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Hydrocarbon indication in Rio Bonito Formation sandstone: Implication for CO_2 storage in São Paulo, Brazil

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A B S T R A C T

São Paulo State has witnessed CO_2 storage-based investigations considering the availability of suitable geologic structures and proximity to primary CO_2 source sinks related to bioenergy and carbon capture and storage (BECCS) activities. The current study presents the hydrocarbon viability evaluations and CO_2 storage prospects, focusing on the sandstone units of the Rio Bonito Formation. The objective is to apply petrophysical evaluations with geochemical inputs in predicting future hydrocarbon (gas) production to boost CO_2 storage within the study location. The study used data from eleven wells with associated wireline logs (gamma ray, resistivity, density, neutron, and sonic) to predict potential hydrocarbon accumulation and fluid mobility in the investigated area. Rock samples (shale and carbonate) obtained from depths >200 m within the study location have shown bitumen presence. Organic geochemistry data of the Rio Bonito Formation shale beds suggest they are potential hydrocarbon source rocks and could have contributed to the gas accumulations within the sandstone units. Some drilled well data, e.g., CB-1-SP and TI-1-SP, show hydrocarbon (gas) presence based on the typical resistivity and the combined neutron-density responses at depths up to 3400 m, indicating the possibility of other hydrocarbon members apart from the heavy oil (bitumen) observed from the near-surface rocks samples. From the three-dimensional (3-D) model, the free fluid indicator (FFI) is more significant towards the southwest and southeast of the area with deeper depths of occurrence, indicating portions with reasonable hydrocarbon recovery rates and good prospects for CO_2 injection, circulation and permanent storage. However, future studies based on contemporary datasets are required to establish the hydrocarbon viability further, foster gas production events, and enhance CO_2 storage possibilities within the region.
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1. Introduction

Adapting subsurface reservoir units for CO_2 storage is gaining popularity amongst most scientific publications and events, primarily in organisations biased toward greenhouse gas control measures. The preferences for any chosen geological site for CO_2 storage depend upon a range of geologically-based factors as presented by existing and proven CO_2 storage atlases (e.g., Ketzer et al., 2014; Abraham-A and Tassinari, 2021; CO2CRC Annual Report, 2021; Global CCS Institute, 2021; IEA-GHG Technical Report, 2022). Reservoir depths (usually above 800 m), reservoir thicknesses (above 10 m), good porosity/permeability, reservoir seals/traps/overburden integrities, existing reservoir fluid (hydrocarbon or water) saturation, and hydrocarbon production-related activities form the components of the details in the required factors considered for CO_2 storage in geologic structures. Therefore, the study aims to predict CO_2 storage possibility based on the hydrocarbon indication within the Rio Bonito Formation. It confirms the reservoir properties and confinement required for CO_2 geological storage (Bachu, 2002; Bachu et al., 2007). The objective is to

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propose a hybrid situation involving the injection of supercritical CO_2 to enhance hydrocarbon recoveries (CO_2-EHR) within the reservoir units when further investigations based on newly acquired datasets confirm commercially viable hydrocarbon deposits. Within the Paraná Basin, depending on the reservoir option, other CO_2 storage limiting or enhancing aspects may include thin-bedded layers and igneous intrusions (Abraham-A and Tassinari, 2023).

Depleted hydrocarbon reservoirs are one of the main geological structures suitable for permanent CO_2 storage (Sun and Englezos, 2016; Raza et al., 2018; CO2CRC Annual Report, 2021). The best scenarios for CO_2 storage in depleted fields may be 'hybrid' situations, such as CO_2-EHR or injection into the water leg down-dip of a depleted reservoir (IEA-GHG Technical Report, 2022). The CO_2-EHR option includes supercritical CO_2—based enhanced hydrocarbon production, which involves shutting CO_2 in the reservoir units after it has improved the recovery of the hydrocarbon. Among all the CO_2 storage options, this presents a more economically viable scenario where the processes may not incur further costs. Another expensive CO_2 storage option is dedicated reservoirs delineated purposefully for fluid (CO_2) repositioning. A dedicated CO_2 storage process must engage detailed preliminary geological/geophysical investigations, which is fundamental to deciding whether or not the region meets the standard geological requirements for CO_2 storage (Abraham-A and Tassinari, 2021; 2023). The need for delineating reservoirs dedicated only for CO_2 storage may depend on the amount of the waste CO_2 constantly being released into the atmosphere, proximity to source sinks, availability of depleted hydrocarbon reservoirs, access to oil and gas pipelines, CO_2 injection wells/storage site monitoring potential, and distances away from subsurface aquifers (Abraham-A and Tassinari, 2022). The São Paulo part of the Rio Bonito Formation has no active or past hydrocarbon production events; therefore, detailed geological, geophysical, and geochemical studies are paramount to deciding the CO_2 storage options within the region.

Studies involving fluid identification and differentiation based on neutron-density response are not without uncertainties; however, they have proven dependable in hydrocarbon evaluations (Abraham-A and Taioli, 2019; Abraham-A et al., 2022). Geochemistry-based evaluations have been fundamental in petroleum exploration activities involving hydrocarbon source rocks, generation, maturation, migration, accumulation and composition, among other related subjects. Considering the Paraná Basin, several studies have presented valuable databases indicating organic-rich shales as potential hydrocarbon source rocks (e.g., Milani and Zalán, 1999; Milani et al., 2007; Holanda et al., 2018; Martins et al., 2020; Rocha et al., 2020). Therefore, the study relies primarily on the petrophysical evaluation involving wire-line logs representing higher penetration depths with related geochemical-based analysis to predict possible hydrocarbon production and CO_2 storage prospects. The approach in this study is uncommon within the Rio Bonito Formation. The research results will provide the basis for future hydrocarbon exploration-related studies, preferably with CO_2 storage options.

2. Geology and petroleum systems

The study focuses on the São Paulo State portion of the Paraná Basin. Research results further confirm the Paraná sedimentary basin as a product of the Upper Proterozoic to Early Paleozoic geological evolutions at the end of the Neoproterozoic Brasiliano Orogenic Cycle (Milani, 1997; Zalán et al., 1990; Santos et al., 2006). The Paraná Basin has an extensive sedimentary-magmatic sequence, covering an area above 1,500,000 km^2 and 7000 m in total thickness consisting of Palaeozoic to Mesozoic rock units. The Basin includes six super-sequences; Rio Ivaí (Ordovician-Silurian), Paraná (Devonian), Gondwana I (Carboniferous to Eotriassic), Gondwana II (Medium to Neotriassic), Gondwana III (Neojurassic to Eocretaceous) and Bauru (Neocretaceous), that cover a time interval of 450 Ma to 65 Ma (Milani, 1997). The first three super-sequences (Rio Ivaí, Paraná and Gondwana I) represent transgressive-regressive cycles associated with sea-level oscillation, characteristic of the Paleozoic (Milani, 1997). The other super-sequences (Gondwana II, Gondwana III and Bauru) date from the Mesozoic and are continental sedimentary packages associated with igneous intrusions (Milani, 1997; Milani et al., 1998, 2006, 2007; Milani and Zalán, 1999; Santos et al., 2006).

