Origin and Evolution of a CO_2-Rich Gas Reservoir Offshore Angola: Insights from the Gas Composition and Isotope Analysis

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Highlights

- A pre-salt reservoir in the Kwanza Basin is rich in bitumen, CO_2 and methane;
- This reservoir is SHGS with mantle-derived CO_2 and late mature thermogenic CH_4;
- The $\delta^{13}C$ indicates mixed sapropelic, humic and abiotic origins for hydrocarbons;
- Rapid oil generation occurred due to high thermal gradient or fast deposition;
- Similarity to Brazilian basins may indicate great petroleum potential for Angola.

Abstract

The pre-salt sections of the offshore Kwanza Basin, Angola are potentially petroliferous reservoirs like their Brazilian counterparts on the other side of the South Atlantic Ocean. In this study, a pre-salt reservoir of the offshore Kwanza Basin was found to contain solid bitumen and gas of high portions of CO_2 (ca. 83%) and methane (ca. 16%). The chemical and isotopic (C, H and He) compositions of the gas indicate that the CO_2 is primarily mantle-derived while the gaseous hydrocarbons are mainly late mature thermogenic gas. The Barremian-Aptian Red Cuvo Formation with sapropelic and humic organic matter and an average TOC content of 1.7% could be the principal source of the bitumen and gaseous hydrocarbons in the reservoir. Rapid oil generation since the source rock sedimentation could have occurred as a result of the fast and thick salt deposition or the high thermal gradient created by the crustal thinning and magmatism during the South Atlantic Ocean opening. The $\delta^{13}C$ of gaseous hydrocarbons also indicates their mixed origins of sapropelic and humic organic matters and possible abiotic processes.

This reservoir is similar in the origin of CO_2 and geological background to some pre-salt reservoirs in the Brazilian basins. Such similarities with prolific petroleum systems may imply great petroleum potential in the pre-salt sections of the offshore Kwanza Basin, Angola.

Keywords: Kwanza Basin, Angola; Pre-salt reservoir; CO_2; petroleum potential; South Atlantic Ocean opening.

1. **Introduction**

The separation of Southern Africa and South America during the opening of the South Atlantic Ocean in the Early Cretaceous resulted in the development of conjugated passive continental marginal basins that share a common tectonic evolution and sedimentary history (Figure 1; Blaich et al., 2011; Kukla et al., 2018; Quirk et al., 2013). Confined between the volcanic lineaments of the Walvis Ridge and the Rio Grande Rise to the south and the Ascension Fracture Zone to the north, the central segment of the South Atlantic Ocean is characterized by pervasive Aptian salt deposition and considerable petroleum reserves discovered in the pre-salt carbonate reservoirs in the offshore Brazilian Santos and Campos basins (Aslanian et al., 2009; Ceraldi and Green, 2017; Karner and Gambôa, 2007; Kukla et al., 2018; Quirk et al., 2013). This has led to the increase of petroleum exploration activities in the pre-salt plays on the Western African side of the South Atlantic Ocean with discoveries, e.g., in the Orca, Cameia, and Azul areas of the offshore Kwanza Basin, Angola (Figure 1; Despinois et al., 2014; Greenhalgh et al., 2012; Koning, 2014).

A recent study discovered a pre-salt reservoir of the offshore Kwanza Basin, Angola containing bitumen and gas (Liu et al., 2022) and proposed a bitumen formation model. Here, we present the study on the gas of this reservoir through chemical and isotopic composition analysis to understand its fluid origin and evolution history as an example to understand the petroleum potential of the Angolan pre-salt reservoirs.

2. Geological background

The Early Cretaceous deposition of the central segment of the South Atlantic Ocean can be defined as pre-rift, rift, sag, salt basin and post-salt stages in the context of the

South Atlantic Ocean opening (Ceraldi and Green, 2017). Before the invasion of seawater and formation of the salt basin, the Walvis Ridge and the Rio Grande Rise volcanic lineaments formed by mantle plume activities blocked the seawater to the south and thus the rift basins of the central segment of the South Atlantic Ocean were fluvial-deltaic and lacustrine basins (Thompson et al., 2015). As a result, the pre-salt sedimentary stratigraphy can be divided into three phases (Ceraldi and Green, 2017). The first phase was composed of the fluvial-lacustrine deposition from freshwater deep basins created by the syn-rift grabens during the onset of continental break-up. The second phase (Sag 1) was composed of mainly carbonate deposition from the possibly interconnected fresh to brackish lakes during the widespread subsidence created by the syn-kinematic stretching of the continental crust and/or continuous rifting. Lastly, the third phase (Sag 2) was composed of microbial deposition from the under-filled, alkaline and hyperalkaline lake formed as a result of the continuous subsidence (Ceraldi and Green, 2017). Organic-rich mudstones were deposited in the deep lacustrine environment which was limited in the grabens during the syn-rift phase but more widespread during the Sag phase, e.g., the Bucomazi Formation and its equivalents in the Lower Congo and Kwanza basins and the Lagoa Feia and Guaratiba formations of the Brazilian Campos and Santos basins (Brownfield and Charpentier, 2006; Burwood, 1999; Saller et al., 2016).

The subsidence of the volcanic barriers due to the northward-propagating rifting of the supercontinent Gondwana during the Late Aptian induced periodic or episodic seawater invasion and the deposition of thick and extensive salt deposits in the central segment of the South Atlantic Ocean (Ceraldi and Green, 2017; Karner and Gambôa, 2007; Quirk et al., 2013; Torsvik et al., 2009). Sea-level rose progressively following the salt

deposition, leaving deposits of restricted marine carbonate and evaporite before the open marine sedimentation took over from the Late Cretaceous (Saller et al., 2016; Torsvik et al., 2009).

In the southern offshore Kwanza Basin (or named the Benguela Basin), a well has been drilled through the studied reservoir which penetrates through the salt of the Aptian Loeme Formation (2616.5 m; 2687.5–5304 m), the pre-salt Chela Formation (216 m; 5304–5520 m) with carbonate and silicified carbonate deposits, the Grey Cuvo Formation (133 m; 5520–5653 m) with fine grain siliciclastic sandstone and clay deposits and the Barremian-Aptian lacustrine Red Cuvo Formation (397 m; 5653–6050 m) with mixed deposits of siltstone, black shale, thin carbonate interlayer, and igneous units (Figure 1).

