Journal of Sedimentary Environments
Published by Universidade do Estado do Rio de Janeiro
2 (4): 274-282 October-December, 2017
doi: 10.12957/jse.2017.32495

JSE
RESEARCH PAPER

AROMATIC STEROIDS BIOMARKERS APPLIED TO HIGH RESOLUTION STRATIGRAPHY: IRATI FORMATION, SOUTHERN OF PARANÁ BASIN, BRAZIL

LINA LILIANA OSORIO[1], DARLLY ERIKA SILVA DOS REIS[2, 3] AND RENÉ RODRIGUES[2*]

1. Universidad de los Andes Colombia, UNIANDES, Departamento de Geociencias, Bogotá. Colômbia. linalili63@hotmail.com
2. Universidade do Estado do Rio de Janeiro - UERJ, Faculdade de Geologia, Depto. de Estratigrafia e Paleontologia. Av. São Francisco Xavier, 524, Maracanã. 20550-013 Rio de Janeiro, RJ, Brazil. rene@uerj.br
3. Depto de Geologia, Instituto de Geociências, Universidade Federal do Rio de Janeiro, Av. Brigadeiro Trompowski s/n, Ilha do Fundão, CCMN, Bloco G, CEP. 21949-900 – darllyreis@gmail.com

* CORRESPONDING AUTHOR, rene@uerj.br

Received on 18 August 2017
Received in revised form on 10 January 2018
Accepted on 25 January 2018

Editor: Maria Virginia Alves Martins, Universidade do Estado do Rio de Janeiro, Brazil

Citation:
Osorio, L.L., Reis, D.E.S., Rodrigues, R., 2017. Aromatic steroids biomarkers applied to high resolution stratigraphy: Irati Formation, Southern of Paraná Basin, Brazil. Journal of Sedimentary Environments, 2 (4): 274- 282.

Abstract

The use of aromatic steroids in geochemical studies is almost absent in Brazilian sedimentary basins. For this reason, it is intended to test the application of these compounds in high-resolution stratigraphy in the relatively well known Lower Permian Irati Formation. The Irati Formation is about 40 meters thick. It is thermally immature, and comprise two lithological distinct members: the lower siliciclastic Taquaral Member and the upper calcareous-siliciclastic Assistência Member. Based on the whole rock data, mostly total organic carbon, total sulfur, insoluble residue, Rock-Eval pyrolysis and aromatic steroids biomarkers, was possible to split the Irati Formation into seven chemostratigraphic units, named from A to C in the Taquaral Member and from D to G in the Assistência Member. Each of these units represents: distinct inputs of land derived organic matter type (chemostratigraphic units C and F) and/or; the response of living organisms to salinity changing of the water system (chemostratigraphic unit D) and; anoxia (chemostratigraphic unit E) during sedimentation. The methodology applied in this work can be used in other sedimentary basins but considering the lithology and sedimentary environment particularities.

Keywords: Organic Geochemistry. Aromatic Biomarkers. High Resolution Chemostratigraphy. Intracratonic Basin. Irati Formation. Lower Permian. Paraná Basin. Brazil.

1. Introduction

The Irati Formation is a sedimentary unit of the Paraná Basin that extends over an area of more than 4 million km^2 (South America). It has been considered one of the most important oil source horizon within this basin due to the presence of organic-rich rocks (e.g. Milani et al., 2007).

Paraná Basin covers approximately 1,500,000 km^2, from which 1,100,000 km^2 are located in Brazil (Fig. 1; Milani et al., 2007). It contains a stratigraphic record from the Ordovician to the Upper Cretaceous, with a maximum cumulative thickness of 7000 m (Milani et al., 2007).

Journal of Sedimentary Environments
Published by Universidade do Estado do Rio de Janeiro
2 (4): 274-282 October-December, 2017
doi: 10.12957/jse.2017.32495

Milani et al. (2007) subdivided the stratigraphic units of the Paraná Basin in six second order sequences or supersequences (Fig. 2).

The Irati Formation is included in Gondwana I Supersequence (Westphalian-Scythian), at the beginning of the regressive third order cycle. It is subdivided into the Taquaral and Assistência members. The lower member, Taquaral, is essentially siliciclastic, deposited in an open marine environment, and the upper member, Assistência, is characterized by carbonates interbedded with bituminous shale, deposited in a restricted marine environment (Northfleet et al., 1969; Hachiro and Coimbra, 1991; Santos Neto and Cerqueira, 1993; Rodrigues et al., 2010a, b; Alferes et al., 2011; Gama and Rodrigues, 2011; Reis (2012), Reis and Rodrigues, 2014; Euzébio et al., 2016).

The use of aromatic steroids in geochemical studies is almost absent in Brazilian sedimentary basins. For this reason, it is intended to test the application of these compounds in high-resolution stratigraphy in the relatively well known Lower Permian Irati Formation, Paraná Basin (Santos et al., 2006; Gutiérrez et al., 2010; Rocha-Campos et al., 2011, Euzébio et al., 2016).

2. Material and methods

A total of 29 rock samples previously analyzed for bulk geochemical parameters were selected from the well SC-20-RS (UTM coordinates: N 6496095.77 m, E 232067.79 m) drilled by Companhia de Pesquisa de Recursos Minerais (Mineral Resources Research Company; CPRM) 6 Km at southern of the Pinheiro Machado city, Rio Grande do Sul State, Brazil (Fig. 3). The analyzed interval ranges from 10 m to 55 m. The upper section was not studied because it was severely weathered.

The total organic carbon (TOC), total sulfur (S), insoluble residue (IR) and Rock-Eval pyrolysis data are derived from the work done by Reis (2012) and Reis and Rodrigues (2014) jointly with newly acquired from aromatic biomarkers results.

