

Mineralogy of Palygorskite Occurrences from Guadalupe, Piauí, Parnaíba Basin

Mineralogia das Ocorrências de Palygorskita em Guadalupe, Piauí, Bacia do Parnaíba

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Abstract

Palygorskite is a clay mineral with structural units forming ribbons, whose economic importance is directly related to its unusual structure and physicochemical properties, which give it a wide variety of uses in industry. The formation stability field of palygorskite is very limited, which makes deposits of this clay rare around the world. In Brazil, the only exploitable deposits of this mineral are located in the municipality of Guadalupe, Piauí state, inserted in the geological context of the Parnaíba Basin, specifically in the Carboniferous and Permian sequence represented by the Piauí, Poti and Pedra de Fogo formations. The objective of this study was the geological and mineralogical description of palygorskite occurrences in the Guadalupe region. Six occurrences were studied, and 25 samples were collected. These raw samples were processed to concentrate particles with size smaller than 44 µm. XRD, SEM/EDS, density and particle size analysis were performed. Most of the samples were composed of palygorskite, quartz and kaolinite; however, according to the diffractograms, there are three samples with the absence of palygorskite, two with the absence of kaolinite and one with presence of dolomite. From these results, it is possible to correlate hypotheses for palygorskite formation with the local geological context. The environmental conditions of Piauí and Pedra de Fogo formations were favorable to this clay mineral formation, the association of dolomite and palygorskite in an upper layer may indicate a greater association with Pedra de Fogo Formation, however the field descriptions, as the levels of silicite, and the analyses results are not enough to define in which one of these formations the occurrences of palygorskite are inserted.

Keywords: Clay minerals; Fibrous clay; Applied mineralogy

Resumo

Palygorskita é um argilomineral com unidades estruturais em formato de fitas, sua importância econômica está diretamente relacionada a sua estrutura incomum e suas propriedades físico-químicas que lhe dão uma vasta variedade de uso na indústria. O campo de estabilidade de formação da palygorskita é muito limitado, o que torna seus depósitos raros pelo mundo, no Brasil os únicos depósitos exploráveis deste mineral estão situados no município de Guadalupe, no estado Piauí, e estão inseridos no contexto geológico da Bacia do Parnaíba, especificamente nas sequências do Carbonífero e Permiano representadas pelas Formações Piauí, Poti e Pedra de Fogo. Este trabalho teve como objetivo fazer uma descrição geológica e mineralógica de ocorrências de palygorskita da região de Guadalupe-PI, foram estudadas 6 ocorrências e coletadas 25 amostras. As amostras de trabalho foram as amostras brutas e que passaram por um processo de beneficiamento, foram realizadas análises de DRX, MEV/EDS, densidade e granulométrica. A maioria das amostras são constituídas por palygorskita, quartzo e caulinita, no entanto, a partir dos difratogramas, em três amostras há a ausência de palygorskita, duas com ausência de caulinita e uma amostra com a presença de dolomita. A partir dos resultados, principalmente com a diferença mineralógica observada em alguns perfis, é possível relacionar hipóteses de formação da palygorskita com o contexto geológico local. As condições ambientais das Formações Piauí e Pedra de Fogo são propícias para a formação do argilomineral, a associação de dolomita e palygorskita observada em uma camada mais superior que as demais pode indicar uma maior relação com a Fm. Pedra de Fogo, no entanto as observações de campo, como os níveis de silicite encontrados, e os demais resultados não são suficientes para definir em qual das duas formações essas ocorrências estão inseridas.

Palavras-chave: Argilominerais; Argilas fibrosas; Mineralogia aplicada

1 Introduction

Palygorskite is a magnesian clay mineral of the 2:1 type that is not expansive. It differs from most clay minerals in that its structural units have the shape of ribbons, not sheets, as is characteristic of the phyllosilicates group (Galan & Aparicio 2015). Palygorskite is usually found as a mixture of two polymorphs: one monoclinic and the other orthorhombic (Giustetto & Chiari 2004).

The term attapulgitite is also used as a synonym for this mineral, although the Association Internationale pour l'Etude des Argiles (AIPEA) has established palygorskite as the official name (Guggenheim et al. 2006). Nevertheless, attapulgitite is still used as a commercial term and in some publications and technical works, especially those aimed at its applications.

The economic importance of this mineral is directly related to its physicochemical properties, which give it a wide variety of uses in industry. Among these properties are the high specific surface area (190 m²/g) and cation exchange capacity – CEC (< 25 meqiv/100g), which give it a high absorbance capacity, along with the unusual morphology of its needle-shaped crystals (Murray 2002, 2006).

Regarding its formation process, palygorskite is mainly formed by authigenesis, a term that covers several diagenetic processes and stages that in the case of clay minerals basically consist of the formation of minerals from the direct precipitation of solutions, called neof ormation, or the formation of minerals from the transformation of others already existing in the environment (Pozo & Calvo 2018). The stability field of palygorskite crystallization is very limited. Palygorskite deposits and occurrences are found in regions with semiarid to arid climates, with alkaline pH (approximately 8) and with high Si, Mg and Al activity (Guggenheim & Krekeler 2011; Krekeler, Guggenheim & Rakovan 2004).

Deposits of this mineral have been described in different geological environments, such as epicontinental evaporite basins, saline lake systems, soil formations in arid regions, supergene hydrothermal alterations of mafic and ultramafic rocks on land and in oceans, and formations associated with percolation of fluids in fault zones. In the United States, palygorskite deposits are found along the west coast associated with fault and fractures zones and hydrothermalism (Post & Crawford 2007). However, the country's main deposit, providing 66% Fuller's earth, is located in Georgia in the context of the Gulf Trough-Apalachicola Embayment area, where palygorskite was formed by the alteration of montmorillonite in shallow

water in a perimarine lagoon environment (Murray, Pozo & Galán 2011). Spain also has deposits of palygorskite, mainly in Tertiary continental basins (Duero and Torrejón basins). The palygorskite deposits in these two basins are related to the alteration of other minerals in a lacustrine system. In the Duero basin, it is formed from the alteration of detrital phyllosilicates in an alluvial fan, while in the Torrejón basin the precipitated solutions for the formation of palygorskite originate from a slate layer (Murray, Pozo & Galán 2011; Pozo & Calvo 2018).

In Brazil, the main palygorskite deposits are in the municipality of Guadalupe in the state of Piauí and are distributed in an area of about 700 km² (Luz & Lins 2008). Guadalupe is located in southwest Piauí, bordering the state of Maranhão in the north, and is 345 km from the state capital Teresina (Figure 1A).

The deposits in the region have been studied since the beginning of the 1980s. Rezende (1997) mentioned that the first references date from 1982 and that studies related to the genesis, local geology and reserves were conducted by Cavalcanti and Bezerra (1992), and that technological studies for use the mineral began with Luz, Almeida and Ramos (1988).

More recent studies of palygorskite from Guadalupe have investigated its applicability in pharmaceutical industry due to its high specific surface area, bleaching power and maintenance of thixotropic properties in the presence of electrolytes (Araújo et al. 2020; Soares et al. 2013), and in environmental remediation as an adsorbent of oils, heavy metals and glyphosates (Câmara et al. 2020; Simões et al. 2017). Other works are related to clay processing techniques to improve its applicability, such as pelletizing, organophilization and acid activation (Furlanetto, Brandão & Bertolino 2018; Novo, Bertolino & Simões 2018; Rodrigues et al. 2019).

Only sparse research has been published focused on the description of palygorskite deposits, especially in relation to their industrial and environmental applications. The main objective of this work was to carry out a geological and mineralogical study of palygorskite deposits in the region of Guadalupe.

