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Holocene Environmental Climatic Changes Based on Palynofacies and Organic Geochemical Analyses from an Inland Pond at Altitude in Southern Brazil

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Abstract

This paper focuses on the interpretations in the analyses of palynofacies and organic geochemistry carried out on a sedimentary profile covering 9542 cal yr BP from a pond located at the mining district from Ametista do Sul, southernmost Brazil. The hydrological isolation renders this pond, located on a hilltop, highly sensitive to climatic change because the water entering in the system is subsidized exclusively by the rainfall. The main goal of this study is to establish relationships between the sedimentary organic record and climatic fluctuations in the Holocene, trying to correlate the alterations in the particulate organic matter with regional climatic changes or perhaps even events on a global scale. Fluctuations in water depth are inferred from the frequency of the autochthonous elements (algae), which predominate in the basal intervals, but tend to decrease progressively toward the top, when begining to alternate periods of high and low frequency with the parautochthonous (spores) and allochthonous (pollen grains) elements, due to changes in the patterns of moisture. *Pseudoschizaea* seems to have a closer relationship with the spores than with all other algae and can serve as a biological marker of transitional intervals or have some role in the successional process of vegetation. The variety of spores of ferns and pollen grains on the topmost interval indicates increased vegetal diversity, and is probably related to the process of successional evolution of the area. An increased rainfall event detected between 8.6 to 7.4 ka yr BP can be responsible for the beginning of the process of water accumulation in the gos-

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san and sedimentation of the pond and can be related with the "Bond Events". The saturation level of the pond, in turn, remained relatively constant until 6.8 ka yr BP, when changes in the patterns of moisture make the environment drier and resulted in an intermittent pattern of water depth, currently existing on the site.

Keywords

Organic Matter (OM); Total Organic Carbon (TOC); Total Sulfur (TS); Paleoclimatic Change; Rainfall Influence

1. Introduction

Altitude ponds can be excellent archives of past changes in depositional and ecological conditions under which they formed, because they only collect sediments from a restricted basin. Part of the story of these changes can be obtained from the analyses of the particulate organic matter (POM) preserved in these deposits; however, more meaningful reconstructions can be achieved by combining palynofacies and geochemical organic analysis. Studies of organic matter (OM) from present-day terrestrial environments are particularly important because of their sensitivity to environmental changes caused by climate and human impacts.

We rely for this investigation on the concept of palynofacies defined by [1] that corresponds to "a body of sediment containing a distinctive assemblage of palynological organic matter thought to reflect a specific set of environmental conditions or to be associated with a characteristic range of hydrocarbon-generating potential". According to this author, the advantage of applying palynofacies technique lies in the fact that it provides direct information about the origin and characteristics of the particulate organic matter, allowing a more detailed analysis of subtle variations in the sedimentary environment.

More of the interpretive models available in the scientific literature that deal with organic geochemical and palynofacies analysis were designed for use in marine and epicontinental sections, because they had hydrocarbon exploration source rocks as the main objective. Although relatively recent, palynofacies analysis has been applied to different depositional systems resulting in a powerful research tool used to characterize the OM of present-day samples in continental deposits [2]-[7], coastal environments [8] [9] and marine deposits [10]-[13].

In Brazil, studies based on palynofacies and organic geochemistry analyses of organic matter were firstly applied by [14] on Permian sedimentary rocks bitumen prone of the Paraná Basin. Later, these studies were widely applied in the investigation of Mezosoic deposits of marine and epicontinental origin [15]-[17] and Cenozoic deposits [18]-[27].

Results for Holocene Brazilian lacustrine systems were also studied through the organic matter content in different regions using Total Organic Carbon, Rock Eval Pyrolisis, C/N determination, petrography, sedimentology and radiocarbon dating (e.g. [28]-[31]) with emphasis on paleonvironmental implications. Nevertheless, only a few papers added to the knowledge of environmental changes in continental areas through palynofacies analyses of peatlands [24] or in inland lacustrine deposits [23] [27].

The palynofacies method provides a valuable contribution connecting particulate OM to the depositional environments in Holocene deposits. This is reinforced by the study of [32] on the main approaches performed for the particulate OM characterization from Quaternary deposits in recent terrestrial environments, as based on applied examples in surficial deposits, soil profiles, wetland, lacustrine ecosystems and within catchments.

We presently use palynofacies and organic geochemical analyses on a particular type of ephemeral pond of altitude in the sub-tropical climatic belt of southernmost Brazil. The pond is located on a hilltop, and this hydrological isolation renders this pond highly sensitive to climatic changes because the water entering the system is subsidized exclusively by the rainfall. According to [33], pools showing similar morphology and that dry up periodically, are common in the studied area and could be originated by the claying of Cretaceous basalts by the action of hydrothermal fluids. Because these amethyst-bearing, smectite-rich basalts underlie directly the ponds, it is understood that the soil at the surface is nearly impermeable because it inherited the expansive clays resultant from weathering of the rocks.

As in the study area, the ingress of water into the system is subsidized exclusively by precipitation index, these peculiar characteristics can provide quite accurate data about the pluviometric regime in that region over the Holocene and also allow a correlation with the global scale paleoclimate records.

The Southern Hemisphere climate changes during the Holocene period have received considerable research attention in recent years, particularly with respect to the timing and correlation of climate events in the history of the northern hemisphere climate [34]. For the Brazilian Holocene, the studies of [35] using speleothems allowed correlations in global scale evidencing strong events of increased precipitation centered at 9.2, 8.2, 7.4, 7.0, 6.6, 5.2, 4.0, 3.2, 2.7, 2.3, 2.2, and 1.9 ka yr BP, which are synchronous with the Bond events [36] [37]. Based on the striking correlation between ice-rafted debris (IRD) records in North Atlantic sediment cores and tropical rainfall, the Bond IRD events have been used to link shifts in the intensity of the Atlantic thermohaline circulation to changes in sea surface temperature (SST) and related precipitation anomalies over areas affected by the monsoons in Oman [38], Asia [39], South America [40]-[42] and Brazil [35] [43] [44]. Unluckily, the absence of any crystalline deposit that could potentially generate speleothems in Rio Grande do Sul State has impeded, until the moment it correlated this kind with the Bond events, the palynological [45] [46] and palynofaciological records [24] that led to inferring cyclical climatic oscillations for the Holocene. However, such paleoclimate data have not been correlated with the Bond events.

In the light of the above considerations, the main goals of the present study are to 1) present the results obtained from palynofacies analyses carried out on a sedimentary profile covering 9542 cal yr BP (median probability) of sedimentation from a Holocene subtropical ephemeral pool of highlands located in Ametista do Sul, southernmost Brazil; 2) consider the paeoenvironmental significance of palynofacies analyses; 3) determinate if the particulate organic matter record was affected by paleoclimatic change, that is, if it was climatically sensitive, 4) determine whether these changes in organic matter record reflect local or regional climatic changes or even events of global scale.

2. Geological Background and Site Description

The present investigation is focused in the sedimentary record recovered from an Holocene inland pool of highland, which in the present-days dries up periodically. The pond is located near the edge of a hill in the Ametista do Sul mining district in Rio Grande do Sul State, southernmost Brazil, at an altitude of 500 m above sea level (**Figure 1**) [33]. The topography is marked by high hills crossed by deeply incised rivers that flow at 250 m elevation; the Uruguay River is the regional reference and runs from east to west at 30 km to the north of Ametista do Sul.

This district is the largest world producer (300 t/month) of amethyst and agate geodes from hydrothermally-altered basalts of Cretaceous age (135 Ma) [33]. Basalts are the only volcanic rock type present in the district, but nearly every lava flow is covered by a sand layer (0.1 - 2.0 m thick). The lava flows are nearly horizontal in the region, but a fault-block structure is recognized with the blocks downthrown to the west [47]-[53]. Extensive NW-directed fault zones can be observed in satellite images, positioned along the river valleys and not registered on hill tops.

The area was selected because of several favourable factors, such as 1) the absence of hidrodynamic influence from alluvial plains, which may cause severe interference upon adjacent systems; 2) the pond area is filled with very fine grained sediments, and 3) the area is directly subordinated to the regional pluviometric regime.