The methodology applied to obtain TOC, S, IR and Rock-Eval pyrolysis data are mentioned in Reis and Rodrigues (2013). For aromatic biomarkers the used procedures are described below.

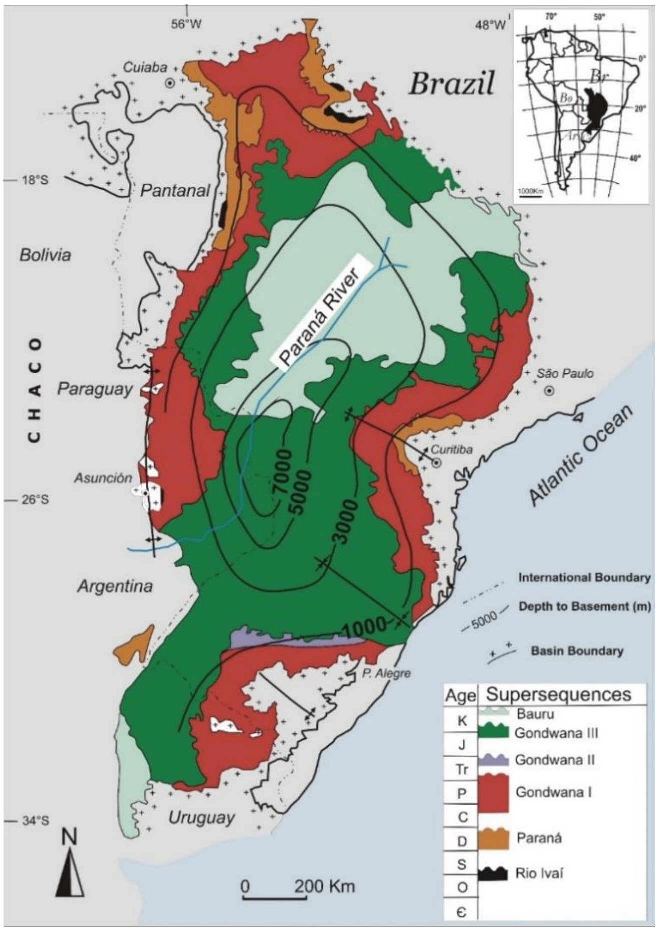

Fig. 1. Geological map of the Paraná Basin and its geographical location. The sedimentary supersequenses that compose this basin are mapped (adapted from Milani et al., 2007).

Journal of Sedimentary Environments
Published by Universidade do Estado do Rio de Janeiro
2 (4): 274-282 October-December, 2017
doi: 10.12957/jse.2017.32495

