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DIEGO NERY DO AMARAL

MARCADORES NITROGENADOS ASSOCADOS A PARÂMETROS GEOQUÍMICOS PARA INTERPRETAÇÕES PALEODEPOSICIONAIS DAS FORMAÇÕES CANDEIAS (BACIA DO RECÔNCAVO) E BARREIRINHA (BACIA DO AMAZONAS)

Salvador
2024

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Orientador: Prof. Dr. Sérgio Luís Costa Ferreira
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“Tudo deve ser feito o mais simples possível, porém não simples demais.”

Albert Einstein

RESUMO

Marcadores nitrogenados (N-marcadores), como carbazóis, benzocarbazóis e seus isômeros alquilados constituem uma pequena fração da composição química do petróleo e/ou extrato de rocha geradora (<4,0%), mas podem fornecer informações sobre origem, migração, ambiente deposicional e maturidade do petróleo, sendo avaliados de forma isolada e/ou através das razões diagnósticas. Presentes em amostras de petróleo e extratos de rocha geradora principalmente em estruturas aromáticas e heterocíclicas, a identificação de N-marcadores envolve certa complexidade, tornando, até o momento, a aplicação desses compostos em avaliações geoquímicas aplicadas a bacias sedimentares brasileiras pouco explorada. Diante disso, a técnica GC-MS/MS tem sido empregada na literatura para determinação de compostos orgânicos em estudos geoquímicos por diminuir etapas de preparo de amostra (como a não necessidade de etapa de fracionamento utilizando sílica ácida, no caso dos compostos nitrogenados) e apresentar alta seletividade e sensibilidade. O objetivo desta pesquisa foi empregar, de forma inovadora, os N-marcadores em conjunto com parâmetros geoquímicos convencionais (como biomarcadores saturados, carbono orgânico total e dados de pirólise Rock-Eval, por exemplo) e também os S-marcadores como novas ferramentas na caracterização de sucessões verticais de afloramentos de rochas geradoras de petróleo em bacias sedimentares com diferentes origens, quanto ao paleoambiente deposicional, tipo de matéria orgânica e condições deposicionais, sendo utilizadas amostras das Formações Candeias (Bacia do Recôncavo) e Barreirinha (Bacia do Amazonas). Para isso, foram otimizados métodos para determinação e quantificação dos marcadores em estudo via GC-MS/MS. Foram coletadas amostras em três diferentes afloramentos: um na Bacia do Recôncavo, com 10 amostras coletadas verticalmente, dois na Bacia do Amazonas, com 7 amostras coletadas verticalmente em cada afloramento. A matéria orgânica contida nas amostras foi extraída via extração acelerada com solventes (ASE) com posterior fracionamento via cromatografia líquida em coluna aberta e análise das frações de compostos aromáticos e NSO combinadas via GC-MS/MS. Em conjunto com parâmetros geoquímicos convencionais, os marcadores nitrogenados e sulfurados se mostraram eficientes na avaliação de distinções e similaridades entre as rochas geradoras em estudo. Amostras da rocha geradora da Bacia do Recôncavo, de origem lacustre, apresentam, no geral, concentrações mais baixas de compostos nitrogenados (carbazóis (CA), metilcarbazóis (MCA) e dimetilcarbazóis (DMCA)) e sulfurados (benzotiofenos (BT), dibenzotiofenos (DBT) e benzonaftotiofenos (BNT)), enquanto amostras da Bacia do Amazonas, de origem marinha, apresentam altas concentrações desses compostos. O *input* de matéria orgânica algálica foi evidenciado por diagramas ternários utilizando isômeros de N-marcadores (1-MCA, 2-MCA e 4-MCA) e S-marcadores (BNT-1,2, BNT-2,1 e BNT-2,3), destacando diferenças isoméricas inerentes aos ambientes deposicionais (lacustre e marinho), que ajudam a entender o comportamento desses compostos nos diferentes ambientes. Os valores da razão pristano/fitano apresentam correspondência com as concentrações dos benzocarbazóis e relação DBT/Fenantreno, indicando que estes compostos podem ser afetados pelas condições redox dos ambientes deposicionais.

Palavras-chave: N-marcadores, Bacia do Recôncavo, Bacia do Amazonas, paleoambiente deposicional.

ABSTRACT

Nitrogen markers (N-markers), such as carbazoles, benzocarbazoles and their alkylated isomers, are specific to a small fraction of the chemical composition of petroleum and/or source rock extract (<4.0%), but can provide information on the origin, migration, depositional environment and maturity of petroleum, being evaluated in isolation and/or through diagnostic ratios. Presented in petroleum samples and source rock extracts mainly in aromatic and heterocyclic structures, the identification of N-markers involves a certain complexity, making, to date, the application of these compositions in geochemical evaluations applied to Brazilian sedimentary basins little explored. In view of this, the GC-MS/MS technique has been used in literature for the determination of organic compounds in geochemical studies to reduce sample preparation steps (such as the elimination of a fractionation step using acidic silica, in the case of nitrogen compounds) and to present high selectivity and sensitivity. The aim of this research was to use, in an innovative way, N-markers in conjunction with occasional geochemical interruptions (such as saturated biomarkers, total organic carbon and Rock-Eval pyrolysis data, for example) and also S-markers as new tools in the characterization of vertical successions of outcrops of oil source rocks in sedimentary basins with different origins, regarding depositional paleoenvironment, type of organic matter and depositional conditions, using samples from the Candeias Formations (Recôncavo Basin) and Barreirinha Formations (Amazon Basin). For this, methods for determination and quantification of the markers under study via GC-MS/MS were optimized. Samples were collected from three different outcrops: one in the Recôncavo Basin, with 10 samples collected vertically, two in the Amazon Basin, with 7 samples collected vertically in each outcrop. The organic matter contained in the samples was extracted via accelerated solvent protection (ASE) with subsequent fractionation via open column liquid chromatography and analysis of the combined aromatic and NSO fractions via GC-MS/MS. Together with conventional geochemical parameters, nitrogen and sulfur markers proved to be efficient in evaluating distinctions and similarities between the source rocks under study. Samples of the source rock from the Recôncavo Basin, of lacustrine origin, present, in general, lower concentrations of nitrogen compounds (carbazoles (CA), methylcarbazoles (MCA) and dimethylcarbazoles (DMCA)) and sulfur compounds (benzothiophenes (BT), dibenzothiophenes (DBT) and benzonaphthothiophenes (BNT)), while samples from the Amazon Basin, of marine origin, present high concentrations of these compounds. The input of algal organic matter was evidenced by ternary diagrams using isomers of N-markers (1-MCA, 2-MCA and 4-MCA) and S-markers (BNT-1,2, BNT-2,1 and BNT-2,3), highlighting isomeric differences inherent to the depositional environments (lacustrine and marine), which help to understand the behavior of these compounds in different environments. The values of the pristane/phytane ratio correspond to the concentrations of benzocarbazoles and the DBT/phenanthrene ratio, indicating that these compounds can be affected by the redox conditions of the depositional environments.

Keywords: N-markers, Recôncavo Basin, Amazon Basin, paleodepositional environment.

SUMÁRIO

APRESENTAÇÃO E ESTRUTURA

A parte experimental dessa tese foi realizada utilizando a infraestrutura do Centro de Excelência em Geoquímica Petróleo, Energia e Meio Ambiente - LEPETRO, localizado no Instituto de Geociências (IGEO) na Universidade Federal da Bahia (UFBA). Os recursos foram oriundos do Projeto GEOQPETROL – inserido no Projeto Pesquisa em Sistemas Petrolíferos em Bacias Sedimentares Brasileiras (UFBA/Shell Brasil/ANP) e também do Programa Doutorado Acadêmico de Inovação (DAI) do CNPq, Edital º 23/2018, processo 142495/2019-0.

A disposição dos capítulos se inicia pela introdução e segue com a apresentação de dois artigos científicos. Na introdução, há a descrição da proposta geral do trabalho, a relevância e aspectos inovadores, abordando os principais aspectos da literatura sobre o tema. O capítulo 3 e o capítulo 4 exibem os resultados da pesquisa na forma de artigos científicos. A formatação dos artigos seguiu a estrutura indicada pelos periódicos nos quais eles foram submetidos. A metodologia empregada nesta tese foi distinta para cada artigo produzido.

No primeiro artigo (apresentado no capítulo 3), intitulado "*Use of nitrogen markers to assess source rock paleodepositional environment of the Candeias (Recôncavo Basin) and Barreirinha (Amazonas Basin) formations*", publicado na *Marine and Petroleum Geology* (2024), foi otimizado um método para identificação e quantificação de N- marcadores via GC-MS/MS, a partir de extratos de rochas geradoras de petróleo para interpretação, de forma inovadora, dos seus paleoambientes deposicionais.

No capítulo 4 é apresentado o segundo artigo gerado nesta tese, intitulado "*Organic sulfur markers as proxies of depositional paleoenvironments related to Recôncavo and Amazon Basins, Brazil*", publicado no periódico *Energy & Fuel*. Nesse artigo é otimizado um método para identificação e quantificação de S-marcadores via GC-MS/MS, que, em conjunto com parâmetros convencionais da geoquímica orgânica, fundamenta a interpretação dos paleoambientes deposicionais das rochas geradoras em estudo e contribui para o entendimento dos S-marcadores, ressaltando dados e interpretações inovadoras. Por fim, são as conclusões gerais, abordando a relação entre os capítulos descritos.

1 INTRODUÇÃO

A Bacia do Recôncavo, localizada no Estado da Bahia, foi a primeira bacia sedimentar a ser explorada e produzir petróleo do Brasil (Rocha *et al.,* 2002). Os sistemas petrolíferos identificados na Bacia do Recôncavo têm em comum a rocha geradora, representada pela Formação Candeias, onde há ocorrência de folhelhos negros, ricos em matéria orgânica (Penteado; Behar, 2000). Já a Bacia do Amazonas está localizada nos Estados do Amazonas e Pará, e tem seu histórico de produção petrolífera mais recente (a partir de 1980), sendo a Formação Barreirinha, portadora de folhelhos negros, betuminosos, a principal geradora da bacia (Cunha *et al*., 2007). Ambas as bacias sedimentares são atualmente produtoras de petróleo e continuam sendo alvo de estudos que visem comprovar ainda mais potencial petrolífero.

Estudos anteriores, incluindo avaliações geoquímicas (Daniel *et al*., 1989; Figueiredo *et al.,* 1994; Gaglianone; Trindade, 1988; Mello *et al*., 1994, Amaral *et al*., 2020) e de petrografia orgânica (Balbinot; Kalkreuth, 2010), identificaram como a principal rocha geradora da Bacia do Recôncavo a Formação Candeias, depositada em ambiente lacustre durante o Cretáceo (Berriasiano). Os autores supracitados definem tal Formação como uma espessa seção de folhelhos cinza-esverdeado a escuro, com intercalações subordinadas de siltitos, calcários e dolomitos, englobando localmente corpos de arenitos maciços e/ou estratificados. Segundo Milani e Araújo (2003), o teor médio de carbono orgânico total (COT) associado ao folhelho Candeias é de 4% e o querogênio é do Tipo I.

Na Bacia do Amazonas, a Formação Barreirinha é reconhecida como principal geradora da bacia, sendo portadora de folhelhos cinza escuros a negros, ocasionalmente silicificados, depositados em ambiente marinho anóxico, associado à preservação de um grande volume de matéria orgânica no Devoniano (Frasniano) (Loboziak *et al.,* 1997; Cunha, 2000). Estudos geoquímicos apontam para valores de COT em torno de 3% e querogênio do tipo II (Gonzaga *et al.,* 2000; Calderón, 2017; Góes *et al.,* 2022).

Nos últimos anos, vários estudos utilizaram compostos nitrogenados (N-compostos) na avaliação de extratos de rochas geradoras e petróleo (Zhang *et al.,* 2018; Ziegs *et al.,* 2018; Chen *et al.,* 2021, Dias *et al.,* 2021). N-compostos como carbazóis e benzocarbazóis (espécies de nitrogênio neutros, que compreendem pirrol, indol, carbazol, benzocarbazol e seus análogos alquilados), são empregados como marcadores (N-marcadores) de fácies deposicionais, maturidade térmica e biodegradação (Li *et al*., 1995; Bennett *et al*., 2002; Larter *et al.,* 2000). Os N-marcadores são avaliados de forma isolada e/ou através das razões diagnósticas (na maioria dos casos) (Dias *et al.,* 2020).

Zhu *et al.* (1998) e Li *et al.* (1999) relatam que a abundância de carbazóis e benzocarbazóis no petróleo de origem marinha é várias vezes superior ao do petróleo de origem lacustre, onde rochas geradoras depositadas em condições marinhas normais exibem proeminência do 1-metilcarbazol (1-MCA) e uma alta concentração de benzo[c]carbazol (B[c]CA) (Clegg *et al.* 1997; Bakr, 2009). Há ainda observações que sugerem correspondências entre N-marcadores e biomarcadores saturados, como a correlação positiva entre a razão de benzocarbazóis: Benzo[a]carbazol/ Benzo[a]carbazol + Benzo[c]carbazol (B[a]CA/B[a]CA+B[a]CA) e os valores de pristano/fitano (marcadores de condições oxi-redutoras de ambiente deposicional) descrita por Zhou e Huang (2010).

Os compostos orgânicos de enxofre permitem inferir correlações entre rochas geradoras de petróleo, avaliar fácies, entrada de matéria orgânica e condições paleodeposicionais, servindo então como S-marcadores (Oliveira *et al.,* 2023). Por exemplo, Hughes (1984) observou que a abundância relativa de dibenzotiofenos em óleos de diferentes ambientes sedimentares aumenta na ordem: água doce < fácies salina <fácies hipersalina. Outro exemplo é sobre a abundância de benzonaftotiofenos e seus isômeros (C_1-BNTs, C_2-BNTs e C_3-BNTs) em petróleos brutos terrestres e marinhos e extratos de rochas geradoras. Hughes (1984), Kohnen *et al.* (1990), Pu et al. (1990) e Huang e Pearson (1999) concluem que os S-marcadores são tipicamente mais baixos em óleos terrestres e extratos de rochas geradoras do que aqueles de origem marinha.

Devido à sua estabilidade diante de altas temperaturas, os S-marcadores são mais comumente utilizados em avaliações de graus de maturidade (Radke, 1987; Yang *et al.,* 2019). Estudos aplicados a avaliações paleodeposicionais utilizando S-marcadores, no entanto, são limitados devido às incertezas associadas, e pesquisas desse tipo geralmente recorrem a biomarcadores saturados, como hopanos e esteranos (Hughes *et al.*, 1995, Radke *et al.,* 2001, Sivan *et al.,* 2008, El Nady; Harb, 2009).

A determinação de N-marcadores e S-marcadores em amostras de petróleo e extratos de rocha geradora envolve certa complexidade, devido aos baixos teores (total menores que 4,0%) e os desafios para o correto isolamento de compostos (Prado *et al.,* 2017; Dias *et al.,* 2020). A cromatografia a gás acoplada a espectrometria de massas (GC-MS) é a técnica mais empregada para identificação de N-marcadores e S-marcadores em extrato de rocha e petróleo (Dias *et al.,* 2020; Oliveira *et al.,* 2023). A GC-MS/MS tem sido empregada para determinação de marcadores em estudos geoquímicos por diminuir etapas de preparo de amostra e apresentar alta seletividade e sensibilidade (Sampaio *et al.,* 2021; Dias *et al.,* 2021; Oliveira *et al,* 2023).

A determinação de N-marcadores e S-marcadores por GC-MS/MS para avaliação geoquímica em bacias brasileiras ainda é pouco explorada na literatura. Por outro lado, indicadores geoquímicos clássicos, como os biomarcadores, são muito empregados para avaliar os mesmos parâmetros obtidos com os N-marcadores e os S-marcadores, como por exemplo, condições deposicionais e maturação termal. Assim, o emprego e interpretação de N-marcadores e S-marcadores associada aos indicadores geoquímicos clássicos pode trazer uma maior confiabilidade para os dados, além de complementar e conferir maior robustez para as interpretações geoquímicas.

2 OBJETIVOS

2.1. GERAL

Empregar os N-marcadores (carbazóis, benzocarbazóis e seus isômeros alquilados) e os S-marcadores (benzotiofenos, dibenzotiofenos, benzonaftotiofenos e seus isômeros alquilados) em conjunto com parâmetros geoquímicos na caracterização de sucessões verticais de afloramentos das Formações Candeias e Barreirinha, quanto ao paleoambiente deposicional, tipo de matéria orgânica e condições deposicionais.

2.2. ESPECÍFICOS

- Empregar GC-MS/MS para identificação e quantificação dos N-marcadores e S-marcadores nas amostras em estudo;
- reunir parâmetros geoquímicos como COT, resíduo insolúvel (RI), hidrocarbonetos totais do petróleo (HTPs), pirólise Rock-Eval das amostras em estudo para auxiliar e confirmar as interpretações dos N-marcadores e S-marcadores;
- interpretar os dados obtidos para os N-marcadores e S-marcadores a fim de avaliar o paleoambiente deposicional, tipo de matéria orgânica e condições deposicionais em afloramentos das Bacias do Recôncavo e Amazonas, em conjunto com os biomarcadores e com indicadores já estabelecidos na literatura.

3 USE OF NITROGEN MARKERS TO ASSESS SOURCE ROCK PALEODEPOSITIONAL ENVIRONMENT OF THE CANDEIAS (RECÔNCAVO BASIN) AND BARREIRINHA (AMAZONAS BASIN) FORMATIONS

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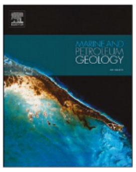

Use of nitrogen markers to assess source rock paleodepositional environment of the Candeias (Recôncavo Basin) and Barreirinha (Amazonas Basin) formations

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Recôncavo Basin

A B S T R A C T

In this study nitrogen markers (N-markers) were employed to evaluate the depositional paleoenvironment of the Candeias and Barreirinha Formations, Recôncavo and Amazonas Basins, respectively. Towards this end, twenty-one N-markers from carbazole (CA), benzocarbazole (BCA), indole (IND), acridine (ACR), and quinolone (QUIN) classes were determined by highly selective and sensitive gas chromatography-triple quadrupole mass spectrometry (GC–MS/MS). Twenty-four (24) samples was collected in vertical sections of outcrops of the Candeias Formation and of the Barreirinha Formation. The N-markers were efficient in evaluating distinctions and similarities between the source rocks and were able to define the origin and input of organic matter, the depositional paleoenvironment conditions of the samples. The samples from the Recôncavo Basin presented low concentrations of CA, methyl carbazole (MCA), and dimethyl carbazole (DMCA), and high concentrations of QUIN and 4-methyl quinoline (4-MQUIN), indicating a lacustrine environment. Samples from the Amazonas Basin present high concentrations of CA, MCA, DMCA, 2,4-dimethyl quinoline (2,4-DMQUIN), benzo[c]quinoline (B[c]QUIN), and ACR, typical of the marine environment. Although the formations are from different paleoenvironments, the organic matter input is similar. The proportions of the 1-, 2- and 4-methyl carbazole (1-MCA, 2-MCA, and 4-MCA), in addition to the low values for the 4-MCA/2-MCA ratio, allowed to affirm that algal input was predominant in the Candeias and Barreirinha formations. The relative concentration of DMCA and of the B[b]CA isomer also indicate the supply of terrigenous material for both formations. BCA concentrations were affected by the conditions of depositional paleoenvironment. Samples deposited under redox conditions presented low concentrations of BCA, and those deposited in oxidizing environments had higher amounts.

1. Introduction

Nitrogen compounds are present in fossil fuels, with concentrations typically less than 2.0%. They are found in the form of polycyclic aromatic structures, classified into basic (pyridine, quinoline, and benzoquinolines) and non-basic (pyrrole, indole, carbazole, and benzocarbazole) species. In geochemistry studies, these compounds play an essential role as markers (N-markers) to assess the depositional paleoenvironment, depositional facies, thermal maturity, and migration (Dias et al., 2020).

Non-basic N-markers provide a convenient way to infer correlations between oil-source rocks, assess facies, organic matter input, and

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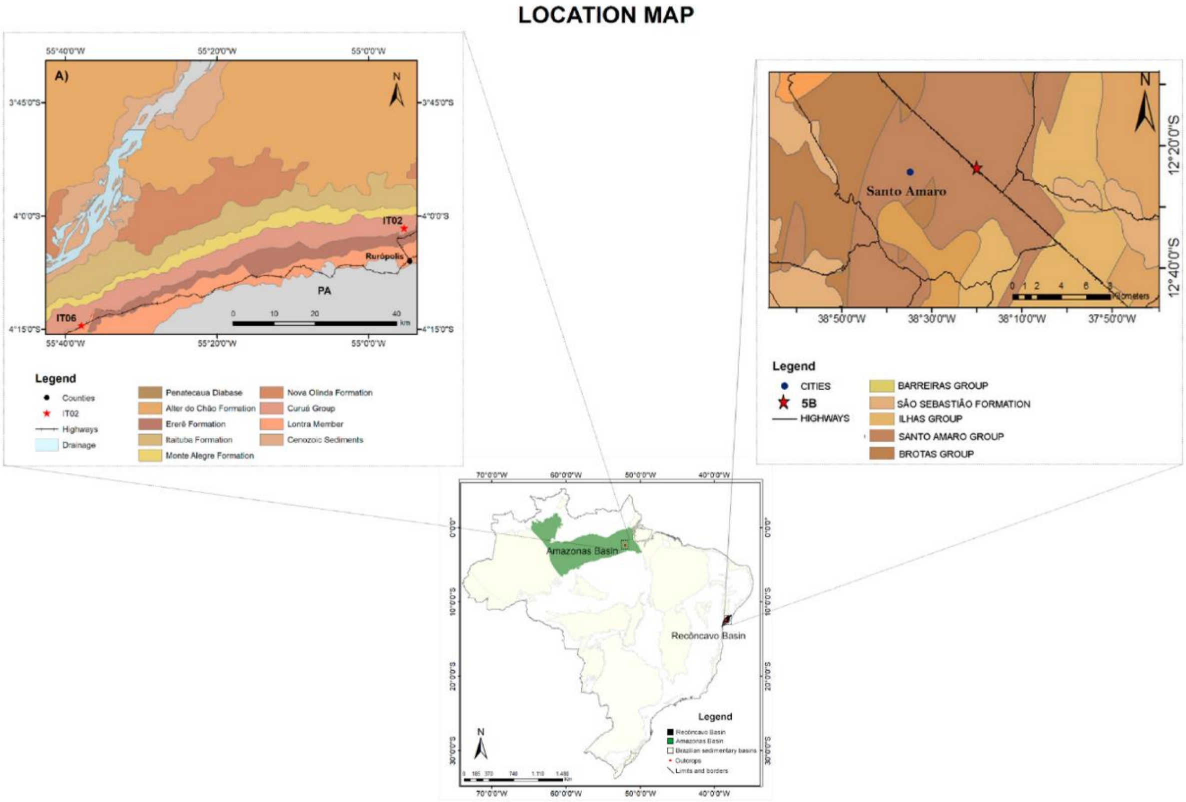


Fig. 1. Map of the location of the Amazon and Recôncavo Basins indicating the location of the outcrops.

