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Reservoir quality evaluation as a measure to forecast hydrocarbon and CO_2 storage prospects in Irati and Rio Bonito Formations, Paraná Basin

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ABSTRACT

Enhanced hydrocarbon recovery processes coupled with CO_2 storage are, by far, the cheapest carbon capture and storage (CCS) options in geological structures. However, reservoirs are also being explored for CO_2 storage in regions without producing/depleted hydrocarbon reservoirs, such as the Irati and Rio Bonito Formations in the southwestern part of São Paulo. Therefore, the study involves petrophysics-based flow unit factors to predict the reservoirs' quality, primarily focusing on hydrocarbon viability with CO_2 storage possibilities based on the shale, carbonate, sandstone and siltstone rock units. The methodology involving the models for the research objective is uncommon for the Irati and Rio Bonito Formations. The porosity range is 0.02 to 0.15 in shales, 0.028 to 0.18 in siltstones, 0.03 to 0.21 in carbonates, and 0.10 to 0.31 in sandstones based on the sonic-density porosity ($\Phi_{S\text{-}D}$) approach. Permeability (k) is 0.00005mD to 36.6mD in shales, 0.0008mD to 132mD in siltstones, 0.025mD to 786mD in carbonates and 8mD to 10000mD in sandstones. The results show more significant fluid transmission indices for the sandstone based on Φ, k, free fluid index-FFI, reservoir quality index-RQI, and flow zone indicator-FZI. Also, the parameters are considerably significant for carbonates in some instances, less effective for siltstone and comparatively insignificant for shale. However, shales` total organic content (TOC) values are up to 10.5%, suggesting their hydrocarbon generation potentials. Significant values (e.g., $\Phi \geq 25\%$ and FFI $\geq 20\%$) in sandstones indicate reservoirs with the potential for hydrocarbon accumulation. Considerable physical qualities, as presented for the sandstone, suggest reservoir rock units with reasonable fluid (e.g., gas) recovery and CO_2 injection rates. Therefore, based on the research results, the Irati Formation shales are viable hydrocarbon source rocks, and the Rio Bonito Formation sandstones are potential hydrocarbon reservoirs. Subsequently, future hydrocarbon production events will enhance CO_2 storage options in the region. Furthermore, the research results may serve as input data in related hydrocarbon exploration studies. However, if further research indicates non-commercially viable hydrocarbon reserves, the findings will also aid in delineating dedicated geological reservoirs for CO_2 storage when needed.

1. Introduction

The carbon capture and storage (CCS) industry emerged from enhanced oil recovery (EOR) practices. CO_2 injected for EOR is permanently trapped in the pore space that previously held the oil. Famous hydrocarbons-bearing rocks include shales (e.g., Blaizot, 2017; Feng et al., 2021), sandstones (e.g., Abraham-A and Taoili, 2019, 2020; Abraham-A et al., 2022; Abraham-A et al., 2023a) and carbonates (e.g., Kargarpour, 2020; Chen et al., 2021). The conditions enabling hydrocarbon accumulation in the reservoir rocks in situ are similar to those controlling the ability to inject and store CO_2 permanently in the geologic structures. Therefore, hydrocarbon exploration methods are also suitable for CO_2 storage reservoirs delineation. Some studies (e.g., Abraham-A and Tassinari, 2019; Abraham-A and Tassinari, 2021; de Oliveira et al., 2021; Abraham-A and Tassinari, 2023; Abraham-A et al., 2023b) indicate the Parana Basin's Irati Formation as a potential CO_2 storage site. Research findings have also referred to the hydrocarbon potentials of the Irati Formation's shales as viable hydrocarbon source rocks (e.g., Santos et al., 2006; Milani et al., 2007; Rocha et al., 2020; Tassinari et al., 2021) and Rio Bonito Formation's sandstones as feasible

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gas reservoirs (Abraham-A et al., 2023a; 2023b).

Currently, the study location has no producing or depleted hydrocarbon reservoirs. Adapting reservoir units associated with hydrocarbon production for CO_2 storage reduces cost, considering enhanced oil recovery procedures involving CO_2, exhausted hydrocarbon reservoirs, and, in most cases, the availability of oil and gas pipelines to ease transportation of the captured CO_2 from source sinks to storage sites. Several presentations (e.g., Steven et al., 2010; Pearce et al., 2011; Gabriela et al., 2013) have emphasised the benefits of adapting depleted and enhanced oil-recovery-driven reservoirs for CO_2 storage. Nonetheless, exploring non-hydrocarbon reservoir units for CO_2 storage is also gaining popularity (The Global CCS Institute Report, 2021; Abraham-A and Tassinari, 2021; de Oliveira et al., 2021). The Global CCS Institute (2020) reported some CO_2 storage sites worldwide that are fully operational, and others still developing or under evaluation. The report shows that the functioning CO_2 storage sites are predominantly enhanced oil recovery (EOR)-based, while most reservoirs still developing are dedicated CO_2 storage sites. In the Global CCS Institute Report (2021), far more dedicated CO_2 storage reservoir units are under development than EOR-based alternatives. The Global CCS Institute (2022) reported that most future storage would not be associated with EOR. Operational and developing dedicated geological reservoirs for CO_2 storage worldwide have increased from 31 to 82 between 2020 and 2021, and 82 to 114 between 2021 and 2022 (The Global CCS Institute Report, 2020; 2021; 2022). Although harnessing geological structures mainly for CO_2 storage comes with cost implications; however, the urgent call for CCS-related events to mitigate global warming seems to have overwhelmed the concerns about the cost. Therefore, this study aims at predicting the hydraulic unit of the Irati and Rio Bonito Formations to forecast the hydrocarbon viability and CO_2 storage potentials of the reservoirs. The results may also be applicable in delineating suitable portions for CO_2 storage considering dedicated CO_2 repositories if future studies indicate non-viable hydrocarbon reservoirs.

São Paulo has the highest population in Brazil, and it is heavily industrialised with significant carbon dioxide emissions, majorly attributed to production from the biomass and energy sectors. The state has the highest percentages of waste CO_2 via its various activities. 25.8% of domestic carbon dioxide emissions and 31.4% of CO_2 acquisition via importation activities come from São Paulo (Imori and Guilhoto, 2016). The Irati Formation consists of varying proportions of shales, carbonates (limestone and dolomite), and siltstones. The Rio Bonito Formation consists mainly of sandstone layers with siltstone and shale. Locating potential hydrocarbon reservoir units within the Irati and Rio Bonito Formations close to the CO_2 emitting sources will boost the CO_2 storage activities. Considering CO_2-based enhanced hydrocarbon recovery approaches, shale gas production will encourage CO_2 injection events. Future CCS-related events can also engage the evaluated parameter as inputs in delineating dedicated underground reservoirs for CO_2 storage if further studies indicate non-viable hydrocarbon units within the region.

The study applies petrophysical models to evaluate the reservoir quality while relating the results to hydrocarbon potentials and CCS. Petrophysics has been a proven geophysical method for various studies with diverse objectives (e.g., Zhong et al., 2017; Abraham-A and Taioli, 2017; Gogoi and Chatterjee, 2019; Olierook et al., 2021). Therefore, this study hopes to present models based on porosity (Φ), free fluid index (FFI), and permeability (k) are crucial in the hydraulic unit [reservoir quality index (RQI) and flow zone indicator (FZI)] prediction. FFI indicates the moveable fluid in a reservoir (Nzekwu and Abraham-A, 2022; Abraham-A et al., 2022). RQI and FZI are theoretical parameters for predicting geological attributes such as grain sizes, grain sorting, textures, pore sizes, pore throats and cementation (Tiab and Donaldson, 2012; Abraham-A and Taioli, 2017; Abraham-A and Taoili, 2019). The organic matter in the rock influences the distribution of most of the above-referred attributes. Therefore, this study would harness the relationship between total organic content (TOC) and the reservoir flow units to access the hydrocarbon viability of the rocks. The evaluated flow unit factors are essential in hydrocarbon prospecting, involving reservoir quality evaluation to access fluid transmissibility and predict reservoir capacity concerning fluid recovery or storage. Hence, flow-unit-based models are vital in predicting reservoirs' hydrocarbon and CO_2 storage potentials considering the shale, carbonate, sandstone and siltstone units of the Irati and Rio Bonito Formations.

Shales are fined-grained clastic sedimentary rocks consisting of mud or clay minerals, tiny quartz and calcite particles and other materials depending on the organic and chemical composition and the area geology. The hydraulic units of the shale reservoir rock in situ may not support large volumes of CO_2 storage. Already fractured and depleted oil and gas reservoirs provide easy access to CO_2 storage (Steven et al., 2010; Pearce et al., 2011; Gabriela et al., 2013). Permeability (k) measures the ability of the rock to transmit fluids, expressed in millidarcy (Schlumberger Energy Glossary, 2023). An increase in k comes from shale fracturing. Primarily, free gas occurs in shales within dispersed organic matter, adsorbed by these organic matters or other related minerals based on the composition or physical characteristics of the area where the sedimentation/formation of the rock occurred. In shales, k is proportional to natural cracks/fracture magnitude, allowing fluid passage (Slatt and O'Brien, 2011; Chalmers et al., 2012). Fractured paths, fracture patterns, organic matter content and cementation also contribute to shale k. Other factors include the relative configuration of the building grains of the rock, pore/grain sizes, thermal maturity, and volume of organic matter per unit area/organic matter distribution and mineral composition. The stated characteristics define the reservoirs' flow units and are pertinent to predicting fluid presence, mobility, injection rates, and storage. Gases occur in the intra-particle of organic pores, and inter-particle of organic and inorganic pores in shales (Loucks et al., 2009, 2012; Yang et al., 2015); therefore, reservoir quality evaluations involving physical and chemical properties are fundamental in predicting fluid transmissibility and retention rates.

