



Petrological study of the Iraty Formation Shale Rocks from Paraná Basin, Limeira, São Paulo.

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ABSTRACT

Shales are fine-grained rocks formed by clays and silt-sized particles in thin, relatively impermeable layers. They are originated from rocks that suffered weathering and erosion and their composition is quite variable. When oil production declines, interest arises to improve the understanding of the physicochemical properties of unconventional rocks, like shale. For the characterization of the shale samples of the Iraty Formation, the gamma-ray computed industrial tomography technique has been proposed to be used as an alternative to obtaining information about each element present in the mineral, the pore distribution, through the shale morphology. The tomographic results were compared with those obtained by conventional methodologies used in the petrological analysis, such as scanning electron microscopy (SEM), x-ray fluorescence, and x-ray diffraction.

Keywords: shale rock, rock morphology, gamma-ray tomography.

1. INTRODUCTION

In the current world scenario, there is a growing demand for energy resources, due to the accelerated development of technology and means of production. One of the main raw materials that drive this cycle is oil, but in a few years, the conventional resources for its production will no longer be able to correspond to that increase. For this reason, the study and exploration of non-conventional resources become necessary. Thus, studying shale reservoirs are on the agenda because they are rocks with great potential as oil reservoirs. [1, 2]

Shales are one of the most abundant sedimentary rocks found in sedimentary basins [1]. Brazil is classified by the IEA (International Energy Agency) as the 10th shale gas reserve in the world, with about 245 trillion cubic feet of recoverable shale gas resources, behind countries such as China, the United States, and Argentina [2]. These rocks are formed by the consolidation of silt, mud, or clay, presenting a very thin granulometry. Their chemical composition is quite varied, according to the geomorphology of the place where they have been formed, however, even when this variation is present, shales are rich organic matter rocks when compared to rocks of other types, and they may be a great source of hydrocarbons (HC) [3]. Thus, the study and the exploitation of the shale reservoirs are of great economic interest in the countries.

The deposits of known shales in the world vary from Cambrian to Tertiary period and may be found in several depositional environments such as marshes, marine basins, freshwater lakes, saline lakes, as well as in coastal zones. In Brazil, at least nine deposits of oil shale from the Devonian to Tertiary period have been reported. These deposits may contain little organic matter, being of low economic value and without much interest in their study, or they may contain enormous amounts of oil, attracting attention to their exploitation [4].

Although there are other sources of cheaper energy and a greater focus on investment in other areas, like mining, the shale may represent a very important resource. According to studies in some countries, standing out among them Germany, China, Israel, Estonia, and even Brazil, it is shown that besides oil and gas, it is possible to obtain other resources from these reservoirs, such as electricity, heat, cement, chemicals, and others. All of them present reasonable prices, allowing competitiveness in the market, in addition to an increase in the generation of jobs in various sectors [5].

The reservoir rocks are those that have good porosity and permeability, propitious to keep oil, gas, and/or water. These fluids are retained in the interstices of the rocks. Therefore, greater and better knowledge about the physical properties of these rocks is necessary. Among these properties, it can be quoted: (a) the filling of fluids in their pores, (b) their stratigraphy, and (c) their internal geometry are the most important, having a fundamental role in increasing the recovery factor of hydrocarbons. There is, already, a great deal of information about rocks such as sandstones and carbonates, which are the most common types of reservoir rocks. Also, unconventional reservoirs, such as the bituminous shales, are found. Yet, the porosity and permeability properties of shales as reservoir rocks are still little known. These properties, compared to conventional reservoirs (sandstones and carbonates), are more complex.

Thus, the more information is collected, the more tools engineers and other professionals involved will have so that their work may be improved. With this knowledge in hand, there may be optimization in the extraction of the desired material, as previously mentioned, besides a reduction in the time of the operations and the final costs involved.

The shale samples analyzed in this work were collected from the surrounds of Limeira, in the countryside of São Paulo. Because they are rocks that have impermeable structures, formed by the consolidation of clay in layers with thin laminations, differently from the structures usually explored, deeper characterization is necessary. The rock samples were assessed using the Scanning Electron Microscopy (SEM), X-Ray Fluorescence, and X-Ray Diffraction techniques, conventionally used in petrophysical analyzes. Additionally, an alternative technique for the characterization of the shale rock was proposed using the gamma-ray Industrial Tomography system developed in our laboratory. This technique characterizes rock microstructures through high-resolution images. It is a non-destructive technique and it has the advantage of not requiring preparing the sample and can measure the rock in its original form, in different dimensions and shapes. As far as it is known, a study on the methodology for characterizing shale rocks using gamma-ray tomography has not been found in the literature.

