



## Performance of the SEM (Scanning Electron Microscope), Raman Spectroscopy, and Industrial Computed Tomography used for characterization of the vesicular volcanic rock as applied in Carbon Capture and Storage (CCS)

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### 1. Introduction

The use of carbon capture and storage (CCS) technology is considered an effective tactic to curb climate change. Storage in underground geological formations such as unconventional shale formations, depleted hydrocarbon reservoirs, saline aquifers, and coal seams. According to the International Energy Agency (IEA), carbon dioxide mineralization can reduce about 10–15% of total global emissions, according to the International Energy Agency (IEA) [1].

Igneous rock reservoirs exist in more than 20 countries and in more than 300 basins or blocks around the world. In contrast to sedimentary formations where silicate minerals represent a mineral retention gap, injection of CO<sub>2</sub> into suitable igneous (volcanic) rocks such as basalt can create rapid carbonation and mineral retention [1].

Volcanic rock is a designation given in petrology and geology to extrusive igneous rocks. It is a type of rock formed by the cooling of magma on the surface and underground. The surface magma is called lava and can be expelled through a central conduit or through fissures [2].

In reality, the porous system of volcanic rocks is formed by a complex structure of vesicles, microcracks and fractures resulting from the interaction between primary and secondary processes. Vesicles, in this type of rock, are gas bubbles formed in supersaturated volatile lava (especially water vapor), after rising to the surface [3].

In this case, gamma radiation tomography provides a detailed two-dimensional view of the distribution of minerals in the pores, while scanning electron microscopy allows high-resolution analysis of mineral morphology and texture. Furthermore, Raman spectroscopy provides information about the crystalline structure of the minerals present in the sample.

### 2. Methodology

The samples of vesiculated volcanic rocks were collected in the municipalities of Guaporé and Vista Alegre do Prata, in the State of Rio Grande do Sul.

Petrography is a characterization method that considers aspects such as texture, degree of crystallinity, visibility, geometry, arrangement (plot), size of crystals, characterization of porosity and alteration products. It will be carried out using a specific transmitted light optical Olympus BX40, from the Philips brand, belonging to the Department of Mineralogy and Geotectonics, Institute of Geosciences, University of São Paulo, USP.

The topography and morphology of the minerals that make up the rock will be evaluated using a scanning electron microscope (SEM), from the Philips CECTM, model XL30. The sample was fragmented and its surface was cut, polished and uncovered by carbon evaporation for specific analysis. The images were processed using the free software ImageJ 1.50b.

By changing the frequency of a small fraction of the incident radiation, when it is mirrored by crystalline structures, Raman spectroscopy was used on small basalt fragments of approximately 1 cm<sup>3</sup>. HORIBA Xplora is located at CETER/IPEN, which has a 732 nm laser. The LabSpec6 software (Horiba Scientific) was used to operate the equipment and acquire the spectra. All experimental Raman spectra were compared with the RRUFF database and the literature, identifying the composition of the minerals that fill the vesicles.

Thus, the tomographic measurement will be carried out in the natural shape and size of the rock, without requiring any processing to carry out the tomographic measurements, using a first-generation industrial computerized tomography using gamma rays, developed at the Center for Radiation Technologies CETER from IPEN.

The images from all tomographic experiments carried out will be reconstructed using the ML-ME algorithm, software developed by a member of the group and renewed on the MATLAB platform [4]. Through the results obtained by tomographic measurements, the following will be estimated: (1) estimated the density of the constituent minerals of the rock; (2) the geometry of the vesicles; and (3) visualized the interconnection of the vesicles.

### 3. Results and Discussion

The formation of secondary minerals can change the texture of the rock matrix, creating a more compact and less porous matrix. This can result in a decrease in permeability, as the presence of secondary minerals can reduce pore connectivity and limit the pathways available for fluid flow. Some secondary minerals can act as cements, binding the basalt's mineral grains together and reducing the rock's permeability. This occurs, especially when secondary minerals fill the spaces between the grains and crystallize, forming a more cohesive and compact matrix, as can be seen in Figure 1.

