CHAPTER 9

CLAY MINERALS AND CO_2 GEOLOGICAL STORAGE IN THE PARANÁ BASIN

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ABSTRACT

CO_2 geological storage is the segment within the CCS chain that plays a significant role in mitigating the worst impacts of climate change due to its considerable CO_2 abatement capacity. Overall, the effectiveness of CO_2 geological storage depends on the combination of geological factors, including clay mineralogy. Clay minerals are relevant to CO_2 geological storage since they affect the gas sorption capacity of rock formations. For instance, the concentration of expandable clays, such as smectites, adds to reservoirs' overall CO_2 storage capacity by favouring the development of CO_2 adsorption sites due to interlamellar swelling. In this chapter, the contribution of clay minerals to CO_2 geological storage is discussed. In addition, the Paraná Basin, south and southeast Brazil, was selected as a case study for determining potential reservoirs and caprocks to CO_2 geological storage, based on identified clay mineral assemblages. The result is that the clay mineralogy of various geological formations within the Paraná Basin favours the overall effectiveness and safety of CO_2 geological storage and the deployment of CCS technologies in the region.

Keywords: Clay minerals, CO_2 geological storage, Panará Basin

1. INTRODUCTION

The increase in carbon dioxide (CO_2) concentration in the Earth's atmosphere, especially from the 1950s to the present day, has been scientifically proven with data from different proxies (IPCC, 2021) and widely disseminated in various media. Special attention has been given to CO_2 emitting sources, the greenhouse effect of this gas in the atmosphere, and the possible consequences on the planet's surface in different environments.

On the other hand, the technologies developed to capture the CO_2 released from stationary sources, compress it, transport it, and store it in geological formations placed at depths greater than 500 m are still relatively less known (Tomic et al., 2018). The combination of these technologies is known as CO_2 capture and storage (CCS). According to the IPCC (2005), CCS is an important option to reduce the release of CO_2 into the atmosphere, contributing to stabilizing its concentration. It may lead to a critical emission reduction in a zero-carbon transition scenario (IEA, 2020).

In this chapter, the focus is to evaluate the potential for CO_2 geological storage, also known as CO_2 geological sequestration, of some sedimentary formations of the Paraná Basin, based on the contribution of its clay minerals for the retention of this compound.

2. CLAY MINERALS

Clay minerals are common minerals on the Earth's surface, constituting many soils, sediments, and sedimentary rocks. In sedimentary basins, they are abundant constituents of siliciclastic and some sedimentary carbonate rocks. In these materials, most clay minerals are clay-sized particles, usually less than 2 µm.

Clay minerals' chemical composition and crystal structure classify them as hydrated aluminium phyllosilicates (Guggenheim & Martin, 1995), divided into two groups (1:1 and 2:1), which differ by the number of tetrahedral sheets linked to an octahedral sheet (CMS, 2020). 1:1 clay minerals are formed by repeating the stacking of a tetrahedral sheet and an octahedral sheet. 2:1 clay minerals contain an octahedral sheet between two tetrahedral sheets and interlamellar material (usually cations or chemical compounds) between the 2:1 layers.

The adsorption capacity of clay minerals is one of the most important characteristics to be determined to operate efficiently CO_2 sequestration (Fripiat et al. 1974). The interlamellar distance is a critical parameter determining the sorption of molecules, including CO_2 (Hong and Romanov 2018). This distance depends on the charge and composition of the clay mineral and the size of the charge-compensating cations in that space (Busch et al. 2016, Grekov et al. 2020). For instance, expandable clays, such as clays from the smectite group, lead to higher CO_2 storage capacity (Bertier & Rother, 2016; Busch et al., 2017) due to its volumetric expansion and consequent development of adsorption sites. Additionally, such interlamellar swelling in smectite clays associated with CO_2 adsorption contributes to storage safety and a reduction in reservoir pressure (Busch et al., 2020).