3. Samples and methods

Sidewall core samples were collected from the pre-salt Chela, Grey Cuvo and Red Cuvo formations (Table 1) for the total organic carbon (TOC) content measurements, maceral identification and Rock-Eval analysis. All the analyses were run in CSTJF-TOTAL Facilities in Pau, France. The TOC contents of the powdered samples were determined with a LECO CS-400 carbon/sulfur analyzer after the treatment with hydrochloric acid. The preparation of samples for optical analysis, identification of organic matter type, and measurement of vitrinite reflectance followed standard methods, i.e., ASTM D2797/D2797M-11a (2011a), ASTM D2799-12 (2012), and ASTM D7708-11 (2011b). The maceral examination was performed using a LEICA DM6000M microscope. Reflectance measurements were carried out on vitrinite and bitumen under

reflected white incident light in oil immersion. Rock-Eval analysis was conducted with Rock-Eval 6 (Table 2).

Four down-hole pressurized fluid samples were taken from the Chela and Red Cuvo formations with the Multi-sample Production Sample Receptacle (MPSR) of the Schlumberger MDT Modular Formation Dynamics Tester and measured at CSTJF-TOTAL Facilities (Table 3). The gas composition was measured with an Agilent 8890 GC chromatography equipped with an Agilent HP-PLOT Al_2O_3 S column (25 m × 0.32 mm × 8 μm) and flame ionization and thermal conductivity detectors. The carbon isotope compositions of the hydrocarbons and CO_2 were analyzed by Gas Chromatography-Combustion Isotope-Ratio Mass Spectrometry (GC-C-IRMS) with an Agilent 6890N equipped with an Agilent PoraPLOT Q column (25 m × 0.32 mm × 10 μm) and IsoPrime 100. The hydrogen isotope compositions of the hydrocarbons were measured by Gas Chromatography-Thermal Conversion-Isotope Ratio Mass Spectrometry (GC-TC-IRMS) with a ThermoFisher Trace1310 equipped with a PoraPLOT Q column (25 m × 0.32 mm × 10 μm) and Delta V Advantage. The temperature programs for the C and H isotope composition analyses were starting from 50 °C and kept for 3 mins and then increasing the temperature to 190 °C at 30 °C/min. The carrier gas was Helium. The helium concentration and isotope composition of the samples were analyzed following Györe (2015) with a Mass Analyzer Product (MAP) 215-50 mass spectrometer.

4. Results

The organic matter in the Chela Formation carbonate rock reservoir is characterized as abundant pore-filling anisotropic bitumen with no autochthonous organic matter

(Figure 2a-b). The TOC (purely bitumen) contents are 0.4–4.5% with an average of 1.7% (Table 1). The bitumen has no fluorescence and is characterized by relatively high bitumen reflectance (BR_o) of 1.88–1.98% (equivalent VR_o of 1.56–1.62%; Table 1; Jacob, 1989). The Grey Cuvo Formation samples are carbonate- and argillaceous-rich siltstones with small-size humic coaly fragments, e.g., inertinite and vitrinite (Figure 2c-e). The TOC contents are in the range of 0.6–1% with an average of 0.74% (Table 1). The organic matter exhibits zero fluorescence and the vitrinite reflectance is between 1.45 and 1.52 % (Table 1). The Red Cuvo Formation consists of siliciclastic rocks bearing various contents of carbonate and pyrite. The organic matter is a mix of sapropelic micro-granular organic matter and terrestrial land plant debris (humic coaly fragment; Figure 2f-h). Scarce anisotropic bitumen is also observed (Figure 2h). The TOC contents are 1.1–3.9% with an average of 1.7% (Table 1). Vitrinite reflectance values in the Red Cuvo Formation show a general increase with depth from ca. 1.7% at 5791.5 m to 2.1% at 6015.0 m (Table 1). The low Rock-Eval parameters of the Red Cuvo Formation samples indicate that their hydrocarbon generation potential has been exhausted (Table 2).

The four fluids sampled from the Chela and Red Cuvo formations are predominantly comprised of CO_2 (ca. 82–84%) and CH_4 (ca. 14–17%; Table 3). The CH_4 accounts for ca. 93–96% of the total hydrocarbons. The hydrocarbon composition, $\delta^{13}C$ and $\delta^{2}H$ are homogeneous for the shallower three samples while being slightly different from the deepest 5980.8 m sample in general (Table 3; Figure 3-4). Helium concentrations vary between 1 and 1.4×10^{-4} cm^3/cm^3 (1 atm and 15 °C; Table 3). The molar ratio $^3He/^4He$ is presented as R/R_a, which represents the $^3He/^4He$ value of the sample (R) divided by

that of air (R_a, 1.384×10^{-6}; Clarke et al., 1976). The R/R_a values are 4.4–4.7 while the $CO_2/^3He$ ratios are ca. 0.89 to 1.32×10^9.

5. Discussion

5.1 CO_2 source(s)

The sources for CO_2 in geological reservoirs can be magmatism, regional and contact metamorphism, marine carbonates, biotic decay, and the breakdown of coaly Type III organic matters (Procesi et al., 2019; Wycherley et al., 1999). The natural gases in this study are composed of ca. 82–84 mol% of CO_2. For most reservoirs with abundant CO_2, e.g., > 70 mol%, the major sources of the CO_2 are typically magmatism and metamorphism (Györe, 2015; Wycherley et al., 1999). The fact that the $\delta^{13}C$ values of the CO_2 of the samples in this study are ca. -3.9% (Table 3) also indicates that their dominant CO_2 sources could include magmatism ($\delta^{13}C_{CO2}$ of ca. -7 to -4‰) and regional metamorphism ($\delta^{13}C_{CO2}$ of ca. -10‰ to 0; Györe, 2015; Jenden et al., 1993b; Wycherley et al., 1999).

A clear mantle signature is identified for the studied gas samples through their excessive primordial ^3He compared to air, as the R/R_a values are as high as ca. 4.5 (Table 3) which is often the characteristic of mantle-originated fluids (Porcelli et al., 2002). Meanwhile, the samples possess an evident excess of radiogenic ^4He compared with typical MORB (Mid-Ocean Ridge Basalt) noble gas, as their R/Ra value of ca. 4.5 is lower than the typical value of 8 for MORB-type noble gas (Graham, 2002). Such radiogenic ^4He could be produced by the alpha decay of U and Th, elements that are rare in the reservoir lithologically dominated by carbonates but can be abundant in the clastic sedimentary

rocks and/or igneous rock. The $CO_2/^3He$ ratios of the studied gases are 0.89–1.32 × 10^9 (Table 3) which are consistent with the typical range of $CO_2/^3He$ ratios for pure magmatic-sourced fluids, i.e., around 10^9 to 10^{10} (Ballentine et al., 2002). The value below this range, i.e., 0.89 × 10^9 for the deepest sample, indicates that the gas may have been subjected to CO_2 loss by dissolving into the aquifer. Thus, the CO_2 in the studied reservoir is mainly mantle-derived although there may have been minor contributions from metamorphism and organic matter (Figure 3e-f).

