# PALEOPRECIPITATION CHANGES BASED ON PALEOSOLS PROFILES OF THE MARÍLIA FORMATION (UPPER CRETACEOUS) IN THE EASTERN PORTION OF THE BAURU BASIN IN SOUTHEASTERN BRAZIL

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ABSTRACT - The Marília Formation is a Maastrichtian sequence of the Bauru Basin that crops out in the Southeastern Brazil. This formation consists of an illuvial deposits succession characterized by alternating sedimentary strata and paleosols. Pedogenic features related to climatic factors can be used as a tool for the interpretation of paleoenvironments. Through macro- and microscopic descriptions, mineralogical analysis and geochemical data, twenty paleosol sections were identified and characterized in the Marília Formation. The characterization of C, Ck, Bt, Btk and Gley horizons and the geochemical data allowed the identification of paleoclimatic factors influencing the formation of paleosols. Changes in the formation processes of these paleosols were mainly triggered by moisture variations. Paleoprecipitation estimates (MAP) obtained from CIA-K values in Bt and Btk horizons indicate that the precipitation rates varied from 20 to 1000 mm/year. These contrasting climatic conditions caused the overlap of distinct paleosol profiles, suggesting oscillation between arid to semi-arid conditions. The results from this work contribute to a better understanding of the Upper Cretaceous paleoclimatic in the Southeastern Brazil.

Keywords: Bauru Basin, Marília Formation, Paleosols, Paleoprecipitation, Maastrichtian.

RESUMO - A Formação Marília é sequência Maastrichtiana da Bacia Bauru que aflora na região Sudeste do Brasil. Esta formação é constituída por uma sucessão de depósitos alluviais marcado pela alternância de estratos sedimentares e paleossolos. Feições pedogênicas relacionados a fatores climáticos podem ser usados como uma ferramenta para a interpretação de paleoambientes. Através de descrições macro e microscópicas, análise mineralógica e geoquímica foram identificados vinte perfis de paleossolos na Formação Marília. A caracterização geoquímica de horizontes C, Ck, Bt, Btk e Gley permitiu identificar condições paleoclimáticos que influenciam a formação de paleossolos. Mudanças nos processos de formação desses paleossolos foram provocados principalmente por variações de umidade. Estimativas de paleoprecipitação (MAP) obtidos a partir de valores CIA-K em horizontes Bt e Btk indicam que as taxas de precipitação variou de 20 a 1000 mm/ano. Estas condições climáticas contrastantes causou a sobreposição de perfis de paleossolos distintas, sugerindo períodos de oscilação de árido a semi-árido. Os resultados deste trabalho contribuem para um melhor entendimento do clima do Cretáceo Superior na Região Sudeste do Brasil.

Palavras-chave: Bacia Bauru, Formação Marília, paleossolos, Paleoprecipitação, Maastrichtiano.

#### **INTRODUCTION**

Paleosols are soils formed in the past and preserved from erosion on stable surfaces covered by sedimentary deposits. They are developed during periods of non-deposition, indicating tectonic stability, and exposition to weathering agents, which, according to the evolutionary degree, can correspond to

stratigraphic discordances of different orders (Retallack, 2001).

Pedogenic features can be quantitatively related to climatic factors and are used as tools in paleoenvironment interpretations from the Paleozoic to the Cenozoic (Retallack, 2001, 2007; Sheldon et al., 2002; Sheldon, 2003, 2005; Sheldon and Tabor, 2009). Thus,

paleosol successions in continental sequences can record paleoclimatic cycles.

A distinctive characteristic of the paleosols is the occurrence of root marks, soil horizons, and soil structures. Root marks are the most diagnostic features, since their presence are enough to indicate soil formation when other evidences are lacking (Retallack, 1988).

The Marília Formation, at the top of the Bauru Group (Upper Cretaceous of the Bauru Basin), is characterized by a succession of alluvial and eolian deposits intercalated with paleosol profiles. The identification of the paleosols profiles in the Marília Formation has already been made by several authors (Suguio, 1973: Barcelos, 1984; Fernandes. 1998: Goldberg and Garcia 2000, Dal'Bó and Ladeira, 2006; Basilici et al., 2009, Basilici and Fernandes, 2009; Dal'Bó and Basilici, 2010; Dal'Bó and Basilici 2011).

This study presents the paleosols characterization of the Marília Formation as a tool to identify variations in precipitation during the stratigraphic evolution of the area. A representative 43 m-thick section of the unit was described, and twenty paleosol profiles were recognized based on macro- and micromorphologic characteristics. The analyzed paleosols are constituted by the horizons C (weathered rock), Ck (calcic weathered rock), Bt (argillic horizon), Btk (calcic argillic horizon) and Cg (gley weathered rock).

Geochemical data from X-Ray Fluorescence (XRF) were applied for the determination of the following molecular ratios of major elements: CIA-K, leaching, argillization, loss of base, dolomitization, calcification and oxidation (Nesbit and Young, 1982; Maynard, 1992; Sheldon et al., 2002).

Through the chemical weathering indices for horizons Bt (argillic horizon) and Btk (calcic argillic horizon) it was possible to calculate the paleoprecipitation during the pedogenic events of the Marília Formation (Sheldon and Tabor, 2009). The results suggest that the climate oscillated from arid to semiarid, with distinctive precipitation phases, ranging from 20 to 1000 mm.

## STUDY AREA AND GEOLOGICAL ASPECTS

The study area is located in the eastern portion of the Bauru Basin, in the Triângulo Mineiro area in the Minas Gerais State (Figure 1).

### Bauru Basin

The Bauru Basin, constituted predominantly continental siliciclastic deposits, bv is approximately elliptical in shape, elongated in the N/NNE direction, with 330,000 km<sup>2</sup> in area, distributed in central-western São Paulo, northeastern Mato Grosso do Sul, southeastern Mato Grosso, southern Goiás and western Minas Gerais (Batezelli, 2003). The depocenter of the Bauru Basin locates in the southwest of São Paulo State, where the thickness of the Serra Geral Formation basalts is the greatest (Riccomini, 1995, 1997).