The present-day local climate is included in the subtropical climatic zone framed in the climatic types Cfa (subtropical-humid) of [48] and the modern-day vegetation is dominated by semi-desciduous forests belonging to the Mata Atlantica rain forest. The local mineralized bedrocks are basalts from the Cretaceous (133 Ma) Paraná volcanic province and are included in the Serra Geral Group. These units cover 1,300,000 km^2 of South America, mostly Brazil but also Uruguay, Argentina and Paraguay [49]. The volcanic province is at the top of the sedimentary Paraná Basin, which contains the very large Guarani aquifer directly below the lavas [50]. This aquifer mostly consists of sandstones of the Botucatu Formation [51]. According to [47], heating by volcanism provided a widespread, large volume of hot water and vapour for basalt alteration and related processes of cavity formation and filling.

The formation of amethyst geodes it is explained by [33] [52] [53] by the intense circulation of hot water and its vapor originated in the underlying Guarani aquifer and the consequent alteration of the basalts into clay minerals and zeolites. The hot water also brought fluidized detrital quartz grains from the aquifer, now observed as sandstone layers and breccias in the mines. This made a large volume of silica available for the ore-forming

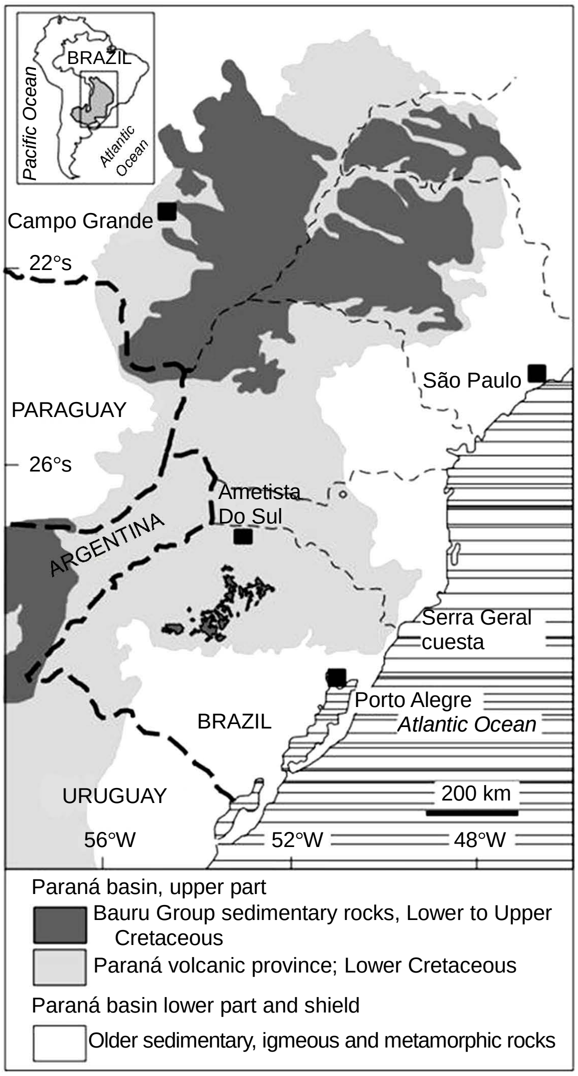

Figure 1. Location map of Ametista do Sul [adapted 47].

hydrothermal event. Weathering of the altered basalt led to the formation of smectite-rich soils at the surface and related ponds identified as "gossans" [33]. These gossans are important guides for mineral prospecting [54] because of their constant relationship whit the underlying amethyst mines (**Figure 2**). Pools showing similar morphology are common in the studied area and according [47] [55] have the same origin, that is, the formation of gossans is due to supergenic processes, where weathering is superimposed on hydrothermal systems, constituting an anomaly coincident with mineralization of amethyst geodes.

3. Material and Methods

3.1. Sampling

The sampling point (27˚19.536'S × 53˚13.579'W) is known as "Mina Modelo" because it is located immediately above an undreground amethyst mine. The site was originally selected with the aid of maps generated by satellite (*e.g. Google Earth*), particularly because of its isolation from the surrounding native woods. Interviews with local residents were essential to confirm the spontaneous nature of the surrounding vegetation of the area. We thus know that the pond exists since "Indian times" and is not built by the white settlers.

Samples for different analyses were recovered from a 160 cm-long sediment core which was collected manually in the center area of the pool. The sampling was performed with the assistance of a tractor backhoe that

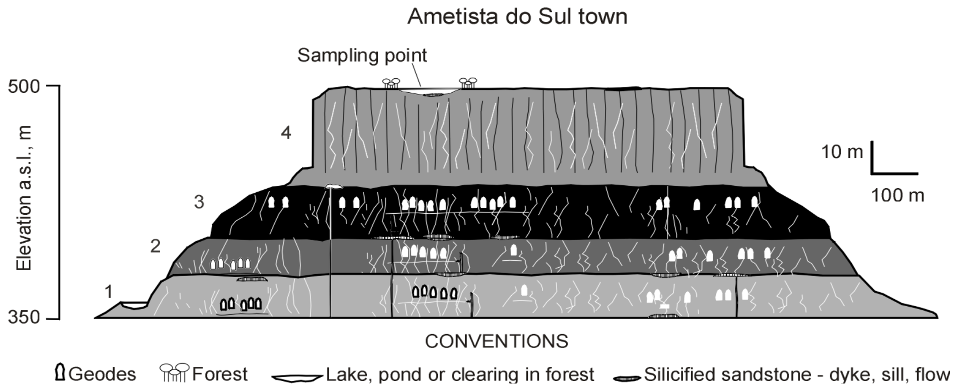

Figure 2. Model sections of lava units in the mining districts from Ametista do Sul [adapted 47].

opened a trench of approximately 2.0 m depth, from the surficial sedimentary level until the boundary with the underlying basalt. The corer consists of a piece of PVC tube 2.0 m long and 7 cm in diameter, previously cut in two halves. For sample collection, the convex side of the semi-split corer was pressed against the wall of the trench. Once filled with sediment, the corer was sealed with a plastic film on both sides to prevent loss of moisture. The core was split into subsamples in the laboratory for sedimentary, geochemical and palynofacies analyses.

3.2. Granulometric Analyses

Granulometric analyses were performed at the "Laboratório de Sedimentologia, Centro de Estudos Costeiros e Oceânicos, Instituto de Geociências, Universidade Federal do Rio Grande do Sul". The method of sieving and pipetting was applied with class intervals of 1 e 1/4 *phi* respectively, following the method proposed by [56].

3.3. Dating

For dating, sampling was done at lithological boundaries to create a consistent age-depth model. Three radiocarbon datings were performed, on the lower boundary (80 cm depth) and middle part (45 cm depth) of the clay-silty mud Interval B and on the upper portion (15 cm depth) of the silt-clayed mud Interval C. We used Accelertion Mass Spectometry (AMS) at the *Beta Analytic Radiocarbon Dating Laboratory* (Miami, Florida, EU). Interpolated and extrapolated ages were calculated using the intercept of the mean conventional age interval in the callibration curve of ^{14}C (CALIB version 4.3, according [57]). The unconsolidated surface sediment (0 - 15 cm) was not sampled because there are roots of recent plants which penetrated on soil and this could affect the resolution of the method of carbon dating (^{14}C). The ambiental and antropic factors, interacting about the surface, also could alter the results of the dating methodology. The top of the core corresponds to the soil surface where the sedimentary profile was collected and, because of this, was assigned age "Recent" to the core top.

3.4. Geochemistry

The accumulation of Organic Matter (OM) in sediments is estimated using Total Organic Carbon (TOC) analyses. According to [1], TOC analyses are a convenient method to determine the relative abundance of OM in sediments. The accumulation of OM is controlled by major factors such as primary productivity, water depth, and sediment grain size. TOC is controlled by three main variables: input of OM, preservation of the supplied OM, and dilution of the OM by sediment accumulation [1]. The values of TOC in marine rocks range [1] from ca. 0.1% (deep-sea pelagic deposits) to 94% (coals).

Total Organic Carbon (TOC) analyses adopted the methods of ASTM D 4239 [58] and NCEA-C-1282 [59]. Following acidification to remove carbonates, the TOC and ST analyses were made in all samples with a LECO SC 144 equipment at Laboratory of Palynofacies and Organic Facies (LAFO).