Dolomite is a common carbonate rock in the Irati Formation. Dolomitisation is a process that involves the substitution of some Ca^{2+} in limestone ($CaCO_3$) by Mg ions to form dolomite [Ca. Mg $(CO_3)_2$]. Dolomitisation enhances crystallisation and pore sizes and thus increases porosity (Φ) and permeability (k) (Weyl, 1960; Tucker and Wright, 1990; Purser et al., 1994; Warren, 2000; David et al., 2008; Ritesh et al., 2014; Wang et al., 2015). Inter-crystalline porosity is a highly interconnected medium that gives dolomite reservoirs good fluid storage capacity and efficient drainage (Warren, 2000). The dolomites are less reactive and less ductile compared to limestone; as such, they are less likely to lose porosity with depth due to dissolution or re-precipitation (Schmoker and Halley, 1982; Purser et al., 1994; Sun, 1995; Saller and Henderson, 1998; Grammer and Harrison, 2003; Davis et al., 2008, 2013; Sharma et al., 2014; Chao et al., 2016). Therefore, dolomites are better reservoirs in the carbonate class. Furthermore, a dolomite bed can retain or create porosity and permeability to greater burial depths and higher temperature realms than a limestone counterpart (Warren, 2000). Hence, where the relative abundance of dolomite is significant compared with limestone, they present better flow units with higher CO_2 storage potentials.

Generally, sandstones include clastic sedimentary materials with grain or sand sizes ranging from 0.0625 mm to 2 mm (Bonewitz, 2012; Schlumberger Energy Glossary, 2022; Geology Science, 2022). They range from unconsolidated and semi-consolidated to consolidated rocks based on cementing materials peculiar to the geologic environment. Sandstone consists of quartz (predominantly), feldspar, mica and other rock mineral grains, which are held together by silica and calcite or clays. In the Rio Bonito Formation, sandstone units are predominant, interlayered with siltstone and shale lithologies. Engaging the presented parameters (FFI, RQI, and FZI) in the models for hydrocarbon viability prediction has been emphasised (Tiab and Donaldson, 2012; Abraham-A and Taioli, 2017; Abraham-A and Taoili, 2019). There is also a highlight involving the applicability of the parameters as CO_2 storage indicators (Abraham-A and Tassinari, 2019). Therefore, this study involves the hydraulic unit characterisation based on the selected parameters to predict the hydrocarbon viability and the reservoirs' adaptability for CO_2 storage based on the rock units of the Irati and Rio Bonito Formations.

2. Study location and geology

The study focuses on the Irati and Rio Bonito Formations of the Paraná Basin in the southwestern part of São Paulo (Fig. 1). The Palaeozoic to Mesozoic Paraná basin is a sedimentary formation confined in the NNE-SSW direction in the central-eastern portion of South America. The intracratonic Parana Basin is about 1700 km long and 900 km wide. It extends via south-central Brazil, Argentina, Uruguay and Paraguay, with a large portion (the Chaco-Paraná basin) located in Argentina and Uruguay. It is about 7000 m deep in its central occupied by Palaeozoic to Mesozoic sediments, basaltic spills and, in some cases, Cenozoic rocks. (Melani and Ramos, 1998; Zalán et al., 1990; Milani et al., 2007; Costa et al., 2016; Darlly et al., 2018).

Six super-sequences are associated with the Parana basin (Milani et al., 1994; Milani and Zalán, 1999; Santos et al., 2006). The associated supersequences include Rio Ivaí (Rio Ivaí Group of Ordovician– Silurian age), Paraná (Paraná Group, Devonian) and Gondwana I (Tubarão and Passa Dois Groups, Carboniferous–Permian). Others are the Gondwana II (Triassic units), Gondwana III (São Bento Group, Jurassic–Cretaceous) and Bauru (Cretaceous) super-sequences.

The Irati Formation spreads through most parts of the Parana Basin. It consists of fossiliferous and soil-bearing rocks having an average thickness of 40 m and a maximum thickness of >80 m (Mendes et al., 1966; Holz et al., 2010). The Irati Formation deposition was after the Gondwana I tectonic sequence during the Permian Artinskian age (Holanda et al., 2018; Santos et al., 2006). It forms part of the Permian Passa Dois Group, divided into the lower Taquaral Member (comprising of siltstones and grey claystone) and the upper Assistência Member (formed by organic-rich clay stones intercalated with limestone lenses) (Holz et al., 2010). The upper Assistência Member consists of a depositional system that includes internal, intermediary and distal ramps tilted southwest (Holanda et al., 2018). It indicates a possible connection to the Panthalassa Ocean in the southernmost region of South America. The Taquaral Member is in a shallow marine environment (Epicontinental Sea) restricted to the open ocean with relatively better water circulation than the overlying Assistência Member (Milani et al., 2006; Holanda et al., 2018). The Paraná Basin unfolded for over 360 million years during the long transgression-regression cycles of an ancient sea, which enclosed the Gondwana (Wit et al., 2007).

With time, these cycles permitted the emergence of the palaeozoic marine, lacustrine, fluvial, and glacial rocks (Zalán et al., 1991; Rocha-Campos et al., 2008). Similarly, during the Jurassic times, the Aeolian deposits of the Botucatu Formation were also documented to have spread for 1500,000 km^2 and covered parts of southern Brazil, Paraguay, Uruguay, and Argentina (Scherer, 2000, 2002; Waichel et al., 2008). The partition of South America and the African plates permitted the South Atlantic Ocean to spread following the Gondwana breakup in the Cretaceous. Upon the separation process, a superposed basalt flow (up to 1500 m) enveloped 1200,000 km^2 of the palaeozoic sedimentary rocks of the Paraná Basin. Bauru Basin (consisting of a desert) spread over the basalt at the end of the Cretaceous (Fernandes et al., 2003). The sediments of the Quaternary age are the youngest geological units in Paraná.

3. Materials and methods

The study involves visiting some mining sites in the southwestern part of São Paulo that reveal alternating shale and carbonate beds ($\geq$200 m) corresponding to the Irati Formation. The research also involves wireline logs representing nine drilled wells, consisting of gamma-ray, density and sonic logs representing Irati and Rio Bonito Formations. The wireline logs are pretty old; they consist of the dataset acquired between the mid-60s and late 80s. The study aims to predict the hydrocarbon viability with CO_2 storage possibilities based on theoretical hydraulic units' evaluation involving the shale, carbonate, sandstone and siltstone layers of the Irati and Rio Bonito Formations of the Parana Basin. The objectives include:

a) Feasibility assessment involving lithological unit identification and rock samples collection at some active and abandoned mining sites;
b) Field observation of porosity and permeability indexes, considering the pattern of the fluid flow on the fresh surfaces of the broken samples and the rocks in situ;

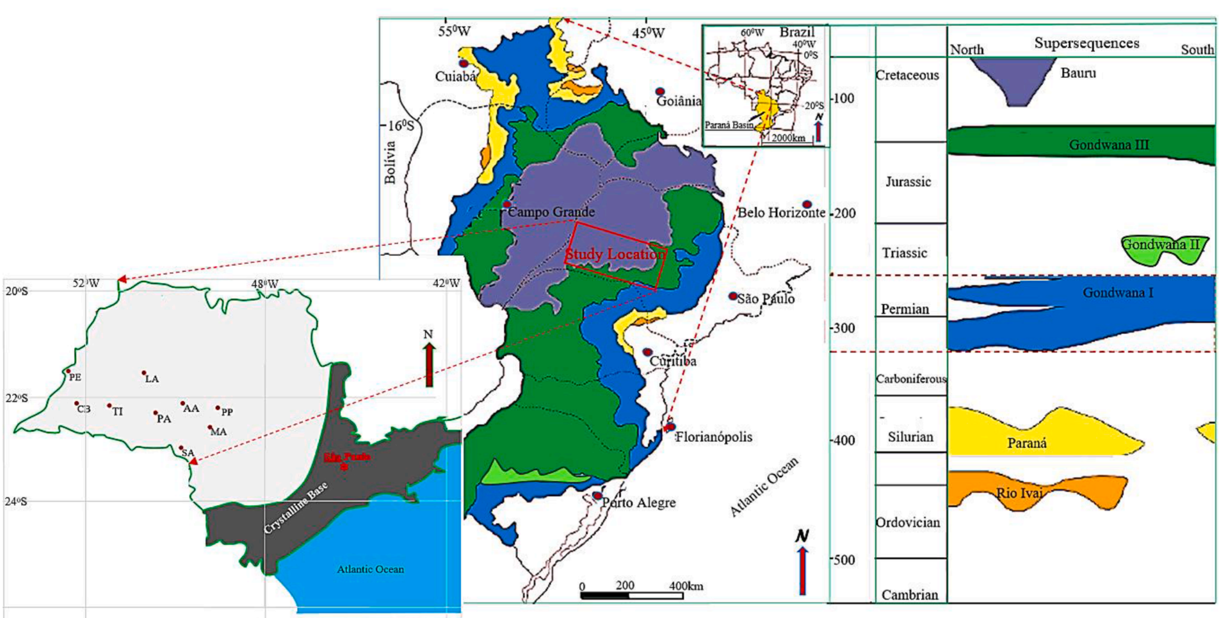

Fig. 1. Geological map (modified from Maahs et al., 2019) indicating the study and well locations generated for the research purpose.

c) Modification of relevant equations and correlation of parameters for the prediction of flow units in carbonate, shale, sandstone and siltstone beds;
d) Evaluation of average porosity values of the rock units based on density and sonic logs;
e) Prediction of the upper limits and average values of the hydraulic units of the rock units and;
f) Petrophysics-based total organic content (TOC) estimation based on the density logs to predict the hydrocarbon potential of the shale and its implications for CO_2 storage viability assessment;

The overview of the geochemical analysis of the associated rock units to further correlate the organic matter of the reservoirs with the physical qualities is pertinent to achieving the research objectives.