The Rio Bonito Formation corresponds to the Early Permian age. The focus of this study is the lowermost unit of the Guatá Group, the Gondwana I super-sequence, consisting of a cyclical sedimentary succession of sandstones, siltstones, and shale units with coalbeds. The existing rock units probably emerged during the transition between fluvial, deltaic, lagoonal and shallow marine paleoenvironments (Schneider et al., 1974; Holz et al., 2010; Pereira et al., 2019; Bicca et al., 2020). An erosional surface separates the Rio Bonito Formation from the underlying Itararé Group. On the other hand, a transitional and erosional contact associated with ravinement processes (Lopes et al., 2003; Holz et al., 2002) separates the overlying Palermo and Irati Formation, representing the maximum flooding surface of the Permian transgression (Lavina and Lopes, 1987; Milani et al., 2007).

As part of the Permian transgression, the Rio Bonito Formation is subdivided into three members according to the lithological predominance: Triunfo, Paraguaçu and Siderópolis (Schneider et al., 1974). The Triunfo Member presents evidence of sedimentary rework influenced by a deltaic and tidal context in the first package. The second member, Paraguaçu, shows the marine influence with pelitic packages of considerable thickness. While the third member, Siderópolis, is characterised by lagoon restriction and the development of peat accumulation, which originated in the coal deposits of the Siderópolis Member, Rio Bonito Formation (Schneider et al., 1974; Lavina and Lopes, 1987; Milani et al., 2006).

The hydrocarbon generation and petroleum systems within the Paraná Basin are highly affected by the major Paraná-Etendeka Large Igneous Province (LIP) of the Lower Cretaceous, showcasing basalts of the Serra Geral Formation, with thicknesses up to 1700 m, including several sills and dykes across the Basin (Milani et al., 2007). Related studies (e.g., Milani and Thomaz Filho, 2000; Mohriak, 2014) show concern about the Basin's geologic complexity, correlating the massive interbedded volcanic sequences with the sedimentary units. Its tectonic-stratigraphic evolution encompasses a succession of continental distension, thermal subsidence, and isostatic adjustment processes. The associated deformations must have altered the sedimentary setting, affecting fluid migration, accumulation, and security.

Milani et al. (2007) indicated the Paraná Basin as a non-conventional petroleum-producing basin associated with oil shale production with two petroleum systems.

(i) the Carboniferous-Devonian Ponta Grossa/Rio Bonito Itararé System and
(ii) the Permian-Triassic Irati-Rio Bonito System.

The Irati-Rio Bonito-Pirambóia petroleum system, which interests this study, was identified as a proven petroleum system (Araújo et al., 2000a,b). The organic-rich shale of the Irati Formation represents the hydrocarbon source rock, the Palermo Formation is portrayed as the caprock, and the Rio Bonito sandstone is the potential reservoir rock. The current study focuses on the sandstone units of the Rio Bonito Formation as potential reservoirs for CO_2 geological storage. Geochemical analysis involving the

Pirambóia Formation tar sands shows similarities to those extracted from the Irati Formation shales, suggesting the shales are the source rocks (Quadros, 1982; Cabral, 2006). A couple of research results presented that the fluvial and eolian sandstones bitumen of the Pirambóia Formation lower portions results from oil that was expelled and migrated from the Assistência Member of the Irati Formation shales (e.g., Araújo, 2001; Cabral, 2006; Thomaz Filho et al., 2008; Mateus et al., 2014).

3. Materials and method

Hydrocarbon production bolsters CO_2 storage options by reducing operational costs considering existing oil/gas pipelines, in most cases, to transport captured CO_2 to the storage sites and already delineated geologic structures, amongst others. The research engaged wire-line log data of 11 wells, including gamma ray, resistivity, density, and sonic signatures, representing the physical properties of the sandstone, siltstone and shale units of the Rio Bonito Formation. The sandstone units dominate the Rio Bonito Formation; therefore, they are explored as potential hydrocarbon reservoirs to predict future hydrocarbon production to boost the CO_2 storage prospect of the region. The research methodology also includes the compilation and analysis of organic geochemistry data (e.g., TOC and Rock-Eval pyrolysis) from the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP) database.

The research focuses on evaluating the hydrocarbon viability of the Rio Bonito Formation and predicting the CO_2 storage prospect of the region. Primarily, the objectives of the study include petrophysics-based evaluations involving probable hydrocarbon-bearing zone identification focusing on the sandstone units considering gamma ray, resistivity, density, neutron, and sonic logs responses. It also involves three-dimensional (3-D) modelling of the free fluid index (FFI) based on the sandstone units to predict fluid transmissibility concerning hydrocarbon production (fluid recovery factor), and CO_2 injection rates within the Rio Bonito Formation. The study also features geochemical-based hydrocarbon indices by involving twenty (20) samples of the Rio Bonito Formation shale obtained from some of the wells (e.g. MA-1-SP, SA-1-SP, TI-1-SP, AR-1-SP, and PP-1-SP). Other value-added hydrocarbon indices data include rock samples from research-based fieldwork, showcasing the availability of hydrocarbon contents on the shale and carbonate rock surfaces.

3.1. Hydrocarbon indices

The study engages petrophysical- and geochemical-based inputs in predicting the hydrocarbon viability to foresee the CO_2 storage prospect of the concerned region. The evaluated wire-line logs in the wells include gamma ray, resistivity (dual induction and short regular), neutron, density and sonic logs. Resistivity and gamma-ray records are fundamentals in identifying lithologic units and delineating hydrocarbon zone. The gamma ray log calibration is from 0 to 150 in API units. The wire-line logs showcase multi-layered rock units (sandstones, siltstones and shales). Radioactive contents should decrease from shales to siltstones and sandstones. Therefore, based on the Rio Bonito Formation, a low gamma-ray response is taken as sandstones, moderate reactions represent siltstones, and high responses correspond to shale units. The resistivity tools (Deep Induction and Short Normal), calibrated from 0.2 to 2000 in ohm-metre, indicate hydrocarbon (usually oil and gas) presence when they show a high response within the reservoirs. Low resistivity response may represent water-filled reservoirs in water-saturated zones.

