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CHARACTERIZATION OF THE ASSISTÊNCIA MEMBER, IRATI FORMATION, PARANÁ BASIN, BRAZIL: ORGANIC MATTER AND MINERALOGY

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Abstract

Currently, the Irati Formation, in Paraná Basin, Brazil, represents one of the world's largest reserves of oil shale. Among the shale-derived products stands out the fuel oil, gas, naphtha, fuel, liquefied gas, and sulfur, in addition to byproducts that can be used by the asphalt, cement, agricultural, and ceramics industries. This study describes and illustrates features of organic-rich shales of the Lower Permian Assistência Member, Irati Formation, scanning electron microscopy (SEM) was combined with energy-dispersive X-Ray Spectrometry (EDS), X-Ray Diffraction (XRD), total organic carbon (TOC), total sulfur (S), insoluble residue (IR) and Rock-Eval pyrolysis to characterize the mineral composition, organic matter distribution and different types of pore at the micrometric scale. These analyses were performed on samples from well SP-32-PR located in the Sapopema township, Northeast Paraná State, in South of Brazil. The investigations demonstrated that the Assistance Member has high total organic carbon (TOC) content, generation potential (S2) and hydrogen index (HI), but is in an immature stage. The mineralogical content of the Assistência Member presents intervals rich in quartz, plagioclase, carbonates and clay minerals. Pores distribution includes intraparticle within organic matter and interparticle pores in pyrite framboids, surrounding quartz grains and between organic matter and mineral grains.

Keywords: Organic-rich shale. X-Ray Spectrometry (EDS). X-Ray Diffraction (XRD). Organic geochemistry. Rock-Eval pyrolysis.

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1 Introduction

The Irati Formation (Lower Permian of the Paraná Basin, Brazil) is one of the most studied geological formations among Brazilian sedimentary formations, due to its unique fossil-bearing occurrences and highs values of organic matter recorded on shales. In the past few years, the search for alternative sources of raw materials has been concentrated on shale deposits. These rocks with high organic content often represent important source rocks for oil exploration. Unconventional oil and shale gas reshaped the future energy of the planet. It has been suggested that these reserves can cover the energy needs of humanity for at least the next 135 years (Conti et al., 2011).

Recent exploration technology advances (horizontal drilling and hydraulic fracture) have opened vast new oil and natural gas sources in shale formations. The U.S Energy Information Administration (EIA) estimates that about 15.8 trillion cubic feet of dry natural gas was produced directly from shale in the United States in 2016. This was about 60% of total dry natural gas. Shale gas production has also been established in Canada, and initial exploration drilling has begun outside North America, most notably in Poland, Argentina, India, Australia and China (Camp et al., 2013).

In Brazil, PETROBRAS has been operating an industrial plant to explore hydrocarbons from organic-rich shale of Irati Formation. At the beginning, the Petrosix® process was established as a pilot plant in 1991, which includes procedures for mining, crushing and thermochemical processing (pyrolysis) of the organic-rich shale. Among the shale-derived products (byproducts) are fuel oil, gas, naphtha, fuel, liquefied gas, and sulfur, which in addition can be used to manufacture asphalt, cement, agricultural, and ceramics industries. According to Maraschin and Ramos (2015), the plant processes 7800 tons/day, resulting 3870 barrels of oil, 120 tons of gas, 45 tons of liquid gas and 75 tons of sulfur.

Historically, shales were thought to perform two key functions in petroleum systems: seal for conventional reservoirs and act as a source rock for hydrocarbons. Recently, several shale formations have also proven to be major self-sourcing hydrocarbon reservoirs (Driskill et al., 2013).

Because of their extremely fine grain size, shale is difficult to be observed and described using conventional optical microscope techniques. However, the high magnification capability of electron microscopy allows the study of fine-scale rock features. Recent advances in electron microscopy technology have resulted in improved images and analytical methods to better describe, evaluate and understand shale hydrocarbon reservoir. Scanning electron microscopy (SEM) is a standard technique for identify nanometer and micrometer scale features of shales. Shale fabric at these scales provides substantial information about the origin, sedimentary and diagenetic processes, organic matter distribution and pore networks (Slatt and O'brien, 2013).

Only a few studies were performed to analyze the exploratory potential of shales in Brazil (Dyni, 2006; Ramos, 2014; Maraschin and Ramos, 2015). These studies suggested that the Irati Formation is one of the main formations of the Brazilian basins with exploratory potential for shale gas and oil. Therefore, the purpose of this study is to document the primary constituents, like organic matter distribution and pore types of the Irati Formation, in the Sapopema area, located at Northeast of Paraná State, southeast of Brazil.