The Bauru Basin in the west of Minas Gerais is constituted by the Bauru Group (Figure 2), which is divided into the following lithostratigraphic units: Araçatuba, Adamantina, Uberaba and Marília formations. The latter formation is further divided into Ponte Alta, Serra da Galga and Echaporã members (Batezelli, 2003).

### Marília Formation

The Marília Formation was defined by Almeida and Barbosa (1953), when these authors were studying the Bauru Series in São Until stratigraphic Paulo State. the formalization as Marília Formation (Soares et al., 1980), this unit was informally named: calcconglomeratic facies, facies C, Marília lithofacies, Superior Member, Marília facies, and Superior Unit (IPT, 1981).

The Echaporã Member corresponds to the Marília Formation cropping out in the western region of Minas Gerais State (Barcelos, 1984). It is composed of fine- to coarse-grained sandstones with conglomeratic intercalations, according to fining-upward and coarseningupward cycles, cemented by calcium carbonate. For this reason, the region also presents ridges in the form of broad plateaus.

The Marília Formation was dated as Maastrichtian by means of vertebrate fossils (Santucci and Bertini, 2001) and



Figure 1. Distribution of the Bauru Basin in southeastern Brazil and the study area in Minas Gerais State (Batezelli, 2003 - mod.).



Figure 2. Chronostratigraphic column of the Bauru Group in the Triângulo Mineiro (Minas Gerais State) and adjacent areas in São Paulo State (Batezelli, 2012 - mod.).

### Paleosol Micromorphology

Twenty paleosol profiles were described and macromorphologic using the analysis 2001) diagnostic features (Retallack, of paleosols were identified. These characteristics the identification included of horizons. (MÜNSELL thickness. colors COLOR CHART, 1975), transitions type, bioturbation, root marks, soil structures, textural variations between horizons and cementation. Additionally to the field descriptions, the horizons were sampled for micromorphology, mineralogy, and geochemical analysis.

### Paleosol Micromorphology

The samples collected in the field were cut, impregnated with resin, glued to glass slides and polished to a thickness of up to 30  $\mu$ m. Since paleosol samples disaggregate easily, even when almost completely cemented by calcium carbonate, they were impregnated with a polyester resin that hardens by polymerization, making the preparation of thin sections possible without significant material loss.

The micromorphologic description was made according to the procedures of Castro (2008). A binocular stereograph and an optical microscope under plane-polarized light and crossed nicols were used to determine the constituents and the organization of pores, plasma and skeleton and to recognize the pedologic features that characterize the textural B horizons.

## X-Ray Diffraction Analyzes

The samples were analyzed by X-Ray diffraction using the powder method at the UNICAMP Institute of Geosciences. The Bruker D2 Phaser diffractometer is equipped with a vertical scanning goniometer and a 400 W copper tube ( $\lambda$  CuK $\alpha$  = 1.5406 Å), which adopts the Bragg–Brentano geometry in continuous mode, with a scanning speed of 0.25°/min. The detection system includes a Bruker LvnxEve detector. Voltage and current were adjusted to 30 kV and 10 mA, respectively. The diffractograms were obtained from a 8°- 65° (2 $\Theta$ ) exposition interval, with 0.02° steps. The crystalline phases were identified using the PDF-2 catalog of the International Center for Diffraction Data (ICDD).

### **Geochemical Analysis**

The collected samples were taken to the Sample Preparation Laboratory of the Department of Geology and Natural Resources of the Unicamp Institute of Geosciences to be fragmented in a crusher and pulverized in a ball mill or ring mill, when necessary. The resulting material was tested for loss on ignition at 1000 °C (LOI %).

Glass disks were prepared using 1 g of the powdered sample for trace element analysis and pressed powder pellets with ca. 8 g of sample were prepared for major element analysis. The chemical analyzes were performed on a Philips PW 2404 x-ray fluorescence spectrometer at the Analytical Geochemistry Laboratory of the Unicamp Institute of Geosciences.

Bt/Btk/C/Ck horizons, with the exception of a

Gley profile. No profile exhibits preserved

superficial A horizon. An eroded surface marks

most of the upper portion of the horizons. The

colors vary from red (10R5/8), light red

(10R6/8) to variegated yellowish (2,5Y8/4, 2,5Y6/6, 7,5Y6) colors. The fine- to medium-

grained sandy textures predominate.

## RESULTS

### **Paleosol Macromorphology**

A 43 m-thick lithologic section representing the Marília Formation in western Minas Gerais was described. The paleosols described are indicated as numbered profiles from 1 to 20 (from top to bottom of the section), and most of the profiles can be composed of 1, 2 or 3 horizons (Figures 3, 4, 5 and 6).

Twenty paleosol profiles were identified with thickness varying from 300 cm to 500 cm (Figure 7). They usually contain sequences of reaching more than 30 cm in horizons B (Figure 8A). Occasionally the prismatic structures can be broken into secondary angular blocks, revealing a high pedogenic development

degree. Other structures, such as massive (Figure 8B), are associated with horizons C, Ck, and Bk.



**Figure 3.** General view of section 1, representing the Marilia Formation cropping out in the study area. A) Detail of the profile 1. B) Detail of the profile 2.



**Figure 4.** Continuation of section 1, representing the Marilia Formation cropping out in the study area. A) Detail of the profiles 3, 4 and 5. B) Detail of the profiles 6, 7 and 8.



**Figure 5.** Continuation of section 1, representing the Marilia Formation cropping out in the study area. A) Detail of the profile 9. B) Detail of the profiles 10, 11, 12 and 13.