In this study, the neutron porosity (w/w) increasing from right to left and density (g/cm^3) increasing from left to right aided gas zone identification within the hydrocarbon-bearing units. Depending on the calibration, within the hydrocarbon-bearing zones, minimum deflections of the logs are characterised by neutron signatures crossing to the right and density signatures to the left, creating a considerable separation indicating gas zones. The fundamental petrophysical-based parameters derived from the wire-line logs include porosity (Φ) and irreducible water saturation (S_{wirr}). They are essential in predicting the physical properties and estimating the fluid transmissibility of reservoirs. Therefore, Φ is calculated based on the averaged density and sonic porosity within each sandstone unit; this way, the values obtained are not from a single Φ tool, and uncertainties concerning Φ and other dependent parameters are presumably reduced (Abraham-A and Tassinari, 2021).

Hence;

$$\Phi_{average} = \frac{\Phi_S + \Phi_D}{2} \tag{1}$$

Where Φ_S is sonic-derived porosity and Φ_D is density-derived porosity. Fluid (water, oil or gas) in the pore space, which can flow under normal reservoir conditions during production or injection, is called free fluid (Schlumberger, 1989; Schlumberger Energy Glossary, 2022). Therefore, the phenomenon applies to predicting fluid production (e.g., primary hydrocarbon recoveries) and injection rates (e.g., CO_2 storage). Abraham-A and Taoili (2019) showcased a simplified expression for free fluid index (FFI) in sandstone reservoirs considering some intrinsic parameters as equation (2):

$$FFI = \Phi - 0.02 \tag{2}$$

Where 0.02 is an approximated constant, a function of the reservoir intrinsic parameters such as cementation exponent (a), tortuosity factor (a) and S_{wirr} (Abraham-A and Taoili, 2019).

Therefore, the study presents a 3-D geological model showing the FFI distribution across the study location by interpolating the FFI data inside the Rio Bonito Formation domain (3-D solid) to permit a spatial analysis. Related models (e.g. de Oliveira et al., 2021) have been applied considering other objectives within the Paraná Basin; however, using the model to represent the fluid recovery rates, transmissibility, and injection rates is new.

There are also petrographic evaluations from existing studies indicating the bitumen-bearing sandstone of the Paraná Basin (Maraschin et al., 2019) to further buttress the hydrocarbon viability of the region. Furthermore, physically identified rock samples from research-based field activities and hydrocarbon-related studies (e.g., White, 1908; Weniger et al., 2010; Kalkreuth et al., 2013; da Costa et al., 2014; Bicca et al., 2020; Rocha et al., 2020; Tassinari et al., 2021) have stated the hydrocarbon presence in the Paraná Basin. The parameters from these evaluations serve as value-added inputs indicating the hydrocarbon viability of the Rio Bonito Formation.

4. Results

The research presents petrophysics-based models in the form of suites of wire-line logs with the appropriate signatures representing the properties of the rock units within the Rio Bonito Formation. It indicates the hydrocarbon presence and free fluid index (FFI). The evaluation showcases an FFI-based 3-D geological model derived from parameters generated from the eleven wells representing the sandstone units. The study also highlights some value-added geochemical- and petrographic-based evaluations to bolster the study objectives.

4.1. Petrophysics-based hydrocarbon indices

The effectiveness of the wire-line logs in formation evaluation has been gainfully productive in hydrocarbon-related studies. Therefore, eleven (11) drilled wells were engaged, representing São Paulo State within the extension of the Paraná Basin (Fig. 1). Although the wells are not at regular intervals across the field, they reveal the section of the Rio Bonito Formation significant enough to predict the reservoir parameters required to meet the research objectives.

Well PA-1-SP (Fig. 2) with the Rio Bonito Formation sandstone delineated between 700 m and 740 m shows hydrocarbon (mostly gas) indication; however, the depth of occurrence may increase the uncertainty concerning the hydrocarbon-in-place. The available data are old, dating from the 1960s to the 1980s. Therefore, unless further studies based on newly acquired wire-line logs and 3-D/4-D seismic interpretations confirm the hydrocarbon viability of the reservoir, the gas presence in well PA-1-SP may remain questionable. However, gas accumulation at such depths is not entirely impossible. Suppose reasonable thicknesses of low permeability units (e.g., shales) of the overlaying Palermo Formation, as indicated at the top of Rio Bonito Formation in well PA-1-SP, are available to provide the required overburden with other seal configurations to secure the gas in place. In that case, the sandstone will offer a prominent reservoir system.

In well TI-1-SP (Fig. 3), the Rio Bonito Formation is below 3315 m. Zones with hydrocarbon indication have a maximum thickness of 15 m in the middle. The top of Rio Bonito Formation in well TI-1-SP, between 3315 m and 3335 m (about 20 m thick), has sandstone units interlayered with siltstone beds and shows gas indication. There is also a similar instance at the bottom of the Formation in well measuring up to 11 m thick.

The Rio Bonito Formation is below 1029 m in well MA-1-SP (Fig. 4) with visible gas indication based on the neutron-density response. The thickness of the hydrocarbon-bearing units (mostly the sandstone layers) is up to 10 m. Also, in C.B.-1-SP (Fig. 5), the Rio Bonito Formation's top is at a depth of 3480 m, with a gas indication at about 3520 m. The delineated gas zone is about 11 m thick.

4.1.1. Fluid mobility and recovery indices

The primary hydrocarbon recovery rate, which depends on the fluid ability to move freely within the reservoir unit, is a function of the FFI (Nzekwu and Abraham-A, 2020; Abraham-A et al., 2022). Therefore, the ability of the injected fluid (e.g., CO_2) in the underground geologic units to circulate freely can also relate to FFI. Hence, portions of the field with significant values for FFI indicate reservoirs with reasonable hydrocarbon recovery and CO_2 injection rates. The 3-D model (Fig. 6) represents the FFI distribution across the sandstone reservoir within the Rio Bonito Formation in São Paulo.

4.2. Physically observed hydrocarbon indices

Within the southwestern São Paulo State, there are no current petroleum-producing events. Therefore, the hydrocarbon indication of the areas is best described by the available wire-line logs presented in the previous section and the physical identification of hydrocarbon (bitumen) traces involving accessible rock units. Furthermore, a related study associated with the concerned location has indicated the bitumen-rich sandstone outcrop, showcasing the hydrocarbon potential of the region (Maraschin et al., 019).

