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**CO₂ GEOLOGICAL STORAGE IN ORGANIC-RICH SHALES OF THE IRATI
FORMATION, PARANÁ BASIN, BRAZIL**

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**CO₂ GEOLOGICAL STORAGE IN ORGANIC-RICH SHALES OF THE IRATI
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*Aos meus pais e irmã,
que sempre apoiaram meus estudos e escolhas*

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RESUMO

ROCHA, Haline de Vasconcellos. **Armazenamento geológico de CO₂ em folhelhos enriquecidos em matéria orgânica da Formação Irati, Bacia do Paraná, Brasil**. 2021. Tese (Doutorado) – Programa de Pós-Graduação em Energia, Instituto de Energia e Ambiente, Universidade de São Paulo, 2021.

O armazenamento geológico de dióxido de carbono (CO₂) corresponde a uma tecnologia eficiente e segura para a mitigação deste gás contribuinte ao efeito estufa em longo prazo. Quando aplicada a folhelhos, a injeção de CO₂ pode aumentar a taxa de recuperação de *shale gas*, bem como contribuir para a redução de emissões de CO₂ através do armazenando geológico em folhelhos enriquecidos em matéria orgânica. Os folhelhos são classificados como reservatórios não convencionais e o armazenamento de CO₂ nesta litologia possui características peculiares: armazenamento por adsorção à microporosidade orgânica e à argilominerais. Portanto, compreender a porosidade do folhelho e os padrões de sorção de gases associados requer uma caracterização detalhada de sua composição orgânica e mineralógica. Parâmetros como quantidade, tipo e maturidade do conteúdo orgânico são fatores de controle da porosidade orgânica e dos processos de adsorção de CO₂ e dessorção de CH₄ e, consequentemente, impulsionam a capacidade de armazenamento de CO₂ e produção de hidrocarbonetos. Esta pesquisa visa reduzir as incertezas quanto ao armazenamento de CO₂ em folhelhos, ao testar a hipótese de que a Formação Irati, na Bacia do Paraná, pode ser um reservatório viável para tecnologias CCUS e para a produção de *shale gas* e/ou de *shale oil* no Brasil, devido ao seu alto conteúdo orgânico, ampla ocorrência territorial e sua proximidade das principais fontes emissoras de CO₂ no país. Devido à heterogeneidade dos folhelhos Irati - que é atribuída à complexa história térmica da bacia, a caracterização de seu conteúdo orgânico e inorgânico em escala regional impõe desafios. Neste estudo, uma análise combinada de geoquímica orgânica, petrologia, mineralogia e isothermas de sorção de gás é aplicada à caracterização dos folhelhos Irati. Além disso, a interação entre os componentes orgânicos e inorgânicos com o CO₂, bem como os mecanismos rocha-fluido em folhelhos é investigada. O resultado é a determinação da capacidade de armazenamento de CO₂ e de potencial gerador de hidrocarbonetos não convencionais da Formação Irati, além da viabilidade geológica deste processo. Além da geologia, a tese traz uma abordagem multidisciplinar para as perspectivas de armazenamento de CO₂ no Brasil, apresentando uma visão geral do potencial do CCUS no país e identificando as principais barreiras legais e regulatórias para a implantação dessa tecnologia em larga escala.

Palavras-chave: Captura, utilização e armazenamento geológico de carbono, folhelhos enriquecidos em matéria orgânica, gás em folhelho, isothermas de sorção, Formação Irati, Bacia do Paraná, barreiras regulatórias, Brasil.

ABSTRACT

ROCHA, Haline de Vasconcellos. **CO₂ geological storage in organic-rich shales of the Irati Formation, Paraná Basin, Brazil.** 2021. Thesis (Doctorate) - Energy Postgraduate Program, Institute of Energy and Environment, University of São Paulo, 2021.

Geological storage of carbon dioxide (CO₂) is an efficient and safe long-term storage of this greenhouse-contributing gas. When applied to shales, CO₂ injection can enhance shale gas recovery, as well as contribute to CO₂ abatement by storing significant amounts of CO₂ into its organic porosity and clay content. Shales are classified as unconventional reservoirs and the CO₂ storage into this lithology has peculiar characteristics: storage through adsorption into the surface area microporous organic particles and clay minerals. Therefore, understanding shale's porosity and associated gas sorption patterns requires a detailed characterization of its organic and mineralogical composition. Parameters such as kerogen quantity, type, and maturity, are controlling factors of organic porosity and of CO₂ adsorption and CH₄ desorption processes, and consequently drive CO₂ storage capacity and hydrocarbon production of organic-rich shales. This research aims to reduce uncertainties regarding CO₂ storage in shales. It tests the hypothesis that the Irati Formation at Paraná Basin, can be a feasible target for both CCUS and shale gas production in Brazil, due to its high organic content, large occurrence and proximity to major CO₂ emitting sources within the country. Due to heterogeneity of Irati shales - which are attributed to the basin's complex thermal history, characterizing its organic and inorganic aspects in a regional scale is a challenging task. In this study, a combined analysis of organic geochemistry, petrology, mineralogy, and gas sorption isotherms is applied to Irati shale's characterization. Additionally, the interaction between the organic and inorganic component with CO₂ as well as rock-fluid mechanisms in shales are investigated. The result is determining Irati shale's storage capacity and overall geological feasibility as a CO₂ reservoir and as an unconventional hydrocarbon source-rock. Besides the geological aspects, the thesis brings a multidisciplinary approach towards CO₂ storage prospects in Brazil. It presents a general overview of the potential for CCUS in the country and identifies the main legal and regulatory barriers to large-scale CCUS deployment.

Keywords: Carbon capture, utilization, and storage (CCUS), CO₂ geological storage; organic-rich shale; shale gas, sorption isotherms; Irati Formation, Paraná Basin, regulatory barriers, Brazil.

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LIST OF ABBREVIATIONS AND ACRONYMS

ANM - Brazilian National Mining Agency

ANP - Brazilian National Agency of Petroleum, Natural Gas and Biofuels

BECCS - Bioenergy with CCS

BECCUS - Bioenergy with CCUS

BET - Brunauer–Emmett–Teller method

CAPES - Coordination for the Improvement of Higher Education Personnel

CNPq - Brazilian National Council for Scientific and Technological Development

CBM - Coalbed methane

CCS - Carbon Capture and Storage

CCUS - Carbon Capture Utilization and Storage

CEPAC - Center of Excellence in Research and Innovation in Petroleum, Mineral Resources and Carbon Storage

CIMA - Center for Marine and Environmental Research

COM - Commission to the European Parliament

COP - Conference of the Parties

DAC - Direct Air Capture

EASAC - European Academies Science Advisory Council

EC - European Commission

ECBM - Enhanced Coalbed Methane

E&P - Exploration and Production

EIR - Environmental Impact Report

EOR - Enhanced Oil Recovery

ESG - Enhanced Shale Gas Recovery

EU - European Union

Fm - Formation (Geological)

FP-ENAS - Fernando Pessoa Energy, Environment and Health Research Unit

GCCSI - Global CCS Institute

GHG - Greenhouse Gas

GIS - Geographic Information System

GO - Goiás State

Gt - Gigatonne

GW - Gigawatt

HI - Hydrogen Index

IBAMA - Brazilian Institute of Environment and Renewable Natural Resources

ICL - Imperial College London

ICCP - International Committee for Coal and Organic Petrology

ICDD - International Centre for Diffraction Data

IEA - International Energy Agency

IEAGHG - GHG Technology Collaboration Programme of International Energy Agency

IEE - Institute of Energy and Environment

IUPAC - International Union of Pure and Applied Chemistry

IPCC - Intergovernmental Panel on Climate Change

LNEG - Portuguese Geological Survey

Mb - Member (of a Geological Formation)

MME - Brazilian Ministry of Mines and Energy

Mpa - Mega Pascal

MT - Mato Grosso State

Mt - Million Metric Tonnes

MtCO₂ - Million tons of carbon dioxide

MW - Megawatt

NDC - Nationally Determined Contribution

OI - Oxygen Index

PB - Paraná Basin

PND - Brazilian National Development Plan

PR - Paraná State

R&D - Research and Development

RCGI - Research Centre for Gas Innovation

SDG - Sustainable Development Goals

SP - São Paulo State

TAI - Thermal alteration index

TOC - Total Organic Carbon

UAlg - University of Algarve

UNFCCC - United Nations Framework Convention on Climate Change

UK - United Kingdom

US - United States of America

US DOE - United States Department of Energy

UERJ - Rio de Janeiro State University

UFP - Fernando Pessoa University

USP - University of São Paulo

VR - Vitrinite Reflectance

XRD - X-Ray Diffractogram

SUMMARY

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1. INTRODUCTION TO THE THESIS

This doctoral thesis was submitted to the Energy Postgraduate Program of the Institute of Energy and Environment of the University of São Paulo (PPGE/ IEE/USP), in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Science. It is entitled 'CO₂ Geological Storage in Organic-Rich Shales of the Irati Formation, Paraná Basin, Brazil'.

The research was conducted with a multidisciplinary approach, covering areas of knowledge of Energy and Geology, and aims to search for synergies between geological studies, energy planning and CO₂ abatement strategies by discussing the potential for CO₂ geological storage in Brazil. Overall, this thesis aims to demonstrate the geological significance of organic-rich shale formations as potential reservoirs for CO₂ storage. Organic-rich shales hosts significant CO₂ storage capacity, mainly due to the organic porosity, and in despite of the low-permeability that characterize unconventional reservoirs. To do so, the thesis considers principles of organic geochemistry, petrology, petrography, and mineralogy, aligned with principles of pore-space flow and reaction with CO₂ through gas sorption experiments. It is applied to organic-rich shales of the Irati Formation, Paraná Basin, south-eastern Brazil. The general objective is to determine if Irati Formation organic-rich shales should be a target for CO₂ geological storage and for shale oil or shale gas exploration and production in Brazil.

This introductory section frames the research topic and presents the research motivation, problem characterization, followed by research questions, hypothesis, objectives, and concludes by presenting the structure of the thesis.

1.1 Introduction to research topic

Carbon dioxide capture, utilization, and storage (CCUS) is a key suite of technologies for reducing carbon dioxide emissions. It is essential to decarbonize the power and industrial sectors worldwide (IPCC, 2005; 2014) and already resulted in 260 million tonnes of CO₂ been stored to date (Global CCS Institute, 2020). Besides its significant role since the 2015 Paris Agreement of the United Nations Framework Convention on Climate Change (UNFCCC) and on the global effort outcome to limit global warming below 2 degrees Celsius, CCUS is necessary to meet net-zero goals in developing nations, such as Brazil, where it works as a transitional technology to a more sustainable energy mix by providing CO₂ mitigation to its continued use of fossil fuels. Accordingly, Brazil has substantial opportunities for large-scale CCUS deployment.

Although CCUS technologies only gained recognition and became essential in 2005 by the Intergovernmental Panel on Climate Change (IPCC) 1.5°C target, CCUS has been in operation for 45 years and currently applied to 26 large-scale facilities operating in commercial scale worldwide, that capture approximately 40 Mt of CO₂ per year (GCCSI, 2020). There are 65 commercial CCUS facilities globally, and hundreds that operate at different stages of development (IPCC, 2005; GCCSI, 2020). However, existing commercial and legal barriers still limit the expansion of large-scale CCUS projects at the required scale.

Overall, CCUS became so important in the net-zero emissions scenario that global efforts are taken place to surpass such barriers and provide legal and regulatory support its deployment. For instance, the European Commission established the Directive 2009/21/EC - here referred as 'CCS Directive', which regulates CO₂ geological storage activities within the European Union, and it is an important first step towards a legal and regulatory regime for CCUS technologies worldwide.

Besides existent commercial barriers to CO₂ geological storage, due to associated costs and lack of carbon market mechanisms, there are also economic interest associated to CCUS large-scale deployment. The CCUS strategy is significantly cheaper than climate change consequences and other strategy costs (Adelman & Duncan, 2011; IPCC, 2014; Pop, 2015). According to the International Energy Agency (IEA), there is an estimated cost increase by 71% for meeting 2050 targets without CCUS (IEA, 2015). Moreover, the development and deployment of CCUS technologies can bring revenue through CO₂ utilization and by exporting and improving this worldwide demanded strategy and emerging global CCUS industry (Pop,

2015). For instance, carbon capture, utilization, and storage (CCUS) can reduce the global warming potential (GWP) of fossil fuelled power plants in 63% to 82%, and CO₂-enhanced oil recovery has the GWP 2.3 times lower compared to discharging CO₂ to the atmosphere (Cuéllar-Franca & Azapagic, 2015). The combined potential for mitigating CO₂ emissions and for supporting a sustainable energy transition, coupled with economic development opportunities, is what brings efforts worldwide to support CCUS projects and research.

CO₂ geological storage is the segment within the CCUS chain that plays the major role in mitigating the worst impacts of climate change by its significant CO₂ abatement capacity. This role arises from the capacity of injecting large volumes of CO₂ into adequate geologic formations for a geologically significant period (Bachu, 2002). For instance, global targets are estimated in 10 Gt CO₂ emission abatement per year by 2050 and this can only be achieved with geological CO₂ storage (Krevor et al. 2019), which despite the yet few large-scale facilities, the already reached 97.5 million tonnes of CO₂ been stored annually (GCCSI, 2020).

Brazil has a high potential for CO₂ geological storage due to the large occurrence of sedimentary basins within its territory – a total of twelve prospective basins that cover an area of approximately 12000.000 km² (Ketzer et al., 2015), with an estimated storage capacity of 2030 GtCO₂ (GCCSI, 2019). However, it is important to highlight that CO₂ storage sites are not simply associated with the occurrence of a sedimentary basin and a suitable geological formation. It relies on the reservoir's characteristics, such as its mineralogy, petrography, geochemistry and petrophysics, as well as on properties such as porosity, permeability, and CO₂ trapping mechanisms, as well as on caprock integrity, injectivity and fluid dynamics (Haszeldine, 2019; Krevor, et al., 2019).

In addition to geological feasibility, the logistics of CO₂ capture from emitting sources and its transport to storage sites play a major role on the economic feasibility of the CCUS chain. In the Brazilian case study, most of the CO₂-emitting stationary sources are concentrated in the highly industrialized Southeast region of Brazil and lay on top of sedimentary basins (Figure 1), which brings synergies between CO₂ capture and storage by reducing CO₂ transportation costs and efforts. Estimates show that CO₂ emissions in the surroundings of these basins (within a 300 km radius) reach approximately 368 Mt/year, from which 49% are from the Brazilian power generation sector (Ketzer et al., 2015).

Figure 1. Map of Brazil with sedimentary basins with estimated potential for CO₂ geological storage. Adapted from Ketzer et al. (2015).

Regarding its energy mix, Brazil stands out among the developing countries for its comparatively low CO₂ equivalent footprint in the power generation sector, with 80.2% of its electricity mix and 43.5% of primary energy mix derived from renewable sources (MME, 2019). However, similarly to most developing countries, fossil fuels tend to play a continuously increasing share in the Brazilian energy and electricity mix, especially with the growing exploration of the Brazilian Presalt – one of the largest hydrocarbons reserves worldwide. For instance, oil production in Brazil will account 23% of the total increase in oil production worldwide until 2030, and will double its natural gas production capacity, from 112 to 220 million m³ per day (MME, 2019).

Brazil additionally has a national energy security establishment continuously being dependent on fossil fuels. In accordance with the oil and gas expansion supply, the energy expansion plan (from the Portuguese, Plano Decenal de Expansão de Energia - PDE), which reports expansion prospects for the Brazilian energy sector over a ten-year timeframe, address natural gas power plants as essential to energy capacity supply in a current scenario of hydraulic potentials

exhaustion (PDE, 2029; EPE, 2020). Consequently, CO₂ emissions in the Brazilian energy generation sector have an upward tendency.

In this context, Brazil voluntarily committed in the 2015 Paris Agreement to reduce 37% of its CO₂ emission by 2025, and to reduce 43% by 2030, based on 2005 levels. This accounts for mitigating 6.2 tonnes of CO₂ equivalent (NDC Brazil, 2015; Brazil, 2016). However, Brazil is facing challenges to meet such ambitious target: deep economic recessions and political crisis difficult the future of climate action in Brazil. Since 2018, flexibilization of existing national climate and environmental policies resulted in increasing deforestation and, consequently, cumulative CO₂ emissions (Morgan et al. 2019; Nobre et al. 2019).

Aiming to surpass these challenges and fulfil the NDC Brazil commitment towards net-zero emissions, CCUS technologies represent a promising solution to meet the national increasing energy demand and limit the associated CO₂ emissions: CO₂ geological storage could lead to a major CO₂ abatement within the power and industrial sectors and could make national GHG reduction efforts achievable. Additionally, CCUS could work as transitional technology towards a more sustainable energy future in Brazil.

Facing the presented scenario of urgent deployment of large-scale CCUS technologies, worldwide abundant and widespread rock formations, such as shales, gain relevance for its potential to contribute to CO₂ geological storage capacity. Despite the low permeability that characterize these unconventional reservoirs, the microporosity of organic particles and clay minerals that constitute shales, in addition to the displacement efficiency between the pre-existent methane (CH₄) with the injected CO₂, attribute to these formations significant CO₂ storage capacity. Involved properties and trapping mechanisms are presented and discussed in this research, with the aim to evaluate if organic-rich shales of the Irati Formation at the Paraná Basin can be economically feasible targets to deploy CCUS technologies in Southeast Brazil. Moreover, CO₂ storage in shale gas reservoirs can not only provide CO₂ abatement, but also lead to the enhanced recovery of shale gas and shale oil and, consequently, bring economic feasibility to the process through the associated hydrocarbon production, facing the still absent carbon taxation and pricing in Brazil.

1.2 Research questions, hypothesis, and objectives

This Ph.D. thesis investigates the hypothesis that organic-rich shales can store significant amounts of CO₂ due to rock-fluid properties that attribute to these unconventional reservoirs a remarkably high CO₂ storage capacity. The hypothesis is tested in Irati Formation organic-rich shales of the Paraná Basin, Brazil, with the aim to discuss if such geological formation can be a feasible target for both CO₂ abatement and shale gas production under small-scale CO₂ emitting-sinking/closed-cycle systems in southern Brazil, where the CO₂ emitting sources are geographically proximal to potential geological reservoirs.

This study also raises questions about the (i) Irati Formation organic-rich shales potential for unconventional hydrocarbons (e.g. shale oil and/or shale gas), (ii) Irati Formation organic-rich shales composition and porous system characterization and implications on CO₂ geological storage, (iii) the effect of the organic content on storage capacity in shales, (iv) the effect of the mineralogical content on storage capacity in shales, (v) the most suitable areas for CO₂ geological storage and for hydrocarbon production in the Irati Formation and within the Paraná Basin, (vi) the potential geologic risks and environmental impacts associated to CCUS technologies, and (vii) potential regulatory barriers to CCUS deployment in Brazil.

The main directions of this research can be expressed in the following questions:

1. Do Irati Formation organic-rich shales have potential for unconventional hydrocarbons (e.g., shale gas and shale oil) and/or for CO₂ geological storage?
2. What are the main characteristics and components of Irati Formation shales and how are these relevant to shale gas and shale oil potential and to CO₂ geological storage?
3. How the Irati Formation organic-rich shales' mineralogy and organic content type and maturation affect CO₂ adsorption and how does its heterogeneity interfere with its potential for CO₂ geological storage?
4. In which portions of the Paraná Basin, the Irati Formation is more suitable to shale gas, to shale oil, and to CO₂ geological storage?
5. Would Irati Formation organic-rich shales be a feasible CO₂ reservoir, and should these be a target for CCUS in southeast Brazil, and which are the conditioning factors and potential barriers?

To achieve answers for these questions, this research methodological framework comprises two main routes of investigation. The first is a detailed characterization of the organic and inorganic (mineralogical) composition of Irati Formation shales. The second comprises the estimation of its CO₂ storage capacity through gas sorption isotherms analysis. In organic-rich shales, CO₂ storage is controlled by gas adsorption into the micropores of organic matter and clay minerals (Rodrigues, 2002). Therefore, a detailed characterization of these elements is essential and the first step to determining the CO₂ storage capacity in shales.

Applied methodology includes quantitative and qualitative approaches to provide a thorough analysis on the subject. Besides bibliographical research, rock samples were object of study, alongside with several geochemical, petrological, and petrographic techniques, such as determining its total organic carbon, kerogen typing and maturation through Rock-Eval pyrolysis screening, palynofacies, and vitrinite reflectance and spore fluorescence, respectively, followed by conducted experiments with gas sorption isotherms. The combination of analysis and experimental procedures provides a general overview of the geological feasibility of Irati Formation organic-rich shales been used for CO₂ storage, at a regional scale of the Paraná Basin. In addition to the geology, the potential for CCUS in the Irati Formation is analysed under a multidisciplinary perspective, considering also environmental, technical, economic, and regulatory aspects.

In addition to the geological feasibility, a general evaluation of regulatory aspects of CCUS technologies is also presented in this study. Regarding economic feasibility, the study considers that CO₂ storage in shales can be economically feasible as CO₂ reservoirs in the context of shale gas/shale oil exploration, where the deployment of enhanced recovery using CO₂ injection can potentially improve production rates as well as lead to the permanent sequestration of CO₂.

The study intended contribution is to enhance the knowledge regarding unconventional reservoirs and CO₂ geological storage in Brazil. The obtained results can contribute to reducing uncertainty about CO₂ geological storage in low-permeability, organic-rich shale formations, through analysing parameters that affect rock-fluid interactions. It also investigates to which extent the organic content and clay minerals contribute to shale's storage capacity and how it affects CO₂ sorption and hydrocarbon generation in this lithology that is very abundant worldwide. Additionally, the thesis also contributes to the characterization of Irati Formation shales and to the analysis of the complex thermal history of the Paraná Basin.

Besides the scientific contribution, the primary propose of the study is to contribute to CCUS and CO₂ geological storage deployment in Brazil by providing data and discussion for future determining the Brazilian overall geological storage capacity for CO₂.

1.3 Structure of the thesis

The Ph.D. thesis is divided in seven sections, which follow the sequence of the research objectives. The first consist of an introduction to the thesis and to the study. It presents the research problem, motivations, questions, hypothesis, and objectives.

The second presents the theoretical background with an introductory approach to carbon capture, utilization, and storage (CCUS) technologies. It starts with general aspects of CCUS and then focus on the concept of CO₂ geological storage, addressing specificities of shales as reservoirs and applied CO₂ trapping mechanisms, as well as potential risks associated to these processes. The section concludes by presenting the Brazilian case study, discussing the overall potential for CCUS in Brazil with associated challenges and barriers based on international experience.

Subsequently, section three presents the Paraná Basin case study, with a description of its geological setting and study area location. This section concludes with a characterization of the organic-rich shales from the Irati Formation based on literature review.

Section four address the materials and methods applied in this research. It describes sample sites, collection and preparation, and the applied analytical procedures and apparatus used in this study.

Section five presents the obtained results. It includes data on organic geochemistry, organic petrography, mineralogy, porosity, and storage capacity. It also briefly discusses the obtained results.

Section six brings an integrated discussion and the combined interpretation of results. It discusses the Irati Formation shale's whole-rock and clay mineralogy, organic matter content type, source, maturation, and depositional environment, as well as its heterogeneity. Additionally, this section presents the correlation between shale's composition and gas sorption pattern and compares the obtained results with previous studies.

Section seven includes a synopsis of the thesis's main findings, presenting the final remarks and conclusions. Additionally, it contextualizes the Irati Formation study case with the overall Brazilian study case scenario.

2. THEORETICAL APPROACH

This section presents the fundamental literature background of the study. It addresses, respectively, the technical background of CCU technologies, CO₂ geological storage requirements, CO₂ trapping mechanisms, and the prospects of shales as CO₂ reservoirs and its specificities, followed by potential geologic risks and environmental impacts that can relate to CO₂ storage, also addressing risk mitigation strategies, as well as legal and regulatory aspects. The section concludes with a general overview of CCUS in Brazil, including identified regulatory barriers to its deployment.

2.1 CCUS and CO₂ geological storage technologies

Carbon capture, utilization, and storage (CCUS) refers to a suite of technological processes. These are: (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 into a service and/or product with economic value; and/or (iv) CO₂ storage into suitable geological formations (Lal, 2005; Bradshaw et al. 2007; IPCC, 2005, 2014;), as illustrated in Figure 2.

Figure 2. Illustrative diagram of CCUS technologies integrated chain and possible applications. Retrieved from IPCC (2005).

CO₂ capture consists of the separation of CO₂ from other effluent gases, compression for volume reduction and fluid accommodation (IPCC, 2014; Ramirez, 2019). It can be categorized into three different CO₂ capture processes: (i) pre-combustion - fuel conversion into CO₂ and H₂ gaseous mixture, followed by H₂ separation and combustion without producing CO₂, being usually applied to natural gas processing; (ii) post-combustion – separation of CO₂ from combustion exhaust gases through solvents or adsorption processes, being a highly applied method within food and beverage industries; and (iii) oxyfuel with post-combustion – utilization of oxygen for the combustion of fuels, which produces H₂O and CO₂ that can easily be captured afterwards (GCCSI, 2014, 2019). CO₂ capture can be efficiently applied to industrial and energy generation facilities, such as thermoelectric power plants or cement, steel, paper, chemical, and natural gas processing industries, through different methods, such as CO₂ absorption, desorption, membrane separation and cryogenic separation (IEA, 2009, 2015).

CO₂ transport includes its compression through pipelines, or adequate ships and trucks, from the capture unit to the storage site (IEA, 2019).

CO₂ utilization is a broad term that refers either to the direct usage of CO₂ in physical processes, such as enhanced oil recovery (EOR), or to its indirect usage as feedstock supply to industrial processes, such as in the production of chemicals, materials, and fuels (Ramirez, 2019). CO₂ subsurface utilization accounts for the exploitation of energy resources, such as oil (enhanced oil recovery - EOR), natural gas (enhanced gas recovery – EGR, enhanced shale gas recovery – ESG, and enhanced coalbed methane – ECBM), and geothermal power and heat (enhanced geothermal systems). Among these technologies, CO₂-EOR is the most used and mature technology, routinely used by the petroleum industry worldwide. This technology can potentially produce 470 billion barrels of oil and could facilitate the storage of 140 billion tonnes of CO₂ (GCCSI, 2014, 2019). Consequently, CO₂-EOR represents a cost-effective pathway within the CCUS chain. However, there are concerns and legal uncertainties associated to CO₂-EOR being used for increment oil production and, understandably, a debate around it being addressed as a CO₂ abatement technology (GCCSI, 2012; Ramirez, 2019).

CO₂ storage is the segment within the CCUS chain that has major contribution to net-zero goals. It stands out among a diverse portfolio of CO₂ mitigation strategies, together with hydrogen production, energy efficiency and renewable energy generation, and it is required as a component for other CO₂ abatement technologies such as bioenergy with CCS (BECCS) and

direct air capture (DAC) (Bui & Mac Dowell, 2019), which also can result in negative emissions.

CO₂ storage can occur through two different technological segments: biological fixation (biotic sequestration) and geological storage (abiotic sequestration) (Herzog & Colomb, 2004; Rodrigues, et al. 2015). Regarding economic feasibility, CO₂ geological sequestration is far more advanced than the biotic sequestration pathway, being already widely implemented at commercial scale worldwide in subsurface geological formations such as depleted oil and gas reservoirs, deep saline aquifers, coal seams, organic-rich shale formations, and basalts (Rodrigues et al. 2015).

CO₂ geological storage consists of CO₂ injection and storage into adequate reservoirs for a geologically significant period (Bachu, 2002). Suitable reservoirs must present suitable porosity and permeability, satisfactory seal, and a stable tectonic environment to avoid compromising the integrity of the storage site (Bachu, et al. 2007). Reservoirs should be permanently monitored to ensure that the CO₂ remains stored within the geological formation (Bachu et al. 2017). These combinations of features are found in sedimentary geological systems around the world, that include both conventional (e.g., sandstones and carbonates) and unconventional reservoirs (e.g., coal seams and organic-rich shales). However, it is important to highlight that CO₂ storage sites are not simply associated with the occurrence of a sedimentary basin. It relies on geological, geochemical and petrophysical processes and properties such as porosity, permeability, caprock integrity, injectivity and fluid dynamics (Krevor et al. 2019; Haszeldine, 2019).

Conventional geological reservoirs considered favourable to carbon storage must have the following characteristics (Bachu et al. 2007; Bachu, 2008): (i) sufficient capacity to store large volumes of CO₂; (ii) adequate "injectivity" to allow the injection of carbon into the geological formation; and reservoir (iii) confinement or integrity, (i.e., geological configuration with traps and sealing that retain the upward CO₂ leakage for the desired period of time).

Besides geological aspects, it is important to understand the CO₂ trapping mechanisms for each reservoir type for the CO₂ storage to be safe and effective. There are diverse trapping mechanisms of CO₂ into geological formations. These traps are classified as structural, stratigraphic, solubility, mineral and capillary trapping mechanisms, as well as adsorption.

Structural and stratigraphic trapping are common in conventional reservoirs, such as depleted oil and gas reservoirs since it is configured as a physical barrier to upward flow of CO₂. The CO₂ accumulated above brine due to buoyancy and it becomes trapped below the caprock (Bachu et al., 1994).

Solubility trapping of CO₂ occurs by its dissolution into the brine, usually in an aquifer formation. As CO₂ saturated brine is denser than host brine, it sinks deeper into the formation resulting in convective mixing. This process is slow and can take from one year to thousands of years depending on the reservoir permeability (Riaz et al., 2006, Lindeberg et al., 1997, Ennis-King et al., 2005).

Mineral trapping occurs after CO₂ dissolves in the brine to form carbonic acid (H₂CO₃) which then reacts with the formation rock to generate solid minerals. This trapping mechanism requires an exceedingly long time and is considered the slowest trapping mechanism (Gunter et al., 1997, Lin et al., 2008).

Capillary trapping, also called residual trapping, occurs through CO₂ trapping into pore space. It does not rely on the caprock, but on the porosity and pore size distribution within the geological formation. It is the fastest CO₂ trapping mechanism and one of the most efficient in ensuring CO₂ remains permanently stored in the subsurface (IPCC, 2014; Krevor et al., 2015). The safety of this trapping mechanisms relies on its capacity of CO₂ buoyancy avoidance and consequently limits CO₂ plume migration, since the CO₂ remains within pore space.

In regard to CO₂ trapping and the overall safety and efficiency of the CO₂ geological storage, and similarly to petroleum production, there are environmental risks associated, mainly represented by fluid leakage. Leakage can be caused by improper sealing of the reservoir, integrity/confinement loss due to drilling and abandoned wells, and by geological faults and fractures (Barros et al, 2016).

2.2. CO₂ storage in shale formations

Shales were historically recognized as hydrocarbon source rocks and as caprocks to conventional petroleum systems, and most recently recognized as unconventional reservoirs to shale gas and shale oil. With the growing importance of shale gas as the future supply of natural gas - which is known as the transitional fossil fuel until the global energy mix shifts towards renewable energy - these organic-rich shale formations gained relevance in the energy scenario worldwide. Besides its role as natural gas source-rocks, shales can be reservoirs to either hydrocarbons or to other fluids, such as CO₂. The behaviour of organic-rich shales as a reservoir depends on its composition and mainly on the characteristics of the organic matter compound. In organic-rich shale formations, the migration of hydrocarbons generated within the lithology is restricted and, consequently, all the elements of a petroleum system (e.g., source rock, reservoir and caprock) are constrained to the same shale formation, configuring an unconventional petroleum system and either one shale gas or shale oil reservoir, according to the organic content type and maturation. In the case of shale gas reservoirs, CO₂ injection in organic-rich shale reservoirs enhance shale gas recovery (CO₂-ESG) and effectively replace water as the stimulation fluid in the hydraulic fracturing technological process (Lyu et al., 2021). Moreover, part of the injected CO₂ gets permanently stored due to the adsorption trapping mechanism (Godec, et al., 2013; Kang, et al., 2011).

In resemblance to coal due to the high organic content, the adsorption inherent characteristics of organic-rich shales lead to fluids been stored in the organic matter microporous structure (Bemani, et al., 2020; Chen & Xiao, 2014; Zhou et al., 2020). Therefore, the organic component in these unconventional reservoirs plays a major role on its porous system and, consequently, on its storage capacity (Rodrigues, 2002). For instance, in organic-rich rocks, the adsorption process control storage and trapping mechanisms, and accounts for 95% to 98% of the total gas storage, while 2% to 5% are stored as free gas and due to the absorption (Dinis, et al., 2010, 2015; Rodrigues, et al., 2018). As shown in Figure 3 and in contrast to conventional reservoirs, in organic-rich shales smaller pores imply a higher internal surface area and, consequently, in a higher storage capacity due to the adsorption trapping mechanism of CO₂.

Figure 3. Porous media, CO₂ trapping and storage capacity illustration scheme for unconventional and conventional reservoirs, focusing on the role of organic porosity and pore-size distribution on internal surface area. Adapted from Rodrigues & Lemos de Sousa (2008).

Shales are widely known as impermeable rocks, and the complexity of fluid-flow mechanisms in shales that lead to such low-permeability (usually <0.01 mD) is attributed to its complex porous system. The coexistence of organic and intergranular (inorganic) porosity in shales results in a wide range of pore volumes and pore size distribution, which affects gas flow and sorption patterns in shales. According to Kuila & Prasad (2011) and Mastarlez, 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. This differs from the gas flow pattern in conventional reservoirs, such as sandstones, which is Darcy-like flow in micrometre to larger pore sizes (Mastarlez, 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.

CO₂ sequestration in organic-rich shales is also driven by its organic porosity (Boruah, et al., 2019; Chen & Xiao, 2014; Gu, et al., 2017; Hackley & Cardott, 2016; Han, et al., 2017; Pan et al., 2015; Rodrigues, et al., 2013; Romero-Sarmiento et al., 2012). This organic porosity is mainly attributed to maceral groups with microporosity, such as vitrinite, whose surface area provides sorption sites (e.g., on organic surface area of micropores and nanopores) (Bustin et al. 2008; Mastarlez, et al. 2013). Moreover, the storage capacity of shales relies in the kerogen evolution, more specifically to its thermal cracking during catagenesis and to hydrocarbon generation and migration (Ross & Bustin, 2009).

Overall, influencing factors of CO₂ storage capacity of organic-rich shales include the following parameters: TOC, kerogen type, thermal maturity, as well as mineral composition (Bemani et al., 2020; Boruah et al., 2019; Klewiah, et al., 2020; Liu, et al., 2018; Pan et al., 2015; Romero-Sarmiento et al., 2012). For instance, shale gas reservoirs are usually over-mature source-rocks mainly composed of type III kerogen and that contain elevated organic matter content (TOC from 0.5 to 2%), vitrinite reflectance (%R_r) ranging from 1.75 and 3.0%, and that usually occurs in the field of thermogenic gas (temperature range, between 120 and 180 °C, and burial sufficiently high (usually above 1.000 meters) to convert oil to natural gas (Aliouane, et al., 2014; Bruner & Smosna, 2011; Ryder, 2008).

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

During early stages of thermal maturation, the total organic content (TOC) controls fluid adsorption in organic-rich shales (Han et al., 2017). This is due to the kerogen swelling and shrinkage effect and the associated organic porosity generation. Kerogen swelling reaches its maximum at the transitioning oil to gas window, at a T_{max} of approximately 445°C and vitrinite reflectance of 0.8% R_o. At that point, after 0.8% R_o, organic nanopores are formed by the shrinkage of kerogen and by the release of hydrocarbons, leading to an increase in internal surface area and of organic porosity. The continued kerogen cracking results in a more rigid kerogen residue, and subsequently, the swelling and retention ability of 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_o and below 3.5% R_o are more suitable to CO₂ storage through adsorption.

Overall, the effectiveness of CO₂ geological storage depends on the combination of physical factors that define the trapping system, or a geological trap, which consist of three-dimensional arrangements of rocks in the subsurface that prevent the buoyant CO₂ from migration upwards (Krevor et al. 2019). In general, reservoir-seal-trapping systems are well known by the oil industry, since there are analogous to the petroleum systems exploited by them. Petroleum systems' elements and processes configure a trapping mechanism that store hydrocarbons for million or even tens of millions of years (Bachu, 2008), which supports the statement that these geological mechanisms can be used for CO₂ storage effectively.

Clay minerals are also 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 largest amounts, followed by Na-exchanged smectite, illite and kaolinite, and negligible amounts of CO₂ adsorbed on chlorite (Busch, et al., 2020; Busch et al., 2008).

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 pathway and result in reduced permeability over time, 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 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, which contributes to storage safety and to a reduction in reservoir pressure (Busch et al. 2020).

Considering that shale's organic and mineralogical composition determine gas sorption patterns and, consequently, its storage capacity, a detailed characterization of these components in organic-shale formations is the first step towards evaluating its potential for CO₂ geological storage. Additionally, the organic matter and clay mineralogy affect the overall safety and efficiency of CO₂ sequestration, and should be considered in risk assessments and monitoring of CO₂ geological storage.

2.3. Geologic risk assessment and monitoring of CO₂ storage

The environmental impacts of CO₂ geological storage can be divided into global and local environmental risks. Global risks arise by the lack of efficiency of the CO₂ storage process and the consequent CO₂ release to the atmosphere. Local risks are usually associated to CO₂ leakage, which may result from high CO₂ concentrations in the gas phase near the surface, CO₂ dissolution in groundwater (aquifers), and effects induced by displacement of fluids with the injection of CO₂ (seismic activity) (Zhang & Bachu, 2011; Rodrigues et al. 2015; Almeida et al, 2017).

Local large-scale onshore leakages of CO₂ can result in direct risks to human health, both through immediate deaths resulting from asphyxiation or health impacts of prolonged exposure to high concentrations of carbon dioxide (Graus et al., 2011). The effects of CO₂ leakage on the local fauna and flora, however, are less certain and could disrupt the local ecology and agriculture (Gerard and Wilson, 2009). The main concern relates to the contamination of drinking water and surface water through the displacement of saline water and/or CO₂ into the aquifers. Moreover, subsurface CO₂ injection can trigger small seismic events. Although there is low probability of risk occurrence, it is essential to safely manage CO₂ injection to guarantee human and ecological safety (Gerard and Wilson, 2009).

