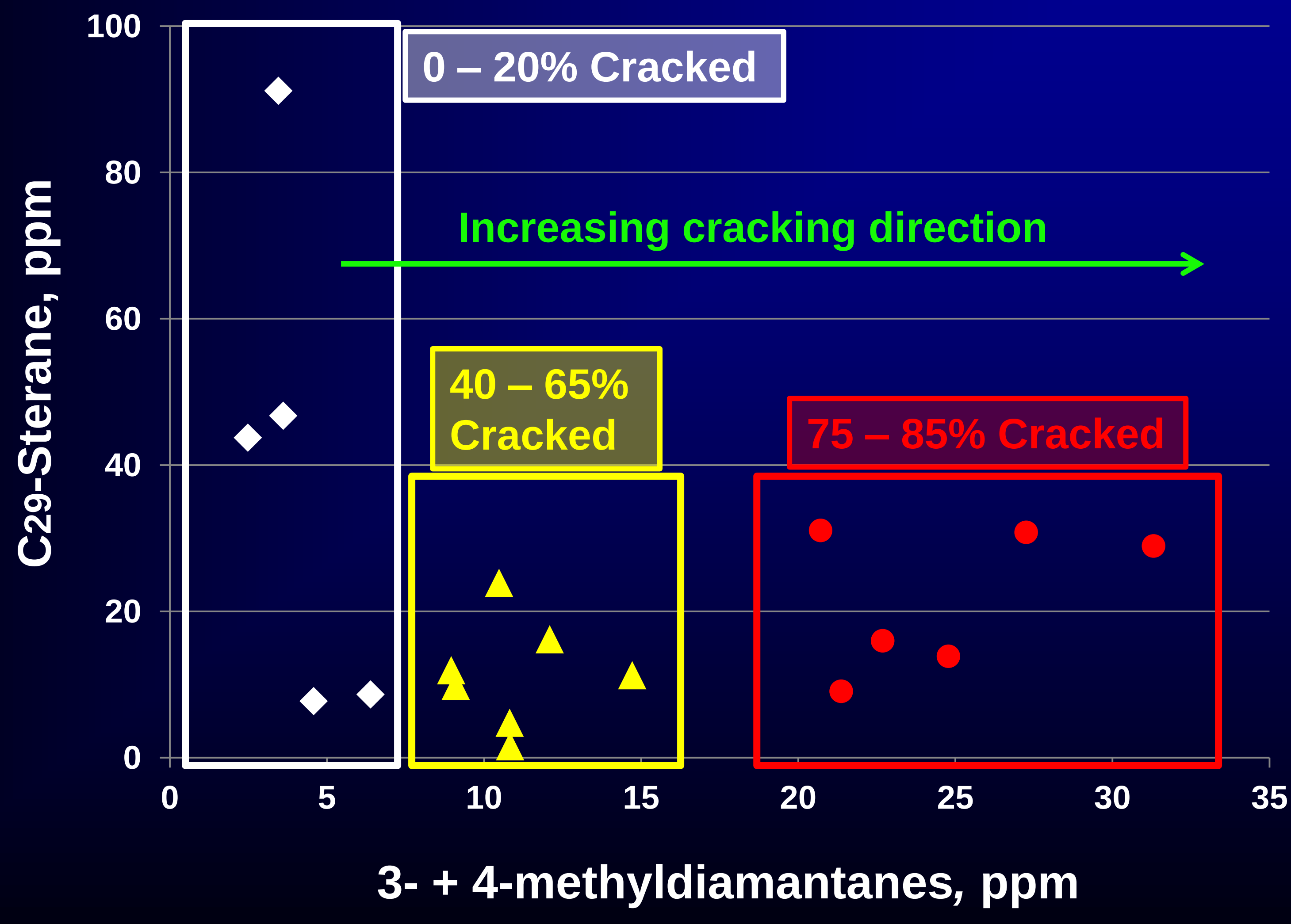
Moral: don’t throw the baby out with the bath water!

