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UNDERGROUND CO_2 MINERALIZATION POTENTIAL IN PARANÁ STATE: PRELIMINARY ASSESSMENT OF BASALTIC ROCKS FROM SERRA GERAL GROUP

Erico Albuquerque dos Santos[1], João Pedro Tauscheck Zielinski[1], Stéphanie Carvalho da Silva[1], Antônio Rosales Gonçalves Oliveira[1], William Jeovanini Fucks[1], Pedro Costabile de Souza[1], Rodrigo Sebastian Iglesias[1], Breno Leitão Waichel[2], Victor Hugo Jacks Mendes dos Santos[1], Felipe Dalla Vecchia[1], Leonildes Soares de Melo Filho[3], Cassiane Maria Nunes Ferreira[3]

1 - Instituto do Petróleo e dos Recursos Naturais (IPR) - Pontifícia Universidade Católica do Rio Grande do Sul (PUCRS). Av. Ipiranga, 6681, Prédio 96J - Partenon, Porto Alegre - RS, 90619-900. E-mail: erico.santos@pucrs.br ; joao.zielinski@pucrs.br ; stephanie.silva@pucrs.br ; rosales.antonio@pucrs.br ; william.fucks@pucrs.br ; pedro.costabile@gmail.com ; rodrigo.iglesias@pucrs.br ; victor.santos@pucrs.br ; felipe.vecchia@pucrs.br

2 - Departamento de Geologia - Universidade Federal de Santa Catarina (UFSC). R. Eng. Agronômico Andrei Cristian Ferreira, s/n - Trindade, Florianópolis - SC, 88040-900. E-mail: breno@cfh.ufsc.br

3 - Repsol Sinopec Brasil. Praia de Botafogo, 300 - Botafogo, Rio de Janeiro - RJ, 22250-040. E-mail: leonildes.soares@repsolsinopec.com ; cassiane.ferreira@repsolsinopec.com

Abstract: *The Paraná Basin's CO_2 geological storage potential is significant due to its coal deposits, saline formations, CO_2 emission sources, and pipeline network. Recent interest has shifted to volcanic rocks containing divalent cations, facilitating mineral carbonation. The basin's volcanic rocks have an estimated CO_2 storage capacity of 2,840 Gt and areas of ca. 174,000 km^2 in total were identified in different parts of Brazil. The Paraná State, with its vast geological data, is ideal for a detailed assessment, especially in the Serra Geral Group, which covers over half of the state. Using different methodologies, the CO_2 storage capacity in this area was estimated between 79 to 654 Gt, with further research required for precise quantification and identification of possible reservoirs for CO_2 injection.*

Keywords*: CO_2 mineralization; Potential site; Paraná State; Assessment; Northern State*

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1. INTRODUCTION

The potential for CO_2 geological storage in the Paraná Basin (PB) has been historically emphasized due to its abundant coal deposits, saline formations and existing CO_2 emission sources, as well as a minimally established pipeline network (Rockett et al., 2011; CEPAC, 2014). In recent years, attention has been directed toward volcanic rocks due to the presence of divalent cations (e.g., Ca^{2+}, Mg^{2+}, Mn^{2+} and Fe^{2+}) that can be released from minerals through reactions with CO_2-dissolved water, facilitating mineral carbonation (e.g., calcite, magnesite and siderite) (Oelkers et al., 2008). The CO_2 storage capacity of volcanic rocks from the PB has been estimated in 2,840 Gt (Oelkers et al., 2023) and areas of ca. 174,000 km^2 in total were identified in parts of the states of Rio Grande do Sul, Santa Catarina, Paraná, São Paulo and Mato Grosso do Sul as the most suitable for CO_2 geological storage (Zielinski et al., 2024). To select specific sites for injection in those areas, complementary studies are necessary and the Paraná State emerges as an interesting region to conduct a detailed analysis due to the larger availability of geological data.

