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JOSÉ DIEGO DIAS VERAS

INTERPRETAÇÃO PALEOAMBIENTAL DA FORMAÇÃO TAMBABA (EOCENO) DA SUB-BACIA ALHANDRA, BACIA PARAÍBA, POR MEIO DE ESTUDOS SEDIMENTOLÓGICOS, ESTRATIGRÁFICOS E GEOQUÍMICOS

Recife
2022

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Tese apresentada ao Programa de Pós-Graduação em Geociências da Universidade Federal de Pernambuco, como requisito parcial para a obtenção do título de Doutor em Geociências.

Área de concentração: Geologia Sedimentar e Ambiental.

Orientador: Prof. Dr. Virgínio Henrique de Miranda Lopes Neumann

Coorientador: Prof. Dr. João Adauto de Souza Neto

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RESUMO

A Formação Tambaba possui idade Eocênica e ocorre de forma restrita em superfície na região costeira norte da Bacia Paraíba. Anteriormente, os depósitos carbonáticos constituintes desta unidade eram frequentemente citados como Formação Marinha Farinha Superior, admitindo-se uma formação estratigráfica distinta da Formação Marinha Farinha (de idade Paleocênica). Este trabalho teve como objetivo a construção de um modelo paleoambiental dos calcários recifais da referida formação através de estudos sedimentológicos, estratigráficos e geoquímicos. Os afloramentos estudados estão localizados na faixa costeira entre as praias de Tambaba, Coqueirinho e Jacumã, no estado da Paraíba. Estes depósitos carbonáticos apresentam um aspecto coquinoide e devido à erosão, um aspecto ruiniforme irregular. Porções acumuladoras de bivalves e gastrópodes propiciaram um intenso processo de bioerosão, causado principalmente por organismos perfuradores. Além disso, esses depósitos apresentam uma intensa variação de fácies que foram caracterizadas através de microscopia óptica e catodoluminescência entre Mudstones, Wackestones e Packstones. São compostas essencialmente por uma matriz micrítica com a presença ainda de pirita e sílica em menores proporções, entretanto, as fácies sofrem o processo diagenético de substituição de calcita por dolomita (dolomitização). Outros processos diagenéticos como dissolução, cimentação e compactação foram identificados nos estudos petrográficos. A evidência de bastante piritização substituindo valvas e fragmentos de bioclastos, e substituindo tubos de Thallassinoides, e indicam um estágio eodiagenético. Os valores de $\delta^{13}C$ variam de 1.0 a 2.8‰ e os de $\delta^{18}O$, de -1.3 a 1.8‰ VPDB, sugerindo deposição em ambiente de plataforma rasa restrito. Análises químicas de rocha total sugeriram alterações diagenéticas, como dedolomitização (Mn/Sr varia de 0.6 a 28) e dolomitização sugerido pela alta razão Mg/Ca (0.5 a 0.6). Além disso, os baixos teores de SiO_2 e Al_2O_3 (0.0 a 0.5) corroboram o baixo influxo de materiais terrígenos. Esses dados sugerem mudanças ambientais, como aumento ou diminuição da bioprodutividade dos organismos que compõem esses calcários recifais. Essas mudanças também são registradas no comportamento dos elementos maiores e traços - por exemplo, a relação entre SiO_2, Al_2O_3, MgO e CaO, caracterizando dois ciclos diferentes durante a deposição desses calcários: o primeiro caracterizado por uma deposição predominantemente carbonática, e o segundo apresentando pulso de conteúdo siliciclástico. Além disso, os valores de paleotemperatura (9-15°C, estimados a partir de dados de $\delta^{18}O$) obtidos, juntamente com os perfis quimioestratigráficos (por exemplo, $\delta^{13}C$, CaO, MgO, SiO_2, Al_2O_3), indicam que os calcários de recife da Formação Tambaba foram provavelmente depositados cerca de 5 Ma após o evento Paleoceno-Eoceno Térmico Máximo.

Palavras-chave: Formação Tambaba; calcários recifais; Bacia Paraíba.

ABSTRACT

The Tambaba Formation is Eocene Age and occurs in surface restricted way in the northern coastal region of the Paraíba Basin. Previously, the carbonaceous deposits constituent of this unit were frequently cited as Upper Maria Farinha Formation, assuming a stratigraphic formation distinct from the Maria Farinha Formation (Paleocenic Age). The objective of this work was the construction of a paleoenvironmental model of reef limestones of this formation through sedimentological, stratigraphical and geochemical studies. The outcrops studied are located in the coastal strip between the beaches of Tambaba, Coqueirinho and Jacumã, in the state of Paraíba. These carbonate deposits have a coquinoid aspect and due to erosion, an irregular ruiniform aspect. Accumulating portions of biválvios and gastropods provided an intense process of bioerosão, caused mainly by perforating organisms. In addition, they present an intense variation of facies that were characterized by optical microscopy and cathodoluminescence between Mudstones, Wackestones and Packstones. They are composed essentially of a micritic matrix with the presence of pyrite and silica in smaller proportions, however, the facies undergo the diagenetic process of replacement of calcite by dolomite (dolomite). Other diagenetic processes such as dissolution, cementation and compaction were identified in the petrographic studies. The evidence of sufficient pyritization replacing valves and fragments of bioclasts, and also replacing Thallassinoides tubes, indicates an eodiagenetic stage. The $\delta^{13}C$ values ranged from 1.0 to 2.8‰ VPDB while the $\delta^{18}O$ values ranged from -1.3 to 1.8‰ VPDB, thus suggest a restricted shallow-platform depositional environment. Bulk chemistry analyses suggested diagenetic changes, such dedolomitization (Mn/Sr ratios from 0.6 to 28) and dolomitization, which was identified by high Mg/Ca ratios (0.5 to 0.6). The very low SiO_2 and Al_2O_3 (0.0 to 0.5) content attested to the low terrigenous material influx. These data suggest environmental changes, such as an increase or decrease in bioproductivity of the organisms that make up these reef limestones. These changes are also recorded in the behaviour of the major and trace elements – for example, the relationship between SiO_2, Al_2O_3, MgO and CaO, characterizing two different cycles during the deposition of these limestones: the first one characterized by a predominantly carbonate deposition, and the second one presenting a pulse of siliciclastic content. In addition, palaeotemperature values (9-15°C, estimated from $\delta^{18}O$ data) obtained, together with chemostratigraphic profiles (e.g. $\delta^{13}C$, CaO, MgO, SiO_2, Al_2O_3), indicate that the reef limestones of the Tambaba Formation were probably deposited about 5 Myr after the Paleocene–Eocene Thermal Maximum event.

Keywords: Tambaba Formation; reef limestones; Paraiba Basin.

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1 INTRODUÇÃO

A faixa costeira da Bacia Paraíba está compreendida entre a Zona de Cisalhamento Pernambuco (ZCPE) e o Alto Estrutural de Mamanguape, que está relacionado a uma ramificação da Zona de Cisalhamento Patos (ZCPA), na porção oriental do Nordeste do Brasil. O conhecimento geológico, onshore e offshore, dessa área ainda é deficiente quando comparado com bacias vizinhas, como a Bacia Potiguar ou a Bacia de Alagoas.

Dentro da coluna sedimentar da Bacia Paraíba, entre a sequência carbonática de idade Campaniano-Daniano (Formações Itamaracá, Gramame e Maria Farinha), e a sequência siliciclástica continental, de idade Mioceno-Holoceno (Formação Barreiras e coberturas holocênicas) (Beurlen 1967, Mabesoone & Alheiros 1988, Arai *et al*. 1988, 1994, Arai 1997, Barbosa 2004, Rosseti 2006b), ocorrem depósitos de origem recifal-lagunar que afloram nas Sub-Bacias Alhandra e Miriri (Beurlen 1967, Costa *et al*. 2001). Embora poucos trabalhos tenham tratado a ocorrência destes depósitos, Almeida (2000, 2007), realizou um estudo mais sistemático desses depósitos nomeados por Beurlen (1967) como Maria Farinha Superior. Este último autor caracterizou a fáunula de moluscos presentes nestes depósitos e sua paleocologia, além de seu importante conteúdo icnofossilífero, e sugeriu que estes calcários seriam de possível idade Eocênica.

Estes depósitos sempre foram citados como pertencente à Formação Maria Farinha, conforme sugerido por Beurlen (1967), que os correlacionou aos depósitos Paleocênicos que ocorrem sobre o topo da Formação Gramame na região sul da faixa costeira. Contudo, este autor observou a diferença entre a faciologia dos calcários classicamente denominados de Maria Farinha, e os depósitos que ocorrem na porção norte da faixa costeira, e denominou estes últimos de Formação "Maria Farinha Superior".

Com base no estudo das relações estratigráficas, na análise de modelos de fácies carbonáticas e na aplicação dos conceitos de estratigrafia de sequências, Correia Filho *et al*. (2015) definiu esses depósitos recifais como Formação Tambaba.

Apesar disso, algumas lacunas estratigráficas ainda persistem sobre a definição da abrangência lateral das unidades ao longo da faixa Recife-João Pessoa, e da relação vertical das formações reconhecidas. O presente estudo irá fornecer subsídios sedimentológicos, estratigráficos e geoquímicos da Formação Tambaba, citada como Formação Maria Farinha por outros autores.

Os resultados desta pesquisa contribuirão para um conhecimento mais detalhado dos calcários recifais da Formação Tambaba, assim como um melhor entendimento da evolução geológica de uma região muito carente de pesquisas mais detalhadas que é a Bacia Paraíba.

A pesquisa foi dividida em X capítulos estruturados da seguinte forma:

O capítulo 1 consiste em uma introdução geral detalhando as características geológicas dos calcários da Formação Tambaba diante do histórico bibliográfico da Bacia Paraíba e dessas rochas carbonáticas.

O capítulo 2 aborda as necessidades de estudo das rochas da Formação Tambaba, refletindo o foco principal do projeto.

O capítulo 3 traz os objetivos deste referido estudo (geral e específicos).

O capítulo 4 aborda as características da área de estudo: localização de descrição da área (geograficamente), os aspectos fisiográficos da área e o contexto geológico na qual a área de estudo está inserida.

O capítulo 5 descreve todo o conjunto de materiais e métodos que foram utilizados para a confecção deste documento. As etapas estão descritas separadamente, já que são fases distintas do estudo (etapas de campo e laboratório), e detalhadas por equipamentos e métodos utilizados.

Os resultados deste trabalho de Defesa de Tese são apresentados no capítulo 6 e estão divididos, inicialmente, em 1 artigo submetido e 2 artigos que já se encontram publicados em dois periódicos.

O item 6.1 traz uma contribuição sedimentológica detalhada ao nível de microfácies e correlações estratigráficas. O artigo foi submetido no ano de 2022 no periódico *"Brazilian Journal of Geology"* (Qualis A3) intitulado "*Texture and compositional characterization of the microfacies of the Reef Limestones of the Tambaba Formation, Paraíba Sedimentary Basin, NE Brazil* ".

O item 6.2 é referente ao artigo publicado no ano de 2019 no periódico *"Anuário do Instituto de Geociências – UFRJ"* (Qualis B2) intitulado "*C and O Isotope Chemostratigraphy and Bulk Chemistry of Reef Limestones of the Tambaba Formation, Paraíba Basin, Northeastern Brazil*". Este artigo trata de resultados geoquímicos gerais, entre isótopos estáveis de carbono e oxigênio e geoquímica de rocha total abordando as principais composições presentes nas rochas carbonáticas.

O item 6.3 também traz uma contribuição geoquímica mais detalhada devido à maior quantidade de dados fornecidos. O artigo foi publicado no ano de 2021 no periódico *"Geological Society of London – Special Publications"* (Qualis A2) intitulado "*Stable isotope and chemical stratigraphy of the Eocene Tambaba Formation: correlations with the Paleocene-Eocene Thermal Maximum event*".

E, finalmente, o capítulo 7 consiste nas conclusões da Tese, o qual apresentará a síntese dos resultados que serviram de base para a conclusão dos artigos precedentes

2 HIPÓTESES DO ESTUDO

Segundo a hipótese já existente, os calcários recifais tratados nesse estudo são denominados como Formação Maria Farinha Superior. No entanto, estudos mais recentes (Correia Filho *et al*., 2015) propuseram a formalização desta unidade como Formação Tambaba, através de seu conteúdo textural macro e microscópico. Esta pesquisa visa definir a diferença paleodeposicional entre as formações Maria Farinha e Tambaba, já que apresentam características sedimentológicas e geoquímicas que diferem entre si.

3 OBJETIVOS

3.1 OBJETIVO GERAL

Caracterizar o paleoambiente deposicional da Formação Tambaba durante o preenchimento da bacia, através de estudos sedimentológicos, estratigráficos e geoquímicos.

3.2 OBJETIVOS ESPECÍFICOS

a) Identificar e caracterizar as macrofácies e microfácies carbonáticas;

b) Analisar as microfácies carbonáticas através de microscopia óptica e catodoluminescência;

c) Estabelecer a posição temporal da referida unidade e sua relação com as unidades sobre e sotopostas a ela;

d) Analisar os resultados geoquímicos e estabelecer padrões que refletem o paleoambiente deposicional.

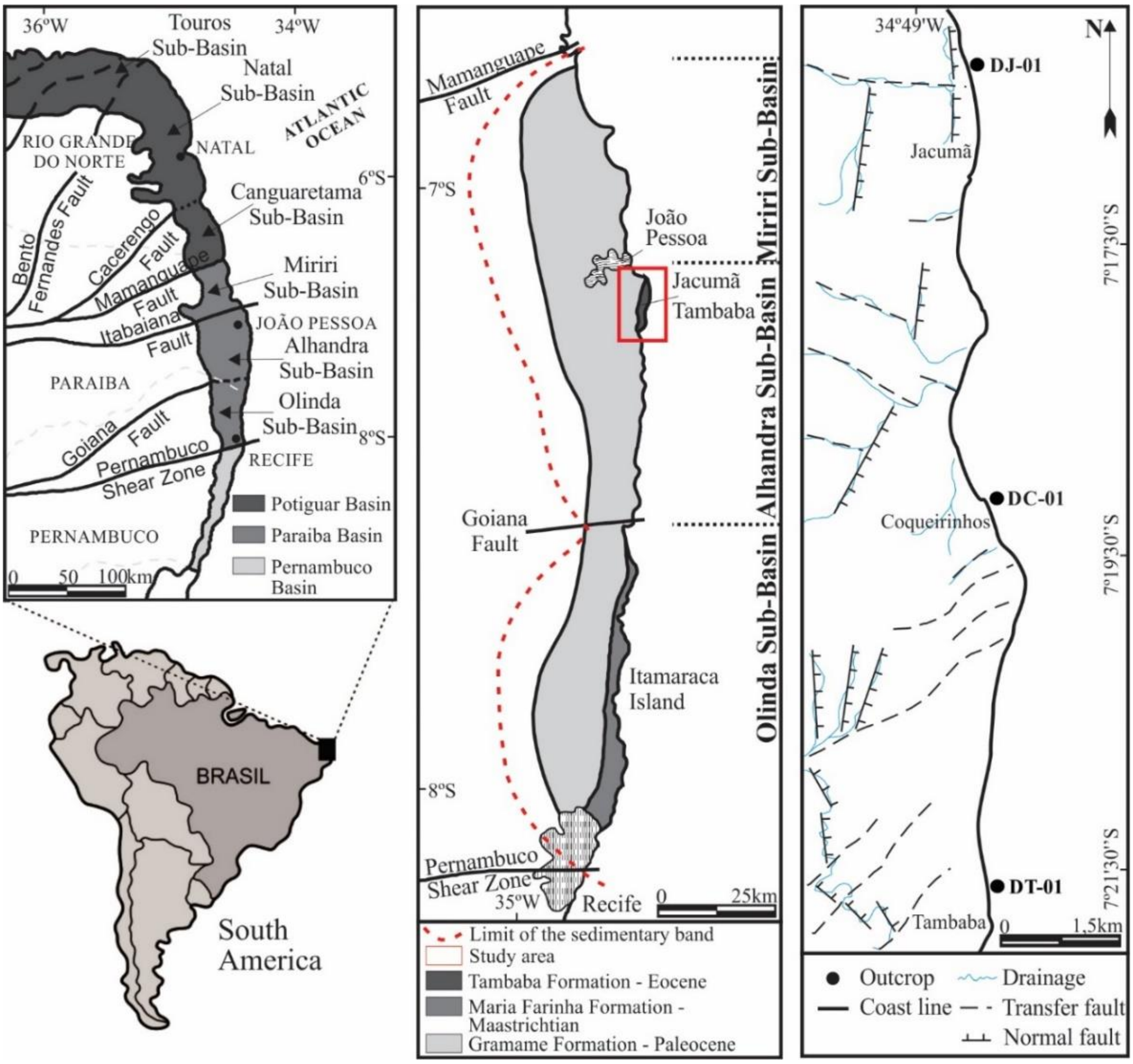
4 CARACTERIZAÇÃO DA ÁREA DE ESTUDO

4.1 LOCALIZAÇÃO E DESCRIÇÃO DA ÁREA

A região estudada está localizada a sul da capital paraibana, João Pessoa, e inserida no município de Conde, pertencente ao estado da Paraíba. Os afloramentos estão situados na linha de costa paraibana por uma extensão de aproximadamente 10 km entre as praias de Jacumã e Tambaba (Figura 1).

Tomando como referência a capital do estado de Pernambuco, Recife, a principal via de acesso é a BR-101 no sentido João Pessoa. O extremo norte da faixa estudada pode ser acessado através da PB-018 (aproximadamente 113 km de Recife) e o extremo sul através da PB-044 (aproximadamente 100 km).

Figura 1 - Localização da região estudada. Faixa costeira de ocorrência dos calcários recifais entre as praias de Jacumã e Tambaba.



Fonte: o autor, 2019.

4.2 ASPECTOS FISIOGRÁFICOS

O município de Conde, está inserido na unidade Geoambiental dos Tabuleiros Costeiros. Esta unidade acompanha o litoral de todo o Nordeste, apresenta altitude média de 50 a 100 metros. Compreende platôs de origem sedimentar, que apresentam grau de entalhamento variável, ora com vales estreitos e encostas abruptas, ora abertos com encostas suaves e fundos com amplas várzeas. De modo geral, os solos são profundos e de baixa fertilidade natural.

O clima é do tipo Tropical Chuvoso com verão seco. O período chuvoso começa no outono tendo início em fevereiro e término em outubro. A precipitação média anual é de 1.634.2 mm.

A vegetação é predominantemente do tipo Floresta Subperenifólia, com partes de Floresta Subcaducifólia e Cerrado/ Floresta.

Os solos dessa unidade geoambiental são representados pelos Latossolos e Argissolos nos topos de chapadas e topos residuais; pelos Argissolos com Fragipã, Argissolos Plínticos e Neossolos Quartzarêmicos nas pequenas depressões nos tabuleiros; pelos Argissolos Concrecionários em áreas dissecadas e encostas e Gleissolos e Neossolos Flúvicos nas áreas de várzeas.

4.3 GEOLOGIA

A gênese da Bacia Paraíba, como também das bacias sedimentares marginais do atlântico sul, está relacionada à abertura do Oceano Atlântico Sul, que ocorreu a partir da fragmentação do continente Gondwana. A evolução deste processo de rifteamento resultou na formação de bacias de margem passiva, que atualmente representam os principais alvos exploratórios petrolíferos na margem Atlântica do Brasil.

O sistema rifte que progrediu até o Aptiano-Albiano, começou sua evolução no Sul (Argentina), e se propagou para norte, acompanhado de intenso magmatismo na província Paraná Etendeka, cujo pico de atividade foi datado entre 133 e 130 Ma, do Jurássico Superior ao Cretáceo Inferior. Este processo deu origem a importantes sequências vulcano-sedimentares nas bacias da margem sudeste (Renne *et al*., 1992a, 1996a, b; Turner *et al*.,1994; Ernesto *et al.*, 1999, 2002; Mincato *et al*., 2003).

Conforme o modelo de rifte propagante de Bueno (2004), a evolução do Atlântico Sul se deu a partir de três estágios de abertura, de sul para norte. Segundo esse autor, o terceiro estágio, que culminou no Aptiano, chegou até a região das bacias de Sergipe e Alagoas. No entanto, trabalhos mais antigos como Matos (1992, 1999), e recentes (Córdoba *et al*., 2007; Barbosa *et al*., 2014), tem sugerido que o rifte na região entre Recife e Natal pode ter se estendido até o Albiano. Matos (1999), já havia sugerido que esse trecho do nordeste do Brasil teria apresentado uma evolução tardia em relação as demais bacias da margem sudeste.

4.3.1 Embasamento Pré-Cambriano

A Bacia Paraíba está inserida no contexto regional da Província Borborema. Almeida *et al*. (1977) definiram o nome para região de dobramentos do nordeste de Brito Neves (1975), situada ao norte do Cráton São Francisco e afetada pela Orogênese Brasiliana.

Oliveira & Santos (1993) e Santos (1995, 1996), baseando-se no modelo de evolução do tipo colagem tectônica, implantaram o conceito de "terrenos" ou processo de colagem de terrenos tectono-estratigráficos distintos na qual os terrenos da Província Borborema, na evolução pré-cambriana, teriam sido colados durante eventos orogênicos: Cariris Velhos (de idade Greenville) e Brasiliana (Pan-Africana). Esta última teria sido responsável pela justaposição e dispersão dos terrenos (Figura 2)

A Bacia Paraíba foi implantada sobre três terrenos distintos da Província Borborema, Terreno Rio Capibaribe, Terreno Alto Moxotó e o Terreno Alto Pajeú (Figura 2). Esses domínios fazem parte da Zona Transversal da Província Borborema que é limitada pelas duas principais zonas de Cisalhamento da região, a Zona de Cisalhamento Pernambuco (ZCPE), a sul, e a Zona de Cisalhamento Patos (ZCPA), a norte.

O embasamento do Terreno Rio Capibaribe é representado por ortognaisses paleoproterozoicos datados em 1,97 a 2,12 Ga (Neves *et al*., 2006), e pelo ortognaisse Taquaritinga, Mesoproterozoico, com idade 1,5 Ga (Sá *et al*., 2002). A cobertura, metassedimentar, é composta pelo Complexo Surubim, representado por xistos e gnaisse pelíticos com granada e/ou sillimanita, mármores, quartzitos e rochas calcissilicáticas.

Datações em zircões detríticos do complexo surubim forneceram idades arqueanas a neoproterozoicas, com a idade mais jovem em 665 ± 17 Ma. A idade de metamorfismo foi obtida a partir da leucossoma da porção migmatizada, o intercepto inferior da discórdia apresenta idades de 626 ± 15 Ma, interpretada como a idade de cristalização do leucossoma, portanto, idade de metamorfismo de alto grau.

O Terreno Alto do Moxotó, delimitado pelas falhas de Itabaiana e a de Goiana, é representado por uma associação basal, exposta em extensas áreas do terreno, e uma sequência supracrustal metavulcanossedimentar. O embasamento datado pelo método U-PB em zircão, forneceu uma concórdia superior de 2,11 ± 30 Ga. Para as rochas supracrustais, Complexo Lagoa das Contendas foram encontradas idades em torno de 1.012 ± 18 Ma (Santos *et al.*, 1994 e Santos, 1995a). A sequência Caroalina engloba micaxisto e o Complexo Sertânia compreende rochas metassedimentares originadas em ambiente continental. Estas sequências foram datadas, pelo método U-Pb SHRIMP e obtidas idades em torno de 2,0 Ga (Santos *et al*., 2004).

O Terreno Alto Pajeú, principal representante do evento geológico Cariris Velhos, delimitado pela Falha de Itabaiana e a ZCPA, é representado por uma associação metassedimentar intercalada com rochas metavulcânicas e metavulcanoclásticas pertencentes ao Grupo São Caetano. Esta associação foi datada, pelo método U-Pb SHRIMP, resultando em uma discórdia, onde o intercepto inferior cortou a idade 1.089 ± 143 Ga (Santos *et al*.,1994).

Nas décadas anteriores, toda a plataforma continental entre o Alto de Maragogi e o Alto de Mamanguape, foi interpretada como uma única bacia marginal denominada Bacia Pernambuco-Paraíba (Mabesoone & Alheiros 1988; 1993). Outros trabalhos incluíram a porção sedimentar costeira para o norte, até o Alto de Touros, em uma única área então denominada Bacia Pernambuco-Paraíba-Rio Grande do Norte (Mabesoone; 1995, 1996a; 1996b). No entanto, essa área da plataforma pode ser dividida em pelo menos três trechos, que apresentam estilo estrutural e preenchimento sedimentar diferenciados entre si. O trecho a norte da ZCPE apresenta enorme diferença em relação à porção a sul desta. Este fato levou a divisão deste trecho em duas bacias sedimentares distintas, a faixa a sul da ZCPE foi definida como Bacia Pernambuco, e a região a Norte ficou definida como Bacia Paraíba (Figura 2) (Lima Filho, 1998; Barbosa, 2004).

A compartimentação da Bacia Paraíba foi condicionada por falhas transcorrentes com direção NE-SW, que formaram altos estruturais e seus principais depocentros. As falhas de borda, com trend dominante NNW-SSE, representam as falhas relacionadas ao processo de abertura da bacia. Estas falhas de transferência, geralmente, são falhas de pequeno rejeito favorecendo uma sedimentação rasa, que preencheu grabéns de pouca expressão na região emersa da bacia. A literatura sobre a bacia inclui algumas publicações dedicadas à descrição de feições neotectônicas que evidenciam reativações tardias. Estas reativações podem ser observadas principalmente através de falhas que afetaram a Formação Barreiras (Mioceno-Pleistoceno), assim como mudanças no padrão de drenagem observadas na faixa costeira (Furrier *et al*., 2006, Bezerra *et al*., 2014).

Os principais depocentros da Bacia Paraíba estão relacionados ao Graben de Itamaracá, a norte da ZCPE, onde foi perfurado o poço estratigráfico 2-IST-1-PE, que atingiu o embasamento a 400m de profundidade, e o Graben de João Pessoa. Através de dados de poços hidrogeológicos, Barbosa (2004) elaborou uma seção geológica com os principais domínios estruturais na região da faixa costeira da Bacia da Paraíba entre Recife e João Pessoa (Figura 3). Este perfil foi comparado com o perfil estrutural inferido, construído a partir do perfil de elevação topográfico obtido através de dados de elevação do terreno a partir do

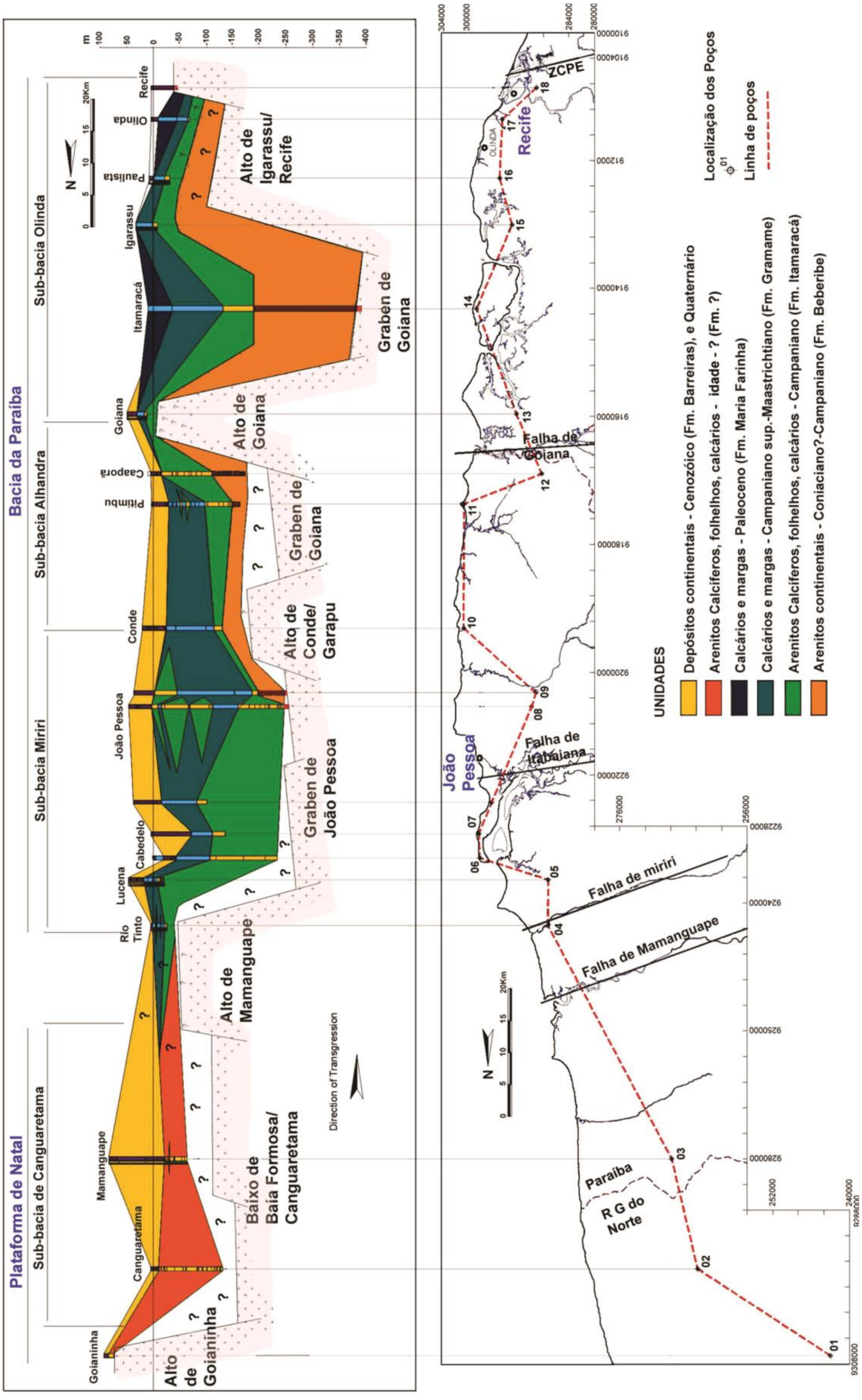
Figura 2 - Subdivisão das bacias marginais da porção oriental do nordeste do Brasil. Em destaque, os terrenos pré-cambrianos que compõem o embasamento da Bacia Paraíba, cujos domínios coincidem com a Zona Transversal do Nordeste, limitada pelas grandes Zonas de Cisalhamento Pernambuco e Patos (modificada de Barbosa, 2007).