Similar instances involving samples collected at a depth less than 200 m from a mining site at Piracicaba in São Paulo State also show the physical present of bitumen within the Irati Formation of

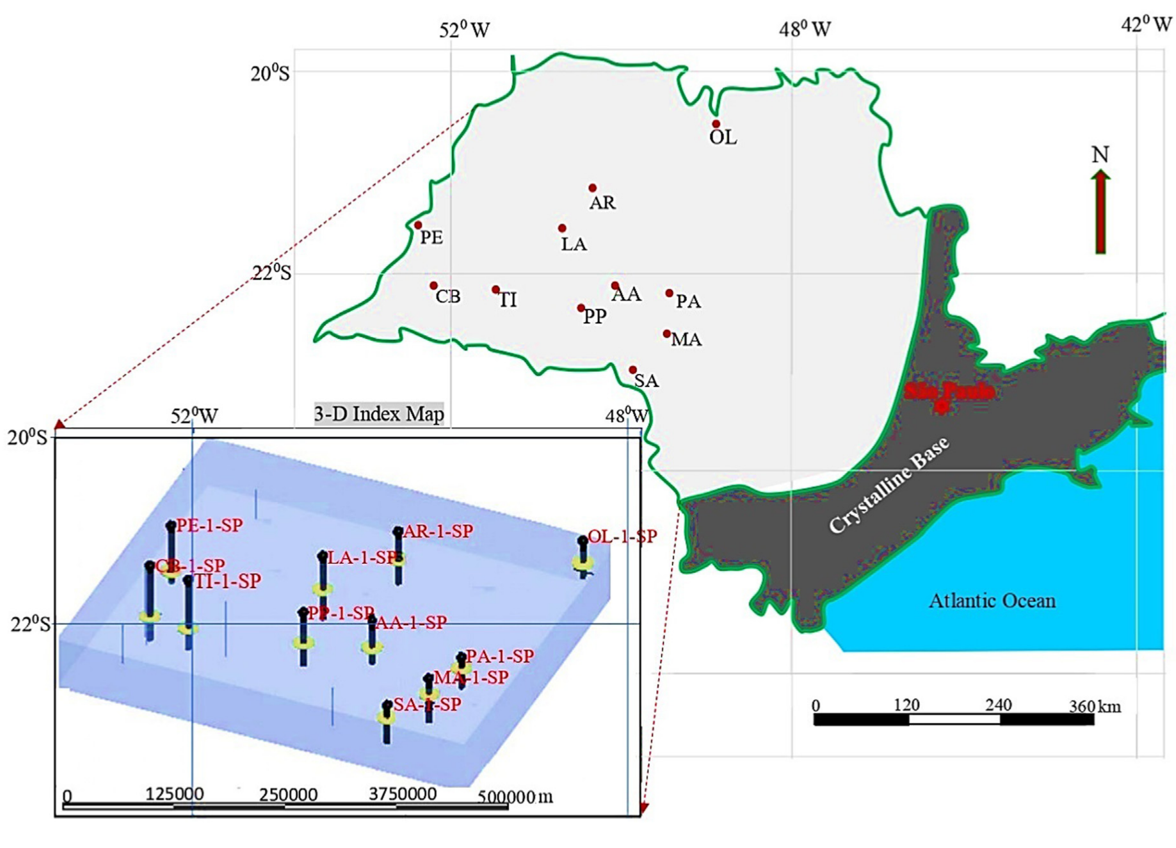

Fig. 1. Study location with the 3-D index map of the well points.

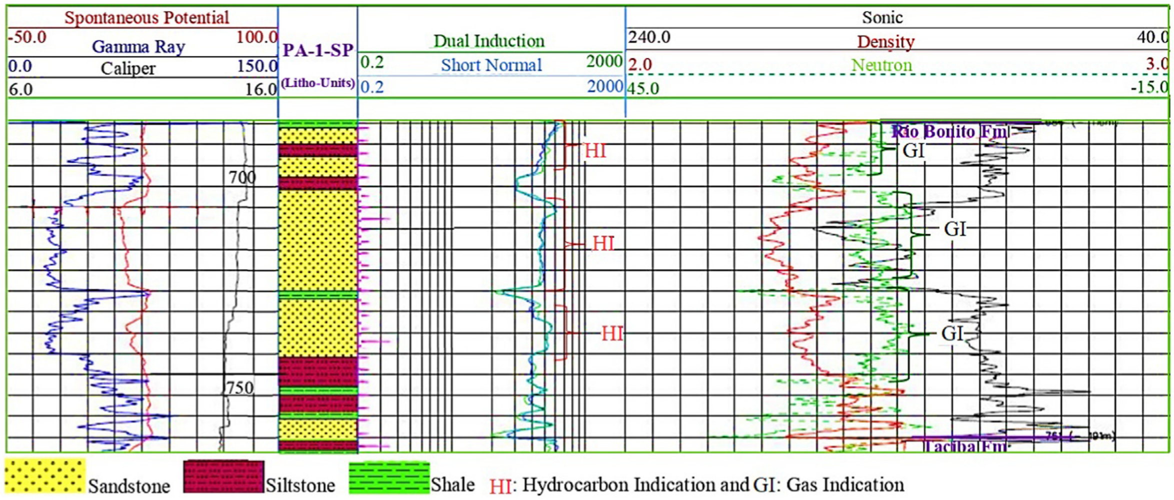

Fig. 2. Gas indication below 705 m

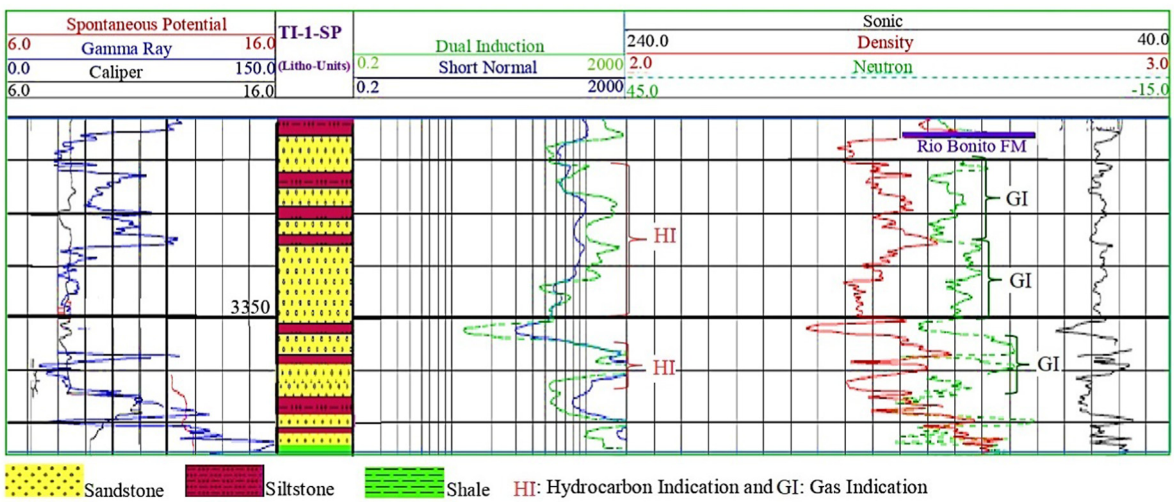

Fig. 3. Hydrocarbon indication below 3315 m

the Paraná Basin (Fig. 7), indicating the hydrocarbon viability of the area. Therefore, there are possibilities for lighter/less dense crude oil or gas at higher penetration depths. Schlumberger Energy Glossary (2022) defines bitumen as naturally occurring, flammable organic matter formed from kerogen during petroleum generation.

