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Experimental investigation of the Carbon dioxide storage potential of the Cunga Formation at Cabo de São Braz Region, Kwanza Basin, Angola

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Abstract
The Cunga Formation is one of the geological formations located on the Kwanza Basin onshore, consisting of predominantly black clay (which indicates the possibility of organic matter), marl, limestone, siltstone and sandstones. In the present study, analyses of X-ray diffraction (XRD - 24 samples), analyses of the scope of organic petrology and geochemistry were carried out; that is, analysis of palynomorphs (2 samples), total organic carbon (TOC - 47 samples) and pyrolysis (Rock-Eval) (49 samples). From the XRD analyses it was possible to know the mineral associations, with the predominance of quartz, albite, microcline, muscovite, orthoclase, and heulandite being found in the analysed samples. The analysis of palynomorphs revealed the presence of marine palynomorphs, namely dinoflagellates (Gonyaulacales and Peridiniales) and foraminifers, and continental palynomorphs, namely fungi and spores. From the TOC analysis it was possible to quantify the organic matter, with the analysed samples presenting values between 0.14% and 7,52%. The pyrolysis analysis (Rock-Eval) provided insights into the quality of the organic matter in the analysed samples, revealing the presence of kerogen types II, II/III, and III. Additionally, the Tmax parameter was used for the determination of the maximum temperatures that the samples have undergone (417 ºC – 431 ºC). From the interpretation of the results, it was determined that the Cunga Formation in the Cabo de São Braz Zone was deposited in a sedimentary marine coastal to neritic environment. The Cunga formation has a good potential to generate gas and oil; however, due to insufficient thermal maturation (Tmax values ranging from 417°C to 431°C), it has not been an effective source rock. On the other hand, these same petrological and geochemical properties allowed the sequence under study to be characterized as a reservoir for CO_2 storage, which could therefore have wide applicability in the context of the energy transition.
Keywords: *Cunga formation, Shale, Kwanza basin, Organic matter, Organic geochemistry, Organic petrology, Energy transition, CO_2 reservoirs, Petroleum potential and vitrinite*
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1. Introduction

As global energy demand continues to rise, there is a need to enhance energy generation, transport and distribution systems. These improvements are essentials to ensure that end consumers can access energy with minimal limitations. Consequently, the issues of energy efficiency and energy security are becoming increasingly critical. Addressing these challenges involves adopting advanced technologies and that optimize the entire energy supply chain, thereby ensuring reliable and sustainable energy access for all.

Currently, the global energy matrix is predominantly reliant on fossil fuels, necessitating the combustion of significant quantities to meet energy demands (IEA, 2021; CC, 2015). This reliance results in substantial CO_2 emissions, which accumulate in the atmosphere accelerating global warming and climate changes warming and climate change (Soeder, 2021). Therefore, balancing energy demand with the imperative to reduce atmospheric CO_2 emissions is a significant challenge. In response to that, several leading nations are actively engaging in the study, development, and implementation of clean energy technologies, such as photovoltaics, wind, and geothermal energy. Additionally, there is a focus on integrating carbon capture and storage systems to sequester CO_2 in geological formations, rather than allowing it to enter the atmosphere post-combustion (Das et al., 2023; Hassan, 2024; Baines, 2004).

In the context of Angola, it is crucial to follow the dynamics of other countries while focusing on our sedimentary basins. For this study, we have selected the Kwanza Basin due to its geological characteristics, extensive reach, and significant potential. Therefore, conducting research related to the Kwanza Basin is increasingly pertinent, with the aim of identifying possible reservoirs for the long-term and safe storage of CO_2, specifically in the form of shale gas and shale oil, akin to initiatives in various countries across the Americas, Asia, Europe, and some African nations. Currently, there is limited scientific literature regarding the unconventional reservoirs of the Kwanza Basin, with one of the few recent studies conducted by Cacama (2021).

The specific objectives of this work include: (1) Understanding the geodynamic context in which the Cunga Formation was formed, at both regional and local scales (Cabo de São Braz); (2) Identifying, quantifying, and characterizing the organic matter (OM) preserved in the collected samples; (3) Determining the maturation stages that the Cunga Formation has undergone in the study area; (4) Identifying the types of hydrocarbons generated; and (5) Characterizing the Cunga Formation as a potential reservoir for CO_2 storage. This study entails performing the same types of analyses utilized in conventional petroleum system studies, including X-ray diffraction analysis (XRD), palynomorph analysis, total organic carbon (TOC) analysis, and pyrolysis (Rock-Eval).

2. Tectonosedimentary evolution

The origin and evolution of Kwanza Basin resulted from the movement of the tectonic plates that caused the fracturing of the supercontinent Gondwana in the late Jurassic (Lundin, 1992; Hudec and Jackson, 2002; Karner et al., 2003; Jian-Ping et al., 2008; Rodrigues et al., 2017). The evolution of this basin occurred according to several distinct tectonic phases, each of them creating a specific stratigraphy and structural style. These phases are usually classified as: pre-rift, sin-rift (I and II), post-rift and regional subsidence (Horn, 1980; Hudec and Jackson, 2002; Brownfield and Charpentier, 2006). The stratigraphic sequences in the Kwanza Basin are represented by the pre-salt and post-salt sequences, separated by a salt sequence of variable thickness, marking the transition from continental deposition conditions to predominantly marine deposition conditions (Stark et al., 1991).

As a result of gravity-induced deformation, an extension of thin layer was deposited on the Aptian salt in the Kwanza Basin (Wu et al., 1990; Demercian et al., 1993; Letouzey et al., 1995; Peel et al., 1995; Morley and Guerin, 1996), first performed by Duval et al. (1992). According to Fort et al. (2004), in passive margins, gravity-driven deformation above the salt usually leads to the development of extensional domains on the slope and contraction toward the base of the slope. The study carried out by Fort et al. (2004) establishes the existence of a structural zoning characteristic of the Angolan margin in which it is possible to identify comparable characteristics with three main structural domains, that is, ascending extensional domains and contractional domains towards the base of the slope separated by a transition domain, which is characterized by inverted extensional structures.

The ascending extensional domain is subdivided into three subdomains with (1) sealed slanted blocks, (2) growth failure systems and rollovers, and lastly, (3) extensional diapirs (Fort et al., 2004). The contractional domain toward the base of the slope is subdivided into three parts: (1) delayed compression of diapirs, (2) early onset of polyharmonic folds and push faults, (3) late stage folding and pushing. The results obtained by Fort et al. (2004) in studies based on seismic interpretation and also on laboratory experiments, indicate that the overall structural zoning is mainly controlled by the basal slope angle, while the type of structures in the structural domains depends strongly on the sedimentation rate. In the extensional domain, structures and structural zoning depend on the coupling between brittle (sediments) and ductile (salt) layers, while in the contractional domain, structures and structural zoning are mainly linked to contraction migration in time and space. Due to the structural similarity between the models and the Angolan margin, it is possible to say that the initial geometry of the salt basin was united both to the mainland and to the sea, and that the salt was entirely covered by sediments at the beginning of the gravity-driven deformation.

3. Contextualizing the Cunga formation within the petroleum systems of the Kwanza Basin

There are four relatively well-known regional petroleum systems in the Kwanza Basin, described by various authors (Brognon & Verrier, 1966; Burwood, 1999; Schiefelbein et al., 1999), namely: (1) Pre-salt/Pre-salt Petroleum System, (2) Pre-

salt/Post-salt Petroleum System (?), (3) Binga Post-salt Petroleum System (?) and (4) Paleogenic-Neogene Post-salt Petroleum System (?).

For the present study, the Cunga Formation in the Cabo de São Braz region was selected due to its diverse facies, predominantly consisting of shales, argillites, and black marls. This formation is regarded as the source rock for the Paleogene-Neogene Post-salt Petroleum System. The geochemical, petrographic, petrophysical, and structural parameters associated with this petroleum system are documented in the existing literature (Burwood, 1999; Brownfield and Charpentier, 2006; Série et al., 2016; Beglinger et al., 2012; Cacama, 2021).

