

Organic Geochemistry of Shale Outcrop From the Morro Do Chaves Formation, Lowercretaceous, Sergipe-Alagoas Basin, Northeastern Brazil

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1 ORGANIC GEOCHEMISTRY OF SHALE OUTCROP FROM THE MORRO DO
2 CHAVES FORMATION, LOWER CRETACEOUS, SERGIPE-ALAGOAS BASIN,
3 NORTHEASTERN BRAZIL

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20 **Keywords:** Barremian; Depositional Environment; Marine Incursions; Organic
21 Geochemistry; Proto-South Atlantic.

1 **ABSTRACT**

2 The Morro do Chaves Formation (Barremian-Aptian) was deposited in a complex
3 lake rift-system with marked oscillations in salinity related to climatic fluctuations
4 during the Lower Cretaceous. However, the majority of geochemical studies in the
5 locality are focused on coquina, while the depositional origin of shales is poorly known.
6 In this paper, we present the geochemical characterization of the organic matter as
7 well as the paleodepositional conditions of shales of the Morro do Chaves Formation
8 (InterCement Quarry). The positive relationship between Hydrocarbon Index (HI) and
9 Total Organic Carbon (TOC) revealed the presence of type I and II kerogen, which
10 reflects a predominantly lacustrine biomass preserved in a redox paleoenvironment.
11 This hypothesis is supported by the presence of pyrite and fluorescent amorphous
12 organic matter. However, although the data analyzed reflect a strong continental
13 influence, they are also indicative of lagoon ecosystems. In addition, the relative
14 abundance of type II kerogen was interpreted as an indicator of probable redox
15 paleoenvironments, deposited during calm and humid periods. Moreover, the
16 presence of *n*-alkanes nC_{16} - nC_{22} in P05 was interpreted as an indicator of a
17 transitional paleoenvironment with bacterial action on algal material.
18 These data reinforce the interpretation of a disturbed paleoenvironmental setting,
19 characterized by possible periodic marine incursions associated with tectonic–climatic
20 oscillations during the breakup of Gondwana, as documented at the InterCement
21 Quarry.

1. INTRODUCTION

The Early Cretaceous is characterized by significant paleoclimatic, paleoceanographic, and paleogeographic changes that allowed the distribution of marine biota on a worldwide scale [1-4]. Moreover, this period is marked by the break-up of Gondwana and the opening of the South Atlantic Ocean [3,5].

Evidence of the break-up of Gondwana can be observed along the Brazilian and African continental marginal basins, characterized by relatively continuous onshore and offshore Early Cretaceous records [3,6]. However, the most remarkable marine stratigraphic record of this period is observed in the Sergipe-Alagoas Basin, located on the northeastern Brazilian Continental Margin [4, 7-9].

The Morro do Chaves Formation (Figure 1) belongs to the Coruripe Group and is composed of a mixed carbonate-siliciclastic succession deposited during the Rift and Post-rift stages of the Sergipe-Alagoas Basin [3, 8-10]. In addition, the geological record of the Morro do Chaves Formation is representative of a complex lake rift-system with marked oscillations in salinity related to climatic fluctuations during the Lower Cretaceous (Barremian-Aptian) [8, 9, 12-16].

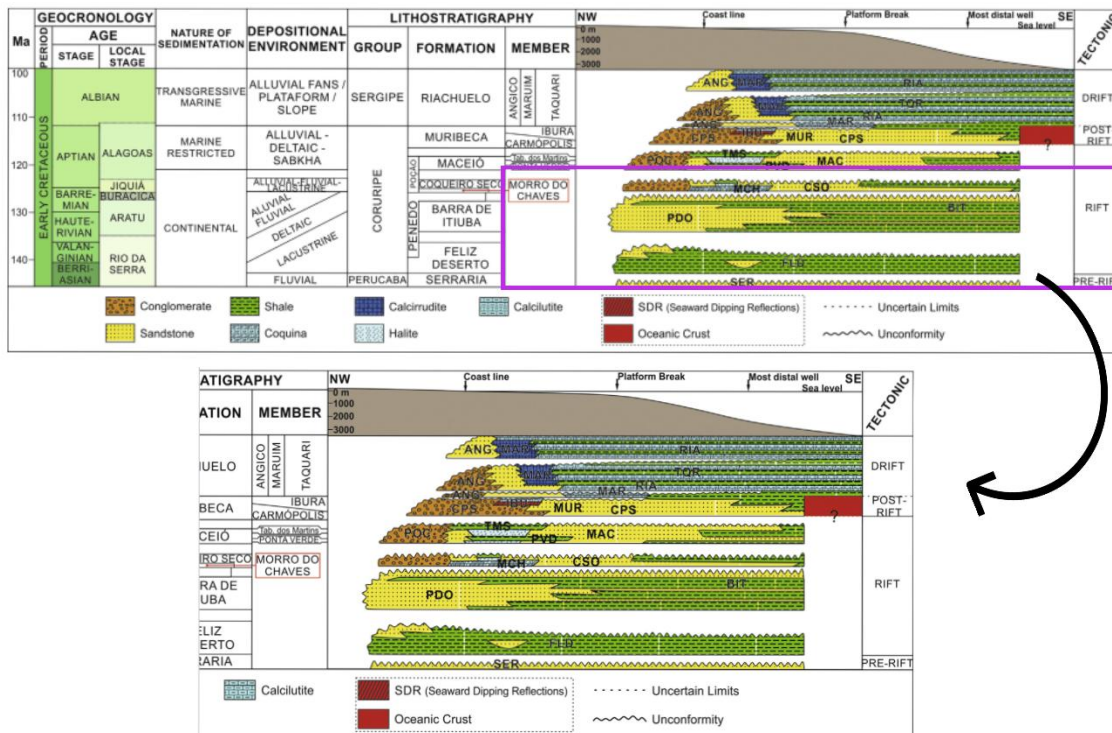


Fig.1 Stratigraphic framework of Sergipe-Alagoas Basin (modified from Garcia et al., 2018). Abbreviations: SER: Serraria Formation; FLD: Feliz Deserto Formation; PDO: Penedo Formation; BIT: Barra de Itiuba Formation; MCH: Morro do Chaves Formation; CSO: Coqueiro Seco Formation; POC: Poção Formation; MAC: Maceió Formation; TMS: Tabuleiro dos Martins Member; PVD: Ponta Verde Member; MUR: Muribeca Formation; CPS: Carmopolis

The most representative outcrop of the Morro do Chaves Formation is the Intercement Quarry (formerly Atol Quarry), located in Alagoas state [8, 9]. It is known as the most remarkable coquina outcrop in Brazil, composed mainly of an agglomeration of shells of bivalves and gastropods in association with shales rich in fish remains [9].

Due to their economic importance, several studies [7, 16, 17] cover the geological development, as well as the depositional paleoenvironment of coquinas in the Morro do Chaves Formation.

1 According to some authors [17, 18], the coquina of the Morro do Chaves
2 Formation is thought to have been deposited in a lacustrine setting during the Rift
3 phase of the Sergipe-Alagoas Basin, whose bivalve shells are supposed to have lived
4 in shallow and oxic lake waters. In addition, the absence of bivalves in live position as
5 well as the presence of fragmented shells could be indicative of an extensive transport
6 of bioclasts along paleolake shores, influenced by the action of storms, and reworked
7 by currents and waves [16, 17, 19].

8 On the other hand, the shales of the Morro do Chaves Formation have been
9 primarily examined for their paleontological content. Since the late 19th century,
10 numerous studies on flora and fauna have revealed a rich and significant fossil record.
11 However, the comprehension of the depositional development of these shales remains
12 poorly understood. Notable contributions include the studies with detailed evaluations
13 of the paleoenvironmental conditions of deposition in the locality [20, 21].

14 The authors suggest that the Morro do Chaves Formation was a lacustrine
15 paleoenvironment influenced by marine and continental episodic deposition which was
16 also a mass mortality scenario. These hypotheses were corroborated by
17 paleontological (i.e. aulopiform fishes, brackish mollusks, foraminiferans, poriferans
18 and microbivalvians) and paleoecological pieces of evidence that supported the
19 finding that Morro do Chaves Formation is a lacustrine, highly disturbed
20 paleoenvironment due to marine incursions in the northern sector of the Sergipe-
21 Alagoas Basin during the Lower Cretaceous [8, 9, 14, 16, 22-24].

22 In the most recent taphonomic study of the Morro do Chaves Formation the
23 authors also interpreted this unit as a seasonal lacustrine paleoenvironment, based
24 on cyclic deposits of coquinas, shales, and sandstones, as well as sedimentary
25 structures such as mud cracks [25]. The study also proposed a revised depositional

1 framework for the area, in which the Sergipe sector represents the paleolake margin,
2 whereas the Alagoas sector corresponds to a more distal lacustrine setting [25].

3 In addition, recent advances in paleontology and paleoecology [9, 25, 26]
4 emphasize the need for a more detailed paleoenvironmental framework for the Morro
5 do Chaves Formation. Accordingly, the main objective of this study is to evaluate the
6 geochemical characteristics of organic matter and extracts from shales of the Morro
7 do Chaves Formation (InterCement Quarry), in order to improve the understanding of
8 the depositional evolution of this system, using modern geochemical tools.

9 Among the most widely used geochemical methods, Total Organic Carbon
10 (TOC) is a fundamental parameter in the exploration and development of
11 unconventional shale reservoirs [27]. It provides semi-quantitative information on the
12 organic carbon content of rock samples, reflecting the production and preservation
13 conditions of the depositional environment [28-31].

14 Also, Rock-Eval pyrolysis is a rapid and widely used geochemical technique that
15 involves the programmed heating of rock samples under an inert (oxygen-free)
16 atmosphere to assess their hydrocarbon generation potential (Tissot and Welt, 1984).
17 This method enables the quantification, characterization, and evaluation of the thermal
18 maturity of organic matter (kerogen), providing key parameters (S1, S2, and S3) for
19 the identification and assessment of potential source rocks [28].

20 Biomarkers analysis were also used in this paper. They are complex organic
21 compounds found in sediments, rocks, and petroleum that preserve a carbon skeleton
22 directly related to a specific biological precursor [32]. Biomarkers serve as chemical
23 indicators that trace the origin, thermal evolution, and degradation history of organic
24 matter deposited in the geological past [32].

These tools enable a more robust interpretation of the depositional evolution of the shales of the Morro do Chaves Formation, as well as an improved understanding of the paleoenvironmental context of the study area.

