

AAPG HEDBERG RESEARCH CONFERENCE
“NATURAL GAS GEOCHEMISTRY: RECENT DEVELOPMENTS, APPLICATIONS AND
TECHNOLOGIES”
MAY 9-12, 2011 – BEIJING, CHINA

Distinction between Lacustrine and Marine Thermogenic Gases
Based on Hydrogen and Carbon Isotopic Compositions

Jose Roberto Cerqueira and Eugenio Vaz dos Santos Neto

Petrobras R&D Center/PDEXP/Geochemistry, Rio de Janeiro, Brazil

INTRODUCTION

Carbon and hydrogen isotopic compositions in *n*-C₁₅₊ alkanes have been used for oil classification, as proxy for paleoenvironmental and paleoclimatic conditions of source rocks (Santos Neto and Hayes, 1997; Li *et al.*, 2001; Santos Neto and Takaki, 2000; Santos Neto *et al.*, 2004; Schimmelmann *et al.*, 2004). Compound specific isotope analysis of stable carbon for the C₁-C₄ range has been used to determine the origin of biogenic and thermogenic natural gases and aspects related to kerogen type and thermal evolution (James, 1983, 1990; Schoell, 1980, 1983; Prinzhofer and Huc, 1995; Lorant *et al.*, 1998; Boreham *et al.*, 2001). Although newly developed technologies have allowed reliable and fast measurements of δ D in C₁-C₄ hydrocarbons, there are relatively few results published using them as indicators of the source rocks paleoenvironment (Boreham *et al.*, 2001; Boreham and Edwards, 2007). The objective of this work was to study the combined use of carbon and hydrogen isotopes in thermogenic gases on investigation of the depositional paleoenvironment of their source rocks.

The samples studied in this work were gases obtained by MSSV-micropyrolysis (Micro Scale Sealed Vessel) of asphaltenes precipitated from marine and lacustrine oils, and marine and lacustrine source rocks, under different temperatures. Additionally, gases collected in representative petroleum fields from South American basins were also studied. ¹³C/¹²C and D/H ratios were measured using different Agilent 6890 GCs, each one connected to Thermo Electron isotope ratio mass spectrometers: MAT 252 and Delta Plus XL, respectively. Isotopic compositions are expressed in parts per thousand using delta notation, $\delta = [(R_{\text{spl}} - R_{\text{std}})/R_{\text{std}}] \times 1000$, and were reported against VPDB for carbon and VSMOW for hydrogen. R_{spl} and R_{std} stand for ¹³C/¹²C or D/H of the sample and of the standard, respectively.

DISCUSSION

$\delta^{13}\text{C}$ and δD values of the gaseous hydrocarbons obtained by micropyrolysis (MSSV) of lacustrine and marine oil asphaltenes showed the already expected depletion in ¹²C and H, and the lost of the heavier components due to the increment of the thermal evolution (Figure 1).

Regarding the composition of the profiles showed in figure 1 for carbon isotopes, there was a trend in $\delta^{13}\text{C}$ towards relatively more negative values for the lacustrine sample. On the other hand the marine sample presented more negative values for δD under the same pyrolysis temperatures. Such variations are probably reflecting the geochemical characteristics of the organic matter sources from which asphaltenes were originated, and the genetic influence of the physicochemical conditions of the lacustrine and marine paleoenvironments.

Based on Schoell's approach for differentiating oil and gas windows, where $\delta^{13}\text{C}$ values for methane range from -50‰ to -40‰ and from -40‰ to -30‰, respectively (Schoell, 1983), it was possible to compare simultaneously $\delta^{13}\text{C}$ and δD values for methane generated in the MSSV experiments (asphaltenes and source rocks) and methane present in natural gases with different degrees of thermal evolution, associated to lacustrine and marine petroleum systems from South American basins (Figure 2). The trends of isotopic ratios are consistent with the thermal evolution, and the methane in the lacustrine gases is depleted in hydrogen when compared to the marine gases. Such variations are typical of each depositional environment of the gas source rocks.

CONCLUSIONS

Lacustrine $\text{C}_1\text{-C}_4$ hydrocarbons generated by MSSV experiments using asphaltenes and source rocks samples are D and ^{12}C enriched compared with their marine counterparts.

Within the estimated oil and gas windows marine gases presented more negative δD values for methane in comparison with lacustrine gases.

The interpretative scheme presented here can be very useful in cases where gases did not experience significant post-genetic alterations in the reservoirs.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the valuable contributions of Alexandre de Andrade Ferreira and other colleagues from Petrobras Geochemistry Division and PETROBRAS for the authorization to publish this paper.