Recognition of Mixed Oil

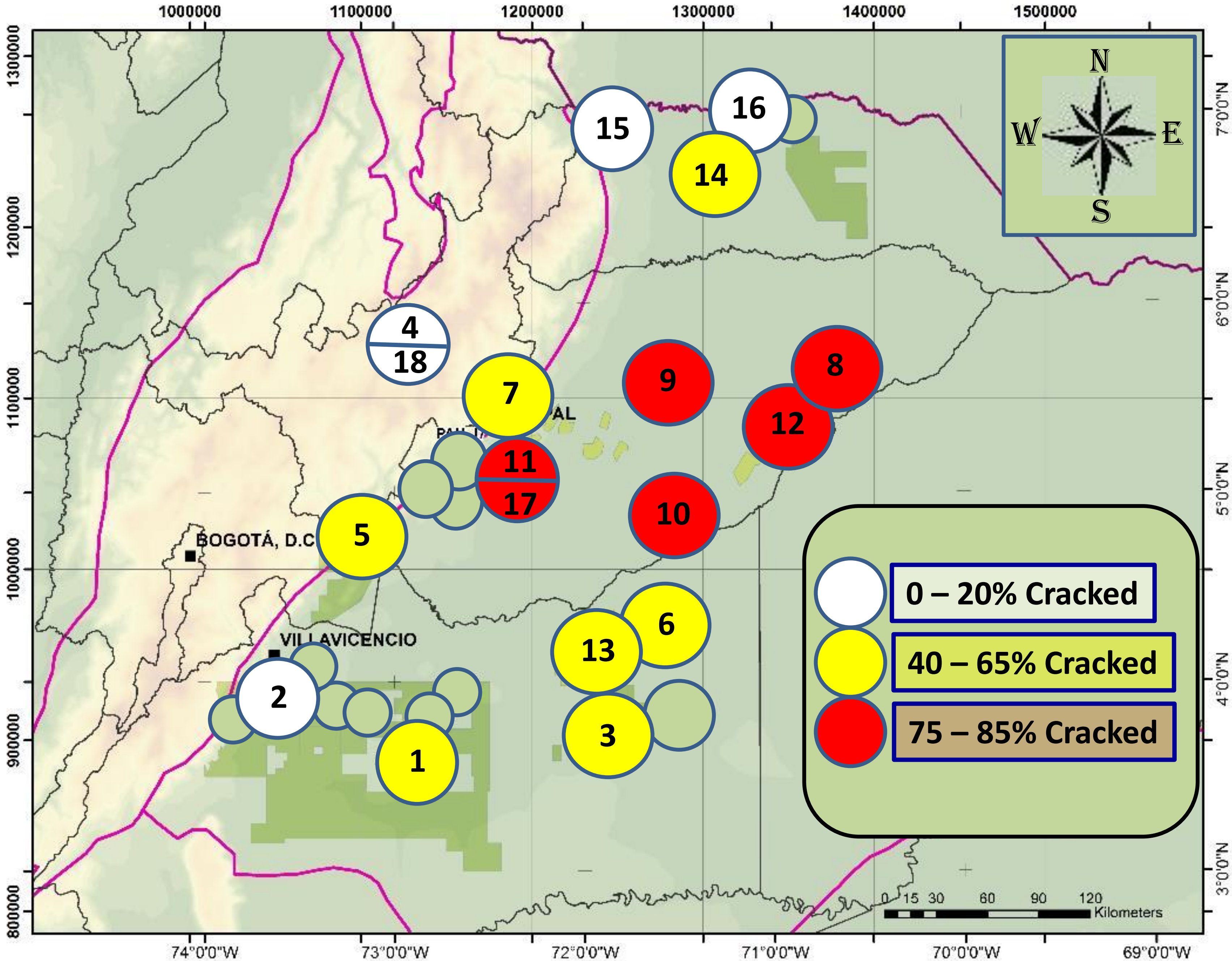


Dahl et al., 1999

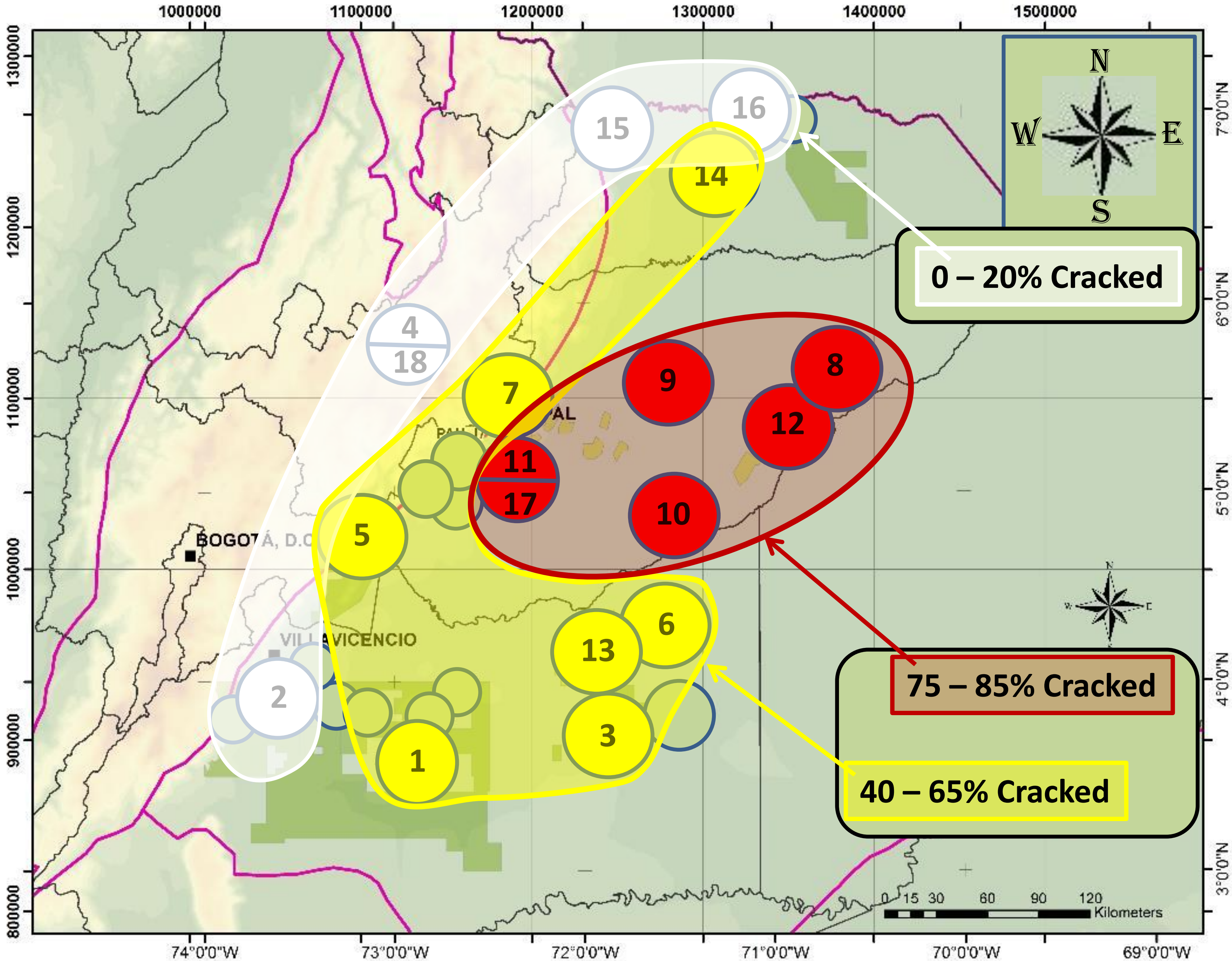
The Diamondoid-Biomarker Cracking Plot Shows Many Mixed-maturity Oils in the Llanos