2. GEOLOGICAL BACKGROUND AND PALEOENVIRONMENT

2.1. The Sergipe-Alagoas Basin

The Sergipe-Alagoas Basin (Figure 2) encompasses an onshore area of 44,370 km² of Sergipe and Alagoas states [6]. It represents the most complete sedimentary evolution among Brazilian marginal basins, a fact related to the break-up of Gondwana and the opening of the South Atlantic Ocean during the Jurassic-Cretaceous [7, 8]. In addition, the Sergipe-Alagoas Basin is divided into Cabo, Alagoas, Sergipe and Jacuípe sub-basins, characterized by evidence of unstable tectonic conditions and a variable complexity in chrono and lithostratigraphic distributions [6-8, 21, 33].

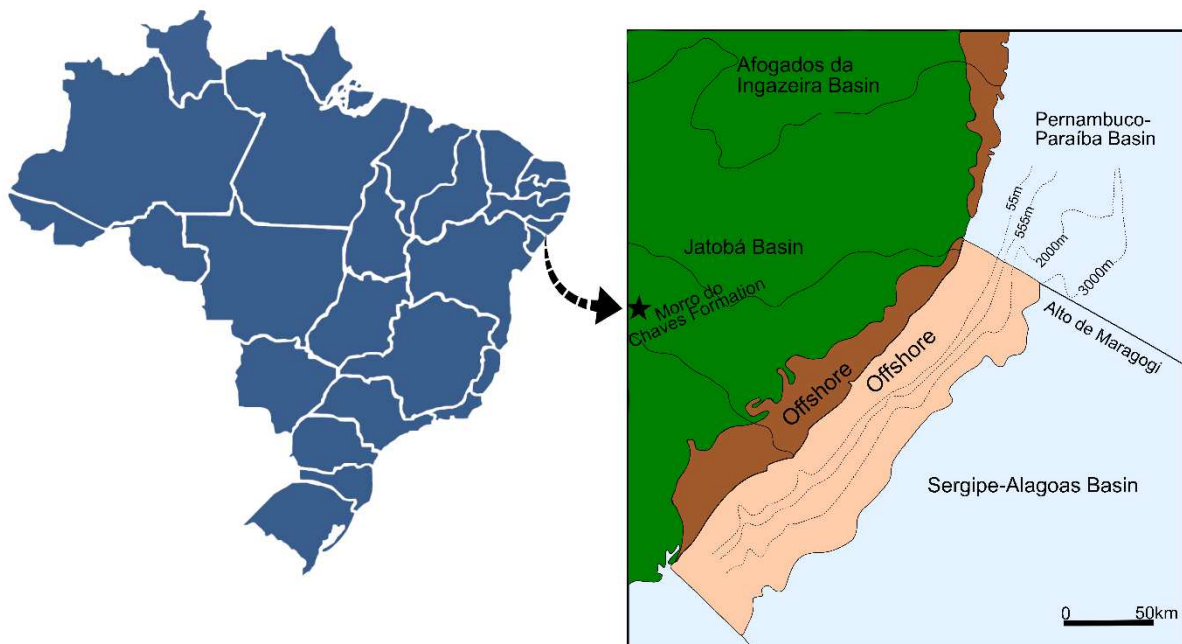


Fig.2 Location map of Sergipe-Alagoas Basin in the northeastern Brazil (modified from Antonietto, 2015).

The sedimentary succession of the Sergipe-Alagoas Basin is subdivided into five main super sequences: Paleozoic, Pre-rift, Rift, Post-rift (gulf/restricted sea) and Drift (open sea/ocean). The Paleozoic super sequence is characterized by a glacial system which was influenced by fluvial and marine deposits in the Batinga Formation (Late Carboniferous) [34, 35]. In addition, a transgressive-regressive stratigraphic succession was observed in the Aracaré Formation (Late Permian) [6, 35-37].

The Pre-rift super sequence is filled by continental deposits in the Bananeiras, Candeeiro, and Serraria formations from the Late Jurassic to the Early Cretaceous [7, 37]. This super sequence is also marked by the Afro-Brazilian Depression during the Late Jurassic. It occupies at least 300,000 km² and extends from northeastern Brazil (Sergipe-Alagoas Basin) to Africa (Equatorial Guinea, Gabon, Congo, the Democratic Republic of Congo, and Angola) [38, 39].

The Rift super sequence is characterized by fluvial-deltaic-lacustrine deposits in the Early Cretaceous of Penedo and Barra de Itiúba formations [6,34]. In addition, the periods of low sedimentary input formed the coquina levels of the Morro do Chaves Formation [6, 37, 40].

The Post-rift (gulf/restricted sea) super sequence is filled by evaporite depositions related to the first unequivocal marine incursion in the Sergipe-Alagoas Basin that generated the Muribeca Formation in the Early Cretaceous [6, 7, 34]. On the other hand, the Drift (open sea/ocean) super sequence is marked by a transgressive-regressive environment of the Riachuelo and Contiguiba formations in the Early Cretaceous [6, 7].

2.2. The Morro do Chaves Formation – InterCement Quarry (formerly Atol quarry)

The Morro do Chaves Formation was deposited during the Rift and Post-rift stages of the Sergipe-Alagoas Basin, dating from the late Barremian to the Aptian [8, 10, 14]. It is concordant with the Penedo Formation (lower contact) and transitional to the Coqueiro Seco Formation (upper contact) [7,9].

Additionally, the Morro do Chaves Formation contains a 108-meter thick hybrid sedimentary succession exposed along 1 km of the quarry face (Figures 3, 4 and 5). It is composed of coquinas, mudstones, sandstones, and conglomerates [8, 12, 13, 15, 16, 18].

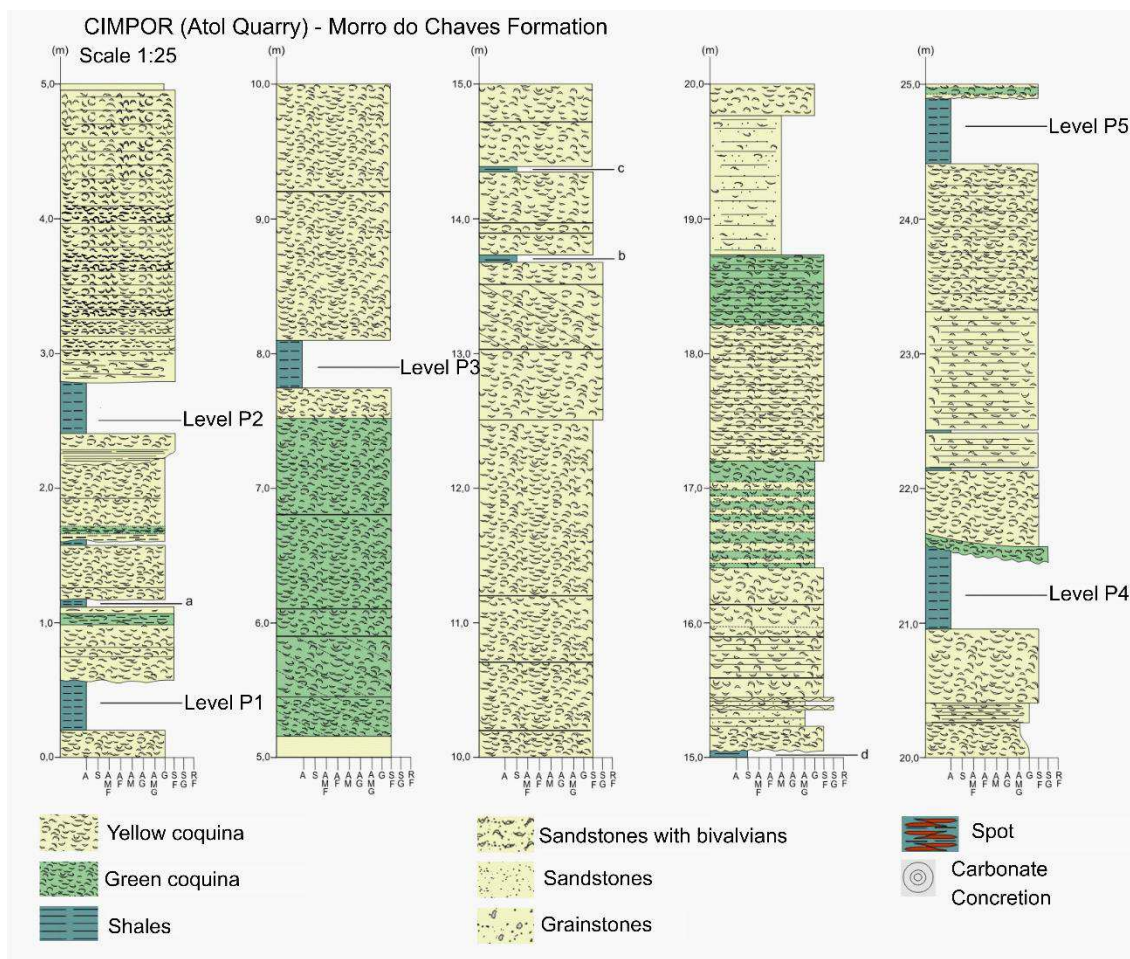
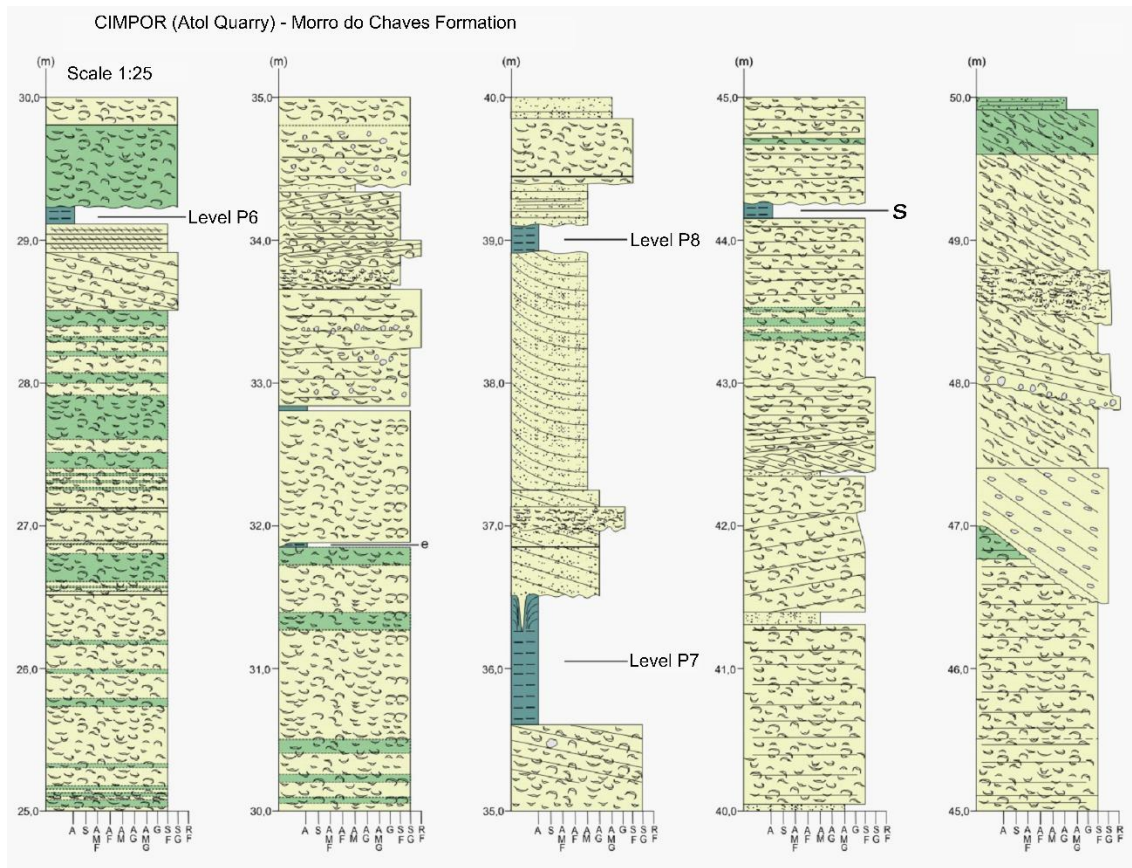


Fig.3 Detailed stratigraphic section (P1-P5) of the Morro dos Chaves Formation (InterCement quarry), Sergipe-Alagoas basin, Brazil (modified from Melo, 2011).