3.1. Feasibility study

The mining sites show stratified rocks, such as carbonates (limestone/dolomite) and shale (Fig. 2). The collected samples and the fresh rock surface (in situ) indicate the presence of heavy oil (bitumen). The sites have experienced mining-related activities, exposing depths ranging from 10 m to ≥200 m, which consist of carbonate and shale strata across the area. There are fractured carbonate units and exfoliating shale surfaces, probably due to the vibrations from the excavation processes. However, a closer observation also suggests they may have been cracked/exfoliated in situ already.

Samples of the rocks (shale and dolomite) corresponding to the Irati Formation were taken from the site and showed heavy oil (bitumen) evidence. The rock units were observed in situ based on vertical sections of dolomite and shale surfaces and ex-situ, considering broken rock samples obtained from abandoned and active mining sites. The patterns of fluid (bitumen) flow on the rock surfaces indicate the porosity (Φ) and permeability (k) distributions in the dolomite and shale rocks. Based on the on-site and off-site observations, the oil drains from almost the entire dolomite unit, with some of them making linear formations across the exposed rock surface, indicating randomly interconnected and closely distributed Φ and k networks (Fig. 3). Conversely, the oil drains from point sources, which are far apart on the surfaces of the shale samples, indicating sparsely distributed Φ and k networks (Fig. 4).

Furthermore, the bitumen flow on the broken surface of the dolomite was almost instantaneous. On the other hand, the oil smell is the principal physical characteristic indicating bitumen presence in the shale rock, and it took a bit of time before the fluid started flowing slowly from dispersed point sources. During the fieldwork, sandstone and siltstone of the Rio Bonito Formation were not accessed to investigate the fluid behaviour physically; therefore, they are presented based on wireline logs information alone.

3.2. Hydraulic (flow) unit factors

The Irati Formation consists of carbonate, shale and siltstones, and in the Rio Bonito Formation, sandstone lithologies are more frequent in occurrence and thicknesses than siltstone and shale units. This study predicts the flow unit factors in the carbonate, shale, sandstone and siltstone units of the Irati and Rio Bonito Formations. Therefore, the parameters evaluated for each of the four rock units include porosity

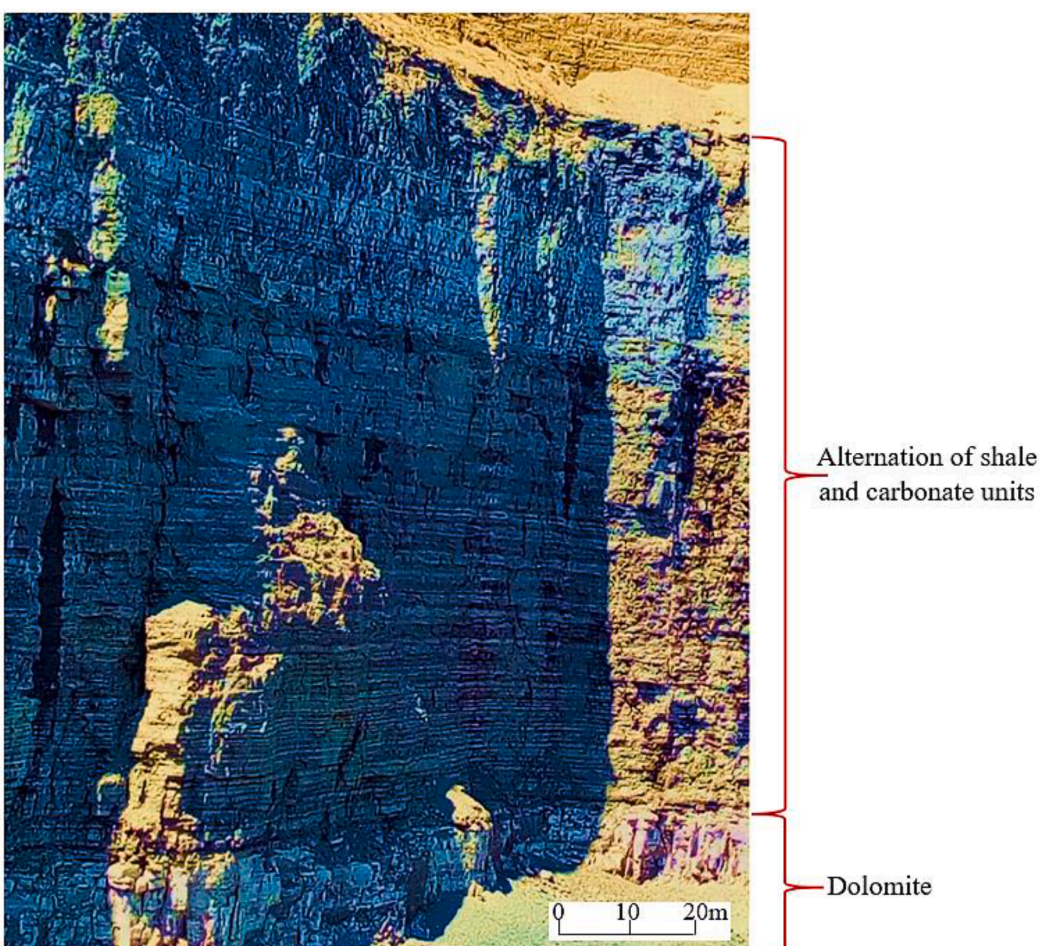

Fig. 2. A vertical section consisting of alternating layers of carbonate and shale beds.

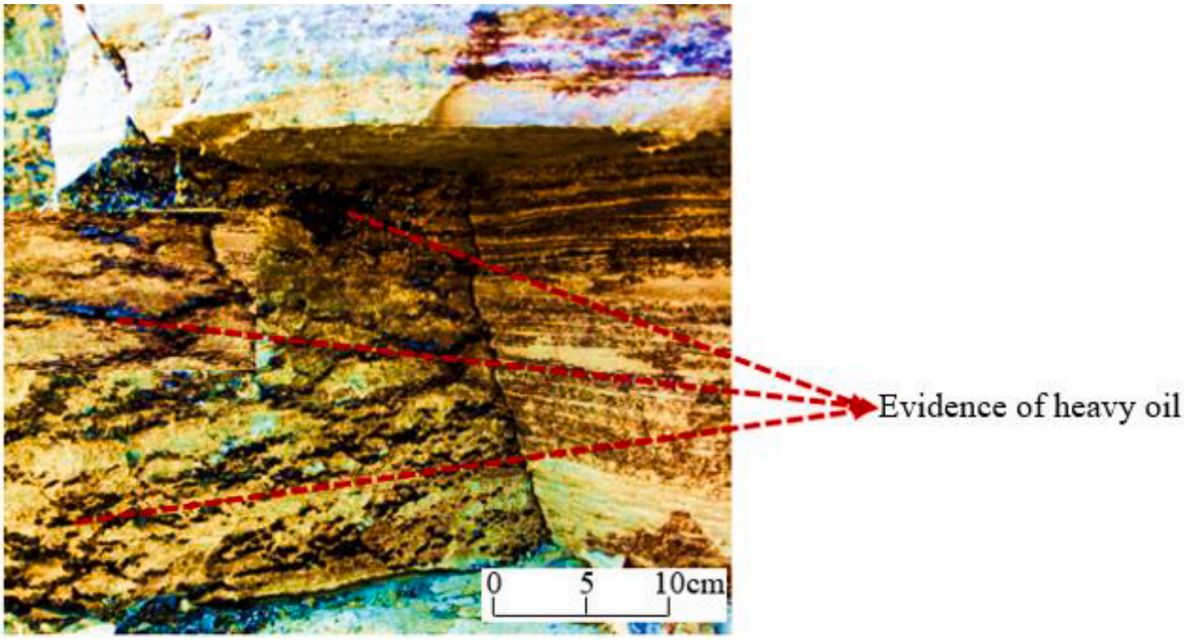

Fig. 3. Evidence of heavy oil in dolomite (in situ).