2 Geological Context

The study area is located in the Parnaíba Basin (Figure 1B), where the occurrences of palygorskite are associated with rocks from the Poti and Piauí formations, and are linked to permo-carboniferous marine incursions, including associations with the Pedra de Fogo Formation (Luz & Almeida 2008; Rezende 1997).

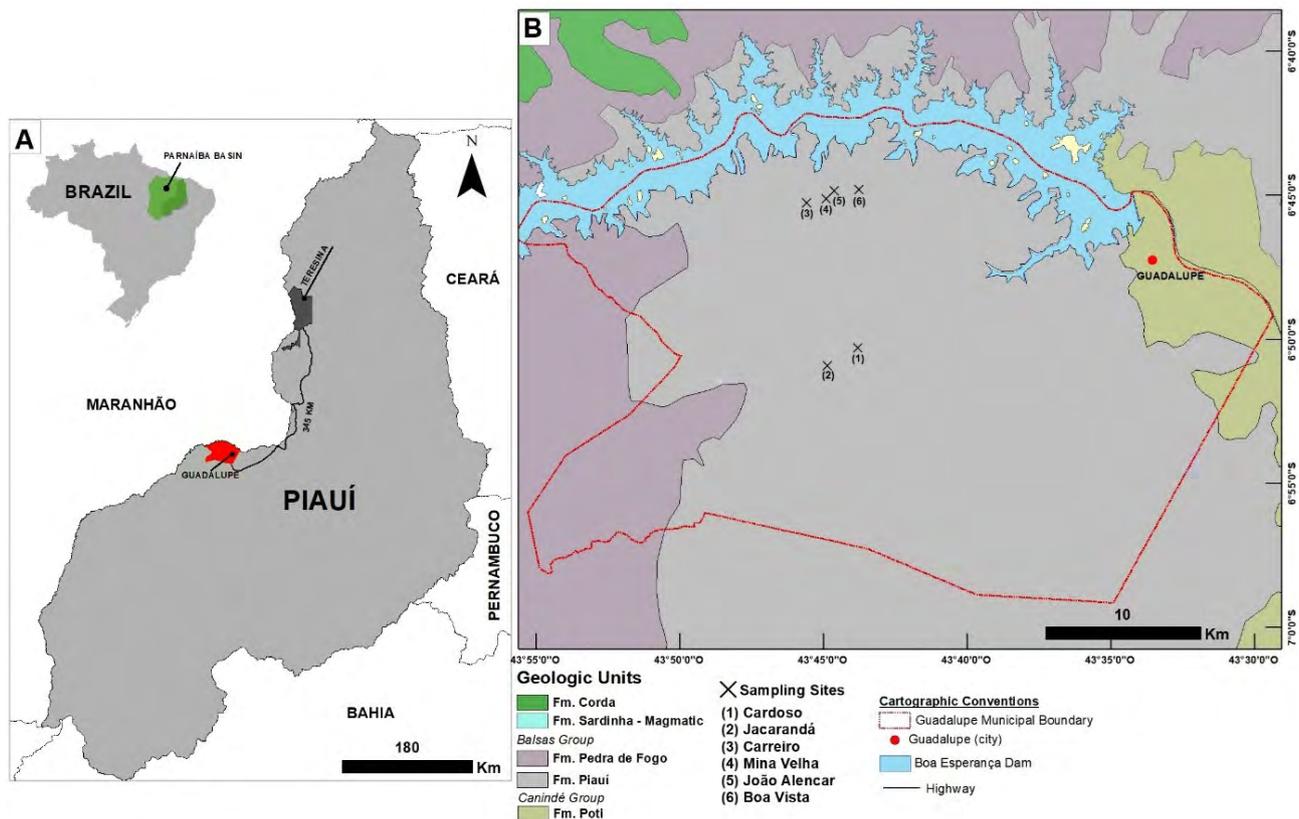


Figure 1 Maps of the study area: A. Location map of the municipality of Guadalupe – PI; B. Geological map of the region, with the sampling sites. Adapted from CPRM (2006) and IBGE (2019)

The Poti, Piauí and Pedra de Fogo formations belong to the Paleozoic sequences, which are influenced by the great transgressions of that period, and their discordances are related to the fluctuations of the high eustatic levels of the epicontinental seas of the Eopaleozoic era (Almeida & Carneiro 2004). Orogenetic processes in the southern active margin of Gondwana may also have influenced these fluctuations, which consequently influence the sedimentary features (Vaz et al. 2007).

The Poti Formation is the last constituent of the Canindé Group, from the Lower Carboniferous, where global conditions of shallow seas prevailed over cratons, called epicontinental seas, with cold to moderate climates. The deposition of this formation is related to an environment of deltas and plains under the influence of storms, presenting a Mesocarboniferous erosive unconformity in the top layer, related to regression of the global extension (Caputo 1984; Goés & Feijó 1994; Ribeiro 2000; Vaz et al. 2007).

The Piauí Formation, from the Neocarboniferous and the oldest of the Balsas Group, deposited on the Mesocarboniferous erosive unconformity, has a deposition environment described as fluvial with aeolian contribution and small marine incursions, in a semiarid to desert

climate, with signs of the onset of continentalization and establishment of desert conditions in the Parnaíba Basin (Ribeiro 2000; Vaz et al. 2007). Pedra de Fogo Formation, dating from the Permian (Dino, Antonioli & Braz 2002). The depositional environment was described by Goés & Feijó (1994) as a shallow to coastal marine environment, with sabkha plains under the influence of storms, while Araújo et al. (2016), based on faciological and stratigraphic analyses of this formation, defined the environment as a shallow lacustrine system induced by the climate, with retreat and expansion phases. A differential of this formation in relation to others found in the region is the presence of lithological varieties such as flint, oolitic and pisolitic limestone and occasionally stromatolite, interspersed with fine to medium sandstone, gray shale, anhydrite, and occasionally dolomite (Vaz et al. 2007).

Palygorskite deposits in the Guadalupe region are described as palygorskite layers occurring together with kaolinitic clays with presence of manganese nodules, carbonates, silicite and gastropod, suggesting that palygorskite was neoformed in a marine environment (Cavalcanti & Bezerra, 1992; Rezende, 1997). However, there are insufficient data to establish a correlation between

these clay layers with some of the formations found in the region (Rezende 1997). Cavalcanti and Bezerra (1992) described the clayey sequence in which the mineral occurs in three distinct facies: São Pedro, Terra Branca and Cemitério, all of which have mineralogy similar to palygorskite in association with kaolinite, smectite, illite, quartz, nodules and concretions of silexite, dendrites and Mn films, and rarely dolomite and calcite, with differences in these associations and density of the ore from one location to the other (Rezende 1997). In these deposits, the presence of minerals with lower concentrations, such as tourmaline, micas, rutile and feldspars, have also been reported, which reinforces the idea of a detrital contribution to the sedimentation basin (Luz, Almeida & Ramos 1988).

3 Materials and Methods

We collected 25 samples (Table 1) of clays from 6 sites (Figure 1B) to describe their mineralogical constituents: three active mines, one occurrence area and two deactivated mines (closed more than 30 years ago).

At these sites, we chose some vertical profiles to perform the sampling. The number of profiles and samples

collected varied at each site, depending mainly on the dimensions of the deposit, whether the mines (active or deactivated) had more than one pit or mining front (Figure 2A, D and E) and whether it was possible to identify layers with different textural characteristics (Figure 2B and C). The criterion adopted for sampling was to consider the most clayey layer of a profile as the main layer, the ore layer in the case of active mines (01), overlying layers (02) and underlying layers (00) (Figure 2B and C).