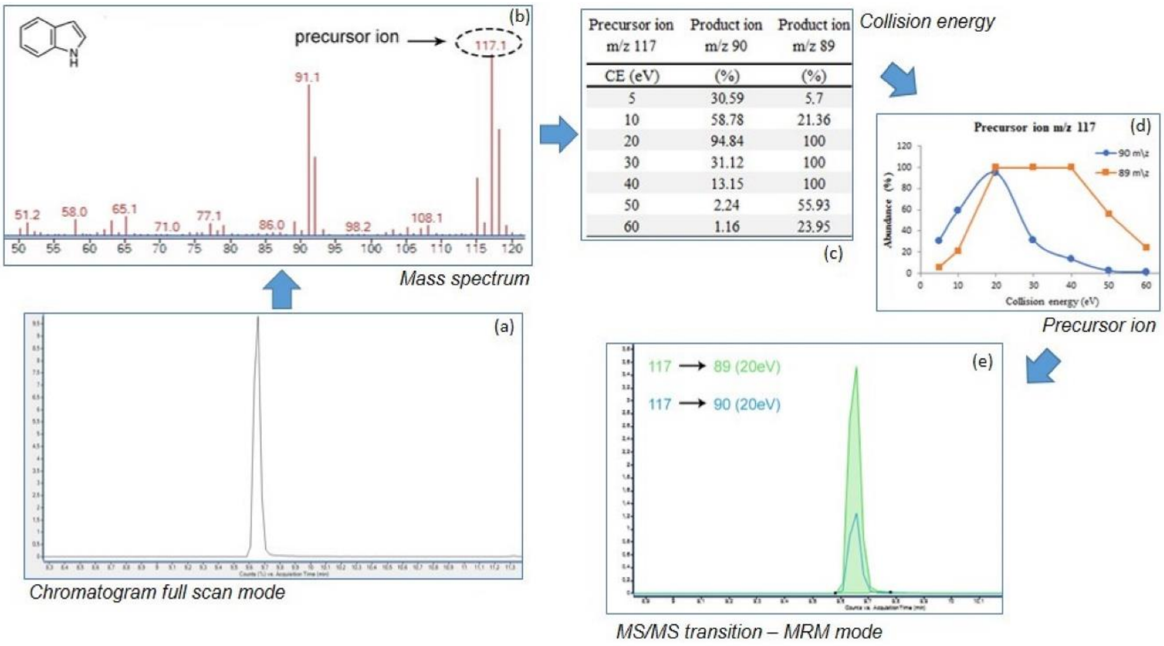
depositional paleoenvironment conditions. For example, Clegg et al. (1997) observed a predominance of 1-methylcarbazole (1-MCA) in source rock extracts deposited under normal marine conditions and the prominence of carbazole (CA), 1-MCA and benzo[c]carbazole (B[c]CA) in deposition under regressive conditions of higher salinity. Zhu et al. (1998) and Li et al. (1999) reported that the abundance of CA and benzocarbazoles (BCA) in oil generated from marine source rocks is several times higher than in oil generated from fresh water source rocks (lacustrine). Ternary diagrams with different proportions of 1-MCA, 2-MCA, and 4-MCA differentiate oils generated from organic matter in marine and terrigenous source rocks (Bennett and Larter, 2000). Depositional paleoenvironments (oxide and suboxide) are distinguished through correlations of the diagnostic ratios of N-markers using concentrations of alkyl-CA such as benzo[a]carbazole/benzo[a]carbazole + benzo[c]carbazole (B[a]CA/B[a]CA + B[c]CA) in association with saturated hydrocarbon biomarkers (Bakr and Wilkes, 2002).

As a traditional geochemical tool for oil source evaluation, biomarkers can provide various information about the origin and depositional environment (Peters and Moldowan, 2005). This information is used to determine the inherited relationship between crude oil and residual organic matter in source rocks and has already been applied to oil and source rocks in the Recôncavo Basin (Balbinot and Kalkreuth, 2010; Amaral et al., 2020; Morais et al., 2023) and Amazonas Basin (Souza et al., 2021; Góes et al., 2022). The Barreirinha Formation is recognized as the primary hydrocarbon source rock of the Amazonas basin and consists of dark gray to black shales. The Candeias formation in the Recôncavo basin, based on biomarkers, is a lacustrine source rock with excellent organic matter preservation (Balbinot and Kalkreuth, 2010; Amaral et al., 2020; Penteado and Behar, 2000). However, biomarkers may be affected by biodegradation, water washing, and thermal alteration (Penteado and Behar, 2000; Jiang and Xiong, 2020). In these cases, N-markers can overcome instances where ratios of biomarker-related parameters are not sufficiently accurate (Horsfield et al., 1998; Huang et al., 2003; Zhang et al., 2008, 2011; Bechtel et al., 2013). Therefore, the combined information based on the cross-validation of saturated hydrocarbon biomarkers and N-markers can more accurately evaluate the depositional paleoenvironment of source rocks in the Recôncavo and Amazonas basins.

Despite several studies proving the efficiency of N-markers for geochemical assessments, they are still not widely used. One of the main reasons is coelution problems and their low concentrations, which require laborious and selective sample preparation steps and compatible instrumentation. In general, a separation of the maltene fraction is necessary, followed by fractionation of the oil or organic rock extracts using a SARA method (Bechtel et al., 2013; Zhang et al., 2018; Dias et al., 2020). An additional method is often needed for isolating concentrates free of non-nitrogen compounds, followed by chromatographic separation into two subfractions (neutral and basic N compounds) with known molecular weight and known structural type (Bechtel et al., 2013; Li et al., 1995).

Traditionally, gas chromatography coupled to mass spectrometry (GC-MS) in selected ion-monitoring (SIM) mode has been the first technique of choice for the determination of N-markers in geochemistry studies (Dias et al., 2020). However, even though such a technique is sensitive, disadvantages such as selectivity that depend on laborious fractionation steps, as well as the limitation of compounds with specific and distinct masses, are limitations.

GC–MS/MS has the advantage of increasing the selectivity and



Precursor ion m/z 117	Product ion m/z 90	Product ion m/z 89
CE (eV)	(%)	(%)
5	30.59	5.7
10	58.78	21.36
20	94.84	100
30	31.12	100
40	13.15	100
50	2.24	55.93
60	1.16	23.95

Fig. 2. Steps for MS/MS method optimization: (a) chromatogram indicating the retention time of indole, (b) mass spectrum of indole used for selection of the precursor ion. (c) collision energies (eV) and abundances of the most intense product ions, (d) collision energy graph versus product ion abundance, (e) chromatogram indicating MRM transitions.

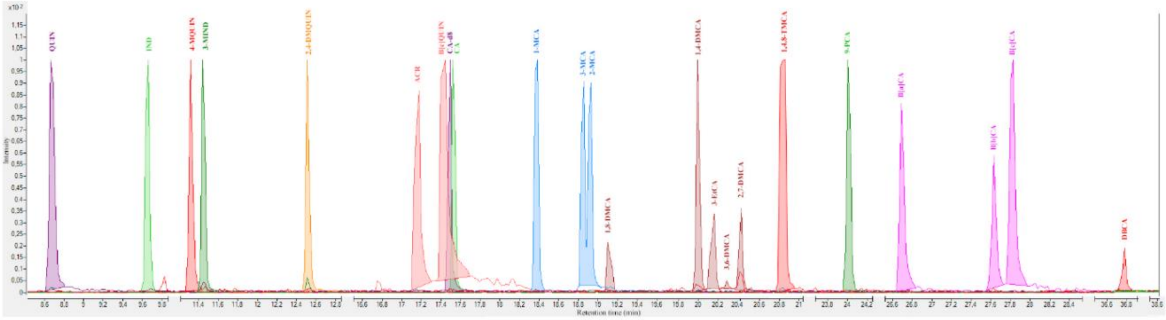


Fig. 3. GC-MS/MS chromatogram in MRM mode for analysis of N-markers standards. For abbreviations see Table 1.

sensitivity because uses quadrupoles in tandem allows the elimination of background interference and the detection of target compounds with increased sensitivity. Recently, the technique was found to have good performance in the analysis of some N-markers in geochemical evaluation (Dias et al., 2021; Easley et al., 2022). However, a limited number of compounds were evaluated, and geochemistry interpretation was not the primary aim of either study.

The aim of this study was to employ N-markers to assess source rock depositional paleoenvironment of Brazilian formations located in the Recôncavo and Amazonas basins. A GC–MS/MS method was optimized for the determination of 21 N-markers in source rock extracts. Interpretations focused on individual and/or diagnostic ratios of basic and non-basic species, for the first time, to analyze differences and similarities between the geological formations under study and interpret the conditions of their depositional paleoenvironments.

2. Geological setting

The Amazonas Basin is located in the northern region of Brazil, covering part of the Amazonas and Pará states, with an area of approximately 500,000 km^2. This basin is of the intracratonic syneclisis type, with sediments from the Paleozoic to Mesozoic, as seen on the stratigraphic chart of the basin (Fig. S1a).

The deposition of the Barreirinha Formation in the Amazonas Basin was associated with a rapid relative sea level rise that occurred when the South American Platform underwent a major marine transgression in the Frasnian (Caputo, 1984). The initial depositional phase of this formation is represented by a thick section of radioactive black shales – dark gray, laminated, fissile, and bituminous – that is the Abacaxis Member, considered the primary hydrocarbon source rock in the Amazonas Basin. Abacaxis Member is overlapped by two other members: Urubu Member (dark gray shales) and Uraria Member (gray shales and dark to light

Table 1
Summary of optimized MRM transitions used for quantifying N-marker compounds.

N-marker	Abbreviation	Window width	T_R	Quantification transition			Confirmation transition		
		(±T_R min)	(min)	Precursor ion *(m/z)*	Product ion *(m/z)*	CE[a] (eV)	Precursor ion *(m/z)*	Product ion *(m/z)*	CE[a] (eV)
Quinoline*	QUIN	4.00–10.00	8.66	129	102	30	129	128	20
Indole*	IND	4.00–10.00	9.66	117	89	20	117	90	20
4-methylquinoline*	4-MQUIN	10.00–12.00	11.32	143	115	30	143	142	20
3-methylindole*	3-MIND	10.00–12.00	11.44	130	77	30	130	103	20
2,4-dimethylquinoline*	2,4-DMQUIN	12.00–15.50	12.51	157	115	30	157	156	20
Acridine*	ACR	15.50–17.80	17.17	179	178	30	179	152	30
Benzo[c]quinoline*	B[c]QUIN	15.50–17.80	17.44	179	151	30	179	125	30
Carbazole-d_8	CA-d_8	15.50–17.80	17.49	175	173	40	175	145	30
Carbazole	CA	15.50–17.80	17.52	167	139	40	167	140	30
1-methylcarbazole	1-MCA	17.80–20.70	18.38	181	152	40	181	127	50
3-methylcarbazole	3-MCA	17.80–20.70	18.86	181	152	40	181	127	50
2-methylcarbazole	2-MCA	17.80–20.70	18.93	181	152	40	181	127	50
1,8-dimethylcarbazole	1,8-DMCA	17.80–20.70	19.10	195	180	40	195	152	50
1,4-dimethylcarbazole	1,4-DMCA	17.80–20.70	19.99	195	180	40	195	152	50
3-ethylcarbazole	3-ETCA	17.80–20.70	20.15	180	152	30	195	180	5
3,6 dimethylcarbazole	3,6-DMCA	17.80–20.70	20.29	195	180	40	195	152	50
2,7-dimethylcarbazole	2,7-DMCA	17.80–20.70	20.44	195	180	40	195	152	50
1,4,8 Trimethylcarbazole	1,4,8-TMCA	20.70–23.60	20.86	209	194	20	209	193	40
9-phenylcarbazole*	9-PhCA	23.60–24.80	24.00	243	241	30	243	242	30
Benzo[a]carbazole	B[a]CA	24.80–32.00	26.69	217	189	40	217	190	40
Benzo[b]carbazole	B[b]CA	24.80–32.00	27.63	217	189	40	217	190	40
Benzo[c]carbazole	B[c]CA	24.80–32.00	27.83	217	189	40	217	190	40
Dibenzocarbazole	DBCA	32.00–38.60	36.78	267	239	50	267	139	40

*Compounds optimized in this study.
[a] Collision energy.

siltstones) (Caputo, 1984). Previous studies indicate that the Barreirinha Formation contains marine organic matter with average TOC contents between 2 and 3%, type II kerogen (mostly) and varying levels of thermal maturation (Souza et al., 2021; Góes et al., 2022).

The Recôncavo Basin located in the State of Bahia, Brazil, covers approximately 11,500 km^2 and corresponds to the southern portion of the Recôncavo-Tucano-Jatobá Rift (RTJ). The RTJ system developed during the Cretaceous and is interpreted as an aulacogen associated with South Atlantic Rift (Castro et al., 2023). The deposition of the Candeias Formation, widely recognized as the primary source rock in the Recôncavo Basin, occurred in the context of increased tectonic activity as a time of humid climate, generating conditions for the development of deep lakes. This marked the beginning of the rift phase, in the Berriasian (Fig. S1b). In this scenario, initially, there was a transgression represented by the dark pelites of the Tauá Member, which is an overlapping gray-green shale with carbonate intercalation of the Gomo Member (Caixeta et al., 1994).

The Candeias Formation has been the subject of several geochemistry studies (Balbinot and Kalkreuth, 2010; Amaral et al., 2020; Penteado and Behar, 2000; Mello et al., 1994). The authors define the Candeias Formation as a thick section of dark-green, gray shale with subordinate interspersed limestone and dolomites, locally encompassing bodies of massive and/or stratified sandstones. The amorphous organic matter with intense fluorescence averages total organic carbon content (TOC) of approximately 3% and Type I kerogen with high potential for hydrocarbon generation.

3. Material and methods

3.1. Sampling

The same collection sample procedure was employed for both outcrops in Candeias and Barreirinha Formations. The superficial layers of altered rocks were removed, digging deep enough (12–23 m) to reach below the weathering zone to access source rocks without alteration/oxidation features. The location of each outcrop is shown in Fig. 1.

In the Recôncavo Basin, samples were collected from an outcrop (named 5B) along the BR-324 Highway (km 557), near the city of Santo Amaro, Bahia State, Brazil. The sampling was carried out every 20 cm, for a total of 10 samples (Fig. S2a), to investigate possible vertical variations of the geochemical parameters. In the Amazonas Basin, 14 samples (Fig. S2b) were taken vertically every 1 m (named IT-02 and IT-06) from an outcrop along the BR-230 (Transamazônica Highway) in the municipality of Rurópolis, Pará State, Brazil.

3.2. Extraction of soluble organic matter from the rock samples

Prior to extraction, all rock samples were ground with an agate mortar and pestle, pulverized in a Retsch planetary ball mill (Retsch, PM 400, Haan, Germany), and subsequently sieved to a particle size of less than 0.18 mm.

To obtain the source rock extract, accelerated solvent extraction (ASE) was used in a Dionex ASE 350 instrument (Thermo Scientific, Massachusetts, USA). The procedure consisted of weighing approximately 50 g of sample mass and 10 g of diatomaceous earth (dehumidifying agent) in metal extractor cells and heating at 75 °C with a pressure of 5×10^6 Pa for 15 min using dichloromethane (DCM), in a volume of 150 mL. The extraction process was repeated three times to ensure that all soluble OM compounds were extracted (Bechtel et al., 2013). All extracts were concentrated in a rotary evaporator (Model R-210 Labortechnik, AG Switzerland) and subsequently fractionated as described below.

3.3. Fractionation of organic extract

Each of the 24 extracts was fractionated into saturate, aromatic, resin, and asphaltene (SARA) by the ASTM D2007-11(ASTM 2007) method. The saturate fraction was eluted with 25 mL of *n*-hexane, the aromatic fraction (ARO) with 30 mL of a 4:1 mixture of *n*-hexane:DCM and the resin fraction (NSO), 30 mL of a 4:1 mixture of DCM:methanol.

Table 2

Concentrations of N-markers (mg kg^{-1} of extract) in samples from the Recôncavo (5B) and Amazonas basins (IT).

N marker	Samples (mg kg^{-1})																							
	Candeias Formation										Barreirinha Formation													
	5B01	5B02	5B03	5B04	5B05	5B06	5B07	5B08	5B09	5B10	IT02-02	IT02-03	IT02-04	IT02-05	IT02-06	IT02-07	IT02-08	IT06-54	IT06-55	IT06-56	IT06-57	IT06-58	IT06-59	IT06-60
QUIN	0.07	0.13	0.02	0.04	0.04	0.19	0.06	0.05	0.01	0.07	0.02	0.00	0.02	0.01	0.01	0.01	0.03	0.02	0.03	0.03	0.02	0.02	0.01	0.01
IND	0.04	0.02	0.03	0.04	0.06	0.05	0.05	0.07	0.05	0.11	0.08	0.02	0.07	0.08	0.11	0.04	0.09	0.11	0.28	0.31	0.24	0.17	0.05	0.06
4-MQUIN	0.05	0.05	0.04	0.03	0.00	0.03	0.03	0.03	0.03	0.05	0.01	0.00	0.01	0.01	0.02	0.01	0.03	0.01	0.01	0.00	0.00	0.00	0.01	0.00
3-MIND	0.04	0.03	0.02	0.02	0.04	0.02	0.03	0.03	0.01	0.03	0.04	0.02	0.04	0.04	0.04	0.01	0.04	0.03	0.02	0.02	0.02	0.03	0.01	0.03
2,4-DMQUIN	0.25	0.18	0.15	0.16	0.26	0.10	0.11	0.10	0.02	0.21	0.33	0.61	2.94	2.39	1.63	0.96	1.48	0.63	0.69	0.71	0.44	0.18	0.59	0.33
ACR	0.08	0.09	0.04	0.04	0.18	0.01	0.05	0.07	0.05	0.01	2.60	0.58	2.79	2.11	1.56	1.74	1.80	1.59	1.44	1.22	1.19	0.71	0.79	1.44
B[c]QUIN	0.17	0.10	0.08	0.10	0.17	0.04	0.05	0.05	0.09	0.03	7.74	1.04	2.31	3.39	4.17	0.99	1.06	5.31	2.35	1.01	2.69	3.37	1.86	3.06
CA	0.22	0.05	0.06	0.05	0.43	0.14	0.12	0.06	0.09	0.07	0.15	0.24	0.86	0.90	0.53	0.52	0.42	0.43	0.23	0.27	0.21	0.35	0.34	0.15
1-MCA	0.04	0.02	0.01	0.01	0.03	0.01	0.00	0.02	0.02	0.01	0.70	0.24	1.24	1.10	0.80	0.17	0.21	0.12	0.09	0.23	0.33	0.21	0.11	0.17
3-MCA	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.16	0.08	0.33	0.27	0.26	0.04	0.13	0.11	0.12	0.10	0.08	0.05	0.09	0.05
2-MCA	0.03	0.01	0.01	0.02	0.02	0.00	0.00	0.00	0.02	0.02	0.20	0.08	0.34	0.38	0.25	0.18	0.13	0.08	0.09	0.10	0.18	0.05	0.06	0.04
4-MCA	0.04	0.02	0.01	0.04	0.11	0.02	0.03	0.03	0.03	0.05	0.11	0.04	0.13	0.12	0.11	0.12	0.07	0.06	0.06	0.07	0.08	0.10	0.05	0.06
1,3 DMCA	0.01	0.00	0.00	0.62	0.03	0.01	0.08	0.00	0.00	0.12	0.09	0.03	0.07	0.11	0.12	0.05	0.02	0.73	0.74	0.75	0.46	0.10	0.40	0.11
1,8-DMCA	0.05	0.01	0.00	0.02	0.01	0.00	0.01	0.00	0.00	0.05	0.09	0.04	0.22	0.10	0.17	0.04	0.08	0.53	0.63	0.48	0.24	0.08	0.26	0.04
1,4 DMCA	0.05	0.02	0.01	0.02	0.06	0.01	0.05	0.00	0.00	0.07	0.25	0.05	0.43	1.10	0.30	0.16	0.16	0.58	1.28	0.40	0.11	0.10	0.48	0.10
3-EtCA	0.01	0.01	0.00	0.10	0.01	0.00	0.03	0.00	0.00	0.83	0.32	0.03	0.15	0.28	0.15	0.19	0.12	0.48	0.22	0.34	0.11	0.10	0.46	0.03
3,6 DMCA	0.03	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00	1.62	0.08	0.01	0.12	0.13	0.02	0.01	0.01	0.40	0.31	0.31	0.05	0.05	0.08	0.04
2,7-DMCA	0.04	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.20	0.12	0.02	0.20	0.06	0.12	0.08	0.07	0.84	0.66	0.61	2.40	0.07	0.26	0.07
2,4-DMCA	0.02	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.00	0.15	0.09	0.01	0.09	0.08	0.07	0.06	0.04	0.08	0.08	0.08	0.04	0.01	0.11	0.03
1,4,8 TMCA	0.12	0.10	0.02	0.04	0.26	0.04	0.08	0.08	0.02	0.02	8.44	1.30	5.41	6.09	6.59	3.83	3.25	3.14	3.16	3.73	2.94	2.38	0.34	2.64
B[a]CA	0.04	0.03	0.01	0.03	0.07	0.01	0.01	0.02	0.01	0.03	1.53	0.21	0.87	1.09	1.18	0.73	0.60	0.53	0.38	0.50	0.61	0.44	0.50	0.75
B[b]CA	0.01	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.00	0.10	0.04	0.06	0.22	0.19	0.11	0.12	0.08	0.15	0.08	0.09	0.10	0.07	0.14
B[c]CA	0.21	0.09	0.04	0.09	0.21	0.04	0.04	0.07	0.01	0.13	4.50	1.39	3.31	0.23	7.35	2.83	5.45	3.15	2.84	4.29	0.97	4.56	2.39	1.98
DBCA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.02	0.01	0.02	0.00	0.02	0.00	0.01	0.00	0.00	0.00

QUIN: Quinoline; IND: Indole; 4-MQUIN: 4-methylquinoline; 3-MIND:3-methylindole; 2,4-DMQUIN: 2,4-dimethylquinoline; ACR: Acridine; B[c]QUIN: Benzo[c]quinoline; CA: Carbazole; 1-MCA: 1-methylcarbazole; 3-MCA: 3-methylcarbazole; 2-MCA: 2-methylcarbazole; 4-MCA: 4-methylcarbazole; 1,3-DMCA: 1,3-dimethylcarbazole; 1,8-DMCA:1,8-dimethylcarbazole; 1,4-DMCA: 1,4-dimethylcarbazole; 3-EtCA:3-ethylcarbazole; 3,6-DMCA: 3,6 dimethylcarbazole; 2,7-DMCA: 2,7-dimethylcarbazole; 2,4-DMCA: 2,4-dimethylcarbazole; 1,4,8-TMCA: 1,4,8 Trimethylcarbazole; B[a]CA: Benzo[a]carbazole; B[b]CA:Benzo[b]carbazole; B[c]CA: Benzo[c] carbazole; DBCA: Dibenzocarbazole.

