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STUDY OF CHEMICAL REACTIVITY FOR CO_2 MINERALIZATION POTENTIAL IN VOLCANIC ROCK PLUGS FROM THE SERRA GERAL GROUP

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Abstract: *This study investigates the potential of basalts from the Serra Geral Group for geological CO_2 storage, focusing on the geochemical behavior of the rocks under reservoir-like conditions at a depth of 900 m. Massive and brecciated basalt samples were characterized in terms of porosity, permeability, and petrography. Closed-system reactor experiments will be conducted at 50 bar and 40 °C for 24 weeks to simulate fluid-rock interactions. Post-experimental analyses will include SEM-EDS, X-ray microtomography, petrographic descriptions to assess mineralogical alterations, and for the fluid; analysis of pH, electrical conductivity, total alkalinity, and chemical composition (ICP-MS and IC). The goal is to evaluate basalt reactivity and its potential for carbonate mineralization and long-term CO2 sequestration.*

Keywords – CCUS, CO_2 mineralization, reactivity of basalts, Serra Geral Group.

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1. INTRODUCTION

The geological storage of CO_2 in basaltic rock reservoirs has driven laboratory and field studies in Large Igneous Provinces (LIPs) worldwide. In Brazil, the Serra Geral Group (SGG) stands out, with thicknesses exceeding 1,700 m and covering a large portion of the Paraná Basin. Experimental studies and field-scale projects have demonstrated the potential of volcanic rocks as geological reservoirs for carbon storage worldwide, such as studies carried out by Matter et al. (2016), Polites et al. (2022) and Oelkers et al. (2022). Basaltic rocks exhibit reactive potential for CO_2 mineralization due to their mineralogical composition, which is rich in divalent cations such as Ca^{2+}, Mg^{2+}, and Fe^{2+}.

These elements have a high electrochemical affinity with carbonate (CO_3^{2}) and bicarbonate (HCO^{3-}) anions, forming stable carbonate minerals such as siderite ($FeCO_3$), magnesite ($MgCO_3$), and calcite ($CaCO_3$), as demonstrated by Xiong et al. (2017).

This study presents preliminary data resulting from CO_2-fluid-rock interaction after six weeks of experimentation in a batch reactor maintained at 40 °C and 50 bar pressure in Fig. 1 area. By the end of the experimental phase (twenty-four weeks), the objective is to characterize the reactive potential of basaltic rocks from the Serra Geral Group for CO_2 mineralization in the form of stable carbonate minerals.

