

GEOCHEMICAL CHARACTERIZATION AND CLASSIFICATION OF CUBAN ASPHALTITES

Z. DOMINGUEZ^{1,2*}, J. V. P. GUZZO³, J.O. LOPEZ², D.A. AZEVEDO⁴

¹LAMCE/COPPE, Federal University of Rio de Janeiro, Ilha do Fundão, Rio de Janeiro, Brazil. guzzo@petrobras.com.br

²Oil Research Center (CEINPET), Washington #169 Havana, Cuba.

³Petrobras/CENPES/PDEXP/GEOQ, Ilha do Fundão, 21949-900, Rio de Janeiro, Brazil.

⁴Chemistry Institute, Federal University of Rio de Janeiro, 21949-900, Brazil.

Traditional biomarkers derived from steranes, terpanes and aromatic compounds were determined to characterize and classify eight asphaltites (asphaltene rich petroleum samples occurring as seeps or filling veins, joints, cavities and fissures). These samples correspond to several locations in Cuban island, and are intensely affected by biodegradation and weathering process.

Previous works have classified the Cuban oils in three main families according to their molecular and isotopic compositions (López *et al.*, 2004; 2006; Pascual *et al.* 2006; Dominguez *et al.*, 2005; 2006). The principal objective of this study was to correlate the genetic identity of the asphaltites studied to the well-known oil families. To achieve this, genetic molecular parameters were compared in order to establish oil-oil correlations. In spite of the absence of steranes in one of the eight samples, and low concentration in the rest of them, it was possible to determine the C₂₇, C₂₈ and C₂₉ steranes percentages and 20S/(20S+20R) and $\frac{C_{27}}{C_{27} + C_{28}}$ ratios.

Concerning the study of aromatic compounds, three samples (MC, CA and ME) revealed the predominance of dibenzothiophene (DBT) over phenantrene (P), as well as predominance of methyl-dibenzothiophene (MDBT) over methyl-phenantrene (MP), suggesting a sulphur rich carbonate source rock (Hugues, 1984). These samples, and also LB and SM samples, show the following MDBT distribution: 4MDBT > 2 3MDBT < 1MDBT, suggesting a carbonate source paleoenvironment, although Radke and Willsch (1994) have previously interpreted this feature as an indication of low maturity rather than a carbonatic character. The samples: CB, MN and FS, on the other hand, showed a distinct pattern, with 4MDBT > 2,3MDBT > 1MDBT, which is typical of siliciclastic origin (Hugues, *ibid*).

Thermal evolution was investigated using several biomarker maturity parameters, such as C₂₉ steranes isomers (20S/20S+20R and $\frac{C_{27}}{C_{27} + C_{28}}$), 22S/22S+22R homohopane C₃₁,

Ts/Tm ratio (Peters & Moldowan, 1993; Peters et al., 2005), and C23/C21 tricyclic ratios (Ekweozor and Strauz, 1983; Cassani, 1986), all of them applied to the saturate fraction. Other ratios were calculated from the aromatic fraction: Methyl-Phenanthrene Index (MPI1), Maturity Index (PP-1) and Methyl-Dibenzothiophene ratio (MDR) (Radke *et al.*, 1982b; 1986; Cassani *et al.*, 1988). There was a general agreement between all the different maturity parameters used. All samples seem to represent petroleum in the early catagenetic stage, as shown in table 1 and figure 1.