3.1 Sample Processing

At the Mineral Technology Center (CETEM), the samples were dried at room temperature, crushed in a jaw crusher and homogenized using the prismatic pile method. The aliquots separated for processing (1 kg) were wet milled in a bar mill, the wet classified with a vibrating classifier with a set of sieves of 212, 150, 104, 74, 53 e 44 μm . The fractions retained in each sieve were dried in an oven at around 60 °C and weighed. The fractions smaller than 44 μm were passed through a BoxmagRapid magnetic separator with high intensity magnetic field (15,000 Gauss).

Table 1 List of samples collected at the sampling sites and the products that were analyzed.

Sampling Sites	Field Sample	Analyzed Sample
Cardoso	CA-P01-00	Raw (R)
		<44 μm N.M (P)
	CA-P01-01	Raw (R)
		<44 μm N.M (P)
	CA-P01-02	Raw (R)
		<44 μm N.M (P)
	CA-P02-01	Raw (R)
		<44 μm N.M (P)
CA-P03-02	Raw (R)	
	<44 μm N.M (P)	
CA-P04-01	Raw (R)	
	<44 μm N.M (P)	
Jacarandá	JA-P01-01	Raw (R)
		<44 μm N.M (P)
	JA-P02-01	Raw (R)
		<44 μm N.M (P)
	MJA-P01-01	Raw (R)
		<44 μm N.M (P)
	MJA-P02-01	Raw (R)
		<44 μm N.M (P)
MJA-P03-01	Raw (R)	
	<44 μm N.M (P)	

Table 1 Cont.

Sampling Sites	Field Sample	Analyzed Sample
Carrero	CAR-P01-01	Raw (R) <44 μm N.M (P)
	CAR-P02-01	Raw (R) <44 μm N.M (P)
Mina Velha	MV-P01-01	Raw (R) <44 μm N.M (P)
	MV-P02-01	Raw (R) <44 μm N.M (P)
	MV-P03-01	Raw (R) <44 μm N.M (P)
João Alencar	JAL-P01-01	Raw (R) <44 μm N.M (P)
	JAL-P02-00	Raw (R) <44 μm N.M (P)
	JAL-P02-01	Raw (R) <44 μm N.M (P)
	JAL-P03-01	Raw (R) <44 μm N.M (P)
	JAL-P04-01	Raw (R) <44 μm N.M (P)
Boa Vista	BV-P01-01	Raw (R) <44 μm N.M (P)
	BV-P01-02	Raw (R) <44 μm N.M (P)
	BV-P02-01	Raw (R) <44 μm N.M (P)
	BV-P02-01	Raw (R) <44 μm N.M (P)
	BV-P02-02	Raw (R) <44 μm N.M (P)

The non-magnetic fractions were filtered in a filter press (5 bar), and dried in an oven at around 60 °C. At the end of this process, the non-magnetic fractions with particle size smaller than 44 μm (<44 μm N.M – F) were generated, which together with the raw samples (R) were used in the analyses (Table 1).

3.2 Mineralogical Characterization

The mineralogical characterization of the raw samples (R) and processed fractions (P) was performed using X-ray diffraction (XRD) by the powder method, in a Bruker AXS D8 Advance Eco diffractometer, with $\text{CuK}\alpha$

radiation (40 kV/25 mA), with 0.02° 2θ step and counting time of 0.52 seconds per step, coupled to a LynxEye XE silicon drift (with energy discrimination), collected from 4° to 70° 2θ . Qualitative spectrum interpretation was performed by comparison with patterns contained in the relational database PDF 4+ (ICDD, 2014) in the Bruker Diffrac EVA software. The microtextural study was carried out with a Hitachi TM3030 Plus microscope, equipped with a Bruker Quantax energy dispersion system (SEM/EDS) for chemical microanalysis to identify minerals, their composition and textural relationships. Density analysis was performed using Micromeritics AccuPyc II 1340 helium pycnometer.

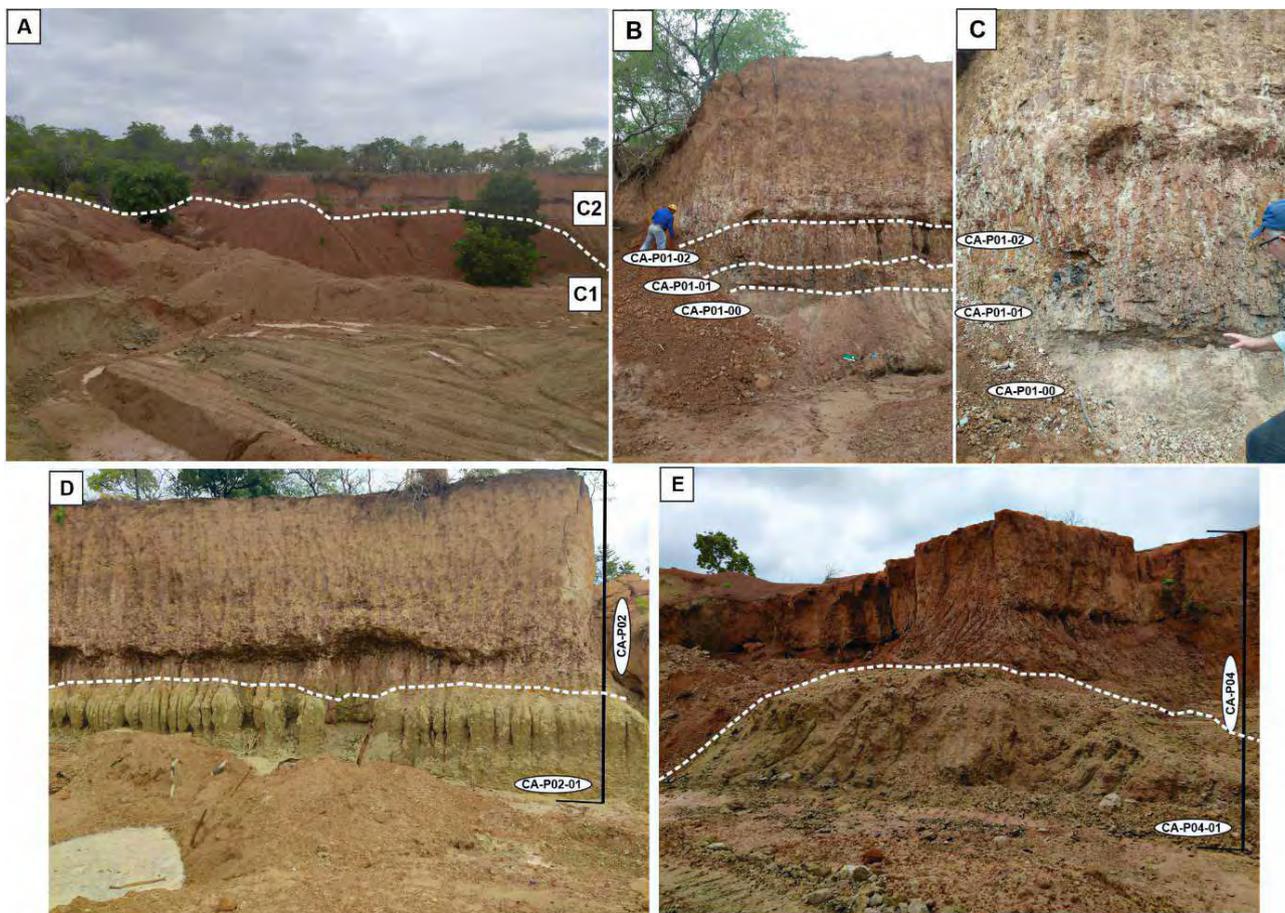


Figure 2 Cardoso mine sampling site; A. Overview of the mine, showing the two extraction pits (C1 and C2); B. Example of how the identification of layers was carried out to collect samples in the vertical profile at CA-P01; C. Detail of the layers in the profile CA-P01; D. Second vertical profile, in front of the mine at site C2; E. Vertical profile of sampling in pit C1.