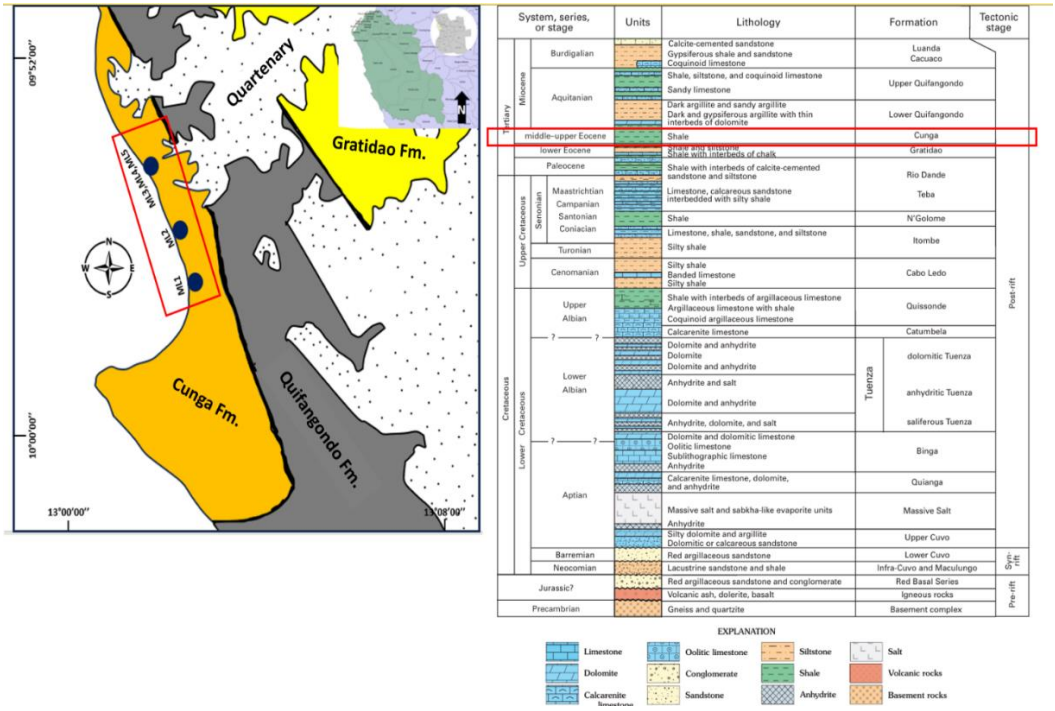

Fig. 1: Geological framework of the study area (Modified from the Geological Map of the Kwanza Sonangol Basin-TOTAL, 1987 and Brownfield & Charpentier, 2006)

4. Methodology and techniques

This section outlines the steps and techniques used in conducting this study. The adopted methodology covers everything from the definition of the theme and objectives to the analysis of the obtained data, and is divided into subsections that detail the specific procedures for each phase of the work, and takes in consideration all the qualitativy and quantitativy aspects. The specifications related to data collection, sample analysis, and interpretation will be presented in subsections 4.1 to 4.3.

4.1. Fieldwork

Based on previous studies, the Geological Map of the Kwanza Basin (Sonangol-TOTAL, 1987), topographic map-sheet No. 125, SC-33/ C-I of the IGCA (Scale 1/100 000, 1981) and aerial photographs (Google Earth), it was possible to select the profile to be studied. This profile is located along the coast of Cabo de São Braz, with a general NE-SW orientation, rises 95 meters high and extends 3 kilometres in length. It is divided into five distinct exposed rocks, labelled ML1, ML2, ML3, ML4, and ML5.

In situ studies were conducted on the exposed rocks, allowing the observation and identification of variations in lithology, sedimentary structures, strata thickness, attitudes, and the intensity of weathering. This provided a reliable basis for the sampling process. The quality and quantity of the samples were critical, as they could influence the results of subsequent laboratory analyses. Given the specific focus of the study, preference was given to fine-grained, dark-colored, and less weathered rocks, as these are more likely to preserve organic matter. A total of 49 samples were collected along the profile, with each sample weighing between 2 kg and 4 kg.

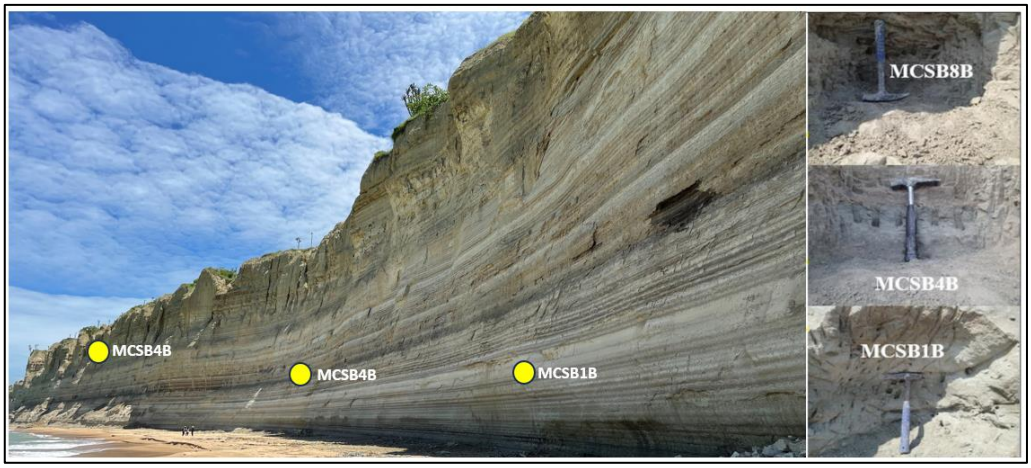

Fig. 2: Indication of some sampling points in the ML2 outcrop

4.2. Laboratory techniques

4.2.1. Preliminary preparation of samples

Initially, the samples were fragmented, followed by cleaning and the selection of fragments with potential for the desired analyses. Subsequently, 50 mg to 400 mg of each sample was accurately weighed using analog scales for the respective analyses. The samples were then packaged in transparent plastic bags, clearly labeled with the identifiers MCSBn and MCSBnB.

4.2.2. X-ray diffraction

This stage involved the preparation of the samples, which included several procedures: fragmentation, crushing, quartering, grinding, and homogenization. These steps were essential for reducing the samples to the appropriate particle size for X-ray diffraction (XRD) analysis (da Silva, 2013). The analyses were conducted using the X'Pert PRO device from PANalytical, following the protocols outlined by da Silva (2013). This analytical method enabled the acquisition of diffraction spectra, or diffractograms, for 24 samples, allowing for the identification, individualization, and quantification of the mineral species present. Consequently, this facilitated an assessment of the mineralogical composition of the rocks. The data are summarized in Figures 4 and 5.

4.2.3. TOC

The total organic carbon (TOC) analysis revealed the hydrocarbon-generating potential of 47 samples. The organic matter (OM) present in the sediments comprises both soluble (bitumen) and insoluble (kerogen) components in organic solvents (Silva, 2010). To determine the TOC in the samples, inorganic carbon was first removed by reacting the samples with hydrochloric acid (HCl). Subsequently, the samples were combusted in a Leco® SC-144 analyzer, which is equipped with an infrared detector. During this process, the samples were oxidized at a temperature of 1350 ºC, allowing for accurate TOC quantification. The results are summarized in Table 2.

4.2.4. Pyrolise rock-eval

In the present work, 49 samples were submitted to Rock-Eval pyrolysis analysis, with a view to defining its hydrocarbon generating potential, as well as the degree of maturation. For this purpose, 250 mg of each previously ground sample was placed in the equipment at a temperature of 300ºC to 600ºC for 25 minutes for each sample, and throughout this period the parameters were read according to the procedures adopted by (Espitalié et al., 1977):

- **S1 (mgHC/gRock):** This measurement was obtained following the vaporization of the free hydrocarbons present in the sample. It therefore represents the quantity of free hydrocarbons, indicating the amount that has been generated naturally and stored within the porous structure of the sample.
- **S2 (mgHC/gRock):** At temperatures ranging from 300 ºC to 600 ºC, the degradation of kerogen and the generation of hydrocarbons occurred. These hydrocarbons were quantified using a flame ionization detector and are represented by the S2 peak, which reflects the generating potential of the

sample. This peak indicates the hydrocarbons produced by pyrolysis and represents the potential of the rock to generate additional hydrocarbons under optimal thermal conditions.