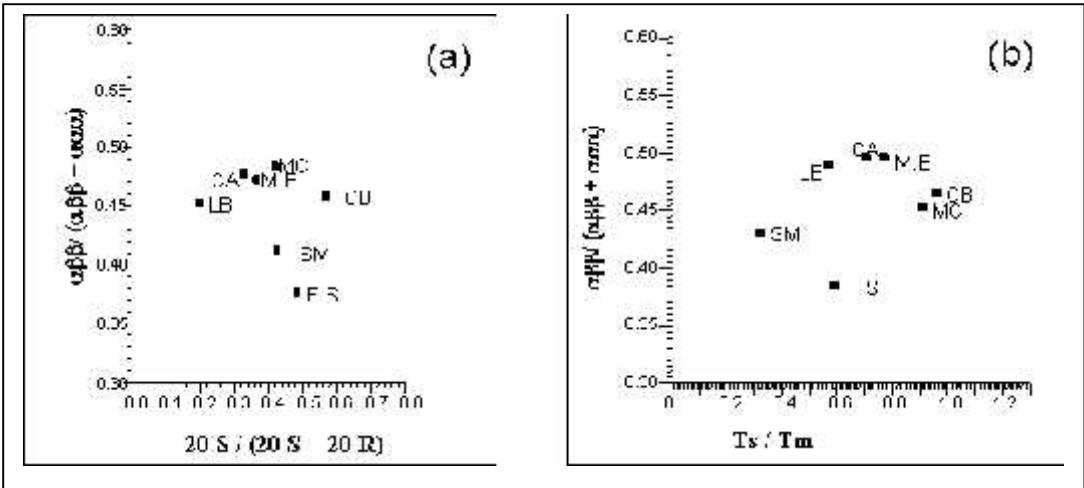


Figure 1. Some of maturity parameters analysed.

Statistical procedures (PCA and Cluster Analysis, figure 2) were used as auxiliary techniques to the genetic characterization and classification of samples and pointed that the majority of the samples were classified as Family II oils (marine anoxic carbonate sourced). Exception was observed in two samples (CB and MN), interpreted as belonging to Family III oils (normal marine siliciclastic suboxic sourced). The use of refractory aromatic compounds (*e.g.* phenanthrene, dibenzothiophene and their alkyl derivatives) showed to be useful in oil-oil correlation of biodegrade surface petroleum shows.

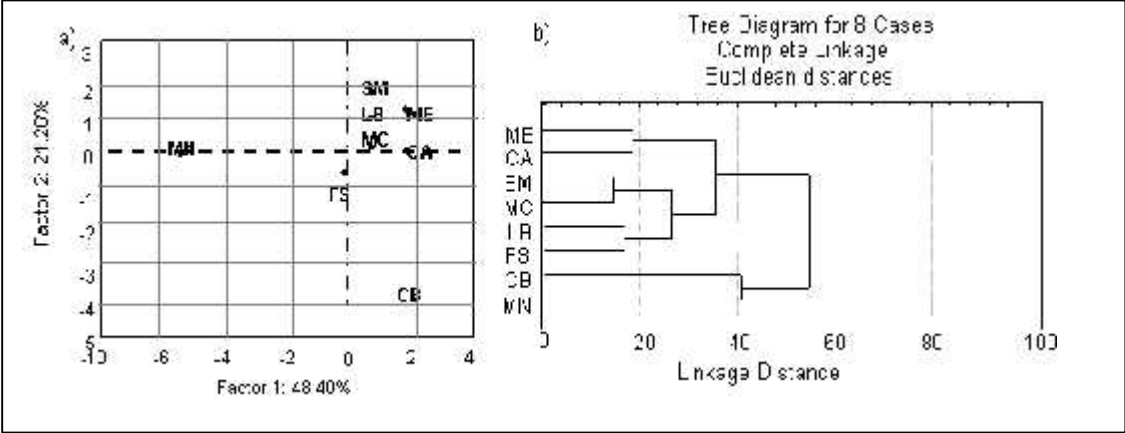


Figure 2. Statistic analysis of the samples, a) PCA analysis, b) Cluster analysis.

Table1. Principal parameters values used.

Samples	CB	MC	CA	ME	LB	FS	SM	MN
$\delta^{13}\text{C}$	-28.66	-26.86	-27.67	-27.94	-26.22	-26.63	-26.27	-28.59
C23/C21 Tr	3.75	1.96	2.25	2.92	3.38	3	2.34	2.36
H29/H30	0.51	1.68	1.16	1.55	0.91	4.57	0.94	0.75
H35/H34	0.62	0.99	1.08	1.1	1.22	0.9	0.98	2.0
TET 24/26Tr	0.63	8.16	2.75	5.74	2.43	1.1	1.16	1.71
TET 24/H30	0.04	0.38	0.12	0.15	0.08	0.18	0.13	0.78
TPP	0.84	0.78	0.52	0.48	0.41	0.46	0.42	0.77
G/H30	0.02	0.07	0.26	0.14	0.1	0.09	0.3	0.33
Diast/ St. reg	0.34	0.06	0.4	0.17	0.19	0.8	0.84	n.d
C29/C27 St.	1.57	0.46	1.12	1.05	1	2.35	0.96	n.d
Hop/St	8.52	8.76	7.37	5.73	3.36	2.31	3.08	n.d
Ts/Tm	0.98	0.94	0.26	0.23	0.15	0.6	0.72	0.8
PP- 1	0.94	1.22	1.08	1.93	1.37	0.91	2.71	1.19
MPI1	1	0.82	0.93	0.52	0.73	1.1	0.37	0.84
DBT/P	0.3	1.21	2.62	2.5	0.32	0.05	0.36	0.27
DBT/MDBT	0.12	0.06	0.34	0.08	0.12	0.65	0.03	0.33
MDR	2.2	1.82	2.62	1.46	1.28	0.94	1.03	2.96

PP-1= (1MP+9MF)/(2MP+3MP), MPI1= 1.89(2MP+3MP)/P+1.26(1MP+9MP),

MDR= 4MDBT/1MDBT, RMFI= 0.3*(MFI-1)+0.68.