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3 **Fig.4** Detailed stratigraphic section (P6-P8) of the Morro dos Chaves Formation
 4 (InterCement quarry), Sergipe-Alagoas basin, Brazil (modified from Melo, 2011).

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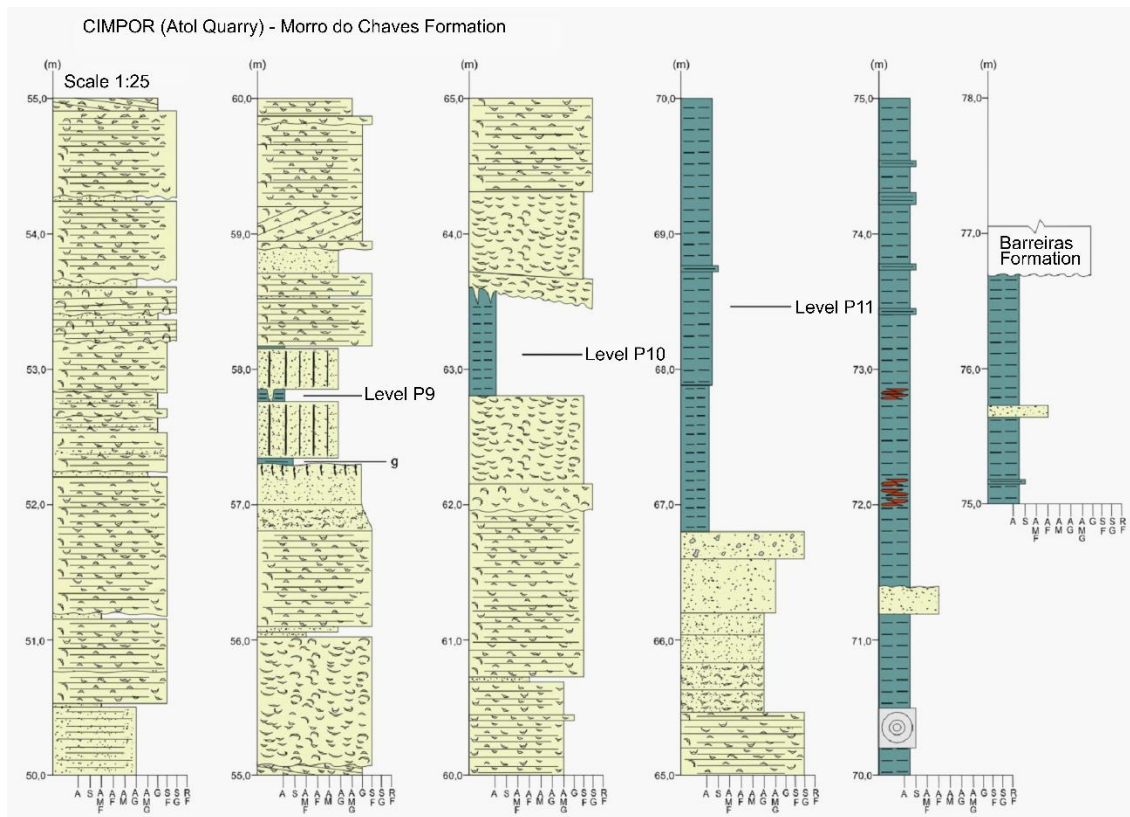


Fig.5 Detailed stratigraphic section (P9-P11) of the Morro dos Chaves Formation (InterCement quarry), Sergipe-Alagoas basin, Brazil (modified from Melo, 2011).

The most representative outcrop of the Morro do Chaves Formation is located in the InterCement Quarry (formerly Atol Quarry), composed mainly of an agglomeration of bivalve and gastropod shells in association with shales rich in fish remains [9].

Moreover, from base to top, the stratigraphic succession of the Intercement Quarry is formed by bioclastic limestones (i.e., so-called coquina), calcilutites, and grayish shales, interbedded with rocks of the Pitanga, Poção, and Coqueiro Seco formations [9]. It corresponds to the first tectonic pulse after the rift phase, associated with the formation of a great lake and marked oscillations in salinity, as observed in the Pitanga, Barra de Itiúba, and Penedo formations [15, 20, 41].

2.3. Paleoenvironmental Context

The shales of the Morro do Chaves Formation are characterized by a relatively diversified fossil content deposited in a lake isolated from adjacent depocenters by rollover structures [8]. In addition, the fish fauna is thought to have developed in a seasonal lacustrine paleoenvironment inferred from the cyclic arrangement of coquinas, shales, and sandstones with mud cracks [9, 23].

Moreover, the presence of pyrite and organic matter (predominantly represented by bryophyte, gymnosperm, and angiosperm remains) are indicative of a shallow lacustrine paleoenvironment with reducing, anoxic waters, marked by oscillating water levels determined by warming in episodic pulses [8, 9, 21].

Nevertheless, according to paleontological evidence (i.e. aulopiform fishes, brackish mollusks, foraminiferans, poriferans, and microbivalvians), the Morro do Chaves Formation was a scenario of episodic marine incursions and brackish influence [14, 20, 21]. These events produced occasional variation in salinity, as well as periodically oxygenated conditions [8, 14, 16, 22-24].

Furthermore, the botanical affinities indicate two distinct depositional environments in the Morro do Chaves Formation [8]. The first depositional environment is represented by a plain with sparse herbaceous plants, surrounded by remote mountainous regions with arboreal plants submitted to hot and humid climatic conditions [8]. The second depositional environment was subject to episodic storm events and marine incursions, thus changed to an alluvial-deltaic lacustrine *sabkha* interbedded with reduced lake-level episodes and associated with a closed lake basin [8].

3. MATERIAL AND METHODS

3.1. *Geological Dataset*

The analysis was based on 14 shale samples extracted from 11 pelitic levels (P01 to P11) of the Morro do Chaves Formation (InterCement Quarry). The outcrop studied is located in São Miguel dos Campos county (10°15'S; 36°06'W), in Alagoas state (Figure 6). Some pelitic levels (i.e. P04, P07, P08 and P11) were represented by more than one rock sample (top, middle, and basis), labeled in accordance with A-G subdivisions as shown in Table 1. The material was obtained from excavations conducted between 2008-2011, previously studied in taphonomic analyzes [21]. It is housed at the Paleozoological Collection of the Zoology Department of the Universidade do Estado do Rio de Janeiro. All samples were catalogued and submitted to analysis at the Fluid Technology Management Petrobras Research and Development Center (CENPES) laboratories.

Table 1 TOC and Rock Eval pyrolysis parameters of samples from the Morro do Chaves Formation.

Samples	TOC (%)	Ins Res (%)	S1	S2	S3	TMax (°C)	HI	OI	Sulfur
P01	2.14	66	0.25	12.5	0.57	425	584.11	26.63	2.26
P02	0.06	94	-	-	-	-	-	-	0.56
P03	0.15	52	-	-	-	-	-	-	1.02
P04-D	1.73	94	0.11	8.07	0.24	429	466.47	13.87	0.97
P04-C	0.2	92	-	-	-	-	-	-	0.74
P04-B	0.06	57	-	-	-	-	-	-	0.28
P04-A	0.18	87	-	-	-	-	-	-	0.58
P05	1.03	82	0.08	3.81	0.41	426	369.9	39.8	0.62
P06	0.12	79	-	-	-	-	-	-	0.67
P07-D	0.05	84	-	-	-	-	-	-	0.53
P07-C	0.11	83	-	-	-	-	-	-	0.44
P07-B	1.7	80	0.11	7.32	0.33	427	430.58	19.41	2.6
P07-A	0.09	76	-	-	-	-	-	-	1.82
P08	3.03	70	0.32	18.82	0.69	424	621.12	22.77	1.03
P09	0.23	89	-	-	-	-	-	-	-
P10-B	0.04	81	-	-	-	-	-	-	-
P10-A	0.03	93	-	-	-	-	-	-	-
P11-G	0.05	86	-	-	-	-	-	-	-
P11-F	0.05	89	-	-	-	-	-	-	-
P11-E	0.02	88	-	-	-	-	-	-	-

1

2 **3.2. *Methods***

3 The analytical methods employed in this study were selected for their
4 robustness, as their sensitivity is not affected by sample quality, even if derived from

1 relatively old samples. Nevertheless, all samples were carefully processed in the
2 laboratory and stored under controlled conditions to prevent exposure to chemical or
3 environmental contaminants. This approach ensures the reliability and integrity of the
4 results obtained.

5 The samples were submitted to analytical techniques in Organic Geochemistry,
6 such as Total Organic Carbon (TOC) and Rock-Eval Pyrolysis, extraction and
7 separation of fractions by Medium Pressure Liquid Chromatography (MLMP), Gas
8 Chromatography (GC), and Gas Chromatography Coupled to Mass Spectrometry
9 (GC-MS).

10 To achieve reliable TOC values, the shale samples were analyzed following
11 Killops and Killops [29]. Moreover, the quantification of TOC and sulfur contents were
12 performed on the SC-444 Leco Elementary Analyzer. Finally, Insoluble Residues (IR)
13 were obtained from the decarbonation of the samples.

