

CO₂ GEOLOGICAL STORAGE THROUGH ADSORPTION IN ORGANIC-RICH SHALES: A CASE STUDY OF IRATI FORMATION SHALES FROM THE PARANÁ BASIN, BRAZIL

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ABSTRACT

Geological sequestration of carbon dioxide (CO₂) can represent an efficient and safe long-term storage of this greenhouse-contributing gas. When applied to shales, CO₂ injection can enhance shale gas recovery (CO₂-ESG) and contribute to CO₂ abatement through geological storage. Shale is considered an unconventional reservoir due to its reduced permeability, consequently CO₂ storage in shales has peculiar characteristics: storage through adsorption into the microporosity of organic particles and clay minerals. The efficacy of CO₂ adsorption and CH₄ desorption processes drive CO₂ storage capacity and hydrocarbon production of organic-rich shale. Therefore, understanding gas sorption patterns in shale and how these are affected by its organic and inorganic composition is essential to evaluate shale's CO₂ storage capacity, organic matter quantity, type and maturation

are vital parameters considering CO₂ adsorption in shale because it controls organic porosity, pore size, and internal surface area within this lithology. Besides the organic component, clay mineralogy also affects CO₂ storage capacity in shale. Expandable clay minerals, such as smectites, contribute as CO₂ adsorption sites and add to shale's overall CO₂ storage capacity. Thus, such organic and mineralogical characterisation should be the first step towards CO₂ storage capacity assessment in shale. This chapter investigates the complexity of the interaction between the organic and inorganic components in shale with CO₂. Due to the heterogeneity regarding the organic content and maturation stage of shales from Irati Formation, Paraná Basin, Brazil, these were selected as a case study in this research. Selected Irati Formation organic-rich shale samples went through the following experimental procedures: total organic carbon and Rock-Eval pyrolysis screening, paired with palynofacies, vitrinite reflectance and spore fluorescence to characterise the organic component; followed by x-ray diffraction and scanning electron microscopy to determine mineralogical composition; together with gas sorption isotherms (BET and Langmuir methods) to characterise the porous media and CO₂ storage capacity. The relation between shale's composition and sequestration was analysed and demonstrated in this study to improve the knowledge on CO₂ geological storage into organic-rich rock formations and scientifically communicate how these unconventional reservoirs can significantly contribute to CO₂ abatement.

Keywords: CO₂ geological storage; organic-rich shales; shale gas, sorption isotherms; CO₂ adsorption Irati Formation, Paraná Basin, Brazil.

1. INTRODUCTION

Carbon capture, utilization, and storage (CCUS) refer to a suite of technological processes to reduce carbon dioxide emissions. These technologies include: (i) CO₂ capture and separation from gaseous effluents; (ii) CO₂ transport through pipelines or ships from the capture facility to a storage site or industrial facility; (iii) CO₂ utilization via service or product with economic value and (iv) CO₂ storage in suitable geological formations (Bachu, 2002; Bachu et al., 2007; GCCSI, 2019; Lal, 2005).

CCUS technologies stand out among a diverse portfolio of CO₂ mitigation strategies due to their potential to decarbonize the carbon-intensive power and industrial sectors worldwide (IPCC, 2005; 2014). Additionally, CCUS is required as a component for other essential CO₂ abatement technologies, such as bioenergy with CCS (BECCS) and direct air capture (DAC), which are vital to reaching

net-zero by providing negative emissions (Budinis et al., 2018; Daggash, Fajardy, & Mac Dowell, 2020; Leeson, Ramirez, & Mac Dowell, 2020).

CO₂ geological storage is the segment within the CCUS chain that plays a significant role in mitigating the worst impacts of climate change and meeting net-zero emission targets (IPCC, 2005, 2014). This role arises from the capacity of injecting large volumes of CO₂ into adequate geologic formations. For instance, global targets are estimated at 10 Gt CO₂ emission abatement per year by 2050 (IPCC, 2014), and this could only be achieved with geological CO₂ storage (Zahasky & Krevor, 2020), which despite the yet few large-scale facilities, the already reached 97.5 million tonnes of CO₂ been stored annually (GCCSI, 2019).

