

Article

The Occurrence of Authigenic Clay Minerals in Alkaline-Saline Lakes, Pantanal Wetland (*Nhecolândia* Region, Brazil)

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Abstract: Mg clay minerals are usually associated with carbonates in alkaline-saline environments, precipitated from solution and/or transformation from other minerals. The aim of this research is to identify the mineralogy and geochemistry of clay minerals in different alkaline lakes in the *Nhecolândia* region, the southernmost region of the Pantanal wetland (Brazil). Sediment samples were analyzed by X-ray diffraction, X-ray fluorescence, scanning electron microscopy and transmission electron microscopy. Water samples were analyzed, determining their main cations and anions, in order to understand their relationship with the clays. The analyses allowed classifying the water bodies as saline, oligosaline and freshwater lakes. The sediments are composed mainly of quartz and a fine-clay fraction, dominated by illite, kaolinite and smectite. The XRD results showed illite and smectite mixed-layered in the saline lakes at *Barranco Alto* farm, whereas at *Nhumirim* farm, trioctahedral smectite was only observed in one lake. The smectite minerals were normally identified coupled with calcite at the top of the sequences, associated with exopolymeric substances (EPS) in the lakes, suggesting that these minerals are precipitating due to the physical-chemical and biological conditions of the water bodies.

Keywords: alkaline lakes; clay minerals; EPS; chemical precipitation

1. Introduction

Clay minerals occur in different geological environments under varying climate, geological and chemical conditions. The weathering environment, rock type, topography and the presence of organisms and organic matter also play a prominent role in the formation of clay minerals [1]. The clays correspond to nearly 70% of the sedimentary rocks found worldwide and can be designated as detrital, transformed and neoformed clays [2]. The detrital clays are derived from erosion of soils and weathered rocks, being transported and accumulated; transformed clays are secondary clay minerals originated by reactions undergone at the deposition, burial and diagenesis processes and neoformed clays precipitate directly from solutions [1–5]. The last two types of clay minerals formation are associated with



diagenesis and authigenic clays that normally take place in soil profiles in alkaline-saline environments under certain concentrations in arid to semi-arid conditions [6,7].

The authigenic clay minerals have frequently been reported as magnesium silicate minerals, e.g., kerolite, trioctahedral smectites, palygorskite and sepiolite [5–8]. The authigenic clay minerals can also comprise corrensite, dioctahedral smectite minerals, a variety of mixed-layer minerals, as well as illite formed by illitization processes [6]. Regarding the smectite minerals, depending on the concentration of the solution and the amount of detrital material available, dioctahedral or trioctahedral minerals are favored [7,8]. Dioctahedral smectites are mainly formed through transformation of detrital material and they are associated with environments rich in Al^{3+} and Fe^{3+} , while trioctahedral smectites are formed by precipitation from aqueous solutions, associated with Mg^{2+} [7,9,10].

The *Nhecolândia* sub-region of the Pantanal wetland is known as a modern alkaline-saline environment, influenced by seasonal weather conditions, located in western Brazil [11,12]. The *Nhecolândia* region comprises thousands of fresh-water and alkaline-saline lakes, which are distributed next to each other, but display a wide chemical variability [7]. The salinity of the lakes used to be attributed to an inherited past, but more recently it has been related to a continuous evaporitic concentration of the freshwater [13]. The chemical variability is possibly related to precipitation of calcite or Mg-calcite and formation of Mg-silicates as the solutions become more saline [13,14].

Several works have already discussed the distribution, classification and geochemistry of the lakes, as well as the main mineral compositions of the sediments. Researches in alkaline-saline lakes in the *Nhecolândia* studied the mineralogy of smectite minerals, indicating magnesium clay minerals precipitate under exogenous conditions by organic control [8,14]. In this context, the aim of this research is to study the mineralogical and geochemical features of the clay minerals and lakes from two distinct regions at the *Nhecolândia* region, as well as to identify a possible relation to carbonate precipitation through biologically influenced mineralization.

2. Geological Setting

The Pantanal is the largest tropical wetland of the world and its origin is dated to the Proterozoic times [15]. The Pantanal is currently an active sedimentary basin, one of the four geographic areas of the Central Andean foreland basin system, corresponding to the most eastern region, also referred to as back-bulge depozones [16]. The third depozone described by the aforementioned authors is known as forebulge and it is found in eastern Bolivia and northern Paraguay, located west, parallel to the Pantanal wetland. The subsidence of the Pantanal is related to an elastic response caused by the extension of the upper crust when the forebulge initiated its development [17].

The floodplains of Pantanal are surrounded by highlands and plateaus, where the Proterozoic and Cambrian basement rocks are exposed [15,17]. Besides the magmatic and low-grade metamorphic rocks of the Cuiabá Group basement rocks, the highlands also comprise rocks of the Corumbá Group at the west edge, and Paleozoic and Mesozoic rocks of the Paraná Basin, at the east edge of the Pantanal wetland [12].

The depocenter of the Pantanal basin reaches approximately 500 m [17]. The basin is filled by siliciclastic sediments (primarily quartzose sands) from different source areas, mainly from the adjacent highlands, such as Paleozoic and Mesozoic sediments from the Paraná Basin on the eastern limit and quaternary sediments from the alluvial fans of Taquari River to the northeast, which consists in the Quaternary Pantanal Formation [12,18,19]. The Pantanal Formation includes conglomerates and coarse-grained sandstones in the bottom part, with fining upward sequences, where fine and medium quartz sands prevail. Locally, the presence of iron oxide cements and reddish sands are observed [19].

The Pantanal wetland is inserted in the Upper Paraguay River drainage basin, where the Paraguay River flows to N–S and cross-cutting the marginal alluvial fans, which flows to E–W [19]. Most of the Pantanal area is dominated by hydrodynamic alluvial fans and the most important of them is the Taquari River alluvial fan, extending over an area of 54,125 km², with a 250 km diameter and circular shape; [12,19].

The southern half of the Taquari alluvial fan is called *Nhecolândia*, showing a very low topographic gradient and corresponds to the oldest depositional lobe of the Taquari alluvial fan [12,20]. The *Nhecolândia* region is characterized by thousands of lakes which vary widely on the basis of spatial, physical, chemical and biological features [20], surrounded by elevations of 3–4 m, locally called *"cordilheiras"*.

The physiography of the region, the formation of the lakes, as well as their variabilities and the sediment features may be related to different origins [21]. Several works have related the lakes and the quartzose sands to an eolian origin, once the sands are white fine to medium-grained, and the *cordilheiras* would be morphological expressions of ancient dunes [12,21]. On the other hand, there is a hypothesis that indicates a fluvial genesis for the lakes, and the textural features of the sediments might be related to their source area, therefore being an inherited feature [22]. The authors have proposed that the current landscape was formed after the Late Pleistocene glaciation, when the elevation of the regional phreatic level would have formed the lakes, and the waters would have become progressively briny. The morphology of the lakes and the sand banks (*cordilheiras*) could be explained by the shifting of the river channels, being the result of the cut-off meanders. In all these studies, the evolution of the *Nhecolândia* is related to wet and arid phases during the Pleistocene [13].

Currently, the Pantanal experiences annual flooding from September to April and a dry season from May to August [19]. The annual rainfall provides a heterogeneous filling of rivers, lakes and groundwater, promoting a high chemical variability to the waters. The lakes generally show high alkalinity values and, some of them, high salinity. The origin of different types of water in the lakes is still under debate: there is the hypothesis that lakes have become progressively brinier [22] and another hypothesis indicates that the lakes derived from the same water source and underwent different degrees of evaporation and, thus, different concentrations of ions [7,13]. Additionally, the last hypothesis was complemented with studies showing that the evaporation rates are the same on the region and the distinct degrees of concentration are related to dissimilar insulation degrees, caused by a sub-superficial continuous horizon of low-porosity materials, as amorphous silica and smectites [23].

Several works have been conducted to investigate and classify these lakes according to pH, electric conductivity (EC) and total dissolved solids (TDS) values [13,18,21,24]. These lakes can be distinguished between hyperalkaline and alkaline lakes, despite showing a huge variance [18]. They can also be classified between freshwater and saline lakes, based on EC values [21] and finally, discriminated into five types according to EC and TDS values: freshwater; water with low to medium salinity; water with high salinity; water with very high salinity; and hypersaline water [24].