Oil Cracking by Sample



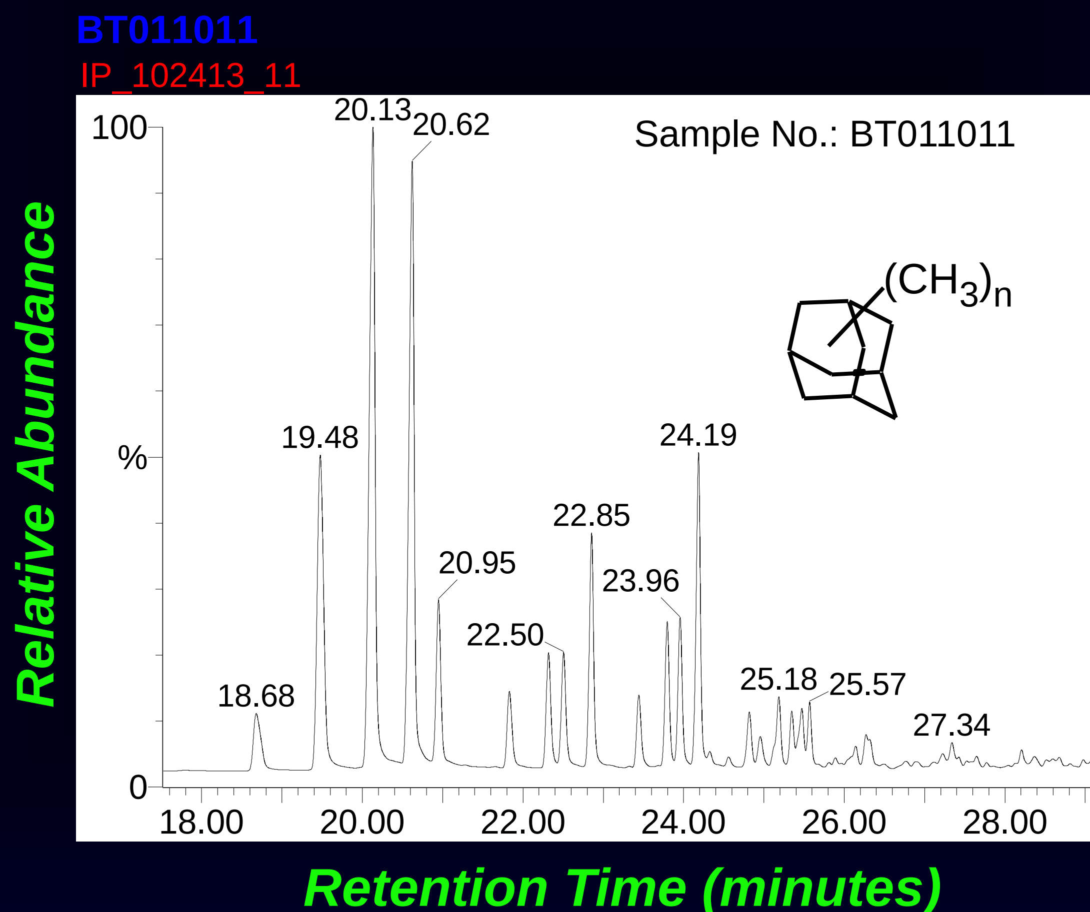
Cracking Contours Are Evident



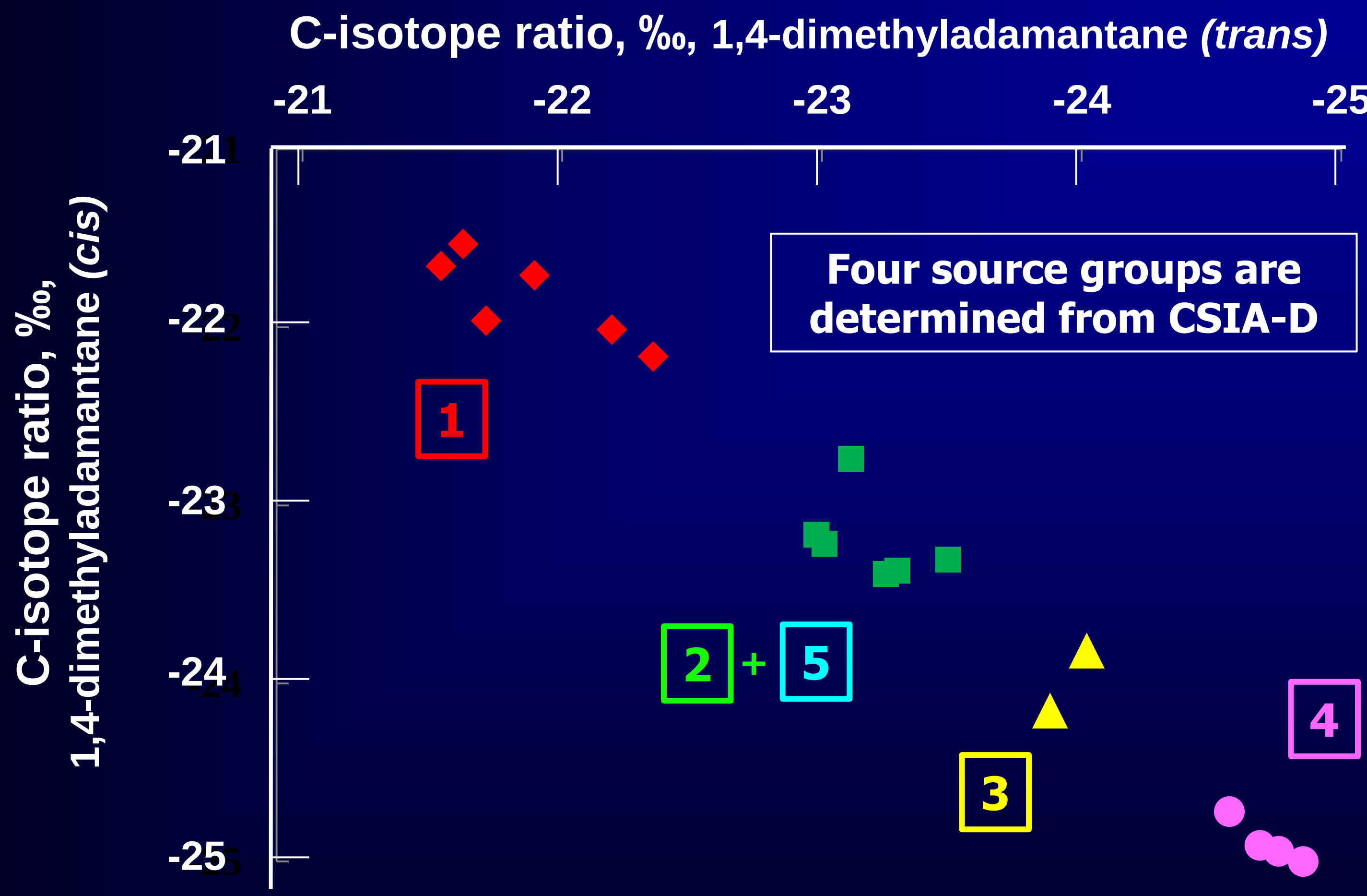
Adamantanes isolated from petroleum for CSIA-D

(compound specific isotope analysis of diamondoids)