Similarly, petroleum is a complex mixture of naturally occurring hydrocarbon compounds, ranging from solid to gas; however, the term generally refers to liquid crude oil. Furthermore, previous studies indicated that the bitumen in the associated sandstones of the lower part of the Pirambóia Formation resulted from crude oil, which was expelled and migrated from the Assistência Member of the Irati Formation shales (e.g., Araújo et al., 2001; Thomaz Filho et al., 2008; Mateus et al., 2014). Therefore, the presence of bitumen may indicate the availability of other hydrocarbon members within and around any geological basin.

4.3. Geochemical-based hydrocarbon indices

The Paraná basin consists of organic-rich shales among its associated geological units (e.g., the Irati and Rio Bonito Formations). Shales are associated with oil deposits and source rocks worldwide (EIA-ARI, 2013). Previous research has referred to the Permian Irati Formation organic-rich shales as potential hydrocarbon source rocks (Cerqueira and Santos Neto, 1986; Milani and Zalán, 1999; Milani et al., 2007; Euzébio et al., 2016; Holanda et al., 2018; Martins et al., 2020; Rocha et al., 2020). Abraham-A and Tassinari (2021) calculated up to 11.2% with an average value of 8.8% for the total organic content (TOC) of the Paraná Basin shale within São Paulo using density log inputs in a modified expression (Schmoker, 1993; Godec et al., 2013). Similarly, according to Rocha (2021), the Irati Formation shales have TOC values ranging between 4.42 % and 9.64 %, and are known for hydrogen index (HI) mostly above 600 mg HC/g of TOC and high hydrocarbon generating potential with S_2 peak values up to 130.33 mg HC/g of rock. Therefore, these parameters show the Irati shales as excellent potential hydrocarbon source rocks, predominantly oil-prone (type I-II kerogen).

The hydrocarbon indication in the Rio Bonito Formation sandstones reported in this study is probably attributed to the Irati-Rio Bonito-Pirambóia petroleum system (Araújo et al., 2000a,b, 2001). However, due to the broad occurrence of organic-rich lithologies

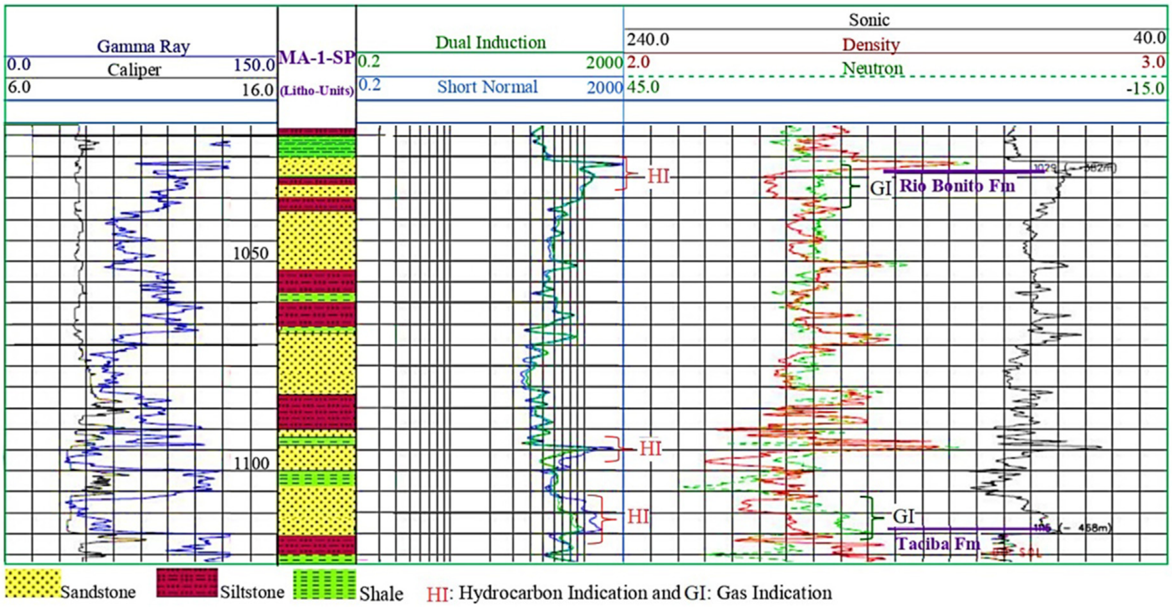

Fig. 4. Hydrocarbon indication below 1029 m

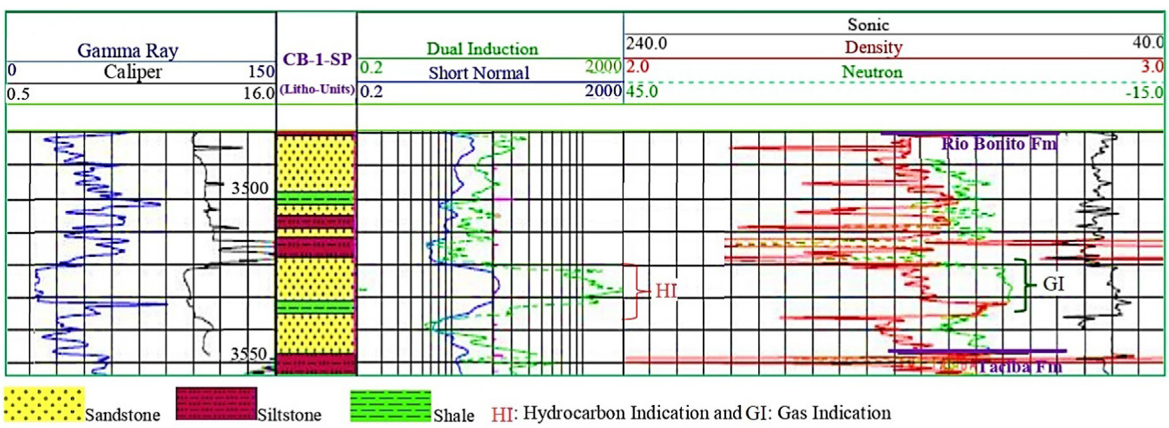

Fig. 5. Gas indication below 3520 m

within the Rio Bonito Formation (e.g., shale and coalbeds), it could act as hydrocarbon source rocks due to the oil- and gas-window thermal maturities reached across the Paraná Basin (Kalkreuth et al., 2003, 2006, 2010, 2013; Weniger et al., 2010; Bicca et al., 2020). The heterogeneity in thermal maturity, characteristic of the Paraná Basin organic-rich beds, resulted from the thermal effect of igneous intrusions from the Paraná-Etendeka LIP. The intrusion was one of the most significant magmatic events in the Phanerozoic, preceding the breakup of the southern Gondwana and the opening of the South Atlantic Ocean (Melfi et al., 1988; Leonard et al., 2018).