2. Study Area: Geologic Settings

The study area is within the tectonic and stratigraphic context of Parana Basin, a Paleozoic syneclise composed of magmatic and sedimentary rocks with ages ranging from Ordovician to Cretaceous (Zalán et al., 1991). According to Milani et al. (2007), the stratigraphic record of the basin is divided into six tectonic sequences separated by interregional unconformities: the Ivaí River (Ordovician Silurian), Paraná (Devonian), Gondwana I (Carboniferous Lower Triassic), Gondwana II (Middle to Upper Triassic), Gondwana III (Upper Jurassic-Lower Cretaceous), and Bauru (Upper Cretaceous). It covers the Brazilian meridional portions and part of Paraguay, Argentina and Uruguay, with a total area of approximately 1.4 million km² (Fig. 1).

The Irati Formation was deposited during the Gondwana I tectonic sequence, in the Permian, Artinskian age (Santos et al., 2006). It is the basal part of the Passa Dois Group and extends almost throughout the Paraná Basin. It has an average thickness of 40 m, with local peaks of about 70 m (Holz et al., 2010); it occurs in the subsurface and is exposed in outcrops around the eastern edge of the basin.

According to Holz et al. (2010), the Irati Formation is divided into the lower Taquaral Member, comprising siltstones and gray mudstones, and the upper Assistência Member, formed by organic-rich shales interbedded with limestones. The Taquaral Member was deposited in a shallow marine environment (Epicontinental Sea) with restricted connection to the open ocean, and with relatively good (better) water circulation compared to the overlying Assistência Member. The depositional system of the Assistência Member includes internal, intermediary and distal ramps tilted to southwest, suggesting a possible connection to the Panthalassa Ocean only at the southernmost region of South America. Relatively deeper depositional conditions are interpreted in southern parts of the basin, which organic-rich shales predominate and total organic carbon (TOC) reaches values as high as 23% (Milani et al., 2006).

Despite the high TOC contents, the Irati Formation is thermally immature in most of the Paraná Basin. Several

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JSE
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authors (e.g. Milani and Zalán,1999; Araújo et al., 2000; Correa and Pereira, 2005; Costa et al., 2016) emphasized the role of the heat effect deriving from the diabase sills in the maturation of organic matter present in the shales.

In this way, the main petroleum system of the Parana Basin, Irati-Rio Bonito/Piramboia, is defined as a non-conventional petroleum system (Milani et al., 2006).

Based on biomarkers and isotope data, Loutfi (2011) has shown a very good correlation between the oil samples recovered from Rio Bonito Formation and the organic extract from organic rich shales of Assistência Member, of Irati Formation. Other authors (Cabral, 2006; Serafim, 2011; Vital, 2012) also found a good correlation between the oil extracted from the Piramboia oil sands and the shales of Irati Formation.

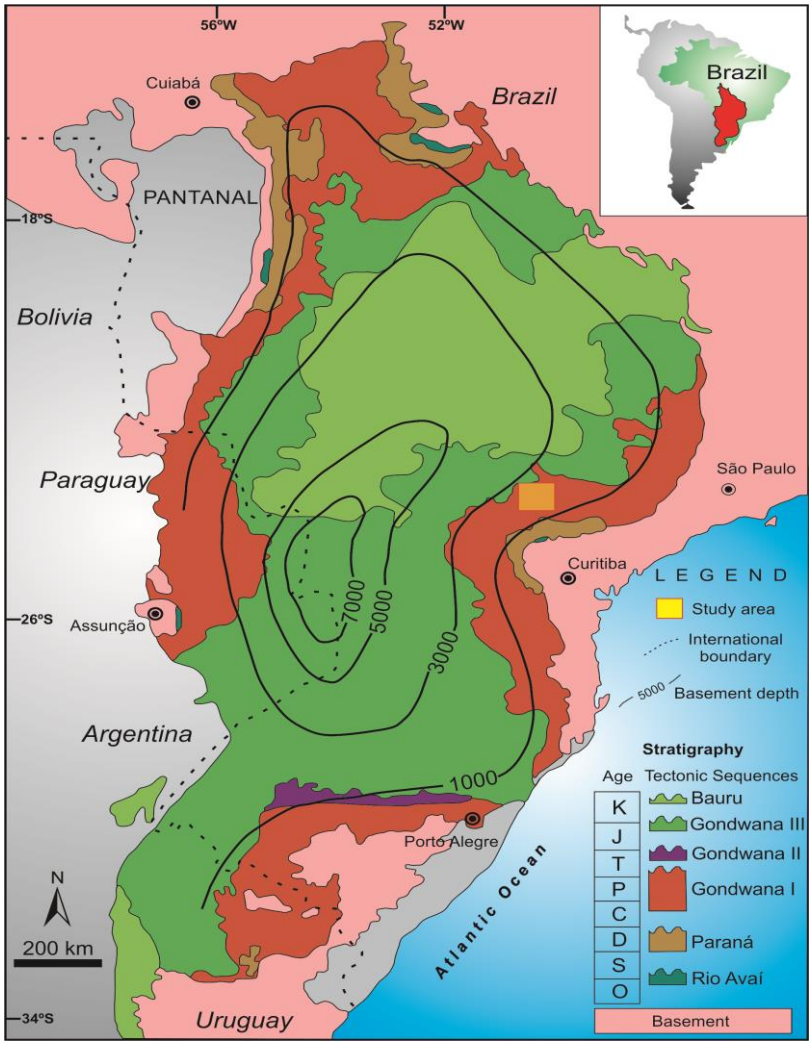

Fig. 1. Location and simplified geological map of the Paraná Basin. Modified from Zalán et al. (1991) and Costa et al. (2016).