The South Atlantic Ocean opening was associated with active magma activities (Masse and Laurent, 2016). Three main episodes of magma activities are recognized in the South Kwanza Basin and they could have been significant source(s) of CO_2 (Comin-Chiaramonti et al., 2011; Denis and Kluska, 2017; Jerram et al., 2019; Kukla et al., 2018; Marzoli et al., 1999; Masse and Laurent, 2016). The earliest major magmatic episode is the Paraná-Etendeka flood basalt province (ca. 132 Ma; Marzoli et al., 1999) which is characterized by tholeiitic lava flows, dykes and volcanoclastic sediments underlying the Early Cretaceous sedimentary succession. It only lasted for a short duration of 3–4 m.y. (Jerram et al., 2019; Marzoli et al., 1999) and took place much earlier than the deposition of caprock of the reservoir in this study, i.e., the Loeme Formation salt (ca. 117–113 Ma; Quirk et al., 2013). Thus, it is unlikely to be the main source of CO_2 in the studied reservoir.

The second is an Aptian episode of tholeiitic magmatism during the syn- to early post-rift phase of the South Atlantic Ridge breakup which intruded the Barremian to Aptian sedimentary units including the salt (Denis and Kluska, 2017; Jerram et al., 2019; Marsh and Swart, 2018; Marzoli et al., 1999; Quirk et al., 2013). This magmatic episode is well-developed offshore. The latest one is an Albian-Turonian alkaline magmatic

episode (Jerram et al., 2019; Marzoli et al., 1999; Quirk et al., 2013) which has been interpreted to originate from a mantle perturbation at the base of the lithosphere like the Cameroon Volcanic Line (Reusch et al., 2010). The origin of CO_2 cannot be unambiguously constrained to either of these two later magmatic episodes through the $\delta^{13}C$ of CO_2 and He signatures.

In a recent study, CO_2 was believed to have induced the bitumen formation through asphaltene precipitation and thermal cracking in this reservoir (Liu et al., 2022). The timing of this CO_2-induced bitumen formation process was constrained by the Re-Os radioisotope geochronometer to be 116 ± 29 Ma (2σ; Liu et al., 2022). Thus, the CO_2 responsible for the bitumen formation should be originated from the second episode (Aptian) magma activity. The third Albian magmatic episode may have also contributed CO_2 to the studied reservoir, although the amount is difficult to estimate. It is worth noting that there is still a considerable quantity of gaseous hydrocarbons left in the reservoir currently as will be discussed in the following sections. The gaseous hydrocarbons are mainly thermogenic and should be generated through the source rock maturation and possibly the oil thermal cracking during the Aptian CO_2 alteration. If there has been Albian CO_2 charged into the studied reservoir, it was incapable of clearly expelling these antecedent hydrocarbons, and the earlier CO_2 as well. Besides mantle CO_2, these two magma episodes could also produce CO_2 through contact metamorphism of carbonates (Wycherley et al., 1999).

5.2 Gaseous hydrocarbon source(s)

Natural gas may have either biotic or abiotic origins. Biotic gas is generated from organic matter through thermogenic and microbial processes. Abiotic gases can form

from magmatism and gas-water-rock reactions, e.g., Fischer-Tropsch Type (FTT) synthesis (Etiope and Oze, 2022; Etiope and Sherwood Lollar, 2013; Etiope and Whiticar, 2019). The gas composition and stable C ad and H isotope composition are often used to identify the origins of the gas. The $\delta^{13}C$ trend of the gaseous hydrocarbons of the fluids in this study are $\delta^{13}C_1 \approx \delta^{13}C_2 < \delta^{13}C_3 < \delta^{13}C_4$ (Table 3; Figure 4), indicating their predominantly biotic origin rather than a reversed $\delta^{13}C$ trend of $\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3 > \delta^{13}C_4$ for common abiotic gaseous hydrocarbons (Chung et al., 1988; Dai et al., 2008; Jenden et al., 1993b).

It is indicated on the genetic diagrams of $\delta^{2}H$-CH_4, $C_1/(C_2 + C_3)$ and $\delta^{13}C$-CO_2 versus $\delta^{13}C$-CH_4 that the gaseous hydrocarbons in the studied reservoir are dominant of late mature thermogenic gas (Figure 3; Milkov and Etiope, 2018). Although close to the secondary microbial zone (Figure 3a, c and e) and the arrow indicating oxidation process (Figure 3d), the studied samples are unlikely to have such origin or to be affected by such processes considering their burial depth of ca. 5000–6000 m. Although it is indicated that the gas samples may have been altered by thermochemical sulfate reduction (TSR) processes (Figure 3b and d), it is not supported by the absence of H_2S (Table 3). The $\delta^{13}C$-CO_2 versus $\delta^{13}C$-CH_4 diagrams (Figure 3e-f) indicate that the CO_2 is compatible with the C stable isotope range of late mature thermogenic gas. There may have also been some thermogenic CO_2, although we have concluded that the CO_2 is mainly mantle-derived.

The organic-rich intervals of the pre-salt section in the Kwanza Basin are the mudstone, marl and shales deposited in the deep lacustrine environment during both the Barremian to Aptian syn-rift and sag stages (Brownfield and Charpentier, 2006; Burwood, 1999; Ceraldi and Green, 2017; Danforth, 1998; Saller et al., 2016). The organic-rich strata

drilled through by the studied well are the Barremian-Aptian Red and Grey Cuvo formations. The vitrinite R_o values of these two formations are 1.7–2.1% and ca. 1.5%, respectively, indicating that they have been mature and are in the stages of wet to dry gas and condensate generation, respectively. Considering their thickness (397 m vs 133 m), average TOC contents (1.7% vs 0.74%) and generation potential (sapropelic organic matter vs humic coaly fragments), the Red Cuvo Formation is more likely to be the major source for the hydrocarbons in the studied reservoir than the Grey Cuvo Formation. Besides, the presence of the pore-filling bitumen in the Chela Formation carbonate reservoir indicates that there was charge(s) of crude oil for which the sapropelic organic matter of the Red Cuvo Formation should be the principal source. Moreover, the humic contribution to the gas could be attributed to the coaly fragments and terrestrial land plants of the Grey and Red Cuvo formations. Partial thermal cracking of crude oil during the bitumen formation process could also generate light hydrocarbons (Liu et al., 2022).