- **Tmax (ºC):** A few minutes later, the Tmax was recorded, serving as an indicative parameter of the thermal evolution stage. Tmax represents the temperature at which the maximum quantity of hydrocarbons was generated, as reflected in the S2 peak.
- **S3 ($mgCO_2/gRock$):** At the end of the process, the carbon dioxide (CO_2) produced in the furnace is measured, which constitutes the S3 parameter. This parameter represents the loss of oxygenated functional groups and indicates the CO_2 generated by the organic matter (OM) present in the rock.
- **PI:** This characterizes the level of evolution of organic matter. In a closed system, the Production Index (PI) increases with the extent of hydrocarbon generation. The PI value is dimensionless and is calculated using Equation (1).
- **HI (mgHC/gTOC):** This parameter is used to determine the type, origin, and preservation status of kerogen and is calculated using Equation (2).
- **OI ($mgCO_2/gTOC$):** This parameter is used to determine the type of kerogen when analysed in conjunction with the HI on the modified van Krevelen diagram (Fig. 7). It is calculated using Equation (3).

$$PI = \frac{S1}{(S1 + S2)} \quad (1)$$

$$HI = \frac{S2}{TOC} \times 100 \quad (2)$$

$$OI = \frac{S3}{TOC} \times 100 \quad (3)$$

4.3. Palynological techniques

Two samples were processed for palynological analysis at the Geological Survey of Portugal (LNEG). A procedure using HCl and HF acids was used to extract and concentrate the organic matter (Wood et al., 1996; Riding and Warny, 2008; Rodrigues et al., 2021). The samples were not oxidized and all residues were sieved with 7 μm and 10 μm meshes. The final residue was stained with safranin-O and mounted on microscope slides using Entelan®, a commercial resin-based mounting medium. The slides were examined under transmitted light, using an Olympus BX40 microscope equipped with an Olympus C5050 digital camera, as well as a Nikon eclipse Ci microscope. The analysis was carried out at LNEG, and to determine the relative abundance, the criterion of counting at least 150 palynomorphs using the 40x objective was established, a procedure adopted by Rodrigues et al. (2021) in recent studies. Based on the results of the microscopic observations, it was possible to group the palynomorphs into main classes, which comprise dinoflagellate cysts, foraminifera linings, terrestrial palymorphs (spores and fungal remains) and other marine palynomorphs.

5. Presentation and discussion of results

5.1. Paleoenvironmental interpretation

Paleoenvironmental interpretation is essential for understanding the processes and conditions that contribute to the genesis and development of the sedimentary sequence under investigation, as well as its context within the sedimentary basin. To achieve this, we evaluated the mineralogical composition, characterized the palynomorphs, and assessed the organic matter content preserved in the samples.

5.2. Mineralogy

The study profile, extending 3 km in length and 100 m in height, was divided into five outcrops (ML1, ML2, ML3, ML4, and ML5). It primarily consists of intercalations of shales, black marls, siltstones, and sandstones, as well as marls and limestones, each exhibiting distinct sedimentological and structural features, including bioturbation, calcareous nodules, and pyrite nodules. Based on the facies characteristics observed at the macroscopic level, it was determined that during the deposition and formation of the rock package, processes of suspended sediment transport predominated. Additionally, variations in sea level contributed to the alternation between materials with lower and higher marly content, as well as the reworking of organic matter and chemical precipitation processes.

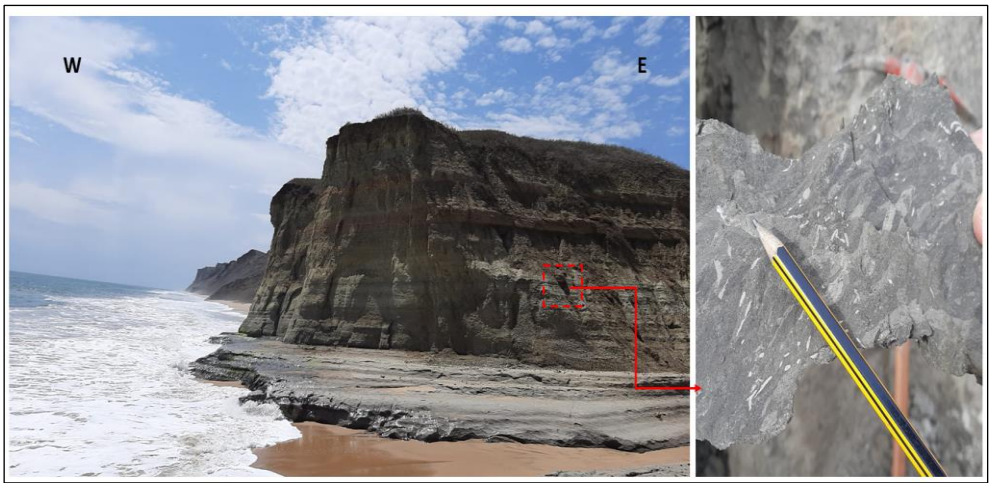

Fig. 3: Evidence of the bioturbation process in the samples

The results of the XRD analysis allowed for the determination of the mineralogical composition of the samples. As shown in Figure 5, the most abundant minerals identified are calcite and quartz, while orthoclase, muscovite, microcline, albite, clinoptilolite, gypsum, halite, ankerite, kaolinite, heulandite, dolomite, and pyrite are present in lower quantities. These mineral associations support the conclusion that the rocks are silico-carbonated, indicating deposition in both internal and external neritic marine environments, as corroborated by previous studies (Mulanda, 2020; Pereira et al., 2021; Rodrigues et al., 2021; Cacama, 2021). Furthermore, the mineralogical characteristics depicted in Figure 5 suggest that the source of the sedimentary input was primarily granitoid and low-grade metamorphic rocks, indicating that the sediment source and the sedimentary basin were in close proximity.

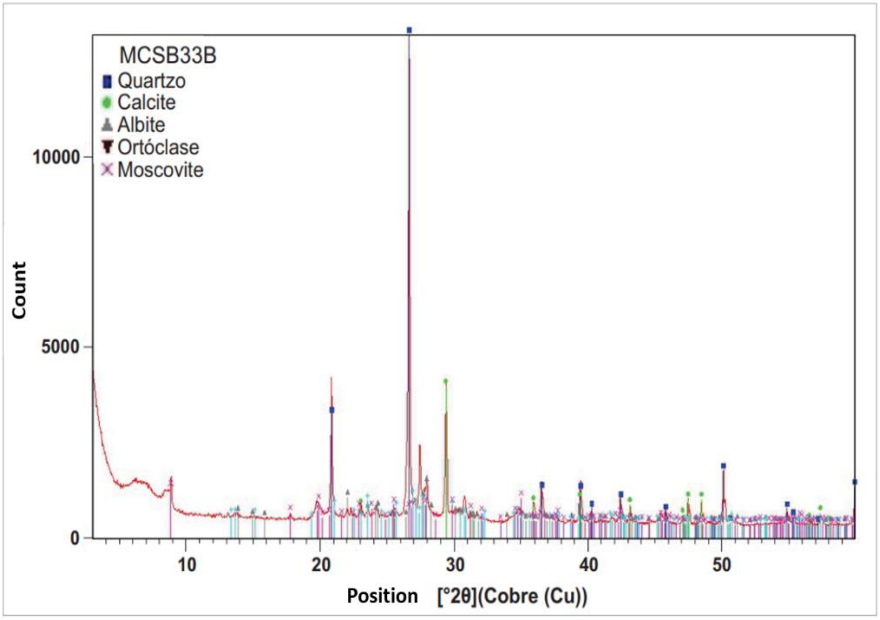

Fig. 4: Diffractogram of the MCSB33B sample (one of the most representative samples)