3.5. Samples Preparation

The preparation of the material for the palynofacies analyses used the standard non-oxidative palynological procedures described by [1] [14] [60] [61]. For kerogen concentrate preparation procedure, the studied samples were ground to approximately 2 mm size. Samples were treated successively to remove carbonates (HCl 37% for 18 h), silicates (HF 40% for 24 h), and neoformed fluorides (HCl 37% for 3 h). Between steps, samples were washed with distilled water until washing water was neutral. After this procedure, ZnCl2 (density = 1.9 to 2 g/cm^3) was added, stirred, and then centrifuged to separate sulphides. The floated material was washed similarly and HCl (10%) drops + distilled water were added to eliminate the heavy liquid. The isolated kerogen was sieved at 10 µm. After this procedure, strew slides were made with the organic residue.

The strew slides analysed in "Laboratório de Palinologia, Instituto de Geociências, Universidade Federal do Rio Grande do Sul" under the numbers: MP-P 7139 to MP-P 7152 and MP-P 7485 to MP-P 7488.

3.6. Palynofacies Analyses

The palynofacies analyses involved the quantitative—counting of 300 to 500 particles—and the qualitative—organic particle component identification—of the kerogen component groups and subgroups. These were achieved by means of microscopic techniques under transmitted white light and blue/ultraviolet incident light (fluorescence). The count followed the organic matter groups and subgroups classification proposed by [1] [14] [60] [61]. In this classification, the particulate organic matter is organized into three main groups according to their optical properties: Phytoclasts, Amorphous Product (AP) and Palynomorphs.

In the present paper, all organic matter without form, no sharp edges, without angular contours, or any type of feature permitting its classification in any other group of POM was classificated as AP (Amorphous Product). Such particles probably derive from algae or plant debris in an advanced state of degradation, which may have resulted either from microbial action as from other transformation processes of POM active in the studied depositional environment, or by both processes concurrently. The term "Amorphous Product" was chosen because of the exclusively continental origin of analysed sediment so as to avoid conflicts with the Amorphous Organic Matter (AOM), commonly related to marine environments or depositional systems that suffer the influence of eustatic variations.

The classification of the subgroups of palynomorphs was established based on the peculiarities of the studied environment in which only freshwater algae are present, associated with spores and pollen grains of exclusively continental origin (**Figure 3**).

3.7. Statistical Treatment

The statistical treatment of the data was based on quantitative analysis of the organic particulate components related in **Figure 3**. These data were recalculated for percentage values and submitted to the multivariate statistical

GROUP	SUBGROUP			ABREVIATTION
PHYTOCLAST	Opaque	Lath		POL
		Equidimensional		POE
	Translucent	Structured		PTS
		No Structured		PTNS
		Amorphous		PTA
		Cuticle		CUT
		Membrane		MEMB
PALYNOMORPH	Sporomorph	Spores	Briophyte	Spores
			Pteridophyte	
		Pollen grains	Gymnosperm	Pollen
			Angiosperm	
	Freshwater microplankton	*Botryococcus* (Chlorophyceae)		Botry
		Other algae (Zygnemaphyceae)	*Spyrogira*	Algae
			Debaria	
			Mougeotia	
			Zignema	
			Desmídia	
	Incertae sedis	*Pseudoschizaea*		Pseud
AMORPHOUS PRODUCT				AP

Figure 3. General classification of POM used in this work.

analyses (cluster analysis), to check similarities among the variables (organic particles) and determinate the Palynofacies (correlation coefficient Pearson/R-Mode) and to observe the degree of similarity between the samples (correlation coefficient Pearson/Q-Mode) for determination the Associations (depths) and, subsequently, the Intervals (ages). The same date matrix (**Table 1**) was used for generated de R-Mode and Q-Mode dendograms using the Statistic Basic program version 6.0 [62]-[65].

4. Results

4.1. Profile Description

Visual observations associated to granulometric analyses allowed the identification of four sedimentary intervals (**Figure 4**), from the base (160 cm) to the surficial unconsolidated level:

Interval A. Corresponds to the lower part of the core (160 - 80 cm) and shows a predominance of fragmented basalts with yellowish-gray colour ocurring as coarse gravel mixed with sand and clay-silty mud, this latter probably originated from suprajacent levels by precolation through the basalt.

*Interval B. C*orresponds to the lower middle section of the core (80 - 30 cm) where a significant discordance is observed because the finer grained texture, granulometry and colour patterns relative to the interval A. It is composed of a dark greywish, semi-compact and texturally homogeneous mud. Granulometric analysis allowed to classify the sediment as a degraded, clay-silty mud with the predominance of the clay fraction in this section of the profile (**Table 2**). The fine grain size indicates a low energy depositional setting and the absence of sedimentary structures adds to the interpretation that the sediment was deposited through decantation under quiet lacustrine conditions.

Interval C. Corresponds to the upper middle section of the core (30 - 10 cm). It is composed of a greywish, semi-compact mud, texturally homogeneous and showing few thin vegetal remains. Granulometric analysis

Table 1. Table showing the frequency peaks of major subgroups of particulate organic matter. The percentage values of the subgroups are related to the total organic matter, including the palynomorphs and the frequency peaks are highlighted. Abbreviations are in accordance with **Figure 3**. Assoc (Association).

DEPTH	AP	POL	POE	PTS	PTNS	PTA	CUT	MEMB	Spore	Pollen	Botry	Pseudos	Other algae	ASSOC
0	10.18	0.60	1.80	13.17	10.48	14.67	19.76	5.99	2.99	6.29	13.77	0.30	0.00	IV
5	11.01	0.60	1.49	9.82	8.93	16.37	25.00	4.17	12.80	3.27	5.95	0.60	0.00	IV
10	5.00	0.00	0.59	11.18	17.65	17.65	30.59	6.47	7.35	2.35	0.88	0.29	0.00	IV
15	3.07	0.51	1.53	9.21	2.81	2.56	30.18	6.91	24.30	3.32	5.12	7.67	2.81	II
20	9.00	0.00	0.25	5.25	2.50	27.00	24.75	10.00	16.50	0.75	1.25	2.50	0.25	IV
25	6.32	0.27	0.55	7.69	1.92	3.30	40.66	10.16	19.23	1.65	2.75	4.12	1.37	II
30	4.99	0.29	0.59	6.74	3.52	2.35	45.45	7.04	11.44	2.35	8.80	4.40	2.05	II
35	4.74	0.26	1.05	5.53	1.84	1.32	36.32	6.32	20.00	1.58	13.16	5.26	2.63	II
40	3.29	0.25	0.76	5.06	5.32	1.52	44.81	5.82	10.13	1.01	16.46	1.77	3.80	I
45	6.79	0.27	0.54	5.16	2.99	1.63	38.59	5.71	9.78	2.17	23.10	1.36	1.90	I
50	7.43	0.24	0.72	3.84	4.32	1.20	34.53	6.47	11.75	2.64	22.78	1.68	2.40	I
55	3.96	0.26	1.06	9.23	2.90	0.79	39.84	4.49	12.66	2.11	19.79	1.32	1.58	I
60	4.81	0.25	1.52	8.86	4.05	1.27	39.49	7.34	7.09	4.56	17.72	1.27	1.77	I
65	4.08	0.29	1.17	7.58	4.37	2.04	40.52	5.83	6.71	2.33	21.87	1.17	2.04	I
70	3.99	0.27	0.80	12.50	6.12	3.19	38.03	7.98	7.98	2.93	13.30	0.27	2.66	I
75	4.61	1.15	1.73	19.60	8.07	2.59	24.78	7.20	9.22	5.48	11.53	1.44	2.59	III
80	5.71	0.57	2.29	14.57	8.00	0.86	21.14	17.14	4.29	11.71	8.57	0.29	4.86	III

