The influence of ancient soil biota on the precipitation and distribution of pedogenic carbonate in paleosols of the Marília Formation (Upper Cretaceous, Brazil)

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ABSTRACT

In arid and semi-arid climates, soil development is strongly influenced by seasonal patterns and biogenic activity, and often results in pervasive pedogenic horizons consisting of highly concentrated carbonate. In Brazil, such horizons enriched in calcium carbonate are common and relatively well-studied in paleosols of the Upper Cretaceous Marília Formation. However, detailed analyses on the sequence of mineral precipitation phases and the role of organisms in these processes are still lacking. The present work describes eight argillic and calcic horizons characterized by different degrees of carbonate accumulation. Argillic horizons show translocation clay structures and weak to moderate cementation by calcium carbonate. Calcic horizons contain moderate to high carbonate accumulations ranging from powdery coatings to nodular masses of micrite. Carbonate distribution in these horizons is preserved largely as carbonate-cemented macropores produced by such ichnofossils as *Planolites*, *Taenidium*, *Naktodemasis*, *Skolithos*, *Palaeophycus* and calcareous rhizocretions. Moreover, stable isotope data, respired soil CO₂ function, and cathodoluminescence (CL) of the paleosol samples were used to evaluate soil paleovegetation, paleoproductivity, and the distinctive stages of calcite precipitation. Stable isotopic analysis suggests that paleovegetation cover in the paleosols was predominantly C₃-photosynthesizing plants. The relationship between bioturbation indices and soil respiration suggests a positive pattern of paleoproductivity controlled by higher moisture conditions and the increased activity of soil fauna. Finally, CL imaging shows that there were multiple stages of carbonate precipitation with both α -type and β -type fabrics that are interpreted as abiotic and biotic processes during pedogenesis.

1. Introduction

The spatial distribution of carbonate accumulations in soil horizons under arid to subhumid conditions is controlled by such parameters as soil moisture, soil pCO₂, temperature, topography, soil-dwelling organisms and texture (Gile et al., 1966; Machette, 1985; Meyer et al., 2014; Zamanian et al., 2016). The role of organisms in the precipitation and accumulation of calcium carbonate has been documented by many authors (e.g., Klappa, 1980; Jaillard, 1987; Wright, 1990; Jaillard et al., 1991; Verrecchia and Verrecchia, 1994; Verrecchia et al., 1995; Canti, 1998; Kosir, 2004; Cunningham et al., 2008). Plants and

microorganisms in particular induce calcite precipitation in active or passive ways through metabolic process that generate different biogenic features (Wright et al., 1996; Kosir, 2004; Alonso-Zarza et al., 2008; Zhou and Chafetz, 2009; Verrecchia, 2011). While much research into the plant-induced concentration of CaCO₃ has focused on modern soils and Quaternary paleosols (e.g., Gocke et al., 2011; Gocke and Kuzyakov, 2011; Kosir, 2004; Sun et al., 2020), there is a smaller body of work examining more ancient paleosols and the paleoenvironmental and paleoclimatic information they can provide (e.g., Cerling, 1991; Wright et al., 1995; Kraus and Hasiotis, 2006). In addition, the burrows, nests, and tunneling of such soil-dwelling invertebrates as termites, bees, ants,

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wasps and earthworms produce soil macropores and permeable pathways that increase horizontal and vertical fluid flow and also act as nucleation sites for carbonate precipitation (Canti, 1998; Cunningham et al., 2009; Smith et al., 2011; Genise, 2017).

In the last two decades, paleosols of the Marília Formation (Upper Cretaceous, Bauru Basin, Brazil, have been the focus of diverse studies regarding their paleoenvironmental and paleoclimate aspects, as well as abiotic influences on the distribution of calcium carbonate (e.g., Basilici et al., 2009; Dal' Bó et al., 2009; Dal' Bó et al., 2010; Basilici et al., 2016; Dal' Bó et al., 2018; Delgado et al., 2019; Batezelli et al., 2019). In addition, Nascimento et al. (2019) and Rodrigues et al. (2019) recognized the importance of plant root metabolism in the distribution of carbonate in the paleosols. Despite an abundance of ichnofossils associated with paleosols and other facies in the Marília Formation (Silva et al., 2017; Nascimento et al., 2019; Rodrigues et al., 2019), few studies have suggested a large role for ancient soil biota in the development and distribution of calcic horizons in the ancient soil profiles.