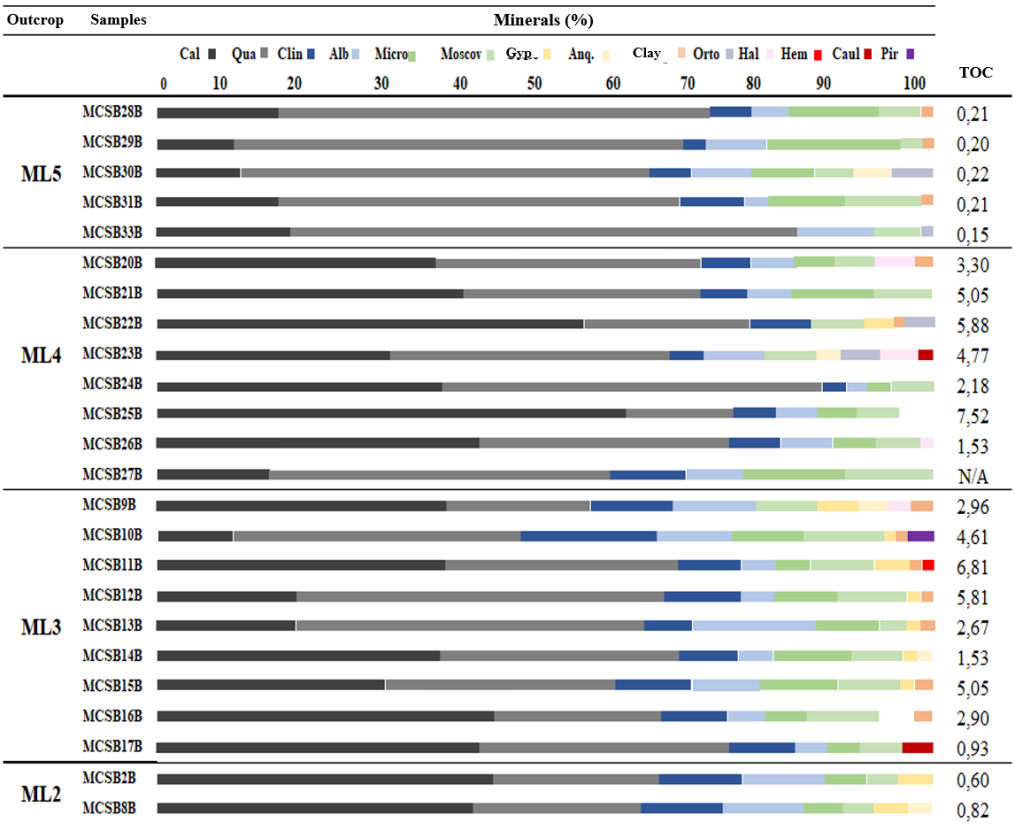

Fig. 5: Distribution of the TOC value as a function of the minerals identified by XRD in the samples

The samples from the ML3 and ML4 exposed rocks consist of argillites and marls and exhibit high levels of calcite. Additionally, these samples show elevated total organic carbon (TOC) values. This suggests a greater capacity for the retention and preservation of organic matter, likely due to the fine sediment characteristics and the hypersaline environment with low hydrodynamics, as indicated by the high calcite content.

5.3. Characterization of palynomorphs

Two samples (MCSB6 and MCSB9) from the ML1 outcrop were analysed, both containing organic matter of continental and marine origin. The analysis revealed a predominance of palynomorphs indicative of a marine environment (Table 1). In the MCSB6 sample, 18 palynomorphs were counted, of which 16.70% were of continental origin, specifically from the order Fungi, while 83.30% were of marine origin. In the MCSB9 sample, a total of 145 palynomorphs were identified, with only 4.12% belonging to the continental environment (2.06% spores and 2.06% fungi), while 95.88% were marine. These results suggest a coastal to neritic environment, as evidenced by the dominance of organisms such as radiolarians, Corrudinum regularis, and foraminiferal linings, which are characteristic of such environments, as supported by the literature (Mulanda, 2020; Rodrigues et al., 2021; Cacama, 2021). Furthermore, the studied sequence dates to the Eocene, as confirmed by the organisms identified in the laboratory analyses, which have been used to date Eocene sequences in Angolan coastal basins (Mulanda, 2020; Rodrigues et al., 2021; Cacama, 2021) and similar formations globally.

Table 1: Palynological data from the MCSB6 and MCSB9 samples

				Distribution per sample (%)	
Environment	**Group**	**Family**		**MCSB6**	**MCSB9**
Continental	**Palynomorphs**	**Fungi**	Fungi	16.70	2.06
		Spores	*Cicatricosiorites sp.*		2.06
Marine	**Palynomorphs**	**Dinoflagellates**	*Impagidinium Sp*	5.55	2.06
			Spiniferites Spp.	5.55	7.58
			Selenopemphixnephroides	5.55	1.37
			Homotrybliumtrenuispinosum		3.44
			Homotryblium Sp.		3.44
			Hystrichosphaeridium Sp.		1.37
			Impagidinium dispertitum		2.06
			Nematosphaeropsis Sp		0.68
			Spiniferites pseudofurcatus		1.37
			Dynocist Sp. B		3.44
			Deflandrea phosphoritica		2.75
			Deflandrea Sp.		3.44
			Trinovantenidium sp.		6.20
	Zoomorphs	**Palynomorphs**	*Radiolaria*	27.77	22.90
			Foraminiferous linings	38.88	32.41
	Palynomorphs	**Other marine palynomorphs**			1.37
				100	**100**

6. Evaluation of petroleum potential and characterization of organic matter

The total organic carbon (TOC) values of the 49 samples range from 0.14% to 7.52%. Based on the classification by Espitalié et al. (1977), the oil potential of a source rock can be assessed from these TOC values, indicating that the studied samples exhibit a range from poor to excellent oil potential. The ML1 exposed rock, represented by samples MCSB1 to MCSB15, is located in the lower part of the sequence and predominantly consists of black to greenish argillites, with an average TOC of 3.17%. The ML2 exposed rock, represented by samples MCSB1B to MCSB8B, is positioned directly above the ML1 exposed rock and is predominantly composed of claystones, showing an average TOC of 0.60%. The ML3 exposed rock, represented by samples MCSB9B to MCSB19B, is situated in the intermediate part of the sequence and mainly comprises marly argillites, with an average TOC of 3.32%. The ML4 exposed rock, represented by samples MCSB20B to MCSB26B, is also located in the intermediate part of the sequence and consists predominantly of claystones, yielding an average TOC of 4.29%. Finally, the ML5 exposed rock, represented by samples MCSB28B to MCSB34B, is positioned at the top of the sequence and comprises claystone-silty sediments with a considerable sand component, showing a low average TOC of 0.18%.

Comparing the average TOC values across the exposed rocks reveals that the highest TOC values are associated with those outcrops dominated by clay-sized sediments, with the exception of ML2. For the ML2 outcrop, it is suggested that there may have been limited availability of organic matter or significant oxidation of organic matter prior to deposition, as its other characteristics are similar to those of the ML1, ML3, and ML4 outcrops, which contain good TOC levels. In contrast, samples with a higher silty component exhibit the lowest TOC values. These findings suggest that during the deposition of organic matter, clay-sized sediments had a greater capacity for retaining and preserving organic material due to their low permeability, which significantly limits water circulation in the porous structure and consequently reduces the activity of aerobic bacteria. Conversely, in sediment packages with a high silty component, there was a diminished capacity for the retention and preservation of organic matter, making them more susceptible to biodegradation driven by microbial activity.