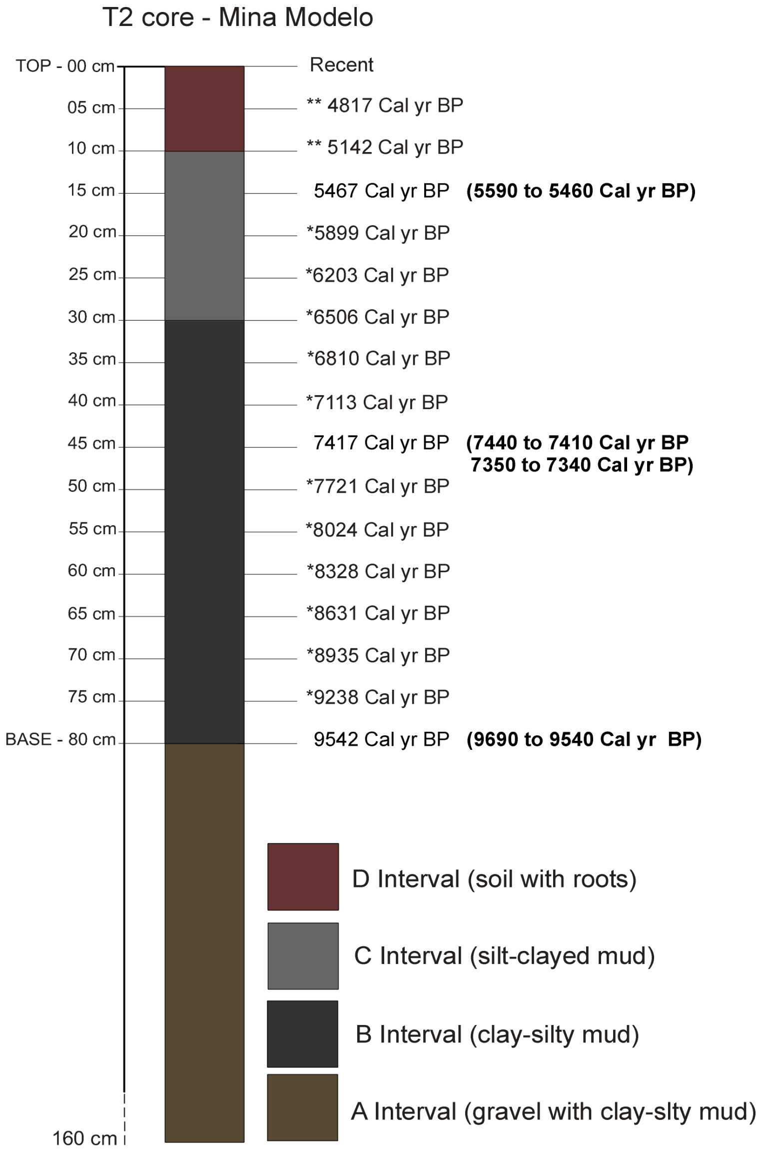

Figure 4. Chronological framework for the sedimentary profile of the T2 core (Mina Modelo), showing the calibrated radiocarbonic age (cal yr BP), the interpolated ages (*) and the extrapolated ages (**). The analyses performed by Beta Analytic are highlighted in bold. The other ages are calculated as the median probability.

allowed to classify the sediment as a silt-clayed mud with the predominance of the silt fraction in this section of the profile (**Table 2**).

Interval D. Represents the surficial sediments of the core (10 - 0 cm) and corresponds to a brownish-gray soil, showing thin rootlets and bioturbation.

Only the intervals B, C and D were selected for this study because of their sedimentary composition, showing potential for preservation of organic matter. Due to the great homogeneity of the sediment in the interval B and C, only three samples were selected for granulometric analyzes, named Base (80 cm), Midst (45 cm) and Top (15 cm) (**Table 2**).

4.2. Radiocarbon Dating

A chronological framework for the B and C sedimentary intervals was provided by the radiocarbon date (**Figure 4**,

Table 3). A gradually low mass accumulation rate in the pond can be inferred from the relation of the long time interval with the short interval of sedimentation (80 cm). Additionally, the age of 9690 to 9540 years cal BP (median probability of 9542 cal yr BP) obtained from 80 cm depth offers important data because it represents the beginning of the pond sedimentation, directly overlying the basalt at the roof of the underlying amethyst mine, and should represent the own age of the pond.

4.3. Geochemical Organic Analysis

The geochemical organic characterization (Total Organic Carbon—TOC) expresses the amount of organic matter contained in the sediment [1]. Geochemical organic parameters are widely applied in deposits of marine and epicontinental origin (and applied to prospecting of hydrocarbon source rocks). Few studies have been developed

Table 2. Values in percentage of the TOC and ST and granulometric analysis of the T2 core (Mina Modelo).

Age (Cal yr BP)	Depth (cm)	Geochemical organic analysis				Granulometric analysis				
		COT %	ST %	C:S Rato	RI %	Sand%	Silt %	Clay%	Sample	Texture
Recent	00	0.18	<0.01	18	84					
4918	05	0.15	<0.01	15	81					
5222	10	0.25	<0.01	25	85					
5828	15	1.27	0.01	127	83	0.01	30.79	39.18	Top	Silt-clayed mud
5550	20	1.08	0.04	27	87					
6132	25	1.10	0.06	18.3	90					
6435	30	0.86	0.03	28.6	90					
6738	25	0.81	0.01	81	88					
7042	40	0.77	0.03	25.6	92					
7440	45	0.76	0.03	25.3	92	0.45	46.46	53.07	Midst	Clay-silty mud
7669	50	0.68	0.03	22.6	93					
7994	55	0.74	0.01	74	90					
8318	60	0.65	0.02	32.5	94					
8642	65	0.66	0.02	33	92					
8966	70	0.71	0.01	71	92					
9291	75	0.70	0.01	70	89					
9690	80	0.67	0.01	67	92	6.37	23.78	69.84	Base	Clay-silty mud

Table 3. AMS (Accelerator Mass Spectrometry) radiocarbon ages from the sediments of the T2 core. The analyses were performed by Beta Analytic, Inc.

Depth (cm)	Lab. number	$^{13}C/^{12}C$ (‰)	Conventional ^{14}C age BP	Calendar age cal yr BP (median probability)†	Calendar age range (cal yr BP)§	Elevation a.m.s.l.(m)#
15	Beta 295198	−17.9	4770 ± 30	5467	5590 to 5460	500
45	Beta 295199	−21.4	6500 ± 30	7417	7440 to 7410 7350 to 7340	500
80	Beta 295200	−19.5	8650 ± 40	9542	9690 to 9540	500

BP = before present, AD 1950; cal = calibrated.
†Calibrated ages are calculated from SHCAL04 [63]
§Calibrated ages are calculated from INTCAL 04 [64] [65], which assumes a two-sigma error on radiocarbon measurements with an error multiplier of 1.0.
#a.m.s.l. = actual altitude above mean sea level

in strictly continental areas that evolved without the influence of eustatic variations. However, according to [66], "in order to make sense of TOC data we must appreciate the way in which these three variables (the input, the preservation, and the dilution of organic) interact; this can only be done for Recent sediments as these are the only place where there is a possibility of quantifying the full set of critical parameters with sufficient accuracy".

In the T2 core samples (Mina Modelo), the TOC contents reached the maximum percentage of 1.27% at 15 cm depth and the maximum TS content attained was 0.06% in the sample at 25 cm depth (**Table 2**). The phytoclast group is predominant in the organic matter over the entire the segment (80 - 0 cm) analised, significantly influencing the carbon content of the sediment. The low concentrations of TOC and TS are related to oxic phases [66] and the continental aquatic environments contain a very low concentration of dissolved sulphate [1]. In the analyzed samples, the low values of ST indicate that sulfate-reducing processes, typical of anoxic environment, were not significant along the sedimentary deposition. This evidence, associated with low amounts of TOC of most samples, confirms the relatively oxic conditions of the depositional environment and can be related to a low to moderate sedimentation rate. Even considering that the percentage of TOC does not reach 1% in some intervals, the high C/S ratio (>15) is typical of freshwater environments, according to the model proposed by [67].

Despite the references that assert that the silt fraction is less favorable to the preservation of organic matter compared to clay, in the present paper, the amendment of predominant grain size in the interval of 15 - 25 cm coincides with the increase of TOC contents (**Table 2**).

In the samples of 25 and 15 cm, the TOC contents above 1% can be related with a high percentage of "associated cuticles" (containing appended subcuticular remnants).

In the sample of 20 cm, in turn, the TOC contens above 1% can be related with the peak of PTA and increase of AP. All these elements may have influenced the moderate increase in the concentration of TOC, since such particles tend to contribute to high contents of organic Cabon on the system, due to the more advanced stage of molecular degradation.

The lowest TOC concentrations in the samples of 10, 5 e 0 cm (**Table 2**), may be related to a more surficial (and exposed to oxidation) position of the sediment.

4.4. Palynofacies Analysis

The fluorescence intensity of the particles is usually very intense, due to the recent age of the sediment. Among the sporomorphs (**Figure 5**), the fluorescence varies from yellowish-green (*Botryococcus*) to yellow or yellow-orange (spore e pollen) and among the phytoclasts (**Figure 6**, A-K), it varies from yellow (cuticle and membrane) to yellow-orange or orange-brown (PTS, PTNS and PTA).The AP group (**Figure 6**, L-M), in turn, exhibits fluorescence ranging from yellow-orange and reddish-orange to orange-brown.