The consequences associated with CO₂ leakage are highly dependent on the location of the storage site and on how the country deals with such incidents. For instance, leakage from onshore storage sites is likely to affect a much more significant number of people than in the case of offshore sites. However, CO₂ leakage from offshore can trigger ocean acidification and, consequently, have adverse effects on marine ecosystems and on livelihood of coastal populations (van der Zwaan & Gerlagh, 2016).

On the other hand, CO₂ leakage from a CCUS site most probably will to be a gradual seepage rather than sudden and rapid leakage, which lower CO₂ concentrations and associated consequences and more easily predicted and remediated than natural events (Pop, 2015). While this means that the likelihood of catastrophic accidents leading to extensive and uncontrollable leakage is extremely low, a degree of uncertainty remains as to the possibility of CO₂ escaping from transport pipelines, through operational or abandoned wells on the site, as well as through fault lines, depending on the characteristics of the reservoir (Lako et al., 2011). Importantly, this risk is dictated to a significant extent by the level of maintenance of both active and abandoned infrastructure and by safety standards and regulations on well's design and

construction (IEAGHG, 2019). Overall, the risk of CO₂ leakage from CCUS facilities relies significantly on human action and are mainly mitigated with the storage site control, through appropriate subsurface monitoring and remediation measures.

Monitoring is essential to the safe deployment of CO₂ geological storage. It required since the permitting process and should be carried out during all stages of CO₂ injection, from planning to completion. Monitoring includes a characterization of the reservoir and caprock properties, to select appropriate storage sites with adequate capacity, injectivity and integrity to handle high-pressure CO₂ injection (Dino & Gallo, 2009). Appropriate monitoring includes: (i) tracking the location of the CO₂ plume; (ii) ensuring that injection and abandoned wells are not leaking; and (iii) verifying the quantity of CO₂ that has been injected underground. Additionally, depending on site-specific considerations, monitoring may be required to (iv) ensure that natural resources, such as groundwater and ecosystems, are protected and that the local population is not exposed to unsafe concentrations of CO₂ (Bachu, 2017). Together with monitoring requirements it is important to quantify the volume of CO₂ injected underground to estimate the storage effectiveness. In addition to monitoring activities, a detailed risk assessment is required to ensure that any CO₂ injection associated impact can be appropriately identified, monitored, and mitigated (EC, 2015).

Evidence indicates that CO₂ leakage is not likely to occur if site selection, characterization and storage project design are undertaken correctly. However, there is a minor risk that inevitably remains associated with the up-to-date insufficient deployment of CCUS projects and the consequent lack of practical experience within the emerging learning curve. This risk should be addressed in the legal framework to be minimized.

Nevertheless, addressing the geologic risk adds complexity to the regulatory regime, since the geological sequestration exceeds the lifespan of conventional commercial scale projects and entities. Accordingly, large-scale, and long-term environmental safety of CO₂ storage requires a well-designed and comprehensive policy and regulation framework, that can address specific barriers to this technology deployment, such as the geologic risk and long-term liabilities.

In this concern, the Europe Commission created the Storage Directive (i.e., Directive 2009/31/EC), which provides a legislative framework for the CO₂ geological storage component of the CCUS chain. The Directive guides European Commission Member States by requirements of appropriate project design to ensure the storage of CO₂ is permanent and safe (EC, 2009)

Regarding geologic risk, the CCS Directive determines that the absence of CO₂ leakage risk, as well as the absence of significant risks to health and the environment, are fundamental first steps to storage site selection (EC, 2009).

To identify and assess the potential hazards associated with a storage location, a thorough characterization of the site and surrounding areas should be performed in accordance to the best practices adopted by Costa et al (2018, 2019) and Mussara et al (2019). These consist on: (i) data collection, to construct a 3-D static model of the reservoir, sealing rock/trap and the surrounding area, including hydraulically connected areas; (ii) construction of the 3-D static terrestrial geological model, by developing a series of scenarios for each parameter and calculating the appropriate confidence limits and associated uncertainty; (iii) characterization of the dynamic behaviour of the storage complex, sensitivity characterization and risk assessment, through computerized simulations of CO₂ injection at the storage site.

Furthermore, the EU CCS Directive demands a constantly updated monitoring plan of the storage complex. According to the monitoring requirements of the CAC Directive, the plan should consider: (i) detection of CO₂ migration; (ii) detection of CO₂ leakage; and (iii) effects on the surrounding environment, including the biosphere and all its resources, and particularly human populations (EC, 2009). The monitoring plan should be detailed for each of the main stages of the project, including (i) baseline, (ii) operational and (iii) post-closure monitoring. In addition to the monitoring plan, a plan for mitigation and corrective measures should be addressed. This would update the safety evaluation of the storage complex integrity both in short and long-term, assuring that the CO₂ storage would be environmentally safe (Barros et al. 2016; Oliveira, 2016).

The safety evaluation of the CO₂ storage site integrity should be based on an environmental impact assessment (EIA) and/or by a leakage risk assessment, carried out at various stages of the CCUS operation. In this sense, large-scale CCUS projects - that deal with more than 100 kilotonnes of CO₂ being stored, are regulated by Directive 2009/31/EC and by Directive EIA 2011/92/EU (EU, 2011; Commission, 2009, European Union, 2012). The latter been an update of the Directive 85/337/EEC, regarding Environmental Impact Assessment (EIA), capture and transport of CO₂ for geological storage, as well as storage sites. Accordingly, the Directive 2009/31/EC added amendments related to CCUS and projects phases, in addition to EIA obligation (Annexes I and II of the former EIA Directive) (Barros et al. 2016; Oliveira, 2016). CCUS projects phases and obligations are presented in Table 1.

Table 1. Life cycle of CCS projects considering the obligations established in the CCS and EIA Directives, according to the analysis of Oliveira (2016).

CCS Project/activity phase	CCS Directive (2009/31/EC)	EIA Directive (2011/92/EU)
Phase 0 Site selection; Planning; Project feasibility evaluation; Local storage risks assessment	Detailed project description. Storage complex characterization	
	Explorations permits request. Development of site-specific monitoring, control and corrective measures plan	Selected site and surroundings environmental characterization regarding: Natural resources and human population. Environmental Impact Assessment (EIA)
Phase 1 Construction and substructures for on-site testing and operation.	EIA full report submitted and approved: required for the storage permit; Site-specific monitoring and control, and development of a corrective action plan. Consider possible environmental impacts as criteria in strategic decision making. Mitigation measures incorporated into the installation project and project review.	Monitoring of significant impacts to the environment, and the effectiveness of corrective measures. Quantitative risk assessment and re-evaluation of the EIA report.
Phase 2 Testing: CO ₂ Injection tests		
Phase 3 Exploration: CO ₂ storage at commercial scale		
Phase 4 Deactivation: site closure	Maintenance of the specific Plan of Monitoring, Control Plan and Corrective Measures; Records and quantitative assessment of risks and associated impacts.	

According to Barros et al. (2016) and Oliveira (2016), the Environmental Impact Assessment of a CCUS project should consider the entire life cycle of the projected unit, analysing not only environmental issues, but also the social and economic effects of the project and the risk assessment. Thus, the purpose of the EIA is to identify the possible origins of the problems, propose alternatives and define measures to avoid, reduce and, if possible, remedy significant adverse effects.

CO₂ geological storage projects introduces to the EIA the concept of permanent storage, which means the CO₂ being stored for a period of thousands of years. Considering this perpetual underground storage, some authors tend to establish comparisons between the geological sequestration of CO₂ and the disposal of radioactive waste. However, in addition to the permanent storage required in underground rock formations, there are no other similarities between these two situations (Barros et al., 2016). In this sense, there is no reference in the legal

system for dealing with the permanent storage concept – which far exceed the conventional lifespan of commercial projects and entities. Overall, the permanent storage concept brings legal uncertainties to the liability regime. And these associated uncertainties restrain stakeholder investment and technology development, which are essential to commercial scale CCUS deployment.

2.4. Legal and regulatory aspects of CCUS

The European Parliament together with the Council on the Geological Storage of Carbon Dioxide agreed on 23 April 2009 and implemented on June 25th, 2009, the Directive 2009/31/EC. The so-called Carbon Capture and Storage Directive – here referred to as ‘CCS Directive’) establishes a regulatory regime for an environmentally secure geological storage of CO₂. And guides European Commission Member States by requirements of appropriate project design to ensure the storage of CO₂ is permanent and safe (EC, 2009)

As previously mentioned, the CCS Directive focuses on the geological storage component of the CCUS chain, more especially on the prevention of CO₂ leakage and on geologic risk. The CCS Directive addresses the exploration of potential CO₂ storage sites, storage operations, closure and post-closure obligations, transfer of responsibility, financial security, and commercial mechanisms (EC, 2009).

To ensure the coherent implementation of the CCS Directive throughout the European Union (EU), State Members are required to present a report every four years on the implantation of the Directive (EC, 2009). Subsequently, the EC reports to the European Parliament and the Council on the CCS Directive implementation. These include reporting on the implementation, facilitating exchanges between the competent authorities, publishing guidance documents, and adopting Commission Opinions on draft storage permits. The first implementation report was released in 2013, and it was based on Member States` reports delivered between 2011 and 2013, such as the report carbon capture and storage in Europe - published by the EC in partnership with the European Academies Science Advisory Council (EASAC) in 2013, on how to secure CCS as a viable strategy towards net-zero emissions (EASAC, 2013). A second report was released in 2017, based on practical applications of the Directive. The third and last implementation report was released in 2019, based on national reports produced from 2016 to 2019 focused on the progress towards the CCS Directive implementation. These guidance documents assist the insurance industry and regulators to gain a better understanding of the

risks involved and their significance in terms of likelihood of occurrence and their potential to cause harm to the environment.

The Directive 2009/31/EC, contributed to the knowledge and development of CCUS in Europe, especially thought requiring assessments for available storage capacity and for technical and economic feasibility for CCUS projects. The CCS Directive promoted national research programmes, demonstration projects and funds, together with transboundary collaborative projects towards CCUS deployment (Shogenova et al. 2013).

Concerning CCUS retrofitting, the CCS Directive requires that when applying for licence, operators assess the technical and economic feasibility of carbon capture, transport, and storage (Article 4(2) of the CCS Directive, 2009). If the assessment is positive, `space on the installation site must be set aside for the equipment necessary to capture and compress CO<sub>2</sub>` (EC, 2009, 2015, 2018). However, technical assessments carried out in Belgium, the Czech Republic, Germany, Romania, Poland, Slovenia, and Spain, found that CCS was not economically feasible (EC, 2018). The unfeasibility was mainly associated with lack of access to suitable geological storage sites (e.g., the case of Belgium and Estonia), or associated to technical incompatibility for power plants retrofitting.

In contrast, newly built power plants have been going beyond the established legal requirements and setting aside land for future CO₂ capture installations and are being designed in such way that is suitable to further CCUS installations (e.g., Czech Republic, Estonia, Germany, and Poland) (COM, 2017). Other national initiatives have been proven successful, such as the case of Norway, Sweden, and the United Kingdom. In Norway, for instance, new gas fired power plants must apply CO₂ capture and storage since the start of power plant operation. In Sweden, power plants installations that surpass 300MW are conducting preliminary studies on CCUS retrofitting (COM, 2013, 2017, 2019).

In regards to CO₂ transport and storage networks, the CCS Directive promoted international collaborations to develop `common and transboundary solutions to access CO₂ transport networks and geological storage sites (e.g. the North Sea and the Baltic Sea Basins case - cooperation between Member States bordering the North Sea and the Baltic Sea, which has proven geological suitability and ongoing CO₂ storage - evolving the UK, the Netherlands, Norway, Germany, Belgium and the Baltic Sea Region CCS network with Estonia, Germany, Finland, Norway and Sweden). These cross-chain integration initiatives ensure that each capture facility will have full access to transport and storage infrastructure (COM, 2017, 2019).

Storage capacity assessments are the first step towards CCUS large-scale deployment and have been highly promoted through the CCS directive: Article 4(2) of the CCS Directive requires that Member States that intend to allow geological sequestration on their territory must carry out assessments of the available storage capacity (EC, 2009). In this sense, many European countries are analysis theoretical storage capacities of saline aquifers, depleted oil and gas fields and hydrocarbon producing suitable for CO₂-EOR. Once carried out, these assessments are used for explorations and storage permit applications, also addressed in the CCS Directive.

In concern to geological storage, the CCS Directive states that ‘all available evidence indicates that the stored CO₂ will be completely and permanently contained’ (EC, 2009). According to Article 18 of the CCS Directive, most of the liabilities associated with storage sites are to be transferred to the national competent authority after post-closure stability – that can be determined after 20 years minimum (EC, 2009).

The long timescale and associated uncertainties add complexity to the legal and regulatory framework. Consequently, risk allocation becomes imbalanced and mostly carried by the operator. Considering that risk allocation overlaps with financial obligations, the liability issue associated costs can be prohibitively expensive for CCUS projects operators. Such liability regime can place barriers to CCUS deployment, since it does not incentivize the competent authority to accept the responsibility transfer and to move towards equal risk allocation which could also undermine investment in CCUS projects (Pop, 2015; Elkerbout & Bryhn, 2019).

Overall, the CCS Directive effectively created a general legal framework to storage site selection, permitting of exploration and storage, monitoring, reporting, and management of storage sites. It established a legislative framework for CO₂ geological storage by requiring appropriate project design to ensure the storage of CO₂ is permanent and safe (Lions et al., 2014; Patil, 2012).

Nevertheless, the CCS Directive left regulatory uncertainties towards responsibility allocation between operator and the competent national authority in the case of geologic risk in a CCUS project (e.g., CO₂ leakage). This general approach towards long-term liability created an unbalance risk-sharing: the operator is left with a high degree of uncertainty in estimating the financial magnitudes of potential leakages. Consequently, undefined liability provisions became a significant barrier to CCUS investment and deployment.

2.5. An overview of CCUS in Brazil

The first step towards CCUS development in Brazil is to provide a legal and regulatory regime that is supportive to CCUS, evaluate the country's geological storage capacity; and identify potential storage sites that geographically close to CO₂ emitting sources and to storage infrastructure (Ketzer et al., 2015).

Based on preliminary geological studies, numerous opportunities to CO₂ geological storage Brazil were identified, due its geology and occurrence of favourable storage sites. These opportunities include CO₂ storage in saline aquifers, CO₂ storage in depleted oil and gas fields, CO₂ storage through mineral carbonation in basalts, CO₂ storage in organic-rich formations such as coal seams and shales – potentially applied to unconventional hydrocarbon production (e.g., coalbed methane and shale gas), CO₂ storage in salt caverns within the Brazilian Pre-salt complex. Additionally, there is a clear potential for CO₂ utilization, such as enhanced oil recovery (CO₂ -EOR), which can bring economic feasibility to CCUS projects (Beck et al. 2011; Ketzer et al. 2015; Godoi e Matai 2021).

CO₂ utilization and geological storage technologies are already being deployed in Brazil. However, CCUS projects has been mainly restricted to the oil industry, through enhanced oil recovery (EOR) (Godoi & Matai, 2021). The CO₂-EOR technology has been applied by the Brazilian national oil and gas company - Petrobras, since 1982. The company has accumulated 25 years of experience on onshore CO₂-EOR in the northeast of Brazil, Bahia State, where 130.000 tonnes of CO₂ were injected per year into the Buracica oil field and into the Rio Pojuca aquifer, both at Recôncavo Basin (Ketzer et al. 2015). Additionally, CCUS demonstration projects are applied to saline aquifers and depleted reservoirs, such as the Petrobras Miranga Project, and to coal seams with enhanced coalbed methane production (ECBM) in the CEPAC Carbometano Porto Batista Project (Beck et al., 2011).

The Petrobras expertise with CO₂ injection advanced towards CO₂-EOR research and development in offshore environments. In 2015, 3 million tonnes of CO₂ were reinjected to deep-water producing oil fields in the Santos Basin, southeast of Brazil: Libra and Sapinhoá (Hatimondi et al. 2011). Until 2020, the Petrobras Santos Basin CCS facility, surpassed 14 million tonnes of CO₂ stored since its inception (GCCSI, 2020). This CO₂ injection can be crucial to oil production in certain pre-salt reservoirs, due to elevated CO₂ concentrations, which can vary from 8 to 20% (Petrobras, 2019). According to Godoi & Matai (2021), CO₂-EOR applied to the pre-salt reservoirs can result in 5.7 billion additional oil barrels been produced

and on 266 Mt CO₂ been stored until 2040. Accordingly, Petrobras has investing in operating and planned CCUS demonstration projects, in assembly with partners, to promote CO₂ geological sequestration from the Santos and Campos basin's pre-salt oil fields cluster (Hatimondi et al., 2011; Beck et al., 2011). Additional onshore storage sites will be targeted for carbon intensive industrial facilities, fossil fuelled power plants and biofuel production (Bioenergy with CCS - BECCS).

Within the energy generation sector there are also various opportunities for CO₂ capture in Brazil, such as retrofitting of existing coal and diesel-fuelled power plants and incorporating post-combustion CO₂ capture technologies, and CO₂ capture implementation on new natural gas-fuelled power plants - with pre-combustion CO₂ capture integrated with combined cycle technologies (Rochedo et al., 2016).

Regarding CO₂ transportation, Brazil has a limited natural gas pipeline network. This network is geographically located in the proximities of potential CO₂ capture facilities and storage sites (e.g., the southeast region of Brazil, that concentrates most of industrialization within the country), and these existing pipelines can be retrofitted to CO₂ transportation. Contrarily, CO₂ transportation in Brazil can rely on trucks and/or ships, which are already consolidated as primary means of products transportation and distribution within the country.

CO₂-EOR concentrates financial investments and is the most deployed technology among the CCUS chain - to date, 84% of stored CO₂ worldwide is used for CO₂-EOR operations (Zahasky & Krevor, 2020). This is mainly due to economic viability, overlapped by technical similarities, such as the injection infrastructure, and to petroleum companies been familiar with the subsurface geology complexities and R&D.

In addition to economic and technical aspects, there are legal and regulatory mechanisms to the oil sector that are relatable to CO₂ geological storage, such as fluid injection into geological formations and associated geologic risks, environmental impacts, and liabilities. This applicability makes large scale CO₂ geologic sequestration mostly likely to be deployed within the petroleum sector, especially in countries that have no regulation specific to CCUS, such as Brazil.

Once knowledge and potential for shale gas generation is consolidated in Brazil, these shales may become alternatives for carbon storage with associated natural gas production (CO₂-EOR). (Ketzer et al., 2015; Weniger, et al., 2010). Although there are few studies refer to this theme

in Brazil, the country holds a big potential for shale oil and shale gas. Brazil is ranked in the 10th position on the rank of countries with technically recoverable shale gas resources, estimated in 245 Tcf (EIA, 2012). However, estimates made by the National Petroleum, Gas and Biofuels Agency (ANP) indicate most promising numbers for the country: 414 Tcf in only five of the main Brazilian sedimentary basins (e.g., Paraná, São Francisco, Parecis, Recôncavo and Parnaíba), being the Paraná basin the one with highest potential (226 Tcf) (ANP, 2015).

This potential of the Paraná Basin comprises the large occurrence of oil shales, attributed to the Assistência Member of the Irati Formation, and its high organic matter content and oil occurrence. In addition to this source rock potential, there is geographic proximity to major natural gas demand centres and main stationary CO₂ emitting sources in Brazil – southeast region. Therefore, these organic-rich shales can be an attractive national target to economic feasible CO₂ storage and to unconventional hydrocarbon production in Brazil.

3.1. Challenges and regulatory barriers

CCUS legislation and CO₂ geological storage regulation provides social-environmental protection against potential leakage of CO₂ from storage sites. However, legislative instruments for CCUS activities are yet inexistent in Brazil.

In Brazil, and in most developing countries, absent legislative and regulatory incentives to CCUS added to the lack of carbon trading or taxation policies, to CCUS not yet being mandatory to new oil production instalments, and to other initiatives that could encourage CCUS deployment without the revenue of the CO₂ utilization, initially constrain CCUS to CO₂-EOR and to the oil industry. Additionally, specificities such as the elevated CO₂ content in the offshore pre-salt reservoirs, and petroleum regulatory mechanisms being relatable to CCUS, make CCUS mostly likely to be deployed by the oil and gas industry. In this scenario, to propose a supportive regulatory regime to CCUS in Brazil, it is essential to analyse the existing legislation and competent authorities of the Brazilian petroleum sector. Additionally, CO₂ geological storage in Brazil includes the analysis of the Brazilian Civil Code and the Civil Liability concept, the petroleum sector regulation with the national Oil and Gas laws, and the environmental legal and regulatory regime.

As previously mentioned, risks regarding CO₂ geological storage are primarily associated with CO₂ leakage, which goes beyond generations, ongoing to hundreds to thousands of years -

geological time scale rather than human time scale. Such a time scale goes way beyond the lifespan of conventional entities and/or operators that may be managing CCUS projects and storage sites and has regulatory implications on property on the subsoil as well as on the direct ownership over the storage fluid. Consequently, to date, risk allocation and liability uncertainties of CO₂ geological storage projects are the main regulatory barriers to CCUS large-scale deployment in Brazil.

Additionally, heterogeneities on national and subnational (state-level) jurisdictions can barrier transboundary aspects of CCUS projects, such as interstate tax regulation, CO₂ transportation (e.g., gas pipelines) and storage (CO₂ plume and its possible migration) that might go across several Brazilian states and municipalities. As the 5th largest country of the world, Brazil has a very heterogeneous territory. This contributes to different regulatory demands from each state, due to the divergent nature of its natural resources and even the lack of access to these, adding complexity to the regulatory systems.

Other barrier is the lack of jurisdiction regarding the classification of CO₂, which also present heterogeneities: CO₂ can be classified as polluting or as a commodity, depending on its origin and end-usage (Costa et al., 2018).

To surpass these regulatory barriers and promote safe and economic CO₂ storage projects in Brazil, a specific regulatory framework for CCUS is necessary. Accordingly, this new legal/regulatory regime for CCUS in Brazil should address issues yet unresolved by international existing regulation (e.g., the European Union CCS Directive). These issues mainly relate to long-term liability ownership transfer, which barrier large industrial-scale CCUS programs (Rocha & Costa, 2021). The CCUS regulatory regime should also include mandatory monitoring requirements and risk assessments, as well as provisions on regulatory agents, licensing, and environmental impact assessment procedures. In addition, it is important to create a competent national authority on CCUS - or attribute regulatory capacity to an existing national entity (Costa et al., 2018).

Overall, large-scale deployment of CCUS is still subject to political, economic, environmental, and social challenges. In Brazil, regarding CCUS activities, it is necessary to increase regulatory capacity and build support for government authorities to develop a deeper understanding of how this technology and liabilities should be applied (IEAGHG, 2013; Romeiro-Conturbia, 2014).

Besides geologic feasibility, CO₂ geological storage deployment in Brazil requires legal and regulatory regime that is supportive to CCUS and to unconventional hydrocarbons exploration.

In this concern, the European Parliament together with the Council on the Geological Storage of Carbon Dioxide agreed on 23 April 2009 and implemented on June 25th, 2009, the Directive 2009/31/EC. The so-called Carbon Capture and Storage Directive – here referred as ‘CCS Directive’) establishes a regulatory regime for an environmentally secure geological storage of CO₂. The CCS Directive focuses on the geological storage component of the CCUS chain, more specifically on the prevention of CO₂ leakage and on geologic risk. The CCS European Directive 2009/31/EC is an important first-step towards a legal and regulatory regime for CCUS technologies worldwide. It addresses the main challenges and difficulties of regulating this complex chain of CCUS, and especially the questions regarding the geologic risk and long-term liability associated with the CO₂ geological storage (EC, 2015, 2018).

In summary, the lessons learned for more of 10 years since the CCS Directive has been implemented include the (i) review on long-term liability regime, adopting a more balanced risk-sharing approach to CO₂ leakage and revising the concept of permanent storage by attributing a more tangible timescale; (ii) continued mandatory assessments regarding geological storage capacity and technical and economic feasibility of CCUS; (iii) continued support on R&D through funding and grants; (iv) continued support on transboundary collaborations for developing a CO₂ transport and storage network; (v) make CCUS mandatory for the power generation and industrial sectors, through CCUS retrofitting and new installation requirements; (vi) consider the CO₂ utilization as part of the CCS chain, since it brings economic feasibility to the process and could accelerate CCS deployment; and finally (vii) promote supportive perspective from policy makers and general public towards CCUS and its significance to 2050 climate goals. These lessons could help building regulatory support to CCUS in emerging economies, such as Brazil.

In this sense, a CCUS regulation in Brazil should address a clear division of responsibilities between CCUS operators and Member States, and should address the nature, extent, and duration of liabilities very clearly in order to reach balance between legal certainty, security and investment. Additionally, involved parties such as governments and respective national competent authorities, should consider the significance of geological storage of CO₂ towards net-zero ambitions and promote CCUS until it reaches significant deployment scale and progress on the learning curve.

CO₂ geological storage, as well as the injection of fluids into subsurface, such as to enhance oil recovery (EOR), is generally a mature technology, already extensively deployed in Brazil. Although there is no specific regulation for CO₂ geological storage, the Brazilian regulatory regime for the oil and gas industry can be adopted and/or adapted to CCUS. However, the existing regulation is yet insufficient since it poorly addresses the post-operational phase to the injection of fluids, that is, the process of `permanent` CO₂ geological storage that mostly requires specific regulation and public policies worldwide.

Based on the EU experience, most of the regulation challenges are attributed to this geologic CO₂ storage component of the CCUS chain, especially on how to manage CO₂ geological storage risks and how to predict and quantify costs of a potential CO₂ leakage in this long-term liability scenario.

Estimating the CCUS cost is yet challenging due to the lack of enough empirical data, since these are emerging technologies, and to heterogeneity in the existing projects, which operate in different currencies and with different infrastructure, adding complexity to a comparative analysis (Herzog, 2017; Budinis et al. 2018). Consequently, it is important to ensure that potential associated costs and liabilities of the operator are predictable and quantifiable.

Additional barriers to CCUS deployment rely on undefined and unlimited provisions on liabilities in the CCS Directive, such as `evidence of CO<sub>2</sub> being completely and permanently contained`. Such a general approach represents unreasonable guarantees that no entity, private or public, would be able to assure. Therefore, it is important to aim for a balanced distribution of the burden of uncertainty.

This is the main barrier to CCUS, and especially to CO₂ geological storage, which are the same in Brazil and in worldwide: the lack of a specific regulation to this suite of technologies and overlapping economic and regulatory uncertainties. Although there are jurisdictions that present regulatory elements, such as the mentioned Brazilian oil and gas regulation, these are usually incomplete and insufficient to address juridical safety and financial risk prevention to the Brazilian State and operating company.

Additional steps towards CCUS development in Brazil include (i) assessments of Brazilian geological storage capacity, prioritizing storage sites that are geographically close to CO₂ emitting sources and to storage infrastructure, (ii) technical and economic assessments of

potential CCUS projects, (iii) continued search for financial and political support of early-phase CCUS projects to be able to latter meet the long-term goals for net zero GHG emissions, (iv) Investments in R&D and on international partnership, and (v) continuously investigate the mechanisms for carbon prices and how these could promote CO₂ abatement technologies.

Ensuring an environmentally safe deployment of CCUS must remain a priority in every regulatory regime. A very permissive regulation can lead to socioenvironmental risks, which go beyond generations, maybe for hundreds to thousands of years - geologic risks rely on the geological timescale rather than the human time scale. However, long-term liability uncertainties can, instead of incentivizing CCUS deployment, become a significant barrier for investors.

It is important to highlight that CCUS are a suite of climate change mitigation technologies, and that with CO₂ geological storage climate goals can be met until 2050. And that CCUS investment relies on the improvement on liability and cost allocation issues, yet not resolved by the CCS Directive. Therefore, there should be a balance of obligations between stakeholders to prevent binding and establish legal certainty regarding the obligations of each involved entity. This balanced approach could provide legal certainty until sufficient CCUS projects deploy and the financial costs associated with potential risks of CO₂ leakage become quantifiable.

3. PARANÁ BASIN AND IRATI FORMATION GEOLOGICAL SETTING

This section presents a general description of the Paraná Basin's geology, focusing on the Irati Formation and its geological setting. It is based on a systematic literature review and synthesis of relevant articles and thesis that address the organic parameters of Irati Formation organic-rich shales – the focus of this study. The objective is to present the state-of-the-art on the literature regarding Irati Formation shales studies and to point out research gaps, which are mainly related to its maturation and depositional paleoenvironment. The compiled data on organic geochemistry and organic petrography will compose a comparative analysis with the obtained data from this research. Finally, this summary works as a starting point for understanding and evaluating the potential for unconventional hydrocarbons and CO₂ storage of the black shales from Irati Formation.

3.2. Geological Setting of the Paraná Basin

The Paraná Basin is the largest intracratonic basin in South America, located in the central-eastern portion of the South American Platform. The Paraná Basin comprises territorial portions from the centre to the south of Brazil, eastern Paraguay, north-eastern Argentina and northern Uruguay, corresponding to an area of approximately 1.4 million square kilometres, from which 1.1 million square kilometres are in Brazil. The current outline of the basin configures an erosive border, reaching approximately 5.500 kilometres on its major axis (NE-SW). The Brazilian states of SP, PR, SC and RS overlap the basin and, in smaller proportions, the states of MT, MS, GO and southwest of MG, geographically comprising most of the central, south and southeast regions of Brazil (Zálan et al., 1990; Milani, 1997; Milani & Zálan 1999).

The geology of the Paraná Basin has been extensively studied through history, being one of the main research topics in the Brazilian geoscientific bibliography (Milani et al., 2007). The Paraná Basin historical research started with White (1908), whose work is considered the 'ground-zero' of its stratigraphic characterization, followed by Sanford and Lange (1960), Northfleet et al. (1969), Schneider et al. (1974), Soares et al. (1978), Almeida (1980), Fúlfaro et al. (1980) and Zalán et al. (1990), Milani et al., 2007. These scientific reports mainly refer to the regional geology of the Paraná Basin. More recently, research conducted by Petrobras, through the authors Milani (1997), Milani (2004) and Milani et al. (2007), refocused on the stratigraphy of the basin due to its potential for hydrocarbons, especially on its Permian section, the Irati Formation (Cerqueira & Santos Neto, 1986; Milani and Zalán, 1999; Milani et al., 2007; Euzébio et al., 2016; Holanda et al., 2018).

In this context, the national oil company, Petrobras, conducted a geophysical survey and drilling program in the basin to identify optimal sites for hydrocarbon accumulation (Quintas et al 1999). According to Galhano (2006), from 1953 to 1974, a large systematic research effort was implemented, including 71 exploratory wells and data gathering from prospecting methods, such as aeromagnetometry, gravimetry and seismic. Although data collection had a limited territorial range in the Paraná Basin (approximately 30% of the basin was studied), these efforts towards hydrocarbon exploration significantly contributed to the scientific knowledge of its stratigraphy and geological evolution (Figure 4).

Figure 4. Paraná Basin stratigraphic column. Retrieved from Milani et al. (2007).

The geological evolution of the Paraná Basin is attributed to the palaeo-continent Gondwana, dating from the Paleozoic and Mesozoic eras, and varying from the Upper Ordovician to Upper Cretaceous (Zálan et al., 1990; Milani & Ramos, 1994). According to Milani (1997), the geological history of the Paraná Basin started 400 Ma (Silurian), from a lithosphere flexure due to overload associated with collisional belts derived from the Gondwana e Panthalassa convergence during the Phanerozoic (Milani 1997).

The basin contains a sedimentary and magmatic stratigraphic column of approximately 7 thousand meters of maximum total thickness, at the structural depocenter of the syncline. Its tectonic-stratigraphic evolution encompasses a succession of continental distension, thermal subsidence, and isostatic adjustments processes (Maack, 1947; Zálan et al., 1990; Milani & Ramos, 1998; Milani, 2004).

Post-Paleozoic events on the South American continent shaped the current Paraná basin's morphology. The east flank of the basin is attributed to the marginal uplift of the South Atlantic rift and its erosion that significantly exposed the crystalline basement of the Paraná Basin in this portion. The west flank of the basin is bounded by the Asunción Arch, which arises from the lithospheric overload attributed to the Andean belt and segregates the Paraná Basin from Paraguayan-Bolivian Chaco Basin. The northeast of the basin shows an original boundary, represented by a depositional palaeo-border (Milani, 2004).

3.3. Stratigraphy of the Paraná Basin

Six large-scale super-sequences were identified by Milani (1997) in the Paraná basin (Figure 5): Rio Ivaí (Ordovician-Silurian), Paraná (Devonian), Gondwana I (Carboniferous to Eotriassic), Gondwana II (Medium to Neotriassic), Gondwana III (Neojurassic to Eocretaceous) and Bauru (Neocretaceous). The proposed super-sequences cover the time interval of 450 Ma to 65 Ma (Milani, 1997). According to the author, the first three super-sequences (Rio Ivaí, Paraná and Gondwana I) represent transgressive-regressive cycles associated with sea-level oscillation, which are characteristic from the Paleozoic. The other super-sequences (Gondwana II, Gondwana III and Bauru) date from the Mesozoic and are characterized as continental sedimentary packaging associated with igneous intrusions (Milani, 1997; Milani, 2004).

Figure 5. Map (A) and profile section NW-SE (B) showing the super-sequences of Paraná Basin – defined by Milani (1997), and the general geologic context of study areas in GO, SP and PR States (Modified from Milani, 2004).

Overlying the Precambrian syncline's basement, the Rio Ivaí super-sequence corresponds to the first transgressive-regressive sedimentary cycle in the Paraná Basin (Milani et al., 2007). The sequence is essentially composed of marine sediments, being the major transgression represented by the basal units (Alto Garças and Iapó Formations) covered by the fossiliferous pelites of Vila Maria Formation - indicative of the maximum flooding of this sedimentary cycle. The regressive sedimentation is also present, but it has little expression in the Brazilian territory due to the subsequent erosion associated with regional Neosilurian discordance. However, the regressive cycle is well recorded in Paraguay, where the sedimentary package is thicker, corresponding to the fine, micaceous, and fossiliferous sandstones of the Cariy Formation (Milani, 2004; Milani et al., 2007).

The Paraná super-sequence corresponds to the second transgressive-regressive cycle of the Paraná Basin. Its sedimentary package was accumulated along with the basin's subsidence during the Devonian and has varied thickness. The sequence comprises the Furnas Formation and the Ponta Grossa Formation. This lithological sequence is the representation of the first great flood of the Devonian period (Milani et al., 2007). The authors also describe a second episode of marine expansion during the Mesodevonian, which would have resulted in the connection between the Paraná and Parnaíba basins, as evidenced by the paleontological correlation of megafossils and palynomorphs. The top of the sequence is marked by successive erosive events that date from the Neodevonian to the Middle Carboniferous. A gap in the tectono-sedimentary history of the Paraná Basin was identified by the Milani et.al. (2007), represented by a gap of about 70 million years and corresponding to the Mississippian period, absent in the basin record. Such a gap could have been justified by tectonic events associated with the Hercinian Orogeny (Milani et al., 2007).

During the Late Paleozoic Era, the Paraná Basin was flooded by a large epicontinental sea, with restricted or no connections to the Panthalassa Ocean. Therefore, its sedimentary package is predominantly Paleozoic and had been accumulated during Gondwana continental drift, corresponding to a complete cycle of transgression-regression (Milani et al., 2007). Initially described by Derby (1878) and White (1908) (apud Milani et al., 2007), the Gondwana I super-sequence is also known as the Pennsylvanian-Permian tectonic-sedimentary sequence, or as Carboniferous-Eotriassic Sequence. This sedimentation cycle outset is represented by a glacial package at the sequence's base, followed by records of maximum seawater flooding in the Artinskian age (Palermo Formation) and ended by continental deposits that would fill the syncline at the beginning of the Mesozoic period. The closure of the sedimentary super-

sequence occurs at the beginning of the Triassic, due to continental depositional systems (Arthur, P.C. Soares, 2002). Milani et al (2007) state that Gondwana I is concomitant to the progressive closing of the Paraná Basin, initiating its intracratonic aspect since it is progressively imprisoned in the continental interior of Gondwana during the Mesozoic (Araújo et al., 2000; Araújo, 2001; Milani et al., 2007).

The Triassic period in the Paraná Basin is characterized by a generalized distention of the Gondwana palaeocontinent on its southern portion. The distention leads to the accumulation of the Gondwana II super-sequence, whose occurrence is restricted to the southern portion of the basin (in Uruguay and the Brazilian State of Rio Grande do Sul). According to Milani et al. (2007), the Paraná Basin Neotriassic subsidence event, lead to the development of asymmetric grabens, which would have accommodated the river drainage over the system's flexural ramp, and accumulating mudstones in deeper portions (Milani et al., 2007). Large-scale erosive conditions along the Mesozoic, associated with wind abrasion inside the Gondwana palaeocontinent, represent another expressive stratigraphic gap in the basin.

The Gondwana III super-sequence, also called Jurassic-Eotriassic Sequence (Milani et al. 1994), is widely distributed throughout the Paraná Basin and consists of a continental sedimentary package represented predominantly by wind facies (Botucatu Formation) and by magmatism (Serra Geral Formation) (Milani, 2004; Milani et al., 2007).

The Eocretaceous period in the geological record of the Paraná basin is characterized by rupture of the Gondwana supercontinent and the consequent evolution of the South Atlantic Ocean and associated magmatism (Milani 2004). The magmatism corresponds to the basalts from the Serra Geral Formation: sills and dykes that cross the extensive sedimentary package of the basin and altered its thermal history (Araújo et al., 2000; Araújo, 2001; Milani et al., 2007).

During the Neocretaceous, along with the evolution of the South Atlantic Ocean opening and the isostatic adjustment, occurs the accumulation of the Bauru super-sequence. It is described by Milani (1997) as siliciclastic unit accumulated in a semi-arid to desertic paleoenvironmental context. During the deposition of the Bauru super-sequence, igneous activity was also present; represented by intrusive bodies often positioned on the northern edges of the basin (Milani et al. 2007).