4 Results

4.1 Description of Sampling Sites

There were clay variations at the six sampling sites, even within the same vertical profile. Due to the characteristics of the outcrops, it was not possible to observe structural and sedimentary features in a hand sample; it was only possible to observe textural changes in the ore, within the same mine and between different sites.

The Cardoso mine has one of the best layers rich in palygorskite. The profile is approximately 6 meters high (Figure 2D and E), formed by an upper layer of soil, a transition layer between soil and clay, a clayey layer (ore) and a clayey-sandy layer at the base. In the CA-P01 profile, it was possible to observe that the lower layer was sandier than the upper layer (Figure 2B and C), and there were differences in the clay at different points

of the mine. This was particularly the case of samples CA-P02-01 and CA-P04-01. The first was “purer”, i.e., homogeneously whitish, with a sticky sensation to the touch when moistened, characteristic of clays (Figure 3A), while the second (Figure 3B) showed percolation of oxides and a brownish color.

At Jacarandá, 2 km from the Cardoso mine, clay extraction is carried out in a pit, with benches of approximately 3 meters. Samples collected in the old mine pit (Figure 3E) and outside it (Figure 3C and D) had similar characteristics. The clay is lighter in color than that of the Cardoso mine, with little oxide percolation, more compacted and less friable (Figure 3F).

At Carrero, a known ore occurrence site in the region, but which has not yet been exploited, two samples were collected (Figure 4A). The profile of this site is covered by a lateritic soil, supported by a thick and massive ore layer (approximately 80 cm) at its base, approximately

1.5 m thick. Superficially, the layer was much altered, but the collected samples had characteristics similar to those obtained from the Cardoso mine, together with percolation of oxides.

At the site called Mina Velha, an abandoned mine that was last worked in the 1980s, a change in the behavior of the deposit was observed in relation to the other sites. The mine front profile of Mina Velha is approximately 10 meters high, with a topsoil followed by a soil-rock transition zone and a thick layer measuring approximately 75 cm of silexite (Figure 4C and E). The clayey ore layer at the base of the sequence contains dispersed occurrences of silexite. In the region, the silexite is called “fire stone” and hinders advance the ore extraction (Figure 4B). Above the silexite-rich level there is another clayey layer, where the MV-P03-01 sample was collected (Figure 4D).

The occurrence at the former João Alencar mine, operated in the 1980s and 1990s, is the largest in lateral extension (about 200 meters long). The mine front has a profile of approximately 15 meters, with a top cover of soil and approximately 10 meters of clayey layer, in outcrop scale. It was not possible to clearly distinguish the differences between the layers. The samples collected at this site stand out mainly for their low density.

At the Boa Vista mine, the clays have a lighter and more homogeneous color, with no percolation of oxides observed as at the other sites (Figure 4F). There is a difference in the density of the samples between the layers, with samples being lighter than at the other sites. The biggest differential of this mine in relation to the other analyzed sites is a layer above the clayey layer, observed in the second pit, where it is visibly more massive (Figure 4G and H).

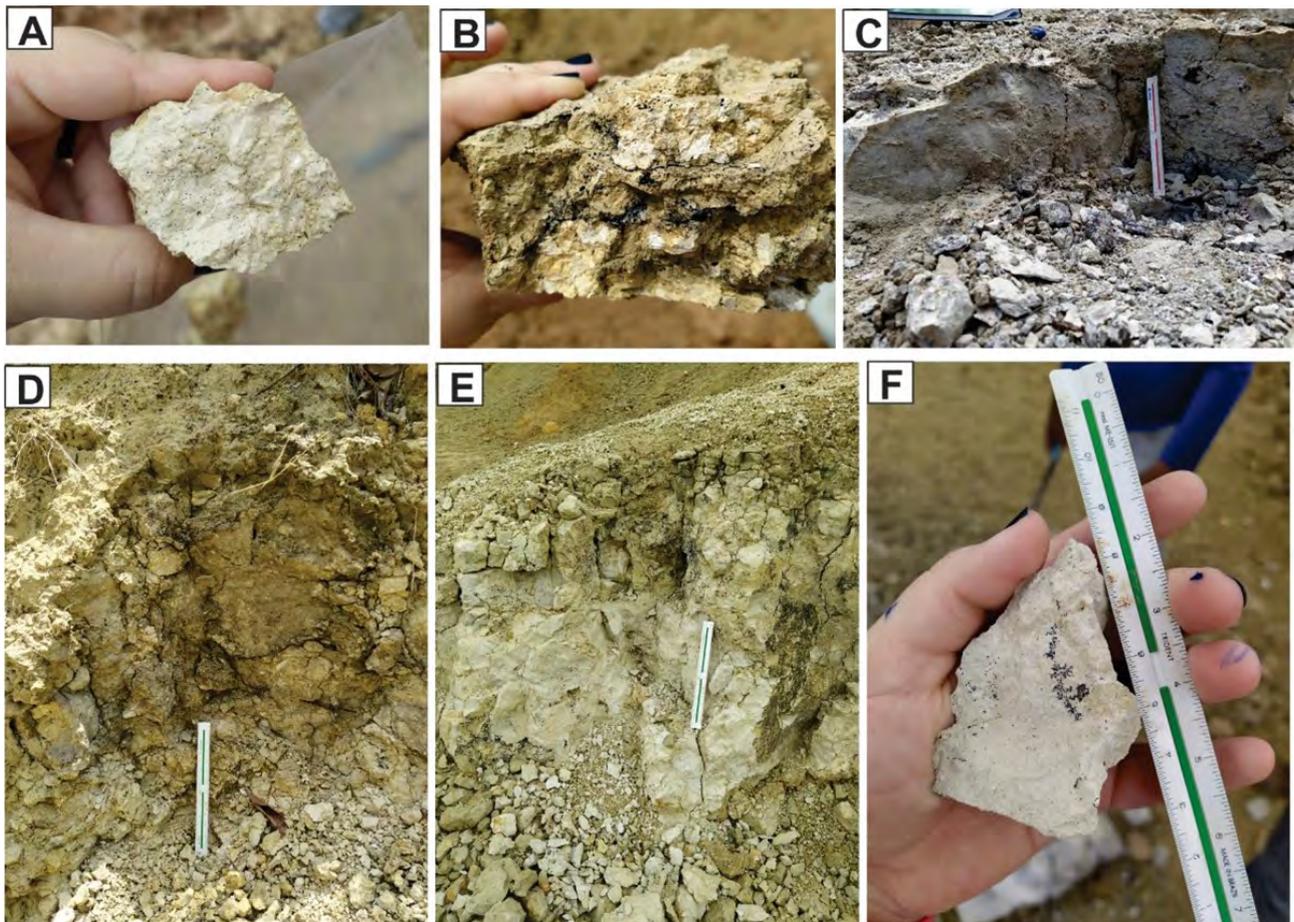


Figure 3 Sampled layers of the Cardoso and Jacarandá sites: A. CA-P02-01 in hand sample; B. CA-P04-01 in hand sample; C. Lajedo where sample JA-P01-01 was collected; D. Sampling layer JA-P02-01 in a former riverbed; E. Sampling layer MJA-P02-01; F. MJA-P02-01 in hand sample.