This paper describes the direct, and sometimes indirect, influence of organisms, mainly invertebrates and roots, on the precipitation and distribution of pedogenic carbonate in argillic and calcic horizons of three pedotypes from the Echaporã Member of the Marília Formation. Additionally, the paleovegetation and paleosol biota, paleoproductivity of horizons and the identification of the different stages of calcite precipitation and biogenic structures are recognized and compared with

other Late Cretaceous examples. These methods, never before applied in the Bauru Basin, suggest that biogenic processes were the primary driving mechanism in the precipitation of pedogenic carbonate in paleosols of the Marília Formation.

2. Geological setting

The Bauru Basin is an intracratonic Mesozoic basin in southern Brazil that developed during the breakup of the Gondwana supercontinent (Fig. 1; Fernandes and Coimbra, 1996). The basin is the result of thermal and lithostatic subsidence subsequent to large basaltic effusion (Serra Geral Formation) in the Early Cretaceous (Fernandes and Coimbra, 1996; Theide and Vasconcelos, 2010). This basin is approximately 370,000 km² in area and has an elliptical shape with its long axis aligned in a northeasterly direction (Fernandes, 1998). Sedimentary deposits in the Bauru Basin have a maximum thickness of ~300 m and are subdivided into the Caiuá and Bauru groups (Fernandes and Coimbra, 1996). The Bauru Group is stratigraphically composed of the Araçatuba, Adamantina, Uberaba and Marília formations (Soares et al., 1980; Barcelos and Suguio, 1987; Batezelli, 2015). The Marília Formation is Maastrichtian in age (Dias-Brito et al., 2001) and is composed mainly of very fine- to medium-grained sandstone with rare conglomeratic sandstone and mudstone beds (Soares et al., 1980). According to Barcelos and Suguio (1987), the Marília Formation is subdivided into three

Fig. 1. Schematic geological map of the research area (modified from Batezelli, 2015). The location of the studied outcrops is indicated by pink stars. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

lithostratigraphic members: Ponte Alta, Serra da Galga and Echaporã; of which only the Echaporã Member is exposed in the study area (Fig. 2). The Ponte Alta and Serra da Galga members are geographically restricted to the northeastern limit of the basin and only crop out in Minas Gerais State. Recently, Soares et al. (2020) proposed a new stratigraphic division for this geographic area, in which the Serra da Galga Member (sensu Barcelos and Suguio, 1987) is lithostratigraphically considered a formation.

The Echaporã Member is ~160-m-thick and is composed of fine- to medium-grained sandstone intercalated with rare conglomerate bodies. In the northwestern part of the Bauru Basin, this member has been interpreted as eolian sand sheet deposits (Basilici et al., 2009; Basilici and Dal' Bó, 2010; Dal' Bó et al., 2010) and as distal deposits of distributive fluvial systems in the southeastern portion (Basilici et al., 2016). Basilici et al. (2009), Dal' Bó et al. (2009), and Basilici and Dal' Bó (2010) indicated that around 66% of the sedimentary thickness of the Echaporã Member consists of paleosols, while the remainder is comprised of interbedded fluvial and eolian deposits. These authors described several paleosol profiles and ascribed them to five soil orders: Aridisols, Alfisols, Entisols, Vertisols and Inceptisols. In the study area, Dal' Bó et al. (2009) and Silva et al. (2019) described Aridisols or Calcisols profiles (sensu Mack et al., 1993) characterized by high concentrations of calcium carbonate in B horizons, forming calcic and petrocalcic horizons. The concentrations of calcium carbonate were interpreted to be mainly derived from airborne dust inputs of CaCO₃ particles (Dal' Bó et al., 2009) in a regional arid to semi-arid paleoclimate.