14 The rock samples are also submitted to the Rock-Eval pyrolysis a chamber filled
15 with inert gas, then gradually heated at 200°C-550°C following Espitalié et al. [42] and
16 Souza et al. [31]. In addition, the samples were submitted to the bitumen extraction,
17 following Peters et al. [43].

18 Moreover, a whole oil gas chromatography was conducted on the organic
19 extracts of the shales. Among them, the Gas Chromatography (GC - Whole oil) was
20 used to recognize the distribution of hydrocarbons, in addition to identifying the
21 distribution of linear chains, branched and cyclic chains, and aromatic compounds.

22 Furthermore, the biomarkers were extracted and identified from the analysis of
23 Gas Chromatography Coupled to Mass Spectrometry (GC-MS). In this analysis, a part

of bitumen (organic extract) is submitted to the $\delta_{13}\text{C}$ ratio of the organic fraction of the TOC using a mass spectrometer (EA-IRMS) [43].

3.3. Use of AI

During the preparation of this manuscript, the GPT-5.5 AI tool was used exclusively to assist with language editing and improve the clarity and readability of the text. No AI tool was used to generate scientific content, analyze or interpret data, or draw scientific conclusions. All analyses, interpretations, and conclusions were conducted by the authors. The authors reviewed and edited the entire manuscript and assume full responsibility for its content.

4. RESULTS AND DISCUSSION

TOC contents varied between 0.02% and 3.03% (Table 1), representing a significant variation in the production/preservation conditions of organic matter in the InterCement Quarry. The samples P01, P04-D, P05, P07-B, and P08 had TOC content values higher than 1%, thus considered with good potential for hydrocarbon generation, according to the literature [28] (Figure 7).

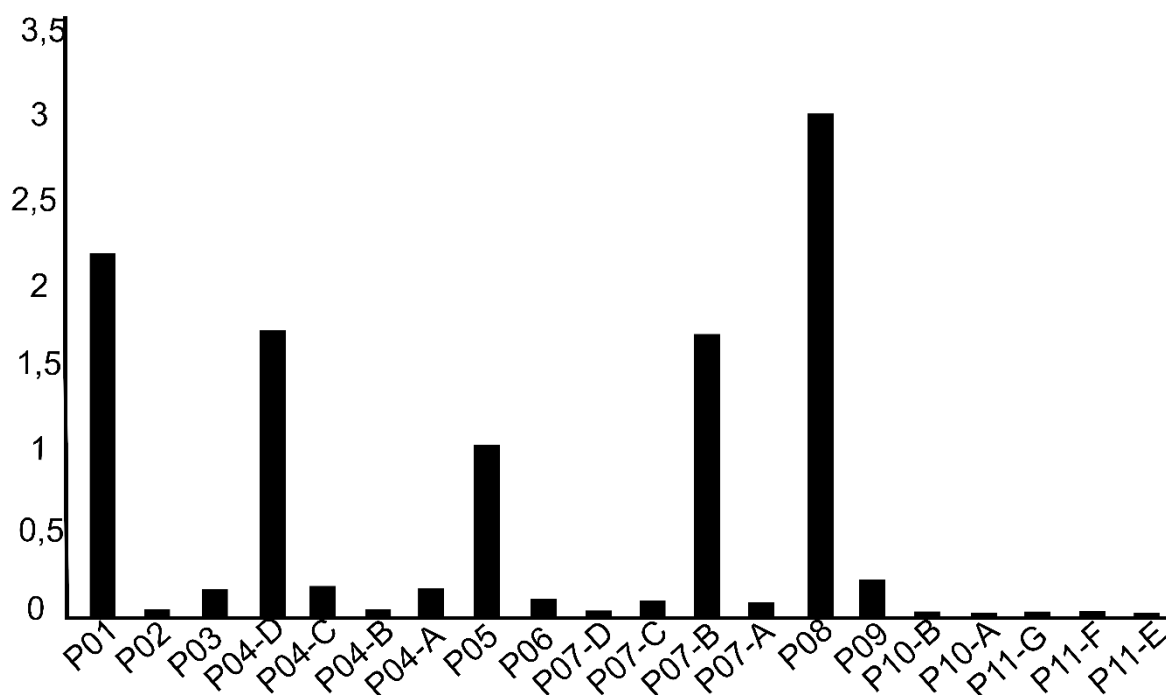


Fig.7 Graphic representation of the TOC content in the InterCement quarry. The highest values represent the best production/preservation conditions of organic matter, as observed in P01, P04-D, P05, P07-B, and P08.

However, an association between the degradation/preservation rates of organic matter and the dynamic of environmental factors, such as transgressive and/or high-energy events, may disturb the deposition process [44, 45]. This condition would explain the low TOC content in the majority of pelitic levels of the InterCement Quarry (P02-P04-C, P06, P07-A, C and D, P09-P11).

Moreover, pieces of evidence of intense active tectonism were recorded between Africa and South America at the time of the Gondwana break-up [46]. These events probably caused a hydrocarbon conversion/elimination, as well as the organic matter cracking, which also resulted in the reduction of the TOC content in InterCement Quarry.

1 The variation in insoluble residue (IR) values are indicative of changes in the
2 depositional paleoenvironment [47]. Therefore, IR values $\leq 70\%$ are more related to
3 marl and carbonate shales, favored by mixed sedimentation, as observed in P01
4 (IR=66%). In contrast, IR values $\geq 70\%$ are indicative of predominantly siliciclastic
5 sedimentation on the depositional paleoenvironment, as observed in P04-D (IR=94%),
6 P05 (IR=82%) and P07-B (IR=80%) (Table 1).

7 Furthermore, the potential of hydrocarbon generation (S_2) is positively related to
8 different depositional paleoenvironmental conditions [47]. The pyrolysis Rock-Eval
9 analysis produced five main S_2 peaks in the InterCement Quarry (Table 1) that varied
10 from 3.81 mg HC/g TOC to 18.8 mg HC/g TOC (P01, P04-D, P05, P07-B and P08).
11 Based on these results, P01, P04-D, P07-B, and P08 were interpreted as possible
12 good potential source rocks ($S_2 \geq 5$ mg HC/g TOC), whereas P05 was considered a
13 poor source rock ($S_2 \leq 5$ mg HC/g TOC) (*sensu* Peters and Cassa [48]).

14 The kerogen-type, as well as the potential of hydrocarbon generation, can be
15 estimated through direct observation of the HI values and/or the S_2 x TOC diagram
16 [47-53].

17 According to both analyses (Figures 8 and 9), the InterCement Quarry is
18 represented by kerogen types I (P08) and II (P01, P04-D, P05 e P07-B). These results
19 are related to the presence of marine organic matter probably deposited in a redox
20 paleoenvironment [46].

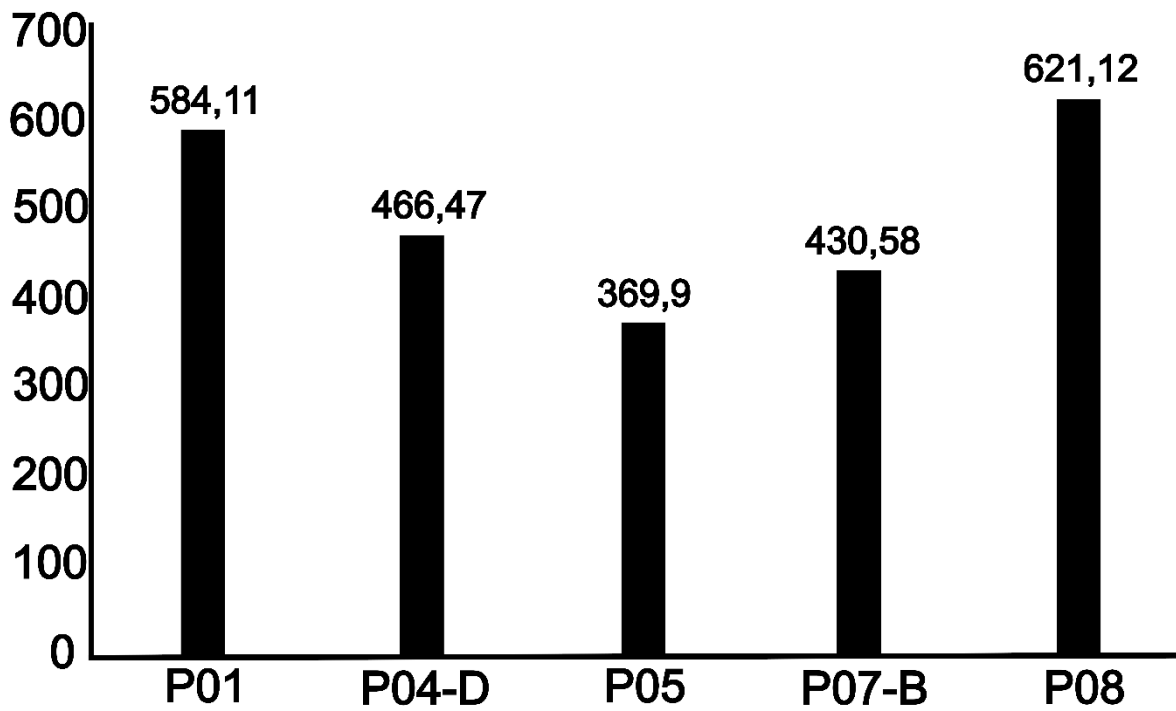


Fig.8 Samples of the InterCement quarry with the highest TOC values plotted on the IH variation diagram.