The most recent classification has distinguished the lakes according to biological and geochemical features [25]. The lakes are classified as macrophyte or freshwater lakes, where autotrophic metabolism predominates above the lake waterline (EC < 2000 μ S/cm and pH < 7.5); bacterial or oligosaline lakes, where heterotrophic metabolism predominates (500 < EC < 5000 μ S/cm and 7.9 < pH < 10.5); or saline lakes, where metabolism is also autotrophic, but predominates below the lake waterline (700 < EC < 65,000 μ S/cm and 7.9 < pH < 10.5).

3. Materials and Methods

3.1. Study Area and Sampling

The study areas are located on the south and southwestern parts of the Taquari alluvial fan, at *Barranco Alto* farm, near to Aquidauana/MS, and *Nhumirim* (*Embrapa*) farm, near to Corumbá/MS, respectively (Figure 1). Three field campaigns were conducted in different seasons. The first was at *Barranco Alto* farm, from 26 to 30 June 2017 at the beginning of the dry season. The second was at *Nhumirim* farm, from 20 to 24 August 2018, and the third again at *Barranco Alto* farm, from 17 to 21 September 2018. The last two campaigns were scheduled to happen at the end of the dry season, however, despite the low rate of rainfall in the region during the wet season and similar rainfall rate during the wet season in 2017–2018, the lakes had not dried and the water level was significantly higher than in 2017.

In *Barranco Alto* farm, we studied twelve lakes and the *Negro* River. In *Nhumirim* farm, we studied five lakes and the *Paraguay* River. In each lake and river, we collected samples of water and sediments following a sequence extending from the border of the lakes to their central part (P1, P2, P3 and P4), resulting in two to four collection points. When it was necessary, the sampling points were divided into bottom, middle and top samples (Figure 2). We collected 160 samples of sediment, but only 95 were analyzed: 31 from the first campaign, 38 from the second and 26 from the third campaign. The samples were chosen according to the amount of sand and clay.

The water temperature (WT °C), the pH, the EC (mS cm⁻¹) and the TDS (mg L⁻¹) were measured in situ with a multiparameter equipment. The lakes were classified adapting recent criteria, which take functional biogeochemistry, pH and EC values to classify them as saline, oligosaline and freshwater lakes [25]. In this work, we differentiate the lakes based on the names proposed by the authors; however, we used the TDS values as the main parameter to differentiate them. According to the TDS data, fresh water has less than 500 mg L⁻¹ and we considered in this work, based on the data obtained on the field campaigns, the oligosaline lakes with TDS values between 501 and 1500 mg L⁻¹ and the saline lakes with values higher than 1500 mg L⁻¹ [26].

3.2. Water Analyses

The water samples were analyzed for cations and anions in the *Laboratório de Pesquisa Hidrogeológica* (LPH-UFPR), whose methods are described on Table 1. The samples were prior filtered in the field through 0.45 µm surfactant-free cellulose acetate (SFCA) syringe filters [27]. In the laboratory, a fiberglass membrane and then a cellulose ester membrane were used to filter the samples from the campaign of 2017, whose water had more suspension material than those from 2018.

Element	Equipment	Methodology	Quantification Limit
Alkalinity			$0.10 \text{ mg L}^{-1} \text{ CaCO}_3$
HCO ₃	Automatic burette	Titration	$0.10 \text{ mg L}^{-1} \text{ HCO}_3$
CO ₃			$0.10 \text{ mg } \text{L}^{-1} \text{ CO}_3$
Ca	Atomic absorption	Atomic absorption	0 10 mg I ⁻¹
Mg	Spectrometer	Spectrometer	0.10 mg L
Cl		REF 918 20 NANOCOLOR [®]	$0.20 \text{ mg } \text{L}^{-1} \text{ Cl}$
Si	Spectrophotometer	REF 936 225 VISOCOLOR®	$2.00 \text{ mg } \text{L}^{-1} \text{ SiO}_2$
Fe	UV/VIS II (190–1100 nm)	REF 918 36 NANOCOLOR®	$0.01 \text{ mg L}^{-1} \text{ Fe}$
SO_4		Turbidimetric determination	$1.00 \text{ mg L}^{-1} \text{ SO}_4$
Na	Flame photometer	Flame photometer	0.10 Na mg L ⁻¹
К	Finite Photoineter	r mile protoineter	$0.10 { m K mg L^{-1}}$

Table 1. Equipment and methodologies used for water analyses.



Figure 1. Map of the *Barranco Alto* and *Nhumirim* farms in the sub-region of *Nhecolândia*, Pantanal wetland (Brazil).



Figure 2. (a) Aerial view of *Barranco Alto* farm; (b) sampling points in the margins (formed by sand or a crust of sediments, carbonate and iron oxide) and inside the lakes; (c) sampling core with the sediments split in bottom, middle and top portions; (d) water samples in plastic containers.

3.3. Mineralogical Analyses

The mineralogical analyses were carried out at Instituto LAMIR (*Laboratório de Análises de minerais e rochas*) of the Geology Department at Federal University of Parana. The composition of the sediments was determined by means of X-ray diffraction (XRD) through a PANalytical diffractometer model Empyrean with an X-celerator detector. Scans from bulk sediments and clay minerals were run from 20 angles of 3° to 70° and 3° to 30°, respectively, using a step-size of 0.016° and count time of 10.16 s per step [27]. A total of 74 bulk sediment samples and 69 clay mineral samples were analyzed, since some of the bulk sediments were composed solely by sand.

To analyze the mineralogy of the clay minerals, approximately 30 g of the bulk sediment was sifted in a 350-mesh sieve with distilled water. The solution was firstly centrifuged for 7 min at 800 rpm to decant the coarser fraction. The supernatant fluid was transferred to another plastic tube and centrifuged again for 30 min at 3000 rpm. The resulting mixture was poured on a glass slide covering at least 1 cm^2 of the glass slide. The samples were air-dried under room temperature and pressure (STP) to obtain oriented analyses with three different treatments: air-dried sample, ethylene-glycol vapor saturation for 8–12 h (EG) and heating at 550 °C for 2 h [27].

The clay minerals were identified mostly by their 001 peak after the three treatments cited above. The dioctahedral and trioctahedral character of smectites were identified by their 060 diffraction /peaks. Table 2 shows some clay minerals and their respective 001 and 060 peaks. Sepiolite and palygorskite present 110 reflections at 12.0–12.3 and 10.4–10.5, respectively.

Clay Minerals	Air Dried	d(001) Ethylene-Glycol	550 °C	d(060) Å
Kaolinite	7.0-7.1	No change	Collapse	1.49
Illite	10.1	No change	No change	1.50
Glauconite	10.1	No change	No change	1.51 - 1.52
Smectite (dioc)	15.0	16.9	10.0	1.49 - 1.52
Smectite (trioc)	15.0	16.9	10.0	1.52 - 1.54
Vermiculite	~14.0	No change	No change	1.54
Chlorite	~14.0	No change	Increase the intensity	1.54

Table 2. Clay minerals and their 001 and 060 peaks [28].

There is a wide variation in 060 diffraction peaks among dioctahedral and trioctahedral smectites. In dioctahedral smectites, for instance, montmorillonite and beidellite show d060 at 1.49–1.50 Å, while nontronite shows d060 at 1.52 Å [28]. In trioctahedral smectites, stevensite and saponite present 060 at 1.52 Å and hectorite presents d060 at 1.53 Å.

Mixed-layered clay minerals are very common in natural environments [2]. The identification of mixed-layered minerals is based on the entire diffraction pattern, like breadth, symmetry, intensity and peak position [28]. Illite/smectite (I/S) are the most common mixed-layered clay minerals in sedimentary rocks and soils. They can be recognized by their altered diffraction pattern under EG solvation treatment and after heating the sample to 375° for 1 h, resulting in a pattern similar to that of illite [28].

Non-clay minerals are very common in sedimentary rocks, such as quartz, feldspar, zeolites, carbonates, apatite, pyrite, gypsum and others [28]. Beyond the carbonates, calcite and dolomite are normally associated with clay minerals. The d-spacings of the most intense peak of calcite and dolomite are 3.04° and 2.89° 20, respectively [28]. The empirical curve of a calcite-disordered dolomite solid-solution series was used to identify the amount of mol% MgCO₃ [29]. The semi-quantitative XRD percentages of each sample were obtained through the Rietveld multi-phase standard analysis, performed in the HighScore Plus PANanytical Software (Version 3.0, Malvern, Amsterdam, The Netherlands).

A thin section of a crust sample was examined under transmitted light using the Zeiss Imager A2m Microscope (Carl Zeiss Microscopy, New York, NY, USA) aiming to observe the contact relations between grains and cements.