Figure 6. Panoramic view of section 2, representing the Marilia Formation cropping out in the study area B). Detail of the profiles 14, 15, 16, 17, 18, 19 and 20.



Figure 7. Paleosol profiles of the Marilia Formation in western Minas Gerais State.



Figure 8. Pedogenic structures. A) angular blocks in Bt horizons e B) massive structure in C horizon.

The primary cementing agent is calcium carbonate. The horizons show variations from weakly cemented (Bt) to strongly (Btk) and extremely cemented (Bk and Ck). The calcium carbonate concentrations frequently form glebules, and mostly nodules. The internal structure of the nodules (Figure 9A) is undifferentiated. They are hard, whitish, vary from <10 mm to 30 mm in diameter and are sub-spherical, ellipsoidal and irregular in shape. Other types of glebules, such as halos, are white, small (2 mm - 10 mm) and irregular. The nodules can constitute up to 50% of the horizons volume, forming hardened horizons of pedogenic calcrete (Figure 9B).

Bioturbation structures such as rhizoconcretions, krotovinas, reduction halos and animal excavations are common in almost all paleosol profiles. In general, ichnofossils correspond to vertically elongated cylindrical structures, with lateral branching and fining downwards, such as rhizoconcretions (Figure 10A), which can reach up to 21 mm in length.

Other structures with sub-spherical shape and longitudinally tubular, such as krotovinas (Figure 10B), were distinguished by means of color contrast or grain size from the matrix and filling material. Bioturbations are frequently filled with fine- to medium-grained sand and calcite.

# Interpretation of the macromorphologic analysis

The horizons of sub-superficial argillic texture (Bt) are yellow, brown or red with iron

oxide and hydroxide minerals, such as hematite and goethite. The presence of this horizon with an illuvial clay enrichment in paleosols typical of semi-arid to arid climatic conditions indicates the occurrence of more humid rainy periods (Khormali et al., 2003). As there is no evidence of illuvial clay movement in soils on younger landscapes, soil scientists have concluded that it takes at least some thousand years for an argillic horizon to form (Soil Taxonomy, 1999).

Massive, prismatic and columnar soil structures (peds) were recognized in the field. Laminar structures are fine, but often with large lateral extent. They are frequently formed by the initial rupture of the material from the relict layer in weakly developed soils. Prismatic and columnar peds are taller than wider and can extend to a considerable portion of the soil. They form in associated argillic soils with alternating moist content (Retallack, 2001).

A typical feature of the Marília Formation is the calcretes found in the study area. Pimentel et al. (1996) listed some characteristics that help distinguish between pedogenesis and forms of calcium carbonate concentration related to percolation of CaCO<sub>3</sub>-rich waters. According to the authors, the main pedogenic features are 2 to 3 m profiles organized in horizons, and the occurrence of nodular, laminar, prismatic and blocky structures. Marbled rhizoliths, when present, reflect the lack of Fe, and rarely present lateral variations such as calcrete – dolocrete – gypcrete.



Figure 9. A) Irregular nodules found in Btk horizons. B) Horizon with pedogenic calcrete.



Figure 10. A) Rhizoconcretions filled with calcite; B) Krotovinas filled with red sand (black arrow).

Root traces can be frequently found in the paleosol profiles. The most abundant are tubular features filled with material distinct from the adjacent one, mainly clay varieties, silt or sand. The root traces are occasionally limited by films of iron or manganese oxides, showing bifurcations and decrease in diameter. The concentrations of other fossil vestiges, such as holes and krotovinas, can also be used to identify paleosols, because they record periods of reduced or no deposition of sediments, during which the surface was extensively modified. Usually, zones with significant vestiges of roots and holes can be interpreted as horizons close to the top of a paleosol (Retallack, 2001).

Among the macromorphologic features seen in the field, evidences of gleization were observed, in special mottling. Within the water table fluctuation zone, the alternating oxidizing and reducing conditions produce nodules or gley (McCarthy et al., 1998). Mottling is an evidence of a reducing environment. The reducing condition is not necessarily produced in the water-saturated portions, but it also occurs in areas influenced by the capillary fringe. Therefore, despite the apparently higher water availability and gleization signs, this does not mean that the environment was wet but that the water drainage in this soil profile was possibly inefficient.

### **Paleosol Micromorphology**

The high content of calcite (as plasm and crystals), bioturbations, nodules, and Iron Oxide (hematite) are the most common micromorphological features described (Figure 11). Calcite can occur as plasma involving siliciclastic grain skeleton or as crystals filling cracks, pores and bioturbações (Figures 11A and 11B). In Ck and Bk horizons calcite can replace siciliclásticos grains, or forming nodules and glebules (Figure 11C).

The bioturbações have tubular shapes and may have branches. Are filling with calcite or sand cemented by calcite or hematite (Figure and hematite 11B. 11C 11D). The concentrations develop at preferred levels as films involving the grains, aggregate filling the micro pores (Figures 11E) or as nodules (Figure 11E). In thin sections analyzed is common to see growth of films and carbonate fringes involving grains with hematítica film (Figure 11A).

Subtle clay accumulations were observed in Bt horizons, as low-developed cutas, often modified by carbonation or development of hematite concentrations. The presence of pedogenic horizons that exhibit intercalations and overlapping calcium carbonate and clay concentrations are common in the paleosols of the study area. In horizons Bt and Btk, the percentage of illuviation cutans that occur in the paleosol matrix exceeded 1% of the area of the thin sections, which is the minimum required for a classification as argillic horizon (Soil Survey Staff, 1999).



**Figure 11.** Photomicrograph of the B horizons in the Marília Formation showing the diagnostic features. A) Hematite and carbonate plasma (red arrows). B) Bioturbation filled by siliciclastic grains. C) Calcite crystal filling bioturbation (yellow arrow). D) Carbonate nodule in Bk horizon (red arrow). E) Hematite plasma (red arrow). F) Hematite nodule (red arrow).

