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ARTICLE

The mineralogy of paleosols in the Marília Formation and their importance in the environmental evolution of the Maastrichtian of the Bauru Basin in southeastern Brazil

Mineralogia de paleossolos da Formação Marília e seu significado na evolução ambiental do Maastrichtiano da Bacia Bauru, sudeste do Brasil

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ABSTRACT: Soils and paleosols reflect the complex interplay between sedimentation, erosion and non-deposition. An analysis of the mineralogical components of paleosols is critical for the reconstitution of the factors, processes and environments in which they were formed. The recognition of mineralogical assemblages can reveal the environmental conditions during pedogenesis and through quantitative analysis it is possible to identify a vertical variation in mineral concentration or leaching over the paleosol profiles, indirectly pointing to environmental processes that dominated during the pedogenetic evolution. The objective of this study is to discuss the significance of mineral phases and to quantify the environmental evolution and degree of development of paleosols of the Marília Formation, Maastrichtian of Bauru Basin. Three sections have been described (A1, A2, A3) in the Marília Formation. The mineralogy was determined by x-ray diffraction, and mineral quantification was obtained through the Rietveld refinement method. The calcretes of the Marília Formation are pedogenic, mostly authigenic minerals. The variation of quartz, calcite, palygorskite and smectite, the micromorphology, and the diversity of subsurface horizons (Bkm, Btkm, Bt) indicate that the studied paleosols did develop in semi-arid conditions, with episodes of higher rainfall rates, humidity, leaching and desilication.

KEYWORDS: Calcrete; Paleoclimate; Palygorskite; Pedogenesis; Upper Cretaceous.

RESUMO: *Solos e paleossolos refletem complexa inter-relação entre sedimentação, erosão e não-deposição. A análise dos constituintes mineralógicos de paleossolos é fundamental para a reconstituição dos fatores, processos e ambientes no qual esses se formaram. O reconhecimento de determinadas assembléias mineralógicas podem revelar as condições ambientais durante a pedogênese e através da análise quantitativa se torna possível constatar variação vertical ao longo dos perfis de paleossolos, identificando horizontes com maior concentração mineral ou lixiviação, apontando indiretamente processos ambientais que dominavam no decorrer da evolução pedogenética. O objetivo desse trabalho foi discutir o significado das fases minerais e sua quantificação na evolução ambiental e no grau de desenvolvimento dos paleossolos da Formação Marília, Maastrichtiano da Bacia Bauru. Foram descritas três seções (A1, A2, A3) da Formação Marília. A mineralogia foi determinada através da difratometria de raios-x e para a quantificação mineral foi utilizado o método de refinamento Rietveld. Os calcretes da Formação Marília são predominantemente pedogênico, com minerais autigênicos em sua maioria. A variação do teor de quartzo, calcita, paligorskita e esmectita, a micromorfologia e a diversidade de horizontes subsuperficiais (Bkm, Btkm, Bt) demonstraram que os paleossolos se desenvolveram em condições gerais semiáridas, com episódios de maiores taxas de precipitação, umidade, lixiviação e dessilicação.*

PALAVRAS-CHAVE: *Calcrete; Paleoclima; Paligorskita; Pedogênese; Cretáceo Superior.*

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INTRODUCTION

Progress in identification and mineralogical quantification techniques has contributed to the study of paleosols. The techniques have become effective tools for performing paleoenvironmental analysis and for identifying the evolution of continental sedimentary basins. Soils and paleosols reflect complex interplay between sedimentation, erosion, non-deposition and pedogenesis. Because soil is an open system that results from the interactions between factors (parent material, relief, time, climate and organisms) (Jenny 1994), and specific processes of formation (Buol *et al.* 1997, Breemen & Buurman 2002, Resende *et al.* 2002), one can infer its origin from top to bottom. Thus, it is possible to define the factors' conditions and the formation processes from the analysis of paleosols.

Paleosols, defined as soil formed in an ancient landscape (Wright 1986), reveal the environmental conditions and characteristics that identify parental material, estimate formation time, and reconstitute paleosurfaces, paleoclimate and paleobiote. In addition, the use of paleosols enables the identification of the relationship between deposition, non-deposition and erosion. They have taken an increasingly prominent role in the study of paleoenvironmental and stratigraphic reconstructions (Andreis 1981, Kraus & Brown 1988, Birkeland 1999, Kraus 1999, Retallack 2001).

The qualification and quantification of the mineralogical constituents of paleosols are critical for the reconstitution of the factors, processes and environments in which they were formed. The recognition of mineralogical assemblages may reveal the chemical, temperature, and hydrological conditions during pedogenesis (Allen & Hajek 1989, Paquet & Clauer 1997, Birkeland 1999, Meunier 2005, Kämpf *et al.* 2009). Through quantitative analysis it is possible to assess the vertical variation of paleosol profiles, and identify horizons with higher mineral concentration (transformation, neoformation or inheritance) or leaching, which indirectly points to chemical processes that dominated during the pedogenetic evolution.

The objective of this study was to discuss the significance and the quantification of mineral phases in the environmental evolution and inthe degree of development of the paleosols of the Marília Formation, Maastrichtian of Bauru Basin.

Several authors have identified mineral assemblages in the Marília Formation and associated them with climatic conditions (Lepsch *et al.* 1977, Suguio & Barcelos 1983a, 1983b, Ribeiro 2001, Barison 2003, Dal'Bó & Basilici 2010, Fernandes 2010, Dal'Bó 2011, Pereira *et al.* 2015, Silva *et al.* 2015, 2016, 2017). However, quantitative studies aimed at the identification of mineralogical changes in time and their relationship with paleoenvironmental evolution was never performed.

The Marília Formation paleosols were developed on sandstones with different degrees of carbonate cementation, mostly calcretes. The mineralogical composition and quantification show that calcite was the second most abundant, followed by palygorskite and smectite. According to Meunier (2005), mineralogical compositions with an assemblage of smectite, sepiolite and palygorskite identify soils derived from sediments exposed to arid or semi-arid conditions. Calcite, on the other hand, is a mineral soil that is very common in dry regions (sub-humid arid) (Hubert 1978, Allen & Hajek 1989, Tanner 2010).

The proposed mineralogical quantification indicates that the paleosols of the Marília Formation were developed in semiarid conditions, with episodes of higher rainfall rates, humidity, leaching and desilication. This information contributes to the knowledge about the evolution of the Maastrichtian in the Bauru Basin. It is expected that these results can corroborate the hypotheses, based on micromorphology and geochemistry, about the evolution conditions of the Marília Formation.

GEOLOGICAL SETTING AND STRATIGRAPHY OF THE BAURU BASIN

The Bauru Basin, located in southeastern Brazil, covers an area of approximately 330,000 km^2, including the center-west of São Paulo, northeastern Mato Grosso do Sul, southern Mato Grosso, southern Goiás and western Minas Gerais (Fig. 1). This basin has an elliptical shape, which is elongated in the N-NE direction and consists primarily of siliciclastic continental deposits (Batezelli 2003).

The Bauru Basin originated in the Late Cretaceous, was developed over the basalt rocks of the Serra Geral Formation, and was generated by the flexural subsidence caused by the weight of thick basalt, the Alto Paranaíba Uplift and the Alkaline Province of Goiás (Fig. 1) (Riccomini 1995, 1997, Fernandes & Coimbra 2000, Batezelli 2003, Batezelli *et al.* 2007, Batezelli, 2010, 2015, Batezelli & Ladeira, 2016).

The Bauru Basin is subdivided into Caiuá and Bauru groups (Figs. 1 and 2). The lithostratigraphic position of these two groups is up for debate. Authors such as Fernandes & Coimbra (1996, 2000) and Fernandes (2004) state that the two groups are contemporary. Other authors (Fúlfaro & Perinotto 1996, Paula e Silva *et al.* 2005, Batezelli 2010, 2015) put the Caiuá in the lower portion of the basin, separated from the Bauru Group with a stratigraphic discordance. This discordance is signaled by a much evolved paleosol (Geosol Santo Anastásio, as in Fúlfaro *et al.* 1999). Batezelli (2010, 2015) and Batezelli & Ladeira (2016) demonstrated, using outcrops and well-logs data, that the two groups are not contemporary (Fig. 2), and proposed chronostratigraphy to understand the basin.

Through facies analysis, architectural elements and paleocurrents, Batezelli et al. (2007) concluded that the deposits of the Bauru Group were formed in a proximal and intermediate

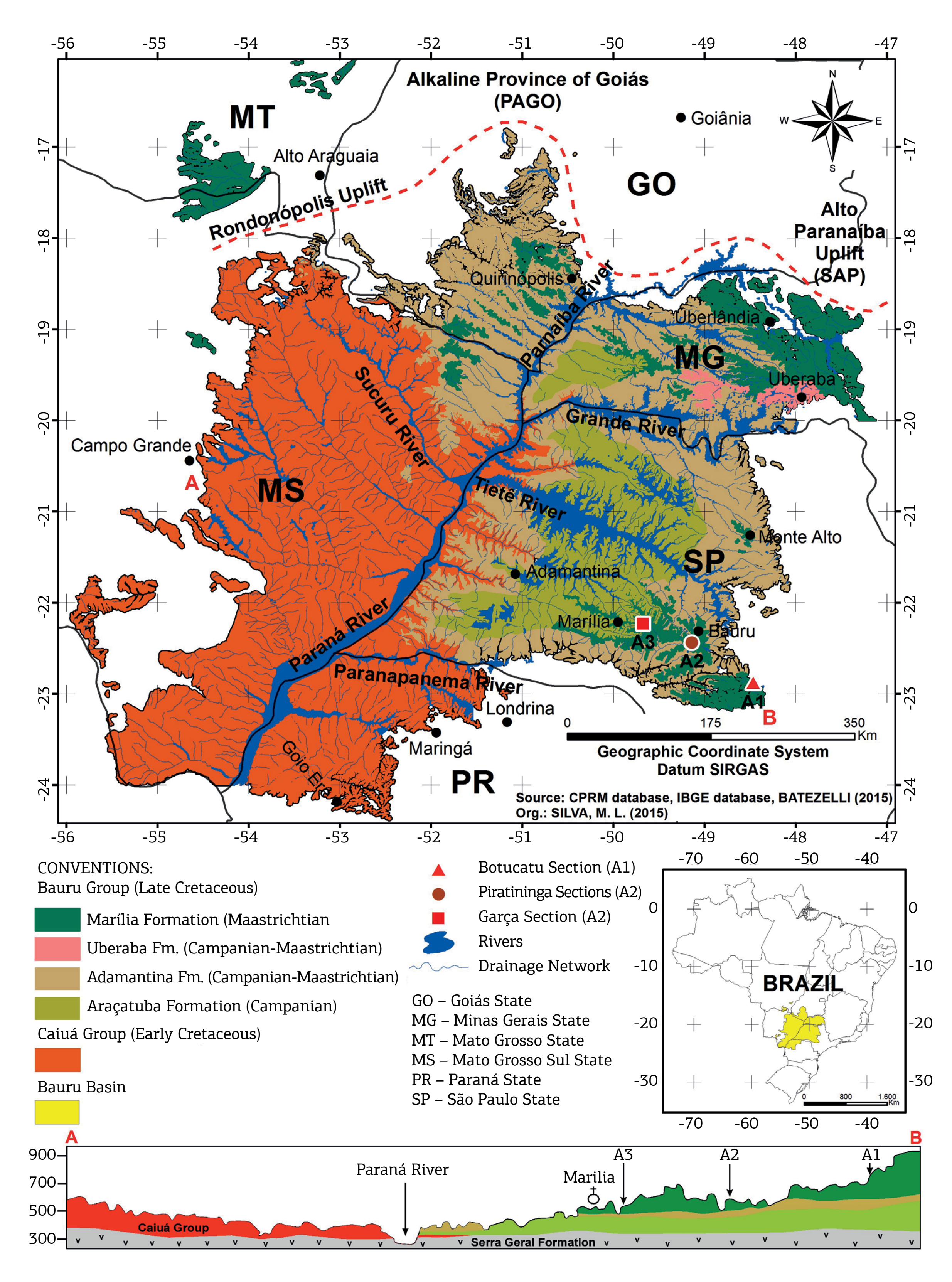

Figure 1. A lithostratigraphic map and a geologic section (A-B) of the Bauru Basin. The red square, cycle and triangle are the positions of the outcrops in the study area.

portion of a braided, river-dominated alluvial system (According Stanistreet & McCarthy, 1993 terminology) arising from the Alto Paranaíba Uplift and the Alkaline Province of Goiás (Fig. 1).