Images and chemical composition of specific points in 10 samples were collected using a JEOL scanning electron microscope (SEM, JEOL Ltd., Peabody, MA, USA) model 6010LA, equipped with an energy dispersive X-ray spectrometer (EDX, JEOL Ltd., Peabody, MA, USA) EX-94410T1L11 for elemental analyses. The morphology of illite crystals consists of ribbon-like flakes projections, as well as filamentous pore-lining and pore-bridging for authigenic illites [30]. The kaolinite occurs as stacks of pseudohexagonal plates or blocks and vermiform crystals. Smectite consists of a webby or highly-crenulated pore lining and thin ribbon of pore-bridging morphologies [30].

Images of one selected fine-clay fraction sample were obtained by transmission electron microscopy (TEM) using a JEOL JEM 1200EX-II instrument (JEOL Ltd., Peabody, MA, USA) operated at 120 kV (medium resolution) at *Centro de Microscopia Eletrônica* (CME) in the Federal University of Parana. Images, qualitative analyses and quantitative chemical analyses of 6 samples collected in 2017 were performed by scanning tunneling electron microscopy (STEM) with a FEI TITAN G2 instrument operated at 300 kV (high resolution—HRTEM) at *Centro de Instrumentación Científica* (CIC) in Granada University (Spain). The chemical composition was determined by analytical electron microscopy (AEM) in the HRTEM and the data were used to calculate the chemical formulae.

The HRTM analyses usually show illite particles as straight and relatively defect-free lattice fringes, with continuous and constant 10 Å interlayer spacings, with a mottled contrast, whereas smectite particles show anastomosing and imperfect 14 Å lattice fringe images [31]. AEM is a technique for quantitative chemical analysis of crystals of clay minerals, where data can be interpreted by phase diagrams [2,31–33]. Muscovite, albite, biotite, spessartite, olivine and titanite were used to obtain

k-factors to the correct energy dispersion X-ray data by the thin-film method [34]. Errors for analyzed elements (two standard deviations) expressed in percentage of the atomic proportions are 6 (Na), 3 (Mg), 2 (Al), 4 (K), 4 (Ca), 5 (Ti), 3 (Mn) and 3 (Fe). Instrumental conditions for spectra acquisition were 200 s of live time for all elements except for K and Na, for which a time of 30 s was used due to volatilization problems.

Contents of the major oxides of 92 bulk-sample sediments were measured by means of X-ray fluorescence (XRF) using a PANalytical spectrometer model AXIOS MAXDY 5297 (Malvern, Amsterdam, The Netherlands), through quantitative analyses at *Instituto* LAMIR (*Laboratório de Análises de minerais e rochas*) of the Geology Department at the Federal University of Parana.

4. Results

4.1. Water Chemistry

Despite the proximity between the studied lakes, they show a high spatial, physical and chemical variability. In the first field campaign at *Barranco Alto* farm (2017), the lakes showed differences related to their physical-chemical parameters. Table 3 shows the mean results of temperature, pH, EC and TDS measured on field and the concentrations of cations and anions in meq L⁻¹ (except SiO₂, whose value is in mmol L⁻¹), measured at the LPH. The two field campaigns of 2018 were scheduled to happen in a drier season than 2017. However, as mentioned before, the region was still flooded, and the physical-chemical aspects of the lakes showed lower values than 2017 (in the case of *Barranco Alto* farm).

In 2017, the northernmost lakes in *Barranco Alto* farm (*Tubarão*, *Burro Branco*, *Coração* and *Mara Maravilha*) were considered saline lakes. These lakes also exhibited the highest pH (10–11) and EC (>3 mS cm⁻¹) values. The *Mineira Grande* and *Sete* lakes were considered as oligosaline lakes and the others (nearest to the *Negro* River) were classified as freshwater lakes. In 2018, the lakes from *Barranco Alto* farm showed a great difference in comparison with the results of 2017. *Mara Maravilha* was the only saline lake, while *Sete*, *Coração*, *Nova*, *Burro Branco*, *Sete C*, *Japão* and *Jacaré* were classified as oligosaline lakes and the others were considered as freshwater lakes.

In *Nhumirim* farm, the *Meio* and *Oito* lakes were considered as oligosaline. Nevertheless, *Meio* lake has shown a pH > 10.18 and TDS value of 926.00 mg L^{-1} , while at *Oito* lake, the pH is 8.60 and TDS value is 651 mg L^{-1} . The other lakes were classified as freshwater.

Considering the average values of pH, the freshwater lakes exhibited values lower than 9, the oligosaline lakes values near 9.5 and the saline lakes values higher than 10.

It was also possible to distinguish the lakes according to their spatial and morphological features in 2017. The saline lakes have an average depth of 50 cm with a distinctive white beach devoid of vegetation around them, which is ringed by *carandas* palm trees, *Gramineae*, *Bromeliaceae* and the forest towards the "*cordilheiras*" [20]. The freshwater lakes, on the other hand, show depths higher than 1 m, do not have beaches surrounding them, and aquatic vegetation is very common, as well as the presence of animals, like alligators. In 2018, however, those features were not evident, and all the lakes showed similar morphological features.

Similarly, the measured elements in the water and listed in Table 3 show the same proportion related to the pH, EC and TDS values, when the data are split in milliequivalent per liter (Figure 3). Comparing the average values of saline, oligosaline and freshwater lakes in the three field campaigns (in meq L^{-1}), it is possible to recognize the highest values among saline and oligosaline lakes.

Regarding the anion content, bicarbonate shows the highest value in almost all of the campaigns, except for the saline lakes from *Barranco Alto* 2017 and freshwater lakes from *Nhumirim* 2018, where the carbonate ions were higher. The results from *Barranco Alto* in 2018, on the other hand, have exhibited larger amounts of Cl^- than CO_3^{2-} in all types of lakes. This feature is only observed in 2017 in the freshwater lakes.