Organic geochemistry data from 5 wells (MA-1-SP, SA-1-SP, TI-1-SP, AR-1-SP, and PP-1-SP) located in the southwestern part of São Paulo State (the same wells analysed for the petrophysics-based hydrocarbon indices in section 4.1), is presented in Table 1. The total organic carbon content (TOC) of 21 analysed samples from various depths (between 792 m and 3513 m) ranges from 0.11% to 1.07%, with an average of 0.62%, characterising the shale of Rio Bonito Formation as potential hydrocarbon source rocks. Regarding Rock-Eval pyrolysis data, hydrogen index (HI) values range between 11 mg HC/g TOC and 310 mg HC/g TOC of the rock, with an average value of 133.6 mg HC/g. In contrast, oxygen index (OI) values range from 9 mg CO_2/g TOC to 107 mg CO_2/g TOC (average 34 mg CO_2/g TOC). T_{max} values range from 427 °C to 440 °C (average 432 °C).

OI versus HI data applied to the modified van Krevelan Diagram suggests a prevailing type II-III kerogen (Fig. 8A) in shale samples from the Rio Bonito Formation. T_{max} values indicate a mature (oil window) stage for most samples. Samples were collected at similar depths; however, wells MA-1-SP and SA-1-AP present different maturation patterns, showing that the events are unrelated to the depth and thermal subsidence of the Basin. The explanation for this could probably be that heat changes affected the thermal maturity of the Rio Bonito shale due to the igneous intrusions from the Paraná-Etendeka LIP, which accounts for the heterogeneity and lack of positive correlations between thermal maturity and depth (Fig. 8B). Overall, the organic geochemistry data indicate that the Rio Bonito Formation shale beds are potentially hydrocarbon source rocks and could have contributed to the hydrocarbon indication in the Rio Bonito Formation sandstones reported in this study.

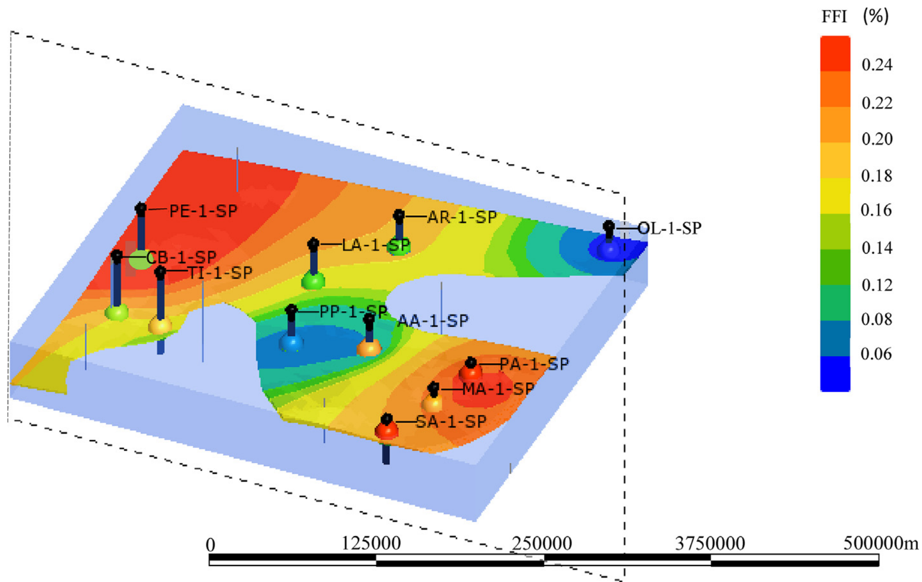

Fig. 6. 3-D model representing the sandstone reservoir free fluid index (FFI).

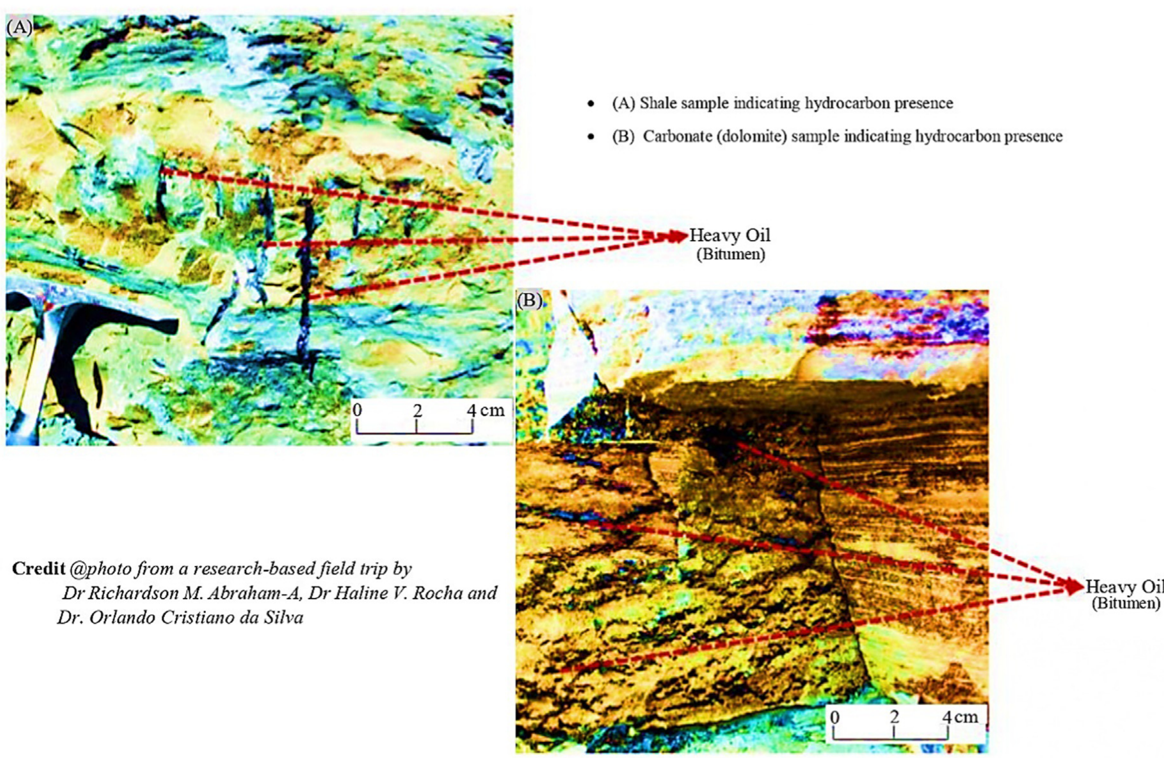

Fig. 7. (A) Shale sample with bitumen indication from a mining site in Piracicaba, southwest Sao Paulo. It corresponds to the Irati Formation, whose shale is tagged as the potential hydrocarbon source rocks of the Parana Basin. It indicates porosity (Φ) and permeability (K) distribution in shales based on the fluid flow pattern on the sample. (B) Bitumen-bearing carbonate (dolomite) sample also from the mining site in Piracicaba, corresponding to the Irati Formation. The rock sample indicates porosity (Φ) and permeability (K) distribution in carbonate rocks of the study location, considering the pattern of fluid seepages from the rock surface.