Table 2: Data from rock-eval pyrolysis analysis

Outcrop	Sample	TOC (%)	S1 (mg HC/g rock)	S2 (mg HC/g rock)	S3 (mg CO2/g rock)	Tmax (°C)	HI (mg HC/g TOC)	OI (mg CO2/g TOC)	PI
ML5	MCSB 34B	0.14							
	MCSB 33B	0.15							
	MCSB 32B	0.14							
	MCSB 31B	0.21							
	MCSB 30B	0.22							
	MCSB 29B	0.20							
	MCSB 28B	0.21							
ML4	MCSB 26B	1.35	0.10	2.96	4.05	427	219	300	0.03
	MCSB 25B	7.52	0.40	31.09	4.75	424	413	63	0.01
	MCSB 24B	2.18	0.11	5.56	4.23	429	255	194	0.02
	MCSB 23B	4.77	0.26	17.62	3.88	428	369	81	0.01
	MCSB 22B	5.88	0.35	18.68	3.74	429	318	64	0.02
	MCSB 21B	5.05	0.20	15.01	3.48	429	297	69	0.01
	MCSB 20B	3.30	0.24	10.76	2.85	422	326	86	0.02
ML3	MCSB 19B	1.10	0.03	0.80	1.18	428	73	107	0.04
	MCSB 18B	2.19	0.14	6.61	4.42	428	302	202	0.02
	MCSB 17B	0.93	0.07	1.73	2.62	430	186	282	0.04
	MCSB 16B	2.90	0.18	10.24	3.97	429	353	137	0.02
	MCSB 15B	5.05	0.49	18.08	3.17	424	358	63	0.03
	MCSB 14B	1.53	0.11	3.49	2.08	428	228	136	0.03
	MCSB 13B	2.67	0.34	7.87	2.44	426	295	91	0.04
	MCSB 12B	5.81	0.47	25.08	2.34	426	432	40	0.02
	MCSB 11B	6.81	0.32	16.93	2.05	421	249	30	0.02
	MCSB 10B	4.61	0.36	16.57	2.30	427	359	50	0.02
	MCSB 9B	2.96	0.31	10.62	2.41	429	359	81	0.03
ML2	MCSB 7B	0.82							
	MCSB 6B	0.53							
	MCSB 5B	0.66	0.10	0.23	2.21	426	186	335	0.30
	MCSB 4B	0.53	0.10	0.55	2.46	417	104	464	0.15
	MCSB 3B	0.51	0.12	0.60	2.30	417	118	451	0.17
	MCSB 2B	0.60	0.12	0.82	1.85	421	137	308	0.13
	MCSB 1B	0.57	0.11	0.75	1.45	420	132	254	0.13
ML1	MCSB 15	1.13	0.15	9.83	2.21	424	314	71	0.02
	MCSB 14	5.59	0.57	20.70	3.01	422	370	54	0.03
	MCSB 13	2.66	0.41	6.55	2.66	426	246	100	0.06
	MCSB 12	3.78	0.47	13.25	3.63	425	351	96	0.03
	MCSB 11	4.78	0.52	17.88	2.61	426	374	55	0.03
	MCSB 10	4.44	0.47	13.62	3.81	424	307	86	0.03
	MCSB 9	1.42	0.30	4.18	2.15	430	294	151	0.07
	MCSB 8	1.38	0.30	2.85	3.27	427	207	237	0.10
	MCSB 7	2.36	0.50	7.51	2.29	426	318	97	0.06

MCSB 6	0.88	0.20	1.31	1.70	422	149	193	0.13
MCSB 5	1.36	0.23	2.13	2.36	424	157	174	0.10
MCSB 4	4.30	0.34	16.20	3.06	426	377	71	0.02
MCSB 3	2.27	0.17	6.27	3.11	428	276	137	0.03
MCSB 2	4.67	0.25	16.02	2.99	431	343	64	0.02
MCSB 1	4.67	0.48	14.44	4.21	429	309	90	0.03

In general, the S1 values (determined only for samples with TOC equal to or greater than 0.5%) in the studied sequence are less than 0.5 mg HC/g rock (Table 2), indicating that these samples have poor oil potential. The exceptions are the MCSB11 and MCSB14 samples, which exhibited S1 values of 0.52 mg HC/g rock and 0.57 mg HC/g rock, respectively, suggesting a reasonable oil potential. The S1 values indicate that the analysed sequence did not mature sufficiently and therefore did not generate significant amounts of hydrocarbons due to temperature effects.

The residual hydrocarbon generation potential of the analysed samples was assessed using the S2 parameter, which varies significantly across the sequence, ranging from 0.55 mg HC/g rock to 31.09 mg HC/g rock (Table 2). The ML2 exposed rock samples exhibited low S2 values, indicating a poor residual potential for hydrocarbon generation in this specific part of the sequence. Conversely, the samples from the ML1, ML3, and ML4 exposed rock s showed higher average S2 values, suggesting that their residual potential for hydrocarbon generation ranges from reasonable to excellent.

To enhance the robustness of the oil potential analysis, the TOC-S2 diagram (Figure 6) was employed, revealing a proportional relationship between S2 values and TOC in the samples. Specifically, higher TOC values corresponded to higher S2 values, as noted by Cacama (2021) in a study conducted in the same region. However, the combined analysis of the TOC and S2 parameters highlighted a slight discrepancy in oil potential assessment. Some samples classified as having reasonable oil potential based on TOC values—namely MCSB5, MCSB6, MCSB1B, MCSB2B, MCSB3B, MCSB4B, MCSB5B, MCSB17B, and MCSB19B—demonstrated poor oil potential according to S2 values. In other words, despite containing substantial amounts of organic matter (as indicated by TOC values), these samples may not generate economically viable hydrocarbon accumulations due to the unfavourable quality of the organic matter (as indicated by S2 values).

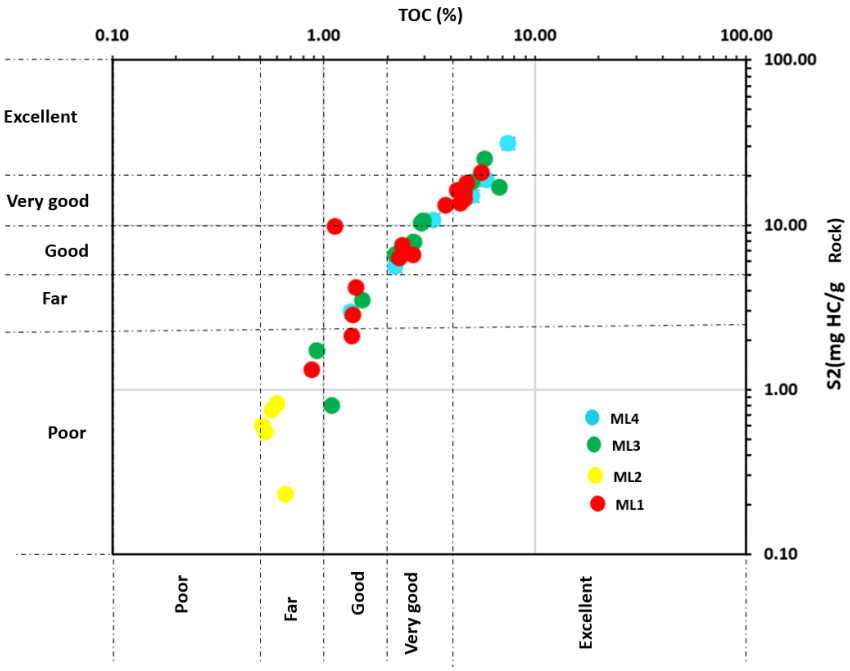

Fig. 6: Relationship between TOC and S2 of the samples of the sequence under study.

To identify the type of kerogen in the analysed samples, the HI/OI relationship was employed, utilizing the modified van Krevelen diagram (Tissot and Welte, 1984), as shown in Fig. 7. The samples from the ML1 exposed rock exhibited HI values ranging from 149 mg HC/g TOC to 377 mg HC/g TOC, with IO values between 54 mg CO_2/g TOC and 237 mg CO_2/g TOC. These results indicate a predominant presence of type II/III kerogen, with type III kerogen occurring in smaller proportions.

In the ML2 outcrop, the samples displayed HI values from 104 mg HC/g TOC to 186 mg HC/g TOC, and OI values ranging from 218 mg CO_2/g TOC to 464 mg CO_2/g TOC, indicating a dominant occurrence of type III kerogen. The samples from the ML3 outcrop showed HI values spanning 73 mg HC/g TOC to 432 mg HC/g TOC, and IO values from 30 mg CO_2/g TOC to 282 mg CO_2/g TOC, suggesting the predominant presence of both type III and II/III kerogen, with type II kerogen in smaller amounts. The ML4 outcrop samples presented HI values ranging from 219 mg HC/g TOC to 413 mg HC/g TOC, and IO values between 63 mg CO_2/g TOC and 300 mg CO_2/g TOC, indicating a predominant occurrence of type II/III kerogen, along with type II and type III kerogen in lesser amounts.

In summary, the results indicate that types II/III and III kerogens are predominant throughout the sequence, with type II kerogen occurring in smaller proportions. Based on these characteristics, it can be inferred that the sedimentary sequence under study was deposited in a coastal to neritic environment, which primarily favoured the formation of macerals from the vitrinite group.