The Bauru Group in the State of São Paulo consists of Araçatuba, Adamantina (Vale do Rio do Peixe according to Fernandes & Coimbra, 2000) and Marília (Echaporã Member) formations, from its base to the top (Batezelli, 2003, 2010, 2015). According to Batezelli (2003, 2010, 2015), the Araçatuba Formation was formed in a lacustrine environment (playa-lake) that served as the base level for the river system (Adamantina and Marília formations). The filling occurred because of the progradational advance of an alluvial system dominated by a braided river that gave rise to the Marília Formation.

The sedimentary evolution of the alluvial system was marked by periods of fluvial sedimentation and eolian reworking, interspersed with periods of non-deposition (Batezelli 2010, 2015, Batezelli & Ladeira 2016). During non-deposition times the floodplain would be covered by vegetation, and as such, soils could develop. Thus, the Marília Formation consists of a succession of deposits and paleosols that record sedimentation and pedogenesis during the Maastrichtian of the Bauru Basin.

In the Marília Formation, paleosols are made up of argillic horizons (Btk and Bt) and a calcic horizon (Bk) with different degrees of cementation, constituting calcretes. The irregular distribution and different thicknesses of the profiles are related to the type of parent material, hydrology, topography and biology, as well as the time of exposure of deposits to weathering agents.

MATERIALS AND METHODS

Field descriptions

The facies analysis method was based on Miall (1985, 1996) and the characterization of paleosols was performed according to Andreis (1981), Retallack (1988, 2001) and Catt (1990).

Three sections have been described (A1, A2 and A3) at the Marília Formation (Figs. 1 and 3), and nine samples profiles were obtained.

Three main lithofacies were identified: Gm (conglomerates), Sm (sandstones) and Fm (pelites or mudstones).

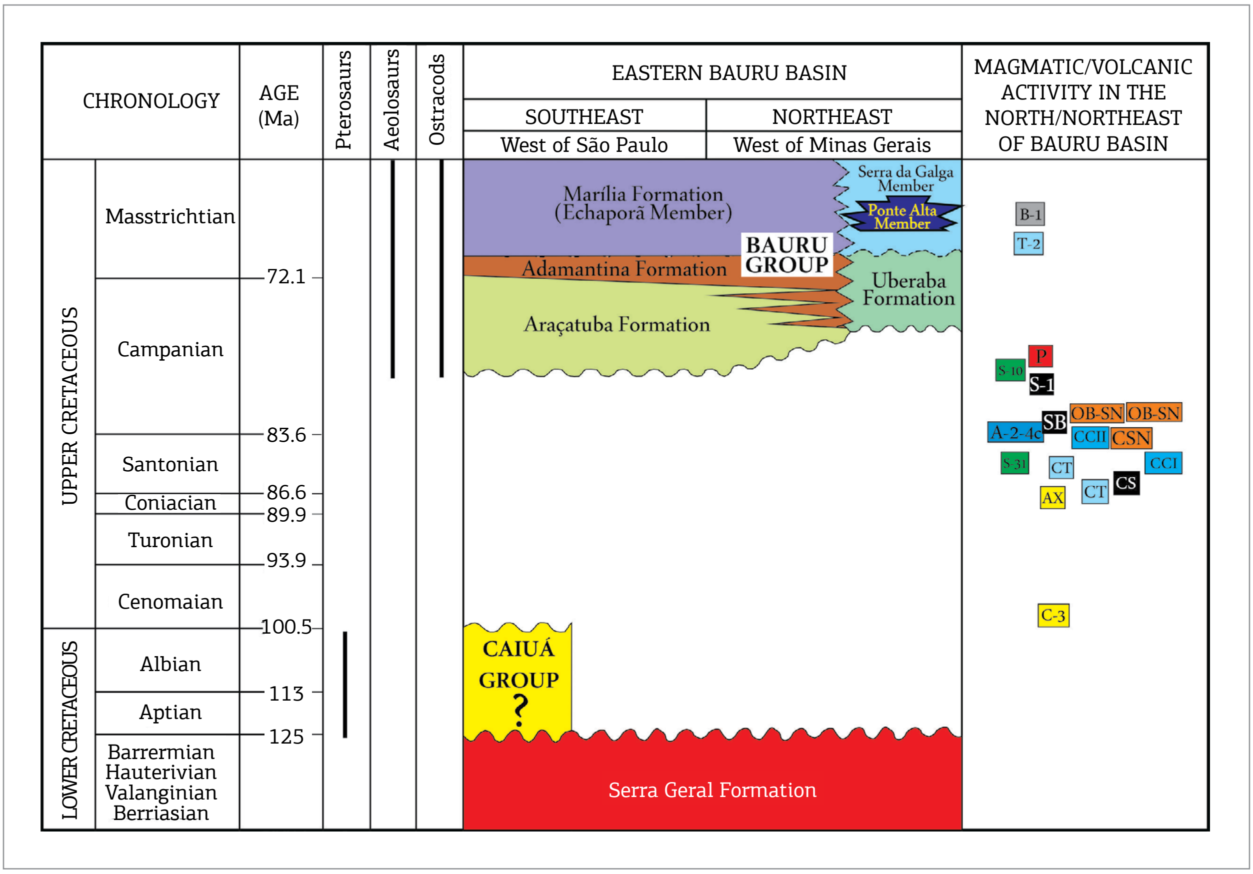

Figure 2. A chronostratigraphic chart of the eastern portion of the Bauru Basin, based on Amaral *et al.* 1967 (CSN sample); Hasui & Cordani 1968 (samples AX, C-3, S-10, S-31, A-C2-4, OB-SN, SB, S-1, P, T-2, B-1); Sonoki & Garda 1988 (samples CT, CS, CCI); Machado Junior 1992 (sample CCII); Guimarães *et al.* 2012 and Fragoso *et al.* 2013 (Pterosaurs); Gobbo-Rodrigues 2001 and Dias-Brito *et al.* 2001 (Ostracods); Santucci & Bertini 2001 and Martinelli *et al.* 2011 (Allosaurus) (Batezelli 2015).

The fieldwork consisted of identifying horizons, ped structures, and root marks which are the main attributes of paleosols (Andreis 1981, Retallack 1988, Catt 1990, Retallack 2001). The horizons were defined through descriptions of texture, structure, color (Munsell Color Chart), thickness and depth, types of contact — cutans, nodules or cementing — bioturbations, presence or absence of mottling, gleyzation and friction surfaces (slickensides). Calcic (Bkm)

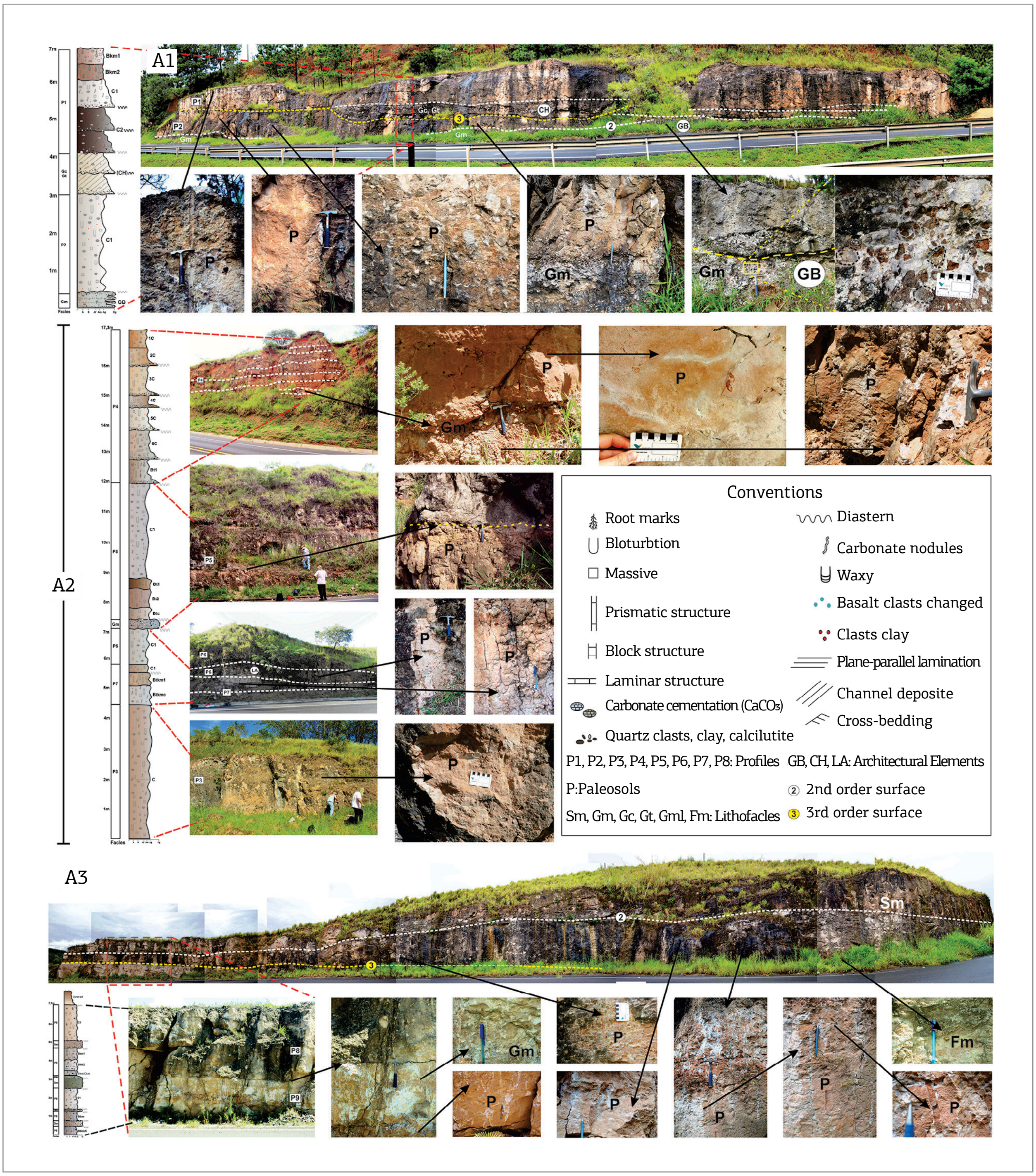

Figure 3. Described sections. Botucatu section (A1): Located in the homonymous municipality (Marechal Rondon Highway, km 151), and stratigraphic section with the lithofacies (Gc, Gt, Gm) and profiles (P1, P2); Piratininga section (A2): Located in the homonymous municipality (Bauru-Ourinhos Highway, km 248), and stratigraphic section with the lithofacies (Gm, Gmi) and profiles (P3, P4, P5, P6, P7); Garça section (A3): Located in the homonymous municipality (João Ribeiro de Barros Highway), and stratigraphic section with the lithofacies (Sm, Gm, Fm) and profiles (P8, P9). The identification and description of facies are based on proposals from Miall (1985, 1996).

and argillic (Btkm and Bt) horizons were identified in the paleosols of the study area.

Micromorphological analysis

The description of the oriented thin sections was made according to Bullock *et al.* (1985) and Stoops (2003) using a binocular magnifying glass to separate domains on the blade, and a petrographic microscope, with increases in magnification of 2.5X to 40X, for the analysis of the groundmass (S-matrix) and pedofeatures.

Scanning electron microscopy analyzes were performed on four samples, which are representative of the different horizons of paleosols.

Interpretations of the groundmass and pedofeatures were based on Delvigne (1998) and Stoops *et al.* (2010).

X-ray diffraction

X-ray diffractometry (XRD) was used to determine mineralogy. It is a particularly useful technique in sedimentology and paleopedology for the characterization of minerals. XRD was performed in thirty representative samples of paleosol horizons and it used the powder method. The analysis followed the methodology proposed by Camargo *et al.* (1986), Jenkins & Snyder (1996) and Pecharsky & Zavalij (2009).

Quantitative analysis

The mineralogical analysis was refined, and the mineral phases were quantified using the Rietveld Method (Jenkins & Snyder 1996, Fabris *et al.* 2009).

The basic principle of the method is the fitting of a diffraction pattern (real) with a theoretical standard (crystalline structure) in order to minimize the difference between calculated and measured points (Jenkins & Snyder 1996). According to Fabris *et al.* (2009), the diffraction pattern's best fit is obtained through the least squares method for all intensity values (y_i), simultaneously from the minimization of the residue (S_y) given by Equation 1:

$$S_y = \sum_i w_i (y_i - y_{ci})^2 \quad (1)$$

Where:
w_i is the weight of each intensity given by $w_i = 1/y_i$,
y_i is the intensity observed in the *i*-th step, and
y_{ci} is the intensity calculated in the *i*-th step, and the sum is over all the points.