# Interpretation of the micromorphologic analysis

Calcic horizons that contain clay illuviation features are commonly interpreted as resulting from climatic changes (Reheis, 1987). The hematite associated with clay were firstly formed in more humid conditions and were later covered by calcium carbonate when climatic became drier, with accompanying decrease in leaching at depth (Gile et al., 1966; Khormali et al., 2003). The occurrence of an argillic horizon in material of calcareous origin from a semi-arid to arid climate could point to a paleoprocess in stable geomorphological conditions (Khormali et al., 2003).

Absence of clay skins has been reported for the B horizon of a Mojave soil (Typic Haplargid) by Buol and Yesiloy (1964) and soils in Arizona, California and Orego by Nettleton *et al.* (1967), and has been attributed to natural soilturbation.

## Mineralogy

Mineralogical analysis was carried out on ten samples from horizons Bt and Btk of paleosol profiles of the study area. Palygorskite was found in profiles 1 and 6 (horizons Bt, Bt1 and Bt2 respectively). These analyzes confirm previous studies where palygorskite and smectite were described as frequent clay minerals in the Marília Formation (Suguio and Barcelos, 1983).

## Interpretation

Palygorskite is a dominant clay mineral (Figure 12) in horizons Bt, thus indicating the occurrence of carbonates in the horizon compositon. The presence of this clay mineral in an illuvial horizon evidences the occurrence of small illuvial calcium carbonate nodules or filaments around grains (Dal'Bó and Basilici, 2010). Palygorskite is an unstable clay mineral in soils under precipitation conditions higher than 300 mm, and it is mostly transformed in smectite (Paquet and Millot, 1972).

The coexistence of pedogenic carbonate nodules with palygorskite and illuvial clay films on calcite crystals in the argillic horizon from Aridisols in Central Iran suggests that palygorskite was captured by pedogenic carbonate and that the argillic horizon formed when the climate was more humid than nowadays (Khormali et al., 2003).

# Chemical Analysis

The data and the results of the x-ray fluorescence spectrometric analyzes are listed in Table 1. The indices of chemical alteration (Table 2; Figure 13) were calculated to evaluate the degree of chemical weathering in paleosols (Retallack, 2001; Sheldon and Tabor, 2009).

 $SiO_2$  contents are the highest among the oxides (Table 1). There is a constant distribution in all profiles, varying from 70 to 85%, which decreases to ca. 65 and 38% when CaO increases. The most relevant variations in the SiO<sub>2</sub> contents are related to CaO variations

(Table 1), which decrease when CaO increases. CaO variations mark carbonate concentration in (Table and calcic horizons nodules 1). Minimum CaO concentrations were found in Gley (10) and horizons C, stressing out the strong CaO leaching. MgO concentrations are low, with slight increases in horizons Bk. indicating the probable presence of dolomite. Low Na<sub>2</sub>O concentrations, in contrast to higher K<sub>2</sub>O contents, show that there was enough water to remove most of the sodium from the paleosols, but insufficient to remove potassium. which is less mobile. Thus, these estimates can indicate strong precipitation seasonality during the Maastrichtian (Retallack, 2001).

The chemical index of alteration without potassium [CIA-K =  $100 \times Al_2O_3/(Al_2O_3+CaO+Na_2O)$ ] measures the degree of weathering of paleosols in different horizons (Maynard, 1992). When CIA-K increases, there is an increase in leaching (Ba/Sr) and consequently a decrease in loss of bases (m $\Sigma$ bases/mAl<sub>2</sub>O<sub>3</sub>). High CIA-K values reflect high precipitation, indicating that these soils underwent intense chemical alteration. In general, this alteration culminated with leaching of soluble alkaline and alkaline earth metals and the concentration of less soluble elements, such as aluminum (Dal'Bó and Basilici, 2010).

Strontium is significantly more soluble than barium during leaching, so that higher Ba/Sr values are expected in more leached horizons (Retallack, 2001). Leaching indices vary inversely with loss of bases; thus, higher leaching is expected with decreasing loss of bases. The highest Ba/Sr values were found in profiles 2 and 10.

Clay formation is indicated by the alumina/silica ratio  $(Al_2O_3/SiO_2)$ . This molecular proportion shows very low resistance values (0.013-0.051), whereas argillic soils show values higher than 0.3. Higher values in the paleosol profiles were used to recognize clay concentration in horizons Bt (Hamer et al., 2007b).

Calcification [(mCaO + mMgO)/mAl<sub>2</sub>O<sub>3</sub>] was very irregular in the paleosol horizons. This irregular pattern is a characteristic of pedogenic horizons enriched in calcium carbonate. The profiles that present horizons Btk, Bk, and Ck contain higher calcium carbonate concentrations. This variability probably results from an external calcium carbonate source, such the addition of eolian

dust or carbonate dissolved in rainwater (Machette, 1985).



Figure 12. X-ray diffraction pattern of Bt horizons (Profiles 1 and 6). Palygorskite is the dominant clay mineral.