2. MATERIALS AND METHODS

Samples of shale rock containing hydrocarbons in their pores were found in the city of Limeira, in the interior of São Paulo, at the coordinates (22°32'47 "S - 47°26'33" W). Specific petrographic hammers and mallets were used for fieldwork on outcrops (rocks exposed to the surface). The shale samples were analyzed using X-Ray Diffraction (XRD), X-Ray Fluorescence, Scanning Electron Microscopy (SEM) with and without the use of energy dispersive spectroscopy (DES) and Gamma-Ray Industrial Process Tomography.

2.1. Sample preparation

Previously, the shale samples were prepared for use in analytical measurements. For the fluorescence technique measurements, the shale rock was pulverized and, then, 0.009 kg of powdered shale was mixed with 0.001 kg of microcrystalline wax, which was pressed as a tablet in a 0.036 m diameter matrix, for analysis. For use in the electron microscopy technique, the powdered shale samples were dispersed in carbon adhesive and covered with carbon, to be inserted in the equipment sample holder. For the X-ray diffractometry technique, powder samples were added to the glass sample holder. In the tomography technique, the collected shale sample has been used without requiring prior preparation, only adjusting the sample on the tomograph carefully so that the entire structure is in the path of the radiation beam and no "edge" is omitted from the measurements.

2.2. X-ray fluorescence

The X-ray fluorescence technique is very useful for the detection and quantification of heavy metals, based on the measurement of the characteristic X-ray intensities that are emitted by the chemical elements contained in the sample. The mode of operation of this technique consists of the use of a source of controlled excitation, to cause an increase in the agitation of the molecules of the atoms present in the analyzed substances, obtaining a fluorescence emission spectrum characteristic of the chemical elements present in the sample. The source used may be an alpha or gamma particle from radioactive sources or even a bundle of charged particles from accelerators or X-ray tubes. After the molecules are excited, the atom absorbs a large amount of energy and moves to an unstable state,

causing some transition to its electrons between the energetic layers (layers L and M to layer K, layers M and N to layer L and/or in outer layers). Due to these movements among layers, characteristic spectra of the elements are emitted and may be measured qualitatively and quantitatively [6,7]. The X-ray fluorescence equipment used to carry out the measurements was the EDX-900HS model, from the SHIMADZU brand.

2.3. X-ray diffraction

X-ray diffraction is a rapid analysis technique most often used to identify the crystalline phase of the rock. The equipment used, the diffractometer, consists of three basic elements: an X-ray emitter tube, an X-ray detector and a holder for the sample to be placed. For the execution of this technique, the sample of interest is placed in the support where it will be bombarded by fast electron beams. A cathode ray emitter tube will emit X-rays to heat a filament; electrons are produced and, then, accelerated toward the target of interest. When the emitted electrons reach enough energy to remove the electrons present in the target material, electronic transitions will start in the energetic layers of the sample and a single-layer electron will be pulled out; when it is filled again, there will be an emission of radiation with a length of the characteristic wave of this transition (diffracted rays). As the sample and the detector are rotated, the intensity of the reflected X-rays is recorded, being the ratio between the angle that the electrons were bombarded and collected the most important component of the diffraction. When the geometry of the incident X-rays contemplates the Bragg Equation ($n\lambda = 2d \sin \theta$), there is constructive interference and a peak of intensity is generated. This signal is collected and processed by a detector that sends it to the equipment, where it may be seen or printed. The instrument that is used to hold the angle and rotate the sample is called a goniometer; this sample rotates in the path of the X-ray beam at an angle θ , while the detector rotates at an angle of 2θ [8,9]. The X-ray diffraction equipment used to carry out the measurements was the BRUKER D8 Advanced 3kW diffractometer, equipped with a copper radiation tube, 0.25 m goniometer, a graphite monochromator, and a scintillation detector.

2.4. Scanning electron microscope (SEM)

To evaluate the morphology, topography, and elemental chemical composition of the shale, a scanning electron microscope was used to observe the homogeneity and the structural quality with high

resolution (magnification of 10-20.000X), having a scale with order values of 2 to 5 nanometers (20-50Å). The principle of a scanning electron microscope consists in the use of a beam of small diameter electrons, incident on the surface of the sample, for the production of electrons and photons, which may be collected by suitable detectors and, subsequently, converted into a signal of video. Later, this signal is transmitted to a cathode screen with scanning perfectly synchronized with that of the incident beam. To be detected, the electromagnetic rays resulting from this interaction between the beam and the sample have to be returned to the detector. Their results are influenced by the intensity of the particle energy incident on the detector or captured by the detector. Most of these instruments used, such as a source of electrons and a heated tungsten (W) filament, operate in a range of 1 to 50 kV acceleration voltages [10].