3. Materials and methods

This study was carried out in three localities of the São Paulo State: in the Avencas district (22°15'24"S;50°04'05"W); Monte Alto municipality (21°18'11"S;48°30'16"W); and Garça municipality (22°13'46"S;49°40'20"W) (Fig. 1, inset polygons in detail). The outcrops described herein represent well-exposed successions of paleosols with prominent calcium carbonate accumulation in pedogenic horizons. The profiles are grouped in three pedotypes composed of paleosols with similar physical and chemical properties (Retallack, 1994). Each pedotype represents a unique set of horizons within the study area.

Fig. 2. Chronostratigraphic chart of the Bauru Basin modified from Bazzoli (2015).

Paleosols were recognized in the field based on soil structures, horizonation, rhizoliths, and textural variations (Catt, 1990; Retallack, 2001). Paleosol horizon descriptions follow the recommendations of Schoeneberger et al. (2012). Paleosol taxonomy is referred to US Soil Taxonomy (Soil Survey Staff, 1999). Pedogenic carbonate concentrations are reported in accordance with the morphogenetic stages proposed by Gile et al. (1966) and Machette (1985). Invertebrate trace fossil and rhizolith identifications are based on in situ outcrop observation followed by comparison with ichnofossils previously described in the literature. The bioturbation index (BI) description includes the size analysis, density, amount of trace fossils overlapping and sharpness of primary sedimentary structure (Taylor and Goldring, 1993; Taylor et al., 2003). Oriented samples from calcic paleosol horizons were collected for petrographic and geochemical characterization (Table 1).

Detailed micromorphological analysis was done using 20 thin sections, according to descriptive methods of Bullock et al. (1985) and Stoops et al. (2010). Primary constituents were quantified according to Gazzi-Dickinson method (Zuffa, 1985) and classified in McBride (1963) compositional diagram. Carbonate mineral species were identified with a solution of potassium ferricyanide and Alizarin Red-S (Dickson, 1965). Ten thin sections with different pedogenic carbonate features were described under cathodoluminescence (CL). The CL was operated with an electron source CITL MK 5–2, operating 12 kV, 215 µA in vacuum (<0.050 mBar), linked in the microscope Scope A1 Zeiss, located in Laboratory of Sedimentary Geology, Federal University of Rio de Janeiro (Table 2).

Two samples of calcic horizons were selected for X-ray CT scans to evaluate the internal arrangement of biogenic structures. The scans were done in Nuclear Instrumentation Laboratory (LIN-COPPE/UFRJ, Brazil) using a Skyscan 1173 (Bruker system) and processed in Dragonfly software (version 2.0). Stable isotopic analyses were performed on ten samples collected using a dental drill in rhizoliths and carbonate coatings from calcic horizons of the three pedotypes. Stable carbon and oxygen isotopes were measured using a Kiel IV Carbonate Devise and a Delta V Plus – Isotope Ratio Mass Spectrometer (Thermo Scientific), the results of which were expressed as parts per thousand (‰) differences from the Vienna Pee Dee Belemnite (VPDB) standard. One internal lab (LGQM/UERJ, Brazil) standard of the Calcite ($\delta^{13}\text{C} = +2.429\text{‰}$, $\delta^{18}\text{O} = -9.855\text{‰}$, relative to VPDB) and one international standard IAEA-C-01 ($\delta^{13}\text{C} = +2.492\text{‰}$, $\delta^{18}\text{O} = -2.400\text{‰}$, relative to VPDB) were used to calibration, with analysis accuracy of 0.04‰ to $\delta^{13}\text{C}$ and 0.08‰ to $\delta^{18}\text{O}$.