Fonte: Barbosa & Lima Filho, 2006.

Google Earth. A comparação do perfil topográfico com a seção geológica sugere a ocorrência de blocos relativamente rebaixados, sendo eles, o Graben de Goiana, de Itamaracá e o de João Pessoa, individualizados por dois altos estruturais principais, o Horst de Goiana e o Horst de Conde. A formação de vales fluviais, relacionados a zonas de cisalhamento do embasamento na região do litoral da Bacia Paraíba também foi estudada por Bezerra et al. (2014), que evidenciaram o papel de reativações tardias dessas grandes estruturas.

No aspecto regional, os principais trends são representados por falhamentos normais que estão associados à borda da bacia, com direções principais NNW-SSE. Além desse padrão observa-se que antigas zonas de cisalhamento do embasamento foram reativadas como falhas de transferência, com direção NE-SW. Desta maneira, as reativações são controladas pela trama dúctil e rúptil do embasamento (Bezerra *et al*., 2011, Bezerra *et al*., 2014).

Figura 3 - Seção geológica elaborada a partir de perfis de poços ao longo da faixa costeira entre a ZCPE e o Alto de Mamanguape.



Fonte: Barbosa, 2004.

4.3.2 Unidades Litoestratigráficas Fanerozoicas

O arcabouço tectono-estratigráfico das bacias marginais inicia-se com a megassequência sin-rifte, onde predominam os depósitos flúvio-lacustres que foram condicionados pelos esforços distensionais. Em seguida ocorreu a megassequência transicional, associada à formação do golfo marinho, representado por espessos depósitos evaporíticos. Esta última foi seguida pela megassequência pós-rifte, relacionada à fase de subsidência térmica, e instalação de extensas plataformas carbonáticas, controladas, principalmente, pela variação do nível do mar (Asmus & Ponte, 1973; Milani, 1989; Feijó, 1994).

A Bacia Paraíba, em sua faixa costeira, apresenta algumas diferenças, no tocante a idade das litologias que a preencheram, em relação a essas principais fases de evolução do Atlântico Sul. É possível inclusive, que como sugerido acima, a fase rifte nessa faixa tenha se iniciado de forma tardia em relação às demais bacias da margem sudeste, e que esta tenha se estendido até o Albiano. Até o presente, não há registro de rochas de idade Aptiana, ou mais antigas, na faixa Recife-Natal (Beurlen, 1967; Mabesoone & Alheiros, 1988; Barbosa, 2004).

4.3.2.1 Formação Beberibe

O preenchimento sedimentar da faixa costeira da Bacia Paraíba iniciou-se de forma tardia em relação a outras bacias sedimentares da margem continental brasileira. A sequência basal representada pela Formação Beberibe é um importante sistema aquífero para Região Metropolitana do Recife e é composta por arenitos flúvio-lacustres continentais, cuja idade ainda é pouco estudada, sendo considerada Coniaciano?-Santoniano (Kegel, 1954; Beurlen, 1967a, 1967b; Mabesoone & Alheiros, 1988; Souza, 1998; Barbosa, 2004; Souza, 2006). Esta unidade apresenta depósitos areno-argilosos, onde são encontrados arenitos médios a grossos, localmente conglomeráticos. Os depósitos podem se apresentar friáveis de coloração cinzenta a creme, e eventualmente bem litificados.

A idade da Formação Beberibe foi estimada por Beurlen (1967b), através de macrofósseis, em especial fragmentos de amonoides, como sendo Santoniana. No entanto, na época os autores costumavam incluir os depósitos da Formação Itamaracá, de natureza transicional, dentro da Formação Beberibe, de natureza continental. Por isso, é possível que a Formação Beberibe tenha idade Turoniana, ou pós Turoniana (Coniaciano?), conforme descrito para depósitos que ocorrem na porção basal da faixa mais a norte, a Plataforma de Natal (Barbosa, 2007).

4.3.2.2 Formação Itamaracá

Esta unidade ocorre sobreposta aos arenitos da Formação Beberibe, e representa o registro de quando a Bacia Paraíba recebeu influência transicional, ou seja, depósitos com influência marinha. A unidade é composta por arenitos calcíferos, carbonatos com siliciclásticos e no topo da sequência, depósitos fosfáticos e dolomíticos, que em alguns trechos da bacia apresentam nível rico de fosfato ou fosforita. O horizonte rico em fosfato, caracterizado por pico de raios gama em poços, ocorre ao longo de toda a Bacia (Barbosa, 2004). Este nível foi interpretado como uma superfície de condensação, durante um máximo transgressivo, que promoveu na região proximal da bacia um evento de alta produtividade orgânica que está ligado à formação dos níveis de fosfato orgânico com a acumulação de argilominerais, matéria orgânica (pelotas fecais) e de macro e microfósseis (Kegel, 1954). Este evento esteve relacionado à alta produtividade marinha e baixa taxa de sedimentação (Kegel, 1954, 1955; Menor *et al*., 1977; Menor & Amaral, 1979; Amaral *et al*., 1977; Souza, 1998; Lima Filho *et al*., 1998; Barbosa, 2004; Souza, 2006). Este horizonte tem sido proposto como um marco estratigráfico, uma superfície de inundação máxima (SIM), que ocorreu durante a fase transgressiva que possivelmente apresenta idade Meso-Campaniano-Eo-Maastrichtiano (Souza, 2006; Barbosa, 2004, 2007). Vale à pena ressaltar que não há registro do nível fosfático a sul da ZCPE e a norte da Falha de Mamanguape, mostrando que o ambiente de sedimentação da Bacia Paraíba seria diferenciado das áreas adjacentes da faixa costeira.

Embora alguns autores tenham incluído os depósitos do evento transgressivo dentro da unidade posterior, a Formação Gramame, ou tenham tratado esses depósitos como um membro da Formação Beberibe (Kegel, 1955), Barbosa (2004, 2007) e Souza (2006), sugeriram a individualização dessa formação considerando os conceitos da estratigrafia de sequências.

4.3.2.3 Formação Gramame

Essa unidade é composta por carbonatos e margas depositados sobre os depósitos transicionais da Formação Itamaracá, comumente, biomicritos e bioesparitos, que formaram uma plataforma estreita sobre a atual faixa costeira da bacia. Estes carbonatos ocorrem em afloramentos ao longo da linha de litoral e apresentam importância econômica, pois são minerados e empregados como matéria prima na fabricação de cimento. Apesar de terem sido inicialmente interpretados como carbonatos de plataforma mais profunda (Tinoco, 1971), estudos mais recentes têm demonstrado que estes foram depositados em plataforma rasa a média com relativa influência de estuários (Barbosa, 2007). Estes depósitos, possivelmente, estão ligados a um estágio de mar alto, que resultou no estabelecimento da plataforma após o evento transgressivo. A Formação Gramame é principalmente composta por calcários margosos, calcários bioclásticos e margas, e sua idade seria Maastrichtiana (Beurlen, 1967a, 1967b; Tinoco, 1971; Muniz, 1993; Lima & Koutsoukos, 2002).

Embora a porção média e superior desta formação não apresente a mesma quantidade de fósseis observados nos estratos da Formação Itamaracá, esta unidade contém fósseis de corais, peixes cartilaginosos (tubarões e raias), peixes, crocodilos marinhos, moluscos, plantas e crustáceos (Muniz, 1993; Barbosa, 2004, 2007). A maior parte dos fósseis de moluscos descritos para a unidade Gramame foi encontrada na região norte da bacia, nas proximidades do Rio Gramame, e nesta porção da bacia a Formação Gramame apresenta apenas a porção do Maastrichtiano médio a basal (Lima & Koutsoukos, 2002).

4.3.2.4 Formação Maria Farinha

Acima da Formação Gramame, na faixa sul da bacia, entre a cidade de Recife e a Falha de Goiana ocorrem calcários de coloração cinza a amarelados, que representam a Formação Maria Farinha, de idade Daniano, e que repousa sobre o Maastrichtiano Superior através da Passagem K-T (Beurlen, 1967b, Muniz, 1993; Albertão, 1993). A idade desses depósitos, a partir de análise bioestratigráfica realizada com vários microfósseis ficou estabelecida a idade daniana, do começo do Paleoceno (Albertão, 1993; Albertão & Martins Jr.,1996; Stinnesbeck & Keller, 1996).

Conforme descrito por Beurlen (1967) ocorrem também, na faixa de litoral a sul de João Pessoa, calcários recifais, chamados por este autor de "detríticos", cuja afinidade com a Formação Maria Farinha descrita na Faixa Recife-Goiana foi proposta apenas pelo fato de que ambos os conjuntos de depósitos seriam pós-Cretáceo. De fato, como comprovado através do estudo de nanofósseis, da Falha de Goiana até o Norte de João Pessoa, ocorre um desaparecimento de depósitos da Formação Gramame de idade Maastrichtiano Superior, fazendo com que estes depósitos estejam posicionados de forma discordante sobre o Maastrichtiano médio a basal (Lima & Koutsoukos, 2002).

A transição entre as unidades Gramame e Maria Farinha, preservada na porção sul da Bacia Paraíba representa um registro geológico importante, a passagem K-T (Albertão, 1993; Morgan *et al*., 2006; Neumann *et al*., 2009, Nascimento-Silva *et al*., 2011). Interpretado como um período de crise biótica catastrófica na história geológica, associado ao impacto de corpos extraterrestres, cujo reconhecimento foi feito através da identificação de anomalia de irídio em vários locais no planeta (Alvarez *et al*., 1980, 1984; Alvarez, 1986; Albertão, 1993; Albertão *et al*., 1993, 1994a, 1994b; Keller *et al*., 2002; Keller, 2001, 2003, 2005). Este período é caracterizado como uma época de intensas mudanças nas condições ambientais (clima, variação do nível do mar), o que afetou a sobrevivência dos organismos, principalmente do plâncton marinho, invertebrados marinhos e os grandes répteis terrestres (Keller, 1996a, 1996b, 2001; Archibaldi, 1996).

Beurlen (1967a), e posteriormente Mabesoone & Alheiros (1988), já haviam interpretado que os calcários e margas de idade paleocênica encontrados na faixa Recife-Goiana teriam sido depositados sob um regime regressivo, que afetou a bacia, e possivelmente teve seu clímax no início do Daniano (Barbosa, 2004, 2007). De forma especial na exposição da Mina Poty, é possível perceber a intensificação do evento regressivo com a transição do ambiente carbonático para um sistema influenciado por siliciclásticos, com a presença de quartzo detrítico (Barbosa, 2004, 2007).

É possível que este evento tenha sido influenciado por soerguimento tectônico, induzindo uma regressão forçada, mais intensa nas sub-bacias Alhandra e Miriri (Barbosa *et al*., 2003; Barbosa, 2004). Neste caso, a erosão mais expressiva da plataforma exposta nestas sub-bacias resultou na perda dos carbonatos do topo da Formação Gramame e, possivelmente, dos depósitos pertencentes à Formação Maria Farinha, que ficou restrita a porção sul.

4.3.2.5 Formação Tambaba

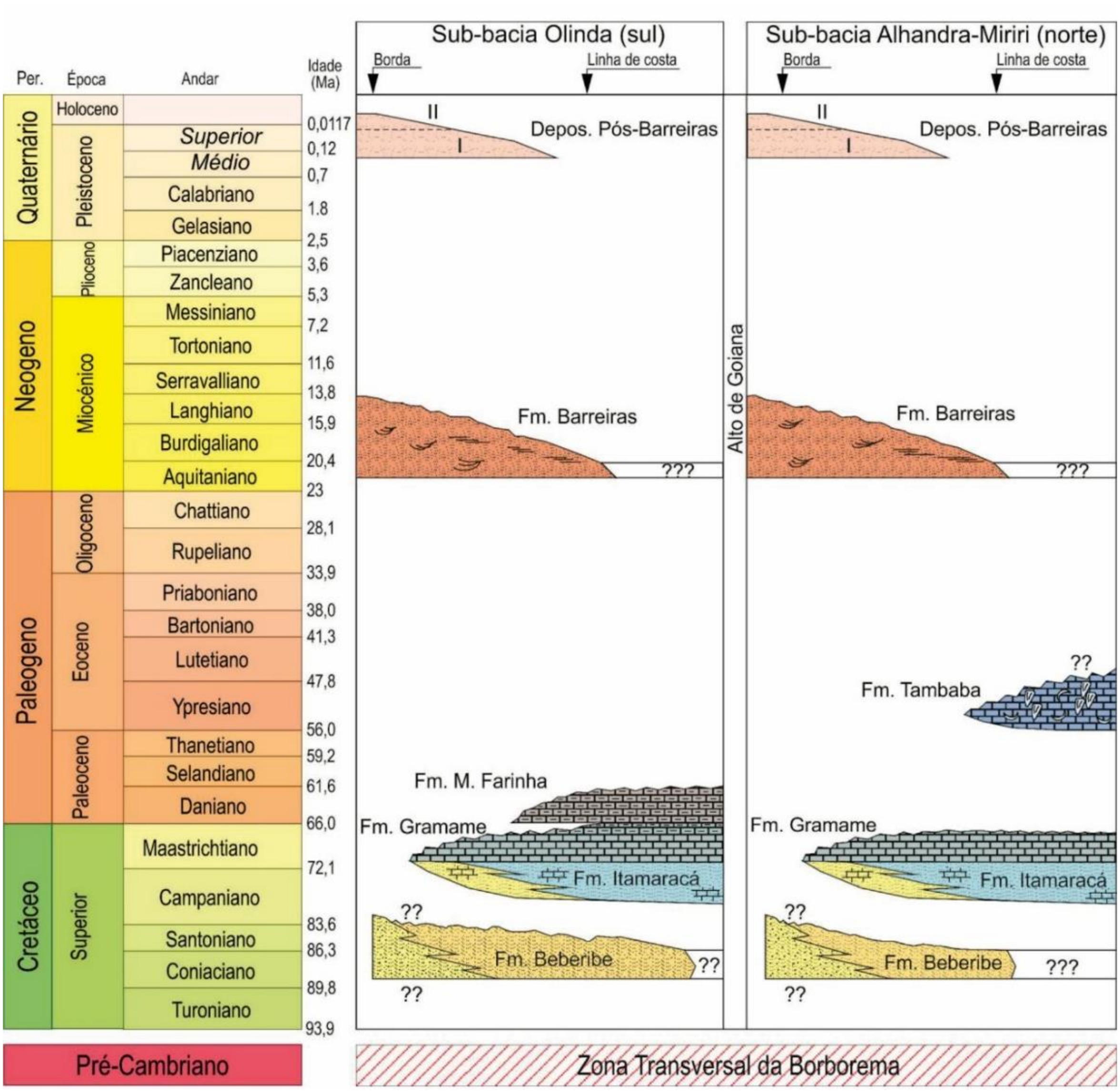
Embora poucos trabalhos tenham tratado a ocorrência destes depósitos, Almeida (2000, 2007), realizou um estudo mais sistemático desses depósitos nomeados por Beurlen (1967) como Maria Farinha Superior. Este último autor caracterizou a fáunula de moluscos presentes nestes depósitos e sua paleocologia, além de seu importante conteúdo icnofossilífero, e sugeriu que estes calcários seriam de possível idade Eocênica.

Correia Filho (2015) baseado no estudo das relações estratigráficas, na análise de modelos de fácies carbonáticas e na aplicação dos conceitos de estratigrafia de sequências definiu esses depósitos como Formação Tambaba. Essa unidade é composta por calcários recifais de coloração creme, variando entre calcilutito, calcarenito e calcirudito ricos em fósseis ou icnofósseis.

4.3.2.6 Formação Barreiras

Depositados sobre uma extensa faixa ao longo das bacias marginais brasileiras, do Pará ao Rio de Janeiro, e recobrindo de forma discordante, as sequências sedimentares mais antigas, bem como trechos do embasamento pré-cambriano, que formam as bordas adjacentes dessas bacias, afloram os depósitos da Formação Barreiras. Esta unidade está relacionada à existência de leques aluviais e sistemas fluviais, que possivelmente gradavam para sistemas deltáicos (Rossetti & Truckenbrodt 1989, Rossetti *et al.*, 1990, Rossetti 2000, 2001, 2006a, b, Netto & Rossetti 2003, Rossetti & Santos Jr. 2004). Sua variação faciológica compreende desde conglomerados até argilitos. Comumente apresenta estratificações cruzadas planares e acanaladas. Segundo autores mais antigos a idade dessa formação seria Plio-pleistocênica (Beurlen, 1967a, 1967c; Mabesoone & Alheiros, 1988, 1993). No entanto, trabalhos recentes têm sugerido idade miocência (Arai *et al.*, 1988, 1994, Arai 1997, Leite *et al.*, 1997a, b).

Figura 4 - Carta estratigráfica para a porção emersa da Bacia Paraíba, considerando o registro das unidades nas duas sub-bacias (norte-sul).



Fonte: Correia Filho, 2015.

5 MATERIAIS E MÉTODOS

O presente trabalho foi realizado através das seguintes etapas: revisão bibliográfica, etapas de campo, análises laboratoriais e elaboração de um modelo deposicional e de evolução diagenética dos depósitos.

A revisão bibliográfica foi realizada com foco nas principais contribuições científicas no âmbito regional e local a respeito da área de interesse, com ênfase nos aspectos sedimentológicos e no preenchimento sedimentar.

5.1 ETAPAS DE CAMPO

Foram realizadas etapas de campo com a utilização dos instrumentos básicos de campo (martelo, lupa, bússola, canivete, ácido clorídrico, trena e GPS) para o estudo dos afloramentos. Nos afloramentos foram realizadas descrições sedimentológicas, estruturais, seções estratigráficas nos mais representativos e coleta de amostras para posterior confecção de seções delgadas e análises químicas.

Para a determinação em campo dos diferentes tipos de rochas carbonáticas, foi utilizada a classificação de Gabrau (1904) que é baseada na granulação da rocha.

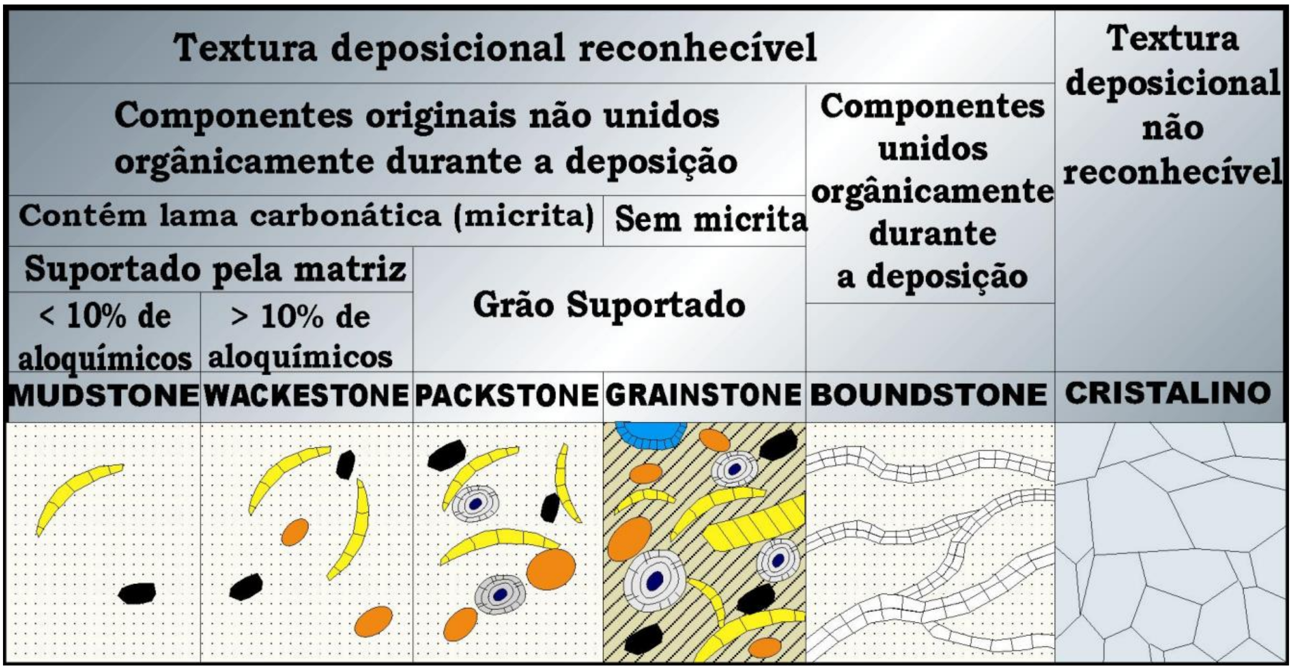
5.2 ANÁLISES LABORATORIAIS

Na descrição das fotomicrografias foi utilizada uma simbologia simplificada: (//) para indicar fotomicrografias obtidas com nicois paralelos e (+) para nicois cruzados. Para o estudo microscópico, foram aplicados os métodos de classificação de Dunham (1962).

5.2.1 Microscopia Óptica de Luz Transmitida

A análise petrográfica foi realizada com base em microscópio polarizado modelo OLYMPUS BX-51, com uma câmera digital modelo OLYMPUS DP26 acoplada ao microscópio do Laboratório Gemologia da UFPE. Foram descritas e interpretadas seções delgadas a partir de feições texturais e estruturais, composição mineralógica e paleontológica, porosidades e processos diagenéticos.

Figura 5 - Classificação de Dunham (1962) de rochas carbonáticas de acordo com suas texturas deposicionais.



Fonte: Dunham, 1962.

5.2.2 Catodoluminescência

Também foi realizado o estudo das seções delgadas em equipamento de catodoluminescência Cambridge Image Technology Ltd. (CITL) modelo CL8200, acoplado à um microscópio óptico, do Laboratório de Catodoluminescência no Departamento de Geologia da UFPE, tendo como objetivo de complementar a petrografia convencional, visto que, realça feições que não são perceptíveis na microscopia óptica de luz transmitida. A técnica de catodoluminescência (CL) resulta do bombardeamento de elétrons sobre a amostra, que ao produzir a excitação da estrutura atômica dos minerais presentes produz luminescência. A técnica de CL, no caso de rochas carbonáticas, apresenta enorme aplicação na caracterização de processos diagenéticos, evolução de cimentos autigênicos e na descrição de componentes microfaciológicos (Boggs & Krinsley, 2006).

5.2.3 Análises Geoquímicas

Uma fração representativa das amostras coletadas foi pulverizada no Núcleo de Estudos Geoquímicos e Laboratório de Isótopos Estáveis (NEG-LABISE) do Departamento de Geologia da UFPE em moinho de disco de carboneto de volfrâmio. As amostras em pó foram então submetidas a análises geoquímicas.

Os dados de isótopos estáveis (carbono e oxigênio) foram obtidos no NEG-LABISE e no Laboratório de Geocronologia da Universidade de Brasília e seguiram uma metodologia de espectrometria de massa de razão isotópica, onde foram utilizados um espectrômetro de massa de razão isotópica de fluxo contínuo (DELTA V™ Plus IRMS) e uma fonte gasosa com setor magnético. Usando o acessório Thermo™ GasBench II, 600-800 μg de amostra foram inseridos em frascos de vidro limpos com tampas de septo de borracha condicionadas em um bloco com temperatura controlada de 70°C. Uma agulha de cromatografia gasosa foi então usada para realizar o processo flushfill. Isso troca o ar atmosférico no frasco para tornar o ambiente reativo livre de interferência, injetando um fluxo contínuo de hélio por 6 min. Usando uma bomba doseadora, cinco gotas de H_3PO_4 99% foram adicionadas aos frascos para uma reação de extração de CO_2 por 1h:

$$2H_3PO_{4(l)} + 3CaCO_{3(s)} \rightarrow Ca_3(PO_4)_{2(aq)} + 3H_2O_{(l)} + 3CO_{2(g)}$$

Após a extração do CO_2, uma segunda agulha cromatográfica foi utilizada para coletar o gás do frasco e passá-lo por uma coluna cromatográfica em fluxo contínuo de hélio. Depois de passar pela coluna, o gás foi injetado na fonte de íons a ser medido. Os valores de $\delta^{13}C$ e $\delta^{18}O$ são apresentados em partes por mil (‰) com base no padrão Vienna Pee Dee Belemnite (VPDB).

Para a análise dos elementos maiores, foi utilizada uma porção (2,25g) de cada amostra foi colocada em uma estufa para secar a 110°C, e a seguir foi colocada em uma mufla a 1000°C por 2h para determinar a perda ao fogo. Pérolas fundidas foram geradas usando tetraborato de lítio como fundente. As pérolas foram analisadas em Espectrômetro de Fluorescência de Raios-X Rigaku modelo ZSX Primus II equipado com tubo de Rh, e sete análises de cristais foram realizadas pelo método da curva de calibração, que se baseou em materiais de referência internacional. Os resultados são exibidos com base em% de peso (elementos principais) ou ppm (elementos traços).

6 RESULTADOS

Os resultados obtidos até o momento no referido trabalho já estão publicados na forma de dois artigos em dois periódicos de qualis B2 e A2, respectivamente. Enquanto um terceiro artigo foi submetido em periódico de qualis A3.

6.1 TEXTURE AND COMPOSITIONAL CHARACTERIZATION OF THE MICROFACIES OF THE REEF LIMESTONES OF THE TAMBABA FORMATION, PARAÍBA SEDIMENTARY BASIN, NE BRAZIL

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Keyword:	Carbonate Facies, Sedimentology, Tambaba Formation, Reef Limestones, Paraiba Basin

Texture and compositional characterization of the microfacies of the Reef Limestones of the Tambaba Formation, Paraíba Sedimentary Basin, NE Brazil

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Abstract: The Tambaba Formation has an Eocene age and is restricted to the surface in the northern coastal region of the Paraiba Basin. Previously, the carbonate deposits constituting this unit were often considered as the Upper Maria Farinha Formation, admitting a distinct stratigraphic portion of the Paleocene Maria Farinha Formation. This work aimed to build a paleoenvironmental model of the reef limestones of that formation through sedimentological studies. The studied outcrops are located in the coastal strip on the beaches of Tambaba, Coqueirinho and Jacumã, in the state of Paraíba. These carbonate deposits present a cochinoidal aspect and, due to erosion, an irregular ruiniform aspect. Accumulating portions of bivalves and gastropods provided an intense process of bioerosion, caused mainly by perforating organisms. In addition, they present an intense variation of facies that were characterized through optical microscopy and cathodoluminescence between Mudstones, Wackestones and Packstones. They are essentially composed of a micritic matrix with the presence of pyrite and quartz in smaller proportions, however, the facies undergo the diagenetic process of replacement of calcite by dolomite (dolomitization). Other diagenetic processes such as compaction, dissolution and cementation were identified in the petrographic studies. Evidence of intense pyritization replacing valves, and fragments of bioclasts and tubes of Thallassinoides indicate an eodiagenetic stage.

Keywords: Carbonate Facies, Sedimentology, Tambaba Formation, Reef Limestones, Paraiba Basin

1 INTRODUCTION

The Tambaba Formation is a lithostratigraphic unit of the Eocene of the Paraíba Basin. This unit is represented by carbonate rocks deposited in a marine reef environment. They usually have a light yellow color, bioclastic texture and layering, with reef constructions presenting an irregular weathered appearance due to erosion (Veras, 2017).

For a long time, this unit was considered the upper part of the Maria Farinha Formation. However, it has specific faciological, stratigraphic and petrographic features that differ considerably from the stratification described for the typical stretch of the Maria Farinha Formation, which was established in the southern portion of the coastal strip of the Paraíba Basin. The Tambaba Formation occurs in the Paraíba Basin and in the Alhandra and Miriri Sub Basins, and is mappable at a scale of 1:25,000 (Correia Filho *et al.*, 2015).

Based on the study of stratigraphic relationships, the analysis of carbonate facies models and the application of sequence stratigraphy concepts, Correia Filho *et al*. (2015) defined these reef deposits as the Tambaba Formation.

The objective of this work is to characterize the reef limestones of the Tambaba Formation in sedimentological, petrographic, microfaciological, microstructural and diagenetic terms. The results of this research will contribute to a more detailed knowledge of the reef limestones of the Tambaba Formation, as well as a better understanding of the geological evolution of a region that lacks more detailed research, which is the Paraíba Basin.

2 GEOLOGICAL CONTEXT

The coastal strip of the Paraíba Basin is located in the eastern portion of Northeast Brazil between the Pernambuco Shear Zone and the Mamanguape High Structural Zone, which is related to a branch of the Patos Shear Zone (Figure 1). The geological knowledge, onshore and offshore, of this area is still deficient in comparison with neighboring basins, such as the Potiguar Basin or the Pernambuco Basin.