3.3.1. Gondwana I Super-sequence

The Gondwana I super-sequence has the largest sedimentary volume within the Paraná Basin's super-sequences, occurring almost continuously along the perimeter of the syncline and reaching a maximum thickness around 2.500 meters (Zálan et al., 1990; Milani, 1997; Milani et al., 2007). Its sedimentary package is predominantly Paleozoic and has been the focus of many studies due to the occurrence of deposits with economic value, such as mineral coal beds with potential for coalbed methane (CBM) (Rio Bonito Formation), and of petroleum systems (Almeida, 2019). Initially described by Derby (1878) and White (1908), the Gondwana I super-sequence is also known as the Pensilvanian-Permian tectono-sedimentary Sequence, or as the Carboniferous-Eotriassic Sequence.

The Gondwana I super-sequence encompasses a wide variety of depositional conditions, ranging from glacial to desertic/arid continental environments, which indicate the arrival of the Mesozoic period (Milani, 1997). The super-sequence is divided by Milani et al. (2007) into the following sedimentary packages: Itararé Group (Lago Azul, Campo Mourão, Taciba, and Aquidauana Formations), Guatá Group (Rio Bonito and Palermo Formations), Passa Dois Group (Irati, Serra Alta, Teresina, Corumbataí and Rio do Rasto Formations), and Pirambóia, Botucatu and Sanga do Cabral Formations (Milani 2004; Milani et al., 2007).

During the Eocarboniferous period, the south-western portion of the supercontinent Gondwana was exposed to high latitudes and, consequently, to extensive continental glaciation (França et al., 1995). The glaciation represented an inhibiting factor to sedimentary deposition and lead to the absence of geological record in the interval between the Neo-Devonian and the Neo-Carboniferous periods (between the Ponta Grossa Formation and the Itararé Group - Aquidauana Formation, strata). The sedimentation proceeded with the progressive migration of the palaeocontinent towards the north, thus moving away from the focus of glaciation (Milani et al. 2007). These glaciogenic deposits in the Paraná Basin are represented by (i) massive or stratified diamictites, with the occurrence of pebbles and blocks of different lithology, which were transported by glaciers; and by (ii) massive sandy facies, coarse graded or with unidirectional undulations, corresponding to a geological context of turbiditic sedimentation. The pelitic packages within the sequence were associated with the decantation process (uniform texture and unstructured lithology) or to turbiditic sedimentation (laminated mudstones). Other glaciogenic lithotypes such as rhythms (varvites) and tillites (locally in the Itararé Group) are also present, although on a smaller scale (Rocha-Campos, 1967; Santos et al. 1996; Rocha-Campos et al. 2000). The glaciogenic section of the Gondwana I super-sequence is more evident

in the central-north portion of the basin, where it reaches its maximum thickness, of approximately 1.300 meters (Milani et al. 2007).

From the deglaciation phenomenon, the consequent increase in the relative sea level was registered by Lavina & Lopes (1987) as the “Permian transgression” of the basin. The associated sedimentary package, Rio Bonito Formation, is composed of sandstones and mudstones, and is subdivided into 3 members, according to the lithological predominance: Triunfo, Paraguaçu and Siderópolis (Schneider et.al.1974). In the first package, the Triunfo Member presents evidence of sedimentary rework, influenced by a deltaic and tidal context. The second member, Paraguaçu, presents the marine influence, with pelitic packages of considerable thickness. While the third member, Siderópolis is characterized by lagoon restriction and the development of peat accumulation, which originated the coal deposits of the Siderópolis Member, Rio Bonito Formation (Milani et al., 2007; Almeida, 2019).

The deglaciation process of the Gondwana palaeocontinent is attributed to the Itararé Group. The deposition of the Itararé Group is followed by an onlap sedimentation pattern, from south to north of the Paraná Basin, which characterizes the deposition of the Guatá Group (Neo-Permian). The following sedimentary section had a coastline regressive pattern, attributed to the Passa Dois Group (Milani & Ramos, 1998).

3.3.1.1. Passa Dois Group

Due to its economic potential for hydrocarbons through conventional and unconventional source rocks, the Passa Dois Group, Gondwana I super-sequence, has been the focus of several studies throughout the years (e.g., Milani et al., 2007; Santos et al., 2006; Mateus et al., 2014; Simões; et al., 2016). It includes the Irati, Serra Alta, Teresina, Rio do Rasto, and Corumbataí Formations (Figure 6). The lowermost unit of the Passa Dois Group, the Irati Formation, is one of the most studied Brazilian geological formations due to its unique fossil-bearing content (Mezzalira, 1971), and potential on hydrocarbons exploitation, being considered one of world's largest oil-shale deposit (e.g., Padula, 1969; Tissot and Welte, 1984; França et al., 1995; Goldberg and Humayun, 2016).

Figure 6. Stratigraphic sequence of the Gondwana I super-sequence, defined by Milani (1997). (Modified from Santos et al., 2006).

The Passa Dois Group units are described in detail by Krebs and Menezes Filho (1984), and Holz et al. (2010). Dark grey shales and siltstones with local calcareous lenses, concretions, and fossil-rich content composed of fish, pelecypods, and conchostrachans specimens comprise the Serra Alta Formation, which was conformably deposited over the Irati Formation. This formation was deposited in a low energy marine environment, in the context of the shrinkage of the Irati Gulf and a marine transgression, below the fair-weather wave base (Milani et al., 2007). The Teresina Formation was conformably deposited over the Serra Alta Formation and comprehends mudstones and shales, interbedded with sandstone beds, calcareous lenses, and concretions. This unit's fossil content includes plant debris, lamellibranch, and palynomorphs (Neregato et al., 2008). The Teresina Formation was deposited in a marine environment marked by high energy shallow waters, which were dominated by wave and tidal processes (Milani et al., 2007). The following unit, the Rio do Rasto Formation, comprehends two members, the oldest Serrinha Member, consisting of fine-grained sandstones and interbedded grey to red siltstones, mudstones, and local limestone lenses; and the Morro Pelado Member, consisting of red beds deposited in a continental environment. The fossil content includes pelecypods, conchostracans, plant remains, and vertebrates, reaching the basal Lopingian age (Holz et al., 2010). At the top of the Rio do Rasto Formation, an erosive surface marks the passage to the overlying Botucatu Formation (Krebs & Menezes Filho, 1984; Holz et al., 2010). The Corumbataí Formation, recognized in the northern part of the basin and in the State of São Paulo, represents the greater hydrodynamic circulation towards the borders of the Paraná Basin, with deposition of non-bituminous pelites interbedded with fine layers of carbonates and sandstones (Riccomini 1995; Hachiro, 1996).

3.4. Irati Formation

The organic-rich shales of the Irati Formation 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 was initially recognized and described in 1827, by Silva & Andrada, followed by Cope (1886), Campos (1887, 1888), and Oliveira (1889) (apud Hachiro, 1996). Studies about its potential as a source rock date back from 1897, with Collon (apud Hachiro, 1996), followed by White

(1908), who named the formation after the Irati river and the homonyms city where the first outcrops were recognized in Paraná State, south of Brazil. The Irati Formation studies have been continuous and ongoing to date, due to its relevance and maturation complexity.

The Irati Formation shales configure the source rock for the conventional petroleum system: Irati - Rio Bonito – Pirambóia, with potential for accumulation of liquid hydrocarbons (Quadros 1982; Zalán et al. 1990; Araújo et al., 2000; Araújo 2001; Arthur & Soares, 2002; Ferreira, 2017). Additionally, the Irati Formation also configure unconventional petroleum systems, due to organic-rich shale content, with potential for shale oil and shale gas (Rocha, 2016; Riccomini, 2016; Tassinari et al., 2017; Mabecua, 2018), and also for CO₂ geological storage (Masulino, 2020; San Martín Cañas, 2020).

According to the Energy Information Administration - World Shale Gas and Shale Oil Resource Assessment, Brazil ranks in the 10th position of countries with technically recoverable shale gas and shale oil resources, estimated in 245 Tcf and 5.4 billion barrels (EIA/ARI, 2015). Most of this potential is attributed to the Paraná Basin and the organic-rich shales of the Irati Formation, with shale gas reserves estimated at 226 Tcf (ANP, 2013, 2015, 2016). However, this potential is based on the net shale thickness - in an analogy with the Barnett shale, Fort Worth, Texas, and, therefore, it does not consider the organic content.

Shale gas potential assessment of organic-rich shales usually consider the following requirements (Table 2): total organic carbon content (TOC) (above 2%), thermal maturity (VR between 0.8 and 1.1%Ro.), thickness (> 15 m), mineralogy (clay content < 40%), kerogen type (II/III kerogen), gas-in-place, porosity (> 4%) and permeability (> 100 mD) (Boyer et al., 2006; Curtis and Zumberge, 2010; Jarvie et al., 2007; Kiersnowski and Dyrka, 2013; Zou et al., 2010; Mustafa et al., 2015). Based on a comparative analysis, the Irati Formation black shale's organic parameters meet a few of the mentioned requirements: TOC, kerogen type, maturity, and thickness. However, there is not enough data from the Irati shales on a regional scale, and further studies are required. Therefore, this study will focus on the Irati shales and its heterogeneity to address its potential for unconventional hydrocarbons and associated CO₂ storage.

Table 2. Unconventional hydrocarbons prospect parameters (Chen, et al., 2018; Hennissen et al., 2017; Josh et al., 2012; McGlade, et al., 2013).

Prospect parameters		Required values
TOC		$\geq 2\%$
Maturity	R _o	0.8 - 1.2%R _o (shale oil) 1.1-3.5 Rr% (shale gas)
	Tmax	455 °C
Kerogen type		Type I-II (shale oil), type II – type II-III (shale gas)
Thickness		> 15m
Burial depth		1500 – 3000m
Mineralogy	Clay content	< 40%
	Siliceous and carbonates content	> 40%
Porosity		> 4%
Permeability		> 100 mD
Water saturation		<45%
Overpressure		0.45psi/ft

In the southern portion of the Paraná Basin, the Irati Formation organic-rich shales are already exploited, through thermochemical processing (pyrolysis), by the national oil company, Petrobras, in the São Mateus do Sul municipality, Paraná State. The PETROBRAS-SIX called unit represents one of the largest reserves of oil shale in the world, with shale layers that reach 9.1% of oil content (Santos et al., 2006; Petrobras, 2020). From these shales are produced fuel oil, gas, naphtha, liquefied gas, and sulphur, which is used to manufacture asphalt, cement, and consumed by agricultural and ceramics industries (Holanda et al., 2018). According to Maraschin and Ramos (2015), the plant processes 7800 tons/day, resulting in 3870 barrels of oil, 120 tons of gas, 45 tons of liquid gas and 75 tons of sulphur.

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 (Milani & Zalán, 1999; Milani et al., 2007). The Irati Formation presents a heterogeneous lithologic distribution within the basin: accumulations of carbonates and evaporites in the northern portion of the Paraná Basin; and bituminous shales in the southern portion (Santos Neto, 1993; Milani et al., 1994). 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). The Irati Formation presents an average thickness of 40 m (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) (Figure 7.A).

The Irati Formation is subdivided into two members: Taquaral and Assistência. The Taquaral Member is composed of 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; Xavier et al., 2018). 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 (Schneider et al., 1974; Hachiro, 1996; Milani, et.al., 2007) (Figure 7.B).

Figure 7. 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 organic-rich 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, being less predominant in the southern part of the Ponta Grossa arch (Hachiro et al., 1993; Hachiro, 1996; Padula, 1969; Araújo, 2001). Hachiro (2006) attributes the intercalation of shales and carbonates to paleoclimate variability, which is characterized by well-marked alternation between arid and humid seasons. According to the author, the 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) and Reis et al. (2018), the Taquaral Member was deposited in a marine epicontinental to a restricted environment, while the Assistência Member was originated in a vast and shallow sea where there was 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 and Cornford, 1985; De Castro, 1988; Rocha et al., 2020).

Dolomitic carbonate levels in the Irati Formation can result from the mixture between inorganic carbon enriched meteoric waters with Mg enriched deep waters (Banerjee, 2016). However, Almeida (2018) attribute the dolomite to bio-precipitation: the microbial content enrichment associated with the Irati deposition (Bertassoli et al., 2016), and to consequent biogenic methane generation, would have played a role in the precipitation of dolomite (Almeida et al., 2020).

Being an intracratonic basin affected by magmatic events, the Paraná Basin shales units had a complex thermal evolution, due to this igneous influence on paleofluids, such as hydrocarbons. Turner et al (1994), Araújo (2001) and Araújo et al (2001) mainly attributed the shale's maturation to the Lower Cretaceous Serra Geral magmatic event, and its associated high geothermal gradient and subsequent migration pathways due to magmatic activity. Additionally, the authors state that the thermal metamorphism effect would justify the significant variation on total organic carbon (TOC) values within the formation. Following this interpretation, the Paraná Basin thermal history before the Serra Geral magmatism in the Cretaceous, would be characterized by a low diagenetic thermal gradient, reaching maximum temperatures around 60 to 80 °C (Araújo, 2001; Araújo et al., 2001; Mateus et al., 2014).

The Serra Geral magmatism is represented by a basaltic flood that covers an area of approximately 1.000.000 km² and reaches up to 1.700 meters thick basalts, including several levels or intruded sills and dykes along with the Paraná Basin extension (Hurter & Pollack, 1994; Milani et al., 2007). U–Pb zircon ages of Serra Geral Formation samples from São Paulo State indicate 3 Ma timespan for the magmatism (Janasi et al., 2011; Teixeira et al., 2020).

The Irati Formation hosts magmatic sills within its occurrence along the Paraná Basin (Araújo et al., 2000). Hurter and Pollack (1994) attribute an average thickness of 15 meters for the magmatic sills, although some can reach hundreds of meters in certain areas of the basin. In the south-eastern border of the Paraná Basin, at São Paulo State, the Serra Geral basalts reach 400 m of preserved thickness (Janasi et al., 2007). In this region, the Irati Formation is situated in approximately 300 m beneath the Serra Geral flood basalts (Teixeira et al., 2020), and are consequently affected by thermal metamorphism.

Regarding paleotemperatures, fluid inclusions studies also indicate that the Paraná Basin presented a higher diagenetic gradient. Mateus et al. (2014) affirm that the paleogeothermal gradient reached 125°C, during the Permian-Triassic, in deeper portions of the Paraná Basin. In accordance, paleotemperatures reported by Nomura et al. (2014), indicate a thermal gradient from 90 to 140 °C. This thermal gradient could propitiate conditions to interstitial fluid flow within the basin. Furthermore, it could stimulate organic matter maturation in large-scale and liquid hydrocarbon generation. These studies highlight a second interpretation for the Irati shales maturation, which would be most probably controlled by burial (Mateus et al., 2014), and, at certain portions of the basin, by the associated overburden pressure from the hundred-meters thick overlaying Serra Geral flood basalts (Nomura et al., 2014; Teixeira et al., 2020).

Based on this interpretation, the hydrocarbon generation and migration processes within the Irati Formation were heterogeneous and performed in multistage phases. Three major flow episodes were identified by Mateus et al. (2014): (i) a confined flow dated from the late Permian to Triassic; (ii) a heterogeneous flow dated from the Lower Cretaceous, associated with the pre-developed permeability within the formation and with a new regime of high geothermal gradient build-up; (iii) and a late flow from the driven by local pressure and temperate gradients, associated to igneous intrusions (Mateus et al., 2014; Ferreira, 2017).

Mateus et al. (2014) state that the first stage of fluid migration resulted in fissured reservoirs due to pressure build-up. This developed permeability was then propitious to hydrocarbon accumulation in the Lower Cretaceous due to this mentioned adequate temperature gradient.

The second stage of fluid migration was considerably heterogeneous, been subjected to the multiphase emplacement of igneous intrusions. This stage propitiated the displacement from oil to gas window of hydrocarbon generation, as well as the relocation of fluids within the basin. The third and late migration stage was related to the cooling process of the magmatic intrusions, driven by local pressure gradients. Posteriorly, with the developed permeability, freshwater infiltration from overlapping aquifers (Pirambóia and Botucatu Formations), favoured the organic-matter degradation by anaerobic microorganisms (methanogenesis) at low-temperature conditions (below 50°C), producing biogenic natural gas (Bertassoli et al., 2016; Mateus et al., 2014), and resulting in a mixture of thermogenic and biogenic natural gas (Almeida, 2018).

4. DATA ACQUIREMENT, MATERIALS AND METHODS

This section presents the applied methodology, including the description of samples and sample's location, as well as sample preparation and applied techniques. Analytical procedure comprises geochemical, petrological, mineralogical and gas sorption analysis. The used apparatus and experimental procedures are also here described.

4.1. Sampling

Sampling for this study was focused on organic-rich levels of oil shales from Assistência Member of the Irati Formation, Paraná Basin, southeast Brazil - due to the previously mentioned correlation between organic matter and CO₂ storage, which is the focus of this study. A total of forty-eight (48) samples of Irati Formation organic-rich shales were collected from boreholes and outcrops at different portions of the Paraná Basin, to represent its heterogeneity. Samples were selected from 12 boreholes and 5 outcrops at the North, Southeast and South portions of the PB, that geographically comprise the States of Goiás (GO), São Paulo (SP) and Paraná (PR), respectively.

Before and during sampling the following criteria were taken into account: (i) Irati Formation shales being the principal hydrocarbons' source rock of the Paraná Basin (Hachiro, 1996; Milani, 2004; Milani et al., 2007; Silva, 2007); (ii) feasibility of access to sampling sites and logistics; (iii) representation of the formation's heterogeneity; and (iv) optimal geographical proximity between the source rocks, natural gas demand of main consuming centres (power sector and industry).. Based on these criteria, three areas within the Paraná Basin (PB) were selected for sampling: (i) the Northern border of the PB – Goiás State; (ii) the Southeastern portion of the PB – São Paulo State; and (iii) the Southern portion of the PB – Paraná State. Sampled areas are indicated in Figure 8.

Figure 8. Geological map of the Paraná Basin with samples' location, per Brazilian state. Sample type (surface or borehole) and identification number are also represented.

Sample collection was performed in two methods: (i) individual sampling, and (ii) regular distance sampling. Individual sampling was predominantly applied to boreholes, collecting organic-rich intervals of the Assistência Member shales, which were identified by colour (black coloured levels). Regular distance sampling was applied in surface/open-pit mining sets, where samples were collected at every 20 cm interval within a 2 m vertical sequence. Additionally, surface samples from each shale strata were also collected laterally, to analyse horizontal heterogeneity and to reconstruct depositional paleoenvironment. Samples were collected after removal of weathered surface material, for approximately 10 cm.

Samples were collected from: (i) outcrops and open-pit mining sets, from each sampling segment (N, SE, and S), and (ii) boreholes obtained from the national company on mineral resources research – the Brazilian Geological Survey (*Companhia de Pesquisa de Recursos*

Minerais – CPRM), at the southeastern and southern (SE and S) portions of the Paraná basin – states of São Paulo and Paraná.

Regarding sample collection in the CPRM boreholes, the selected wells and their location are indicated in Table 3. Sampling was carried out in 13 different well cores, being 12 in the Paraná state and 1 in São Paulo. The selection criteria of the wells were: (i) geographic distribution, (ii) depth - preference for samples at higher depths, seeking higher organic matter maturation rates, and (iii) thickness - preference for thicker shale packages, and (iv) representability of the formation and its heterogeneity. The selected wells intersected the Irati Formation at different depths, in between a depth range from 80 to 477 meters. Samples were collected from the organic-rich intervals, identified by color (black shales).

Table 3. Selected CPRM boreholes for sampling, with respective ID, sampled quota, location, and coordinates.

Borehole ID	Sampled Quota (m)	Location	Coordinates
FP-01-PR	194 - 197	Ibaiti, PR	23°38'56.30"S / 50°23'31.48"W
FP-02-PR	122 - 357	Sapopema, PR	23°50'15.18"S / 50°35'43.58"W
FP-03-PR	226,5 - 231,5	Sapopema, PR	23°52'42.09"S / 50°39'54.17"W
FP-04-PR	185 - 193	Ortigueira, PR	24°15'3.03"S / 50°55'51.76"W
FP-07-PR	80 - 95,5	São Matheus, PR	25°51'49.02"S / 50°26'24.31"W
FP-11-PR	351 - 373	Ortigueira, PR	24° 4'12.20"S / 50°47'32.77"W
FP-12-SP	274 - 276	Anhembi, SP	22°45'31.29"S / 48°16'6.55"W
SP-29-PR	340 - 341	Sapopema, PR	23°46'56.50"S / 50°35'42.15"W
SP-37-PR	211 - 215	Sapopema, PR	23°47'12.55"S / 50°31'36.76"W
SP-47-PR	238 - 242	Sapopema, PR	23°46'29.71"S / 50°32'1.68"W
SP-49-PR	373 - 373,5	Sapopema, PR	23°42'1.12"S / 50°25'45.19"W
SP-55-PR	476 - 477	Sapopema, PR	23°46'14.72"S / 50°32'49.44"W

The samples were collected in the top of the Assistência Member – Irati Formation vertical interval, within 5 metres distant to the overlying formation (Serra Alta Formation or Corumbataí Formation). The top of the Irati formation was identified based on the outcrops and well logs vertical sequence observation, and on the core descriptions from the Brazilian Geological Survey (CPRM). In São Paulo State, samples were also collected from the lowermost portion of the Corumbataí Formation for paleostratigraphic studies. Shale samples were collected at different depths to represent the Assistência Member - Irati Formation heterogeneity. In

boreholes, it was possible to control the depths where the Irati Formation was intersected and the vertical distance of the samples to the contact with the igneous intrusions.

As previously mentioned, sampling was performed in three different segments: in the north border of the Paraná Basin, State of Goiás (GO); in the southeast of the Paraná Basin, at São Paulo State (SP); and at the south of the Paraná Basin, State of Paraná (PR). The local geological aspects of each sampled area, as well as the collected samples, are described in the following section.

4.1.1. Goiás State (GO)

At the northern border (N) of the Paraná Basin, the Assistência Member of Irati Formation can be observed in the States of Goiás (GO) and Mato Grosso (MT). In GO State, the Irati Formation overlaps the Aquidauana Formation and underlies the Corumbataí Formation (Costa et al, 1981; Dos Anjos, 2008), and corresponds to a sequence of black shales interbedded with grey dolomites. The overlapping Corumbataí Formation can also be observed in GO, corresponding to reddish beige sandstones and pelitic rocks (shales, siltstones, and mudstones). Towards the northwest portion of the basin, at Mato Grosso State, the Irati Formation is represented by Inter calations of pink coloured limestones (dolomitic) and shales, with light beige siltstone. This pink carbonate facies can be observed at Alto Garças municipality. However, due to the absence of black shales, no samples were collected in MT.

19 samples were collected at State of GO, in the municipalities of Montividiu and Perolândia, on the mining fronts of the Rio Verde, ELBA and SUCAL quarries (samples 572 to 590). A total of 8 samples were collected at Rio Verde quarry (samples 572 to 579), and 4 samples were collected at ELBA Calcário quarry (samples 587 to 590), both in Montividiu municipality. Additionally, 7 samples were collected at SUCAL quarry (samples 580 to 586), in Perolândia – GO. The samples correspond to 10-20 cm bituminous black shales with pyrite, that are interbedded with 10-30 cm dolomitic limestone beds. An igneous intrusion was identified in the proximity of the sampled succession, at Rio Verde and ELBA quarries (Figure 9).

Figure 9. Map of the Paraná Basin and its geochronological sequence with sampling site's location. Detail for samples collected in the N of the Basin, GO State, and their placement in the geological map and cross-section.

4.1.1.1. Rio Verde Mineração, Montividiu, GO

Eight samples of Irati black shales were collected at Rio Verde mining quarry, at Montividiu – GO (Coordinates: S17 °14'32,2''/ W051 °29'31,5''). Sampling was carried out in an open-pit mining vertical sequence of approximately 3 meters, with fissile black shales interbedded with dolomitic limestones (rhythms). There is predominance of shales over limestones, featuring a pelitic stratigraphic facies.

The black shales had occurrence of pyrite and the carbonate were dolomitic and presented silex nodules. Shales were thicker at the base of the sequence, varying between 23 and 28 cm thick, interbedded with 10 to 12 cm thickness dolomites. Towards the top of the sequence, there was a thickening pattern of the limestone layers, which reach about 30 cm, about the same as the shales. Sample collection follows the sequence from the bottom to the top (Figure 10). The shale layers were sampled at four different levels, with approximate 20 cm distance. At each level, two samples were collected laterally, with the purpose of analysing the horizontal heterogeneity of the layer, with about 2 m of distance between the collection points. In total, 8 samples were collected at this sampling point (572, 573, 574, 575, 576, 577, 578 and 579).

Figure 10. Rio Verde quarry with sampling location and samples' identification number. A: Sampled vertical sequence, with the positioning of the collected samples. B: Detail of silex nodules in limestones, interspersed with shales. C: Levels of sampled shales, in detail, indicating variation in the thickness of the layers.

4.1.1.2. ELBA Calcário Montividiu, GO

A total of 4 samples were collected at the limestone quarry, Elba Calcário, in Montividiu – GO (Coordinates: S17°19'38,7''/W051°12'58,8''). Sampling was performed in a vertical sequence of 29 meters high. The four samples are from two levels of shales sampled with a lateral distance of approximately 10 m.

The exposed vertical sequence is an interbedded association of limestones, black shales, siltstones and, locally, basalts. The Irati Formation is represented by intercalations of cream-to-gray dolomites with an average thickness of 20 cm; black shales, with thickness varying between 20 and 30 cm; and greenish-black basalts, with an average thickness of 30 cm. At the top of the sequence, an erosion surface can be identified by the occurrence of a cream-coloured sandstone layer (30 cm), that divides the Irati Formation (base) with the overlying Corumbataí Formation (top). The Corumbataí Formation comprises a 5 meters thick sequence of interbedded pink limestones and shales. The diabase sill can be observed locally at the base of the vertical sequence, intruding at shale levels. Diabase is sometime amalgamated and is not present throughout the entire lateral sequence. Sampling was carried out at shale levels distant from the diabase, with an average distance of 50 m. A total of 4 samples were collect (587, 588, 589, 590) (Figure 11).

Figure 11. Vertical sequence indicating sampling points (samples 587 to 590), and igneous intrusion (diabase). A: General overview of the vertical sequence with samples location. B: Detail of the sequence: black shales from Assistência Mb, Irati Fm with Serra Geral Fm igneous intrusions, underlying the pink sandstones and mudstones from Corumbataí Fm. C: Vertical sequence at approximately 50 m west of image B, indicating the doleritic sills; D: Stratigraphic column indicating diabase sill at the base, about 20 m east of image B. E, F: Detail of igneous intrusions and the interbedded black shales and dolomites.

4.1.1.3. SUCAL Mineração, Perolândia, GO.

A total of 7 samples were collected at SUCAL mining quarry in Perolândia – GO (Coordinates: S17°18'37,6''/W051°03'33,7''). The samples correspond to 10-20 cm bituminous black shales with pyrite, that are interbedded with 10-30 cm dolomitic limestone beds.

The exposed stratigraphic sequence was approximately 35 meters high, where centimetric intercalations of limestone and shales were observed. At the base of the sequence, there is a predominance of limestones, with variations between 1 m and 30 cm thick, interspersed with thin layers of silty gray shales, with about 5 to 9 cm. At the top, black shales are predominant, and its layers become thicker, reaching 28 cm, while the limestones are approximately 12 cm thick, characterizing a pelitic facies. The change of facies is transitional.

Sampling was carried out on two vertical sequences, the first being on a carbonate facies of about 6 meters high (sample 580 – Figure 12 and 13), and the second on the furthest facies, with about 20 meters (samples 581, 582, 583, 584, 585 and 586 - Figure 13).

Figure 12. General overview of the quarry and sample collection points, whose positioning and ID number of the samples are indicated in black and white. Sample 580 was collected at the base of the stratigraphic column. Samples 581 to 583 were collected at different levels of shale in the central portion of the stratigraphic column. Samples 584 to 586 were collected east of the figure, about 100 m laterally from samples 581 to 583.

Figure 13. Basal portion of the mining vertical sequence, and collection point of sample 580. A, B: Detail of the base of the stratigraphic column - carbonate facies. C: Detail of the sampled level of black shale (sample 0580).

At this first sampling point, the shale levels of this carbonate facies have fossiliferous content (*mesossaurus*). The limestones are laminated, have a dolomitic composition (field verification with hydrochloric acid - HCl), and a light grey to cream colour. The thin layers of shale are grey in colour and consolidated in appearance (not friable). One sample of shale was collected in this facies (580).

Sampling continued at the pelitic section of the stratigraphic sequence, in a vertical sequence of approximately 20 meters high (Figure 14). The sequence was represented by interbedding between gray limestones and bituminous shales, shales being the predominant lithology. Limestone layers with an average thickness between 15 and 20 cm and shales with 20 to 30 cm thick, with more thickening towards the top of the sequence. Interspersed with the limestone, there are also layers of laminated siltstone, dark grey in colour, with an average thickness of 12

cm. The shales are enriched with organic matter, with black colour and fissile aspect. These differ from the shales found in the basal portion of the stratigraphic sequence (carbonate facies), which have a gray color and are more consolidated. In this sequence, 6 samples were collected (581, 582, 583, 584, 585 and 586), in three levels of black shales, located at the top of the pelitic sequence. The lateral distance of the sampling was about 100 meters.

Figure 14. Upper portion of the mining front and sample collection points (samples 0581 to 0586). A: General overview of the vertical sequence and sampling position; B: Detail of the sampled shale levels (0581 to 0583); C: Overview of the observed stratigraphic sequence, where the transition between the carbonate (base) and pelitic (top) facies is evident; D: Detail of lateral sequence where samples 0584 to 0586 were collected, about 100 m east of image A; E: Detail of the sampled shale levels (0584 to 0586).

4.1.1.4. Faciological Description

In the northern portion of the Paraná Basin, two stratigraphic facies were identified for the Assistência Member of the Irati Formation at the sampling points: dolomitic facies, and a pelitic facies. Due to the predominance of black shales in the pelitic facies, most of the sampling was carried out in this facies.

The dolomitic facies can be observed at the base of stratigraphic columns in the region, from the quarries: Rio Verde, SUCAL and ELBA, at the municipalities of Montividiu and Perolândia, GO. This consists mainly of packages of dolomitic carbonate rocks of beige to light gray colour, with varying thicknesses between 30 cm and 2 meters. Interspersed with this lithology, thin layers of shales of black to dark gray colour, about 2 to 5 cm thick can be observed. This sequence of intercalations between carbonates and shales, which characterizes the facies, can reach up to 7 m in thickness. The carbonate rocks of this stratigraphic facies are economically explored in the region, being mainly used in the agricultural sector for soil pH correction.

On top of the dolomitic carbonate facies, a pelitic facies is present, mainly characterized by centimetric intercalations of black fissile shales with gray-coloured laminated dolomitic limestones, representing rhythms. The limestone layers have an average thickness between 15 and 20 cm, while the shales are 20 to 30 cm thick, with a thickening pattern towards the top of the sequence, reaching up to 50 cm thick. Throughout the intercalation, layers of dark gray laminated siltstone are also observed, with an average thickness of 12 cm. The shales are enriched in organic matter, with black colouring and fissile aspect, in addition to the occurrence of pyrite and fossil records (Mesosaurid reptiles). These differ from the shales found in the basal portion of the stratigraphic sequence (carbonate facies), which have a gray colour and are more consolidated (not fissile). In the carbonate rocks there are chert nodules and thin layers of silicites, on average 9 cm thick. In this pelitic facies, diabase sills can be observed locally, featuring igneous intrusions that occurred throughout the Irati Formation, corresponding to the Cretaceous Serra Geral magmatism. These intrusions are represented as greenish-black diabase about 30 cm thick. This layer is sometimes amalgamated, not being present along the entire lateral sequence of the stratigraphic columns.

In Portelândia - GO and Alto Garças - MT, sampling was not performed due to the absence of black shales, the focus of this study. However, faciological variations were observed in Portelândia, where a calcitic carbonate facies was observed, and in Alto Garças, presenting a pink carbonate facies, as shown in Figure 15.

Figure 15. Stratigraphic facies identified in the Assistência Member, Irati Formation, in the municipalities of Portelândia - GO and Alto Garças – MT. A: Calcitic carbonate facies, represented by uniform gray limestone with the occurrence of calcite crystals, located in Calcário Brita Minas Fortaleza mining quarry, Portelândia, GO; B, C: Pink carbonate facies, represented by intercalations of pink limestones with thin layers of shales and pink beige siltstones. At the top are pinkish-coloured sandstones, attributed to the Corumbataí Formation. D: Detail of the intercalation between shales, siltstones, and limestones - in limestone packages, silica nodules are also present.

Anjos (2008) presents a detailed study of the faciological variation present in the Assistance Member of the Irati Formation, in the northern portion of the Paraná Basin, in which six facies were identified by the author: Dolomitic Carbonatic, Lower Pelitic, Oolitic Carbonatic, Upper Pelitic and, locally, Stromatolytic and Pink Carbonate facies (Anjos 2008; Anjos et al., 2010). The Dolomitic Carbonate facies described by Anjos (2008) corresponds to the Dolomitic carbonate facies described in this study. The pelitic facies, on the other hand, are likely to be associated with the Lower Pelitic facies, according to the description of Anjos (2008).

Anjos (2008) describes the Dolomitic Carbonate facies as packages of fine dolomitic sandstone, gray to beige, with thickness ranging from 50 cm to 2 m. These are interspersed with centimetric layers of shales and dark gray mudstones. Plane-parallel and hummocky stratification were identified. The author identified wackstone texture in doloarenites, with pellets and intraclasts dispersed in the micritic matrix. Less often, there are lens of packstone texture, intraclasts and fossiliferous levels (crustacean shells, ostracodes, ossicles) supported by micrite, and locally cemented by sparite. According to the mineralogical analysis carried out by the author, in addition to dolomite, carbonate rocks are constituted by traces of saponite, illite, kaolinite and feldspar. The shales and mudstones also have a carbonate composition, consisting mainly of saponite, quartz and dolomite, with traces of illite and albite (Anjos 2008).

The facies on top of the dolomites is named by Anjos (2008) as Lower Pelitic, described as intercalations predominantly of shales and carbonate rocks. In addition to these, thin layers of black clay, about 10 cm thick, are present. Carbonate rocks are described as laminated dololutes, with the presence of pellets and intraclasts dispersed in the matrix, and styloliths with recrystallization of quartz, calcite, and pyrite at the edge. The shales and black clay are formed by saponite and quartz, with traces of illite, kaolinite, talc, lizardite and dolomite. Near igneous intrusions, talc and calcite crystals of metamorphic origin have been identified (Anjos 2008).

Anjos (2008) also describes the identified Pink Carbonate Facies as centimetric intercalations of pelites and dolomites, both pink in colour, indicating oxidative conditions. The thickness of the layers varies from 20 to 60 cm. Still according to Anjos (2008), the presence of calcitic carbonate rocks would be associated with the presence of intrusions, as in the Facies Carbonatic Oolitic, which presents a dolomitic composition when far from igneous intrusions, and calcitic in the proximity of intrusions.

4.1.2. São Paulo State (SP)

In the southeast of the Paraná Basin, samples were collected at São Paulo state, from both surface and borehole: (i) open-pit mining samples at Saltinho municipality, Vitti and Amaral Machado quarries, and (ii) core samples from the borehole FP-12-SP, at Anhembi municipality. In the area, the Assistência Member of Irati Formation is characterized as bituminous black shales, dark grey mudstones, and gray shales intercalated by limestone beds. In São Paulo State, the Corumbataí Formation was also sampled in the Vitti Quarry (sample Vitti-3). This Formation was sampled for palynostratigraphic analysis and for petrographic and maturation comparison with the Irati Fm. In this region, Corumbataí unit consists of mudstones, siltstones, and fine sandstones intercalated with dolomites. Samples' location on the geological map and on cross-sections are represented in Figure 16.

Figure 16. Geological map of the Paraná Basin and its geochronological sequence with sampling sites location. Detail for samples collected in the SE of the Basin, São Paulo State (SP), and their placement in the geological map and cross-sections.

4.1.2.1. Vitti Quarry

Three samples were collected at the Vitti Quarry, at Saltinho Municipality – SP: samples Vitti-1, Vitti-2 and Vitti-3 (Coordinates: 22°54'48.92"S/ 47°43'2.03"W). Sampling was carried out in a vertical sequence of approximately 22 meters, composed by centimetric layers of grey and black shales rhythmically interbedded with dolomites. At the base of the sequence, dolomites are predominant, constituting meter-thick beds over centimetric shale layers. The Corumbataí Fm is composed by mudstones, siltstones, and fine sandstones intercalated with dolomitic limestones (Figure 17).

Figure 17. Vitti Quarry at Saltinho – SP, with sample's location. A, B: Overview of open-pit mining vertical sequence, showing the contact between the Irati and Corumbataí Formations. C: Vertical sequence with the positioning of samples Vitti-1 and Vitti-2. D, E: Detail of sampled levels - centimetric shales interbedded with carbonates.

4.1.2.2. Amaral Machado Quarry

Two samples were collected at Amaral Machado quarry, also located at Saltinho – SP (Coordinates: 22°53'38.84"S/47°41'53.42"W). One sample of Irati Formation black shale and one sample of the interbedded dolomite, both for mineralogical characterization. The exposed vertical sequence reaches approximately 25 meters, being 5 meters at the base corresponding to a dolomitic limestone package, followed by centimetric intercalations between dolomites and black shales. At the top of the sequence the contact with the overlying Corumbataí Formation can be observed (Figure 18).

Figure 18. Amaral Machado Quarry at Saltinho – SP. A: Overview of the quarry and the sampled vertical sequence, showing the contact between the Irati Formation (base) and the Corumbataí Formation (top). B: Irati Formation with a dolomitic package at the base, followed by the typical Assistência Member rhythmites. C: Detail of the black shales interbedded with dolomites. D: Oil occurrence within the formation. E: Dolomitic package at the base of the sequence.