2. MATERIALS AND METHODS

To provide a preliminary assessment of the potential for underground CO_2 mineralization in the Paraná State, this study analyzed publicly available data (Table 1) to delineate the geological characteristics in surface and subsurface area of the Serra Geral Group (SGG) in the state. The data were analyzed in a geographical information system with the software ArcGIS 10.8.2 (ESRI, 2021). The area of the volcanic rocks was calculated for the continuous polygon estimated from SGB (2022) using the Calculate Geometry command. The depth and thickness were obtained through the interpolation of data from exploratory drilling wells from ANP (2021). The volume was estimated by the multiplication of the calculated area of the estimated polygon for all of SGG in the state by the estimated average thickness of the volcanic rocks. The geochemistry was described using the major elements (wt.%) analyzed from samples (n = 857) of exploratory drilling wells, made available by ITCG (2018). The geothermal gradient (°C/km) was estimated through the interpolation of data from boreholes (n = 2,397) from the Brazilian Geothermal Database, made available by LABGEOT/ON (2022). The depth of water wells was estimated through the interpolation of data from water wells (n = 14,577), provided by SGB (2023).

Table 1 - Geological data used for the preliminary assessment. Source: elaborated by the authors.

Characteristic	Attribute	Source
Geometry	Area (km^2) and volume (km^3)	SGB (2022)
Group	Thickness (m) and depth (m)	ANP (2021)
Geochemistry	Major elements (wt.%)	ITCG (2018)
Geothermal	Geothermal gradient (°C/km)	LABGEOT/ON (2022)
Groundwater	Depth (m) of wells	SGB (2023)

3. RESULTS AND DISCUSSIONS

The SGG occupies most of the western portion of the Paraná State, covering an area of ca. 130,846 km^2, which corresponds to more than half of the state's total area. In the state, there are 5 formations of the SGG which can be found: (i) Vale do Sol - rubbly *pahoehoe* flows of basaltic andesites and subordinate andesites and basalts; (ii) Palmas - domes, lobes and flows of dacites and subordinate rhyolites; (iii)

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Chapecó - flows of trachydacites and dacites, both porphyritic; (iv) Pitanga - *pahoehoe* flows (locally rubbly *pahoehoe* flows) of basalts and basaltic andesites, with intercalated layers of volcaniclastic and sedimentary rocks; and (v) Paranapanema - *pahoehoe* flows (locally rubbly *pahoehoe* flows) of basalts and basaltic andesites with intercalated layers of volcaniclastic and sedimentary rocks (Figure 1). There is also 1 undivided unit in the state. In the northwest portion of the Paraná State, in an area of ca. 25,076 km^2 (around 19% of the area of SGG in the state), these volcanic rocks are covered by sedimentary rocks from the Bauru and Caiuá groups.