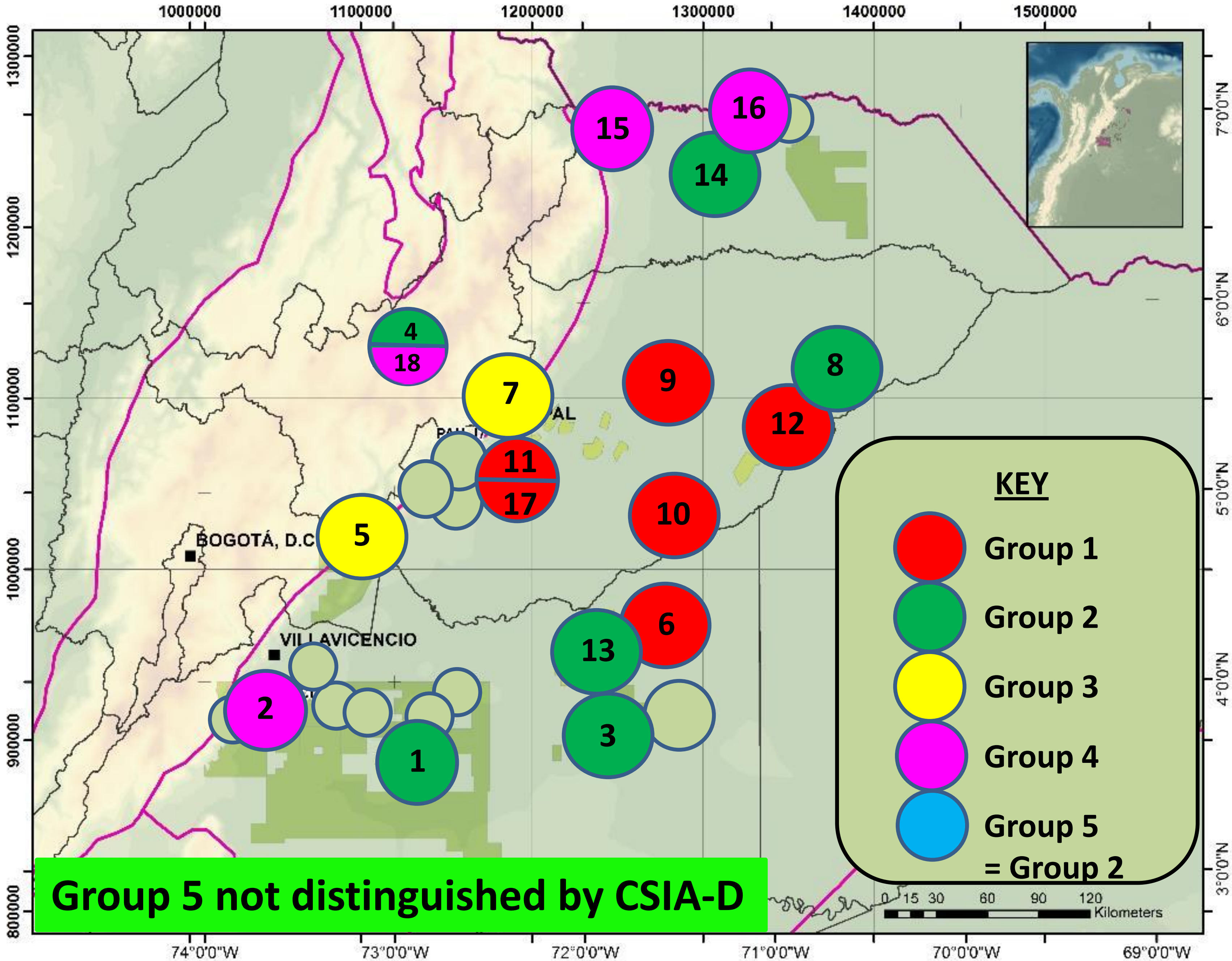
Chromatogram from GC-C-IRMS instrument



Correlation by CSIA-D



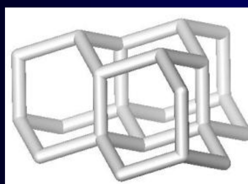
Correlations by CSIA-D



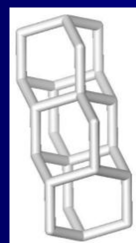
Group 5 not distinguished by CSIA-D

Structures of extended diamondoids measured in QEDA studies

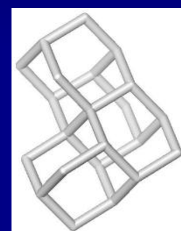
T1



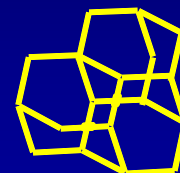
T2



T3



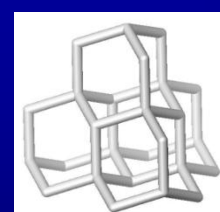
Tetramantanes



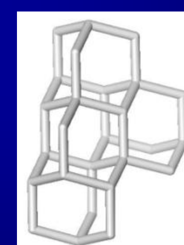
Triamantane

Used for normalization

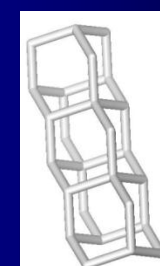
P1



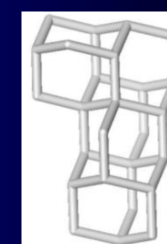
P2



P3

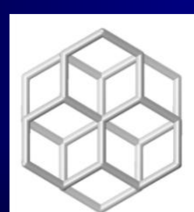


P4



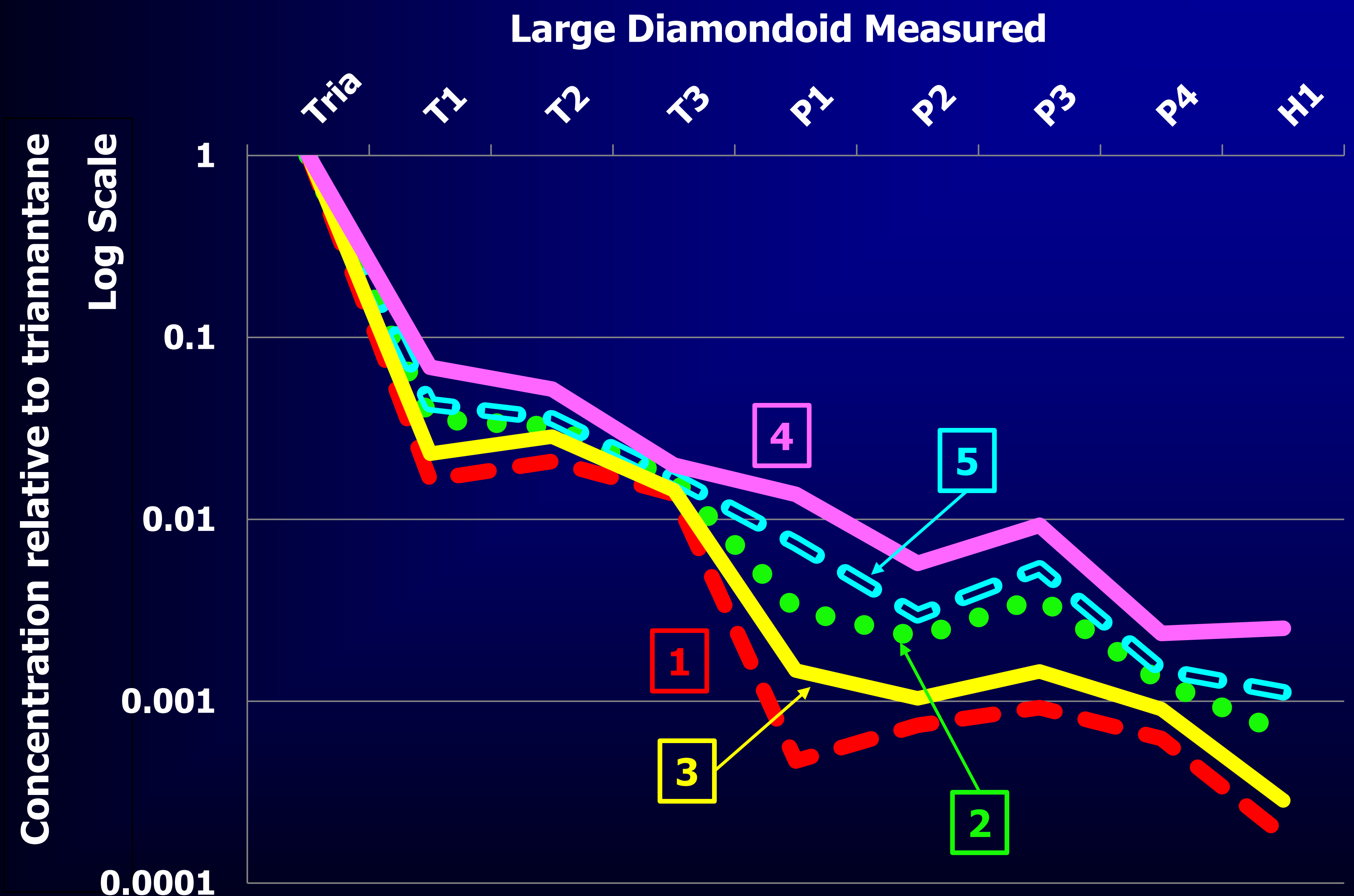
Pentamantanes

H1



Cyclohexamantane

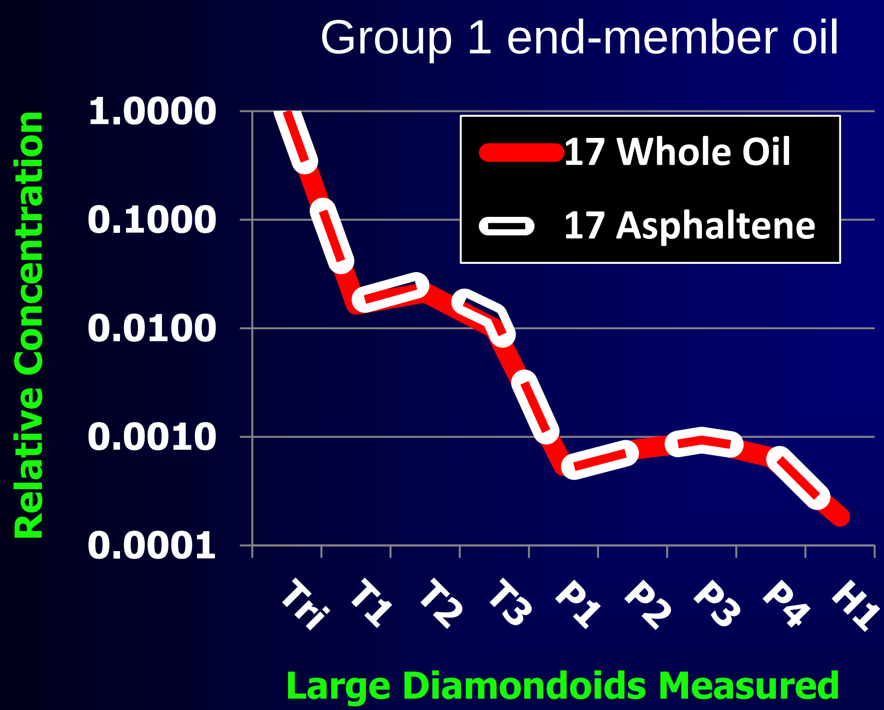
Distinguishing Five Oil Families by QEDA Fingerprints