The Phytoclast Group predominates (61.48%) in all samples, while the palynomorphs are the second dominant group (32.05%) and the AP Group the last (6.47%). Concentrations of TOC in the sediment are regulated by the most abundant group, in this case, the phytoclasts.

4.4.1. Hierarchical Cluster Analysis R-Mode

According to the statistical R-Mode, using the Ward's method with 1-Pearson distance, the samples were classified into four main clusters of the particles, denominated Palynofacies A, B, C and D (**Figures 7** and **8**).

The palynofacies A is represented by autochthonous (*Pseudoschizaea*) and parautochthonous (spores) elements, indicative of moist environments and who have suffered little if any carriage. The palynofacies B is represented by *Botryococcus*, autochthonous elements indicative of the presence of a waterbody and by cuticles, allochthonous, non-woody elements of plant origin. The palynofacies C is represented by amorphous components (AP and PTA) and PTNS, all allochthonous. The palynofacies D comprises autochthonous elements designated by "other algae", that indicate the presence of a sheet of water, and by allochthonous elements (pollen grains, membrane, PTS, POL and POE) of terrigenous origin.

4.4.2. Hierarchical Cluster Analysis Q-Mode

According to the statistical Q-mode, using the Ward's method with Euclidian distance, four main associations of samples were observed and identified as Association I, II, III and IV (**Figures 8** and **9**), which are related to the palynofacies defined by cluster R-mode (**Figure 7**).

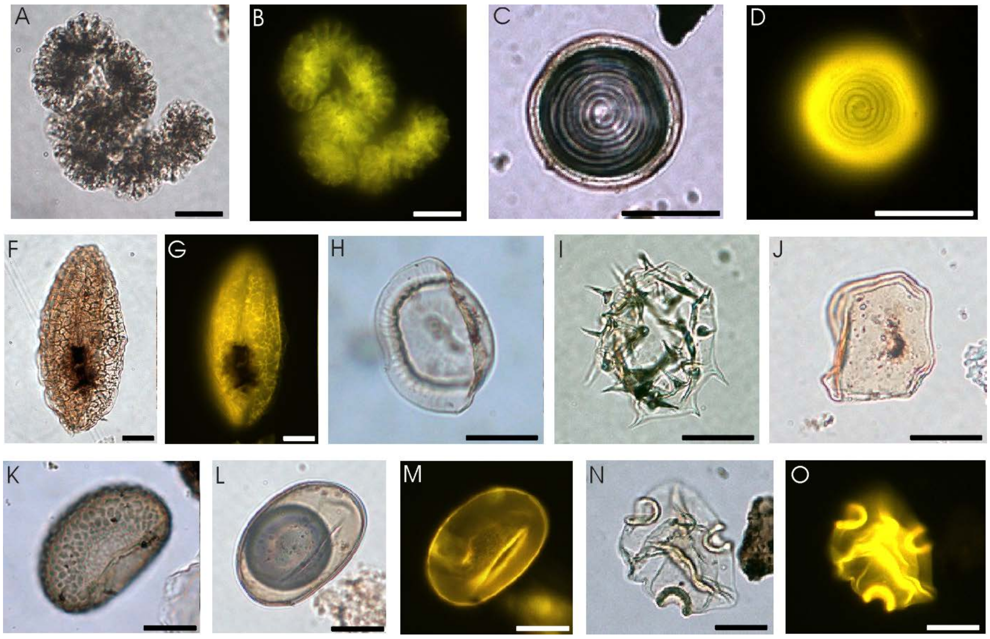

Figure 5. Palynomorphs group. (A) and (B) *Botryococcus*; (C) and (D) *Pseudoschizaea*; (F) and (G) *Spyrogira*; (H) *Debaria*; (I) *Desmídia*; (J) *Mougeotia*; (K)-(M) Pteridophyte spores; (N) and(O) pollen grain. Scale bars: 20 µm.

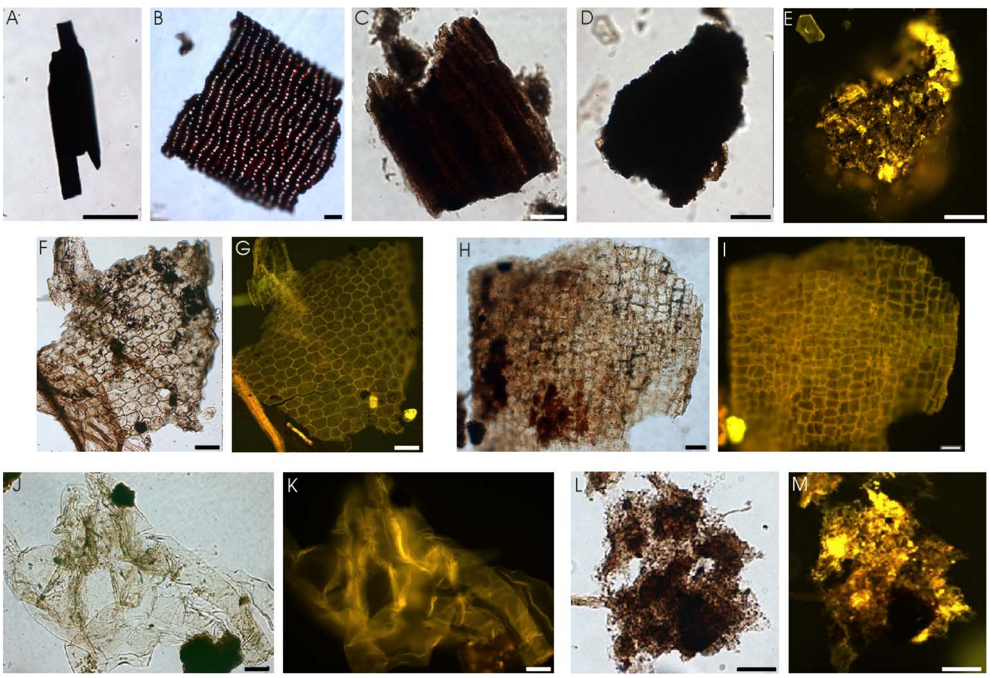

Figure 6. (A)-(E) Phytoclasts group. (F)-(I) cuticles; (J) and (K) membrane; (L) and (M) Amorphous Product (AP). Scale bars: 20 µm.

The Association I is represented by samples from 40, 45, 50, 55, 60, 65 and 70 cm. The particle that reaches the peak frequency in this Association is *Botryococcus*, which are related to Palynofacies B (**Table 1**). The Phytoclast Group predominates (average 58.69%), over the Palynomorph (average 35.75%) and AP (average 5.56%) groups (**Table 4**). The cuticles are the most abundant subgroup of phytoclasts. Among the palynomorphs, the algalics elements prevail over the terrestrial elements in all samples. *Botryococcus* predominates over other

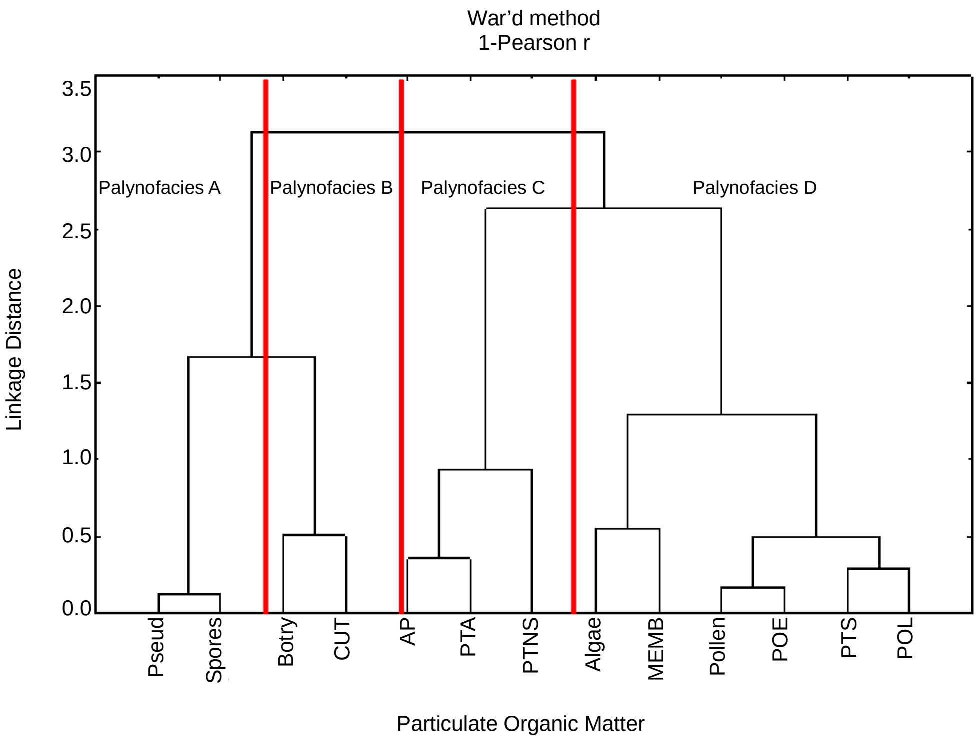

Figure 7. Dendrogram produced by cluster analysis R-mode for groups and subgroups of the POM from the T2 core (Mina Modelo). The red vertical lines divide the four palynofacies. Abbreviations are in accordance with **Figure 3**.