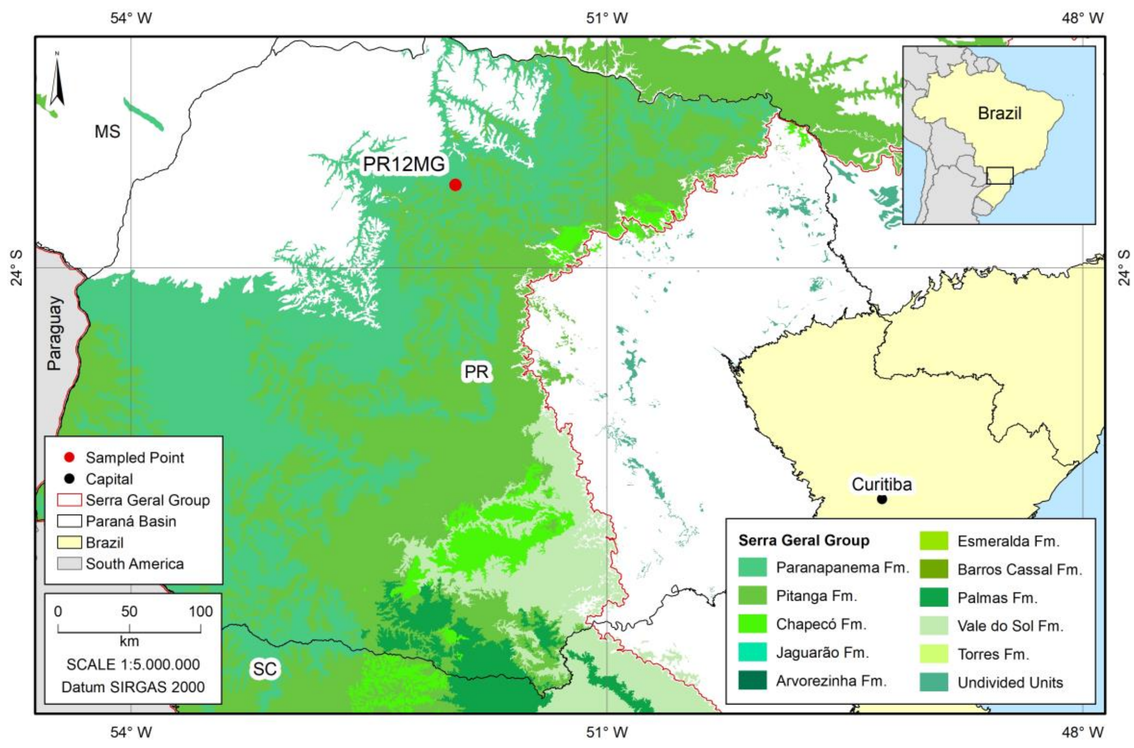

Figure 1– a) Location of Serra Geral Group (SGG) within the Paraná Basin and sample location. Based on data from Horn et al. (2022).

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2. MATERIALS AND METHODS

This study aims to evaluate the geochemical behavior of volcanic rock plug samples from the SGG through CO_2-fluid-rock interaction, simulating pressure and temperature conditions similar to those expected at depths between 900 and 1,200 m. Initially, samples PR12MG_1 and PR12MG_3 were cored into 1-inch diameter cylindrical plugs and subjected to porosity and permeability testing. Pore volume measurements were conducted using the gas expansion method with nitrogen, based on Boyle's Law, employing the AP-608 Porosimeter and Permeameter system. Eight sub-samples, massive volcanic rocks from the flow core (sub-samples SM1, SM2, SM3 and SM4) and vesicular samples collected from the top of rubbly-pahoehoe lava flows (sub-samples SV1, SV2, SV3 and SV4) were used (Fig. 2B), were cut into plugs and subsequently divided in half, resulting in two external portions and a central slice (Fig. 2C). The central slice (~1.5 mm thick) was used to prepare thin sections for petrographic characterization prior to the experiments. The two external portions are placed inside the reactor core holder, with appropriate spacing to simulate fractures, mimicking preferential pathways for fluid flow.

The ongoing experiment is based on the methodology adopted by Xiong et al. (2017), adapted to the conditions of the available materials (Fig. 2A). Pressure and temperature conditions, as well as the CO_2-fluid-rock interaction process, are being simulated experimentally in a closed reactor over a period of approximately twenty-four weeks (6 weeks step time). The reactor was heated to 40 °C and pressurized to 50bar. After each specific step, the reactor will be cooled to room temperature and gradually depressurized over 1 to 2 hours. After opening, immediate measurements of electrical conductivity (EC) and pH will be performed. Total Alkalinity (TA) will be determined by titration, while dissolved metals (Ca, Mg, Fe, Si, Al, Na, etc.) will be analyzed by ICP-MS and anions (Cl^-, Br^-, NO_2^-, NO_3^-, SO_4^{2-}, etc.) by Ion Chromatography. Pre and post-experiment analyses will be performed for characterization of the rock and fluid, as outlined in Table 1.

Table 1. Analytical methods applied according to the sample type and experimental phase:

	Pre	Post
Rock Analysis	XRF Petrography X-Ray MicroCT	XRF Petrography X-Ray MicroCT SEM-EDS
Fluid Analysis	Total Alkalinity EC (Eletrical Cond.) pH ICP-MS (cations) IC (anions)	Total Alkalinity EC (Eletrical Cond.) pH ICP-MS (cations) IC (anions)