3.1. $\delta^{13}\text{C}$ of CO₂ in soil and partial pressure of respired CO₂ calculation

Carbon isotope composition of the CO₂ in soil ($\delta^{13}\text{C}_s$) was calculated using the isotopic composition of pedogenic calcite and calcite formation temperature, according with Romanek et al. (1992) (Table 3), given by:

$$C_s = \frac{C_c + 1000}{\frac{(11.98 - 0.12T)}{1000} + 1} - 1000 \quad (1)$$

where, C_c is carbon isotopic composition of soil carbonate and T (°C), is mean annual temperature derived from salinization (S) molar ratio, following the equation ($R^2 = 0.37$; S.E. = ± 4.4 °C) (Sheldon et al., 2002) (Table 3):

$$T = -18.5S + 17.3 \quad (2)$$

The isotopic pattern of terrestrial plants was attributed to isotopic composition of soil CO₂ (C_s), in which generally reflects the respiration of roots, microorganisms plus the kinetic isotopic effects and transport of CO₂ through the soil profile, which results in the enrichment of plant-derived CO₂ by 4.4‰ compared with soil-respired CO₂.

Partial pressure of respired CO₂ (Pr in ppmv) is a function which is related with original depth to calcic horizons (Ds) ($R^2 = 0.80$, S.E. ± 893 ppmv) (Retallack, 2008, 2009). The calculation of the original depth to

Table 1

Macromorphological properties of eight pedogenic horizons selected from Avenças, Monte Alto and Garça pedotypes.

Locality	Pedotype	Profile	Horizons	Thickness(cm)	Boundary	Color	Pedogenic structure	BI (%)
Marília	Avenças	1	Btk1	20	Abrupt/Smooth	10R 4/8	Subangular Blocky	50
		5	5Btk3	27	Abrupt/Wavy	5YR 8/4	Subangular Blocky	50
		5	5Bkk2	45	Abrupt/Wavy	7.5R 8/4	Subangular Blocky	70
		6	6Bkk3	70	Clear/Wavy	7.5Y 7/4	Subangular Blocky	70
Monte Alto	Monte Alto	2	2Bkk1	10	Clear/Wavy	2.5YR7/4	Angular Blocky	70
		3	3Bkk2	28	Gradual/Wavy	2.5YR 7/4	Subangular Blocky	65
Garça	Garça	4	4Btk2	25	Gradual/Wavy	2.5YR 5/8	Prismatic	50
		5	5Bk3	45	Clear/Wavy	2.5YR 5/8	Subangular Blocky	55

Table 2

Calcite precipitation stages in the argillic and calcic horizons of the Avenças, Monte Alto and Garça pedotypes.

Cement stages	Description	Pedotypes and horizons
S1	Brightly luminescent micrite	Avenças: Argillic (Btk1/5Btk3); Calcic (5Bkk2/6Bkk3) Monte Alto: Calcic (2Bkk1/3Bkk2) Garça: Argillic (4Btk2); Calcic (5Bk3)
S2	Dull-luminescent bladed calcite	Avenças: Argillic (Btk1/5Btk3); Calcic (5Bkk2/6Bkk3) Monte Alto: Calcic (2Bkk1/3Bkk2) Garça: Argillic (4Btk2); Calcic (5Bk3)
S3	Dull-luminescent micrite	Avenças: Argillic (Btk1/5Btk3); Calcic (5Bkk2/6Bkk3) Monte Alto: Calcic (2Bkk1/3Bkk2) Garça: Argillic (4Btk2); Calcic (5Bk3)
S4	Brightly luminescent microspar	Avenças: Calcic (5Bkk2/6Bkk3) Monte Alto: Calcic (2Bkk1/3Bkk2)
S5	Nonluminescent sparry calcite	Avenças: Argillic (Btk1/5Btk3); Calcic (5Bkk2/6Bkk3) Monte Alto: Calcic (2Bkk1/3Bkk2) Garça: Argillic (4Btk2); Calcic (5Bk3)
S6	Sparry calcite zoning	Avenças: Argillic (Btk1/5Btk3); Calcic (5Bkk2/6Bkk3) Monte Alto: Calcic (2Bkk1/3Bkk2)
S7	Brightly luminescent sparry calcite	Avenças: Argillic (Btk1/5Btk3); Calcic (5Bkk2/6Bkk3) Monte Alto: Calcic (2Bkk1/3Bkk2) Garça: Argillic (4Btk2); Calcic (5Bk3)

calcic horizons use compaction estimates of Aridisols, proposed by [Sheldon and Retallack \(2001\)](#) (Table 3).