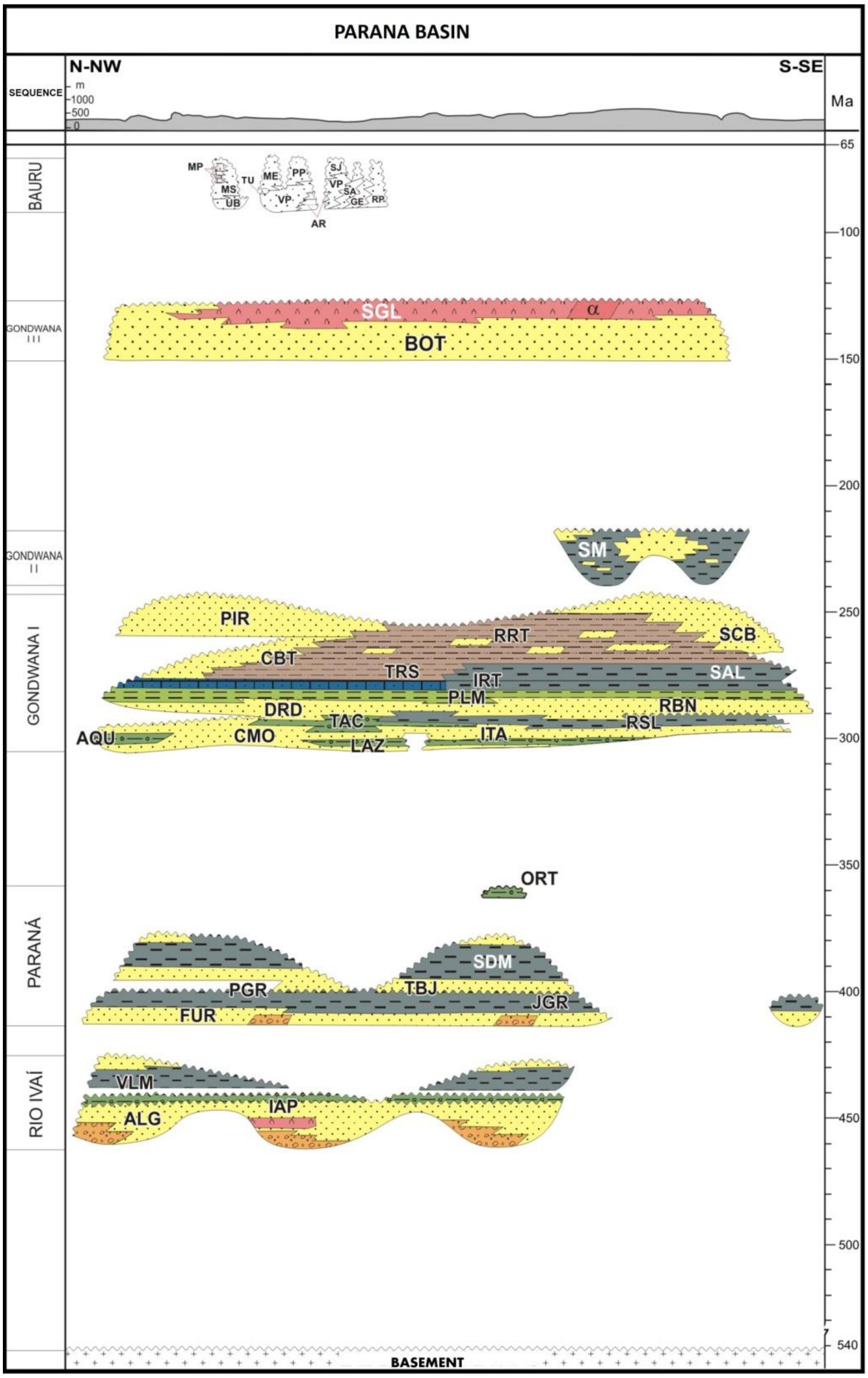

Fig. 2. Stratigraphic chart of Paraná Basin, with the indication of the six sequences (supersequences), according Milani et al. (2007). The Irati Formation is included in Gondwana I Supersequence (Westphalian-Scythian). Legend. ALG = Alto Garças Formation; IAP = Iapó Formation; VLM = Vila Maria Formation; FUR = Furnas Formation; PGR = Ponta Grossa Formation; JGR = Jaguariaíva Member; TBJ = Tibaji Member; SDM = São Domingo Member; ORT = Ortigueira "diamictite"; ITA = Itararé group; LAZ = Lagoa Azul Formation; CMO = Campo Mourão Formation; TAC = Taciba Formation; RSL = Rio do Sul Member; AQU = Aquidauana Formation; DRD = Dourados Formation; RBN = Rio Bonito Formation; PLM = Palermo Formation; IRT = Irati Formation; TRS = Teresina Formation; SAL = Serra Alta Formation; CBT = Corumbataí Formation; RRT = Rio do Rasto Formation; SCB = Sanga do Cabral Formation; PIR = Pirambóia Formation; SM = Santa Maria Formation; BOT = Botucatu; SGL = Serra Geral; AR = Araçatuba Formation; UB = Uberaba Formation; VP = Vale do Rio do Peixe Formation; GE = Goio Erê Formation; RP = Rio Paraná Formation; SA = Santo Anastácio Formation; MS = Serra da Galga Member of Marília Formation; MP = Ponta Alta Member of Marília Formation; ME = Echaporã Member of Marília Formation; TU = Taiúva volcanic rocks; PP = Presidente Prudente Formation; SJ = São José do Rio Preto Formation.

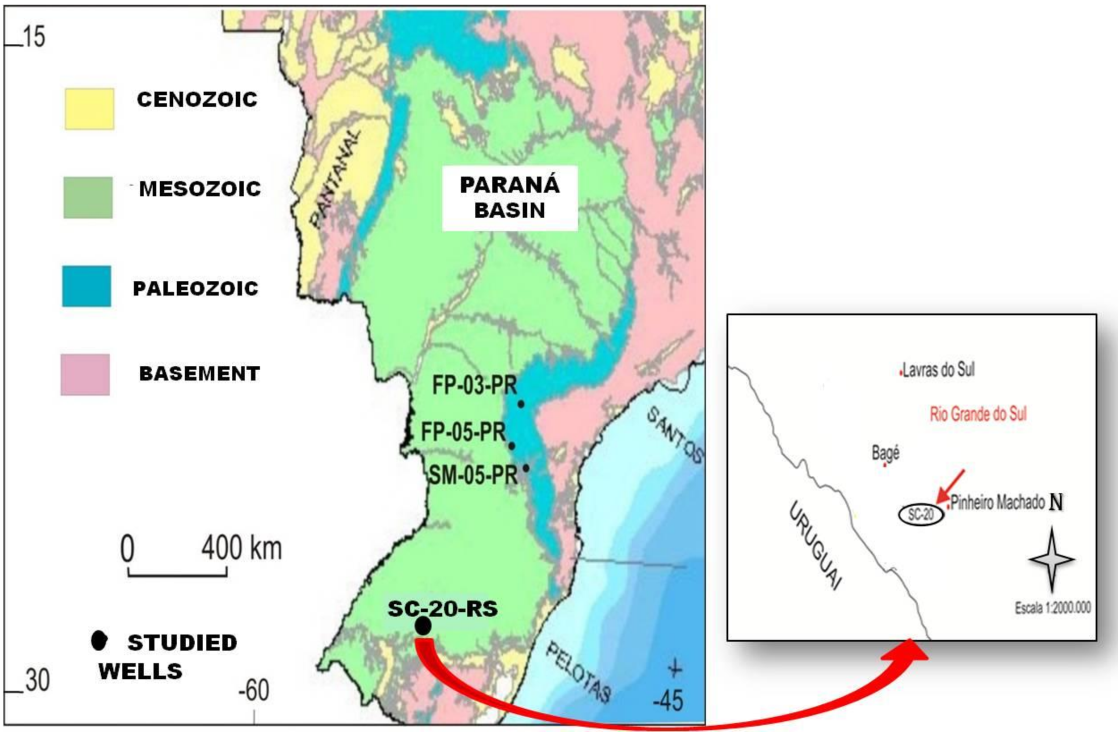

Fig. 3. Location of the studied well and other wells under analysis, in the Southwestern Paraná Basin. Modified from Reis (2012).