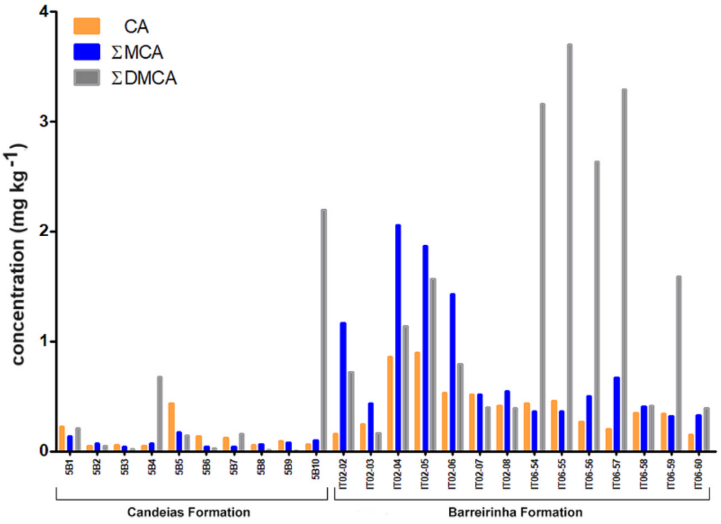


Fig. 4. Concentration of carbazole (CA), methylcarbazoles (MCA) and dimethylcarbazoles (DMCA) in samples for depositional paleoenvironment interpretation.

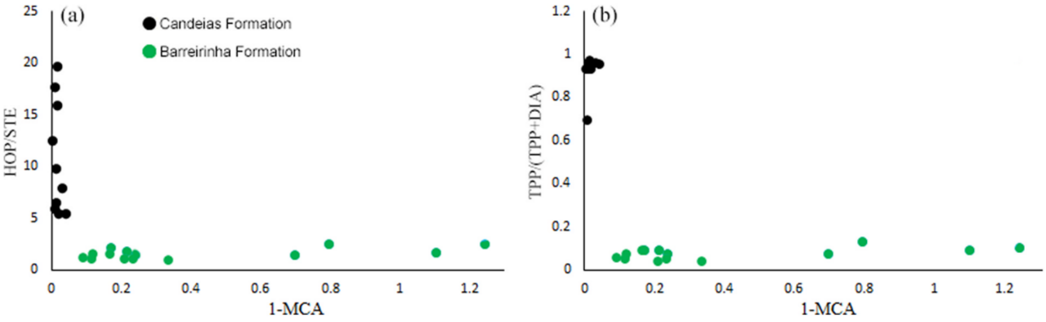


Fig. 5. Correlation of (a) 1-methylcarbazole (1-MCA) versus hopanes/steranes (HOP/STE) ratio and (b) 1-methylcarbazole (1-MCA) versus polyprenoids (TPP) and diasteranes (DIA) TPP/TPP + DIA ratio for samples (Adapted from Holba et al., 2000).

The ARO and NSO fractions were combined. All extracts were concentrated in a rotary evaporator (Model R-210 Labortechnik, AG Switzerland), transferred to 2 mL vials, and re-suspended in toluene to a concentration of 2000 mg L^{-1}

3.4. GC-MS/MS analysis

Chromatographic analyses were performed in a GC-MS/MS system equipped with a 7890B gas chromatograph with split/splitless injector and a 7000C mass detector with linear hexapole collision cell from Agilent (Santa Clara, CA, USA). The chromatographic conditions were optimized from Dias et al. (2021). The column used was a DB5-MS (30 m × 0.25 mm internal diameter × 0.25 μm film thickness). The oven operating conditions were as follows: started at 80 °C for 1 min and ramped to 160 °C at 6 °C min^{-1}, then to 200 °C at 20 °C min^{-1}, increased to 280 °C at 4 °C min^{-1}, and held constant at 310 °C for 2 min. Both the injector and transfer line were held at 300 °C. Helium was used as the carrier gas at 1 mL min^{-1}. The ion source temperature of MS was maintained at 280 °C.

3.4.1. MS/MS optimization

Twenty-one individual N-markers of indole (IND), 3-methylindole (3-MIND), carbazole (CA), carbazole-d8 (CA-d$_8$), 9-phenylcarbazole (9-PCA), quinoline (QUIN), 4-methylquinoline (4-MQUIN), 2,4-dimethylquinoline (2,4-DMQUIN), benzo[c]quinoline (B[c]QUIN), acridine (ACR) 1-methylcarbazole (1-MCA), 2-methylcarbazole (2-MCA), 3-methylcarbazole (3-MCA), 1,8-dimethylcarbazole (1,8-DMCA), 2,7-dimethylcarbazole (2,7-DMCA), 3,6-dimethylcarbazole (3,6-DMCA), 3-ethylcarbazole (3-EtCA), 1,4,8-trimethylcarbazole (1,4,8-TMCA), benzo[a]carbazole (B[a]CA), benzo[b]carbazole (B[b]CA), benzo[c]carbazole (B[c]CA), and dibenzocarbazole (DBCA) were acquired from Chiron (Trondheim, Norway). Stock standard solutions of individual N-markers were prepared at a concentration of 1000 μg L^{-1} by appropriate dilution of the standard solution in toluene. Then, intermediate mixed solutions containing the standards were prepared to a concentration of 1000 μg L^{-1}. A working standard solution was prepared by adding precise volumes of the intermediate mix solution at a concentration of 100 μg L^{-1}. All solutions were stored in capped amber vials in the freezer at 20 °C. The internal standards 9-PCA and CA-d$_8$ were prepared at 10 μg L^{-1}.

For MS/MS, two overlapping precursor-to-product ion transitions (multiple reaction monitoring, MRM) were employed based on Dias et al. (2021). In addition to standards previously optimized by Dias et al. (2021), were added IND, 3-MIND, QUIN, 4-MQUIN, 2,4-DMQUIN, B[c]QUIN, ACR, and 9-PCA acquired from Chiron (Trondheim, Norway). For these, the collision energy (CE, 5–60 eV) and MRM transitions were

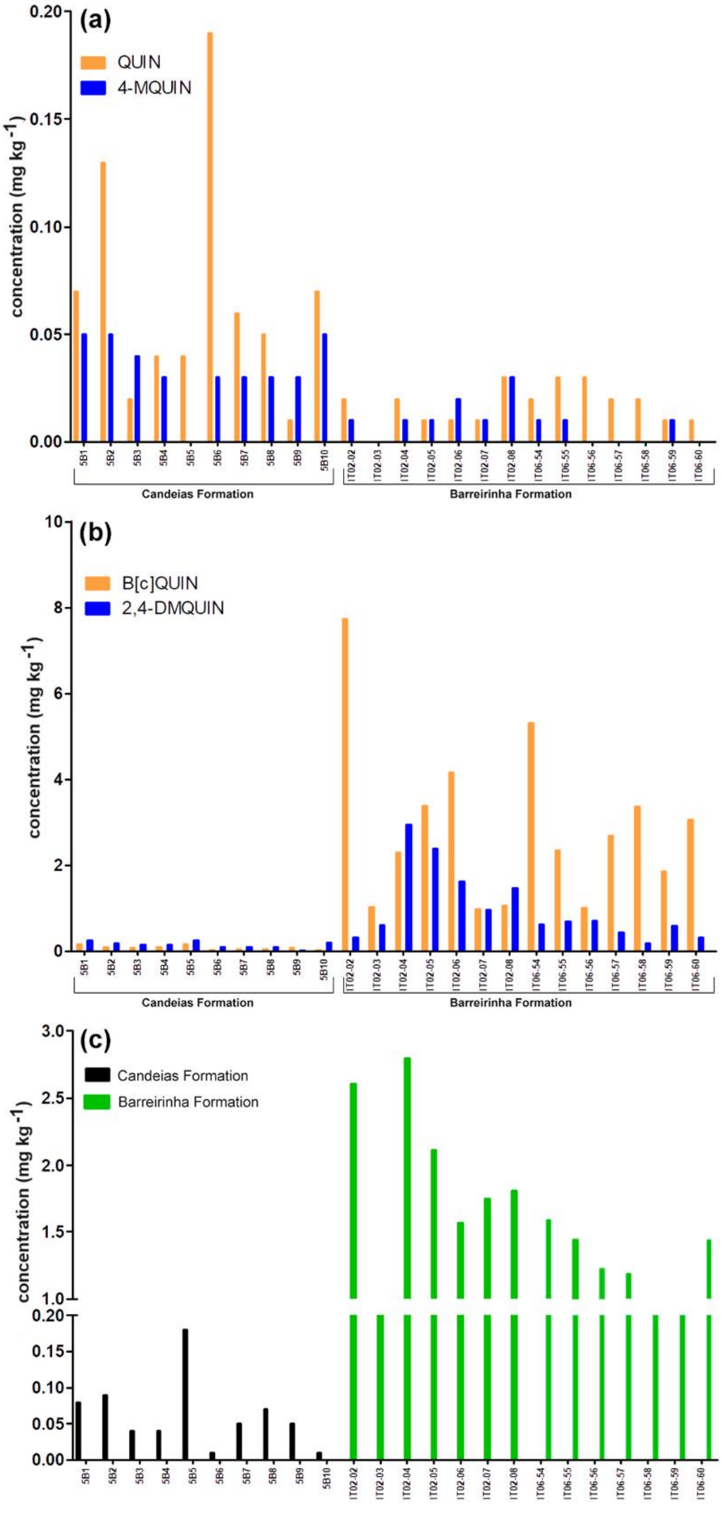


Fig. 6. Basics nitrogen compounds for depositional paleoenvironment interpretation. (a) Concentrations of quinoline and 4-methylquinoline (4-MCA); (b) Concentrations of benzo[c]quinoline (B[c]QUIN) and 2,4-dimethylquinoline (2,4-DMQUIN); (c) Concentrations of acridine (ACR) in samples.

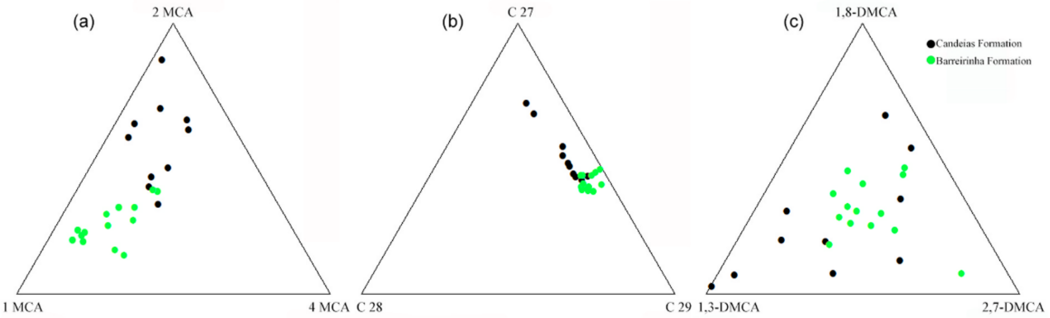


Fig. 7. Ternary diagrams for input evaluation. (a) isomers distribution of methylcarbazoles, (b) distribution of steranes C_{27}, C_{28} and C_{29}, (c) distribution of dimethylcarbazoles for samples.

definite.

3.4.2. Quantification

The concentration of the N-markers was calculated considering the concentration of the internal standards 9-PCA, CA-d_8 and the relation between the peak areas referring to the compounds in the samples, according to the equation:

$$C\ (\mathrm{mg\ L^{-1}}) = (A_{\mathrm{comp}} / A_{\mathrm{IS}}) \times C_{(\mathrm{IS})} \qquad \text{(Equation 1)}$$

C = desired concentration in mg L^{-1}
A_{comp} = area of the compound of interest.
A_{IS} = internal standard area.
$C_{(\mathrm{IS})}$ = internal standard concentration.

After determining the concentration in mg L^{-1}, the conversion to mg kg^{-1} was performed:

$$C\ (\mathrm{mg\ kg^{-1}}) = (C_{\mathrm{Comp}}\ (\mathrm{mg\ L^{-1}}) \times V_{\mathrm{sol}}) / M_{\mathrm{ext}} \qquad \text{(Equation 2)}$$

C_{Comp} = concentration of the desired compound in mg kg^{-1}
C_{Comp} (mg L^{-1}) = compound concentration in mg L^{-1}
V_{sol} = volume of solvent used.
M_{ext} = source rock extract mass.

3.5. Total organic carbon, total sulfur and Rock-Eval pyrolysis

The TOC values were determined from 1.0 g of each rock sample previously separated into the 80 mesh fraction. These samples were subjected to an acid (37% HCl) reaction to remove the inorganic carbon (decarbonization). The decarbonated samples were inserted in the LECO 628CN Elementary Analyzer to quantify the TOC contents. In rock sample aliquots without acid treatment, total sulfur contents were determined on the LECO 628S Elementary Analyzer. For Rock-Eval analysis, approximately 100 mg aliquot of each sample was sieved with a 0.177 mm sieve was encapsulated in tin capsules and analyzed with Rock-Eval 6 instrument, following a procedure proposed by Espitalié et al. (1977). These steps were performed and described in previous studies (Amaral et al., 2020; Góes et al., 2022).

3.6. Biomarkers analysis

Saturated biomarkers analyses were performed previously (Amaral et al., 2020; Góes et al., 2022) using gas chromatography coupled to a mass spectrometer (DSM5977A, Agilent) in a capillary column DB-5 (60 m × 0.25 mm × 0.25 μm) with oven temperature program from 60 °C to 310 °C with a heating ramp of 2 °C min^{-1}. Helium was used as the carrier gas with a 1 mL min^{-1} flow and a constant pressure of 30 psi. The injection volume was 1 μL. The ions monitored were: m/z 183 (isoprenoids), m/z 217 (steranes), m/z 191 (triterpanes) and m/z 259 (tetracyclic polyprenoids and diasteranes).

4. Results and discussion

4.1. Optimization of the GC-MS/MS method for N-markers determination

Initially, the mix of N-markers was injected in full scan mode (m/z 50–450) to obtain the retention time and mass spectrum of each compound. Then, for compounds indicated in Section 3.4.1 (IND, 3-MIND, QUIN, 4-MQUIN, 2,4-DMQUIN, B[c]QUIN, ACR, and 9-PCA) the product and precursor ions were optimized employing different collision energies. Fig. 2 shows the optimization steps using the IND compound as an example.

The transitions for the MRM method were selected from the product ions with the highest abundance (Fig. 2b). The evaluated collision energies varied from 5 eV to 60 eV (acquired every 10 eV). The ions with greater intensities (Fig. 2c) defined two transitions: quantification transition and qualification transition. For indole, the quantitative MRM transition was m/z 117 → m/z 89 at a collision energy of 20 eV, and to confirm the identity of the compounds (qualifier transition), the MRM transition was m/z 117 → m/z 90 at 20 eV (Fig. 2e). Fig. 3 shows the optimized chromatogram of the N-markers standards. Table 1 lists the respective retention times, window widths, transitions, and collision energies for all compounds under optimized conditions.

4.2. Origin of organic matter

Table 2 lists the concentration values (mg kg^{-1} of extract) of the N-markers analyzed in the samples from the Candeias and Barreirinha Formations. To determine the depositional paleoenvironments, the interpretations based on N-marker concentrations were confirmed by saturated biomarkers (hopanes and steranes), total organic carbon (TOC), total sulfur, and Rock-Eval pyrolysis (Amaral et al., 2020; Góes et al., 2022) to confirm the N-markers data.

The concentrations of CA and DMCA in extracts of source rocks and crude oils can be employed to correlate and interpret organic matter origin (Bakr and Wilkes, 2002; Zhang et al., 2008; Espitalié et al., 1977). In the analyzed samples, the concentrations of these compounds (CA, MCA and DMCA) are different in the Candeias and Barreirinha formations (Fig. 4), making it possible to differentiate the source rocks of these basins where high concentrations are indicative of marine origin and low concentrations represent a more terrigenous origin.

The difference in carbazole concentration (Fig. 4) may indicate that the occurrence and distribution of N-markers are controlled by paleoenvironment during organic matter sedimentation. The samples from the Candeias Formation (Recôncavo Basin) have lower concentrations of CA, MCA, and DMCA than those of Barreirinha Formation (Amazonas Basin). These results are consistent with the low concentrations of N-markers generally observed in non-marine source rock extracts (Zhang et al., 2008).

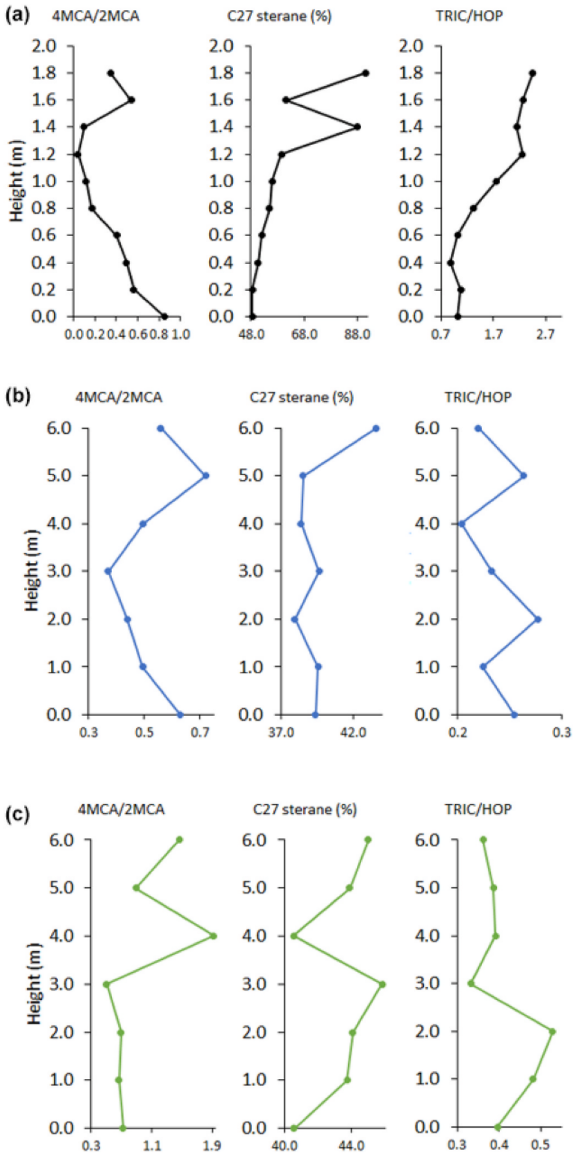


Fig. 8. Vertical variations of the 4-MC/2-MC ratio for samples from the Candeias (a) and Barreirinha (b) formations to evaluate the organic matter input of the outcrops.

The differentiation of sedimentary paleoenvironments obtained by N-markers was confirmed by previous studies that employed saturated biomarkers. Saturated biomarkers demonstrate that the organic matter present in the Candeias Formation is lacustrine (Amaral et al., 2020) and the organic matter present in the Barreirinha Formation is marine Góes et al. (2022).

In source rocks deposited under normal marine conditions, the abundance of carbazole and their isomers, especially 1-MCA, is many times higher than source rocks of lacustrine origin (Clegg et al., 1997; Zhu et al., 1998; Li et al., 1999). In the present study, the relationship between 1-MCA and the hopane/sterane ratio (HOP/STE) (Fig. 5a) and the ratio between tetracyclic polyprenoids (TPP) and diasteranes (DIA) (TPP/TPP + DIA) (Fig. 5b) highlights the distinction between the depositional environments, according to the range defined by Holba et al. (2000). Samples from the Candeias Formation have the lowest concentrations of 1-MCA and highest values for HOP/STE and TPP/TPP + DIA ratios, characteristic of a freshwater lacustrine paleoenvironment. Samples from the Amazonas Basin present the highest concentrations of 1-MCA and lower values for the HOP/STE and TPP/TPP + DIA ratios, typical of a marine paleoenvironment.

When evaluating basic N-markers in organic source rock extracts, Yamamoto (1992) concluded that they are not affected by the source variations (marine or non-marine). Since then, research using basic nitrogen markers has been carried out to assess thermal maturation and migration distances (Yamamoto, 1999; Covas et al., 2019). However, in the present study, differences in the concentrations of basic nitrogen markers were observed between marine and non-marine samples. Samples from the Candeias Formation show the highest concentrations of QUIN and 4-MQUIN (Fig. 6a), while samples from the Barreirinha Formation show the highest concentrations of 2,4-DMQUIN, B[c]QUIN (Fig. 6b) and ACR (Fig. 6c).

Diaz et al. (2015) related the origin of quinoline to terrestrial plants, algae, and various microorganisms, among other sources. Therefore, understanding what reasons affect the concentrations of basic nitrogen compounds in organic source rock extracts from different origins is promising, and requires further studies.

4.3. *Input of organic matter*

Algae-rich samples (lacustrine or marine) exhibit higher proportions of 1-MCA and 2-MCA than of 4-MCA(Clegg et al., 1997; Han et al., 2018). In the samples, even though they are in notably different concentrations (Fig. 4), the relative proportions of methylcarbazoles allow us to refine the assessment of the type of organic matter in the depositional paleoenvironment. The ternary diagram with the isomeric distribution of MCAs (Fig. 7a) shows that both formations present higher proportions of 1-MCA and 2-MCA to the detriment of 4-MCA, indicating that the algal input occurred in the Candeias Formation and in the Barreirinha Formation.