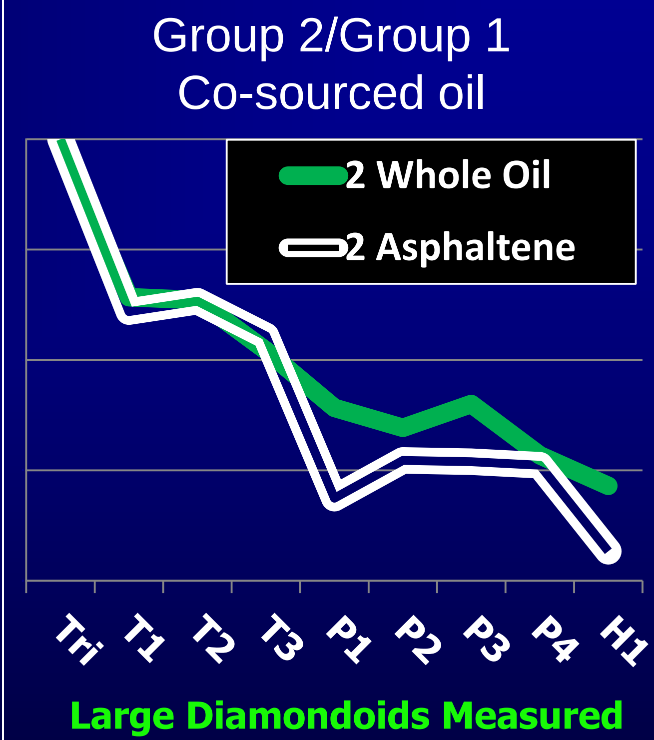
ASPHALTENE ANALYSIS UNCOVERS MIXTURES

- Hydrous pyrolysis of asphaltenes releases fresh oil
- Correlation of the pyrolysate with whole oil reveals mixtures

Hydrous pyrolysates of asphaltenes show co-sources and end-members by their QEDA fingerprints



Same QEDA fingerprint for whole oil and asphaltenes

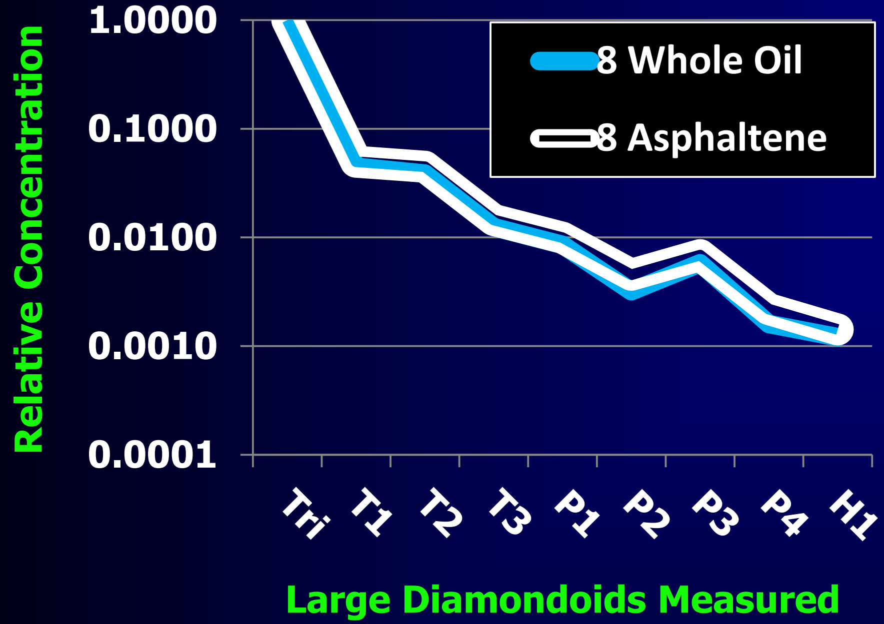


Whole oil QEDA fingerprint correlates with Group 2

Asphaltene QEDA fingerprint correlates with Group 1

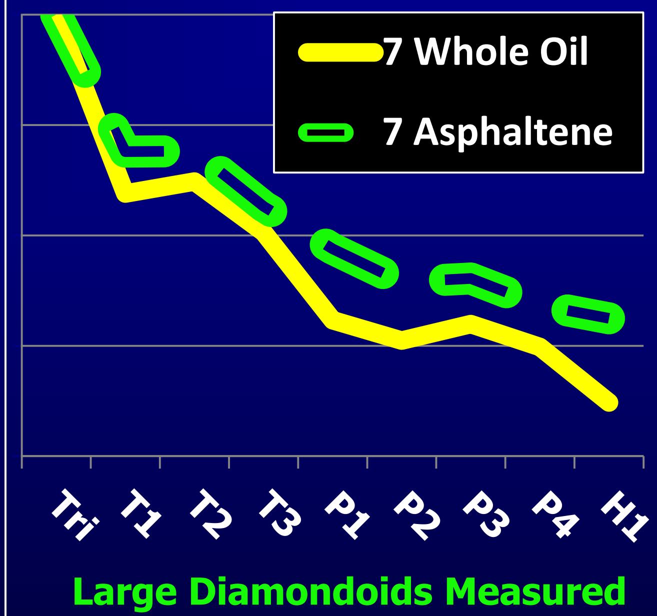
Asphaltenes show co-sources and end-members by QEDA fingerprints