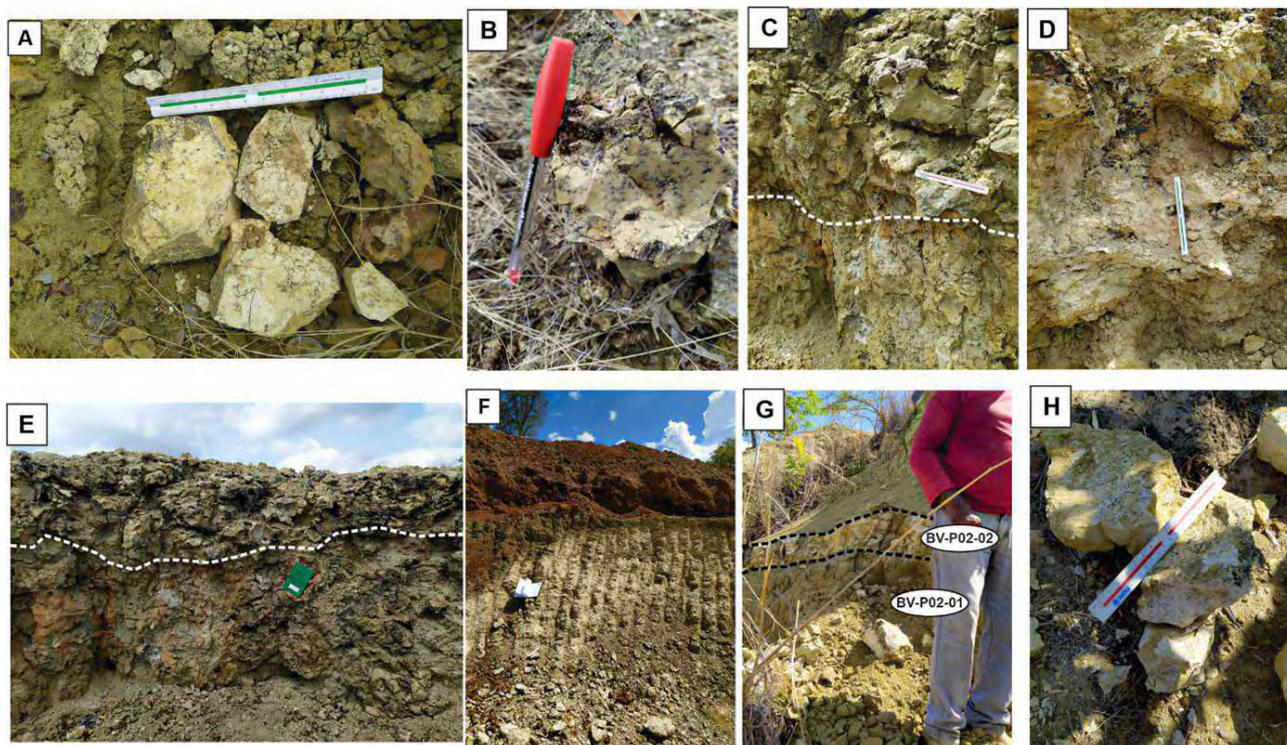


Figure 4 Sampled layers of the Carrero, Mina Velha and Boa Vista sites: A. Sample CAR-P01-01 from Carrero; B. Silixite from Mina Velha; C. Profile MV-P01 with silixite in the top layer and clayey layer below MV-P01-01; D. MV-P03-01; E. Profile MV-P01, showing the thick top layer of silixite; F. Mina Boa Vista, sampling profile BV-P01-01; G. Profile BV-P02, showing the difference between the layers BV-P02-02 and BV-P02-01; H. Samples from the stiffer layer BV-P02-02

The sample collected in this layer was called BV-P02 -02, and below it clays samples were collected (BV-P02-01).

4.2 Particle Size Analysis

Figure 5 presents the graphs of the particle size distribution of the samples. All samples had more than 60% passing mass in a sieve of 0.044 mm (44 μm). Sample BV-P01-01 had the lowest yield from this process, in which 60.44% was below 44 μm . The samples CAR-P01-01 and JAL-P02-01 showed the highest yields, with 97% and 95.08% of fraction with particle size smaller than 44 μm , while the two samples collected at Carrero site showed the best yield (Figure 5C), having more than 90% passing mass through the 44 μm sieve. The two samples from Mina Velha (Figure 5D) had coarser particle size, with mass retained by the sieve with mesh of 0.210 mm and 66.40% (MV-P01-01) and 71.80% (MV-P02-01) yield of the fraction with particle size smaller than 44 μm .

4.3 Mineralogical Characterization

We used X-ray diffraction to analyze the raw samples (R) and the non-magnetic fractions smaller than 44 μm (P). Comparison of the diffractograms of the raw samples with the processed samples showed no change in the mineral composition after processing, although this can change the concentration of clay minerals. The samples consisted mostly of palygorskite determined by diagnostic reflections at 10.5 \AA , quartz (3.34 \AA) and kaolinite (7.00 \AA). Sample BV-P02-02 (Figure 6F) showed peaks characteristic of the mineral dolomite (2.88 \AA). In all analyzed diffractograms, palygorskite was identified by the referring to the monoclinic and orthorhombic polymorphs.

Differences were observed in the mineralogical composition of the occurrences of palygorskite. In the samples collected in the first profile of Cardoso mine, the presence of palygorskite was not observed (CA-P01-00, CA-P01-01 and CA-P01-02); only kaolinite and quartz

reflection peaks were observed. In the samples CA-P02-01, CA-P03-02 and CA-P04-01, there were peaks related to palygorskite, kaolinite and quartz (Figure 6A).

In the samples collected at the Jacarandá mine, the presence of kaolinite was not identified in samples MJA-P03-01 and MJA-P02-01, where it only appeared

in samples JA-P01-01 and JA-P02-01 (Figure 6B). The samples from Carrero (Figure 6C), Mina Velha (Figure 6D) and João Alencar (Figure 6E) were composed of palygorskite, kaolinite and quartz, and no differences were observed in the diffractograms of the samples collected from the same site.