The 4-MCA/2-MCA ratio was applied by Clegg et al. (1997) to evaluate algae proportions in oil source rock samples and variations over the time of deposition were observed. The use of this ratio to the samples under study, indicated variations in algal input over the time of deposition of the Candeias and Barreirinha Formations (Fig. 8). While the outcrop 5B of Candeias Formation (Fig. 8a) and the outcrop IT-02 of the Barreirinha Formation (Fig. 8b) show a downward trend in values from the bottom to the middle, followed by an increase from the middle to the top of the profiles, outcrop IT-06 of the Barreirinha Formation (Fig. 8c) shows a decrease from base to middle, followed by alternation in the ratio value at the top of the outcrop. Although the 4-MCA/2-MCA ratio provides information about algal input, the values for the total tricyclic terpanes (TRI)/hopanes (HOP), and % of C_{27} sterane do not exhibit the same vertical variations along the outcrops. Therefore, the variations observed in the outcrops under study indicate that the algal input was not the only input type during the sediment deposition.

The ternary diagram from regular steranes C_{27}, C_{28}, and C_{29} (Fig. 7b) confirms the presence of different organic matter inputs and algal types of inputs (represented by the relative proportion of C_{27}). The C_{29} sterane in samples indicates that the paleoenvironments received contributions from higher land plants (Mello et al., 1988; Waples and Machihara, 1991).

Several studies have shown substantial variability of dimethylcarbazoles in paleoenvironments with different sources of organic matter (Li et al., 1995; Han et al., 2018; Clegg et al., 1998). For example, in oils from different source rocks, there is no pattern of abundance between 2,7–DMCA, 1,8–DMCA, and 1,3–DMCA isomers, and this lack of pattern is related to different origins of organic matter (marine and terrigenous). The same behavior was observed in Candeias and Barreirinha formation samples with substantial variations in the

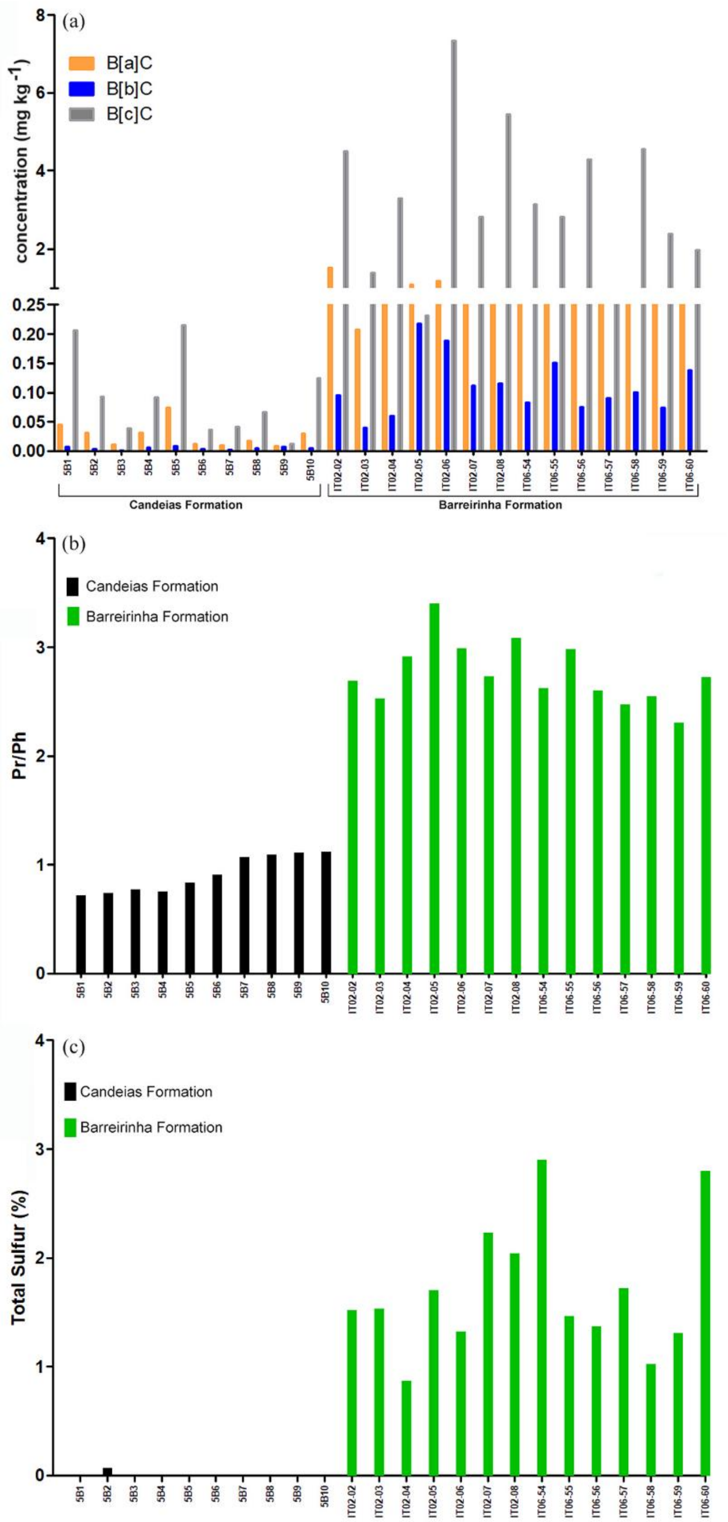


Fig. 9. (a) Concentrations of benzocarbazoles, (b) values for the pristane/phytane ratio (Pr/Ph) and (c) total sulfur for the samples.

proportions of DMCA isomers (Fig. 7c), indicating different inputs of organic matter.

Benzocarbazoles are another N-marker class used to identify depositional organic facies (Bakr and Wilkes, 2002; Horsfield et al., 1998; Clegg et al., 1998; Larter et al., 1996). The evaluation is made by individual compounds or for diagnostic ratios. For example, the benzo[b] carbazole isomer has not been observed in oils of marine origin. When detected, even in low concentrations, it is indicative of samples that received terrigenous material (Oldenburg et al., 1999). In this sense, the values calculated for the B[a]CA/B[b]CA diagnostic ratio (Table 2) were low (<1.0) for all samples (except for IT02-05), indicating terrigenous organic matter contributions, albeit in small amounts.

4.4. Depositional paleoenvironment conditions

Benzocarbazoles are also used to assess depositional paleoenvironment, either from the isolated compounds or from diagnostic ratios, such as the ratio of benzocarbazoles (B[a]C/(B[a]C + B[c]C) (Bechtel et al., 2013; Bakr, 2009).

In Fig. 9a, the difference in BCA concentrations is accentuated among the samples from the Recôncavo Basin (minor concentrations) and the Amazonas Basin (higher concentrations). In addition to suggesting different organic matter inputs (as discussed in item 4.2). This difference in benzocarbazole concentrations, as in previous study (Bakr and Wilkes, 2002), is related to oxidizing conditions in depositional paleoenvironments, where samples deposited under reducing conditions present low values for the benzocarbazole ratio. In contrast, those deposited under oxidizing conditions exhibit high ratio values.

Based on the analysis of the isoprenoids pristane and phytane (presented as the Pr/Ph ratio), it is possible to distinguish oxidizing (Pr/Ph > 1) or reducing (Pr/Ph < 1) conditions of the paleodepositional environment of the organic matter (Peters et al., 2005). As shown in Fig. 9b, there are differences between the samples from the Candeias Formation (deposited under reducing conditions) and the Barreirinha Formation (deposited under oxidizing conditions), although within each sample group there is significant similarity in Pr/Ph values and benzocarbazole concentrations.

Bakr and Wilkes (2002) have reported that redox conditions affect the concentrations of benzocarbazoles. The more reducing the depositional environment, the greater the amounts of sulfur. However, a negative correlation between the total sulfur values and the benzocarbazoles ratio was observed. The samples from the Barreirinha Formation presented the highest concentrations of benzocarbazoles and the highest values of total sulfur (Fig. 9c). In this case, the benzocarbazoles concentrations can be related to depositional paleoenvironment and possible source rock retention effects, although the samples are thermally immature for hydrocarbon generation. The distributions of benzocarbazoles in the samples under investigation can be affected by the N–H bond that has an affinity with the hydroxyl groups of clay minerals, favoring their adsorption and subsequent fixation in source rocks (Li et al., 1995; Dorban et al., 1984; Tang et al., 2022).

5. Conclusions

The N-markers were applied for the first time to samples of formations with already known depositional paleoenvironment through biomarkers. The results obtained by N-markers allowed to evaluate and prove distinctions and similarities between the source rocks, defining the origin of organic matter, the organic matter input, the depositional paleoenvironment conditions of the samples.

Source rock samples from the Recôncavo Basin, of lacustrine origin, have lower concentrations of CA, MCA, and DMCA, while samples from the Amazonas Basin, of marine origin, present high concentrations of these compounds. Basic nitrogen compounds were also found in different concentrations in the samples, where samples of lacustrine origin had higher concentrations of QUIN and 4-MQUIN. In contrast, samples of marine origin had higher values for 2,4-DMQUIN, B[c]QUIN, and ACR.

The concentrations of the 1-MCA, 2-MCA, and 4-MCA isomers, in addition to the low values for the 4-MCA/2MCA ratio indicate that algal input was predominant in the Candeias and Barreirinha formations. The relative proportions of DMCA and the recognition of the B[b]CA isomer also indicate the relative amount of terrigenous material deposited into both formations.

Similarities between benzocarbazoles concentrations and Pr/Ph values indicate that N-markers are affected by the depositional setting. Samples deposited in reducing conditions presented low concentrations of benzocarbazoles, while those deposited in oxidizing environments presented higher amounts of benzocarbazoles.

CRediT authorship contribution statement

Diego Nery do Amaral: Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Flávia Lima e Cima Miranda:** Formal analysis, Methodology, Writing – original draft. **Luise Carvalho Dias:** Methodology. **José Roberto Cerqueira:** Data curation, Methodology, Writing – review & editing. **Hélio Jorge Severiano Ribeiro:** Methodology, Writing – review & editing. **Olívia Maria Cordeiro de Oliveira:** Funding acquisition, Project administration. **Antônio Fernando de Souza Queiroz:** Funding acquisition, Project administration, Writing – review & editing. **Maria Elisabete Machado:** Conceptualization, Investigation, Supervision, Writing – review & editing. **Sérgio Luís Costa Ferreira:** Investigation, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpetgeo.2024.106977.

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4 ORGANIC SULFUR MARKERS AS PROXIES OF DEPOSITIONAL PALEOENVIRONMENTS RELATED TO RECÔNCAVO AND AMAZON BASINS, BRAZIL

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Organic Sulfur Markers as Proxies of Depositional Paleoenvironments Related to Recôncavo and Amazon Basins, Brazil

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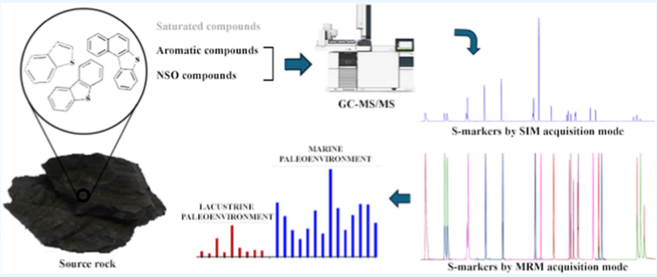

ABSTRACT: This study employed organic sulfur markers (S-markers) associated with geochemistry parameters to evaluate the paleoenvironment of different depositional settings in 24 samples collected in vertical sections of outcrops of the Candeias and Barreirinha Formations in Recôncavo and Amazon basins, respectively. A total of twenty-one S-markers from benzothiophene (BT), dibenzothiophene (DBT), and benzonaphtothiophenes (BNT) classes were optimized and quantified by gas chromatography-triple quadrupole mass spectrometry (GC−MS/MS). S-markers efficiently evaluated and differentiated the depositional paleoenvironment in the source rocks based on the individual compound, in cross-validation with saturated biomarkers, and associated with parameters such as total organic carbon (TOC) and Rock-Eval pyrolysis. Samples from the lacustrine environment presented low concentrations of BT, DBT, and BNT, and samples from the marine environment showed high BT, DBT, and BNT concentrations. The variations in $\sum$DBT and TOC indicated that the quantity and/or the type of organic matter exert some control over the distribution of DBTs. Although the formations are from different paleoenvironments, the organic matter input was similar, as indicated by high proportions of 1,2-BNT and 2,1-BNT relative to 2,3-BNT, thus characterizing the algal input with a microbial contribution for both sites. The sum of the BNTs was directly related to the amounts of amorphous organic matter (AOM) in the vertical distribution of outcrops. These results are in accordance with the finding that BNTs may originate from the microbial activity. The DBT/Phen vs pristane/phytane (Pr/Ph) relationship attested to differences in the redox conditions of the depositional paleoenvironments of the formations under study. The 4,6-DMDBT/2,4,6-TMDBT and 2,4,6-TMDBT/(2,4,7 + 2,4,8)-TMDBT ratios indicated immaturity for hydrocarbon generation.

1. INTRODUCTION

Sulfur is an abundant heteroatom in fossil fuels with total concentrations usually less than 4.0%. The polycyclic aromatic sulfur heterocycle (PASH) structures are the most abundant form of organic sulfur in crude oils and source rocks and include benzothiophenes (BTs), dibenzothiophenes (DBTs), benzonaphthothiophenes (BNTs), and their C_1-C_3 alkyl derivatives.[1] In geochemistry studies, the PASHs have been used as markers (S-markers) to assess the depositional paleoenvironment, maturity degree, migration, and organic facies from crude oils and source rock extracts.[1−3]

S-markers provide a convenient way to correlate oils with source rocks, to assess facies, organic matter input, and depositional paleoenvironment conditions. For example, the

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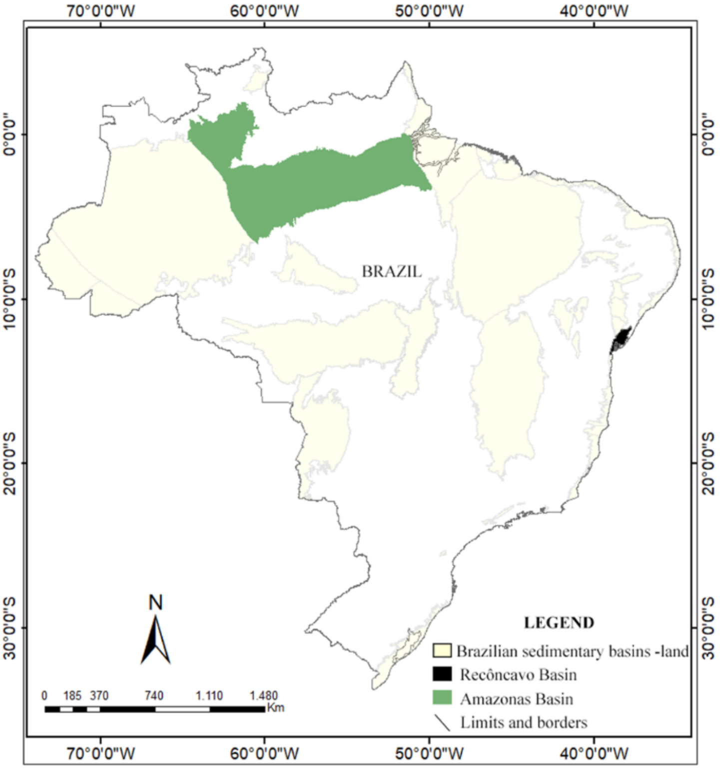

Figure 1. Map of Brazilian terrestrial sedimentary basins highlighting the Recôncavo and Amazon basins.

abundance of dibenzothiophenes (e.g., DBT and methyl-DBTs) in oils from different sedimentary environments increases in the order of freshwater < saline < hypersaline facies.[4] For the benzonaphthothiophenes and their isomers (C_1-BNTs, C_2-BNTs, and C_3-BNTs), the abundances in crude oils and source rocks of terrigenous origin are lower than marine equivalents.[4−7] In addition, due to their stability in high temperatures, S-markers can be ideally used to assess the state of maturity.[8,9] However, the studies based on S-markers to assess paleodepositional settings are limited.[2,10−12]

Saturated hydrocarbons, such as *n*-alkanes, pristane, phytane, hopanes, and steranes, are biomarkers conventionally employed in geochemistry studies to provide information about the origin and depositional paleoenvironment of the organic matter.[13] These compounds determine the relationship between crude oil and residual organic matter in source rocks all over the world. In Brazil, the oils and source rocks from the Recôncavo and Amazon basins have already been characterized in terms of their paleoenvironment using different biomarkers.[14−18] However, biomarkers may be affected by biodegradation, water washing, and thermal alteration.[19,20] In these cases where parameters are not sufficiently diagnostic, S-markers can provide a better application.[7,21] Therefore, the combined information based on the cross-validation of saturated biomarkers and S-markers allows a more accurate evaluation of source rocks' depositional paleoenvironments.

In the Amazon Basin, the Barreirinha Formation is known as the primary hydrocarbon source rock composed of dark gray to black shale. Data from saturated biomarkers indicate that these black shales, highly enriched in organic matter, were deposited in a marine paleoenvironment.[22,23] In the Recôncavo basin, as biomarker data indicate, the Candeias Formation is recognized as a hydrocarbon source rock deposited in a lake context with good organic matter preservation.[14,15,24] Considering that the two sedimentary basins were deposited in different paleoenvironments (marine and lacustrine), a detailed study based on specific S-markers using these basins as a model can be an excellent tool for paleodepositional assessment.

Determination of S-markers in crude oils is made primarily by gas chromatography coupled to mass spectrometry (GC−MS) in the selected ion monitoring (SIM) mode.[1] However, it is necessary to perform previous laborious fractionation steps, and there are limitations to the identification of compounds with the same mass fragment ions. The gas chromatography coupled to triple quadrupole spectroscopy (GC−MS/MS) is able to increase the selectivity and sensitivity for S-markers because it eliminates the background interference. The GC−MS/MS has been proven to good performance in the analysis of individual S-markers in petroleum samples.[25−29] However, a limited number of compounds was evaluated, and the geochemistry interpretation of results was not the aim of those studies.

This work aimed to employ S-markers in combination with geochemistry parameters to assess the depositional paleoenvironment of source rocks of different origins. A GC−MS/MS method was optimized to determine twenty-one S-markers in source rock extracts. Interpretations focused on individual and diagnostic ratios from S-markers were used, for the first time, to analyze differences and similarities between the geological formations under study and to interpret the paleoenvironment conditions of their depositional settings.

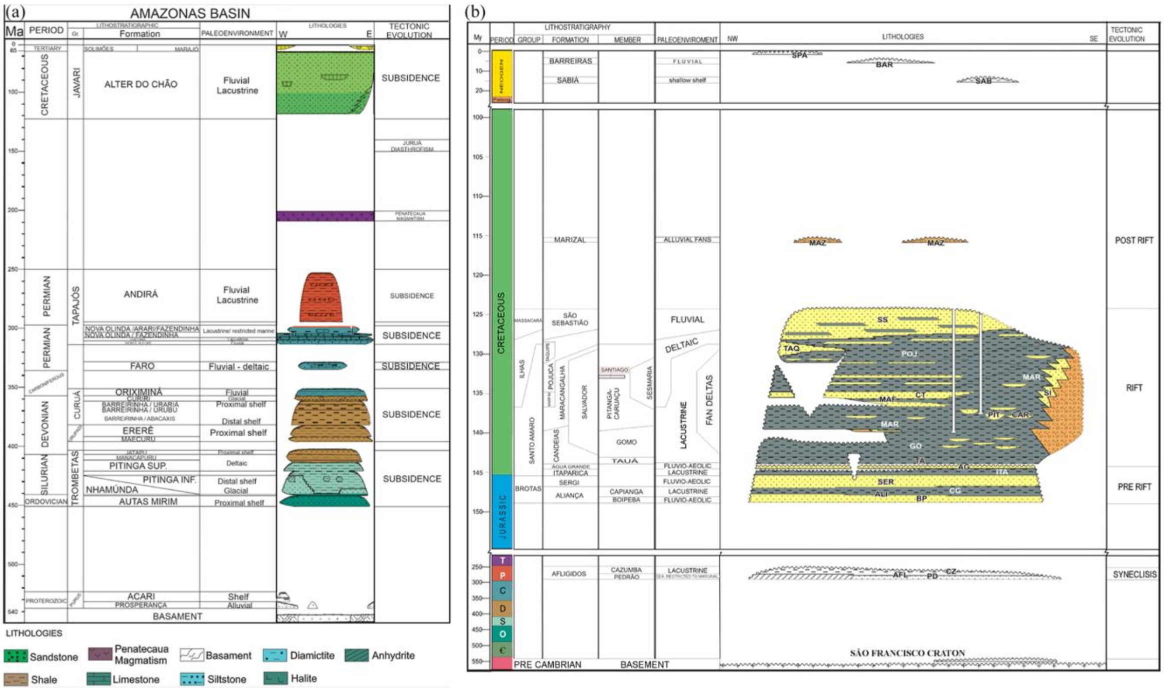

Figure 2. Stratigraphic charts: (a) Amazon basin. (b) Recôncavo basin, adapted from refs 17,34.

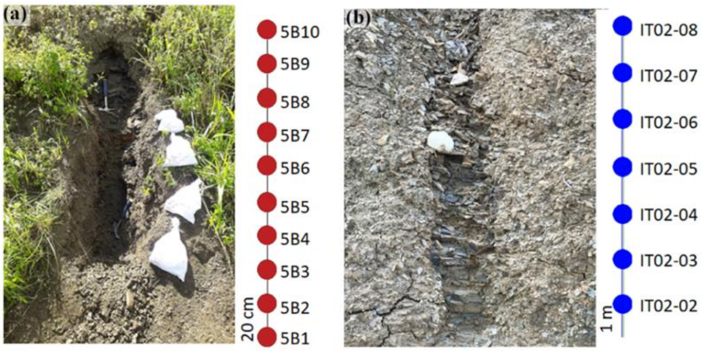

Figure 3. Sampling points with vertical spacing in outcrops of the Candeias (a) and Barreirinha (b) formations.

2. GEOLOGICAL SETTINGS

2.1. Amazon Basin. The Amazon basin is located in the northern region of Brazil (Figure 1), covering part of the states of Amazon and Pará, with an area of approximately 500,000 km^2. It is classified as a Paleozoic basin of the intracratonic syneclisis type, whose sedimentation began in the Paleozoic and lasted until the Mesozoic,[16,17] as seen on the stratigraphic chart of the basin (Figure 2a).