PALYNOFACIES	PARTICLES
A	*Pseudoschizaea* and spores
B	*Botryococcus* and CUT
C	PTNS, PTA and AP
D	Pollen, Other algae, MEMB, PTS, POL and POE

ASSOCIATION	PARTICLES	PALYNOFACIES
I	*Botryococcus* and CUT	B
II	*Pseudoschizaea,* spores and CUT	A and B
III	Pollen, Other algae, MEMB, PTS, POL and POE	D
IV	PTNS, PTA and AP	C

INTERVAL	PARTICLES	ASSOC.	PALYNOFACIES
1	Pollen, Other algae, MEMB, PTS, POL and POE	III	D
2	*Botryococcus* and CUT	I	B
3	*Pseudoschizaea,* spores, and CUT	II	A and B
4	PTNS, PTA and AP	IV	C
5	*Pseudoschizaea,* spores and CUT	II	A and B
6	PTNS, PTA and AP	IV	C

Figure 8. Chart showing the Palynofacies, the Associations and the Intervals generated by statistical analyses.

freshwater algae, while the spores predominate over the pollen grains in the whole Association.

The Association II is characterized by samples from 15, 25, 30 and 35 cm. The particles that reach the peak frequency in this Association are cuticles, spores and *Pseudoschizaea*, which are related to Palynofacies A (spores and *Pseudoschizaea*) and B (cuticles) (**Table 1**). The phytoclasts are the dominant group (average 58.47%), while the AP Group is the least abundant (5.60%) The Palynomorph Group, although reach the higher frequency in this association (average 35.93%), has secondary dominance (**Table 4**). In this association, the

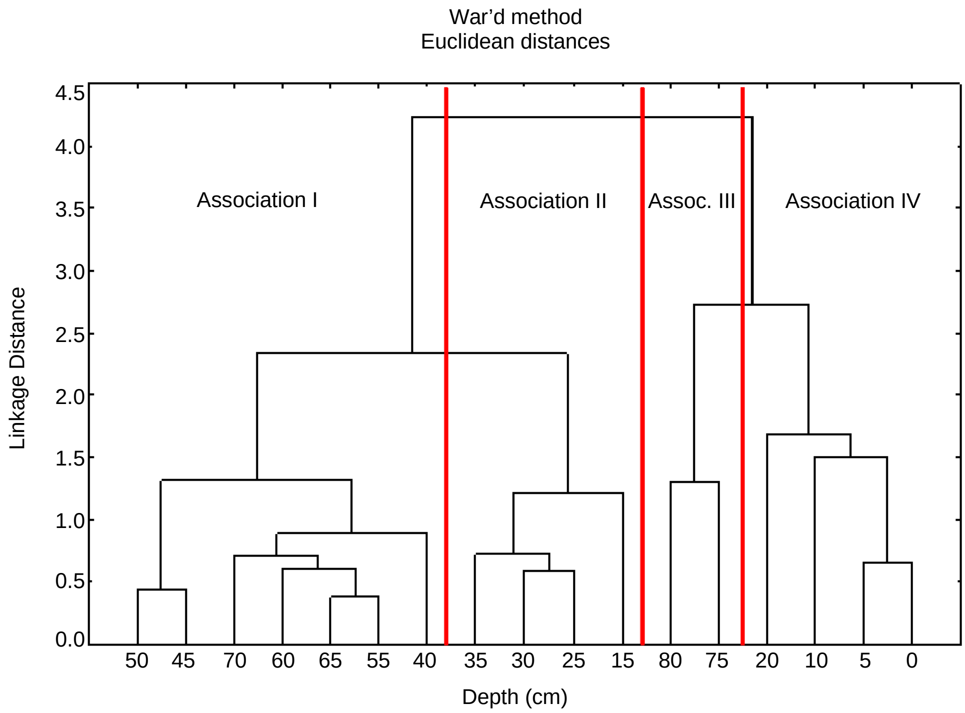

Figure 9. Dendrogram produced by cluster analysis Q-mode for groups and subgroups of the POM from the T2 core (Mina Modelo) in relation to depth. The red vertical lines divide the four Associations. Abbreviations are in accordance with **Figure 3**.

average percentage of the three major groups OM (phytoclasts, palynomorphs and AP) are very similar to those of the Association I; however, the subgroup prevailing and the dominant kind of particles differs greatly. The terrestrial sporomorphs (especially the spores) predominate among the palynomorphs. One exception is the sample of 30 cm, in which the algalic elements are more abundant (52.52%) by influence of *Pseudoschizaea*, that reaches high percentage in this Association, even surpassing *Botryococcus* in the samples of 25 and 15 cm. *Pseudoschizaea* shows slightly different behavior from other algae, because its percentage increases in samples in which the frequency of *Botryococcus* and other algae decreases, but seems to have sync with the distribution of spores.

The Association III is represented by samples from 75 and 80 cm. The particles that reach the peak frequency in this Association are other algae, pollen grains, membrane, PTS, POL and POE comprising the Palynofacies D (**Table 1**). The phytoclast predominates (average 62.20%) over the palynomorphs (average 31.83%) and AP (average 5.97%) (**Table 4**). Among the(palynomorphs, the terrestrial sporomorphs (53.84%) predominate over the algalic in the sample of base (80 cm), standing out the pollen grains (39.42%). In the next sample (75 cm), the algalics sporomorphs become dominant (51.43%), because of increase of *Botryococcus* (38.10%). The spores frequency (30.48%) also exceed that of pollen grains (18.10%) in the sample of 75 cm.

The Association IV is characterized by samples from 0, 5, 10 e 20 cm. The particles that reach the peak frequency in this Association are AP, PTNS e PTA, which are related to Palynofacies C (**Table 1**). The Phytoclast Group and the AP Group achieve their higher averages frequencies in this Association, respectively 70.01% and 9.28% (**Table 4**). The Palynomorph Group, in turn, reaches the lowest average (20.70%). Among the palynomorphs, the terrestrial sporomorphs dominate in the intervals of 20, 10 and 5 cm, but they are surpassed by algalics sporomorphs in the top of core, because of the significant increase in frequency of *Botryococcus*. Pollen grains also become predominant over the spores in the top sample.

4.4.3. Palaeoenvironmental Characterization Based on Intervals Generated by Cluster Analysis Q-Mode

Based on the associations generated by cluster analysis (Q-mode) the sedimentary section (**Figure 4**) was subdivided in six intervals (**Figure 10**), from the base to the top of the core, aiming to inferring the hydrological fluctuation which occurred during a time interval of 9542 cal yr BP to the present day on the pond and surrounding

Table 4. Table showing the percentages of the TOC and ST and the percentages of the major groups and subgroups of the POM and of the averages of the sample groups. (*) Percentage value of the three main groups of POM related to total organic matter. (**) Percentage value of sporomorphs related to the total palynomorph group. Abbreviations are in accordance with **Figure 3**.