Deposits of reef-lagoon origin occur in the Alhandra and Miriri sub-basins in the sedimentary column of the Paraíba Basin between the Campanian-Danian carbonate sequence (Itamaracá, Gramame and Maria Farinha formations) and the Miocene continental siliciclastic sequence (Barreiras Formation and Quaternary Sediments) (Mabessone & Alheiros, 1988; Barbosa, 2004) (Figure 2). Although few studies have evaluated the occurrence of these deposits, Almeida (2000, 2007) carried out a more systematic study of these deposits, which were named by Beurlen (1967a) as the Maria Farinha Superior Formation. The latter author characterized the molluscs present in these deposits and their paleoecology, in addition to their important ichnofosilliferous content, and suggested that these limestones were possibly of Eocene age. However, an erosive/depositional gap of at least 7 million years may have occurred between the top of the Maria Farinha Formation and the lagoon-reef limestones.

These deposits have always been cited as belonging to the Maria Farinha Formation as suggested by Beurlen (1967a), who correlated them with Paleocene deposits that occur at the top of the Gramame Formation in the southern region of the coastal strip.

However, this author observed a difference between the limestone faciology of the classical name of Maria Farinha and the deposits that occur in the northern portion of the coastal strip and referred to the latter as the “Upper Maria Farinha” Formation.

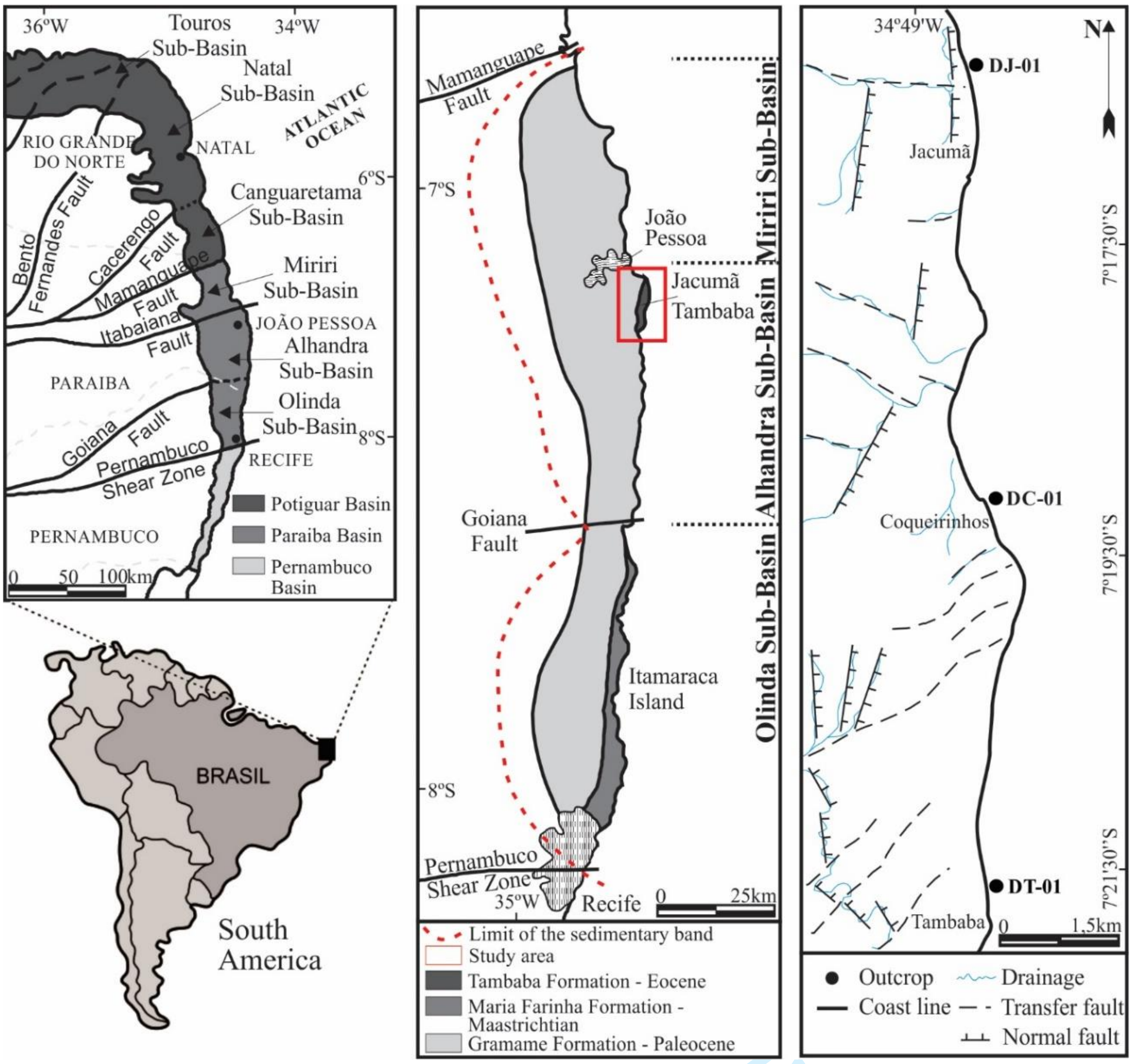

Figure 1. Location map of the Paraíba Basin and the Tambaba Formation occurrence area.

Considering lithofaciological, paleontological, biochronological and depositional aspects, Correia Filho *et al*. (2015) proposed the individualization of these carbonate deposits, previously named Upper Maria Farinha Formation by Beurlen (1967a), as the Tambaba Formation. These deposits outcrop in the Alhandra and Miriri sub-basins to the north of the Paraíba Basin along a strip of beach between the beaches of Tambaba and Jacumã (Correia Filho *et al*., 2015; Veras, 2017). Petrographic studies by Correia Filho *et al*. (2015), Távora *et al*. (2017) and Veras (2017) highlighted the carbonate microfacies and the diagenetic changes that occurred in these deposits.

The outcrops of these reef limestones have a rounded general morphology (“egg box pattern”), are locally stratified, have a bioclastic texture and eroded appearance (Veras, 2017). These outcrops are located between 0 and 10 m above sea level, vary in grain size between calcilutite and calcirudite, and have molds of rhodoliths, bivalve shells and tubes of drilling and excavating organisms (Correia Filho *et al*., 2015; Távora *et al*., 2017; Veras, 2017).

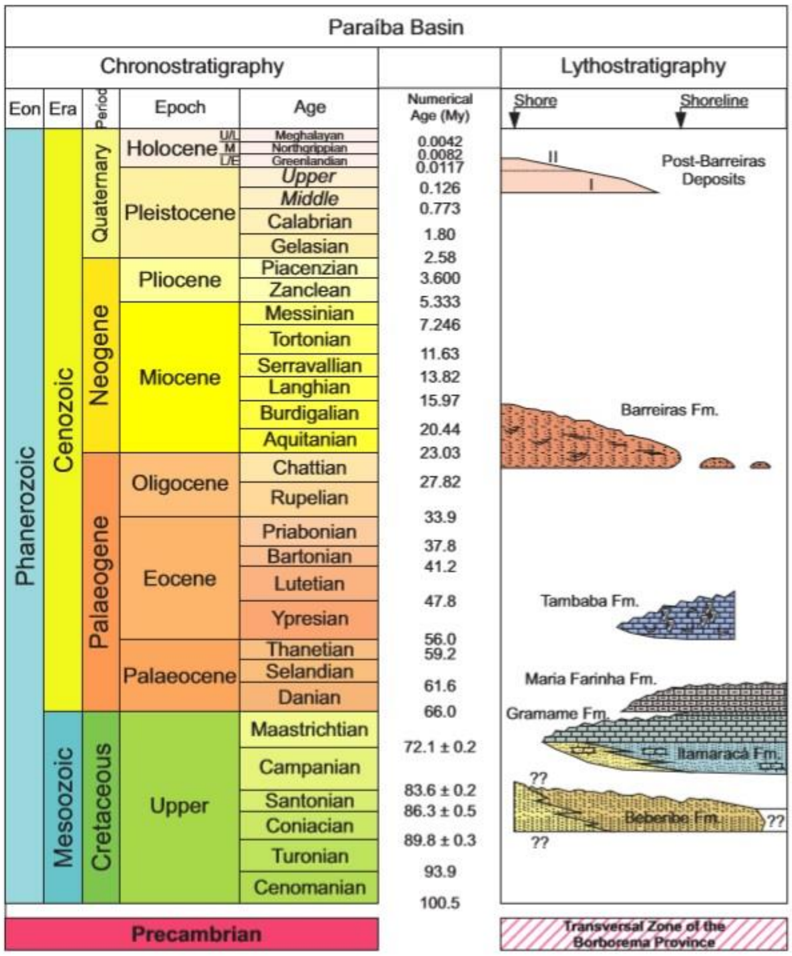

Figure 2. Chronostratigraphy and lithostratigraphy of the onshore portion of the Paraíba Basin, taking into consideration the record of the units in the two sub-basins (north and south), including the newly identified unit of the Tambaba Formation (modified from Correia Filho *et al*. 2015). Geochronology according to the chart of the International Commission on Stratigraphy (May, 2019). The positioning of deposits is according to available data (Almeida 2000; Barbosa *et al*. 2006b; Rossetti *et al*. 2011, 2012).

3 REEFS

Reefs are unique sedimentary systems. The interrelationship of physical, chemical and biological processes makes them especially interesting and, in addition, fossil reefs are large repositories of hydrocarbons (Tucker & Wright, 1990).

In simple terms, two characteristics characterize reefs. First, they are somewhat constrained laterally, although they may cover large areas and/or have significant relief. Second, they show evidence of a biological influence during growth, although this is not always clear in some ancient reefs such as mud mounds. The term reef has been used by some researchers to describe any discrete accumulation of carbonate, but Dunham (1970a) suggested that a distinction be made between stratigraphic reefs, which are laterally restricted accumulations of carbonate, perhaps composed of small overlapping reefs, and ecological reefs, which he considered rigid, wave resistant, topographically distinct and biogenically formed. The connotation that to be a 'reef' the structure must have been resistant to waves is a requirement of many reef definitions, but proving 'wave resistance' on ancient reefs is difficult. In this work, the term is used in a general sense for any biologically influenced carbonate accumulation that was large enough during formation to possess some topographic relief. It should be noted that a variety of organisms can build reefs (Longman, 1981), involving many different processes. As a result, a broad spectrum of reefs can be formed.

Ancient reefs exhibit a vertical succession of litho and biofacies, starting with a basal bioclastic accumulation, followed by colonization of structural constructs that become increasingly diverse towards the top and culminate in a unit of fouling organisms with low specific diversity (Davis Jr, 1983). Four stages of growth can be recognized: **I- Stabilization**: characterized by accumulations of skeletal calcareous sands composed of fragments of massive invertebrate carapaces (corals, poriferans, bryozoans and branched red algae) and mats of green algae, which serve as a substrate for sessile organisms; **II- Colonization**: thin level of the reef, which reflects the initial colonization by branched and encrusting metazoans, the main builders of reefs (algae, bryozoans, porifera and corals); **III- Diversification**: Diversity increases and a greater variety of growth forms occurs. This stage forms most of the reef; **IV- Domain**: this phase is characterized by lamellar (encrusting) forms reflecting a lamellar frame to the reef. Evidence of higher energy is present when a rudstone forms.

Stages I, II and III appear to reflect autogenic succession, as each stage prepares the environment for the next. While stage IV presents an allogenic succession, as the reef development occurs in shallow water conditions and progressively higher energy (Tucker & Wright, 1990).

4 MATERIALS AND METHODS

Reef limestone classification, microfacies interpretation, diagenetic evolution and depositional environments are based on field observations, in addition to detailed description of samples and thin sections. The fieldwork was carried out in a coastal strip of the state of Paraíba on the beaches of Tambaba and Jacumã, represented by 08 outcrops.

These outcrops were sampled along a vertical profile perpendicular to the layers, where samples were taken following a base-top sequence of approximately 5.5 m in height (example: from DT-01A to DT-01E). For this, a small two-stroke engine drill was used that provides cores of 25 mm in diameter and up to 10 cm in length.

The laboratory analysis consisted of petrographic descriptions of 30 thin slides of representative samples, using a petrographic microscope model BX-41 Olympus. Cathodoluminescence analysis was also performed using a Cambridge Image Technology Ltd (CITL) CL8200 cathodoluminescence optical system, coupled to a Zeiss Axioscope A1 optical microscope, at the Department of Geology at the Federal University of Pernambuco (UFPE).

The integrated analysis allowed the classification of the reef limestones of the Tambaba Formation using the propositions of Grabau (1904) and Dunham (1962). In addition, it was possible to characterize the microfacies of these reef limestones based on textural and microstructural characteristics and fossil content, in addition to defining the diagenetic evolution undergone by these rocks.

5 RESULTS

The reef limestone deposits studied occur both on the beach strip, up to where they are covered by the Barreiras Formation strata, and in the intertidal region, where they are partially or totally covered by seawater during high tide, and by recent beach sediments (Figure 3). They present a limited lateral extent, but an intense vertical variation of facies and are between 0 and 10 meters above sea level.

Figure 3. The reef limestones of the Tambaba Formation occur both on the beach strip and in the intertidal region, where they are partially or totally covered during high tide (red arrows). Outcrops located on Tambaba Beach.

In general, these deposits have a cream color, cochinoidal appearance, locally layered and, due to erosion, the reef constructions have an irregular ruiniform appearance (Figure 4). According to the classification by Gabrau (1904), in the reef limestones investigated there is a predominance of calcilutites, but due to their facies variation, calcarenites and calcirudites were also found. The stratigraphic sections constructed illustrate this intense faciological variation (Figures 5 and 6).

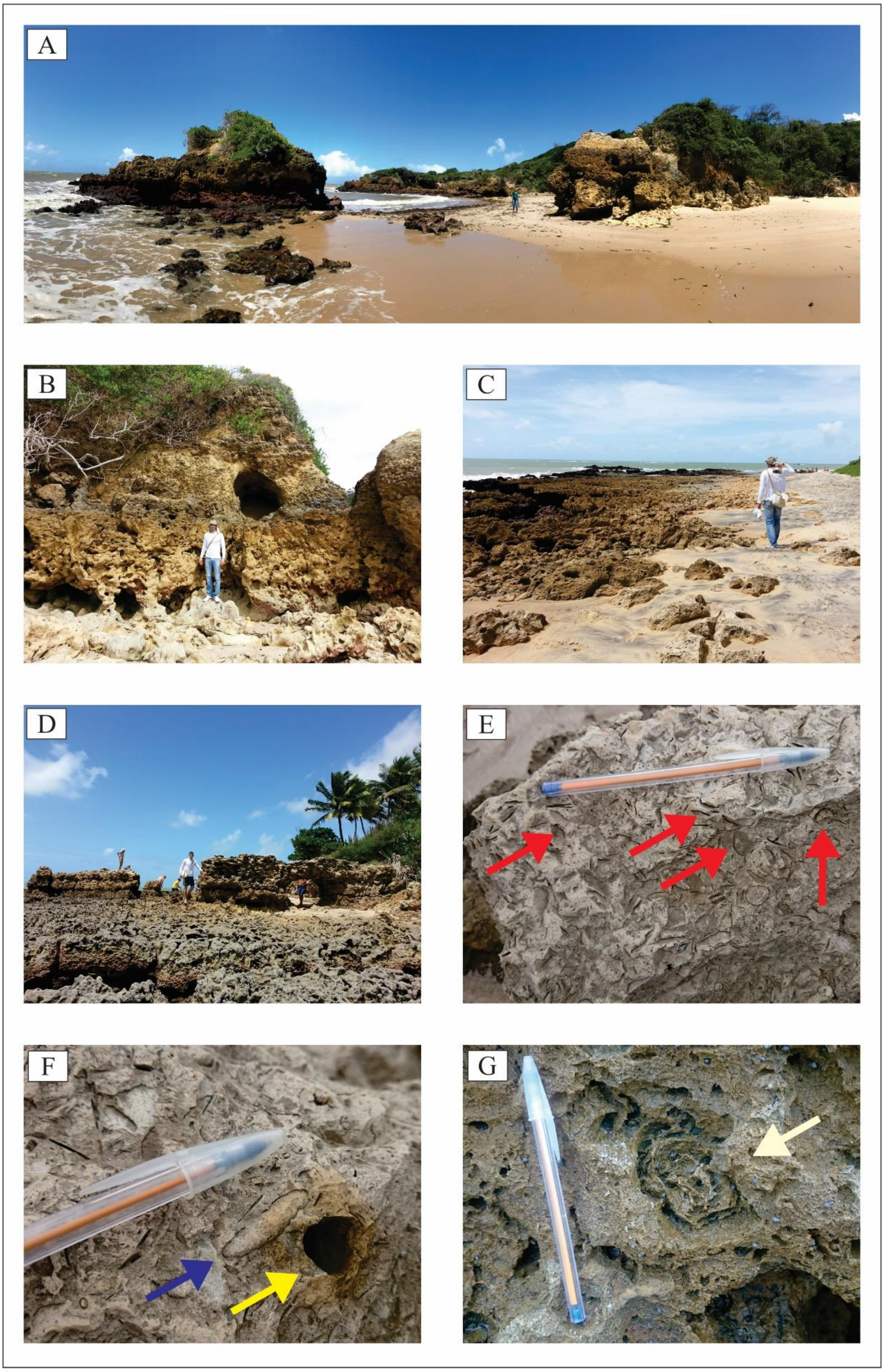

Figure 4. Reef limestone outcrops. A) General appearance of limestones; B) Tambaba Outcrop (DT-01); C) Coqueirinho Outcrop (DC-01); D) Jacumã Outcrop (DJ-01); E) bivalves molds (red arrows); F) bioturbation molds (blue and yellow arrows); and G) molds of encrusting organisms, e.g. algae (rhodoliths – white arrow).

The abundant levels of bivalves and gastropod shells that form the layers interspersed with bodies of reef-algal constructions, provided the intense process of bioerosion, caused mainly by scraping and perforating organisms (Figures 4E and 4F).

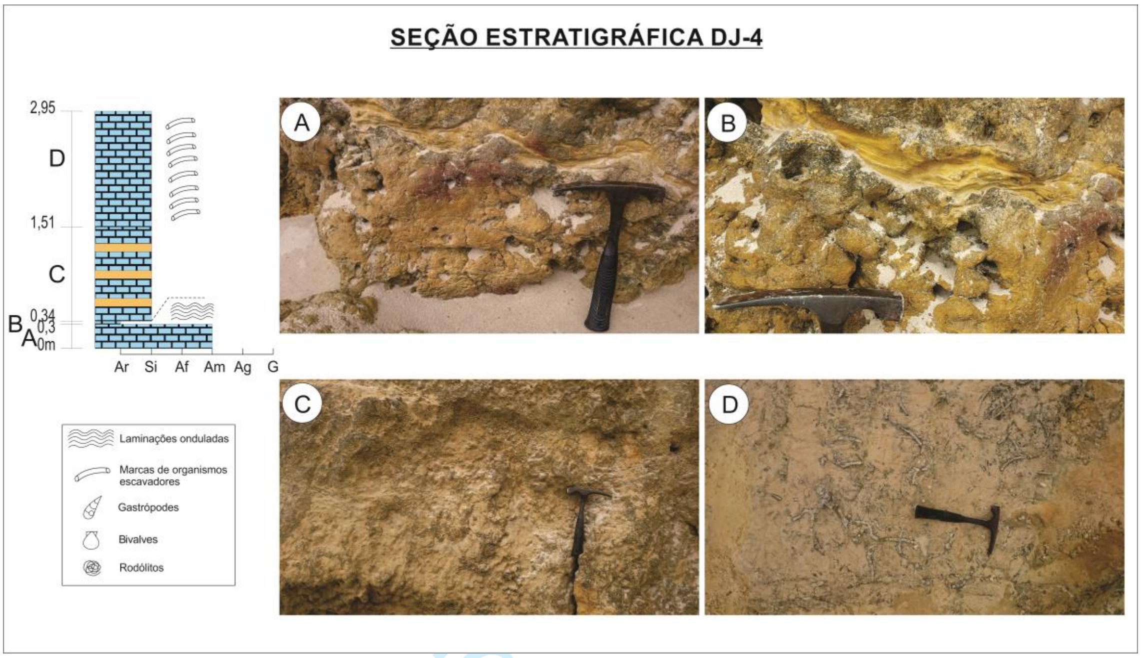

Figure 5. Stratigraphic section performed at Jacumã beach (Ar: Clay; Si: Silt; Af: Fine Sand; Am: Medium Sand; Ag: Coarse Sand; G: Granule). A) Calcarenite with molds of bivalves and gastropods; B) Calcilutite with plane-parallel lamination and wavy geometry; C) Intercalation of calcissiltite with marl; D) Calcissiltite with bioturbation.

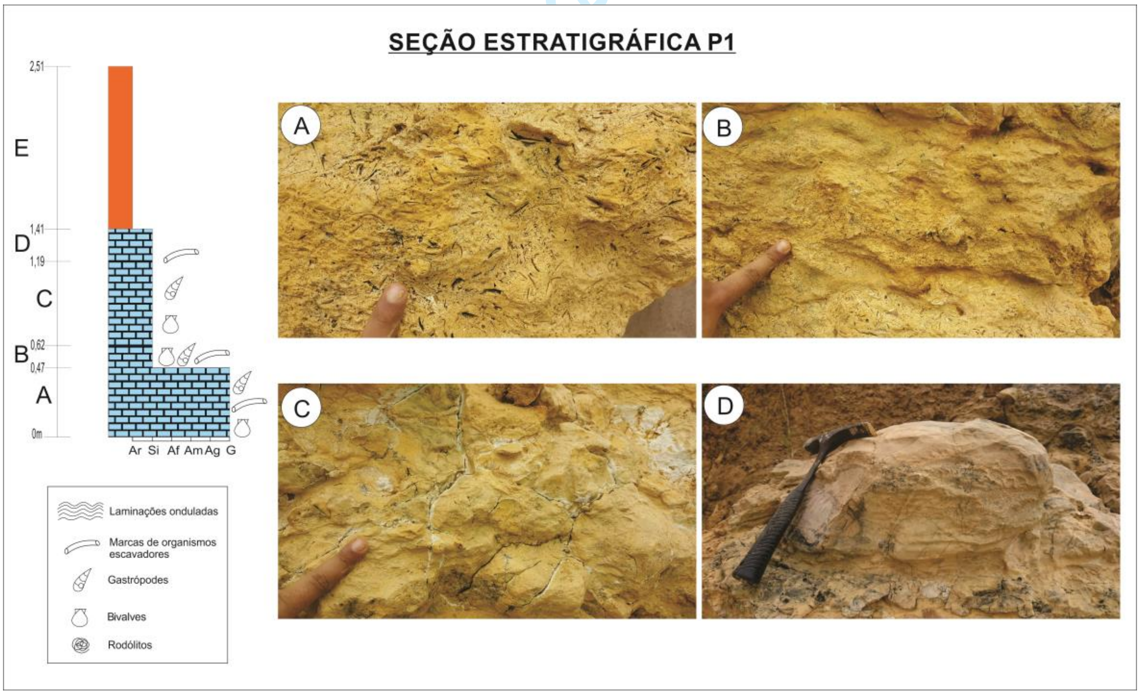

Figure 6. Stratigraphic section performed on Tambaba beach (Ar: Clay; Si: Silt; Af: Fine Sand; Am: Medium Sand; Ag: Coarse Sand; G: Granule). A) Calcirudite with molds and counter-molds of bivalves and gastropods; B) Calcissiltite with cochinoidal aspect; C) Calcissiltite with almost non-existent molds; D) Calcissiltite with incipient stratification.

It is possible to identify the direct contact between the Tambaba Formation and the Barreiras Formation (overlying unit) at only one point along the range of reef limestone occurrence (Figures 7 and 8). There is also evidence of strong erosion of the Barreiras Formation, possibly caused by seawater and rain, where these agents excavated the unit, giving rise to cliffs and exposing the reef limestone deposits.

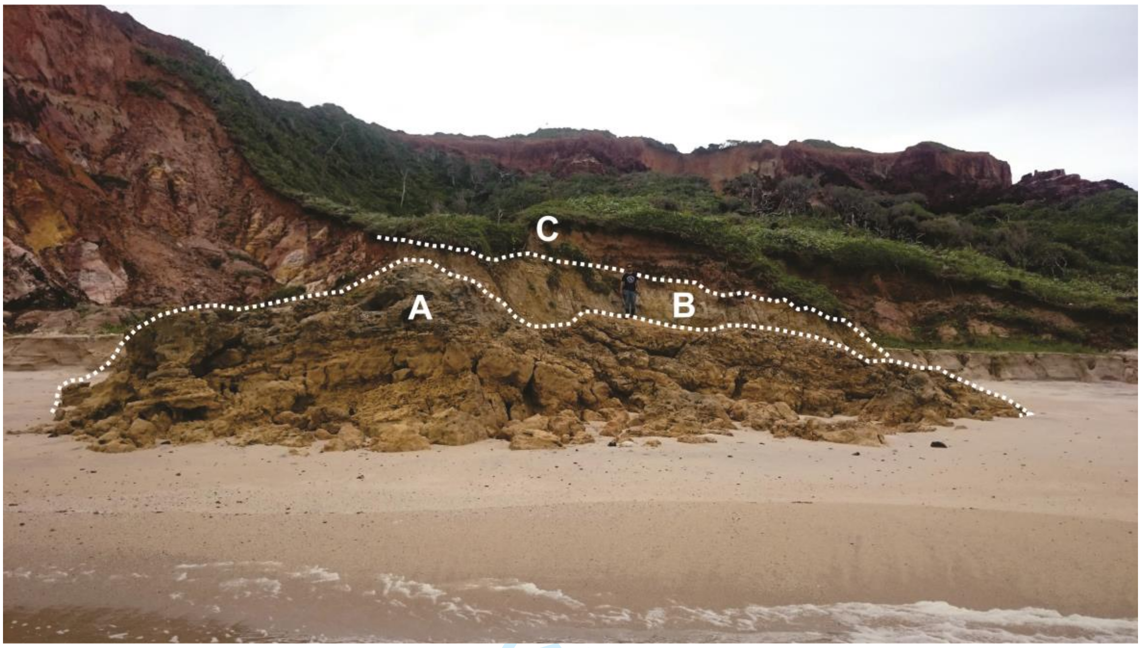

Figure 7. Outcrop located at Praia de Tambaba showing contact between the Tambaba Formation and the Barreiras Formation. A) Reef limestones of the Tambaba Formation; B) Weathering mantle between the units; C) Sandstone of the Barreiras Formation.

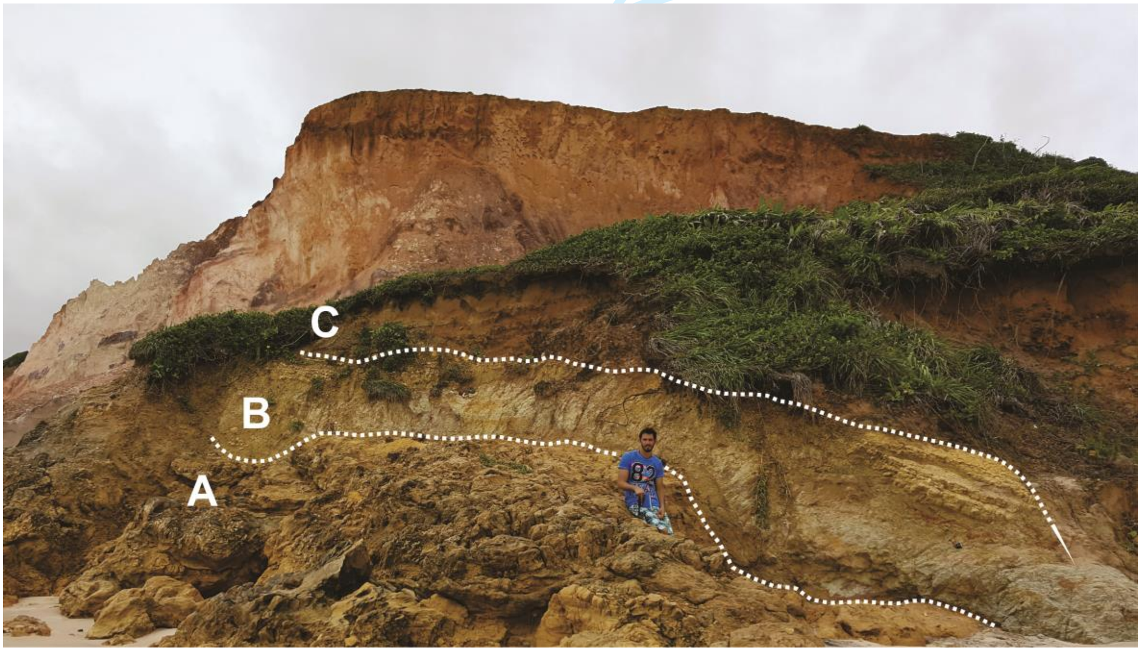

Figure 8. Lateral view of the outcrop showing the contact between the Tambaba Formation and the Barreiras Formation. A) Tambaba Formation; B) Weathering mantle between the units; C) Barrier Training.