CO₂ geological storage consists of CO₂ injection and storage into adequate reservoirs for a geologically significant period (Bachu, 2002). Suitable reservoirs must present (i) sufficient capacity to store large volumes of CO₂; (ii) adequate “injectivity” to allow the injection and flow of CO₂ into the geological formation; and (iii) confinement or integrity of the reservoir (e. g., geological configuration with traps and sealing that retain the upward CO₂ buoyancy and prevent leakage for the desired period) (Bachu et al., 2007; Krevor, Blunt, Trusler, & Simone, 2019). Additionally, reservoirs should be permanently monitored to ensure that the CO₂ remains stored within the geological formation (EC, 2009).

Such a combination of geological features is common in both conventional (e. g., sandstones and carbonates) and unconventional reservoirs (e. g., coal seams and organic-rich shales) (Rodrigues, 2002). However, it is essential to highlight that CO₂ storage sites are not simply associated with a sedimentary basin and a suitable geological formation. It relies on geological, geochemical and petrophysical processes and properties such as porosity, permeability, caprock integrity, injectivity and fluid dynamics (Haszeldine, 2019; Krevor et al., 2019)

This chapter raises the hypothesis that organic-rich shales can store substantial volumes of CO₂ due to rock-fluid properties that attribute a remarkably high CO₂ storage capacity to these unconventional reservoirs. The hypothesis was tested by Rocha (2021) on Irati Formation organic-rich shales to discuss if the Irati Formation can be a feasible target for both CO₂ reduction and shale gas production under small-scale CO₂ emitting-sinking/closed-cycle systems in southern Brazil, where the CO₂ emitting sources are close to the geological reservoir. Moreover, the chapter aims to project the understanding of the geological requirements for CO₂ storage in shale reservoirs and further assess storage capacity in organic-rich shales.

2. CO₂ STORAGE IN SHALE RESERVOIRS

Shales are considered unconventional reservoirs, and the CO₂ storage in shales has peculiar characteristics: storage through adsorption in pore internal surface areas (Bemani et al., 2020; Chen & Xiao, 2014; Yu et al., 2019; Zhou et al., 2019, 2020). As shown in Figure 1 and in contrast to the conventional reservoir, smaller pores in organic-rich shale imply a higher internal surface area. Thus, smaller pores in organic-rich shale suggest a higher internal surface area; therefore, a higher storage capacity due to the adsorption trapping mechanism.

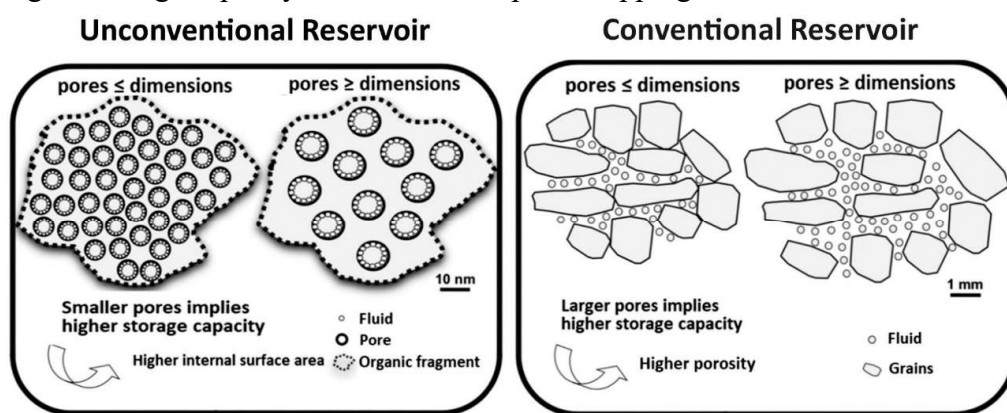


Figure 1. Porous media, CO₂ trapping mechanism and storage capacity illustration scheme for unconventional (on the left) and conventional reservoirs (on the right side of the image), focusing on the role of organic porosity and pore-size distribution. Adapted from de Rodrigues & Lemos de Sousa (2008)

The co-existence of organic and intergranular porosity in shales results in a wide range of pore volumes and pore size distribution, affecting gas flow patterns within this lithology. According to Mastalerz et al. (2013), gas flow in shales occurs through Knudsen diffusion and slip flow in nanometre-size pores, and through Darcy-like flow, in larger pores. It differs from the gas flow pattern in conventional reservoirs, such as sandstones, which is Darcy-like flow in the micrometre to larger pore sizes (Chen & Xiao, 2014; Curtis et al., 2011; Han et al., 2017; Mastalerz et al., 2013). Therefore, understanding shale's organic porous systems and the CO₂ adsorption process is essential to evaluate the potential for CO₂ storage into this geological formation.