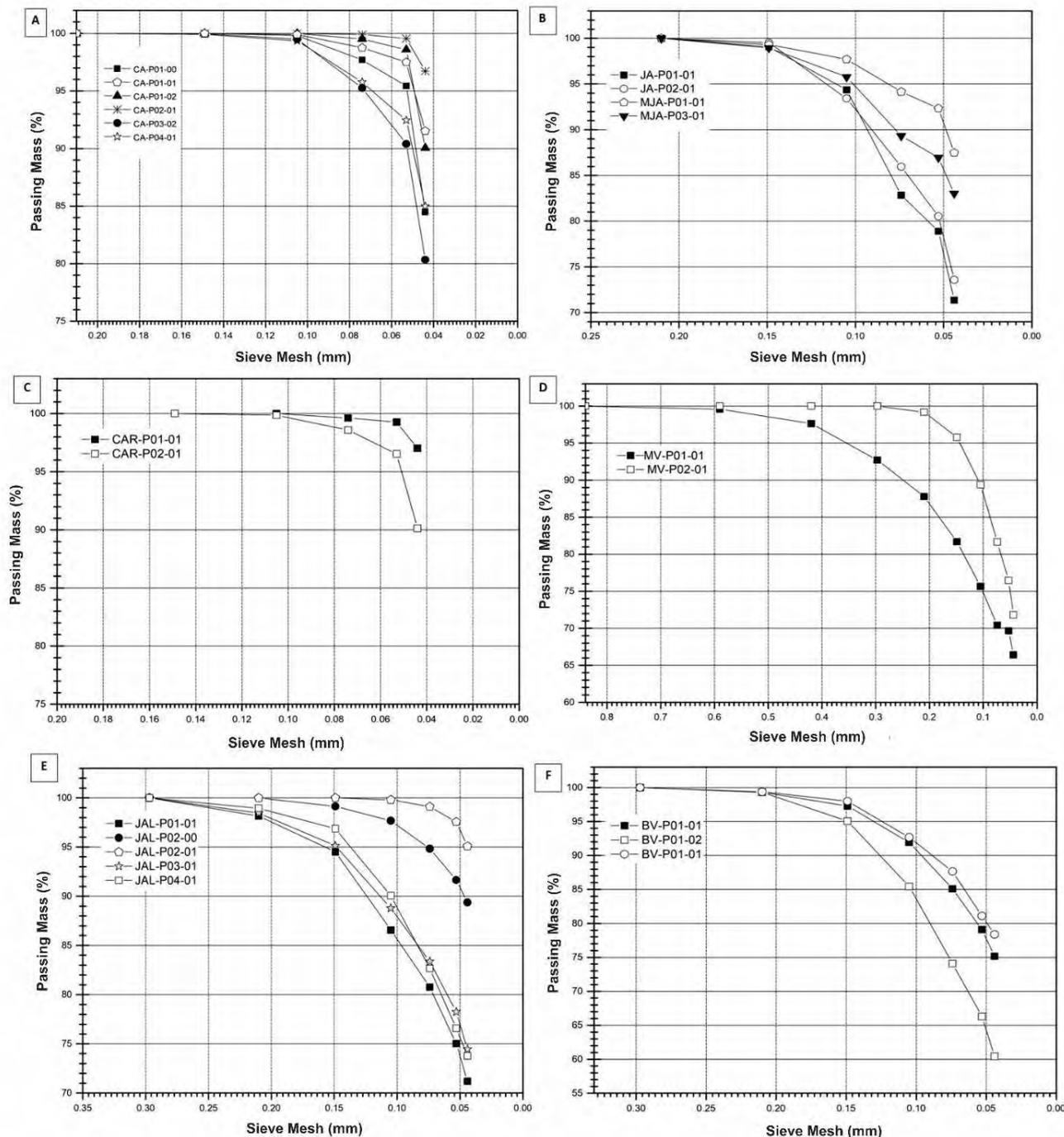


Figure 5 Particle size distribution of the samples: A. Cardoso; B. Jacarandá; C. Carrero; D. Mina Velha; E. João Alencar; F. Boa Vista

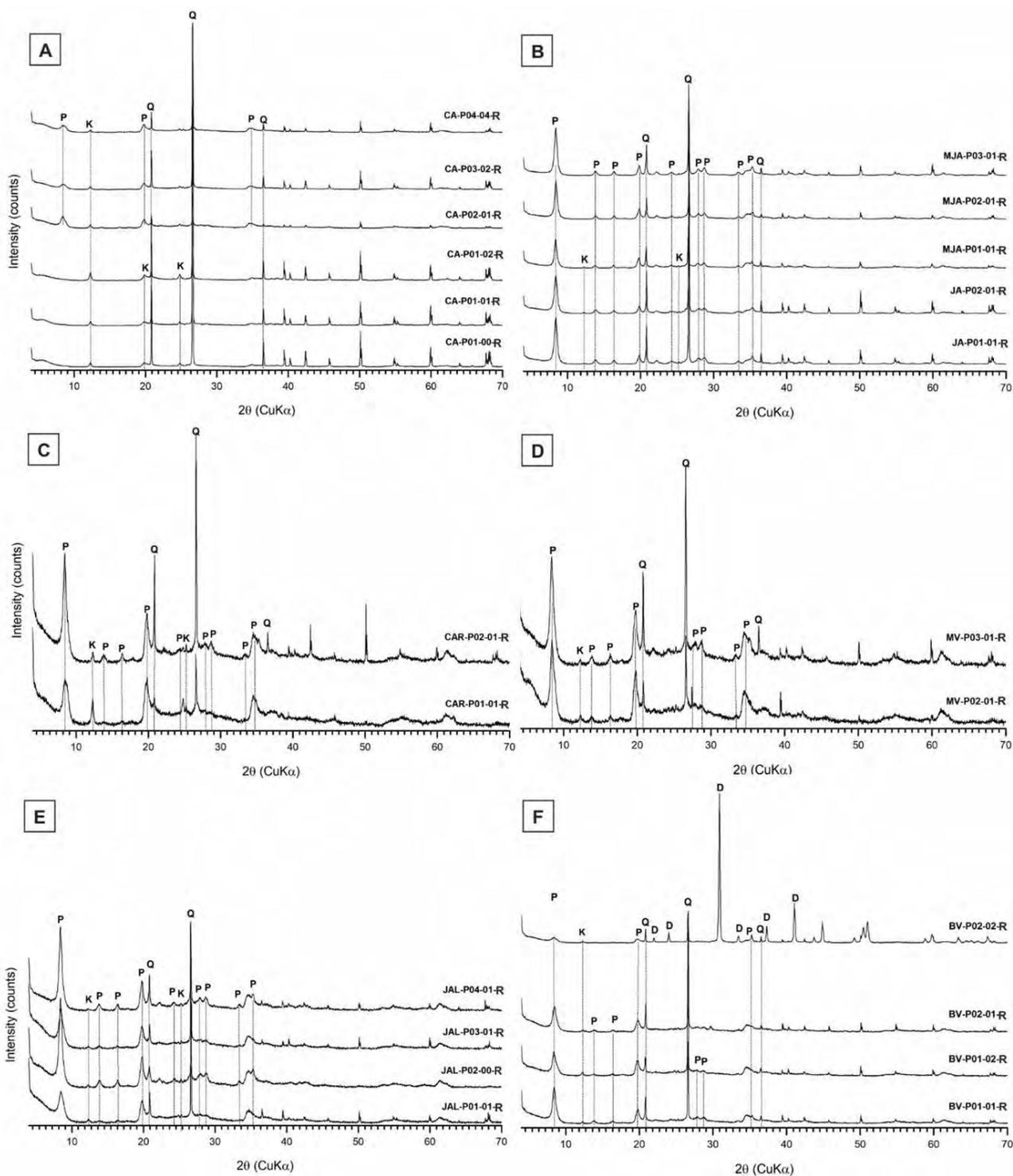


Figure 6 X-ray diffractograms of raw samples: A. Cardoso; B. Jacarandá; C. Carrero; D. Mina Velha; E. João Alencar; F. Boa Vista. Legend: P – palygorskite; K – kaolinite; Q – quartz; D – dolomite.

The sample BV-P02-02, from the Boa Vista mine, showed characteristic peaks of dolomite, palygorskite, kaolinite and quartz, but the other three samples collected at this site, did not present peaks indicating dolomite in their diffractograms (Figure 6F).

The results of the analysis carried out with scanning electron microscopy (SEM/EDS) indicated the characteristic morphology of palygorskite in the form of fibers, both in the raw samples (R) and those that underwent processing (P)

(Figure 7). The chemical analyses of the samples showed the elements oxygen, silicon, aluminum, iron, magnesium and potassium (Table 2). The amount of silicon in the processed samples (P) was lower than in the samples without treatment (R), while the magnesium concentration remained practically the same, which can indicate a decrease in quartz content after processing. The samples from the Cardoso mine analyzed by EDS showed a lower concentration of Mg compared to samples from the Carrero and Jacarandá.