Farm	Vaar	Laka	WT	pН	EC	TDS	Alkalinity	Si	HCO ₃ -	CO32-	Cl-	Ca	Mg	Na	К	Fe
Palli	Ieal	Lake	(°C)		(mS cm ⁻¹)	(mg	L ⁻¹)	(mmol L ⁻¹)				(meq	L−1)			
		Tubarão	28.77	10.10	3.20	1811.00	1560.65	0.7706	18.1514	13.0547	1.7860	0.2031	0.1094	24.0107	5.9849	0.4244
		Burro Branco	30.93	11.15	8.30	4596.00	4456.80	2.2219	40.2987	48.8194	7.2011	32.1373	22.5468	25.2286	8.4403	0.0645
		Coração	26.70	11.00	4.25	1987.00	1836.40	0.0083	1.7176	35.0048	7.5396	16.8671	7.5705	16.9641	4.0922	0.0501
		Mara Maravilha	26.88	11.35	9.07	5570.00	3788.60	0.7739	25.8535	49.9059	42.8878	38.8243	16.0461	30.6658	11.8931	0.0125
		Mineira G.	28.77	7.80	0.78	1071.00	723.36	0.7739	9.4010	5.0629	1.7742	0.1856	0.1111	13.8322	4.9107	0.0716
	2017	Mineira P.	29.31	7.82	0.56	369.00	262.58	0.4497	5.2502	0.00	0.2547	0.2675	0.1267	3.3058	1.2942	0.0004
	2017	Sete	23.15	9.78	1.50	845.00	646.50	0.7223	5.5503	7.3772	1.4916	0.0589	0.0214	12.1793	3.2482	0.2944
		Boi Preto	20.82	6.81	0.11	89.00	54.79	0.3332	1.0956	0.00	0.0860	0.1722	0.1070	0.5959	0.1709	0.0002
		Jacaré	21.23	9.90	1.40	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
		Japão	NM	10.70	1.90	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
		Negro River	NM	NM	NM	369.00	17.72	0.1012	0.3543	0.00	0.2462	0.1856	0.1736	0.1087	0.0726	0.0082
Parranco -		Well	NM	NM	NM	224.00	81.02	0.6141	1.6199	0.00	1.3350	0.4875	0.2864	1.2701	0.9438	0.0007
Alto		Tubarão	32.40	9.52	0.53	471.32	365.70	0.3678	6.7921	0.4999	0.2905	0.1597	0.0494	3.2275	1.4374	0.1450
		Burro Branco	30.80	9.31	1.91	1203.15	245.10	0.7746	0.7418	4.1594	3.4327	0.2675	0.0387	15.4851	3.7342	0.0376
		Coração	31.80	10.86	0.92	806.00	545.20	0.6511	9.7812	1.1198	2.7010	0.2051	0.0642	7.8296	1.9950	0.0398
		Mara Maravilha	33.10	10.40	2.78	2522.00	1092.50	0.7406	19.2447	4.1594	17.5139	0.2001	0.0634	24.2717	6.6499	0.0290
		Mineira G.	30.60	9.53	0.60	263.77	390.00	0.4986	7.7978	0.00	1.7663	0.5065	0.0848	5.5677	2.0461	0.0437
		Sete C	32.40	10.09	1.42	1272.70	860.30	0.4492	15.6417	1.5598	4.6439	0.1432	0.0592	11.6574	2.4042	0.0057
	2018	Sete B	31.40	10.18	0.49	447.53	149.00	0.3217	0.2599	2.7196	0.5272	0.0419	0.0485	1.4833	0.5422	0.0140
	2010	Sete	31.80	9.39	0.79	729.30	514.00	0.6424	8.8376	1.4398	1.2806	0.0948	0.0617	8.1776	2.7623	0.4154
		Nova	30.80	10.13	1.25	1160.25	512.90	0.3974	4.7767	5.4792	0.0231	0.2001	0.0568	11.3964	4.8084	0.0061
		Boi Preto	37.2	8.3	0.07	50.0	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
		Jacaré	31.10	10.48	1.49	1387.60	583.80	0.3938	6.5543	5.1192	9.6677	0.1747	0.0625	10.9614	2.1996	0.0179
		Japão	30.40	9.81	1.29	325.33	500.50	0.3542	8.1278	1.8797	8.3612	0.1367	0.0568	10.5264	2.0973	0.0118
		Negro River	32.80	7.44	0.02	339.37	14.10	0.0449	0.2819	0.0000	0.1077	0.0778	0.0905	0.1131	0.1228	0.0444
		Well	NM	NM	NM	179.14	74.90	0.3981	1.4976	0.00	1.2495	0.5439	0.3818	0.9134	0.3581	0.0050
		Oito	15.60	8.60	1.09	651.00	453.26	0.2447	8.9828	0.0800	0.1089	0.7885	0.4921	5.4807	3.1971	0.00
		Meio	20.30	10.18	1.36	926.00	353.31	0.2670	3.5451	3.5195	1.6966	0.2630	0.2617	6.1332	2.4362	0.0004
Mhumirim	2018	Seis	20.03	10.00	0.35	350.00	267.12	0.1731	0.9017	4.4393	0.2036	0.1841	0.1563	3.9583	2.1356	0.00
- 1111111111111111	2010	Salitrada	28.80	7.73	0.31	163.00	133.66	0.3062	0.5336	2.1390	0.0578	0.9317	1.2499	0.5742	0.4834	0.0047
		SalvinaDoce	25.40	6.57	0.14	53.00	34.79	0.0766	0.6955	0.00	0.0062	0.2670	0.3259	0.2175	0.1458	0.0004
		Paraguay River	NM	NM	NM	30.00	25.46	0.1082	0.5189	0.00	0.0138	0.2021	0.2321	0.1000	0.0384	0.0072

Table 3. Elements concentration in the water lakes of *Barranco Alto* farm (2017 and 2018) and *Nhumirim* farm (2018). WT—water temperature, EC—electric conductivity, TDS—total dissolved solids, NM—not measured, NS—not sampled.

2017 and freshwater lakes at *Nhumirim* 2018, where the carbonate ions were higher. Both saline and oligosaline lakes of 2018's campaigns have exhibited similar compositions of silica, Ca²⁺, Mg²⁺ and Fe²⁺.

For all the studied parameters, *Barranco Alto* has shown the highest concentrations, highlighting Na⁺, K⁺, Cl⁻, C.E and TDS. Only Ca²⁺ and Mg²⁺ mean concentrations are higher in the *Nhumirim* farm than in the *Barranco Alto*, where there are lower amounts of Na⁺ and K⁺.



Figure 3. Distribution of the main elements in the saline, oligosaline and freshwater lakes from the three sampling campaigns. The values are given in meq L^{-1} , except for SiO₂, whose values are normally given in mmol L^{-1} .

Exopolymeric substances (EPS) have been observed in both studied sites. In *Barranco Alto*, there were EPS in the *Sete*, *Sete B*, *Mineira Pequena* and *Tubarão* lakes, mainly in 2017, with a green color and a viscous aspect (Figure 4b). In those lakes, the EPS were normally associated with algae, forming a green viscous algalic net with some bubbles. In *Nhumirim*, EPS were observed in the *Oito* and *Seis* lakes and showed an orange color, formed just by bubbles (Figure 4a). At some points of some lakes, the algae were observed with no association with the EPS, and were identified as *charophyte* (Figure 4c). A microbial mat was identified above the sediments on the crust of *Seis* lake, showing green and red interbedded sheets of 2–3 mm each (Figure 4d).



Figure 4. (a) Orange bubbles forming the exopolymeric substances (EPS) at Seis Lake, in *Nhumirim* 2018; (b) green viscous EPS at Sete lake, in *Barranco Alto* in 2017; (c) the algae type charophyte observed at *Sete* B lake in 2017 and (d) The sediment crust from *Seis* lake, with the microbial mat on the top the sample.

4.3. Petrographic Characterization

White unconsolidated sands predominate in "cordilheiras" and lakes' margins at Pantanal, they are composed mainly of quartz, feldspar and iron minerals, and the grains are fine, homogeneous and rounded, probably associated with the top sequences of the Pantanal Formation. The "beach" around the saline and oligosaline lakes is also formed by carbonate. The carbonate was observed as a thin white crust over the sand. Two thin sections were made of a consolidated rock of *Coração* lake and *Negro* River (*Barranco Alto* farm) from the 2017 and 2018 campaigns, respectively. Both samples are composed mostly of quartz. The grains show a mottled aspect, varying from fine to medium granulometry and sub-rounded morphology with high sphericity.

In 2017, *Coração* lake exhibited a wide area composed of a concentric crust of interbedded sandstones, carbonates and iron nodules (Figure 5a). Microscopically, besides the quartz grains, it was also noticed a very thin light brown material around the grains (Figure 5b), which could be constituted of clay minerals.

At higher magnification, the fine-grained material shows wispy laminations and it seems to be coating the quartz grain boundaries and pores (Figure 5c).

The sample collected on the banks of the *Negro* River could be described as a massive agglomerate of sandy clay (Figure 5d). In thin sections, there are clays with brown color (black arrow) and clays with greenish-brown color (red arrow), the latter being the most common in the sample (Figure 5e). Observing these greenish-brown clays in a higher magnification (red arrows), it is noticed that they form a "bridge" (red circle) between the quartz grains (Figure 5f), which widely occurs in the section.



Figure 5. (a) Layered crust around *Coração* lake in 2017; (b) photomicrograph of the crust composed by quartz grains, vugy pores and brown clay material coatings; (c) detail of the lamination in the clayey material; (d) the banks in the margins of the *Negro* River. The rock is described as a consolidated sandy clay; (e) photomicrograph of the sample, with predominance of quartz grains. The black and red arrows indicate, respectively, the brown and the greenish-brown clays; (f) detail of the greenish-brown clays between the quartz grains. They usually develop a "bridge" aspect (red polygons) between adjacent grains.

4.4. Mineral Characterization

XRD analyses of the bulk samples confirmed the dominance of quartz, mainly in the samples from the crust and border. The second mineral is potassium feldspar, followed in some samples by calcite, that is usually present in the saline and oligosaline lakes. Table 4 shows the abundance of three

representative samples from each campaign. This abundance represents a relative proportion of the phases, measured by using the automatic semi-quantification program.

Farms	Year	Lakes		Bul	k Rock	(%)	Clay Fraction (%)				
		Lunco	Qz	Kfs	Ilt	Kln	Cal	Ilt	Kln	Sme	Cal
		Burro Branco	78	17	-	-	5	66	29	-	5
	2017	Coração	84	12	-	-	4	26	71	3	-
Barranco Alto		Negro River	69	16	-	15	-	25	70	4	-
	2018	Sete C	90	10	-	-	-	70	28	-	2
		Mineira	89	11	-	-	-	41	59	*	-
		Negro River	85	15	-	-	-	32	52	16	-
		Meio Lake-P2	92	8	-	-	-	63	30	5	2
Nhumirim	2018	Meio Lake-P3	91	8	-	-	1	51	24	25	-
		Meio Lake-P4	90	8	-	-	2	85.9	8	*	6

 Table 4. Relative abundance of selected samples from each campaign. Qz—quartz; Kfs—K-feldspar;

 Ilt—illite; Kln—kaolinite; Cal—calcite; Sme—smectite; (-) not observed; (*) not measured.