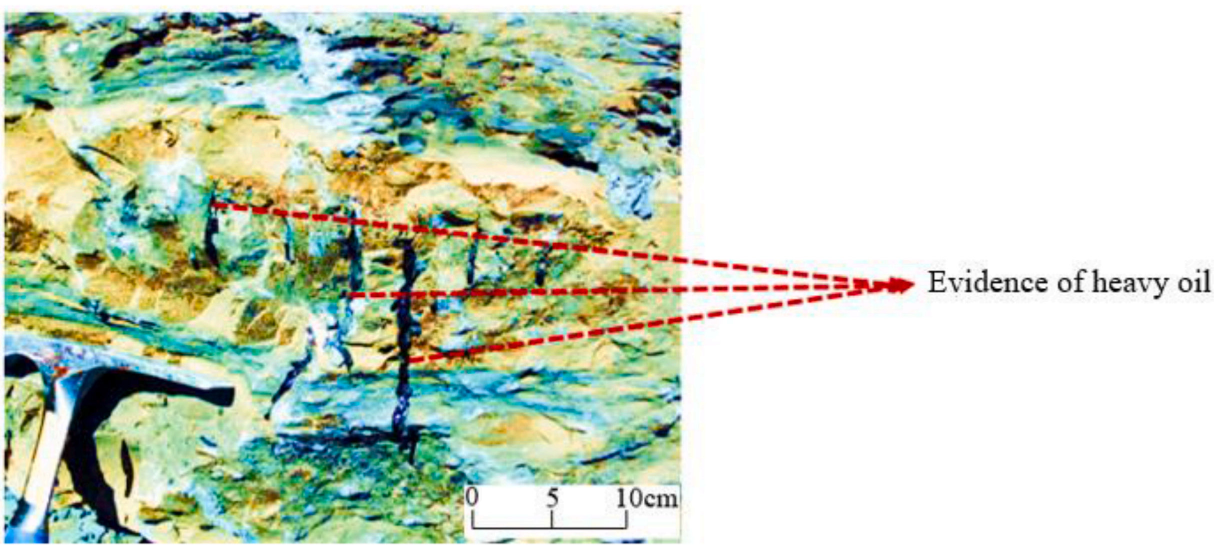

Fig. 4. Evidence of heavy oil in a shale boulder.

(Φ), free fluid index (FFI), permeability (k), reservoir quality index (RQI) and flow zone indicator (FZI). Total organic content (TOC) was estimated for the shale and carbonate units of the Irati Formation.

3.2.1. Porosity (Φ)

The sonic-derived porosity takes the form of Eq. (1)

$$\Phi_s = \frac{\Delta t_{log} - \Delta t_{ma}}{\Delta t_f - \Delta t_{ma}} \times \frac{1}{C_p} \tag{1}$$

where:

Δt_{log} = acoustic transit time (μsec/ft), Δt_f = acoustic transit time of interstitial fluids (μsec/ft),
Δt_{ma} = acoustic transit time of the rock matrix (μsec/ft) and
C_p = the compaction correction factor expressed by Eq. (2)

$$C_p = \frac{\Delta t_{sh}(C)}{100} \tag{2}$$

such that: Δt_{sh}= specific acoustic transit time in adjacent shales (μsec/ft), 100 = acoustic transit time in compacted shales (μsec/ft) and C = Compaction coefficient (Usually in the range of 1.0 to 1.3, based on the geology of the area).

Similarly, the density-derived porosity takes the form of Eq. (3)

$$\Phi_D = \frac{\rho_{ma} - \rho_b}{\rho_{ma} - \rho_f} \tag{3}$$

[Φ_D = density-derived porosity, ρ_{ma} = matrix density of the Formation (up to 3.0 gcc depending on the Formation and rock type), ρ_b= bulk density of the Formation, ρ_f= fluid density of the Formation (1.0 gm/

cc)].

Average porosity (Φ_{S-D}) was calculated based on Φ_S and Φ_D, especially where the sonic and density logs are available. Therefore, the average values of the sum of the density-derived porosity (Φ_D) and sonic-derived porosity (Φ_S) were presented as the Φ of the potential reservoir rocks and used as inputs in the theoretical hydraulic unit factor expressions. Such that;

$$\Phi_{S-D} = \frac{\Phi_S + \Phi_D}{2} \quad (4)$$

Nine wells (AA, MA, PE, LA, SA, TI, PP, PA and CB) were evaluated considering the hydraulic units of the rocks (Shale, carbonates, sandstone and siltstone) reservoirs to predict the CO_2 storage possibilities within the Irati and Rio Bonito Formations of Paraná Basin, Brazil.

3.2.2. Organic content

Theoretically, the total organic content (TOC) takes the form of Eq. (5) (Schmoker, 1993; Godec et al., 2013).

$$TOC = 55.822 \times \left[\left(\frac{\rho_{\max}}{\rho_{\log}}\right) - 1\right] \quad (5)$$

The relationship between organic content and the flow unit factors is essential in predicting hydrocarbon viability involving generation, migration and accumulation in potential reservoir units. Consequently, the understanding of petroleum systems based on the evaluated parameters aids in forecasting hydrocarbon production events with the tendency to inject and store captured fluid (CO_2). Therefore, TOC estimation and overviews of geochemical-related studies concerning the region are vital to achieving the research's key objectives.

3.2.3. Permeability (k), reservoir quality index (RQI) and flow zone indicator (FZI)

The study engages permeability equations redefined by Abraham-A and Taoili (2017; 2019) and Abraham-A and Tassinari (2019) based on Tixier et al. (1963), Timur (1968) and Coates and Denoo (1981) expressions. The equations were modified considering values ranging from 0.6 to 1.65 for the factor of tortuosity (***a***) and 2 to 2.5 for the cementation exponent (***m***) depending on the type of rock (Carothers, 1968; Archie, 1942; Asquith and Gibson, 1982; Schlumberger, 1989; Hilmi and George, 1999; Asquith and Krygowski, 2004). The porosity and reservoir quality index/flow zone indicator (RQI/FZI) relationship are good tools for checking reservoir flow units (Tiab and Donaldson, 2012; Abraham-A and Taioli, 2017). The study presents reconceived expressions for permeability (K), RQI and FZI in shale, carbonate, sandstone and siltstone based on Tiab and Donaldson (2012).

Hence, the expression for permeability takes the form of Eq. (6) in carbonates, Eq. (7) in shales, Eq. (8) in sandstone and Eq. (9) in siltstone.

$$k_{ca} = \left(4472\Phi^{3.25}\right)^2 \quad (6)$$

$$k_{sh} = \frac{\left(2\times10^7\Phi^{6.7}\right)}{a} \quad (7)$$

$$k_{st} = \left[\frac{4472\Phi^{3.25}}{a^{0.5}}\right]^2 \quad (8)$$

$$k_{sst} = \frac{\left(2\times10^7\Phi^{6.7}\right)}{a} \quad (9)$$

Therefore, the reservoir quality index (RQI) takes the form of Eq. (10) in carbonates, Eq. (11) in shales, Eq. (12) in sandstone and Eq. (13) in siltstone.

$$RQI_{Ca} = \frac{140.4\Phi^{3.25}}{\Phi^{0.5}} \quad (10)$$

$$RQI_{sh} = \frac{0.0314\left(2\times10^7\Phi^{6.7}\right)^{0.5}}{a\Phi^{0.5}} \quad (11)$$

$$RQI_{st} = \left[\frac{140.4\Phi^{3.25}}{a^{0.5}\Phi}\right]^{0.5} \quad (12)$$

$$RQI_{sst} = \frac{0.0314\left(2\times10^7\Phi^{6.7}\right)^{0.5}}{a\Phi^{0.5}} \quad (13)$$

Similarly, the expression for FZI takes the form of Eq. (14) in carbonates, Eq. (15) in shales, Eq. (16) in sandstone and Eq. (17) in siltstone.

$$FZI_{ca} = \frac{140.4\Phi^{3.25}}{\Phi^{0.5}\times\Phi_R} \quad (14)$$

$$FZI_{sh} = \frac{0.0314*\left(2\times10^7\Phi^{6.7}\right)^{0.5}}{a\Phi^{0.5}\times\Phi_R} \quad (15)$$

$$FZI_{st} = \left[\frac{140.4\Phi^{3.25}}{a^{0.5}\Phi}\right]^{0.5}\times\frac{1}{\Phi_R} \quad (16)$$

$$FZI_{sst} = \frac{0.0314*\left(2\times10^7\Phi^{6.7}\right)^{0.5}}{a\Phi^{0.5}\Phi_R} \quad (17)$$

Where Φ_R is expressed by Eq. (18) (After Tiab and Donaldson, 2012)

$$\Phi_R = \frac{\Phi}{1-\Phi} \quad (18)$$

Consequently, the research uses correlation plots based on the equations to predict and compare the physical qualities of carbonates, shales, sandstones and siltstones corresponding to the Irati and Rio Bonito Formations.

The free fluid index (FFI) takes the form of Eq. (19) (Schlumberger, 1989).

$$FFI = \Phi(1 - S_{wirr}) \quad (19)$$

However, according to Abraham-A and Taioli (2019), FFI could also take the form of Eq. (20) based on a sensitivity evaluation involving the associated parameters [cementation exponent (m) and the factor of tortuosity (***a***)] for sandstone. Therefore, the study engaged a similar approach to define the parameters in shales, carbonates and siltstones.

$$FFI = \Phi - 0.02 \quad (20)$$

According to Schlumberger (1989), FFI defines the moveable fluid in the reservoir; therefore, it relates to the reservoir unit's effective porosity and may be engaged in the expressions for RQI and FZI to predict the flow units (Abraham-A and Taioli, 2019).