Regarding the sorption capacity of different clay mineral assemblages, Ca-exchanged smectite can adsorb the most significant amounts of CO_2, followed by Na-exchanged smectite, illite, and kaolinite, and negligible amounts of CO_2 adsorbed to chlorite (Busch et al., 2020; Busch et al., 2008).

Overall, clay minerals are essential to CO_2 geological storage due to their gas sorption capacity. In low-permeability reservoirs, such as shale formations, clay minerals contribute to the gas sorption capacity of these unconventional reservoirs and, consequently, its overall CO_2 storage potential (Busch et al., 2008). Clay minerals in conventional reservoirs determine the caprock integrity, storage safety, and effectiveness (Busch et al., 2017). Therefore, determining mineralogical assemblages, especially clay mineral content, type, and composition, is essential to characterize potential CO_2 reservoirs and caprocks.

3. POTENTIAL GEOLOGICAL FORMATIONS FOR CCS IN THE PARANÁ BASIN BASED ON THEIR CLAY MINERALS CONTENT

The Paraná Basin is a Paleozoic-Mesozoic cratonic basin (Ordovician to Cretaceous) that occupies a significant and wide area in the central portion of South America, located mainly in southern Brazil (just over 1,120,000 km^2) (REATE 2020). The basin is filled, essentially, with siliciclastic rocks, and subordinately, with sedimentary carbonate rocks, adding up to about 6 km in thickness.

Volcanic igneous rocks of the Serra Geral Formation, about 1700 m thick, complete the stratigraphic column of the basin. They present themselves as spills, sills, and dikes (Melfi et al. 1988) and close the evolutionary history of the Paraná Basin in the Early Cretaceous (Riccomini 1995).

In total, the sedimentary and igneous rocks of Paraná Basin amount to just over 7600 m, according to the thicknesses mentioned by Milani et al. (2007). They are overlaid by the sedimentary deposits of the Bauru Basin, at least 300 m thick.

Clay minerals are present in siliciclastic rocks along the entire stratigraphic column of the Paraná Basin, with variations in their types and proportions. The most comprehensive study of the characterization of clay minerals was carried out by Ramos & Formoso (1975), who analysed 1052 samples collected in 43 drill cores drilled by Petrobrás until 1967, as shown in Figure 1.