The samples are also very close to and even within the abiotic zone on the genetic diagrams indicating possible abiotic contribution to the gaseous hydrocarbons in the studied reservoir (Figure 3). Gases from pure and active magmatic systems generally contain 10^{-4} to 0.5% CH_4 (Procesi et al., 2019) which could account for 0.05–2.56% of the current methane in the studied reservoir if the loss and the contributions other than magmatism of CO_2 are neglected. Besides, the geometric mean molar ratio of $CH_4/^3He$ is 3×10^6 for the uncontaminated mantle-derived fluids from spreading ridges (Jenden et al., 1993b). The $CH_4/^3He$ values of the fluids from the reservoir in this study are in the range of $1.7–2.6 \times 10^8$ (Table 3). Thus, the methane derived from magmatism along with the noble gases and CO_2 may account for ca. 1.2–1.8% of the total methane of the

reservoir in this study, although the result can be very different from this estimation considering mantle heterogeneity. Both calculations from CO_2 and ^3He indicate a low contribution of CH_4 (maximum of 2.56%) from mantle or magmatism to the methane budget of the studied reservoir. Besides, there hasn't been any hydrocarbon larger than C_2H_6 found in mantle-derived gases so far (Liu et al., 2019).

Among the gas-water-rock reactions, Fischer-Tropsch Type (FTT) synthesis (Sabatier reaction in the free gas phase) within ultramafic rocks is likely the only one that can generate a considerable amount of methane (Etiope and Oze, 2022; Etiope and Sherwood Lollar, 2013; Etiope and Whiticar, 2019). Abiotic methane can be generated through FTT synthesis within the ultramafic rocks associated with magma activities, e.g., the Albian-Turonian alkaline magmatic episode (Jerram et al., 2019; Marzoli et al., 1999; Quirk et al., 2013). There are limitations on the FTT synthesis methane production, e.g., catalysts; however, it can be a long-term active generating source for methane and its production can potentially be comparable to thermogenic methane over geological time (Etiope and Whiticar, 2019). Unfortunately, it is hard to quantify the FTT synthesis contribution of methane in this reservoir.

Thus, the gaseous hydrocarbons in the reservoir of this study are mainly late mature thermogenic gas with possible abiotic methane contributions from magmatism and FTT synthesis according to the chemical and isotopic gas compositions of the gas.

5.3 Further implications from the $\delta^{13}C$ of hydrocarbons

The kinetic nature of the thermogenic natural gas generation process leads to the expectation for the hydrocarbons with higher carbon numbers and the hydrocarbons

generated under higher maturity to have more positive $\delta^{13}C$ values (Tang et al., 2000; Xia et al., 2013). Chung et al. (1988) reported the $\delta^{13}C$ of hydrocarbons on a plot as the function of inverse carbon number, i.e., $\delta^{13}C_n$ vs 1/n (e.g., Figure 4). Based on an ideal equation, the hydrocarbons should be on a straight line in such a diagram if they are generated in a single pulse from the organic matter of the source rocks with homogeneous $\delta^{13}C$ (Chung et al., 1988). However, deviation from the straight line and even the $\delta^{13}C$ reversal to carbon number and maturity are often observed (Burruss and Laughrey, 2010; Dai et al., 2004; Jenden et al., 1993a; Tilley et al., 2011; Xia et al., 1999; Zumberge et al., 2012). Mixing of gases from different sources and/or generation pulses, secondary cracking of crude oil and wet gas, diffusion and methane cracking are proposed to be the causes of the $\delta^{13}C$ deviation and reversal of biotic hydrocarbons (Burruss and Laughrey, 2010; Cheng et al., 2020; Dai et al., 2016; Jenden et al., 1993a; Tilley et al., 2011; Tilley and Muehlenbachs, 2013; Xia et al., 2013; Zumberge et al., 2012).

For the gas samples from the studied reservoir, the actual $\delta^{13}C_1$ of the shallower three samples and the actual $\delta^{13}C_1$ and $\delta^{13}C_2$ of the deepest sample are heavier than the projections, making the curves to be concave (Figure 4). The $\delta^{13}C_1$ and $\delta^{13}C_2$ are nearly identical for the shallower three samples. The $\delta^{13}C_1$ is slightly heavier than the $\delta^{13}C_2$ for the 5980.8 m sample, i.e., the $\delta^{13}C$ is slightly reversed (Table 3).

The mixing of gases generated from either different sources or maturities is often considered the cause of the isotope reversal first (Liu et al., 2019). Gases of humic origin are often heavier in $\delta^{13}C$ than those of sapropelic origin in the same maturation stages while abiotic methane is often heavier in $\delta^{13}C$ than biotic methane (Hunt, 1996).

The gaseous hydrocarbons in the studied reservoir are mainly of sapropelic origin, the deviation of $\delta^{13}C_1$ and $\delta^{13}C_2$ to be heavier than the projections from the propane and butanes in Chung's plot (Figure 4) can be attributed to the humic and abiotic (e.g., magmatic and FTT synthesis) contributions of methane and ethane. The humic contribution should take the major responsibility for shifting the $\delta^{13}C$ positively considering the appreciable amount of humic organic matter in both the over 100 m thick Grey Cuvo Formation with average TOC content of 0.74% and the ca. 400 m thick Red Cuvo Formation. Mantle-derived methane is generally characterized by $\delta^{13}C$ and $\delta^{2}H$ heavier than -20‰ and -200‰, respectively (Etiope and Sherwood Lollar, 2013). Although they are distinctly different from the corresponding values of ca. -32‰ and -131 to -140‰ of the studied gas, the change it can make is limited due to its trace contribution to the total methane (< 2.56%). The exact $\delta^{13}C$ and contribution of methane from FTT synthesis are unknown.

The generation of gas through the secondary cracking of the crude oil expelled from and retained in the source rock may also lead to the isotope reversal of natural gas through its mix with gas generated directly from kerogen (Xia et al., 2013). The relatively high BR_o of the bitumen from both the Red Cuvo Formation source rock (e.g., 6015 m, BR_o of 2.62%) and the Chela Formation reservoir (BR_o of 1.88~1.98%; Table 1) could serve as the evidence for the thermal cracking of crude oils both retained in the Red Cuvo Formation source rock and expelled into the reservoir, and thus the generation of oil-cracking gases. The Tmax of the Chela Formation bitumen is as high as 470 °C (Liu et al., 2022). Besides, the fact that the Chela Formation reservoir bitumen cannot fully dissolve in dichloromethane may also indicate the occurrence of thermal cracking (Liu et al., 2022).

Furthermore, methane cracking and diffusion could also lead to the reversal of $\delta^{13}C$. The cracking of methane under high temperatures can also lead to the reversal of $\delta^{13}C_1$ and $\delta^{13}C_2$ by generating ethane of light $\delta^{13}C$ and leaving the residual methane $\delta^{13}C$ progressively heavier (Cheng et al., 2020). However, such a situation is linked to shale gas in overmature shales with R_o > 2% and thus unlikely to be a major reason for this studied reservoir. Migration and diffusion can change the gas composition and isotope composition and leave the residual methane with heavy $\delta^{13}C$ (Burruss and Laughrey, 2010; Stainforth, 2009). However, the Loeme salt Formation may have acted as a good seal preventing significant diffusion of light hydrocarbons. Migration also shows no significant influence on the $\delta^{13}C$-CH_4 and $C_1/(C_2 + C_3)$ in Figure 3d. Nevertheless, the compositional and isotopic signatures of gaseous hydrocarbons may be fractionated through the movement induced by CO_2 flux.

