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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 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 to 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 by the third generation Gamma-ray industrial tomography technique

Keywords: volcanic, vesicular, rock

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1. INTRODUCTION

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

Due to its high mineralogical degree heterogeneities, mechanical and problems concerning clays plus physical, 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 lava (especially water vapor), after rising to the surface. There are several articles on the genesis and composition of extrusive volcanic rocks. However, few studies have been found on the internal properties of vulcanic rock, regarding the interconnectivity and directions of the vesicles from these 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 volcanic rock 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 and quantifying the chemical elements present in a sample, . In X-ray fluorescence spectrometry, a high energy radiation source (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.

Petrographic tests were carried out using an Olympus BX40 transmitted light optical microscope, from Philips, belonging to the Department of Mineralogy and Geotectonics, Institute of Geosciences, University of São Paulo, USP, Brazil. Initially, five petrographic slides were made for the analysis of the rock. Petrography is a characterization method that considers aspects such as texture, degree of crystallinity, visibility, geometry, arrangement (weft), the size of the crystals, characterization of porosity, and alteration products. For the preparation of the blades, the rock is cut with a diamond saw, obtaining a flat slice. Then, it is impregnated at 60 ° by a mixture of acetone and resin, and the excess resin removed with the help of a stylus [8].

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

Figure 1: *Volcanic Vesicular 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 [9]. The image was reconstructed using Filtered Back Projection (FBP) [10], in the grid matrix of 512 x 512.

3. RESULTS AND DISCUSSION

In the analysis of the composition of elements present in a vesicular volcanic rock sample, using X-Ray Fluorescence, the major elements are in % wt in oxides and the trace elements in ppm, as presented in Table 1. As it may be observed in this table, the analyzed rock is, predominantly, composed of SiO_2 (51,87%), what means that the rock has basic composition.

Table 1: concentration of the elements present in a vesicular volcanic rock sample.

Formula	Z	Concentration	Status
SiO_2	14	51,87%	XRF1
Fe_2O_3	26	15,70%	XRF1
Al_2O_3	13	13,50%	XRF1
CaO	20	6,99%	XRF1
MgO	12	7,11%	XRF1
K_2O	19	2,05%	XRF1
TiO_2	22	1,79%	XRF1
Na_2O	11	0,93%	XRF1
P_20_5	15	0,21%	XRF1
MnO	25	0,14%	XRF1
BaO	56	450 PPM	XRF1
SrO	38	262 PPM	XRF1
CuO	29	255 PPM	XRF1
ZrO_2	40	247 PPM	XRF1
ZnO	30	188 PPM	XRF1
SO_3	16	94.2 PPM	XRF1
Rb_2O	37	80.4 PPM	XRF1
NiO	28	61.7 PPM	XRF1
Y_2O_3	39	61.6 PPM	XRF1
Ag	47	31.2 PPM	XRF1
Ga_2O_3	31	22.1 PPM	XRF1
Nb_2O_5	41	16.3 PPM	XRF1
Tb_4O_7	65	1.27 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, plus the combination of analyses 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.*