Profile	Horizons	SiO	TiO	ALO	Fe <sub>2</sub> O <sub>2</sub>	MnO	ΜσΟ	<b>CaO</b>	Na.O	K.O	P.O.	Ba	Sr
P20	Ck	83 34	0.493	4 53	1.87	0.036	17	2.78	0.17	1 29	0.041	269	81
P20	C	77 81	0 563	4.92	2.14	0.042	2.09	6 58	0.19	1 44	0.051	280	193
P19	Bk	72.15	0.446	3.43	1.61	0.092	4.39	13.8	0.15	1.02	0.043	268	479
P19	Bt	80.43	0.474	3.69	1.69	0.051	3.08	6.55	0.16	1.08	0.042	258	327
P18	C1	78.05	0.466	3.58	1.68	0.047	2.07	10.17	0.12	1.02	0.042	277	304
P18	C2	71.97	0.442	3.28	1.5	0.039	1.24	17.91	0.13	0.94	0.045	270	596
P17	Ck	80.77	0.58	5.11	2.27	0.037	1.09	4.7	0.18	1.54	0.048	305	147
P17	C1	80.28	0.562	4.42	2.11	0.053	0.9	6.99	0.21	1.24	0.045	273	149
P17	C2	80.66	0.691	5.78	2.3	0.037	1.18	3.68	0.26	1.82	0.048	325	120
P17	C3	76.62	0.516	3.73	1.87	0.067	1.12	12.14	0.2	1.17	0.046	285	263
P16	Btk1	48.3	0.523	3.52	2.02	0.105	7.02	34.46	0.04	0.53	0.055	178	720
P16	Btk2	77.03	0.869	6.04	3.61	0.048	2.91	2.14	0.2	1.09	0.064	245	92
P15	Ck	45.18	0.595	3.84	2.55	0.135	13.61	29.96	0.18	0.82	0.07	264	1577
P14	Btk	73.79	0.683	5.04	2.55	0.077	4.41	8.14	0.28	0.98	0.048	257	358
P13	C1	85.8	0.553	3.66	3.03	0.088	0.87	2.23	0.1	0.65	0.059	219	75
P13	C2	80.4	0.782	6.42	3.51	0.085	1.43	0.88	0.16	1.4	0.09	335	81
P12	Ck	67.66	0.553	3.97	2.53	0.077	0.97	18.45	0.17	0.96	1.42	341	450
P11	С	85.68	0.712	4.27	3.18	0.076	0.77	0.54	0.04	0.59	0.043	206	35
P10	Cg1	88.13	0.81	4.06	2.65	0.085	0.52	0.43	0.09	0.73	0.055	1.74	99.3
P10	Cg2	90.26	0.51	3.1	2.85	0.101	0.38	0.27	0.02	0.46	0.06	1.64	99.6
P10	Cg3	93.81	0.22	2.2	1.09	0.039	0.24	0.18	0.02	0.43	0.035	142	17.5
P10	Cg4	82.09	0.774	6.78	4.13	0.221	0.72	0.48	0.09	1.15	0.072	403	43
<b>P9</b>	С	73.32	0.628	3.78	2.13	0.061	2.12	8.09	0.07	0.84	0.037	8.62	99.7
P8	Ck	82.31	0.66	4.01	2.61	0.061	1.89	2.82	0.06	0.95	0.037	244	91
P7	C1	64.7	0.648	5.25	2.82	0.082	2.87	10.37	0.16	1.41	0.049	11.3	99.6
P7	C2	78.64	0.655	4.6	2.98	0.079	1.77	4.31	0.13	1.09	0.045	5.47	99.8
P6	Bt1	68.24	0.72	5.08	2.91	0.079	2.83	8.41	0.2	1.34	0.048	9.79	99.6
P6	Bt2	67.08	0.699	5.82	2.88	0.087	3.32	8.26	0.18	1.58	0.05	10.1	100.1
P5	Ck	69.14	0.602	4.91	3.09	0.085	3.28	7.56	0.14	1.19	0.046	257	275
P4	2Ck	46.71	0.38	2.25	2.8	0.143	3.87	21.18	0.1	0.52	0.055	224	587
P3	Btk	38.35	0.336	2.41	1.48	0.076	2.78	27.64	0.1	0.67	0.039	239	585
P3	C	61.58	0.564	4.74	2.82	0.074	1.12	14.23	0.15	1.14	0.045	262	328
P2		86.51	0.746	4.93	2.58	0.063	0.84	0.42	0.1	1.26	0.037	301	64 70
P2	C2	85.58	0.91	5.49	2.81	0.062	0.89	0.49	0.09	1.38	0.037	313	70
P2	C3	80.8/	0.745	4.57	2.80	0.072	0.73	0.4	0.06	1.17	0.035	280	50
P2 D1	D4	07.3 70.27	0.317	5.9 7.01	2.57	0.000	2.00	1.22	0.07	2.02	0.035	237	90
Г1 D1		17.21 65.87	0.743	7.01	5.59 2 1 2	0.051	2.23 17	1.23	0.23	2.02	0.040	204 225	00 252
Г1 D1	$C^{2}$	05.82 77.01	0.44	5.50 3.87	2.12 2.17	0.008	1./ 1.67	12.04 5.76	0.08	0.79	0.038	200 267	200 107
r1	02	11.91	0.550	5.07	2.47	0.079	1.07	5.70	0.12	0.09	0.030	207	107

 Table 1. Major and trace elements for each paleosol horizon, reported in oxide wt.% or ppm.

 Table 2. Indices of chemical alteration calculated for the Marília Formation paleosols.

Profile	Horizons	CIA-K	Leaching	Argillization	Loss of Bases	Calcification
P20	Ck	45.92	2.12	0.03	6.14	5.15
P20	С	28.61	0.93	0.04	24.69	23.15
P19	Bk	11.92	0.36	0.03	10.84	1.86