5.4 Temporal evolution of the reservoir fluids

Multiple possibilities have been proposed for the maturation timing of the Western African pre-salt source rocks. In the central segment of the South Atlantic Ocean, they could have reached the oil window during the Late Cretaceous in response to salt remobilization and a possibly climate-driven increased sedimentation rate (Brownfield and Charpentier, 2006; Marcano et al., 2013). For the Kwanza pre-salt source rocks in specific, Danforth (1998) suggested that they entered the oil window only since the Early Paleogene while White et al. (2003) proposed rapid oil generation after source rock deposition due to abnormally high thermal regime. It was also suggested that early oil generation could be possible for source rocks in the deeper parts of syn-rift grabens due to the fast and thick salt deposition (Saller et al., 2016). Liu et al. (2022) constrained

the bitumen formation age in the studied reservoir to be 116 ± 29 Ma with the Re-Os radioisotope system. Oil accumulation is earlier than bitumen formation, thus the oil generation occurred rapidly after Red and Grey Cuvo formations source rock deposition during the Barremian-Aptian. This is possibly a result of an abnormally high thermal regime due to the continental crust thinning and active magmatism during the South Atlantic Ocean opening and/or the fast and thick salt deposition (Liu et al., 2022; Saller et al., 2016; White et al., 2003). Thus, all the key processes of this reservoir, i.e., the source rock deposition and maturation, oil accumulation, magmatic CO_2 charge and bitumen formation, occurred in a very short duration.

5.5 Petroleum potential of the Kwanza Basin, Angola

The South Atlantic Ocean opening process was associated with rifting and magma activities accompanied by the release of massive CO_2 (Comin-Chiaramonti et al., 2011). Reservoirs with CO_2 > 20% are relatively rare in petroleum basins, however, they have been discovered in the pre-salt sections on both sides of the central segment of the South Atlantic Ocean (Gamboa et al., 2019; Ma et al., 2015; Santos Neto et al., 2012; this study). In the Brazilian Campos and Santos basins, pre-salt reservoirs with a wide range of CO_2 percentages are discovered (Gamboa et al., 2019). There are two types of sources recognized for the CO_2 in these reservoirs, one being almost exclusively mantle-derived, and the other being mainly organic matter through microbiological and diagenetic processes with occasional mantle influences (Gamboa et al., 2019; Ma et al., 2015). In addition to the gas reservoir with ca. 80% CO_2 of this study, ubiquitous CO_2 gas inclusions have been also discovered near the Benguela Transfer Fault Zone in the southwestern part of the offshore Kwanza Basin, suggesting that there were multiple episodes of CO_2 influx (Girard and Miguel, 2017). The offshore

Kwanza Basin pre-salt section demonstrates a similar origin and influence of CO_2 with the Brazilian counterparts.

Gas reservoirs located in volcanic-sedimentary interacting domains characterized by a mixture of geothermal (thermometamorphic or mantle-derived) CO_2 and biotic (microbial or thermogenic) CH_4 are recognized as Sediment-Hosted Geothermal Systems (SHGSs; Procesi et al., 2019). The maturity of source rocks in SHGSs is often high due to active tectonic movement and anomalous heat flow (Procesi et al., 2019). The injection of CO_2 into reservoirs could reduce the hydrocarbon potential by the thermal alteration of crude oil into pyrobitumen and dry gas and the expulsion of crude oil and gas from reservoirs (Liu et al., 2022 and this study). Nevertheless, the CO_2 could also leach the carbonate reservoirs and may profoundly increase the porosity and permeability, thus enhancing the reservoir quality. In addition to petroleum exploration, the study of the fluid origin and evolution history of SHGSs could also contribute to global climate change studies due to the possible emission of greenhouse gases CH_4 and CO_2 to the atmosphere (Procesi et al., 2019).

As demonstrated by the studied reservoir, the configuration of source rock, reservoir and seal created during the rift and sag phases of the South Atlantic Ocean opening, and the maturation of the source rock due to magmatism or sedimentation, imply potential petroleum reserves for the pre-salt section of the offshore Kwanza basin. The Brazilian Campos and Santos basins sharing common tectonic and sedimentary history with the Kwanza Basin have reached tremendous success in petroleum exploration in the pre-salt section (Aslanian et al., 2009; Ceraldi and Green, 2017; Karner and Gambôa, 2007; Kukla et al., 2018; Quirk et al., 2013), which may imply great opportunities for the

Kwanza Basin. Dry wells and CO_2-rich reservoirs discovered during the primitive exploration stage do not necessarily mean that the pre-salt plays of Angolan offshore basins are poor in petroleum, as they are also discovered in the prolific Brazilian basins (Gamboa et al., 2019; Ma et al., 2015; Santos Neto et al., 2012). There have already been oil and gas accumulations discovered in the Kwanza Basin, too (Despinois et al., 2014; Greenhalgh et al., 2012; Koning, 2014). Yet, the pre-salt reservoirs in the Kwanza Basin are spatially limited and complex which is incomparable to the high-quality pre-salt reservoirs of thick and homogenous microbial carbonates on the Brazilian side. Considerable additional research is required to reveal the actual and full petroleum potential of the extensive Kwanza Basin.

6. Conclusions

The pre-salt gas reservoir of the offshore Kwanza Basin, Angola is a Sediment-Host Geothermal System (SHGS) containing mantle-derived CO_2 from an Aptian magmatic episode and late mature thermogenic CH_4 from the Barremian-Aptian Red and Grey Cuvo formations which reached maturation rapidly after deposition due to the abnormally high thermal regime or the fast and thick salt deposition in the context of South Atlantic Ocean opening. This reservoir demonstrates similar fluid origin and possibly similar evolution history to the pre-salt SHGSs of the Brazilian Campos and Santos basins. The conjugated Brazilian and Angolan basins also share common tectonic and sedimentary history throughout the Cretaceous creating a similar configuration of source, reservoir and seal. The great success of petroleum exploitation in the pre-salt carbonate reservoir of the Brazilian basins may thus imply great reserves in the counterparts of the offshore Kwanza Basin, Angola. Nevertheless, the Kwanza

Basin has its unique characteristics and further research is required to reveal its full petroleum potential.

Data availability statement

The data presented in this study are available upon request from the corresponding author.