3. Materials and Methods

The analyzed samples in this study belong to the SP-32-PR core collected in Sapopema township, Northeast of Paraná State, southeast of Brazil (UTM coordinates 7368384N; 548618E). This region was studied in the past due to the occurrence of continuous coal layers, which led to drill news exploratory wells in the area, made by the Brazilian Geologic Survey (CPRM).

The 11 samples were analyzed in this study area and refer to the Assistência Member from well SP-32-PR. Rock samples were cut and prepared for scanning electron microscopic (SEM) analysis. They were also analyzed by energy-dispersive X-Ray Spectrometry (EDS), X-Ray Diffraction (XRD), total organic carbon (TOC), total sulfur (S), insoluble residue (IR) and Rock-Eval pyrolysis.

3.1 Organic geochemistry data

The samples collected along the SP-32-PR core (between 141.5 m and 180.8 m) were submitted to geochemical analysis, including total organic carbon (TOC), total sulfur (S), insoluble residue (IR) and Rock- Eval pyrolysis. Geochemical analyzes were performed at the "Laboratório de Estratigrafia Química e Geoquímica Orgânica" (Chemostratigraphy and Organic Geochemistry

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JSE
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Laboratory), of Universidade do Estado do Rio de Janeiro (LGQM/DEPA/FGEL/UERJ). The applied procedures are described in the following sub-items.

The samples were analyzed with the Leco SC-632 equipment. The first step was the elimination of carbonates using 50% hydrochloric acid. The TOC, S and IR values were plotted against the core depth. The depth plots allowed to make a semi-quantitative assessment of organic matter concentration in the analyzed sedimentary layers.

Selected samples were analyzed with the Rock-Eval 6 equipment, of Vinci Technologies, for the determination of S1 values (in mg HC/g rock), S2 (in mg HC/g rock) and the temperature at which occurs the maximum peak height of S2 (T_{max}; °C). Considering TOC (%) concentrations, the hydrogen index was calculated [HI = (S2/TOC) x100 in mg HC/g TOC], as well as the oxygen index [OI = (S3/TOC) x100 in mg CO_2/g TOC], following the procedures of Espitalié et al. (1985). With values of S2, HI and T_{max}, semi-quantitative evaluations of the hydrocarbon generation potential, type and stage of thermal evolution of organic matter were carried out.

3.2 X-Ray Diffraction (XRD)

The XRD measurements were performed using a Bruker–AXS D8 Advanced Eco X-ray diffractometer, with Ni-filtered CuKα irradiation, at a voltage of 40 kV and a current of 25 mA, and a 2θ scanning speed of 0.01/s. Thus, step scanning from 5 to 70 and 4 to 30 2θ degrees were used for the bulk (< 63 μm) and clay mineralogy (< 2 μm) purposes, respectively. The qualitative interpretation of the spectrum was performed by comparison with standards contained in the PDF 4+ database (ICDD, 2014) in Bruker Diffrac.EVA software.

To enhance the weak peaks of clay minerals, all the identified non-clay minerals were removed with both standard physical and chemical treatments (Moore and Reynolds, 1997). For XRD purposes, mineralogical analyses followed the method described by Martins et al. (2017, 2016). On oriented clay samples, about 3 g of fine sediment fraction of each sample were first decomposed (disaggregated by ultrasonic vibration for 1 min) and then left to stand for 20 min so that all particle sizes greater than clay-sized (<2 μm) would settle to the bottom of the tube and leave the clay particles in suspension (according to Stoke's law), using a 0.1% solution of $Na(PO_4)_6$ to avoid the aggregation of submicroscopic polymineralic flocculates. The suspension was removed and oriented, and dried clay preparations were made. The first slide was air-dried while the second was saturated with ethylene glycol. The third was analyzed after heating to 550°C for 1 h.

The samples were submitted to semi-quantitative analysis for the identification of all crystalline phases. This analysis is performed considering the relative height of the diffractive peaks and the $I/_{Icor}$ values, which are read importing information from the Diffrac.EVA software database.

3.3 Scanning electron microscopy (SEM) and energy-dispersive X-Ray Spectrometrie (EDS)

The preparation of samples for analysis in the SEM/EDS followed the standard established by the Laboratory of Pesquisa e Desenvolvimento em Exploração e Produção (Laboratory of Research and Development in Exploration and Production) from CENPES/PETROBRAS. Samples were initially fragmented in order to provide a fresh and irregular surface, adhered in a brass conductor and covered by a thin layer of gold-palladium, from EMITECH K750X metallizer. Then, it was adhered to aluminum conductive support and analyzed by scanning electron microscope ZEISS EVO LS-15, in backscattered electron images, operating in a high vacuum at 20 kV and with a working distance of 12.50 mm.