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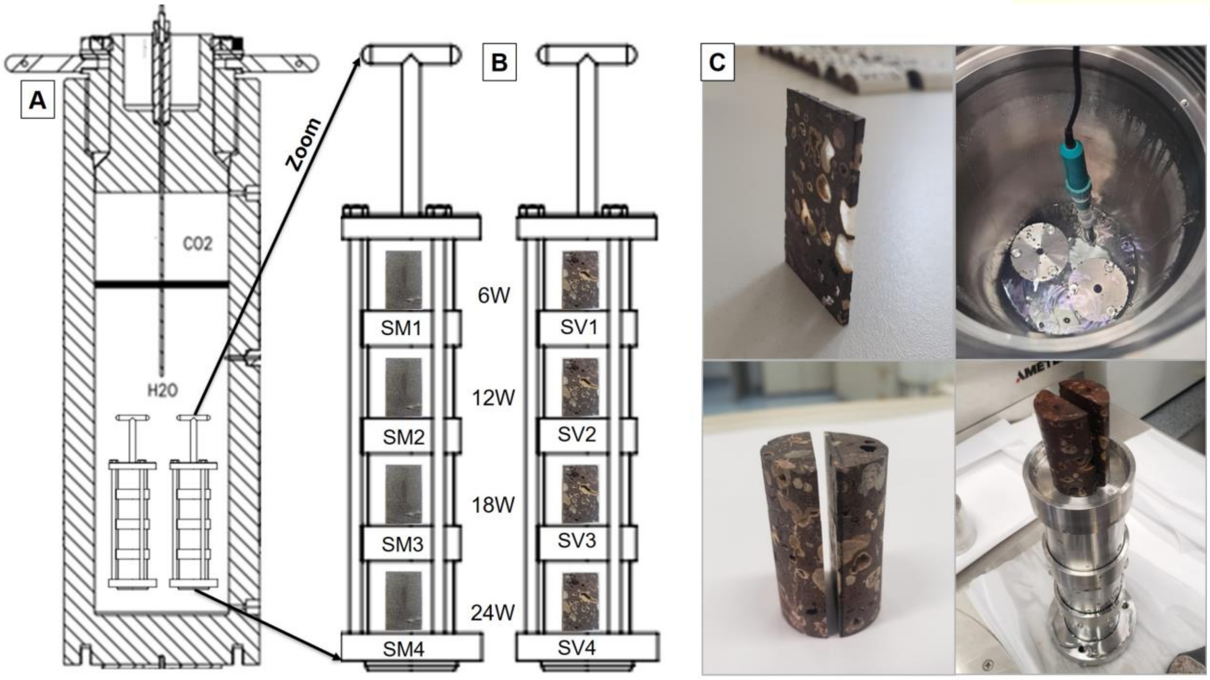

Figure 2. Experimental setup: (A) reactor's internal structure; (B) layout of the samples inside the reactor's vessel; and (C) rock plug setting and pH measurement during sampling

3. RESULTS

3.1. Preliminary petrographic

The sample PR12MG_1 (plugs: SM1, SM2, SM3, and SM4) corresponds to a rock with an intersertal texture, characterized by subhedral to euhedral interlocking plagioclase crystals. Anhedral pyroxenes are present in lesser amounts, along with interstitial glassy matrix and clay minerals (Fig. 3A and 3B). The photomicrograph of sample PR12MG_3, corresponding to plugs SV1, SV2, SV3, and SV4, exhibits a porphyritic texture with an aphanitic, glassy matrix. It is dominated by plagioclase phenocrysts and anhedral pyroxene phenocrysts (Fig. 3C), along with disseminated iddingsite (Fig. 3D). Amygdales up to 2 mm in diameter are filled with subhedral to euhedral zeolite crystals, as well as calcite, quartz, and clays (Fig. 3E and 3F). Vesicle diameters range from 0.2 to 10 mm.

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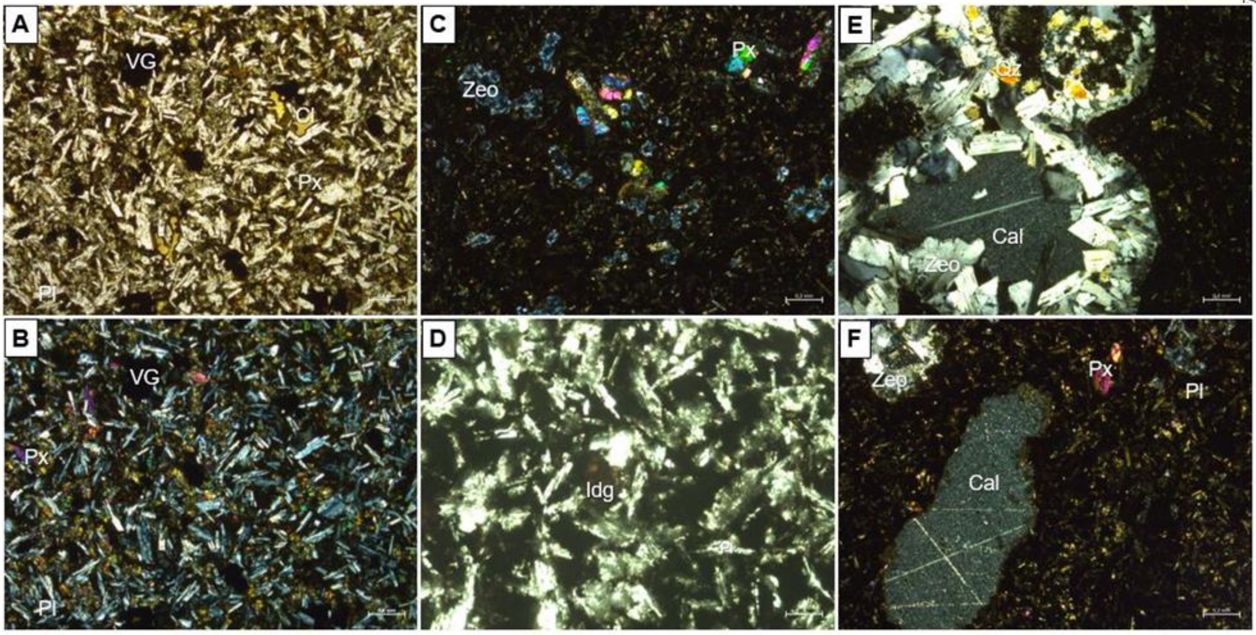

Figura 3. Photomicrographs of the samples in under plane-polarized and cross-polarized light. A e B: Massive sample PR12MG_1; C, D, E e F: Vesiculated sample PR12MG_3.