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Figures

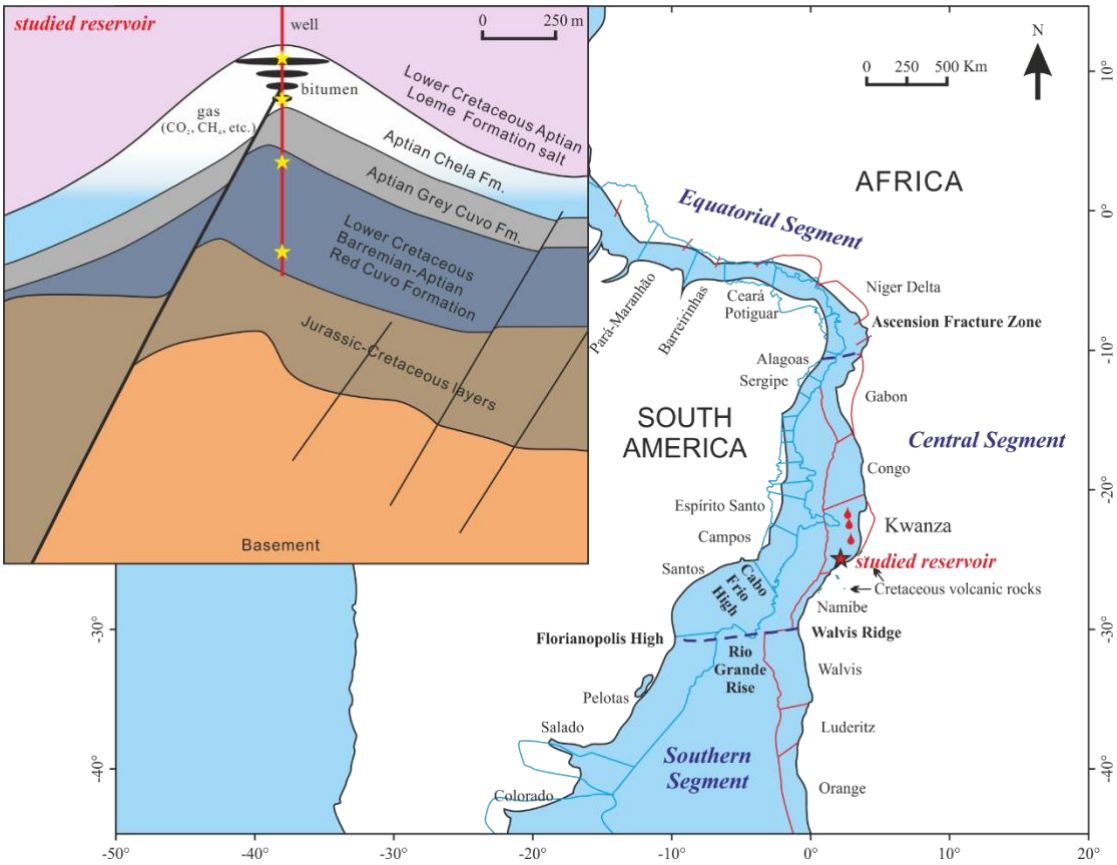
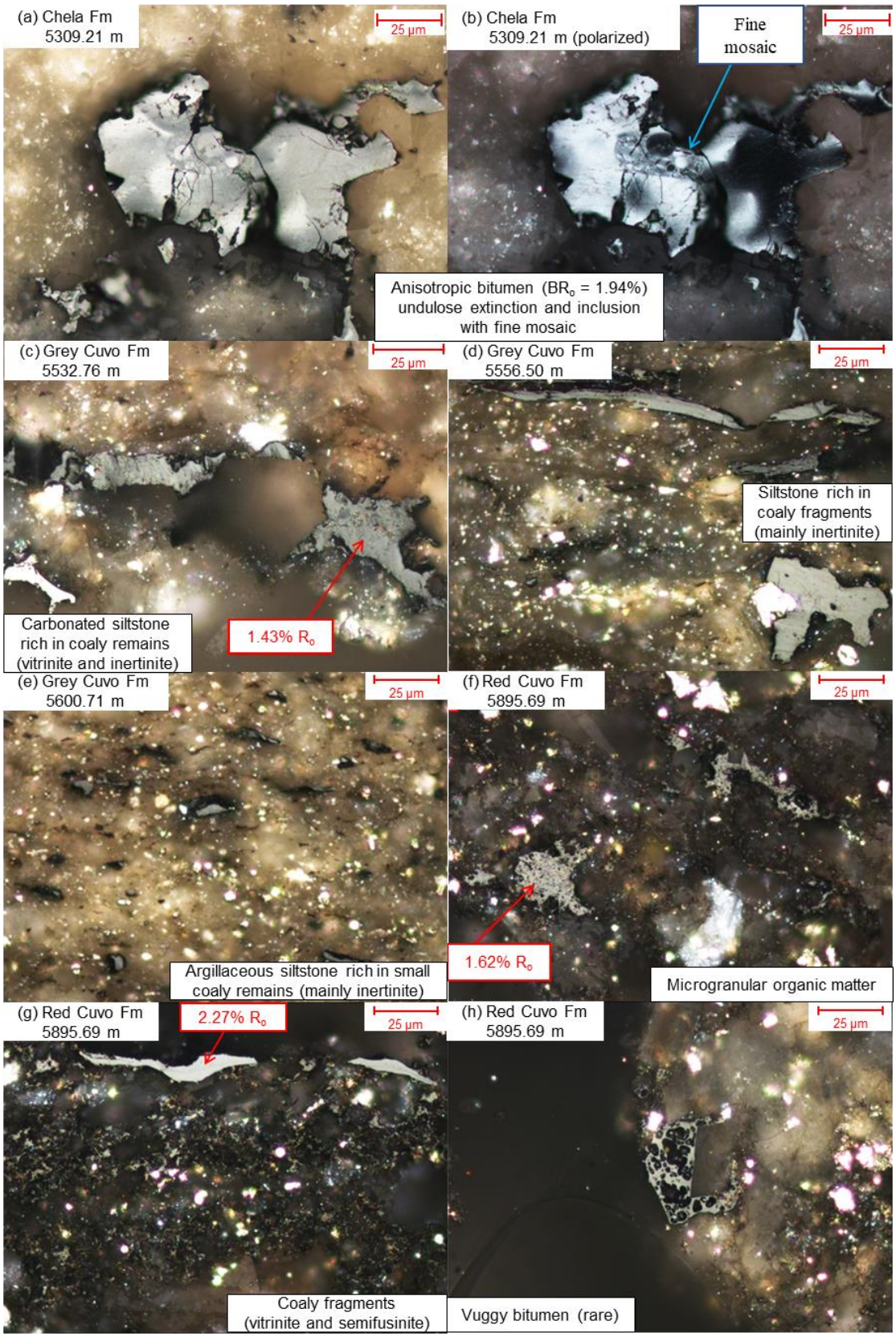


Figure 1 The Aptian South Atlantic Ocean margin (Masse and Laurent, 2016; Thompson et al., 2015) and the seismic profile interpretation of structure and stratigraphy of the studied reservoir (the inset; Liu et al., 2022). The red star marks the location of the studied reservoir. The red drops are locations with pre-salt petroleum discoveries. The yellow stars of the inset are the fluid sampling positions.