4.1.2.3. Borehole FP-12-SP

The well FP-12-SP is located at the Anhembi municipality (coordinates: 22°45'31.29"S/ 48°16'6.55"W), north-eastern flank of the Ponta Grossa Arch, in São Paulo, and it intersects the Irati Formation at 274,5 meters deep. Samples were collected at the upper part of the Assistência Member around 274 m depth. In this borehole the Irati Formation thickness is of 39,5 meters: Taquaral Member being 6 meters thick and Assistência Member with thickness of 33,5 m. The Assistência Member corresponds to dark gray to black shales interbedded with calcilutites – with layers alternating between millimetres to 1 meter of thickness and constituting rhythms. Two samples were collected: samples 658 and 659, at 274,20 and 274,56 meters deep, respectively. Sample selection was based on colour - black shales as an indicative of organic-rich intervals at the upper Assistência Member.

4.1.3. Paraná State (PR)

At the southern portion of the Paraná Basin, borehole samples were collected at various locations of the Paraná State. In addition, surface samples were collected at the Petro-SIX mining unit, in the São Mateus do Sul municipality: samples CCM-1, CCM-2, and CCM-3 (coordinates: 25°51'39.82"S/ 50°23'48.77"W). The boreholes were from the lithological collection of the Brazilian Geological Survey (*Companhia de Pesquisa de Recursos Minerais* – CPRM), located in Araraquara municipality, São Paulo State (Figure 19).

Figure 19. Boreholes from the Brazilian Geological Survey (CPRM). A: Borehole collection from São Paulo and Paraná States. B, C: Shales of Irati Formation, Assistência Member and its heterogeneity among the wells: samples were collected from organic-rich (black coloured) intervals.

The corresponding wells were part of CPRM project focused on carboniferous deposits for coal prospection in the Paraná State, carried out between 1979 and 1982, through which 20 drill holes were drilled. The drilling was performed in the surrounding of Sapopema, Ortigueira, Ibaiti, and São Mateus do Sul municipalities, at Paraná State. And one well was drilled in São Paulo State, proximal to Anhembi city (CPRM, 1982).

A total of 24 samples were collected from the following boreholes: FP-01-PR, FP-02-PR, FP-03-PR, FP-04-PR, FP-07-PR, FP-11-PR, SP-29-PR, SP-37-PR, SP-47-PR, SP-49-PR, and SP-55-PR (Figure 20). To address the Irati Formation heterogeneity, samples were collected at different depths, in between a depth range from 80 to 477 meters, where the wells reached the Irati Formation (top of the Assistência Member). Samples were collected from the organic-rich intervals, identified by color (black shales).

Figure 20. Cross-section of the Assistência Member (Irati Formation) vertical interval. The sequence illustrates sample's location and their proximity to igneous intrusions (in red colour).

In the studied boreholes the Irati Formation is represented by bituminous black shales, dark gray argillites, and gray shales with associated limestones. The Assistência Member characterized by the intercalation sequence between black pyro-bituminous shales and gray, clayey limestones, with a slight bitumen odor, in addition to possible concretions of silex. The Taquaral Member was composed of dark gray shales and argillites, with rare calciferous intercalations. In general, the formation presents fracture filled with calcite and/or pyrite. Regarding sedimentary structures, plane-parallel laminations are the most characteristic. The contact with the underlying formation is concordant transitional (CPRM, 1982).

The local stratigraphic column, intersected by the studied CPRM wells, is represented in Figure 21. It is representative of Permian in the southern portion of the Paraná Basin, at the Paraná State. It is based on borehole description and on the CPRM reports.

Period	Lithostratigraphy			Thickness (m)	Lithological description
Quaternary	—	—		—	Sand and clay deposits. Unconsolidated
Permian	Passa Dois Group	Teresina Fm		200	Siltstones, with flaser bedding and contraction cracks-like structure. Greenish-gray coloured. Sandstones, fine-grained, with micro cross-stratification and light-gray colour. Oolitic limestone.
		Serra Alta Fm		40	Shales, dark gray colour, with conchoidal fracture pattern.
		Irati Fm		40	Bituminous shales, interbedded with limestones with nodular flint. Colour varies between dark gray to black. Sampled level.
	Guatá Group	Palermo Fm		80	Siltstones, laminated and with bioturbations. Gray coloured. Mudstones (argillites), compacted and uniform, with levels of silex. Dark gray coloured.
		Rio Bonito Fm		100 — 110	Siltstones with plane-parallel, lenticular and wavy lamination. Colour vary between greenish gray, purplish and brown. Limestone, argillaceous and beige. Sandstones, very fine-grained and cross-laminated. Whitish gray coloured. Carbonaceous shales and coal beds. Conglomerate, with rounded pebbles in a sandy-clayey matrix. Gray coloured.
	Itararé Group	Undifferentiated		600 — 800	Diamictites with heterogeneous composition fragments: granites, quartzites, quartz, metasediments and others, dispersed in silica matrix, sometimes sandy. Gray coloured. Shales and mudstones, constituting varvites. Dark gray coloured. Sandstones, plane-parallel and cross-stratified. Whitish coloured. Mudstones (argillites) with plane-parallel lamination. Brown coloured.

Figure 21. Local stratigraphic column of the southern Paraná Basin (Paraná State). It represents the geological formations intersected by the studied CPRM wells, together with its thickness and lithological description, based on borehole description and on the CPRM reports.

4.2. Selected Samples

The selected samples for further analysis are listed in Table 4. The total of 43 samples of Irati black shales are identified with respective ID, location, depth, and coordinates.

Table 4. Samples selected for this study.

Sample ID	Location	Depth (m)	Coordinates
Goiás State (N)			
Rio Verde quarry			17°15'0.02"S / 51°28'53.07"W
572	Montividiu - GO	0	
573	Montividiu - GO	0	
574	Montividiu - GO	0	
575	Montividiu - GO	0	
576	Montividiu - GO	0	
577	Montividiu - GO	0	
578	Montividiu - GO	0	
579	Montividiu - GO	0	
SUCAL quarry (N)			17°28'56.73"S / 52° 3'10.62"W
580	Perolândia - GO		
581	Perolândia - GO	0	
582	Perolândia - GO	0	
583	Perolândia - GO	0	
584	Perolândia - GO	0	
585	Perolândia - GO	0	
586	Perolândia - GO	0	
ELBA quarry (N)			17°27'2.03"S / 51°10'34.12"W
587	Montividiu - GO	0	
588	Montividiu - GO	0	
589	Montividiu - GO	0	
590	Montividiu - GO	0	
São Paulo State (SE)			
Vitti quarry			22°54'48.92"S/ 47°43'2.03"W
Vitti-1	Saltinho - SP	0	
Vitti-2	Saltinho - SP	0	
Vitti-3	Saltinho - SP	0	
Amaral Machado quarry			22°53'38.84"S/47°41'53.42"W
AM-01	Saltinho - SP	0	
AM-02	Saltinho - SP	0	
Borehole FP-12-SP			22°45'31.29"S/ 48°16'6.55"W
658	Anhembi - SP	274.2	

659	Anhembi - SP	274.38	
Paraná State (S)			
Borehole FP-11-PR			24° 4'12.20"S / 50°47'32.77"W
660	Ortigueira - PR	351.34	
661	Ortigueira - PR	272.3	
Borehole FP-01-PR			23°38'56.30"S / 50°23'31.48"W
662	Ibati - PR	194.5	
663	Ibati - PR	195.07	
664	Ibati - PR	196.95	
665	Ibati - PR	197.45	
Borehole FP-02-PR			23°50'15.18"S / 50°35'43.58"W
666	Sapopema - PR	122.8	
Borehole FP-03-PR			23°52'42.09"S / 50°39'54.17"W
667	Sapopema - PR	227.16	
Borehole FP-04-PR			24°15'3.03"S / 50°55'51.76"W
668	Ortigueira - PR	185.61	
Borehole FP-07-PR			25°51'49.02"S / 50°26'24.31"W
669	São Mateus - PR	81.07	
670	São Mateus – PR	81.73	
671	São Mateus – PR	84.05	
672	São Mateus - PR	95.45	
Borehole SP-29-PR			23°46'56.50"S / 50°35'42.15"W
673	Sapopema - PR	340.65	
674	Sapopema - PR	340.85	
Borehole SP-37-PR			23°47'12.55"S / 50°31'36.76"W
675	Sapopema - PR	213.72	
Borehole SP-47-PR			23°46'29.71"S / 50°32'1.68"W
676	Sapopema - PR	241.74	
677	Sapopema - PR	242.05	
Borehole SP-49-PR			23°42'1.12"S / 50°25'45.19"W
678	Sapopema - PR	373.13	
679	Sapopema - PR	373.27	
680	Sapopema - PR	373.4	
Borehole SP-55-PR			23°46'14.72"S / 50°32'49.44"W
681	Sapopema - PR	477	
PETROSIX quarry			25°50'10.14"S / 50°25'19.09"W
CCM-1	São Mateus do Sul – PR	0	
CCM-2	São Mateus do Sul – PR	0	
CCM-3	São Mateus do Sul - PR	0	

The Irati Formation was intruded by doleritic sills in 3 boreholes: FP-02-PR, SP-37-PR, SP-47-PR. The boreholes SP-49-PR, SP-55-PR were intruded in the Teresina Formation. Doleritic sills were also identified on two outcrops, at the northern portion of the PB, GO State: Rio Verde and ELBA quarries. The igneous intrusion identified at the well FP-02-PR is very expressive (216 meters thick) and presents microcrystalline structure, characteristic ophitic texture and its fractures are filled by calcite and/or pyrite (CPRM, 1982). This information was estimated for outcrops and determined based on the Brazilian Geological Survey well log reports. Samples that were thermally affected, as well as its distance to the igneous intrusion and the thickness of the sill are listed in Table 5.

Table 5. Samples that are in proximity with igneous intrusions.

Sample ID	Location	Depth (m)	Distance to nearest intrusion wall (m)	Thickness of nearest intrusion wall (m)
Rio Verde quarry (GO)				
574	Montividiu - GO	0	1.5	1
577	Montividiu - GO	0	2.5	1
579	Montividiu - GO	0	2.5	1
ELBA quarry (GO)				
587	Montividiu – GO	0	3	1.5
588	Montividiu – GO	0	3	1.5
589	Montividiu – GO	0	4	1.5
Paraná State (S)				
Borehole FP-02-PR				
666	Sapopema - PR	122.8	2.2	220
Borehole SP-37-PR				
675	Sapopema - PR	213.72	6.28	2
Borehole SP-47-PR				
676	Sapopema - PR	241.74	4.26	20
Borehole SP-49-PR				
679	Sapopema - PR	373.27	346.27	19
680	Sapopema - PR	373.4	346.4	19
Borehole SP-55-PR				
681	Sapopema - PR	477	142.03	60

The selected samples were then prepared to the following analytical procedures: organic geochemical and petrographic analysis, such as total organic carbon content measurement,

Rock-Eval pyrolysis, maceral analysis and vitrinite reflectance; mineral characterization through X-Ray diffraction; and gas sorption analysis through the Langmuir model (with pure CO₂) and BET model (N₂ and CO₂). The first to determine gas sorption capacity and the second to determine pore volume, size, and surface area.

4.3. Sample preparation

Sample preparation includes cleaning, cutting, drying, crushing, pulverizing and transport to analytical laboratories. Initially, collected samples were transported in bags from field to the lithological collection of the Institute of Energy and Environment (IEE) - Scientific Division of Petroleum, Natural Gas and Bioenergy Technologies, located at University of São Paulo (USP), where they were stored.

Selected samples were left open for drying at room temperature for at least 24 hours. Dried samples were cut transversally to the sedimentary bedding with a rock-cutter, to preserve part of the sampled level for further analysis in Portugal, where part of this project was carried out, as below explained.

After cutting, samples were cleaned by scraping of superficial dirt with a knife. Cleaned samples went through a second drying process: placed in an incubator, at 45°C for 24 hours – temperature was relatively low to avoid alteration of the organic-content. Thereafter, samples were fragmented, crushed, and powdered, using an agate pestle and mortar (Figure 22). Grain size control during powdering was performed using a 60 mesh (250 µm) sieve.

Figure 22. Sample preparation steps for analytical experiments. A: sample storage at the IEE lithological collection. B: sample transversal cutting – half of the sample was powdered, and the other half is preserved for future analysis. C, D: sample cleaning and crushing into smaller fragments. E: Elements for sample pulverization: pestle, mortar, and a sieve to reach the adequate granulometry (60 mesh or 250 μm).

A total of 15 grams of pulverized material was prepared for each sample and stored in acrylic recipients. From this quantity, 10 g were set for TOC and Rock Eval pyrolysis and 5 g were set for XRD diffraction analysis. Sample preparation and storage was performed at the Laboratory of Petroleum Systems Rock Characterization (LABPETRO), at IEE/USP. Selected samples were sent from Brazil to partner intuitions in Portugal and England for further analysis. A flow chart explaining lab methodology and sample preparation is presented in Figure 23.

Figure 23. Flow chart of the experimental section, including sample preparation and analytical procedures.

4.4. Analytical procedures

This section presents a brief description of the applied analytical procedures. These include (i) organic geochemistry analysis, such as TOC and Rock-Eval pyrolysis; (ii) organic petrography techniques, such as palynological studies, maceral group analysis (palynofacies and kerogen typing), vitrinite reflectance (VR) measurements, and spore colour and fluorescence identification; (iii) mineral characterization through XRD, and (iv) gas sorption isotherms, low-pressure (BET method) and high-pressure (Langmuir method), for petrophysics data acquirement and storage capacity estimates, respectively.

These analytical procedures were performed in the following institutions: University of São Paulo (USP), Rio de Janeiro State University (UERJ), Fernando Pessoa University (UFP), Portuguese Geological Survey (LNEG), Algarve University (UAlg), and Imperial College London (ICL), all of them partners of the research project 36 of RCGI.

Organic geochemistry and petrography techniques were applied to determine organic composition and thermal maturity windows. Kerogen typing and palynofacies association was determined based on relative frequency and maceral group classification. Organic maturation levels were assessed by different optical method: vitrinite reflectance (VR), spore colour and spore fluorescence, together with Rock-Eval pyrolysis data. The results contribute to Irati shales characterization and to the Paraná Basin thermal history. Additionally, the organic geochemistry and petrography provide data to analyze the association between the organic matter type, quantity and quality with the adsorption and desorption capacity. In addition to identify geological facies with the highest potential to CO₂ sequestration within Irati oil shales.

The XRD analysis was performed to provide detailed mineral characterization and to investigate possible correlation between adsorption capacity and mineralogy, specially of clay-minerals. CO₂ and N₂ low pressure adsorption measurements, based on the Brunauer–Emmett–Teller (BET) theory, were applied to quantify pore volumes, pore sizes, and pore-size distributions within the samples. Additionally, CO₂ high pressure adsorption and CH₄ desorption isotherms were analysed, through Langmuir method, to estimate gas sorption and storage capacity.

4.4.1. Total Organic Carbon (TOC)

Total organic carbon analysis is essential to source-rocks evaluation. TOC measurements are 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 both the insoluble fraction (kerogen) and the soluble in organic solvents fraction (bitumen).

TOC measurements followed the steps of weighing, acidification, washing, drying, second weighing and, finally, measuring TOC and sulfur (S) in the LECO SC632 equipment. These analyzes were carried out at the Laboratory of Organic Geochemistry and Chemical Stratigraphy of the State University of Rio de Janeiro, under the supervision of Prof. Dr. Egberto Pereira.

Initially, aliquots with 0.250g of powdered samples go through an acid treatment for inorganic carbon removal: immersion into an acid solution (HCl + distilled water in a concentration of 1: 1) for 24 hours, followed by a washing step with distilled water to remove excess acid content. The decalcified samples are then dried in a light booth (60W incandescent lamps, with temperature below 80°C), for about 24 hours. Dried samples are weighted and finally taken to the TOC and sulphur content measuring equipment (LECO SC632). The apparatus components include an oven, refractory tube, vacuum pump, and infrared cell. The process consists of the complete and instantaneous oxidation of the sample, by flash combustion (at 1.350 ° C) whereby combustion products are determined by the infrared cell reading of the emitted wavelengths. The described steps and equipment are illustrated in Figure 24.

Figure 24. TOC preparation steps and equipment. A. Aliquots with powdered samples and high precision scale for weighting. B. Acid dissolution step. C. Decalcified samples. D. Washed samples drying in a light booth. E. LECO SC632 equipment.

4.4.2. Rock-Eval Pyrolysis

After determining the TOC and S levels, samples with TOC values greater than 1% proceeded to the pyrolysis *Rock-Eval 6* analysis. This analysis can be used for identifying the type and maturity stage of the organic matter and determining hydrocarbon potential of source rocks (Espitalié et al. 1977).

Rock-Eval pyrolysis is a rapid screening technique for source-rock evaluation. It simulates, under laboratory conditions, the metagenesis and catagenesis 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, but there is no combustion.

The Rock-Eval 6-unit apparatus basically consists of an oven in a helium atmosphere and ionization detectors that record gas release ratios by means of a pyrogram, in which three different peaks are measured: S_1 , S_2 and S_3 . Initially, free hydrocarbons are determined by thermo-vaporization at 300°C (S_1). Then, the heating ramp gradually increases the temperature to 650°C, determining the peak of induced cracking of organic matter and generation of HC (S_2). Peak values S_1 and S_2 are measured in milligrams of HC generated per gram of rock (mgHC/gRock).

The CO and CO₂ expelled from the pyrolysis (S_3), and the temperature at which the maximum amount of S_2 hydrocarbons is generated (Tmax) are also recorded. Additionally, hydrogen index (IH) and oxygen index (IO) are calculated: $HI = (S_2 \times 100) / TOC$; $OI = (S_3 \times 100) / TOC$ (Espitalié et al. 1977). The used Rock-Eval 6 equipment is shown in Figure 25 and is located at the Laboratory of Organic Geochemistry and Chemical Stratigraphy of the State University of Rio de Janeiro.

Figure 25. Rock-Eval 6 apparatus located at the Laboratory of Organic Geochemistry and Chemical Stratigraphy of the State University of Rio de Janeiro (UERJ).

4.4.3. Palynological Studies

Palynology was carried out for palynostratigraphic age determinations, depositional environment interpretations, and for stratigraphic correlations with other South American Gondwana basins.

Standard palynological laboratory procedures were applied to shale samples to extract and concentrate the organic residues (Wood et al., 1996; Riding and Warny, 2008). Fifty grams of shale were crushed and placed in a Teflon jar. To the crushed rocks was added a few drops of HCl to test for carbonates. Since all the samples proved to be devoid of carbonates, the crushed shale samples were treated with HF (40%) until all the silicates were dissolved. Then the organic residue obtained was rinsed and decanted several times using distilled water until the organic residue was fully neutralized. Then, the samples were sieved using a 15 μm mesh sieve. For palynology, spore fluorescence, spore colour analysis, the organic residues were mounted on palynological slides using acrylic resin Elvacite[®].

The organic residues were oxidized using fuming nitric acid for about 30 seconds to 1 minute (Wood et al., 1996; Riding and Warny, 2008) and placed in slides for further microscopic

analysis. The taxonomic study and photomicrographs were performed using optical light BX40 Olympus microscope equipped with an Olympus C5050 digital camera facility. The analytical procedures were conducted in the Portuguese Geological Survey (LNEG), at São Mamede de Infesta, Portugal, under the supervision of Dr. Zélia Pereira. The described methodology is illustrated in Figure 26.

Figure 26. Methodology for palynological studies. A. Samples to be prepared. B, C and E. Acidification and organic matter concentration processes. D, F. Optical light BX40 Olympus microscope coupled with a digital camera for palynomorphs' imaging.

Petrographic composition was determined through a quantitative and qualitative analysis of organic matter compounds, in terms of relative frequency and maceral group analysis (ISO 7404-3, 2009). Petrographic composition was determined on 19 samples, where the organic content was well-preserved based on the palynological analysis. 300 to 600 organic particles were identified and counted for each sample, and absolute values were recalculated for percentages and normalized to 100%. Maceral classification was in accordance with the International Committee for Coal and Organic Petrology (ICCP, 1963, 1998, 2001). Organic compounds are arranged in three morphological constituents: amorphous organic matter, palynomorphs, and phytoclasts. The last group was divided between non-opaque/translucent and opaque phytoclasts.

4.4.4. Vitrinite Reflectance

Vitrinite reflectance (VR) measurements constitute an optical petrographic methodology, based on reflected light microscopy, for determining organic maturity. 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; Fernandes, 2000). This analytical method was developed to classify the coals' rank, being also applied to other organic-enriched lithologies, such as shales.

Vitrinite identification, measurement and presentation of results followed the guidelines recommended by the ASTM D7708-14 (2014), ISO 7404-5 (2009) and ICCP (1998). Vitrinite reflectance ($R_r\%$) measurements were applied to palynological residue and to fragments of dry samples, with a particle size between 0.84 and 1 mm. The organic residues were washed and sieved using 15 μm nylon mesh to remove the acid component. The remaining fraction of organic matter, concentrated in aqueous medium, was mounted in slides for further analysis using polytetrafluoroethylene (PTFE). Two slides were prepared for each sample, and were dried in 45°C, until the application of an epoxy resin on the dry organic fraction (EPOFIX, ratio 15/2 by volume). This process was followed by a second drying process, lamella removal, and resin polishing, preparing the sample for study.

VR was measured on, at least 30 non-oriented, vitrinite particles, using an Olympus BX 51 microscope equipped with an Olympus SC20 digital camera, at the Center for Marine and Environmental Research (CIMA), Faculty of Sciences and Technology of the University of Algarve, Portugal. The greyscale (8-bit) digital images of vitrinite particles were analysed using

the graphical tool VITRINITE, which runs within the MIRONE Suite and calibrates the scale of 256 grey levels with standards of known reflectivity (Fernandes et al., 2015). The reflectance values of the standards used were: 0.00%, 0.428%, 0.595%, 0.897%, 1.314%, 1.715%, 3.15% and 5.37%. VR was measured in non-polarized incident light with a wavelength of 546 nm and immersion oil with a refractive index of 1.518 at a room temperature of 20 °C. The described method was based on Fernandes, (2000); Fernandes et al, (2010), and Lopes (2013).

4.4.5. Spore fluorescence and colour

Qualitative spore fluorescence and spore colour are two optical parameters of thermal maturity of organic maturation, useful for evaluating maturation levels of low-rank rocks until the end of the oil window (McPhilemy, 1988; Suárez- Ruiz et al., 2012). When correlated with the quantitative VR method, spore fluorescence and colour parameters can provide additional support for the thermal maturity of the rocks. Maturation causes a gradual shift in organic matter fluorescence colours (redshift) from the shorter to the longer wavelengths, that is, blue and green to yellow, orange and finally red. Of all the macerals of the liptinite group, sporinite is the one that shows the most consistent changes in fluorescence colour spectra and intensity with increasing maturation.

The analysis of qualitative spore fluorescence colours was undertaken in the University of the Algarve using an Olympus BX 51 microscope equipped with a metal halide lamp fluorescence unit; XCite Series 120Q and with Violet and Blue +12 filter block that generates a wavelength band of 390–490 nm. This system was allowed to stabilize for 5 min before any observation of the fluorescence of palynomorphs was attempted. Suitable spore species with smooth and medium thick exine, such as *Densoisporites* spp., were subjected to 5 min of excitation, after which their fluorescence colours were recorded. The terminology used for describing fluorescence colours was blue (B), green (G), yellow (Y), dark yellow (DY), orange (O), dark orange (DO) and red (R). According to the scale, colours vary from blue and green for an immature sample to orange to red for more mature rocks. The qualitative analysis of the fluorescence was made in the macerals of the liptinite and vitrinite group according to the ICCP Standard (International Committee for Coal and Organic Petrology, 1976; 1993).

Spore exine colour is a method to assess the thermal maturity of sedimentary rocks, because, with increasing burial depth, spore colour changes from light to dark and that the change is irreversible (Correia, 1971; Staplin, 1982). In this study, spore colour was recorded using the

Phillips Petroleum Colour Standard version no. 2 (Pearson, 1984), which is an adaptation of Staplin's Thermal Alteration Index (TAI) chart, because it includes more shades for the same colour index. The spore colour index for the samples was given by the colour of the dominant and lightest spores observed and compared with the Phillips Petroleum Colour Standard chart. The results of spore colour determination were analysed together with VR measurements and spore fluorescence colours for each sample, based on the correlation expressed in Figure 27.

Organic thermal maturity	Spores/ Pollen colour	Correlation to other scales		
		TAI 1-5	Vitrinite reflectance	Fluorescence
Immature		1	0.2%	Blue
		1+		Green
		2-	0.3%	Greenish yellow
		2		
Mature main phase of liquid petroleum generation		2+	0.5%	Golden yellow
		3-		
		3	0.9%	Orange
		3+		Red
Dry gas or Barren		4-	1.3%	Nonfluorescence
		4	2.0%	
	Deformed	5	2.5%	

Figure 27. Correlation chart between the polymorphs colour, thermal alteration index (TAI) and fluorescence, (Adapted from Stach et al., 1982).

4.4.6. X-Ray Diffraction

X-ray diffraction (XRD) technique was applied for mineral content characterization and identification of expandable clay minerals.

In this technique, the sample is scanned through a range of 2θ angles by directing a concentrated and monochromatic x-ray to a flat surface of powdered sample that has been mounted in a holder. The diffracted rays can be counted by a detector and converted to peaks that have different intensities according to their abundance in the sample. The position of a set of peaks on the 2θ angles and their relative intensities can be used for identification of an unknown mineral.

Whole-rock sample preparation and analysis followed Moore & Reynolds (1997) powder pressing technique. Initially, fragments of selected samples were manually grinded using agate mortar and pistil. Then, an aliquot of homogenized powder was pressed onto an acrylic sample holder for analysis. The clay fraction below 2 μ m was used to identify the clay minerals. Sample preparation for clay mineral analysis included the steps of (i) drying the samples in an oven with controlled temperature below 40°C, (ii) manual grinding of selected fragments from each sample, with the aid of a mortar and agate pistil, (iii) treatment with H₂O₂ and ultra-pure water under controlled temperature below 60°C for a maximum of 40 minutes, followed by washing; and (iv) pipetting of the clay fraction.

Sample's preparation was carried out at the Laboratory of Petroleum Systems Rock Characterization (LABPETRO - *Laboratório de Caracterização de Rochas de Sistemas Petrolíferos*) at the Institute of Energy and Environment (IEE) of University of São Paulo (USP).

Initial XRD analyses and mineral phase identification were carried out at the Polytechnic School (POLI/USP), at the Laboratory of Technological Characterization (LCT - *Laboratório de Caracterização Tecnológica*) and are attached to this thesis (Appendix A).

Further XRD analyses were carried out on a Bruker D8 Advance Diffractometer with LYNXEYE XE detector and theta-theta system, at the Non-Destructive Testing *Laboratório de Caracterização* Laboratory of the Petroleum, Natural Gas and Bioenergy Division of IEE/USP.

The diffractograms were obtained with Cu K α radiation, 40 kV, 25 mA, automatic Air-scatter at a scanning rate of 0.02° 2 θ step and with 3.1 seconds acquisition time. The total sample diffractograms were obtained between 0.15° and 100° 2 θ , using 0.2° primary slit and 9.5mm secondary slit. Clay fraction ($\leq 2 \mu$ m) diffractograms were obtained between 2° and 30° 2 θ , with 0.5 mm primary slit and 1.0 mm secondary slit. The clay minerals were analysed under natural conditions (air dried) and after specific treatments such as solvation with ethylene glycol for at least 48 hours, and heating at 500°C for 4 hours in a muffle furnace (e.g., Brindley & Brown 1980). Mineralogical identifications and graphic data treatment of the diffractograms were carried out using DiffracEva software version 4.2.2 (Bruker ASX GmbH), and were based on the International Centre for Diffraction Data (ICDD) database.

4.4.7. Gas sorption isotherms

Gas sorption isotherms and models are an efficient method to evaluate the CO₂ storage potential in a geological reservoir, especially in coals and shales, where CO₂ storage is driven by the adsorption process, that is accumulating onto mineral and organic surfaces (Kalkreuth et al., 2013; Khosrokhavar, et al., 2014; Klewiah, et al., 2020; Weniger, et al., 2010; Rodrigues, 2002).

Sorption of CO₂ or CH₄ onto shales are determined in laboratorial experiments through isotherms. Sorption isotherms quantifies 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.

4.4.7.1. High Pressure-CO₂ sorption isotherms (Langmuir method)

In this study, sorption isotherms volumetric technique, based on the Langmuir isotherm model, were applied to measure the maximum CO₂ sorption capacity of Irati shales.

The Langmuir sorption model is the most adequate to explain the behaviour of gas storage in the coal and shale's organic porosity, based on experimental analysis (Rodrigues, 2002; Rodrigues et al., 2016; Dang et al., 2020; Weniger et al., 2010; Yu, et al., 2016; Zhou et al., 2019). It provides a good description of adsorption into microporous sorbents and of the existing equilibrium between stored/adsorbed gas and free gas by determining saturation limits (Rodrigues, 2002). The Langmuir isotherm models is the following:

$$G_{CS} = V_L \frac{P}{P + P_L}$$

G_{cs} is the gas content at saturation (scf/ton), P 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).

Sorption isotherms calculations were based on volumetric techniques or PVT (pressure–volume-temperature). The called volumetric method considers gas expandability aspects for determining volume, in accordance with the Boyle-Mariotte principle.

The Langmuir equation is mainly used for microporous material characterization, exhibiting Type I Isotherms. In the Langmuir model it is assumed that the adsorption is limited to one monolayer (with pressure increase, gas molecules cover the sample surface to form a one molecule thick layer).

Sorption isotherms and gas storage capacity are affected by numerous variables, that can either related to the reservoir sample or to the sorption gas (individual or mixture). The main variables attributed to the samples are minerology, 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 significant effect in the sorption process (Rodrigues, 2002; Fatah, et al., 2020; Klewiah et al., 2020; Rodrigues et al., 2018).

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) gas volume that is released 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).

The equipment used to measure the adsorption and desorption isotherms (Figure 28) was built by Professor Dr. Cristina Rodrigues – co-author of this research, with assistance of Professor Dr. João Manuel Lemos de Sousa, and in partnership with the Department of Organic Petrology and Geochemistry, Faculty of Sciences of Porto University. The equipment is currently located at the Energy, Environment and Health Laboratory of the Fernando Pessoa University, in the city of Porto, Portugal.

Figure 28. Gas sorption isotherms apparatus. A. Isothermal bath with temperature of 35°C. B. Sorption isotherms measurement equipment and software, at the Fernando Pessoa University.

The equipment includes a set of valves (system supply valve, cells connection valve, purge valve and a safety valve), an isothermal bath, and two cells: a reference cell (where the pressure can reach 17.5 Mpa or 2538.2 psi) and a sample cell (which reaches a maximum pressure of 7 Mpa or 1015.3 psi). The reference cell has a volume of 100 cm³, while the sample cell has a volume of 200 cm³. These values are systematically measured in the equipment calibration phase to detect minimal changes in the pressure and temperature laboratory conditions - since small changes in temperature can imply pressure changes in the equipment cells. To maintain the effectiveness of the method, the volume values are calculated with precision in the order of 10⁻⁴ cm³ (Rodrigues et al, 2002).

10 selected samples initially went through the physical disaggregation process, being crushed to 60 Mesh ($\leq 250 \mu\text{m}$) granulometry. Sample crushing to this granulometry allows the release of remaining gases from the sample, in addition to increasing the contact surface between the sample and the fluid medium. However, due to this increase in the contact surface, the results of adsorption isotherms tend to be overestimated in the order of 0.3 to 0.1% (Rodrigues, 2002). Afterwards, 100g of each selected sample went to the experimental procedure.

The experimental procedure starts with (i) purging the system (cleaning of remaining gases), followed by the (ii) calibration step, and (iii) sample volume, void volume, and density measurements, using helium gas, and finally (iv) adsorption and desorption with the sorption gases (CO₂ and CH₄).

After the purge, the calibration process is carried out for determining volumes of the reference and sample cells. Initially, the reference cell should be calibrated with standard empty volumes (values of pressure and volume of the empty sample cells are recorded for reference). Then, the sample cell calibration step is performed. In this step, the empty sample cell is calibrated with standard empty volumes, then filled with spherical cells of known size and volumes (calibration with standard empty volumes with cells), to assure measurement effectiveness. The next step is to determine the sample volume. Initially, the pulverized rock sample is placed in the calibrated sample cell, followed by the measurement of (i) void volume, (ii) rock sample volume and (iii) sample density. These are measured by the expansion of helium gas. Subsequently, the reference cell is filled with the adsorption gas, which is carbon dioxide (CO₂) for this study. Once the system is fed with this gas, the communication valve between the cells is opened, so that they reach kinetic balance. The pressure values are measured and monitored until equilibrium is reached. The system temperature is maintained by immersing the equipment

into the distilled water isothermal bath, at a constant temperature of 35°C. Finally, the adsorption and desorption processes are carried out, using CO₂ and CH₄, respectively. The pressure and temperature values obtained are processed using the Hewlett-Packard software.

According to Rodrigues (2002), the precision of the experimental data relies on stabilization at each step of increasing or decreasing pressure during the sorption and desorption processes. This means that the adsorbed phase and the free phase must be in dynamic equilibrium under each pressure stage measurement for enough time. Therefore, for this experimental procedure the pressure was stabilized (allowed variance ≤ 0.1 psi $\cong 6.9 \times 10^{-4}$ Mpa) for a period of 30 minutes for each pressure step, to achieve the required dynamic balance.

4.4.7.2. Low Pressure-N₂ and CO₂ sorption isotherms (BET method)

Low-pressure sorption isotherms were applied to 11 selected samples (10 shales and 1 dolomitic rock sample) to determine porosity and surface area through the Brunauer, Emmett and Teller (BET) method. The obtained N₂ and CO₂ BET sorption isotherms data will compose a comparative analysis with the Langmuir high-pressure isotherms.

BET sorption isotherms were used for porous material characterization, determining surface area, pore size distribution and pore volume of the analysed 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 called Brunauer, Emmett and Teller (BET) sorption isotherm equation was developed in 1938 and it is a well-known model for porous material characterization, being until now the conventional method for specific surface area evaluation. The BET theory derived from adsorption analysis, and 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.

$$\frac{1}{\left[V_a \left(\frac{P_0}{P} - 1 \right) \right]} = \frac{C - 1}{V_m C} \times \frac{P}{P_0} + \frac{1}{V_m C}$$

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, at 77.4 K (temperature of liquid nitrogen). C refers to a dimensionless constant that is 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). Average pore size is estimated from the pore volume.

In this study, BET isotherms were measured with nitrogen (N_2) and carbon dioxide (CO_2) as the gaseous adsorbates.

First, approximately 300 mg of pulverized selected samples are placed in sample holder, then the necessary measurements are taken for reference (tube mass + sample mass). Secondly, samples go through a degassing process (cleaning sample surface from water/organic vapours), under vacuum conditions at a set temperature of 45°C – to prevent organic alterations, for 24 hours.

Degassed samples are then weighted, and the sample mass is recorded and inserted into the software for isotherms calculations. After degassing, sample holders are placed into the equipment and the adsorbate (liquid nitrogen) is introduced into the manifold. The valve to the sample cell is opened allowing the adsorbate to interact with the sample material. Afterwards, pressure is repeatedly measured until equilibrium is reached. Once a stable reading is achieved, the analysis is concluded. After the measurements with N_2 , the analysis is repeated with CO_2 as the gas sorbate.

BET Micrometrics 3Flex equipment was the used gas sorption analyser. Analysis was carried out at the Chemical Engineering Department of Imperial College London (Figure 29).

Figure 29. Facility for low-pressure gas sorption isotherms measurements, at the Chemical Engineering Department at Imperial College London. A: Apparatus for BET adsorption isotherms, including the analyser, CO₂ cylinder, and vacuum degasser. B: Analysis taking place with CO₂ as the gas sorbate. C: Detail of the Micromeritics 3Flex.

5. RESULTS

This chapter presents and briefly discuss the obtained results of the research. The results will be presented in five different sections: (1) organic geochemistry assessment, (2) organic petrography assessment, (3) thermal maturation assessment, (4) mineral composition and (5) gas sorption isotherms analysis. This chapter is structured in the following chronology: it starts with sections 1, containing TOC and Rock-Eval pyrolysis data, followed by section 2, presenting organic petrographic composition and maceral group classification, and followed by section 3, with vitrinite reflectance and palynomorphs fluorescence data. These topics address the organic content of analysed samples through different perspectives (geochemistry and petrography), and provide data to classify the organic matter quantity, type, and maturation, in addition to paleoenvironmental depositional conditions. This organic content assessment of Irati oil shales was used to select samples to determine its mineralogical content (section 4), and further to go through gas sorption isotherms experiments, addressed in section 5. Finally, section 5 will include low-pressure N₂ and CO₂ sorption isotherms, for porosity determination, including pore volume, pore size distribution and surface area, through BET method (section 5.1), and high-pressure gas sorption isotherms, through Langmuir method, with CO₂ adsorption and CH₄ desorption data patterns (section 5.2).

5.1. Organic Geochemical Assessment

This section addresses the organic geochemistry of Irati oil shales. Organic geochemical techniques (TOC and Rock-Eval pyrolysis) were applied to source-rock evaluation. Based on previous studies, there is a positive correlation between TOC and stored gas volume (Bemani, et al., 2020; Mahmoud et al., 2020). Therefore, TOC analysis was conducted in 45 samples. Additionally, Rock-Eval pyrolysis analysis data was integrated with organic petrography data for determining kerogen type and thermal maturity assessment. These analytical experiments were conducted at Rio de Janeiro State University (UERJ) (sections 4.4.1 and 4.4.2, p.78-80).

5.1.1. TOC and Rock-Eval screening

Organic geochemical characterization through Rock Eval 6 pyrolysis and TOC data of 45 Irati shale samples is shown in Table 6. Based on the organic geochemical analysis, the studied Irati samples correspond to bituminous shales with remarkably high TOC content (in average 5.4 wt%, reaching up to 20.8 wt% mg HC/g rock), hydrogen-rich, with hydrogen index (HI) mostly above 600 mg HC/g TOC, and with high hydrocarbon generative potential (S₂ peak values reaching 130.33 mg HC/g of rock). These values portray the Irati shales as excellent potential source-rocks, despite the high heterogeneity that will be discussed below.