Group 5 end-member oil



Same QEDA fingerprint for whole oil and asphaltenes

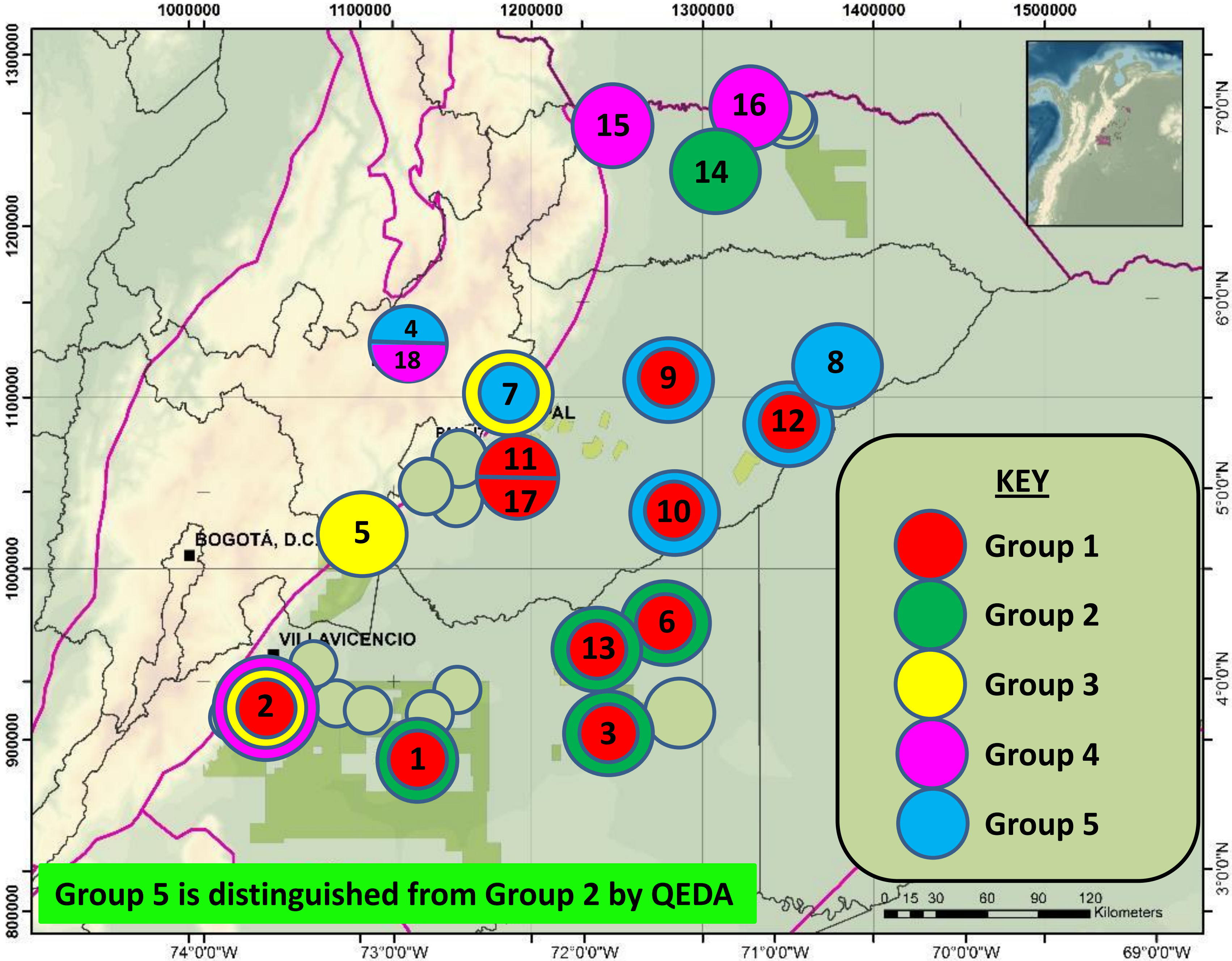
Group 3/Group 5
Co-sourced oil



Whole oil QEDA fingerprint correlates with Group 3

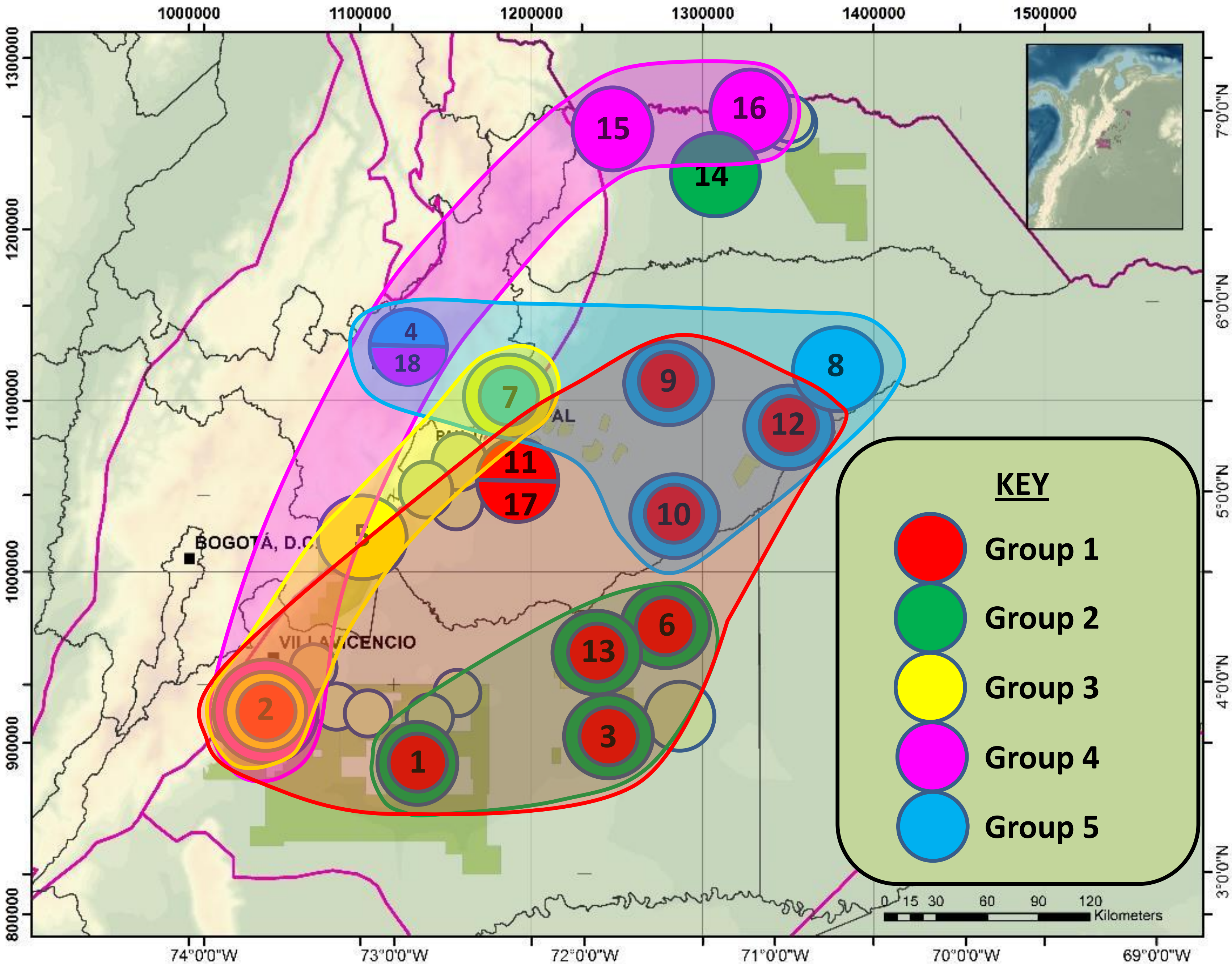
Asphaltene QEDA fingerprint correlates with Group 5