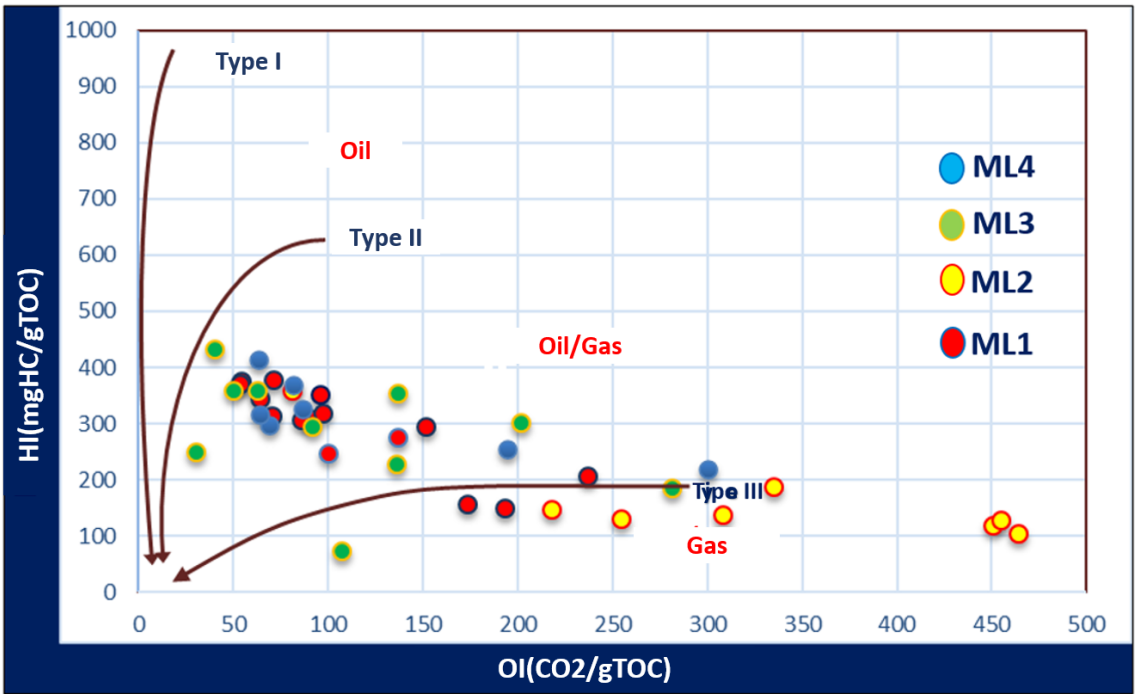

Fig. 7: Relationship between HI and IO of the samples of the sequence under study

7. Thermal maturation assessment

The samples in the analysed sequence exhibit Tmax values ranging from 417 ºC to 431 ºC (Table 2 and Fig. 8), placing them within the diagenesis stage. This indicates that the organic matter in these samples is classified as immature concerning the oil window (Espitalié et al., 1977; Peters and Cassa, 1994). The samples from the ML1 exposed rock are situated predominantly in the immature area for type II/III kerogen, with some samples extending into the type III kerogen range. In contrast, the samples from the ML2 outcrop are primarily located within the type III kerogen range. The ML3 outcrop samples predominantly fall within the ranges for both type III and II/III kerogen, with a smaller proportion appearing in the type II kerogen range. Finally, the ML4 outcrop samples are mainly projected into the type II/III kerogen range, with a minor presence in the type II and III kerogen ranges, as depicted in the HI and Tmax graph from Rock-Eval pyrolysis (Chiagham et al., 2014; Al-Areeq and Albaroot, 2019; Albriki et al., 2021).

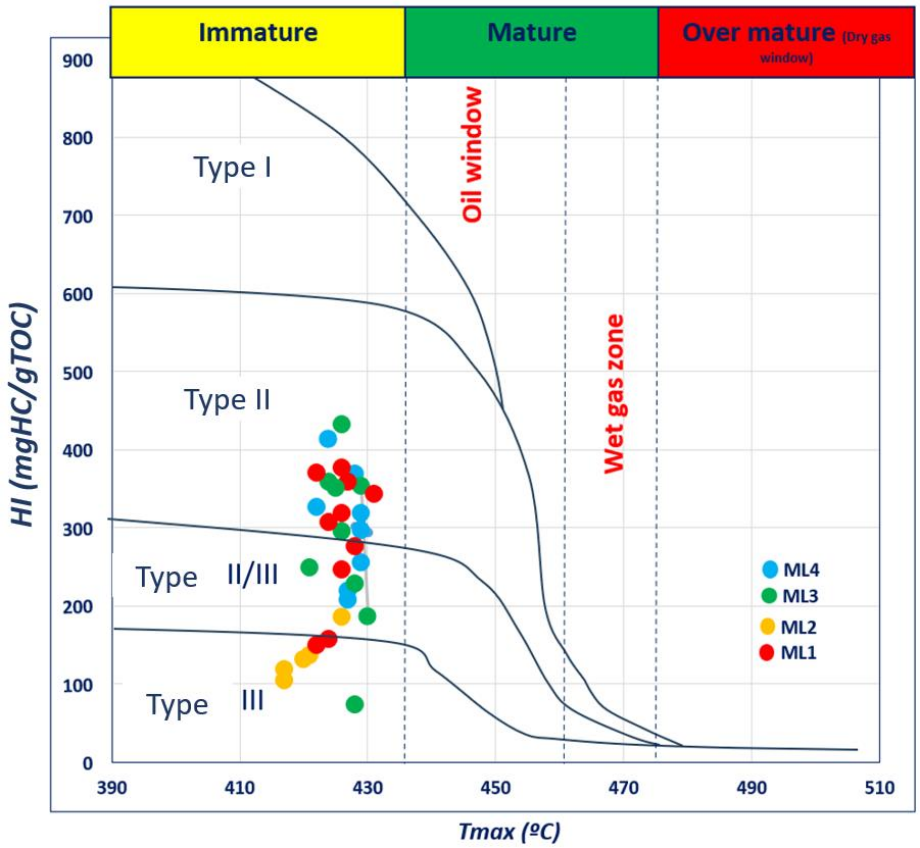

Fig. 8: Relationship between HI and Tmax of the samples of the sequence under study.

8. Characterization of Cunga Formation as a CO_2 reservoir

As previously emphasized, global warming and climate change have emerged as priority issues on the international agenda. Consequently, the adoption of environmentally friendly practices is imperative. By 2050, nations are expected to demonstrate their commitment to clean energy (IEA, 2021) with the goal of reducing CO_2 emissions and other greenhouse gases, a significant portion of which originates from fossil fuels (Martins et al., 2021; Gurney et al., 2002). Proposed solutions include the effective implementation of solar, wind, and green hydrogen energy systems, as well as the deployment of CO2 capture and storage technologies in geological reservoirs (Das et al., 2023; Hassan, 2024; Baines, 2004).

Currently, various techniques are employed to assess the potential of geological formations for use as CO_2 storage reservoirs. These methods include in situ measurements, well data analysis, seismic surveys, computational modelling, sorption isotherms, and organic petrology and geochemistry techniques (Fuji et al., 2010; Abraham-A et al., 2023; Fawad, 2021). Historically, many of these techniques were focused solely on evaluating the oil potential of geological formations for hydrocarbon exploration. Understanding the oil potential of a geological formation is crucial for investigating its suitability as a CO_2 reservoir, as there is a direct relationship between a formation's oil potential and its capacity for CO_2 storage.

Analysing the oil potential of a geological formation involves characterizing the organic matter (both quantity and quality), assessing the stage of thermal evolution of that organic matter, and determining the type of hydrocarbon generated. These factors, along with the mineralogical, geometric, and volumetric properties of the rocks, are critical for selecting the appropriate method for CO_2 storage (Luan et al., 2024; Fujii et al., 2010; Hamdi et al., 2022; Golding et al., 2011) and for measuring the rock's capacity for CO_2 storage (Fujii et al., 2010; Benson and Cole, 2008; Abraham-A et al., 2023).