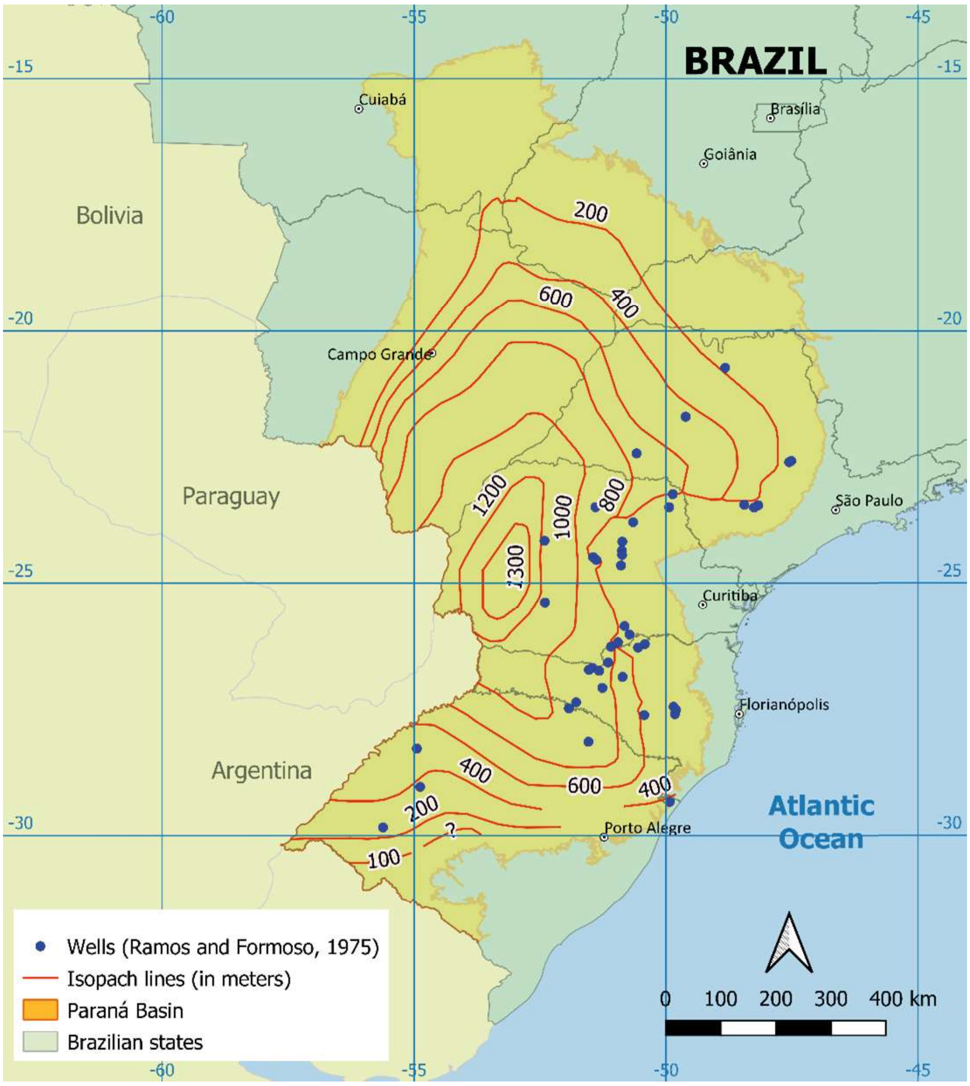

Figure 1 - Isopaque map (in meters) of the Permian section above Irati Formation and the location of the 43 wells analyzed by Ramos & Formoso (1975) in the Paraná Basin (Source: Lima 2021).

The boreholes used by the authors were drilled in the southern (Paraná, Santa Catarina, and the Rio Grande do Sul states) and east (São Paulo state) parts of the basin, reaching a depth of 4378 m in a sample collected in the core 2-CM-1-PR (Paraná state). The authors analysed the clay fraction (< 2µm) by X-ray diffraction (Cu K alpha radiation, 35 kV, 20 mA, Ni filter, goniometer speed of 2o 2Ɵ/min), using oriented preparations and conventional treatments (natural drying, solvation with ethylene glycol and calcination at 490oC). The lithology of the samples accompanies the mineralogical results for groups of clay minerals. Several similar types of research by later authors complement this collection, carried out with samples collected from natural exposures and mine fronts in the outcropping area of the basin along its borders, and in shallow cores drilled close to this area.

The set of information collected is presented in Table 1 and considered representative of the lithological variation and assemblage of clay minerals from various geological formations in the Paraná Basin, given the geographic coverage of the boreholes and exposures as the wide vertical distribution of the samples.

Due to the differences in the methods used for the semi-quantification of mineral phases in the X-ray diffractograms used by the various authors, table 1 shows the dominant clay mineral and those with subordinate presence in each geological formation. Since the objective of this work is to indicate the training potential for deploying CCS technology based on the clay mineral content, the lack of absolute values does not affect this analysis. Thus, information regarding the maximum thickness, dominant and subordinate lithologies, and principal and secondary clay mineral assemblages were compiled for the geological sedimentary formations of the Paraná, Itararé, Guatá, Passa Dois, and São Bento groups (Table 1).

The total thicknesses recorded for each group are hundreds of meters (Table 1): i) Paraná Group with 996 m; ii) Itararé Group reaching 1281 m, the thickest in the basin; iii) Guatá Group with a thickness of 586 m, the thinnest in the basin; iv) Passa Dois Group with 1159 m, and v) São Bento Group with 800 m only in the sum of sedimentary units (Pirambóia and Botucatu formations), not including the volcanic rocks of the Serra Geral Formation, which can reach 1500 m in maximum thickness.