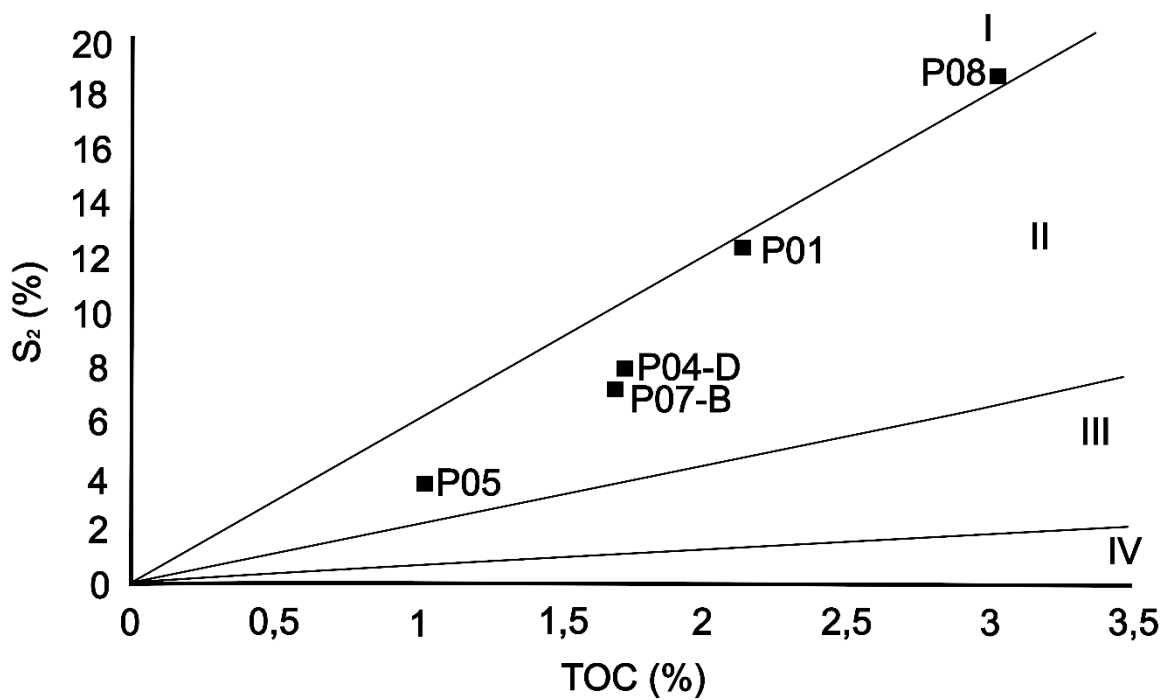


Fig.9 Classification of potential for hydrocarbon generation as a function of the S2xTOC ratio of samples from the outcrops in the InterCement quarry.

In addition, this hypothesis corroborates the first findings in the literature [11, 21]. Based on fish palynology [11] and taphonomy [21], respectively, the authors related the presence of nodular pyrite with a redox disturbed scenario that caused mass mortality of organisms throughout the deposition of pelitic levels.

Thermal maturity can be evaluated using various geochemical proxies, including vitrinite reflectance, Rock-Eval analyzes (e.g., T_{max} and production index), and biomarker maturity ratios [43, 54].

The geological samples of the InterCement Quarry varied from 424°C to 429°C (T_{max}). These values would be indicative of thermally immature rocks [48, 53].

However, the uppermost temperature (429°C) observed only in the P04-D should be related with the transition to a thermally mature zone in the InterCement Quarry due to the burial process effect [53] near the base of the outcrop.

Both biomarkers and isotopic composition also reflect the conditions of thermal maturity, as well as the system in which the organic matter was deposited [43]. The extracts shales of the InterCement quarry present composed by saturated hydrocarbons (20.25% and 25.7%), aromatic hydrocarbons (13.84% and 25.17%), and resins + asphaltenes (NSO) (52.07% and 61.59%) (Tables 2 and 3; Figure 10).

Table 2 Percentage of saturated, aromatic and resin+asphaltene hydrocarbons of the InterCement quarry

Sample	% Sat	% Aro	% NSO	% LOSS
--------	-------	-------	-------	--------

P01	25,7	19,01	55,29	2,74
P04-D	22,76	25,17	52,07	4,3
P05	24,57	13,84	61,59	4,93
P07-B				
P08	20,25	19,32	60,43	0,62

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8 The relative abundance of the NSO-compounds mainly suggests the presence
9 of immature extracts [28] and corroborates the interpretation of T_{max} results, as
10 previously discussed.

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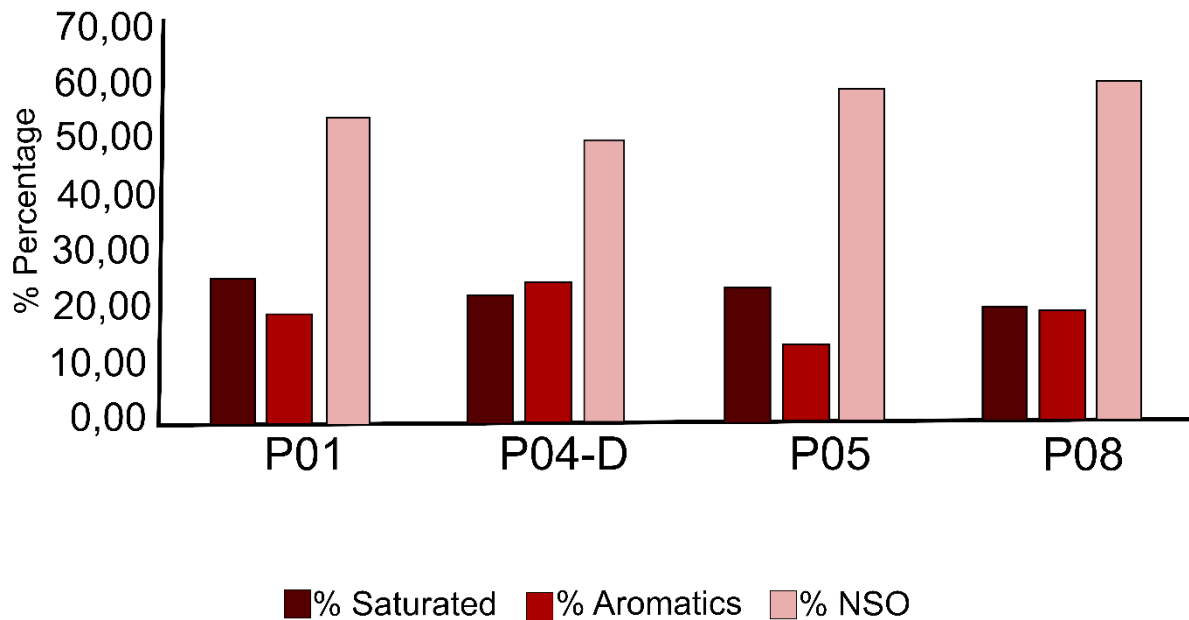


Fig.10 Distribution of the relative abundance of the main compounds, indicating the predominance of the NSO group in the InterCement quarry.

These findings are further supported by the presence of fossiliferous material in the InterCement Quarry. Thermally mature rocks rarely preserve macroscopic fossils, as they are typically destroyed under high-temperature conditions [54]. Therefore, although vitrinite reflectance analysis was not performed in this study, the occurrence of fossils with varying degrees of preservation indicates that the rocks at the InterCement Quarry are thermally immature [54].

The variations of oxy-reductive conditions can be observed from the biomarker compounds such as Pristane/Phytane (Pr/Ph), Pri/C17, and Phy/C18 ratio [29, 47]. According to the results, P01, P05, P07-B, and P08 probably represent a reducing paleoenvironment (Pri/Phi ratio ≤ 1.0), although P04-D (Pri/Phi ratio = 3.0) may be indicative of an oxic scenario (Figures 11, 12, 13).

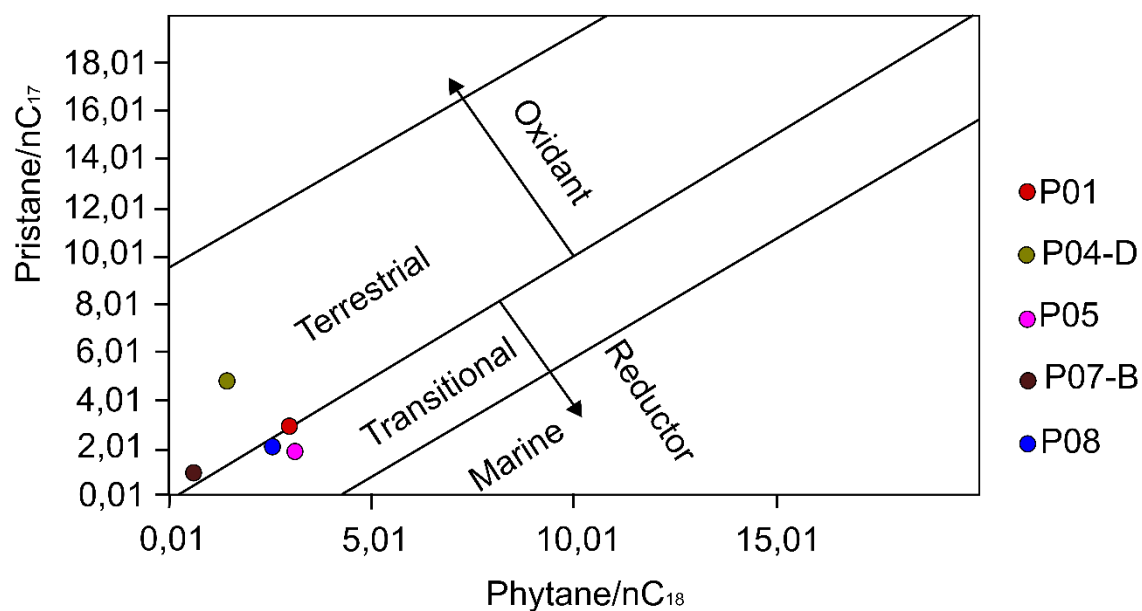


Fig.11 Distribution of paleoenvironmental conditions in the InterCement quarry based on Pristane/Phytane abundance.