Table 3: Summary of the geochemical characteristics of the sequence under study

Exposed rock	High (m)	TOC (average) %	Kerogen	Maceral	Potential for HC generation	Tmax (average) ºC	Grau de Maturação	Estágio de Evolução	HC generated
ML5	68 m - 95 m	0.18	Data not available						
ML4	64 m - 68 m	4.29	III	Vitrinite	Mixture of oil and gas, gas and oil	427	Immature	Diagenesis	Biogenic gas
	59 m - 64 m		II						
	50 m - 59 m		II/III						
ML3	45 m - 50 m	3.32	II	Vitrinite	Mixture of oil and gas, gas and oil	427	Immature	Diagenesis	Biogenic gas
	41 m - 45 m		II/III						
	32 m - 41 m		III						
ML2	7 m - 32 m	0.60	III	Vitrinite	Gas	421	Immature	Diagenesis	Biogenic gas
ML1	5 m - 7 m	3.17	II/III	Vitrinite	Mixture of oil and gas, gas and oil	426	Immature	Diagenesis	Biogenic gas
	4 m - 5 m		II						
	0 m - 4 m		III						

According to the study conducted by Cacama (2021) in Cabo de São Braz, sorption analysis revealed that the samples exhibit varying capacities for CO_2 gas storage, ranging from 17.04 scf/ton to 64.11 scf/ton. Notably, these different storage capacities are closely linked to the type of organic matter present, with the highest capacities found in samples with elevated vitrinite content compared to other maceral groups. Similarly, the shales analysed in the present study are characterized by significant amounts of clay minerals, a predominance of vitrinite macerals, and exposure to temperatures exceeding 400 ºC, all of which contribute to their potential for hydrocarbon generation. Therefore, the petrological and geochemical results obtained in this study suggest that this sequence could serve as a viable reservoir for CO_2 storage through the adsorption method.

9. Conclusion

Based on the results obtained, the following conclusions can be drawn:

1. At the regional level, the Cunga Formation is recognized as belonging to the post-rift stage and is subsequently part of the post-salt sequence. These post-salt formations reflect increasingly deep marine conditions that prevailed in the basin. According to Stark et al. (1991) and Brownfield & Charpentier (2006), the Cunga Formation consists of pelagic limestones and argillites with planktonic organisms, indicating its deposition in a distal environment. However, this study reveals that, at the local level—in the Cabo de São Braz area—the Cunga Formation was deposited in a more proximal environment, specifically coastal to neritic. This conclusion is supported by the predominance of palynomorphs such as radiolarians, Corrudinum regularis, and foraminiferal linings, which are characteristic of these environments.

2. During the deposition of the Cunga Formation in the Cabo de São Braz area, the dynamics within the sedimentary basin varied throughout the process, influencing the production, accumulation, and preservation of organic matter (OM). This variation is evidenced by the lithological differences observed, as well as the dispersion of total organic carbon (TOC) values and the quality of the organic matter identified along the studied sequence.

3. The Cunga Formation in the study area has an average total organic carbon (TOC) value of 2.31%, with a predominance of types II/III and III kerogens, indicating a favorable potential for generating oil and gas mixtures. However, the average Tmax value is 425 ºC, suggesting that the formation is immature and remains in the diagenesis stage. As a result, it has not yet generated hydrocarbons due to the prevailing temperature conditions.

4. Although the studied sequence does not function as an effective source rock, the geochemical characteristics of this formation support its potential use as a CO2 reservoir. The predominance of pelitic sediments (shales and claystones) in its lithology, along with the dominance of vitrinite-type macerals that have been subjected to temperatures approaching the oil generation window, enhances the capacity for adsorption.

5. Geological reservoirs for CO_2 storage present a viable option for reducing emissions and lowering CO_2 concentrations, aligning with global targets set for 2050. In the context of the Kwanza Basin and the realities of Angola, the implementation of such storage solutions could significantly contribute to mitigating climate change and its associated impacts. Continued research and improvement in the understanding of these geological formations will enhance our knowledge of their CO_2 storage capabilities. This ongoing investigation could serve as a critical pivot for achieving the anticipated reduction of CO_2 emissions into the atmosphere, fostering a more sustainable future for Angola and contributing to global climate goals.

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References

Abraham-A, R.M., Rocha, H.V., De Oliveira, S.B., Tassinarri, C.C.G. and Da Silva, O.C. (2023) Hydrocarbon indication in Rio Bonito Formation sandstone: Implication for CO_2 storage in São Paulo, Brazil. Journal Energy Geoscience, 5 (1): 1-11.

Al-Areeq, N.M. and Albaroot, M. (2019) Source Rocks Evaluation and Thermal Maturity of the Dhamar Ali Field, Sab'Atayn Basin, Yemen. Asian Journal of Science and Technology, 10 (1): 9364-9374.

Albriki, K., Wang, F., Li, M. and El Zaroug, R. (2021) Source rock maturity evaluation and its implication for regional petroleum charge, Sirt Basin, Libya: Insights from regional geochemical assessments and modelling study. Journal of African Earth Sciences 176: 1-25.

Baines, S. and Worden, R.H. (2004) Geological storage of carbon dioxide. Geological Society London Special publications, 233 (1):1-6.

Beglinger, S.E., Doust, H. and Cloetingh, S. (2012) Relating petroleum system and play development to basin evolution: West African South Atlantic basins. Marine and Petroleum Geology, 30: 1-25.

Benson, S.M. and Cole, D.R. (2008) CO_2 Sequestration in Deep Sedimentary Formations. Journal Elements, 4: 325-331.

Brognon, G.P. and Verrier, G.R. (1966) Oil and Geology in Kwanza Basin of Angola. Bulletin of the American Association of Petroleum Geologists, 50(1): 108-158.

Brownfield, M.E. and Charpentier, R.R. (2006) Geology and total petroleum systems of the West-central coastal province (7203), West Africa. U.S. Geological Survey Bulletin 2207-B, 1: 1–52.

Burwood, R. (1999) Angola: source rock control for Lower Congo Coastal and Kwanza Basin petroleum systems. Geological Society Special Publications, 153: 181-194.

Cacama, M.S.J.B. (2021) Avaliação do Potencial da Formação Cunga (Bacia do Kwanza) Como Resrvatório Não-Convencional: Implicações no Armazenamento de Dióxido de Carbono, Porto, Portugal. Repositório Institucional da Universidade Fernando Pessoa. https://bdigital.ufp.pt /handle/ 10284/10899. Acessed 13 May 2024.

Climate Council of Australia. (2015) Unburnable carbon: Why we need to leave fossil fuels in the ground. https://climatecouncil.org.au/uploads/a904b54ce67740c4b4ee2753134154b0.pdf. Acessed 6 August 2024.

Chiaghanam, O.I., Chiadikobi, K.C., Ikegwuonwu, A.O., Onyemesili, O.C. and Yikarebogha, Y. (2014) Source Rock Potential and Thermal Maturity of the Eocene Nanka Formation (Ameki Group) in Anambra Basin: An Appraisal of Ogbunike Reference Locality, South Eastern Nigeria. IOSR Journal of Applied Geology and Geophysics, 2: 11-17.

Da Silva, A.L. (2013) Caracterização mineralógica por difracção de raios-X e determinação de terras raras por ICP-MS de Rochas da Região Sul da Bahia. Repositório Institucional da Universidade Federal de Minas Gerais. https://repositorio.ufmg.br/handle/1843/BUBD-97XP2T. Acessed 12 July 2024.

Das, A., Saini, V., Parikh, K., Parikh, J., Ghosh, P. and Tot, M. (2023) Pathways to net zero emissions for the Indian power sector. Energy Strategy Reviews, 45: 759-764.

Demercian, S., Szatmari, P. and Cobbold, P.R. (1993) Style and pattern of salt diapirs due to thin-skinned gravitational gliding, Campos and Santos basins, offshore Brazil. Tectonophysics, 228: 393–433.

Duval, B., Cramez, C. and Jackson, M.P.A. (1992) Raft tectonics in the Kwanza Basin, Angola. Marine and Petroleum Geology, 9: 389–404.

Espitalié, J., Laporte, J.L., Madec, M., Marquis, F., Leplat, P., Paulet, J. and Boutefeu, A. (1977) Methode rapide de caracterisation des roches mères, de leur potential petrolier et de leur degré d'evolution. Revue de l'Institut Français du Petrole, 32: 23-42.