3.2. Porosity

Original rock plugs from sample PR12MG_1, a massive basalt, exhibits an average effective porosity of 0.34% and a permeability of 0.00 millidarcies. In contrast, sample PR12MG_3 shows an average effective porosity of 2.23% and a permeability of 0.03 millidarcies.

3.3. Preliminary analysis of fluid and rock (after 6 weeks)

Physicochemical parameters were measured after the system was opened and cooled following six weeks of reaction. Fluid analysis revealed a significant decrease in solution pH, from 9.86 to 5.73, accompanied by a substantial increase in electrical conductivity, from 194.6 to 848.9 mS/cm (336.1% increase). Alkalinity remained relatively stable, ranging from 90.58 to 89.04 mg/L as CaCO3. In samples SV1A and SV1B, a pronounced dissolution of the vesicle-filling calcite was observed (Fig. 3), indicating a relatively rapid and significant dissolution of this original secondary mineral during this early experimental stage.

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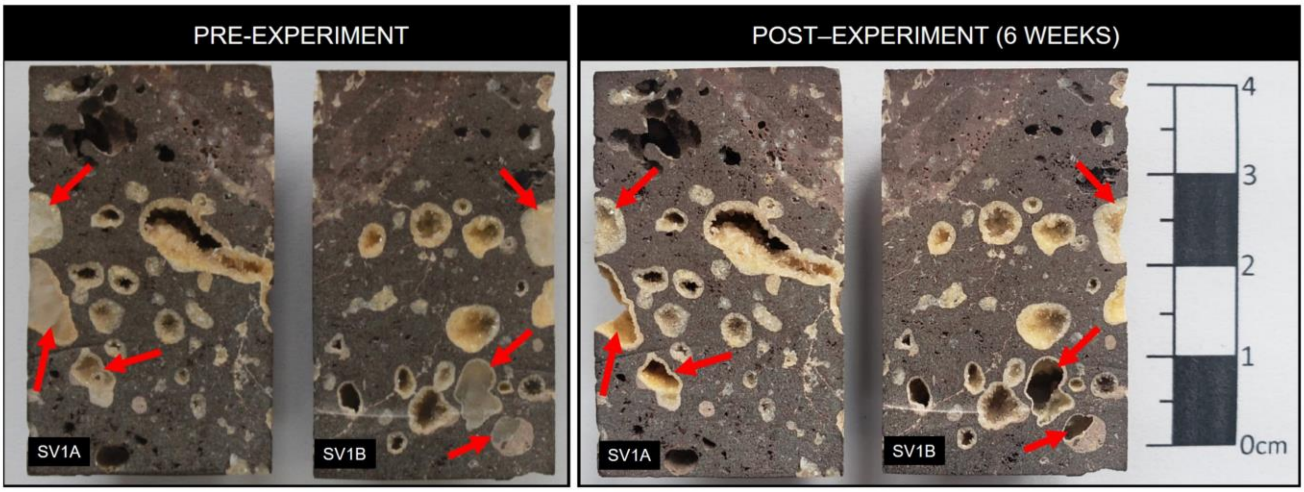

Figure 4. Photograph os sample SV1 before and after the experiment, highlighting mineral dissolution after 6 weeks of experiment.

4. FINAL REMARKS

The ultimate objetive of this study is to provide insights into the reactivity of basaltic rocks and their interaction with fluids in the context of reservoirs for carbonate mineralization, under exposure to a naturally reactive surface area, by assessing the effective capacity of the analyzed SGG basalts for permanent CO_2 storage. To date, based on the comparison between pre- and post-experiment data from the first six weeks of reaction, it was observed that the CO_2-fluid-rock interaction initially promoted mineral dissolution (specially of a significant proportion of fast-reacting calcite), which altered physicochemical parameters and enriched the fluid with divalent cations. This mineral dissolution also led to an increase in porosity and possibly in the permeability of the analyzed sample. Further experimental observations will be investigated during the next sampling steps (12w, 18w and 24w), which will lead to new insights on this reactive process.

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