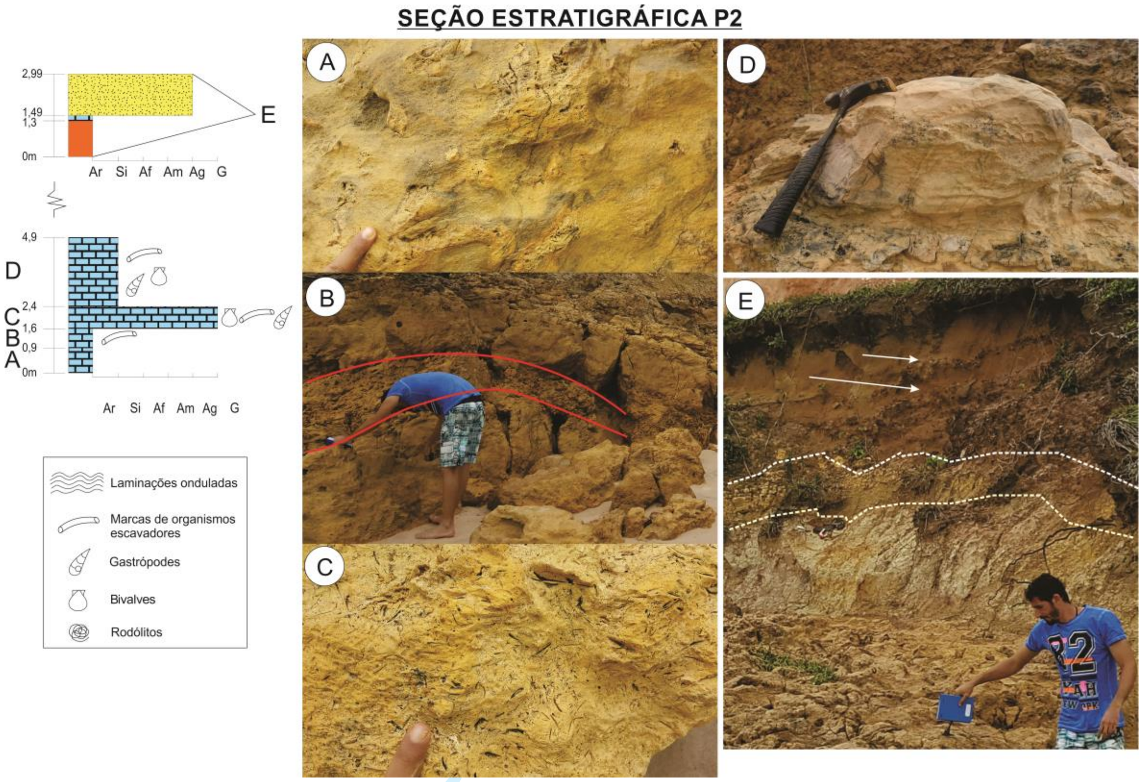

Figure 9. Stratigraphic section carried out on Tambaba beach. A) Calcilutite with low concentration of bioclasts; B) Calcilutite with bioturbation; C) Calcirudite with molds and counter-molds of bivalves and gastropods; D) Calcissiltite with incipient stratification; E) At the base, the weathered claystone of the Barreiras Formation; Calcilutite with incipient stratification delimited by white dashed lines and concretion levels in the Barreiras Formation indicated by white arrows.

Optical Petrography and Cathodoluminescence

Mudstones

Dunham (1962) defines mudstones as matrix-supported rocks with less than 10% allochemical grains. The samples analyzed petrographically define a very fine matrix carbonate mud. They present a difference in texture (Figure 10), where the grayer portion reflects a purer mineralogy, with a lower amount of iron oxide, and another where the oxidation is well marked and it is possible to visualize some nodules. However, this oxidation occurs in a widespread way in the purest and most concentrated portion in the second texture. These features favor the formation of pyrite (FeS_2), which characteristically appears with a framboidal habit.

In the cathodoluminescence study, it was possible to observe that the rock is essentially composed of calcite due to its high luminescence (Figures 12B and 12D). The dedolomitization process was identified by this high luminescence, since the "dolomite" crystals are composed of calcite, evidencing a late replacement process. There are also siliciclastic (quartz) grains that are disseminated and have a rounded morphology. Quartz is identified in dark brown and pale blue cathodoluminescence stains (Figure 12D). This contribution of siliciclastics may be the result of pulses of fluvial sedimentation during marine sedimentation.

These reef limestones present a high concentration of bioclasts, among them, fragments of bivalves, gastropods and tubes of perforating organisms predominate. From this, mold porosities are characterized, which result from the dissolution of allochemical grains, as well as intragranular (as an example of selective weft porosity), as well as fracture and vugular porosity (non-selective weft porosity). Some of these fractures are partially filled with iron oxide. Micritic (brown) calcite is being replaced by spastic (white) calcite, characterizing a marked cementation as a diagenetic process.

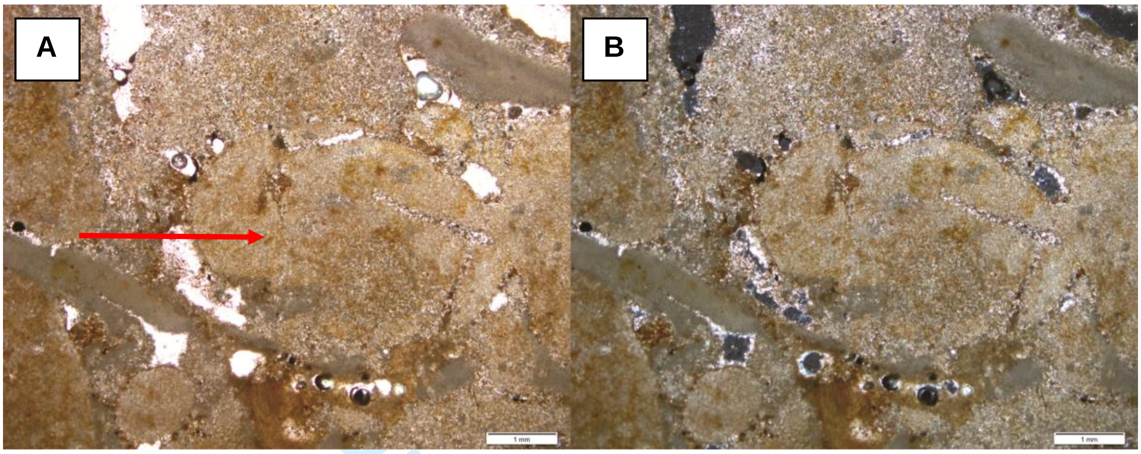

Figure 10. Photomicrograph showing the two existing textures (// parallel nicols; + crossed nicols). A) (4x, //) and B (4x, +); The grayer portion (blue arrow) reflects a purer mineralogy, with a lower amount of iron oxide, and another where oxidation is well marked (red arrow).

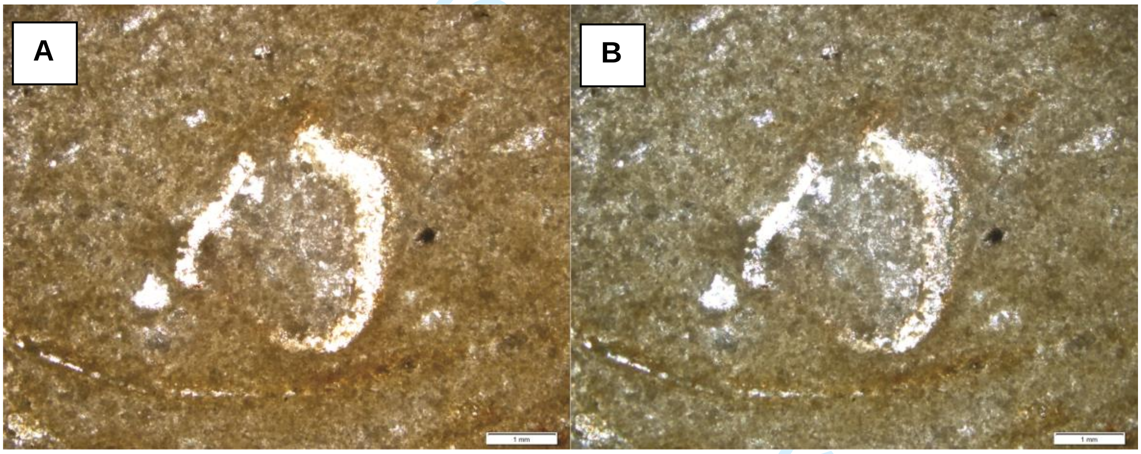

Figure 11. Photomicrograph showing a possible cross-section of an alga or piercing organism (// parallel nicols; + crossed nicols). A) (4x, //) and B (4x, +).

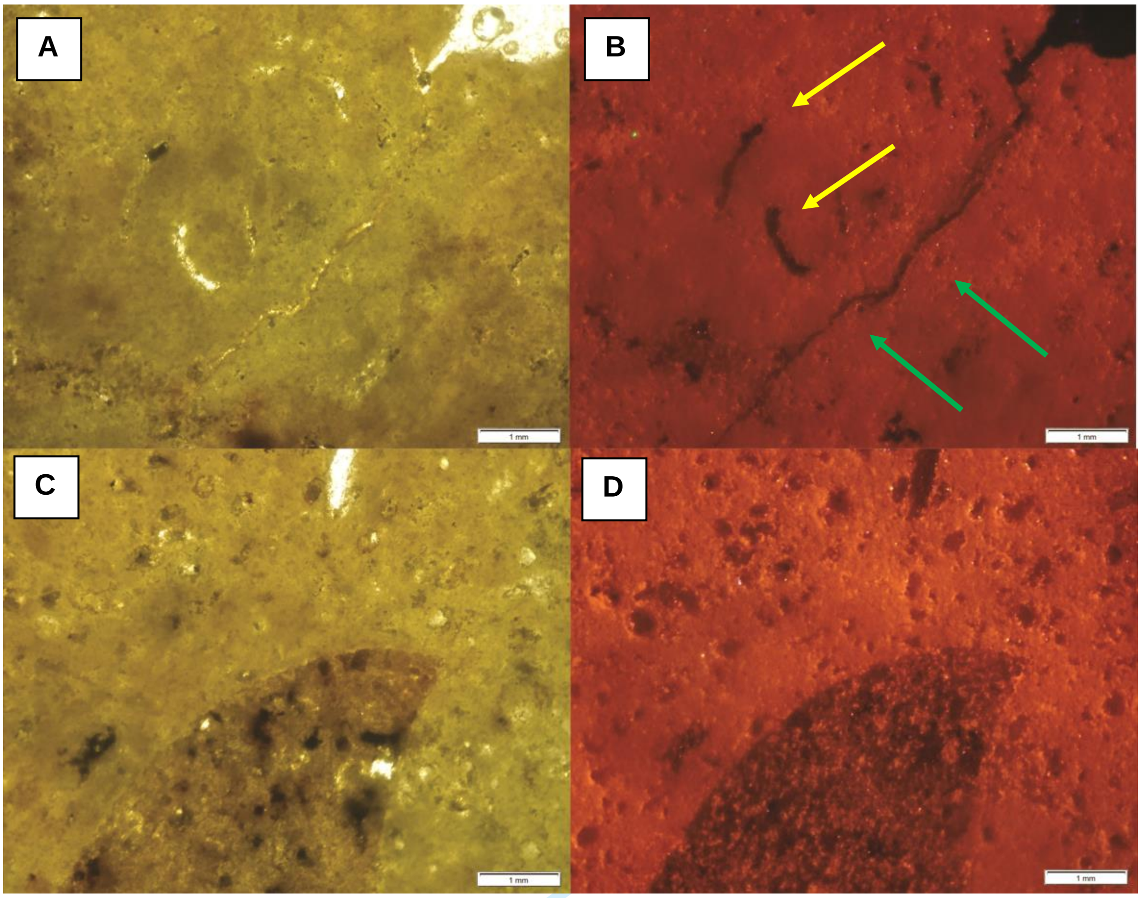

Figure 12. Photomicrographs. (// parallel nicols; + crossed nicols; CL: under cathodoluminescence): A) (4x, //) and B) (4x, CL) Carbonate mud with mold-like porosities (yellow arrows) and microfracture (green arrows)); C) (4x, //) and D) (4x, CL) Detail of part of bioclast exhibiting intragranular porosity.

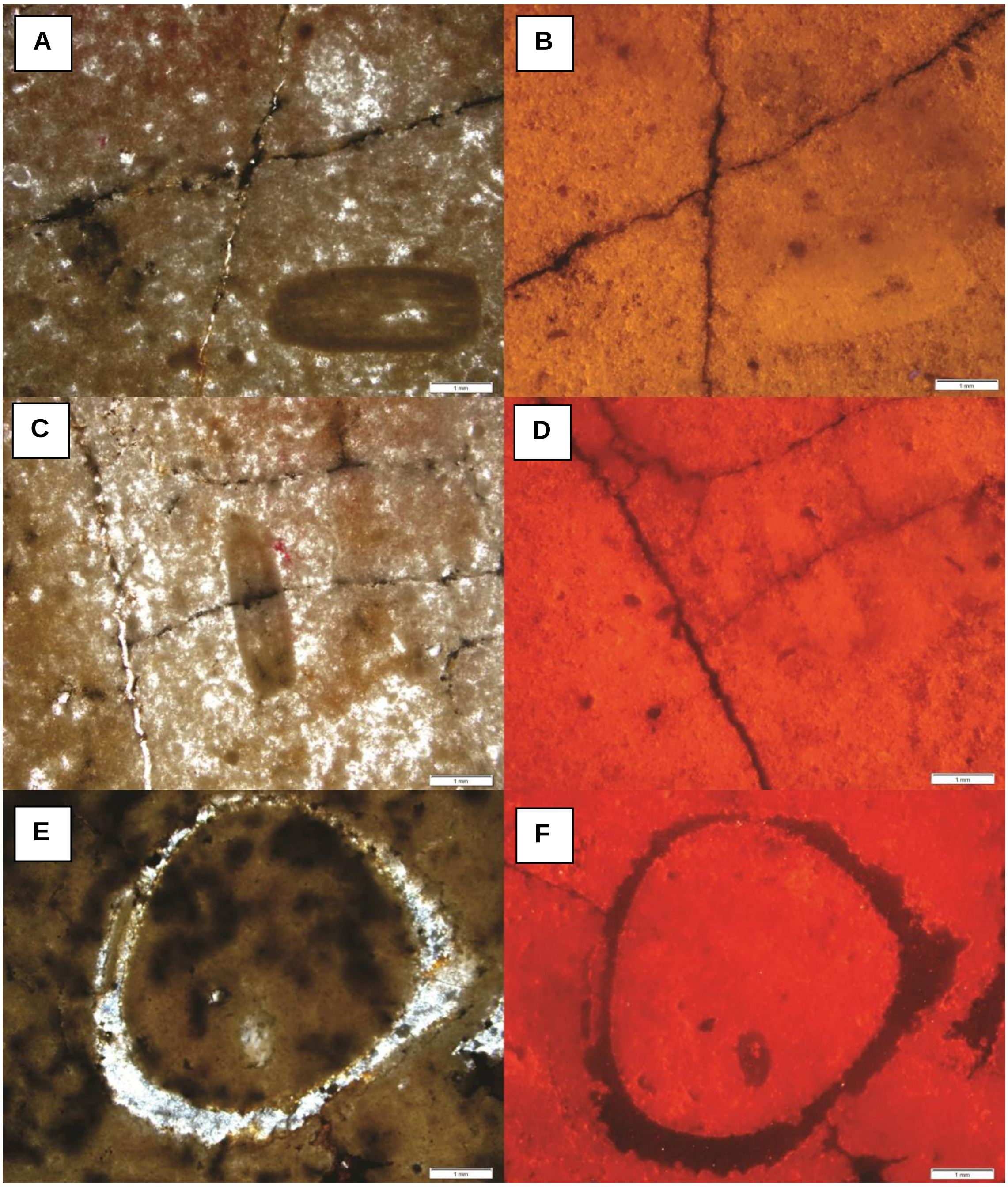

Figure 13. Photomicrographs (// parallel nicols; + crossed nicols; CL: under cathodoluminescence). A) Carbonate mud with a pair of conjugated microfractures and bioclast showing intragranular porosity (4x, +); B) Image A analyzed in cathodoluminescence (4x, CL); C) Late event characterized by failure cutting bioclast (4x, +); D) Image C analyzed in cathodoluminescence (4x, CL); E) Possible cross-section of an alga or a perforating organism (4x, +); F) Image E analyzed in cathodoluminescence (4x, CL).

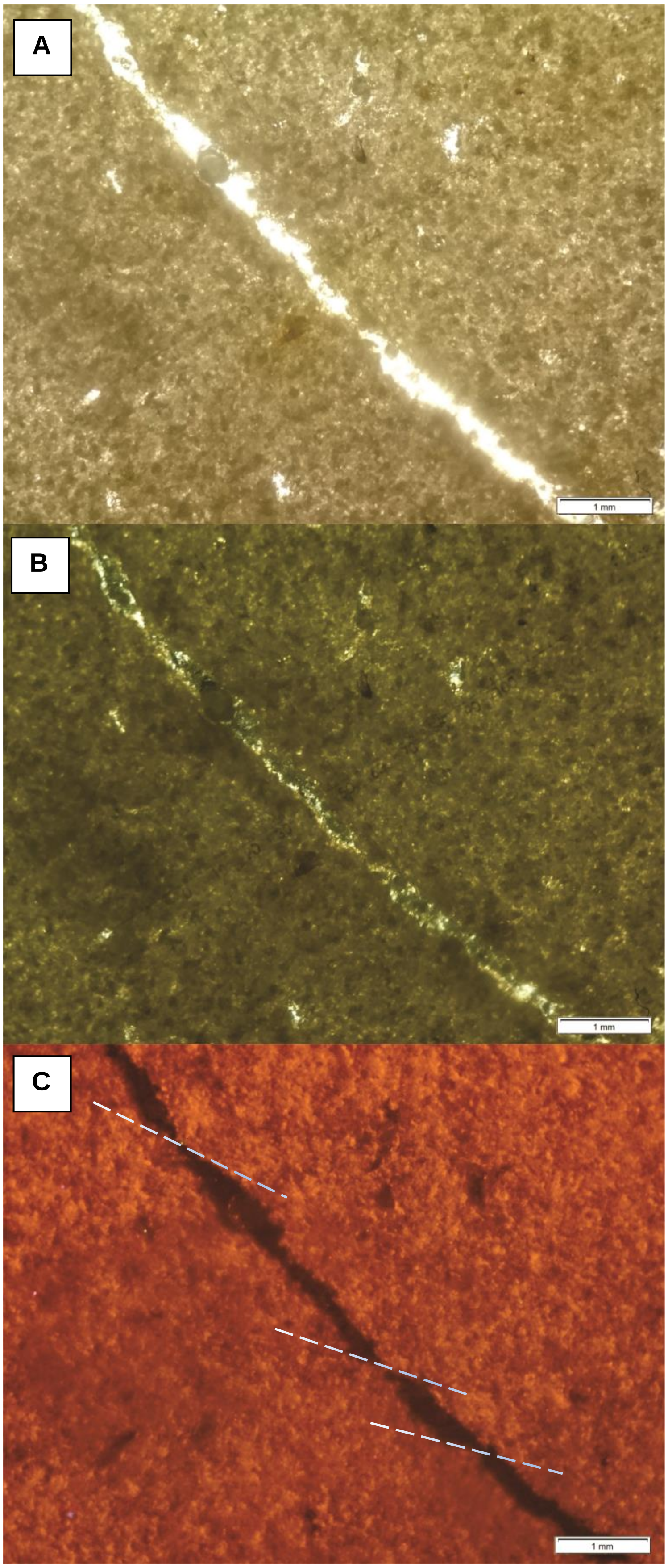

Figure 14. Photomicrograph showing microfaults following a main stress pattern (dashed white lines) (// parallel nicols; + crossed nicols; CL: under cathodoluminescence). A) (4x, //); B) (4x, +); C) (4x, CL).

Wackestones

According to the classification by Dunham (1962) (Figure 2), wackestones are rocks supported by the matrix with more than 10% allochemical grains. This criterion was verified petrographically, this percentage in the thin sections analyzed, which allowed the characterization of this microfacies. Despite being classified in a different microfacies, the analyzed samples and which here represent this facies have characteristics similar to the mudstones described above, since they are limestones formed in a relatively short period of time. The greater amount of bioclasts found in this microfacies directly reflects the increase in porosity (Figure 15). But in addition to these moldic porosities, vugular and intragranular porosities are also found.

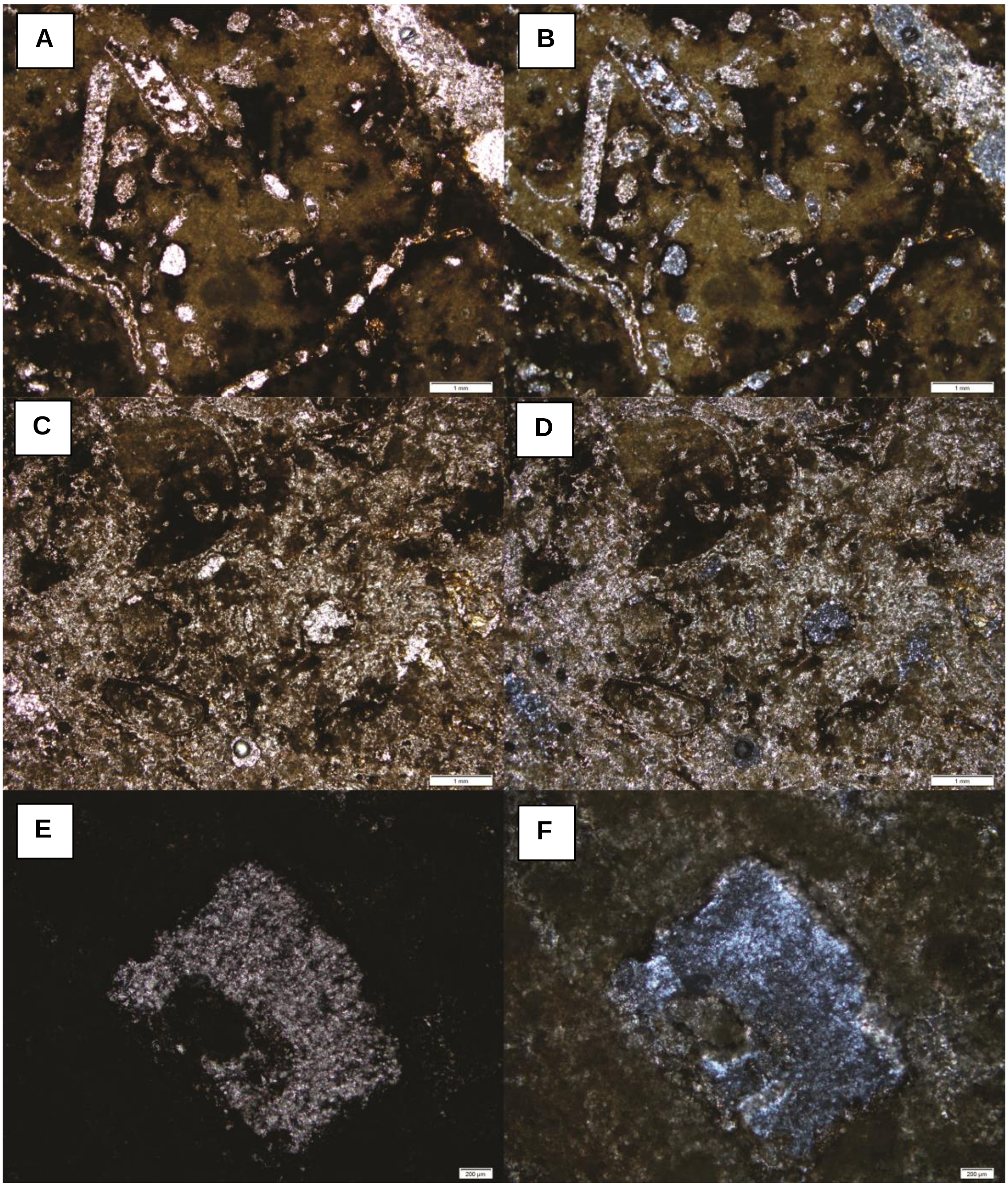

Figure 15. Photomicrographs of wackestone microfacies (// parallel nicols; + crossed nicols). A) and C) Abundance of bioclasts of different sizes and shapes (red arrows) (4x, //); B) and D) Image of A and C at crossed nicols (4x, +); E) Example of regular porosity (10x, //); F) Image of E at crossed nicols (10x, +).

Through the analysis performed in cathodoluminescence, the samples show a predominance of micritic calcite in their matrix, but as in mudstones, spathetic calcite is present through the cementation process. This response is configured by the high luminescence of calcite (Figures 16B, 16D and 16F). The presence of siliciclastic phases is also visible, but not in a widespread and rounded way as occurred in the mudstones, but larger crystals present, almost entirely, in the porosities (Figures 16E and 16F). In addition to all these characteristics mentioned, it is still possible to verify the pyritization process in its most common habit in the studied area, the framboidal..

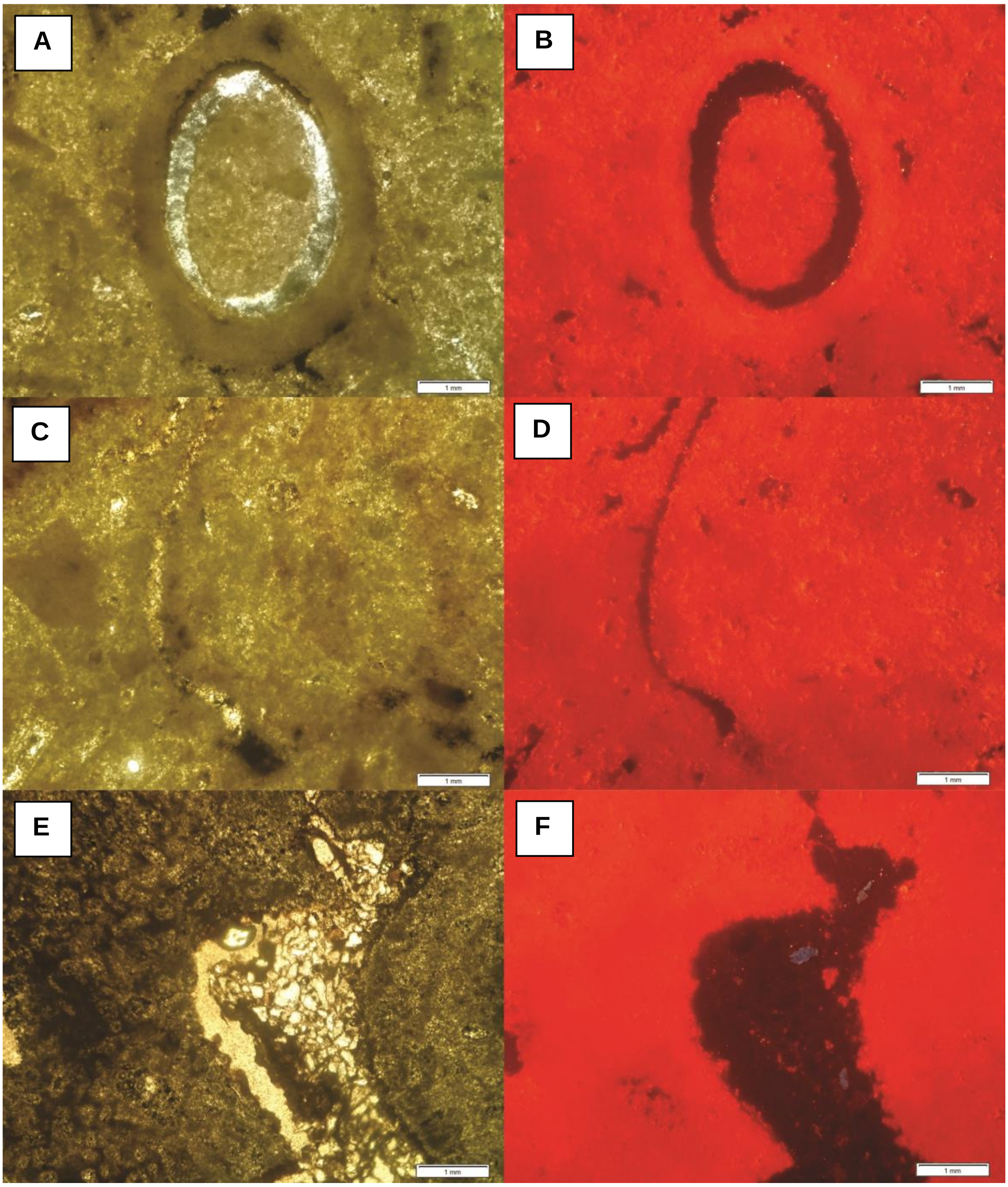

Figure 16. Photomicrographs of wackestone microfacies (// parallel nicols; + crossed nicols; CL: under cathodoluminescence). A) Possible cross-section of an alga or a perforating organism (4x, +); B)

Cathodoluminescence image of A (4x, CL); C) (4x, //); D) Cathodoluminescence C image (4x, CL); E) (4x, //); F) Image of E in cathodoluminescence and the presence of quartz grains (yellow arrows) (4x, CL).