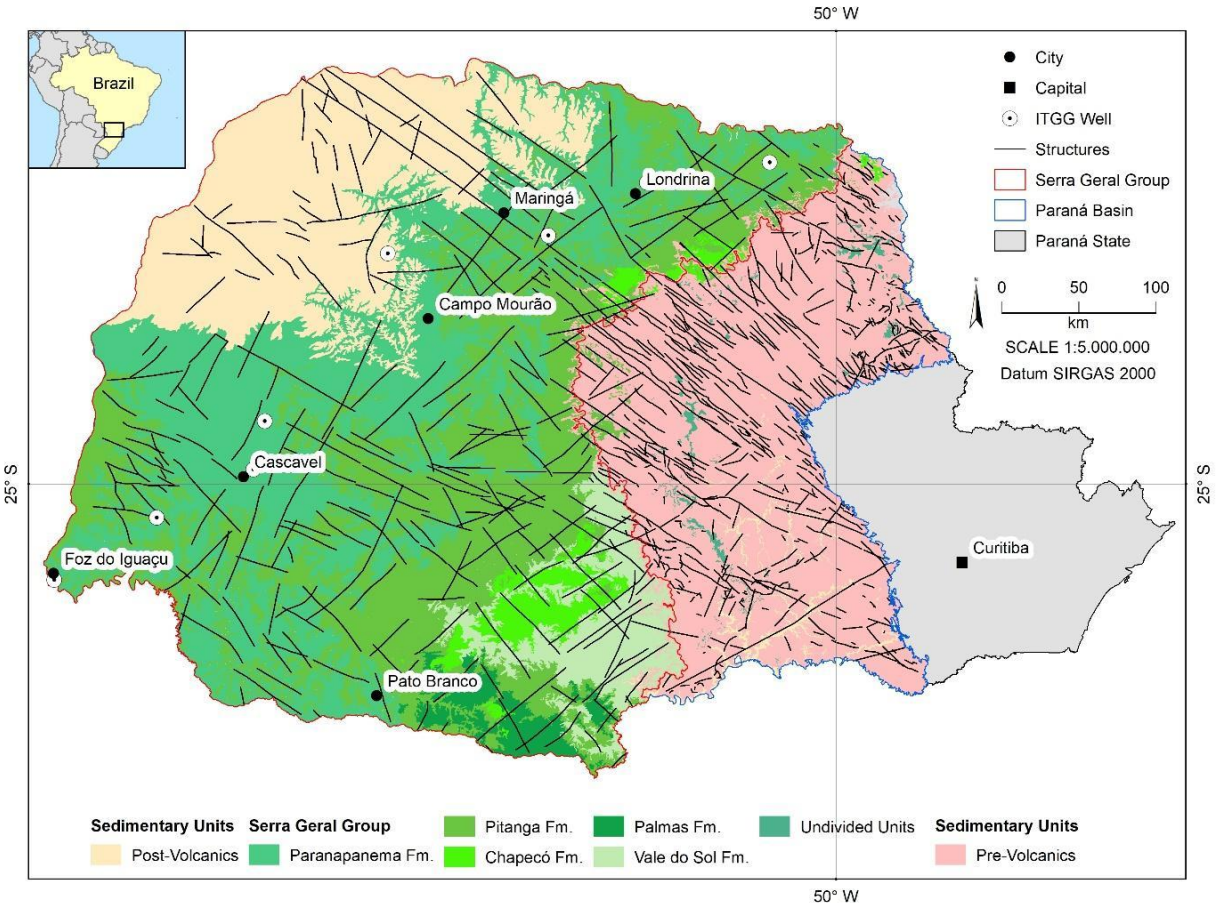

Figure 1 - Formations of volcanic rocks from the Serra Geral Group in the Paraná State. Source: elaborated by the authors with data from SGB (2022).

The Pitanga and Paranapanema formations could have considerable carbon storage potential because of their physical characteristics, such as: (i) the size of the lava flows, (ii) the brecciated portion in rubbly *pahoehoe* flows and (iii) the intercalation with volcaniclastic rocks (Zielinski et al., 2024).

Chemical composition of samples from drilled wells (BOURBON, CA, CIAN, COPACOL, LAR, MANDI, P-03 AND P-2 LOND) of the SGG in the Paraná State (Table 2) ranged from: 41.22 to 61.42 wt.% SiO_2 (avg.: 51.16 wt.%); 1.16 to 5.61 wt.% TiO_2 (avg.: 2.90 wt.%); 10.49 to 26.03 wt.% Al_2O_3 (avg.: 12.84 wt.%); 0.13 to 5.25 wt.% Na_2O (avg.: 2.96 wt.%); 0.16 to 4.41 wt.% K_2O (avg.: 1.35 wt.%); and 17.28 to 32.22 wt.% FeO + MnO + MgO + CaO (avg.: 24.58 wt.%) with approximately 80% of these rocks classified as basaltic andesites. The sum of divalent cations of SGG in the Paraná State showed a wider range of values if compared with the geochemical data from the HN-2 injection well of CarbFix 1 Project in Iceland (values from 22.45 to 29.81 wt.%) (Alfredsson et al., 2013) and the Wallula Basalt Pilot #1 injection well of Wallula Project in the United States of America (values from 19.59 to 30.98 wt.%) (McGrail et al., 2009). This fact attests to the presence of these divalent cations in the volcanic rocks of

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SGG and indicates the possibility for mineralization in lava flows with high content of calcium, magnesium and iron, as suggested by Oelkers et al. (2008).