It is a 2-column fitting image.


(a) Chela Fm
5309.21 m
25 µm
(b) Chela Fm
5309.21 m (polarized)
Fine mosaic
25 µm
Anisotropic bitumen (BR$_o$ = 1.94%) undulose extinction and inclusion with fine mosaic
(c) Grey Cuvo Fm
5532.76 m
25 µm
Carbonated siltstone rich in coaly remains (vitrinite and inertinite)
1.43% R$_o$
(d) Grey Cuvo Fm
5556.50 m
25 µm
Siltstone rich in coaly fragments (mainly inertinite)
(e) Grey Cuvo Fm
5600.71 m
25 µm
Argillaceous siltstone rich in small coaly remains (mainly inertinite)
(f) Red Cuvo Fm
5895.69 m
25 µm
1.62% R$_o$
Microgranular organic matter
(g) Red Cuvo Fm
5895.69 m
2.27% R$_o$
25 µm
Coaly fragments (vitrinite and semifusinite)
(h) Red Cuvo Fm
5895.69 m
25 µm
Vuggy bitumen (rare)

473

Figure 2 Matrices and macerals of the Chela, Grey and Red Cuvo formations. The only organic matter observed in the Chela Formation is the anisotropic bitumen with undulose extinction and no fluorescence filling the intercrystalline pores of carbonate (a-b). The Grey Cuvo Formation carbonated and argillaceous siltstones are rich in humic coaly remains (c- e). The occasionally carbonated siliciclastic rocks of the Red Cuvo Formation contain sapropelic micro-granular organic matter as thin reflective networks (f), humic coaly remains in lower content than the Grey Cuvo Formation (g), and scarce vuggy bitumen (h). Fluorescence of organic matter is absent under high maturity.

It is a 2-column fitting image.

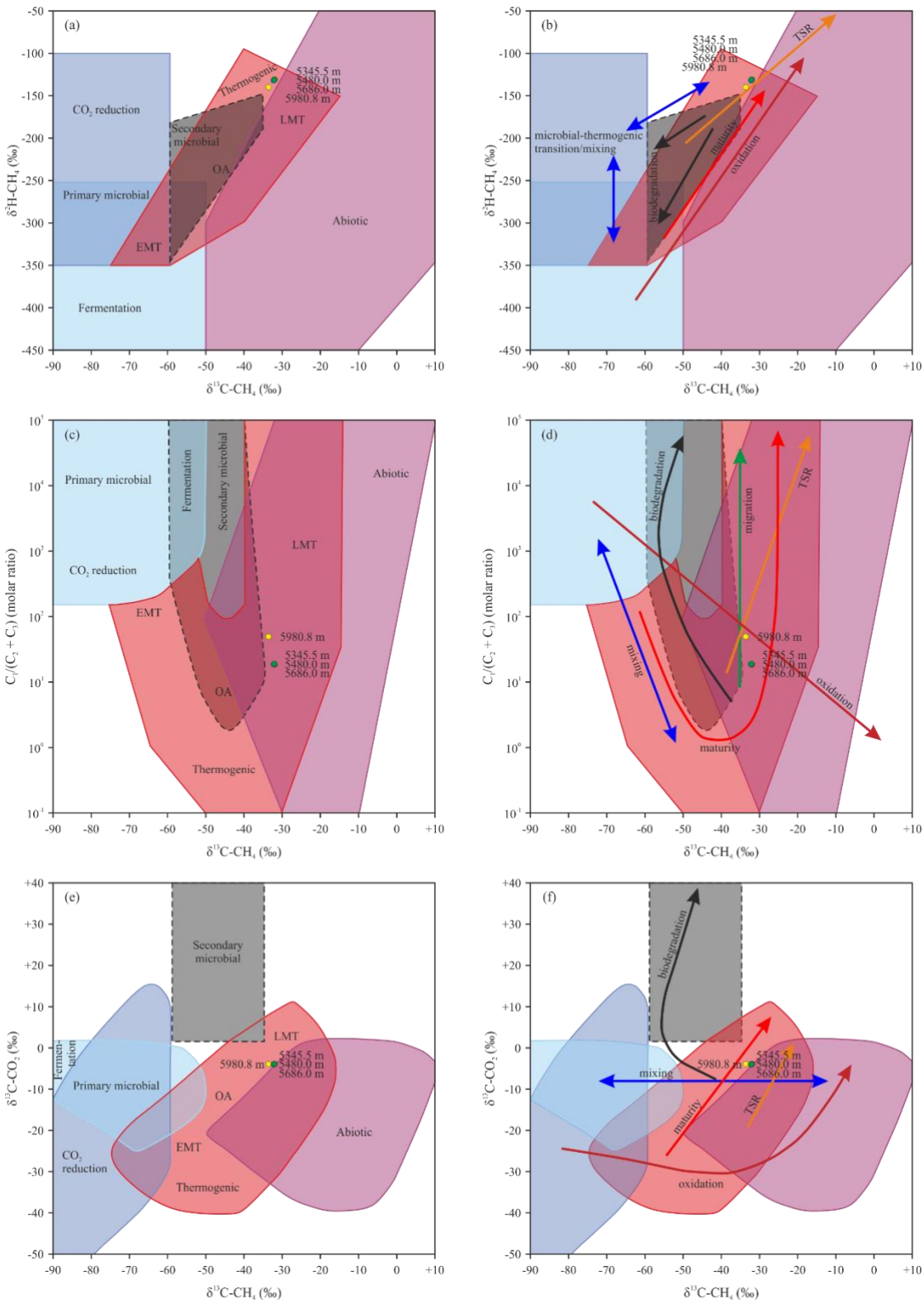


Figure 3 The genetic diagrams indicating the origin and alteration processes of the gas samples (Milkov and Etiope, 2018). EMT – early mature thermogenic gas; OA – oil-associated thermogenic gas; LMT – late mature thermogenic gas; TSR –

thermochemical sulfate reduction. The gas samples in this study are late mature thermogenic gas in general.

It is a 2-column fitting image.