The model parameters that can be refined relate to atomic position of occupation sites and thermal switch (Fabris *et al.* 2009, Pecharsky & Zavalij 2009). The most commonly used program functions that model the profiles of reflection peaks are the Gaussian, Lorentzian, Voigt, Pseudo-Voigt and Pearson VII functions (Fabris *et al.* 2009). The refining process continues until "the best adjustment" is reached.

The Rietveld refinement, which aimed at quantifying the minerals, was performed through the X'Pert Highscore Plus v2.0a, using the Crystallographic Information File (CIF) data files, which originated from the Crystallographic Open Database.

RESULTS

The characterization of Facies and paleosols

Conglomerate (Gc, Gm and Gt), sandstone (Sm) and mudstone (Fm) facies, typical of fluvial depositional systems, were described in the sections (A1, A2 and A3) of the Marília Formation (Fig. 4). Sandstones facies (Sm) were described and interpreted as the C horizons of paleosols, because of intense bioturbation and the predominance of massive structures,.

The identification of pedogenic structures (blocky, prismatic and laminar) and root marks, associated with the absence of stratification, the predominance of massive structures and the discontinuity of carbonate cementation on the base of outcrop, were the main factors used to determine that the profiles were predominantly pedological.

In the morphological characterization, paleosols were identified with a Bkm horizon and blocky structures in the Botucatu section (A1), argillics horizons (Btkm and Bt) with prismatic and blocky structures in the Piratininga section (A2), and Btkm and Bkm horizons in the Garça section (A3) with laminar, prismatic and blocky structures (Fig. 4).

The synthesis of macro-morphological characteristics of paleosol profiles is summarized in Table 1.

The profiles also showed horizons (Bkm, Btkm, Bt), pedological structures (blocky, laminar, prismatic) and root marks (Figs. 5 and 6), which gives them the status of paleosols (Andreis 1981, Retallack 2001). Rhizoliths, rhizoconcretions, krotovines and bioturbations also occur in different proportions in the Marília Formation (Figures 5A, 5B, 5C, 5D, 5E).

In addition to these diagnostic features of paleosols, it was noted that the outcrops showed no stratifications, as they displayed massive structures, especially in horizon C profiles.

Micromorphology revealed the predominance of porphyric c/f-related distribution in three sections, with some chitonic, enaulic, and gefuric regions. Features of coatings, infillings, nodules and *microcodium* were identified in the paleosol horizons (Figs. 7, 8 and 9).

Mineralogy

X-ray diffraction identified eight minerals in the paleosol profiles: ankerite, calcite, hydrated halloysite, montmorillonite (bentonite), nontronite, quartz, palygorskite and saponite (Tab. 2).

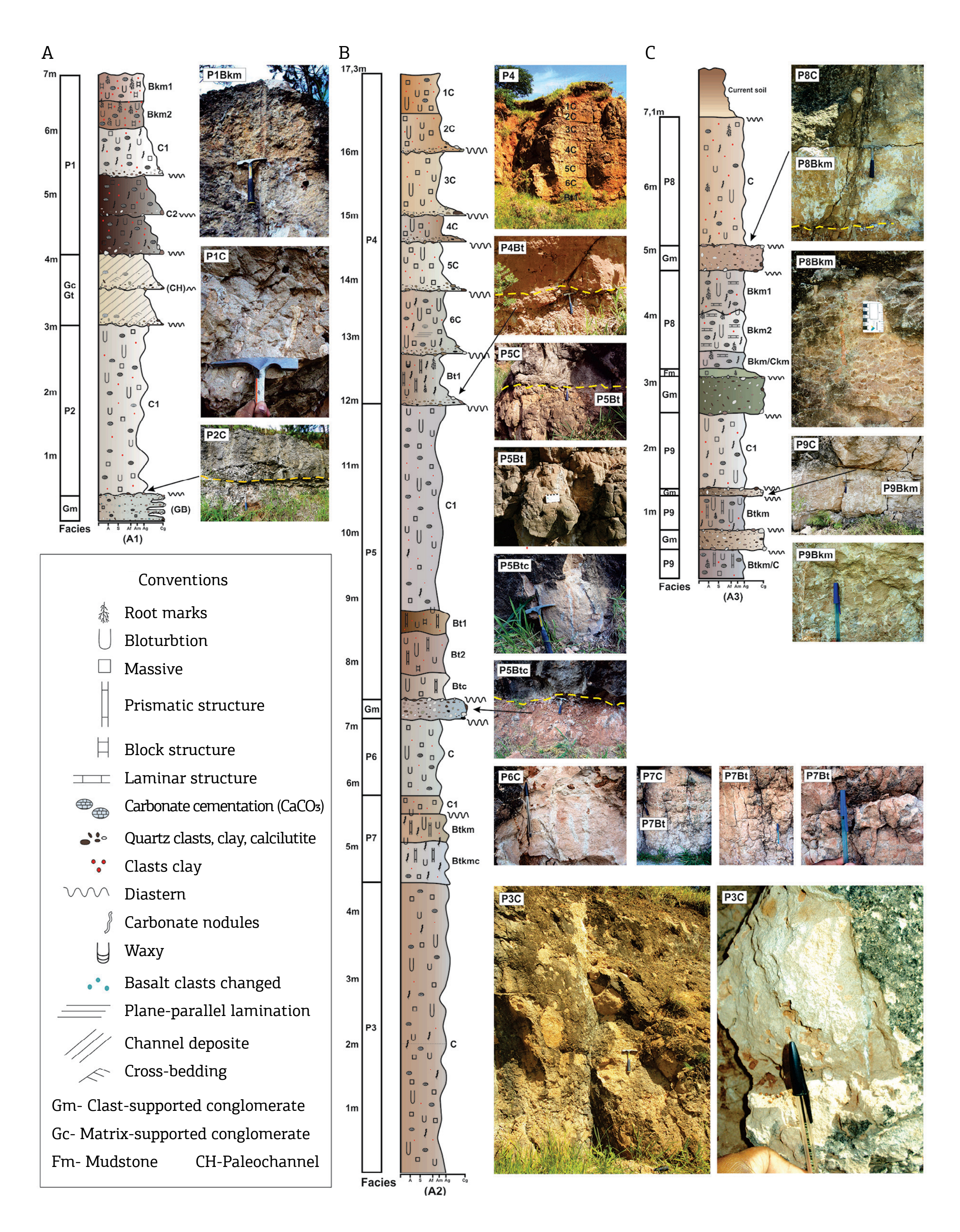

Figure 4. Facies and the macromorphology of paleosol profiles. (A) column with the lithofacies (Gc, Gt, Gm), profiles (P1, P2) and horizons of the Botucatu Section (A1); (B) column with the lithofacies (Gm), profiles (P3, P4, P5, P6, P7) and horizons of the Piratininga Section (A2); (C) column with the lithofacies (Gm, Fm), profiles (P8, P9) and A3 horizons.

Table 1. Summary of morphological characteristics of paleosols in the A1, A2 and A3 sections.

S	PH	Meters	EST	Texture	Colors	B	N	RHCl	TRS
A1	P1Bkm1	0-0.42	EB	Sandy (SP)	10YR 8/1, 2.5YR 5/6, 2.5YR 6/6	A	Cc	Re	SC
	P1Bkm2	0.42-0.81	EB	Sandy (SP)	10YR 8/1, 2.5YR 3/6, 2.5YR 5/8	A	Cc	SR	SG
	P1C1	0.81-1.56	M	Sandy (SP)	10YR 8/1, 2.5YR 5/6	R	CCQ	SR	AS
	P1C2	1.56-2.78	M	Sandy (SP)	10YR 8/1, 5YR 4/6, 5Y 8/6	R	CCQ	Re	-
	P2C1	0-2.65	M	Sandy (SP)	5YR 7/4, 10YR 7/8, 10YR 8/1	A	-	Re	AS
	P2C2	2.65-3.04	M	Sandy (SP)	10YR 8/1, 10R 3/6, 7.5YR 7/8, 5Y 2.5/1	R	-	Re	-
A2	P3C	0-4.50	M	VFF (BS)	5YR 7/4, 5YR 6/8, 2.5YR 4/8, 10YR 8/1	A	SCN	RSR	-
	P4-1C	2.30-2.90	M	FSA (SP)	5YR 7/4, 10YR 8/1	C	CQc	LRN	SC
	P4-2C	2.90-3.50	M	FSA (SP)	5YR 8/3, 10YR 8/1, 2.5YR 5/8	C	FCc	NR	AS
	P4-3C	3.50-4.50	M	FSA (SP)	5YR 8/3, 10YR 8/1, 5YR 7/6	C	FCc	NR	AS
	P4-4C	4.50-4.90	M	FSA (SP)	5YR 8/3, 10YR 8/1, 5YR 7/6	C	Cc	NR	AS
	P4-5C	4.90-5.67	M	FSA (SP)	5YR 7/4, 2.5YR 4/8, 10YR 8/1	C	Cc	NR	AS
	P4-6C	5.67-6.64	M	FCS (SM)	5YR 8/3, 10YR 8/1, 5YR 7/6, 5YR 4/6	A	Cfc	Re	SC
	P4Bt1	6.64-7.42	P	FMS (SMB)	5YR 7/4, 5YR 5/8, 10YR 8/1	CP	Ccn	Re	SG
	P5C1	0-3.20	M	FMS (SMB)	5YR 7/4, 2.5YR 4/8, 10YR 8/1	A	FCc	Re	SG
	P5Bt1	3.20-3.56	PB	FCS (SM)	5YR 7/4, 2.5YR 5/8, 10YR 8/1	A	FCc	LR	SG
	P5Bt2	3.56-4.18	PB	FCS (SM)	5YR 7/4, 2.5YR 6/8, 10YR 8/1	A	Cn	RSR	SG
	P5Btc	4.18-4.59	PM	FCS (SM)	5YR 7/4, 10YR 8/1	A	FCc	Re	-
	P6C1	0-1.19	M	MMS (SM)	5YR 7/4, 5YR 6/8, 10YR 8/1	A	FCc	LR	-
	P7C1	0-0.28	M	FMS (SMB)	5YR 6/6, 5YR 5/6, 2.5YR 4/8, 10R 6/4, 10YR 8/1	C	FCc	LR	AS
	P7Btkm1	0.28-0.72	P	FCS (SM)	5YR 7/4, 2.5YR 5/6, 10YR 8/1	A	Acc	Re	SC
	P7Btkmc	0.72-1.35	PM	FCS (SM)	5YR 7/4, 5YR 8/4, 2.5YR 6/8, 10YR 8/1	F	Acc	RSR	-
A3	P8C1	0.72-2.72	M	MCS (SP)	5YR 7/4, 10YR 8/1, 2YR 7/6	C	Sparse	LR	AS
	P8Bkm1	3.10-3.75	L	Fine sand (SM)	2.5YR 8/1, 2.5YR 7/4	A	Acf	RSR	WC
	P8Bkm2	3.75-4.36	L	Fine sand (SM)	10YR 5/4, 2.5YR 7/4, 10YR 8/1, 10YR 7/8	A	Ccf	Re	SC
	P8Bk/Ck	4.36-4.63	LM	Fine sand (SM)	2.5YR 4/8, 5YR 7/4, 10YR 8/1	R	FC	Re	AS
	P8Ckm1	4.63-5.31	M	-	-	R	-	-	AS
	P9C1	0-1.18	M	FCS (SP)	5YR 7/3, 10YR 8/1, 2YR 7/6	C	Rcf	Re	AS
	P9Btkm	1.29-1.82	P	Fine sand (SM)	5 YR 4/6, 5YR 7/4, 5YR 7/1, 7.5YR 8/6	A	Fsc	RSR	SC
	P9Btkm/C	1.82-2.27	PM	FMS (SM)	5 YR 4/6, 5YR 7/4, 5YR 7/1, 7.5YR 8/6	R	-	Re	AS

S: sections; A1: P1Bkm1, P1Bkm2, P1C1, P1C2, P2C1 and P2C2; A2: P3C1, P3C2, P4-1C, P4-2C, P4-3C, P4-4C, P4-5C, P4-6C, P4Bt1, P5C1, P5Bt1, P5Bt2, P5Btc, P6C1, P7C1, P7Btkm1 and P7Btkmc; A3: P8C1, P8Bkm1, P8Bkm2, P8Bk/Ck, P9C1, P9Btkm and P9Btkm/C; PH: profile and horizon; EST: structure; B: bioturbations; N: nodules; TRS: transition between horizons; EB: blocky; L: laminar; LM: laminar tending to massive; M: massive; P: prismatic; PB: prismatic tending to blocky; PM: prismatic tending to massive; FSA: fine sandy bar to the average; MCS: medium to coarse sand; FCS: fine to coarse sand; VFF: very fine sand to fine; FMS: fine to medium sand; MMS: medium sand; BS: well selected; SP: poorly selected; SM: moderately selected; SMB: good to moderate selection; RHCl: reaction to hydrochloric acid; A: abundant (< 5% of exposed area); C: common (3–5% of exposed area); CP: common to a few (1–5% of exposed area); F: few (1–3% of exposed area); R: rare (< 1% of exposed area); Cc: clay clasts; CCQ: carbonate, clay and quartz clasts; SCN: Sandy clasts with oxide films, nodule $CaCO_3$; CQc: Quartz and clay clasts; FCc: Few clay clasts; Cfc: carbonate, few clay clasts; Ccn: clay clasts and carbonate nodules; Cn: clay nodules; Acc: abundant carbonates, clay clasts; Acf: abundant carbonate, few clay clasts; Ccf: common carbonate, few clay clasts; FC: few carbonates; Rcf: rare carbonates, few clay clasts; Fsc: few carbonates, scarse clay clasts; Re: reactive; RSR: reactive to strongly reactive; SR: strongly reactive; LRN: weakly reactive to nothing; NR: no reaction; LR: weakly reactive; SC: smooth and clear; SG: smooth and gradual; AS: smooth and abrupt; WC: wavy and clear.