The great advantage of SEM over other types of microscopes is the possibility of combining a microstructural analysis with a chemical microanalysis, as well as enabling the generation of images with a large focus and a three-dimensional appearance [10, 11]. The dispersive energy spectroscopy (DES) analysis was also used and is a very important tool of this SEM, since it allows the characterization of metallic and semiconductor materials, identifying the composition of the sample, even if qualitatively, in specific points of the image [11]. In this study, the equipment used for the analyzes was the scanning electron microscope LX-30, from Philips.

2.5. Gamma-ray industrial tomography

The industrial tomography used in this work consists of the transmission of gamma rays through a heterogeneous medium, accompanied by attenuation, which will provide the integral measure of the mass distribution line, through the path traveled by the beam. The measurement of several beams with a different orientation, both spatial and angular concerning the studied volume, followed by an image reconstruction process, provides the density distribution of the phases with a high degree of spatial resolution [12]. With this technique, it is possible to generate images that are not influenced by the external structure, being able to obtain detailed information on the internal structure of the object of interest [13].

For the characterization of these shale rock samples, tomography measurements were carried out using a third-generation computed tomography developed at IPEN/CNEN-SP [14,15]. This system

comprised eight NaI(Tl) detectors of 25 x 50 mm² (diameter, thickness) shielded with lead and ¹⁹²Ir radioactive source, with an activity of 7.4 GBq (200 mCi), placed into a radioactive shield-case, with an aperture angle of 36 degrees. The eight NaI(Tl) detectors were placed on a gantry in fan-beam geometry, opposite to a radioactive shield-case containing ¹⁹²Ir gamma-ray source. The eight detectors were individually collimated with lead-containing septa of 2 x 5 x 50 mm³ (width, height, depth). The movement of the detector and radioactive source assembly is controlled by a stepper motor, which rotates one degree forward, and this process goes on up to complete 360 degrees, totalizing 360 projections. The counting time for sampling was 6 seconds. This system was, previously, described by Mesquita et al [14,15]. The image was reconstructed using Filtered Back Projection (FBP), in the grid matrix of 512 x 512 [15].

3. RESULTS AND DISCUSSION

The composition of the elements present in the shale rock was estimated semi-quantitatively by the X-ray fluorescence technique. The elements found by this technique in the shale sample are presented in Table 1. As it may be observed, the main element constituting this sample is SiO₂ (22.4%), followed by other elements, such as Fe₂O₃ (5.9%), MgO (5.6%), and CaO (6,0%), with very close concentrations among them. Also, elements with lower concentrations, called trace elements (concentration below 1%), such as Na₂O (0.3%), SrO (0.2%), P₂O₅ and BaO (0.1%) were found.

Table 1: Concentration of the elements present in the shale, by the fluorescence method

Z	Element	Oxide	Concentration
14	Silicon	SiO ₂	22.4%
26	Iron	Fe ₂ O ₃	5.9%
12	Magnesium	MgO	5.6%
20	Calcium	CaO	4.6%
13	Aluminum	Al ₂ O ₃	2.6%
16	Sulfur	SO ₃	1.2%
19	Potassium	K ₂ O	1.1%
11	Sodium	Na ₂ O	0.3%
22	Titanium	TiO ₂	0.3%
38	Strontium	SrO	0.2%
15	Phosphorus	P ₂ O ₅	0.1%
25	Manganese	MnO	0.1%
36	Barium	BaO	0.1%

In the diffractogram of the shale sample shown in Figure 1, several intensity peaks were observed: however, only three of these peaks stand out with higher values. Figures 2 and 3 show diffractograms with the patterns of elements from the EVA database, used as a parameter to identify the elements present in the sample. From the analysis of these diffractograms, specifically at higher intensity peaks, it may be stated that the element with the highest concentration is quartz, highlighted with red circles in Figure 1. At lower intensity peaks from the standard diffractogram (Fig. 2), it is possible to observe the presence of pyrite (FeS₂) in the blue line and some silicates, such as Calcium Silicate (Ca₂SiO₄) and Potassium, Magnesium Aluminum Silicate (KMg₂AlSi₄O₁₂), traced in light and dark green lines, respectively, in Figures 2 and 3. These peaks are pointed out with a green circle in Figure 1.

From the results of X-ray fluorescence and X-ray diffraction, it may be stated that both show similar results to the chemical composition present in the sample.