The deposition of the Barreirinha Formation is associated with a rapid relative sea level rise that occurred when the South American Platform underwent a major marine transgression in Frasnian.[30] The initial depositional phase of this formation is represented by a thick section of radioactive black shales (dark gray, laminated, fissile, and bituminous) denoted as the abacaxis member, which is considered the primary hydrocarbon source rock in the Amazon basin. The abacaxis member is overlapped by two other members: Urubu (dark gray shales) and Uraria (gray shales and dark to light siltstones).[30] Previous studies indicate that the Barreirinha Formation is the carrier of marine organic matter, with average TOC contents between 2 and 3%, mostly type II kerogen, and varying levels of thermal maturation.[16,23]

2.2. Recôncavo Basin. The Recôncavo basin covers approximately 11,500 km^2 from Bahia state in Brazil (Figure 1) and corresponds to the southern portion of the Recôncavo-Tucano-Jatobá Rift (RTJ). The RTJ system developed in the Cretaceous can be interpreted as an aulacogen segment associated with South Atlantic Rift.[31]

The deposition of the Candeias Formation, recognized as source rocks in the Recôncavo basin, occurred with increased tectonic activity added to the predominance of climate humidification, generating conditions for the development of deep lakes, which marked the beginning of the rift phase in the

Berriasian (Figure 2b). In this scenario, initially there was the transgression generating the dark pelite of the Tauá Member, which is overlapped by gray-green shale with carbonatic intercalation of the Gomo Member.[32] Various geochemical evaluation studies in Candeias Formation have been performed, including the identification of strata with multiple amounts of total organic carbon (TOC), suggesting internal faciological changes in this geological formation.[14,15,24,33]

Thus, the Candeias Formation is defined as a thick section of dark-green, gray shales, with subordinate intersperses of limestone and dolomites, locally encompassing bodies of massive and/or stratified sandstones.[24,34] According to Amaral et al.[15] the Candeias shales (Gomo Member) are bearers of amorphous organic matter (AOM) with intense fluorescence, average total organic carbon (TOC) content of approximately 3% and kerogen type I, with a high potential for hydrocarbon generation.

3. MATERIALS AND METHODS

3.1. Sampling. Samples in the Recôncavo basin were collected from an outcrop on the side of highway BR 324, km 557, in the municipality of Santo Amaro, Bahia, Brazil. The sampling was carried out every 20 cm for a total of 10 samples (labeled 5B1 to 5B10, Figure 3a), to investigate possible vertical variations of the geochemical parameters.

Two outcrops of the Amazon basin were selected, identified as IT02 and IT06 (representative image of the IT02 outcrop in Figure 3b), and both were collected vertically with a spacing of 1 m at different points ($n = 14$) along the BR 230 highway in the Rurópolis municipality, Pará state, Brazil. Figure 3 shows the sampling in the Recôncavo basin (Figure 3a) and a representative outcrop of the Amazon basin (Figure 3b). The collection procedure was the same for all of the outcrops. The initial layers of altered rocks were removed, digging deep enough (between 1 and 2 m) to reach below the weathering zone to access examples of source rocks without alteration/oxidation features.

3.2. Extraction of Soluble Organic Matter. Prior to extraction, the rock samples were ground with an agate mortar and pestle, pulverized in a Retsch planetary ball mill (Retsch, PM 400, Haan, Germany) and subsequently sieved through a steel mesh sieve with an opening of 0.180 mm (80 mesh), and stored in glass recipients.

Accelerated solvent extraction (Dionex ASE 350, Thermo Scientific, Massachusetts) was employed to obtain the soluble organic matter present in rock samples.[35] Initially, 50 g of sample and 10 g of diatomaceous earth, a dehumidifying agent (Celite 545, Exodo Cientfica, Brazil), were added to metal extractor cells. Thus, the system was heated at 75 °C at a pressure of 5×10^6 Pa for 15 min using 150 mL of dichloromethane. The procedure was repeated three times to ensure that all soluble organic matter compounds were extracted. Then, the source rock extract was concentrated (solvent evaporated) using a rotary evaporator (R-100, Buchi, Meierseggstrasse, Switzerland).

3.3. Fractionation of Soluble Organic Matter. The extracts were fractionated by open column chromatography using silica as the stationary phase (ASTM D2007-11).[36] The saturated hydrocarbon fractions were eluted with 25 mL of *n*-hexane, and the aromatic hydrocarbon fractions containing the S-markers were eluted with 30 mL of *n*-hexane:DCM (4:1, v/v) and 30 mL of DCM:methanol (4:1, v/v). All fractions were concentrated in a rotary evaporator (Model R-210 Labortechnik, AG Switzerland) and transferred to 2 mL vials.

3.4. GC–MS/MS Analyses of S-Markers. The GC–MS/MS analyses of the S-markers were performed on an Agilent 7890B gas chromatograph equipped with a split/splitless injector, a DB5MS column (5% phenylmethylpolysiloxane, 30 m × 0.25 mm internal diameter ×0.25 μm film thickness) coupled to an Agilent 7000C mass spectrometer (Santa Clara, CA). The GC operating conditions are as follows: the oven temperature was held isothermally at 100 °C for 2 min, ramped to 310 °C at 5 °C min^{-1}, and held isothermal for 1.5 min. Helium was used as the carrier gas with a constant flow rate of 1.0 mL min^{-1}. The MS was operated in the electron ionization (EI) mode at 70 eV, ion source at 280 °C, and injector and transfer line temperature of 300 °C.[29]

3.4.1. MS/MS Optimization. The MS/MS transitions for some BTs, DBTs, and BNTs were determined by Sampaio et al.[29] However, in the present study, the number of compounds was twenty-one and tested the collision energy (CE) for each individual S-marker. Thus, to optimize the multiple reaction monitoring (MRM) conditions for the compounds used in this study, a full scan and product ion scan (PIS) were performed in MS/MS. Initially, the mass spectra of all individual standards were obtained in the full scan mode (m/z mass range 45–450), and the fragments with the highest abundance for each one were selected, observing their retention times. Windows were defined based on the retention times of the compounds of interest in the SIM mode. The PIS was selected using collision energy variation from 5 to 60 eV (5, 10, 20, 30, 40, 50, and 60 eV). The product ions exhibiting the highest sensitivity were selected as quantification ions, whereas those exhibiting the second highest sensitivity were selected as qualification ions. Thus, two transitions were defined in the MRM mode under optimized collision energies.

For the method optimization, the following individual standards were employed at a concentration of 100 ug L^{-1}: benzothiophene (BT), 2-methylbenzothiophene (2-MBT), 3-methylbenzothiophene (3-MBT), 2,4-dimethylbenzothiophene (2,4-DMBT), 2,6-dimethylbenzothiophene (2,6-DMBT), 2,3,4-trimethylbenzothiophene (2,3,4-TMBT), 2,5,7-trimethylbenzothiophene (2,5,7-TMBT), dibenzothiophene (DBT), dibenzothiophene-d_8 (DBT-d_8), phenanthrene (Phen), 4-methyldibenzothiophene (4-MDBT), 1-methyldibenzothiophene (1-MDBT), 2,8-dimethyldibenzothiophene (2,8-DMDBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), 2,4-dimethyldibenzothiophene (2,4-DMDBT), 1,4-dimethyldibenzothiophene (1,4-DMDBT), 3,6/2,6-dimethyldibenzothiophene (3,6/2,6-DMDBT), 2,4,7-trimethyldibenzothiophene (2,4,7-TMDBT), 4,6-diethyldibenzothiophene (4,6-DEDBT), benzo[*b*]naphto[1,2-*d*]thiophene (BNT- 1,2), benzo[*b*]naphtho[2,1-*d*]thiophene (BNT-2,1), and benzo[*b*]naphtho[2,3-*d*]thiophene (BNT-2,3).

For BT, DBT-d_8, 3-MBT, 2,4-DMBT, 2,3,4-TMBT, DBT, Phen, 4-MDBT, 1-MDBT, 4,6-DMDBT, 2,4-DMDBT, 1,4-DMDBT, 2,4,7-TMDBT, 4,6-DEDBT and BNT-1,2 the same MRM transitions defined by Sampaio et al.[29] were employed. For 2-MBT, 2,6-DMBT, 2,5,7-TMBT, 2,8-DMDBT, 3,6/2,6-DMDBT, BNT-2,1 and BNT-2,3, the MS/MS conditions were optimized and definite.

3.5. Total Organic Carbon, Total Sulfur, and Rock-Eval Pyrolysis. The TOC content was determined from 1.0 g of each sample (80 mesh) subjected to acid digestion (HCl, 37%) to carbonate removal and measured using a LECO 628CN

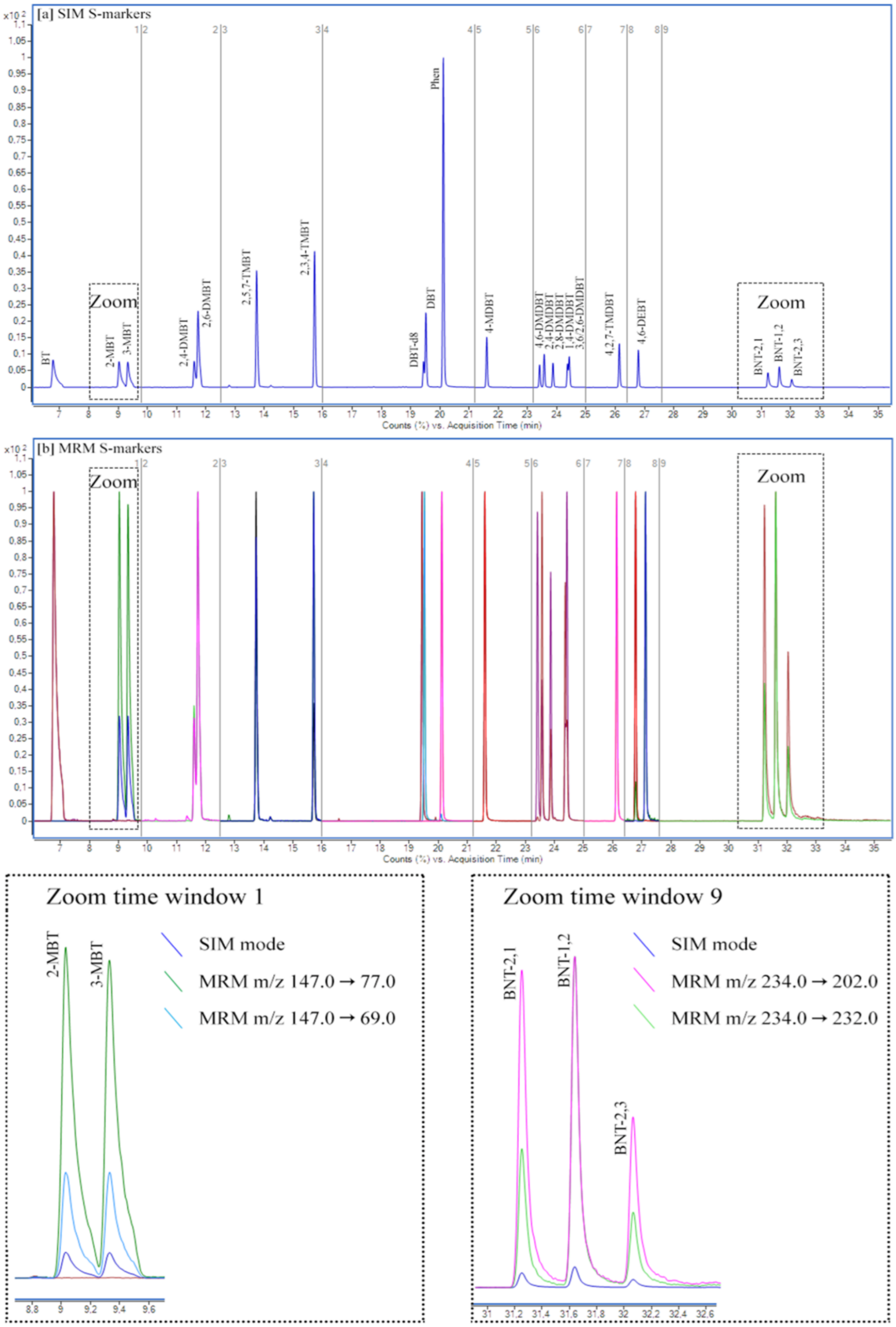

Figure 4. Chromatograms of S-markers in (a) SIM mode and (b) MRM mode. Different colors in (b) and (c) refer to individual MRM transitions.

Table 1. Summary of Optimized MRM Transitions Used for Quantifying S-Marker Compounds

	window	R_t	quantification transition			confirmation transition		
S-markers	(±R_t min)	(min)	precursor ion (m/z)	product ion (m/z)	CE[b] (eV)	precursor ion (m/z)	product ion (m/z)	CE[b] (eV)
BT	4.00−10.00	6.77	134	89	20	134	69	20
2-MBT[a]	4.00−10.00	9.03	147	77	30	147	69	30
3-MBT	4.00−10.00	9.32	147	77	40	147	69	30
2,4-DMBT	10.00−12.00	11.60	162	161	20	162	128	40
2,6-DMBT[a]	10.00−12.00	11.73	162	161	20	162	147	30
2,5,7-TMBT[a]	12.00−17.00	13.73	176	161	20	176	128	40
2,3,4-TMBT	12.00−17.00	15.71	176	161	20	176	175	40
DBT-d_8	17.00−21.00	19.44	192	146	30	192	160	40
DBT	17.00−21.00	19.52	184	139	30	184	152	20
Phen	17.00−21.00	20.12	178	176	30	178	152	40
4-MDBT	21.00−23.00	21.60	198	197	30	198	165	30
4,6-DMDBT	23.00−25.00	23.41	212	197	20	212	211	40
2,4-DMDBT	23.00−25.00	23.57	212	211	20	212	197	40
2,8-DMDBT[a]	23.00−25.00	23.87	212	197	40	212	211	50
1,4-DMDBT	23.00−25.00	24.37	212	211	20	212	197	40
3,6/2,6-DMDBT[a]	23.00−25.00	24.48	212	197	30	212	211	30
2,4,7-TMDBT	25.00−30.00	26.13	226	211	20	226	225	40
4,6-DEDBT	25.00−30.00	26.79	240	210	20	240	225	40
BNT-2,1[a]	30.00−45.50	31.22	234	202	30	234	189	40
BNT-1,2	30.00−45.50	31.61	234	202	40	234	189	30
BNT-2,3[a]	30.00−45.50	32.04	234	202	30	234	189	40

[a] Compounds optimized in this study. [b] Collision energy.

Elementary Analyzer. Total sulfur contents were performed on the LECO 628S Elementary Analyzer. Rock-Eval analysis was performed using a Rock-Eval 6 instrument according to the procedure proposed by Behar et al.[37] The parameters included 100 mg of each sample (0.177 mm) added to a tin device. Analyses were previously performed by Amaral et al. and Góes et al.[15,23]

3.6. Biomarkers Analysis. Saturated biomarkers were previously analyzed in a gas chromatograph coupled to a mass spectrometer (GC/MS-DSM5977A, Agilent) using a DB-5MS capillary column (60 m × 0.25 mm × 0.25 μm). Helium was used as the carrier gas at a flow of 1 mL min^{-1}. The samples were diluted in hexane at 0.05 mg for each 1 mL of solvent. The injection volume was 1 μL in the splitless mode. The oven temperature program was from 60 to 310 °C with a heating rate of 2 °C min^{-1}. The following ions were monitored in MS: m/z 217 (steranes), m/z 191 (terpanes), and m/z 259 (tetracyclic polyprenoids and diasteranes).[15,23]

3.7. Palynofacies. The palynofacies analysis was carried out qualitatively and quantitatively[15,23] by counting 300 organic components (amorphous organic matter, phytoclasts, and palynomorphs) on each slide using a Zeiss Axio Imager A2m microscope, equipped with a white (halogen) light source (from a 12 V/100 W halogen lamp with stabilized current) and a UV light (fluorescence) source (from a high-pressure 100 W mercury lamp with stabilized current). Counting was performed under 20 times magnification following the procedure proposed by Tyson.[60] Qualitatively, organic matter was evaluated for the degree of preservation, appearance, color, presence, and intensity of fluorescence under excitation with UV/blue-violet light.

4. RESULTS AND DISCUSSION

4.1. Identification and Quantification of S-Markers by GC−MS/MS. The critical parameters for the identification and quantification of compounds in the GC−MS/MS method include the choice of the precursor ion and the product ion for each MRM transition with specific collision energy (CE). The more intense ion in the mass spectrum was chosen as the precursor ion, and the two fragment ions with the highest response were selected as the product ion. For example, m/z 147 → 77 and 147 → 69 were used for MBTs (Sampaio et al.,[29]) and substantially reduced the baseline level with the signal-to-noise ratio increased approximately 10 times when compared to GC−MS (m/z 147) (Figure 4).

The optimized GC−MS/MS conditions for the analysis of 21 standards of S-markers are summarized in Table 1, including the retention times (R_t), window widths, quantification and confirmation transitions, and collision energies (CE).

The concentration of S-markers obtained from source rock extracts by optimized conditions of GC−MS/MS are shown in Table 2. In general, higher concentrations were found in samples from the Barreirinha Formation. The 2,6-DMBT was the compound with the lowest concentration (nd to 0.01 $\mu g\ g^{-1}$ for 5B-06), while 2 + 3MDBT showed the highest concentration (1938 $\mu g\ g^{-1}$ to IT06-59).

Throughout the literature, it is uncommon to find geochemistry studies aimed at the quantification of individual S-markers by GC−MS.[38−41] The results are mainly expressed as the sum of classes[10,7,12,42,43] or in area percentage values[3,25,44] because of the commercial limitations and the high cost associated with acquiring the standards. However, GC−MS is not sufficiently selective for S-markers since coelutions with matrix compounds with the same m/z might interfere.[1,45]

A representative chromatogram of a source rock extract sample is shown in Figure 5. The triple quadrupole analyzer is considered one of the best alternatives to analyze S-markers.[1,29] It minimizes interference by improving the selectivity based on the selection of appropriate precursor and product ions (Figure 5a). In addition, a significant decrease of chemical noise in the chromatogram is obtained when compared to that in the SIM mode (Figure 5b). Thus, thanks to the improved sensitivity,

Table 2. Concentrations of Sulfur Markers Applied to This Study ($\mu g\ g^{-1}$ of Extract) in Samples from the Recôncavo (5B) and Amazon Basins (IT)[a]

	Recôncavo basin									
S-marker	5B-01	5B-02	5B-03	5B-04	5B-05	5B-06	5B-07	5B-08	5B-09	5B-10
BT	0.08	0.02	0.03	0.75	0.35	0.16	0.37	0.41	0.16	1.26
2-MBT	0.04	0.01	nd	0.02	0.01	0.10	0.01	0.01	nd	0.02
3-MBT	0.04	0.01	0.01	0.02	0.05	0.14	0.01	0.01	nd	nd
2,4-DMBT	0.01	nd	nd	0.01	0.01	0.01	0.01	0.01	nd	0.01
2,6-DMBT	nd	nd	nd	nd	nd	0.01	nd	nd	nd	nd
2,5,7-TMBT	0.15	0.04	0.06	0.10	0.26	0.24	0.08	0.18	0.01	0.09
2,3,4-TMBT	0.01	nd	nd	0.01	0.01	nd	nd	nd	nd	nd
DBT	0.10	0.08	0.33	0.20	0.18	0.24	0.24	0.25	0.17	0.23
Phen	0.64	0.92	5.83	0.95	0.82	1.30	0.57	0.43	0.28	0.36
1-MDBT	0.18	0.15	0.64	0.23	0.23	0.37	0.19	0.17	0.13	0.26
(2 + 3)-MDBT	0.15	0.07	0.39	0.15	0.13	0.22	0.12	0.05	0.07	0.10
4-MDBT	0.22	0.16	0.62	0.34	0.30	0.58	0.25	0.22	0.17	0.19
4,6-DMBT	0.05	0.03	0.08	0.05	0.06	0.07	0.05	0.05	0.04	0.13
2,3-DMBT	0.05	0.04	0.03	0.07	0.04	0.02	0.05	0.05	0.12	0.20
2,4-DMBT	0.05	0.05	0.19	0.07	0.05	0.19	0.04	0.02	0.03	0.02
2,8-DMBT	0.04	0.02	0.07	0.04	0.06	0.06	0.04	0.05	0.04	0.05
1,4-DMBT	0.02	0.01	0.01	0.04	0.03	0.01	0.02	0.02	0.01	0.05
3,6/2,6-DMBT	0.03	nd	0.04	0.04	0.03	0.15	0.06	0.04	0.02	0.03
2,4,6-TMDBT	0.10	0.04	0.24	0.19	0.16	0.25	0.20	0.17	0.23	0.25
2,4,7-TMDBT	0.13	0.06	0.18	0.19	0.18	0.17	0.15	0.14	0.14	0.23
2,4,8-TMDBT	0.10	0.04	0.18	0.14	0.12	0.18	0.11	0.10	0.10	0.16
4,6-DEBT	nd	nd	nd	0.01	nd	nd	nd	nd	nd	nd
BNT-2,1	0.79	0.39	0.55	2.07	1.85	0.89	1.25	2.22	3.01	3.62
BNT-1,2	0.02	0.01	0.02	0.05	0.05	0.02	0.03	0.04	0.02	0.08
BNT-2,3	0.02	0.01	0.01	0.07	0.08	0.06	0.09	0.14	0.13	0.16

	Amazon basin													
S-marker	IT02-02	IT02-03	IT02-04	IT02-05	IT02-06	IT02-07	IT02-08	IT06-54	IT06-55	IT06-56	IT06-57	IT06-58	IT06-59	IT06-60
BT	7.18	0.39	5.44	4.44	3.08	14.20	5.09	10.90	11.43	11.83	11.54	9.43	15.54	10.46
2-MBT	0.47	0.07	7.89	3.85	1.90	2.34	6.07	2.87	3.78	4.48	3.88	3.39	2.56	4.76
3-MBT	4.23	0.45	34.94	11.43	8.89	17.98	23.43	41.42	30.55	20.02	26.94	29.68	22.19	26.98
2,4-DMBT	0.40	0.22	0.91	1.66	1.81	8.94	3.04	0.52	0.69	0.79	0.46	0.28	3.50	0.58
2,6-DMBT	0.27	0.08	0.79	0.71	0.53	0.87	0.71	0.56	0.59	0.48	0.56	0.18	0.71	0.30
2,5,7-TMBT	46.79	8.12	198	205.7	217	73.73	49.82	89.22	89.43	105	90.69	41.18	113	53.33
2,3,4-TMBT	4.37	0.69	9.50	9.89	10.04	14.34	10.53	25.77	22.56	21.36	15.96	5.72	23.19	13.88
DBT	306	60.25	631	637	639	845	892	1135	1061	700	759	369	1103	728
Phen	2133	168	2779	2620	2474	3147	2358	2626	2384	2293	2261	1269	2891	2398
1-MDBT	979	84.95	1088	1139	1197	1680	1490	1646	1334	1248	1135	1117	1486	1291
(2 + 3)-MDBT	1022	89.28	1160	1200	1294	1649	1601	1938	1675	1644	1441	1245	1665	1333
4-MDBT	867	80.65	987	1007	1100	1603	1349	1602	1441	1372	1317	1103	1220	1207
4,6-DMBT	91.31	7.91	91.51	101	107	166	118	154	134	124	124	121	147	128
2,3-DMBT	30.73	2.70	36.29	47.43	49.46	40.81	22.70	32.32	40.29	41.64	38.44	27.51	61.03	32.15

Table 2. continued

	Amazon basin													
S-marker	IT02-02	IT02-03	IT02-04	IT02-05	IT02-06	IT02-07	IT02-08	IT06-54	IT06-55	IT06-56	IT06-57	IT06-58	IT06-59	IT06-60
2,4-DMBT	89.68	6.07	73.95	81.96	87.05	139	117	129	120	106	101	91.13	98.32	97.01
2,8-DMBT	57.45	1.99	30.50	41.47	68.29	105	90.48	110	95.64	74.76	78.37	67.61	84.67	76.03
1,4-DMBT	52.76	3.16	50.64	51.96	56.62	81.09	68.49	84.58	76.56	67.50	67.64	67.52	79.68	56.07
3,6/2,6-DMBT	213	12.39	164	179	222	317	271	316	314	257	237	225.8	255	217
2,4,6-TMDBT	71.55	4.42	57.34	59.64	68.78	105	19.84	112	87.86	74.52	75.93	77.77	82.04	85.13
2,4,7-TMDBT	102	6.51	81.16	86.86	107	155	21.99	144	136	106	102	112	127	124
2,4,8-TMDBT	106	6.12	73.82	87.96	94.36	153	39.65	150	134	108	99.65	96.93	109	110
4,6-DEBT	1.50	0.10	1.24	1.36	1.63	2.39	1.97	2.49	2.25	1.82	1.74	1.64	1.71	1.65
BNT-2,1	77.36	4.54	71.74	72.06	73.41	78.23	61.43	92.43	91.14	90.44	90.39	85.40	82.26	77.90
BNT-1,2	44.92	2.44	38.40	44.43	47.01	61.96	45.35	55.72	53.44	52.71	49.61	46.63	48.66	48.20
BNT-2,3	18.45	1.21	21.39	26.43	27.78	30.49	20.10	25.21	23.46	19.86	26.90	30.22	28.05	23.19

[a]nd = not detected.

performing reliable determination of S-markers at trace levels, as those required in geochemistry studies is feasible.