	SiO_2	TiO_2	Al_2O_3	FeO(t)	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI
Max.	61.42	5.61	26.03	27.13	0.50	6.98	6.98	5.25	4.41	1.02	14.30
Min.	41.22	1.16	10.49	10.03	0.15	0.64	0.64	0.13	0.16	0.14	-0.30
Avg.	51.16	2.90	12.84	14.98	0.22	4.69	4.69	2.96	1.35	0.39	2.10

Table 2 - Geochemical data used for the preliminary assessment. Source: elaborated by the authors with data from ITCG (2018).

Thickness ranged from 456 to 1,662 m (avg. 1,002 m) (Figure 2) and - based on this obtained average thickness and the total calculated area of the SGG in the Paraná State - the volume of these volcanic rocks was estimated at ca. 131,108 km^3. The thicker portion of SGG (> 1,200 m) is predominantly situated in the northern part of the Paraná State, close to the municipality of Maringá. The potential for mineralization in thicker volcanic piles is higher due to the probability of finding one thick lava flow or various lava flows (e.g., stacked basalts as mentioned by White et al., 2020 and Cao et al., 2024) with brecciated/vesiculated top that has more porosity and permeability for CO_2 injection.

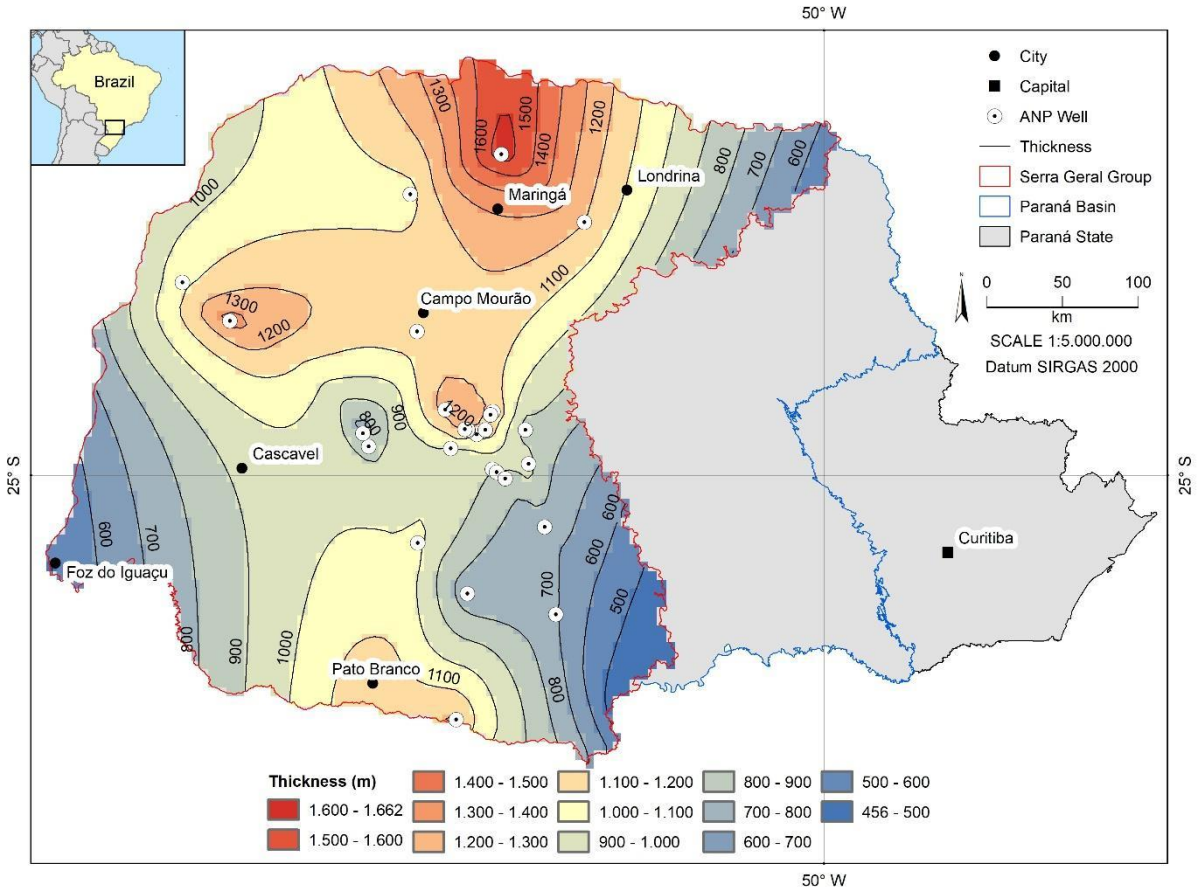

Figure 2 - Thickness of volcanic rocks from the Serra Geral Group in the Paraná State. Source: elaborated by the authors with data from ANP (2021).

Depths ranged from 461 to 1,772 m (avg. 1,052 m) (Figure 3). The deeper portion of SGG (> 1,200 m) is predominantly situated in the northern part of the Paraná State, close to the municipality of Maringá, and it has depth similar to the ones found in the HN-2 injection well of the CarbFix 1 Project in Iceland (1,184 m) (Alfredsson et al., 2013) and the Wallula Basalt Pilot #1 injection well of the Wallula Project in the United States of America (1,253

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m) (McGrail et al., 2009). The potential for mineralization in deeper volcanic piles is higher due to the higher pressure and higher geothermal gradient found in these rocks, which facilitate the CO_2 mineralization. Depths > 900 m are preferable due to lithospheric pressure and temperature conditions that are more suitable for CO_2 mineralization.