4. Results

The results include a set of wireline logs (Figs. 4–6), a table (Table 1) and cross-plots (Figs. 7–10) indicating the relationship between the evaluated parameters within the presented rock units.

4.1. Flow unit factors

The hydraulic (flow) units in shale, carbonate, sandstone, and siltstone reservoirs based on nine drilled wells, consisting of gamma ray, density and sonic logs, were evaluated. Three wells (AA, MA, and PE) reveal the Irati Formation at depths greater than 950m (Figs. 5–7). Generally, the wells reveal depths above 800m and up to 3500m across Irati and Rio Bonito Formations. The thicknesses of the rock units (carbonates, shales, sandstones and siltstones) range from 1m to ≥ 20m across the study location.

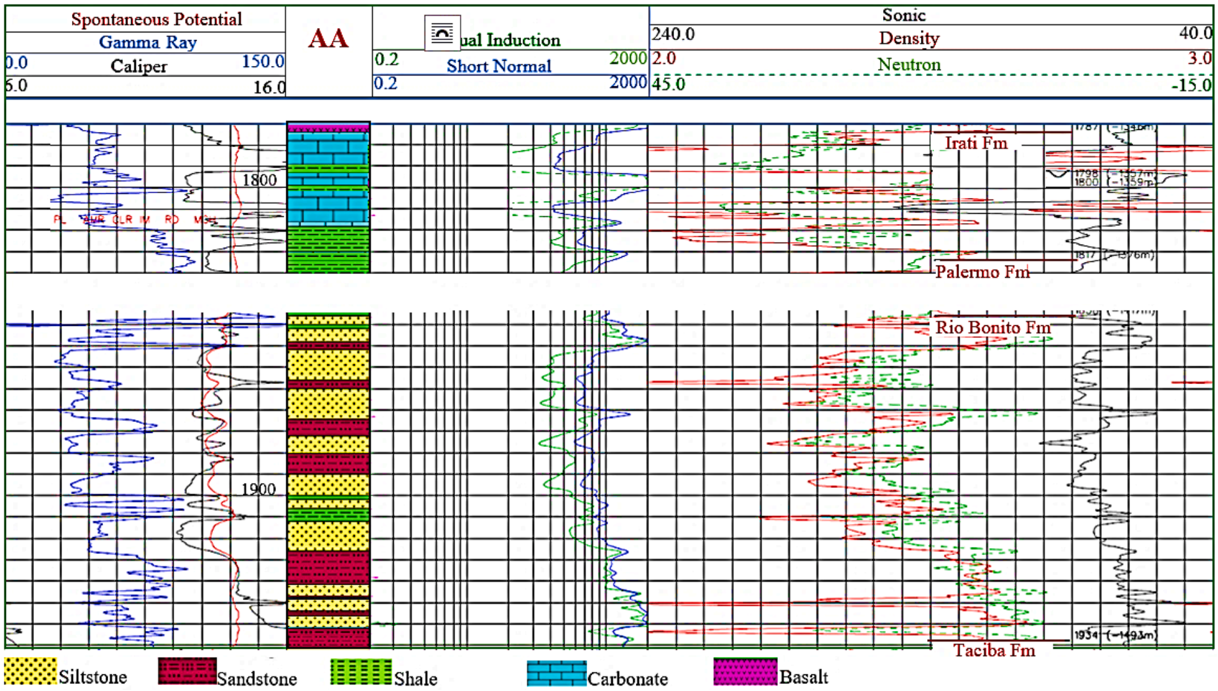

Fig. 5. Well AA showing the lithologic units down the Irati and Rio Bonito Formations.

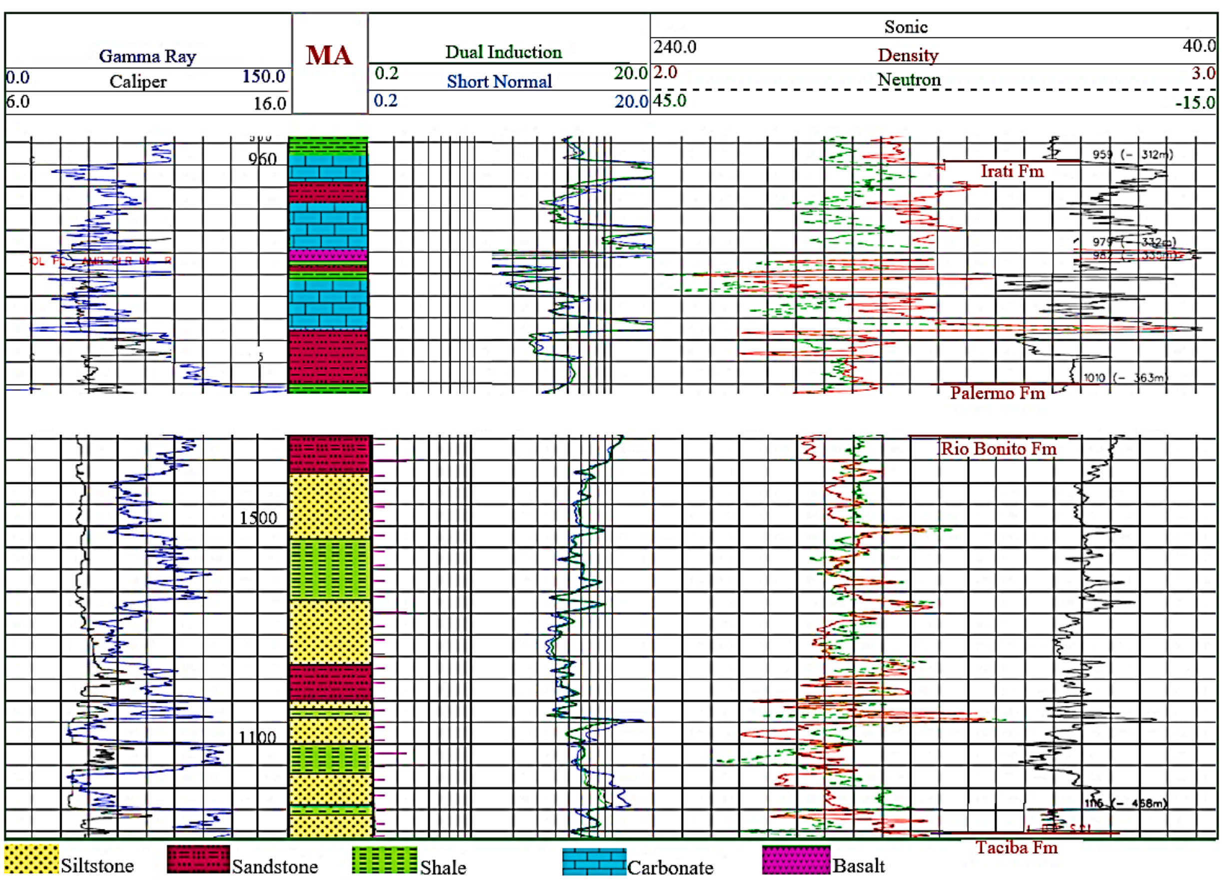

Fig. 6. Well MA showing the lithologic units down the Irati and Rio Bonito Formations.

Total organic content (TOC) was estimated from the density log. The study engaged the wells (e.g. AA and MA) with the density log to present shale and carbonate rocks' TOC values. Table 1 shows the ranges of the parameters estimated for the shale, carbonate, sandstone and siltstone unit. The background objectives feature CO_2 storage prospects; however, the hydrocarbon indication of the study location, considering the

Table 1
Ranges of the hydraulic unit parameters across the wells.

Depth(m)	Rock type	Φ_D(%)	Φ_S (%)	(%)	FFI (%)	TOC(%)	k (mD)	RQI (μm)	FZI (μm)
≥ 800	Shale	2 to ≤ 16	1 to ≤ 13	2 to ≤ 14	0.01to ≤10	3 to ≤10.5	0.000052 to ≤ 36.6	0.0012 to ≤ 0.5	0.06 to ≤ 2.16
	Carbonate	3 to ≤ 22	3 to ≤ 19	3 to ≤ 21	1.8 to ≤ 18	1 to ≤ 5.6	0.0025 to ≤ 786	0.009 to ≤ 1.9	0.29to ≤ 7.2
	Sandstone	10 to ≤ 33	5 to ≤ 28	10 to ≤ 31	8.0 to ≤ 28	-	8.0 to ≤ 12352	0.28 to ≤ 6.3	2.5 to ≤ 13.9
	Siltstone	3 to ≤ 19	2 to ≤ 17	2 to ≤ 18	0.5 to ≤16	-	0.00081 to ≤ 132	0.004 to ≤ 0.68	0.13 to ≤ 3.1