4.2. Paleoenvironment Interpretation Based on S-Markers.

4.2.1. Origin of Organic Matter. The concentrations of BT, DBT, BNT, and its alkylated homologues in source rock extracts and crude oils have been employed to evaluate organic matter origin.[44,46] The highest concentrations of these compounds are found in samples of marine origin compared to those of continental origin.[12,47]

The concentrations of individual S-markers in samples from the Recôncavo and Amazon basins were different (Table 2 and Figure 6). High concentrations of BT, DBT, and BNT, consistent with a marine paleoenvironment, were observed in the Barreirinha Formation. In contrast, low concentrations of these compounds were found in the Candeias Formation, which are typical of a continental freshwater paleoenvironment.

The differentiation of sedimentary paleoenvironments obtained by S-markers was confirmed by biomarkers, such as hopane/sterane (HOP/STE) (Figures S1−S4) and polyprenoids and diasteranes (TPP/TPP + DIA) ratios (Table S1). The palynofacies based on the relative proportions between amorphous organic matter (AOM), palynomorphs, and phytoclasts (Table S1) also confirmed the S-markers data. HOP/STE ratios greater than 5 and the presence of *Botryococcus* algae indicated that the organic matter present in the Candeias Formation had a lacustrine origin.[15] In addition, values of HOP/STE were lower than 5, and the types of palynomorph found indicate the Barreirinha Formation's marine origin.[23]

Another evaluation of the origin of organic matter based on S-markers is by DBTs, where the highest concentrations of these compounds are present in oils and extracts from source rocks of marine origin, compared to those of freshwater lacustrine origin.[10] The classical biomarkers such as HOP/STE and TPP/[TPP + DIA] ratios are frequently employed to evaluate origin, where lake environments usually present values greater than 5 for the HOP/STE ratio and greater than 0.4 for the TPP/[TPP + DIA], while marine environments generally present values lower than 5 for the HOP/STE ratio and lower than 0.4 for the TPP/[TPP + DIA] ratio.[13]

The relationships between ∑DBT versus HOP/STE (Figure 7a) and TPP/[TPP + DIA] (Figure 7b) showed a good distinction between the depositional paleoenvironments. Samples from the Candeias Formation presented the lowest concentrations of ∑DBT and highest values for HOP/STE and TPP/[TPP + DIA] ratios, which are the characteristics of a freshwater lacustrine paleoenvironment.[10,13] Samples from the Barreirinha Formation presented the highest concentrations of DBT and lower values for the HOP/STE and TPP/[TPP + DIA] ratios, typical of a marine paleoenvironment.

According to the theory of bacterial sulfate reduction, organosulfur compounds are formed from the production of inorganic sulfur by bacteria during diagenesis.[1] In general, samples from the Candeias Formation show indications of a high microbial contribution (high values for the HOP/STE ratio) and low concentrations of organosulfur compounds. In this case, the low S-markers concentrations are due to the low availability of sulfate ions in the freshwater lacustrine environment.[48]

The BT class distribution can be applied to evaluate differences in source material/depositional paleoenvironment and/or maturity.[47] All samples analyzed in this study are thermally immature (as will be discussed in subsection 4.5); thus, the differences in BT and alkyl-BT concentrations reflect different depositional paleoenvironments. For example, the 3-

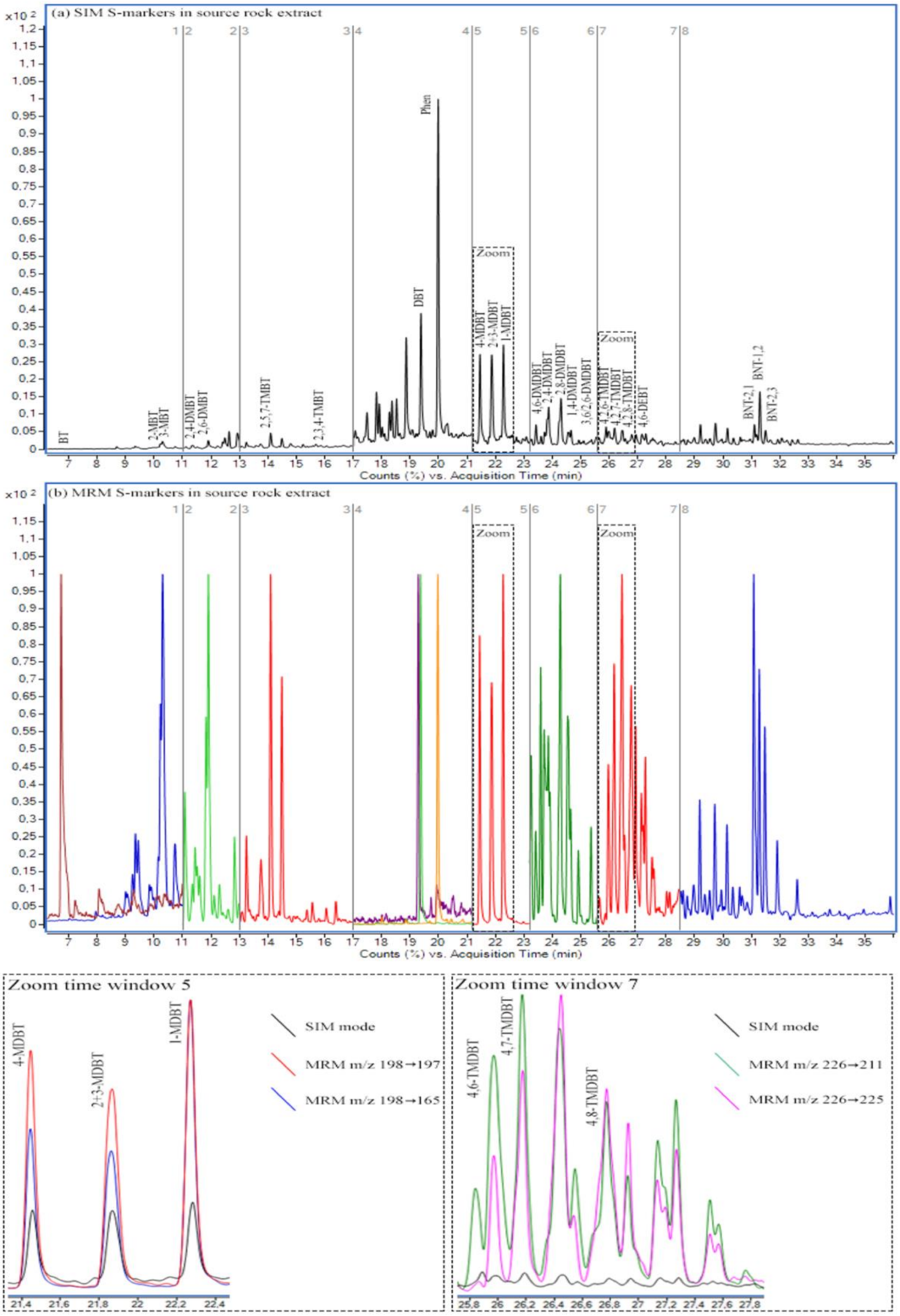

Figure 5. GC−MS/MS chromatogram of S-markers in source rock extract by the (a) SIM and (b) MRM mode.

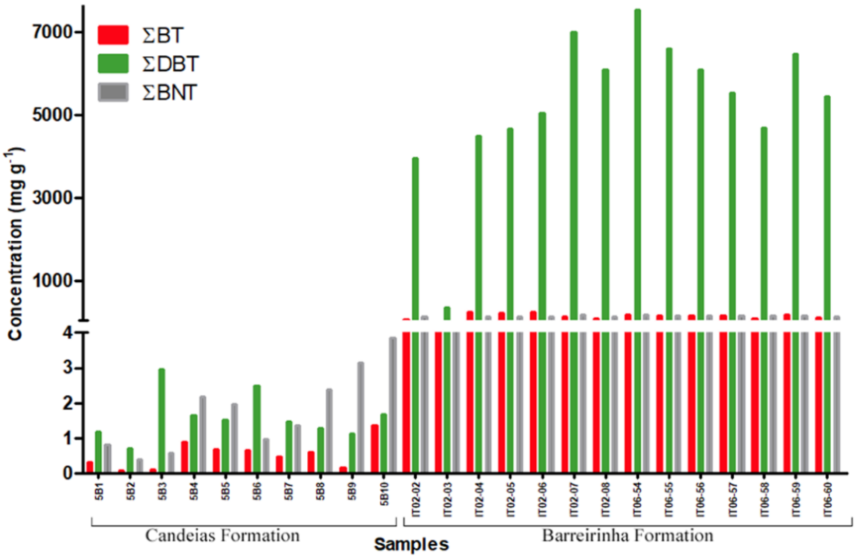

Figure 6. Histogram of the concentrations of benzothiophenes (∑BT), dibenzothiophenes (∑DBT), and benzonaphthothiophenes (∑BNT) in the samples.

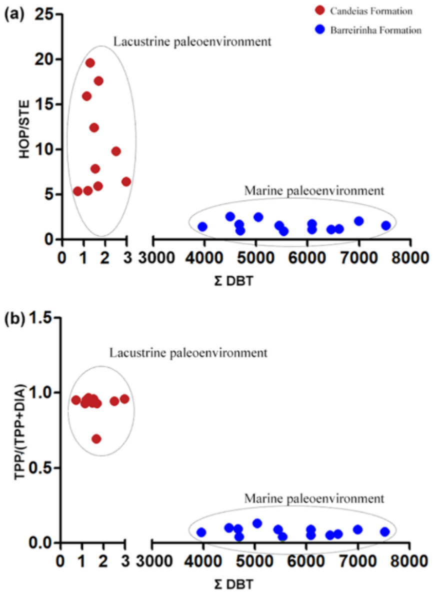

Figure 7. Relationships between: (a) dibenzothiophenes (∑DBT) and the hopanes/steranes (HOP/EST) ratio and (b) TPP/TPP + DIA ratio of samples from the Candeias Formation (Recôncavo basin) and Barreirinha Formation (Amazon basin). Red dotted points are Candeias Formation. Blue dotted points are the Barreirinha Formation.

MBT/2-MBT ratio allows close inspection of the data to evaluate crude oils from different paleoenvironments.[12,49] The application of this ratio (Figure 8) in samples indicates the predominance of the lacustrine paleoenvironment in the Candeias Formation (values ≤ 5.22, average of 1.50) and marine paleoenvironment in the Barreirinha Formation (values ≤ 14.42, average of 6.88).

In the outcrops, vertical variations in the concentrations of BTs and, consequently, in the values of the 3-MBT/2-MBT ratio are observed. Such variations may reflect changes over the time of sediment deposition of the geological formations in question. However, this fact has not been completely understood since no correlations were observed between the concentrations of BTs and other geochemical parameters, such as TOC, Rock-Eval pyrolysis data, or saturated biomarkers data.

BTs/DBTs ratio >3 indicates marine paleoenvironments, from 1 to 3 marine or lacustrine paleoenvironments, and <1 suggests lacustrine paleoenvironments.[8] DBTs are predominant over BTs for the entire set of samples studied (Figure 6). However, the application of the ∑BTs/∑DBTs ratio to the samples (Figure 9) exhibits contradictory values to those reported previously,[8] with marine samples showing the lowest values (<0.2). This behavior can be explained by the influence of the depositional paleoenvironment on these compounds, where higher concentrations of DBTs result in lower values in the ∑BTs/∑DBTs ratio in samples from marine paleoenvironment (Barreirinha Formation). Thermochemical sulfate reduction (TSR) associated with relatively high temperatures between 100 and 180 °C can be the abiotic alteration process responsible for the high DBT values observed in the Barreirinha Formation samples.

The variations in ∑DBT and TOC in the outcrop of the Candeias Formation show an inversely proportional relationship, while in the Barreirinha Formation, there is a proportional increase in DBT and TOC (Figure 10a,b). These results could indicate that the source of organic matter exerts some control over the distribution of DBTs. On the other hand, in the evaluation of the ∑DBT with the geochemical parameters such as hydrogen index (HI), HOP/STE, and Pr/Ph the vertical variations do not agree. Thus, there is uncertainty as to whether the DBT is predominantly controlled by environmental, source, or both factors.

4.3. Input of Organic Matter.

The evaluation of organic matter input by S-markers can amplify the interpretations generated from saturated biomarkers already extensively described in the literature. Therefore, combining S-markers with biomarkers and other geochemical data allows for increased

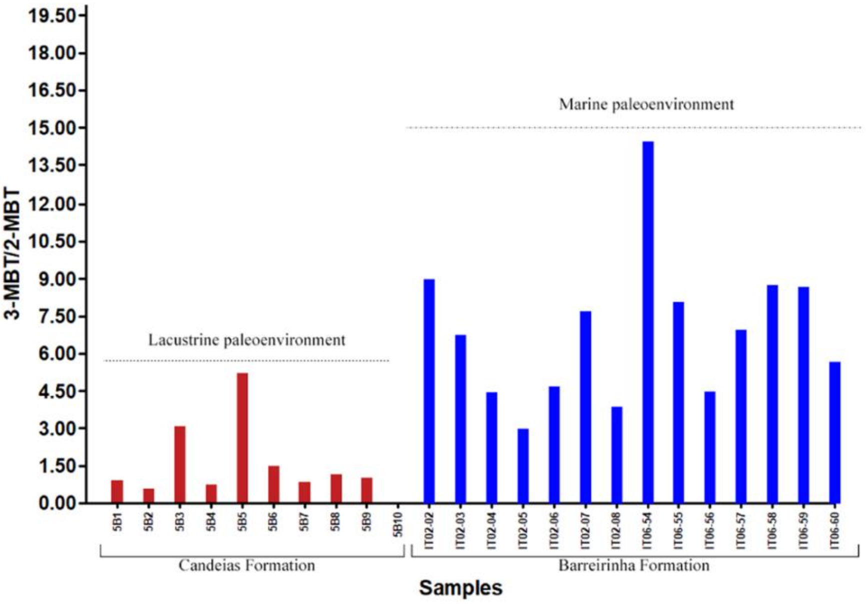

Figure 8. 3-MBT/2-MBT ratio for depositional paleoenvironment interpretations of samples from the Candeias Formation (Recôncavo basin) and Barreirinha Formation (Amazon basin).

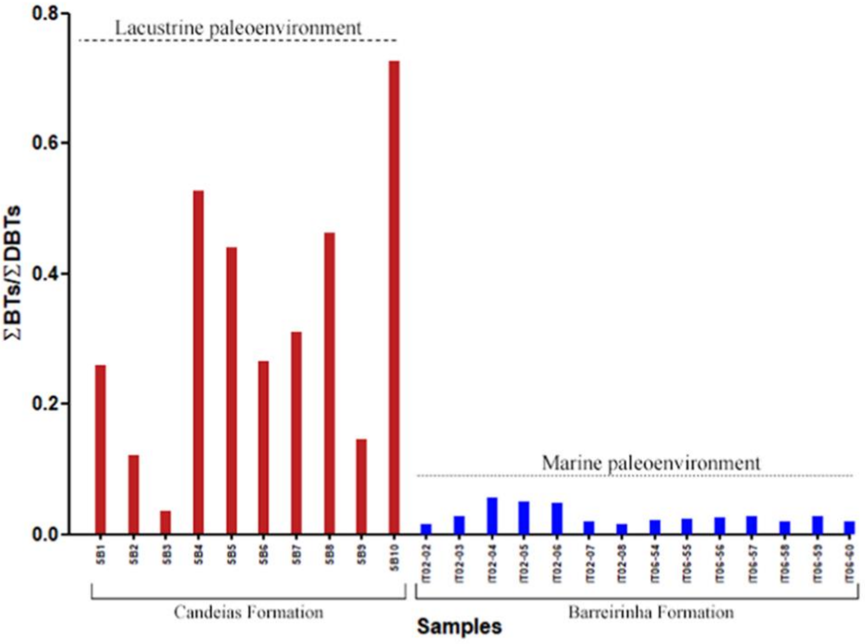

Figure 9. $\sum$BTs/$\sum$DBTs ratio for depositional paleoenvironment interpretations of samples from the Candeias Formation (Recôncavo basin) and Barreirinha Formation (Amazon basin).

interpretations of organic matter input into depositional environments.

Although BNTs have no confirmed origin, a previous study carried out under aerobic conditions indicated that they could be microbially produced from BNT with *Pseudomonas*.[50] Recent studies have affirmed the possibility that BNTs originate from microbial action.[51−53] In the evaluation of the vertical variations in two outcrops (Figure 11), there is a similarity in the distribution of the sum of BNTs to the amounts of AOM, which is congruent with the idea that BNTs can come from microbial activity. Furthermore, the DBT/Phen ratio, which can provide information about the E_h conditions of depositional paleoenvironments,[10] shows different behavior in the outcrops (Table 3). For the Candeias Formation (Figure 11a), the DBT/Phen ratio varies proportionally with the BNTs and AOM values. In contrast, for the Barreirinha Formation (Figure 11b), the DBT/

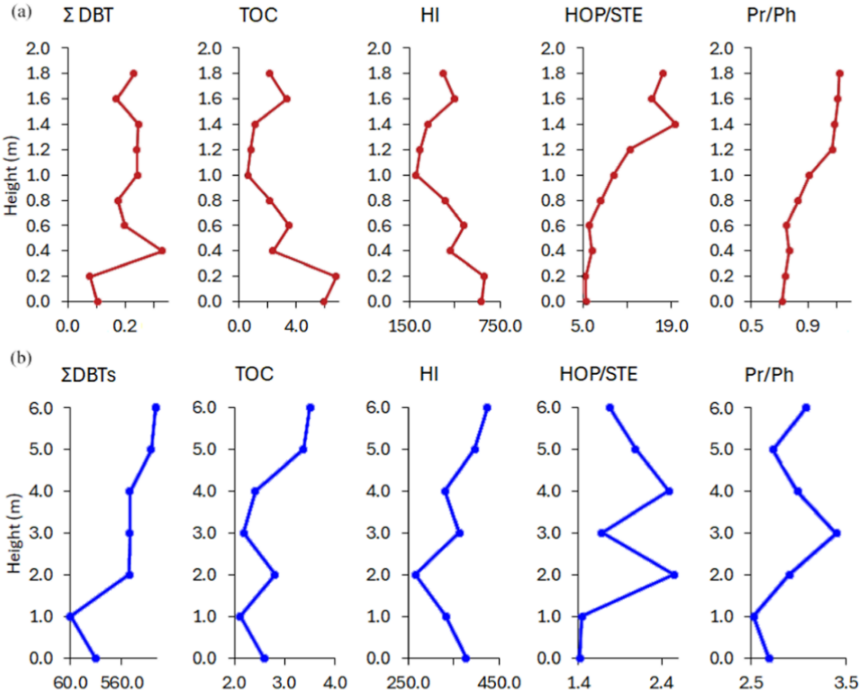

Figure 10. Vertical variations to ∑BNT, TOC, HI, HOP/STE, and Pr/Ph ratios from the (a) Candeias Formation and (b) Barreirinha Formation. For individual values, see Table S2.

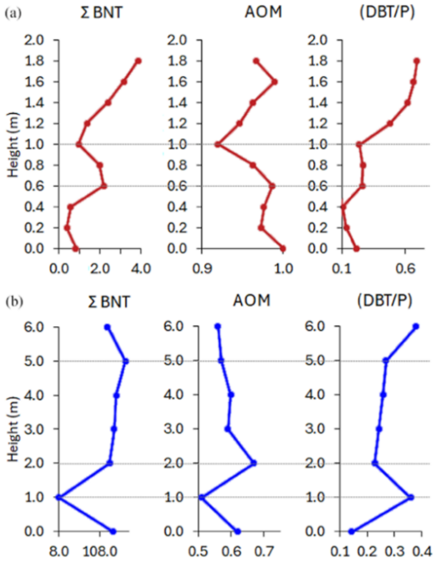

Figure 11. Vertical variations to BNTs, AOM, and DBT/Phen ratios from (a) Candeias Formation and (b) Barreirinha Formation.