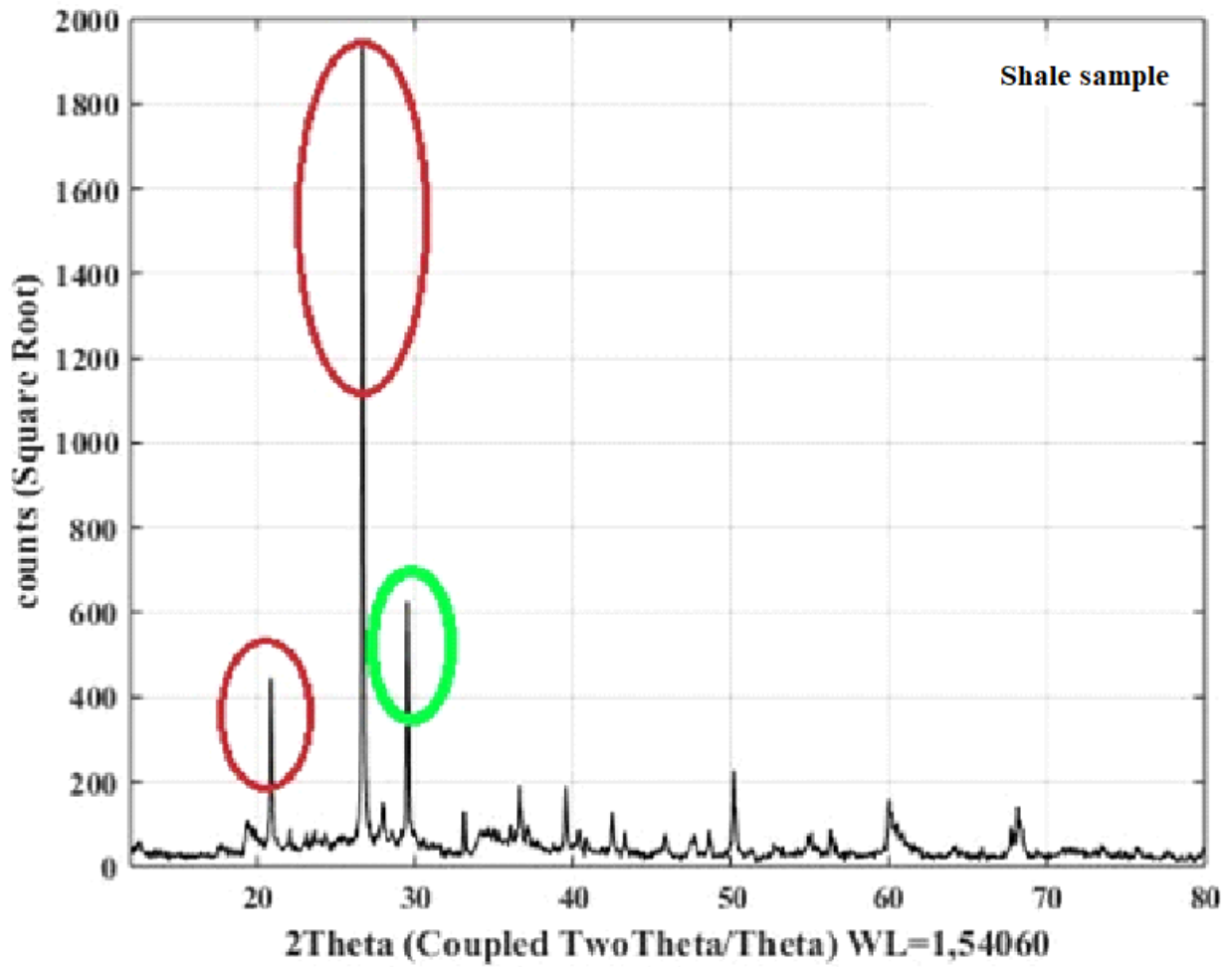


Figure 1: Diffractogram of the shale sample.