Composite maps and EDS microanalyses were obtained through the OXFORD Inca-AZtec Microanalyses, coupled to the SEM, which provided compositional (semi-quantitative) tables of the chemical elements identified in the oxide forms.

4. Results and Discussion

Table 1 presents the following information about each analyzed sample in the Assistência Member (core SP-32-PR): depth (m), lithology and organic geochemistry analyses.

The TOC content of the samples average 3.8 wt.%, ranging from 0.8 to 14.4 wt%. The highest TOC values are associated with black shales located at the top of the Assistência Member. The S average value is about 0.96% and its higher values are associated with black shales in the top of Assistência Member. The higher IR values (>88 wt.%) in the top of Assistência Member spread in a thickness of approximately 4.4 m, are linked with the essentially siliciclastic nature of this interval. However, bellow this depth, the Assistência Member is characterized by alternating intervals of high and low IR content, ranging from 34% to 81%. These values are associated with gray limestone interbedded by dark-gray shale.

The S_1 values range from 0-4.5 mg/g. The highest value determined for this parameter corresponds to a black shale sample (143.3 m), while the lowest value was obtained in the sample of dark-grey shale (153.1 m). The S_2 values ranged from 0.4 mg/g to 85.6 mg/g, with the highest and lowest values recorded in samples of black shale (143.3 m) and dark-gray shale (153.1 m), respectively. The average value of HI was 446.7 mg/g: the highest value of this parameter was found in the black shale sample (143.3 m) and the lowest in the dark-gray limestone sample (153.1 m). In the study

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JSE
RESEARCH PAPER

section, the organic material is thermally immature (Tmax <430 °C).

Scanning electron microscopic images showed that black shales are composed by fine-grained sediments (particles size <20 μm), with high organic matter content. The organic matter not only coat the mineral particles but also fills most of the intergranular and grain contact regions (Fig. 2).

Tab. 1. Organic carbon contents and Rock-Eval pyrolysis results. Notes: TOC = total organic carbon. S_1 and S_2 = peaks corresponding to free and kerogen-bound HC, respectively, generated by Rock-Eval pyrolysis; HI = Hydrogen index; OI = Oxygen Index; T_{max} = peak temperature of kerogen breakdown.

Sample nº	Depth (m)	Lithostratigraphy	Organic geochemistry							
			TOC %	S %	IR %	S1 (mg/g)	S2 (mg/g)	HI (mg/g)	OI (mg/g)	T_{max} °C
1	141.8	Black shale	5.4	0.8	88	0.9	23.8	437	9.4	426
2	142.7	Black shale	3.8	2	90	2.2	19.8	526	16.5	415
3	143.3	Black shale	14.4	0.9	94	4.5	85.6	594	8.3	422
4	146.2	Black shale	8.2	3.7	88	3.4	44.7	547.3	7.7	413
5	148.3	Dark-Gray shale	3.2	0.8	34	3	19.2	594.7	17.4	417
6	151.8	Dark-Gray Shale	1.5	0.4	38	1	6.1	396.8	31.8	407
7	153.1	Dark-Gray Shale	0.8	0.4	81	0	0.4	50	90.8	425
8	155.5	Dark-Gray Shale	1.6	0.4	68	1.7	6.4	394.4	70.4	383
9	156.8	Dark-Gray Shale	0.9	0.4	71	1.1	5.6	592.6	46.8	412
10	158.5	Gray limestone	1.1	0.3	40	0.7	4.2	377.3	35.5	402
11	159.5	Gray limestone	1.1	0.3	37	0.7	4.5	403.6	29.7	406