Phen ratio varies inversely with the other factors under analysis. This behavior may be indicative that BNTs are generated from the AOM under varying E_h conditions (anoxic for the Candeias Formation and suboxic for the Barreirinha Formation).

In this sense, the abundance of BNTs suggests a microbial contribution to the source rocks that expelled the oils. The concentrations of BNTs in samples are very different (Figure 6), and their relative proportions allow the assessment of the type of organic matter in the depositional paleoenvironment. The BNT concentrations indicate diverse microbial participation in the alteration of the samples. The ternary diagram (Figure 12a) shows the BNTs isomers with the distribution of samples into two groups. In addition, the chart from regular steranes C_{27}, C_{28}, and C_{29} (Figure 12b) indicates the presence of different organic matter inputs and algae inputs (relative proportion of C_{27} sterane). The C_{29} concentration in samples indicate terrestrial material imputs.[54,55]

Table 3. Classification of Depositional Paleoenvironments According to the Redox Condition

zone	redox conditions	[Fe]/[S]	Pr/Ph	DBT/Phen
1A, 1B	anoxic/sulfidic[a]	[Fe] < [S]	<1	>1
2	anoxic/fermentative	[Fe] > [S]	<1	<1
1A, 1B, 2	anoxic/hypersaline	variable	<0.4	variable
3	anoxic/nonsulfidic[a]	[Fe] > [S]	1−3	<1
4	periodically oxic or dysoxic	[Fe] ≫ [S]	>3	<1

[a] The term sulfidic refers to conditions where free H_2S_n species are present. [Fe] represents the concentration of iron capable of reacting with reduced sulfur to form iron sulfides. [S] represents the concentration of reduced sulfur capable of reacting with iron to form iron sulfides. Adapted from Hughes et al.[10]

The C_{27}/C_{29} steranes ratio (Figure 12b) indicates inputs of algal and terrigenous material predominant in the Candeias and Barreirinha Formations, respectively. However, the results of the relative proportions of BNT (Figure 12a) indicate an isomeric differentiation among the samples under study. The benzo[*b*]naphtho[2,1-*d*]thiophene isomer is present in higher concentrations in samples from the Candeias Formation of freshwater lacustrine origin (Figure 12a). The predominance of the benzo[*b*]naphtho[1,2-*d*]thiophene isomer is noted in the

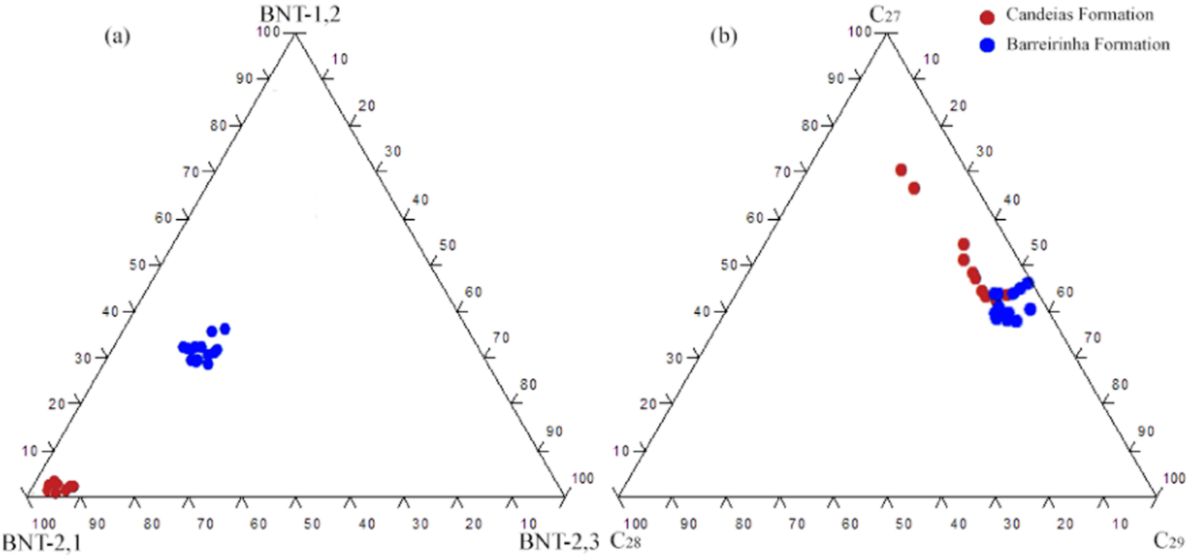

Figure 12. Ternary diagrams for input evaluation. (a) Isomeric distribution of benzothiophenes and (b) distribution of regular steranes C_{27}, C_{28}, and C_{29} for samples.

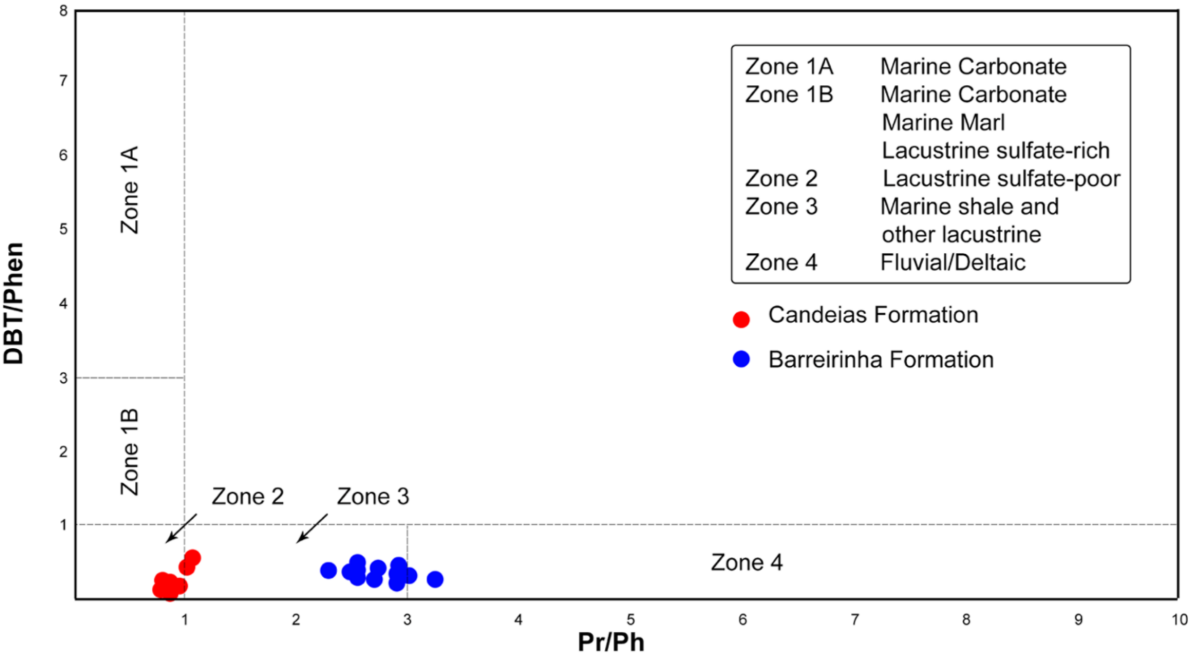

Figure 13. Cross plot of pristane/phytane (Pr/Ph) vs dibenzothiophene/phenanthrene (DBT/PHEN). Red dot points are Candeias Formation. Blue dot points are Barreirinha Formation.

Barreirinha Formation, of marine origin (Figure 12a). This observation indicates that the isomeric distribution of BNTs has the potential to distinguish marine and nonmarine depositional environments. Therefore, the benzonaphthothiophenes isomers differences may be associated with different origins (marine or lacustrine) or different oxygenation conditions in depositional paleoenvironments, a fact that alters microbial production[56]

4.4. Depositional Paleoenvironment Conditions. The DBT/Phen ratio, together with the Pr/Ph ratio (Figure 13), provides a powerful way to classify source rock depositional paleoenvironments relative to their most important microbiological and chemical processes.[10] Applying the relationship between the DBT/Phen and Pr/Ph ratios for the samples from both Formations (Candeias and Barreirinha) indicates zones 2 and 3 as defined by Hughes et al.[10] These zones distinguish the depositional paleoenvironments of the samples in studies compatible with the interpretations already made: lacustrine paleoenvironment for samples from the Candeias Formation

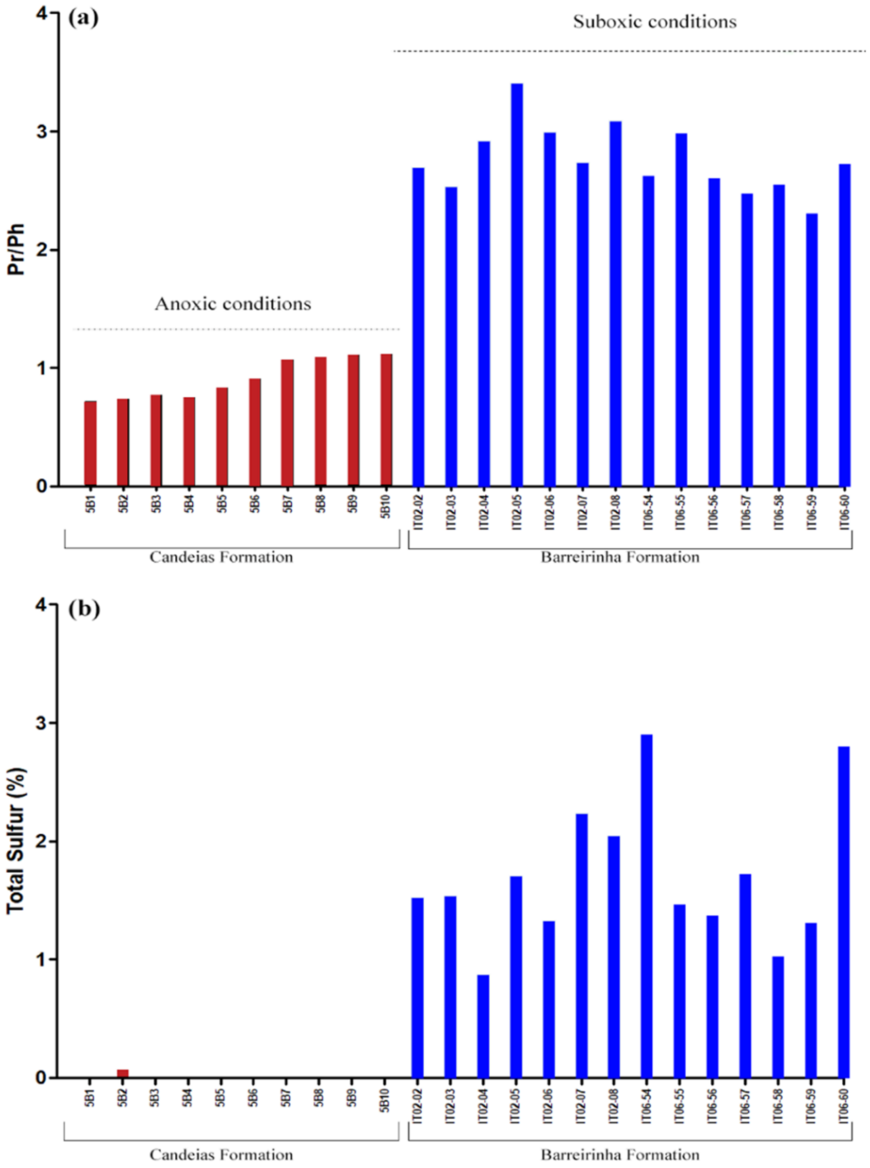

Figure 14. (a) values for the pristane/phytane ratio (Pr/Ph) and (b) total sulfur for the samples of Candeias and Barreirinha Formations applied to evaluate the depositional paleoenvironmental conditions of these formations. For individual values, see Table S2.

and marine paleoenvironment for samples from the Barreirinha Formation.

The isoprenoids Pr/Ph ratio indicates oxidizing (Pr/Ph > 1) or reducing (Pr/Ph < 1) conditions of the depositional paleoenvironment of the organic matter.[13] In Figure 14a, the differences between the samples from the Candeias Formation (deposited under more reducing conditions) and the Barreirinha Formation (deposited under more oxidizing conditions) confirm the previous depositional conditions observed.

Variations in the values for the Pr/Ph ratio can be noted in the vertical sections of the outcrops (Figure 14a). In the Candeias Formation, values grade linearly from base to top, with 0.72 at the base and 1.12 at the top. In the outcrops of the Barreirinha Formation, greater vertical variations are observed with values varying between 2.30 and 3.40 (Table S2). Although values greater than 1 were noted in all outcrops studied, due to the good preservation of organic matter, depositional paleoenvironments with these high values were interpreted as presenting suboxic conditions.

The DBT/Phen ratio also reflects the availability of reactive sulfur, primarily hydrogen sulfide (H_2S), and polysulfides (H_2S_n), for interaction with organic matter.[10] Candeias and Barreirinha Formations had low values for this ratio (Figure 14b).

Deposited in a freshwater lacustrine context, samples from the Candeias Formation present low values for the DBT/Phen ratio (Table S3) due to the sulfate concentration in freshwater that varies between ∼10 and 500 μM, which is many times lower than in seawater (28 mM).[57] In this case, the low E_h may be caused by fermentation and not sulfate reduction.[48] Therefore, Pr/Ph < 1 and DBT/Phen <1 may be due to fermentation under low sulfate concentrations.

Barreirinha Formation samples have high values of total sulfur (Figure 14b), originating from the reduction of sulfate present in the marine paleoenvironment. However, the DBT/Phen ratio values for these samples are low (Table S3). This behavior is similar to a previous study with crude oils, where levels of organic sulfides were higher than thiophenes.[58] Furthermore, Barreirinha Formation source rocks were deposited under conditions of sulfate reduction, and the supply of reactive iron was greater than that of the sulfide. The presence of pyrite in samples from the Barreirinha Formation is geological evidence of this process.[23]

The DBT/Phen values for the outcrops remain between 0 and 1 along the vertical sections, varying between 0.06 and 0.64 in the Candeias Formation and between 0.14 and 0.44 in the Barreirinha Formation. Therefore, it is possible to classify the samples in zones 2 (Candeias Formation) and 3 (Barreirinha Formation), according to the proposed by Hughes et al.[10] (Table 4).

4.5. Thermal Maturation. Sulfur compounds are good markers of the thermal maturation stage due to their highest stability at elevated temperatures.[8,9] Generally, the concentrations of BTs, DBTs, and BNTs increase with thermal maturation. Diagnostic ratios such as 4,6-DMDBT/2,4,6-TMDBT and 2,4,6-TMDBT/(2,4,7 + 2,4,8)-TMDBT are employed to evaluate this parameter.[1]

The low values of the S-markers ratios (Table 2) for all samples analyzed indicated that they are thermally immature, in accordance with the interpretations reported in the literature for these compounds.[49,59] In addition, low values of the ratio $T_s/(T_s + T_m)$ and T_{max} values less than 440 °C confirm the thermal immaturity of the samples for hydrocarbon generation.[13]

In addition, there is a correlation between the maturation values tested in kerogen samples (evaluated by T_{max} from Rock-Eval pyrolysis) and the values calculated from molecular parameters. For the entire set of samples, the T_{max} values are low (less than 440 °C), ranging between 412 and 438 °C for the samples from the Candeias Formation and between 425 and 437 °C for the samples from the Barreirinha Formation. The ratio of biomarkers $T_s/(T_s + T_m)$ also shows low values for the samples under study, attesting to thermal immaturity of the samples for hydrocarbon generation.[13]

Although they allow the same interpretation regarding thermal immaturity, the values calculated from the molecular ratios are not directly proportional to the T_{max} values, indicating that both analyses must be performed in such a way that they corroborate the other.

5. CONCLUSIONS

The application of GC–MS/MS instead of GC–MS for individual quantification of twenty-one S-markers allowed an increase in the reliability and accuracy of data results. The results obtained by S-markers allowed us to evaluate and prove distinctions and similarities between the source rocks, defining the origin of organic matter, the organic matter input, the depositional paleoenvironment conditions, and the level of thermal maturity of the samples.

The samples from the Recôncavo basin, of lacustrine origin, have lower concentrations of BT, DBT, and BNT, while samples from the Amazon basin, of marine origin, present high concentrations of these compounds. There is an inversely proportional relationship between variations in ∑DBT and

Table 4. Diagnostic Ratios of Sulfur Markers and Biomarkers Used to Evaluate Thermal Maturation in the Outcrop Samples

	Candeias formation									
ratio	SB01	SB02	SB03	SB04	SB05	SB06	SB07	SB08	SB09	SB10
4,6-DMDBT/2,4,6-TMDBT	0.35	0.57	0.45	0.25	0.34	0.43	0.34	0.34	0.32	0.55
2,4,6-TMDBT/2,4,7 + 2,4,8-TMDBT	0.43	0.42	0.68	0.56	0.54	0.72	0.76	0.69	1.01	0.65
$T_s/T_s + T_m$	0.03	0.05	0.02	0.02	0.05	0.02	0.02	0.01	0.03	0.04
T_{max} (°C)	434	437	438	438	436	412	414	416	415	415

	Barreirinha formation													
ratio	IT02-02	IT02-03	IT02-04	IT02-05	IT02-06	IT02-07	IT02-08	IT06-54	IT06-55	IT06-56	IT06-57	IT06-58	IT06-59	IT06-60
4,6-DMDBT/2,4,6-TMDBT	0.89	1.21	1.13	1.16	1.00	1.07	5.37	1.07	0.99	1.17	1.22	1.08	1.16	1.03
2,4,6-TMDBT/2,4,7 + 2,4,8-TMDBT	0.34	0.35	0.37	0.34	0.34	0.34	0.32	0.38	0.32	0.35	0.38	0.37	0.35	0.36
$T_s/T_s + T_m$	0.16	0.17	0.16	0.13	0.14	0.15	0.17	0.15	0.16	0.15	0.17	0.02	0.14	0.17
T_{max} (°C)	435	436	433	437	436	434	433	426	434	434	428	427	429	425

TOC in the outcrop of the Candeias Formation, while in the Barreirinha Formation, this proportion increases. This observation is indicative that the source of organic matter exerts some control of the distribution of DBTs.

The relative proportions of the BNT-2,1, BNT-1,2, and BNT-2,3 isomers, in addition to the C_{27}, C_{28}, and C_{29} regular steranes, indicated that the inputs of algal and terrigenous materials were predominant in the Candeias and Barreirinha Formations, respectively, with different levels of microbial participation. In addition, in the vertical variations of the outcrops, there is a similarity in the distribution of the sum of BNTs with the amounts of AOM, which indicates that BNTs can come from microbial activity.

Similarities between DBT/Phen concentrations and Pr/Ph values indicated that S-markers are affected by the conditions of the depositional paleoenvironments. Candeias Formation presented low values for the DBT/Phen and Pr/Ph ratios due to the absence of sulfate in the paleodepositional environment and the fermentation of organic matter. Although the source rocks of the Barreirinha Formation were formed under conditions of sulfate reduction, the supply of reactive iron exceeded that of sulfide, resulting in the predominant formation of pyrite.

The thermal maturity was evaluated using T_{max} values from Rock-Eval pyrolysis from kerogen samples, and the molecular values were calculated using S-markers. Low values to ratios 4,6-DMDBT/2,4,6-TMDBT and 2,4,6-TMDBT/(2,4,7 + 2,4,8)-TMDBT associated with low values to T_{max} (less than 440 °C) indicated that the Formations are thermally immature for hydrocarbon generation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c07344.

> Palynofacies data, saturated biomarkers, and BNTs concentrations in samples (Table S1); TOC, total sulfur, Rock-Eval pyrolysis parameters (Table S2); diagnostic ratios and concentration of saturated and S-markers in samples (Table S3); GC–MS chromatograms of the biomarkers in saturated fractions (Figures S1–S4) (PDF)

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5 CONCLUSÕES GERAIS

O emprego de marcadores nitrogenados e sulfurados associados a parâmetros geoquímicos tradicionais se mostrou eficiente para refinar as interpretações dos paleoambientes deposicionais das rochas geradoras de petróleo representadas pelas Formações Candeias (Bacia do Recôncavo) e Barreirinha (Bacia do Amazonas).

Avaliados nas rochas geradoras de petróleo citadas acima, os N-marcadores e S-marcadores evidenciaram distinções e similaridades entre as formações geológicas em estudo, definindo a origem da matéria orgânica, o *input* e as condições paleoambientais deposicionais das amostras.

Amostras da rocha geradora da Bacia do Recôncavo, de origem lacustre, apresentam, no geral, concentrações mais baixas de compostos nitrogenados (carbazóis (CA), metilcarbazóis (MCA) e dimetilcarbazóis (DMCA)) e sulfurados (benzotiofenos (BT), dibenzotiofenos (DBT) e benzonaftotiofenos (BNT)), enquanto amostras da Bacia do Amazonas, de origem marinha, apresentam altas concentrações desses compostos. Exceção para os compostos nitrogenados básicos (quinolina (QUIN) e 4-metilquinolina (4-MQUIN)), em que as amostras de origem lacustre apresentaram maiores concentrações que aquelas de origem marinha.

Diagramas ternários utilizando isômeros de N-marcadores (1-MCA, 2-MCA e 4-MCA) e S-marcadores (BNT-1,2, BNT-2,1 e BNT-2,3), em conjunto com diagrama ternário utilizando esteranos regulares (C_{27}, C_{28} e C_{29}), foram efetivos na análise do *input* de matéria orgânica no tempo de deposição das rochas geradoras em estudo, destacando que as algas foram os principais constituintes preservados nas formações geradoras e destacando diferenças isoméricas inerentes ao ambientes deposicionais (lacustre e marinho), que ajudam a entender o comportamento desses compostos nos diferentes ambientes.

Conformidades e correlações entre os valores da razão pristano/fitano e concentrações dos benzocarbazóis e relação DBT/Phen indicam os N-marcadores e S-marcadores são afetados pelas condições redox dos ambientes deposicionais.

Portanto, este estudo demonstra a eficiência dos N-marcadores e S-marcadores nas interpretações paleoambientais de rochas geradoras de petróleo, pois, ainda que sejam encontrados em baixas concentrações, as suas utilizações conferem maior robustez aos estudos geoquímicos, permitindo entendimentos mais apurados e embasando decisões mais assertivas acerca dos elementos que compõem um sistema petrolífero.