Shale composition determines its porosity, therefore, its CO₂ sorption capacity and storage potential. In organic-rich shale, gas storage capacity mainly relies on organic porosity and clay mineralogy, where the CO₂ gets stored through adsorption.

Additionally, part of the CO₂ is held in a 'free' way into larger pores and fractures (Al-Mutarreb et al., 2018; Klewiah et al., 2020).

Shale's porous system (e. g., primary and secondary porosities) result from a complex interaction of physical and chemical processes before and after deposition (Al-Mutarreb et al., 2018; Fatah et al., 2020; Romero-Sarmiento et al., 2012). In this sense, shale's pore size/type, interconnectivity, and distribution, rely on the inorganic matrix and the organic matter content. It can be divided into clay matrix porosity, non-clayey matrix porosity, and organic porosity (kerogen) – which hosts most of the porosity fraction in organic-rich shales. organic parameters to be considered include kerogen quantity (TOC wt. %), type and maturity level, while inorganic aspects rely on mineralogy, such as ratios of silica/quartz, carbonates, and predominant clay minerals (Goodman et al., 2020; Schaef et al., 2014; Weniger et al., 2010).

2.1. The Role of the Organic Matter

CO₂ sequestration in organic-rich shales is mainly driven by its organic porosity (Boruah et al., 2019; J. Chen & Xiao, 2014; Chen et al., 2020; Hackley & Cardott, 2016; Han et al., 2017; Pan et al., 2015; Sihra & Head, 2010). Moreover, the storage capacity of shales relies on kerogen evolution, more specifically to its thermal cracking during catagenesis and to hydrocarbon generation and migration (Romero-Sarmiento et al., 2012).

Organic maturation is crucial for organic porosity and CO₂ geological storage and hydrocarbon recovery processes in shale reservoirs. It controls organic porosity, pore size and surface area within these lithologies; therefore, the efficacy of CO₂ adsorption and CH₄ desorption processes, which drive CO₂ sequestration in shales and enhanced shale gas and oil recovery associated processes.

During the early stages of thermal maturation, the total organic content (TOC) controls fluid adsorption in organic-rich shales (Han et al., 2017) due to the kerogen swelling and shrinkage effect and the associated organic porosity generation. Kerogen swelling reaches its maximum at the transitioning oil to the gas window, at a Tmax of approximately 445°C and vitrinite reflectance of 0.8% Rr. After 0.8% Rr, organic nanopores are formed by the shrinkage of kerogen and by the release of hydrocarbons, leading to an increase in internal surface area and organic porosity. The continued cracking of the kerogen results in a more rigid kerogen residue, and subsequently, the swelling and retention ability of the kerogen network is decreased. Therefore, fluid sorption in shales tends to increase with maturity until a maximum sorption capacity is reached (Chen & Xiao, 2014;

Han et al., 2017). In this sense, organic-rich shales with vitrinite reflectance above 0.8% R_r and below 3.5% R_r are more suitable for CO₂ storage through adsorption.

According to Chen & Xiao (2014), the evolution of organic porosity in shales is divided into three stages. The first stage of nanopores formation, with vitrinite reflectance measurements between 0.6% and 2.0% R_r. In this stage, there is an initial decrease in nanopores during oil generation (0.6% < R_r < 0.8%), followed by a nanoporosity increase during oil cracking to gaseous hydrocarbons, (0.8% < R_r < 2.0%). There is a second stage of nanoporosity development, with R_r between 2.0% and 3.5%. In this stage, further methane generation and kerogen cracking result in an even more matured solid, graphitic-like structure and nano and microporous kerogen residue. In the third and last stage of organic porosity development, with the R_r > 3.5%, high temperature and pressure decomposes the organic matter and transforms the nano and micropores to mesopores and macropores. At this stage, the shale has no longer sufficient sorption capacity to CO₂ adsorption.