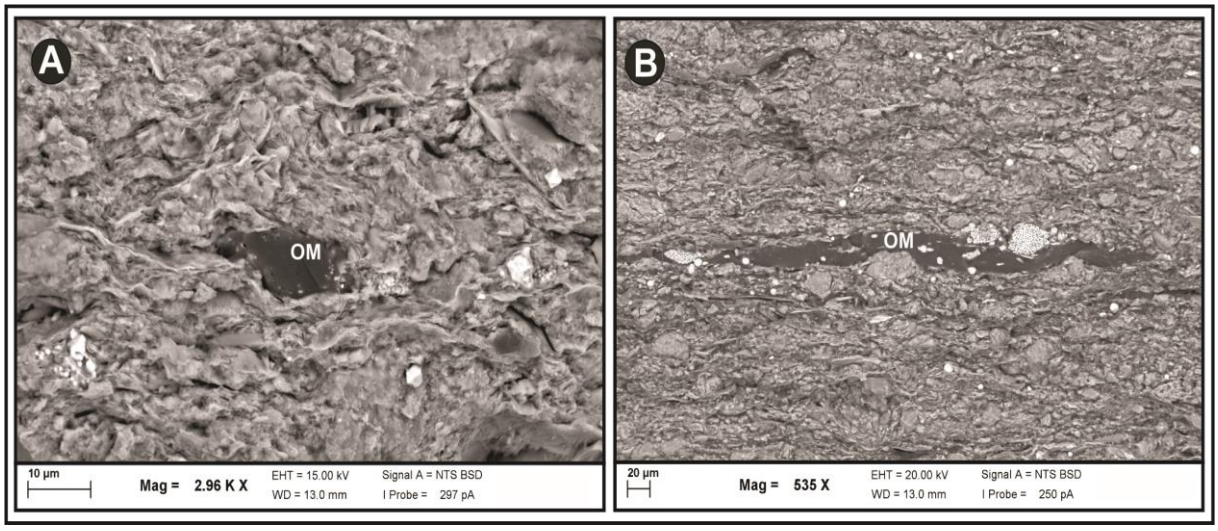

Fig. 2. SEM images of the Assistência Member (sample 143.3 m) showing (A) organic matter (OM) coat mineral and (B) filling of intergranular regions.

The black shale samples had about 36.1-40.5% of quartz and about 14-15.6% of plagioclase with small amounts of pyrite, analcime and gypsum. Among the clay minerals, there is a predominance of illite/muscovite. The dark-gray shale samples showed about 29.2-37.1% of quartz and 14.8-18.4% of plagioclase. Among clay minerals occur illite/muscovite, chlorite, expanded chlorite and kaolinite. The gray limestones have about 33.9-36.6% of dolomite, 18-19.7% of quartz and 17.8-19.0% of calcite. They also include illite/muscovite, expanded chlorite and kaolinite.

SEM images indicated that a final microfabric can be influenced by the amount of silt-size particles. Examples of the most common silt-size minerals are quartz, plagioclase, carbonates (calcite and dolomite), mica and pyrite in framboids (Fig. 3). Their identification was confirmed by EDS analysis.

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JSE
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The clay flakes on burial could easily rotate into a parallel or sub parallel position (Fig. 4). The samples from the Assistência Member had clay contents between 25.9 and 54.7% (Table 1) and were composed of illite/muscovite and occasionally small amounts of chlorite and kaolinite. Scanning electron microscopic images showed that most clay minerals often formed fibrous or platelet aggregates on the surface of other minerals (Fig. 5).

Different types of pore and microfractures were recognized in the Assistência Member. Intraparticle pores were found predominantly within organic matter and rarely in inorganic particles. Interparticle pores were present in pyrite framboids, surrounding quartz grains and between organic matter and mineral grains.

In some images, microfractures containing porosity have been observed. Different kinds of pores morphology were observed. In general, interparticle pores are irregular and polyhedral, whereas intraparticle pores are rounded and ellipsoidal (Fig. 6).