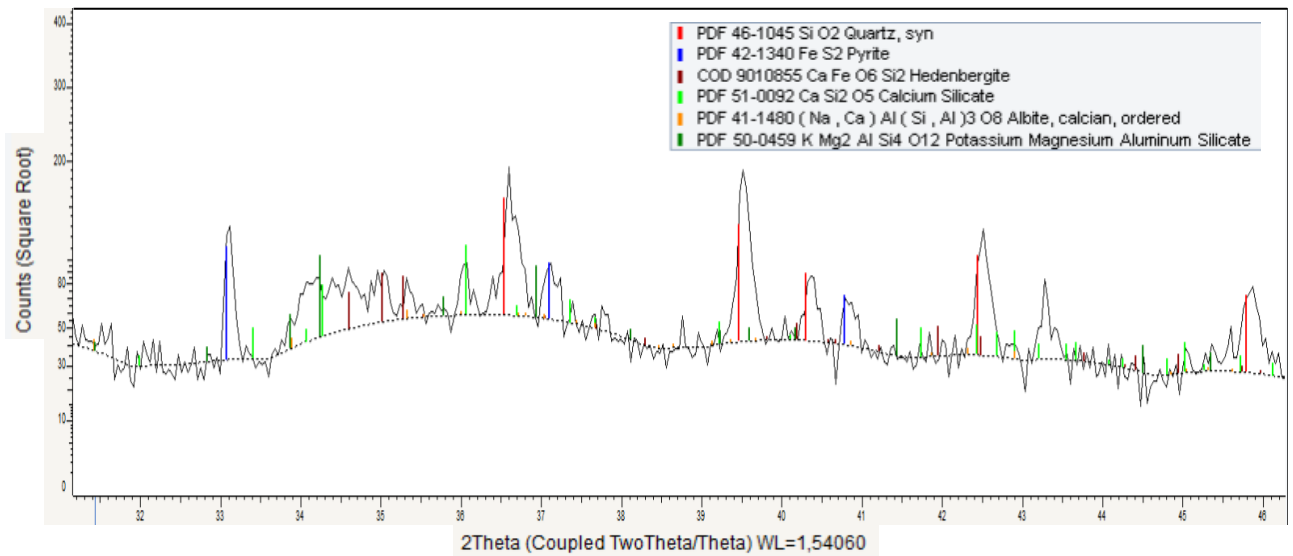


Figure 2: Diffractogram with the patterns of elements and peak of the shale overlapped (black line).

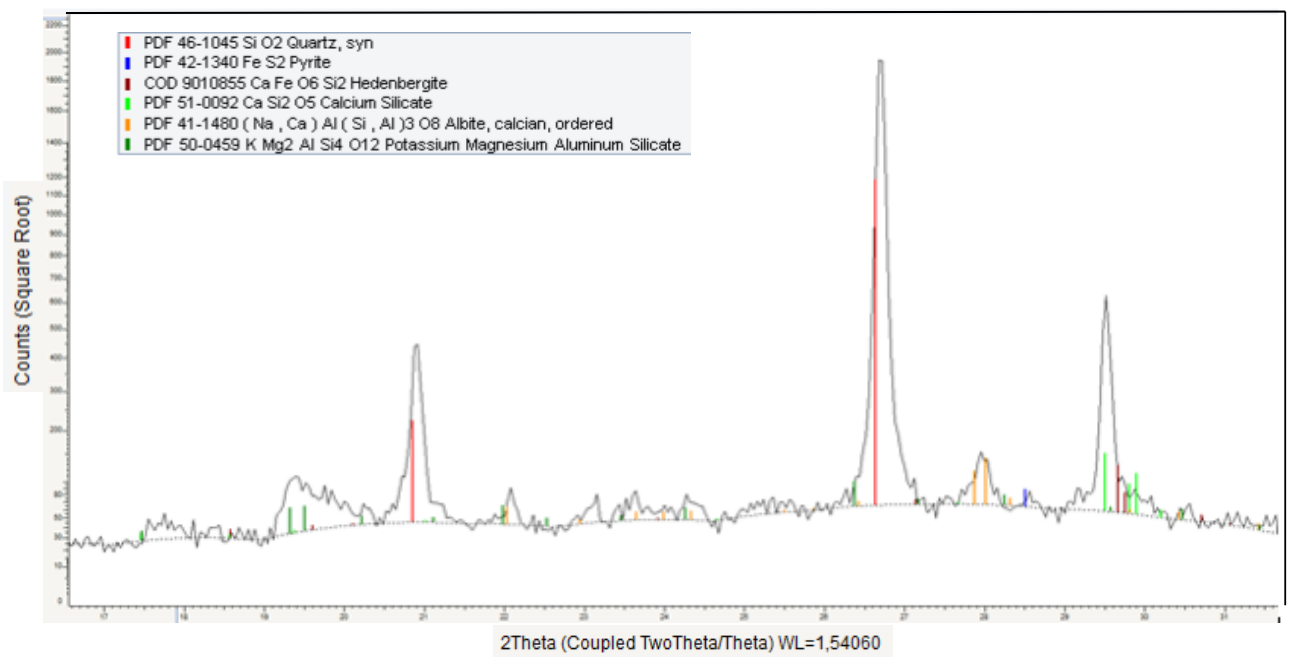


Figure 3: Diffractogram with the patterns of elements and peak of the shale overlapped (black line).

In the images obtained by the scanning electron microscope technique, it was possible to observe that the sample is composed of a fine granulation, characteristic of the shales, with grains dispersed

as it may be seen in Figure 4 (a), increasing by 1000 times its normal size and Figure 4(b), increasing by 2500 times. As it may be observed in these images, apparently there is no cementation, thus, several void spaces are present, which confers to this rock the condition for storing hydrocarbons. From these images, it is, also, possible to notice that the structure of the grains does not follow a defined pattern, with grains of several formats (sub-angular, rounded, sub-rounded).