P19	Bt	23.26	0.5	0.03	3.06	22.84
P18	C1	16.08	0.58	0.03	2.74	6.68
P18	C2	9.1	0.29	0.03	2.79	1.67
P17	Ck	36.63	1.32	0.04	3.51	3.39
P17	C1	25.29	1.17	0.03	14.07	2.21
P17	C2	44.81	1.73	0.04	46.08	10.88
P17	C3	14.27	0.69	0.03	64.49	6.63
P16	Btk1	5.31	0.16	0.04	21.3	5.34
P16	Btk2	58.87	1.7	0.05	6.21	10.55
P15	Ck	6.55	0.11	0.05	16.22	3.51
P14	Btk	24.83	0.46	0.04	8.1	2.06
P13	C1	46.45	1.86	0.03	12.59	0.69
P13	C2	77.51	2.64	0.05	13.56	9.07
P12	Ck	10.5	0.48	0.03	12.41	0.81
P11	С	80.3	3.76	0.03	1.85	1.71
P10	Cg1	81.37	0.01	0.03	1.84	0.4
P10	Cg2	85.55	0.01	0.02	3.5	0.42
P10	Cg3	85.93	5.18	0.01	2.75	0.47
P10	Cg4	86.91	5.98	0.05	5.15	0.52
P9	C	20.32	0.06	0.03	3.98	5.31
P8	Ck	43.42	1.71	0.03	26.59	4.02
P7	C1	21.55	0.07	0.05	2.1	4.42
P7	C2	36.36	0.03	0.03	9.05	2.68
P6	Bt1	24.54	0.06	0.04	13.35	4.97
P6	Bt2	27.54	0.06	0.05	29.64	2.47
P5	Ck	26	0.6	0.04	15.93	6.06
P4	2Ck	5.5	0.24	0.03	20.34	23.77
P3	Btk	4.56	0.26	0.04	32.59	21.46
P3	С	15.36	0.51	0.05	10.01	4.49
P2	C1	84.16	3	0.03	12.43	0.58
P2	C2	84.09	2.85	0.04	8	0.56
P2	C3	84.69	3.15	0.03	20.58	0.57
P2	C4	84.84	3.28	0.03	54.27	0.59
P1	Bt	72.83	2.78	0.05	5.08	3.8
P1	C1	12.59	0.59	0.03	48.74	8.18
P1	C2	26.62	1.59	0.03	13.63	1.13

### Interpretation of the chemical analysis

In profile 1, there was a decrease in CIA-K and leaching in horizon C1 with increasing calcification. This change can be explained by a hotter and drier climatic period, whereas in the superficial horizon of this profile (Bt) there was a significant increase in CIA-K and leaching, as well as in argillization, and a corresponding decrease in calcification. These variations in the indices of alteration can indicate a climatic seasonality during the formation of this paleosol profile. In profile 2, the index of molecular alteration shows high chemical weathering and leaching rates in all horizons (C1, C2, C3, and C4), whereas calcification in this profile is practically absent. High chemical weathering and leaching indices can indicate a wet and hot climatic period, with the loss of bases.

Profiles 3, 4 and 5 present a significant decrease in weathering and leaching rates with increasing calcification, forming horizons Ck and Btk. A punctual climatic variation may have occurred during the formation of these paleosols.





Profile 6 presents a continuous variation of CIA-K values and leaching, with an increase in argillization in the argillic horizons Bt1 and Bt2. Profiles 8 and 9 present weathering and leaching rates with no significant changes.

Besides being a gleysol, profile 10 also yields high CIA-K and leaching, which may be related to a higher paleoprecipitation index with hot climate or that this soil profile possibly presented inefficient water drainage in a plane relief.

The base of profile 11 (horizon C) shows a continuity of profile 10 in leaching and weathering indices, whereas in the upper profiles there is a punctual modification in horizon Ck, with significant drop in weathering and leaching indices, as well as an increase in calcification, probably corresponding to a climatic change to a drier period. The superficial horizons of profile 13 (C1 and C2) present an increase in weathering and leaching rates, which gradually decrease towards profile 15. In this profile, horizon Ck shows an abrupt drop in leaching and weathering rates, with a significant increase in calcification.

Profiles 18,19 and 20 present small gradual variations in weathering, leaching, argillization and calcification rates, with moderate leaching and weathering rates indicating a hot and dry climate, with no major rainfall variations.

These analyses corroborate with previous studies on the climate of the Upper Cretaceous in the Bauru Basin, which was arid in general (Suguio and Barcelos, 1983), with well-defined seasons, distinguished by alternating dry and rainy periods (Goldberg and Garcia, 2000).

## Paleoprecipitation Estimates

important challenge for An paleoenvironmental interpretation of continental deposits is the identification of features that indicate the prevailing climatic conditions. In this sense, the paleosols indicate mineralogical and chemical changes associated the processes of training with provide information on climate, including rainfall rates, temperatures, and evapotranspiration.

An exponential equation that relates precipitation (MAP) with chemical alteration

indices (CIA-K) of argillic horizons Bt and Btk employed to check the annual was paleoprecipitation estimates (Sheldon et al., 2002). The first step for the application of the equation is to calculate the chemical index of alteration without potassium (Maynard, 1992) CIA-K follows: 100 as = x  $Al_2O_3/(Al_2O_3+CaO+Na_2O)$ , in % molar mass. This index is used with the objective of controlling the potassium metasomatic effects in paleosols. Sheldon et al. (2002) proposed the following equation to evaluate the precipitation rates:

$$P(mm) = 14.265(CIA-K) - 37.632$$

with slightly higher accuracy:  $R^2 = 0.73$  (determination coefficient).

It was possible to use chemical alteration indices for horizons Bt and Btk in the study area since they are based on the characteristics of horizons B and do not require a preserved superficial horizon A. The results presented in this study (Figure 14) reflect two distinct moments of paleoclimatic evolution during the deposition and formation of soils in the Marília Formation.

The estimates calculated through the geochemistry for horizons Bt revealed considerable increase in precipitation, with average values of 490 mm/year (Figure 14). The values reflect a distinct evolutionary moment in the Marília Formation, in which carbonates deposited in drier phases underwent leaching and the dominant process change to the genesis of the hematite and subtle clay illuviation in horizons Bt.

These paleoprecipitation data in horizons Bt and Btk in the Marília Formation reveal two distinct moments in its paleoclimatic evolution, one characterized by more arid moments, which allowed the development of calcic horizons, and another with mean values of 490 mm/year, enough for carbonate leaching and favoring dispersion, translocation and accumulation of clays in argillic horizons. This polygenetic sequence shows the vertical changes in soil properties that are related to changes in soil moisture.