4.4. Uncertainties

The wire-line log data, in Portable Document Format (PDF), are up to six decades old. Some of the logs, mostly the resistivity signatures, appear unreliable, especially within the areas (e.g. Irati Formation) invaded by the associated igneous rock of the Paraná Basin, as presented by Abraham-A and Tassinari (2021). Therefore, such portions require some editing, following the usual log-log calibration within the affected rock units to interpret the physical properties of the reservoirs. Porosity (Φ) estimation, which is fundamental to predicting the free fluid index (FFI), was estimated using the averaged value of sonic-derived and density-derived Φ to reduce the uncertainty. The referred hydrocarbon indices based on rock samples collected from the mining site represent near-surface

Table 1
TOC and Rock-Eval pyrolysis data of Rio Bonito Formation shale samples from Paraná Basin within the southwestern part of São Paulo state.

Well ID	Depth (m)	TOC (wt%)	S_1 (mg HC/g rock)	S_2 (mg HC/g rock)	S_3 mg CO_2/g rock	HI (mg HC/g TOC)	OI (mg CO_2/g TOC)	T_{max} (°C)
MA-1-SP	**966**	**0.98**	**0.11**	**2.7**		**275.5102**		**427**
MA-1-SP	**1002**	**0.87**	**0.69**	**2.58**		**296.5517**		**432**
SA-1-SP	**792**	**0.6**	**0.11**	**1.06**	**0.17**	**176.6667**	**28.33333**	**430**
SA-1-SP	**795**	**0.7**	**0.11**	**2.17**	**0.13**	**310**	**18.57143**	**433**
SA-1-SP	**798**	**0.7**	**0.06**	**1.84**	**0.18**	**262.8572**	**25.71429**	**434**
SA-1-SP	**801**	**0.6**	**0.17**	**1.77**	**0.19**	**295**	**31.66667**	**429**
SA-1-SP	**804**	**0.6**	**0.09**	**1.06**	**0.07**	**176.6667**	**11.66667**	**434**
TI-1-SP	**3372**	**0.62**	**0.09**	**0.07**		**11.29032**		
TI-1-SP	**3462**	**0.47**	**0.32**	**0.1**	**0.41**	**21.2766**	**87.23405**	
TI-1-SP	**3471**	**0.55**	**0.7**	**0.73**	**0.41**	**132.7273**	**74.54546**	**440**
TI-1-SP	**3492**	**0.21**	**0.04**	**0.04**	**0.04**	**19.04762**	**19.04762**	
TI-1-SP	**3513**	**0.22**	**0.1**	**0.05**	**0.02**	**22.72727**	**9.09091**	
AR-1-SP	**1836**	**0.87**	**1.64**		**0.25**		**28.73563**	
AR-1-SP	**1842**	**1.07**	**1.81**		**0.28**		**26.16822**	
AR-1-SP	**1845**	**0.73**	**0.87**		**0.42**		**57.53424**	
AR-1-SP	**1848**	**0.95**	**0.32**		**0.1**		**10.52632**	
AR-1-SP	**1851**	**0.96**	**0.39**	**0.47**		**48.95834**		
AR-1-SP	**1881**	**0.9**	**0.31**	**0.39**	**0.15**	**43.33333**	**16.66667**	
AR-1-SP	**1944**	**0.27**	**0.08**	**0.03**	**0.29**	**11.11111**	**107.4074**	
PP-1-SP	**2115**	**0.79**	**0.58**	**0.27**	**0.17**	**34.17722**	**21.51899**	

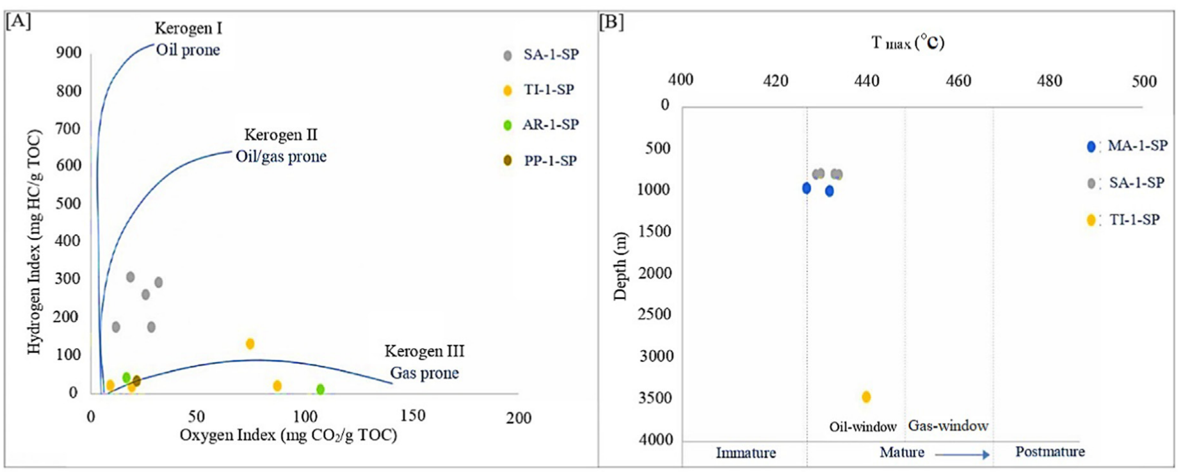

Fig. 8. (A): A cross-plot showing a prevailing type II-III kerogen for the Rio Bonito Formation's shale samples in the southwestern part of São Paulo State. (B): A cross-plot of maximum pyrolysis temperature (T_{max}) and depth, demonstrating the thermal maturity of the samples.

depths within the study location. Arguably, bitumen in the surface or near-surface rocks may not necessarily point to the presence of other hydrocarbon members at higher depths; however, the neutron-density response confirming gas presence at higher penetration depths (e.g. TI-1-SP and CB-1-SP) is noteworthy. The geochemical data were also taken from old PDF archives and some existing related studies; therefore, there are likely some uncertainties associated with the interpretations.