2.2. The Role of Mineralogy

Clay minerals are genuinely relevant to CO₂ geological storage and affect the gas sorption capacity in shales. For instance, high surface area clay mineral-rich shale formations (e. g., clays of the smectite group) tend to have higher CO₂ storage capacity (BERTIER & ROTHER, 2016; BUSCH et al., 2008, 2017). Regarding sorption capacity, Ca-exchanged smectite can adsorb the most significant amounts, followed by Na-exchanged smectite, illite and kaolinite, and negligible amounts of CO₂ adsorbed on chlorite (BUSCH et al., 2008, 2020).

For smectites, which are expandable clays, CO₂ adsorption can lead to volumetric expansion followed by the generation of swelling pressures (BUSCH et al., 2008). Such volumetric expansion leads to dehydration cracks that work as pathways for CO₂ flow rates into the formation, possibly accelerating the CO₂ storage process. However, consequent swelling pressures can close the generated fractured path and result in reduced permeability overtime after a CO₂ saturation breakthrough point is reached (BUSCH et al., 2008). In summary, CO₂ sorption on clay minerals in shale formations will increase flux rates after CO₂ breakthrough, while times scales for a breakthrough are still far above the critical time scale of 10,000 years requested by most regulators. At the same time, depending on the details of the CO₂ concentration gradients across the seal, significant amounts of CO₂ will be temporarily immobilized, contributing to storage safety and reducing reservoir pressure (BUSCH et al. 2020).

3. RESEARCH METHODS

To evaluate the potential of shale gas reservoirs for CO₂ sequestration, the research methodological must comprise a general characterization of the geological formation, followed by a detailed analysis of its organic and mineralogical content. Additionally, gas sorption isotherms measurements and reservoir properties must be considered.

Besides bibliographical research and sampling the studied formation, it is essential to apply further analytical procedures, including organic geochemistry, petrography, mineralogy, and gas sorption isotherms. These analytical procedures must include: (i) organic geochemistry analysis, such as TOC and Rock-Eval pyrolysis; (ii) organic petrography techniques, such palynofacies and kerogen typing, vitrinite reflectance measurements and spore colour and fluorescence identification; (iii) mineral characterization through x-ray spectrometry, and (iv) gas sorption isotherms, such as low-pressure (BET method) and high-pressure (Langmuir method) adsorption and desorption measurements, for petrophysics data acquirement and storage capacity estimates, respectively. This combination of analysis and experimental procedures provides the overall geological feasibility of organic-rich shales for CO₂ storage.

3.1. TOC and Rock-Eval screening

Total organic carbon (TOC) analysis is essential to source-rocks evaluation. It is usually the first analytical procedure to be carried out to determine hydrocarbon generation potential since it quantifies the preserved organic matter within the rock, expressed as a percentage. The measured organic content includes the insoluble fraction (kerogen) and the soluble in organic solvents fraction (bitumen). TOC classifies the shale into four categories: (i) shale containing less than 0.5% TOC is considered as poor source rock, (ii) shales containing a TOC between 0.5% and 1% indicate fair source rocks, (iii) shales containing TOC values between 1% and 2% indicate good source rocks, and (iv) shales containing TOC values above 2% often indicate a highly reducing environment and preserved organic content and indicate excellent source-rock potential (BOSTICK & DAWS, 1994; HUTTON, 1987; MUSTAFA et al., 2015). After determining the TOC levels, samples with significant TOC values (usually greater than 1%) proceeded to the pyrolysis Rock-Eval analysis.

Rock-Eval pyrolysis is a rapid screening technique for source-rock evaluation. Under laboratory conditions, it simulates the catagenesis and metagenesis processes by which the rock was exposed, determining the stage of maturation

in which the preserved organic matter is found. It consists of the volatilization of the sample's hydrocarbons by a controlled temperature increase and wavelength reading via an infrared cell – in a similar process for determining TOC, there is no combustion. Overall, Rock-Eval pyrolysis can be used to identify the type and maturity stage of the organic matter and determine the hydrocarbon potential of source rocks (ESPITALIÉ et al. 1977).

Besides organic geochemistry, organic petrography techniques are essential to characterise and classify the organic content of organic-rich shales, such as organic matter quantity, type, and maturation.

