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Performance of the X-ray powder diffraction (XRD), X-ray fluorescence (XRF) and the industrial computed tomography used for characterization of the vesicular volcanic rock.

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ABSTRACT

Volcanic rock is a designation in geology given to extrusive igneous rocks. One type of igneous rock of interest, in economic terms, is the vesicular, since besides the knowledge of the morphology (positioning, size, direction and interconnectivity of the vesicles) of these structures within the spill, there is also an economic interest regarding the possibility of this rock as a reservoir of fluids (water and hydrocarbons). In this work, samples of vesicular volcanic rock from the Paraná Basin were studied for their characterization, aiming to contribute in the knowledge of this rock proprieties as a reservoir of fluids. The elements present inside the rocks were identified and quantified by X-ray fluorescence and X-ray diffraction. The dimensions of the vesicles and the interconnection between them could be clearly observed in the reconstructed images of the rocks measured, using the third generation gamma ray industrial tomography.

1. INTRODUCTION

Volcanic rock is a designation given in petrology and geology for the igneous rocks of volcanic origin. It is a type of rock that is formed by cooling the surface magma and it is extrusive. The surface magma is called lava and it may be expelled through a central conduit or through cracks [1].

Due to its high chemical degree, problems concerning clays plus physical and mechanical heterogeneities, the volcanic rock has been, dominantly, considered as secondary targets for hydrocarbon exploration [2]. A relative lack of detailed studies on the hydrocarbon associated system in a volcanic rock has led to a simplified vision of the volcanic poor system, with reservoir properties commonly being attributed to the presence of tectonic fractures and weathering [3].

In reality, the porous system in volcanic rocks is formed by a complex framework of vesicles, microcracks and fractures with the result of interplay between primary and secondary processes [4]. The vesicles, in this type of rocks, are bubbles of gas formed in volatile supersaturated liquefied lava (especially water vapor), after rising to the surface. There are several articles on the genesis and composition of igneous rocks. However, few studies have been found on the internal properties of this rock type, regarding the interconnectivity and directions of the vesicles from volcanic rocks. In this work, samples of vesicular volcanic rocks from the Paraná Basin were studied, concerning their composition and internal vesicle rearrangement.

2. EXPERIMENTAL PART

Samples of the vesicular volcanic rocks were collected between the municipalities of Guaporé and Vista Alegre do Prata, located in the northeast region of Rio Grande do Sul State, Brazil, following the NBR 16434/2015 standard, which describes recommended procedures for the collection, handling and preparation of solid waste, soil and sediment samples [5].

The evaluation of the crystalline phases of the volcanic rock collected was performed using the Multiflex X-ray diffractometer model, RIGAKU. In this analysis, the directions to which the planes of the crystal are preferentially oriented (Miller indices) are identified. X-ray diffraction patterns were obtained in the diffractometer from CuKα radiations (2θ ranging from 20º to 60º). To generate the diffractogram and calculate the degree of the sample crystallinity, the Origin 2019 program and Excel software were used, respectively [6].

The qualitative and quantitative chemical composition of the collected sandstone sample was identified using the X-ray fluorescence technique and the X-ray Fluorescence Model EDX-900HS, SHIMADZU brand. X-ray fluorescence spectrometry is a technique for identifying the elements present in a sample, as well as establishing the concentration at which each element is present in the sample. In X-ray fluorescence spectrometry a high energy radiation source (gamma radiation or X radiation) causes excitation of the substance atoms to be analyzed. When an atom in the ground state is under the action of an external source of energy, it absorbs this energy, promoting electrons to more energetic levels. In this state, the atom will be in an unstable situation, called "Excited State". In nature, everything tends to seek the state of stability and, hence, the excited atom tends, naturally, to return to its ground state, occurring, then, an emission of energy. This energy involved in the absorption is a specific characteristic of each chemical element, allowing its identification and corresponding quantification [7]. Previously, the rock sample was pulverized in the Department of Mineralogy and Geotectonics, Institute of Geosciences, University of São Paulo, USP, Brazil.

For the internal visualization of the vesicular igneous rock collected, samples of 25 cm x 35 cm from this rock (Figure 1), tomography measurements were carried out using a third generation computed tomography, developed at IPEN/CNEN-SP. This system comprised eight NaI(Tl) detectors of 25 x 50 mm^2 (diameter, thickness) shielded with lead and ^{192}Ir radioactive source with the activity of 7.4 GBq (200 mCi), placed into a radioactive shield-case having an aperture angle of 36 degrees.