Packstones

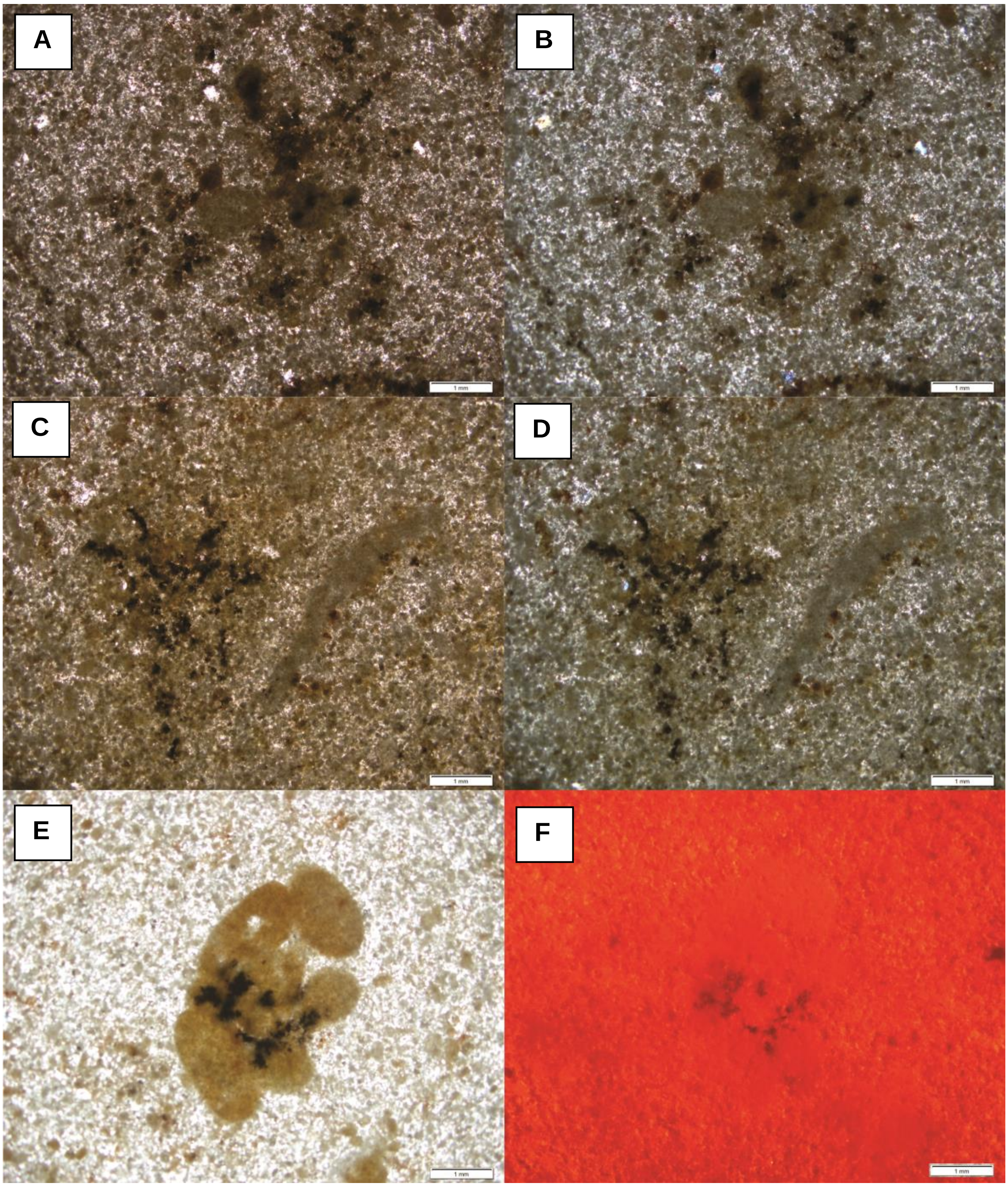

Figure 17. Photomicrographs of packstone microfacies (// parallel nicols; + crossed nicols; CL: under cathodoluminescence). A) Overview of the sample showing a supported grain texture (4x, +); B) Image from A to crossed nicols (4x, +); C) Detail of the abundance of pyrite with a framboidal habit (4x, //); D) Image of C to crossed nicols (4x, +); E) Presence of unidentified shells (4x, //); F) Image of E in cathodoluminescence showing spastic calcite (4x, CL).

In this microfacies, there is also a predominance of spastic calcite (Figure 17E) as a rock-incorporating cement. This microfacies is also rich in allochemical grains such as bivalves fragments and carapaces of unidentified organisms (Figure 17F). The non-skeletal grains are represented by calcite, and as in all other previous microfacies, this mineral came from a recrystallization from dolomite crystals (dedolomitization process). Furthermore, it is possible to observe the presence of pyrite with a framboidal habit (Figures 17C and 17D). No influence of diagenetic processes responsible for porosity formation was observed. Therefore, the porosity is greatly reduced. The allochemical grains are micritized and partially cemented.

6 DISCUSSIONS

The reef limestones of the Tambaba Formation, interpreted by Almeida (2000) as Eocene, mapped in the coastal strip between the beaches of Jacumã and Tambaba, were deposited directly on the carbonates of the Gramame Formation (Middle to Lower Maastrichtian). The observation of a sampling in the gutter of a water hole, carried out close (approximately 6 km to the west) to the area of occurrence of reef limestones, added to the contact outcrop between the units found, also allowed to prove that in the coastal region (Tambaba Beach) the Barreiras Formation also rests directly on the carbonates of the Gramame Formation, without the presence of the studied reef-lagoon limestones.

Stratigraphic relationships suggest that there are no intermediate limestones, such as the Danian limestones of the southern portion (Tambaba Beach), and that there is an erosive hiatus that must have included the Maastrichtian top and any Paleocene deposits that may have existed. Barbosa (2004, 2007) recognized that these deposits could represent deposition levels formed during the initial stretch of the regressive event, which in the literature is treated by Hunt & Tucker (1992) as Falling Stages System Tract. However, the occurrence of hardgrounds with suppression of the sedimentation rate and the formation of bioerosion surfaces, with considerable variation of facies in a thin interval, suggest that these deposits were deposited during the stabilization of the low sea tract that followed the regressive process.

A second alternative is that these limestones, interspersed with hardgrounds and bioerosion, in which Trypanites ichnofacies occur, as already discussed for reef limestones (Barbosa *et al*., 2006), would correspond to a Transgressive Surface, which overlapped the surface. erosion that marks the exposure of the Gramame platform. In this case, these deposits would mark a new event of resumption of marine sedimentation after the erosive event that must have affected the Gramame Formation. According to Catuneanu (2006), if no deposits related to Falling Stage or Low Stand events are preserved on the exposed erosive surface (sequence limit), then the Transgressive Surface can join it. It is also suggested that if the sediment inflow rate is low, the Transgressive Surface and the Maximum Flood Surface may merge into the continent.

The second hypothesis seems to be the most acceptable, according to the characteristics of the record of reef limestones in the Paraíba Basin. And in this way, these would correspond to a depositional sequence distinct from the sequence composed by the Itamaracá, Gramame and Maria Farinha formations.

The reef limestones of the Alhandra Sub-Basin have an abundant ichnofosilliferous content. Muniz & Almeida (1989) observed the presence of trace fossils from drilling in mollusc shells and coral skeletons. Almeida (2000) studied these limestones and described the occurrence of the ichnogenera Ophiomorpha, Trypanites, Gastrochaenolites, Rogerella, Caulostrepsis and Entobia. These trace fossils are associated with the action of organisms that pierce hard substrate, rocky coasts, bed of bone and shell accumulation, as well as hard substrates of reef colonies (Buatois *et al*., 2002). These ichnofacies are usually associated with discontinuities in the sedimentation process, or absence of sedimentation, which allows the floors of bones, shells and corals to be exposed for a long period, allowing bioerosive action (Pemberton & MacEachern, 1995; Taylor & Wilson, 2003). In the studied deposits, the levels of carbonate abundant in Ophiomorpha occur interspersed with levels containing floors of shell accumulation, which suggests that in a reef-beach marine environment, there were episodic stops of sedimentary input, which favored the formation of hardgrounds and bioerosion. In some carbonate levels, there is an intense network of Ophiomorpha galleries, which suggests that the construction of tube networks was continuously affected by the action of high energy events, such as storms, which causes organisms to leave a lower level and build another level of tube weaves (Barbosa *et al*., 2006). This research also observed the presence of Thalassinoides tubes. The association of these ichnofossils suggests a variation in the energy level, during periods of greater contribution of carbonate sediments. This also suggests an alternation of ichnofacies, related to hard substrate and soft substrate, according to variations in climate and sedimentary input.

Távora *et al*. (2017) integrated the data obtained in the field and recognized three stages of reef accretion: colonization (bafflestone lithofacies), diversification (framestone lithofacies) and dominance (bindstone lithofacies). The colonization, diversification and dominance stages, as well as the superposition surfaces are related to the most important style of carbonate accumulation of this deposit and its rigid structural portion, the reef core.

The Eocene reef deposits are separated from the Maria Farinha Formation, probably, by an unconformity, which shows the establishment of a shallow, internal and restricted platform characterized by the existence of isolated subdomains of reef cores and fringe reefs, as well as by the overlap of these environments by facies related to beach environments and very shallow lagoons (Figure 18).

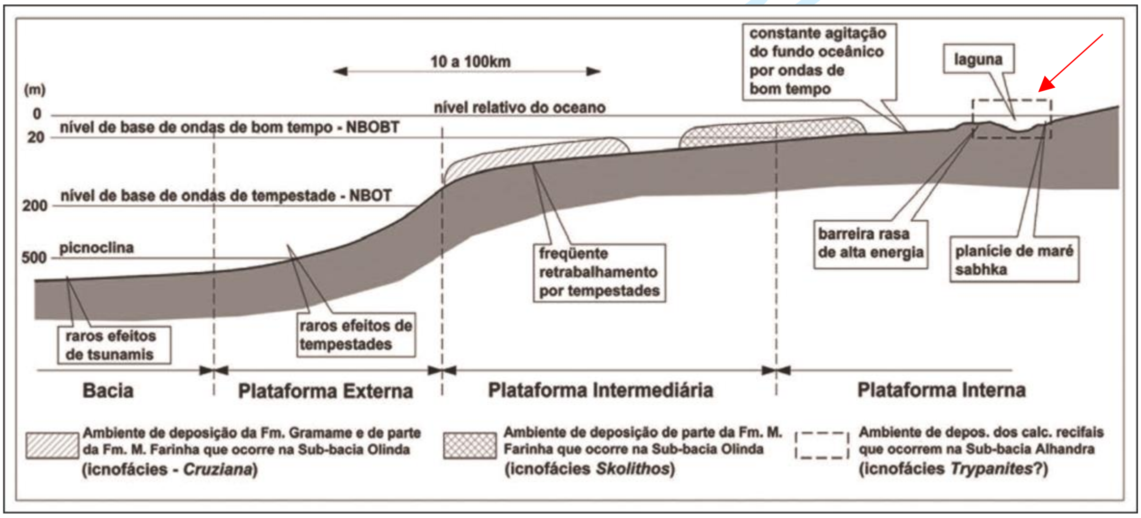

Figure 18. Depositional model of carbonate units that occur in the Paraíba Basin (Barbosa *et al*., 2006), with the positioning of the reef limestones of the Tambaba Formation studied in the present contribution (arrow in red).

The petrographic studies indicate a diagenetic stage as the Eogenetic, or even, the Early Diagenesis stage. The main indicator of this formation environment is the pyrite mineral with a framboidal habit, as there is evidence of a lot of pyritization replacing valves, fractures and bioclast fragments, and replacing Thallassinoid tubes. Several other minerals are also associated with this diagenetic environment of carbonate formation, which were identified according to optical microscopy parameters.

The microfacies analysis clearly shows the predominance of moldy, fracture, vugular and intragranular porosities. The samples are predominantly considered to be porous. The fact that some samples are not very porous may be related to compaction and dolomite crystals, which cause a decrease in porosity.

The intragranular and vugular porosities are indicative that there was a dissolution of the carbonate components of the Tambaba Formation, and they are secondary porosities, being indicative of a post-depositional diagenetic state.

The dolomitization process occurs intensively in some of the studied reef limestone layers of the Tambaba Formation, which masks the original rock texture. However, most of the slides studied present well-preserved bioclast molds, indicating that there was a mild weathering action on these carbonates.

Despite the great bioturbation (mainly Thallassinoides) in the limestones of the Tambaba Formation, which implies an oxygenation of the environment, many tubes of Thallassinoides conjugated with a pyritization process were evidenced, indicating that there was a return to the reduction conditions during diagenesis.

Recent microfacies studies have identified stages of reef accretion (colonization, diversification and dominance). Távora *et al*. (2017) describes these stages associated with depositional microfacies. The allochemical constituents observed in this study were also identified (fragments of calcareous algae, corals, bivalves, gastropods and echinoids, as well as bioturbation structures, in addition to reduced siliciclastic contribution.

It is possible to correlate the microfacies studied here with those described by Távora *et al*. (2017). Here we present the microfacies in terms of Dunham's classification (1962), while in addition to this we have the classification of Embry & Klovan (1971) in the descriptions by Távora *et al*. (2017). In the colonization stage, we have a reef core represented by mudstones (dolomudstones), where this microfacies is characterized by a micritic matrix framework, brown in color, texturally homogeneous and, sometimes, a carbonate mud without individual crystals, with little allochemical constituents. abundant and poorly preserved.

In the diversification stage, the reef cores formed by dolowackestones and dolopackstones from Távora *et al*. (2017) are seen here as the carbonate microfacies wackestones and packstones, respectively, thus maintaining the positive correlation between the results.

7 CONCLUSIONS

The reef limestones of the Tambaba Formation outcrop in a coastal strip of the municipality of Conde, approximately 10 km south of the city of João Pessoa (Paraíba), and occur in the form of elongated bioconstructions parallel to the coastline, called Jacumã, Coqueirinhos and Tambaba, with similar compositional, textural, stratigraphic and paleontological aspects, configuring a fringing reef system, controlled by basement fault reactivations.

These outcrops are lithologically composed of yellowish and layered limestones, heavily weathered, with a ruiniform and irregular appearance, classified from calcilutite to calcirudite, according to Grabau (1904).

The spatial distribution of the outcrops of this geological unit and their stratigraphic relationships allowed us to recognize the formation characteristics that make up the reef core, the most important style of carbonate accumulation in this deposit, defined by a compact, resistant and massive structure.

Three microfacies were defined based on their textural features (Dunham, 1962). All microfacies were correlated with the stages of mudstone (colonization), wackestone (diversification) and packstone (diversification) reef development).

The fraction of allochemicals is frequent and is represented by fragments of algae, corals, bivalves and gastropods. Fossil traces and bioturbation structures are also common.

Reef limestone deposition is associated with periods of subsidence in the Paraíba Basin, where marine sedimentation and warm climate typical of equatorial regions were conducive to the formation of a topographically higher margin in a carbonate ramp, allowing the formation of reefs. The hardgrounds, equivalent to the reef superposition surfaces, were formed in the uplift periods and with the resumption of subsidence the reef accretion process was restarted from the diversification stage, defining successive generations of reefs, vertically characterizing superimposed reefs.

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6.2 C AND O ISOTOPE CHEMOSTRATIGRAPHY AND BULK CHEMISTRY OF REEF LIMESTONES OF THE TAMBABA FORMATION, PARAÍBA BASIN, NORTHEASTERN BRAZIL

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C and O Isotope Chemostratigraphy and Bulk Chemistry of Reef Limestones of the Tambaba Formation, Paraíba Basin, Northeastern Brazil

Quimioestratigrafia Isotópica (C e O) e Geoquímica de Calcários Recifais da Formação Tambaba, Bacia Paraíba, Nordeste do Brasil

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Abstract

This work focuses on the behavior of the C and O isotopes and major and trace element chemistry of the carbonate rocks of the Tambaba Formation, Paraíba Basin, Northeastern Brazil. Thirteen carbonate samples collected from three vertical profiles located perpendicular to the bedding along the coast of the state of Paraíba were analyzed. The $\delta^{13}C$ values ranged from 1.6 to 2.8‰ VPDB while the $\delta^{18}O$ values ranged from -1.2 to 1.8‰ VPDB, thus suggest a restricted shallow-platform depositional environment. X-ray fluorescence analyses suggested diagenetic changes, such as the replacement of dolomite by calcite (Mn/Sr ratios from 0.6 to 28) and dolomitization, which was identified by high Mg/Ca ratios (0.5 to 0.6). The very low SiO_2 and Al_2O_3 content attested to the low terrigenous material influx. The carbon isotope values suggest that the carbonate rocks were deposited after the Paleocene-Eocene Thermal Maximum (PETM) event.
Keywords: Paraíba Basin; Tambaba Formation; isotope analysis

Resumo

Este trabalho discute o comportamento de isótopos de C e O e a química de elementos maiores e traços de rochas carbonáticas da Formação Tambaba, Bacia Paraíba, Nordeste do Brasil. Amostras de treze rochas carbonáticas de três perfis perpendiculares a estratos, localizados na costa do estado da Paraíba, foram analisadas. Os valores de $\delta^{13}C$ variam de 1.6 a 2.8‰ e os de $\delta^{18}O$, de -1.2 a 1.8‰ VPDB, sugerindo deposição em ambiente de plataforma rasa restrito. Análises por fluorescência de raios-X sugeriram alterações diagenéticas, como substituição da dolomita por calcita (Mn/Sr varia de 0.6 a 28) e dolomitização sugerido pela alta razão Mg/Ca (0.5 a 0.6). Além disso, os baixos teores de SiO_2 e Al_2O_3 corroboram o baixo influxo de materiais terrígenos. Os valores de isótopos de carbono sugerem que as rochas carbonáticas foram depositadas após o evento de máxima temperatura no Paleoceno-Eoceno.
Palavras-chave: Bacia Paraíba; Formação Tambaba; análise isotópica

1 Introduction

The Tambaba Formation is a lithostratigraphic unit of the Eocene of the Paraíba Basin. Such unit is represented by carbonate rocks deposited in a reef marine environment, and they generally present a light yellow color, bioclastic texture, and beds, with the reef constructions presenting an irregular weathered aspect due to erosion (Veras, 2017).

For a long time, this unit was considered the upper part of the Maria Farinha Formation. However, it presents specific faciological, stratigraphic and petrographic features that differ considerably from the bedding described for the typical section of the Maria Farinha Formation, which was established in the southern portion of the coastal strip of the Paraíba Basin. The Tambaba Formation occurs in the Paraíba Basin and the Alhandra and Miriri Sub-Basins, and it is mappable at 1:25.000 scale.

The age proposed by Almeida (2000) for the reef limestones of the Tambaba Formation based on the fossil content differs from that proposed for the Maria Farinha Formation, which is considered Danian (Lower Paleocene) in the Olinda Sub-Basin. Compared with the Maria Farinha Formation, which has been a target of several micropaleontological studies (e.g., Albertão, 1993; Albertão & Martins Jr., 1996; Stinnesbeck & Keller, 1996; Fauth, 2000; Gertsch et al., 2013), the ages of these reef limestones have not yet been established.

A number of chemostratigraphic studies have been performed in the Paraíba Basin due to the Cretaceous-Paleogene boundary (Sial et al., 1992; Barbosa et al., 2005; Barbosa, 2007; Veras et al., 2018). The Cretaceous-Paleogene boundary (KPB) mass extinction (~66.02 Ma) and the Paleocene-Eocene Thermal Maximum (PETM) (~55.8 Ma) are two remarkable climatic and faunal events in Earth's history that have implications for the current Anthropocene global warming and rapid diversity loss (Keller et al., 2018).

In the present work, the behavior of δ13C and δ18O chemostratigraphic curves and the chemistry of major and trace elements obtained for the Tambaba Formation are evaluated and compared with chemostratigraphic curves obtained in the Global Stratotype Section and Point (GSSP) section for the PETM transition in Dababiya (55.8 Ma), Egypt (Keller et al., 2018).

2 Location

The studied region is located to the south of the capital of Paraíba State, João Pessoa, in the city of Conde. The outcrops are located on the coast of Paraíba over an extension of approximately 10 km between the beaches of Jacumã and Tambaba (Figure 1). Using Recife (Pernambuco) as a reference, and the main access road is BR-101 towards João Pessoa, the northern end of the studied range can be accessed via PB-018 (approximately 113 km), and the southern end can be accessed via PB-044 (approximately 100 km).

3 Materials and Methods
3.1 Fieldwork

The fieldwork was conducted along the coastal strip of the state of Paraíba between the beaches of Tambaba and Jacumã, and three outcrops located in the municipality of Conde-PB were visited. One outcrop is located on Tambaba beach, one on Coqueirinho beach and one on Jacumã beach, and they were named DT-01, DC-01 and DJ-01, respectively. Outcrops were sampled through a vertical profile perpendicular to the strata observed at each outcrop, where a sample of each strata was taken following a bottom-up sequence (e.g., DJ-01A, DJ-01B, DJ-01C, DJ -01D – Figure 2).

UTM – DATUM WGS 1984		
OUTCROP	**N (UTM)**	**E (UTM)**
DT-01	9.185.755	301.400
DC-01	9.189.314	301.843
DJ-01	9.195.399	301.306

Table 1 Nomenclature of the outcrops and their respective UTM coordinates.

3.2 Laboratory Analysis

A total of 13 samples were collected along the coast of Paraiba at the Tambaba-Coqueirinho-Jacumã stretch, which is approximately 10 km

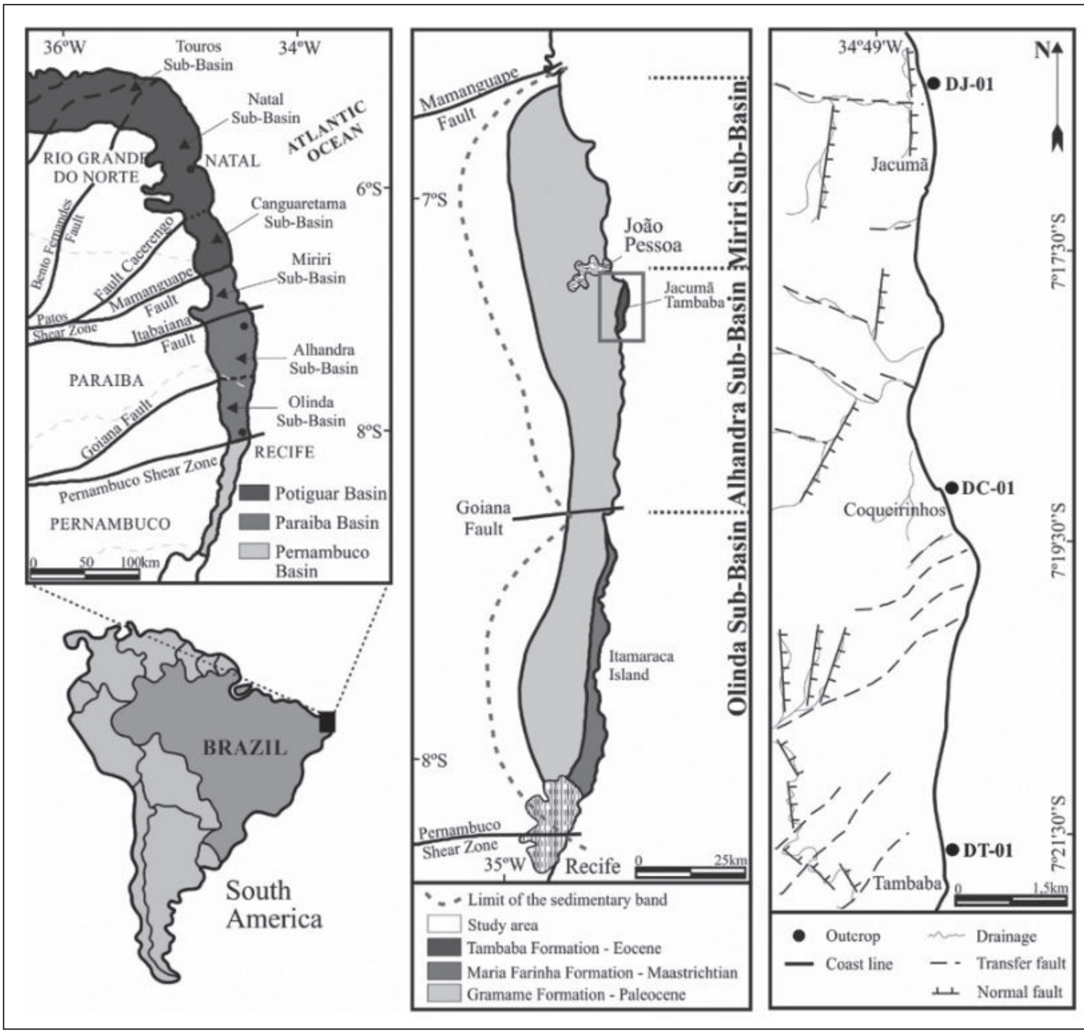

Figure 1 Location map of the occurrence area of the Tambaba Formation in the Paraíba Basin (modified from Távora *et al.*, 2017).

Figure 2 Example of the numbering of the samples collected in the field at reef limestone outcrops (outcrop DJ-01, in Jacumã). The dotted yellow lines show the boundary of the beds.

long, for a stable carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) isotope analyses and chemical analyses of major and trace elements. These analyses were carried out at the Nucleus of Geochemical Studies-Stable Isotope Laboratory (NEG-LABISE) of the Department of Geology of the Federal University of Pernambuco.

The samples were powdered to analysis. For the stable isotope analyses, 20 mg of whole rock were used, and these samples were subjected to CO_2 gas extraction in a conventional high vacuum extraction line after reacting with 100% orthophosphoric acid at 25ºC for 1 day (3 days when dolomite is present).

The liberated CO_2 gas was cryogenically purified and analyzed in a VG Micromass or Delta V (Thermofinnigan Advantage) double-mass spectrometer, and a SIRA II triple collector (using the BSC reference gas (Borborema skarn calcite) was used to determine the isotopic ratios. The results are expressed in the notation of a per mil (‰) relative to a standard VPDB (Vienna PeeDee Belemnite). The uncertainties of the isotopic measurements are better than 0.1‰ for carbon and 0.2‰ for oxygen, based on multiple analyses of an internal LABISE standard.

Prior to the geochemical analysis, a portion (2,25g) of each sample was placed in an oven to dry at 110°C, and then it was placed in a muffle furnace at 1000°C for 2 h to determine the fire loss. Molten beads were generated using lithium tetraborate as the flux. The pearls were analyzed in a Rigaku X-ray Fluorescence Spectrometer model ZSX Primus II equipped with a Rh tube, and seven crystal analyses were performed by the calibration curve method, which was based on international reference materials. The results are displayed based on weight % (major elements) or ppm (trace elements).

4 Geology

The coastal strip of the Paraíba Basin is located between the Pernambuco Shear Zone and the Mamanguape Structural High, which is related to a branch of the Patos Shear Zone in the eastern portion of Northeast Brazil. The geological knowledge, onshore and offshore, of this area is still deficient compared with the neighboring basins, such as the Potiguar Basin or the Alagoas Basin.

Deposits of reef-lagoon origin occur in the Alhandra and Miriri sub-basins within the sedimentary column of the Paraíba Basin between the Campanian-Danian age carbonate sequence (Itamaracá, Gramame and Maria Farinha formations) and the Miocene continental siliciclastic sequence (Barreiras Formation and Quaternary sediments) (Mabessone & Alheiros 1988, Barbosa 2004). Although few studies have evaluated the occurrence of these deposits, Almeida (2000, 2007) conducted a more systematic study of these deposits, which were named by Beurlen (1967a) as Upper Maria Farinha Formation. This last author characterized the mollusks present in these deposits and their paleoecology in addition to their important ichnofossiliferous content and suggested that these limestones were possible of Eocene age. However, an erosional/depositional gap of at least 7 million years may have occurred between the top of the Maria Farinha Formation and the reef limestones.

These deposits were always cited as belonging to the Maria Farinha Formation as suggested by Beurlen (1967a), who correlated them with Paleocene deposits that occur on the top of the Gramame Formation in the southern region of the coastal strip. However, this author observed a difference between the faciology of the classically named limestone of Maria Farinha and the deposits that occur in the northern portion of the coastal strip and referred to the latter as the "Maria Farinha Superior" Formation.

Taking into account the lithofaciological, paleontological, biochronological and depositional aspects, Correia Filho *et al*. (2015) proposed the individualization of these carbonate deposits previously named the Upper Maria Farinha Formation by Beurlen (1967a) as the Tambaba Formation. These deposits surface in the Alhandra and Miriri sub-basins north of the Paraíba Basin along a beach strip between the Tambaba and Jacumã beaches (Correia Filho *et al*., 2015; Veras, 2017). Petrographic studies by Correia Filho *et al*. (2015), Távora *et al*. (2017), and Veras (2017) highlighted the carbonate

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microfacies and diagenetic changes that occurred in these deposits.

The outcrops of these reef limestones present a rounded general morphology ("egg box pattern"), are locally layered, and exhibit a bioclastic texture and eroded appearance, with the latter due to erosion (Veras, 2017). These outcrops are between 10 and 0 m above sea level, and they vary in grain size between calcilutite and calcirudite and have molds of rhodolites, shells of bivalves and tubes of boring and burrowing organisms (Correia Filho *et al*., 2015; Távora *et al*., (2017), and Veras, 2017) (Figure 3).

Correia Filho *et al*. (2015), Távora *et al*. (2017), and Veras (2017) also studied these rocks across petrographic and catodoluminescence analyses, and observed the presence of a micritic matrix, well-formed dolomite crystals, bioclasts, framboidal pyrite, fine-grain quartz and low concentration feldspars.

In addition, the effect of dolomitization of the carbonate matrix was observed, as well as of dedolomitization reflecting evidence of diagenetic events (mineral replacement). The contribution of detrital siliciclastic components is very small, mainly represented by fine-grains quartz and feldspar, which increase the evidence of low input from the continent (Correia Filho *et al*., 2015).