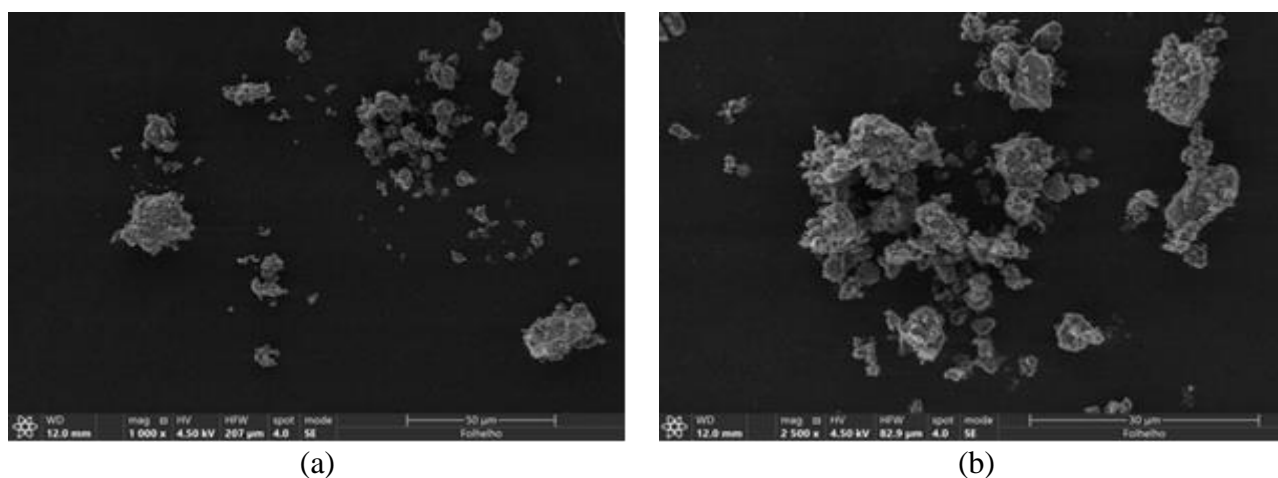
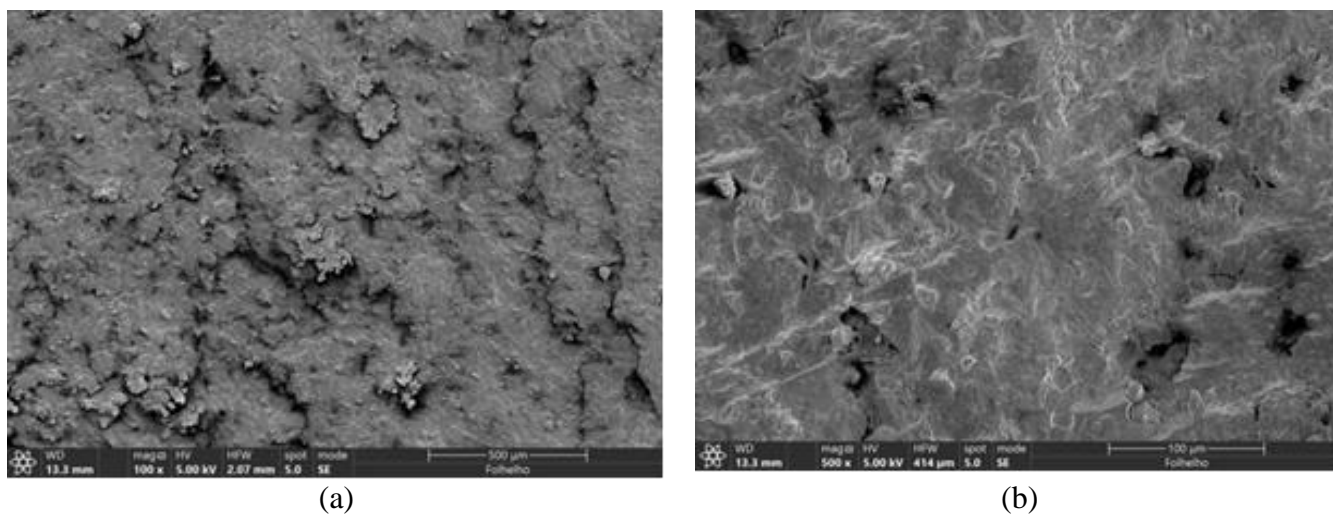


Figure 4: Shale structure images increased by 1000 (a), and 2500 (b) times.

The images of the grain surface in this sample, magnified 100 and 500 times, are shown in Figure 5. As observed in these figures, the images exhibit two contrasting gray colors, a lighter shade, and a darker tone. This signal contrast may be an indication of the differences in the composition of the shale grains, light areas indicating grains with high atomic numbers and dark areas, grains with low atomic numbers. This fact suggests that the lighter area is the rock matrix, mainly composed of SiO_2 , similar to what was found by the other techniques studied in this work. The dark area represents the hydrocarbon present inside.