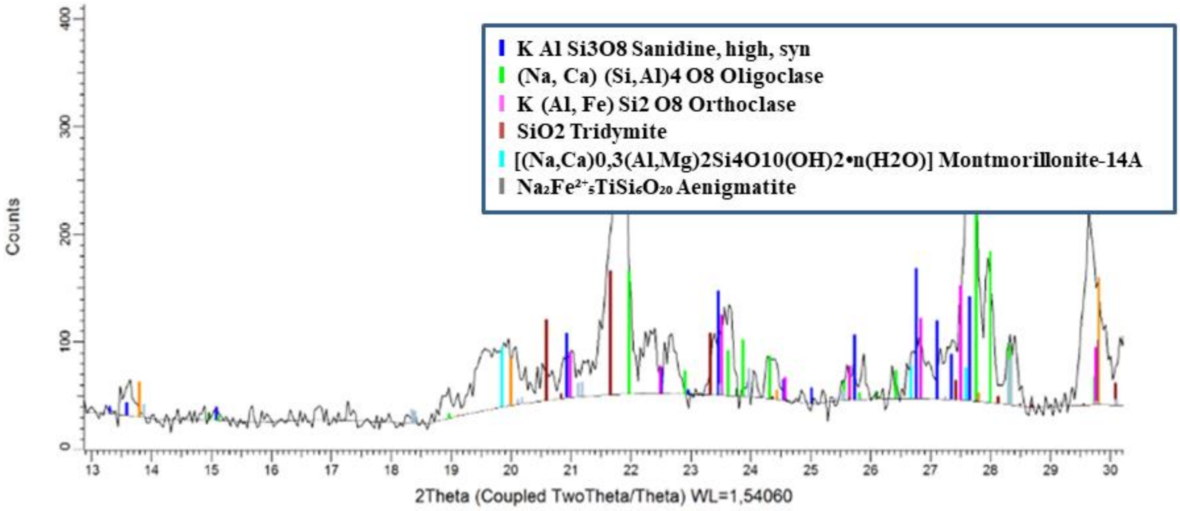
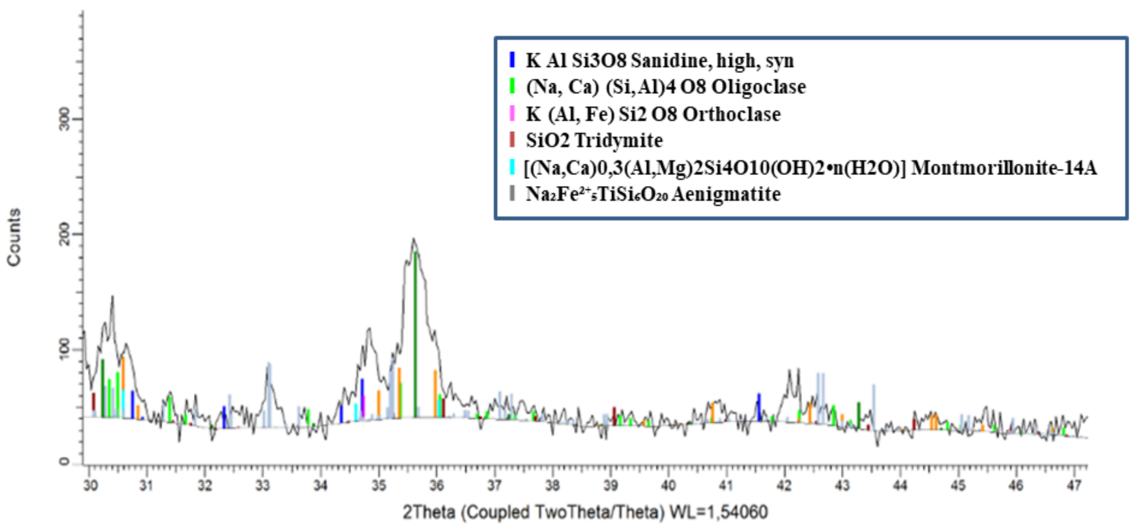


Figure 3: *Diffractograms with phases belonging to the analyzed sample and the several reference databases, with abscissa range from 30 to 47 Two Theta.*



In both graphs, Figures 2 and 3, it may be observed that sanidine [$K(AlSi_3O_8)$] and Orthoclase ($K(Al,Fe)Si_2O_8$), tridymite (SiO_2), OLIGOCLASE [$(Na,Ca)(Si,Al)_4O_8$], Montmorilonite [$(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2{\bullet}n(H2O)$] and (Aenigmatite is a primary constituent in sodium-rich alkalic volcanics). The Montmorilonite and Aenigmatite are proposed as the main phases, which indicate that is an alterated volcanic rock.

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 presents a vesicle filled partially by zeolite and silica (tridymite). The zeolite is a mineral secondary formed hydration of silicates of Al, Ca and Na.