Figure 1: Vesicular igneous rock sample.

The eight NaI(Tl) detectors were placed on a gantry in fan-beam geometry, opposite to a radioactive shield-case containing a ^{192}Ir gamma-ray source. The eight detectors were individually collimated with lead-containing septa of 2 x 5 x 50 mm^3 (width, height, depth). The detectors move 35 times in a step angle of 0.165 degrees, emulating 144 detectors per projection (8 detectors x 18 steps). The counting time for sampling was 6 seconds. Thereafter, the support table containing the gantry and the ^{192}Ir gamma source rotates one degree forward, and this process goes on up to completing 360 degrees, totalizing 360 projections. For a total of 51840 samples (144 'virtual detectors' x 360 projections), it takes the system, approximately, 12 hours to obtain each tomographic image. This system was previously described by [8] . The image was reconstructed using Filtered Back Projection (FBP) [9], in the grid matrix of 512 x 512.

3. RESULTS AND DISCUSSION

In the analysis of the elements composition present in a vesicular igneous rock sample, using X-Ray Fluorescence, several elements were determined, as presented in Table 1. As it may be observed in this table, the analyzed rock is, predominantly, composed of O (56.3%), Si (21.1), Fe (8.88%), Al (6.69%, Ca (2.43%), K (1.46%) and Mg (1.21%). Other oxides identified are present in the ppm range.

Table 1: Composition and concentration of the elements present in a vesicular igneous rock sample.

Fomula	Z	Concentration	Status
O	8	56.3%	Matrix
Si	14	21.1%	XRF1
Fe	26	8.88%	XRF1
Al	13	6.69%	XRF1
Ca	20	2.43%	XRF1
K	19	1.46%	XRF1
Mg	12	1.21%	XRF1
Ti	22	0.898%	XRF1
Na	11	0.666%	XRF1
Mn	25	873 PPM	XRF1
P	15	807 PPM	XRF1
Ba	56	400 PPM	XRF1
Sr	38	170 PPM	XRF1
Cu	29	157 PPM	XRF1
Zr	40	144 PPM	XRF1
Zn	30	116 PPM	XRF1
Rb	37	56.5 PPM	XRF1
Y	39	38.6 PPM	XRF1
Ni	28	37.5 PPM	XRF1
S	16	32.7 PPM	XRF1
Ag	47	24.3 PPM	XRF1
Ga	31	12.7 PPM	XRF1
Nb	41	9.04 PPM	XRF1
Tb	65	0.882 PPM	XRF1

From the chemical composition of the elements found by the X-ray fluorescence and the diffractogram obtained by the X-ray diffraction, the EVA software was used to infer the possible phases belonging to the rock sample, according to simultaneous research in several reference databases and the combination of analyzes of the peaks obtained from the rock analyzed and those from the reference databases, as illustrated in Figures 2 and 3.