Quartz was the predominant mineral, due mainly to a large presence of sandstones in the Marília Formation, followed by calcite and palygorskite. Other mineral phases were present in a lower percentage.

Nontronite, saponite and palygorskite have more than one chemical formula (Tab. 3). Therefore, these phases received different designations (symbols) such as N and N_1, P, P_1 and P_2, or S and S_1 (Tab. 2).

The mineral identification and quantification of the Botucatu, Piratininga and Garça sections (A1, A2 and A3) are compiled in Table 3 and in Figures 10 and 11.

Palygorskite was identified in all of the paleosol profiles. In the profiles with a B horizon of the sections A1, A2 and A3, the percentage of palygorskite was quite variable (Figs. 10, 11 and 12).

The mineralogy of the sections of the Marília Formation showed that, after quartz, calcite was the second most abundant mineral, followed by palygorskite (Tab. 3). The calcite may be inherited or have an authigenic formation. Often it takes up much of the groundmass especially in petrocalcic horizons (featuring calcretes). Some calcretes consist of more than 900 g^{-1} kg of calcite (Allen & Hajek 1989). The high calcite content of the paleosol horizons matched the condition of calcretes, a fact that had already been examined in the field.

Palygorskite was found to be the third most abundant mineral in the horizons and had speciation, indicating changes in the environment during its formation.

Clay minerals of the smectite group (montmorillonite, nontronite, and saponite) were present in low amounts. Bentonite, a type of montmorillonite was present in a

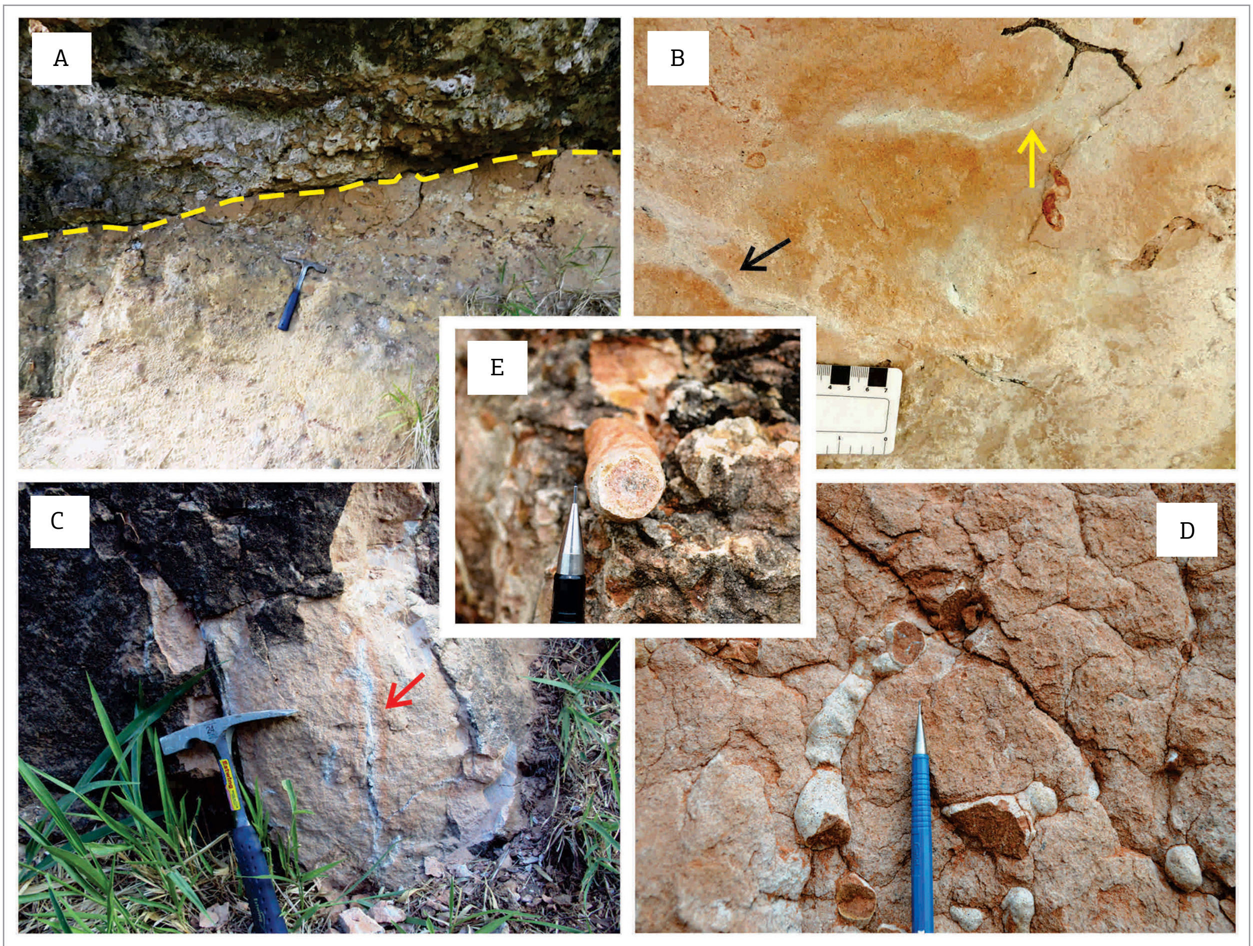

Figure 5. Morphological aspects of paleosol profiles. (A) Horizon base C2 of P (the base does not have $CaCO_3$ cementation indicating if it is a pedogenic calcrete); (B) bioturbations with and without carbonate filler material in the profile 4. The black arrow indicates a rhizolith (a precipitated carbonates tube, which filled former burrows), a common feature in paleosols of the Marília Formation. The rhizoliths are organo-sedimentary structures produced by decomposition and plant root activity (Durand *et al.* 2010). The yellow arrow indicates a krotovine (bioturbation mark filled with other materials) on top; (C) the red arrow indicates a large bioturbation (rhizolith) on the Btc horizon profile 5 with a reduction of halos (white) and oxidation (redder feature); (D) bioturbations in the Bt horizon of the A2 section; (E) Rhizoconcretion present in the Marília Formation.

percentage lower than 1% in the paleosol horizons, and it was not considered for interpretation. The clay mineral halloysite was present in a percentage of 0.5% in the horizon Bt1 of the profile 5, and was also not considered (Fig. 12, Tab. 3).

Smectites can be found in several geological materials and remain in the soils during pedogenesis (Azevedo & Vidal-Torrado 2009). Saponite and nontronite rarely occur in soils. However these smectites can form through hydrothermalism in some types of source materials (Garcia-Romero *et al.* 2005). Regarding the origin of smectites through transformation, we emphasize that smectites can be formed by changes in thestructure and the load on the micas layersso that theydo not cause dissolution and reprecipitation. Smectites can also be formed through the transformation of chrolites, mainly Fe-Mg chrolites. For smectites to form through precipitation from solution, it is necessary to have solutions rich in Si with Mg or Fe (Azevedo & Vidal-Torrado 2009). These authors state that the neoformation of smectites occurs more often in soils with little leaching. Examples include soils formed in drainage-limited or arid locations. These conditions allow for the maintenance of the high ion concentration required for the precipitation of these minerals.

DISCUSSION

Pedogenesis of calcretes

Plenty of calcretes in the Marília Formation records are environments with a semi-arid paleoclimate, because they are rare in arid or humid climates and develop completely in semi-arid climates (Fedoroff & Courty 1989). Another factor that endorses this thesis is the lack of gley horizons associated with calcretes. Generally calcretes from humid climates are associated with horizons of reducing environments, because their position is in relief.

Morphological characteristics led to the interpretation that calcretes are pedogenic, because the profiles showed most of the features inherent to calcretization pedological processes (Pimentel *et al.* 1996, Alonso-Zarza 2003, Wright 2007). Discontinuous carbonate cementation on the basis of the profiles (Figure 5A) and the absence of a pseudogley feature also contributed to the interpretation of calcretes as having a pedogenic origin. Unlike pedogenic calcretes, groundwater calcretes have intense mottling (with gray-green tones), a feature restricted to fracture zones or roots within oxidized horizons, called pseudogley (Pipujol & Buurman 1994, Pimentel *et al.* 1996).

Prismatic and blocky structures recorded in the profile (Figs. 6A, 6C, 6D) are typical products of pedogenesis, and may even be preserved in paleosols of the Paleozoic age (Andreis 1981).

The micromorphologic interpretation of secondary processes, the accumulation of carbonate as recrystallization and replacement, the variety of weathering patterns, root marks, bioturbation, *microcodium*, nodules, the authigenesis of paligorskita, the coating features of carbonates on quartz and coating clay, pisolite and pending calcite (Figs. 7, 8 and 9) supported the hypothesis that the profiles have a pedogenic origin.

Usually *microcodium* is associated with a rizogenic horizon (Kosir 2004). Calcite pendants (pending calcite) are another striking feature of pedogenic calcretes (Manafi & Poch 2012). Microfabric *Beta* type (biogenic/microbial related to the presence of roots, carbonates with cellular factory,

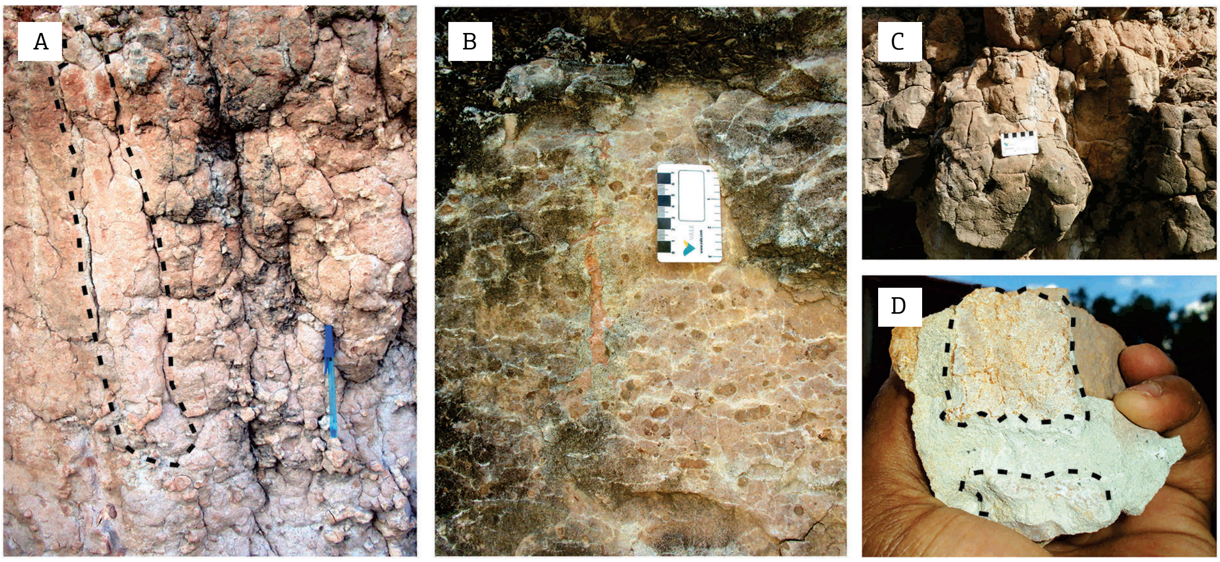

Figure 6. Structures of the Marília Formation paleosols. (A) Prismatic structure Btkm1 horizon (P7), with carbonate nodules; (B) laminar structure profile 8 (P8); (C) blocky structures Bt horizon (P5), especially lots of bioturbation; (D) details of the blocky structures, and carbonate cementation involving *peds* (calcan).

fibrous calcite, *microcodium*), the presence of meniscus structures and pendent cementation are typical and striking features of pedogenic calcretes (Pimentel *et al.* 1996).