5 Results

The results obtained for all samples (Table 2) range from 1.60‰ to 2.75‰ (VPDB) for $\delta^{13}C$ and -1.18‰ to 1.76‰ (VPDB) for $\delta^{18}O$. According to Figure 4, the values obtained for the Tambaba samples vary between 1.60‰ and 2.61‰ (VPDB) for $\delta^{13}C$ and 0.66‰ and 1.76‰ (VPDB) for $\delta^{18}O$. The isotopic curves show both isotopes vary with the same trend up the penultimate point analyzed (arrows in yellow), which occur a negative curve isotope excursion. After this excursion, the last sample value (DT-01F = 1.60‰) is similar to initial profile value (DT-01A = 1.62‰).

The values obtained for the Coqueirinho samples vary between 2.05‰ and 2.53‰ (VPDB) for $\delta^{13}C$ and 0.28‰ and 0.60‰ (VPDB) for $\delta^{18}O$ (Figure 5), and do not show great variations. The curves obtained through the Jacumã outcrop do not show any abrupt variations and maintain an isotopic pattern. Their values vary between 2.32‰ and 2.75‰ (VPDB) for $\delta^{13}C$ and -1.18‰ and -0.01‰ (VPDB) for $\delta^{18}O$.

The Mn/Sr ratio is in a range from 0.59 to 27.19, thus reflecting the high predominance of the manganese concentration relative to strontium, which can reach up to 27-times higher. The Mn/Sr ratio shows strong variations with high manganese concentrations in DT-01D (red arrow – Figure 4). Compared with the Tambaba samples, the Mn/Sr ratio found in Coqueirinho reflects considerable variation but expresses a lower manganese content (DC-01A = 2.50; DC-01B = 0.86; DC-01C = 3.36). In the Jacumã section, the Mn/Sr ratio varies between 0.59 and 3.92.

The Mg/Ca ratio has a certain proportionality, where the calcium concentration for all the samples is almost twice as high as the magnesium concentration ($0.52 < Mg/Ca < 0.62$). In the Tambaba section, the Mg/Ca ratio values are within a small range without much variation, from 0.55 to 0.61. The values of the Mg/Ca ratio from Coqueirinho are between 0.53 and 0.62, while in the Jacumã section the Mg/Ca ratio varies between 0.52 and 0.59.

Despite presenting not very significant values, the Al_2O_3 values are in a range between 0.00% and 0.52%. The values of the ranges of Al_2O_3 concentrations from Tambaba, Coqueirinho and Jacumã sections are, respectively, 0.00% to 0.24%, 0.13 to 0.41, 0.21% to 0.52%.

The Figures 4, 5 and 6 show the chemostratigraphic composite logs generated from the stratigraphic sections described in the field.

6 Discussion

Attention is required when using stable C and O isotopes in carbonate chemostratigraphy for paleoenvironmental studies. Diagenetic processes may change the isotopic composition of carbonates (Hoefs, 2018). Takaki and Rodrigues (1984) assert that during diagenesis the isotopic composition of

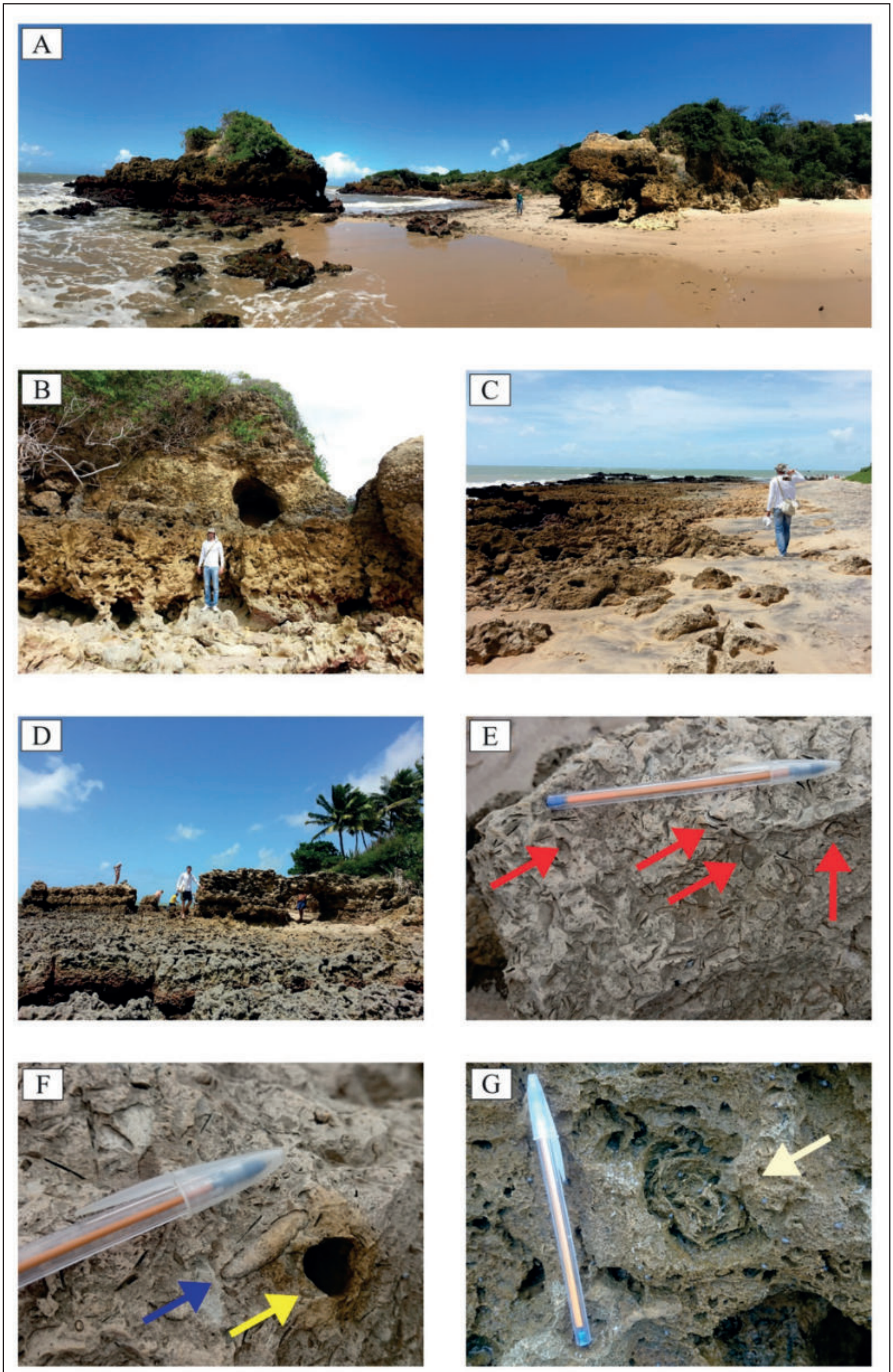

Figure 3 Outcrops of reef limestones. A) General appearance of limestones; B) Tambaba outcrop (DT-01); C) Coqueirinho outcrop (DC-01); D) Jacumã outcrop (DJ-01); E) bivalves molds (red arrows); F) bioturbation molds (blue and yellow arrows); and G) mold of incrusting organisms, i.e., algae (rhodolites – white arrow).

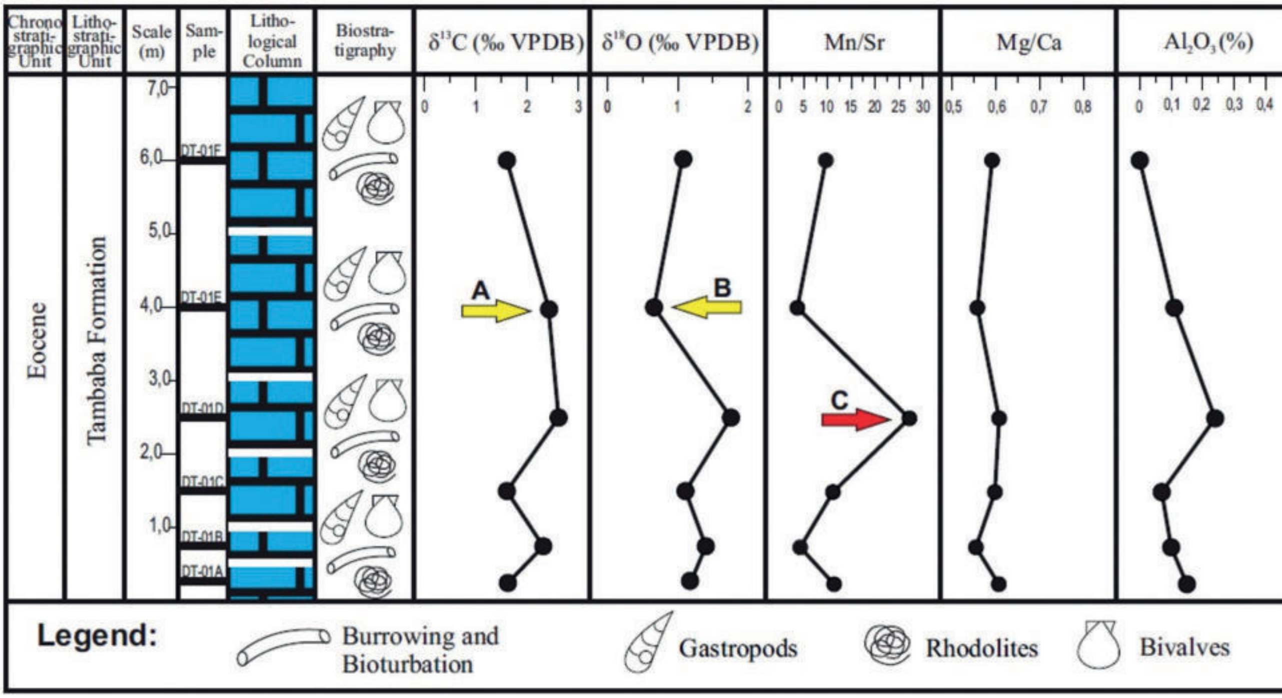

Figure 4 Chemostratigraphic profile of the section located on Tambaba beach. Both isotopes vary with the same trend up the penultimate point analyzed (yellow arrows); High concentration of manganese in DT-01D (red arrow).

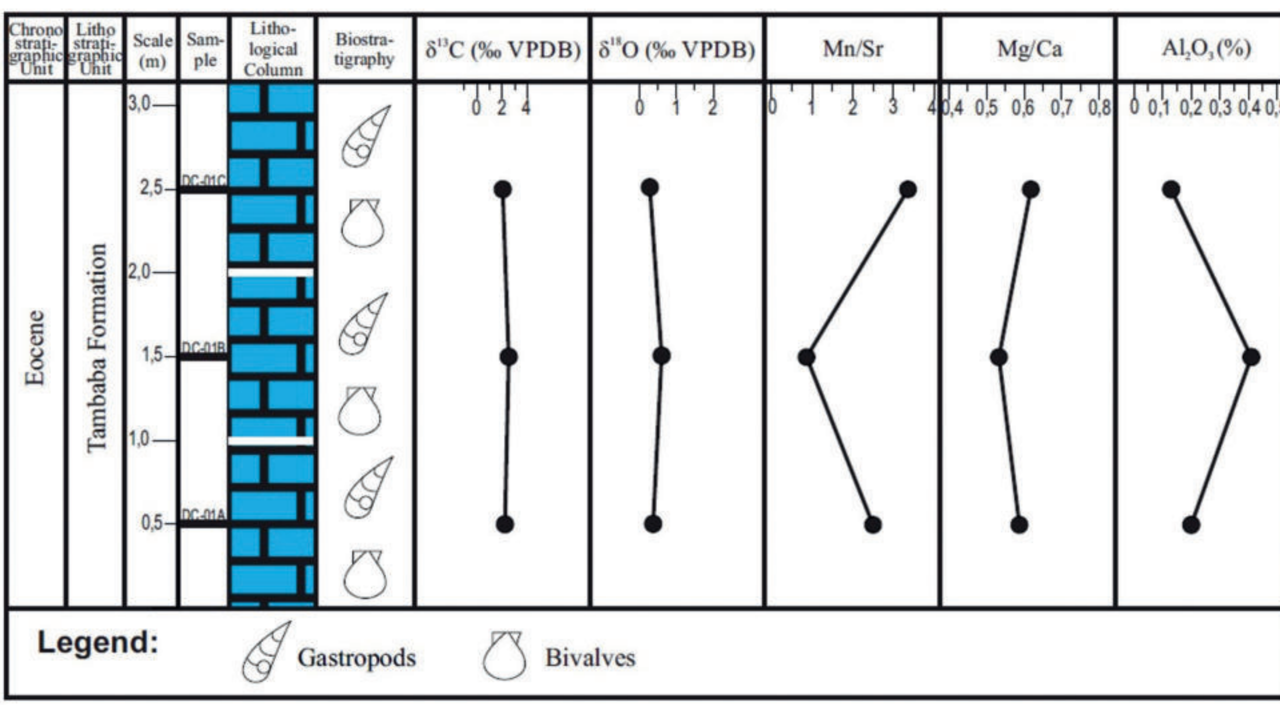

Figure 5 Chemostratigraphic profile of the section located on Coqueirinho beach.

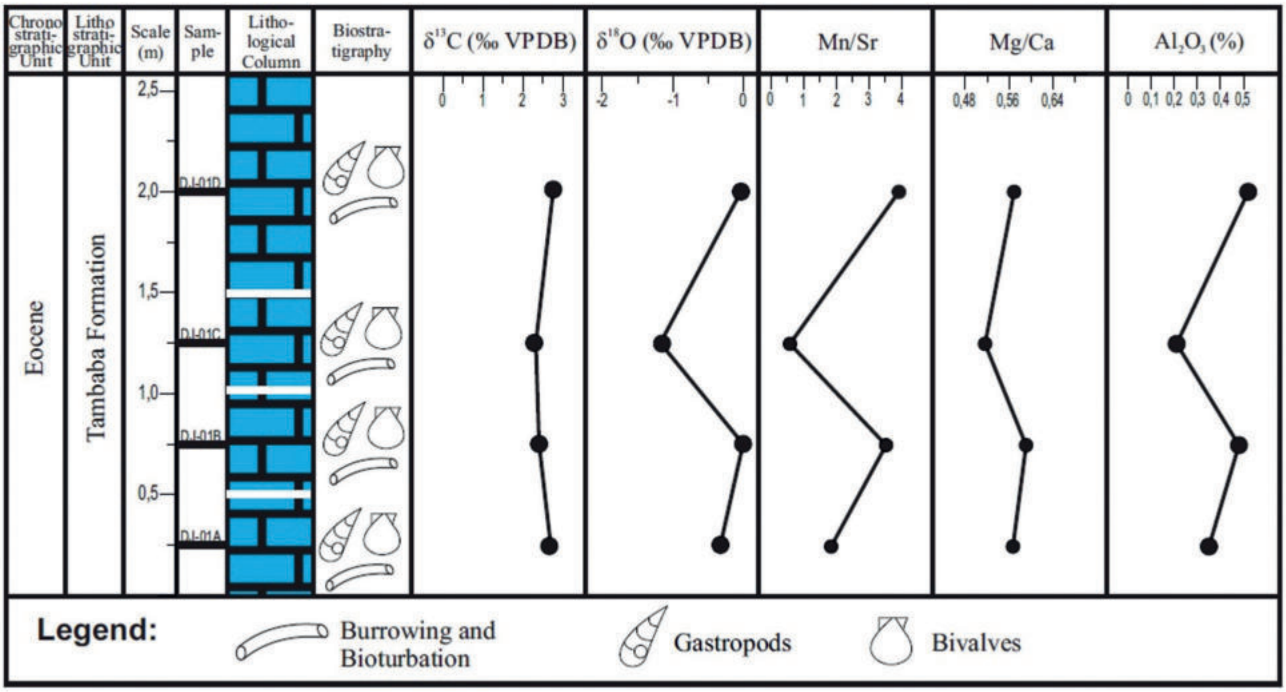

Figure 6 Chemostratigraphic profile of the section located on Jacumã beach.

Sample	d13C$_{VPDB}$‰	d18O$_{VPDB}$‰	Mn/Sr	Mg/Ca	Al_2O_3
DT-01A	1.62	1.18	11.36	0.61	0.15
DT-01B	2.31	1.40	4.25	0.55	0.10
DT-01C	1.60	1.11	11.13	0.60	0.07
DT-01D	2.61	1.76	27.19	0.61	0.24
DT-01E	2.41	0.66	3.64	0.56	0.11
DT-01F	1.60	1.06	9.62	0.59	0.00
DC-01A	2.23	0.37	2.50	0.59	0.20
DC-01B	2.53	0.60	0.86	0.53	0.41
DC-01C	2.05	0.28	3.36	0.62	0.13
DJ-01A	2.69	-0.33	1.85	0.57	0.35
DJ-01B	2.40	-0.01	3.53	0.59	0.48
DJ-01C	2.32	-1.18	0.59	0.52	0.21
DJ-01D	2.75	-0.04	3.92	0.57	0.52

Table 2 Results of isotopic and lithogeochemical chemostratigraphy for the described reef limestones.

carbon in relation to the total rock would not change much, because the carbonate volume in carbonates is much higher than in the formation water.

The isotopic curves in DT-01 (Figure 4) show that both isotopes vary with the same trend up to the penultimate sample, where δ^{13}C undergoes a negative excursion (arrow A) and δ^{18}O undergoes a positive excursion (arrow B), which may indicate: a fall in productivity, during transgressions there was an anormal proliferation of organisms that extract the δ^{13}C from seawater and cause an enrichment of δ^{13}C in seawater and precipitated carbonates. This droping productivity may also be linked to a regression event; and a cooling of the temperature, according to studies by Barbosa (2007) on the Cretaceous-Paleogene (K-Pg) boundary of the Paraíba Basin carbonate platform, where the behavior of the δ^{18}O curve shows more negative values close to the K-Pg boundary. These values corroborate the heating and subsequent cooling of a period of environmental stress (Li & Keller, 1998; Keller, 2001; Keller *et al*., 2002; Keller *et al*., 2003; Keller *et al*., 2004a). According Barbosa (2007), the enrichment in Mn is associated to the replacement of dolomite by calcite during diagenetic events (dedolomitization), where this replacement occurred after the dolomitization process that is evidenced by the Mg/Ca ratio.

In the Coqueirinho section there is not much variation between the values obtained (from 2.05‰ to 2.53‰ for δ^{13}C, and δ^{18}O from 0.28‰ to 0.60‰ - figure 5). C- and O-isotope studies of carbonate rocks from the Paraíba Basin (Nascimento-Silva *et al*., 2011) reveal that the behavior of $\delta^{13}C$ e $\delta^{18}O$ provides information on productivity, temperature and paleoenvironment. Our samples show a carbon and oxygen variation with the same trend are observed with no abrupt variation, indicating a period of environmental stability, without major changes in productivity, temperature or eustatic variations. It is also possible to observe that there is still a predominance of manganese over strontium, especially the reasons found are lower than those in the Tambaba section (<4), and may imply that the intensity of diagenetic events was lower in the DC samples when compared to the DT.

As in Tambaba, Jacumã also presents variation in the behavior $\delta^{18}O$ curve, indicating again a change in the environmental conditions during the deposition period, diagenetic changes (dolomitization and replacement of dolomite by calcite) and little contribution of siliciclastics. The ratio Mn/Sr in figure 6 presents a variation similar to that observed in Coqueirinho.

The values presented from the mineral chemistry (table 2) indicate that in all three outcrops: i) replacement of dolomite by calcite (dedolomitization) due to the high concentration of manganese on strontium, establishing an order of diagenetic intensity of Tambaba to Jacumã (DT > DC ≥ DJ); (ii) Reef limestones are classified as dolomitic limestones, since they have MgO contents above 12%, however, considering that the CaO > MgO contents and the occurrence of diagenesis previously mentioned, it is possible to conclude that there was initially precipitation of the calcite, then a dolomitization causing the occurrence of dolomites, and finally, a phase of replacement where the dolomites were dedolomitized and returned to the calcite mineral phase; iii) all Al_2O_3 values are below 0.50%, indicating a low terrigenous influx over the entire occurrence area of the Tambaba Formation.

Variations in the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ value in the world's oceans through time have been documented through chemostratigraphic studies of marine carbonate rocks ($^{13}C_{carb}$). This variation has been used to date and correlate sediments. Saltzman and Thomas (2012) analyzed isotope curves between different authors and geological time periods and built a $\delta^{13}C$ curve from Archean until Pleistocene explaining the isotope behavior.

Keller *et al*. (2018) studied environmental changes in two remarkable climatic and faunal events in Earth's history: The Cretaceous-Paleogene Mass Extinction (KPB) and Paleocene-Eocene Thermal Maximum (PETM). For this study They chose the globally recognized most complete sections for the KPB and PETM events. For the KPB these are the Global Stratotype Section and Point (GSSP) at El Kef, Tunisia, and for the PETM, the global GSSP at the Dababiya quarry in Egypt. They analyzed the carbon isotope behavior across chemostratigraphic sections before, during and after the main events (KPB and PETM), which show excursions (positives and negatives), environmental changes and isotope signal recovery.

Comparing the isotope curves from the reef limestones of the Tambaba Formation (Eocene) with the PETM event (Keller *et al*., 2018) and the curves built by Saltzman and Thomas (2012), it is possible that the reef limestones are fit well after the PETM event when there is a recovery of the $\delta^{13}C$ values. The curves built by these authors are in a range from 0‰ to 2‰, as such as the reef limestones here studied.

7 Conclusions

The carbon isotope ($\delta^{13}C$) behavior in the analyzed samples is generally constant, and the values vary from 1.6 to 2.8‰ and are fit well with the previous values of PETM event. However, the PETM event produced a strong negative excursion that reached values up to -4‰ for $\delta^{13}C$. This finding added to the previous data from Tambaba Formation corroborates that the carbonate deposits were formed after the PETM event since the $\delta^{13}C$ values had stabilized by approximately 2‰. The field data were correlated with the chemostratigraphic profiles of the studied outcrops and the bibliographic data, and they favor the hypothesis of a shallow and restricted platform environment with a low sedimentation rate that formed along with the coastal systems. Therefore, the isotopic variations suggest the occurrence of such a paleoenvironment during a transgression event of smaller magnitude, which allowed for variations in the water blade and generated the deposits studied here.

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6.3 STABLE ISOTOPE AND CHEMICAL STRATIGRAPHY OF THE EOCENE TAMBABA FORMATION: CORRELATIONS WITH THE PALEOCENE-EOCENE THERMAL MAXIMUM EVENT

Stable isotope and chemical stratigraphy of the Eocene Tambaba Formation: correlations with the Paleocene–Eocene Thermal Maximum event

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Abstract: The Paraíba Basin has a well-defined carbonate depositional sequence from the Upper Cretaceous (Campanian) to the Eocene. The carbonate sequence consists of the Itamaracá, Gramame, Maria Farinha and Tambaba formations, which mainly contain calcareous sandstones and carbonates with siliciclastics, limestone–marl alternations, limestones and marls, and limestones, respectively. The Tambaba Formation is composed of reef limestones, ranging from fossil- and ichnofossil-rich calcilutite to calcarenite. We investigated rocks of this unit located in a representative geological section at the Tambaba Beach, northeastern Brazil, in order to elucidate the environmental responses recorded in geochemical proxies (C and O isotopic composition, and distribution of major and trace elements). The $\delta^{13}C$ and $\delta^{18}O$ values ranged from 1.0 to 2.7‰ VPDB and from −1.3 to 1.1‰ VPDB, respectively. The interpretation of this response suggests environmental changes, such as an increase or decrease in bioproductivity of the organisms that make up these reef limestones. These changes are also recorded in the behaviour of the major and trace elements – for example, the relationship between SiO_2, Al_2O_3, MgO and CaO, characterizing two different cycles during the deposition of these limestones: the first one characterized by a predominantly carbonate deposition, and the second one presenting a pulse of siliciclastic content. In addition, palaeotemperature values (9–15°C, from $\delta^{18}O$ data) obtained, together with chemostratigraphic profiles of previous studies (e.g. $\delta^{13}C$, CaO, MgO, SiO_2, Al_2O_3), indicate that the reef limestones of the Tambaba Formation were probably deposited about 5 myr after the Paleocene–Eocene Thermal Maximum event.

Many studies have indicated that the carbon and oxygen isotopic compositions of carbonate rocks provide useful information regarding the physico-chemical conditions of precipitation, palaeoclimatology, palaeooceanography, palaeoecology and diagenetic conditions (e.g. James and Choquette 1984; Wright 1990). The carbon isotopic composition in carbonate minerals is mainly determined by the $\delta^{13}C$ values of the bicarbonate/carbonate ions in the palaeowater, whereas the $\delta^{18}O$ values are largely influenced by the isotopic composition of water and the palaeotemperature of precipitation (James and Choquette 1984).

Furthermore, carbon isotope studies are an important tool in the reconstruction of palaeoenvironmental conditions (Madhavaraju *et al.* 2004). Carbonates deposited in marine environments record the carbon isotopic composition of ocean water (Scholle and Arthur 1980). Climate changes have been well documented in marine sedimentary rocks, in which the oxygen isotopes suggest variations in temperature. Li and Keller (1998) and Keller (2001) studied this behaviour of global palaeotemperatures and verified a relatively cold climate (10–12°C) even before the Cretaceous–Paleogene boundary (KPB), when slight warming occurred.

Hsu and Wissert (1980) and Huber *et al.* (1995) studied the oxygen isotopic composition of the late Maastrichtian, and suggested that in the southern Atlantic Ocean the temperature was 18–25°C, with

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cooling (*c.* 10°C) occurring before the Cretaceous–Paleogene transition. A number of chemostratigraphic studies have been performed in the Paraíba Basin due to the presence of the KPB and its carbonate sequence (e.g. Sial *et al.* 1992; Barbosa 2007; Nascimento-Silva *et al.* 2011). Veras *et al.* (2018) studied a post-KPB carbonate sequence, the Tambaba Formation.

The Tambaba Formation occurs in the Paraíba Basin, and the Alhandra and Miriri sub-basins, and is mappable at the 1:25 000 scale (Fig. 1) (Correia Filho *et al.* 2015). In the Paraíba Basin (Fig. 1), the Tambaba Formation of Eocene age is represented by carbonate rocks deposited in a reef marine environment. The carbonate rocks present with a light-yellow colour, bioclastic texture, and beds, observed in reef constructions, with an irregular weathered and erosional aspect (Veras 2017).

Previously, this unit was considered to be the upper part of the Maria Farinha Formation (limestones and marls from the Paleocene) (Beurlen 1967*a*, *b*). However, this unit presents specific facies, stratigraphic and petrographical features that differ considerably from the bedding described for typical sections of the Maria Farinha Formation (Correia Filho *et al.* 2015).

The age proposed by Almeida (2000) for the reef limestones of the Tambaba Formation, based on the fossil content (gastropod: *Serrathocerithium* sp. and *Proadusta* sp.; corals: *Pocillopora* sp., *Paracyathus* sp. and *Caulastrea* sp.), differs from that proposed for the Maria Farinha Formation, which is considered to be Danian (Lower Paleocene) in the Olinda Sub-basin. Almeida (2000) compared the Tambaba Formation with the Maria Farinha Formation, which has been the target of several

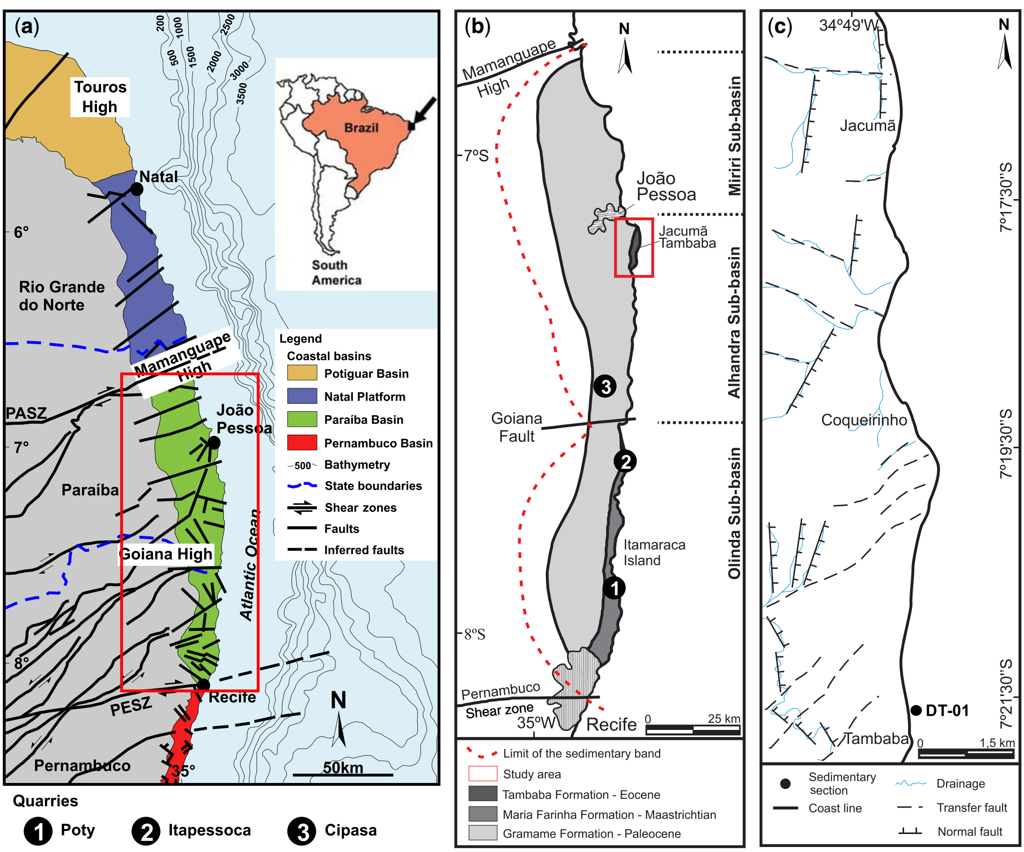

Fig. 1. (**a**) Location map of northeastern Brazil and the Paraíba Basin (modified from Neumann *et al.* 2009). PESZ, Pernambuco Shear Zone; PASZ, Patos Shear Zone. Some quarries studied by Barbosa (2007) are indicated (Poty, Itapessoca and Cipasa). (**b**) Geological and subdivision map of the Paraíba Basin and the occurrence area of the Tambaba Formation (modified from Távora *et al.* 2017). (**c**) Location of the samples studied in the Paraíba Basin (modified from Veras *et al.* 2019).

micropalaeontological studies (e.g. Albertão 1993; Albertão and Martins 1996; Stinnesbeck and Keller 1996; Fauth 2000; Gertsch *et al.* 2013), and determined a possible Eocene age. The genus *Serrathocerithium* was found in some deposits in France (Bois-Gouët, NW France) and was defined as Lutetian–Bartonian. This may suggest a more restricted age range for the Tambaba Formation rocks.