The powdered rock samples were extracted using dichloromethane and fractionated in alkanes and aromatic hydrocarbons. The aromatic biomarker analyses were performed using a GC-MS (Agilent Technologies 6890 GC coupled to an Agilent 5973 Mass Detector) and Mass Spectrometry Agilent 7000 GC-MS-MS System with a triple quadripole analyzer system. The attempt to identify the organic compounds was performed by comparison with literature mass spectra, retention time and elution order (Peters et al., 2005).

Geochemical analyzes were carried out at the Laboratório de Estratigrafia Química e Geoquímica Orgânica (Chemostratigraphy and Organic Geochemistry Laboratory), of the Universidade do Estado do Rio de Janeiro (LGQM/UERJ).

3. Results and discussion

The studied samples presented a great variability of valuesTOC (0.08-16.90%), S (0.01-4.07%) and IR (14-96.40%). The results of Rock-Eval pyrolysis also vary greatly: S2 ranged from 0.04 to 72.4 mg HC/g rock; hydrogen index (HI) varied between 7.78-516 mg HC/g TOC and; Tmax oscillated between 401-426 °C. The detailed distribution of these parameters as well as the aromatic biomarkers identified in the different chemostratigraphic units is presented in the following sub-items.

3.1. Chemostratigraphy and High-Resolution Stratigraphy Characterization

The Irati Formation is about 40 meters thick and is thermally immature. Based on whole rock data, mostly TOC, S and IR, as well as Rock-Eval pyrolysis data and aromatic biomarkers, it was possible to split the Irati Formation in seven chemostratigraphic units, named from A to C in the Taquaral Member and from D to G in the Assistência Member. Based on these data, was proposed a high-resolution sequence stratigraphic for the Lower Permian Irati Formation section of well SC-20-RS, where the maximum flooding surface is characterized by the higher TOC and HI values according to Reis (2012) e Reis and Rodrigues (2014).

3.2. Distribution patterns of demethylated and methylated triaromatic steroids

3.2.1. Taquaral Member

Units A, B and C are essentially siliciclastic, as shown by the RI data (85-96%). Units A is characterized by the presence of C26(R)+C27(S) and C28 (S+R) demethylated triaromatic steroids occurring in equivalent proportions. The predominance of C28 (S+R) can be observed in the interval B (TOC >2%), whereas higher abundance of C26(R)+C27(S) was detected in unit C (Fig. 4).

Journal of Sedimentary Environments
Published by Universidade do Estado do Rio de Janeiro
2 (4): 274-282 October-December, 2017
doi: 10.12957/jse.2017.32495

RESEARCH PAPER

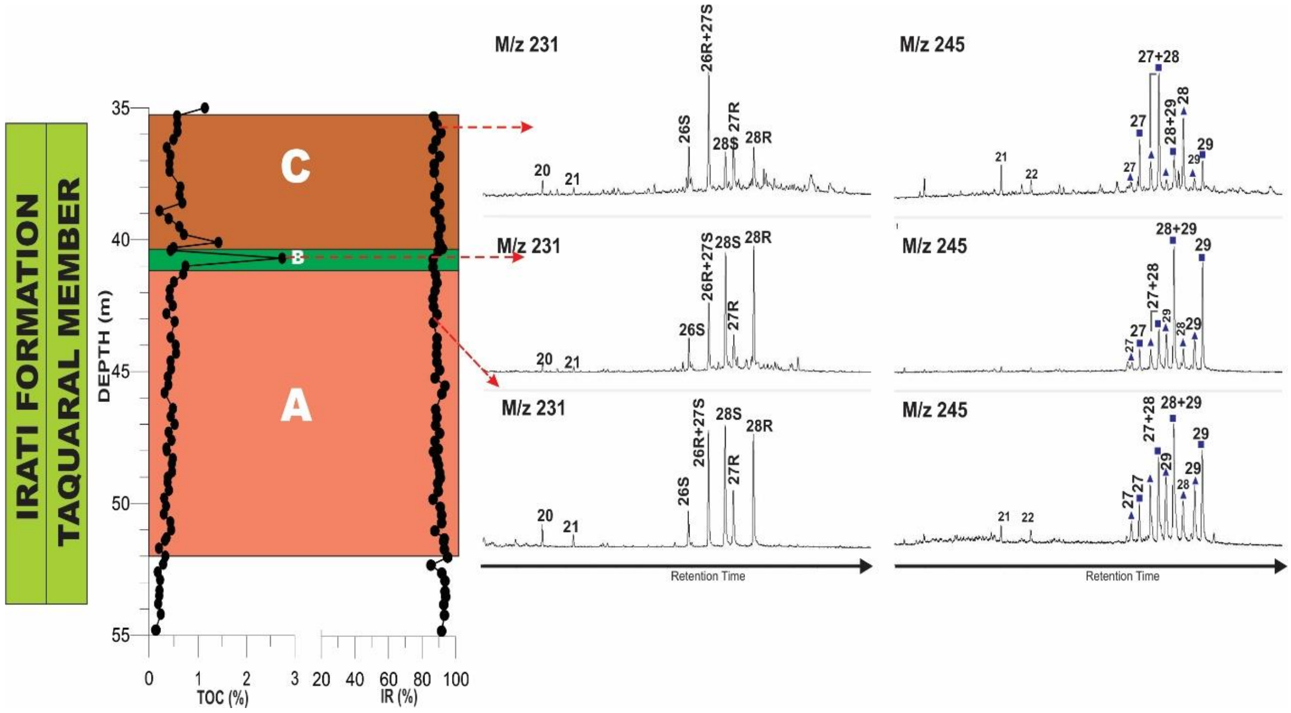

Fig. 4. Mass fragmentograms (*m/z* 231, *m/z* 245 of aromatic fractions) showing distribution of demethylated and methylated triaromatic steroids in the Taquaral Member (Chemostratigraphic Units A, B and C), respectively. Peak numbers represent the number of carbon (C) atoms.