Infillings and coatings were common features found in the calcretes (Figs. 7, 8 and 9). Coatings, hypocoatings, quasicoatings and infillings are practically the result of a

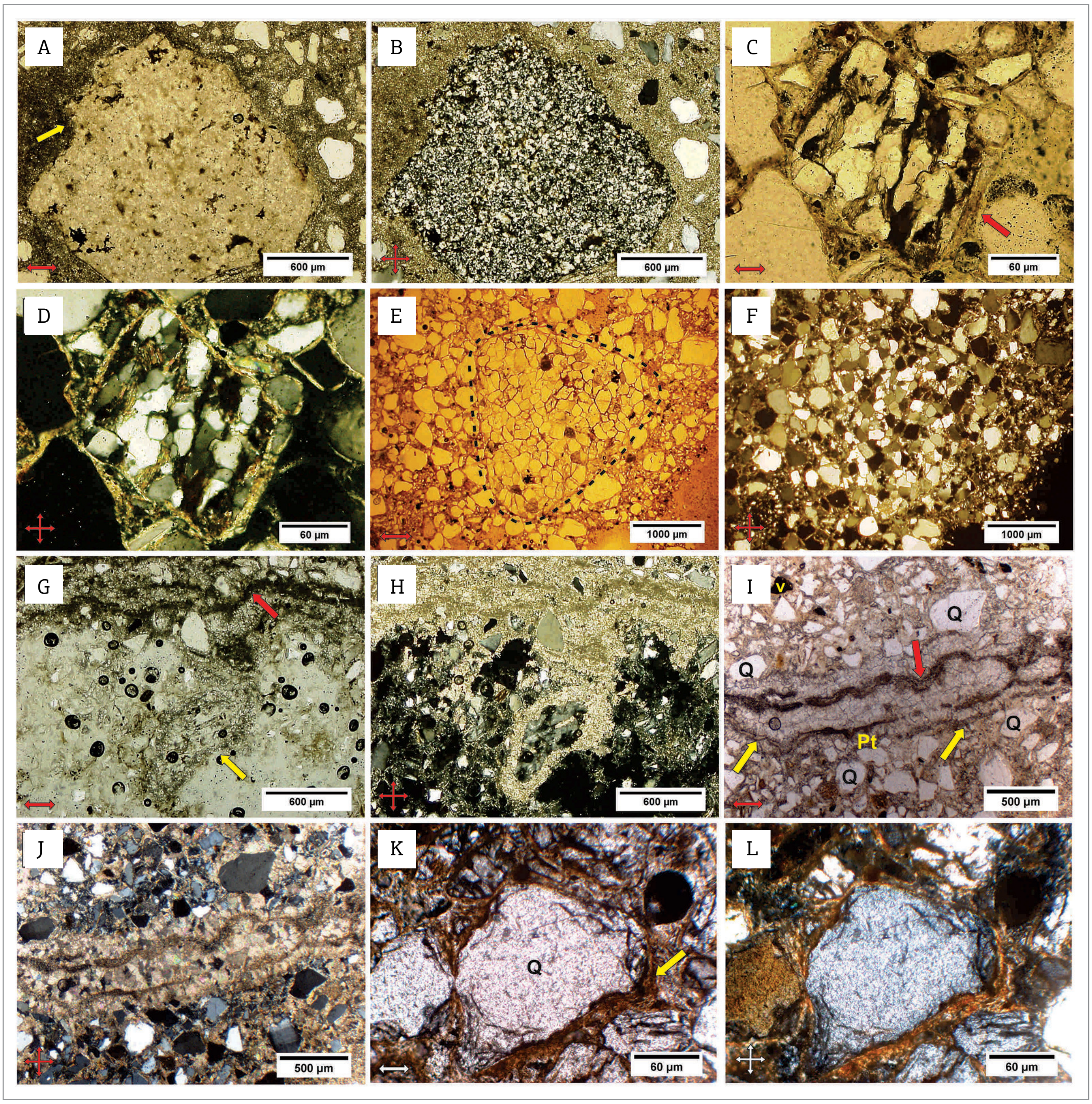

Figure 7. Characteristics of the groundmass. (A) $CaCO_3$ recrystallization process in the C2 horizon (P1), resulting in crystalline pedological features (crystalline pedofeatures) represented by carbonate nodules (yellow arrow); (B) with crossed nicols (NC); (C) simultaneous processes and weathering replacement of the quartz polycrystalline calcite (red arrow) in the Bt1 horizon (P5); (D) with NC. With a polarized light, it is possible to perceive a superimposition process of clayey material (iron oxides) in the carbonate features; (E) bioturbation in the Bt1 horizon (P5) filled by quartz grains (krotovine); (F) with NC; (G) replacement process and bioturbation feature in laminar horizon Bkm1 (P8). There is a change and partial replacement of quartz with microsparitic calcite coating, which is indicated by the yellow arrow. Coating quartz carbonate is a typical feature of soil profiles (Bedelean 2004). The red arrow indicates a calcified root mark, common in rizogenic calcrete; (H) with NC; (I) pendant calcite (Pt) in the Btkm horizon (P9) below the quartz grains (Q) indicated by the arrows; (J) with NC; (K) Feature coating in the Bt2 horizon (P5). The yellow arrow indicates coatings with iron oxides around the quartz grains (Q), typical autochthonous pedological feature; (L) with NC.

pedological formation, a weathering product in situ (Stoops 2008). Figure 7D shows the change and partial replacement of quartz with calcite that has a microsparitic coating, indicated by the yellow arrow. Quartz coating carbonate is a typical feature of soil profiles (Bedelean 2004).

Concentric bands of clay in pisolites (Fig. 8F), resulting from the new formation of clay with Si and Al, and their concentric layers may indicate the control from microorganisms that are associated with the roots (Durand *et al.* 2010).

Calcification-decalcification pedofeatures, common in calcretes of the Marília Formation, are associated with the impregnation of the root tissue and are often observed in semi-arid calcareous soils (Durand *et al.* 2010).

The paleoenvironmental significance of clay mineralogy

Mineral phases and mineralogical measurements allow for the comparison of paleosol profiles and a discussion on the evolution of the Marilia Formation (Fig. 12, Tab. 3). According to

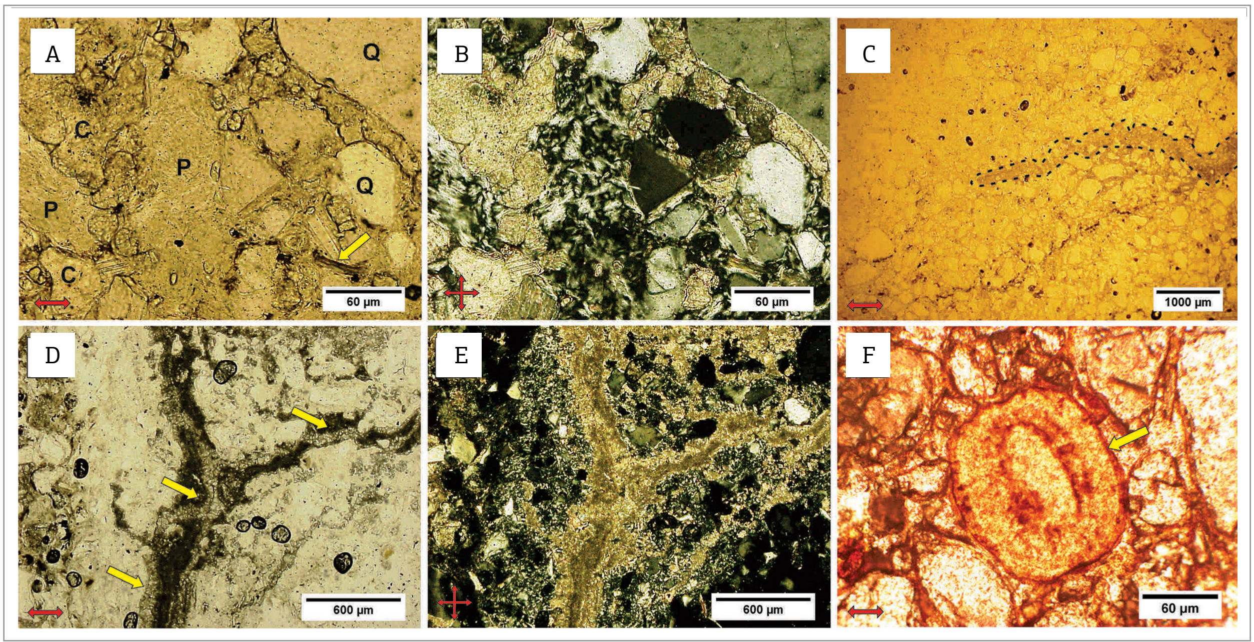

Figure 8. Features of the groundmass. (A) Chronology in the Bkm horizon (P1). The chronology revealed that palygorskite (P) precipitated in the paleosol void, as a secondary mineral. The yellow arrow indicates weathered biotite; (B) with NC; (C) crystalline pedofeature, represented by the root mark (rhizolith $CaCO_3$) in the Bk/Ck horizon (P8); (D) *Microcodium* in the Bkm1 horizon profile 8 (arrows); (E) with NC; (F) pisolite shows concentric rings of iron-containing material (Bt1 horizon of P5), with natural light (LN or PPL). The yellow arrow also shows clay with iron oxides coating the pisolite.

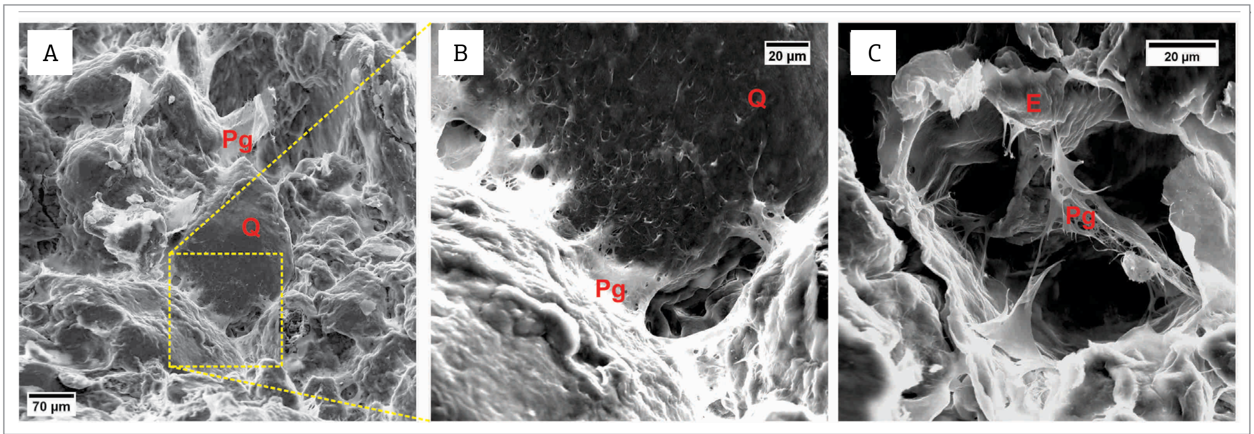

Figure 9. C1 horizon (P3) SEM. (A) Authigenesis of palygorskite (Pg), coating grains of quartz (Q) and calcite; (B) detailed palygorskite (Pg) in the form of aggregate of entangled fibers coating the quartz grain (Q); (C) the formation of palygorskite (Pg) through changing smectite (E). It is possible to observe palygorskite in the form of aggregate filling the voids intertwined fibers, a typical feature of paleosol (Singer 2002).