Figure 4: *Vesicles partially filled with zeolite.*

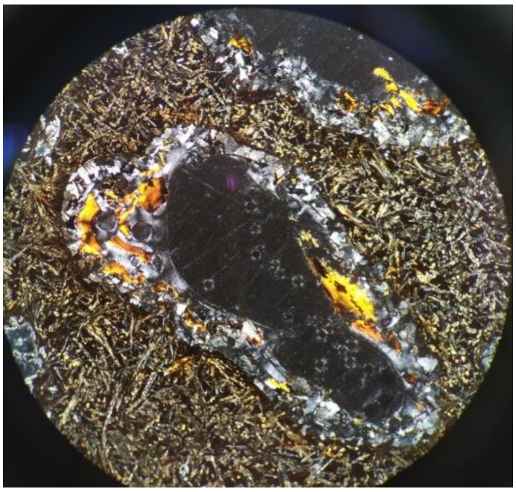
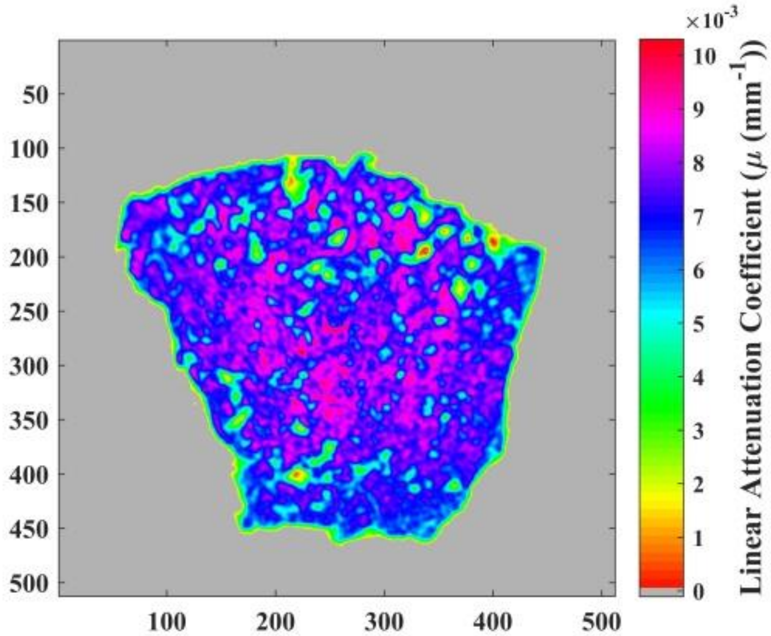


Figure 5, it is noted that a rock is hypocrystalline due to the predominant presence of crystalline and cryptocristaline material. The particle size of the matrix is fine, microvesicular, which varies from fine to medium, formed by euhedral and subhedral micro-crystals of oxidized plagiocase (oligoclase), with intergranular mineral (red circle). Note the presence of plagioclase around some pores, featuring a dikititexitic texture (orange circle). It is also possible to observe the presence of montmorillonite including minuscule, euhedral and subhedral plagioclase (oligoclase) strips, characterizing the offitic texture.

Figure 5*: Matrix granulometry, intergranular mineral and* diktytaxitic *texture.*

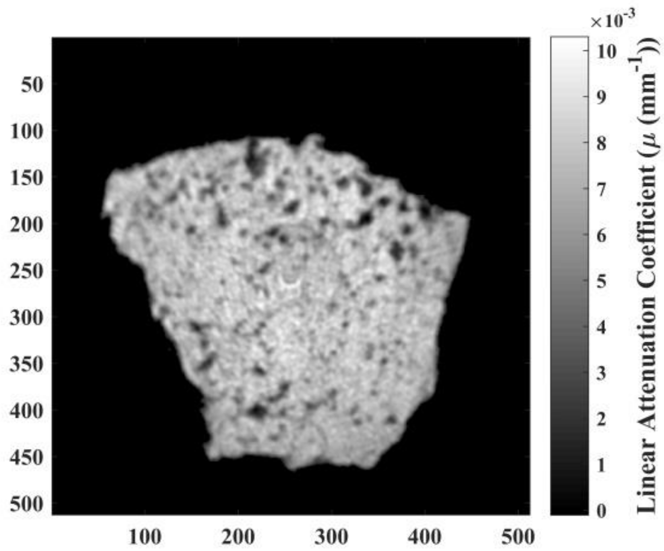
Figure 6 presents the reconstructed images of the igneous rock measured using a third generation Gamma ray industrial tomography, developed at IPEN [10]. The color-bar index value represents the linear attenuation coefficient (μ (cm-1)). The pores and their interconnectivity in the rock may be seen clearly, as observed in Fig 6 and Fig 7. It is possible to note 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].**