Methylated triaromatic (M/z 245) steroids in units A and B can be distinguished by the higher proportion of C29 steroids mainly in unit B where TOC is also higher, whereas in Unit C an increasing of C27+C28 steroids were observed in the top session (Fig. 4).

3.2.2. Assistência Member

The lower carbonate, interbedded marls and shale section (unit D; RI values ranging from 14-94%), deposited in hypersaline conditions, based on alkanes biomarkers according to Reis and Rodrigues (2013), are characterized by: higher abundance of C28 (S+R); absence of C26 (S) and; low proportion of C21-C22 short chain of triaromatic steroids (Fig. 5). Similar results were also obtained by Riolo et al. (1986) in the same sedimentary conditions. In the oil shale section (unit E; RI: 80-95%; TOC: 1.51-16.90%; IH: 203-516 mg HC/g TOC), deposited under lower salinity and strongest anoxic conditions, according to Reis and Rodrigues (2013), there is a predominance of C26(R)+C27(S) with increasing of C26(S) and C28 (S+R) in equivalent proportion towards to the top, along with a corresponding increase in TOC (Fig. 5). In the siliciclastic unit F (RI values ranging from 90-96%), there is a predominance of C28 (S+R), lower C27R, and a relative increase of lower homologues C21-C22 (Fig. 5). The upper carbonate and marl section (unit G) deposited in oxic (RI: 24-34 %; TOC: 0.53-1.02%; IH 39-132 mg HC/g TOC; S2: 0.7-0.91 HC/g rock) and less restrict sedimentary conditions, according to Reis and Rodrigues (2013), display different demethylated steroids distributions compared to the lower carbonate and marls (unit D) (Fig, 5).

The chemostratigraphic Units D and G (carbonate, interbedded marls and shale as revealed by the RI data ranging for the Unit D between14-94% and for the Unit G between 24-34%, display equivalent proportions of C27/28, C28/29 and C29 steroids, as also observed by Li et al. (2012) in the same depositional conditions. An important variation in the oil shale section (Unit E; RI: 80-95%; TOC: 1.51-16.90%; IH: 203-516 mg HC/g TOC) occurs, related to the predominance of C27/C28 and C28 steroids, and absence or low proportions of C27 and C29 steroids (Fig. 6).

In the shale interval (RI values ranging from 90-96%), of low TOC content (Unit F), deposited in oxic conditions (TOC: 0.24-0.82 %; IH: 9-55 mg HC/g TOC), there is a predominance of C29 steroid, which is quite similar to that observed in the siliciclastic section of Taquaral Member (Fig. 6).

3.3. Distribution patterns of monoaromatic steroids

3.3.1. Taquaral Member

The siliciclastic units A and B are characterized by the strong presence of rearranged structures, but in greater relative abundance in unit A, probably related to its more oxic depositional conditions (Riolo et al., 1986). Nonetheless, a slight reduction of these isomers and a decrease in C28 steroids can be observed in unit B. However, unit C is especially enriched with C27, C27+28 steroids, and rearranged structures are absent (Fig. 7).