It is well known that during the Eocene, a rapid global warming event that began in the Paleocene was recorded worldwide (e.g. Zachos *et al.* 2001; Keller *et al.* 2018). This time interval, which represents the Paleocene–Eocene Thermal Maximum (PETM) event (*c.* 55.8 Ma), is marked by a negative isotope excursion of $\delta^{13}C$ values. The PETM event, which lasted for *c.* 170 kyr, is a remarkable climatic event in Earth's history that greatly influenced the fauna (Keller *et al.* 2018). Rapid warming (*c.* 5°C), extinctions of benthic and planktonic foraminifera, and anoxic conditions were some of the striking features of the PETM event.

In the present study, we analysed $\delta^{13}C$ and $\delta^{18}O$ values and the distribution of concentrations of some major and trace elements in carbonate samples from the Tambaba Formation in a representative sedimentary section from the Paraíba Basin (Alhandra Subbasin: Fig. 1a, b), and compared these results with chemostratigraphic curves obtained in some Global Stratotype Section and Point (GSSP) sections for the PETM transition (e.g. Dababiya quarry, Egypt: Keller *et al.* 2018).

Geological and stratigraphic setting

The Paraíba Basin is located on the continental bank of northeastern Brazil, and its coastal strip covers the state of Paraíba and a portion of the northern coast of Pernambuco (Barbosa 2004) (Fig. 1a). The Paraíba Basin occupies an onshore area of approximately 7600 km^2 and an offshore area of approximately 31 400 km^2, extending from the continental shelf to a bathymetric depth of 3000 m. This basin is limited by the Pernambuco Shear Zone and the Mamanguape Fault (which joins the Patos Shear Zone (PASZ)), and is subdivided into three sub-basins: the Olinda (southern), Alhandra (central) and Miriri (northern) sub-basins (Fig. 1b).

The origin of the Paraíba Basin is related to the opening of the South Atlantic Ocean during the Upper Jurassic–Lower Cretaceous (Chang *et al.* 1988; Matos 1999; Bueno 2004). The evolution of this rifting process resulted in the formation of passive-margin basins but among the marginal basins of northeastern Brazil, the strip between the Pernambuco Shear Zone (PESZ) and the Touros High (Potiguar Basin) represents a poorly studied stretch with tectonic characteristics somewhat different from the neighbouring marginal basins (Barbosa and Lima Filho 2006). There are differences in the evolution and distribution of the formations that cover the strip due to a different tectonic evolution. Such evolution divided the area into sectors, which are limited by the extension of lineaments and major faults in the Precambrian basement (Feitosa and Feitosa 1986; Lima Filho *et al.* 1998; Souza 1998; Feitosa *et al.* 2002; Barbosa *et al.* 2003; Barbosa 2004).

The sedimentary infill of the Paraíba Basin (Fig. 2) began with the sandstones of the Beberibe Formation during the Santonian–Campanian (Beurlen 1967*a*), followed by sandstones and carbonates of the Itamaracá Formation (Kegel 1955), limestones and marls of the Gramame Formation (Beurlen 1967*b*), the Maria Farinha Formation (Beurlen 1967*a*, *b*), also composed by limestones and marls, and reef limestones of the Tambaba Formation (Correia Filho *et al.* 2015) and of the Barreiras Formation. These units were deposited on a carbonate ramp, initially defined as an homoclinal one with shallow sedimentary cover (Mabesoone and Alheiros 1988, 1991, 1993). However, Barbosa and Lima Filho (2006) considered this ramp to be a distally inclined ramp. In what follows, we described in detail, from bottom to top, all the units of the Paraíba sedimentary basin.

Beberibe Formation

The Beberibe Formation is composed of continental fluvio-lake sandstones whose age is still little studied, being considered Coniacian–Santonian (Kegel 1954; Beurlen 1967*a*, *b*; Mabesoone and Alheiros 1988; Souza 1998; Barbosa 2004; Souza 2006). This formation has sandy-clay deposits of medium–coarse sandstones, which are locally conglomeratic. The deposits can be friable grey to beige, and eventually well lithified.

Itamaracá Formation

This unit overlies the sandstones of the Beberibe Formation and represents the moment when the Paraíba Basin had a transitional marine influence. This unit consists of calcareous sandstones, carbonates with siliciclastics, and phosphatic and dolomitic deposits at the top of the sequence, which in some stretches of the basin have a high level of phosphate or phosphorite. The phosphate-rich horizon, characterized by gamma-ray peaks (up to 1200 cps) in well logs, occurs throughout the basin (Barbosa 2004). This horizon was interpreted as a condensation surface that was deposited during a transgressive maximum, which promoted an event of high organic productivity in the proximal region of the basin. This event is linked to the formation of

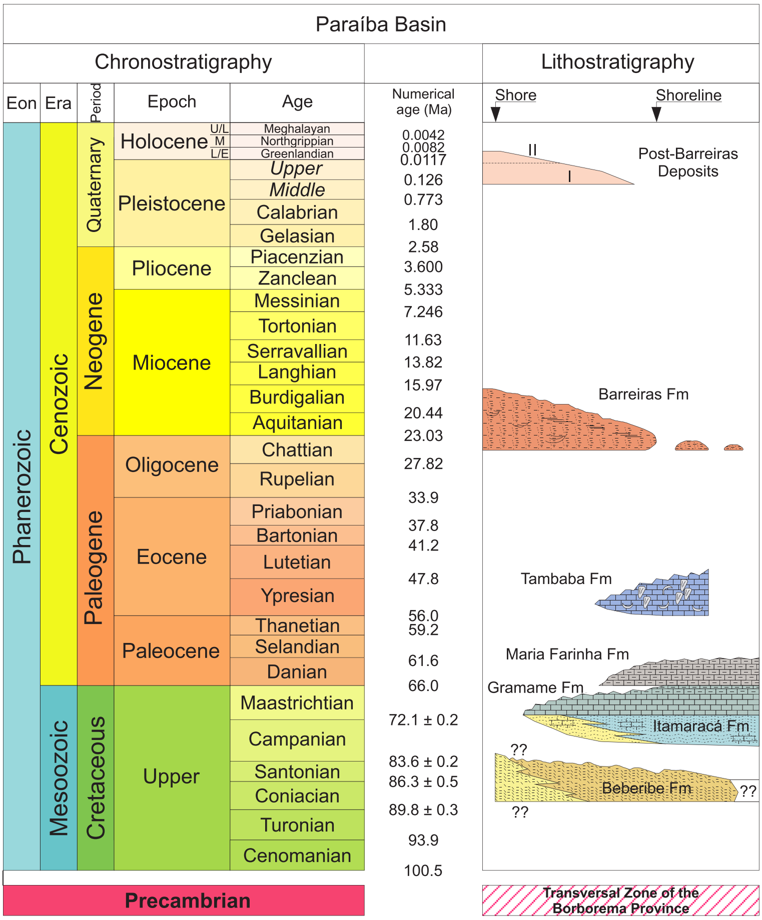

Fig. 2. Chronostratigraphy and lithostratigraphy of the onshore portion of the Paraíba Basin, taking into consideration the record of the units in the two sub-basins (north and south), including the newly identified unit of the Tambaba Formation (modified from Correia Filho *et al.* 2015). Geochronology according to the chart of the International Commission on Stratigraphy (May 2019). The positioning of deposits is according to available data (Almeida 2000; Barbosa *et al.* 2006*b*; Rossetti *et al.* 2011, 2012).

organic phosphate levels, with the accumulation of clay minerals, organic matter (faecal pellets), and macro- and microfossils (Kegel 1954). This horizon has been proposed as a stratigraphic landmark, a maximum flooding surface, which occurred during the transgressive phase and possibly has a middle Campanian–early Maastrichtian age (Barbosa 2004, 2007; Souza 2006).

Gramame Formation

The Gramame Formation overlies the Itamaracá Formation and is composed of limestone–marl alternations deposited on 100–150 m-deep carbonate platforms, and directly reflects high-frequency environmental changes (Westphal 2006). This formation displays characteristics of a highstand tract, and in its upper part it presents traces of a regression caused by tectonic uplift, just before the transition to the Paleogene (Barbosa *et al.* 2003; Barbosa 2007).

Maria Farinha Formation

The Maria Farinha Formation consists of limestone and marls. These strata were deposited in the Olinda Sub-basin during the regressive event that occurred in the basin (Barbosa *et al.* 2003, 2004; Barbosa 2004). Beurlen (1967*a*, *b*) named these deposits the Maria Farinha Formation.

Barbosa (2007) defined the following microfacies: dolosparite, biomicrite (mudstone, wackestone, packstone) and biosparite (wackestone, packstone). It was observed that there was a gradual increase in the content of clay and detritic siliciclastic from the bottom to the top, characterized by the action of the regressive event in the basin.

Albertão (1993) performed a characterization of the Cretaceous–Paleogene transition from foraminifera and palynomorphs, and stated that the Paleogene is marked by the appearance of pollens from *Echitriporites trianguliformis* sp. and *Proxapertites cursus* sp. There is also an increase in the abundance of acritarca *Baltisphaeridium* sp. and spore smooth and spiked triletes, and the appearance of the foraminifera *Globigerina (E) fringe* sp.

The transition between the Gramame and Maria Farinha formations, preserved in the southern sector of the Paraíba Basin, represents an important geological record, namely the Cretaceous–Paleogene transition (Albertão 1993; Morgan *et al.* 2006; Neumann *et al.* 2009; Nascimento-Silva *et al.* 2011). This transition in the area is characterized by a 1 cm layer of clay with an iridium positive anomaly (up to 0.69 ppb), being interpreted as a period of catastrophic biotic crisis in the geological history worldwide associated with the impact of extraterrestrial bodies (Keller *et al.* 2004). This period was characterized by intense changes in environmental conditions (climate and sea-level variations) that affected the survival of organisms, especially marine plankton, marine invertebrates and large terrestrial reptiles (Albertão *et al.* 1993, 1994*a*, *b*; Alvarez *et al.* 1980, 1984; Alvarez 1986; Archibald 1996; Keller 1996*a*, *b*, 2001).

Tambaba Formation

The Tambaba Formation of Eocene age is represented by carbonate rocks deposited in a reef marine environment. The rocks generally present a light-yellow colour, bioclastic texture, and beds where the reef constructions present an irregular weathered and erosional aspect (Veras 2017). This erosion is also strongly evidenced in small caves distributed in some outcrops that document karstification. These reef limestones, which range from calcilutite to calcarenite, are both fossil and ichnofossil rich.

These reef limestone deposits occur both on the beach strip, which may be covered by the Barreiras Formation, as well as in the intertidal region, where they are partially or totally covered by seawater during high tide and by recent beach sediments. They have a limited lateral extension and crop out in a strip approximately 10 km on the coastline.

Almeida (2000, 2007) conducted a more systematic study of these deposits, which were first appointed by Beurlen (1967*a*, *b*) as the Upper Maria Farinha Formation. The last author characterized the mollusca fauna present in these deposits and their palaeoecology (reef environment), in addition to its important ichnofossils content. This author also suggested that these limestones are possibly of Eocene age, based on gastropods (*Serrathocerithium* sp. and *Proadusta* sp.) and some corals (*Pocillopora* sp., *Paracyathus* sp. and *Caulastrea* sp.).

These deposits had previously been considered to be part of the Maria Farinha Formation, eventually treated as the Upper Maria Farinha Formation (Beurlen 1967*a*, *b*; Almeida 2000; Barbosa 2007). More recently, Correia Filho *et al.* (2015), based on the mapping scale (*c.* 1 km^2 of occurrence area at a 1:25 000 scale), stratigraphic relationships, analysis of carbonate facies models and application of sequence stratigraphy concepts, defined these deposits as an individual formation and named it the Tambaba Formation.

Barreiras Formation

These deposits are related to the existence of alluvial fans and fluvial systems, which possibly went to delta systems (Rossetti and Truckenbrodt 1989; Rossetti *et al.* 1990; Rossetti 2000, 2001, 2006*a*, *b*; Netto and Rossetti 2003; Rossetti and Santos 2004).

The Barreiras Formation was deposited along an extensive strip over the Brazilian marginal basins, from Pará to Rio de Janeiro (about 4000 km long). This unit covers others sedimentary sequences in a discordant way, as well as structural characteristics of these basins that are important components.

The facies variations of the Barreiras Formation range from conglomerates to claystones and commonly presents planar-stratifications through to cross-stratifications. According to previous studies, the age of this formation is Plio-Pleistocene (Beurlen 1967*a*, *c*; Mabesoone and Alheiros 1988, 1993). However, recent work has suggested an older age, linked to the Oligocene–Miocene (Arai *et al.* 1988, 1994; Arai 1997; Leite *et al.* 1997*a*, *b*).

Post-Barreiras deposits

These deposits are composed of weakly cemented quartz-sandy sediments that occur in channels dug out by river streams in the Barreiras Formation. Lateritic crusts were also found at the top of the Barreiras Formation, which possibly mark a subaerial exposure level and the beginning of post-Barreiras sedimentation (Rossetti and Truckenbrodt 1989; Rossetti 2006*b*).

Methods and analytical techniques

Fieldwork

Previous studies on the carbonates from the Paraíba Basin were carried out by Veras (2017) and Veras *et al.* (2019), and examined facies and geochemistry composition of the reef limestones from the Tambaba Formation. In these studies fieldwork was conducted along a coastal strip in the state of Paraíba between the Tambaba and Jacumã beaches, and also included three outcrops located in Conde city (Fig. 1b).

In this work, we investigated a representative outcrop located on Tambaba beach (Fig. 1c). This outcrop was sampled along a vertical profile perpendicular to the layers, where samples were taken following an approximately 5.5 m bottom-up sequence (from DT-01A to DT-01K: see Figs 3 & 4), with a interval of about 30 cm between each. In order to do this, a two-stroke Shaw rock drill was used (Fig. 4) which delivers cores 25 mm in diameter and up to 10 cm long. Eleven carbonate samples collected at centimetre intervals were analysed for C and O isotopes, and for the geochemistry of major and trace elements.

Laboratory work

The laboratory analysis consisted of petrographical descriptions of 30 thin sections (Veras 2017) using a model BX-41 Olympus petrographical microscope; cathodoluminescence analysis was also performed using a Cambridge Image Technology Ltd (CITL) CL8200 optical cathodoluminescence system coupled to a Zeiss Axioscope A1 optical microscope at the Department of Geology, Universidade Federal de Pernambuco (UFPE). The integrated analysis allowed the limestones of the Tambaba Formation to be classified using the classifications of Grabau (1904) and Dunham (1962).

A representative fraction of the collected samples was powdered in the Nucleus of Geochemical Studies and Stable Isotope Laboratory (NEG-LABISE) at the UFPE in a wolfram carbide disc mill. The powdered samples were then subjected to geochemical analyses.

Geochemistry investigations

The stable isotope data were obtained at the University of Brasília Geochronology Laboratory and followed an isotopic ratio mass spectrometry methodology, where a continuous-flow isotope ratio mass spectrometer (DELTA V™ Plus IRMS) and a gaseous source with magnetic sector were used. Using the Thermo™ GasBench II accessory, 600–800 µg of sample were inserted into clean glass vials with rubber septum lids conditioned in a block with a controlled temperature of 70°C. A gas chromatography needle was then used to perform the flushfill process; this exchanges the atmospheric air in the flask to make the reactive environment free from interference by injecting a continuous flow of helium for 6 min. Using a dosing pump, five drops of 99% H_3PO_4 were added to the vials for a CO_2 extraction reaction for 1 h:

$$2H_3PO_{4(l)} + 3CaCO_{3(s)} \rightarrow Ca_3(PO_4)_2(aq) + 3H_2O_{(l)} + 3CO_{2(g)}.$$

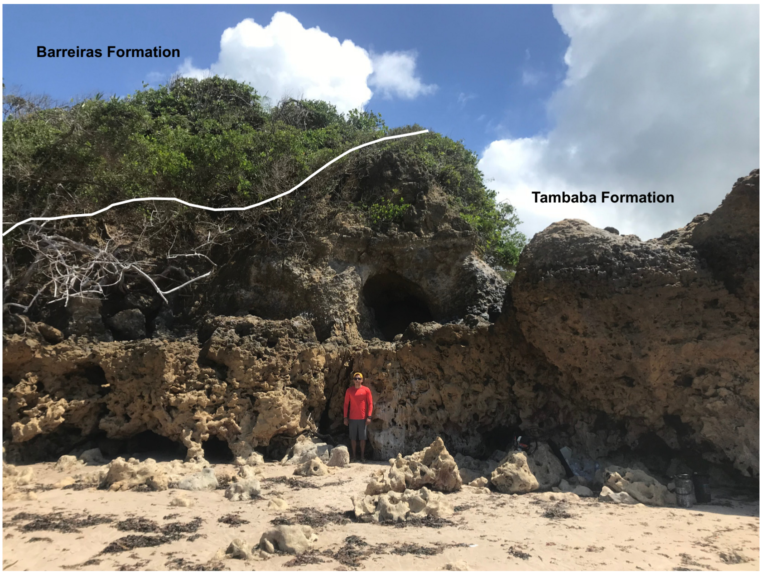

Fig. 3. Representative outcrop of reef limestones of the Tambaba Formation (Eocene: outcrop DT-01 located in Fig. 1c) covered by sandstones–claystones of the Barreiras Formation (Oligocene–Miocene).

Fig. 4. Example of the samples collected in the field at reef limestone outcrops (DT-01B, DT-01C and DT-01D) of calcarenites of the Tambaba Formation (outcrop DT-01 located in Fig. 1c).

After the CO_2 extraction, a second chromatographic needle was used to collect the gas from the flask and pass it through a chromatographic column using a continuous flow of helium. After passing through the column, the gas was then injected into the ion source to be measured. Values of $\delta^{13}C$ and $\delta^{18}O$ are presented in parts per thousand (‰) based on the Vienna Pee Dee Belemnite (VPDB) standard.

From the isotopic data, the palaeotemperature (T) and palaeosalinity (Z) for the reef limestone of the Tambaba Formation were calculated using equation (1) (Deocampo 2010) and equation (2) (Keith and Weber 1964), respectively:

$$\delta^{18}O = 0.49(T) - 12.65 \quad (1)$$

$$Z = 2.048(\delta^{13}C + 50) + 0.498(\delta^{18}O + 50). \quad (2)$$

Prior to the geochemical analysis, a portion (2.25 g) of each sample was placed in an oven to dry at 110°C and then placed in a muffle furnace at 1000°C for 2 h to determine the lost on ignition contents. Molten beads were generated using lithium tetraborate as the flux. The pearls were analysed in a Rigaku ZSX Primus II X-ray fluorescence spectrometer equipped with a Rh tube, and seven crystal analyses were performed using the calibration curve method, which is based on international reference materials. The results are displayed in wt% (major elements) and ppm (trace elements).

The oxidation–reduction conditions are deduced from the relationship:

$$Mn^* = \log\left(\frac{\text{Mn sample}}{\text{Mn shale}} \Big/ \frac{\text{Fe sample}}{\text{Fe shale}}\right)$$

which provides an indication of the redox potential of the depositional environment. The mean values for Mn shales and Fe shales are those suggested by Wedepohl (1978).

Results

The outcrops of these reef limestones present a rounded general morphology (‘egg-box pattern’), are locally layered, and exhibit a bioclastic texture and eroded appearance, with the latter due to erosion (Fig. 3). These outcrops are between 0 and 10 m above sea level, vary in grain size between calcilutite and calcirudite, and have molds of rhodolites, shells of bivalves, and tubes of boring and burrowing organisms. The communities of algae and corals, as well as the macrobioerosion ichnofossils, are responsible for the formation of the layers of accumulated shells that generate the hardgrounds.

Optical and cathodoluminescence petrography

The representative samples analysed petrographically define a mudstone that presents a compositional

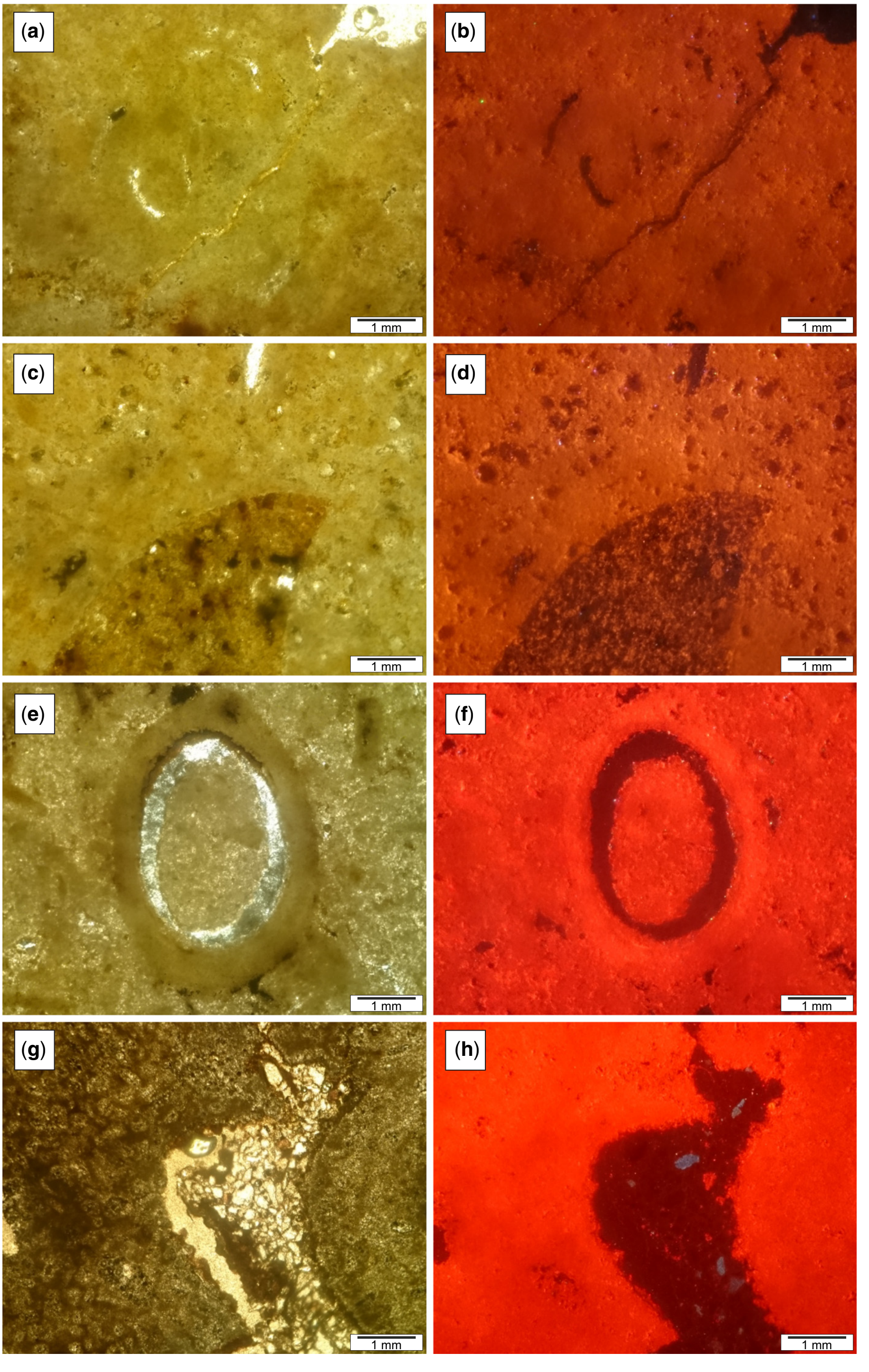

Fig. 5. Microphotographs of representative samples of reef limestones from the Tambaba Formation (Veras 2017). (**a**), (**c**), (**e**) & (**g**) Parallel nicols and (**b**), (**d**), (**f**) & (**h**) Cathodoluminiscence. (**a**) & (**b**) Mudstone with some moldic porosity. (**c**) & (**d**) Bioclast portion displaying an intragranular porosity. (**e**) & (**f**) Cross-section of seaweed or burrow/boring. (**g**) & (**h**) The presence of quartz grains (CL, pale-blue colour).

difference (Fig. 5) which reflects one mineralogy with a low presence of iron oxide, and another mineralogy in which this oxidation-bearing compound is relatively abundant. These features favour pyrite formation (FeS_2), which appears characteristically with framboidal habits.

Via cathodoluminescence (CL), it is possible to observe, due to its high luminescence, that the rock is essentially composed of calcite (Fig. 5b, d, f & h). The dedolomitization process was identified by the high luminescence of calcite, even in dolomite crystals because dolomites had been replaced by calcite. The influence of siliciclastic grains (quartz) was also observed, with a low (2%) content and presenting a rounded morphology occurring as disseminated as well as in the matrix porosity (Fig. 5g). Moreover, in the CL analysis, quartz identified in the dark brown area showed as a pale-blue colour (Fig. 5h).

These reef limestones present a large concentration (*c.* 35 vol%) of bioclasts. Among these, the presence of fragments of bivalves, gastropods, and burrows and borings predominate (Fig. 5c–f). Related to this, moldic porosities are characterized that result from the dissolution of allochemical grains, in addition to the intragranular (as an example of fabric-selective porosity), fracture and vuggy porosity (non-fabric-selective porosity) observed.

C and O isotopes

In the analysed samples of the Tambaba Formation, the $\delta^{13}C$ and $\delta^{18}O$ values range from 1.0 to 2.7‰ and from −1.3 to 1.1‰, respectively (Table 1). Carbon and oxygen isotope stratigraphic profiles from the Tambaba limestone outcrop are shown in Figures 6 and 7.

SiO_2 and Al_2O_3 contents

SiO_2 was not detected, as all samples presented SiO_2 concentrations below the limit of detection (LOD) for the method (<0.001%). Despite not being very significant, the values of the Al_2O_3 concentrations from the Tambaba Formation representative section are between the LOD (<0.001%) and 0.35% (Table 1).

Mg/Ca ratio

The Mg/Ca ratio, ranging from 0.47 to 0.54, has a certain homogeneity between the analysed samples, where the calcium concentration for all the samples is almost twice as high as the magnesium concentration (Table 1).

Mn/Sr and Rb/Sr ratios

The Mn/Sr ratio ranges from 3.15 to 21.41 (Table 1); thus reflecting the high predominance of the manganese concentration relative to strontium, The Mn/Sr

Table 1. *The isotope (VPDB), major (%) and trace element (ppm) compositions and ratios in reef limestones samples from the Tambaba Formation*

Sample	$\delta^{13}C$ (VPDB ‰)	$\delta^{18}O$ (VPDB ‰)	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	Rb (ppm)	Sr (ppm)	Mn (ppm)	Mg/Ca	Mn/Sr	Rb/Sr	Sr/Ca	*T* (°C)	Mn*	Z
DT-01A	1.93	−0.2	<LOD	<LOD	<LOD	0.80	0.06	21.75	34.16	0.03	<LOD	0.01	3	116	464	0.54	4.00	0.03	0.00048	12.22	0.80	131.15
DT-01B	2.19	−0.1	<LOD	<LOD	<LOD	0.72	0.06	21.74	34.06	0.03	<LOD	0.01	5	110	445	0.54	4.05	0.05	0.00045	12.45	0.83	131.74
DT-01C	1.31	−0.9	<LOD	0.01	<LOD	0.74	0.06	21.40	33.60	0.01	<LOD	0.01	1	108	488	0.54	4.52	0.01	0.00045	10.79	0.86	129.53
DT-01D	1.01	−1.4	<LOD	<LOD	<LOD	0.85	0.08	21.42	33.83	0.13	<LOD	0.01	3	107	624	0.53	5.83	0.03	0.00044	9.87	0.91	128.69
DT-01E	1.96	0.00	<LOD	0.01	<LOD	0.78	0.01	21.12	33.57	0.21	<LOD	0.02	2	118	765	0.53	6.48	0.02	0.00049	12.65	1.03	131.31
DT-01F	1.54	−0.4	<LOD	0.01	<LOD	0.90	0.17	21.20	33.50	0.17	<LOD	0.01	1	112	1311	0.53	11.71	0.01	0.00047	11.79	1.20	130.24
DT-01G	1.24	−0.6	<LOD	0.01	<LOD	1.34	0.30	20.98	33.25	0.15	<LOD	0.02	3	111	2377	0.53	21.41	0.03	0.00047	11.43	1.29	129.54
DT-01H	1.62	−0.4	<LOD	<LOD	<LOD	1.34	0.13	20.75	32.98	0.35	<LOD	0.01	3	131	1045	0.53	7.98	0.02	0.00056	11.81	0.93	130.41
DT-01I	2.73	1.14	<LOD	0.02	0.31	0.75	0.17	19.87	33.65	0.25	<LOD	0.02	4	233	1299	0.50	5.58	0.02	0.00097	14.98	1.28	133.46
DT-01J	2.1	0.61	<LOD	0.03	0.35	0.80	0.13	20.15	33.51	0.08	<LOD	0.02	4	187	1048	0.51	5.60	0.02	0.00078	13.89	1.16	131.90
DT-01K	2.71	0.82	<LOD	0.02	0.23	0.47	0.10	19.36	34.40	0.04	0.01	0.03	5	255	803	0.47	3.15	0.02	0.00104	14.32	1.27	133.26

Mn*, Mn index.
Z, salinity.
Precision for C and O isotopes: 0.1‰.
International standard:
- NBS 18 C = −5.014 VPDB; O = −23.20.
- NBS 19 C = 1.95 VPDB; O = −2.20.