Table 2. Phase minerals found in three sections (A1, A2 and A3).

Mineral Phase	2θ (CuKα)	d (Å)	I (%)	Mineral Phase	2θ (CuKα)	d (Å)	I (%)
Ankerite (A) Reference Code: file PDF-3 01-084-2066 of ICSD	23.976	3.70855	14	Quartz (Q) Reference Code: file PDF-3 01-086-1629 of ICSD	39.522	2.27836	7.4
	30.804	2.90032	100		40.373	2.23223	3.4
	37.257	2.4115	13.9		42.548	2.12306	5.2
	40.989	2.20013	19.5		45.892	1.97583	2.8
	44.908	2.01682	8.6		50.227	1.81497	11
Calcite (C) Reference Code: file PDF-3 01-072-1652 of ICSD	23.069	3.85229	9.8		55.396	1.65722	1.6
	29.452	3.03034	100		57.367	1.60488	0.2
	31.547	2.83367	2.1	Quartz (Q) Reference Code: file PDF-3 01-083-0539 of ICSD	20.827	4.26171	21.7
	35.966	2.495	13.9		36.488	2.4605	6.5
	39.429	2.28351	18.4		50.046	1.82111	11.3
	43.164	2.09415	14.5		59.857	1.54395	7.9
	47.646	1.9071	18.4	Palygorskite (P) Reference Code: file PDF-3 00-021-0550 of ICSD	8.495	10.4	100
	48.58	1.87258	19.3		13.913	6.36	14
	56.559	1.62588	3.2		16.402	5.4	10
	57.401	1.60402	8.8		19.846	4.47	20
Hydrated Halloysite (H) Reference Code: file PDF-3 00-029-1489 of ICSD	8.836	10	100		24.165	3.68	16
				Palygorskite (P_1) Reference Code: file PDF-3 01-082-1873 of ICSD	22.493	3.94967	12.6
Montmorillonite - Bentonite (M) Reference Code: file PDF-3 00-003-0015 of ICSD	5.887	15	100		25.726	3.46018	4.2
					27.439	3.24789	0.6
					35.681	2.51427	3.3
					41.256	2.18648	2.2
					51.872	1.76123	1
Nontronite (N) Reference Code: file PDF-3 00-029-1497 of ICSD	5.81	15.2	100	Palygorskite (P_2) Reference Code: file PDF-3 00-005-0099 of ICSD	8.414	10.5	100
	19.801	4.48	55		27.594	3.23	100
					34.331	2.61	80
Nontronite (N_1) Reference Code: file PDF-3 00-002-0017 of ICSD	6.008	14.7	100	Saponite (S) Reference Code: file PDF-3 00-029-1491 of ICSD	5.697	15.5	100
Quartz (Q) Reference Code: file PDF-3 01-086-1629 of ICSD	20.904	4.24612	21.2	Saponite (S_1) Reference Code: file PDF-3 00-005-0068 of ICSD	5.734	15.4	100
	26.686	3.3378	100				
	36.627	2.4515	7.3				

2θ (CuKα): annulus 2 Theta, in a vertical Bragg-Brentano geometry, operating with copper tubes (λ = 1.54Å) in Kα radiation originating from the innermost K layer of the target metal atom. d (Å): "d" spacing (interatomic distance) of the mineral. I (%): peak intensity of mineral phases.

Meunier (2005), mineralogical compositions that are associated with smectite, sepiolite and palygorskite, reveal a diagnosis of the soils' arid to semi-arid conditions. Calcite ($CaCO_3$) is a very common mineral in soils from dry regions.

However, blocky, prismatic and laminar structures at different B horizons (Bkm, Btkm Bt) (Figs. 4 and 6, Tab. 3) indicate changes in the environment, mainly with regard to the degree of moisture, weathering and leaching.

Table 3. Quantification of minerals in percentage using Rietveld refinement (Sections A1, A2 and A3).

S	PH	(%)								
		Calcite	Quartz	Palygorskite	Montmorillonite	Ankerite	Nontronite	Saponite	Halloysite	Total
A1	P1Bkm1	60.3	22.2	17.5						100
	P1Bkm2	73.9	16.5	9.6						100
	P1C1	53.1	30.9	16						100
	P1C2	43	19.2	17.5		20.3				100
	P2C1	23.9	31.5	13.4		31.2				100
	P2C2	51	18.1	14.5		16.4				100
A2	P3C1	41.3	41.9	10.2			6.6			100
	P3C2	24.2	58.8	16.6	0.4					100
	P4-1C		70.4	29.6						100
	P4-2C		74.8	25.2						100
	P4-3C		77.5	22.5						100
	P4-4C		85.5	14.5						100
	P4-5C		77.6	22.4						100
	P4-6C		77.9	22.1						100
	P4Bt1		70.2	9.8			20			100
	P5C1		73.9	25.7	0.4					100
	P5Bt1		79.2	20.1	0.7					100
	P5Bt2		61.1	12.6				26.3		100
	P5Btc		47.5	23.7				28.8		100
	P6C1		72.6	27.4						100
	P7C1	46.8	35.6	17.6						100
	P7Btkm1	33.8	43	22.7					0.5	100
	P7Btkmc	43.6	44.6	11.8						100
A3	P8C1	22.5	60.7	16.8						100
	P8Bkm1	54.1	34	11.9						100
	P8Bkm2	37.4	44.2	18.4						100
	P8Bk/Ck	13.6	57.6	22.1			6.7			100
	P9C1	39.8	41.8	17.7	0.7					100
	P9Btkm	16.1	37.4	27.1				19.4		100
	P9Btkm/C	5.6	46.7	18.1				29.6		100

S: sections; A1: P1Bkm1, P1Bkm2, P1C1, P1C2, P2C1 and P2C2; A2: P3C1, P3C2, P4-1C, P4-2C, P4-3C, P4-4C, P4-5C, P4-6C, P4Bt1, P5C1, P5Bt1, P5Bt2, P5Btc, P6C1, P7C1, P7Btkm1 and P7Btkmc; A3: P8C1, P8Bkm1, P8Bkm2, P8Bk/Ck, P9C1, P9Btkm and P9Btkm/C; PH: profile and horizon.

The environmental significance of calcite and quartz

Pedogenic calcretes are formed from the secondary accumulations of $CaCO_3$ in well-differentiated horizons on a macro and microscopic scale. The progressive $CaCO_3$ accumulation on the pedogenic profiles is indicated by different morphological stages (Gile *et al.* 1966, Bachman & Machette 1977). These stages vary according to the availability of the calcium ion, the organisms' activity, the relationship between precipitation/evapotranspiration, the time of the evolution and the type of parent material.

According to Birkeland (1999), the formation of carbonatic horizons in the soil is strongly dependent on moisture availability. Pedogenic carbonate accumulations are common in Holocene soils in regions where the climate is warm and seasonally dry most of the year. Seasonally dry climates with an average annual precipitation from 100 to 500 mm favor the formation of calcareous horizons in soil profiles (Birkeland 1999).

The calcite content in the Marília Formation ranges from 22 to 53% in the profiles with a C horizon. In profiles with the Bkm horizon, the calcite ranges from 37 to 73%. The content of calcite in paleosol profiles with Bt and Btkm horizons ranges from 16 to 33% (Fig. 12, Tab. 3).

According to Allen & Hajek (1989), calcite content increases with the depth of soil profiles in dry regions, due to dissolution in the upper part of the profile and subsequent precipitation in the lower portion. This increase in carbonate content with profile depth characterizes most soils in dry regions, except for those in areas without a source of carbonates (Allen & Hajek 1989). Excluding the Bkm horizons, there was an increase in the calcite content in the C horizons (Fig. 12), according to Allen & Hajek (1989).

The presence or absence of calcic horizons in paleosols is usually evidence of dryness (Tanner 2010). Hubert (1978) indicated a well-developed calcrete in alluvial deposits in the Hartford Basin (Upper Triassic) as evidence of a

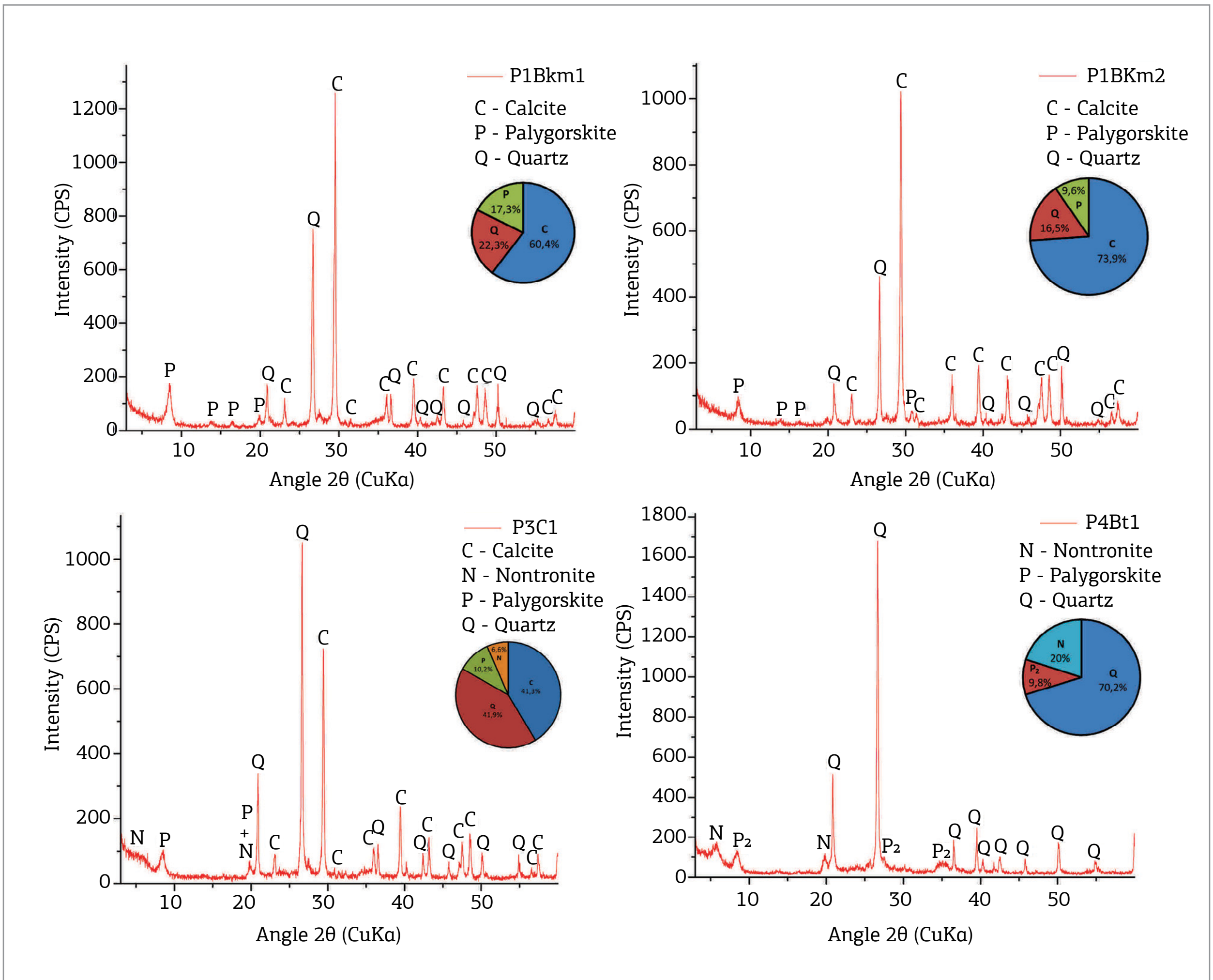

Figure 10. XRD patterns with a quantitative analysis using the Rietveld refinement of the profile 3 of the Piratininga (P3C1) section and profiles with the B horizon of the Botucatu (P1Bkm1, P1Bkm2) and Piratininga (P4Bt1) sections.

semi-arid climate, with an average annual precipitation of 100–500 mm.