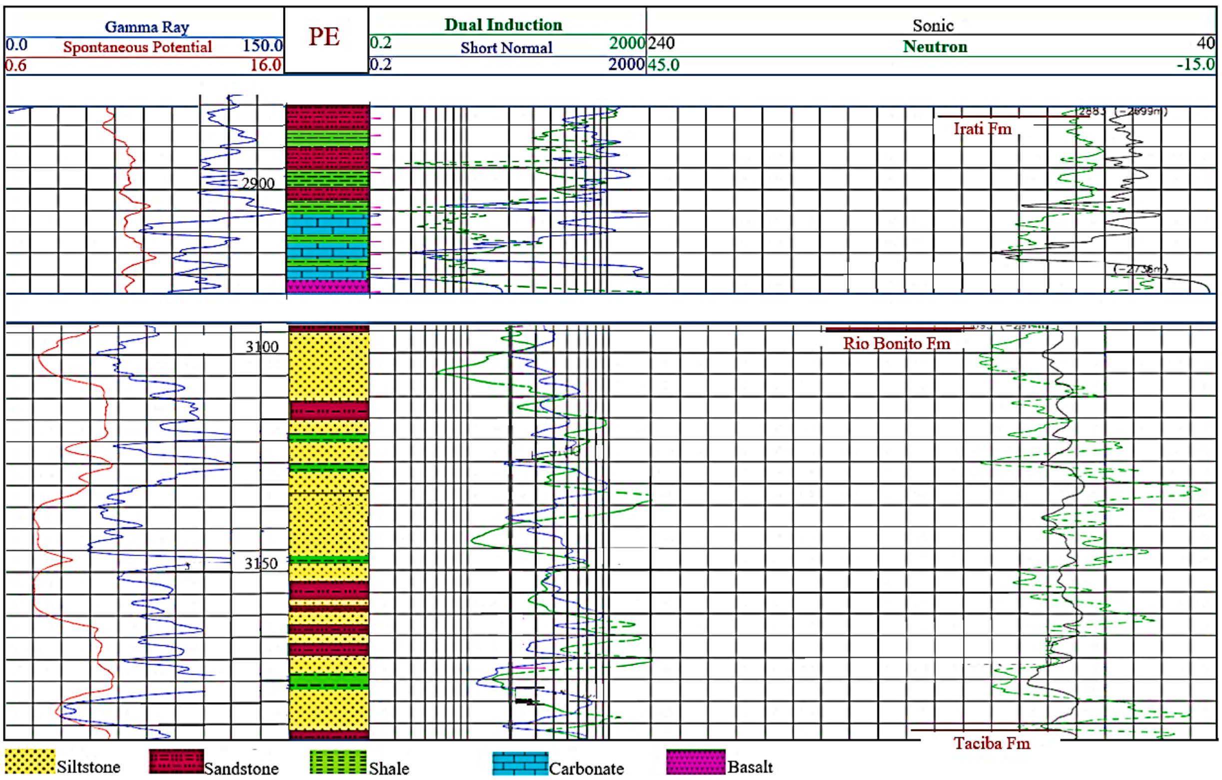

Fig. 7. Well PE showing the lithologic units down the Irati and Rio Bonito Formations.

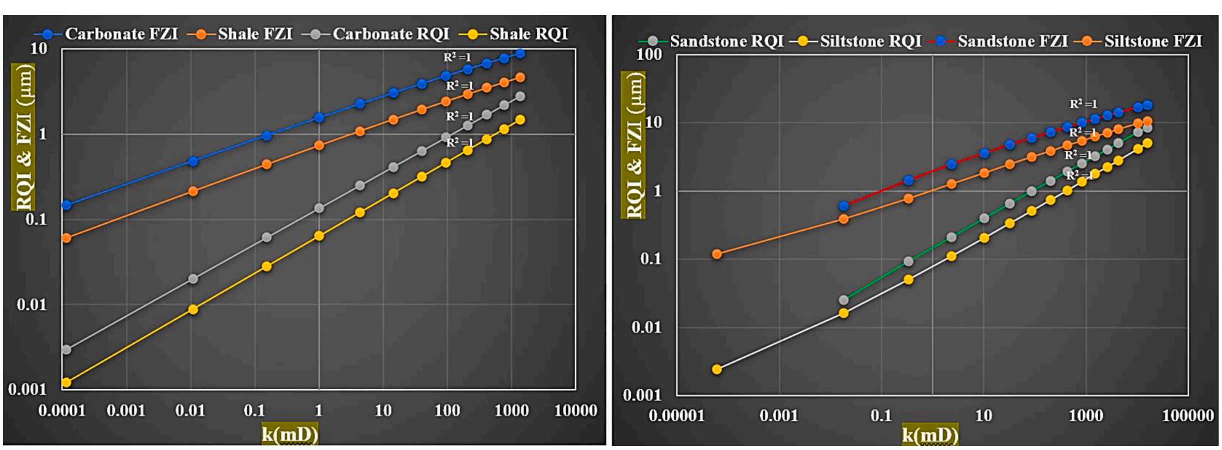

Fig. 8. Reservoir quality index (RQI) with Flow zone indicator (FZI) and permeability (k) correlation Plots.

Irati formation shales as potential source rocks based on the shale TOC, is noteworthy. Furthermore, the Rio Bonito Formation consist of sandstone units at considerable depths favourable for hydrocarbon accumulation. Generally, the parameters (porosity- Φ, free fluid index-FFI, permeability-k, reservoir quality index-RQI andflow zone indicator-FZI) point to reservoirs with the potential totransmit and store fluid. In practice, hydrocarbon production favours CO_2 storage processes; therefore, the study harnesses the parameters to predict the hydrocarbon prospect with the possibility of CO_2 storage. The organic-rich shales of the Irati Formation are perceived as potential source rocks, and the porous Rio Bonito Formation sandstone units are seen as suitable hydrocarbon reservoirs.

Fig. 8 shows a positive correlation between permeability and the other flow (hydraulic) unit factors. Figs. 9, 10 and 11 show the upper

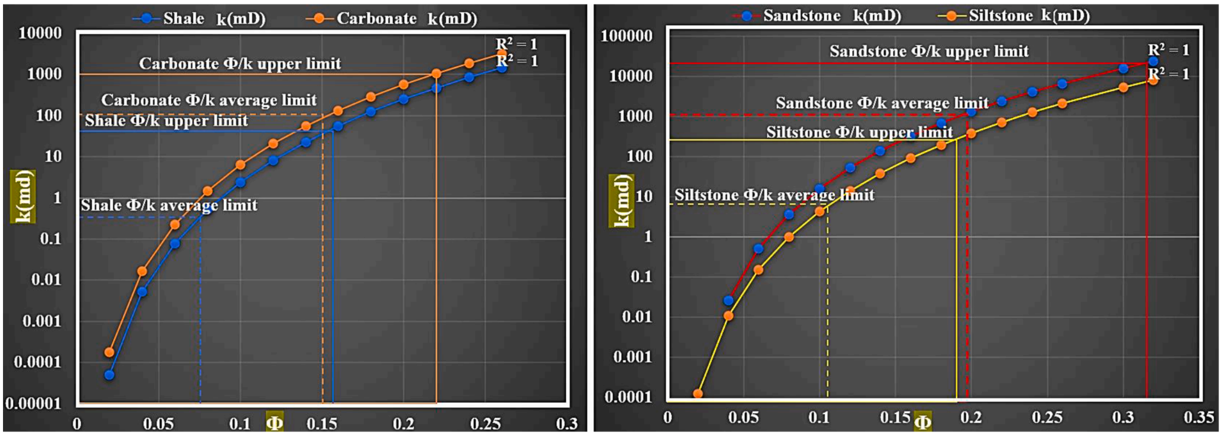

Fig. 9. Correlation involving the upper limits and average values for Φ and k defined for the rock units.

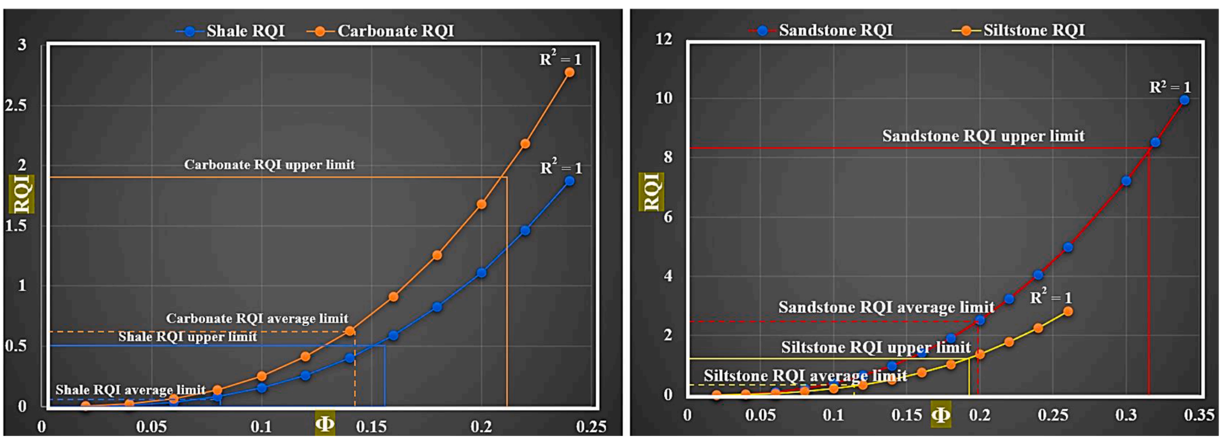

Fig. 10. Reservoir quality index (RQI) and porosity (Φ) correlation considering the upper limits and average value.