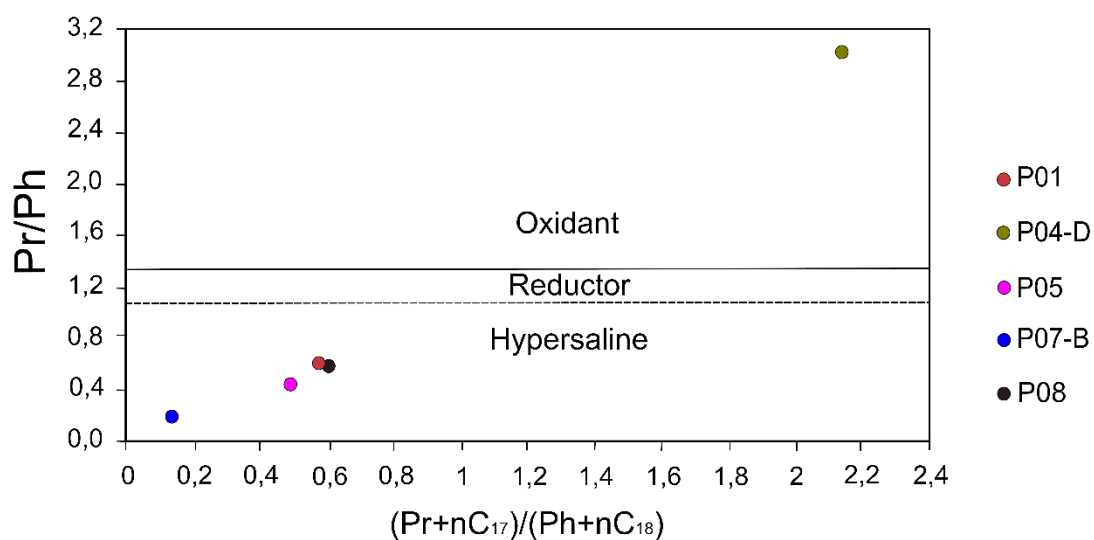
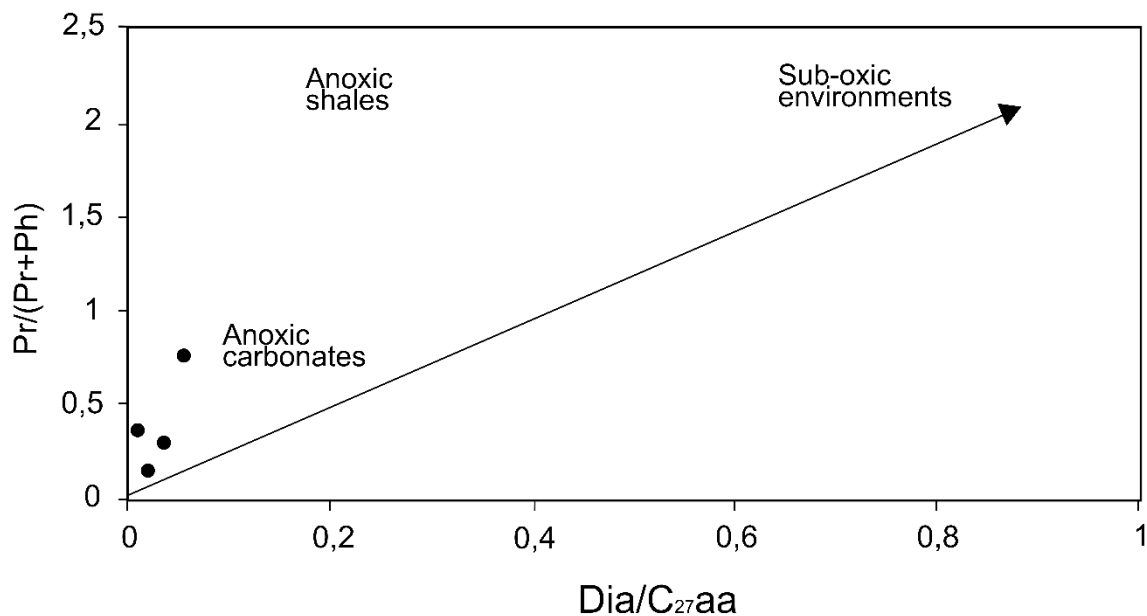


Fig.12 Depositional conditions of the InterCement quarry paleoenvironment based on Pri/nC₁₇ and Phy/nC₁₈ rates.

1



2

3 **Fig.13** Paleoenvironmental conditions of the InterCement quarry represented by the
 4 relationship between pristanes/phytanes and diasterans.

5

6 There is a relative abundance of isoparaffins and cycloparaffins (P01 and P04-
 7 D), as well as an abundance of odd-numbered normal paraffins in the chromatographic
 8 sequences from C_{23} to C_{29} . Moreover, all the samples analyzed had PCI (Preferential
 9 Carbon Index) values ≥ 1.0 (Figure 14; Tables 3 and 4).

10

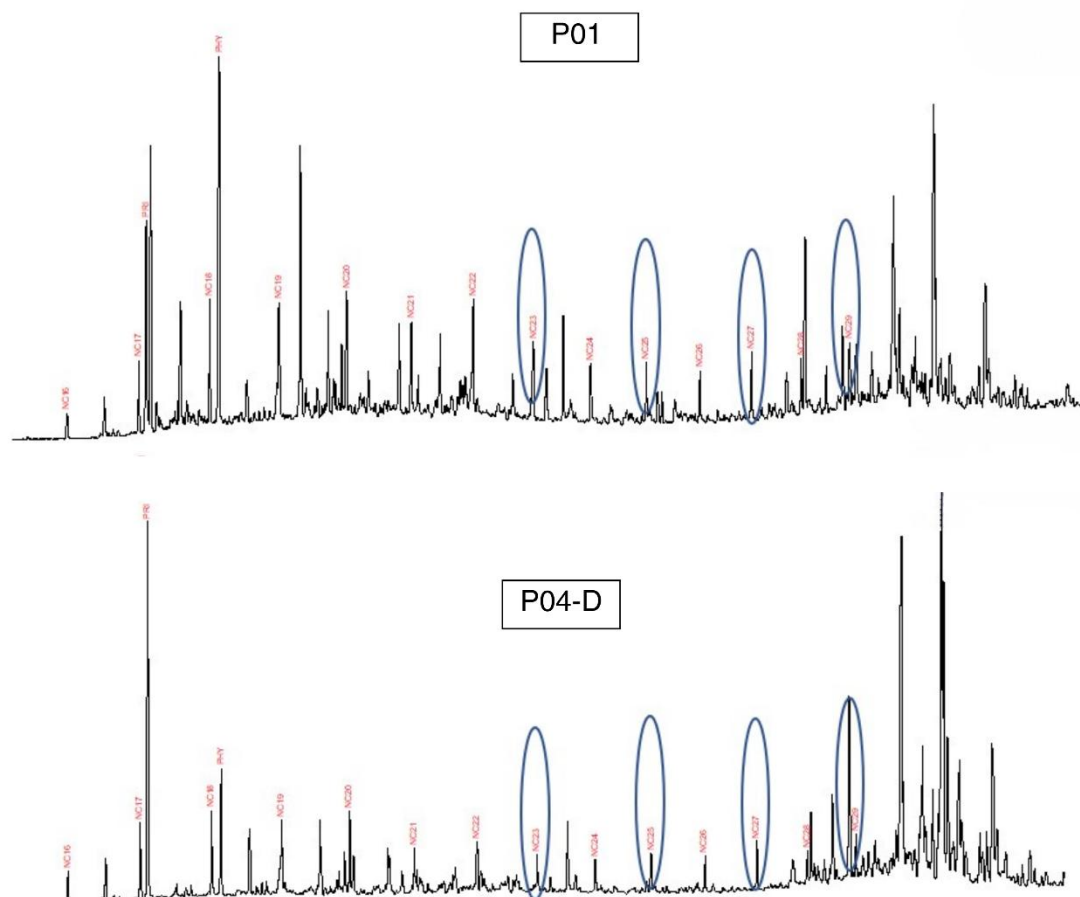


Fig.14 Gas Chromatography profiles of P01 and P04-D samples.

Table 3 Biomarkers and isotopic composition of organic extracts of the InterCement quarry.

TRIC/HOP	H28/H30	H29/H30	GAM/H30	H35/H34
0,6364	0,1115	0,41884	0,53532	1,02225
0,11907	0,02227	0,71126	0,31387	0,59234
0,1556	0,01843	0,27659	0,40611	0,8441
0,35331	0,05309	0,68485	0,64486	0,56714
0,82356	0,09445	0,43241	0,69165	0,90123
21/23TRI	26/25TRI	NORNEO/H29	TS/(TS+TM)	20S/(20S+20R) St
1,65417	2,81432	0,20244	0,14838	0,11065
1,32022	2,17939	0,15078	0,1479	0,15046
1,76758	2,87436	0,26753	0,1807	0,1071
1,12458	1,79321	0,15033	0,16155	0,1223

1,39944	2,60072	0,25182	0,14748	0,11994
aßß/(aßß+aaa)	% 27 aßßR&S (218)	% 28 aßßR&S (218)	% 29 aßßR&S (218)	TPP (m/z 259)
0,20945	27,60929	19,50537	52,88534	0,88867
0,25359	36,54444	18,43381	45,02175	0,83219
0,21128	28,83494	22,29762	48,86744	0,91015
0,20812	34,06751	21,57051	44,36198	0,9613
0,1956	30,36513	21,51648	48,11839	0,96076
TET24/H30	H29/C29TS			
0,02227	4,93979			
0,02174	6,6324			
0,01077	3,73783			
0,05476	6,65203			
0,02859	3,97104			

Table 4 Preferential Carbon Index-PCI ratio values of the InterCement quarry samples.

Sample	PCI
P01	1,5
P04-D	1,6
P05	1,5
P07-B	1,2
P08	1,6

In other words, the InterCement Quarry contains a predominance of odd *n*-alkanes, typical of hydrocarbons generated from lacustrine organic matter, also indicative of low thermal maturity with plant contribution [43, 55]. A bimodal distribution between odd and even paraffins, as well as the predominance of normal paraffins, was also observed in P05, P07-B, and P08. Furthermore, the presence of *n*-alkanes

(nC_{15} to nC_{37}) in the extracts and the predominance of normal high molecular weight alkanes (between nC_{23} and nC_{33}) suggests a contribution of terrestrial organic matter.

The distribution of normal paraffin chains suggests a deposition of organic matter in transitional environments with contributions by algae (predominant low molecular weight paraffins in the C_{15} to C_{22} range) or vascular plants (high molecular weight paraffins in the C_{15} to C_{22} range) [43,56]. P05 had a relative abundance of n -alkanes nC_{16} - nC_{22} and was therefore interpreted as a transitional paleoenvironment with bacterial action on algal material (Figure 15). These findings were supported by the biomarkers Hopane/Sterane, Gammacerane/H30, and Hopane35/Hopane34, as well as by higher concentrations of regular sterols (Table 3; Figure 16). C_{27} and C_{29} were derivative of phytoplankton, while C_{28} originated from contributions of vascular plant material [47, 57].