Fawad, M. (2021) Seismic reservoir characterization of potential CO_2 storage reservoir sandstone in Smeaheia area, Northern North Sea. Journal of Petroleum Science and Engineering, 205: 1-16.

Fort, X., Brun, J.P. and Chauvel, F. (2004) Salt tectonics on the Angolan margin, synsedimentary deformation processes. AAPG Bulletin, 88 (11): 1523-1544.

Fujii, T., Nakagawa, S., Sato, Y., Inomata, H. and Hashida, T. (2010) Sorption Characteristics of CO_2 on Rocks and Minerals in Storing CO_2 Processes. Journal Natural Resources, 1: 1-10.

Golding, S.D., Uysal, I.T., Boreham, C.J., Kirste, D., Baublys, K.A. and Esterle, J.S. (2011) Adsorption and mineral trapping dominate CO_2 storage in coal systems. Journal Energy Procedia, 4: 3131-3138.

Gurney, K.R., Mendoza, D.L., Zhou, Y., Fischer, M.L., Miller, C.C., Geethakumar, S. and Du Can, S.R. (2002) High resolution fossil combustion CO_2 emission fluxes for the United States. Department of Earth and Atmospheric Sciences/Department of Agronomy, Purdue University, pp 1-24.

Hamdi, Z., Raffik, R.Z.A., Talabi, O. and Patel, U. (2022) CO2 Mineral Trapping in Basaltic Formation During CO2 Storage. SPE Canadian Energy Technology Conference. https:// researchgate.net/ publication/359174350_CO2_Mineral_Trapping _in_Basaltic_Formation_ During_CO2_Storage. Acessed 10 May 2024.

Hassan, Q., Algburi, S., Sameen, A.Z., Salman, H.M. and Jaszczur, M. (2024) Green hydrogen: A pathway to a sustainable energy future. International Journal of Hydrogen Energy, 50: 310-333.

Horn, M.K. (1980) The habitat of oil and gas on continental margins. SEAPEX Proceedings V, pp 23-62.

Hudec, M.R. and Jackson, M.P.A. (2002) Regional restoration across the Kwanza Basin, Angola: salt tectonics triggered by repeated uplift of a metastable passive margin. American Association of Petroleum Geologists Bulletin, 88(7):971–990.

IEA – International Energy Agency (2021) Net Zero by 2050: A Roadmap for the Global Energy Sector. https://www.iea.org/reports/net-zero-by-2050. Acessed August 12 2024

Jian-Ping, L., Xiao-hua, P., Zuo-ji, T., Yong-jin, C. and Lun-kun, W. (2008) Petroleum geology and resources in West Africa: an overview. Petrololeum Exploration and Development, 35(3): 378–384.

Karner, G.D., Driscoll, N.W. and Barker, D.H.N. (2003) Syn-rift regional subsidence across the West African continental margin: the role of lower plate ductile extension. Geological Society of London Special Publication, 207(1): 105–129.

Letouzey, J., Colletta, B., Vially, R. and Chermette, J.C. (1995) Evolution of salt-related structures in compressional settings, in Jackson, M.P.A., Roberts, D.G., and Snelson, S., eds., Salt tectonics, a global perspective: AAPG Memoir, 65: 41–60.

Luan, J., Zhang, R., Zhao, H., Zhang, X., Mao, L., Zhang, Y., Hu, F., Tian, H., Dong, Y., Jiang, L. and Chen, F. (2024) Geological Storage Conditions and Potential Analysis of Carbon Dioxide in the High-steep Fold Belt in Eastern Sichuan Basin. E3S Web of Conferences, pp 79-83.

Lundin, E.R. (1992) Thin-skinned extensional tectonics on a salt detachment, northern Kwanza basin, Angola. Marine Petroleum Geology, 9: 405–411.

Martins, T., Barreto, A.C., Souza, F.M. and Souza, A.M. (2021) Fossil fuels consuption and carbon dioxide emissions in G7 countries: Empirical evidence from ARDL bounds testing approach. Environmmental Pollution Journal, 291: 1-7.

Morley, C.K., and Guerin, G. (1996) Comparison of gravity-driven deformation styles and behavior associated with mobile shales and salt. Tectonics, 15: 1154–1170.

Mulanda, N.P.T. F. (2020). Contribuição para o estudo palinológico da Formação Quifangondo na região de Cabo São Brás, Bacia do Kwanza (Angola). Universidade Agostinho Neto, Luanda. (Dissertação de Mestrado).

Peel, F.J., Travis, C.J., and Hossack, J.R. (1995) Genetic structural provinces and salt tectonics of the Cenozoic offshore U.S. Gulf of Mexico: A preliminary analysis, in M. P. A. Jackson, D. G. Roberts, and S. Snelson, eds., Salt tectonics, a global perspective. AAPG Memoir, 65: 153–175.

Pereira, Z., Mendes, M., Rodrigues, C., Mulanda, N., Cacama, M. and Nsungani, P.C. (2021) Dinoflagellate cyst assemblages of the Cunga - Quifangondo cenozoic formations in the Cabo São Brás section, Kwanza Basin (Angola): towards a first stratigraphic and paleoenvironmental interpretation. Revue de Micropaléontologie, 72: 1-20.

Peters, K.E. and Cassa, M.R. (1994) Applied source rock geochemistry. In: Magoon, L. B., Dow, W. (Eds.), The Petroleum System – From Source to Trap. Tulsa: American Association of Petroleum Geologists Memoir, 60: 93-120.

Rodrigues, C.F.A, Pereira, Z., Mendes, M., Nsungani, P.C., Fernandes, P., Lopes, G.,

Duarte, L.V., Aboelkomsan, W., Taylor, E., Tyrrell, M., Fernando, M.F. and Machado, V. (2021) Preliminary late Miocene palynomorph assemblages from the Quifangondo and Luanda formations, Onshore Kwanza Basin, Angola. Journal of African Earth Sciences, 178: 1-20

Rodrigues, C., Fernandes, P., Pereira, Z. and Barata, S. (2017) Source Rocks of the Onshore Kwanza Basin-A New Geochemical approach. Conference of Associação de Geofísica de Angola, Halliburton, Rua Kwame N'Krumah, 217/221, Luanda, Angola, pp 1-5.

Schiefelbein, C.F., Zumberge, J.E., Cameron, N.R., Brown, S.W. (1999) Petroleum systems in the South Atlantic margins. In: Cameron, N. R., Bate, R. H., Clure, V. S. (Eds.), The Oil and Gas Habitats of the South Atlantic. London Geological Society Special Publications, 153: 169-179.

Serié, C., Huuse, M., Schødt, N. H., Brooks, J. M., Williams, A. (2016) Subsurface fluid flow in the deep-water Kwanza Basin, offshore Angola. Basin Research, 29: 149-179.

Soeder, D.J. (2021) Fossil fuel and Climate Change. In: Fracking and the Environment, 1st edition, Springer Nature Switzerland AG, 155-185.

Stark, D.M., Alagoa, A., Baird, T., Belaud, D., Charron, M., Dodds, K., Domzalski, S., Faivre, O., Fosset, C., Gibbs, M., Joli, F., Kumar, R., Lane, G., Lefèbvre, L., Marca, C., Miranda, V., Motet, D., Pousset, M., Ségéral, G., Serra, O., Tan, T.H., Trayner, P., Varotsis, N., Vergel, P., Vu Hoang, D., Walker, C. and Yver, J. P. (1991) Well Evaluation Conference of Angola, pp 1-352.

Tissot, B.P. and Welte, D.H. (1984) Petroleum formation and occurrence: a new approach to oil and gas exploration, 2nd edition, Heidelberg Springer Verlang, New York.

Total, S. (1987) Carte Geologique du Bassin du Kwanza. Angola 1, 250 000.

Wood, G.D., Gabriel, A.M. and Lawson, J.C. (1996). Palynological techniques processing and microscopy. American Association of Stratigraphic Palynologists Foundation, 1: 29-50.

Wu, S., Bally, A.W., and Cramez, C. (1990) Allochtonous salt, structure and stratigraphy of the Northeastern Gulf of Mexico: Part II Structure. Marine and Petroleum Geology, 7: 334–370.