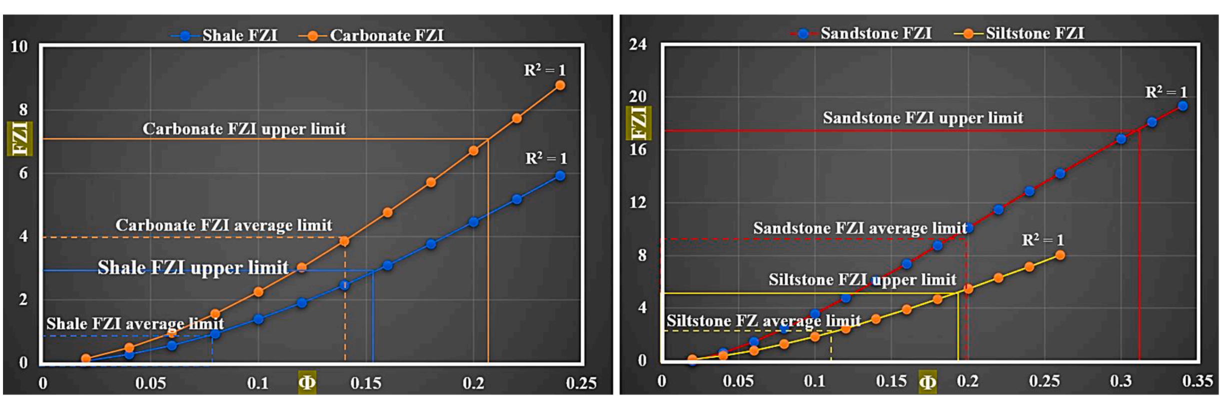

Fig. 11. Flow zone indicator (FZI) and porosity (Φ) correlation considering the upper limits and average value.

limits and the average values of the hydraulic units defined for each rock unit corresponding to the Irati and Rio Bonito Formations. In shales, few instances show porosity (Φ) above 15%, but generally, it is less than 14%, with an average value of ≤ 8%. In carbonates, there are instances with Φ up to 22%; however, Φ is vastly less than 20% with an average value of ≤ 14%. Similarly, in siltstones, Φ is mostly less than 20%, with an average value of ≤ 11%. Sandstones show Φ up to 33% in some cases, but Φ is vastly less than 31%, with an average value above 16%. Free fluid index-FFI values are generally significant in sandstones, low in carbonates and insignificant in shale and siltstones. The charts compare Φ, permeability (k), reservoir quality index (RQI) and flow zone indicator (FZI) of the rocks. The relationships confirm that sandstone presents more significant flow units than others, even at the same range of Φ. Considering the equal value of Φ in all the rocks, RQI and FZI in sandstones are far better and will support fluid movement and storage more than the others. The significance of the flow units increases from shales to siltstones, carbonates and sandstone in that order. However, TOC is higher in shales. The correlation plots indicate the influence of Φ on other parameters. Considering that TOC influences Φ in shales, the correlations indicate a strong relationship between the hydraulic unit factors and Φ and, by extension, TOC. Therefore, this association is essential, representing the potential for hydrocarbon generation, considering existing shale-based geochemical analyses (e.g., Rocha, 2021).

4.2. Organic contents and flow units' relationship

Organic-rich shales are potential hydrocarbon source rocks (Doust and Omatsola, 1990; Stacher, 1995). As such, information regarding the TOC of the rock units is essential to predicting the hydrocarbon potential of the study location. The organic-rich shales of the Irati Formation are considered parts of the largest shale oil deposits in the world (EIA, 2013). These shales are recognised source rock units for various hydrocarbon accumulations within the Paraná Basin (Espitalie et al., 1983; Hachiro, 1996; Araújo et al., 2000; Milani et al., 2007). The hydrocarbon potentials include the oil accumulations in carbonate units at São Paulo State (Araújo et al., 2000; Araújo 2001, 2001; Mateus et al., 2014) and in oil shales at Paraná State (Corrêa da Silva and Cornford 1985; Santos et al., 2006).

Based on the organic geochemical analysis, the Irati Formation shale at the southeast border of the Paraná Basin (São Paulo State) is bituminous, having remarkably high TOC content ranging from 4.42% to 9.64%. The shale hydrogen index (HI) is above 600 mg HC/g, with a high potential for hydrocarbon generation. The peak values of hydrocarbons generated through thermal cracking of non-volatile organic matter (denoted as S_2) reached 130.33 mg HC/g. These values portray the Irati shales as excellent potential source rocks with prevailing type I-II kerogen (Rocha, 2021). Previous research also classifies the Irati organic-rich shales as notable 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). Other geochemical analyses also reveal that the total organic carbon content (TOC) varies from 0.1 to 23%, with an average of 2.0% (Milani and Zalán, 1999; Araújo et al., 2000; Milani et al., 2007; EIA/ARI, 2013).

Reservoir attributes, including grain sizes/sorting, textures, pore volumes/throats, and cementation, amongst others, are estimated theoretically via the computation of reservoir quality index (RQI) and flow zone indicator (FZI)(Tiab and Donaldson, 2012; Abraham-A and Taioli, 2017; Abraham-A and Taoili, 2019). To a large extent, the organic content of the parent rock controls the above-stated attributes. Higher TOC enhances the reservoir flow unit factors (Φ, k, FFI, RQI and FZI). Hence, an approach based on the combination of all the presented parameters is advisable in predicting the hydrocarbon availability, fluid recoverability, and fluid (e.g., CO_2) injection rates within the geologic structures.

4.3. Uncertainties

The wireline logs consist of a dataset from the mid-60s to the late 80s. Some log signatures (e.g., resistivity and spontaneous potential) show unusual and unreliable responses, probably due to digitisation or other data acquisition and computation errors. However, the evaluation is based mainly on the porosity tools (sonic and density logs) with considerably legible signatures. Furthermore, hydrocarbon exploration and production methods are always risks and uncertainties-prone. The fact that there are existing databases and studies (though very old and needed to be more detailed) that could not establish the economic viability involving volumetric estimation of the hydrocarbon in the study location increases the uncertainties. Most existing reports duel more on the shale being a potential source rock based on the organic matter content and related geochemical properties. There are no reports on the Irati and Rio Bonito Formations involving detailed qualitative and quantitative hydrocarbon evaluations based on petrophysics and seismic models.

There are also uncertainties concerning the equations and the choice of shale and carbonate units for future CO_2 storage. However, the study presents models that allow the direct computation of porosity (Φ) in the expressions for the evaluated parameters. Therefore, the expressions avoid the approximation of Φ over a range of equations to get other parameters as they are usually estimated. Considering that a slight change in Φ often results in significant changes in all the parameters; therefore, the assumption is that this approach has aided in avoiding exaggerating or underestimating the hydraulic unit factors, thereby reducing the level of uncertainties involving the equations. Low porosity and relative permeability will affect fluid production or storage within the shale unit. However, if future studies confirm shale gas in a commercial quantity, it will encourage fracturing to enhance gas production with subsequent CO_2 storage. The chemical relationship between CO_2 and rocks such as shale, sandstone and siltstones may not be an issue concerning CO_2 storage potentials. However, CO_2-carbonate reaction in the presence of water may limit CO_2 storage potentials (Abraham-A and Tassinari, 2021). Therefore, detailed geochemical evaluations and petrophysics-based water saturation (S_w) estimations are necessary before considering carbonate reservoirs for CO_2 storage (Rötting et al., 2015; Siqueira et al., 2017; Zhang et al., 2019; Abraham-A and Tassinari, 2021). However, the CO_2-carbonate reaction is inactive without water (Wang et al., 2013); therefore, if water saturation (S_w) is not significant enough to spike the CO_2-carbonate response, carbonate reservoirs may present effective CO_2 storage units.

5. Discussion

Porosity (Φ) is fundamental in predicting the quality and volumes of the reservoir concerning fluid transmissibility and storage. The study suggest that the combined sonic-density porosity ($\Phi_{S\text{-}D}$) approach validates the estimated Φ, being a key input in the hydraulic unit expressions. Via a sensitivity analysis, Abraham-A and Taoili (2019) validated the use of the modified equations for free fluid index (FFI), permeability (k), reservoir quality index (RQI) and flow zone indication (FZI) within sandstone reservoir units. Modifying these expressions to evaluate the required parameters for flow unit prediction and as hydrocarbon potential indicators with storage of CO_2 possibilities within the rock units is uncommon in the Irati and Rio Bonito Formations. From the results, Φ could be high in shales in some cases. However, shales are composed of tiny grain sizes that diminish the fluid flow and storage capacity. Shales are detrital sedimentary rocks formed via the consolidation of clay, mud, and silt (usually fine-grained). Shales are typically porous and contain hydrocarbons but generally exhibit deficient k (Schlumberger, 1989; Halliburton, 2001) compared to other rock units (e.g., sandstone and carbonate reservoirs). High Φ values in shales may not correspond to high k. In sandstones, high Φ indicates well-interconnected pores for fluid paths and high k. Also, k can be lower than 0.0001mD in clay/-clayey rocks (Electric logs, 2019), and the evaluation results are in tune with these values.