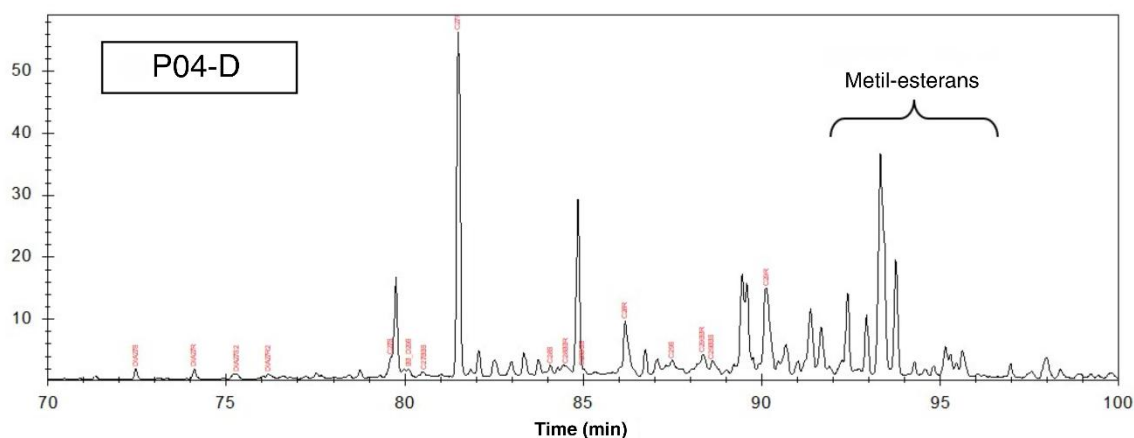
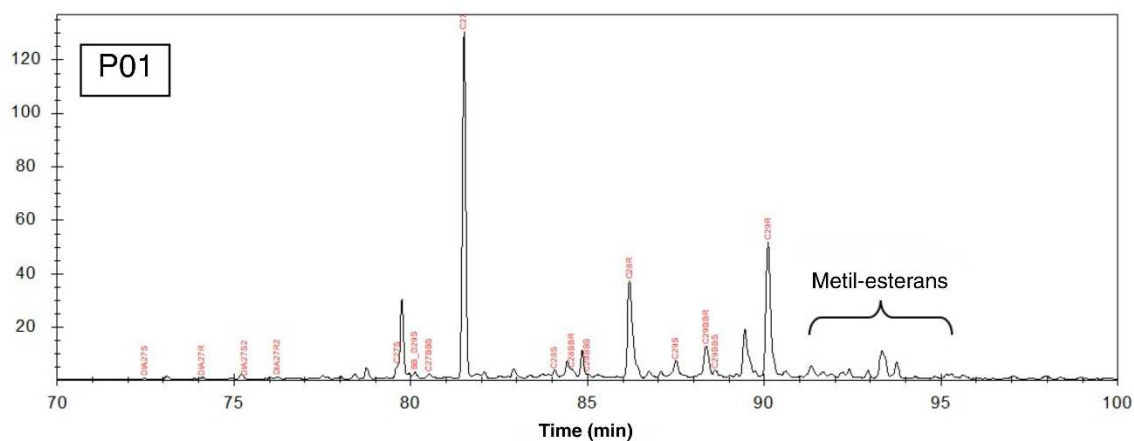
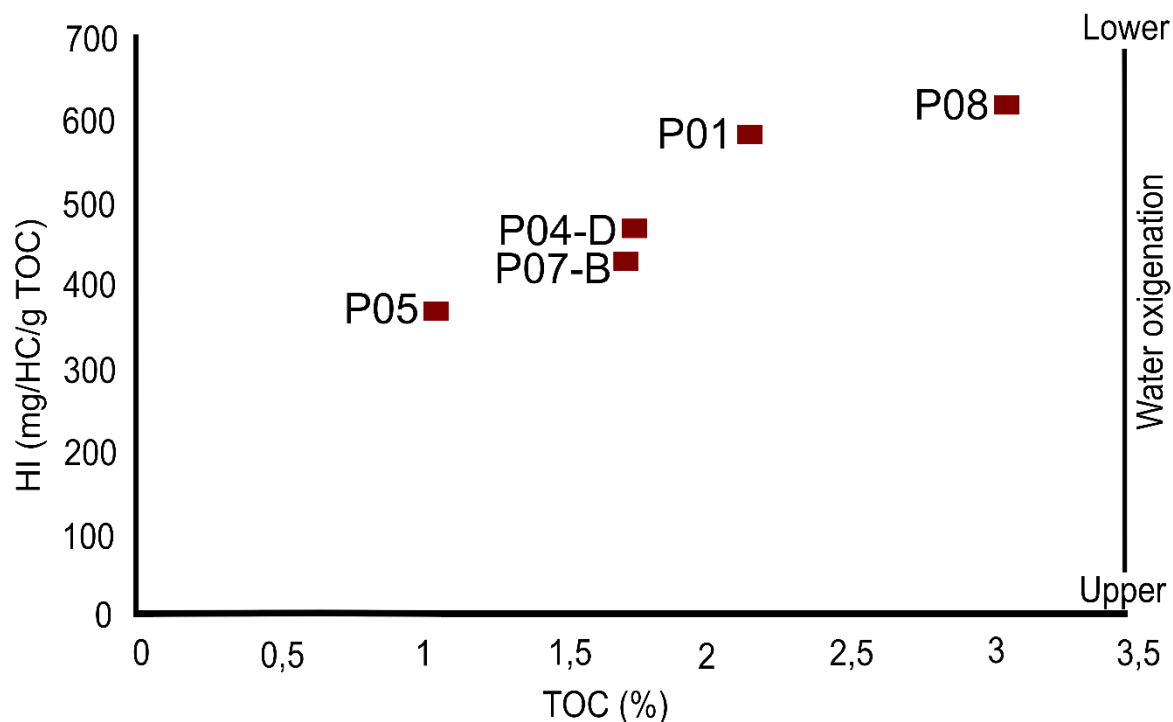


Fig.16 Chromatogram ion 217 esteranes. Em detail, the occurrence of metil-esteranes.

4.1. Depositional paleoenvironment

Since this study focuses exclusively on geochemical characterization, we draw on previously published paleontological data from the literature to support our analysis. An association between the abundance of primary producers and low energy conditions, in addition to a positive relationship between HI and TOC, can be indicative of organic matter input, as well as oxygen rates in different depositional paleoenvironments [29, 58, 59]. The positive relationship between HI and TOC observed in the InterCement Quarry (Figure 17) is interpreted as an improvement in marine algal lipid richness.

1



2

3 **Fig.17** Oxidic conditions of the InterCement quarry plotted in the HI x TOC diagram.

4

5 This finding is supported by the predominance of type II kerogen, which indicates
 6 that marine biomass was deposited in redox paleoenvironments [46, 60] on occasion
 7 of the sporadic marine incursions in the locality (lagoonal paleoenvironments) [9].

8 Lagoonal paleoenvironments are inherently complex due to the interaction
 9 between marine and continental waters, resulting in dynamic, highly productive, and
 10 diverse ecosystems with unique taxonomic composition [61]. In this context, the co-
 11 occurrence of both lacustrine and marine taxa within the same locality is expected, as
 12 documented by [8, 11, 62]. These authors reported the presence of Prasinophyceae
 13 (recorded in proximal deposits and marine sediments) associated with *Scenedesmus*
 14 Meyen, 1829 [63] and *Botryococcus* Kützing, 1849 [64] (colonial lacustrine alginite) in
 15 the InterCement Quarry, interpreting this assemblage as an indicative of marine
 16 incursions at the site. This interpretation is further supported by additional

1 paleontological evidences, as the occurrence of marine fish taxa (e.g. Aulopiformes)
2 associated with lacustrine ones (e.g. Ginglymodi) along the outcrop that reinforces the
3 hypothesis of lagoon deposition.

4 Paleontological evidence, such as the occurrence of marine fish taxa (e.g.,
5 Aulopiformes) alongside lacustrine forms (e.g., Ginglymodi) throughout the outcrop,
6 reinforcing the hypothesis of a lagoonal depositional environment.

7 On the other hand, the occurrence of fluorescent amorphous organic matter in
8 the locality was previously observed [11] and here is considered type I kerogen. This
9 material is produced by algae of lacustrine or marine origin enriched by microbial
10 action related with good oil source rocks [28, 46, 60].

11 The marine biota recorded in the InterCement Quarry [14, 21, 22, 65] reinforces
12 the hypothesis of transgressive events or marine incursions, as well as the
13 paleogeographical model of a global Mid-Cretaceous marine transgression [66].
14 According to this model, marine incursions originated in South America from the
15 Tethys Sea during the Aptian/Albian [67]. These events produced a seaway system in
16 the continent that allowed the access of marine fauna to lacustrine environments of
17 the Araripe, Camamu, Parnaíba, São Luís, Sergipe-Alagoas, and Tucano basins [11,
18 66-70].

19 Moreover, periodic marine incursions caused by sea level oscillations would
20 have been reflected in the oxygen, hydrogen and TOC fluctuations in the InterCement
21 Quarry. The reduction in oxygen rates would have been caused by the decomposition
22 of organic matter or increase in ambient temperature [72,73].

23 The cycles in the InterCement Quarry were widely studied [20,21]. Therefore,
24 P02-P04 and P07-P10 would have been scenarios of a warm and dry period, whereas
25 P05 and P11 are probable representatives of a cold and humid period with a profuse

1 water column and lower temperatures [21]. These hypotheses are corroborated in the
2 present analysis. Moreover, the highest temperatures events recorded in the
3 InterCement Quarry are inversely related to oxygen availability.

4 Furthermore, paleoenvironments with carbonate richness are favored by higher
5 levels of water pH due to anaerobic decomposition [21, 47]. Based on the IR rates, the
6 InterCement Quarry was interpreted as a periodic redox paleoenvironment (P01 and
7 P08) subjected to high temperatures that allowed the preservation of organic matter.
8 On the other hand, P05 was interpreted as a calm, humid paleoenvironment marked
9 by an improvement in oxygen availability that preserved a reduced amount of organic
10 matter.

11 The parameters of biomarkers like according to the data to the 26/25Tri ratio and
12 TPP (tetracyclic polyprenoides) values, the sediments of the InterCement Quarry are
13 representative of continental, lacustrine and transitional (lagoon) depositional
14 conditions. In addition, only P04-D had an abundance of methyl steranes in relation to
15 C₂₉, an indicator of continentality (lacustrine environment). In contrast, P01, P05, P07-
16 B and P08 would be indicators of marine environments.

17 Furthermore, the Gam/H₃₀, 26/25Tri and H₃₅/H₃₄ parameters (Table 3) were
18 interpreted as representatives of restricted carbonate paleoenvironments of high
19 salinity and associated anoxia. The H₂₉/H₃₀ and H₃₅/H₃₄ ratios are important in the
20 interpretations of the carbonate/siliciclastic contribution in the system, as well as of the
21 possibility of stratification of the water column. Thus, upper H₂₉ values indicate marine
22 carbonate conditions with siliciclastic influence. In opposite, lower H₂₉ values are
23 indicative of marine carbonate conditions. These values can be related to the H₃₅/H₃₄
24 ratio and suggest the presence ($H_{35}/H_{34} \geq 1.0$) or absence ($H_{35}/H_{34} \leq 1.0$) of stratification
25 in the water column (Figures 17 and 18).