Further studies based on newly acquired datasets are required to verify the physical parameters of presented reservoirs and to establish the availability (or otherwise) of other hydrocarbon members within São Paulo. Furthermore, it will also reduce the uncertainty and risk involving the CO_2 storage reservoir options in the study location. Some of the wire-line logs, such as PE-1-SP and OL-1-SP, do not have the density log; therefore, it was impossible to identify possible gas zones in all the well locations in the field.

5. Discussions

The petrophysics-based evaluation indicates hydrocarbon-bearing (mostly gas-bearing) reservoirs in the study location. Apart from well PA-1-SP, where the Rio Bonito Formation appears at a depth of about 700 m with gas indication, other wells (e.g., MA-1-SP, TI-A-SP and CB-1-SP) show the sandstone units of the Rio Bonito at far greater depths up to 3500 m and above. The gas indication in well PA-1-SP is unavoidably noticeable based on the usual neutron log interaction with the associated density log. However, concerning the trapped fluid's security, the reservoir's depth of occurrence (700 m) seems questionable. In another school of thought, the well (PA-1-SP) shows siltstone units and a shale bed extending from the upper Palermo Formation overlaying the sandstone beds (gas reservoirs), indicating potential overburden units or cap rocks. Therefore, regardless of the reservoir depth, it seems to have the configurations to trap and secure the detected gas.

Furthermore, the associated igneous intrusions of the Paraná LIP will also play a significant role in fluid migration, accumulation and entrapment within the geologic units. Therefore, at a depth of 700 m with very low porosity and permeability overlying rock and other factors favouring fluid security, gas accumulation is possible, as indicated. However, depths (less than 800 m) are not suitable for CO_2 storage based on recommended best practices (Chadwick et al., 2008; IEA-GHG et al., 2009; Smith et al., 2011, Miocic et al., 2016; de Oliveira et al., 2021; Abraham-A and Tassinari, 2021). On the other hand, wells TI-1-SP and CB-1-SP with gas indications at depths greater than 3200 m are excellent pointers to viable hydrocarbon units within the Rio Bonito Formation. Furthermore, organic geochemistry data based on the Rio Bonito Formation point to the shale beds as potential hydrocarbon source rocks. The petrophysical- and geochemical-based hydrocarbon indices collectively show that the Rio Bonito Formation configures a petroleum system (e.g., source rocks, reservoirs and caprock) in the southwestern part of São Paulo State, Paraná Basin. Therefore, more wells with modern databases acquired around this region are fundamental to explicitly define the hydrocarbon potentials of the sandstone unit and encourage future CO_2 storage.

The 3-D model represents FFI distribution considering the sandstone units of the study locations. From the model, wells AA-1-SP, PP-1-SP and OL-1-SP are in portions with low FFI, indicating low hydrocarbon recovery factor and, by extension, low fluid transmissibility and injection with circulation rates. Conversely, FFI, up to 25% as recorded for some parts of the study location, is significant, indicating a reservoir with potential for substantial fluid recovery with good injection and circulation rates. Therefore, when future study confirms economically viable hydrocarbon-bearing strata within the field, it has high prospects for hydrocarbon recovery with reasonable CO_2 storage injection rates. However, when future evaluations reveal insignificant recoverable hydrocarbon reserves, the area will support effective fluid injection rates if it is engaged purposely as a dedicated CO_2 storage unit. In Rio Bonito Formation sandstones, the multiphase flow (e.g., CO_2, CH_4 and H_2O) and rock-fluid interaction properties in the porous media, considering hydrocarbon occurrence, either in economically viable reserves or otherwise, must be studied. Previous studies (e.g., Bandilla and Celia, 2019) indicate the alteration in rock wettability during CO_2 sequestration due to carbonic acid (H_2CO_3) formation, which leads to lower pH in the system and, consequently, could change the reservoir permeability by mineral dissolution. Furthermore, the multiphase flow has implications on capillary pressure and relative permeability.

Besides well PP-1-SP, which reveals the Rio Bonito Formation at a depths greater than 800 m, others show the geologic units of the study location at depths generally ranging between less than 800 m and up to 3550 m. Therefore, future evaluation involving potential reservoir volume estimation for CO_2 storage must consider portions deeper than 800 m near well PP-1-SP in predicting the fluid storage efficiency factor (E_a), which is the fractional reduction in area useable for CO_2 storage considering depths and other associated parameters. After all, considering the evaluated parameters, Rio Bonito Formation presents potential geologic (mainly sandstone) units capable of accumulating hydrocarbon (gas), whose production will enhance CO_2 storage options within the region. Furthermore, the potential for CO_2 storage with (or without) hydrocarbon production options abounds in the study location, considering the free fluid index (FFI) estimated for the sandstone units, depth of reservoir occurrence, and proximity to CO_2 source sinks.

6. Conclusion

The study presents the hydrocarbon indication of the Rio Bonito Formation sandstone and its implications for CO_2 storage. Wire-line logs (neutron and density) aided in identifying probable gas zones. Bitumen-bearing rock samples from the surface (outcrop) and near-surface collected from a mining site at depths of about 200 m were consulted and contributred to predicting the hydrocarbon viability of the region . Furthermore, references involving petrographic-based evaluations also point to the presence of bitumen, which may imply the presence of other hydrocarbon members at more significant depths. The presented geochemical-based indices suggested the organic-rich shales of the region as viable hydrocarbon source rocks. The petrophysics-based evaluation points to other hydrocarbon members (mainly gas) at higher penetration depths within the Rio Bonito Formation. The 3-D model aided in identifying portions with higher prospects for fluid (CO_2) injection and transmission. Overall, the deduction from this study are as follows:

a) The sandstones of the Rio Bonito Formation within the São Paulo State are potential hydrocarbon (mainly gas) reservoirs, and shale beds are potential hydrocarbon source rocks;
b) Further study involving seismic methods with newly acquired data sets based on modern tools and approaches is pertinent to further confirm the reservoirs' gas viabilities and boost production events with the CO_2 storage option;
c) Future studies should also ensure that all the wells contain the required wire-line logs (neutron and density log) to aid fluid identification/differentiation and also include multiphase flow and rock-fluid interaction in the porous media, considering the presence of CO_2, hydrocarbon and water, especially in portions where the gas reservoirs are not commercially viable;
d) The reservoirs portray good prospects for gas recovery with fluid (e.g. CO_2) injection and circulation, considering the values computed for FFI;
e) The study will be a reference for future research by providing input data based on the evaluated parameters for related findings involving hydrocarbon exploration and CO_2 storage within the region.

CRediT authorship contribution statement

Richardson M Abraham-A: Conceptualisation, Investigation, Formal analysis, Writing − original draft. **Haline V. Rocha:** Formal analysis, Writing − review & editing. **Saulo B de Oliveira:** Formal analysis, **Colombo C.C.G. Tassinari:** Resources. **Orlando C da Silva:** Resources.

Declaration of competing interest

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

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