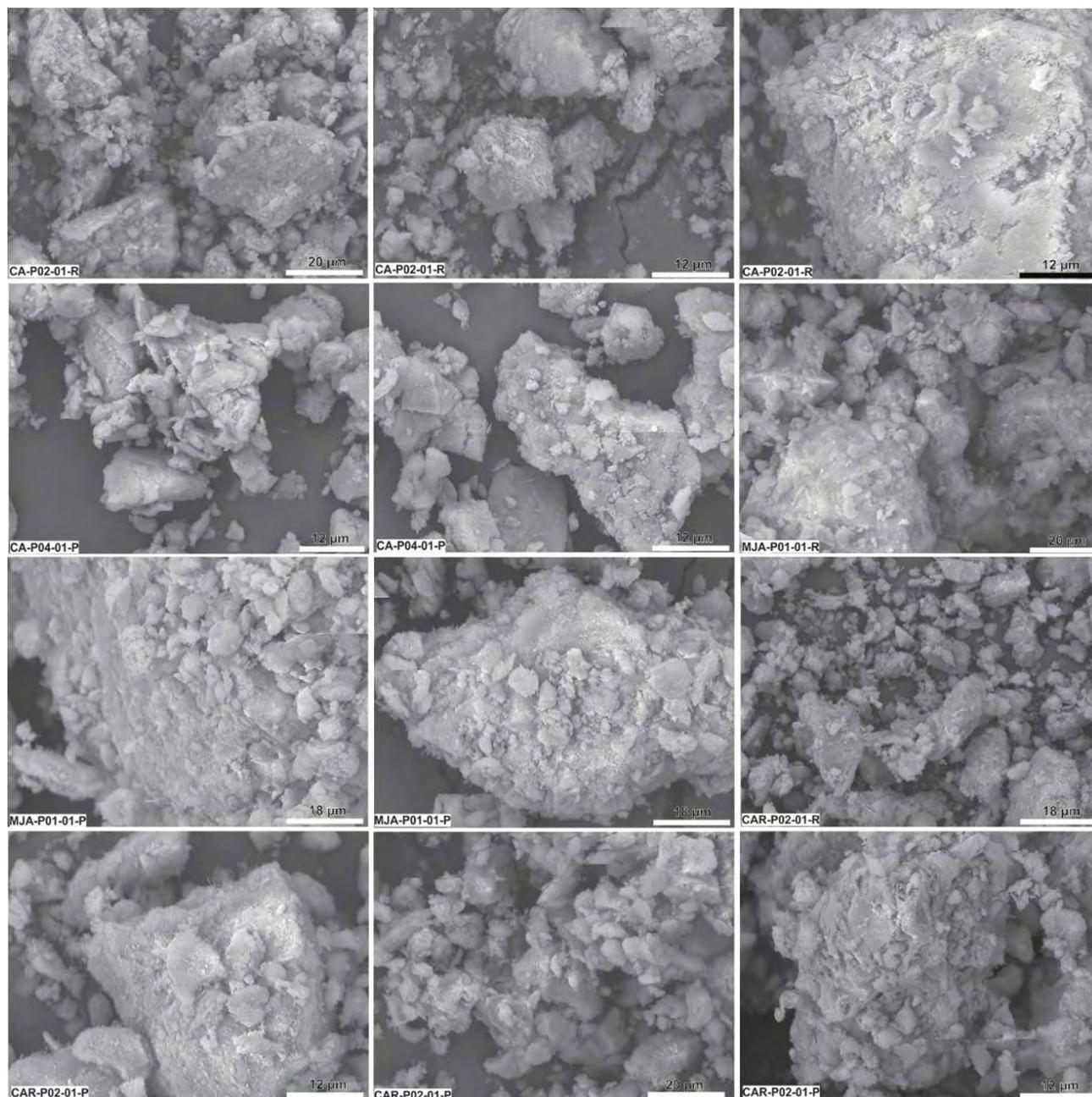


Figure 7 Scanning electron microscopy (SEM) images in secondary mode of raw (R) and processed (P) samples

Table 2 Semi-quantitative spot chemical analysis of samples in relation to weight percentage (wt.%) and atomic percentage (at.%).

Element	O		Si		Al		Fe		K		Mg	
	wt.%	at%	wt.%	at%	wt.%	at%	wt.%	at%	wt.%	at%	wt.%	at%
Samples												
CA-P02-01-R	43.83	58.97	36.09	27.66	10.19	8.13	07.03	2.71	*	*	2.86	2.53
CA-P02-01-P	50.64	65.64	30.79	22.73	8.24	6.33	5.66	2.10	2.44	1.29	2.23	1.91
CA-P04-01-R	39.5	54.85	37.19	29.42	11.85	9.76	8.71	3.46	*	*	2.74	2.51
CA-P04-01-P	43.56	58.75	37.03	28.46	10.33	8.26	7.03	2.72	*	*	2.04	1.81
CAR-P01-01-R	43.09	58.36	35.65	27.51	11.14	8.95	7.61	2.95	*	*	2.50	2.23
CAR-P01-01-P	49.35	64.85	27.57	20.56	9.22	7.15	6.01	2.25	4.02	2.15	3.83	3.30
CAR-P02-01-R	40.43	55.25	39.96	31.11	9.40	7.62	6.24	2.44	*	*	3.97	3.57
CAR-P02-01-P	44.64	60.64	29.59	22.90	9.54	7.68	7.91	3.08	5.14	2.86	3.19	2.85
MJA-P01-01-R	46.78	60.25	40.44	29.67	8.80	6.72	*	*	*	*	3.98	3.37
MJA-P01-01-R(2)	44.12	59.15	33.39	25.25	9.06	7.20	5.16	1.98	3.39	1.86	4.87	4.30
MJA-P01-01-P	51.37	65.62	29.81	21.69	8.97	6.79	5.03	1.84	*	*	4.82	4.05

The results of the density analysis using the helium pycnometer indicated that the samples had a density between 2.38 g/cm³ (CA-P04-01-B) and 2.71 g/cm³ (CA P01-02-F) (Figure 8), with the average density of the constituent minerals being 2.15 g/cm³ for palygorskite, 2.62 g/cm³ for quartz, 2.6 g/cm³ for kaolinite and 2.84 g/cm³ for dolomite. The samples with greater density were those that did not show a peak of palygorskite in the X-ray diffraction (the samples collected in the CA-P01 profile). With the exception of these samples, all the others only had approximate values, so it is not possible to state that a site of occurrence had ore with different density than others

5 Discussion

In the described outcrops it was not possible to observe sedimentary and structural features, mainly because most are in front of the occurrence, thus having undergone many changes due to removal of ore. The characteristics observed in the field, such as the presence of percolation of oxides (Figure 3B and F), probably from manganese, the difference in ore density between the sites, and the presence of flint (observed only at the Mina Velha site) corroborate previous findings for the region (Luz, Almeida & Ramos 1988; Rezende 1997).

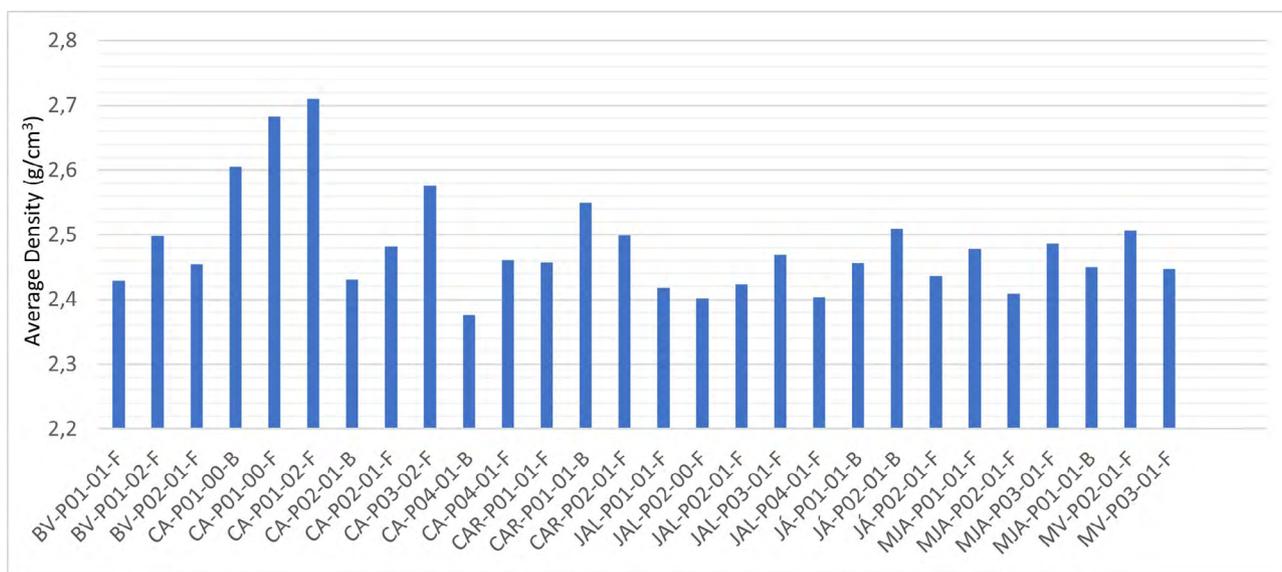


Figure 8 Average density of the analyzed sample according to analysis with a helium pycnometer.