Table 6. Organic geochemistry data of Irati shale samples. Values in red correspond to wide or exceedingly small S₂ peak, resulting in Tmax not been clearly identifiable.

Sample ID	Borehole/ Quarry	Location	Depth (m)	TOC (wt%)	S (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)	Tmax (°C)
572	Rio Verde	Montividiu - GO	0	0.67	0.05	0	0	0.15	0	22.39	505
573	Rio Verde	Montividiu - GO	0	0.48	0.37	0	0	0.16	0	33.33	505
574	Rio Verde	Montividiu - GO	0	0.67	0.07	0.01	0.02	0	3	0.00	394
575	Rio Verde	Montividiu - GO	0	0.5	0.05	0	0	0.08	0	16.00	505
576	Rio Verde	Montividiu - GO	0	0.46	0.04	0	0	0.1	0	21.74	505
577	Rio Verde	Montividiu - GO	0	0.26	0.24	0.03	0.01	0.43	4	17.70	393
578	Rio Verde	Montividiu - GO	0	0.57	0.05	-	-	-	-	-	-
579	Rio Verde	Montividiu - GO	0	0.65	0.08	-	-	-	-	-	-
580	SUCAL	Perolândia - GO	0	4.49	0.13	2.27	27.66	0.13	616	3	408
581	SUCAL	Perolândia - GO	0	4.41	1.77	2.09	25.6	0.42	580.5	9.52	409
582	SUCAL	Perolândia - GO	0	8.19	2.79	2.6	43.49	0.18	531	2.00	412
583	SUCAL	Perolândia - GO	0	5.49	3.02	2.22	33.61	0.2	612	4.00	408
584	SUCAL	Perolândia - GO	0	2.78	1.22	0	0	0.16	0	5.76	504
585	SUCAL	Perolândia - GO	0	2.52	1.17	0	0	0.17	0	6.75	504
586	SUCAL	Perolândia - GO	0	2.65	1.27	0	0	0.21	0	7.92	504
587	ELBA	Montividiu - GO	0	1.64	0.13	0.95	4.82	0.49	293	30.00	392
588	ELBA	Montividiu - GO	0	1.66	0.09	0	0	0.25	0	15.06	505
589	ELBA	Montividiu - GO	0	2.02	0.14	0	0	0	0	15.35	504
590	ELBA	Montividiu - GO	0	1.75	0.12	0	0	0	0	14.86	505
Vitti	VITTI	Saltinho - SP	0	4.42	-	2.72	39.63	0.06	731	1	407
658	FP-12-SP	Anhembi - SP	274.2	9.65	5.7	4.46	48.34	0.69	500.93	7.15	423
659	FP-12-SP	Anhembi - SP	274.38	8.71	2.51	4.06	45.73	0.28	525.03	3.21	426
660	FP-11-PR	Ortigueira - PR	351.34	5.66	1.13	3.83	16.07	0.86	283.92	15.19	434
661	FP-11-PR	Ortigueira - PR	272.3	0.29	0.27	-	-	-	-	-	-
662	FP-01-PR	Ibati - PR	194.5	12.3	1.19	4.33	74.29	0.54	603.98	4.39	422
663	FP-01-PR	Ibati - PR	195.07	13.8	2.17	6.91	93.77	0.64	679.49	4.64	416
664	FP-01-PR	Ibati - PR	196.95	7.98	4.04	4.02	50.56	0.45	633.58	5.64	412
665	FP-01-PR	Ibati - PR	197.45	10.2	5.43	4.74	62.18	1.77	609.61	17.35	418
666	FP-02-PR	Sapopema - PR	122.8	3.73	0.46	0.02	0.06	0.54	1.61	14.48	405
667	FP-03-PR	Sapopema - PR	227.16	6.43	3.61	3.47	43.09	0.33	670.14	5.13	417

668	FP-04-PR	Ortigueira - PR	185.61	12.1	2.12	5.95	72.77	0.34	601.40	2.81	413
669	FP-07-PR	São Mateus - PR	81.07	13.8	3.32	9.27	81.97	0.49	593.99	3.55	419
670	FP-07-PR	São Mateus - PR	81.73	14.4	3.34	6.97	91.21	2.37	633.40	16.46	423
671	FP-07-PR	São Mateus - PR	84.05	11.9	3.75	7.11	80.95	1.07	680.25	8.99	419
672	FP-07-PR	São Mateus - PR	95.45	20.8	3.29	10.15	130.33	0.64	626.59	3.08	421
673	SP-29-PR	Sapopema - PR	340.65	0.39	0.27	-	-	-	-	-	-
674	SP-29-PR	Sapopema - PR	340.85	0.37	0.24	-	-	-	-	-	-
675	SP-37-PR	Sapopema - PR	213.72	5.29	0.75	2.53	20.62	0.17	390	3.21	439
676	SP-47-PR	Sapopema - PR	241.74	0.54	0.26	0.02	0.11	0.03	20	5.53	427
677	SP-47-PR	Sapopema - PR	242.05	1.03	0.78	0.02	0.06	0.55	5.83	53.40	330
678	SP-49-PR	Sapopema - PR	373.13	14.9	1.81	4.36	92.04	1.11	617.72	7.45	419
679	SP-49-PR	Sapopema - PR	373.27	11.4	1.24	4.53	74.83	0.47	656.4	4.12	422
680	SP-49-PR	Sapopema - PR	373.4	7.89	1.66	3.08	47.24	0.16	599	2.00	426
681	SP-55-PR	Sapopema - PR	477	0.43	0.45	-	-	-	-	-	-
CCM-2	PETROSIX	São Mateus - PR	0	1.63	-	0.94	5.25	0.11	322	7	391

Total organic carbon (TOC) measurements provided an estimation of the hydrocarbon generation potential of the studied samples of the Irati Formation. Analysis of 45 Irati shale samples provided a TOC range between 0.26% to 20.8%, with a mean of 5.4% mg HC/g rock, as shown in Table 6. Among these, 65% of the samples are above 2% of TOC content. The heterogeneity regarding the TOC content is mainly attributed to thermal maturity variations and can also be observed among the sampled areas.

In the northern border of the Paraná Basin, the samples from the Goiás (GO) State: Montividiu municipality mining sets - Rio Verde (samples 572 to 579) and ELBA (587 to 590), and from Perolândia municipality - SUCAL mining set (580 to 586), presented significant variance of TOC obtained values. Samples from Rio Verde were under 1% of TOC (ranging from 0.12 to 0.67%), and samples from ELBA were above of 1%, ranging from 1.66 to 2.02% of TOC. Samples from SUCAL presented higher values of TOC: varying from 1 to 5.47% mg HC/g rock. It must be noted that GO State samples presented the lowest TOC content in comparison with the other sampled areas (SP and PR States). This lower TOC content is mainly attributed to exceptionally low TOC range from Rio Verde samples (Table 6).

Samples from São Paulo State (SP) at southeast border of the Paraná Basin, presented a TOC range between 4.42 and 9.64 % - the lowest value is from a surface sample (Vitti quarry at Saltinho municipality) and the other two samples from the FP-12-SP borehole, located at Anhembi municipality (Table 6). These two sampled areas have a 65.2 km distance.

Towards the south of the Paraná Basin, samples present a higher TOC content. About 78.26% of samples from Paraná State (PR) have a TOC values above 1%, with an average of 7.7% of TOC (Table 6). Exceptions are attributed to borehole SP-29-PR (samples 673 and 674), borehole SP-55-PR (sample 681) and to sample 661. It is important to highlight that these low TOC samples are placed in proximity to igneous intrusions and that sample 681 was collected at the highest depth among all samples (at 477 meters deep).

Most samples are rich in hydrogen content and present a hydrogen index (HI) range between 500 and 731mg HC/g TOC (Table 6, Figure 30). 57.7% of samples with reliable pyrolysis data have $HI \geq 600$, 26.9% have HI between 300-600, and 15.3% have $HI \leq 300$ mg HC/g TOC. HI and TOC data indicate rich to very rich-oil prone samples (Figure 30). Exceptionally low HI values, between 0 and 20mg HC/g TOC, are unreliable since were obtained from thermally altered samples, and were not considered in this analysis. The hydrocarbon generative potential (S_2 peak) is highly heterogeneous, ranging from 0.1 to 130.33 mg HC/g of rock, with average

S₂ values of 45.6 HC/g of rock. Low values of S₂ are coincident with low values of HI and TOC, which correspond to thermally affected samples with no source-rock potential (samples 572-579, 584-590 from Montividiu municipality - GO, and samples 666, 676, 677, from Sapopema - PR).

Figure 30. Hydrogen index (IH) versus total organic carbon (TOC) plot showing generative source-rock potential of Irati black shale samples and its distribution.

According to the modified Van Krevelen diagram (Espitalié et al., 1986), studied Irati black shale samples Rock-Eval data reveal mixtures of type I-II and type III kerogen (Figure 31).

Figure 31. Plot of Rock-Eval data (hydrogen index versus oxygen index- modified van Krevelen diagram) showing kerogen types all studied samples of Irati shales.

Total sulphur (S) contents are significant, with concentrations equivalent to marine depositional environments. S values range between 0.04 to 5.7% (sample 658, borehole FP-12-SP) (Table 6). Despite the high heterogeneity, a sulphur increasing trend can be observed towards the south of the basin. Samples from SP and PR have higher S values in comparison to samples from GO State. This could be associated with a greater marine influence/sea water influx to the depositional site, which agrees with paleogeographic maps of the Irati Formation (Faure & Cole, 1999; Matos et al., 2017). Sulphur concentration could also be an indicative of anaerobic organisms and a reductive paleoenvironment (Chaves et al., 2018).

Thermal maturity assessment of analyzed samples include Rock-Eval pyrolysis data. The analyzed samples display a Tmax range between 405-434°C (Table 6) and indicate low to early-maturity stage (Tissot and Welte, 1984; Espitalié et al., 1986). Exceptions are attributed to samples from GO State (samples 572-577, 584-590) and samples 677 and CCM-, in which Tmax was not precisely identifiable (Table 6) - based on a review of the pyrograms, Rock Eval pyrolysis data was inconsistent for most of the samples collected at the Montividiu municipality (GO) (Rio Verde and ELBA quarries), due an absence of a defined S₂ peak. The unreliable Tmax results can also be attributed to the proximity of igneous intrusions.

According to the exposed TOC and Rock-Eval pyrolysis data, is possible to observe the high heterogeneity regarding organic matter content among the oil shales from the Irati Formation. For instance, within the same borehole, even in small (centimetric) depth differences, pyrolysis data (HI, OI, and Tmax) can have a significant variance, such as shown in the borehole SP-47-PR. This heterogeneity can also be observed geographically.

Comparatively, samples from the northern border of the Paraná Basin indicate dominance of type II kerogen: HI values ranges from 531 to 616 mg HC/g TOC (samples 580, 581, 582 and 583). While most samples from the south and southeast of the Paraná Basin are attributed to type I kerogen: HI values ≥ 600 mg HC/g TOC. Type III kerogen is also present among studied portions of the basin, with higher occurrence in the N of PB (e.g., samples 574, 577 and 587). When comparing sampled locations, it is possible to state that samples from GO have higher type II kerogen content, lower TOC, and possibly higher thermal influence from igneous intrusions than samples from SP and PR. Despite that, intrusions are present in every sampled area (GO, SP and PR).

The observed high heterogeneity extends to different patterns of organic matter oxidation and preservation within the region. The elevated content of oxygen within these samples (from 0 to 53,4 mg CO₂/g TOC) (Table 6) suggest a high concentration of reactive oxygenated components (Verheyen, Johns, & Espitalié, 1984). Considering the geological setting of sampled areas, it is possible to attribute the oxidation to contact metamorphism from igneous intrusions, which are well known in the Paraná Basin. Furthermore, as previously mentioned, the presence doleritic intrusions (Serra Geral Formation) in the proximity of the sampling location, reinforce this theory.

Overall, organic geochemical data indicate that most of the Irati black shale samples are classified as excellent source-rocks with prevailing medium-high potential for oil generation, with kerogen type I predominant, with mixed type II kerogen, and locally type III. Tmax values suggest an immature to early mature stage to most samples, with exceptions being associated to the mentioned igneous intrusions (Figure 32).

Figure 32. Cross-plot of hydrogen index (HI) versus maximum pyrolysis temperature (Tmax) – and its equivalence on vitrinite reflectance (Ro), based on kerogen typing to indicate source-rock maturity of Irati black shale samples.

5.2. Organic Petrography Assessment

This section will describe the petrographic composition, thermal maturation levels, and palynostratigraphic framework of Irati oil shales (Assistência Mb.). Petrographic composition and palynofacies were based on maceral group prevalence (counted among 300 to 600 organic particles). To further evaluate thermal maturation levels, optical petrographic methods were applied, such as vitrinite reflectance and spore fluorescence. These procedures were conducted at the University of Algarve, at the Centre for Marine and Environmental Research – CIMA. Palynological studies and palynostratigraphy were based on taxonomic study and photomicrographs, conducted at the Geological Survey of Portugal, LNEG, Sao Mamede de Infesta, Portugal (section 4.4.3, p.81-85). To determine the organic composition in the Irati black shales, maceral analysis was conducted following the ASTM (2014) and SANS 7404-5 (2016)/ISO 7404-5 (2009).

5.2.1. Petrographic composition and palynofacies

The organic petrographic composition of 19 samples of the Irati shales with its respective predominant maceral groups is shown in Table 7. The maceral content within the analyzed samples is highly heterogeneous. Liptinite group macerals are predominant in most samples, ranging from 19 to 91 vol%. Inertinite group macerals range from 4 to 66 vol%; and vitrinite macerals, range from 8 to 56%. Fluoresce of liptinite maceral compounds is also registered, ranging from dull yellow to yellow colored fluorescent amorphous organic matter (AOM).

Table 7. Organic petrographic composition with maceral group distribution (wt.%) and fluorescence of Irati oil shale samples, determined by an optical evaluation analysis. DY = dull yellow, Y = yellow.

Sample ID	Location	Depth (m)	AOM (%)	Palynomorphs (%)	Non-opaque phytoclasts (%)	Opaque phytoclasts (%)	Counted points	Fluorescence	Predominant maceral	Average (%)
574	Montividiu - GO	0	17	1	16	66	300	no	Opaque o.m.	66
577	Montividiu - GO	0	32	0.66	24.33	43	300	no	Opaque o.m.	43
579	Montividiu - GO	0	31	2	16.33	51	300	no	Opaque o.m.	51
581	Perolândia - GO	0	60.33	19.83	1.66	8.16	600	DY	AOM	60.33
582	Perolândia - GO	0	65.28	17.71	10.71	6.28	600	DY	AOM	65.28
583	Perolândia - GO	0	59.16	28.82	7.83	4.16	600	DY	AOM	59.16
584	Perolândia - GO	0	75.83	15.16	4.83	4.36	600	DY	AOM	75.83
585	Perolândia - GO	0	73.5	11.66	8.33	6.5	600	DY	AOM	73.5
587	Montividiu - GO	0	32	16.32	39.16	12.5	600	no	Phytoclasts non-opaque	39.16
588	Montividiu - GO	0	19.33	10.82	55.66	14.16	600	no	Phytoclasts non-opaque	55.66
589	Montividiu - GO	0	53.16	3.33	33.3	10.16	600	no	AOM	53.16
Vitti	Saltinho - SP	0	54.33	33.65	8	4	600	DY	AOM	54.33
658	Anhembi - SP	274.2	47.83	0.83	26.33	30.33	600	no	AOM	47.83
659	Anhembi - SP	274.38	62	3.83	14.66	19.66	600	no	AOM	62
673	Sapopema - PR	340.65	24	19.82	38.33	18	600	Y	Phytoclasts non-opaque	38.33
675	Sapopema - PR	213.72	74	3.33	8	14.66	300	no	AOM	74
676	Sapopema - PR	241.74	-	-	-	100	300	no	Opaque o.m.	100
681	Sapopema - PR	477	41.75	1.75	33.75	23	400	no	AOM	41.75
CCM2	São Mateus do Sul - PR	0	56.5	27.99	9.83	5.66	600	Y	AOM	56.5

The analyzed samples present a fluorescent amorphous organic matter (AOM) dominated palynofacies association (as previously shown in Table 7), ranging from 24% to 76% of total particulate organic matter. Non-opaque phytoclasts represent the second most abundant palynofacies component, varying from 8% to 56%. Palynomorphs, although generally present, are a minor constituent among most of the samples: average 12.2% of total particulate organic matter. However, palynomorphs constituents are moderately high in a few samples, reaching 26% of bisacate pollen and 7% of monosacate pollen. Due to their poor preservation and fragmentation in most of the samples, bisacate and monosacate palynomorphs could not be well distinguished and classified. Spores and algae were identified but with rare occurrence, accounting for < 1.5% of the total recovered palynomorphs. Spores were mostly identified in samples at the northern border of the Irati Formation (Goiás state, samples 0583, 0587, 0588, and 0589). Fluorescence was present for both AOM and palynomorphs.

Opaque organic matter occurrence is highly heterogeneous among the analyzed samples. It varies from 4 to 66% of the total particulate organic matter, in an average of 16.8%. The opaque component is a major constituent among four of the analyzed samples (676, 574, 577, and 579). These samples common characteristic is the proximity to igneous intrusions and, consequently in an overmatured stage. Thermal alteration within these samples is also evidenced by high values of vitrinite reflectance (>1.19% reaching 4.46%), and absence of palynomorphs' fluorescence.

The dominance of AOM, the common-to-abundant presence of spheroidal pollen palynomorphs with presence of marine palynomorphs (algae) correspond to a type I-II prevalent kerogen for the shale samples of Assistência Member of the Irati Formation. Kerogen type III (phytoclasts) is also present and mostly concentrated in samples from the north of the Paraná Basin (GO State).

5.2.1.1. Amorphous organic matter (AOM)

Amorphous organic matter (AOM) is the main constituent of Irati oil shales. The samples predominantly present AOM translucent beige to light brown coloured particles with a granular texture. AOM brown particles with gelified texture are also identified, sometimes containing internal structured and usually associated with the granular AOM. The particles have heterogeneous sizes and have small internal fragment, such as pyrite inclusions (Figure 33).

Figure 33. Amorphous organic matter (AOM) from Irati Formation black shales. The scale bar is 10µm. A, B and C: translucent, light brown AOM with granular texture and opaque inclusions. D, E: AOM with gelified texture, associated with granular AOM.

Most AOM particles have moderate fluorescence, composing a fluorescent matrix that incorporates opaque particles (framboidal pyrite and non-fluorescent inertinite) and strong fluorescent filaments (palynomorphs) inclusions (as shown in Figure 33).

Overall, the predominant content of AOM in Irati shales indicate an original oil-prone sample composition. The predominantly light coloured AOM with granular texture suggest marine OM source with bacterial degradation. A second pattern of dark coloured gelified AOM imply further microbial activity. The dominant fluorescence possibly indicates low oxygen palaeoenvironment (Tyson, 1987, 2006), but it is mostly associated with the microbial composition (Pacton, Gorin, & Vasconcelos, 2011). The record of framboidal pyrite and dominance of AOM support the interpretation of a low energy/restricted marine environment with bacterial degradation.

5.2.1.2. Palynomorphs

The results from performed palynological studies were published as *Rocha et al. 2020* (<https://doi.org/10.1016/j.jsames.2020.102631>), and the published peer-reviewed version is attached to the thesis appendices (Appendix B). This section will briefly present the acquired data and palynological assemblages per sampled area (GO, SP and PR).

Optical analysis of 34 shale samples from the Assistência Member of Irati Formation led to well-preserved palynomorphs being recovered from 13 shale samples (583, 584, 589, 577, 581, 585, 587, 588, 658, 660, 673, 675, and CCM2). In total, 18 pollen genera (34 pollen species), seven spore genera, four microplankton genera (1 species), and Chlorophyceae algae species were identified.

In general aspects, the recovered palynological assemblage is dominated by striate and non-striate bisaccate and monosaccate pollen grains, and subordinated spores, algae, and *Botryococcus* (Figure 34). The palynostratigraphic analysis reveals a clear dominance of bisaccate pollen grains such as *Corisaccites alutas*, *Lueckisporites virkkiae*, and *Weylandites lucifer*. The *Lueckisporites virkkiae* zone was identified in the upper part of the Irati Formation (Assistência Member) and it is also attributed to the lowermost part of the Corumbataí Formation, indicating a Kungurian to Roadian age for this part of the succession (Rocha et al. 2020).

Figure 34. Palynomorphs from Assistência Mb. Irati Fm. A: *Protohaploxylinus* spp. (*P. amplus*, *P. bharadwajii*, *P. hartii*) and Microplanktonic Chlorophyceae algae (e.g., *Brazilea scissa*, *Leiosphaeridia* sp., and algae clusters). B, C: *Lueckisporites* spp. (*L. agoulaensis*, *L. densicarpus*, *L. latisaccus*, *L. stenotaeniatus*, *L. virkkiae*). D: *Vittatina* spp. (*V. costabilis*, *V. fasciolata*, *V. subsaccata*, *V. vittifera*). E, F: spores *Convolutispora* sp. G, H and I: black coloured, oxidized pollen (GO State samples).

GO State recovered palynomorphs assemblage (samples 577, 581, 583, 0584, 585, 587, 588, and 0589) is moderate to well preserved (particularly in samples 585 and 587) with a dominance of bisaccate taeniate pollen grains (35.3-90%). These include the coniferopsida *Lueckisporites* spp. (*L. agoulaensis*, *L. densicarpus*, *L. latisaccus*, *L. stenotaeniatus*, *L. virkkiae*) (Fig. B, C), the lyginopteridopsida *Protohaploxylinus* spp. (*P. amplus*, *P. bharadwajii*, *P. hartii*) (Figure 34 A), *Corisaccites* spp. (*C. alutas*, *C. vanus*), and *Staurosaccites* spp. (*S. cordubensis*, *S. quadrifidus*). In addition to *Vittatina* spp. (*V. costabilis*, *V. fasciolata*, *V. subsaccata*, *V. vittifera*) (Fig. D). Monosaccate pollen are rare (only present in samples 585 and 587) and represented by *Plicatipollenites gondwanensis* and *Potonieisporites novicus* (0.7%) (Figure 34 B). Spores are exceedingly rare in this assemblage (0-0.7%), represented by the pteridophyte fern *Convolutispora* sp. (samples 0585 and 0587) (Figure 34 D, E). Microplanktonic Chlorophyceae algae (e.g., *Brazilea scissa*, *Leiosphaeridia* sp., and algae clusters) are present in several samples and vary from rare to common (0.0-18.5%) (samples 583 and 587). Additionally, dark coloured/oxidized

palynomorphs (Fig. G, H, I), in samples 574, 577 and 579, suggest post-depositional thermal processes, such as thermal metamorphism. This idea is supported by sample's proximity to igneous intrusion (Rocha et al. 2020).

SP State recovered palynomorphs (sample 658 and Vitti) are poorly preserved. Samples present a dominance of microplanktonic algae specimens (70.8%), followed by taeniate bisaccate pollen grains (29%), asaccate pollen grains, such as *Vittatina costabilis* (0.2%). Spores are absent in this assemblage, and very abundant amorphous organic matter was observed (Rocha et al., 2020).

PR State palynological assemblages (samples 660, 673, 675, CCM2) reveal poorly preserved material with a distinctive dominance of taeniate bisaccate pollen grains (57.4%-75.0%), excepting for sample 660 (17.5%) where Chlorophyceae algae dominate (82.5%). Only a few important specimens are identified at a generic level, for instance the taeniate bisaccate pollen *Lueckisporites densicarpus*, *L. latisaccus*, *L. virkkiae*, *Lueckisporites* spp., *Protohaploxypinus amplus*, *Corisaccites alutas*, *Staurosaccites cordubensis*, *S. quadrifidus*, *Staurosaccites* spp., as well as the asaccate pollen grains *Vittatina costabilis*, *V. subsaccata*, and *Weylandites lucifer*. The following non-taeniate bisaccate pollen grains are also present in this assemblage (9.0%-20.7%, samples 673, 675, and CCM2), *Alisporites nuthallensis*, *Alisporites* sp., and *Limistisporites* sp., and rare monosaccate pollen were identified in sample 673, including *Plicatipollenites* sp., *Potonieisporites novicus*, and *Potonieisporites* sp. Rare to common trilete spores could be identified in samples 673 and CCM2 (0.7%-6.7%), including the pteridopsida *Leiotriletes* sp., *Punctatisporites* sp., *Verrucosisporites* sp., and *Convolutispora* spp., as well as the lycopodiopsida *Cristatisporites* sp., *Kraeuselisporites* sp., and *Lundbladispota* sp. Microplanktonic elements like Chlorophyceae algae and incertae algae clusters are common to abundant in all samples (6.7%-82.5%), and the occurrence of *Botryococcus braunii* (about 2%), in sample 673, is also worth noting. Phytoclasts and amorphous organic matter dominate the palynodebris recovered in samples 660 and 675 (Rocha et al., 2020).

Overall, the palynological data gathered in this study in different areas of the Paraná basin, in the States of GO, SP and PR, can be assigned to the *Lueckisporites virkkiae* Zone, and attributes a Kungurian to Roadian age to the Irati Formation (Assistência Member) black shales. The dominant palynomorphs assemblage suggests a shallow marine depositional environment. The presence of microplanktonic algae, such as *Botryococcus braunii*, indicate freshwater influx, indicating a low energy lacustrine depositional regime (Souza & Marques-Toigo, 2005; Rocha

et al. 2020). Comparatively among the Paraná basin sampled regions (N, SE and S), the N portion presents a higher content of terrestrial material (e.g., spores), suggesting a shoreline proximal environment. Palynostratigraphic age and paleoenvironmental implications of this data will be further discussed in section 6.2 (p.138)

5.2.1.3. Non-opaque phytoclasts

Translucent brown to dark-brown phytoclasts with tabular shapes are abundant components among the samples. These particles are either associated with AOM or as separate large size particles. Translucent phytoclasts usually have large size and present preserved cellular biostructures, being sometimes partially oxidized (Figure 35).

Figure 35. Translucent phytoclasts with preserved biostructure. A, B and C: well preserved brown cutinite with internal structure. D: brown phytoclast with partly gelified texture.

Elevated content of translucent phytoclasts are usually associated to fluvial sources proximal palaeoenvironment and/or a marine transgression (Tyson, 1989). Non-opaque phytoclasts are more abundant in samples from the N portion of the PB (samples 574 - 587).

The identified phytoclasts are terrestrially derived, suggesting freshwater influx in the palaeoenvironment (De Andrade et al., 2019; Kemp, et al., 2019) This supports the idea of a

mixture of marine and terrestrial organic matter for the Assistência Member. The size and well preserved biostructure of phytoclasts suggest that these can be either resistant to physical abrasion or fungal degradation (Hart, 1986), or attributed to a low-energy palaeoenvironment (Whitaker et al., 1992).

5.2.1.4. Opaque OM

Completely oxidized black opaque fragments of OM are abundance among the samples. These particles are opaque, non-fluorescent and without biostructure. Opaque particles are usually associated with the AOM, and have either irregular shape or tabular/elongated phytoclast preserved shape (Figure 36) Opaque OM is more abundant in thermally altered samples (574, 577, 579 and 676).

Figure 36. Opaque organic matter from Irati black shales. A: Opaque terrestrial filament (inertinite). B. Disperse opaque organic matter, with irregular shape. C: Amorphous organic matter with opaque inclusions. D: Sample with totality of opaque organic matter (oxidized).

Opaque phytoclasts are less susceptible to degradation (Tyson, 1995). In this sense, opaque OM remains in the depositional environment after the bacterial degradation of non-opaque OM (De Andrade et al., 2019).

5.3. Thermal Maturation Assessment

In addition to bulk geochemical analysis (Tmax from Rock-Eval pyrolysis), organic maturation levels of Irati black shale samples were assessed in detail through optical petrographic methods. These comprise vitrinite reflectance measurements and spore fluorescence qualitative analysis. The thermal maturation assessment determines the organic matter maturity and contributes to the evaluation of Irati black shales source-rock generative potential, to shale oil and/or shale gas prospects, and to CO₂ geological storage capacity estimates. Additionally, thermal maturation data of the Irati Formation contributes to research on the complex thermal history of the Paraná Basin and the role of the Serra Geral magmatism.

5.3.1. Vitrinite reflectance, spore fluorescence and colour

Table 8 presents vitrinite reflectance measurements of 34 shale samples, in addition to qualitative fluoresce data (occurrence and colour). Figure 37 illustrates vitrinite particles used to VR measurements.

Table 8. Vitrinite reflectance and spore fluorescence data. VR = vitrinite reflectance, N = number of particles, SD = standard deviation, FL = fluorescence, Y = yellow, DY = dull-yellow, O = orange, NO = no fluorescence.

Sample ID	Location	Depth (m)	VR	N	SD	FL
Goiás State (N)						
Rio Verde quarry						
574	Montividiu - GO	0	2.46	93	0.29	no
577	Montividiu - GO	0	1.19	37	0.1	Y-O
579	Montividiu - GO	0	1.67	99	0.2	no
SUCAL quarry (N)						
581	Perolândia – GO	0	0.93	95	0.18	DY
582	Perolândia – GO	0	1.33	51	0.27	DY
583	Perolândia - GO	0	1.25	73	0.3	DY
584	Perolândia – GO	0	0.96	32	0.26	DY
585	Perolândia – GO	0	1.03	64	0.1	DY
ELBA quarry (N)						
587	Montividiu – GO	0	1.09	99	0.1	Y-O
588	Montividiu – GO	0	1.07	44	0.13	no
589	Montividiu – GO	0	1.48	12	0.07	no
São Paulo State (SE)						
Vitti	Saltinho – SP	0	0.96	50	0.15	DY
Borehole FP-12-SP						
658	Anhembi - SP	274.2	0.74	10	0.04	no
659	Anhembi - SP	274.38	0.67	31	0.1	no
Paraná State (S)						
Borehole FP-11-PR						
660	Ortigueira - PR	351.34	0.67	31	0.1	Y
Borehole FP-01-PR						
662	Ibati - PR	194.5	0.64	33	0.1	Y
663	Ibati - PR	195.07	0.54	32	0.11	
664	Ibati - PR	196.95	0.55	12	0.07	Y
665	Ibati - PR	197.45	0.55	19	0.12	Y

Borehole FP-02-PR 666	Sapopema - PR	122.8					
Borehole FP-03-PR 667	Sapopema - PR	227.16	0.54	11	0.12	Y	
Borehole FP-04-PR 668	Ortigueira - PR	185.61	0.52	12	0.1	Y	
Borehole FP-07-PR 669	São Mateus - PR	81.07	0.63	43	0.15	Y	
Borehole SP-29-PR 673	Sapopema - PR	340.65	0.69	78	0.06	Y	
Borehole SP-37-PR 675	Sapopema - PR	213.72	0.81	55	0.14	no	
Borehole SP-47-PR 676	Sapopema - PR	241.74	4.46	42	0.4	no	
Borehole SP-49-PR 679	Sapopema - PR	373.27	0.55	21	0.12		
680	Sapopema - PR	373.4	0.63	47	0.11		
Borehole SP-55-PR 681	Sapopema - PR	477	0.62	48	0.1	no	
PETROSIX quarry CCM2	São Mateus do Sul – PR	0	0.61	41	0.07	Y	
CCM3	São Mateus do Sul - PR	0	0.59	41	0.11	Y

Figure 37. Photomicrographs (reflected white light) of vitrinite particles used to reflectance measurements, associated with inertinites and pyrite. (A) vitrinite particle on the left of inertinite particle, (B) tabular vitrinite, (C)

granular vitrinite, (D, E) vitrinite particle next to inertinite particle, (E) vitrinite and framboidal pyrite, (G) framboidal pyrite, (H, I) thermally altered vitrinite.

Organic maturation results attribute an early-maturity stage to Irati black shales in a regional scale, which is probably related to the formation burial subsidence, and local late-maturity levels attributed to samples thermally affected by igneous intrusions.

Liptinite maceral group fluorescence and colour were analyzed to complement VR results in the organic maturation assessment. As shown in Figure 37, palynomorphs and AOM fluorescence is predominantly yellow coloured. Thermally affected samples usually present no fluorescent OM. Exceptions are samples 577 and 589, that show yellow to orange fluorescence in palynomorphs, indicating higher maturation patterns (Figures 38 and 39).

Figure 38. Photomicrographs (incident blue light) of maceral composition from Irati oil shales: (i) non-fluorescent organic particles, (ii) Fluorescent AOM, (iii) fluorescent palynomorphs -yellow, dull-yellow and orange coloured fluorescence.

Figure 39. General overview (incident blue light) of palynomorphs from GO State Irati shale samples, showing yellow-orange coloured fluoresce.

The recorded liptinite fluoresce and colour reinforce that the Irati black shales are mostly oil-prone source rocks that reached oil-window maturities ($\geq 0.6 \%R_r$). Additionally, this qualitative analysis validates the results obtained from VR data, indicating two different maturation levels to Irati black shales: a regional early-maturity stage and a second post-mature stage associated with heat-affected samples that were proximal to igneous intrusions.

Acquired VR measurements were confirmed by fluorescence patterns, and such patterns indicate that the maturity of Irati organic-rich shales is highly heterogeneous along the Paraná Basin. Figure 40 illustrates sample's maturity based on VR and Tmax data. Based on both organic geochemical and petrographic data, there is an early-mature stage attributed to most studied samples, reaching oil generation at a regional scale (Figure 38). Nevertheless, a slight variation between thermal maturity indicators is frequent among clay-rich shales, which can be due the influence of clay minerals on pyrolysis experiments (Yang & Horsfield, 2016; Nascimento et al. 2021).

Figure 40. A cross-plot of maximum pyrolysis temperature (Tmax) and vitrinite reflectance (%Rr) versus depth to demonstrate the distribution of the maturity parameters with increasing depth.

Considering sampled areas, higher VR values were identified in the north and the southeast of the PB (GO and SP states). GO State samples present the higher VR obtained measurements, which range from 0.93 and 2.46% R_r . Comparatively, samples from SUCAL, at Perolândia municipality present dull yellow fluoresce, while samples from Montividiu (Rio Verde and ELBA) have mostly no fluoresce or yellow to orange colored fluoresce (samples 577 and 587). Provided data on VR and fluoresce attribute a gas-window maturity to GO State Irati Formation organic-rich shales.

In SP State, samples present variant VR measurements: samples from the FP-12-SP borehole at Anhembi municipality (659, 658) present 0.67 and 0.74% R_r respectively, while the sample from Vitti quarry, in Saltilho, present 0.96 % R_r . The last correspond to gas-window maturity.

in PR state, the vitrinite reflectance (VR) is mostly consistent, varying between 0.52 and 0.69 % R_r (samples 660, 662, 663, 664, 665, 667, 668, 669, 673, 679, 680, 681, CCM2 and CCM3) with slight increase with depth, as shown in Figure 40). These indicate that most samples were on beginning of the oil window generative zone and are associated to a low maturity gradient to these oil-prone source rocks. Exceptions are attributed to samples 675 and 676, which present 0.81 and 4.46 % R_r , respectively. These reflect the thermal effect from Serra Geral igneous intrusions and are located at the intrusion surroundings, as discussed below.

Samples with VR directly affected by igneous intrusions are represented in Table 9. As well as the sample's distance to the most proximal intrusion wall and the intrusion thickness. The Irati Fm. was intruded by doleritic sills in 3 boreholes: FP-02-PR, SP-37-PR, SP-47-PR (Table 9). The boreholes SP-49-PR, SP-55-PR were intruded in the Teresina Formation. Doleritic sills were also identified on two outcrops: Rio Verde and ELBA, at the N of the PB. This information was estimated for outcrops and determined based on the Brazilian Geological Survey well log reports.

Table 9. Vitritine reflectance and fluorescence data from thermal metamorphism affected samples. In addition to nearest igneous intrusion distance and thickness (in meters).

Sample ID	Location	Depth (m)	VR	N	SD	FL	Distance to nearest intrusion wall (m)	Thickness of nearest intrusion (m)
Rio Verde quarry (N)								
574	Montividiu - GO	0	2.46	93	0.29	no	1.5	1
577	Montividiu - GO	0	1.19	37	0.1	Y-O	2.5	1
579	Montividiu - GO	0	1.67	99	0.2	no	2.5	1
ELBA quarry (N)								
587	Montividiu - GO	0	1.09	99	0.1	Y-O	3	1.5
588	Montividiu - GO	0	1.07	44	0.13	no	3	1.5
589	Montividiu - GO	0	1.48	12	0.07	no	4	1.5
Paraná State (S)								
Borehole FP-02-PR								
666	Sapopema - PR	122.8	-	-	-	-	2.2	220
Borehole SP-37-PR								
675	Sapopema - PR	213.72	0.81	55	0.14	no	6.28	2
Borehole SP-47-PR								
676	Sapopema - PR	241.74	4.46	42	0.4	no	4.26	20
Borehole SP-49-PR								
679	Sapopema - PR	373.27	0.55	21	0.12		346.27	19
680	Sapopema - PR	373.4	0.63	47	0.11		346.4	19
Borehole SP-55-PR								
681	Sapopema - PR	477	0.62	48	0.1	no	142.03	60

To attempt a thermal maturation assessment throughout the Paraná Basin (PB), VR measurements were examined for each sampled sub-region (N, SE, S) of the PB. Comparatively, samples from the N portion of PB, present higher thermal maturation (0.93 – 2.46 %R_r), reaching over-mature stages when proximal to igneous intrusions. Anjos &

Guimarães (2008) confirm a high thermal effect at Goiás State (GO), through mineralogical evidence of metamorphism (Anjos & Guimarães, 2008; Anjos et al., 2010).