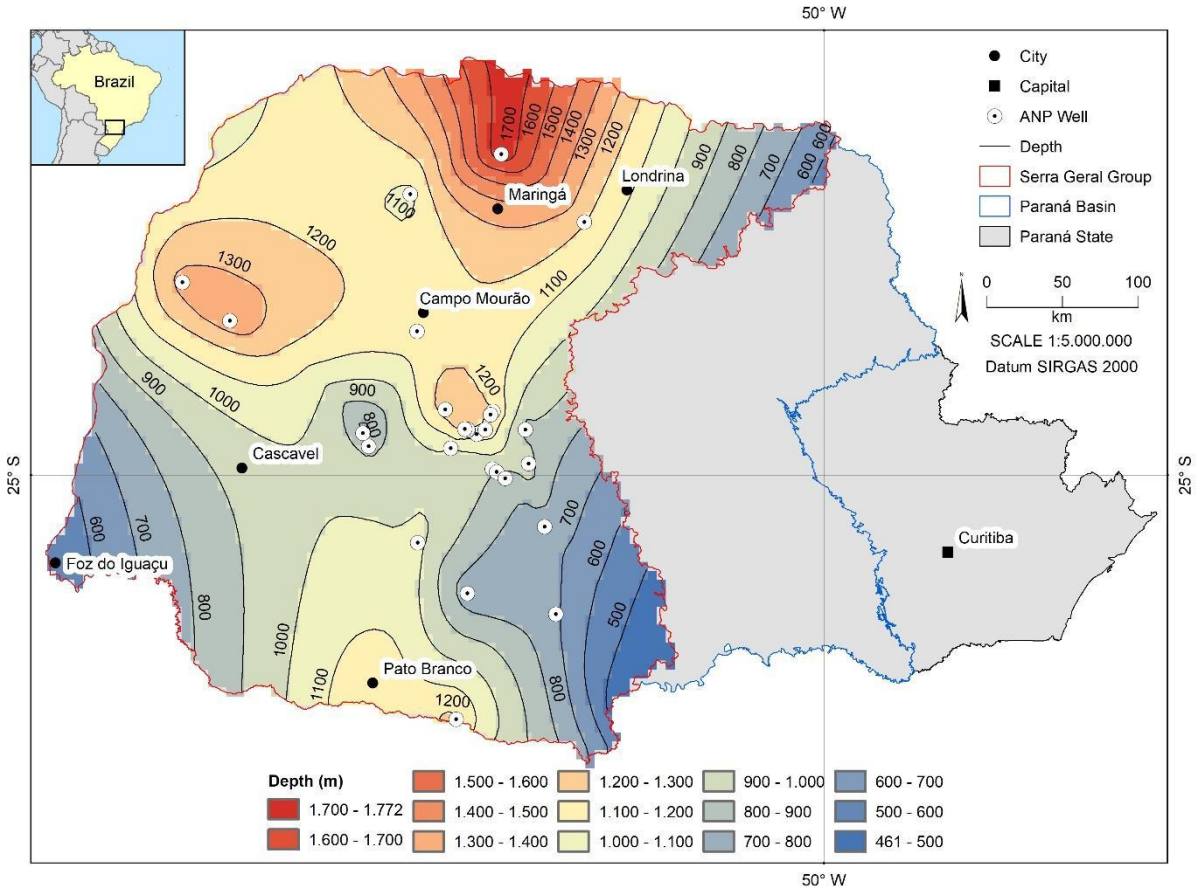

Figure 3 - Depth of volcanic rocks from the Serra Geral Group in the Paraná State. Source: elaborated by the authors with data from ANP (2021).

The geothermal gradient varied from 18.59 to 29.75 °C/km (avg. 23 °C/km) (Figure 4), classifying this region as having a cold geothermal gradient (< 30 °C/km), according to Kaldi & Gibson-Poole (2008). The hotter portions of SGG (> 23 °C/km) are predominantly found in the northern part of the Paraná State, close to the municipalities of Paranavaí, Maringá and Londrina. However this hotter region of SGG in Paraná is still colder, if compared to the geothermal gradient found