Figure 14. Stacked B horizons of the Marília Formation and paleoprecipitation estimates based on Sheldon et al., (2002).

### CONCLUSION

The vertical association of 20 paleosol profiles containing horizons C, Ck, Bt, Btk and Cg in the Marília Formation are cemented with CaCO<sub>3</sub>. In relation to macrofeatures, these present colors that vary from 2.5Y to 10R. The blocky structures suggest a high degree of pedogenetic development, with truncated horizons and lack of horizon A. Glebules, root marks and krotovinas are present in all profiles. Gleization features are recorded in a single profile (10).

The most striking microfeatures are related to subtle clay illuviation, hematite and intense carbonation. Palygorskite associated with carbonation suggests semi-arid climatic conditions.

The chemical alteration indices for the 20 paleosol profiles indicate variation in

weathering conditions. The highest rates indicated by CIA-K, leaching, argillization, and loss of bases and decrease in calcification are recorded at the base of the section and coincide with the period of highest precipitation in the study area (1000 mm, profiles 1 and 2). Profiles 3 to 9 present low molecular variation, although a carbonation increasing tendency is observed profiles. Based in the upper on paleoprecipitation estimates calculated according to Sheldon et al. (2002), it was possible to draw a rainfall variation graph for the Marília Formation paleosol succession, which record two periods of higher precipitation (P1Bt = 1000 mm and P16Btk = 800 mm), intercalated with periods of lower precipitation.

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2. BASILICI, G.; DAL' BO, P.F.F.; LADEIRA, F.S.B. Climate-induced sediment-palaeosol cycles in a Late Cretaceous dry aeolian sand sheet: Marilia Formation (North-West Bauru Basin, Brazil). **Sedimentology**, v. 56, p. 1876– 1904. 2009.

3. BARCELOS, J.H. Reconstrução Paleogeográfica da Sedimentação do Grupo Bauru Baseada na sua Redefinição Estratigráfica Parcial em Território Paulista e no Estudo Preliminar Fora do Estado de São Paulo. Rio Claro, 190p. Tese (Livre Docência) - Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista. 1984.

4. BARCELOS, J.H. & SUGUIO, K. Correlação e extensão das unidades litoestratigráficas do Grupo Bauru, definidas em território paulista e nos estados de Minas Gerais, Goiás, Mato Grosso do Sul e Paraná. In: SIMPÓSIO REGIONAL DE GEOLOGIA, 6. Atas... Rio Claro, p. 313-321. 1987.

5. BATEZELLI, A. Análise da sedimentação cretácea no Triângulo Mineiro esua correlação com áreas adjacentes. Rio Claro, 2003. 183 p. Tese (Doutorado em Geociências) – Instituto de Geociências e Ciências Exatas, Universidade Estadual Paulista, Rio Claro. 2003.

6. BATEZELLI, A. Evolução dos tratos de sistemas continentais Neocretáceos da porção sudeste da Plataforma Sulamericana. **Para Conhecer a Terra**. Memórias e Notícias de Geociências no Espaço Lusófono, Vol. 1, p.92-100, 2012.

7. BUOL, S.W. & YESILOY, M.S. A genesis study of a Mojave sandy loam profile. **Soil Science Society of American Proceedings**, v. 28, 254-256. 1964.

8. CASTRO, S.S. Micromorfologia de solos: bases para descrição de lâminas delgadas. Campinas: Universidade Estadual de Campinas, 143 p. 2008.

9. DAL' BO, P.F.F. & LADEIRA, F.S.B. Ambientes Paleoclimáticos da Formação Marília Baseado em Análise Paleopedológica na Região de Monte Alto (SP). **Geociências**, v.25, p. 127-134. 2006.

10. DAL' BO, P.F.F.; BASILICI, G.; ANGELICA, R. S.; LADEIRA, F. S.B. Paleoclimatic interpretations from pedogenic calcretes in a Maastrichtian semi-arid eolian sandsheet palaeoenvironment: Marília Formation (Bauru Basin, southeastern Brazil). **Cretaceous Research**, v. 30, p. 659-675. 2009.

11. DAL' BO, P.F.F., BASILICI, G.; ANGELICA, R. S. Factors of paleosol formation in a Late Cretaceous eolian sand sheet paleoenvironment, Marilia Formation, Southeastern Brazil, **Palaeogeography, Palaeoclimatology, Palaeoecology**, v. 292, n. 1-2, p. 349-365. 2010.

12. DIAS-BRITO, D.; MUSACCHIO, E.A.; CASTRO, J.C.; MARANHÃO, M.S.A.S.; SUÁREZ, J.M.; RODRIGUES, R. Grupo Bauru: uma unidade continental do Cretáceo no Brasil – concepções baseadas em dados micropaleontológicos, isotópicos e estratigráficos. **Revue de Paléobiologie** v. 20, n. 1, p. 245-304. 2001.

**13.** FERNANDES, L.A. Estratigrafia e evolução geológica da parte oriental da Bacia Bauru (Ks, Brasil). São Paulo, 216 p. Tese (Doutorado) – Instituto de Geociências, Universidade de São Paulo. 1998.

 FERREIRA JR., P. D. Modelo Deposicional e Evolução Diagenética da Formação Uberaba, Cretáceo Superior da Bacia do Paraná, na Região do Triângulo Mineiro. 1996.
 175p. Dissertação de Mestrado. Universidade Federal de Ouro Preto. Ouro Preto, 1996. 15. GILE, L.H.; Peterson, F.F.; Grossman, R.B. Morphological and genetic sequences of carbonate accumulation in desert soils. **Soil Science**, v. 101, p. 347–354. 1966.