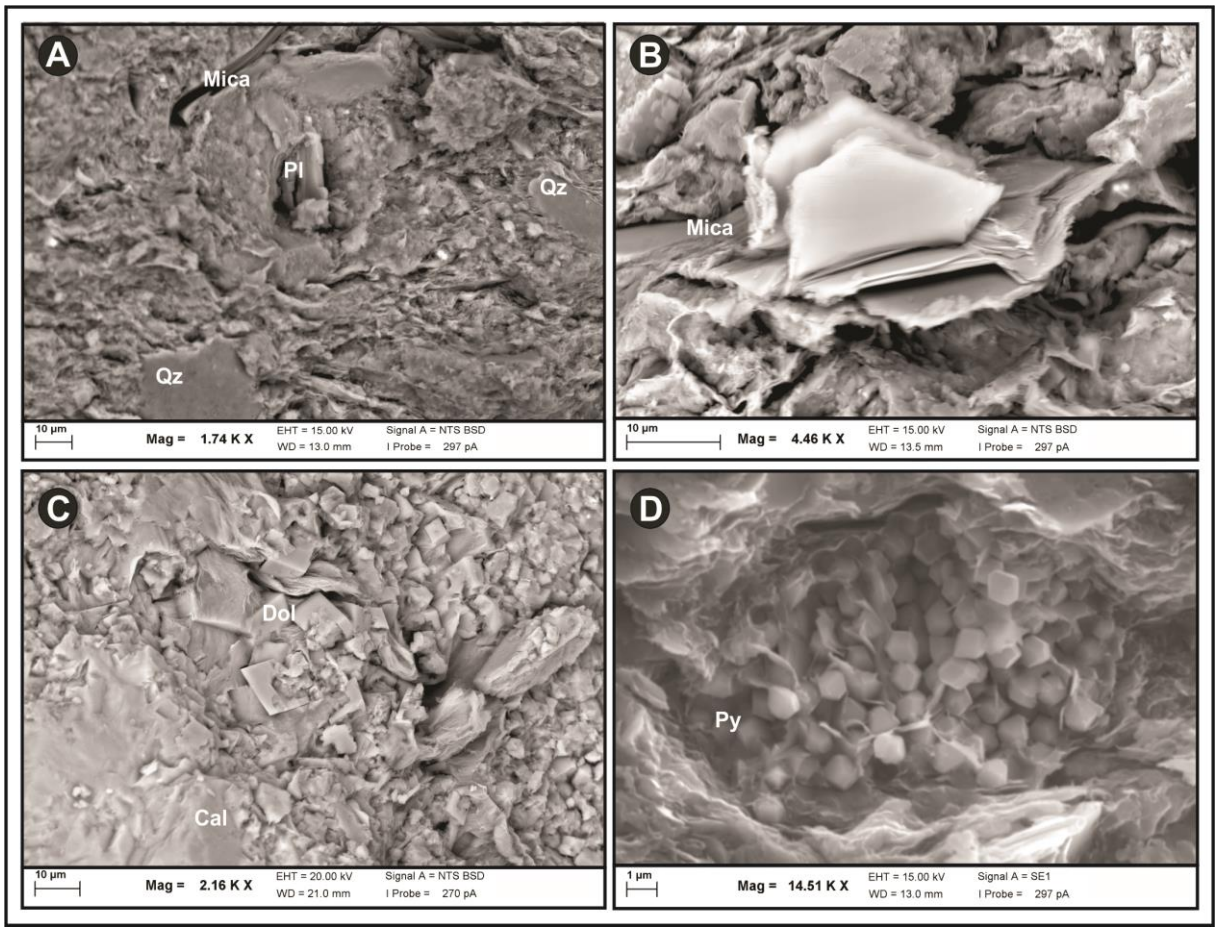

Fig. 3. SEM images of the Assistência Member showing several types of mineral grains in a clay matrix. (A) Sample 146.3 m: Qz = quartz. Pl = plagioclase; (B) sample 158.5 m: embedded mica sheets; (C) sample 158.5 m: carbonate (Dol = Dolomite; Cal = Calcite); (D) sample 142.5 m: framboidal pyrite (Py).

5. DISCUSSION

The bituminous black shales interval (141.8 – 146.3 m) can be distinguished of the dark-gray shale and gray limestone by their IR (> 88%). The highest TOC levels and S are characteristic of an anoxic environment. The TOC (3.8-14.4%), S2 (19.8-85.6 mg HC/g rock) and HI (437-594 mg HC/g TOC) values indicate that the organic-rich black shales of the top of the Assistência Member has an excellent concentration of organic matter with excellent potential for oil generation. These data evidences that this part of Irati Formation is economically the most important interval in the studied area.

The Assistência Member in the SP-32-PR core presents good prospects for oil/gas shale ex situ, in which shale is mined and subsequently retorted (pyrolyzed) to produce oil and gas as it occurs in the São Mateus do Sul. Currently, the Shale Industrialization Unit (SIX) has the capacity to process 5880 t/d. However, the black shales currently exploited in São Mateus do Sul present more advantageous parameters

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JSE
RESEARCH PAPER

(TOC and S2 up to 23% and 273 mg HC/g rock, respectively) according to Padula (1969) and Alferes et al. (2011). On the other hand, for shale gas and shale oil exploration, the best areas to be prospect would be where Irati Formation is close to intrusive rocks as described by several authors (e.g. Milani and Zalán, 1999; Araújo et al., 2000; Correa and Pereira, 2005; Costa et al., 2016).

Tab. 2. Minerals contents and clay minerals data. Legend: Qz - quartz; Pl - plagioclase; Cal - Calcite; Dol - dolomite; Py - pyrite; Anl - analcime; Gp - gypsum; Ilt/Ms- illite/muscovite; Chl- chlorite; Kln- kaolinite; Chlexp – expanded chlorite. Tr – values <2%.

Sample nº.	Depth (m)	Lithology	Semiquantitative XRD analysis										
			Mineral species (wt.%)								Clay minerals (wt.%)		
			Qz	Pl	Cal	Dol	Py	Anl	Gp	Ilt/Ms	Chl	Kln	Chlexp
1	141.8	Black shale	39.2	14	-	-	Tr	2.9	Tr	42.9	-	-	-
2	142.5	Black shale	40.5	14	-	-	2.2	2	Tr	39.5	-	-	-
3	143.3	Black shale	39.7	15.6	-	-	1.9	4.2	Tr	36.8	-	-	-
4	146.3	Black shale	36.1	14.6	-	-	3.2	3.1	Tr	42.5	-	-	-
5	148.3	Dark-gray shale	37.0	15.0	-	-	-	-	-	43.0	-	-	5.0
6	150.5	Dark-gray shale	37.1	14.5	-	-	-	-	-	43.3	-	-	5.1
7	151.8	Dark-gray shale	37	18.4	-	-	-	-	-	44.6	-	-	-
8	153.1	Dark-gray shale	29.2	16.3	-	-	-	-	-	37.7	9.4	7.4	-
9	155.5	Dark-gray shale	32.4	15.9	-	-	-	-	-	37.6	8.5	5.6	-
10	156.8	Dark-gray shale	30.5	14.8	-	-	-	-	-	38.7	11.8	4.2	-
11	158.5	Gray limestone	19.7	-	17.8	36.6	-	-	-	16.5	6.6	2.8	-
12	159.3	Gray limestone	18.5	-	19.0	33.9	-	-	-	17.5	8.9	2.2	-