The dominant lithologies are psammitic (sandstone) to pelitic (siltstone, claystone, and shale) (Table 1). Psephytic rocks (diamictite and conglomerate) are only important in the Itararé Group. Subordinately occurring lithologies include carbonate rocks (limestone, oolitic limestone, and marlstone), calcareous concretion, nodular flint, and coal.

Among the clay minerals mentioned by the consulted authors, illite, interstratified illite/smectite, and smectite are cited as the main phases in several geological formations where they are associated or isolated, constituting the main mineralogical composition. Chlorite is the main clay mineral only in the Rio Bonito and Irati formations. Assemblages of clay minerals that are more varied, with subordinate occurrences, are recognized in the different formations and commonly include kaolinite, in addition to pyrophyllite (Grupo Paraná), palygorskite (Grupo Itararé), and corrensite (Grupo Passa Dois).

The presence of smectite as the main or subordinate clay mineral in several geological formations of the Paraná Basin meets one of the critical criteria for selecting the reservoir rock for CO_2, that is, the presence of appropriate mineralogical composition for the interaction with the carbon dioxide. Several studies have demonstrated the role of this expandable clay mineral in CO_2 adsorption.

In addition, the presence of interstratified illite/smectite and corrensite may be important for the effectiveness of the geological storage of CO_2 in the Paraná Basin. These clay minerals are still poorly studied in their interactions with CO_2, but both contain interstratified smectite and are expandable, which suggests a good sorption capacity. The other clay minerals (illite, kaolinite, chlorite) interact with CO_2, although lesser (e. g., Hu et al. 2019).

The varied lithology of sedimentary formations that contain expandable clay minerals as dominant or subordinate clay suggests that the study to determine the potential for CO_2 storage will have a local character. The characterization of sedimentary facies and mineralogical composition, together with other local geological attributes (e. g., deformation structures), will be the basis of information for selecting reservoir rocks.

4. CONCLUSION

The geological storage of CO_2 is a technological alternative to reduce the emission of greenhouse gases worldwide. It may eventually compensate for the various stationary sources that emit this gas in Brazil's southeast and south regions. Several geological sedimentary formations within the Paraná Basin contain lithologies that might be suitable for CO_2 retention. The overall suitability of reservoirs to CO_2 storage depends on their clay mineralogy among various geological aspects. This dependence is due to the gas sorption capacity of clay minerals, which affects the CO_2 storage potential of clay-rich geological formations. Inthe Paraná Basin, the occurrence of expandable clays, such as smectites, contributes to the overall potential for CO_2 geological storage and CCS deployment in the region. However, the lithological and compositional heterogeneity of geological formation suggests that a local scale approach will be necessary to determine its behaviour as a reservoir and/or caprock and its real contribution to emissions mitigation.