From the evaluation, for the same or less Φ, other parameters (k, RQI and FZI) are better in the Rio Bonito Formation sandstone than the other rock units. The significance of the flow units decreases from sandstones (showing higher values) to carbonates, siltstones and shales (with the least values). For the Irati Formation, carbonate offers more significant flow units than shales. Mostly, the combined sonic-density-based porosity ($\Phi_{S\text{-}D}$) values across the wells range from 0.08 (2%) to 0.106 (10.6%) in shales, with a few cases showing up to 0.15 (15%). Also, total organic content (TOC) ranges from 3.0% to 10.5%, k varies from 0.00005mD to 36.59mD, RQI ranges from 0.001μm to 0.5 μm, and FZI ranges from 0.06 μm to 2.16 μm in shales. Within the carbonate reservoirs, ($\Phi_{S\text{-}D}$) ranges from 0.02 (2%) to 0.22 (22%), TOC ranges between 2.8% to 5.2%, k has a range of 0.0025 mD to 786 mD, RQI goes from 0.009 μm to 1.9 μm, and FZI ranges from 0.29 μm to 7.2 μm. In siltstones, $\Phi_{S\text{-}D}$ ranges from 0.02 (2%) to 0.18 (18%), K has a range of 0.0008 mD to 132 mD, RQI ranges from 0.004 μm to 0.68 μm, and FZI ranges from 0.13 μm to 3.1 μm. Within the Rio Bonito Formation sandstone, $\Phi_{S\text{-}D}$ range from 0.1 (10%) to 0.31 (31%) (Up to 32% in some instances), k has a range of 8 mD to 12352 mD, RQI range from 0.28 μm to 6.3 μm, and FZI ranges from 2.5 μm to 13.9 μm. For the sandstone units, the parameters are significant for a potential reservoir rock with a recovery factor expected to be above 20% based on the value estimated for the porosity-dependent free fluid index (FFI) (e.g., Abraham-A et al., 2022). The theoretical TOC (up to 10%) calculated for the shale units indicates potential hydrocarbon source rocks. In addition, the shale hydrogen index (HI) rates above 600 mg HC/g with type I-III kerogen, pointing to high hydrocarbon generation potentials. All these parameters indicate that the organic-rich shales of the Irati Formation are potential hydrocarbon kitchens with unquantified reserves within the associated rocks. Therefore, the study area is a possible hydrocarbon reservoir location with CO_2 storage options. While anticipating shale gas exploitation, there are indications of hydrocarbon accumulation in the sandstone units.

Newly acquired datasets based on up-to-date equipment could reveal the presence of hydrocarbons (e.g., shale gas) at higher depths to encourage CO_2–based fracturing and enhance gas production with post-production CO_2 storage options. Similarly, detailed studies with sophisticated methodologies to explore the carbonate units of the Irati Formation and the Rio Bonito Formation sandstone units for possible hydrocarbon extraction will also encourage post-production CO_2 storage. The study shows that flow units are usually more significant in sandstones. Carbonates and siltstones indicate better flow unit indicators than shale lithology. At higher burial depths, dolomitisation processes enhance pore interconnectivity (Warren, 2000; Wang et al., 2015; Chao et al., 2016). Therefore, dolomites may present better reservoir units to boost possible hydrocarbon recoveries with subsequent CO_2 storage based on the hydraulic units. While the shale units are potential hydrocarbon source rocks, thick carbonate units trapped between shale layers will present well-protected reservoirs for hydrocarbon accumulation and CO_2 storage. Areas overlaid by basalt sills and low-permeability shale of the upper Serra Alta Formation can provide the required overburden for the Irati Formation to serve as a shale-carbonate hybrid geological reservoir. Based on this study, the critical factor determining the hydrocarbon viability and CO_2 storage potential of the sandstone units of the Rio Bonito Formation is significant porosity with other reservoir quality indicators. Therefore, sandstones at significant depths are potential hydrocarbon reservoir units with reasonable fluid transmissibility/recovery rates, which will boost CO_2 storage processes in the future. Siltstones sandwiched between two sandstone units are apparent within the Rio Bonito Formation; therefore, sandstone-siltstone-sandstone hybrid reservoir scenarios are foreseeable in the Rio Bonito Formation. For the Irati Formation, Abraham-A and Tassinari (2021) already proposed the viability of the shale-carbonate hybrid reservoir option for CO_2 storage based on detailed petrophysical and seismic evaluations.

The chemical reaction between CO_2 and carbonate rocks is crucial in the CO_2 storage processes. The CO_2-water-carbonate interaction, in some ways, alters the petrophysical parameter of the reservoir. Related studies have shown that CO_2 in carbonate rocks results in dissolution, precipitation and re-precipitation, leading to rapid physicochemical modifications within the carbonate rocks (Andreani et al., 2009; Bacci et al., 2011; Rötting et al., 2015; Siqueira et al., 2017; Lebedeva et al., 2017; Zhang et al., 2019). Other effects include changes in the texture/structure of the reservoir rocks and disequilibrium of the pore pressures and fluid chemistry. Physically, some of these processes increase Φ and k in carbonate rocks to enhance fluid mobility and storage. However, CO_2 storage in carbonates is still questionable based on CO_2-water-carbonate reactions that may result in some geochemical imbalances within the reservoirs. Abraham-A and Tassinari (2021) indicated decreases in water saturation (S_w) (below 14% at depths greater than 950m) with corresponding depth increases considering the carbonate units within the Irati Formation. Supercritical CO_2 has no reaction with carbonate rocks in the absence of water. Therefore, if the ratios of CO_2 are higher in the carbonate reservoirs and S_w is not enough to encourage a complete CO_2-carbonate reaction, the Irati Formation carbonates reservoirs at higher depths will support CO_2 storage, provided all other efficiency factors are sufficient.

Based on the hydraulic units and the overview of the geochemical analysis of some of the associated reservoir rocks, the Irati and Rio Bonito Formations have the potential for hydrocarbon generation considering the organic-rich shales and CO_2 storage based on depths, thicknesses and evaluated parameters in shales, carbonates, sandstones and siltstones units. The development of the reservoirs for two purposes, i.e., hydrocarbon production and CO_2 storage, will reduce costs. Further detailed geophysical evaluations may reveal non-economically viable hydrocarbon deposits. In this case, oil/gas production activities may still be encouraged to minimise costs considering CO_2 storage as the primary objective. In the worst-case scenario of the absence of hydrocarbon in some targeted reservoirs, such units may be engaged as dedicated geological storage for CO_2 repositioning when needed. Detailed studies involving 3D-4D seismic interpretation are crucial to confirm the hydrocarbon availability, estimate the reserves and predict the hydrocarbon recovery rates to foster CO_2 storage options.

6. Conclusion

The density-based porosity (Φ_D) and sonic-based porosity (Φ_S) results are almost within the same range of values for each rock unit within the Irati and Rio Bonito Formations. The combined sonic-density approach for porosity estimation validated the values derived with each log and aided the prediction of flow units. The significance of the hydraulic (flow) units increases from shale to siltstones, carbonates and sandstones. The flow unit factors (Φ, k, RQI and FZI) are better in the Rio Bonito Formation sandstones. Therefore, it holds potential reservoir units capable of accumulating hydrocarbon for future production events to boost CO_2 injection and permanent storage. Although shale shows the least values estimated for the flow unit factors; however, it has considerable total organic content (TOC) coupled with related geochemical analysis findings to represent a viable hydrocarbon source rock. The region shows potential for hydrocarbon production with CO_2 storage possibilities considering reservoirs in sandstones and carbonate rocks. The CO_2 storage potential in shale is limited based on the flow units. If further studies reveal viable shale gas units, fracturing to enhance gas production will increase effective porosity and permeability, thereby boosting the shale reservoirs' CO_2 injection and storage potentials. The limitation concerning the carbonates reservoirs for CO_2 storage could be in the CO_2-water-carbonate reactions. The wireline logs show significant thicknesses of carbonate units trapped between shale layers, indicating reservoir units with the potential to accumulate migrated or injected fluids. The indication of the decrease in water saturation (S_w) with depth increases may boost the CO_2 storage potential in carbonates. The results indicate the carbonate rocks of the Irati Formation with better flow unit factors as possible CO_2 storage tanks, such that the shale and siltstone potential serve as viable overburden layers and traps. The sandstone units of the Rio Bonito Formation are potential hydrocarbon reservoirs and viable CO_2 storage tanks based on their abundance and significance of the flow unit factors. However, considering the frequency of thin-bedded layers of siltstone units sandwiched between sandstone beds, sandstone-siltstone-sandstone hybrid CO_2 storage reservoir options are possible in the Rio Bonito Formation. The study's results remain relevant when considering the associated rocks as dedicated CO_2 storage units, especially if further studies indicate non-economically viable oil and gas reserves. The research findings can also contribute to future exploration events involving modern equipment and methodology to confirm the hydrocarbon reserves and establish the CO_2 storage capacity.

CRediT authorship contribution statement

Richardson M. Abraham-A: Conceptualization, Investigation, Resources, Formal analysis, Writing – original draft, Writing – review & editing. **Colombo C.C.G. Tassinari:** Investigation, Resources, Formal analysis, Writing – review & editing. **Fabio Taioli:** Formal analysis, Writing – review & editing. **Haline V. Rocha:** Formal analysis, Writing – review & editing. **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.

Data availability

The authors do not have permission to share data.

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