In 2017, calcite widely occurred in the sediments of the *Mara Maravilha* and *Burro Branco* lakes, as well as in the crusts of the *Coração*, *Tubarão* and *Sete B* lakes. In 2018, calcite occurred in the sediments of the *Coração*, *Burro Branco*, *Tubarão*, *Mara Maravilha* and *Sete B* lakes in *Barranco Alto* farm and in the *Seis*, *Oito* and *Meio* lakes in *Nhumirim* farm. In the clay fraction, calcite only occurred in the middle of those lakes, often at the top of the sequences.

The clay fraction is dominated by illite and kaolinite and secondly by smectite [28]. The clays were identified mostly by their 001 peaks. Illite and kaolinite were distinguished by their distinctive peaks at 10.0–10.1 and 7.0–7.1 Å, respectively [28]. Smectite was identified by its 001 peak ~15 Å in the air-dried sample and the shift to 16–18.5 Å after EG treatment, and by the shift to ~10 Å after heating at 550 °C. The dioctahedral and trioctahedral characters were identified by its 060 diffraction peak, between 1.49–1.52 and 1.52–1.54 Å, respectively [28,35,36].

Some samples from *Barranco Alto* farm did not show the illite 001 peaks ranging from 10 to 12 Å in air-dried condition, exhibiting a broad reflection, with an inclination toward the small angles (Figure 6). Most of the samples have not shown a shifting after the EG treatment, however, after heating the samples at 550 °C, the peaks became sharper and more intense, as it is shown in the first row (*Burro Branco* and *Sete C* lakes). The *Coração* and *Mineira* lakes show broader peaks in air-dried condition (second row) and although these peaks are connected, they exhibit two points of maximum intensity at 13 and 14 Å. After heating, these peaks shift to the peak of 10 Å.

Smectites have been observed in the sediments of the *Negro* River and in (third row) *Meio* lake. They were identified by a shift of the 001 peak from ~15 Å under air-dried condition to 17–18 Å under EG treatment and to ~10 Å after heating the samples at 550 °C (Figure 6). In *Meio* lake, the smectite was identified at the top of the three collection points inside the lake, normally associated with calcite. The XRD pattern was accompanied by a high background, which hampered the identification of the 060 peaks. The 060 diffraction peak of smectite from the *Negro* River was not distinguished in 2017, but in 2018 showed values of 1.542 Å. The smectite of *Meio* lake showed 060 peaks at 1.521 (P3) and 1.524 Å (P4), but the peak from sample P2 was not distinguished. The other lakes of *Nhumirim* farm are composed mainly of illite and kaolinite. On the lakes *Seis* and *Oito*, there is also calcite present, normally at the center of the lakes and in the top of the sequences.



Figure 6. XRD patterns of the clay fraction of some samples from the *Barranco Alto* and *Nhumirim* farms. All the sediments are from the top of the sequences collected at the center of the lakes. At the first row of the diffractograms of *Barranco Alto* (*Burro Branco* and 7C lakes), there is no peak at 15 Å; in the second row (*Coração* and *Mineira* lakes), a broad peak is observed between 10 and 14 Å and the diffractograms of *Negro* River showed two different peaks at 10 and 15 Å, the latter being more intense. The numbers above the dashed lines represent the d—spacing values. Sme—smectite, Ilt—illite, K—kaolinite, Qz—quartz, Cal—calcite.

4.5. Microstructure of the Clay Minerals

The SEM observations of samples of the *Mara Maravilha*, *Coração* and *Meio* lakes allowed the investigation of the morphologies and contact relationships between the crystals. The observations indicated dominance of quartz. The grains display spherical and angular morphologies, with smooth surfaces. There are few visible calcite crystals displaying angular and irregular morphologies. The significant amount of fine-grained minerals is observed over and between quartz and calcite grains. They can be distinguished as small aggregations (Figure 7a) or as a thin sheet coating the other grains (Figure 7b). Furthermore, whole structures and pieces of diatoms are noticed along the samples.

EDX analyses are consistent with XRD and the morphological observations. The fine-grained minerals are composed of Si, Ca, Fe, Al, K, Mg and Na. The composition of these minerals is indicative of clay minerals, which do not show a specific morphology, but in some samples, it is possible to distinguish a filamentous pore-bridging structure (structure 1, Figure 7c) and a crenulate/webby shape (structure 2, Figure 7c) between the quartz grains.

Observing the morphologies and their chemical composition, it is possible to establish that there are illite and smectite minerals among the clay minerals.

In Figure 7e, it is possible to observe a thin and elongated structure (indicated as 1) above the quartz grain at the center of the image. This mineral phase is composed of Si, Al and Mg. The mineral

type - 2 is composed of Si, Al and K, and the rounded structure indicated in "3" is composed of a high content of Ca, corresponding to calcite. TEM images of the sample from *Coração* lake show a large thin euhedral sheet mineral, which overlaps, probably in the basal plane, and a lenticular shape, representing a longitudinal plane or other kind of clay mineral. Different shades among the crystals were noticed, which might represent a different electric absorption pattern (Figure 8a).

The thin euhedral and subhedral sheets are arranged close to lenticular crystals in the same aggregate and they exhibit different shades. Besides these characteristics, the samples have also shown irregular morphologies, as "cotton-like", with a filamentous pore lining growing up from the core of the boundaries of some material (Figure 8b). It is possible to notice crystals with thin euhedral morphologies and elongated sheets associated with a cotton-like material disposed together (Figure 8c,d), as well as rounded shapes among a cotton-like mineral, as Figure 8e shows.



Figure 7. Scanning electron photomicrographs. (**a**) General overview of the sediments. The yellow arrows indicate the aggregations of clay minerals; (**b**) thin sheet of clay minerals coating quartz crystals; (**c**) two different structures of clays between the grains (structure 1—pore-bridging and structure 2—webby shape); (**d**) acicular clay minerals scattered on the surface of other crystals; (**e**) elongated Mg-rich clays above quartz (1), associated with clays rich in Al and K (2) and calcite (3). Qz—quartz, Cal—calcite, Dt—diatom.

Despite the different morphologies observed, in the EDX analyses of several points along the minerals, they showed similar chemical composition. Observing different points from similar morphologies, it was not possible to establish a specific chemical composition for each one of them. Si and O are dominant, followed by Al (3.0–15.0 wt.%), Fe (2.6–17.4 wt.%), K (0.5–8.0 wt.%) and Mg (1.1–4.2 wt.%) and some other elements as Ca, Mn and Na. The "cotton-like" morphology mentioned above seems to be growing up from a barite grain in Figure 8b. The cotton-like shaped clay mineral is bound with the organic material through pore-lining or pore-bridging projections, which may indicate

an authigenic clay [30]. In Figure 8d, the structure highlighted by the dashed line show a composition rich in P and Ca, which was not observed in any other sample and might indicate an apatite grain. In Figure 8e, the crystal surrounded by a dashed line is composed only of Si and Al, which corresponds to kaolinite.



Figure 8. Transmission electron photomicrographs. (a) Lath-like clay particles (red line) and flakes (blue line) in the same aggregate; (b) "cotton-like" clays with filamentous pore-lining (red arrows) bond in the core (yellow dashed line) composed of S and Ba; (c) "cotton-like" clays associated with elongated clays; (d) different types of morphologies of clay minerals. The yellow dashed line indicates a portion rich in Ca and P; (e) aggregation of "cotton-like" and pseudohexagonal clays. The circulated area (yellow dashed line) is composed mainly of Si and Al, comprising kaolinite; (f) detail of the pseudohexagonal kaolinite. Kln—kaolinite.

4.6. Chemical Composition and Structural Formulae of the Clay Minerals

The XRF analysis of major elements (expressed as oxides) in the bulk sediments confirm the dominance of SiO_2 and Al_2O_3 , followed by Fe_2O_3 , CaO and K_2O (Table 5).

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The Table 5 presents the average of each lake and it is possible to notice the higher concentrations of the oxides (except SiO_2) in the *Barranco Alto* lakes in 2017, possibly related to the lower water level, caused by higher evaporation rates. In 2018, the SiO_2 concentration increased from a mean value of 83.79% (2017) to 93.80%, while the other oxides decreased from a mean value of 1.63% in 2017 to 0.63% in 2018. Furthermore, comparing the averages of the two farms in 2018, just Al_2O_3 has shown significant differences.