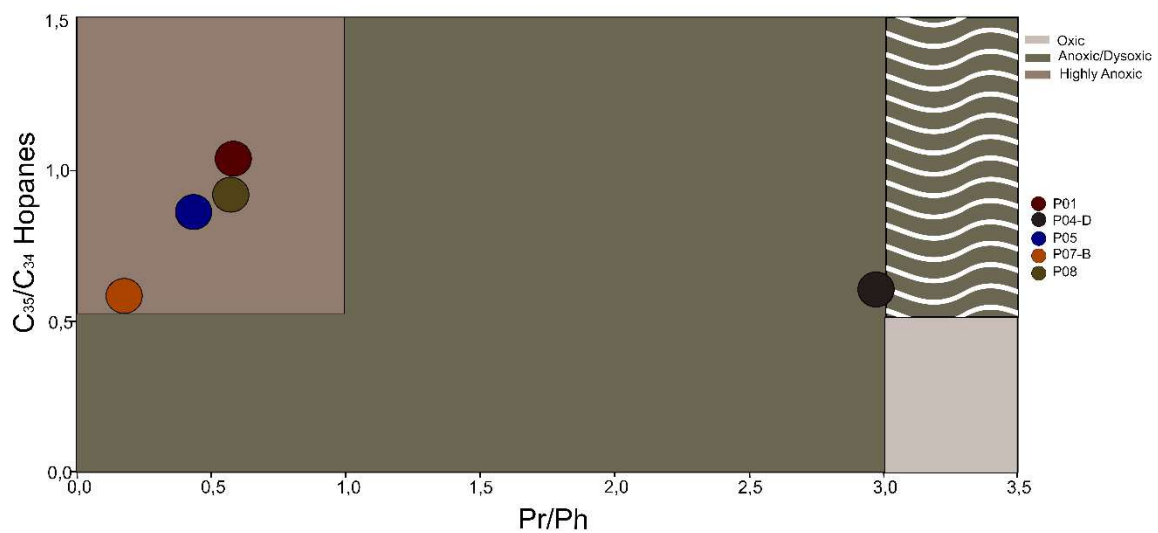
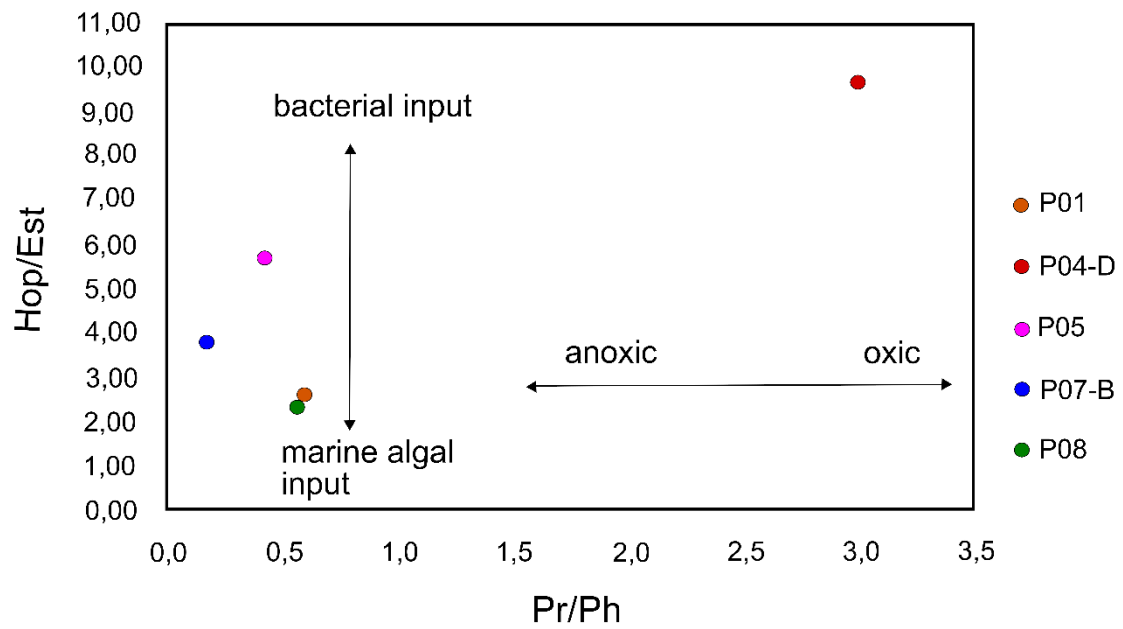


Fig.18 Oxidic conditions of the InterCement quarry plotted in a Pr/Ph x H35/H34 diagram. Except for P04, the InterCement quarry was mostly deposited in a highly anoxic paleoenvironment.

The proportions of C₂₇, C₂₈, and C₂₉ steranes in the analyzed extracts suggest a transitional biological and depositional ecosystem for the deposits InterCement Quarry (Figures 19 and 20). This hypothesis can be corroborated by the relationships of geochemical parameters between biomarkers and non-biomarkers demonstrated by [43, 71].



1

2 **Fig.19** Paleoenvironmental conditions of the InterCement quarry plotted in Hop/Est x

3 Pr/Ph diagram. P04-D was probably deposited in oxic conditions. On the other hand,

4 P01 and P08 are more related to marine algal input.

5

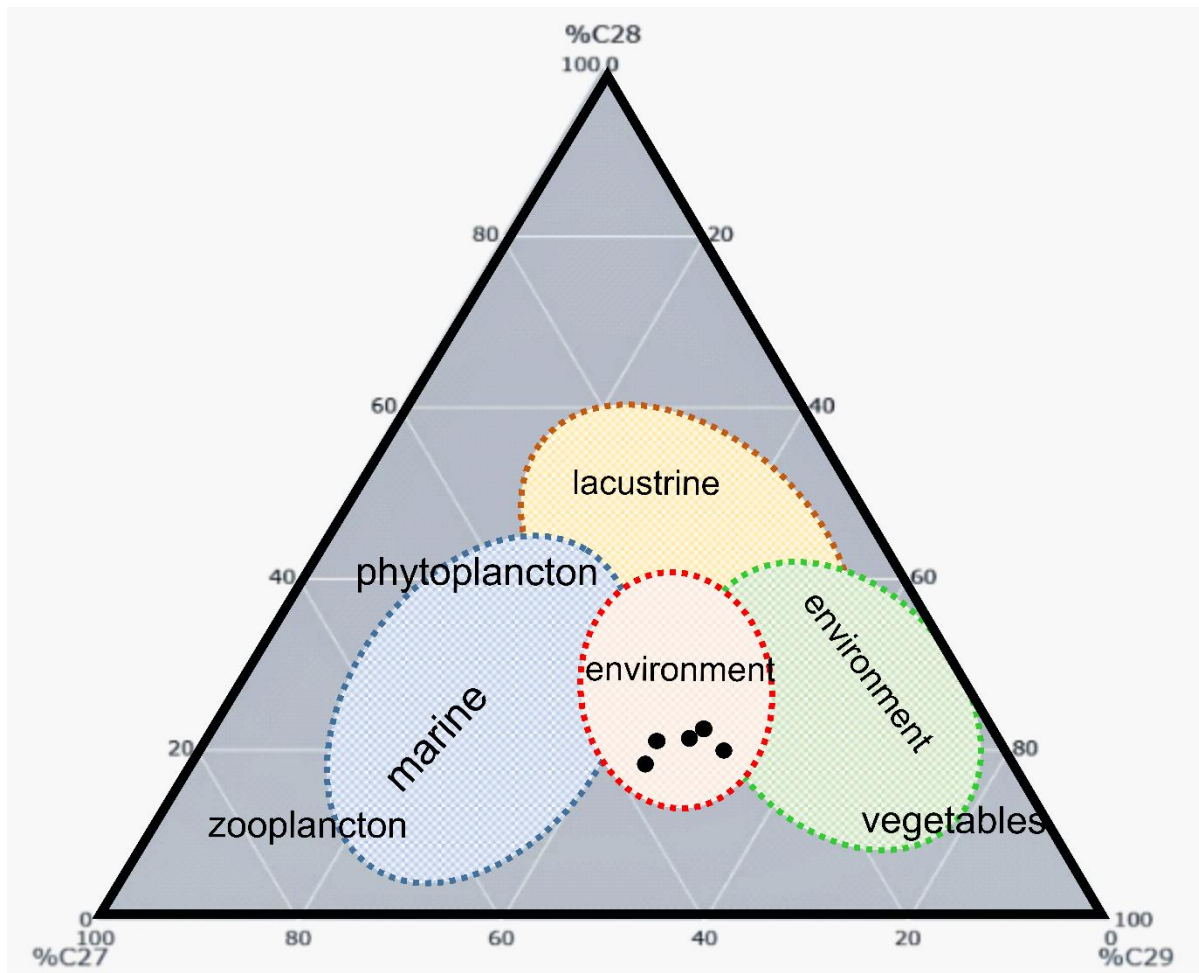


Fig.20 Ternary diagram with the proportions of steranes C27, C28, and C29 from extracts obtained from the mudstones of the InterCement quarry. The ellipses show the depositional sources of transitional biological and depositional ecosystems. Modified from Huang and Meinschein (1979).

5. CONCLUSIONS

Geochemical characterization of sediments collected from the InterCement Quarry (Sergipe–Alagoas Basin, municipality of São Miguel dos Campos, Alagoas) provides significant insights into the depositional and paleoenvironmental conditions of the shales in this part of the basin. The geochemical data suggest that organic

1 matter was deposited predominantly under continental conditions, with a significant
2 marine influence, consistent with a transitional environment. Despite the strong
3 continental influence, several geochemical features indicate a contribution of marine-
4 derived organic matter, pointing to a coastal setting, possibly associated with lagoonal
5 ecosystems.

6 These interpretations are supported by the predominance of Type I and II
7 kerogens in several samples, together with the presence of fluorescent amorphous
8 organic matter resulting from microbial reworking. The low Total Organic Carbon
9 (TOC) contents observed in most samples may reflect the influence of high-energy
10 depositional events associated with periodic marine incursions at the site. The relative
11 abundance of Type II kerogen suggests the development of reducing
12 paleoenvironments during periods of relatively calm and humid conditions.

13 Furthermore, the HI–TOC relationship indicates alternating periods of drier
14 conditions and elevated temperatures, which may have influenced organic matter
15 preservation. In particular, sample P05 is interpreted as representing a relatively calm
16 and humid paleoenvironment with greater oxygen availability, resulting in the
17 preservation of a comparatively lower amount of organic matter.

18 Biomarker distributions and isotopic compositions further reflect the
19 depositional conditions and relative thermal maturity of the sedimentary deposits at
20 the InterCement Quarry. Collectively, these data indicate a depositional system
21 characterized by continental lacustrine and transitional, possibly lagoonal, conditions.

22
23
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ETHICS, CONSENT TO PARTICIPATE, AND CONSENT TO PUBLISH

Ethics, Consent to Participate, and Consent to Publish declarations: not applicable.

DATA AVAILABILITY STATEMENT

All data generated or analysed during this study are included in this published article.

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