<table>
<tr><th rowspan="2">Group</th><th colspan="2">Formation</th><th rowspan="2" colspan="2">Maximum thickness (m)</th><th rowspan="2" colspan="2">Main lithology</th><th rowspan="2" colspan="2">Other lithologies</th><th rowspan="2" colspan="2">Main clay mineral(s)</th><th rowspan="2" colspan="2">Other clay minerals</th></tr>
<tr><th>SSE</th><th>NNW</th></tr>
<tr><td rowspan="2">São Bento</td><td colspan="2">Botucatu</td><td colspan="2">450 [5]</td><td colspan="2">sandstone [1]</td><td colspan="2">claystone [1]
clayey sandstone</td><td colspan="2">smectite [1]</td><td colspan="2">illite, chlorite, I/S, kaolinite [1]</td></tr>
<tr><td colspan="2">Pirambóia</td><td colspan="2">350 [3]</td><td colspan="2">sandstone [3]</td><td colspan="2">claystone, siltstone [3]</td><td colspan="2">smectite, I/S [6]</td><td colspan="2"></td></tr>
<tr><td rowspan="4">Passa Dois</td><td>Rio do Rasto</td><td rowspan="3">Corumbataí</td><td>650 [5]</td><td rowspan="3">130 [7]</td><td colspan="2">siltstone [3]
claystone</td><td>sandstone [1]
limestone
silex</td><td rowspan="3">shale [3]
sandstone
oolitic
limestone</td><td>illite [1]
smectite</td><td rowspan="3">smectite [2]</td><td>I/S, chlorite, corrensite, kaolinite [1]</td><td rowspan="3">illite [2]
chlorite
I/S</td></tr>
<tr><td>Teresina</td><td>318 [3]</td><td colspan="2">siltstone, shale, claystone [1]</td><td>oolitic limestone, silex, sandstone [1]</td><td>illite [1]</td><td>I/S, smectite, chlorite, corrensite [1]</td></tr>
<tr><td>Serra Alta</td><td>120 [1]</td><td colspan="2">shale, siltstone, claystone [1]</td><td>calcareous concretion [1]</td><td>illite [1]</td><td>I/S, chlorite, smectite, corrensite, kaolinite [1]</td></tr>
<tr><td colspan="2">Irati</td><td colspan="2">71 [3]</td><td colspan="2">claystone, shale [1]</td><td colspan="2">limestone, nodular silex [1]
calcareous concretions, siltstone</td><td colspan="2">illite, I/S, chlorite [1]</td><td colspan="2">smectite, corrensite, kaolinite [1]</td></tr>
<tr><td rowspan="2">Guatá</td><td>Palermo</td><td rowspan="2">Tatuí [4]</td><td>300 [5]</td><td rowspan="2">70 [4]</td><td>siltstone [1]</td><td rowspan="2">siltstone [4]</td><td>shale [1]
sandstone</td><td rowspan="2">limestone [4]
silex
sandstone</td><td>I/S [1]</td><td rowspan="2">illite [9]</td><td>chlorite [1]
illite
kaolinite
smectite</td><td rowspan="2">kaolinite [9]
smectite</td></tr>
<tr><td>Rio Bonito</td><td>286 [1]</td><td>sandstone [1]</td><td>shale [1]
siltstone claystone
marlstone coal</td><td>I/S [1]</td><td>kaolinite [1]
chlorite
illite smectite</td></tr>
<tr><td rowspan="3">Itararé</td><td>Taciba</td><td rowspan="2"></td><td rowspan="3">1281 [1]</td><td rowspan="2"></td><td rowspan="3" colspan="2">diamictite [1]
conglomerate
sandstone
claystone</td><td rowspan="3" colspan="2">shale, siltstone [1]</td><td rowspan="3">illite [1]
chlorite</td><td rowspan="2"></td><td rowspan="3">smectite [1]
kaolinite, I/S, palygorskite</td><td rowspan="2"></td></tr>
<tr><td>C. Mourão</td></tr>
<tr><td>Lagoa Azul</td><td>Aquidauana</td><td>799 [3]</td><td>smectite, illite [8]</td><td>kaolinite
chlorite [8]</td></tr>
<tr><td rowspan="2">Paraná</td><td colspan="2">Ponta Grossa</td><td colspan="2">653 [1]</td><td colspan="2">shale [1]</td><td colspan="2">siltstone, sandstone [1]</td><td colspan="2">illite [1]</td><td colspan="2">chlorite, I/S [1]
kaolinite, pirofilite</td></tr>
<tr><td colspan="2">Furnas</td><td colspan="2">343 [3]</td><td colspan="2">sandstone [1]</td><td colspan="2">siltstone [3]</td><td colspan="2">illite [1]</td><td colspan="2">kaolinite, chlorite [1]
I/S, pyrophyllite</td></tr>
</table>

Table 1 – Maximum thicknesses, lithologies and assemblages of clay minerals from geological sedimentary formations in the Paraná Basin. The information in each frame comes from: 1 Ramos and Formoso (1975); 2 Ramos and Formoso (1976); 3 Schneider et al. (1974); 4 Soares (1972), Assine et al. (2003), Chahud (2011); 5 Milani et al. (2007); 6 Gesicki (2007); 7 Zanardo et al. (2011), 8 Gesicki (1997); 9 Curtolo (2019).

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