ASSOCIATION	DEPTH	AGE	TOC	TS	AP*	PHYTOCLASTS*	PALYNOMORPHS*	Spore**	Pollen**	Botryococcus**	Pseudoschizaea**	Other algae**
IV	0	Recent	0.18	0.01	11.11	63.41	25.47	12.82	26.92	58.97	1.28	0.00
IV	5	4817	0.15	0.01	10.96	66.58	22.47	56.58	14.47	26.32	2.63	0.00
IV	10	5142	0.25	0.01	5.11	82.10	12.78	67.57	21.62	8.11	2.70	0.00
IV	20	5899	1.08	0.04	9.95	67.96	22.09	77.65	3.53	5.88	11.76	1.18
AVERAGE			0.42	0.02	9.28	70.01	20.70	53.65	16.64	24.82	4.60	0.29
II	15	5467	1.27	0.01	3.65	52.31	44.04	56.21	7.69	11.83	17.75	6.51
II	25	6203	1.10	0.06	7.43	63.66	28.91	66.04	5.66	9.43	14.15	4.72
II	30	6506	0.86	0.03	6.20	65.35	28.45	39.39	8.08	30.30	15.15	7.07
II	35	6810	0.81	0.01	5.13	52.56	42.31	46.91	3.70	30.86	12.35	6.17
AVERAGE			1.01	0.03	5.60	58.47	35.93	52.14	6.28	20.61	14.85	6.12
I	40	7113	0.77	0.03	3.92	62.50	33.58	30.53	3.05	49.62	5.34	11.45
I	45	7417	0.76	0.03	7.85	53.66	38.48	25.53	5.67	60.28	3.55	4.96
I	50	7721	0.68	0.03	8.01	50.34	41.65	28.49	6.40	55.23	4.07	5.81
I	55	8024	0.74	0.01	4.30	56.96	38.73	33.80	5.63	52.82	3.52	4.23
I	60	8328	0.65	0.02	5.02	61.24	33.73	21.88	14.06	54.69	3.91	5.47
I	65	8631	0.66	0.02	4.99	59.56	35.46	19.66	6.84	64.10	3.42	5.98
I	70	8935	0.71	0.01	4.81	66.58	28.61	29.41	10.78	49.02	0.98	9.80
AVERAGE			0.71	0.02	5.56	58.69	35.75	27.04	7.49	55.11	3.54	6.82
III	75	9238	0.70	0.01	5.32	62.23	32.45	30.48	18.10	38.10	4.76	8.57
III	80	9542	0.67	0.01	6.61	62.17	31.22	14.42	39.42	28.85	0.96	16.35
AVERAGE			0.69	0.01	5.97	62.20	31.83	22.45	28.76	33.47	2.86	12.46

area, from the influences of autochtonous and allochthonous particles (**Figures 8** and **10**).

Estimative of the pond water level was constructed based in the frequency of *Botryococcus* and other algae. *Pseudoschizaea* is considered a genus *incertae sedis* [68] and shows a somewhat different behavior when compared to *Botryococcus* and other algae. Hence, the construction of the water level curve does not consider their distribution.

The interval 1 (9542 to 9238 cal yr BP) corresponds to Association III (80 - 75 cm), marked by peak of other algae, pollen grains, membrane, PTS, POL and POE, particles related to Palynofacies D (**Figures 8** and **10**). Starting from the base (80 cm) up to the immediately subsequent sample (75 cm) is observed a change in the dominance of terrestrial sporomorphs by algalics. *Botryococcus* and other algae indicate the presence of a waterbody sufficient enough to support this type of biomass, which tends to increase in the next samples. Among the terrestrial sporomorphs it was observed the domination of fern spores and pollen grains (Cyperaceae and *Ludwigia*) which are indicative of moist environments [69] [70]. This interval marks the beginning of the

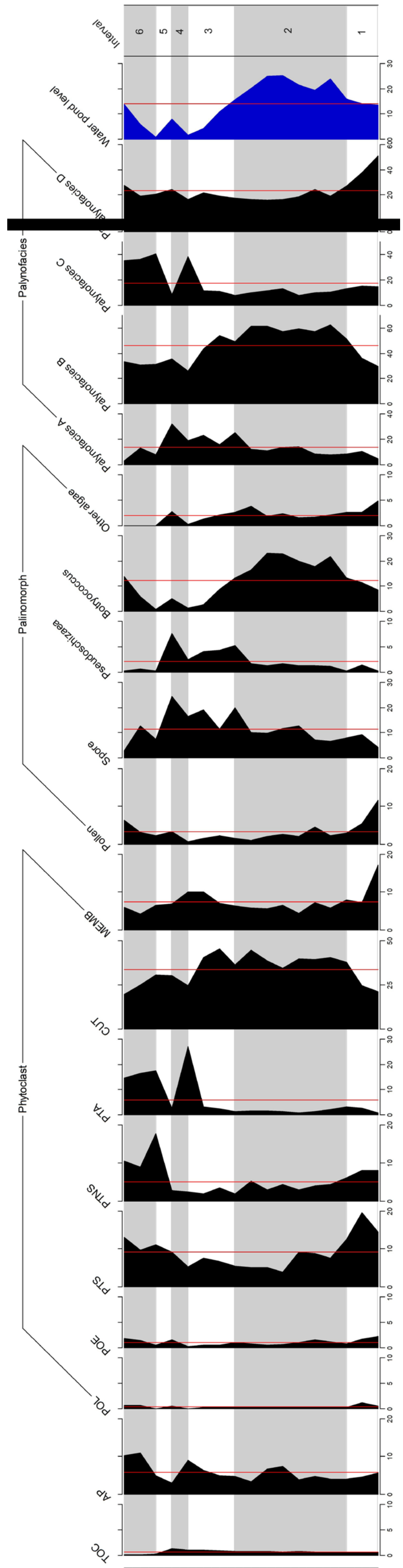

Figure 10. Variation of the palynofacial and geochemical parameters of the main groups and subgroups of POM. The red vertical lines indicate the midline. Abbreviations are in accordance with **Figure 3**.

process of accumulation of water in the gossan and of pond sedimentation. The high frequency of woody phytoclasts (PTS), non-woody (membrane) and opaques (POL and POE) in this interval are result of the entrainment of these terrigenous elements within the deposicional system by rainwater.

The interval 2 (8935 to 7113 cal years BP) corresponds to Association I (70 - 40 cm), marked by peak of *Botryococcus* and high frequency of cuticles, particles related to Palynofacies B (**Figures 8** and **10**). The average frequency of algalics sporomorphs (65.47%) is much higher than that of terrestrial sporomorphs (34.53%), pointing the level of the highest water depth reached by the pond in this interval. This allows us to infer a period of wetness, especially in samples of 65 cm (8631 cal years BP) and 45 cm (7417 cal years BP), in which the *Botryococcus* frequency is too high (above 60%). Among the terrestrial sporomorphs, the spores predominate over the pollen grains, possibly due to the saturation level of soil water or due to vegetational evolution of area. The high frequency of cuticles also could be related to increased sedimentation rate, regulated by a high rainfall periodicity.

The interval 3 (6810 to 6203 cal yr BP) corresponds to Association II (35 - 25 cm), marked by peak of cuticles (related to palynofacies B), and increased frequency of *Pseudoschizaea* and spores (related to Palynofacies A) (**Figures 8** and **10**). The average frequency of terrestrial sporomorphs increases in relation to algalics sporomorphs. *Botryococcus* and other algae begin to undergo oscillations in their frequency, with a tendency to decrease gradually. However, the same does not occur with *Pseudoschizaea* that seems to have a closer relationship with the spores than with all other algae with regard the abundance peaks. This allows us to speculate that this form is an algalic taxon that can serve as biological markers of transitional intervals [71] [72] and has some role in the successional process of vegetation, once its distribution pattern along the core interleaves expansion phases of the algalics and terrigenous elements. Although the reducing of algalics elements indicates a decrease in aquous saturation, the increase of frequency of spores and *Pseudoschizaea* demonstrates the persistence of a high level of local humidity. [73] observed that *Pseudoschizea* can be an indicator for local seazonal drying, because is a common form in in recent environments of relatively warm areas of the world where moisture is available. Possibly, the variation in water depth, that will result in the intermittent pattern of pond, start to become more meaningful from the inicial portions of this interval (35 - 30 cm) when the alternation between periods of greater and lesser moisture seems to acquire a seasonal pattern.

The interval 4 (5899 cal years BP) corresponds to Association IV (20 cm), marked by peak of PTA and high frequency of AP, particles related to palynofacies C (**Figures 8** and **10**). The average frequency of algalics sporomorphs (18.82%) and terrigenous (81.18%) are striking distinct, with predominance of ferns spores. This interval, however, is characterized by a significant reduction in the frequency of all palynomorphs, possibly due to a decrease in moisture, regulated by accented oscillations in rainfall patterns. It is from this interval that the intermittent pattern of pond is probably established. The predominance of amorphous particles is a result of prolonged exposure of organic matter to degradation processes oxic, resulting from decreased water depth.