REFERENCES

- Boreham, C.J., Hope, J.M. and Hartung-Kagi, B. 2001. Understanding source, distribution and preservation of Australian natural gas: a geochemical perspective. *APPEA Journal*, 41 (1), 523-547.
- Boreham, C.J. and Edwards, S. 2007. Effect of source, maturity and biodegradation on the D/H ratio of Australian natural gas. Book of Abstracts of the 23rd International Meeting on Organic Geochemistry, Torquay, England, 1085-1086.
- F. Lorant, A. Prinzhofer, F. Behar and A.Y. Huc, Carbon isotopic and molecular constraints on the formation and the expulsion of thermogenic hydrocarbon gases, *Chemical Geology* 147 (1998), pp. 240-264.
- James, A.T. 1983. Correlation of natural gas by use of carbon isotopic distribution between hydrocarbon components. *AAPG Bulletin* 67, 1176-1191.
- James, A.T. 1990. Correlation of reservoir gases using the carbon isotopic compositions of wet gas components. *AAPG Bulletin* 74, 1441-1458.
- Li, M., Huang, Y., Obermajer, M., Jiang, C., Snowdon, L.R., Fowler, M.G. 2001. Hydrogen isotopic compositions of individual alkanes as a new approach to petroleum correlation: case studies from the Western Canada sedimentary basin. *Organic Geochemistry*, 31, 1387-1399.
- Prinzhofer, A., Huc, A.Y. 1995. Genetic and post-genetic molecular and isotopic fractionations in natural gases. *Chemical Geology*, 126, 281-290.

Santos Neto, E.V., Hayes, J. M. 1997. Hydrogen- and carbon-isotopic indicators of paleoenvironmental conditions and processes during a Cretaceous lacustrine-to-marine transition. 18th International Meeting on Organic Geochemistry, Abstracts Part I, Maastricht, The Netherlands, 22-26/September/1997, 27-28.

Santos Neto, E.V., Takaki, T. 2000 – Isotopic and molecular heterogeneities in lacustrine oils from the Potiguar Basin, Brazil. 7th Latin-American Congress on Organic Geochemistry. New Perspectives on Organic Geochemistry for the Third Millennium, Proceedings, 22-26/October/2000, Foz de Iguaçú, Brazil, 338-340.

Santos Neto, E.V., Cerqueira, J.R., Rangel, M.D. 2004. Classification of oils based on hydrogen isotopic composition of *n*-alkanes: case history of Brazilian offshore oils. Memórias del 9th Congreso Latinoamericano de Geoquímica Orgánica, 05-09/Diciembre/2004, Mérida, México, 31.

Schimmelmann, A., Sessions, A.L., Boreham, C.J., Edwards, D.S., Logan, G.A., Summons, R.E. 2004. D/H ratios in terrestrially sourced petroleum systems. Organic Geochemistry, 35, 1169-1195.

Schoell, M. 1980. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. Geochimica et Cosmochimica Acta, 44, 649-661.

Schoell, M. 1983. Genetic characterization of natural gases. AAPG Bull. 67, 2225-2238.