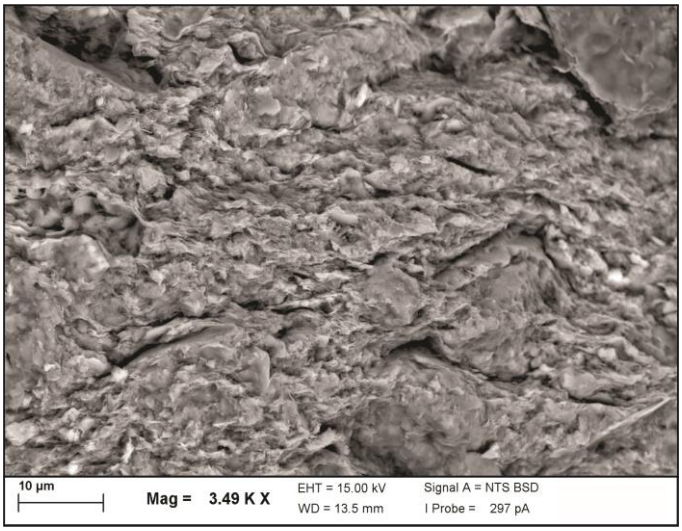

Fig. 4. SEM images of the Assistência Member showing subparallel clay flake orientation slightly disrupted by silt grains. Sample 158.5 m.

The mineralogical content of the Assistência Member presents intervals rich in quartz, plagioclase, carbonates and clay minerals. These major constituents often occur in areas where shale gas and shale oil are explored around the world. For example, the Lower Triassic Montney Formation in British Columbia and Alberta, both in Canada, is composed of organic-rich marine sediments associated with quartz, feldspar, carbonates, clay minerals and pyrite (Wüst et al., 2013).

Although initial focus had been centered on the conventional targets, recent research and developments in horizontal drilling and hydraulic fracture simulation have allowed for the exploitation of the unconventional source rock horizons (Wüst et al., 2013). Another example is the Marcellus Shale which has an average composition of 20% quartz, 50% clay minerals (illite predominantly), 5% pyrite and 25% carbonates (Hosterman and Whitlow, 1983). These values are relatively close to those observed in the Assistance Member.

Pore size distribution based on SEM images analysis provided important information about where pores are localized. According to Dong and Harris (2003) this kind of information can be used to develop models for permeability in unconventional resources.

However, care should be taken in this type of evaluation, due to the potential of creating artificial pores during samples preparation and polishing. Also, mechanically polished samples often contain residual topographic features that can influence the interpretability of subtle structures in SEM images (Driskill et al., 2013).

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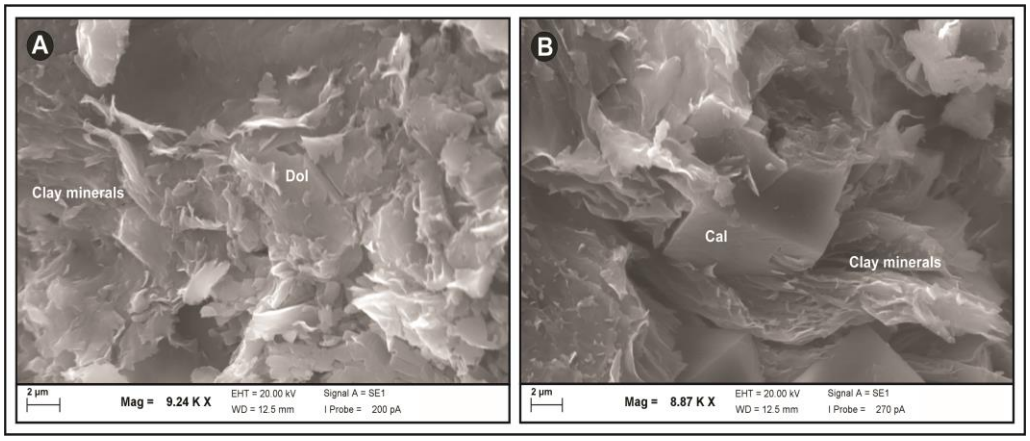

Fig. 5. SEM images of the Assistência Member showing clay minerals coating carbonate grains: (A) sample 148.3 m: Dol = Dolomite; (B) sample 159.3 m: Cal = Calcite.