in the HN-2 injection well of the CarbFix 1 Project in Iceland (80 °C/km) (Alfredsson et al., 2013) and to the Wallula Basalt Pilot #1 injection well of the Wallula Project in the United States of America (39 °C/km) (McGrail et al., 2009). This fact can represent a constraint in basalt dissolution and carbonate precipitation rates. The potential for mineralization is higher in hotter conditions due to the increase in dissolution rates of forsterite, wollastonite, serpentine, anorthite and basaltic glass caused by temperature, as mentioned by Oelkers et al. (2008).

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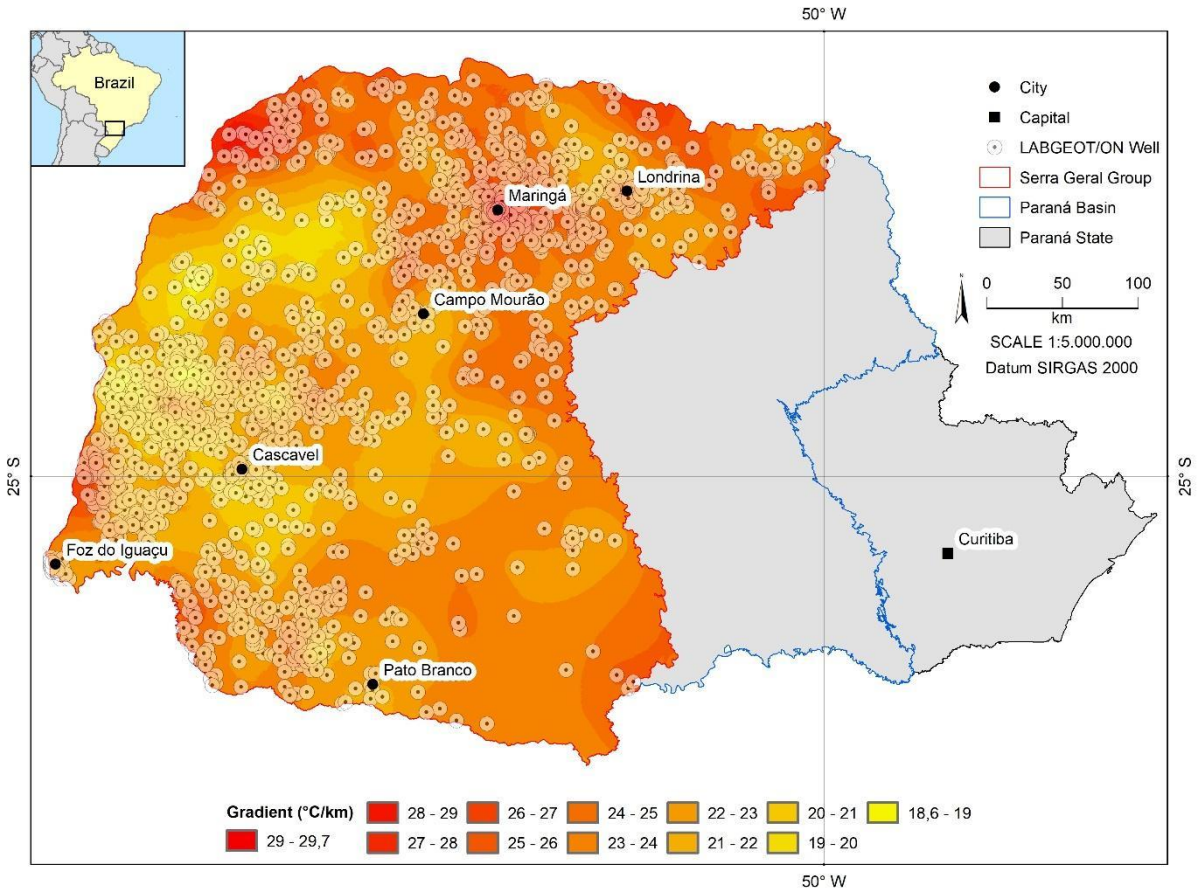