International standard:
- GEFA C = −5.0 VPDB; O = −9.60.

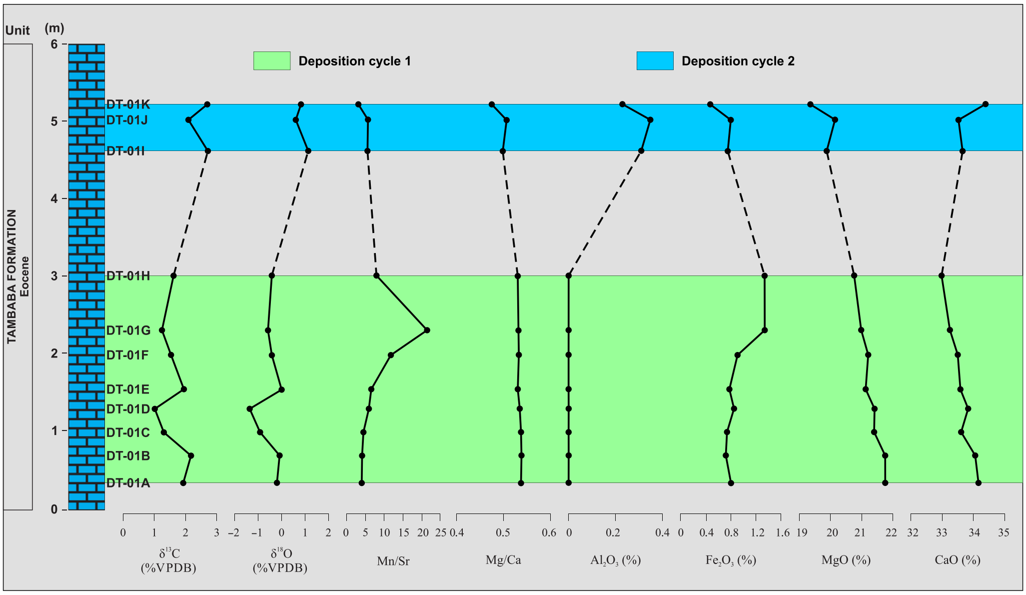

Fig. 6. Isotope and chemical stratigraphy profiles in the Tambaba Formation section. The section is divided into two environments: the first one (at the bottom) is marked by a carbonate-rich layer, justified by the low content of Al_2O_3; and the second with a relatively high Al_2O_3 content, with the input of relatively more siliciclastics.

ratio shows large variations, with relatively high manganese concentrations in sample DT-01G that can be attributed to a diagenetic effect. The Rb/Sr ratios ranged from 0.008 to 0.045.

The C and O isotope stratigraphy, along with main and secondary elements (Mn/Sr, Mg/Ca, Al_2O_3, Fe_2O_3, MgO, CaO, Rb/Sr, Rb, Sr, Sr/Ca), of the Tambaba Formation section are shown in

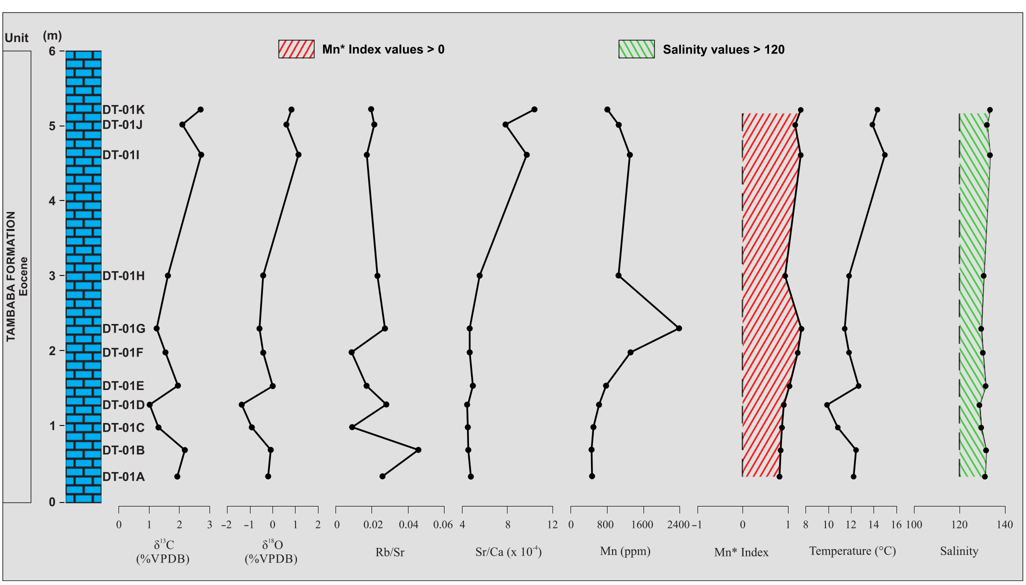

Fig. 7. Isotope, chemical stratigraphy, calculated temperature and salinity profiles in the investigated representative section of the Tambaba Formation.

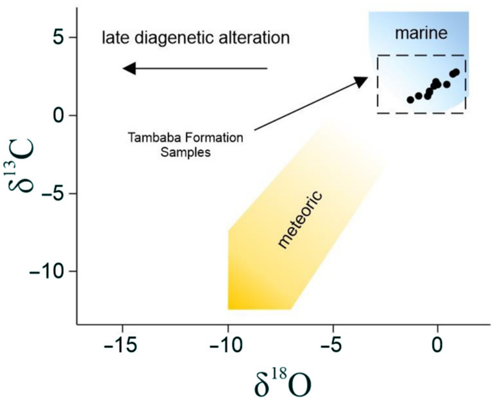

Fig. 8. Cross-plot of δ^{13}C (VPDB per mil) v. δ^{18}O (VPDB per mil) discerning primary v. diagenetic signals in carbonate carbon and oxygen isotope records (modified from Schobben *et al.* 2016).

Figures 6 and 7, and are interpreted in the following Discussion section.

Discussions

Diagenesis v. preserved original isotopic composition

Previous work involving the Tambaba Formation identified the presence of diagenetic processes such as dolomitization and dedolomitization (Fig. 8) (Correia Filho *et al.* 2015; Távora *et al.* 2017; Veras 2017). The enrichment in Mn observed in our analysed samples from the Tambaba Formation (Fig. 7) is probably associated with the replacement of dolomite by calcite during diagenetic events (dedolomitization). These high Mn contents are similar to others marine carbonates studied by Jacobsen and Kaufman (1999) and Barbosa (2007).

We note our Mn/Sr ratios in Table 1 and verify their agreement with the proposed observation by Kaufman and Knoll (1995), which states that carbonates with a Mn/Sr ratio <10 (Fig. 9) would retain values close to the primary trends for δ^{13}C. The Sr concentrations in our samples range from 107 to 255 ppm and the Sr/Ca ratios in the reef limestones of the Tambaba Formation are less than 5×10^{-4}, almost constant. On the other hand, our low Sr/Ca ratios and Mn enrichment (Fig. 7) can indicate that the Sr content from the reef limestones of the Tambaba Formation was not altered during diagenesis and their marine signature was preserved. This idea agrees with studies conducted by Kah (2000) on the dolomitization process with regard to the Sr/Ca ratio and Mn content, which provide a sensitive indication of diagenesis during exchange with diagenetic fluids. Brand and Veizer (1980) and Veizer (1983) stated that Mn is commonly incorporated into carbonates, while Sr is flushed from the carbonate lattice.

Still concerning the diagenetic processes, the original isotopic composition of carbonates can be diagenetically altered, as indicated by several authors (Kaufman *et al.* 1993; Kaufman and Knoll 1995; Jacobsen and Kaufman 1999; Fölling and Frimmel 2002; Hoefs 2018). However, Swart (2015) and Schobben *et al.* (2016) argued that this interpretation is too simplistic and explained that a correlation does

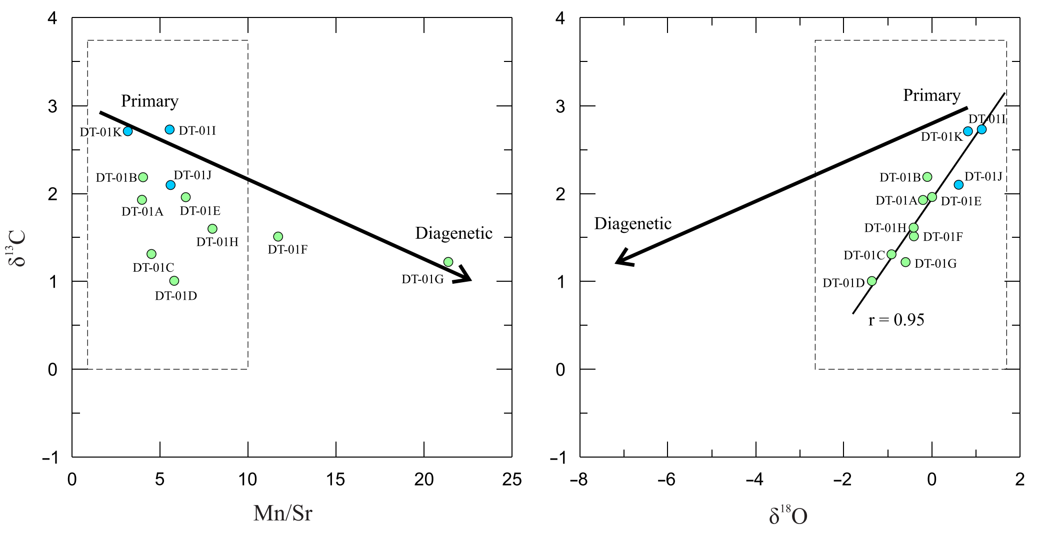

Fig. 9. Correlation geochemical diagram for δ^{13}C, δ^{18}O and Mn/Sr values of the analysed samples from reef limestones of the Tambaba Formation (based on Jacobsen and Kaufman 1999).

not necessarily provide information about the diagenetic modifications; they also suggested that this interpretation should be used with caution and be supported by detailed petrographical analyses. Petrographical analysis and a description of the microfacies of these reef limestones from the Tambaba Formation were performed by Veras (2017), and geochemistry analyses were carried out by Veras *et al.* (2019). These studies showed that even with the presence of diagenetic processes, the original isotopic composition was retained.

During diagenesis, the isotopic composition of carbon would not change when the formation water had a low dissolved inorganic content (Takaki and Rodrigues 1984). Thus, the formation water of these reef limestones was probably the same as that involved in the diagenetic processes (as stated before), mainly dolomitization and dedolomitization, as observed through petrography and CL analyses. From the calculation of Pearson's statistical parameter (r), our samples present a strong positive correlation between $\delta^{13}C$ and $\delta^{18}O$ ($r = 0.95$: Fig. 9). Even with this positive correlation, these reef limestones are part of a single diagenetic zone, as argued by Oehlert and Swart (2014), which means that it has only been affected by diagenesis. Therefore, assuming this, it is possible to indicate that the fluids that interacted with the studied limestones are of seawater origin only.

Investigations using carbon and oxygen stable isotopes may contribute to a better understanding of environmental and climatic changes. Trends in $\delta^{13}C$ values can help to reconstruct the carbon cycle (Kaufman and Knoll 1995; Jacobsen and Kaufman 1999). Local, regional or global responses can be reflected by the chemical variations occuring at the time of deposition. The variations in the stable isotope compositions for both oxygen and carbon are shown in Figure 6. The $\delta^{18}O$ profile shows negative values for sample DT-01I and positive values for the last three samples. In this case, the change to positive values suggests that there was an environmental variation, possibly a slight cooling of the climate (Keller 2005; Keller *et al.* 2002, 2003).

The $\delta^{13}C$ isotope curve (Fig. 6) displays a slight variation in the positive values, where the antepenultimate point analysed (DT-01I: 2.7‰) shows an approximate resumption of the initial value (1.9‰). This suggests changes in the marine bioproductivity, which is observed via the decrease in values within 2.5 m. For the same outcrop, Veras *et al.* (2019) identified a similar chemostratigraphic profile indicating a fall in productivity. During transgressive pulses, a proliferation of primary producers extracted ^{12}C preferentially from seawater, leaving the dissolved inorganic carbon pool enriched in ^{13}C; a fact reflected by the isotopic composition of the precipitated carbonates. Even with this proliferation, there were changes that could represent a slight drop in productivity, which may also be linked to a regressive pulse and a cooling of the temperature.

Palaeoenvironment

This is confirmed by the equation proposed by Keith and Weber (1964), which is used here (equation 2) to discriminate between marine and freshwater limestones, where the limestones with Z values above 120 are considered as marine, whereas those with Z values below 120 would be classified as freshwater types. In the present study (whole-rock samples), 13 samples show Z values above 120. The carbonate deposition phases in the Paraíba Basin are marked by transgressive and regressive cycles. The reef limestones of the Tambaba Formation were formed after the regressive cycle responsible for the deposition of the Maria Farinha Formation. Figure 6 shows the predominance of the carbonates represented by CaO and MgO contents, suggesting a transgressive cycle of small magnitude which was the main vehicle for this deposition after the regressive cycle of the Maria Farinha Formation. The Mg/Ca ratio values are within a small range without much variation (0.47–0.54); however, the CaO content is higher than the MgO content. This homogeneity in the Mg/Ca ratio probably reflects the mineralogy (essentially calcite) and, consequently, the homogeneous palaeotemperature conditions of the depositional environment. The relatively large amount of Mg (up to 21.75 wt% of MgO) could also suggest relatively warm seawater.

We can identify two different cycles. The first cycle (samples DT-01A–DT-01H) is marked by an essentially carbonate deposition without the presence of siliciclastic contents where the SiO_2 and Al_2O_3 contents were not detected (0%: <0.001% (LOD value)). The Fe_2O_3 content (<1.5%: attested by the presence of pyrite (FeS_2)) is associated with this carbonate phase. The second cycle (samples DT-01I, DT-01J and DT-01K) demonstrates an Al_2O_3 content (*c.* 0.3%), even at relatively low concentrations, indicating that there was a change in the first cycle that was essentially carbonate. This change can be explained by the supply of onshore material (probably sediments of the Barreiras Formation) during the environment deposition. This siliciclastic contribution may indicate a decrease in the sea level that could either represent just a pulse or a regressive cycle just before the deposition of the Barreiras Formation. This siliciclastic input is further evidenced by CL analyses that show quartz microcrystalline grains in the carbonate matrix (Fig. 5).

The distribution and concentration of some trace elements may indicate the palaeoclimate and palaeoenvironment (Worash 2002). In the present case, the values of Rb/Sr are relatively low (<0.1:

Fig. 7), which could be interpreted as them being deposited under warm conditions (arid), according to Cao *et al.* (2012), for mudstones from Qaidam Basin, NW China, and Moradi *et al.* (2016).

The analysed samples from the Tambaba Formation present positive values for the Mn* index (Mn* >0: Fig. 7). In oxidizing environments, the Mn* index is characterized by positive values, while in reducing environments these values are negative (Maillot 1983; Machhour 1988); so the oxidation–reduction conditions deduced for the Tambaba Formation deposition indicates an oxidizing environment. For this evaluation, we use the Mn* index, and the results are shown in Table 1.

Palaeotemperatures

The Rb/Sr ratio ranged from 0.008 to 0.045 and can be used to indicate the palaeotemperature conditions of the depositional environment (Cao *et al.* 2012; Moradi *et al.* 2016). From the mathematical equation used by Deocampo (2010), we calculated palaeotemperature values for the Tambaba Formation to be between 9.9 and 15°C (Fig. 7), with a ΔT of 5.1°C. This is similar to the observations of Zachos *et al.* (2001) in a study of the palaeoclimate of the Cenozoic, where determined temperatures for the PETM also suggest a strong relationship with the studies of the late Maastrichtian mentioned previously in this paper.

Paleocene–Eocene Thermal Maximum (PETM)

Despite some previous work addressing isotopic carbon and oxygen signatures in the Paleocene of the Paraíba Basin (e.g. Barbosa 2007; Neumann *et al.* 2009; Nascimento-Silva *et al.* 2011), none of them reported the occurrence of the PETM event, because their investigations focused on the late Cretaceous and early Paleocene (Cretaceous–Paleogene transition). Therefore, we compared our isotopic and geochemical data from the Eocene with data from Barbosa (2007) for the late Cretaceous–Paleocene in order to build a chemostratigraphic scale for the investigated period of time (Fig. 10), in addition to the stratigraphic correlations carried out between each depositional unit (the Gramame, Maria Farinha and Tambaba formations).

Our samples presented positive $\delta^{13}C$ values that ranged from 1.0 to 2.7‰ belonging to the Eocene, as defined by Almeida (2000). Keller *et al.* (2018) studied environmental changes and recognized the most complete sections for the PETM event. The

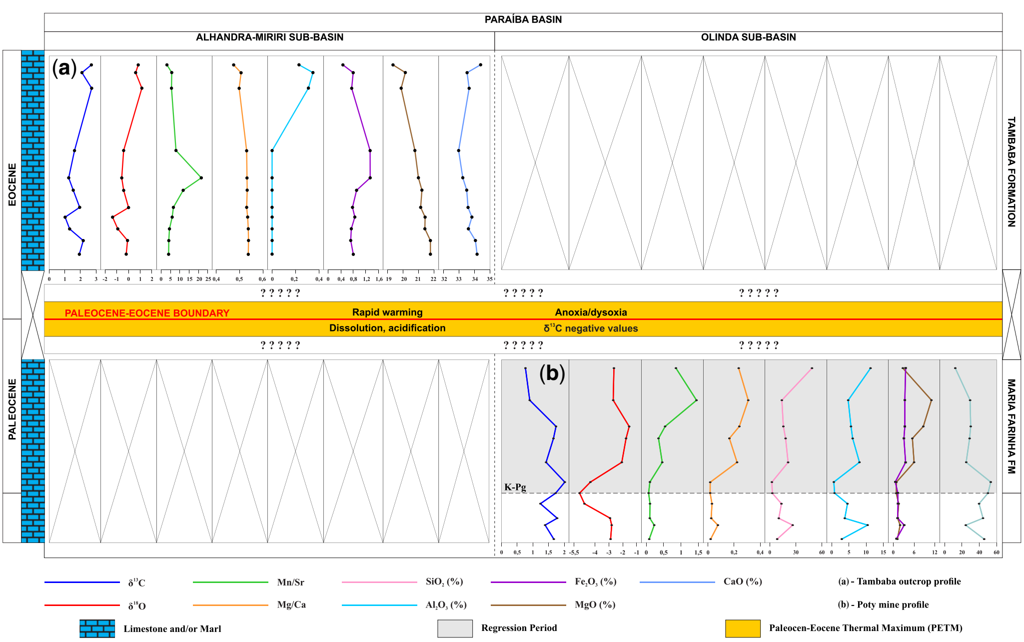

Fig. 10. (**a**) Composite chemostratigraphic and geochemical data of the Tambaba Formation, which were placed after the Paleocene–Eocene Thermal Maximum (PETM) event due to its $\delta^{13}C$ positive values. (**b**) Geochemical data of the carbonate sequence of the Paraíba Basin (Maria Farinha Formation) from Barbosa (2007), including the Cretaceous–Paleogene boundary.

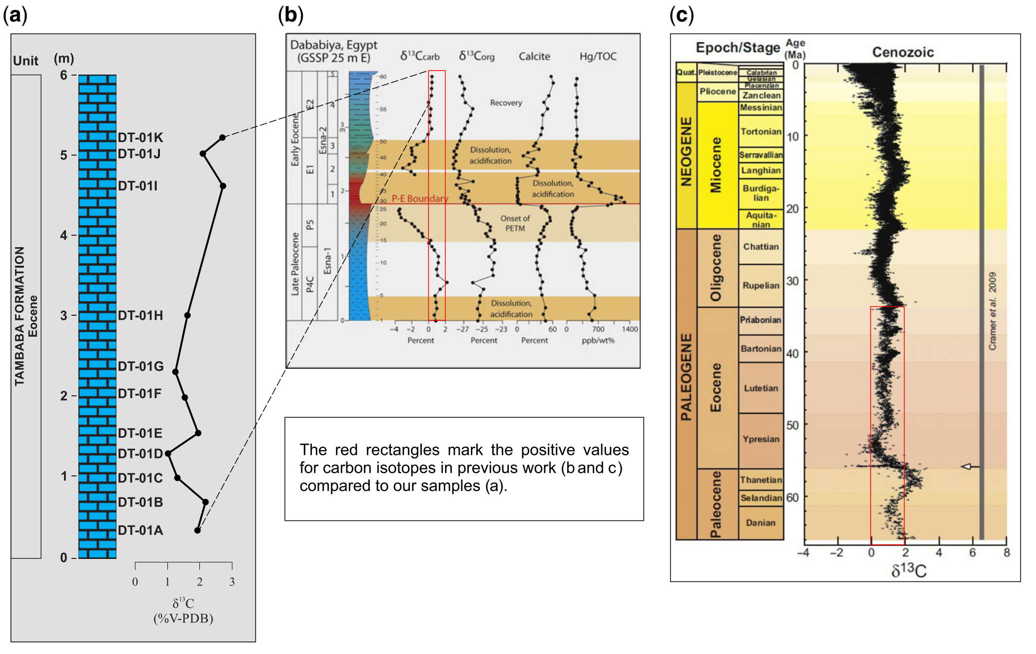

Fig. 11. Comparison of δ^{13}C values with previous work: (**a**) our analysed samples; (**b**) the study carried out by Keller *et al.* (2018) for the PETM transition at Dababiya, Egypt; and (**c**) the carbon curve constructed by Saltzman and Thomas (2012) based on work by Cramer *et al.* (2009) for geological time periods.

GSSP at the Dababiya quarry in Egypt shows excursions (positives and negatives), environmental changes and isotope signal recovery. According to the study of Keller *et al.* (2018) and the δ^{13}C values from this study, it is possible that the reef limestone data fit well after the PETM event when the δ^{13}C values were recovered (to *c.* 2.0‰).

During the Late Paleocene the negative δ^{13}C excursion (*c.* −4 to −1‰) persisted until the Early Eocene, at the time when the PETM had ended and the δ^{13}C values recovered (to *c.* 1‰). The results of Keller *et al.* (2018) showed positive δ^{13}C values (*c.* 0–1‰) after the PETM event. As shown in Figure 11, this suggests that the present investigated section belonging to the Eocene was deposited after the PETM, when the isotopic signal was recovered to positive δ^{13}C values (1–2.5‰).

In this work it is possible to verify a period of stability in the carbon isotope values for the Eocene (δ^{13}C values ranged from 0 to 2‰) after a negative excursion (δ^{13}C down to −2.0‰), like those discussed by Saltzman and Thomas (2012). This negative excursion possibly reflects the PETM event and, soon afterwards, stability would suggest the positioning of the reef limestones studied here. In addition, the palaeotemperature values calculated here in this work are compatible with those mentioned by Zachos *et al.* (2001).

Conclusions

Despite the identification of diagenetic processes, such as dolomitization and dedolomitization, the environment for the formation of reef limestones in the Tambaba Formation was restricted and unique. This is supported by the fact that the only fluid that interacted with these deposits was the same fluid that formed them: that is, seawater. In addition, our geochemical data indicate that the isotopic signal does not change with diagenesis.

The carbon and oxygen isotopes from the samples of the Tambaba Formation show values ranging from 1.0 to 2.7‰ (δ^{13}C) and from −1.4 to 1.1‰ (δ^{18}O) with small variations. However, these values can reveal substantial environmental changes, such as increased or decreased primary marine bioproductivity, as well as a variation in climate (warming or cooling).

When the carbon and oxygen isotope curves are observed and analysed together, and compared with data for similar rock and geological time worldwide, we can conclude that these deposits were formed, at least 50 myr, after the Paleocene–Eocene Thermal Maximum (PETM). In addition, the temperatures found for the Tambaba Formation samples are in agreement with the characterized palaeoenvironment (oxidizing: Mn* >0), since the anoxic environment is a well-defined feature of the PETM event.

The major and trace chemistry results reveal two deposition cycles that show enrichment/depletion in some elements/components (e.g. Al_2O_3, Fe_2O_3, MgO) associated with the presence/absence of terrigenous materials (Fig. 6). The first cycle (bottom 3 m thickness) has a mainly carbonate component, showing the predominance of CaO and MgO. The content of Fe_2O_3 is linked to the carbonate phase, in the form of sulfide (pyrite), and not to a siliciclastic phase. At the top it is possible to observe terrigenous sediments via the Al_2O_3 content, evidencing a second cycle with a thickness of 0.6 m.

Stratigraphic correlations between the Tambaba Formation and the Maria Farinha carbonate sequence are shown in Figure 10, and suggest deposition of the Maria Farinha Formation after the regression event. The integrated field and chemostratigraphic profiles support the hypothesis of a shallow and restricted platform environment (with a sedimentation rate of *c.* 3 mm a^{-1}) that was formed in a coastal system. This palaeoenvironment was formed during a transgression event of smaller magnitude.

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Author contributions **JDDV**: conceptualization (equal), investigation (equal), resources (equal), writing – original draft (lead); **JASN**: conceptualization (equal), investigation (equal), methodology (supporting), supervision (supporting); **ANS**: conceptualization (equal), investigation (supporting), methodology (supporting); **VPF**: conceptualization (supporting), investigation (supporting), methodology (supporting); **VHLMN**: conceptualization (lead), funding acquisition (equal), investigation (equal), methodology (equal), project administration (equal), resources (equal), supervision (lead), writing – review & editing (lead).

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Data availability The data are part of an ongoing survey and can be made available.

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7 CONSIDERAÇÕES FINAIS

Apesar da identificação de processos diagenéticos, tais como dolomitização e dedolomitização, o ambiente para a formação de calcários recifais da Formação Tambaba era restrito e único. Isso é apoiado pelo fato de que o único fluido que interagiu com esses depósitos foi o mesmo fluido que os formou: isto é, água do mar. Além disso, os dados geoquímicos indicam que o sinal isotópico não muda com a diagênese. Os isótopos de carbono e oxigênio das amostras da Formação Tambaba apresentam valores que variam de 1,0 a 2,8‰ ($\delta^{13}C$) e de -1,3 a 1,8 ‰ ($\delta^{18}O$) com pequenas variações. No entanto, esses valores podem revelar mudanças ambientais substanciais, como aumento ou diminuição da bioprodutividade marinha primária, bem como uma variação no clima (aquecimento ou resfriamento).

Quando as curvas de isótopos de carbono e oxigênio são observadas e analisadas juntas e comparadas com dados de rochas semelhantes e tempos geológicos em todo o mundo. Podemos concluir que esses depósitos foram formados, pelo menos 50 mil anos, após o Máximo Termal Paleoceno-Eoceno (PETM). Além disso, as temperaturas encontradas para as amostras da Formação Tambaba estão de acordo com o paleoambiente caracterizado (oxidante: Mn* >0), uma vez que o ambiente anóxico é uma característica bem definida do evento PETM.

Os resultados da química de elementos maiores e traços revelam dois ciclos de deposição que mostram enriquecimento / depleção em alguns elementos / componentes (por exemplo, Al_2O_3, Fe_2O_3, MgO) associado à presença / ausência de materiais terrígenos. O primeiro ciclo (inferior a 3 m de espessura) tem principalmente um componente carbonático, mostrando a predominância de CaO e MgO. O conteúdo de Fe_2O_3 está ligado à fase do carbonato, na forma de sulfeto (pirita), e não a uma fase siliciclástica. No topo é possível observar sedimentos terrígenos através do conteúdo de Al_2O_3, evidenciando um segundo ciclo com espessura de 0,6 m.

Correlações estratigráficas entre a Formação Tambaba e a sequência da Formação Maria Farinha verificadas em campo, na análise das microfácies e resultados geoquímicos sugerem deposição da Formação Tambaba após o evento de regressão da Formação Maria Farinha. A integração do campo com os perfis quimioestratigráfico apoia a hipótese de um ambiente de plataforma raso e restrito (com uma taxa de sedimentação de cerca de 3mm/a) que foi formado em um sistema costeiro. Este paleoambiente foi formado durante um evento de transgressão de menor magnitude, com pulsos isolados.

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