Farm	Year	Lake	SiO ₂	TiO ₂	Al_2O_3	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5	LOI
		Tubarão	88.33	0.20	2.18	1.98	0.27	0.63	0.78	0.98	1.73	0.10	2.80
		Burro Branco	82.20	0.20	3.36	2.10	0.28	0.60	1.28	2.14	1.84	0.16	5.70
		Coração	87.43	0.28	3.33	2.28	0.90	0.50	0.98	0.38	1.28	0.17	2.47
		Mara Maravilha	69.17	0.36	5.63	4.04	0.77	2.09	4.01	1.20	3.04	0.12	9.00
		Mineira G.	78.40	0.30	3.30	1.50	0.20	100	3.00	0.40	1.40	0.50	9.65
	2017	Mineira P.	78.60	0.40	4.60	2.20	0.10	0.50	0.80	0.20	1.20	0.20	11.08
	2017	Sete B	66.00	0.30	4.90	5.80	0.40	1.50	5.60	0.20	2.60	0.10	11.90
		Sete	94.83	0.13	1.90	0.53	0.00	0.17	0.20	0.13	0.90	0.10	1.05
		Boi Preto	96.90	0.10	1.20	0.20	0.00	< 0.1	< 0.1	< 0.1	0.60	0.10	0.76
		Jacaré	95.70	0.20	1.40	0.20	0.00	< 0.1	0.10	0.10	0.90	0.10	1.21
		Japão	97.80	0.10	0.90	0.20	0.00	0.00	< 0.1	0.10	0.50	0.10	0.40
Barranco		Negro River	71.95	0.80	14.80	4.80	0.20	0.85	0.30	0.10	1.65	0.10	4.30
Alto		Tubarão	88.99	0.15	1.82	1.94	0.17	0.43	0.61	0.14	1.27	0.04	4.48
		Burro Branco	97.10	0.09	0.85	0.38	0.03	0.04	0.36	0.10	0.53	0.05	0.80
		Coração	97.25	0.08	0.67	0.17	0.03	0.13	0.54	0.09	0.41	0.02	0.83
		Mara Maravilha	89.37	0.21	2.13	1.51	0.25	0.49	1.18	0.38	1.31	0.04	3.42
		Mineira G.	83.70	0.25	2.82	1.12	0.09	0.38	0.84	0.18	0.85	0.10	9.98
		Sete C	97.22	0.13	1.28	0.34	0.01	0.07	0.07	0.10	0.55	0.01	0.76
	2018	Sete B	82.43	0.24	3.11	3.43	0.20	0.67	1.67	0.12	1.61	0.03	6.55
		Sete	97.41	0.10	1.04	0.32	0.01	0.07	0.05	0.06	0.50	0.01	0.50
		Nova	98.30	0.06	0.53	0.16	0.01	0.05	0.04	0.05	0.31	0.01	0.61
		Boi Preto	97.99	0.08	0.66	0.16	0.01	< 0.01	0.03	0.03	0.32	0.01	0.76
		Jacaré	98.83	0.07	0.51	0.11	< 0.01	0.01	0.02	0.04	0.26	0.01	0.24
		Japão	98.24	0.09	0.65	0.14	0.01	0.01	0.03	0.05	0.32	0.02	0.56
		Negro River	92.54	0.23	3.01	1.00	0.03	0.18	0.09	0.06	0.68	0.02	1.74
		Oito Lake	96.75	0.10	0.72	0.37	0.07	0.13	0.31	0.07	0.47	0.02	0.99
		Meio Lake	96.45	0.13	0.81	0.19	0.04	0.20	0.52	0.12	0.49	0.02	1.02
Nhumirim	2018	Seis Lake	88.57	0.21	1.14	3.33	0.28	0.52	1.16	0.11	1.58	0.27	3.18
		Salitrada	93.39	0.25	1.51	0.38	0.02	0.05	0.10	0.06	0.56	0.03	3.66
		SalvinaDoce	95.59	0.12	0.85	0.43	0.04	0.06	0.07	0.05	0.42	0.02	2.35

Table 5. Major elements (wt.% of the bulk sediments, measured by XRF).

Regarding CaO, MgO and Na₂O, in the farthest lakes from the *Negro* River (*Tubarão* and *Burro Branco*) in 2017, Na₂O prevailed over CaO and MgO. In the other saline and oligosaline lakes (*Mara Maravilha* and *Coração*), CaO predominates over MgO and Na₂O. In the *Negro* River, the sequence of predominance is MgO-CaO-Na₂O.

In 2018, the dominant sequence CaO-MgO-Na₂O continued in most of the lakes. However, some of them showed a preponderance of Na₂O. Nevertheless, the concentrations of these three oxides continued the same for *Negro* River in the two years. The *Nhumirim* lakes showed the same sequence of concentrations than *Barranco Alto* lakes (CaO-MgO-Na₂O), except for *Salitrada* lake, where Na₂O prevails over MgO. Analyzing each collection point (Table S1 in Supplementary Materials), there is an increasing trend of the oxides towards the top of the collected sequences, except for SiO₂. This trend is also observed towards the center of the lakes. Therefore, the concentrations of the oxides are higher in the center of the lakes and in the top of the sequences (in contact with the water), except for SiO₂, which demonstrates a reverse trend.

The clay formulae obtained from chemical analyses by AEM. All samples were collected at *Barranco Alto* farm in 2017. Contrasting the large dimensions of the areas of analysis $(100 \times 20 \text{ nm}^2)$ with the small particle sizes of clays (5–20 nm) and considering the presence of intimate intergrowth of smectites, non-crystalline phases and mixed-layers, the results may not represent a single crystal of clay. The results have been discriminated as illite, I/S and smectite (Table 6).

Detrital Micas	Illite	I/S	Smectites
Si = 3.05–3.15	$Si = \approx 3.20$	K = 0.40 - 0.52	Si = 3.50 - 4.00
	Mg: 0.10-0.25		Mg: 0.30–0.70
	Fe: 0.05–0.10 K: 0.57–0.70		$\Sigma^{(\text{VI})}$: 1.95–2.20 or 2.80–3.05
			$\sum^{(XII)}: <0.65$

Table 6. Criteria to determinate the chemical formulae by AEM analysis [32,37,38].

 $\Sigma^{(VI)}$: Sum of octahedral cations; $\Sigma^{(XII)}$: Sum of interlayer cations.

The I/S species with >90% of illite show K > 0.65 atoms per formula unit (apfu) and Si = 3.34-3.49 apfu [39]. Some of the interlayer charge, which results from the summation of interlayer cations multiplied by their respective charges (K + Na + 2Ca), showed particularly high values (0.21–0.83 apfu). The larger interlayer charge values are normally associated with illite, indicating a mixed-layered I/S or an inclusion of amorphous materials in the analyses [32]. The clay formulae are listed in Table 7.

Table 7. Chemical analyses obtained by analytical electron microscopy (AEM) and expressed as smectite formulae *. MM—*Mara Maravilha; P1—crust; P2*—border of the lakes.