Petrographic Composition and Palynofacies

The petrographic composition of organic-rich shales should be carried out for palynostratigraphy and geological age determinations, depositional environment interpretations, and stratigraphic correlations with other sedimentary basins. Additionally, organic petrography techniques are applicable to determine the kerogen type and origin through palynofacies associations based on maceral group classification and its relative frequency among the analysed sample's organic compounds.

Maceral classification should be in accordance with the International Committee for Coal and Organic Petrology (ICCP). It should follow the ISO 7404-3 (2009), which classifies organic compounds based on morphological constituents: amorphous organic matter, palynomorphs, and phytoclasts divided between non-opaque/translucent and opaque phytoclasts, and opaque organic matter (ICCP, 1998, 2001).

Vitrinite reflectance, Spore Fluorescence and Colour

Vitrinite reflectance (Rr%) measurements constitute an optical petrographic methodology for determining organic maturity based on reflected light microscopy. It estimates the degree of thermal maturation of the organic content by measuring the percentage of incident light reflected from the surface of vitrinite particles in the rock sample (TAYLOR et al., 1998). This analytical method was developed to classify the coals' rank, also applied to other organic-enriched lithologies, such as shales. Vitrinite particles identification and reflectance measurements should follow the guidelines recommended by the ASTM D7708-14 (2014), ISO 7404-5 (2009) and ICCP (1998).

Qualitative spore fluorescence and spore colour are two optical parameters of thermal maturity of organic maturation, helpful in evaluating maturation levels

of low-rank rocks until the end of the oil window (RODRIGUES, 2002). When correlated with the quantitative Rr% method, spore fluorescence and colour parameters can provide additional support for the thermal maturity of the rocks.

Spore exine colour is a method to assess the thermal maturity of sedimentary rocks. With increasing burial depth, spore colour changes from light to dark, and it is irreversible. Moreover, maturation causes a gradual shift in organic matter fluorescence colours (redshift) from the shorter to the longer wavelengths: blue and green to yellow, orange and finally red. According to the scale, colours vary from blue and green for an immature sample to orange to red for more mature rocks, following the ICCP Standard (ICCP, 1998).

Whole-rock and Clay-fraction Mineralogy

Mineralogy plays an essential role in CO₂ geological storage reservoirs. Mineralogical content, especially clay minerals, contributes to shale's total porosity (AL-MUTARREB et al., 2018; BUSCH et al., 2020; KLEWIAH et al., 2020). Therefore, it contributes to its adsorption capacity and gas storage potential. Analysing the mineralogical content helps determine the depositional paleoenvironment and paleoclimate and identify post-depositional processes and thermal history of a sedimentary basin (SANT'ANNA et al., 2006). X-ray diffraction (XRD) technique, a scanning electron microscope (SEM) should be applied for mineral content characterization and identification of clay minerals.

Gas Sorption Isotherms

Gas sorption isotherms and models are efficient methods to evaluate the CO₂ storage potential in a geological reservoir, especially in coals and organic-rich shales, where the adsorption drives CO₂ storage that is accumulating in minerals and organic surfaces (KALKREUTH et al., 2013; KLEWIAH et al., 2020; WENIGER et al., 2010; RODRIGUES, 2002). Sorption of CO₂ or CH₄ onto shales are determined in laboratory experiments through isotherms. Sorption isotherms quantify gas storage within the studied sample by measuring gas adsorption and desorption processes at different pressure gradients – from atmospheric pressure to above the reservoir pressure and under constant temperature – analogous to the reservoir temperature. Sorption models quantify the relation between the absorbed/free gas and the adsorbed (stored) gas within the studied sample.

The Langmuir sorption model is the most adequate to explain the behaviour of gas storage in the coal and shale organic porosity, based on experimental analysis

(RODRIGUES, 2002; RODRIGUES et al., 2013, 2016; WENIGER et al., 2010; YU et al., 2016; ZHOU et al., 2019). It provides a good description of adsorption into microporous sorbents and the existing equilibrium between stored/adsorbed gas and free gas by determining saturation limits (RODRIGUES, 2002). The Langmuir isotherm model is the following:

$$G_{cs} = V_L * P / (P + P_L)$$

G_{cs} is the gas content at saturation (scf/ton), P is the pressure, V_L and P_L are the Langmuir volume (scf/ton) and pressure (psi), respectively. The Langmuir volume (V_L) corresponds to the maximum gas adsorption capacity of the studied samples at a given temperature (Bachu et al., 2007). Langmuir sorption isotherms calculations depend on volumetric techniques or PVT (pressure–volume–temperature). The volumetric method considers gas expandability aspects for determining volume based on the Boyle-Mariotte principle. The Langmuir equation is mainly used for microporous material characterization, exhibiting Type I Isotherms. In the Langmuir model, the adsorption is assumed to be limited to one monolayer (with pressure increase, gas molecules cover the sample surface to form a one molecule thick layer).