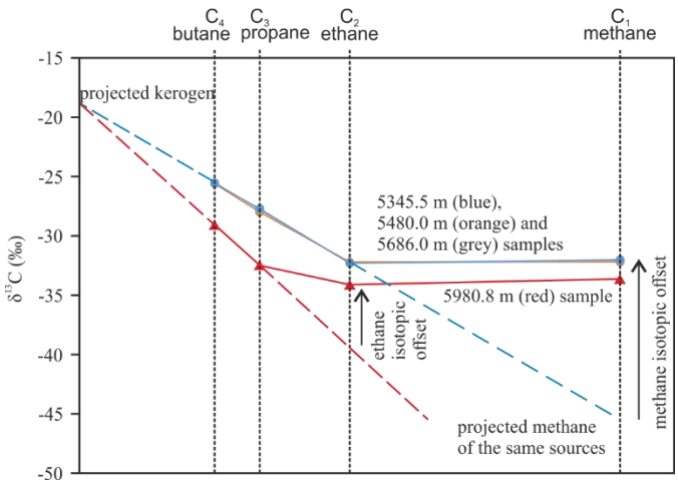


Figure 4 Gas samples on the diagram of $1/C_n$ versus $\delta^{13}C$ (Chung et al., 1988). The shallower three samples are very similar above (the overlapped orange, grey and blue lines and marks) while the deepest sample fits on a lower red line. The $\delta^{13}C$ of the methane (and ethane for the deepest sample) is higher than the projection. The $\delta^{13}C$ of the methane and ethane are slightly reversed, mainly indicating the mixing of humic and sapropelic sources for the gas.

It is a 1-column fitting image.

Tables

Table 1 The TOC contents and maturity (VR_o/BR_o) of the sidewall core samples.

Formation	Depth (m)	TOC (wt.%)	Maceral	VR_o/BR_o [a] (%)	Equivalent VR_o [b] (%)
Chela [c]	5304.00	4.50	bitumen	/	/
	5309.21	3.99	bitumen	1.94	1.60
	5371.75	1.32	bitumen	1.96	1.61
	5408.69	0.99	bitumen	1.88	1.56
	5493.69	0.38	bitumen	1.98	1.62
Grey Cuvo	5532.76	0.60	vitrinite	1.45	/
	5556.50	0.65	vitrinite	1.46	/
	5600.71	0.97	vitrinite	1.52	/
Red Cuvo	5791.50	1.21	vitrinite	1.73	/
	5807.70	3.86	vitrinite	1.69	/
	5844.60	1.21	vitrinite	1.86	/
	5895.69	1.44	vitrinite	2.14	/
	5901.03	1.29	vitrinite	1.97	/
	5958.01	1.99	vitrinite	2.02	/
	5991.61	1.11	vitrinite	2.07	/
	6015.00	1.59	vitrinite	2.13	/
			bitumen	2.62	2.02

[a] VR_o/BR_o: Vitrinite/Bitumen reflectance under white incident light in oil immersion;

[b] Jacob's formula (Jacob, 1989): $VR_o = 0.618 \times BR_o + 0.4$;

[c] Part of the Chela Formation samples data is from Liu et al. (2022).

Table 2 The Rock-Eval parameters of the Red Cuvo Formation.

Depth (m)	S1 (mg HC/g rock)	S2 (mg HC/g rock)	PI [a]	HI [b] (mg HC/g TOC)
5791.50	2.8	0.92	0.75	76
5807.70	5.55	0.98	0.85	25
5844.60	1.81	0.37	0.83	31
5895.69	2.05	0.25	0.89	17
5901.30	1.33	0.27	0.83	21
5958.01	0.84	0.39	0.68	20
5991.61	0.34	0.28	0.55	25
6015.00	0.32	0.19	0.63	12
Average	*1.88*	*0.46*	*0.75*	*28*

[a] PI: S1/(S1 + S2);

[b] HI: S2×100/TOC.

Table 3 Chemical and isotopic composition of the gas samples.

Formation		Chela		Red Cuvo	
Depth (m)		5345.5	5480.0	5686.0	5980.8
Composition of the fluids (In molar fractions (%) and molar ratios)	CO_2	82.85	84.07	82.65	82.15
	H_2S	0.00	0.00	0.00	0.00
	CH_4	15.78	14.23	15.99	16.57
	C_2H_6	0.66	0.60	0.66	0.30
	C_3H_8	0.19	0.16	0.18	0.03
	i-C_4H_{10}	0.03	0.02	0.03	0.00
	n-C_4H_{10}	0.05	0.02	0.05	0.00
	i-C_5H_{12}	0.02	0.01	0.02	0.00
	n-C_5H_{12}	0.01	0.01	0.01	0.00
	CO_2/CH_4	5.25	5.91	5.17	4.96
	$C_1/(C_2 + C_3)$	18.66	18.73	19.01	49.42
	C_2/C_3	3.47	3.74	3.68	9.17
	$\ln(C_1/C_2)$	3.18	3.17	3.19	4.00
	$\ln(C_2/C_3)$	1.24	1.32	1.30	2.22
	Wetness (%) [a]	5.75	5.40	5.63	2.04
$\delta^{13}C$ (‰)	CH_4	-32.00	-32.20	-32.10	-33.60
	C_2H_6	-32.30	-32.20	-32.30	-34.20
	C_3H_8	-27.70	-28.00	-27.80	-32.40
	n-C_4H_{10}	-25.60	-25.60	-25.50	-29.00
	n-C_5H_{12} [b]	*-24.90*	<	*-24.90*	<
	CO_2	-3.90	-4.00	-3.90	-3.90
	$\delta^{13}C_1 - \delta^{13}C_2$	0.30	0.00	0.20	0.60
	$\delta^{13}C_2 - \delta^{13}C_3$	-4.60	-4.20	-4.50	-1.80
δ^2H (‰)	CH_4	-131.00	-132.00	-131.00	-140.00
	C_2H_6	-129.00	-136.00	-133.00	-118.00
Helium	^4He (cm^3 STP/cm^3) [c]	0.99×10^{-4}	1.07×10^{-4}	1.13×10^{-4}	1.44×10^{-4}
	$^3He/^4He$ (R/R_a) [d]	4.60	4.39	4.36	4.65
	$CO_2/^3He$ (mol/mol)	1.32×10^9	1.30×10^9	1.22×10^9	0.89×10^9
	$CH_4/^3He$ (mol/mol)	2.5×10^8	2.2×10^8	2.3×10^8	1.8×10^8

[a] Wetness: $\sum(C_2 - C_5)/\sum(C_1 - C_5)$, %;

[b] Italics: close to detection limits but repeatable; <: under detection limits;

[c] cm^3(STP)/cm^3 = cubic centimeter under standard temperature and pressure (1atm and 15°C) per cubic centimeter;

[d] R/R_a = $^3He/^4He$ of the sample divided by $^3He/^4He$ ratio of the air (1.384×10^{-6}).

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