Samples from SE region present a moderately high maturation stage: 0.67 and 0.74 %R_o in Anhembi municipality (borehole FP-12-SP), reaching 0.96 %R_r in Saltinho (outcrop sample Vitti). Samples from the S portion of the PB vary between 0.52 and 0.69 %R_r for most samples. VR presents a linear increase with depth. Two exceptions are samples 675 and 676, that are very proximal to igneous intrusions and present respectively 0.81 and 4.46 %R_r: sample 675 is approximately 7 m distant to a 2 m thick intrusion, and sample 676 was located 5 m distant to a 20 m thick intrusion, as previously shown in Table 9.

Overall, throughout the thermal maturity assessment carried out in this study, two organic maturation levels can be attributed to Irati Formation organic-rich shale samples. The first corresponds to an early-mature stage, that is consistent towards the south of the PB (PR State) and most probably representative of the burial diagenesis of the original organic content. The second and gas-window-mature stage derived from a further thermal metamorphism event (Cretaceous Serra Geral magmatism) and it is attributed to samples from GO State and from western portion of SP State (Saltinho municipality) and to ≤ 2 m thick intrusions in the Irati Formation. Samples that are proximally located to thick (≥ 20 m) igneous intrusions (e.g., samples 676, 679, 680, 681. from Sapopema, that are proximal to the Ponta Grossa magmatic Arch) have little to none preserved organic content, which represent the effect of thermal metamorphism. Irati Formation shale's maturity and implications on CO₂ geological storage will be further discussed in sections 6.3 and 6.4 (p.13-142).

5.4. Mineralogical composition

Mineralogy plays an essential role in CO₂ geological storage reservoirs. Mineralogical content, especially clay minerals, contributes to shale's total porosity (Chalmers and Bustin, 2008; G.R. Chalmers et al., 2012; Curtis et al., 2010), and therefore to its adsorption capacity and gas storage potential. Analysing the mineralogical content also contributes to determine the depositional paleoenvironment and paleoclimate, as well as to identifying post-depositional processes and thermal history of a sedimentary basin (Chamley 1989, Weaver 1989). In this study, the combined analysis of mineralogical, geochemical, and petrological content of Irati Formation organic-rich shales provide a detailed characterization of the Assistência Member of

Irati Formation in regard to its CO₂ storage capacity and contributes to studies of the complex thermal history of the Paraná Basin.

The mineralogy of the black shales was determined by the X-ray diffraction (XRD) method, using Assistência Member powdered samples for whole-rock and $\leq 2\mu\text{m}$ oriented particles analysis. 16 samples were selected for this mineralogical study, based on organic geochemistry and petrography's previously obtained data, including samples from different maturity ratios and locations in the Paraná Basin. Selected samples were: 574, 577, 581, 582, 583, 587 (GO State), 658, 659, AM01, AM02, Vitti (SP), 673, 675, 676, 680, and CCM2 (PR). Sample's preparation and XRD analysis were carried out at LABPETRO at IEE/USP, as described in section 4.4.6 (p.85).

Based on diffractometric reflections of 16 studied samples, Irati shale's predominant mineralogy is composed of quartz, feldspar (albite and microcline), phyllosilicates, including clay minerals (smectite, chlorite, kaolinite, and interstratified clay) and non-clay minerals (muscovite, serpentine, talc), besides Na bearing zeolites (analcime), carbonates (calcite and dolomite), and sulphides (pyrite). The clay constituents, determined in the $\leq 2\mu\text{m}$ fraction, are mainly represented by smectites, followed by small occurrences of chlorite (sample 676), and kaolinite (possible occurrence on samples Vitti and CCM2). The carbonatic rock interbedded with the Assistência Member organic-rich shales (sample AM02) (section 4.1.2. p.65.) is composed of dolomite (Table 10). XRD diffractograms are shown in Figures 41, 42 and 43.

Table 10. Mineralogical composition of studied Irati Formation shales and carbonate rock. Samples, either from boreholes or quarries, are identified according to ID, location, depth, and lithology. Identified mineral phases are divided into silicates, carbonates, and sulphide with respective mineralogy. Smectite group minerals are divided into 2 categories: low and high-intensity peak.

Sample ID	Borehole/ Quarry	Location	Depth	Lithology	Silicates											Sulphide	Carbonates	
					Tectosilicates			Phyllosilicates										
					Qz	Feld	Ana	Ms	Sme		Il	Chl	Kao	Sp	Tc	Py	Cal	Dol
Low	High																	
574	Rio Verde	Montividiu – GO	0	black shale		●		●		●				●	●			
577	Rio Verde	Montividiu – GO	0	black shale		●		●		●								
581	SUCAL	Perolândia – GO	0	black shale	●	●	●	●	●							●		●
582	SUCAL	Perolândia – GO	0	black shale	●	●	●	●	●							●		●
583	SUCAL	Perolândia – GO	0	black shale	●	●		●	●							●		●
587	ELBA	Montividiu – GO	0	black shale	●	●		●		●								
Vitti	VITTI	Saltinho – SP	0	black shale	●	●		●		●			●					
AM01	Amaral Machado	Saltinho – SP	0	dolomite			●											●
AM02	Amaral Machado	Saltinho – SP	0	black shale	●	●		●		●								
658	FP-12-SP	Anhembi - SP	274.2	black shale	●	●		●	●							●	●	
659	FP-12-SP	Anhembi - SP	274.38	black shale	●	●	●	●	●							●	●	
673	SP-29-PR	Sapopema - PR	340.65	black shale	●	●	●	●	●							●		●
675	SP-37-PR	Sapopema - PR	213.72	black shale	●	●	●	●	●							●		●
676	SP-47-PR	Sapopema - PR	241.74	black shale	●	●		●	●			●				●	●	
680	SP-49-PR	Sapopema - PR	373.4	black shale	●	●	●	●	●							●		●
CCM2	PETROSIX	São Mateus - PR	0	black shale	●	●	●	●	●		●		●			●		●

Figure 41. X-ray diffractograms of analysed samples with correspondent mineral assemblage (main peak of each mineral indicated in angstrom). These mineralogical assemblages characterized by low-intensity basal peak (d001) of smectite clay mineral (14.2 Å).

Figure 42. X-ray diffractograms of analysed whole-rock samples from GO (574, 577 and 587) showing a mineralogical assemblage with high-intensity basal peak (d_{001}) of smectite (14.9 Å), and samples from SP (AM02 and Vitti) also showing high-intensity basal peak (d_{001}) of smectite clay mineral (14.67 Å). Main peak of each mineral indicated in angstrom.

Figure 43. X-ray diffractograms of analysed < 2 μ m fraction of sample 574 from GO state showing the clay minerals assemblage with high-intensity basal peaks in angstrom.

In addition to XRD analysis, SEM imaging was performed in 3 Irati Formation shale samples (574, AM01, AM02, and CCM2) to observe overall mineral aspects, such as structure and texture. SEM images are shown in Figures 44 and 45 (shale samples 574, AM02 and CCM2) and B (dolomite, sample AM01).

Figure 44. SEM images of Irati Formation shales with scale of 100-10 μm , showing general aspects of the mineral texture, structure, and morphology. A,B: sample 0574, showing highly crenulated smectites with webby texture. C, D: sample CCM02. Images shown shale fissility and preferred orientation of clay minerals – parallel to bedding. E, F: sample AM02, E showing general aspect of clay minerals, and F showing in detail the crenulated texture of smectites, that sits on top on the mineral matter matrix.

Figure 45. SEM images and EDS data of carbonate rock sample AM02 (dolomite) from the Assistência Member of Irati Formation. Images were obtained on scale of 100-10µm. A, B,C: SEM images show general aspects of mineral matrix. D,E: SEM Images show in detail the microcrystalline aspect of the micritic dolomite.

Considering the Table 10 data and diffraction profiles observed in the X-ray patterns, the Irati shale's mineralogy above described may be divided in two different mineralogical assemblages. The first mineralogical assemblage (A) is composed of quartz, feldspar (microcline and albite), muscovite, and smectite exhibiting well defined basal d_{001} reflexion with low intensity (samples 658, 659, 673, 581, 582, 583, 675 and 680). The second mineral assemblage (B) comprises smectite (possibly montmorillonite or saponite) exhibiting high intensity and well defined basal d_{001} reflexion, besides analcime, serpentine, talc, chlorite, and pyrite.

As previously mentioned, smectite is the most abundant identified clay mineral group. Diffractometric reflections indicate at least two assemblages of smectite according to their peak pattern and intensity. The first comprised samples 574, 577, 587, AM01, Vitti, 581, 582, 583, 675 and 680, which present medium to high intensity, well defined (d_{001}) peak for this mineral group. The second assemblage from samples 658, 659 and 673 present smectite with well-defined basal peak but exhibiting low intensity. Smectite with lower intensity basal d_{001} peak is most probably detrital in origin, while high intensity d_{001} peak smectite is presumably authigenic, as previously appointed by other authors (Sant'Anna et al. 2006, Ferreria, 2017; Anjos, 2008)

5.5. Gas Sorption Isotherms Assessment

This section addresses the CO₂ sorption capacity of Irati Formation organic-rich shales and describes the shale's porous system through gas sorption isotherms. Langmuir sorption model isotherms were used to determine CO₂ sorption capacity while BET sorption isotherms determined pore volume, surface area, and pore size distribution among the studied samples. Gas sorption analysis will also be used to determine to which extent these are affected by organic and inorganic parameters, such as organic matter quantity, type and maturation, and mineralogy, respectively.

5.5.1. High-pressure sorption isotherms (Langmuir method)

CO₂ sorption capacity of Irati shale samples were quantified in laboratory, by measuring the gas uptake of pulverized shale samples under various pressure conditions at a constant temperature (35°C), defined by a sorption isotherm. High-pressure sorption isotherms laboratorial procedures took place at Universidade Fernando Pessoa, FP-ENAS Research Unit, as previously mentioned (section 4.4.7, p. 87).

High-pressure CO₂ sorption isotherms were measured in 10 Irati Formation organic-rich shale samples: 574, 577, 582, 583, 587, 659, 673, 675, 676 and Vitti. Maximum values of the measured excess sorption capacities and the Langmuir parameters (T , P , V_L , P_L , and G_{Cs}), are listed in Table 11. CO₂ sorption isotherms are shown in Figure 46.

Table 11. List of Langmuir fitting parameters and maximum CO₂ sorption capacity of Irati Formation organic-rich shales, measured at 35 °C. T = temperature (°C), P = pressure (psi), VL = Langmuir volume (scf/ton), PL = Langmuir pressure (psi), Gcs = gas content at saturation (scf/ton and m³/ton of rock).

Sample ID	Borehole/ Quarry	Location	Depth (m)	Mass (g)	T (°C)	P (psi)	V _L (scf/ton)	P _L (psi)	G _{CS} (scf/ton)	G _{CS} (m ³ /ton)
574	Rio Verde	Montividiu- GO	0	100.31	35	520.68	387.13	1026.01	130.32	3.69
577	Rio Verde	Montividiu- GO	0	100.02	35	500.38	299.54	953.23	103.11	2.91
587	ELBA	Montividiu- GO	0	100.00	35	596.80	217.29	595.08	108.80	3.08
582	SUCAL	Perolândia - GO	0	99.97	35	559.78	65.50	525.78	33.77	0.95
583	SUCAL	Perolândia - GO	0	99.80	35	502.32	180.45	1521.86	44.78	1.26
659	FP-12-SP	Anhembi - SP	274.38	99.03	35	554.21	199.57	1607.09	51.17	1.44
673	SP-29-PR	Sapopema - PR	340.65	64.20	35	502.48	11.60	26.77	11.02	0.31
675	SP-37-PR	Sapopema - PR	213.72	98.80	35	703.83	15.18	31.13	14.53	0.41
676	SP-47-PR	Sapopema - PR	241.74	99.99	35	605.42	18.47	211.06	13.70	0.38
Vitti	VITTI	Saltinho - SP	0	99.54	35	655.96	76.88	116.64	65.27	1.84

Figure 46. CO₂ sorption isotherms, measured through the volumetric technique, based on the Langmuir isotherm model, indicating the maximum CO₂ sorption capacity of Irati shales.

Sorption capacities for these samples are highly heterogeneous and range between 11 and 130 standard cubic feet per tonne of rock (scf/ton) (0.3 to 3.7 m³/ton) at 500 psi (3.4 MPa). Samples from GO state: 587, 577, and 574 reached the highest sorption levels, with storage capacity of 103, 108 and 130 tcf/ton (2.9, 3.05 and 3.7 m³/ton), respectively. A second group of samples, comprising 582, 583, from SUCAL quarry (GO State) and 675, and Vitti (SP State), correspond to a lower but still significant storage capacity for shales: ranging between 30 and 60 tcf/ton (0.8 – 1.7 m³/ton). The third sample group, which comprises samples 673, 675 and 676, from Sapopem (PR State), presented the lowest storage capacity among studied samples, estimated in between 11 and 14 scf/ton (0.3 – 0.4 m³/ton).

Regarding isotherms` curve behaviour, samples 574 and 577 - from Rio Verde quarry, and sample 587 - from SUCAL quarry, both at Montividiu municipality - GO State, present a steep increasing sorption pattern with pressure (as shown in Figure 46), while the other samples present a flatter sorption pattern. Sample Vitti reaches its maximum sorption capacity at approximately 200 psi and its isotherms curve follows a flat behaviour in comparison with the previously mentioned samples. Samples 0582, 0583 and 0659 also present increasing sorption capacity with pressure, but with lower storage capacity than the previous samples. Samples 673, 675, and 676 exhibit an inert behaviour to CO₂: these samples reach their maximum storage capacity at approximately 100 psi and remain stable, with no significant increase in gas sorption with increasing pressure, presenting no significant storage capacity.

Isotherm curves attribute the highest CO₂ adsorption capacity to samples from the northern border of the Paraná Basin, GO state. Comparatively, samples from Montividiu municipality (Rio Verde and ELBA quarries) have the highest ability to store CO₂, varying between 2.9 to 3.7 m³/ton, as shown in Figure 46. Samples from SP state (659 and Vitti) also present significant storage capacity, of 1.44 and 1.84 m³/ton of rock, respectively.

Sorption capacity heterogeneity are attributed to variations on mineralogical composition, kerogen typing and maturity, and pore structure. Higher sorption capacity is attributed to clay dominant (authigenic smectite) mature shales (gas window maturity) with low TOC (samples 574, 577 and 587).

5.5.2. Low-pressure gas sorption isotherms (BET method)

In this study, the pore structure of Irati Formation organic-rich shale was analysed through low-pressure sorption experiments with N₂ and CO₂ as adsorptives. Pore structure analyses include pore size distribution, pore volume and specific surface area of 10 Irati organic rich shale samples (574, 577, 582, 583, 587, Vitti, AM02, 659, 675, and 676) and 1 dolomitic rock sample (AM01). Sample preparation and experiment apparatus are described in section 4.4.7. (p.91).

Low-pressure gas sorption experiments applied the BET method, and the pore characterization of Irati Formation shales was carried out based on low-pressure nitrogen (LPN₂) sorption isotherms. Microporous surface area was estimated with low-pressure carbon dioxide isotherms (LPCO₂). The average BET specific surface area, CO₂ micropore surface area, pore sizes and pore volume for all 11 analysed samples are presented in Table 12.

Table 12. List of BET fitting parameters of low-pressure CO₂ adsorbed isotherms for studied Irati shale samples.

Sample ID	Borehole/ Quarry	Location	Lithofacies	Depth (m)	Mass (g)	BET surface area (m ² /g)	Pore volume ¹ (cm ³ /g)	Pore size ² (nm)	CO ₂ Micropore surface area ³ (m ² /g)
0574	Rio Verde	Montividiu- GO	Organic-rich shale	0	0.5409	76.2853	0.087652	4.5960	159.9033
0577	Rio Verde	Montividiu- GO	Organic-rich shale	0	0.5488	61.3775	0.083461	5.4392	116.0020
0582	SUCAL	Perolândia - GO	Organic-rich shale	0	0.7237	4.0725	0.017158	16.8526	21.8862
0583	SUCAL	Perolândia - GO	Organic-rich shale	0	0.5479	10.0247	0.042189	16.8338	37.4848
0587	ELBA	Montividiu- GO	Organic-rich shale	0	0.5322	153.1385	0.146072	3.8154	169.7539
Vitti	VITTI	Saltinho - SP	Organic-rich shale	0	0.6345	9.5850	0.024656	10.2895	46.5330
AM01	Amaral Machado	Saltinho - SP	Dolomite	0	0.3820	2.7740	0.018558	26.7605	-
AM02	Amaral Machado	Saltinho - SP	Organic-rich shale	0	0.3750	6.2656	0.027837	17.7715	-
0659	FP-12-SP	Anhembi - SP	Organic-rich shale	274.38	0.7688	1.8245	0.012358	27.0926	27.4717
0675	SP-37-PR	Sapopema - PR	Organic-rich shale	213.72	0.8007	0.6860	0.000778	4.5340	13.8278
0676	SP-47-PR	Sapopema - PR	Organic-rich shale	241.74	0.5434	39.0475	0.065685	6.7287	69.9613

¹ Single point adsorption total pore volume of pores less than 348.8086 nm diameter at P/Po = 0.994488805.

² Adsorption average pore diameter (4V/A by BET).

³ Dubinin-Astakhov method with CO₂ as adsorbent.

As shown in Table 12, the Irati shale samples have a highly heterogenous pore system. BET specific surface areas of Irati organic rich shale samples range between 0.6 and 153.1 m²/g with an average of 36.22 m²/g. Comparatively, samples from Montividiu municipality (GO state) (574, 577 and 587) present higher BET specific surface areas (≥ 61.3 m²/g). These samples also present the highest pore volume, smallest pore sizes and, consequently, higher microporous surface area in comparison with the other studied samples.

Pore size distribution suggests that pore diameters vary between 3.8 nm and 27 nm and are classified as mesopores (2-50 nm) according to IUPAC (Sing et al. 1985). Samples 659 and AM01 (dolomitic rock) host the largest pore diameters among analysed samples, with 27.09 and 26.76 nm, respectively. The mesopore volume of Irati shales vary between 0.000778 and 0.146072 cm³/g. Samples 574, 577 and 587 have higher average mesopores volumes, ranging between 0.08 and 0.14 cm³/g.

Surface area measurements with CO₂ complement this information, since CO₂ smaller molecules can reach micropore scale (≤ 2 nm). Data on CO₂ micropore surface indicates that Irati shale samples have a high volume of micropores. In this regard, samples 574, 577 and 587 are the most microporous among the studied samples and present significant surface area of micro and meso pores.

Sample AM01 corresponds to a dolomitic rock and its study aims towards a comparative analysis of the porous system with the Irati organic rich shales. As shown in Table 12, sample AM01 BET surface area is 2.7740 m²/g, with pore volume estimated in 0.018 cm³/g and 26.76 nm of average pore size. Based on provided data, the porosity of the dolomitic rock is similar to the porosity of the interbedded black shales within the Irati Formation, although mainly composed of larger/meso pores.

Based on Table 12 data, a possible correlation can be established between BET surface area, pore volume and pore size, as it seems that surface area decreases while pore volume and pore diameter increase (e.g., samples 574, 577 and 583). Sample 675 represents an exception to this inversely proportion pattern, and it is also characterized by a very low-pore volume – smallest among all studied samples (0.000778 cm³/g).

5.5.2.1. Adsorption and desorption patterns

LPN₂ adsorption and desorption isotherms for 10 organic-rich samples and 1 dolomite sample of Irati Formation (Assistência Member) are presented in Figure. 47.

Figure 47. LPN₂ adsorption and desorption isotherms of studied Irati shale and dolomitic rock samples. A: sample 574. B: sample 577. C: sample 582. D: sample 583. E: sample 587. F: sample Vitti. G: sample AM02. H: sample 659. I: sample 675. J: sample 676. K: sample AM01 (dolomitic rock).

LPN₂ sorption isotherms illustrated in Figure 47 show that adsorption and desorption isotherm curves do not overlap and result in a hysteresis loop. According to Boruah et al. (2019), the so-called ‘forced closure’ of the desorption branch (e.g., samples 574, 577, 587, Vitti, AM02 and 576) is a phenomenon that results from an “instability of the hemispherical meniscus during capillary evaporation in pores with diameters smaller than approximately 4.0 nm” (Boruah et al., 2019). According to the authors, such shape of isotherms implies that there is a significant volume of pores with diameters ≤ 4 nm within the samples.

The desorption curves profiles suggest type H2 and H3 hysteresis loop types. Such patterns are characteristic of porous materials (H2 loops) and of aggregates of plate-like particles and slit-shaped pores (H3 loops) (Boruah et al., 2019). The last being mostly associated to clay minerals.

Based on the International Union of Pure and Applied Chemistry (IUPAC) classification of isotherms hysteresis shapes (see Sing et al. 1985), the obtained LPN₂ sorption isotherms from Irati shale samples are type II-IV and typical of nanoporous and mesoporous adsorbents. This information is confirmed by pore size data, which range from 3.8 to 27 nm (mesopore scale), by the CO₂ micropore surface area, and by the ‘forced closure’ hysteresis loop desorption pattern and its association with ≤ 4 nm (nanopore scale).

Overall, it is possible to correlate samples with nano-meter to micron-size pores with higher CO₂ sorption capacity (e.g., samples 574, 577 and 587), as shown in Figure 48. Specificities regarding these samples include its low TOC and gas window maturities, in addition to its mineralogical assemblage which is characterized by high-temperature minerals and, specially, higher clay content. The last comprising high intensity smectite group clay minerals, here interpreted as authigenic, and derived from the thermal effects of local igneous intrusions in the Irati Formation in the north of the Paraná Basin (GO State). These findings add to the hypothesis of clay minerals contribution to CO₂ storage capacity.

Figure 48. Correlation between BET surface area and CO₂ sorption capacity of analysed samples.

Such thermal effect from intrusion can also be identified in borehole samples from Sapopema (PR State) (e.g., sample 676). However, although this sample shows micro-meso porosity and significant surface area, it has no CO₂ storage capacity. Considering that this samples has no preserved organic content, is it possible to state the contribution to organic matter to CO₂ sorption capacity.

6. DISCUSSION AND DATA INTEGRATION

Organic geochemistry (TOC, Rock-Eval pyrolysis), organic petrology and petrography (maceral analysis, vitrinite reflectance, spore fluorescence and palynological studies), mineralogical composition (XRD), high-pressure gas sorption isotherms (CO₂ adsorption capacity through Langmuir method), low-pressure gas sorption experimental studies (pore volume, pore size distribution, surface area through BET method), and low-pressure gas isotherms (pore volume, pore size distribution, and surface area through BET method) were applied to Irati Formation organic-rich shales' characterization. The conducted analysis integrates a detailed assessment on Irati Formation shales and correlated the studied parameters with CO₂ adsorption behaviour in shales.

6.1. Bulk organic matter

Total organic carbon (TOC) is expressed as weight percent (wt%) and indicates source-rock potential for hydrocarbon generation. The TOC classifies the shales into four categories, according to Peters (1986) and Gogoi et al. (2008): (i) shales containing less than 0.5% TOC are considered as poor source rocks, (ii) shales containing a TOC between 0.5% and 1% indicate fair source rocks, (iii) shales containing a TOC values between 1% and 2% indicate good source rocks, and (iv) shales containing a TOC values above 2% often indicate a highly reducing environment and preserved organic content and indicate excellent source-rock potential.

Based on TOC measurements, Irati black shales have excellent potential for hydrocarbon generation, with analysed samples generally containing TOC values above 2% mg HC/g rock (5.4 wt% TOC average). However, a high heterogeneity is identified, and TOC values range from 0.26% to 20.8% among the studied samples. The heterogeneity regarding the TOC content is mainly attributed to depositional paleoenvironment and to thermal maturity variations and can also be observed among the sampled areas. Comparatively, samples from the northern border of the Paraná Basin (GO State), present lower values of TOC (generally $\leq 2\%$) in contrast to samples from SP and PR States (mostly $\geq 2\%$). Exceptional low TOC samples are placed in proximity to igneous intrusions (e.g., samples from the boreholes SP-29-PR, SP-47-PR and SP-55-PR, from Sapopema – PR).

Previous research also classifies the Irati organic-rich shales as excellent hydrocarbon source rocks (Cerqueira and Santos Neto, 1986; Milani and Zalán, 1999; Milani et al., 2007; Euzébio et al., 2016; Rocha, 2016; Holanda et al., 2018, Martins et al., 2020; Rocha et al., 2020).

Geochemical analyses 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). Other authors attribute an average of up to 16.3% TOC (Santos et al., 2009; Loutifi et al., 2010; Euzébio et al., 2016; Holanda et al., 2018; Martins et al., 2020).

The heterogeneity regarding TOC of Irati Formation organic-rich shales is also confirmed by other authors. In the eastern portion of the basin (SP State), TOC ranges from 3.8-14.4% (Holanda et al., 2018; Teixeira et al., 2020), and between 0.14 and 0.5% in the proximity of igneous intrusions (Teixeira et al., 2020). In the south of the Paraná Basin (PR State), TOC values vary between 4.14 to 23 wt% (Padula, 1969; Franco et al., 2010; Alferes et al., 2011; Reis et al., 2018; Martins et al., 2020). Lower TOC values in samples from the northern border of the Paraná Basin (GO State), were also reported by Silva (2007) and Mabecua (2018), with TOC ranging from 0.04 to 3.52% (Silva, 2007; Mabecua, 2018).

6.2. Palynofacies associations, kerogen typing and depositional palaeoenvironment

In this study, the Irati Formation organic-rich shales suite of maceral group components is dominated by liptinite group macerals. The recovered palynofacies were (i) fluorescent amorphous organic matter (AOM), (ii) palynomorphs, (iii) translucent phytoclasts, and (iv) opaque organic matter. Among these, dull-yellow fluorescent AOM was dominant. The palynofacies assemblage correspond to a type I-II prevalent kerogen, with mixture of type III kerogen. The last mostly concentrated in the northern and southeastern borders of the basin.

Kerogen typing is in accordance with obtained Rock-Eval pyrolysis data, from which hydrogen index (HI) confirms the prevailing type I-II kerogen (HI range between 500 and 731 mg HC/g TOC). Samples from GO State present lower hydrogen content ($HI \leq 300$ mg HC/g TOC) in comparison to the other sampled areas of the PB (SP and PR), confirming the occurrence of type III kerogen. Comparatively, samples from the northern portion of the PB present a higher concentration of type II-III kerogen, gas-prone organic matter. This can be associated to freshwater influx and more proximal and/or shallow marine palaeoenvironment.

Still considering Rock-Eval pyrolysis data, samples from SP and PR have higher sulphur (S) values in comparison to samples from GO State. This could be associated with a greater marine influence/sea water influx to the depositional site. Sulphur concentration could also be an indicative of anaerobic organisms and a reductive paleoenvironment (Chaves et al., 2018).

Overall, palynofacies indicate a shallow marine paleoenvironment with fluvio-deltaic influence. The fluorescent intensity of AOM raise the evidence of an anoxic paleoenvironment, which is confirmed by the sulfur content from the pyrolysis. The AOM gelified texture and the occurrence of framboidal pyrite suggest bacterial degradation of the OM.

Paleoenvironmental interpretations of this study are in accordance with previous research that relate the Irati Formation to a restricted, hypersaline anoxic-suboxic marine depositional environment that was subjected to climate oscillations and changing to non-marine oxic transitional conditions, such as fluvial influx and the input of continental organic material (Cerqueira and Santos Neto, 1986; Santos Neto, 1993; Milani, 1997; Araújo et al., 2001; Alferes et al., 2012; Reis et al., 2018; Martins et al., 2020). The intermittency of oxic and anoxic conditions and the consequent variable degree of oxygenation resulted, despite other factors, in the TOC heterogeneity within the Irati Formation shales (Goldberg & Humayun, 2010; 2016)

Based on palynological studies, Schneider et al. (1974) suggest a marine environment below the fair-weather wave base for the deposition of the Irati Formation. However, in this study, the absence of marine palynomorphs, as well as the dominance of taeniate pollen grains, the presence of fresh to brackish water algae specimens, and scarce spores in the studied samples suggest deposition in a shallow marine environment close to the shoreline as the influx of freshwater and terrestrial material in the assemblages is considerable. The record of *Botryococcus braunii*, already described by Corrêa da Silva and Cornford (1985) and De Castro (1988) for the Irati Formation (Paraná Basin), can also support these authors interpretation of a shallow and low energy lacustrine depositional regime (following Traverse, 1992). The record of amorphous organic matter and framboidal pyrite in the studied samples also supports the idea of deposition in shallow and mostly anoxic environments.

6.3. Organic maturation

Although previous studies attribute an immature stage to most of the Assistência Member (Alferes et al., 2013; Araújo, 2001; Araújo L.M. et al., 2000; Da Silva & Cornford, 1985; Holanda et al., 2016; Silva, 2007), obtained organic petrography data in this research show a different maturation trend for these oil shales: being mostly in an early mature stage, beginning of the oil window.

Based on T_{max} values, analysed samples are classified as immature to early maturity stage ($T_{max} \leq 435$ °C). However, due to the complexity of determining thermal maturation in highly heterogeneous shales, such as the Irati Formation organic-rich shales, it is not advisable to use a single parameter for this classification. Therefore, thermal maturity was confirmed through organic petrographic techniques (vitrinite reflectance and spore fluorescence).

Vitrinite reflectance data indicate that most samples reached the beginning of the oil window generative zone ($VR \geq 0.6 \%R_r$). Additionally, recorded liptinite fluorescence and colour reinforce that the Irati Formation shales are mostly oil-prone source rocks that reached oil-window maturities (yellow colored fluorescent palynomorphs). Mature, gas-prone shales were also identified ($VR \geq 1.35 \%R_r$ and yellow to orange coloured fluorescence).

Regarding sample's location, Irati Formation organic-rich shales from the south of the Paraná Basin (PR State) are mostly early mature (oil-window), while samples from the N portion of PB present higher thermal maturation ($0.93 - 2.46 \%R_o$), reaching over-mature stages when proximal to igneous intrusions. Dos Anjos & Guimarães (2008) confirm a high thermal effect at Goiás State (GO), through mineralogical evidence of metamorphism.

Overall, organic petrography data indicate two different maturation levels to Irati Formation organic-rich shales: a regional-scale early-maturity stage and a second mature to post-mature stage. The first is most probably associated with burial palaeotemperatures (e.g., most samples from PR State) and the second attributed to the Cretaceous Serra Geral magmatism influence (e.g., samples from Montividiu, GO).

It is important to highlight the heterogeneity within the studied lithology maturity and the thermal influence from igneous intrusion and their relative proximity to sampled areas and to the thickness of the intrusion. In this sense, it is possible to observe the relation between the thermal aureole and intrusion thickness. Samples that are very proximal to thick ($\geq 2m$) doleritic sills are post-mature and have no source-rock potential (e.g., sample 676), while samples that are proximally located to $\leq 2m$ thick dolerites reached gas-window maturities (e.g., samples from Montividiu, GO). In this regard, studies carried out by Bulguroglu & Milkov (2020), in regard to thermal aureole thicknesses and their relation to intrusion thickness, support the theory that sill intrusions in organic-rich shale have extended thermal influence. The authors state that thermal aureole thicknesses range from 31–137% of the sill thickness, for relatively thick sills ($> 13m$), and can reach up to 1000% for thin sills ($< 5m$) (Bulguroglu &

Milkov, 2020). This pattern can be attributed to shales composition and organic content, which can interfere on the contact metamorphism thermal propagation in the Irati Formation.

In comparison to previous studies, Turner et al (1994), Araújo (2001) and Araújo et al (2001) mainly attributed the shale's maturation to the Lower Cretaceous Serra Geral magmatic event, and its associated high geothermal gradient and subsequent migration pathways due to magmatic activity. Additionally, the authors state that the thermal metamorphism effect would justify the significant variation on total organic carbon (TOC) values within the formation. Following this interpretation, the Paraná Basin thermal history before the Serra Geral magmatism in the Cretaceous, would be characterized by a low diagenetic thermal gradient, reaching maximum temperatures around 60 to 80 °C (Araújo, 2001; Araújo et al., 2001; Mateus et al., 2014).

However, other studies conducted by, Mateus et al. (2014), Nomura et al., (2014), and Teixeira et al. (2018, 2020) sustain that a higher geothermal gradient affected the Paraná Basin before the igneous intrusions. According to these authors, the Irati Formation organic-rich shales reached organic maturation and generated liquid hydrocarbons since the late Permian to the Triassic (Mateus et al., 2014). The authors sustain this hypothesis on hydrothermal activity episodes, due to authigenic and neo-formation of clay minerals from hydrothermal fluids. The hydrothermal activity can also be evidenced by the presence of chert and silica concretions (silicification among irregular fronts, secondary porosity, and fracture infillings), and other typical reactions of high-temperature conditions (Mateus et al., 2014).

Regarding paleotemperatures, fluid inclusions studies also indicate that the Paraná Basin presented a higher diagenetic gradient. Mateus et al. (2014) affirm that the palaeogeothermal gradient reached 125°C, during the Permian-Triassic, in deeper portions of the Paraná Basin. In accordance, paleotemperatures reported by Nomura et al. (2014), indicate a thermal gradient from 90 to 140 °C. This thermal gradient could propitiate conditions to interstitial fluid flow within the basin. Furthermore, it could stimulate organic matter maturation in large-scale and liquid hydrocarbon generation. These studies highlight a second interpretation for the Irati shales maturation, which would be most probably controlled by burial (Mateus et al., 2014), and, at certain portions of the basin, by the associated overburden pressure from the hundred-meters thick overlaying Serra Geral flood basalts (Nomura et al., 2014; Teixeira et al., 2020).

Based on this interpretation, the hydrocarbon generation and migration processes within the Irati Formation were heterogeneous and performed in multistage phases. Three major flow

episodes were identified by Mateus et al. (2014): i) a confined flow dated from the late Permian to Triassic; ii) a heterogeneous flow dated from the Lower Cretaceous, associated with the pre-developed permeability within the formation and with a new regime of high geothermal gradient build-up; iii) and a late flow from the driven by local pressure and temperate gradients, associated to igneous intrusions (Mateus et al., 2014; Ferreira, 2017).

Mateus et al. (2014) state that the first stage of fluid migration resulted in fissured reservoirs due to pressure build-up. This developed permeability was then propitious to hydrocarbon accumulation in the Lower Cretaceous due to this mentioned adequate temperature gradient. The second stage of fluid migration was considerably heterogeneous, been subjected to the multiphase emplacement of igneous intrusions. This stage propitiated the displacement from oil to gas window of hydrocarbon generation, as well as the relocation of fluids within the basin. The third and late migration stage was related to the cooling process of the magmatic intrusions, driven by local pressure gradients. Posteriorly, with the developed permeability, freshwater infiltration from overlapping aquifers (Pirambóia and Botucatu Formations), favoured the organic-matter degradation by anaerobic microorganisms (methanogenesis) at low-temperature conditions (below 50°C), producing biogenic natural gas (Bertassoli et al., 2016; Mateus et al., 2014), and resulting in a mixture of thermogenic and biogenic natural gas (Almeida, 2018).

This theory is in accordance with the results obtained in this study. It implies in a new geological model for hydrocarbon maturation to the black shales of the Irati Formation. Although highly heterogeneous, the Irati Formation organic-rich shales reached thermally mature levels (early oil-window maturities) in a regional-scale, most probably during the Permian-Triassic, being posteriorly thermally affected by the Serra Geral magmatism from the Lower Cretaceous that resulted in local shale gas generation (e.g., GO State and west of SP State).

6.4. The effect of organic matter on gas sorption

Shale composition determines its porosity and therefore its CO₂ sorption capacity and gas storage potential. In organic-rich shales, gas storage capacity mainly relies on organic porosity and clay minerals, where the CO₂ gets stored through adsorption. Additionally, part of the CO₂ gets stored in `free` way into larger pores and fractures (Al-Mutarreb et al., 2018; Klewiah et al., 2020; Romero-Sarmiento et al., 2012).

Shale's porous system (e.g., primary and secondary porosity) result from a complex interaction of physical and chemical processes, before and after deposition (Ahmad, 2014). In this sense, shale's pore size, pore type, interconnectivity, and distribution, rely on the inorganic matrix and on the organic matter content, and 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 include kerogen quantity (TOC wt.%), type and maturity level, while inorganic aspects rely on mineralogy, such as ratios of silica/quartz, carbonates, and clay minerals (Goodman et al., 2020; Schaef et al., 2014; Weniger, et al., 2010).

The impact of organic constituents on CO₂ sorption capacity in shales is analysed in this study. Considered organic parameters comprise TOC, kerogen type and thermal maturity, which were analysed in comparison to BET surface area and to CO₂ sorption capacity to establish possible correlations.

Based on the obtained results, there is no apparent correlation between CO₂ sorption capacity and total organic carbon content (TOC wt.%). As shown in Table 13 and Figure 49, samples with TOC ≤ 1% (e.g., 574 and 577) can still exhibit considerable storage capacity besides the low organic content. Additionally, organic-enriched samples, such as 659, 675 and 676 do not present significant storage capacity. The lack of correlations suggests that TOC does not necessarily contribute to shales' sorption capacity and it is not determinant for CO₂ geological storage in shales.

Table 13. Results of organic matter analysis: TOC, kerogen type, and vitrinite reflectance (VR), and of high-pressure CO₂ sorption experiments (measured at 35 °C) on Irati black shales.

Sample ID	Borehole/ Quarry	Location	Depth	TOC (wt.%)	VR (wt.%)	BET surface area (m ² /g)	G_{CS} (scf/ton)	G_{CS} (m ³ /ton)
0574	Rio Verde	Montividiu – GO	0	0.57	2.46	76.2853	130.32	3.69
0577	Rio Verde	Montividiu – GO	0	0.12	1.19	61.3775	103.11	2.91
0582	SUCAL	Perolândia – GO	0	5.17	1.33	4.0725	33.77	0.95
0583	SUCAL	Perolândia – GO	0	5.47	1.25	10.0247	44.78	1.26
0587	ELBA	Montividiu – GO	0	1.73	1.09	153.1385	108.80	3.08
Vitti	VITTI	Saltinho – SP	0	4.42	0.96	9.5850	65.27	1.84
0659	FP-12-SP	Anhembi - SP	274.38	9.02	0.67	2.7740	51.17	1.44
0673	SP-29-PR	Sapopema - PR	340.65	0.39	0.69	6.2656	11.02	0.31
0675	SP-37-PR	Sapopema - PR	213.72	6.38	0.81	1.8245	14.53	0.41
0676	SP-47-PR	Sapopema - PR	241.74	6.89	4.46	0.6860	13.70	0.38

Figure 49. Correlation between TOC and BET specific surface area for Irati Formation organic-rich shales.