Allen & Hajek (1989) state that carbonates are also common components of soils in humid regions. Carbonates may occur as components inherited from immature profiles that have developed in highly calcareous materials, usually in small geomorphic surfaces. The authigenic precipitation of soils in humid areas occurs on the capillary fringe, where the water table underlies calcareous

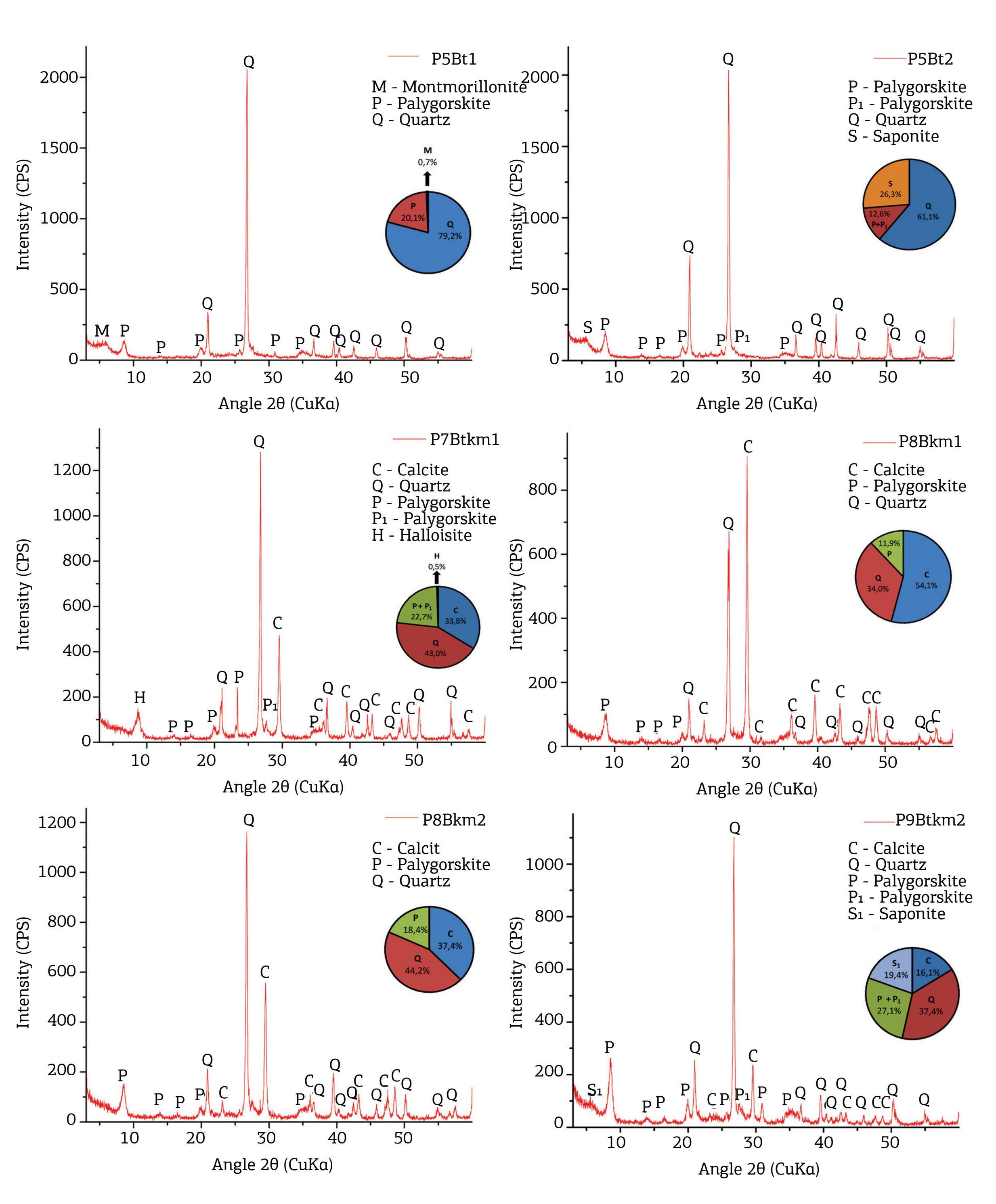

Figure 11. XRD patterns with quantitative analysis using the Rietveld refinement of profiles with a B horizon from the Piratininga (A2) and Garça (A3) sections.

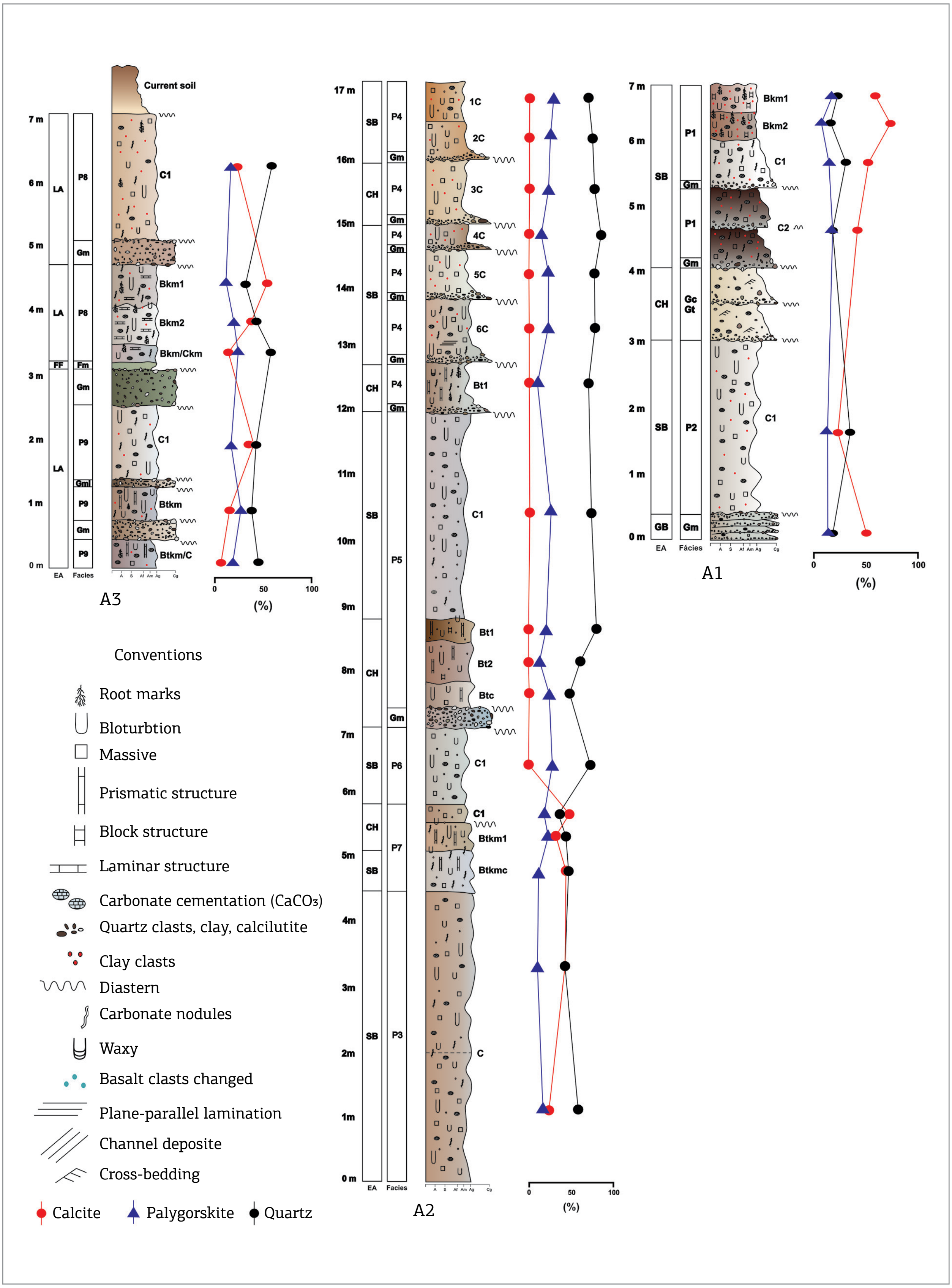

Figure 12. Percentage variation of quartz, calcite and palygorskite in the A1 (Botucatu), A2 (Piratininga) and A3 (Garça) sections of the Marília Formation. The columns on the left (7 m, 17 m and 7 m) of each section (A1, A2 and A3) represent the facie associations and the architectural elements (EA).

sediments. Carbonates can also precipitate in soils from humid regions, from water percolation on slowly permeable materials, or with contact between materials with highly contrasting permeability. Calcretes from humid climates are mostly associated with reducing environments, due to their relief position. Moreover, calcretes are rare in arid and humid climates and predominant in semi-arid climates (Fedoroff & Courty 1989). The absence of Bg (gley) horizons associated with a Bk horizon, as observed in the study area, discards the hypothesis of humid climate conditions for the calcrete formation environment. The discontinuity of carbonates is another factor supporting the hypothesis and evidence of the calcretes' pedogenic origin.

Mineralogical analysis combined with a field characterization provides enough information to define the Marília Formation calcretes as pedogenic. Maoski (2012) concludes that a large percentage of the calcretes of the Marília Formation (Echaporã Member) have a pedogenic origin.

Although mineralogy reveals general semi-arid conditions during the genesis of paleosols in the Marília Formation, local and regional moisture variations were also identified (Fig. 12). The variation in calcite percentage (from 5.6 to 60.3) showed semi-arid conditions for the profile horizons 1, 2, 3, 7 and 8 (P1, P2, P3, P7 and P8) and humid conditions for the profile horizons 4, 5, 6 and 9 (P4, P5, P6 and P9). There was a significant increase in the percentage of calcite in paleosols with a Bkm horizon compared to Btkm and Bt horizons (Fig. 12, Tab. 3). The increase of calcite in the Bkm horizon implies changes in environmental conditions, such as an increase of leaching, precipitation and desilication processes, which leads to a climate with less arid characteristics.

Khormali & Abtahi (2003) affirm the coexistence of carbonate pedogenic nodules with palygorskite and illuvial clay coatings in calcite crystals in the argillic horizon of aridisols in central Iran. These nodules suggest a link between pedogenetic carbonate, palygorskite and the argillic horizon, which formed when the climate was wetter than present day. Bt horizons of the profiles 4 and 5 (P4 and P5) and Btkm of the profile 9 (P9) represented in figure 5 are in agreement with this statement.

In the paleosols of the Marília Formation, the occurrence of carbonates associated with group 2: 1, clay minerals (such as smectites) and sepiolite-palygorskite are common, especially in the C horizon.

However the variation in the quartz content indicates higher percentages in the C horizons and desilication in the B horizons (Fig. 12, Tab. 3).

The environmental significance of palygorskite

Palygorskite was identified in all of the horizons of the nine profiles in the Marília Formation (Fig. 12). Palygorskite and sepiolite are associated with dry soils of arid environments, alkaline pH and relatively high concentrations of Mg and Si (Birkeland 1999). According to the author, the accumulation of carbonates also facilitates the formation of these minerals. However, Fedoroff & Courty (1989) state that palygorskite is not formed in very arid or desert environments, such as the Sahara Desert. According to the authors, authigenic palygorskite is mainly formed in semi-arid environments.

The palygorskite content decreased from bottom to top in the outcrops (A1, A2, and A3). There is no progressive calcite increase in the Bt1 horizons of the profile 4 (P4) and Bt2 of the profile 5 (P7). This may be related to the increase in the precipitation rate and more leaching. An increase in palygorskite content associated with the increasing calcite was found in the Bkm1 horizon (P1) and the profiles 7 and 8 (P7 and P8). This corroborates the thesis that general semi-arid environmental conditions were present during the formation of the paleosols profiles (Fig. 12). The presence of palygorskite in these horizons suggests that semi-arid conditions and low levels of precipitation are required for stability and permanence in this environment. Palygorskite remains stable at an average annual precipitation below 300 mm (Birkeland 1999). For Paquet & Millot (1972). Palygorskite becomes an unstable mineral and turns into smectite in soils that are subjected to an annual precipitation of greater than 300 mm.

Palygorskite and sepiolite were considered rarities in the soils (Allen & Hajek 1989). However as the authors emphasized, these minerals have been reported with increasing frequency as soil components in dry regions in the last three decades. Palygorskites are much more common in pedogenic environments than sepiolites and tend to persist in calcic horizons, in dry places and in environments with very little leachate (Allen & Hajek 1989).

The origin of these clays in the soil is attributed mainly to:

- The inheritance of sedimentary rocks or lacustrine deposits associated with eolian materials;
- Pedogenic neoformation (Allen & Hajek 1989).

Bigham et al. (1980) concluded that sepiolite in soils was derived from lacustrine materials, while palygorskite probably originated from pedogenic materials. Birkeland (1999) states that although palygorskite were originally considered to be a mineral inherited from clays, recent studies have left little doubt as to their pedogenic origin. Palygorskite and sepiolite, although not common in soil or regolith, occur in calcrete and carbonate regolith. These clay minerals are rich in magnesium and are considered by many to be authigenic, as they are closely related to the regolith carbonate formation processes (Chen & Eggleton 2002).