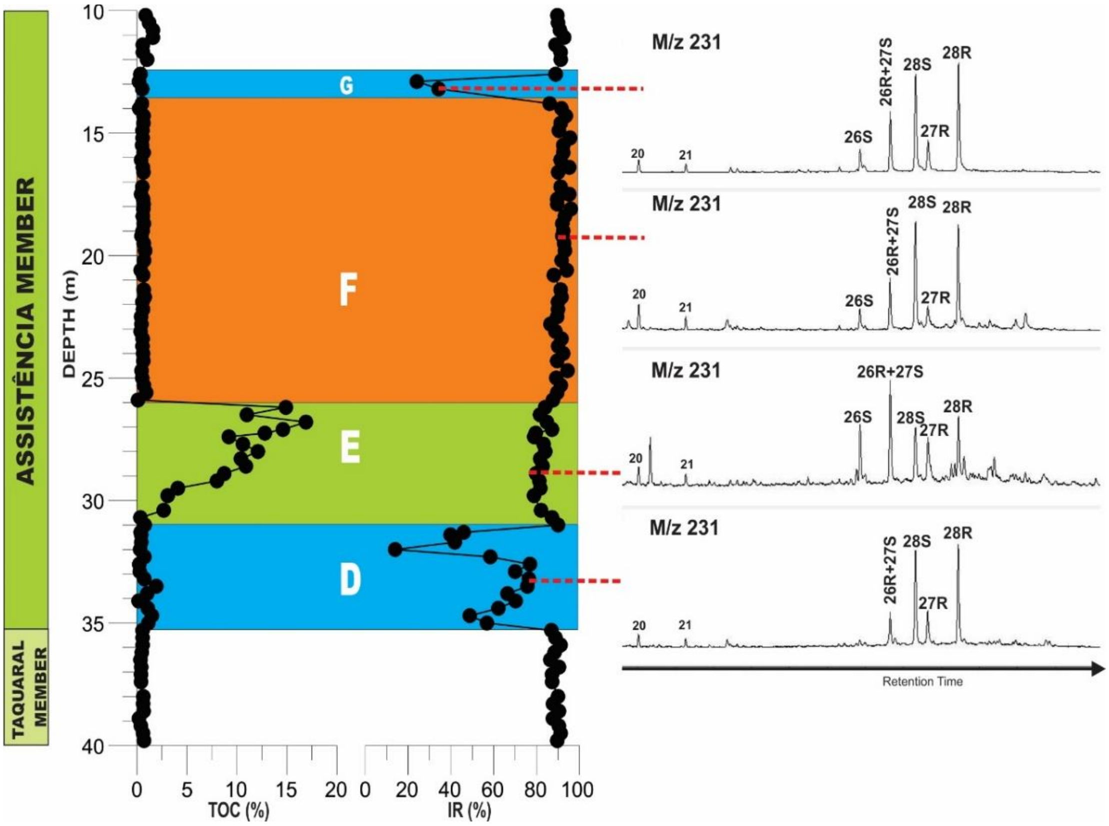

Fig. 5. Representative mass chromatograms.–M/*z* 231, showing distribution of demethylated triaromatic steroid in source rocks extract in the Assistência Member (chemostratigraphic units D-G). Peak numbers represent the number of C atoms.

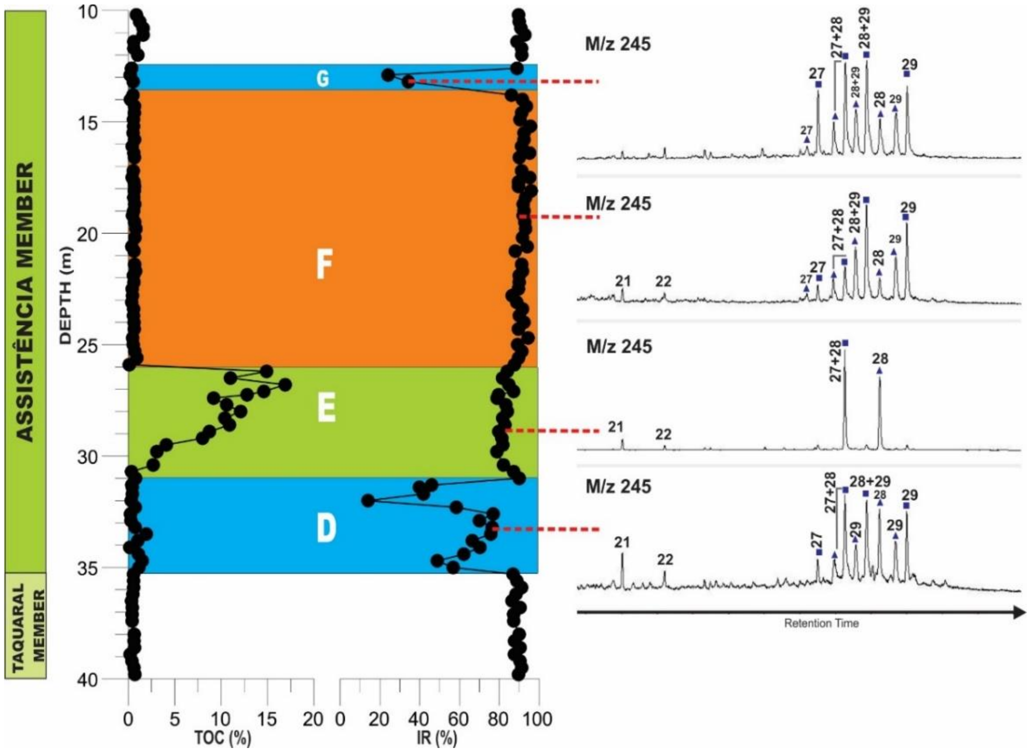

Fig. 6. Representative mass chromatograms. M/*z* 245 showing distribution of methyated triaromatic steroids in the Assistência Member (chemostratigraphic units D-F). Peak numbers represent the number of C atoms.

Journal of Sedimentary Environments
Published by Universidade do Estado do Rio de Janeiro
2 (4): 274-282 October-December, 2017
doi: 10.12957/jse.2017.32495

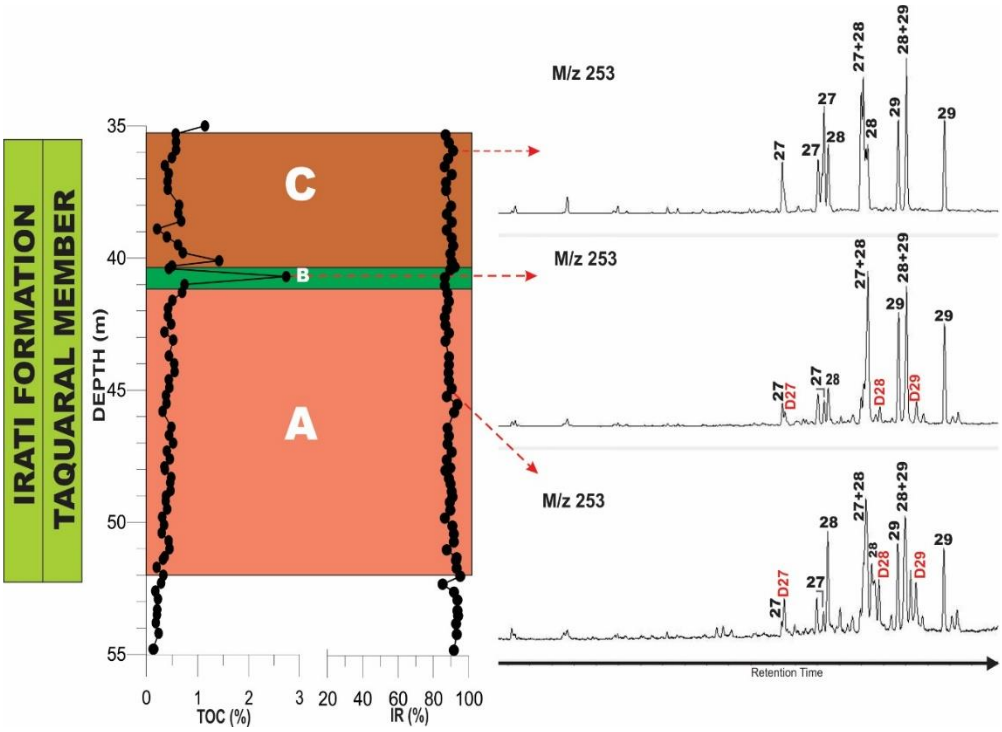

Fig. 7. Distributional variations of monoaromatic steroids~~.~~ (*M/z 253 mass* fragmentograms) from Taquaral Member (chemostratigraphic units A-C). Peak numbers represent the number of C atoms.