Besides the Langmuir model, the called Brunauer, Emmett and Teller (BET) sorption isotherms can be applied to analyse the porous media further. BET sorption isotherms can be used for porous material characterization, determining surface area, pore size distribution and pore volume of the studied sample through adsorption data. The isotherms are obtained by measuring the amount of gas adsorbed to the sample's surface across a wide range of relative pressures at a constant temperature (typically referenced for liquid N₂, at 77.4K). Desorption isotherms are determined by measuring the volume of gas removed as pressure is reduced at the same temperature as adsorption.

The BET sorption isotherm equation was developed in 1938. It is a well-known model for porous material characterization and a conventional method for specific surface area evaluation. The BET theory is derived from adsorption analysis. It is an extension of the Langmuir model, considering multi-layered gas molecule adsorption – the BET model is a derivation of adsorption isotherm equations for multimolecular adsorption (Brunauer et al., 1938). The BET equation is expressed below.

$$1/[V_a (P_0/P-1)] = (C-1)/(V_m C) \times P/P_0 + 1/(V_m C)$$

V_a is the volume of adsorbed gas at standard temperature and pressure (STP), while V_m is the adsorbed gas volume at STP to generate an apparent monolayer on the sample's surface. P_0 is the saturated pressure of the adsorbate gas. P is the pressure of the adsorbate gas in equilibrium with the surface temperature at 77.4 K (temperature of liquid nitrogen). C refers to a dimensionless constant related

to the enthalpy of adsorption of the adsorbate gas on the powder sample (BET constant). Total pore volume is derived from the amount of vapour adsorbed at a relative temperature close to unity (assuming pores are filled with liquid adsorbate). The average pore size is estimated from the pore volume.

Sorption isotherms and gas storage capacity are affected by numerous variables that can either be related to the reservoir sample or the sorption gas (individual or mixture). The main variables attributed to the samples are mineralogy, petrographic composition, and organic maturity. Variables in the experimental procedure are moisture, temperature, pressure, and gas composition, which affect the gas compressibility factor, which, together with gas molecule size, has a significant effect on the sorption process (Rodrigues, 2002; Fatah et al., 2020; Klewiah et al., 2020; Rodrigues et al., 2016).

Overall, gas sorption isotherms applied to geological CO₂ storage in shales and coals can provide the following data: (i) maximum storage capacity in reservoir conditions, (ii) gas saturation estimates by calculating the difference between the maximum storage capacity and the actual gas volume content, (iii) diffusion rate of gas flow, (iv) composition and behaviour of the stored gas, (v) released gas volume from the system due to pressure drop, and (vi) critical desorption pressure, which is the required pressure to gas desorption start at the reservoir (RODRIGUES, 2002).

4. IRATI FORMATION CASE STUDY

Organic-rich shales of the Irati Formation are among Brazil's most studied geological formations worldwide due to its recognized potential for hydrocarbons. They are considered one of the largest shale oil deposits in the world (EIA, 2013). Additionally, these shales are a recognized source rock unit for various accumulations within the Paraná Basin (Hachiro, 1996; Araújo et al., 2000; Milani et al., 2007), such as the oil accumulations in carbonate levels at São Paulo State (ARAÚJO et al., 2000; ARAÚJO 2001; ARAÚJO et al., 2001; MATEUS et al., 2014; FERREIRA, 2017), and in oil shales at Paraná State (CORRÊA DA SILVA & CORNFORD 1985; SANTOS et al., 2006).