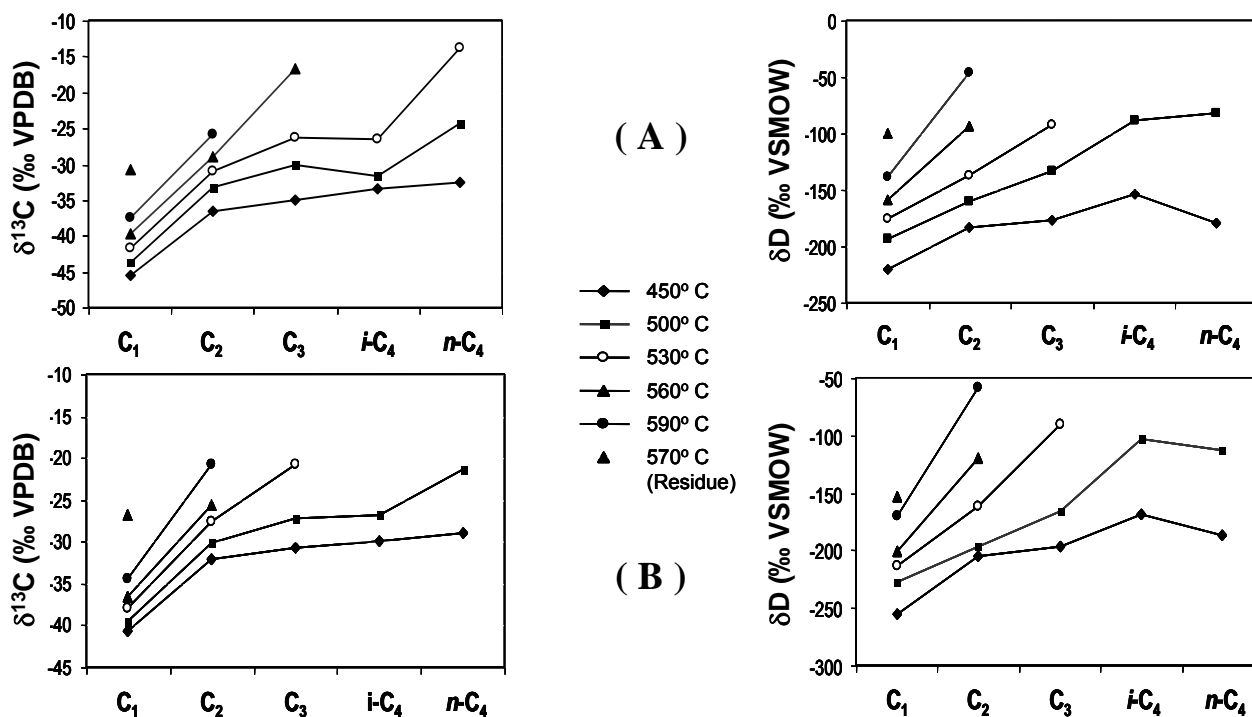


Figure 1: Comparison between $\delta^{13}\text{C}$ and δD for C_1 - C_4 of gases obtained by MSSV-micropyrolysis of lacustrine (A) and marine (B) oil-asphaltenes.

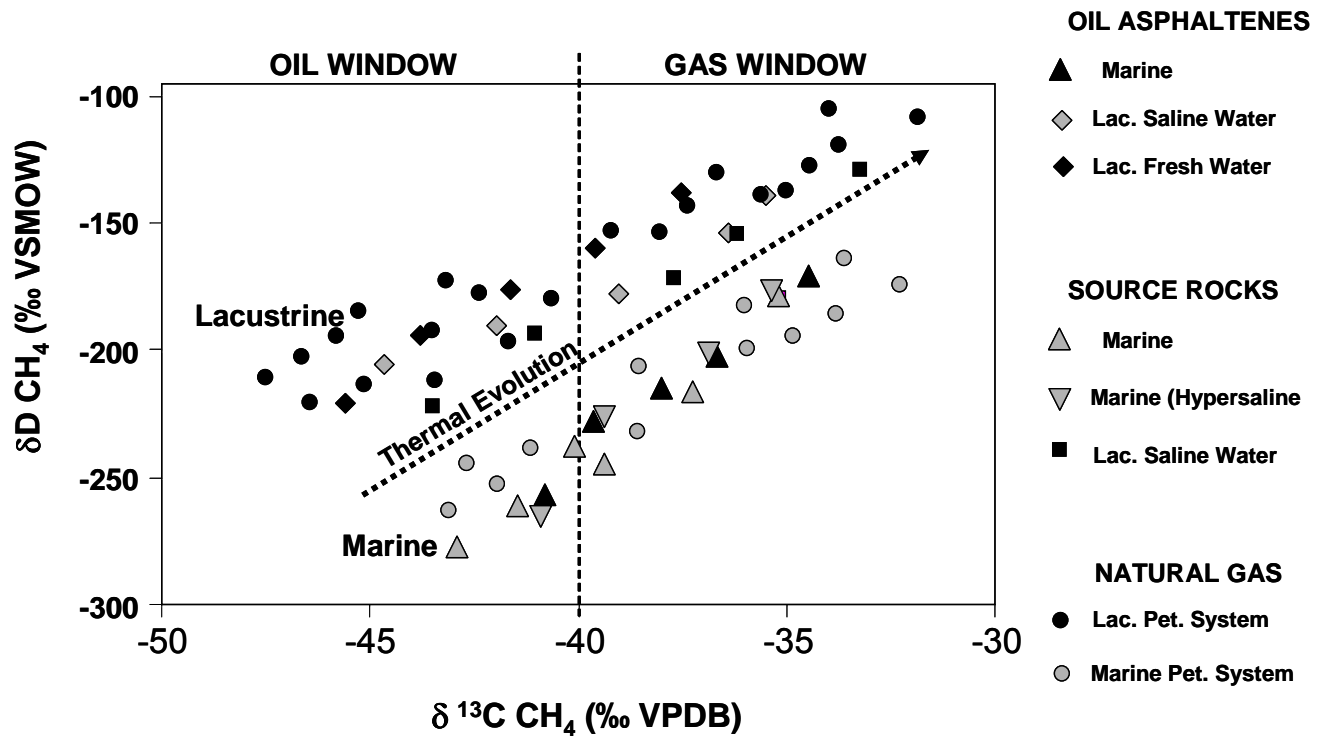


Figure 2: Comparison between $\delta^{13}C$ and δD for C_1 of lacustrine and marine natural gases with gases generated by MSSV-micropyrolysis of lacustrine and marine oil-asphaltenes.