The presence of a silexite-rich layer at Mina Velha is related to the lithologies described of the Balsas Group, where sandstones with the presence of flint was identified in the upper portion of the Piauí Formation and the Pedra de Fogo Formation (Goés, Souza & Teixeira 1990). The presence of silica is an important lithostratigraphic marker of the Pedra de Fogo Formation, although this formation had great lithological diversity (Vaz et al. 2007). The depositional pattern of the Pedra de Fogo Formation, in a shallow coastal marine environment with hot arid to semiarid climate (Dino, Antonioli & Braz 2002) or a lacustrine system in an arid climate (Andrade 2012; Araújo et al. 2016), is favorable for palygorskite formation because the availability of silica and the arid to semiarid climate are critical factors for the crystallization of palygorskite (Guggenheim & Krekeler 2011; Krekeler, Guggenheim & Rakovan 2004). In addition, there are examples of palygorskite deposits in these types of environments, such as in the Senegal Basin in a shallow marine and lacustrine environment, Georgia (USA) and Spain (the Bercimuel and Torrejón deposits) (Murray, Pozo & Galán 2011; Pozo & Calvo 2018).

The X-ray diffractograms indicated that most of the samples had similar mineralogical composition, consisting predominantly of palygorskite, quartz and kaolinite. The BV-P02-02 sample was the only one that contained dolomite together with the minerals already mentioned. It was present in layer above the clayey layers exploited in the Boa Vista mine. In the regional geological context, the Pedra de Fogo Formation is marked by this intercalation of sandstone with flint, limestone and shale (Araújo et al. 2016; Goés, Souza & Teixeira 1990). Other differences observed were the absence of kaolinite peaks in samples MJA-P02-01 and MJA-P03-01 and absence of palygorskite peaks in samples CA-P01-00, CA-P01-01 and CA-P01-02.

The absence of kaolinite and palygorskite peaks in the X-ray diffractograms of these samples and the local geological context of the Piauí Formation, in a coastal desert fluvial environment (Ribeiro 2000; Vaz et al. 2007), shifting to a lacustrine environment with associated sabkha from the Pedra de Fogo Formation (Andrade, Nogueira & Silva 2014; Araújo et al. 2016; Vaz et al. 2007) could be related to a hypothesis that in saline lakes and sabkha environment the reaction between detrital aluminous clay minerals and solutions rich in Si and Mg, in the margins of the lakes, detrital clays transitionally transformed into fibrous clays such as palygorskite and sepiolite in the center of the lakes (Jones & Galán 1988; Pozo & Calvo 2018). In these environments the detrital clay minerals are essentially formed by kaolinite, and to a lesser extent by illite, chlorite and Al-smectite, also the presence of amorphous silica in a lacustrine environment favors the formation of fibrous clays to the detriment of

trioctahedral magnesian smectites (Meunier 2005). Therefore, this could indicate that the formation of palygorskite is related to the transformation of the detrital kaolinite associated with the Piauí Formation into palygorskite during the lacustrine system of the Pedra de Fogo Formation. Thus, the silexites described in the Mina Velha samples and Piauí and Pedra de Fogo formations probably contributed to the formation of palygorskite in the region.

The association of dolomite and palygorskite found in sample BV-P02-02, from a higher layer than the other samples analyzed, in the context of Pedra de Fogo Formation indicates that lower Permian had an arid climate with predominance of siliciclastic sediments with subordinated evaporite deposits (Araújo et al 2016). Many studies have described the genetic relationship of the association of palygorskite with dolomite (Pozo & Calvo 2018; Ryan, Kaczmarek & Rivers 2019; Yenyol 2012), but the data are insufficient to define whether the process of palygorskite formation in this layer differs from that of the other samples.

Particle size and density analyses demonstrated that clays behaved similarly at all sampling sites, although some samples had a better yield from the processing and a lower density, so it is not possible to correlate these characteristics with the sampling sites. For example, a few samples had better yield from processing (e.g., CAR-P01-01 and JAL-P02-01), while other samples collected at the João Alencar site did not show similar yield. The samples from Mina Velha showed the highest retention of material in the sieves used. The presence of silexite disseminated in the clay layer can influence this material's behavior, due to the greater resistance of this rock in the grinding process.

In the density analysis, the samples with the highest mean density (Figure 8) were those that did not show palygorskite peaks in the X-ray diffractograms, namely CA-P01-00, CA-P01-01 and CA-P01-02 (Figure 6A), which were formed by kaolinite and quartz and had average densities of 2.6 g/cm³ and 2.62 g/cm³, greater than that of palygorskite, which has an average density of 2.15 g/cm³. However, the lowest density found was also in a sample from the Cardoso site (CA-P04-01), which may show fluctuations in the concentration of palygorskite in the same deposit or an increase in the quartz content, altering the quality of the ore since quartz is harmful in certain industrial applications.

6 Conclusions

Environmental conditions in the Upper Carboniferous (Fm. Piauí) and the Permian (Fm. Pedra de Fogo) in the Parnaíba Basin were favorable for the formation of

palygorskite. The lithologies described in the two formations and the presence of silexite in the upper portion of the Piauí Formation generated this data inconsistency to define in which formation the palygorskite deposits from Guadalupe are inserted. The hypothesis of formation of fibrous clay minerals in saline lake environments from the alteration of aluminous detrital clay minerals, such as kaolinite, is consistent with the geological context of the region and the data found by X-ray diffraction.

The presence of a layer formed by dolomite and palygorskite can indicate a greater association with the Pedra de Fogo Formation, however to define where within the regional geological context these deposits are inserted and how to define the genesis of palygorskite, whether formed by mineral alteration of detritus or neofomed by solution precipitation, further analysis is needed to investigate textural relationship of its constituent minerals and the quantification of these minerals distributed in the region.

According to the results found, the areas palygorskite that occurs in the municipality of Guadalupe at the sampling sites do not present widely different characteristics regarding commercial applicability. At all sites analyzed, at least one sample had a beneficiation yield greater than 80% and ore density less than 2.5 g/cm³. More technological tests would be needed to compare the quality of the ores at the different sites analyzed, or if there are fluctuations in the concentration of palygorskite in the mineralized and mined layer in the region.

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Author contributions

Jéssica Tiné Pôssa: conceptualization; formal analysis, methodology; validation; writing – original draft; writing review and editing; funding acquisition; visualization; **Luiz Carlos Bertolino:** conceptualization; formal analysis, methodology; validation;; writing review and editing; funding acquisition; supervision.

Conflict of interest

The authors declare no potential conflict of interest.

Data availability statement

All data included in this study are publicly available in the literature.

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