The Irati Formation is part of the Gondwana I sedimentation of the Passa Dois Group, corresponding to the Lower Permian section of the Paraná Basin (ZÁLAN et al., 1990; MILANI & ZALÁN, 1999; MILANI et al., 2007). It presents a heterogeneous lithologic distribution, consisting of carbonates and evaporites in the northern region and bituminous shales in the southern portion of Paraná Basin (MILANI et al., 2007). It has an overly broad geographical occurrence, covering

most of the Paraná Basin in an area of approximately 700,000 km² (MILANI et al., 2007), where it outcrops in a narrow range, resembling an “S” shape, on its northern and south-eastern borders (HACHIRO, 1996). Concerning its thickness, the Irati Formation presents an average thickness of 40m (MENDES et al., 1966), with a typical thickness of 10 m at the margins of the Paraná Basin, reaching up to 70 m in the depocenter (HACHIRO, 1996).

Two distinctive members were identified within the Irati Formation: Taquaral and Assistência (HACHIRO, 1996). The Taquaral Member comprises silty-clayey, non-bituminous, greyish shales with lenticular carbonate interleaves and silex nodules. It varies from 5 to 10 meters of thickness in the marginal areas of the basin and reaches 30 meters in central portions (Hachiro, 1996). The Taquaral Member was deposited under low to moderate oxygenation conditions, below the storm wave base (ARAÚJO, 2001; GOLDBERG & HUMAYUN, 2016). The Assistência Member consists of clayey, bituminous shales, grey-dark to black, locally interbedded with carbonate beds. Its depositional environment ranged from shallow-water and subaerially exposed to stratified and anoxic conditions (ARAÚJO, 2001; GOLDBERG & HUMAYUN, 2016). The thickness of this package varies between 10 and 20 meters in the margins and reaches approximately 40 meters in the basin depocenter (Hachiro, 1996; MILANI et al., 2007) (Figure 2)

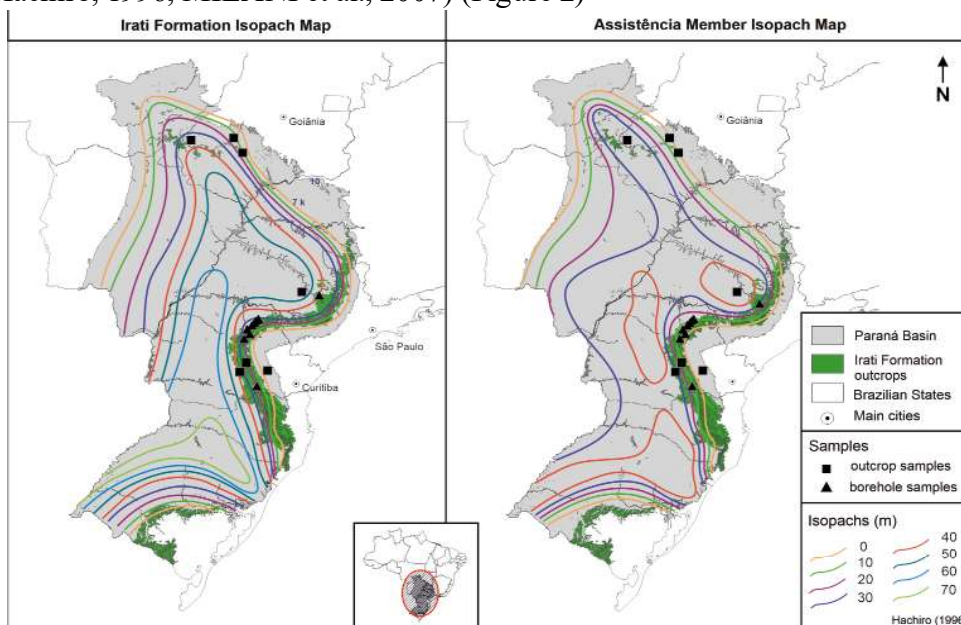


Figure 2. Paraná Basin with outcrops and isopach of the Irati Formation adapted from Hachiro (1996). A: Isopach map of the Irati Formation. B: Isopach map of the Assistência Member. The Irati Formation outcrops along the Paraná Basin are represented in green