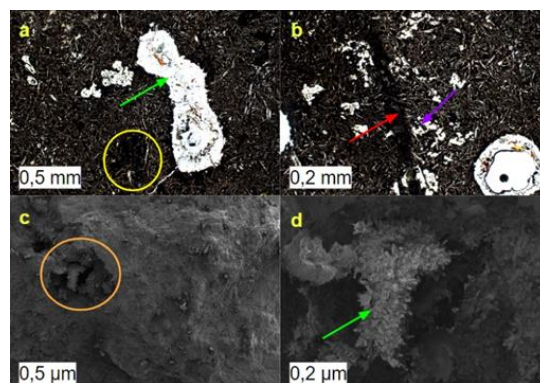


Figure 1: (a): Dikytaxitic texture (yellow circle) and vesicle (green arrow). (b) Intergranular texture (purple arrow) and secondary porosity (red arrow). (c) Partially filled vesicle (orange circle). (d) zeolite (green arrow).

Hydrothermal fluids dissolve some of the primary minerals present in basalts, releasing metal ions and other elements into the solution. The most soluble minerals, such as olivine and pyroxene, may be

the first to be affected by this dissolution process under normal pressure and temperature conditions. Figure 2 illustrates wavelength spectra relating to: augite, calcite, albite, chalcedony and zeolite.

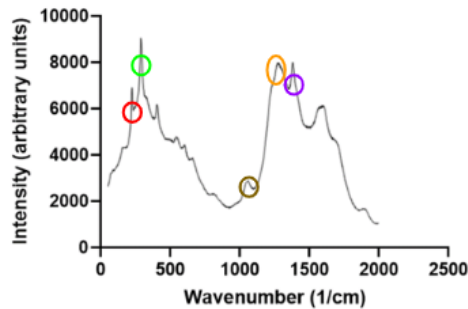


Figure 2: Raman spectroscopy. Augite (green), calcite (brown), albite (orange), chalcedony (red) and zeolite (purple).

Zeolites are formed from the combination of metal ions with aluminosilicates present in the solution, resulting in the formation of porous crystalline structures characteristic of zeolites. Calcite can be introduced into basalts through the processes of metasomatism, which is the chemical alteration of a rock caused by the introduction of new minerals by hydrothermal fluids.

These fluids can contain calcium and carbonate ions that precipitate in the basalt rock, forming calcite. The action of weathering processes, such as the leaching and dissolution of basalt minerals by water and natural acids present in the environment, can concentrate silica in basalt gaps and cavities. This silica can then crystallize and form chalcedony.

The reconstructed image of the igneous rock sample measured after collection is shown in Figure x. The color bar index value represents the linear attenuation coefficient ( $\mu$  (cm<sup>-1</sup>)). High spatial resolution was obtained in the tomography configuration with the selected parameters. The distribution of porosity and permeability can be visualized in the image in Figure 3, observing small vesicles and their interconnections.

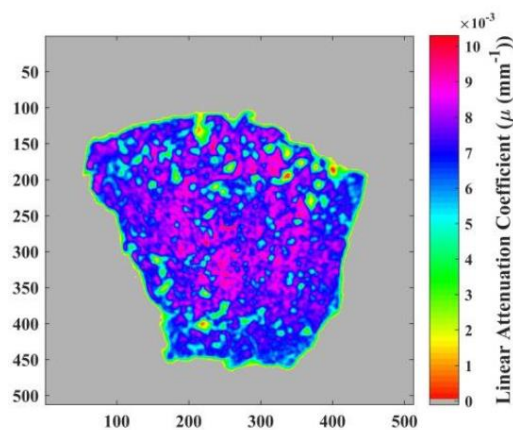


Figure 3: Reconstructed image of volcanic rock.

#### 4. Conclusions

The formation of secondary minerals can change the distribution and size of pores in the rock, thus affecting its ability to transmit fluids. For example, the precipitation of secondary minerals in smaller pores can clog them, reducing the permeability of the rock.

Secondary minerals can fill the void spaces between the basalt's primary mineral grains, thereby reducing the total volume of porosity available for fluid flow. This can decrease the effective permeability of the rock, making it less permeable.

Understanding these processes is crucial for an accurate assessment of basalt permeability by carrying out different types of experiments and for comparison with tomography.

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