Lakes	Si	Al ^(IV)	Al ^(VI)	Fe **	Mg	Mn	Σ ^(VI)	К	Na	Ca	$\Sigma^{(XII)}$
MM (P2)	3.58	0.42	1.82	0.18	0.18	0.02	2.20	0.02	0.00	0.00	0.02
	3.75	0.25	1.04	0.67	0.31		2.02	0.40	0.05	0.03	0.48
	3.80	0.20	1.37	0.36	0.25		1.98	0.29	0.16	0.03	0.48
	4.00		1.24	0.31	0.40		1.95	0.19	0.03		0.22
	3.97	0.03	0.39	1.01	0.59	0.13	2.12	0.34		0.02	0.36
Coração	3.64	0.36	0.80	0.79	0.59	0.09	2.27	0.26		0.02	0.28
(P1)	4.00		0.32	0.88	0.56	0.13	1.89	0.24		0.01	0.25
	3.73	0.27	0.67	0.90	0.32	0.03	1.92	0.77		0.04	0.81
	4.00		0.39	0.64	0.75	0.08	1.86	0.27		0.01	0.28
	3.91	0.09	0.30	1.03	0.64	0.12	2.09	0.55		0.02	0.57
	3.45	0.55	1.79	0.16	0.25		2.20	0.15		0.02	0.17
	4.00		0.75	0.59	0.39	0.08	1.80	0.42	0.11		0.53
Burro	4.00		0.44	0.81	0.49	0.08	1.81	0.50	0.07	0.01	0.58
Branco	4.00		1.06	0.18	0.18		1.41	0.23	0.10	0.01	0.34
(P2)	4.00		0.78	0.49	0.27	0.03	1.57	0.36	0.09	0.01	0.46
(1 2)	4.00		0.95	0.43	0.26	0.05	1.69	0.26	0.08	0.02	0.36
	4.00		1.29	0.27	0.21	0.02	1.80	0.19	0.11	0.02	0.31
	3.64	0.36	1.47	0.4	0.24	0.02	2.13	0.19		0.02	0.21
	3.66	0.34	1.31	0.35	0.31	0.02	1.99	0.62	0.08		0.70
Tubarão	3.94	0.06	0.7	0.82	0.37	0.1	1.99	0.5		0.04	0.54
(P2)	4.00		0.68	0.63	0.41	0.05	1.77	0.44		0.03	0.47
	3.91	0.09	0.41	0.97	0.53	0.10	2.01	0.62		0.04	0.66
	3.26	0.74	1.77	0.08	0.17	0.01	2.03	0.83			0.83
	3.78	0.22	0.36	1.1	0.5	0.05	2.01	0.62		0.07	0.69
	3.82	0.18	0.43	1.03	0.45	0.04	1.95	0.51		0.16	0.67
Sete B	3.74	0.26	0.18	1.35	0.47	0.05	2.05	0.55		0.04	0.59
(P2)	3.83	0.17	0.4	1.1	0.45	0.06	2.01	0.58		0.03	0.61
(1 -)	3.75	0.25	0.57	1.0	0.45	0.03	2.05	0.49		0.05	0.54
	3.61	0.39	1.45	0.41	0.26	0.03	2.15	0.18		0.03	0.21
	3.4	0.60	1.08	0.68	0.22	0.11	2.09	0.27		0.2	0.47
	3.74	0.26	1.49	0.2	0.41		2.10			0.17	0.17
Neoro	3.73	0.27	1.56	0.18	0.42		2.16	0.05		0.08	0.13
River	3.54	0.46	1.27	0.49	0.35		2.11	0.4		0.05	0.45
(P2)	3.5	0.50	1.35	0.59	0.19		2.13	0.08		0.11	0.19
(1 -)	3.39	0.61	1.57	0.22	0.4		2.19	0.47			0.47
	3.51	0.49	1.38	0.46	0.36		2.20	0.17		0.05	0.22

* Units: apfu (atoms per formulae unit). Normalization to 22 charges. ** Total Fe expressed as Fe^{3+} . Values in bold represent octahedral and interlayer sums. Red values represent octahedral sum < 1.92 apfu and interlayer sum > 0.65 apfu.

Despite the wide range among the elements, illite species will be considered in this work as having K > 0.62 pfu. Analyses corresponding to smectites follow the criteria described above. Only five points show K values equal or higher than 0.62 pfu. Besides, almost all Si and $\Sigma^{(VI)}$ values correspond to the range described for smectites [37]. Fourteen analyses (highlighted in red), including all points from *Burro Branco* lake, however, do not correspond to this criterion. The sum of octahedral atoms is lower than 1.92 apfu and they are hereby classified as illite.

5. Discussion

5.1. The Distinct Clay Minerals from Pantanal

The clays identified in *Barranco Alto* farm are mainly of illite and kaolinite composition, with d-spacings at 10–10.1 and 7–7.1 Å, respectively [28,35]. Some illite 001 peaks, however, varied toward 12 Å in air-dried condition, remained constant under EG treatment and shifted to 10 Å after calcination, indicating the ocurrence of illite-smectite interstratification (I/S) [28,40]. The I/S was mainly observed at the *Mara Maravilha*, *Burro Branco*, *Tubarão*, *Coração* and *Sete B* lakes in 2017 (mostly saline and oligosaline lakes), whereas in 2018, it was observed at the *Sete C* and *Mineira* lakes (Table 8). Clays from the *Coração* and *Mineira* lakes exhibited a specific feature in their 001 peaks in air-dried condition: between 10 and 15 Å, two higher intensity peaks occur, confirming the I/S interstratification interpretation.

In the *Negro* River, on the other hand, the smectite diffraction pattern was clearly observed in both campaigns, as shown in Figure 6. Their 060 patterns showed values of 1.541 Å, typical of trioctahedral smectites [28,35]. Differently, the 060 diffraction peaks of the *Mineira* and *Sete* C lakes are at 1.504 and 1.529 Å, respectively, which could be consistent with a mixture of di- and trioctahedral character clays [35,36].

Petrographic analyses, SEM and TEM images have shown different types of clay minerals, based on their morphologies and chemical composition. Figures 5f and 7c exhibit clay crystals forming a "bridge" between quartz grains and Figure 5g shows a pore-lining morphology growing up from a core sample to form a cotton-like structure, indicating a characteristic typical of smectites [30]. The aggregates of clay minerals at Figure 7a and the subhedral and elongated shapes recognized at HRTEM images (Figure 8a–f are common in detrital clays. The different morphologies, however, do not show a specific chemical composition, demonstrating that clay crystals are comprised by distinct components.

Although the calculated chemical formula of some samples showed a very small amount of tetrahedral Al, such a low amount could indicate the presence of trioctahedral smectite [7]. The sum of the octahedral sites, however, does not correspond to the average value of 2.80 apfu for trioctahedral smectite, possibly due to the low amount of Mg [7,37].

Table 8. Interpretation of 001 and 060 peaks from XRD analyses of the clay fraction from the *Barranco Alto* and *Nhumirim* farms (Figure 6). I/S—illite/smectite; Sme—smectite; di—dioctahedral; tri—trioctahedral; d—d-spacing; (-) not observed.

Farm	Year	Lakes	Air-Dried	d(001)Å Ethylene-Glycol	550 °C	d(060) Å	Clay Minerals
	2017	Burro Branco Coração	10.0–12.0 10.0/13.0	No change No change	10 Å more intense 10 Å more intense	- 1.541	I/S I/S
Barranco		Negro River	15.0 17.0		10.0	-	Sme
Alto		Sete C	10.0-12.0	17.0	10 Å more intense	1.529	I/S
	2018	Mineira	10.0/14.0	No change	10 Å more intense	1.504	I/S
		Negro River	15.0	17.0	10.0	1.541	Sme (tri)
		Meio Lake—P2	15.0-16.0	No change	10.0	-	I/S
Nhumirim	2018	Meio Lake—P3	15.0-16.0	17.0	10.0	1.521	Sme (di/tri)
		Meio Lake—P4	15.0-16.0	No change	10.0	1.524	I/S

The di or trioctahedral character in a solid solution is not continuous between its end members in low temperatures [7,37]. The trivalent cation cannot represent less than 65% of the octahedral sites in dioctahedral smectite, which represents 1.3 R³⁺ cations on a Si₄O₁₀ calculation basis, and the natural trioctahedral smectite exhibits a minimum number of 1.83 R²⁺ [41,42]. According to the diagram of octahedral occupancy, AEM analyses mainly display a dioctahedral composition (Figure 9a) [2,7,41,42]. In the Si-Al-Fe triangular composition diagram, the points analyzed formed a gradual trend from montmorillonite to nontronite (Figure 9b). Despite this trend, the analyses of each lake are widely scattered, and a geographic distribution is not feasible. Smectite composition shows a high variation regarding Si, Al, Fe and Mg contents (specially Si and Al). Analyses plotted in the AlAl-AlFe-AlMg ternary diagram (Figure 9c) show they can be designated as Fe-rich beidellite [37].



Figure 9. (a) Diagram showing dioctahedral, trioctahedral and intermediate character of the smectite formulae; (b) triangular Fe-Si-Al composition diagram showing a trend from montmorillonite to nontronite; (c) triangular diagram AlAl-FeAl-AlMg [37] showing that smectite corresponds mainly to a Fe-rich beidellite. Bl—beidellite, Mo—montmorillonite, No—nontronite, FeBl—Fe-rich beidellite, FeMo—Fe-rich montimorillonite.

Clays from *Nhumirim* farm are generally composed of illite and kaolinite, with the exception of the *Salvina Doce* and *Salitrada* lakes, which exhibited just kaolinite and quartz in the clay fraction. In the *Seis, Oito* and *Meio* lakes, calcite appears in the top of sequences, essentially in the regions closest to the center of the lakes. In *Meio* lake, the 060 diffractogram pattern of the sample P3 occurs at 1.521 Å, which could indicate a possible intermediate di- and trioctahedral composition [7,43]. Previous research in *Meio* Lake had indicated 060 XRD patterns typical of trioctahedral minerals in their samples [7]. However, most of their chemical structural formulae displayed an intermediate di- and trioctahedral composition, allowing the authors to indicate that the Mg-rich smectites had a dominant trioctahedral character, but presented a dioctahedral component [7].