In regard to maceral composition, there is a positive correlation between vitrinite and inertinite content and storage capacity. High sorption capacity shale samples (574, 577 and 587) petrographic composition is mainly represented by opaque phytoclasts, indicating that type III kerogen attributes a higher sorption capacity to Irati Formation organic-rich shales (section 5.2.1., p.101).

Organic maturation is a key parameter to CO₂ geological storage and to hydrocarbon recovery processes in shale formations. It controls organic porosity, pore size and surface area within these lithologies and, consequently, the efficacy of CO₂ adsorption and CH₄ desorption processes – which drive CO₂ sequestration in shales, as well as enhanced shale gas and shale oil recovery associated processes.

Regarding the effect of organic maturity on sorption isotherms, in the present study, organic maturity affects sorption capacity of Irati Formation shales and a positive correlation between CO₂ storage capacity and maturity can be observed. Such positive correlation is identified between $VR \geq 1.35 \%R_r$ (gas window-maturity) and storage capacity (e.g., samples 574, 577 and 587), illustrated in Figure 50. Samples with low thermal maturity (e.g., 659 and 673 – immature to early oil window) present exceptionally low storage capacity. However, overmature samples such as 676 (4.46 % R_r) no longer have sorption capacity.

Figure 50. Correlation between vitrinite reflectance and BET specific surface area for Irati Formation organic-rich shales.

The observed correlation between VR and CO₂ sorption capacity of Irati shales is in accordance with previous research (Chen & Xiao, 2014; Han et al., 2017). According to the authors, VR interval between 0.8 and 2 % R_r led to higher sorption capacity in shales (e.g., samples 574, 577 and 587), due to nanoporosity development associated to kerogen cracking and gaseous hydrocarbon release. Still according to the authors, samples with VR above 3.5 % R_r no longer hold storage capacity, which was demonstrated on sample 676 of this study.

Additionally, Table 13 show samples with similar petrographic composition (e.g., vitrinite content in samples 574 and 577) present higher sorption when maturity (VR) is higher. For instance, sample 574 presents a higher sorption curve in comparison with sample 577.

Overall, samples from Rio Verde quarry, and especially sample 574, present higher BET surface area and consequent higher CO₂ sorption capacity among all analysed samples. This can be due to the combination of parameters that affect CO₂ sorption capacity, such as its (i) comparatively higher vitrinite content, (ii) gas-window maturity ($VR \geq 1.35 \%R_r$), and (iii) higher clay content, and (iv) presence of smectite clay type.

Other authors report that gas adsorption capacity rises with the decrease of the TOC, which indicates maturity of organic material in shale (Zhang et al., 2012). Previous studies performed on coal samples report that CO₂ sorption capacity decreases with increasing rank to a minimum

in the medium-volatile bituminous range (Yalcin and Durucan, 1991; Rodrigues, 2002; Faiz et al., 2007). This effect has also been observed for carbon dioxide sorption capacity (Busch et al., 2003; Day et al., 2008, Almeida, 2019).

The effect of maceral composition on methane and carbon dioxide sorption on organic-rich shales is attributed to differences in microporosity of the macerals. Vitrinite is predominantly microporous, whereas inertinite is rather meso-to macroporous (Lamberson and Bustin, 1993; Rodrigues (2002). Some authors report a significant influence of maceral composition on sorption capacities (e.g., Lamberson & Bustin, 1993; Mastalerz et al., 1993, 2004; Chalmers and Bustin, 2007).

6.5. The effect of mineral content on gas sorption

The impact of mineral constituents on CO₂ sorption capacity in shales is analysed in this study. Considered mineralogical parameters comprise the identified mineralogical assemblages and, mainly the clay-content and type, which drive gas adsorption in low-TOC shales (Busch et al., 2008; 2020). Samples with different mineralogical assemblages and with variant smectite peak intensity were analysed in comparison to BET surface area and to CO₂ sorption capacity to establish possible correlations.

In this study, the overall abundant clay content, and the prevalence of expandable clay minerals of the smectite group attribute to Irati Formation organic-rich shales good CO₂ storage capacity. 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 to Irati shales (e.g., samples from Montividiu, GO and from Vitti quarry, SP).

As previously mentioned, smectites are the most abundant identified clay mineral group within studied samples, and it is characterized by variant d₀₀₁ peak intensity. Lower/regular intensity peak smectites are most probably detrital in origin, while high intensity peak smectites are presumably authigenic.

Such differences can be related to varied conditions of the studied samples, which could either be associated with the (i) to variations on redox conditions during sedimentation, (ii) illitization process along diagenesis, and/or (iii) hydrothermal fluids flow and recrystallization episodes, related to the Cretaceous Serra Geral magmatism, as well as (iv) to a combination of these (Sant`Anna et al., 2006).

The two mineral assemblages identified in this study can also be related to the thermal history of the Paraná Basin and, consequently, to the two maturity levels pointed out by the previous results (section 5.3, p.108), which correspond to a diagenetic early-oil window maturity and to a post-depositional thermal maturation, linked to dolerite intrusions. Samples with the predominantly authigenic mineral assemblage (574, 577, 587, AM01, Vitti, and 676) are heat-affected and were proximally located to igneous intrusions (specially samples 574, 577, and 676) and relate to higher maturity samples ($VR \geq 0.96\%$).

In regard to sample location within the Paraná Basin, GO State samples present higher percentages of high-temperature and high-pressure minerals, such as serpentine and talc, comparatively to other sampled areas towards the south of the basin (SP and PR States). This adds to the hypothesis of higher thermal metamorphism in the north of the PB. Additionally, samples from GO (specially from Montividiu), are classified as high intensity smectite clay-dominant mature shales with low TOC and present the higher CO₂ storage capacity. Previous research supports this theory that, at low TOC values, clay becomes dominant in the adsorption process because of the high surface area and swelling effect of some types such as smectite (Heller and Zoback, 2014; Rani et al., 2019; Busch et al., 2020).

Irati Formation shales mineralogy identified in this study is in accordance with previous research (Anjos et al., 2010; Holanda et al., 2016; Ribas et al. 2017, Ferreira, 2017; Holanda et al. 2019). According to Holanda et al. (2019), identified authigenic minerals such as analcime, gypsite, and pyrite contribute to paleoenvironmental interpretations of the Irati Formation. Such mineralogy is attributed to saline and alkaline depositional conditions and to organic matter-enriched sediments, representative of restricted paleoenvironments (Holanda et al. 2019). The described paleoenvironmental conditions are correspondent to the Panthalassa Sea and the Irati Formation geological setting (Holanda et al., 2019; Kemp et al., 2019; Milani, 2004).

Additionally, chemical composition variations can relate to hydrothermal fluids and thermal metamorphism (Cama & Ganor, 2015), and be associated with the Serra Geral Cretaceous magmatism (Sant'Anna et al., 2006). Fe and Mg silicates, such as chlorite, and sulphides may also precipitate from migrating hydrothermal fluids (Hannington, 2014). These minerals are also constituents of the identified mineral assemblages.

Authigenic smectite group minerals are most probably represented by saponite or montmorillonite. Ferreira (2017) reports the occurrence of saponite in SP, while Anjos (2008) reports the occurrence of saponite in samples from GO. According to Kuwahara (2006), a

process of montmorillonite dissolution occurs under alkaline conditions, which are generally correlated to higher pH and higher temperatures. While saponite is characterized as a common product of low-temperature reactions between water and mafic minerals (Sueoka et al., 2019).

High sorption capacity samples (0574, 0577 and 0587) are characterized by low organic content, comparatively to other samples: TOC of 0.57, 0.12 and 1.73 %, respectively. Additionally, sorption capacity can be close to zero even in samples with remarkably high organic content (e.g., samples 0675 and 0676, with 6.38 and 6.89 % TOC, respectively). Such correlations evidence that samples with $\text{TOC} \leq 2\%$ can still exhibit considerable storage capacity besides the low organic content, due to clay-enriched mineral matter.

7. CONCLUSIONS AND FINAL REMARKS

Organic matter type and maturation classifies the Irati shales as mainly oil-prone source-rocks, specially towards the south of the Paraná Basin (PR State), where samples contain mostly type I-II kerogen and maturity ratios between 0.52 and 0.69 % R_r (early oil-window maturities). Gas-prone Irati shales occur in the northern and south-eastern borders of the basin (GO and SP States) and are attributed to higher terrestrial organic matter input (paleogeography) and consequent higher concentration of type III kerogen within samples from these regions. Additionally, gas-window maturities (between 0.9 and 4.46 % R_r) relate to the thermal influence of igneous intrusions derived from the Serra Geral magmatism during the Cretaceous.

CO₂ and N₂ low pressure adsorption measurement (BET method), besides CO₂ high pressure sorption isotherms (Lagmuir method) techniques were applied to quantify pore volumes, pore sizes, and pore-size distributions within the samples, as well as its maximum sorption capacity. Obtained results attribute to the Irati Formation organic-rich shales a significant CO₂ storage capacity in samples with predominance of micropores and with consequent higher internal surface area. Although heterogenous, Irati Formation storage capacity reaches 3.69 m³/ton (sample 0574).

Experimental analysis indicates that organic matter maturity is a controlling variant for total porosity and total pore volumes, affecting also pore-size distribution and the relative proportions of micropores, mesopores and macropores. 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 the observed porosity variation and consequently of storage capacity patterns.

Overall, samples from Montividiu municipality (GO), collected at Rio Verde and ELBA quarries (e.g., samples 574, 577 and 587) present higher CO₂ sorption capacity among all analysed samples. This can be due to the combination of parameters that affect CO₂ sorption capacity, such as its (i) comparatively higher vitrinite and inertinite content, (ii) gas-window thermal maturity, and (iii) higher authigenic clay content, composed of expandable and webby texture smectites.

Paleoenvironmental interpretations explain variations on petrographic composition of analysed samples, attributing a higher content of vitrinite and inertinite group macerals to samples from the north of basin. However, compositional variations were identified even among samples from proximal location (GO state), suggesting that variances on depositional environments are not sufficient to explain the heterogeneity regarding sample's sorption capacity. Consequently, the identified high level of heterogeneity is most probably attributed to a complex combination of processes before and after the Irati Formation deposition during the Permian. For instance, significant post-depositional events such as the Cretaceous Serra Geral magmatism and its effects on organic and mineral matter content.

In general aspects, analysed samples of Irati Formation organic-rich shales are organic-rich and poses moderate to remarkably high potential for hydrocarbon generation, hence been classified as exceptionally good source rocks within the Paraná Basin. Such organic richness of Irati Formation shales is also attributed to depositional conditions that favoured organic matter preservation. The depositional conditions were mainly anoxic, despite been periodically interrupted with oxygenated water influx and leading to a stratified water column. The deposition of the organic content occurred in a shallow-marine restricted environment with local contribution of brackish water and terrestrial material input in the northern border of the basin. The persevered organic content of Irati Formation organic-rich shales is mainly represented by mixed type I-II kerogen, with local concentrations of type III, which is mostly attributed to samples from GO and SP.

Although there is no significant evidence of changes related to the depositional environment, there is a high heterogeneity among Irati Formation organic-rich shales regarding its preserved organic content. Samples from the northern border of the Paraná Basin (GO State) are comparatively poor in organic matter content (TOC) while samples from the south and

southeast of the PB (SP and PR States) are more organic-rich. Additionally, a progressive increase in organic content can be observed towards the south of the Paraná Basin, with samples from PR been more organic-rich than samples from SP. This increase in preserved organic matter can relate to the slight variances on depositional conditions across the basin, with predominance of anoxic to suboxic conditions where is now the southern portion of the PB. Such variances can be confirmed by palynological studies, that point out terrigenous input (e.g., phytoclasts and microplanktonic elements such as *Botryococcus* – brackish water algae) in samples from GO, while a higher content of marine organofacies observed in samples from SP and PR.

In concern to thermal maturity, Irati Formation organic-rich shales have reached distinct levels of organic maturation. The heterogenous maturity range between early to late maturation, with all studied samples reaching sufficient temperature to hydrocarbon generation. Most of studied samples were at early oil-window maturation levels, while few exceptions reached gas-window maturities. This leads to the interpretation that Irati Formation shales reached early oil-window maturity at a regional scale within the Paraná Basin, through burial conditions, while local thermal metamorphism led to gas-window maturities. There is no major correlation between gas-window maturation and burial depth in studied samples and are local and heterogenous. This adds to the hypothesis that such maturity range is associated with the Serra Geral magmatism, and relies on complex factors such as intrusions` thickness and geometry, which vary across the basin.

Regarding the potential for unconventional reservoirs for hydrocarbons, Irati Formation shales have potential for both shale oil and shale gas, with variance based on the region within the Paraná Basin and proximity to the igneous intrusion. Comparatively, samples from GO state present a higher potential for shale gas and, consequently, for CO₂ geological storage, while samples from PR and SP have mostly potential for shale oil, with local occurrence of shale gas in the proximity of igneous intrusions (e.g., geographic surrounding of Sapopema municipality).

The clay mineralogy Irati Formation shales is also heterogenous and it mainly comprises clay minerals from smectite group. This heterogeneity also comprises the proportion of clay minerals and quartz content, which varies along the basin and affect rock brittleness. Therefore, the potential for producing shale gas and shale oil, which requires permeability stimulation techniques, such as hydraulic fracturing, is highly heterogenous and should be analysed locally.

For instance, samples from GO have potential for shale gas and for CO₂ storage due to clay mineral content. Additionally, although organic and mineralogical composition can favour shale gas production locally, the overall thickness of Irati Formation is generally below a hundred meters and cannot go through fracking under current regulation.

The above-mentioned characteristics of analysed shale samples from Irati Formation led to the conclusion that there is geologic feasibility to produce hydrocarbons and for CO₂ geological storage, and that the Irati Formation organic-rich 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 of CO₂ storage capacity and of hydrocarbon generative potential.

Addressing the research problem in a broader and multidisciplinary perspective, besides geologic feasibility, CO₂ geological storage in organic-rich shales deployment in Brazil requires legal and regulatory regime that is supportive to CCUS and to the exploration and production of hydrocarbons unconventional reservoirs.

In this concern, the role of CCUS in Brazil, an in most developing countries and industrial nations, is to provide CO₂ mitigation to its continued usage of fossil fuels, and to be a transitional technology towards a more sustainable energy future. Opportunities for CCUS in Brazil rely on carbon and energy-intensive industries, such as cellulose-based products, cement, steel, aluminium, and fertilizer production, and especially on the power generation sector. Regarding the power sector, Brazil is characterized by an emerging demand for energy resources and by an increase of natural gas fuelled power-plants for baseload energy supply – complementary to intermittent hydropower-generation. Consequently, fossil fuels tend to play a continuous role in the Brazilian energy mix. In addition, fossil fuels' production is expanding within the country, especially due to the offshore exploration and production of the Brazilian Pre-salt. Moreover, the high concentration of CO₂ within these reservoirs urges the necessity of implementing CO₂ abatement technologies, such as CCUS, and especially CO₂ geological storage.

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New palynostratigraphic data of the Irati (Assistência Member) and the Corumbataí formations, Paraná Basin, Brazil, and correlation with other south American basins

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ABSTRACT

This research presents the palynostratigraphy of organic-rich shales from the Irati and the Corumbataí formations, Paraná Basin (PB), Southeastern Brazil, as part of an unconventional hydrocarbon source rock and CO₂ reservoir assessment study. Thirty-four samples from the Corumbataí Formation and the Assistência Member of the Irati Formation were collected in the states of Goiás (northern border of the PB), São Paulo and Paraná (eastern and southern border of the PB, respectively). The acquired data allowed to establish a comprehensive palynostratigraphic study across the basin where a total of 18 pollen genera (34 pollen species), seven spore genera, four microplankton genera (1 species), and Chlorophyceae algae species were identified. The palynostratigraphic analysis also reveals a clear dominance of bisaccate pollen grains such as *Corisaccites alutas*, *Lueckisporites virkkiae*, and *Weylandites lucifer*. The *Lueckisporites virkkiae* zone was identified in the upper part of the Irati Formation (Assistência Member) and the lowermost part of the Corumbataí Formation, indicating a Kungurian to Roadian age for this part of the succession. Differences in the *Guttulapollenites hannonicus* and *Tornopollenites toreutos* biostratigraphic ranges, recovered in the Corumbataí Formation, suggest an earlier development of these species in the Paraná Basin during the middle Permian. Therefore, to evaluate the differences in the first occurrences of key species within the Paraná Basin, a close palynostratigraphic correlation between the main Guadalupian-Lopingian South American Gondwana basins is tentatively established.

1. Introduction

Organic-rich shales are the main conventional source rocks found in petroleum systems. However, with the growing importance of unconventional hydrocarbon resources for the future of fossil fuel supply, such as shale gas and shale oil, these organic-rich rock formations gained even more relevance in the global energy scenario. Brazil ranks in the 10th position of countries with technically recoverable shale gas resources, estimated in 245 Tcf (EIA, 2015). Furthermore, estimates made by the National Petroleum, Gas and Biofuels Agency indicate more auspicious numbers for the country: attributing 226 Tcf of estimated shale gas reserves to the Paraná Basin (EIA, 2015), due mostly to the extensive occurrence of black shales within the Passa Dois Group (Milani et al., 2007; Santos et al., 2006; Mateus et al., 2014).

Despite these estimates, the potential for shale gas and CO₂ geological storage in the Paraná Basin remains unclear. As part of a more comprehensive study aiming for a detailed characterization of the Irati Formation oil shales in order to determine its potential for unconventional hydrocarbons source rock and CO₂ geological storage, palynostratigraphy will be used in a multidisciplinary approach that also includes the analysis of vitrinite reflectance, maceral composition, organic geochemistry (proximate and ultimate analyses, pyrolysis - Rock-Eval), and sorption isotherms.

This work presents a detailed palynostratigraphic study of the basal formations of Passa Dois Group, providing a more comprehensive cross-basin correlation for the unconventional economic hydrocarbon-bearing units in the Paraná Basin.

The Passa Dois Group has been extensively studied, including its

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Fig. 1. Map of the Paraná Basin showing the chronostratigraphy and samples location.

paleoflora and palynostratigraphy (Daemon and Quadros, 1970; Marques-Toigo, 1988, 1991; Souza and Marques-Toigo, 2003, 2005; di Pasquo and Souza, 2014; di Pasquo et al., 2018; Premaor et al., 2006; Neregato et al., 2008; Mori and Souza, 2012). Even so, this paper focuses on the palynostratigraphy and environmental analysis of new outcrop and borehole data collected in the Goiás, Paraná and São Paulo regions, which includes from base to top: the Irati, Serra Alta, Teresina, and Rio do Rasto formations, as well as their lateral equivalent occurring in São Paulo State, the Corumbataí Formation (Figs. 1 and 2). This paper focuses on the uppermost Irati and the lowermost Corumbataí formations.

2. Geological setting

Located in the central-eastern part of the South American Platform, the Paraná Basin is the largest South American intracratonic basin. Comprising territorial areas in southern Brazil, eastern Paraguay, north-eastern Argentina, and northern Uruguay, this basin covers an area of approximately 1.4 million square kilometers, from which 1.1 million square kilometers are located in Brazil. With an outline configuring an

erosive border reaching approximately 5.500 kilometers in diameter, geographically it includes most of the south and southeast regions of Brazil (Milani, 1997; Zalán et al., 1990) (Fig. 1).

The geological evolution of the Paraná Basin is closely linked to the geological history of Gondwana, dating from the Paleozoic and Mesozoic, and varying from the Upper Ordovician to the Upper Cretaceous. In Brazil, the stratigraphic studies of the Paraná Basin started with White, 1908, being followed by Schneider et al. (1974), Zalán et al. (1990), Milani (1997, 2004), and Milani et al. (2007). The two most recent works cited herein, established the current stratigraphic scheme in use for this basin. The basin contains a sedimentary and magmatic stratigraphic column of approximately seven thousand meters of maximum thickness at the structural depocenter of the syncline. During this long-time interval, its tectonic-stratigraphic evolution encompassed continental distension, thermal subsidence, and isostatic adjustment processes (Maack, 1947; Milani, 2004; Zalán et al., 1990).

Six large-scale stratigraphic units, or super-sequences, were identified by Milani (1997) in the Paraná basin: Rio Ivai (Ordovician-Silurian), Paraná (Devonian), Gondwana I (Carboniferous to Eotriassic), Gondwana II (Medium to Neotriassic), Gondwana III (Neojurassic to

Fig. 2. Stratigraphic succession of the Gondwana I super-sequence, defined by Milani (1997) (Modified from Santos et al., 2006).

Eocretaceous), and Bauru (Neocretaceous). According to the author, the first three super-sequences – Rio Ivaí, Paraná and Gondwana I, represent transgressive-regressive cycles associated with sea-level oscillations that occurred during the Paleozoic. The other super-sequences – Gondwana II, Gondwana III, and Bauru, of Mesozoic age, are characterized as continental sedimentary packages associated with igneous intrusions (Milani, 1997, 2004; Milani et al., 2007).

Due to its economic potential for conventional and unconventional hydrocarbons source rocks, the Passa Dois Group, Gondwana I super-sequence, has been the focus of several studies throughout the years (e.g., Milani et al., 2007; Santos et al., 2006; Mateus et al., 2014), including the Irati, Serra Alta, Teresina, and Rio do Rasto formations (Fig. 2). The lowermost unit of the Passa Dois Group, the Irati Formation, is one of the most studied Brazilian geological formations due to its unique fossil-bearing content and potential on hydrocarbons exploitation, being considered one of world's largest oil-shale deposit (e.g., Padula, 1969; Tissot and Welt, 1984; Oelofsen and Araújo, 1987; França et al., 1995; Goldberg and Humayun, 2016). This unit is divided into two distinctive members, the Taquaral Member, located in the lower part of the Irati Formation, which includes dark-grey non-bituminous shales (Barbosa and Gomes, 1958), followed upwards by the Assistência Member comprising bituminous black shales intercalated with dolomites (Barbosa and Gomes, 1958). The intercalation between

dolomite and shale beds has higher rhythmicity in the northern and eastern parts of the Paraná Basin, being less predominant in the southern part of the Ponta Grossa arch (Hachiro et al., 1993; Hachiro, 1996). According to Holz et al. (2010), the Taquaral Member was deposited in a marine epicontinental to restricted environment (Reis et al., 2018), while the Assistência Member was originated in a vast and shallow sea where there was 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.

Several palynological studies performed in the Irati Formation assigned an Artinskian to Roadian age to this unit, based on the identification of the *Lueckisporites virkkiae* zone (Daemon and Quadros, 1970; Menéndez, 1976; Burjack, 1984; Marques-Toigo, 1988; Souza and Marques-Toigo, 2003, 2005; Felix et al., 2006; Santos et al., 2006; Premao et al., 2006; Calça and Fairchild, 2012). Macrofossils are also recorded in this unit, for instance, mesosaurid reptiles, plants, and crustacean fossils (Vasconcelos, 1973; Vieira et al., 1991; Ricardi-Branco et al., 2008). The age of the Irati Formation is also constrained by absolute dating, indicating a Kungurian age (e.g., 278.4 ± 2.2 Ma, 276.4 ± 3.7 Ma, 279.9 ± 4.8 Ma, 278.1 ± 3.4 Ma - SHRIMP zircon ages; Santos et al., 2006; Rocha-Campos et al., 2006, 2019).

The upper units of the Passa Dois Group are described in detail by Krebs and Menezes Filho (1984), Castro et al. (1994), and Holz et al.

Fig. 3. Vitti Quarry with Corumbataí Formation sample's location. A: Overview of open-pit mining front, where the Corumbataí Formation is exposed. B: Vertical sequence with the location of samples Vitti 1 and Vitti 2. C: Detail of sampled levels - centimetric shales interbedded with carbonates.

(2010). Black shales and siltstones with local calcareous lenses, concretions, and fossil-rich content composed of fish, pelecypods, and conchostrachans specimens comprise the Serra Alta Formation rocks which were conformably deposited over the Irati Formation. This unit was deposited in a calm marine environment below the fairweather wave base. The Teresina Formation was conformably deposited over the Serra Alta Formation and comprehends mudstones and shales, interbedded with sandstone beds, calcareous lenses, and concretions. This unit fossil content includes plant debris, lamellibranch, and palynomorphs (Neregato et al., 2008). The Teresina Formation was deposited in a marine environment marked by high energy shallow waters, which were dominated by wave and tidal processes. The following unit, the Rio do Rasto Formation, comprehends two members, the oldest Serinha Member, consisting of fine-grained sandstones and interbedded grey to red siltstones, mudstones, and local limestone lenses; and the Morro Pelado Member, consisting of red beds deposited in a continental environment. The fossil content includes pelecypods, conchostrachans, plant remains, and vertebrates, reaching the basal Lopingian age (Holz et al., 2010). At the top of the Rio do Rasto Formation, an erosive surface marks the passage to the overlying Botucatu Formation (Krebs and Menezes Filho, 1984; Castro et al., 1994; Holz et al., 2010).

The Teresina and Rio do Rasto formations were previously studied for palynology, and provided assemblages assigned to the *Lueckisporites virkkiae* Zone of Kungurian/Roadian age (common *Laevigatosporites vulgaris*) and Roadian/Wordian age (abundance of *Thymospora* spp.). Recent research published by di Pasquo et al. (2018) confirmed the Roadian/Wordian age for the Teresina Formation (Serra do Rio Rasto region, Santa Catarina State), indicating a Capitanian (?Lopingian) age for the Rio do Rasto Formation (Urubici region, southern Santa Catarina State). For the first time in the Paraná Basin, these authors identified palynomorph assemblages that include the following taxa: *Cladaitina veteadensis*, *Guttulapollenites hannonicus*, *Lophotriletes parryensis*, *Protolaploxyrinus microcorpus*, *Staurosaccites quadridifidus*, and *Weylandites cincinnatus*, extending the age range of the Rio do Rasto Formation to the earliest Lopingian.

The Corumbataí Formation, recognized in the northern part of the basin in the S. Paulo State, is considered an equivalent to the Serra Alta and Teresina formations (southern PB). This unit is fossil-rich, containing different fossil groups, such as pelecypods, conchostrachans, ostracods, macroflora remains (Cordaitales), bivalves (Pinzonella neotropica), scales and fish teeth. The palynostratigraphic studies in this

unit are scarce and indicate the *Lueckisporites virkkiae* Zone of Kungurian/Roadian age based on the presence of the taxa *Alisporites cf. nuthalensis*, *Corisaccites vanus*, *Limitisporites* sp., *Lueckisporites virkkiae*, and *Vittatina?* sp. (Daemon and Quadros, 1970; Maranhão, 1995).

In general, the Irati Formation presents a low degree of thermal evolution, ranging from 0.34% to 0.40% R_0 (Corrêa da Silva and Cornford, 1985); except in the basin depocenter where it can reach high values of maturation, ranging from 1.1 to 1.6% R_0 (Córdova-González et al., 2016; Souza et al., 2008) due to the influence of intrusive magmatic bodies (Arthur and Soares, 2002; Goldberg and Humayun, 2016; Hachiro, 1996; Milani et al., 2007; Silva, 2007).

3. Materials and methods

A total of thirty-four shale samples from the Irati Formation (Assistência Member) and from the lowermost part of Corumbataí Formation were collected and analyzed in this study (Fig. 1). The Irati Formation was sampled in detail, and thirty-two samples were collected from several outcrops (open-pit mines) and boreholes (core material) belonging to the Brazilian Geological Survey (*Companhia de Pesquisa de Recursos Minerais* – CPRM). The Corumbataí Formation was sampled in the Vitti Quarry in the São Paulo State (two samples). The sample's location is detailed below and its geographic coordinates are available in Fig. 1 and Appendix A.

3.1. Goiás State (GO)

In the northern part of the Paraná Basin, the Irati Formation outcrops in the State of Goiás (GO). A total of six samples were collected in two Montividiu municipality mining areas, Rio Verde (samples 572 to 579) and ELBA (samples 587 to 590), as well as from the Perolândia municipality, SUCAL mining area (samples 580 to 586). These samples comprise black shales with pyrite and siliceous nodules, which are intercalated by 10–30 cm dolomite beds. An igneous intrusion is also present in the sampled successions (Fig. 1).

3.2. São Paulo state (SP)

In the eastern part of the Paraná Basin in the São Paulo State, borehole FP-12-SP comprising the uppermost part of the Irati Formation (Assistência Member, Fig. 1), was selected for

palynostratigraphic sampling. The sampled lithologies are characterized by bituminous black shales, dark grey argillites, and grey shales intercalated by limestone beds.

In the São Paulo State, the Corumbataí Formation was also sampled in the Vitti Quarry (Figs. 1 and 3, samples Vitti-1, Vitti-2). In this region, this unit consists of mudstones, siltstones, and fine sandstones intercalated with dolomitic limestones.

3.3. Paraná State (PR)

In the southern part of the Paraná Basin, in the Paraná State, the Irati Formation was sampled in an open-pit mine in the São Mateus do Sul municipality (samples CCM-1, CCM-2, and CCM-3). The upper part of this unit in this area comprises bituminous black shales, dark grey shales, and associated limestones. The Irati Formation was sampled in the following boreholes: FP-01-PR, FP-02-PR, FP-03-PR, FP-04-PR, FP-07-PR, FP-11-PR, SP-29-PR, SP-37-PR, SP-47-PR, SP-49-PR, SP-55-PR (Fig. 1, Appendix A).

The analyzed palynological samples were treated with standard palynological laboratory procedures to extract and concentrate the organic residues (Wood et al., 1996; Riding and Warny, 2008). Fifteen of the thirty-four samples processed proved productive and were studied for palynology. The slides were analyzed using an optical light BX40 Olympus microscope equipped with an Olympus C5050 digital camera, as well as a Nikon eclipse Ci microscope. The palynomorph identification was based on its morphological features, and qualitative and quantitative analysis was carried out in this study. A total of 250 palynomorph specimens were counted per slide and the complete slide was scanned for rare taxa, which were then recorded as present but outside of the count. All samples, residues, and slides are held in the Palynological Collection of the Portuguese Geological Survey, LNEG, S. Mamede de Infesta, Portugal.

4. Palynological results

Biostratigraphic schemes used herein follow previous palynostratigraphic works of Souza and Marques-Toigo (2003, 2005), and Souza (2006). The recovered palynomorph assemblages are presented in Fig. 4, and stratigraphically significant palynomorphs are illustrated in Plates 1–3. Relative frequencies of selected groups obtained for each sample are presented in Fig. 5.

The quantitative and qualitative distribution of palynomorphs in the studied samples allow the identification of several assemblages based on the relative abundance of common taxa and the first occurrence of selected taxa distributed by the different states, Goiás State, Assemblage 1 (samples 583, 584, 589, 577, 581, 585, 587, 588), São Paulo State, Assemblage 1 (sample 658) and Assemblage 2 (sample Vitti-1), and Paraná State, Assemblage 1 (samples 660, 673, 675 and CCM-2) (Figs. 1 and 3, and Appendix A).

4.1. Goiás State

4.1.1. Assemblage 1 (samples 583, 584, 589, 577, 581, 585, 587, 588)

In general, the assemblage is characterized by a clear dominance of bisaccate taeniate pollen grains, excepting for sample 0588 where non-taeniate bisaccate pollen are prevailing. Pollen grains are very well preserved, in particular in samples 585 and 587.

The abundant and well preserved taeniate bisaccate pollen grains assemblage (35.3–90%) include the coniferopsida *Lueckisporites* complex (according to Vázquez and Césari, 2017 includes the genus *Lueckisporites*, *Corisaccites* and *Staurosaccites* and presents a wide morphological variation) that comprises in the studied assemblage, the taxa *Lueckisporites agoulaensis*, *L. densicarpus*, *L. latisaccus*, *L. stenotaeniatum*, *L. virkkiae*, *Corisaccites alutas*, *C. vanus*, *Staurosaccites cordubensis*, and *S. quadrifidus*, and the lyginopteridopsida *Protohaploxylinus* spp. (*P. amplus*, *P. bharadwajii*, *P. hartii*). Other abundant and complementary

species are present in the assemblage: *Lunatisporites variesectus*, *Lunatisporites* sp., *Marsupipollenites striatus*, *M. triradiatus*, *Striatoabieites multistriatus*, *Striatopodocarpites cancelatus*, *S. fusus*, *Tiwarisporites simplex*, *Vittatina* spp. (*V. costabilis*, *V. fasciolata*, *V. subsaccata*, *V. vittifera*), *Weylandites lucifer*, and *Weylandites magnus*.

The monosaccate pollen *Plicatipollenites gondwanensis* and *Potonieisporites novicus* are rare and are only present in samples 585 and 587 (0.7%). However, the percentage of non-taeniate bisaccate gymnosperm pollen like *Alisporites nuthallensis*, *Alisporites* sp., *Caheniasaccites flavatus*, *C. ovatus*, *Limitisporites hexagonalis*, *L. rectus*, and *Limitisporites* sp., varies more intensely throughout the samples (3.0%–62.5%) and is dominant in sample 588 (62.5%). Spores are very rare in this assemblage (0–0.7%) and include the pteridophyte fern *Convolutispora* sp. (samples 585 and 587, Fig. 4). Also, microplanktonic Chlorophyceae algae (e.g., *Brazileia scissa*, *Leiosphaeridia* sp., and algae clusters) are present in several samples and vary from rare to common (0.0–18.5%) (samples 583 and 587, Figs. 4 and 5).

4.2. Paulo State

4.2.1. Assemblage 1 (sample 658)

Sample 658 presents a very poorly preserved assemblage with a clear dominance of microplanktonic specimens which comprise approximately 70.8% of the assemblage (e.g., *Brazileia scissa*, *Leiosphaeridia* sp., and algae clusters). Important taxa include poorly preserved taeniate bisaccate pollen grains (29%), such as *Lueckisporites* spp., *Protohaploxylinus amplus*, *Staurosaccites quadrifidus*, and *Staurosaccites* spp., as well as scarce asaccate pollen grains like *Vittatina costabilis* (0.2%). Spores are absent in this assemblage, and very abundant amorphous organic matter was observed.

4.2.2. Assemblage 2 (sample Vitti-1)

This assemblage contains well preserved and characteristic taeniate bisaccate pollen grains (64.3%–82.7%), such as *Lueckisporites* complex (including *Lueckisporites agoulaensis*, *L. densicarpus*, *L. latisaccus*, *L. stenotaeniatum*, and *L. virkkiae*), *Protohaploxylinus* spp. (*P. amplus*, *P. bharadwajii*, *P. hartii*), and asaccate pollen grains (9.0%–15%) including, *Vittatina* spp. (*V. costabilis*, *V. fasciolata*, *V. subsaccata*, *V. vittifera*) and *Weylandites* spp. (*W. lucifer*, *W. magnus*). The following common taxa complete the assemblage: *Lunatisporites variesectus*, *Lunatisporites* sp., *Marsupipollenites striatus*, *Marsupipollenites triradiatus*, *Pakhapites fusus*, *Striatoabieites multistriatus*, *Striatopodocarpites cancelatus*, *Striatopodocarpites fusus*, and *Tiwarisporites simplex*. Scarce *Guttulapollenites hannonicus* and *Tornopollenites toreutos* are observed in sample Vitti-1. Monosaccate pollen are rare to absent (0%–1.3%), and bisaccate non-taeniate pollen grains (6.2%–13.3%) also occur in this assemblage (e.g., *Alisporites nuthallensis*, *Alisporites* sp., *Caheniasaccites flavatus*, *C. ovatus*, *Limitisporites hexagonalis*, *L. rectus*, and *Limitisporites* sp.). Fern spores are rare to absent (0%–0.7% of *Convolutispora* sp. in sample Vitti-1, Figs. 4 and 5), while microplanktonic and Chlorophyceae algae represent 2.1%–5.3% of the assemblage content, including *Brazileia scissa*, *Leiosphaeridia* sp., and indeterminate algae clusters (Figs. 4 and 5).

4.3. Paraná State

4.3.1. Assemblage 1 (samples 660, 673, 675, CCM-2)

The Paraná State palynological assemblages reveal poorly preserved material with a distinctive dominance of taeniate bisaccate pollen grains (57.4%–75.0%), excepting for sample 660 (17.5%) where Chlorophyceae algae dominate (82.5%). Only a few important specimens are identified, for instance the *Lueckisporites* complex (including *Lueckisporites densicarpus*, *L. latisaccus*, *L. virkkiae*, *Lueckisporites* spp., *Corisaccites alutas*, *Staurosaccites cordubensis*, *S. quadrifidus*, and *Staurosaccites* spp.), *Protohaploxylinus amplus*, as well as the asaccate pollen grains *Vittatina costabilis*, *V. subsaccata*, and *Weylandites lucifer*.