Figure 4 - Geothermal gradient in the area of the Serra Geral Group in the Paraná State. Source: elaborated by the authors with data from LABGEOT/ON (2022).

Water well depths ranged from less than 20 to 4,919 m (avg. 139 m) (Figure 5). The deeper water wells in SGG are found in the southern part of the Paraná State. Most of the water wells in the state (~90%) can be considered relatively shallow (< 200 m deep), which prevents water conflict issues since the preferable depth for CO_2 injection is > 900 m. The potential for mineralization in sites with shallower water wells is higher due to the higher distance from the aquifer.

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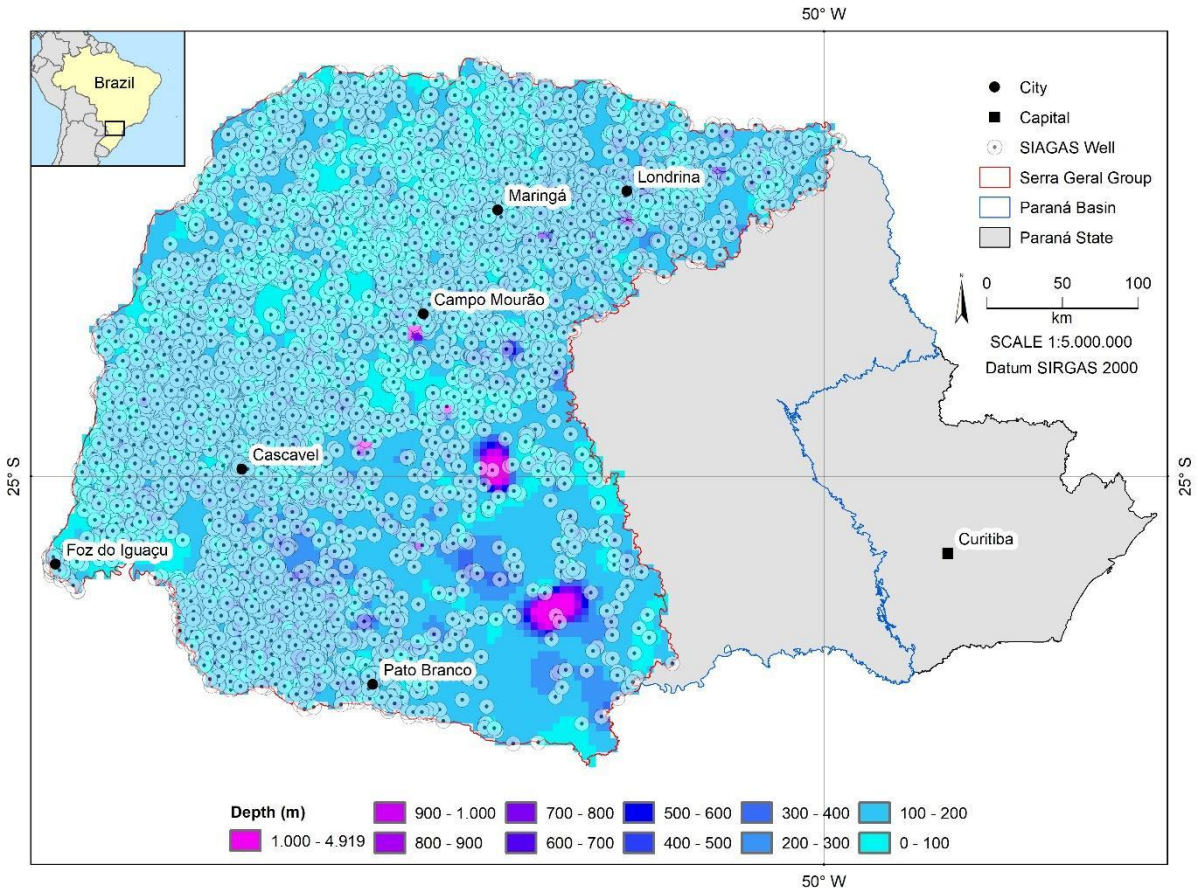