QEDA, QEDA-Asphaltenes & CSIA-D altogether show where five sources are involved



Group 5 is distinguished from Group 2 by QEDA

QEDA, QEDA-Asphaltenes & CSIA-D altogether show where five sources are involved

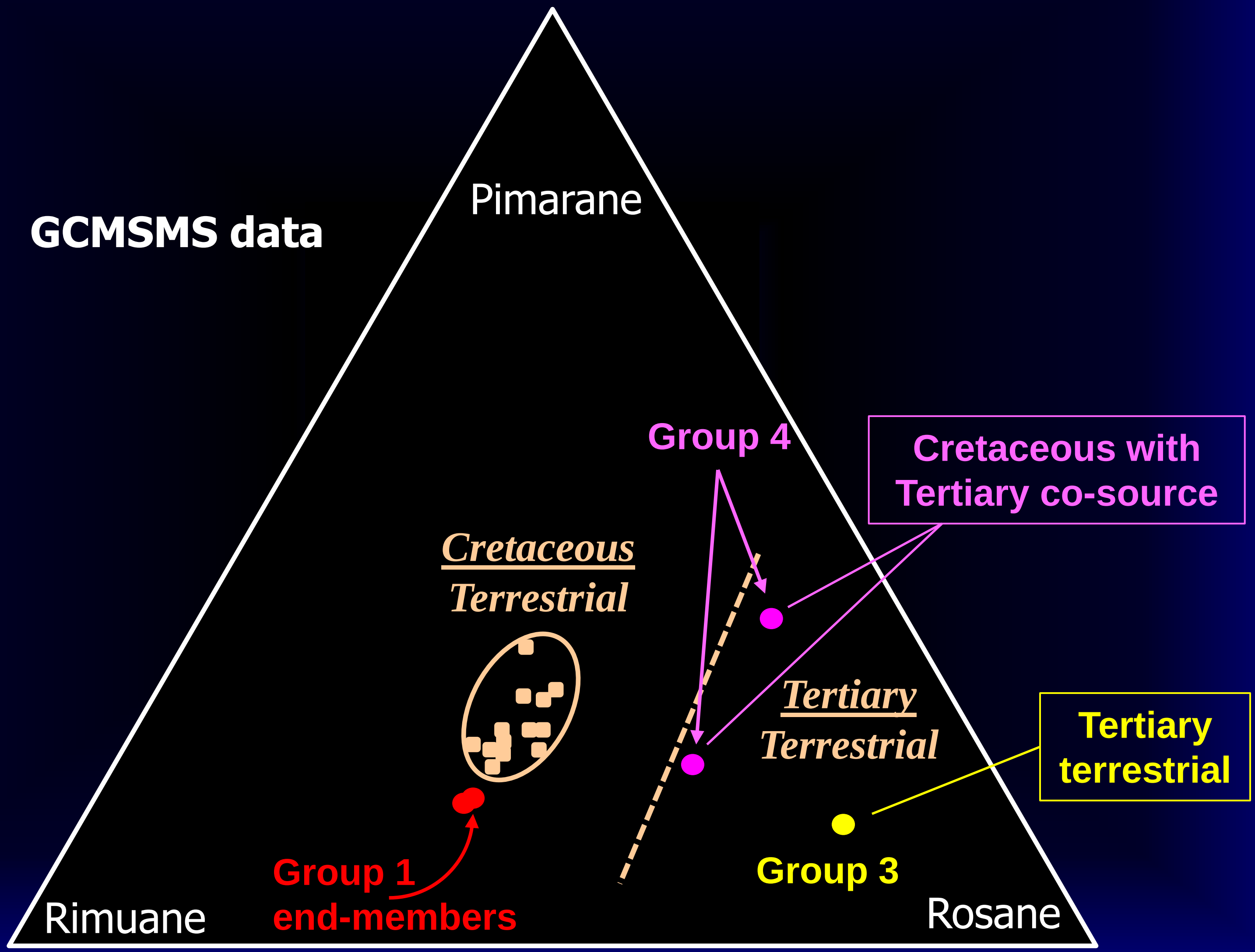


A few biomarker parameters made a huge difference in the overall confidence of the interpretation

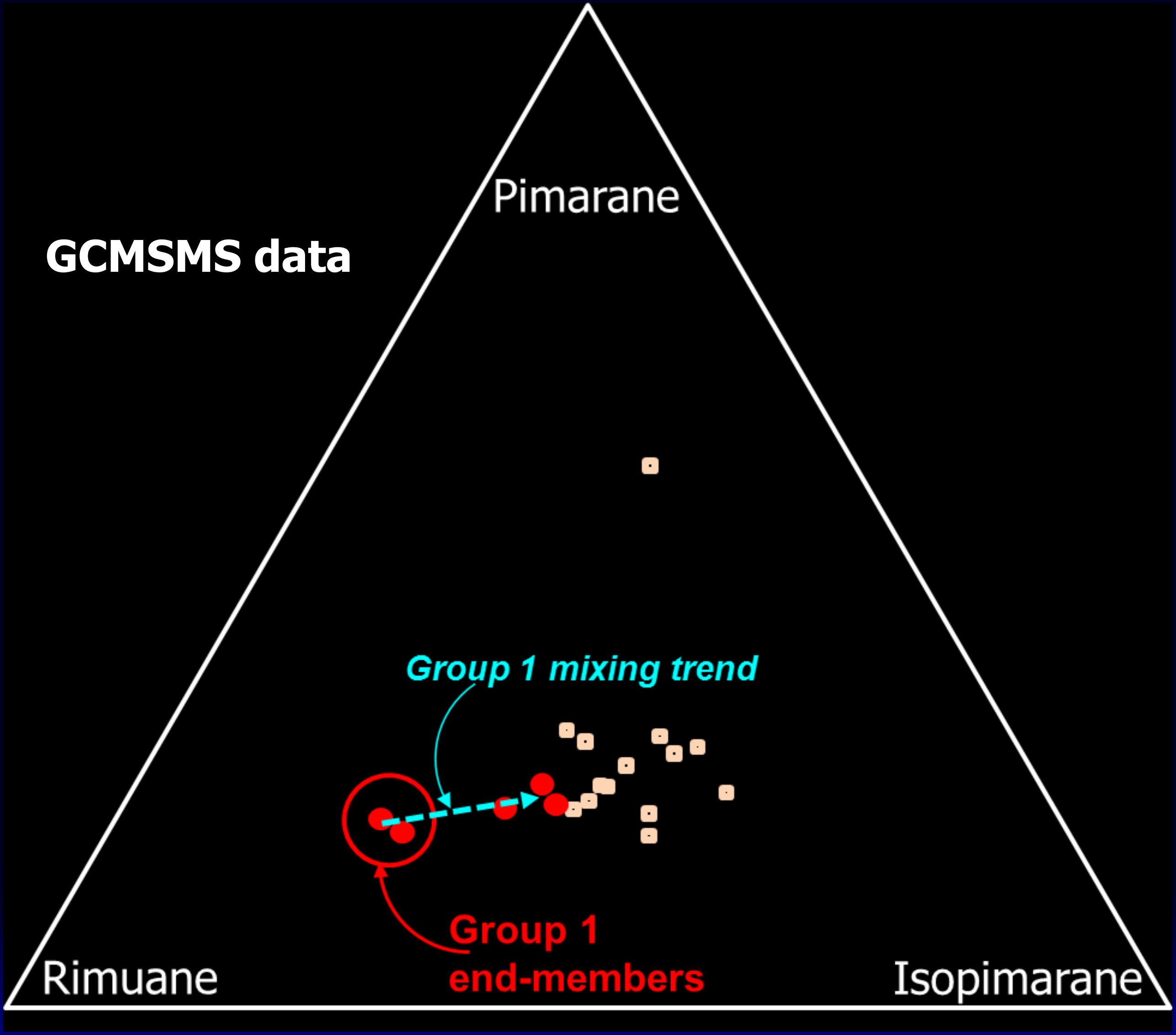
The key parameters were based on terrestrial tricyclic diterpanes and the C_{25}-highly branched isoprenoid

In addition to simple oil-oil correlation, both of these parameters find applications as *Age-Related Biomarkers*