3.3.2. Assistência Member

In the marls and carbonates of chemostratigraphic units D and G, deposited in a hypersaline restricted marine environment according to Reis and Rodrigues (2013), C28+29 and C29 steroids predominate, and rearranged structures are absent (Fig. 8

In the oil shale interval (Unit E) deposited in an anoxic marine environment, there is an increase of C27 compounds and no rearranged structures are observed. Instead, the siliciclastic Unit F is characterized by the presence of rearranged structures (Fig. 8).

4. Conclusion

In the siliciclastic Taquaral Member, deposited in a normal marine environment, the steroid compositional variations observed are mostly related to the changes in oxy-reduction conditions of the depositional environment.

In the Assistência Member, characterized by a siliciclastic-carbonate sedimentation deposited in a hypersaline marine environment, the bituminous shale intervals were deposited in lower salinity conditions. The observed steroid compositional variations are related to changes in the lithology (carbonate-marl versus shale), oxy-reduction conditions and salinity of the depositional environment.

The fingerprint of the demethylated triaromatic steroids normally shows much less variation than their methylated counterpart. However, compositional variations could be observed in the oil shale interval, in which occurs a net increasing of C_{26} e C_{27} homologous compared to the composition of other chemostratigraphic units.

On the other hand, the methylated triaromatic steroids have shown the best possibilities to be applied as a source parameter: the predominance of C_{29} homologous in the low TOC siliciclastic intervals C and F; the increasing of C_{27} and C_{28} homologous in the interbeds of shales, marls and limestones (interval D) and; predominance of C_{28} homologous in the oil shale interval E.

Variations in the relative amount of different homologous of monoaromatic steroids are another geochemical parameter difficult to be considered because of the co-elution of the different isomers and homologues.

Up to now, the best parameter corresponds to the higher amounts of rearranged structures in the low TOC siliciclastic intervals (Taquaral Member and chemostratigraphic unit F of Assistência Member), compared to the other intervals where practically no rearranged structures were observed.

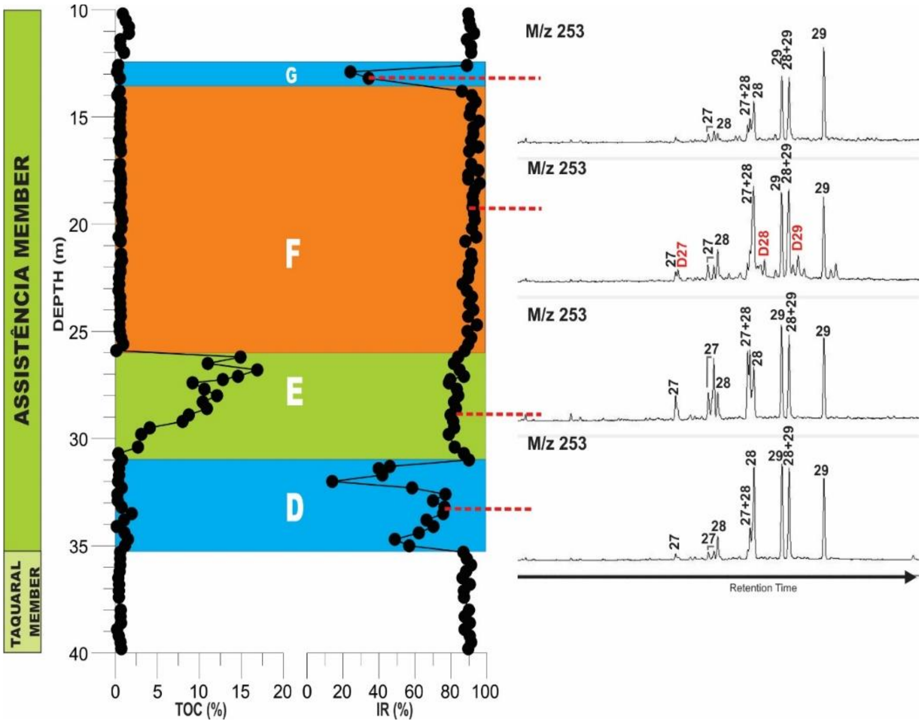

Fig. 8. Variation of rearranged/non-rearranged monoaromatic steroid as a function of TOC and IR. *M/z 253* fragmentograms from Assistência Member (chemostratigraphic units D-G). Peak numbers represent the number of C atoms.

Acknowledgment

The authors thank CNPq (Brazilian research council) and FAPERJ (Rio de Janeiro State research agency), INOG (National Oil and Gas Institute) and UERJ for financial support, to the CPRM, by facilitating the access to data and samples of the studied core and to the LGQM/FGEL/UERJ, for the processing and analysis of samples.

References

Alferes, C.L.F., Rodrigues, R., Pereira, E. 2011. Geoquímica orgânica aplicada à Formação Irati, na área de São Mateus do Sul (PR), Brasil. Geochimica Brasiliensis 25, 47-54.