5.2. A Primary Precursor as a Responsible for the Precipitation of Clay Minerals Associated with Calcite

The subhedral morphologies observed in the SEM and HRTEM images pointed out the occurrence of detrital clays, whose mineralogy could include illite, kaolinite and smectite minerals [2,30,33]. The cotton-like morphologies, however, are associated with transformation and authigenic processes, both related to physical-chemical conditions in the environment, generally in the presence of smectite clays [30] or non-crystalline substances [32].

Clays identified in *Meio* lake are genetically related with transformation processes on the upper zone, where ferribeidellite, vermiculite and illite minerals dominate [7]. In the lower zone, however, saponitic and stevensitic-like smectite minerals prevail, and they are normally related to the authigenic process [7]. This argument was established on the basis of rare-earth elements (REE) concentrations, which are smaller in minerals formed by chemical precipitation, because most natural waters have small REE concentrations in contrast to rocks, generally [7,44]. Magnesium-rich phyllosilicate minerals are commonly precipitated directly from surface water, normally in alkaline lake systems, and parameters like salinity, pH and Mg/Si ratios may play an important role in the nucleation of such minerals [5,8,45]. At high pH (8.7–9.4), high salinity and high Mg/Si ratio (0.67–6.0), kerolite, sepiolite and stevensite-like products are favored [5].

As well as other works already discussed [13,18,21,23–25], we also observed that the lakes from Pantanal show high levels of pH and salinity, especially those classified as oligosaline and saline lakes. The Mg/Si rate, however, reached the maximum value of 0.04 in our studies (based on XRF concentrations), and, therefore, do not reach the necessary chemical conditions [5]. Moreover, the lacustrine Mg-silicate minerals studied in previous works did not contain Al³⁺, and our results display high levels of aluminum [45]. Nevertheless, research carried out in Pantanal [7,13,14] and our work show local occurrences of trioctahedral smectites on XRD patterns, indicating that other physico-chemical agents may be playing a larger role in the studied lakes.

The nucleation of Mg-silicates can take place on pre-existing surfaces, like amorphous silica, detrital clays and biological materials, such as EPS [45,46]. Mg-clay minerals' primary nucleation processes are generally related to a gel-like material, which promotes the binding of Fe, Al, Si, Ca, Mg, Na, K and other elements, increasing the concentration of cations and degrading organic matter and/or particulate sediments [32,44,45,47]. In this work, EPS have been recognized in the surface water, generally with algae and often associated with alkaline-saline lakes. The samples from the top of the sequences in these lakes showed features on SEM and TEM images that could refer to authigenic characteristics, such as the thin laminae covering quartz grains (Figure 7b), filamentous structures bridging quartz grains together (Figure 7c) and a cotton-like material involving organic nuclei (Figure 8b) and other clays (Figure 8a,e) [30,32].

In Figure 7e (*Meio* lake), there are thin and elongated structures (1) composed of Si, Al and Mg on the surface of quartz grains. This structure seems to develop to a more complex material (2), composed of Si, Al, Mg, K and Na. These structures give rise to the rounded material (3), formed only by Ca, C and O. This chemical composition and the morphology resemble spherulitic calcite minerals, which have already been observed in Santos Basin carbonates [45]. Imagery and EDX analysis (Figure 7e) allow to determine that spherulitic-shaped calcite was precipitated after Al-Mg silicates using them as a

template, which, in turn, precipitated probably as a response of the biological and chemical conditions of the water, using a detrital grain as a substrate [48].

Spherulitic calcite crystals might have formed as cement in a stevensitic-like gel, which acted as an ideal substrate, but with no clear evidence of microbial influence in their formation [48]. An association of stevensite and microbialites from Lake Clifton (Western Australia) suggested that Mg-silicates are mediated by high silica activity from dissolving diatoms through biological processes [49]. At Pantanal, for instance, previous work has proposed that the microorganisms in the lakes play an important role in increasing the pH, favoring quartz dissolution and promoting the precipitation of amorphous silica and carbonate during the dry seasons [24]. Other several works in ancient and recent sedimentary basins have identified the association of Mg-silicates with carbonates and evaporitic sequences forming by means of a concentration of elements by EPS in microbial mats [43,50–54].

5.3. Genesis of di and Trioctahedral Clay Minerals

In this work, XRD patterns have demonstrated the predominance of illite, kaolinite and even quartz in the clay fraction. Selected samples, which suggested the presence of smectite, from the first campaign, analyzed by AEM/HRTEM analysis, have shown that most of the smectite minerals have a dioctahedral character, classified as Fe-rich beidellite. The pure crystals of beidelite identified on the *Negro* River may have been transported by the river, as mentioned in previous researches [2], where the colloidal particles on the Amazon River were composed essentially of smectite.

Smectite minerals identified in *Barranco Alto* are mainly beidelite, a mineral comprised of aluminum in the octahedral sheets and mainly by Na and Ca in the interlayers. In *Nhumirim*, only at *Meio* lake, a trioctahedral character was firstly identified. The 060 reflection from one sample of the lake, however, revealed a possible mixture of di- and trioctahedral components, which is in accordance with the structural formulae obtained in the AEM analysis [7].

The two distinctive characteristics of the smectite minerals in the farms are correlated to the types of water found in them. In both farms, sodium bicarbonate water predominates, but in *Nhumirim*, Ca and Mg have higher concentrations than in *Barranco Alto*. This characteristic is compatible with the presence of the trioctahedral components in *Nhumirim*, while in *Barranco Alto*, the smectite is exclusively dioctahedral, rich in Al and Na. Therefore, smectite minerals that have been formed in the lakes should be related to the biological and chemical conditions of the water [8]. Furthermore, the differences in cation concentration and detrital input may control the species of smectite formed: from the least to the most ionic concentrated solution and from the most to the least detrital input, the sequence of smectite formation would be: beidellitic, saponitic and stevensitic components [10].

Although most of the works mention only Mg-silicates with authigenic processes [1,5,7,13,45], the morphologies observed in the SEM and HRTEM images, associated with the EDX analysis, have demonstrated that there are authigenic structures, even though the chemical composition does not correspond to the expected Mg-silicates [8]. According to this author, in an environmental setting with high levels of alkalinity, pH and silica activity, detrital clays favor the authigenic Mg-rich smectite precipitation. *Meio* lake in *Nhumirim* shows an unusual concentration of Mg on the pore water, which enhances the precipitation of trioctahedral clay components. The composition and the biological-physical-chemical characteristics of the saline-alkaline lakes in the studied area also provide the minimum conditions for intermediate di- and trioctahedral smectites to precipitate directly from the water, using the elements available in the water, such as Al, Na and Ca [14,43].

As other research already suggested [48,49,53], calcite has been found to precipitate within Mg-rich silicates. Such silicates probably formed as a primary bacterial gel rich in Si and Mg, giving rise to labile minerals, identified only in the water/sediment interface, where biological and chemical conditions determine the mineral precipitation.

6. Conclusions

The clay minerals from the Pantanal lakes are controlled by distinctive processes of transportation, transformation and neoformation. The biological, physical and chemical conditions of the lakes induce the supersaturation of the water and EPS act as a binding agent, promoting the precipitation of various elements, first as a labile precursor gel and then developing to minerals. Although most of the authigenic minerals have been related to Mg-silicates, an intermediate composition of diand trioctahedral smectites can also be formed directly from the water, considering the presence of microorganisms and chemical conditions available. As well as other works already observed in ancient deposits, calcite precipitates as smectite and I/S minerals at the points with contact with the water, showing that both minerals are genetically related.

Barranco Alto and *Nhumirim* are located in the same geological environment, but display different mineral and geochemical characteristics. The water of *Barranco Alto* has shown higher values of Na, whereas *Nhumirim* has shown significant concentrations of Mg. These features, respectively, are consistent with the dioctahedral and intermediate di- and trioctahedral character of smectites of each farm. The cause of this difference might be related to sediment input, rocks in the basement, fractures and/or faults in the basin, degrees of isolation of each lake, geomorphological features of the environment and the great annual climatic variation which promotes mineral dissolution and precipitation. To evaluate what is promoting the mineralogical and geochemical differences in these two near regions, more studies should be carried out to properly understand them.

Supplementary Materials: The following are available online at http://www.mdpi.com/2075-163X/10/8/718/s1, Table S1: Major oxides (%) of the bulk sediments in different positions of the lakes in distinct depths.

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