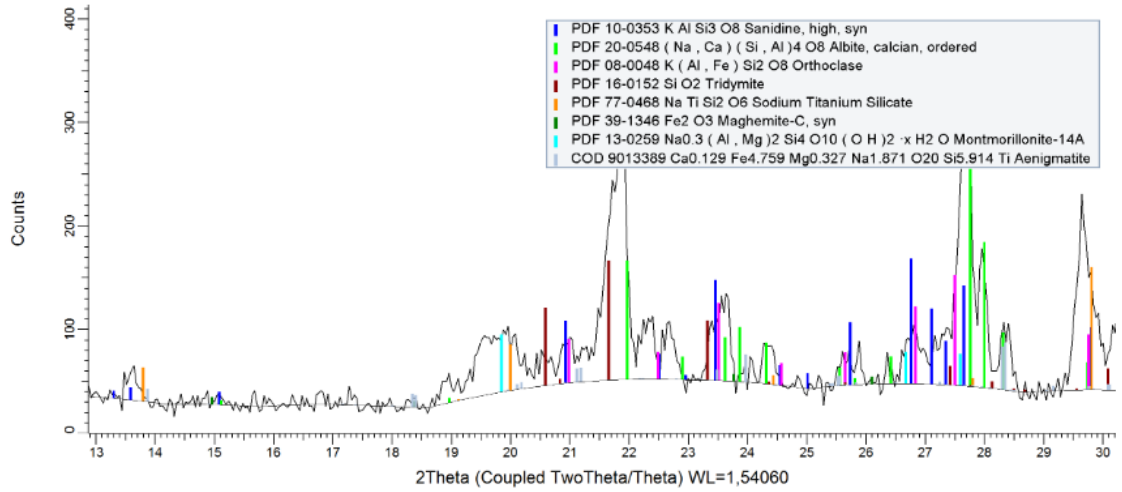

Figure 2: Diffractograms with phases belonging to the analyzed sample and the several reference databases, with abscissa range from 13 to 30 Two Theta.

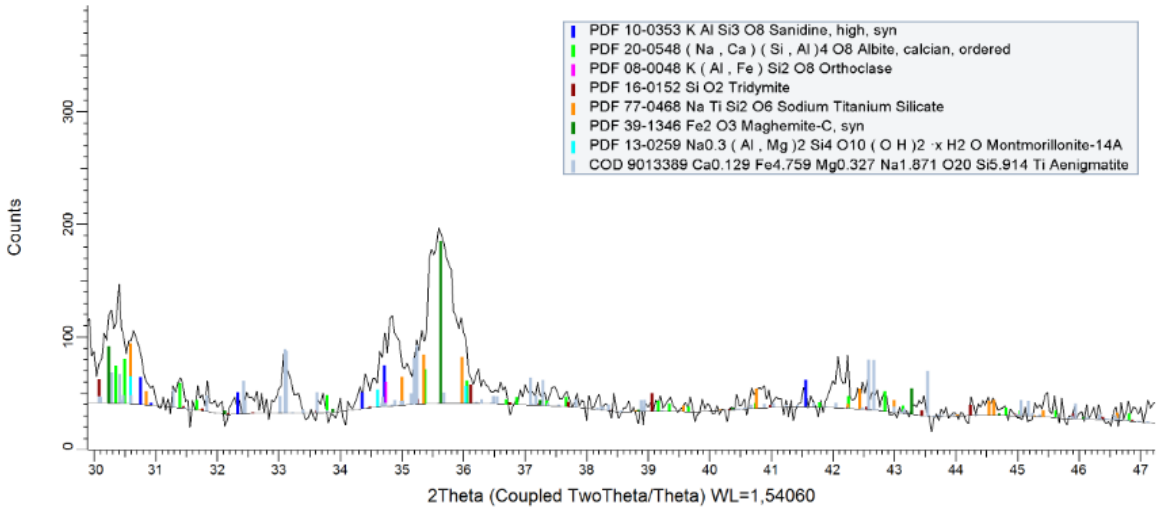

Figure 3: Diffractograms with phases belonging to the analyzed sample and the several reference databases, with abscissa range, from 30 to 47 Two Theta.

In both graphs, Figures 2 and 3, it may be observed that the sanidine [$K(AlSi_3O_8)$], tridymite (SiO_2), albite, sodium silicate, and iron III oxide are proposed as the main phases.

In some areas, marked with a red circle, in the diffractogram of Figure 4, some similar phase peaks of very low intensities may be observed overlapping the peaks belonging to the phases of the analyzed rock. This problem becomes worse by the presence of very small crystalline phases, causing loss of resolution for the diffraction method.