The interval 5 (5467 cal yr BP) corresponds to Association II (15 cm), marked by peak of *Pseudoschizaea* and spores, particles related to palynofacies A (**Figures 8** and **10**). The difference between the average frequency of terrestrial sporomorphs (63.9%) and algalics (36.1%) decreases slightly, although the spores remain prevalent. In this interval, the rainfall conditions necessary to the reestablishment of algalic biomass have returned, although quantitatively more modest than those of the intervals 1 and 2. The increase of moisture is also corroborated by the increased frequency of spores and high frequency of algae. The low frequence of the amorphized elements is probably attributed to the thick water depths which protected the particles from degradation.

The interval 6 (5142 cal yr BP to Recent) corresponds to Association IV (10 - 0 cm), marked by peak of AP and PTNS, particles related to palynofacies C (**Figures 8** and **10**). The frequency of the terrestrial esporomorfos is higher in the samples of 10 and 5 cm while the frequency of the algalics sporomorphs is higher at the top of core (0 cm). Similarly to what occurs in interval 4, the predominance of amorphized elements in the samples of 10 and 5 cm, may be related to the lower level of saturation of water in these layers. The sample of 10 cm revealed conditions of low humidity, which is evidenced by reduced frequency of all palynomorphs (12.78%), especially of algalic origin. From the sample of 5 cm, however, changes in rainfall patterns result in an increased frequency of palynomorphs (22.47%), mainly *Botryococcus*, which increases its frequency, but not enough to prevail. From the next interval (top sample), the frequency of spores decreases, but the pollen increases, indicating a new change of mastery vegetational. Unlike what occurs at the base, the variety of ferns spores and pollen grains of this sample indicates increased vegetal diversity which is probably related to the process of successional evolution of the area. The frequency of *Pseudoschizaea* decreases by half in this interval and the other algae disappears, possibly as a response to the constant fluctuations in water depth. The intermittent pattern of pond starts to act as a limiting factor to the permanence of certain organisms (other algae) initially constant, but seems do not to affect others, as *Botryococcus*, which increases its frequency at the top of core, indicating the return of moisture conditions sufficient enough to maintain this kind of algal biomass. The high frequency of opaque phytoclasts (POL and POE) and non-opaques of woody origin (PTS and PTNS) on the top of core are the result of entrainment of these terrigenous elements into the depositional system by rainwater and corroborate the inferences about raising moisture in this interval. Adittionaly, the presence of opaque particles in the more recent interval can also be indicative of human interference in the environment.

Comparing the age of the top core sample (Recent) with the sample of 5 cm (4817 cal yr BP) is observed a large time interval that could be interpreted as an erosive event. However, it is not possible to observe an erosive boundary between the layer of 5 cm and the top. Nevertheless, is possible infer that the dynamics of sedimentation of pond was dramatically altered by decline or dysregulation in the rainfall frequency that resulted on the establishment of the intermittent pattern of the pond, which corroborates, with the climatic events reported.

Besides to be connected to pluviometric periodicity, the reducing of water level may also be linked with the progressive sedimentary filling of pond over the time. According [74], lakes generally are not permanent features of the landscape and their destination is succumbing to its own metabolism sedimentary over geologic time. Currently, the pond is evident during the rainiest months, but its current depth is possibly lower than the beginning of their sedimentation.

5. Discussion

The curve of pond water level evidences significant changes in the level of aqueous saturation of the pond since the last 9542 cal yr BP, which resulted in reducing water depth and in intermittent flood pattern of the pond, such as currently observed. The present pattern, however, was not prevalent in the past, when the pond maintained high level of aqueous saturation, which is attributed possibly to more intense rainfall, due to wetter periods that prevailed in older time intervals. The higher precipitation events occurred between 8631 to 7417 years cal BP (65 to 45 cm), despite some water-level oscillations. The more conspicuous alteration of wetness patterns started from 6810 cal yr BP (35 cm depth), was intensified from 5899 cal yr BP (20 cm) and, thenceforth, begins to occur interspersed periods of higher and lower moisture which endured until this day. The pond water level, however, is lower than it was in the past.

The process of water accumulation in the gossan and sedimentation of the pond was initiated at approximately 9500 years BP and it was intensified with the increased rainfall, there is nearly 8500 years BP and lasted until about 7400 years BP. The rainfall remained relatively constant until about 7000 years ago. Thereafter, rainfall patterns become irregular. The oscillations between high and low rainfall periods become progressively more frequent and the high moisture levels of early Holocene tend to decrease toward the Recent. The higher precipitation events of early Holocene can be related with the "Bond events" [36] (especially 9.4, 8.2 and 7.4 ka events). These may have been global in scope because they coincide with periods of low solar activity [37] and because the glacial boundary conditions persisted until 7.0 ka yr BP in the Northern Hemisphere [75]. The events subsequent to 7000 years BP reported here, in turn, can be a consequence of abrupt ecological changes intrinsically driven. All changes reported for the Holocene, as indicated by [76], were strongly controlled by local biotic and abiotic processes and also by localized disturbance and regional climatic events that, ultimately, can be linked to events of global scale. The gradual reduction in moisture of middle and late Holocene, in turn, may be related to local climate change, but also can be a reflection of global events related to climate warming.

According to [44], anomalies in the southeastern Brazil show a high degree of correlation with cooler conditions associated with the North Atlantic 8.2 ka event which appears to have affected the environmental equilibrium in South America and intensified the South American summer monsoon. In Brazil, this event had effects of short duration, approximately a few hundred years, and would have increased local precipitation and humidity and sea level rise [44]. The 8.2 ka event is one of the most well-known climate events of global extent [44] [77]-[85]. These results suggest (according with [44]) that a modern-day short-duration North Atlantic climatic event, such as the 8.2 ka event (and perhaps other Bond events), could affect the climate dynamics in South America.

The record of high moisture periods, particularly associated with the Bond events, is of great importance because the global extent of these events is still not well-known. The palaeoclimatic records are still very scarce in

Brazil (35, 44, 86). This is due to small differences between the ages obtained, result of uncertainties in 14C reservoir age corrections.

6. Conclusions

Palynofacies and geochemical organic analyses are a powerful tool in the palaeoenvironmental and palaeoclimatic study of a Holocene strictly continental inland pond in southern Brazil. This study allows the following conclusions:

1) The low amounts of TOC and TS of the samples can be related with the relatively oxic conditions of the depositional environment and with a low to moderate sedimentation rate. The ratio between the concentrations of TOC and TS is high and typical of freshwater environments.

2) The predominance of phytoclasts indicates that this group controls the organic carbon content of sediments in all samples. The palynomorphs are the second group in dominance and the Amorphous Product is the least abundant group.

3) The saturation level of the pond remained relatively constant from 8935 to 6810 cal yr BP, when changes in the patterns of moisture make the environment drier and resulted in an intermittent pattern of water depth, currently existing on the site.

4) Fluctuations in water depth are inferred from the frequency of *Botryococcus* and other algae, which predominate in the basal intervals. However, the autochthonous elements tend to decrease progressively toward the top and begin to alternate periods of high and low frequency with the parautochthonous (spores) and alochthonous (pollen grains) elements. This is due to the reduction of water depth and to the establishment of the intermittent flood pattern of the pond.

5) *Pseudoschizaea* seems to have a closer relationship with the spores than with all other algae. We thus speculate whether this form is an algalic taxon that can serve as a biological marker of transitional intervals related to seasonal drying or that has some role in the successional process of vegetation.

6) Once established, the intermittent pattern of pond acts as a limiting factor to the permanence of certain organisms that were initially constant. But it seems not to affect others, such as *Botryococcus*, because it increases in frequency where *Pseudoschizaea* decreases and the other algae disappear. This may be a response to the constant fluctuations in water depth.

7) The variety of spores of ferns and pollen grains on the topmost interval indicates increased vegetal diversity, and is probably related to the process of successional evolution of the area. On the top sample, the frequency of spores decreases, but the pollen frequency increases, indicating changes of mastery vegetational.

8) An increased rainfall event detected between 8631 to 7417 years cal BP can be related with the "Bond Events", which was responsible for the beginning of the process of water accumulation in the gossan and sedimentation of the pond.

9) The gradual reduction in moisture subsequent to 7000 years BP may be related to local climate change, but can also be a reflection of global events related to climate warming.

10) The present results are of great importance for the understanding of the global extent of "Bond events", not well-known for the Brazilian territory. Further studies are required to improve the understanding of the global climate changes and their local and regional environmental impacts.

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