16. GOBBO, S.R.; SANTUCCI, R.M.; BERTINI, R. J. Considerações sobre a idade da Formação Marília (Grupo Bauru, Cretáceo Superior) na região de Peirópolis, Estado de Minas Gerais. In: XVII Congresso Brasileiro de Paleontologia, 2001, Rio Branco, AC. Boletim de Resumos do XVII Congresso Brasileiro de Paleontologia. Rio Branco, AC: Editora da Universidade Federal do Acre, v. 1. p. 48-48. 2001. 17. GOLDBERG, K. & GARCIA, A.J.V.

Palaeobiogeography of the Bauru Group, a dinosaur-bearing Cretaceous Unit, Northeastern Parana Basin, Brazil. **Cretaceous Research**, v. 21, p. 241-254. 2000.

18. KHORMALI, F., ABTAHI, A. Origin and distribution of clay minerals in calcareous arid and semi-arid soils of Fars Province, southern Iran. **Clay Minerals**, v. 38, p. 511–527. 2003.

19. KHORMALI, F.; ABTAHI, A.; MAHMOODI, S.; STOOPS, G. Argillic horizon development in calcareous soils of arid and semiarid regions of southern Iran. **Catena**, v. 53, p. 273–301. 2003.

20. MAYNARD, J.B. Chemistry of modern soils as a guide to interpreting Precambrian paleosols. **Journal of Geology**, v. 100, p. 279–289. 1992.

21. McCARTHY, P. J. & PLINT, A. G. Recognition of interfluve sequence boundaries: integrating paleopedology and sequence stratigraphy. **Geology**, v. 26, p. 387-390. 1998.

22. MACHETTE, M.N. Calcic soils of the southwestern United States. In: Weide, D.L. (Ed.), Soils and Quaternary Geology of the Southwestern United States, 203. **Geological Society of America**, Special Paper, pp. 1–21. 1985.

23. NESBITT, H.W. & YOUNG, G.M. Early Proterozoic climates and plate motions inferred, from major element chemistry of lutites. **Nature**, v. 299, 715–717. 1982.

**24.** NETTLETON, W.D, FLACH, K. W. & BRASHER, B.R. Argillic Horizons Without Clay Skins. **Soil Science Society of American Proceedings**, v. 33, 121-125. 1969.

25. PAQUET, H. & MILLOT, C. Geochemical evolution of clay minerals in the weathered products and soils of Mediterranean climates. In: INTERNATIONAL CLAY CONFERENCE. **Proceedings...** Madrid, Spain, p. 199-202. 1972.

26. PIMENTEL, N.L.; WRIGHT, V.P.; AZEVEDO, T.M. Distinguishing early groundwater alteration effects from pedogenesis in ancient alluvial basins: examples from the Palaeogene of southern Portugal. **Sedimentary Geology**, v. 105, p. 1-10. 1996.

27. REHEIS, M.C. Climatic implications of alternating clay and carbonate formation in semiarid soils of south-central Montana. **Quaternary Research**, v. 27, 270–282. 1987.

28. RETALLACK, G.J. Core concepts of paleopedology. **Quaternary International**, v. 51/52, p. 203–212. 1998.

29. RETALLACK, G.J. Soils of the Past: An Introduction to Paleopedology. Allen and Unwin, London, pp. 520. 2001.

30. RICCOMINI, C. Tectonismo Gerador e Deformador dos Depósitos Sedimentares Pós-Gondwânicos da Porção Centro-Oriental do Estado de São Paulo e Áreas Vizinhas. 1995. 100p. Tese de Livre-Docência, Instituto de Geociências da Universidade de São Paulo – USP. São Paulo, 1995.

31. RICCOMINI, C. Arcabouço estrutural e aspectos do tectonismo gerador e deformador da Bacia Bauru no estado de São Paulo. **Revista Brasileira de Geociências**, v. 27, n. 2, 153-162. 1997.

32. SANTUCCI, R.M. & BERTINI, R.J. Distribuição paleogeográfica e biocronológica dos Titanossauros

(Saurischia, Sauropoda) do Grupo Bauru, Cretáceo Superior do sudeste brasileiro. **Revista Brasileira de Geociências**, v. 31, n. 3, p. 307-314. 2001.

33. SHELDON, N.D. Pedogenesis and geochemical alteration of the Picture Gorge Subgroup, Columbia River Basalt, Oregon. Geological Society of America Bulletin, v. 115, 1377–1387. 2003.

34. SHELDON, N.D. Do red beds indicate paleoclimatic conditions? A Permian case study. **Palaeogeography**, **Palaeoclimatology**, **Palaeoecology**, v. 228, 305–319. 2005.

35. SHELDON, N. D. & TABOR, N. J. Quantitative paleoenvironmental and paleoclimatic reconstruction using paleosols. **Earth-Science Reviews**, v. 95, 1-52. 2009.

36. SHELDON, N. D.; RETALLACK, G. J.; TANAKA, S. Geochemical climofunctions from North American soils and application to paleosols across the Eocene–Oligocene boundary in Oregon. **Journal of Geology**, v. 110, 687–696. 2002.

 SOIL SURVEY STAFF Soil Taxonomy, 2nd edition.
 U. S. Department of Agriculture, Natural Resource Conservation Service 4362, Washington, DC. 1999.

38. SOARES, P. C.; LANDIM, P. M. B.; FULFARO, V. J.; SOBREIRO NETO, A. F. Ensaio de caracterização estratigráfica do Cretáceo no Estado de São Paulo: Grupo Bauru. **Revista Brasileira de Geociências**, v.10, n. 3, p. 177-185. 1980.

39. SUGUIO, K. Formação Bauru. Calcários e sedimentos detríticos associados. Unpublished Livre Docência Thesis, Universidade de São Paulo, pp. 236. 1973.

40. SUGUIO, K. & BARCELOS, J.H. Calcretes of the Bauru Group (Cretaceous), Brazil: petrology and geological significance. Boletim do Instituto de Geociências da Universidade de São Paulo, v. 14, p. 31-47. 1983.

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