States Assemblages Samples	Irati Fm.								Irati Fm.	Corumbataí Fm.	Irati Fm.			
	Góias								S. Paulo		Paraná			
	Assemblage 1								Assemblage 1	Assemblage 2	Assemblage 1			
	583	584	589	577	581	585	587	588	658	Vitti-1	660	673	675	CCM-2
Pollen Grains														
<i>Alisporites nuthallensis</i>		•	•			•	•	•		•		•		
<i>Alisporites</i> sp.		•	•		•	•	•	•		•		•		•
<i>Caheniasaccites flavatus</i>								•		•				
<i>Caheniasaccites ovatus</i>								•		•				
<i>Corisaccites alutas</i>	•		•	•	•	•	•	•		•			•	•
<i>Corisaccites vanus</i>						•	•	•		•				
<i>Corisaccites</i> spp.							•	•		•				
<i>Guttulapollenites hannonicus</i>										•				
<i>Limistisporites hexagonalis</i>						•	•	•		•				
<i>Limistisporites rectus</i>						•	•	•		•				
<i>Limistisporites</i> sp.	•	•	•			•	•	•		•		•		
<i>Lueckisporites agoulaensis</i>						•	•	•		•				
<i>Lueckisporites densicarpus</i>								•				•		
<i>Lueckisporites latisaccus</i>						•	•	•		•				•
<i>Lueckisporites stenotaeniatus</i>														
<i>Lueckisporites virkiae</i>	•	•	•	•	•	•	•	•	•	•	•	•	•	•
<i>Lueckisporites</i> spp.	•	•	•	•	•	•	•	•	•	•	•	•	•	•
<i>Lunatisporites variesectus</i>						•	•	•		•				
<i>Lunatisporites</i> sp.						•	•	•		•				
<i>Marsupipollenites striatus</i>						•	•	•		•				
<i>Marsupipollenites triradiatus</i>						•	•	•		•				
<i>Plicatipollenites gondwanensis</i>								•						
<i>Plicatipollenites</i> sp.												•		
<i>Protahaploxypinus amplus</i>	•	•	•	•		•	•	•	•	•		•	•	•
<i>Protahaploxypinus bharadwajii</i>						•	•	•		•				
<i>Protahaploxypinus hartii</i>						•	•	•		•				
<i>Protahaploxypinus goraiesis</i>														
<i>Protahaploxypinus</i> sp.						•	•	•		•				
<i>Staurosaccites cordubensis</i>		•	•		•	•	•	•		•	•	•	•	•
<i>Staurosaccites quadrifidus</i>					•	•	•	•	•	•	•	•	•	•
<i>Staurosaccites</i> spp.	•	•	•	•	•	•	•	•	•	•	•	•	•	•
<i>Striatoabieites multistriatus</i>						•	•	•		•				
<i>Striatopodocarpites cancelatus</i>						•	•	•		•				
<i>Striatopodocarpites fusus</i>						•	•	•		•				
<i>Striatopodocarpites</i> cf. <i>gondwanensis</i>														
<i>Pakhapites fusus</i>										•				
<i>Potonieisporites novicus</i>								•				•		
<i>Potonieisporites</i> sp.												•		
<i>Tiwarisporites simplex</i>						•	•	•		•				
<i>Tornipollenites toreutos</i>										•				
<i>Vittatina costabilis</i>	•	•	•			•	•	•	•	•		•		•
<i>Vittatina fasciolata</i>						•	•	•		•				•
<i>Vittatina subsaccata</i>		•				•	•	•		•		•		•
<i>Vittatina vittifera</i>						•	•	•		•				
<i>Vittatina</i> spp.						•	•	•		•				
<i>Weylandites lucifer</i>			•			•	•	•		•		•		•
<i>Weylandites magnus</i>						•	•	•		•				
<i>Weylandites</i> spp.						•	•	•		•				
Spore														
<i>Convolutispora</i> spp.						•	•	•		•		•		•
<i>Cristatisporites</i> sp.												•		
<i>Kraeuselisporites</i> sp.												•		
<i>Leiotriletes</i> sp.												•		
<i>Lundbladispota</i> sp.												•		
<i>Punctatisporites</i> sp.												•		
<i>Verrucosisporites</i> sp.												•		
Algae														
<i>Botryococcus braunii</i>												•		
<i>Brazilea scissa</i>	•				•	•	•	•	•	•		•	•	•
<i>Leiosphaeridia</i> sp.	•	•	•		•	•	•	•	•	•	•	•	•	•
Algae cluster			•						•		•			

Fig. 4. Palynomorph assemblages recovered from the studied Irati Formation, Assistência Member, and Corumbataí Formation (Paraná Basin, Brazil).

The following non-taeniata bisaccate pollen grains are also present in this assemblage (9.0%–20.7%, samples 673, 675, and CCM-2, Figs. 4 and 5), *Alisporites nuthallensis*, *Alisporites* sp., and *Limistisporites* sp., and rare monosaccate pollen were identified in sample 673, including *Plicatipollenites* sp., *Potonieisporites novicus*, and *Potonieisporites* sp.. Rare to common trilete spores could be identified in samples 673 and CCM-2

(0.7%–6.7%), including the pteridopsida *Leiotriletes* sp., *Punctatisporites* sp., *Verrucosisporites* sp., and *Convolutispora* spp., as well as the lycopodiopsida *Cristatisporites* sp., *Kraeuselisporites* sp., and *Lundbladispota* sp. (Figs. 4 and 5).

Microplanktonic elements like Chlorophyceae algae and incertae algae clusters are common to abundant in all samples (6.7%–82.5%),

States	Goiás								S. Paulo		Paraná			
Formations	Irati Fm.								Irati Fm.	Corumbataí Fm.	Irati Fm.			
Assemblages	Assemblage 1								Assemblage 1	Assemblage 2	Assemblage 1			
Samples	583	584	589	577	581	585	587	588	658	Vitti-1	660	673	675	CCM-2
Spores	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.7	0.0	0.7	0.0	6.7	0.0	0.7
Monosaccate pollen	0.7	0.7	0.7	0.0	0.0	0.7	0.7	0.0	0.0	1.3	0.0	1.3	0.0	0.0
Non-taeniate bisaccate pollen	7.8	9.3	20.0	3.0	20.0	23.3	32.7	62.5	0.0	13.3	0.0	20.7	15.6	9.0
Taeniate bisaccate pollen	70.0	85.0	72.3	90.0	70.5	58.0	47.3	35.3	29.0	64.3	17.5	57.4	70.5	75.0
Assacate/Colpate pollen	3.0	4.3	3.0	0.0	0.0	11.3	8.0	2.2	0.2	15.0	0.0	5.3	0.0	5.3
Chlorophycean algae	18.5	0.7	4.0	7.0	9.5	6.0	10.7	0.0	70.8	5.3	82.5	6.7	14.0	10.0
<i>Botryococcus braunii</i>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0

Fig. 5. Relative frequencies of selected palynomorph groups in the studied assemblages (in %).

Fig. 6. Lithostratigraphic and palynostratigraphic taxa distribution of *Lueckisporites virkkiae* Zone established by Souza and Marques-Toigo (2005), and the selected species (bold) obtained in the studied Assistência Member (Irati Formation, Paraná Basin, Brazil). International Chronostratigraphic Chart (ICC), International Commission on Stratigraphy 2019/05.

and the occurrence of *Botryococcus braunii* (about 2%), in sample 673, is also worth noting. Phytoclasts and amorphous organic matter dominate the palynodebris recovered in samples 660 and 675.

5. Palynostratigraphic age interpretations

Assemblage 1, identified in this study for the Irati Formation (Assistência Member) in the Goiás, S. Paulo, and Paraná states, can be assigned to the *Lueckisporites virkkiae* Zone defined for the Paraná Basin by Souza and Marques-Toigo (2005) (Fig. 6). The assemblage indicates a Kungurian to Roadian age and is characterized by abundant taxa assigned to the *Lueckisporites* complex (including *Lueckisporites virkkiae*, *L. densicarpus*, *L. stenotaeniatum*, *Corisaccites* spp. and *Staurosaccites* spp.) and *Protahaploxylinus hartii*, together with common *Alisporites nuthallensis*, *Lunatisporites varisectus*, and *Weylandites lucifer*. Other stratigraphically important taxa such as *Lunatisporites*, *Protahaploxylinus*, and *Pakhapites* are present. The Goiás State palynological results confirm previous ages established by Premar et al. (2006).

The palynological data gathered in this study correlates well with the geochronological ages previously obtained for the Irati Formation (Paraná Basin), confirming that the base of the *Lueckisporites virkkiae* Zone is no older than Kungurian in age (e.g., 278.4 ± 2.2 Ma, 276.4 ± 3.7 Ma, 279.9 ± 4.8 Ma, 278.1 ± 3.4 Ma) (Santos et al., 2006; Rocha-Campos et al., 2006, 2019, Fig. 6), and can reach the Capitanian.

The palynological assemblage identified in the Corumbataí Formation (Assemblage 2), S. Paulo State, presents the typical species of the *Lueckisporites virkkiae* Zone, displaying a dominance of taeniate pollen grains of the following genera: *Lueckisporites* complex (*Lueckisporites*, *Corisaccites*, and *Staurosaccites*), *Lunatisporites*,

Protahaploxylinus, *Pakhapites* and *Weylandites*. Furthermore, *Tornopollenites toreutos* and *Guttulapollenites hannonicus* are rarely identified in this formation, and its occurrence could also be assigned to the *Lueckisporites virkkiae* Zone (Menéndez, 1976; Quadros et al., 1995; Mori, 2010; Mori and Souza, 2012, Fig. 6), confirming a Cisuralian-Guadalupian age for this formation.

The occurrence of *Tornopollenites toreutos* was already known from palynoassemblages of the Amazonas Basin, Brazil (*Tornopollenites toreutos* Zone; Playford and Dino, 2000a, 2000b), the Claromecó Basin, Argentina (*Tornopollenites toreutos*-*Reduviasporonites chalastus* Zone, Balarino, 2014; Gutiérrez et al., 2011), and Paraguay (Perez Loinaze et al., 2010, Figs. 6 and 7), to which it was assigned a Roadian to Guadalupian age.

The recognition of *Guttulapollenites hannonicus* in the Irati, Serra Alta, Teresina, and Rio do Rasto formations (Mori, 2010; Mori and Souza, 2012) highlights the stratigraphic difficulties and complexities of the Paraná Basin. Considering this work and related researches, the similarity of the palynoflora identified in the Irati and Corumbataí formations could suggest a lateral age correlation between the two formations.

6. Stratigraphical significance of the palynoflora and correlation with other main south American gondwana basins

In South American Gondwana basins, several palynostratigraphic studies were already developed throughout the years, resulting in well-established palynological schemes (e.g., Playford and Dino, 2000a, 2000b; Gutiérrez et al., 2003, 2011; 2018; Beri et al., 2011; Balarino, 2014; di Pasquo et al., 2015, 2018; Vázquez and Césari, 2017; Zavattieri et al., 2018). Moreover, recent data obtained by

Fig. 7. Palynological correlation with South American Gondwana basins. International Chronostratigraphic Chart (ICC), International Commission on Stratigraphy 2019/05.

- Plate 1. 1.** *Limitisporites hexagonalis* Bose and Maheshwari 1968; sample vitti, slide 2A_104, MC 1118/454;
- 2.** *Striatopodocarpites fusus* (Balme and Hennelly) Potonié 1958; sample 587, slide F3_108, MC 1157/170;
- 3.** *Guttulapollenites* cf. *hannonicus* Balme 1970; sample Vitti 1, slide D_54, MC 1165/100;
- 4.** *Lueckisporites agoulaensis* Jardiné 1974; sample 587, slide F2_121, MC 1296/134;
- 5.** *Tornopollenites toreutos* Morgan 1972; sample Vitti 1, slide E4_96, MC 1353/100;
- 6.** *Lueckisporites stenotaeniatus* Menéndez (1976); sample 587, slide 1_49, MC 973/388;
- 7.** *Lueckisporites stenotaeniatus* Menéndez (1976); sample 587, slide 1_55; MC 1046/390;
- 8.** *Lueckisporites stenotaeniatus* Menéndez (1976); sample 587, slide F1_55, MC 1407/207.

Plate 2. 1. *Lueckisporites densicarpus* Archangelsky and Gamero 1979; sample 587, slide F1_136, MC 1355/180;
2 - *Lueckisporites densicarpus* Archangelsky and Gamero 1979; sample Vitti 1, slide 2a_15, MC 1046/512;
3 - *Lueckisporites virkkiae* (Potonié and Klaus) Klaus 1963; sample 587, slide F2_25, MC 1340/198;
4 - *Lueckisporites virkkiae* (Potonié and Klaus) Klaus 1963; sample Vitti 1, slide 7D, MC 1275/68;
5 - *Lueckisporites virkkiae* (Potonié and Klaus) Klaus 1963; sample Vitti 1, slide F1_142, MC 1405/233;
6 - *Lueckisporites virkkiae* (Potonié and Klaus) Klaus 1963; sample Vitti 1, slide D_50, MC 1450/99;
7 - *Staurosaccites cordubensis* Archangelsky and Gamero 1979; sample vitti, slide cf2_159, MC 1225/75;
8 - *Staurosaccites quadrifidus* (Dolby) Dolby and Balme 1976; sample 587, slide F3_60, MC 1185/101;
9 - *Staurosaccites quadrifidus* (Dolby) Dolby and Balme 1976; sample Vitti 1, slide D_81, MC 1090/115;
10 - *Staurosaccites quadrifidus* (Dolby) Dolby and Balme 1976; sample Vitti 1, slide 2b_40, MC 1117/347.

geochronology has provided the basis to better constrain the Gondwana palynozones established for example in Brazil (following Souza and Marques-Toigo, 2005; Santos et al., 2006; Mori et al., 2012) and in Argentina (following Césari et al., 2011; Vázquez and Césari, 2017). Therefore, the assemblages characterized in this work can be correlated with palynological assemblages known for other Gondwana basins. This correlation is based on the first occurrence (FO) of selected taxa and abundances of characteristic species, in particular for the Kungurian-Roadian age interval (Fig. 7).

The most important palynoevents with a regional expression that are known for this age interval include, from base to top: the FO of *Lueckisporites virkkiae* of Kungurian/Roadian age, which is followed by the FO of *Tornipollenites toreutos*, *G. hannonicus*, and *Thymospora* spp., in the early Guadalupian, and finally, the abundant presence of *G. hannonicus* and *Cladaitina veteadensis*, which is recognized in palynological assemblages of late Guadalupian/early Lopingian age.

G. hannonicus was described in South America Gondwana basins ranging from the Guadalupian to the Lopingian. More specifically in

Brazil, its base range has been recorded since the middle Permian, in the Serra Alta and Rio do Rasto formations (Mori and Souza, 2012; di Pasquo et al., 2018). In this study, *G. hannonicus* was recorded together with *T. toreutos* (Assemblage 2) in the Corumbataí Formation assemblage, suggesting an earlier occurrence of these taxa during the Kungurian/Roadian (Mori, 2010; Mori and Souza, 2012).

Nevertheless, in Western Argentina, La Veteada Formation, the presence of *G. hannonicus* constitutes a well-defined Lopingian age stratigraphic record (Gutiérrez et al., 2018; Zavattieri et al., 2017, 2018). Even if the assemblages described from the La Veteada Formation also contain *Cladaitina veteadensis* and several other taxa that indicate an end-Permian palynofloral signature, these are not totally recognized in the Irati and the Corumbataí assemblages, suggesting an older age for the Paraná formations.

Likewise, *T. toreutos* was previously recognized in the Amazonas Basin by Playford and Dino (2000a, 2000b), in assemblages assigned a Guadalupian (Capitanian) to Lopingian age. This taxon is also documented from palynological assemblages recovered in the Tunas

Plate 3.1 - *Protohaploxypinus amplius* (Balme and Hennelly) Hart 1964; sample 587, slide 1_22, MC 1004/413;
 2 - *Protohaploxypinus goraiensis* (Potonié and Lele) Hart 1964; sample 673, slide 9B3_4, MC 935/130;
 3 - *Vittatina costabilis* Wilson 1962; sample Vitti 1, slide 2a_142, MC 1014/449;
 4 - *Vittatina costabilis* Wilson 1962; sample Vitti 1, slide c3_42, MC 1192/55;
 5 - *Vittatina fasciolata* (Balme y Hennelly) Bharadwaj 1962; sample Vitti 1, slide 2a_13, MC 1062/522;
 6 - *Vittatina vittifera* (Luber and Waltz) Samoilovich 1953; sample Vitti 1, slide F3_28, MC 1371/135;
 7 - *Weylandites lucifer* (Bharadwaj and Srivastava) Foster 1975; sample 587, slide F2_16, MC 1350/178;
 8 - *Weylandites lucifer* (Bharadwaj and Srivastava) Foster 1975; sample 587, slide F1_111, MC 1430/150;
 9 - *Weylandites lucifer* (Bharadwaj and Srivastava) Foster 1975; sample 587, slide 1_63, MC 1063/389;
 10 - *Marsupipollenites striatus* (Balme and Hennelly) Foster 1975; sample 587, slide F2_28, MC 1340/198;
 11 - *Marsupipollenites striatus* (Balme and Hennelly) Foster 1975; sample 587, slide 1_38, MC 1058/409;
 12 - *Marsupipollenites triradiatus* Balme and Hennelly 1956; sample Vitti 1, slide c3_76, MC 1122/80;
 13 - *Pakhapites fusus* (Bose and Kar) Menéndez 1971; sample Vitti 1, slide E/F2_87, MC 1444/90;
 14 - *Pakhapites fusus* (Bose and Kar) Menéndez 1971; sample 9B, slide F2_166, MC 1331/275.

Formation, Claromecó Basin, Argentina (Balarino, 2014), where the FO of *T. toreutos* marks the base of the *Tornopollenites toreutos*-*Reduviasporonites chalastus* Zone, of lower Guadalupian age. However, radiometric dating obtained from the Tunas Formation (280.8 ± 1.9 Ma, López-Gamundí et al., 2013; 282.4 ± 2.8 Ma, Tohver et al., 2008; 291.7 ± 2.9 Ma and 295.5 ± 8.0 Ma, Arzadún et al., 2018) raises doubts regarding the Guadalupian age assigned by the palynological data, as already suggested by Vázquez and Césari (2017). In the Paraná Basin, the occurrence of this taxon could suggest an earlier occurrence during the Cisuralian/Guadalupian boundary, since it is rare in the studied samples and the lithostratigraphic information of Quadros et al. (1995) is uncertain.

7. Irati and Corumbataí formations environmental interpretation

Schneider et al. (1974) suggest a marine environment below the fairweather wave base for the deposition of the Irati Formation. However, in this study, the absence of marine palynomorphs, as well as the dominance of taeniate pollen grains, the presence of fresh to brackish water algae specimens, and scarce spores in the studied samples suggest deposition in a shallow marine environment close to the shoreline as the influx of freshwater and terrestrial material in the assemblages is considerable. The record of *Botryococcus braunii*, already described by Corrêa da Silva and Cornford (1985) and De Castro (1988) for the Irati Formation (Paraná Basin) can also support these authors interpretation of a shallow and low energy lacustrine depositional regime (following Traverse, 1992). The record of amorphous organic matter and fram-boidal pyrite in the studied samples also supports the idea of deposition

in shallow and anoxic environments.

Deposition in a shallow marine environment in anoxic conditions for the lowermost part of the Corumbataí Formation is the interpretation provided by Schneider et al. (1974). This interpretation highlights the similitude between the depositional environments and the palynofloras found in the Irati and the Corumbataí formations, pointing a dominance of taeniate bisaccate pollen grains (e.g., *Protohaploxypinus*, *Striatopodocarpites*, *Guttulapollenites hannonicus*, and *Tornopollenites toreutos*), scarce spores and rare fresh to brackish water algae elements.

8. Conclusions

The palynostratigraphic data from the Paraná Basin, Brazil, obtained for the Irati Formation in the Goiás, S. Paulo, and the Paraná states can be correlated with the *Lueckisporites virkkiae* Zone of Kungurian to Roadian age (Cisuralian/Guadalupian age). These data confirm previous palynological studies done in the Paraná Basin, as well as previous U–Pb geochronology ages obtained for this unit. Likewise, the lowermost part of the Corumbataí Formation, in the Paraná Basin, allowed the identification of the *Lueckisporites virkkiae* Zone of Kungurian/Roadian age. These assemblages are similar to the palynofloras recorded from the Irati Formation, with rare exceptions of *Guttulapollenites hannonicus* and *Tornopollenites toreutos*.

The dominance of taeniate pollen grains and the presence of fresh to brackish water algae specimens, suggests a deposition in a shallow marine environment, close to the shoreline, highlighted by the influx of freshwater and the presence of considerable terrestrial material in the assemblages.

The new palynological data contributes to the development of a better stratigraphic framework for future unconventional hydrocarbons source rocks and CO₂ geological storage assessment and exploitation in the Paraná Basin.

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.

List of taxa

Spores

Convolutispora spp.

Cristatisporites sp.

Kraeuselisporites sp.

Leiotriletes sp.

Lundbladispora sp.

Punctatisporites sp.

Verrucosisporites sp.

Pollen grains

Alisporites nuthallensis Clarke 1965

Alisporites sp.

Caheniasaccites flavatus Bose and Kar emend. Azcuy and di Pasquo 2000

Caheniasaccites ovatus Bose and Kar 1966

Corisaccites alutas Venkatachala and Kar 1966

Corisaccites vanus Venkatachala and Kar 1966

Corisaccites spp.

Guttulapollenites hannonicus Balme 1970

Limitisporites hexagonalis Bose and Maheshwari 1968

Limitisporites rectus Leschik 1956

Limitisporites sp.

Lueckisporites agoulaensis Jardiné 1974

Lueckisporites densicarpus Archangelsky and Gamero 1979

Lueckisporites latisaccus Archangelsky and Gamero 1979

Lueckisporites stenotaeniatus Menéndez 1976

Lueckisporites virkkiae (Potonié and Klaus) Klaus 1963

Lueckisporites spp.

Lunatisporites variesectus Archangelsky and Gamero 1979

Lunatisporites sp.

Marsupipollenites striatus (Balme and Hennelly) Foster 1975

Marsupipollenites triradiatus Balme and Hennelly 1956

Pakhapites fusus (Bose and Kar) Lele 1964

Plicatipollenites sp.

Potonieisporites novicus Bhardwaj emend. Poort and Veld 1997

Potonieisporites sp.

Protohaploxylinus amplus (Balme and Hennelly) Hart 1964

Protohaploxylinus bharadwajii Foster 1979

Protohaploxylinus hartii Foster 1979

Protohaploxylinus goraiensis (Potonié and Lele) Hart 1964

Protohaploxylinus spp.

Staurosaccites cordubensis Archangelsky and Gamero 1979

Staurosaccites quadrifidus Dolby in Dolby and Balme 1976

Staurosaccites spp.

Striatoabieites multistriatus (Balme and Hennelly) Hart 1964

Striatopodocarpites cancellatus (Balme and Hennelly) Hart 1964

Striatopodocarpites fusus (Balme and Hennelly) Potonié 1958

Tiwarisporites simplex (Tiwari) Maheshwari and Kar 1967

Tornopollenites toreutos Morgan 1972

Vittatina costabilis Wilson 1962

Vittatina fasciolata (Balme and Hennelly) Bharadwaj 1962

Vittatina subsaccata Samoilovich 1953

Vittatina vittifera (Luber and Waltz) Samoilovich 1953

Vittatina spp.

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Weylandites lucifer (Bharadwaj and Srivastava) Foster 1975

Weylandites magmus (Bose and Kar) Backhouse 1991

Weylandites spp.

Chlorophycean algae

Botryococcus braunii Kützing 1849

Brazilea scissa (Balme and Hennelly) Foster 1975

Leiosphaeridia sp.

Appendix A. Sample locations list description (State, Municipality and UTM Coordinates). Bold sample references indicates the productive samples for palynology

Lab ID	Sample ID	Outcrop Sample	Borehole	Depth (m)	Formation	State	Municipality	Coordinates (E, N)	
UTM ZONE 22 L									
15	583	x			Irati	Goiás (GO)	Perolândia	393552.3	8120173.4
16	584	x			Irati	Goiás (GO)	Perolândia	393552.3	8120173.4
22	581	x			Irati	Goiás (GO)	Perolândia	393552.3	8120173.4
23	582	x			Irati	Goiás (GO)	Perolândia	393552.3	8120173.4
24	585	x			Irati	Goiás (GO)	Perolândia	393552.3	8120173.4
14	579	x			Irati	Goiás (GO)	Montividiu	606447.7	8120173.4
17	589	x			Irati	Goiás (GO)	Montividiu	500000	8120445
20	574	x			Irati	Goiás (GO)	Montividiu	606447.7	8120173.4
21	577	x			Irati	Goiás (GO)	Montividiu	606447.7	8120173.4
25	587	x			Irati	Goiás (GO)	Montividiu	500000	8120445
26	588	x			Irati	Goiás (GO)	Montividiu	500000	8120445
UTM ZONE 22 K									
1	658		FP-12-SP	274.2	Irati	São Paulo (SP)	Anhembi	780500	7480600
27	659		FP-12-SP	274.38	Irati	São Paulo (SP)	Anhembi	780500	7480600
19	Vitti-1	x			Corumbataí	São Paulo (SP)	Saltinho	423974.7	4794350.7
34	Vitti-2	x			Corumbataí	São Paulo (SP)	Saltinho	423974.7	4794350.7
UTM ZONE 22 J									
2	660		FP-11-PR	351.34	Irati	Paraná (PR)	Ortigueira	52110	733800
7	668		FP-04-PR	185.61	Irati	Paraná (PR)	Ortigueira	507000	7318000
3	662		FP-01-PR	194.5	Irati	Paraná (PR)	Ibati	562000	7384500
4	663		FP-01-PR	195.07	Irati	Paraná (PR)	Ibati	562000	7384500
30	664		FP-01-PR	196.95	Irati	Paraná (PR)	Ibati	562000	7384500
31	665		FP-01-PR	197.45	Irati	Paraná (PR)	Ibati	562000	7384500
5	666		FP-02-PR	122.8	Irati	Paraná (PR)	Sapopema	541200	7363700
6	667		FP-03-PR	227.16	Irati	Paraná (PR)	Sapopema	534100	7359200
9	673		SP-29-PR	340.65	Irati	Paraná (PR)	Sapopema	541258	7369810
10	675		SP-37-PR	213.72	Irati	Paraná (PR)	Sapopema	548201	7369295
11	676		SP-47-PR	241.74	Irati	Paraná (PR)	Sapopema	547500	7370615
12	679		SP-49-PR	373.27	Irati	Paraná (PR)	Sapopema	558189	7378836
13	681		SP-55-PR	477	Irati	Paraná (PR)	Sapopema	546150	7371080
33	680		SP-49-PR	373.4	Irati	Paraná (PR)	Sapopema	558189	7378836
8	669		FP-07-PR	81.07	Irati	Paraná (PR)	S. Mateus do Sul	55610	713930
18	CCM-2	x			Irati	Paraná (PR)	S. Mateus do Sul	562239	7136074
28	CCM-1	x			Irati	Paraná (PR)	S. Mateus do Sul	559453	7142580
29	CCM-3	x			Irati	Paraná (PR)	S. Mateus do Sul	557652	7147058
32	672		FP-07-PR	95.45	Irati	Paraná (PR)	S. Mateus do Sul	55610	713930

Authorship statement

All persons who meet authorship criteria are listed as authors, and all authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in the concept, design, analysis, writing, or revision of the manuscript. Furthermore, each author certifies that this material or similar material has not been and will not be submitted to or published in any other publication before its appearance in the Journal of South American Earth Sciences.

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REQUISIÇÃO: 345/2020/DRX

Registro de entrada: 0939/20

Dados do cliente

Cliente COLOMBO CELSO GAETA TASSINARI

Projeto FUSP 000036 RCGI_PROJETO 36: ARMAZENAMENTO DE CARBONO EM RESERVATÓRIOS GEOLÓGICOS NO BRASIL: PERSPECTIVAS PARA CCS EM RESERVATÓRIOS DE PETRÓLEO NÃO CONVENCIONAIS "ONSHORE" E DE BACIAS SEDIMENTARES "OFFSHORE" DO SUDESTE DO BRASIL.

Dados gerais

Data de início 25/11/2020 **Prazo de entrega** 09/12/2020

Responsável técnico Gaspar Darin Filho

Método analítico CDRX - Obtenção de difratogramas

Equipamento DRX-04 - Panalytical - Empyrean

Tubo	Tensão (kV/mA)	Ângulo inicial (°)	Ângulo final (°)	Passo angular (°)	Tempo por passo (s)	Configuração
Cu	45-40	2.5	70.0	0.02	150.00	Normal

Recipiente pulverização Planetário aço-cromo (seco)

Amostras

ID LCT	ID Cliente	Método analítico
6968/2020	4	CDRX - Obtenção de difratogramas

RESULTADO DE IDENTIFICAÇÃO DE FASES POR DIFRATOMETRIA DE RAIOS X

RELATÓRIO: DRX 764/20

DATA: 14/12/2020

CLIENTE: COLOMBO CELSO GAETA TASSINARI

AMOSTRA: 1

IDENT. LCT: 343-6965.HPF

1. MÉTODO

O estudo foi efetuado através do método do pó, mediante o emprego de difratômetro de raios X com detector sensível a posição.

A identificação das fases cristalinas, abaixo discriminadas, foi obtida por comparação do difratograma da amostra com os bancos de dados PDF2 do ICDD - International Centre for Diffraction Data e ICSD – Inorganic Crystal Structure Database.

2. RESULTADOS

Os resultados obtidos estão listados na tabela abaixo:

ICDD	Mineral	Fórmula Química	Obs
00-029-1491	Esmectita	$\text{Ca}_{0,2}\text{Mg}_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	
00-025-0645	Serpentina	$\text{Mg}_3(\text{Si}_{2-x}\text{O}_5)(\text{OH})_{4-4x}$	
98-001-1979	Muscovita	$\text{K}(\text{Al}_{1,91}\text{Fe}_{0,09})(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$	
00-029-1493	Talco	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	

O difratograma obtido (cor vermelha), onde são assinaladas as linhas de difração correspondente(s) à(s) fase(s) identificada(s) (cada fase em uma cor distinta) é apresentado anexo.

Executado por: M.Sc. Gaspar Darin Filho (14/12/2020 13:28 BRT)

Revisado por: Dra. Juliana Lívi Antoniassi (15/12/2020 15:18 BRT)

Prof. Dra. Carina Ulsen
Coordenadora do LCT - Poli/USP

NOTA: Os resultados expostos acima referem-se apenas à(s) amostra(s) enviada(s) ao LCT; a representatividade da(s) mesma(s) é de inteira responsabilidade do cliente.

Verifique a autenticidade deste documento em www.lct.poli.usp.br utilizando o código **NJRX-IKVM-PHCD-CVYB**

DIFRATOGRAMA DE RAIOS X

FASES IDENTIFICADAS

RESULTADO DE IDENTIFICAÇÃO DE FASES POR DIFRATOMETRIA DE RAIOS X

RELATÓRIO: DRX 765/20

DATA: 14/12/2020

CLIENTE: COLOMBO CELSO GAETA TASSINARI

AMOSTRA: 2

IDENT. LCT: 344-6966.HPF

1. MÉTODO

O estudo foi efetuado através do método do pó, mediante o emprego de difratômetro de raios X com detector sensível a posição.

A identificação das fases cristalinas, abaixo discriminadas, foi obtida por comparação do difratograma da amostra com os bancos de dados PDF2 do ICDD - International Centre for Diffraction Data e ICSD – Inorganic Crystal Structure Database.

2. RESULTADOS

Os resultados obtidos estão listados na tabela abaixo:

ICDD	Mineral	Fórmula Química	Obs
01-086-1560	Quartzo	SiO ₂	
01-071-0053	Pirita	FeS ₂	
98-005-7049	Albita	(Na _{0,98} Ca _{0,02})(Al _{1,02} Si _{2,98} O ₈)	
01-072-1503	Muscovita	KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂	
00-003-0015	Esmectita	(Na,Ca) _{0,3} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ H ₂ O	
98-004-5719	Microclínio	K(AlSi ₃ O ₈)	
01-075-1593	Caulinita	Al ₂ Si ₂ O ₅ (OH) ₄	pp

Nota: pp = possível presença

O difratograma obtido (cor vermelha), onde são assinaladas as linhas de difração correspondente(s) à(s) fase(s) identificada(s) (cada fase em uma cor distinta) é apresentado anexo.

Executado por: M.Sc. Gaspar Darin Filho (14/12/2020 17:20 BRT)

Revisado por: Dra. Juliana Lívi Antoniassi (14/12/2020 18:47 BRT)

Prof. Dra. Carina Ulsen
Coordenadora do LCT - Poli/USP

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DIFRATOGRAMA DE RAIOS X

FASES IDENTIFICADAS

RESULTADO DE IDENTIFICAÇÃO DE FASES POR DIFRATOMETRIA DE RAIOS X

RELATÓRIO: DRX 766/20

DATA: 14/12/2020

CLIENTE: COLOMBO CELSO GAETA TASSINARI

AMOSTRA: 3

IDENT. LCT: 344-6967.HPF

1. MÉTODO

O estudo foi efetuado através do método do pó, mediante o emprego de difratômetro de raios X com detector sensível a posição.

A identificação das fases cristalinas, abaixo discriminadas, foi obtida por comparação do difratograma da amostra com os bancos de dados PDF2 do ICDD - International Centre for Diffraction Data e ICSD – Inorganic Crystal Structure Database.

2. RESULTADOS

Os resultados obtidos estão listados na tabela abaixo:

ICDD	Mineral	Fórmula Química	Obs
01-086-1560	Quartzo	SiO ₂	
01-071-0053	Pirita	FeS ₂	
98-005-7049	Albita	(Na _{0,98} Ca _{0,02})(Al _{1,02} Si _{2,98} O ₈)	
01-072-1503	Muscovita	KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂	
01-076-0902	Analcima	NaAlSi ₂ O ₆ (H ₂ O)	
01-075-1593	Caulinita	Al ₂ Si ₂ O ₅ (OH) ₄	pp

Nota: pp = possível presença

O difratograma obtido (cor vermelha), onde são assinaladas as linhas de difração correspondente(s) à(s) fase(s) identificada(s) (cada fase em uma cor distinta) é apresentado anexo.

Executado por: M.Sc. Gaspar Darin Filho (14/12/2020 17:20 BRT)
Revisado por: Dra. Juliana Lívi Antoniassi (14/12/2020 18:47 BRT)

Prof. Dra. Carina Ulsen
Coordenadora do LCT - Poli/USP

NOTA: Os resultados expostos acima referem-se apenas à(s) amostra(s) enviada(s) ao LCT; a representatividade da(s) mesma(s) é de inteira responsabilidade do cliente.

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DIFRATOGRAMA DE RAIOS X

FASES IDENTIFICADAS

Equação de Langmuir

P (psi)	VL	PL	V (sfc/ton)
41.16	387.13	1026.01	14.93
125.05	387.13	1026.01	42.06
222.58	387.13	1026.01	69.01
323.32	387.13	1026.01	92.76
434.16	387.13	1026.01	115.11
520.68	387.13	1026.01	130.32

Curva Isotérmica

P (psi)	Isotérmica
41.16	14.93
125.05	42.06
222.58	69.01
323.32	92.76
434.16	115.11
520.68	130.32

Equação de Langmuir

P (psi)	VL	PL	V (sfc/ton)
42.38	299.54	953.23	12.75
119.49	299.54	953.23	33.36
249.23	299.54	953.23	62.08
381.85	299.54	953.23	85.67
500.38	299.54	953.23	103.11

Curva Isotérmica

P (psi)	Isotérmica
42.38	12.75
119.49	33.36
249.23	62.08
381.85	85.67
500.38	103.11

Equação de Langmuir

P (psi)	VL	PL	V (sfc/ton)
43.85	65.50	525.78	5.04
114.74	65.50	525.78	11.73
274.88	65.50	525.78	22.49
414.10	65.50	525.78	28.86
559.78	65.50	525.78	33.77

Curva Isotérmica

P (psi)	Isotérmica
43.85	5.04
114.74	11.73
274.88	22.49
414.10	28.86
559.78	33.77

Equação de Langmuir

P (psi)	VL	PL	V (sfc/ton)
44.38	180.45	1521.86	5.11
115.05	180.45	1521.86	12.68
253.54	180.45	1521.86	25.77
375.44	180.45	1521.86	35.71
502.32	180.45	1521.86	44.78

Curva Isotérmica

P (psi)	Isotérmica
44.38	5.11
115.05	12.68
253.54	25.77
375.44	35.71
502.32	44.78

Equação de Langmuir

P (psi)	VL	PL	V (sfc/ton)
79.23	217.29	595.08	25.53
194.97	217.29	595.08	53.62
345.24	217.29	595.08	79.78
495.84	217.29	595.08	98.76
596.80	217.29	595.08	108.80

Curva Isotérmica

P (psi)	Isotérmica
79.23	25.53
194.97	53.62
345.24	79.78
495.84	98.76
596.80	108.80

Equação de Langmuir

P (psi)	VL	PL	V (sfc/ton)
44.26	199.57	1607.09	5.35
114.40	199.57	1607.09	13.26
274.49	199.57	1607.09	29.11
408.65	199.57	1607.09	40.46
554.21	199.57	1607.09	51.17

Curva Isotérmica

P (psi)	Isotérmica
44.26	5.35
114.40	13.26
274.49	29.11
408.65	40.46
554.21	51.17

Equação de Langmuir

P (psi)	VL	PL	V (sfc/ton)
40.37	11.60	26.77	6.98
109.27	11.60	26.77	9.32
252.59	11.60	26.77	10.49
383.37	11.60	26.77	10.85
502.48	11.60	26.77	11.02

Curva Isotérmica

P (psi)	Isotérmica
40.37	6.98
109.27	9.32
252.59	10.49
383.37	10.85
502.48	11.02

Equação de Langmuir

P (psi)	VL	PL	V (sfc/ton)
112.15	15.18	31.13	11.88
219.42	15.18	31.13	13.29
365.49	15.18	31.13	13.98
500.13	15.18	31.13	14.29
607.90	15.18	31.13	14.44
703.86	15.18	31.13	14.53

Curva Isotérmica

P (psi)	Isotérmica
112.15	11.88
219.42	13.29
365.49	13.98
500.13	14.29
607.90	14.44
703.86	14.53

Equação de Langmuir

P (psi)	VL	PL	V (sfc/ton)
45.41	18.47	211.06	3.27
114.86	18.47	211.06	6.51
271.25	18.47	211.06	10.39
405.42	18.47	211.06	12.15
605.42	18.47	211.06	13.70

Curva Isotérmica

P (psi)	Isotérmica
45.41	3.27
114.86	6.51
271.25	10.39
405.42	12.15
605.42	13.70

Equação de Langmuir

P (psi)	VL	PL	V (sfc/ton)
78.56	76.88	116.64	30.94
194.54	76.88	116.64	48.06
342.53	76.88	116.64	57.35
525.89	76.88	116.64	62.92
655.96	76.88	116.64	65.27

Curva Isotérmica

P (psi)	Isotérmica
78.56	30.94
194.54	48.06
342.53	57.35
525.89	62.92
655.96	65.27