Pedogenic palygorskite and sepiolite occur almost exclusively in soils with dry, ustic and aridic humidity regimes and in climates where the potential evapotranspiration far exceeds the precipitation. In these conditions, the most common clay minerals associated with pedogenic palygorskite are smectite, illite, and interstratified minerals (Singer 2002). According to the author, palygorskite is particularly common in modern soils in North Africa and the Middle East. In the Marília Formation paleosols, palygorskite was associated with smectite and calcite minerals (Fig. 12, Tab. 3).

The results found in this research corroborate previous studies performed in the Marília Formation. Lepsch *et al.* (1977) considered that the presence of palygorskite in sandstones of the Bauru Group was due to relatively high contents of MgO in sediments. For Arakel & McConchie (1982), the smectite and sepiolite found in calcretes are in situ weathering products and reflect the periodic transition between periods of high energy and periods of slow deposition and calcretization. Suguio & Barcelos (1983a, 1983b) described the palygorskite and smectite group as common clays minerals in this area.

Ribeiro (2001) noticed the occurrence of palygorskite, cementing hardened layers of soils ("palicrete") in the Marília Formation sandstones. Barison (2003) highlighted the Quintana and Herculândia regions, where strong carbonate cementation occurs and is associated with palygorskites in quartz-sandstones of the Marília Formation. In Piratininga, a region with lineaments (Fig. 1), there are palygorskites that occur in conjunction to smectite. Palygorskite also occurs nearby basalt outcrop areas, such as near Araçatuba. For Espinosa & Millán (2003), the occurrence of palygorskites indicates dry climates, with 50 to 100 mm of annual precipitation. Durand *et al.* (2006) argued that palygorskite would imply a maximum annual precipitation of 300 mm. Fernandes (2010) found coatings of palygorskite and/or sepiolite in the Marília Formation and suggested that it is an important indicator of arid and semi-arid climates.

The Marília Formation's palygorskite, which occurs in conjunction with calcite and smectite, is pedogenic. It is newly formed or appears as a result of changes in smectites. The speciation of this mineral, as identified in the diffractograms (Figs. 10 and 11, Tab. 3), may show different concentrations of Mg, Si, and Al in solution at the moment of precipitation. These characteristics indicate more than one type of palygorskite in the unit.

2: 1 minerals and their significance in the paleosols of the Marília Formation

The nontronite found in the C (P3C1 and P8Bkm/Ckm) and B (P4Bt1) horizons of the paleosols, was the result of chemical weathering of 2: 1 dioctahedral clay (Azevedo & Vidal-Torrado 2009). The nontronite can be formed by hydrothermal weathering in volcanic rocks or on the ocean floor (Hiller 1995). The saponite of the profile 5 (Bt2 and Btc) and 9 (Btkm and Btkm/C) is a result of the smectite trioctaedral mineral, and can be inherited or formed by hydrothermalism (Garcia-Romero *et al.* 2005, Azevedo & Vidal-Torrado 2009).

We affirm the existence of a possible new formation from smectite minerals, particularly due to the high SiO_2 content found in all of the paleosols profiles (Tab. 3), the necessary conditions for the stability of calcite, and alkaline pH. According to Azevedo & Vidal-Torrado (2009), the new formation of smectite occurs more often in soils with poor leaching, usually in limited drainage sites or arid climate, conditions which enable the maintenance of a high concentration of ions necessary for the precipitation of these minerals.

Often neogenic minerals tend to form in the surface layers of the soil profile, but in the case of smectite, the highest content can be found in the deepest horizons, with a decreasing trend toward the surface, where the weathering conditions were stronger (Azevedo & Vidal-Torrado 2009). Smectite was found mostly in the C horizon while nontronite was common in the profile 8 Bkm/Ckm horizon, but not on the Bkm horizon, which is more superficial than the last.

Watts (1980), studying calcretes in Botswana, observed that montmorillonite is often associated with immature or friable calcrete. Gardner (1972) in Nevada (USA) noted that montmorillonite is very common in friable calcrete horizons and often absent or rare in calcrete horizons dominated by palygorskite. This feature was observed and proven in some of the Marília Formation paleosols, because of an absence of 2:1clay minerals (Figs. 10 and 11, Tab. 3). For Maoski (2012), the whitish crust of hard calcretes in the Marília Formation could be primarily related to the increase in the proportion of cement in the carbonate rock, partial leaching of iron and/or because of the substitution of smectite palygorskite in alkaline medium.

The presence of 2:1 clay minerals possibly formed by precipitation (neoformation), is indicative of semi-arid environmental conditions with poor leaching, a fact demonstrated by the high percentage of quartz in the diffraction patterns (Fig. 12, Tab. 3).

The genesis of the paleosol horizons in a paleoclimatic context during the Maastrichtian of the Bauru Basin

Based on the characterization of paleosols and the mineralogical interpretation of the profiles, we defined three climatic phases during the Maastrichtian of the Bauru Basin, with variations in precipitation, leaching and carbonation (Fig. 13).

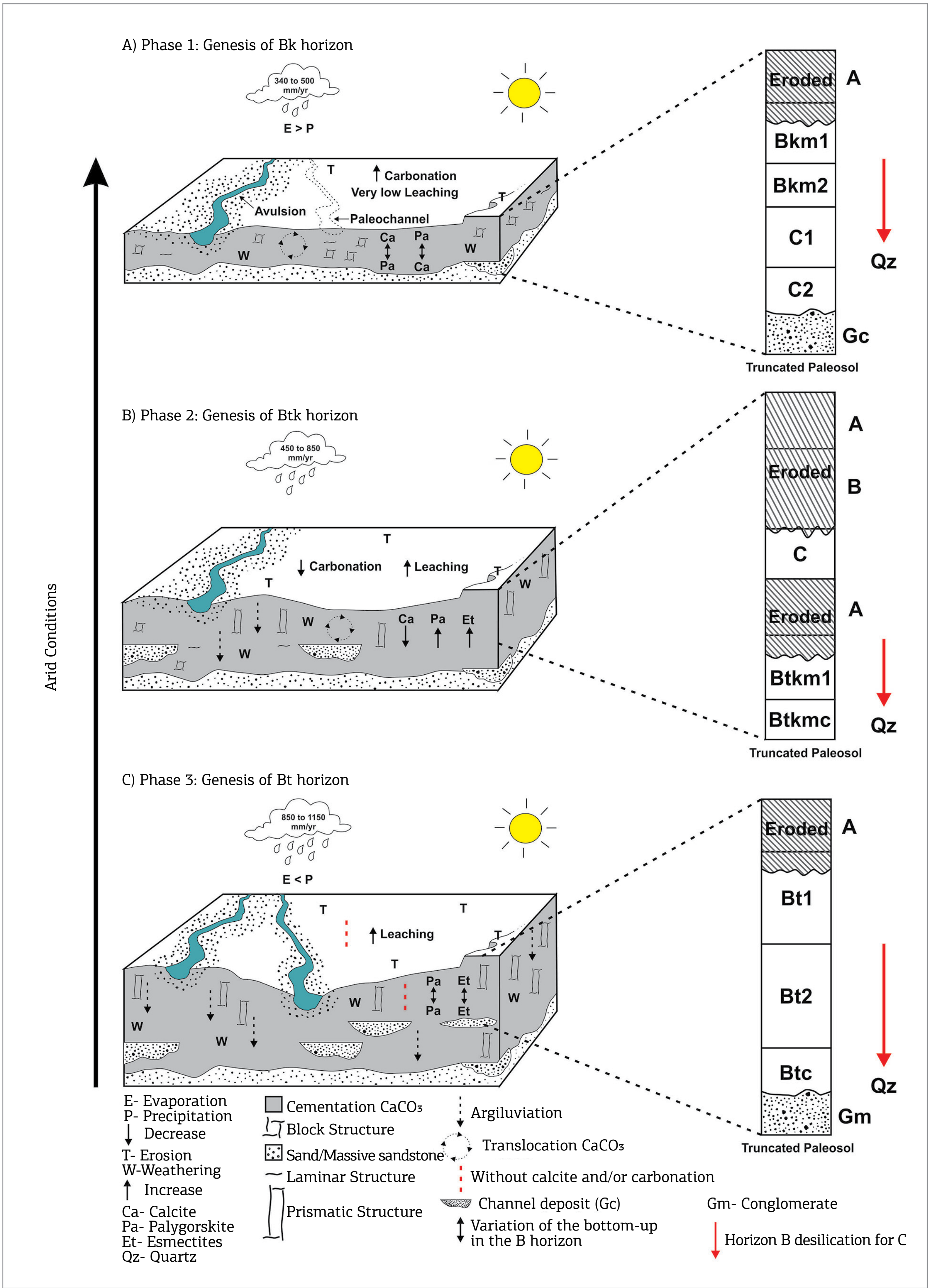

Figure 13. Climate evolution model based on the mineralogy of the profiles for the paleosols of the Marília Formation, Maastrichtian of the Bauru Basin.

Phase 1 (Fig. 13A) consists of the driest conditions, with low precipitation. The intense calcification processes during this phase led to the genesis of paleosols with a Bk horizon, different stages of development, and cementation degrees. The inverse proportional relationship between the contents of calcite and palygorskite and desilication define the Bk horizon at this stage.

Phase 2 (Fig. 13B) marks an increase in precipitation and leaching rates, and a decrease in the calcification process, generating conditions for the formation of a Btk horizon. In this phase, there is an increase in palygorskite and smectites percentages and a decrease in calcite content.

The scarcity of calcite and variations of palygorskite and smectite contents define phase 3 (Fig. 13C). Due to an increase in the precipitation and leaching processes, the conditions for the development of Bt horizons were established.

These results and interpretations complemented and corroborated the conclusions made by Silva *et al.* (2017). Through micromorphological studies, Silva *et al.* (2017) suggested that climatic cyclicity or changes in the hydrology of the Bauru Basin occurred during the Maastrichtian. The studies showed, in light of the micromorphological analysis, three moments or stages in the genesis and evolution of the paleosols (Silva *et al.*, 2017).

Using mineralogical, geochemical and morphology indexes, Silva *et al.* (2015) defined different evolutionary stages for the paleosols of the Marília Formation. The paleosols with a Bt horizon were the most weathered, which is indicative of periods with high precipitation rates and leaching during the Maastrichtian of Bauru Basin. In turn, the paleosols with Bkm horizons had the lowest weathering rates, and therefore, reveal moments of high aridity in the Marília Formation (Silva *et al.* 2015, 2017).

FINAL REMARKS

Based on the field characterization and mineralogical analysis, we were able to define the calcretes of the Marília Formation as being predominantly pedogenic. The discontinuity in the concentration of carbonates at the base of the profiles was an obvious factor from the field, which demonstrated the pedological origin of the calcretes. As such, we indicate the semi-arid climate during the Maastrichtian of the Bauru Basin since there is no relationship between Bk and Bg horizons in the paleosols. The variation in the calcite content and the heterogeneity of subsurface horizons (Bkm, Btkm, and Bt) suggest less arid climatic conditions locally and regionally, and thus an increase in the process of leaching, precipitation, and desilication. The variation in the percentage of quartz along the profiles also indicates higher rates of leaching and desilication in the paleosols' B horizons relative to the C horizons.

The palygorskite associated with calcite under favorable conditions of carbonate accumulation also indicate the occurrence of a semi-arid environment during the Maastrichtian in the Marília Formation. The decrease in palygorskite content without the progressive increase of calcite indicates a rise in precipitation rates and leaching. The increase in both minerals confirms the hypothesis predicting general semi-arid environmental conditions in the formation of paleosol profiles. The absence of sepiolite associated with palygorskite legitimizes the pedogenic origin of calcretes.

Palygorskite, whether formed or transformed, and associated with calcite and smectite, was interpreted as having originated from a pedological environment, under warm and dry conditions that are necessary for mineral stability. The speciation of palygorskite revealed different concentrations of Mg, Si and Al in solution at the time of its precipitation or its transformation from smectite.

The presence of 2:1 clay minerals in possibly neophormed paleosol profiles emerges as another indication of semi-arid environmental conditions with possibly poor leaching, and little evidence of desilication, a fact highlighted by a high percentage of quartz, especially in the C horizons of paleosols.

Regional and local variations in rainfall rates, leaching, and carbonation favored the genesis of paleosols with Bkm, Btkm and Bt horizons, at different times of paleoclimatic evolution in the Marília Formation.

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