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MATERIAIS SUPLEMENTARES DO ARTIGO USE OF NITROGEN MARKERS TO ASSESS SOURCE ROCK PALEODEPOSITIONAL ENVIRONMENT OF THE CANDEIAS (RECÔNCAVO BASIN) AND BARREIRINHA (AMAZONAS BASIN) FORMATIONS

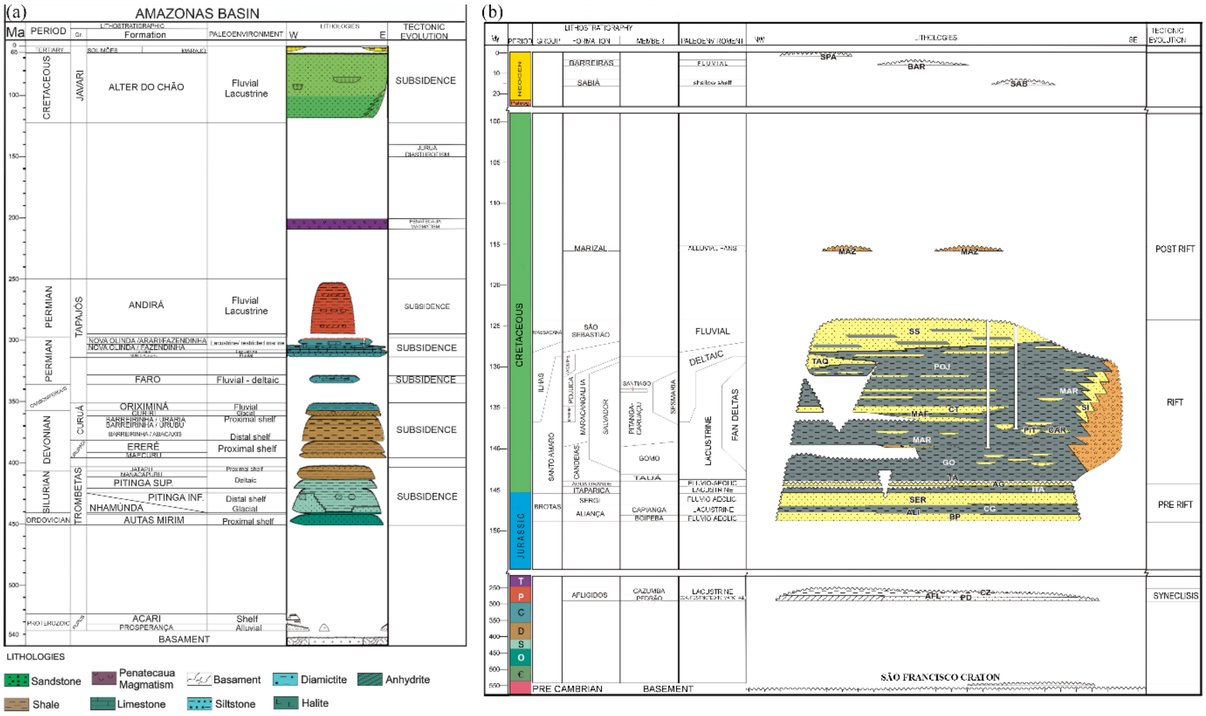

Figure S1 - Stratigraphic charts: (a) Amazonas Basin. (b) Recôncavo Basin, adapted from Penteado and Behar (2000), Souza et al. (2021).

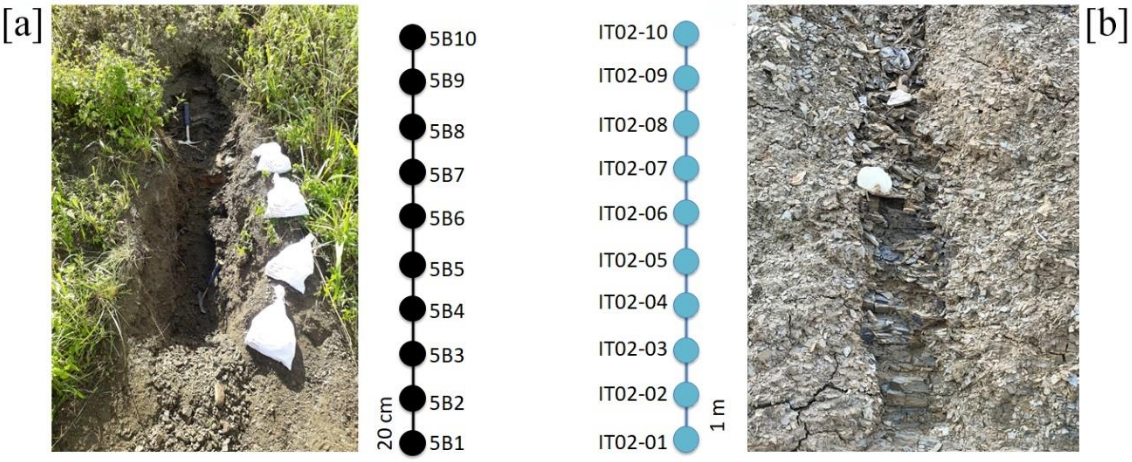

Figure S2 - Sampling points with vertical spacing in outcrops of the Candeias (a) and Barreirinha (b) formations.

MATERIAIS SUPLEMENTARES DO ARTIGO ORGANIC SULFUR MARKERS AS PROXIES OF DEPOSITIONAL PALEOENVIRONMENTS RELATED TO RECÔNCAVO AND AMAZON BASINS, BRAZIL

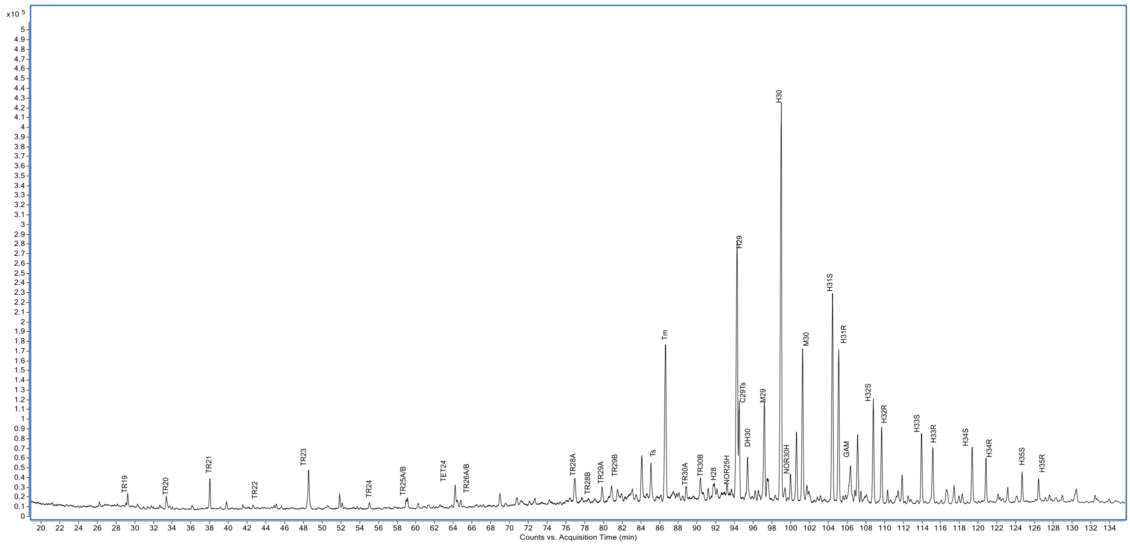

Figure S1 - Representative chromatogram from m/z 191, Barreirinha Formation.

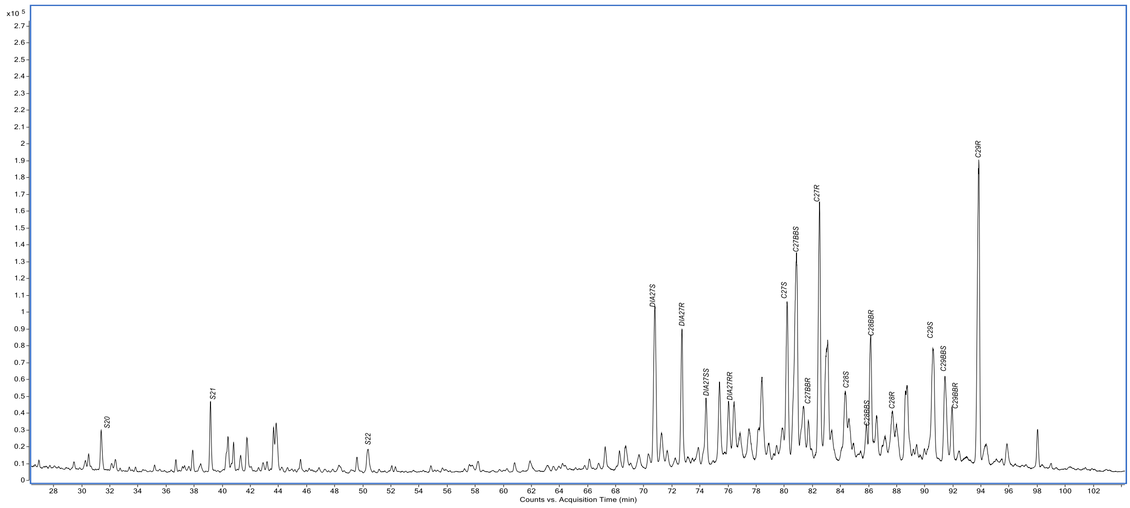

Figure S2– Representative chromatogram from m/z 217, Barreirinha Formation.

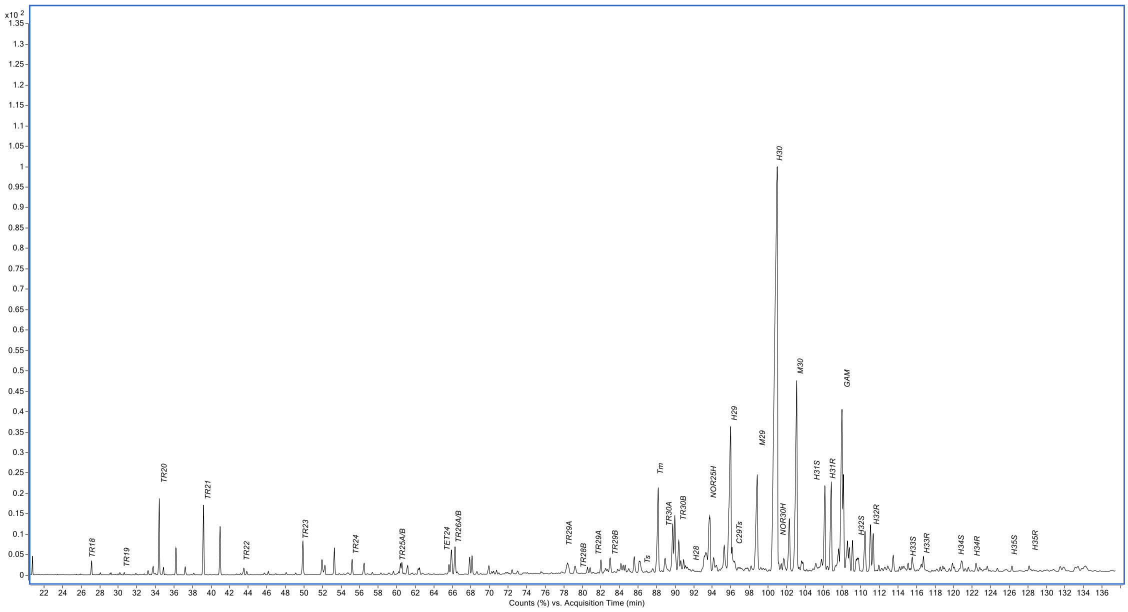

Figure S3– Representative chromatogram from m/z 191, Candeias Formation.

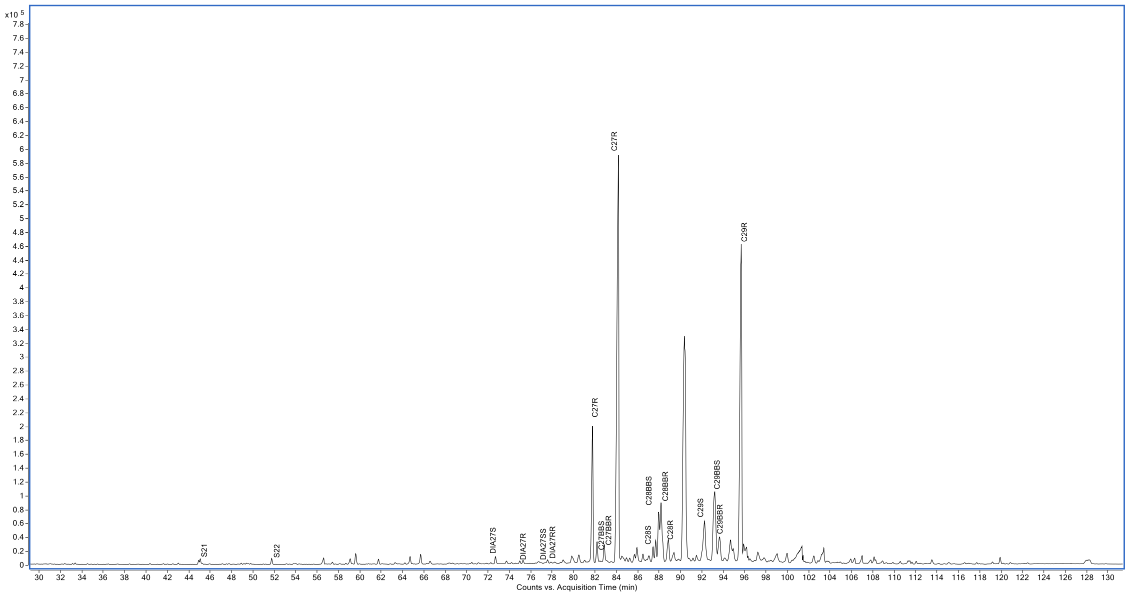

Figure S4– Representative chromatogram from m/z 217, Candeias Formation.

Table S1 - Palynofacies data, saturated biomarkers and proportions of BNTs from the samples under study

Sample	AOM (%)	Palynomorphs (%)	Phytoclats (%)	HOP/STE	TPP/TPP+DIA	C_{27} sterane (%)	C_{28} sterane (%)	C_{29} sterane (%)	BNT-2,1 (%)	BNT-1,2 (%)	BNT-2,3 (%)	Σ BNT
5B1	95%	1.33%	3.66%	5.48	0.95	48.57	2.87	48.56	95.23	2.75	2.02	0.83
5B2	92.30%	5%	2.60%	5.41	0.95	48.42	2.98	48.60	96.05	1.68	2.27	0.40
5B3	92.66%	2.66%	4.66%	6.45	0.96	50.70	3.01	46.28	94.12	3.32	2.56	0.58
5B4	93.66%	3.66%	2.68%	5.95	0.69	52.03	2.94	45.03	94.64	2.28	3.08	2.19
5B5	91.33%	4%	4.66%	7.86	0.96	55.04	2.92	42.03	93.42	2.70	3.88	1.98
5B6	87%	5%	8%	9.84	0.95	55.97	3.02	41.01	91.72	2.41	5.87	0.97
5B7	90%	3.66%	6.34%	12.43	0.93	59.44	2.65	37.91	90.83	2.40	6.77	1.37
5B8	91.33%	2.66%	6.01%	19.65	0.97	88.15	4.12	7.73	92.68	1.53	5.79	2.40
5B9	94.66	3%	2.33%	15.95	0.93	61.16	2.62	36.23	95.19	0.76	4.05	3.16
5B10	91.66%	4.33%	4.01%	17.62	0.93	91.34	3.71	4.95	93.72	2.03	4.24	3.86
IT02-02	57%	40%	4%	1.42	0.07	39.40	8.48	52.11	54.97	31.92	13.11	140.72
IT02-03	46%	50%	3%	1.45	0.08	39.56	10.33	50.12	55.46	29.80	14.74	8.18
IT02-04	62%	34%	3%	2.55	0.10	37.98	7.17	54.85	54.54	29.19	16.26	131.54
IT02-05	54%	43%	2%	1.68	0.09	39.66	7.91	52.43	50.42	31.09	18.50	142.92
IT02-06	55%	41%	3%	2.49	0.13	38.39	8.77	52.83	49.54	31.72	18.75	148.20
IT02-07	52%	47%	1%	2.09	0.09	38.54	10.39	51.07	45.84	36.30	17.86	170.67
IT02-08	51%	47%	1%	1.78	0.09	43.61	7.62	48.76	48.41	35.74	15.85	126.88
IT06-54	66%	33%	1%	1.56	0.08	40.59	9.06	50.34	53.32	32.14	14.54	173.36
IT06-55	69%	29%	3%	1.19	0.06	43.75	8.3	47.95	54.24	31.80	13.96	168.04
IT06-56	59%	38%	2%	1.11	0.05	44.06	8.02	47.93	55.48	32.33	12.19	163.01
IT06-57	67%	31%	2%	0.94	0.04	45.83	1.41	52.76	54.16	29.72	16.12	166.90
IT06-58	63%	35%	2%	1.04	0.04	40.56	3.2	56.24	52.63	28.74	18.63	162.25
IT06-59	67%	32%	3%	1.13	0.05	43.89	4.67	51.44	51.74	30.61	17.64	158.97
IT06-60	60%	36%	3%	1.58	0.09	44.99	3.24	51.77	52.18	32.29	15.53	149.29

Table S2 - TOC, total sulfur, Rock-Eval pyrolysis parameters and Pr/Ph ratio of the samples under study

Sample	TOC (%)	IR (%)	Sulfur (%)	(S1) (mg/g)	(S2) (mg/g)	(S3) (mg/g)	Tmax (ºC)	HI	OI	PI	Pr/Ph
5B1	5.91	74.19	<0,05	0.35	27.11	0.48	434	625	2	0.013	0.72
5B2	6.77	71.4	0.07	0.47	29.86	0.35	437	646	8	0.015	0.74
5B3	2.35	72.32	<0,05	0.12	7.48	0.07	438	418	4	0.016	0.77
5B4	3.51	75.23	<0,05	0.21	14.06	0.11	438	511	4	0.015	0.75
5B5	2.15	75.5	<0,05	0.11	7.07	0.1	436	386	5	0.015	0.83
5B6	0.63	91.01	<0,05	0.04	1.41	0.05	412	193	7	0.028	0.91
5B7	0.83	84.29	<0,05	0.05	2.1	0.1	414	221	11	0.023	1.07
5B8	1.12	82.52	<0,05	0.08	3.3	0.09	416	270	7	0.024	1.09
5B9	3.32	79.88	<0,05	0.19	9.66	0.25	415	451	12	0.019	1.11
5B10	2.16	78.89	<0,05	0.09	5.36	0.12	415	375	8	0.017	1.12
IT02-02	2.59	99.94	1.52	0.15	9.77	0.1	435	377	5	0.015	2.69
IT02-03	2.11	99.92	1.53	0.12	7.3	0.18	436	333	8	0.016	2.53
IT02-04	2.81	99.93	0.87	0.13	7.55	0.26	433	266	9	0.017	2.91
IT02-05	2.19	99.93	1.7	0.13	8.1	0.1	437	363	4	0.016	3.40
IT02-06	2.42	99.93	1.32	0.12	8.28	0.12	436	331	5	0.014	2.99
IT02-07	3.38	99.94	2.23	0.21	13.3	0.13	434	396	4	0.016	2.73
IT02-08	3.51	99.95	2.04	0.26	14.72	0.13	433	424	4	0.017	3.08
IT06-54	5.14	99.86	2.9	0.33	10.18	0.18	426	270	5	0.031	2.62
IT06-55	4.82	99.93	1.46	0.31	20.01	0.82	434	444	18	0.015	2.98
IT06-56	5.56	99.94	1.37	0.47	26.67	1.07	434	532	21	0.017	2.60
IT06-57	3.88	99.89	1.72	0.29	11.86	0.19	428	326	5	0.024	2.47
IT06-58	3.86	99.9	1.02	0.2	10.68	0.24	427	291	7	0.018	2.55
IT06-59	3.36	99.94	1.31	0.22	11.06	0.31	429	346	10	0.02	2.30
IT06-60	3.7	99.89	2.8	0.29	10.57	0.05	425	305	1	0.027	2.72

TOC: total organic carbon; IR: insoluble risidue, HI: hydrogen index; OI: oxygen index; PI: production index.

Table S3 – Ratios using S-markers and Ts/Ts+Tm ratio of the samples under study

Sample	3-MBT/2-MBT	ΣBTs/ΣDBTs	DBT/PHEN	4,6-DMDBT/2,4,6-TMDBT	2,4,6-TMDBT/(2,4,7 + 2,4,8)-TMDBT	Ts/(Ts+Tm)
5B1	0.90	0.26	0.16	0.35	0.43	0.03
5B2	0.59	0.12	0.08	0.57	0.42	0.05
5B3	3.08	0.04	0.06	0.45	0.68	0.02
5B4	0.74	0.53	0.21	0.25	0.56	0.02
5B5	5.22	0.44	0.22	0.34	0.54	0.05
5B6	1.48	0.27	0.19	0.43	0.72	0.02
5B7	0.85	0.31	0.43	0.34	0.76	0.02
5B8	1.15	0.46	0.57	0.34	0.69	0.01
5B9	1.00	0.15	0.62	0.32	1.01	0.03
5B10	0.03	0.73	0.64	0.55	0.65	0.04
IT02-02	8.98	0.02	0.14	0.89	0.34	0.16
IT02-03	6.73	0.03	0.36	1.21	0.35	0.17
IT02-04	4.43	0.06	0.23	1.13	0.37	0.16
IT02-05	2.97	0.05	0.24	1.16	0.34	0.13
IT02-06	4.68	0.05	0.26	1.00	0.34	0.14
IT02-07	7.69	0.02	0.27	1.07	0.34	0.15
IT02-08	3.86	0.02	0.38	5.37	0.32	0.17
IT06-54	14.42	0.02	0.43	1.07	0.38	0.15
IT06-55	8.07	0.02	0.44	0.99	0.32	0.16
IT06-56	4.47	0.03	0.39	1.17	0.35	0.15
IT06-57	6.94	0.03	0.34	1.22	0.38	0.17
IT06-58	8.75	0.02	0.29	1.08	0.37	0.02
IT06-59	8.66	0.03	0.38	1.16	0.35	0.14
IT06-60	5.66	0.02	0.30	1.03	0.36	0.17