Using the dispersive energy spectroscopy tool, with the image shown in Figure 6, it was possible to identify, in the sample, the presence of silicon elements (yellow color) in greater quantity and calcium and magnesium elements (green and blue color, respectively), corroborating the results found by the techniques of X-ray fluorescence and X-ray diffraction. It was, also, possible to notice a dark color in the image, where the porous area is observed, probably, containing hydrocarbon.



(a)

(b)

Figures 5: Images enlarged by 100 times (a) and 500 times (b) of the structure of grains present in the sample analyzed.

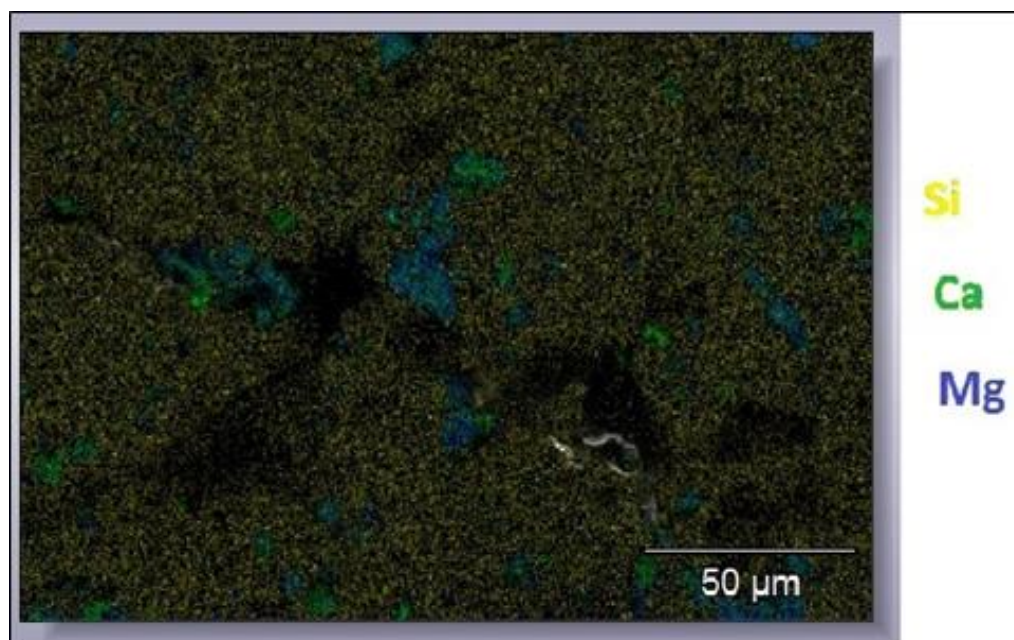


Figure 6: Dispersive energy spectroscopy map performed on a sample grain.

From the analysis of the reconstructed image of a slice of shale rock by gamma-ray industrial tomography shown in Figure 7, and, by inference, the linear attenuation coefficient values (color bars), it may be stated that the rock presents a denser matrix, represented in pink color in the image. Probably, it should be silica (Si), the main element that constitutes the sample. There is, also, a small amount of red dots positioned in the central region, which, from the scale shown in the image, it may confirm that it is an element with a high-density value, maybe iron (Fe). Besides, it is possible to observe the presence of other elements with different densities, represented by the dark blue color. These elements may be calcium (Ca) and magnesium (Mg), both having similar density values, lower than Si and Fe. All of these elements corroborated the results obtained by the conventional techniques used in this work.

Additionally, it is possible to observe some well-spread and poorly connected pores (green color), with some material inside and lower densities, suggesting that this substance could be a hydrocarbon. Further studies should be carried out to corroborate these results. However, these findings showed the feasibility of using this tomographic technique to characterize rocks, with the advantage of not having to fragment or spray as done in the conventional analytical or X-ray microtomography techniques. Thus, the present methodology could be used in large and different dimensions and shapes, as collected in nature. In future studies, it is planned to improve the spatial resolution of the tomograph to evaluate the porosity and its distributions in the interior of rocks, the interconnectivity between the pores, the permeability, and the density.