REFERENCES

- Cassani F. and Eglinton G. (1986) Organic geochemistry of Venezuelan extraheavy oils. 1. Pyrolysis of asphaltenes: a technique for the correlation and maturity evaluation of crude oils. *Chemical Geology*, **56**, 167-183.
- Cassani F., Gallago O. and Talukdar, S., (1988) Methylphenanthrene maturity index of marine source rock extracts and crude oils from the maracaibo Basin, *Organic Geochemistry*, **13**, 73-80.
- Domínguez Z., López J.O., Guzzo J.V.P. and Azevedo, D.A. (2005) Caracterização geoquímica de Petróleos Cubanos, Classificação dos mesmos baseados em informação oferecida pelos biomarcadores. *III Congresso Brasileiro de P&D em Petróleo e Gás. Outubro, Salvador de Bahia, Brasil.*
- Domínguez Z., López J. O., Guzzo J.V.P. and Azevedo, D.A. (2006) Classification of Cuban oil by statistic and geochemical grouping. *Proceedings of X Latinamerican Congress on Organic Geochemistry. Salvador de Bahia, Brazil.*
- Ekweozor C.M. and Strausz, O.P. (1983) Tricyclic terpanes in the Athabasca oil sands: their geochemistry, In: Bjoroy, M. et al (eds), *Advances in Organic Geochemistry 1981*, Wiley, pp. 746-766.
- Hugues W.B. (1984) Use the thiophenic organosulfur compounds in characterising crude oils derived from carbonate versus siliciclastic sources. In: J. B. Palacas (Ed.), *Petroleum Geochemistry and Source Rock Potencial of Carbonate Rock, AAPG Studies in Geology*, **18**, 181-196.
- López J. O., Pascual O., Delgado O. and López J. G. (2004) Familias de petróleos cubanos. Correlación con otras áreas en el Golfo de México. *Proceedings of IX Latinamerican Congress on Organic Geochemistry. Mérida, México.*
- López J. O., Pascual O., López J. G., Delgado O. and Laffita M.C. (2006) The Northern Cuba Heavy Oils Belt: Geochemical Characterisation of Discovered oils. *Proceedings of X Latinamerican Congress on Organic Geochemistry. Salvador de Bahia, Brazil.*
- Pascual O., López J.O., Delgado O. and López J.G. (2006) Characterization and classification of intensely biodegradades oils in a Cuban poor explored region. *Proceedings of X Latinamerican Congress on Organic Geochemistry. Bahía, Brazil.*
- Peters, K.E. Moldowan, J.M. (1993) *The Biomarker Guide; Interpreting Molecular Fossils in Petroleum and Ancient sediment.* Eglewood Cliffs, Prentice Hall. 363p.
- Peters, K. E., Walters, C. C., Moldowan, J. M. (2005) *The Biomarker Guide: Biomarker and isotopes in Petroleum Exploration and Earth History.* 2 ed. V.2, Cambridge University Press. 698p.
- Radke M. and Willsch H. (1994) Extractable alkyldibenzothiophenes in Posidonia Shale (Toarcian) source rock. Relationship of yields to petroleum formation and expulsion. *Geochimica et Cosmochimica Acta*, **58**, 5223-5244.
- Radke M., Welte D.H. and Willisch, H. (1986) Maturity parameter based on Aromatic Hydrocarbons: Influence of the Organic Matter Type. *Organic Geochemistry*, **10**, 51-63.
- Radke, M., Willsch, H., Leythaeuser, D. (1982b) Aromatic component of coal: relation of distribution pattern to rank. *Geochimica et Cosmochimica Acta*, **46**, 1831-1848.
- Williams J.A., Bjoroy M., Dolcater D.L. and Winters J.C. (1986) Biodegradation in South Texas Eocene oils-effect on aromatics and biomarkers. *Organic Geochemistry*, **10**, 451-461.