The black shales of the Assistência Member are rhythmically intercalated with limestones and dolomites. These vary from the millimetre scale (laminae) to meter-thick beds (HACHIRO, 1996). The intercalation between dolomite and shale beds has higher rhythmicity in the northern and eastern parts of the Paraná Basin but is less predominant in the southern part of the Ponta Grossa Arch (HACHIRO, 1996; ARAÚJO, 2001). Hachiro (1996) attributes the intercalation of shales and carbonates to paleoclimate variability, characterized by well-marked alternation between arid and humid seasons. According to the author, carbonate deposition is associated with periods of drier climate – and consequent high evaporation ratio and salinity. While shales were associated with more humid climates and lower salinity - a hypersaline environmental context in the Paraná Basin, due to water circulation restriction between the paleo-ocean Panthalassa and the syncline (AFONSO et al., 1994; HACHIRO, 1996). According to Holz et al. (2010), the Taquaral Member was deposited in a marine epicontinental in a restricted environment while the Assistência Member originated in a vast and shallow sea with an influx of continental waters in some marginal areas of the basin (e. g., presence of *Botryococcus* - brackish to freshwater algae) or hypersaline conditions in other sections (CORRÊA DA SILVA & CORNFORD, 1985; ROCHA et al., 2020).

4.1. Irati Formation Shales Components and Implications to CO₂ Storage

Based on the organic geochemical and petrographic assessments conducted by Rocha (2021), the organic-rich shales of the Irati Formation correspond to excellent hydrocarbon source rocks.

Regarding the role of shale components on CO₂ storage capacity, Rocha (2021) also confirmed the effect of kerogen type and maturity on CO₂ adsorption and storage capacity in organic-rich shales. Experiments conducted on Irati Formation organic-rich shales indicate a positive correlation between total organic carbon (TOC wt. %), vitrinite content (Type III kerogen), organic maturity, and CO₂ storage capacity. Such correlation follows previous studies (CHEN & XIAO, 2014; HAN et al., 2017) attributed to nano and micro-porosity development within the organic particles, associated with kerogen cracking and gaseous hydrocarbon release (ZHOU et al., 2020).

The impact of mineral constituents on CO₂ sorption capacity in shales was also observed. Mineralogical parameters, such as clay content, proportion and type, drive gas adsorption in low-TOC shales (BUSCH et al., 2008; 2020). Additionally, much clay content and the prevalence of expandable clay minerals of the smectite

group contribute to the CO₂ storage capacity of Irati Formation shales. Based on obtained mineralogical and sorption data, a positive correlation is established between samples with a high content of clay minerals from the smectite group and CO₂ storage capacity (ROCHA, 2021).

5. FINAL REMARKS AND CONCLUSIONS

Considering the current scenario of an increasing share of fossil fuels in the Brazilian energy mix and consequently CO₂ emissions upwards, CCUS technologies have become a clear strategy for decarbonising the Brazilian energy and industrial sectors. In this sense, CCUS can enable the continuous participation of fossil fuels in the Brazilian energy mix and still meet national (and international) climate change targets. However, to meet the Paris Agreements and 2050 net-zero goals, a regulatory regime supportive of CCUS is necessary and assesses Brazilian geological storage capacity. Such CO₂ storage capacity assessments must target extensive geological formations with significant rock volume, occurrence, and laterality. It should prioritise storage sites that are geographically close to CO₂ emitting sources and storage infrastructure, such as the Paraná Basin, Irati Formation case study.

CO₂ geological storage and the injection of fluids into the subsurface, such as to enhance oil recovery (EOR), is generally a mature technology already extensively deployed in Brazil. CO₂ injection can lead to enhanced shale gas recovery (CO₂-ESG) and CO₂ sequestration into shale's organic and clay content if applied to shale reservoirs.

Experimental analysis indicates that organic matter maturity is a controlling variant for total porosity and pore volumes, affecting pore size distribution and the relative proportions of micropores, mesopores, and macropores in shales. However, thermal maturity is not the only controlling factor of porosity-related variances in organic-rich rocks. Other contributing factors include quantity and quality of organic content (TOC and kerogen type) and mineralogical composition (clay minerals). These, together with organic maturity, are the pivotal causes of CO₂ adsorption patterns in shales and determine shale reservoirs storage capacity (ROCHA, 2021).

The characteristics of the analysed shale samples from the Irati Formation indicate the geologic potential for unconventional hydrocarbons and CO₂ geological storage. The Irati shales can be targeted for both shale oil and shale gas, according

to the local geology of the Paraná Basin. However, the high level of heterogeneity requires local estimates if the potential is for shale oil or shale gas, besides CCUS.

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