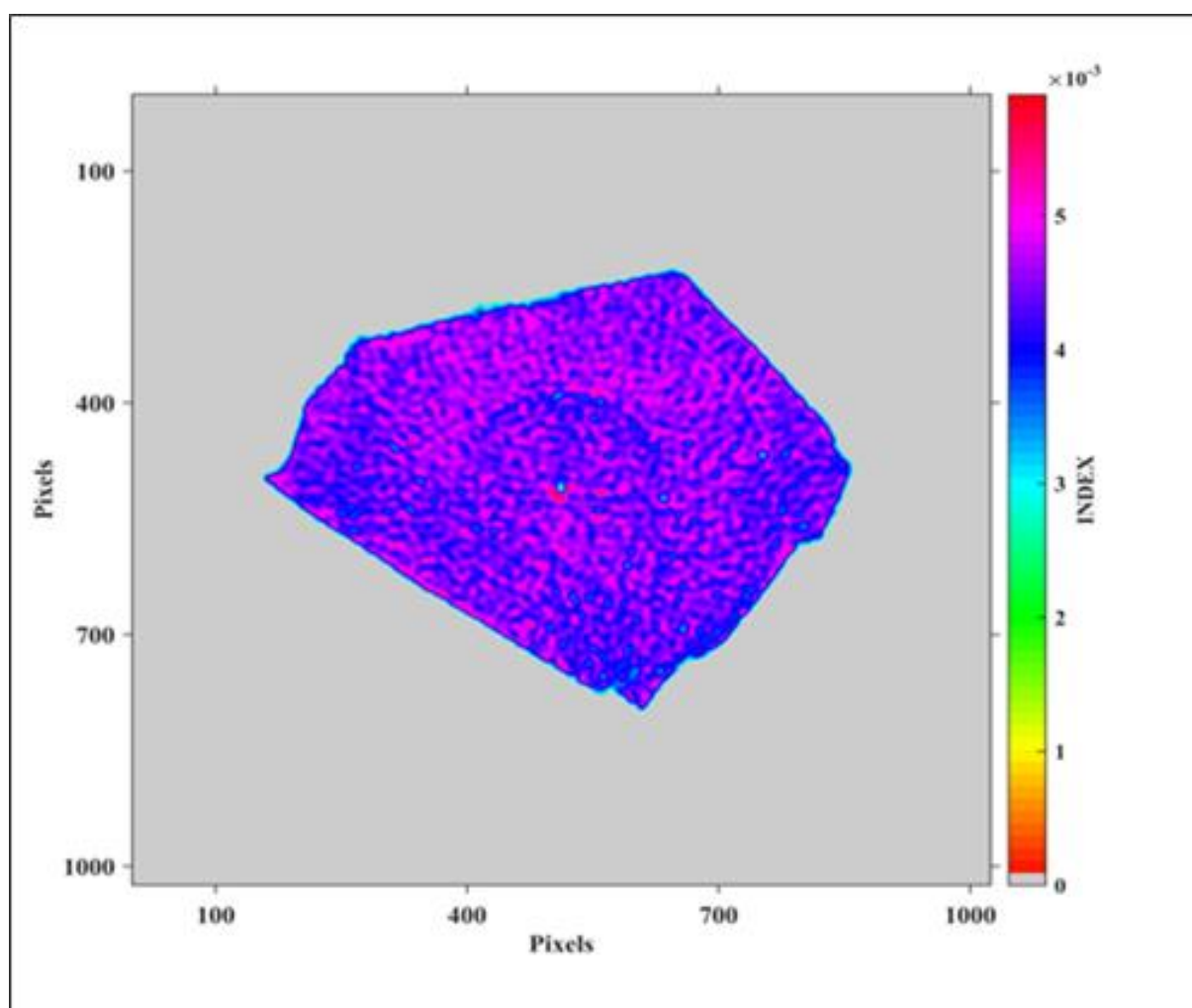


Figure 7: A reconstructed image of the shale rock sample.

4. CONCLUSIONS

From the diffraction analysis, it was possible to conclude that the main components of the shale sample analyzed are silica (Si), one of the most abundant chemical elements in the crust, presenting very high diffraction peaks, followed by other elements such as iron, magnesium, and calcium, but in smaller amounts. The presence of all these elements could be confirmed by the results obtained by the fluorescence method, which determined that the silica value is approximately 22.4%, while, as to the other elements, is between 4% and 6%. Also, the dispersive energy spectroscopy technique corroborated

the results of these elements in the shale sample. From the diffraction analysis, it was possible to conclude that the main components of the shale sample studied are silica (Si), one of the most abundant chemical elements in the crust, presenting very high diffraction peaks, followed by other elements such as iron, magnesium, and calcium, but in smaller amounts. The presence of all these elements could be confirmed by the results obtained by the fluorescence method, showing that the silica value is approximately 22.4%, while, as to the other elements, is between 4% and 6%. Also, the dispersive energy spectroscopy technique corroborated the findings of these elements in the shale sample. It was demonstrated the feasibility of the tomography technique to be used for the characterization of the shale rock, as established in this work. Further studies should be carried out to improve the spatial resolution of the tomograph to obtain more details of the characteristics of the rocks, such as porosity distribution in the interior of the rocks, the interconnectivity among the pores, the permeability, and the density.

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