Figure 5 - Groundwater well depth in the area of the Serra Geral Group (Paraná State). Source: elaborated by the authors with data from SGB (2023).

The theoretical CO_2 storage capacity of SGG in the Paraná State was estimated as ca. 79 Gt, 419 Gt and 654 Gt (Table 3), based on the calculated area and on the methodology and parameters of McGrail et al. (2006), Goldberg et al. (2008) and Oelkers et al. (2023), respectively. More data of effective porosity from the exploratory drilling wells (as obtained by Oliveira et al. in this issue) and of the storage efficiency of these rocks are necessary, in order to better constrain the theoretical CO_2 storage capacity of SGG in the state.

Table 3- Parameters used for the estimation of the theoretical CO_2 storage capacity. Source: elaborated by the authors.

Methodology	Parameter 1	Parameter 2	Parameter 3	Parameter 4	Estimative
McGrail et al. (2006)	Interflow thickness of 10 m	Average porosity of 15%	10 available interflow zones	Average hydrostatic pressure of 100 atm	79 Gt CO_2
Goldberg et al. (2008)	Permeability over 1/6 of the upper 600 m	Average channel porosity of 10%	-	-	419 Gt CO_2
Oelkers et al. (2023)	Average thickness of 500 m	Storage capacity of 10 kg CO_2/m^3	-	-	654 Gt CO_2

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4. FINAL REMARKS

The Paraná State has high potential for CO_2 geological storage, especially in the northern part of the state, where is located an interesting area with thicker and deeper (> 1,200 m) rocks, along with a higher geothermal gradient (> 26 °C/km). The potential for mineralization in these conditions is higher due to: (i) the probability of finding one thick lava flow or or various lava flows (e.g., stacked basalts as mentioned by White et al. [2020] and Cao et al. [2024]) with brecciated/vesiculated top that has more porosity and permeability for CO_2 injection; (ii) the higher pressure and higher geothermal gradient found in these rocks that facilitate the CO_2 mineralization; and (iii) the increase by temperature in dissolution rates of forsterite, wollastonite, serpentine, anorthite and basaltic glass as mentioned by Oelkers et al. (2008). In this context, the Pitanga and Paranapanema formations could have considerable carbon storage potential because of their physical characteristics: (i) the size of the lava flows; (ii) the brecciated portion in rubbly *pahoehoe* flows; and (iii) the intercalation with volcaniclastic rocks (Zielinski et al., 2024). However, attention must be given to the fracture network related to the Ponta Grossa Arch, which could influence the mobility of the injected CO_2 in these rocks. To better understand the state's geological potential, future studies must consider complementary subsurface data (seismic surveys, drilling wells, core samples, petrophysical and geochemical analyses) to locate potential reservoirs for CO_2 injection with more precision.

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