Euzébio, R.S., Reis, D.E.S., Brito, M.A.R.C., Bergamaschi, S., Martins, M.V.A., Rodrigues, R., 2016. Oil generation potential assessment and paleoenvironmental interpretation of Irati Formation (Lower Permian) in northwestern of Paraná Basin (Brazil). Journal of Sedimentary Environments, 1(2), 261-274. https://doi: 10.12957/jse.2016.23388

Gama, R.M.A., Rodrigues, R. 2011. Caracterização dos horizontes geradores da Formação Irati através do uso dos biomarcadores na região de Herval (RS), Bacia do Paraná. In: Atas do 6° Congresso Brasileiro de Pesquisa e Desenvolvimento em Petróleo e Gás – 6º PDPETRO.

Gutiérrez, P.R., Balarino, M.L., Beri, A., 2010. Palynology of the Lower Permian of Paraná Basin, Uruguay. Journal of Systematic Palaeontology, 8 (4) https://doi.org/10.1080/14772011003794546.

Hachiro, J., Coimbra, A.M., 1991. Sucessões sedimentares e ciclos transgressivo-regressivos da Formação Irati no Estado de São Paulo. In: Atas do Simpósio de Geologia do Sudeste, 2, São Paulo. São Paulo: SBG-NSP/NRJ, p. 45-52.

Li, M., Wang, T.G., Lillis, P.G., Wang, C.H., Shi, S., 2012. The significance of 24-norcholestanes, triaromatic steroids and dinosteroids in oils and Cambrian-Ordovician source rocks from the cratonic region of the Tarim Basin, NW china. Applied Geochemistry, v. 27. pp. 1643-1654. https://doi.org/10.1016/j.apgeochem.2012. 03.006

Milani, E.J., França, A.B., Medeiros, R.A. 2007. Rochas geradoras e rochas-reservatório da Bacia do Paraná, faixa oriental de afloramentos, Estado do Paraná. Boletim de Geociências da Petrobras 15, 135-162.

Northfleet, A.A., Medeiros, R.A., Muhlmann, H., 1969 Reavaliação dos dados geológicos da Bacia do Paraná. Boletim Técnico da PETROBRAS 12, 291-346.

Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. The biomarker guide. Cambridge University Press. 1155 p.

Reis, D.E.S., 2012. A Geoquimica Orgânica Aplicada à Formação Irati-Bacia do Paraná, poço SC-20-RS, área de Pinheiro Machado – RS: Identificação Ambiental, Origem da Matéria Orgânica e Potencial Gerador. MsD Thesis UERJ.

Reis, D.E.S., Rodrigues, R. Alkane Biomarker Stratigraphy of Irati Formation in the southern portion of Paraná Basin. Latin American Congresso on Organic Geochemistry – ALAGO, 2014.

Riolo, J., Hussler, G., Albrecht, P., Connan, J., 1986. Distribution of aromatic steroids in geochemical samples: Their evaluation as geochemical parameters. Organic Geochemistry, 10, 981-

Journal of Sedimentary Environments
Published by Universidade do Estado do Rio de Janeiro
2 (4): 274-282 October-December, 2017
doi: 10.12957/jse.2017.32495

990. https://doi.org/10. 1016/S0146-6380(86)80036-5

Rocha-Campos, A.C., Basei, M.A., Nutman, A.P., Kleiman, L.E., Varela, R., Llambias, E., Canile, F.M., da Rosa, O. de C.R., 2011. 30 million years of Permian volcanism recorded in the Choiyoi igneous province (W Argentina) and their source for younger ash fall deposits in the Paraná Basin: SHRIMP U-Pb zircon geochronology evidence. Gondwana Research 19, 509-523. https://doi.org/10.1016/j.gr.2010.07.003

Rodrigues, R., Pereira, E., Bergamaschi, S., Alferes, C.L.F. 2010a. Carbon isotope stratigraphy of organic matter: Irati Formation, Lower Permian of Paraná Basin. In: Proceedings of VII SSAGI – South American Symposium on Isotope Geology, pp. 522-525.

Rodrigues, R., Pereira, E., Bergamaschi, S., Chaves, H.A.F., Alferes, C.L.F. 2010b. Organic Geochemistry of Irati Formation, Lower Permian of Paraná Basin. In: Memórias XII Congresso Latinoamericano de Geoquímica Orgânica, pp. 41-43.

Santos Neto, E.V., Cerqueira, J.R. 1993. Aplicação da Geoquímica Orgânica na cronoestratigrafia e paleogeografia da Formação Irati. I*n*: Anais do Simpósio Sobre Cronoestratigrafia da Bacia do Paraná, 1, Rio Claro. Rio Claro: UNESP, 1, p. 71.

Santos, R.V., Souza, P.A., Souza de Alvarenga, C.J., Dantas, E.L., Pimentel, M.M., Gouveia de Oliveira, C., Medeiros de Araújo, L. 2006. Shrimp U–Pb zircon dating and palynology of bentonitic layers from the Permian Irati Formation, Paraná Basin, Brazil. Gondwana Research 9, 456–463. doi:10.1016/j.gr.2005.12.001.

Zalán, P.V., Wolff, S., Astolfi, M., Vieira, I.S., Conceição, J., Appi, V., Santos Neto, E., Cerqueira, J., Marques, A. 1990. The Paraná Basin, Brazil. *In*: Leighton, M.W., Kolata, D.R., Oltz, D.F., Eidel, J.J. (eds.), Interior cratonic basins. AAPG Memoir 51, 681-708.