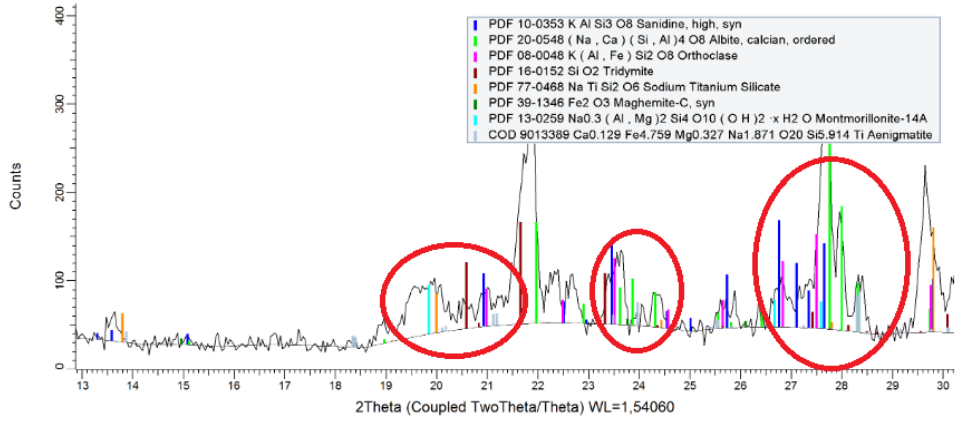

Figure 4: Overlapping of the peaks belonging to the phases from the analyzed rock and from very low intensity elements.

Figure 5 illustrates the diffractogram plotted using the main peaks selected with the help of Excel and Origin 2019 software, making it possible to note the predominance of crystalline phases.

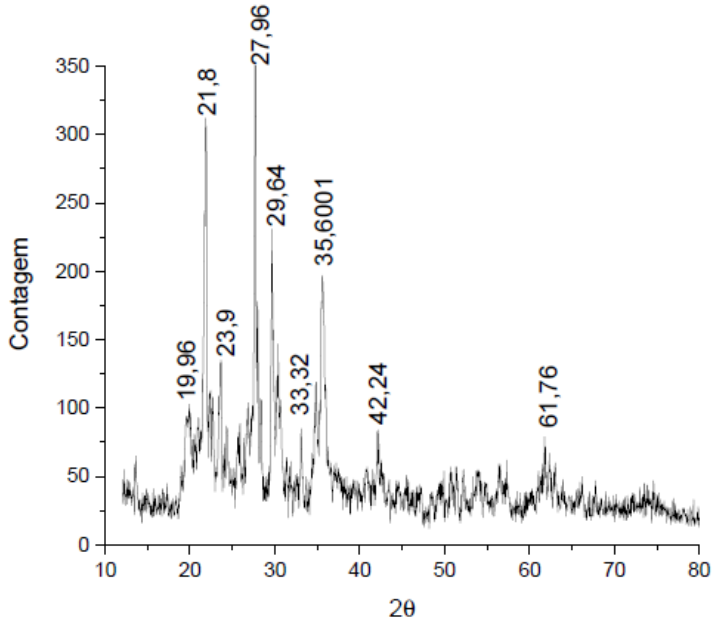

Figure 5: Diffractogram of the peaks representing the peaks of the intensity of crystallines phases.

Figure 6 presents the reconstructed images of the igneous rock measured using a third generation gamma ray industrial tomography, developed at IPEN [10]. The color-bar index value represents the linear attenuation coefficient (μ (cm-1)). The pores and their interconnectivity in the rock may be seen clearly, as it may be seen in Fig.6 and Fig 7b. It may be observed isolated pores, interconnected pores, pore throat size, geometry of the pore, connection and distribution of pores. The porosity is an important feature to be known,

however, only this is not sufficient; the knowledge of how the pores have to be interconnected to allow the passage of fluid and gas through the rock is essential. In other words, the rock should have permeability. The porosity and the permeability of the rocks are the key factors to affect the quality of reservoirs and to control the off-take [11].