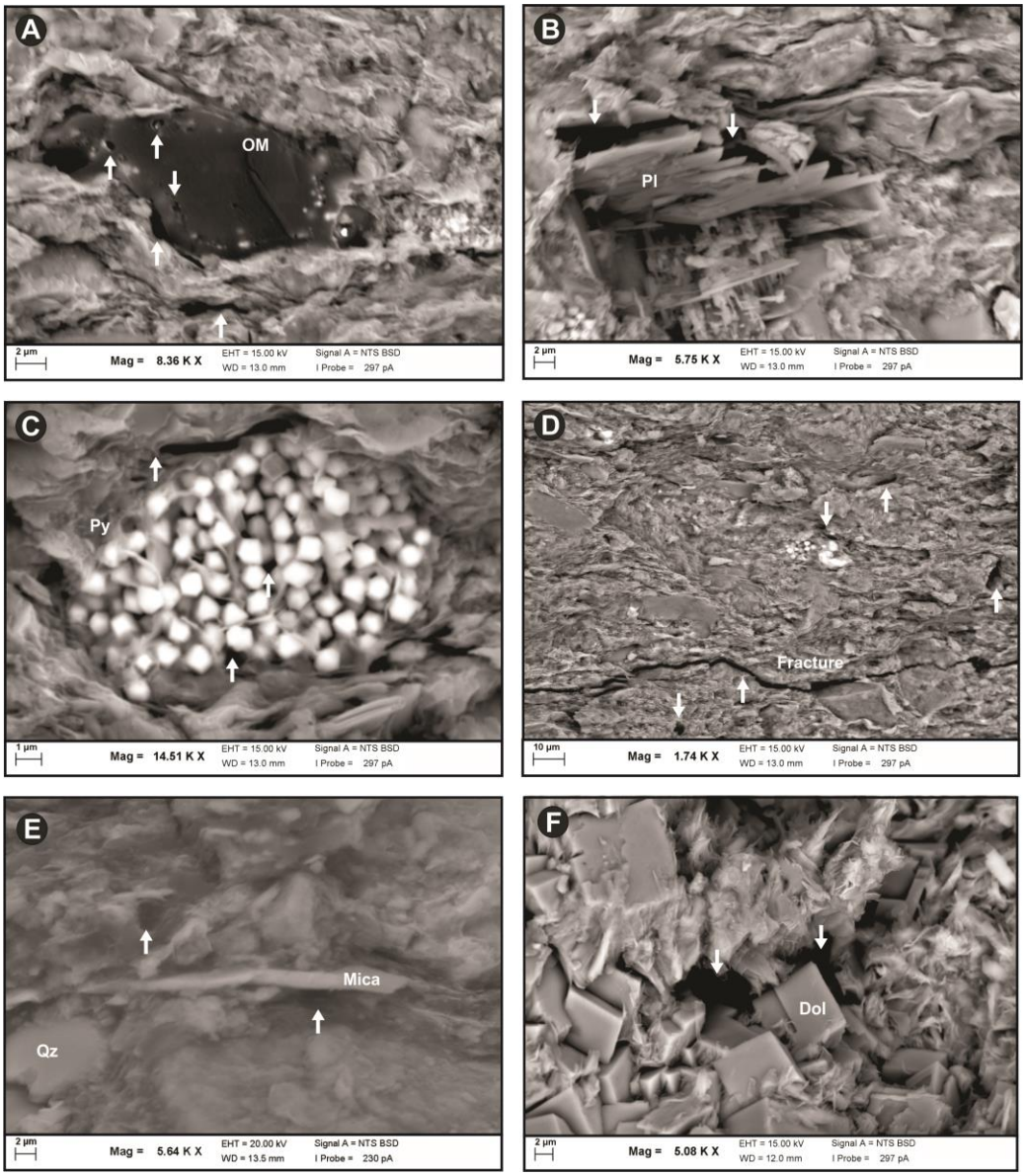

Fig. 6. SEM images of the Assistência Member showing details of different types of pores (arrows). (A) Sample 143.3 m: organic matter intraparticle pore; (B) sample 151.8 m: pore formed from the plagioclase dissolution; (C) sample 146.3 m: pores in typical pyrite framboidal; (D) sample 153. 1 m: fracture porosity; (E) sample 141.8 m: intergranular porosity; (F) sample 148.3 m: pore formed from dissolution.

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JSE
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5. Conclusion

SEM analyzes of organic-rich shale from well SP-32-PR were combined with XRD and source rocks analyses to characterize organic matter, mineral composition and pore distribution of the Assistência Member, Irati Formation. The main finding of this study as follows:

1. Although the organic-rich black shales of the top of the Assistance Member has presented high TOC, S2 and HI levels, it is in an immature state. Therefore, organic-rich shale can only be converted of oil and gas by means of heating (pyrolysis).
2. The organic matter occurs coating mineral and filling most of the intergranular and grain contact regions.
3. The organic-rich black shales and dark-gray shales are composed mainly of quartz, plagioclase and clay minerals with small amount of pyrite, analcime and gypsum at the top of the Assistência Member. Among the clay minerals, there is a predominance of illite/muscovite. The gray-limestones are composed of carbonates (dolomite and calcite) and quartz. It showed predominantly illite/muscovite and subordinately small amount of expanded chlorite and kaolinite.
4. Pores distribution includes intraparticle within organic matter and interparticle pores in pyrite framboids, surround quartz grains and between organic matter and mineral grains.

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