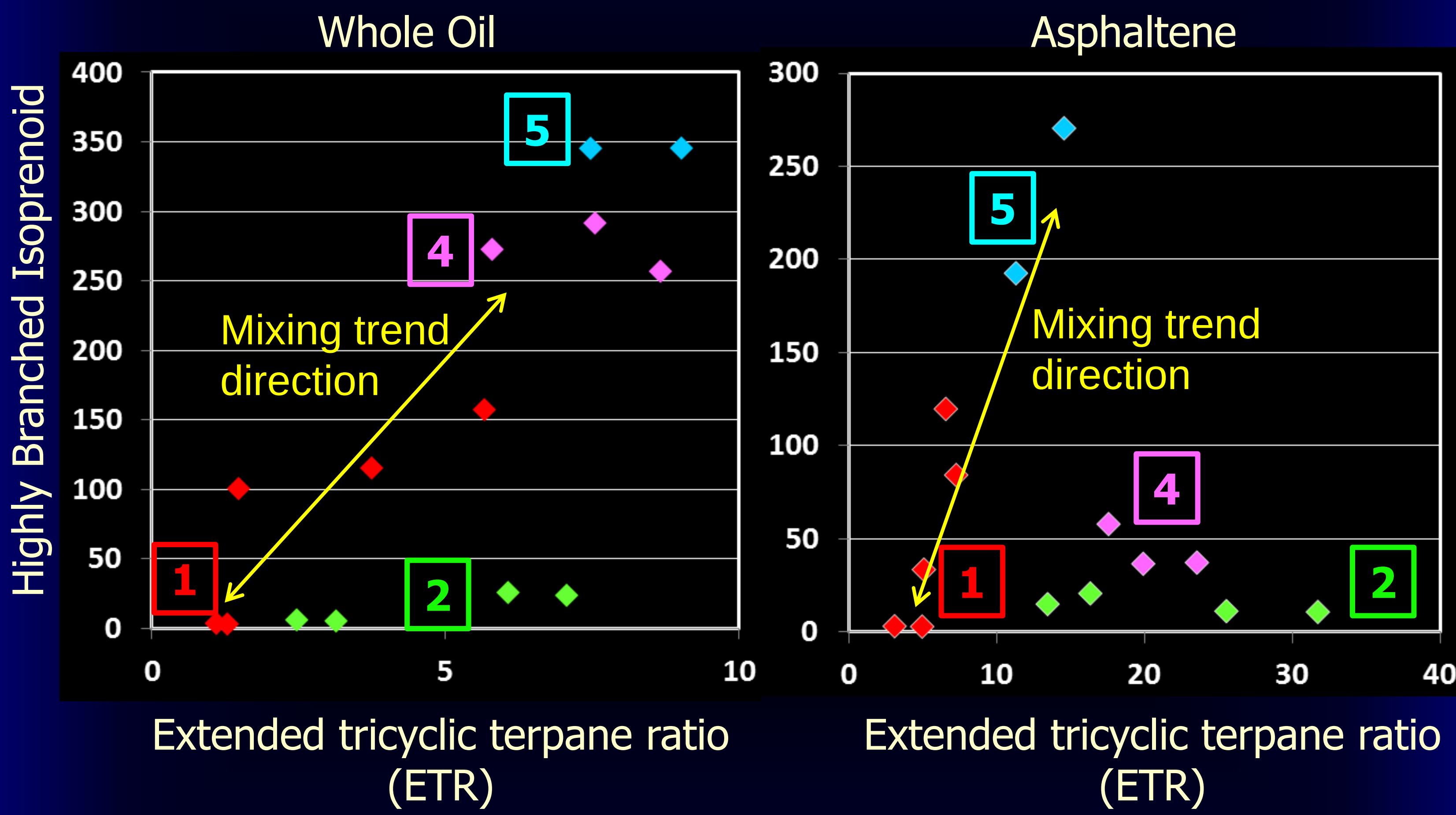
GCMSMS analysis for terrestrial diterpanes identifies co-sourced oils and a Tertiary end-member



Group 1 oils show a terrestrial component unlike the others, consistent with flora from a different age source rock



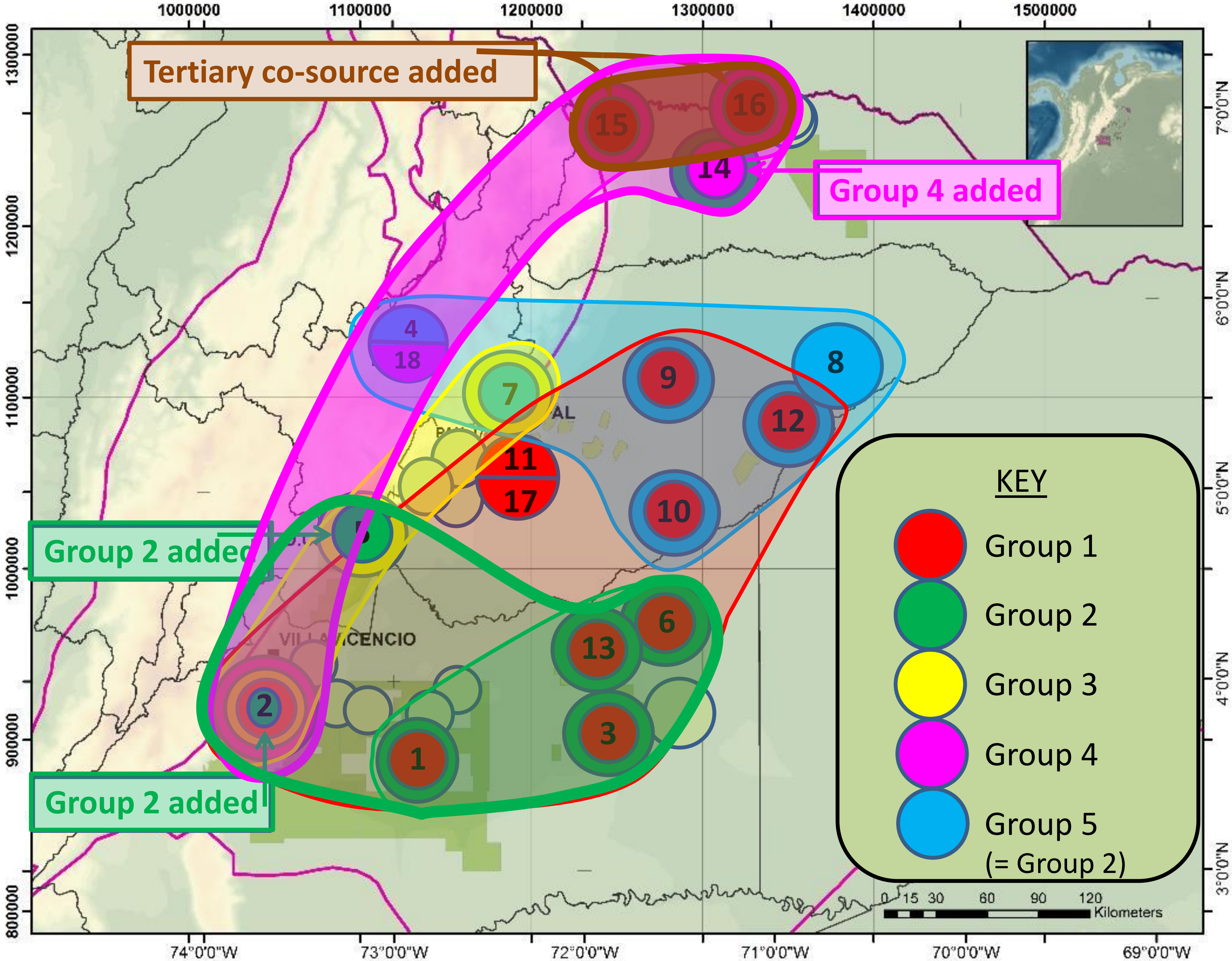
Taxon specific/age-related biomarkers show source relationships
Whole oil versus asphaltene results show mixing trends



Whole Oil result shows mixing trend between Group 1 and Group 4 or 5

Asphaltene result shows mixing is between Group 1 and Group 5

Additional features are revealed by biomarkers



Source Age Based on Age-related Biomarkers and Geologic Circumstances

- Group 1: Lower Cretaceous or pre-Cretaceous (mixed marine-terrestrial, shale)
- Group 2: Late Cretaceous (marine, carbonate)
- Group 3: Tertiary (terrestrial, shale)
- Group 4: Late Cretaceous – Cenomanian/Turonian (marine, shale or marl – Tertiary co-source occurs)
- Group 5: Late Cretaceous – Turonian or younger (marine, shale or marl)

CONCLUSIONS

- **Five source families revealed by diamondoid correlations**
- **Biomarkers constrain depositional environment and age**
- ***Most oils are co-sourced !!!***
- **Asphaltene analysis reveals the co-sources and identifies them**

The most wide-spread major oil source in the Llanos Basin is revealed for the first time