Figure 6: *Reconstructed image of the vesicular volcanic rock sample.*



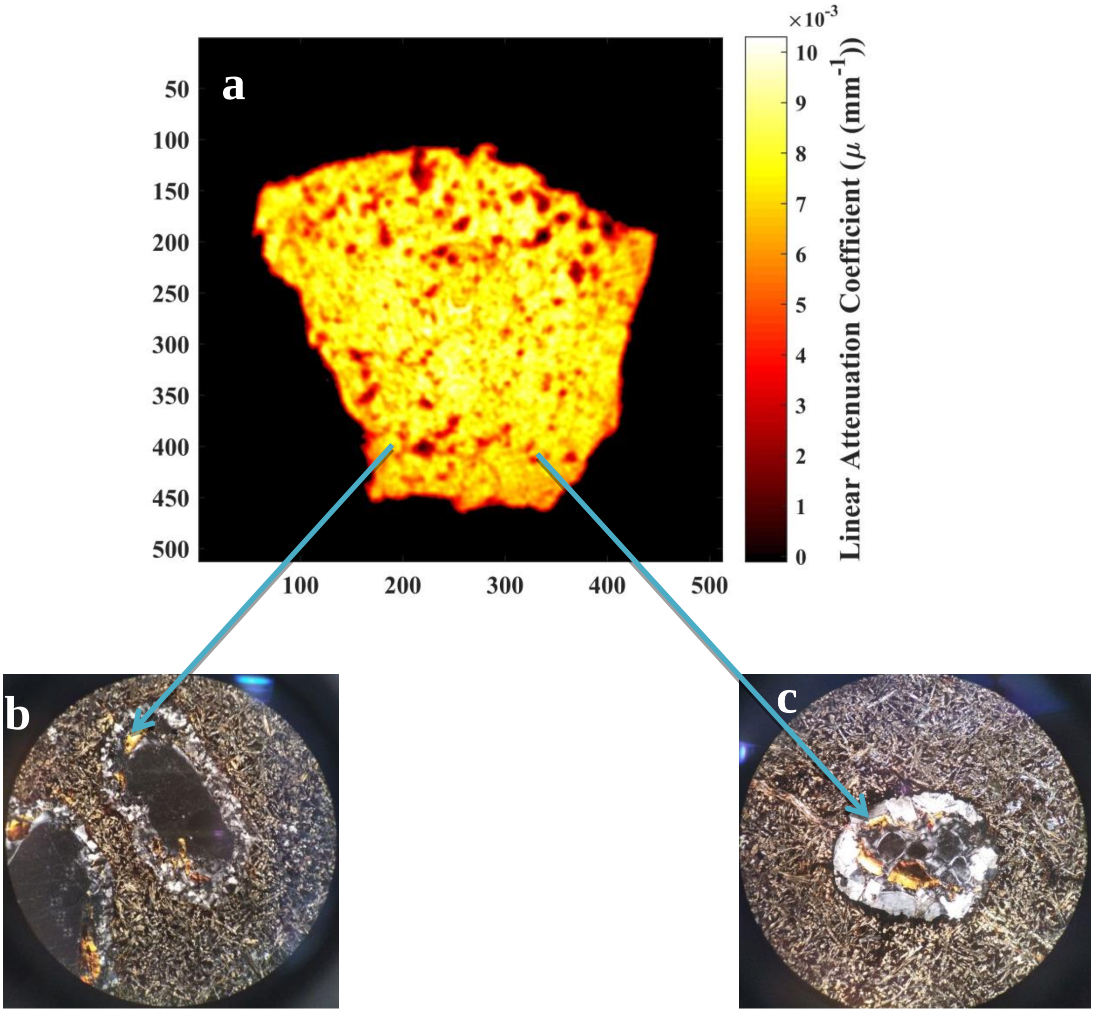
In figure 7, smaller vesicles are observed and the interconnections are more evident. It is noted that some vesicles have interconnecting remnants, before they are filled.

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



In figure 8, corroborates the relationship between petrography and tomographic images (8a) and petrography (8b, c). Note that it is possible to observe how vesicles are partially and fully filled in the two characterization methods.

***Figure 8:** Correlation between optical microscope images and tomography (a) fully filled and partially illustrated vesicles in the tomographic image (b) partially filled vesicle in the petrographic image (c) fully filled vesicle in the petrographic image.*



4. CONCLUSIONS

X-ray fluorescence and diffraction helped to identify mineral paragenesis through chemical composition and crystalline phases not identified by petrography, respectively. The combination of such data helped to identify the mineralogical plot and to understand the processes of primary and secondary porosity.

Through petrography, it was possible to establish a textural relationship of the rock, observe the presence of cryptocrystalline material and visualize the processes of primary and secondary porosity. It is also possible to distinguish the type of porosity in the tomographic image and the post-magmatic filling of the pores by varying the coefficient of linear attenuation. Therefore, petrography validates tomography in this respect.

The presence of secondary minerals, such as smectite in the dikititaxitic cavities of the cryptocrystalline matrix, and zeolite reduces the porosity and permeability of the rock, with a very common occurrence in the regions of Guaporé and Vista Alegre do Prata.

The different sizes and geometries of the vesicles are consequences of the long cooling process.

Obtaining data obtained by established methods such as X-ray fluorescence, X-ray diffraction, and petrography validated industrial 3D gamma radiation tomography, which is a pioneering characterization method in geosciences. The analysis of the sample in natural size and the non-destruction of it, are significant advantages of this characterization method.

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