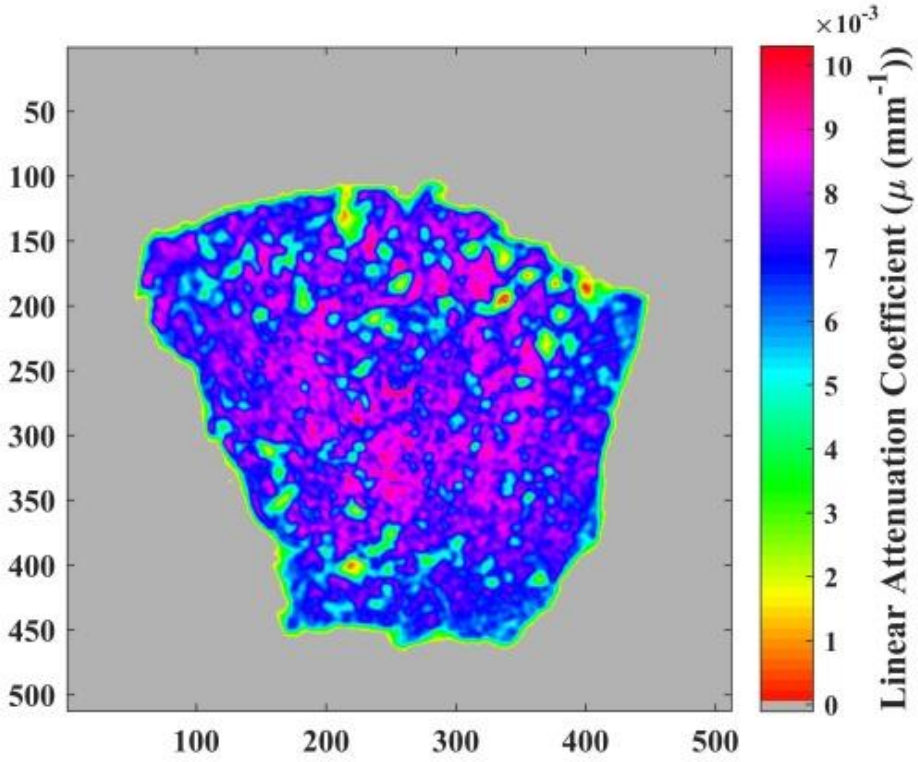

Figura 6: Reconstructed image of the igneous rock sample.

In figure 7, smaller vesicles are observed and the interconnections are more evident. It is noted that some vesicles have interconnecting remnants before they are filled.

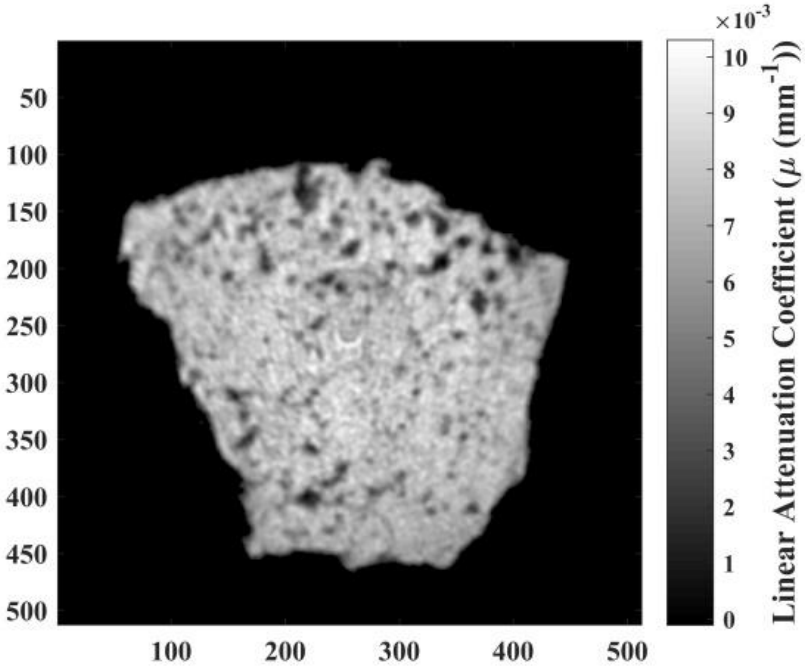

Figura 7: Reconstructed image showing the interconnections between the vesicles, represented by the black color.

4. CONCLUSIONS

The Vesicular Igneous Rock analyzed by the X-ray fluorescence technique was predominantly composed of O (56.3%), Si (21.1), followed by Fe (8.88%), Al (6.69%, Ca (2.43%), K (1.46%) and Mg (1.21%). X-ray Diffractogram analysis results indicate Sanidine [K ($AlSi_3O_8$)], tridymite (SiO_2), albite [Na ($AlSi_3O_8$)], sodium silicate (Na_2SiO_3) and iron oxide III (Fe_2O_3) as the main phases of the rock. From the X-ray Diffractogram data, it was observed that all intensity peaks represent crystalline phases in different proportions. On the other hand, amorphous phase was not evident. The distribution of the porosity and permeability could be clearly seen in the reconstructed image, using the third generation gamma ray industrial process tomography. It was possible to observe that the vesicles had different sizes and geometries. It was also noted that many pores were filled with some material and that some of them had preserved traces of interconnection.

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