$$Pr = 66.7Ds + 588 \quad (3)$$

$$Ds = \frac{Dp}{\left[\frac{-0.62}{0.38} \frac{e^{0.17K} - 1}{e^{0.17K} + 1} \right]} \quad (4)$$

Where Dp (in cm) is depth of calcic horizons in paleosols and K (in km) is burial depth ([Sheldon and Retallack, 2001](#)).

4. Results

4.1. Parent material

Paleosols within the Echaporã Member of the Marília Formation developed primarily on fluvial sandstone deposits ([Basilici et al., 2016](#)). The deposits consist of fine- to medium-grained sandstone with planar-parallel and cross lamination, and rare low-angle cross-stratified sandstone beds. The sandstone is moderately sorted and composed of sub-angular to sub-rounded clasts of quartz, lithic fragments and feldspars ([Fig. 3](#)). In thin section, the sandstones are lithic sub-arkose ([McBride, 1963](#)) composed of mono- and polycrystalline grains of quartz, K-feldspar, plagioclase, muscovite and igneous and metamorphic rock fragments. The deposits form tabular isolated or amalgamated bodies, 5 to 10 m thick and characterized by basal planar erosive surfaces and flat tops showing maximum lateral extent of 10 m. The sandstone bodies are interpreted as in-channel deposits with associated floodplain elements.

4.2. Pedotypes

The Avenças pedotype ([Fig. 4A](#)) comprises six stacked polygenetic paleosol profiles, 0.6–7 m thick, whose complete sequence of horizons includes Bw/Bt/Btk/Bk/Bkk/Ck/Cr. The distinctness of the horizons

Table 3

Data used to calculate paleovegetation and paleoproductivity patterns.

Pedotype	Horizon	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	Na ₂ O (%)	K ₂ O (%)	Al ₂ O ₃ (%)	Na ₂ O+K ₂ O/Al ₂ O ₃	T (°C)	Burial depth (K)	Depth Bk (cm)	$\delta^{13}\text{Cs}$	$\delta^{13}\text{C}$ of plant CO ₂	Soil CO ₂ (ppmv)
Avenças	Btk1	−7.4	−6.52	0.08	0.99	3.87	0.31	11.5	0.085	25	−17.8	−22.2	2270
	5Btk3								0.086	30			2606
	5Bkk2								0.088	80			5972
	6Bkk3	−7.7	−6.0	0.07	0.81	2.47	0.40	9.8	0.09	85	−18.3	−22.7	6310
Monte Alto	2Bkk1	−7.8	−5.9					9.8	0.09	85	−18.4	−22.8	
		−7.8	−5.8					9.8	0.09	85	−18.4	−22.8	
		−8.0	−6.5	0.40	1.44	5.41	0.41	9.7	0.074	105	−18.7	−23.0	7645
		−8.1	−5.7					9.7	0.074	105	−18.7	−23.1	
Garça	3Bkk2	−7.9	−6.7					9.7	0.074	105	−18.5	−22.9	
		−8.1	−6.9	0.41	1.92	6.6	0.41	9.5	0.075	100	−18.8	−23.2	7309
	4Btk2								0.049	45			3604
	5Bk3	−7.8	−6.4	0.21	2.01	5.32	0.47	8.5	0.051	80	−18.5	−22.9	5952
		−7.6	−6.6					8.5	0.051	80	−18.3	−22.7

Fig. 3. Petrographic classification of the fluvial sandstone deposits. (A) Detrital composition of sandstone plotted on the McBride (1963) diagram. (B, C) Fine to medium-grained and moderately sorted sandstone from Avencas, Monte Alto and Garça parent material pedotypes. Lithic fragments (Lh), microcline (MI), quartz (Qz) and albite (Al). Cross polarized light.

boundaries is clear, abrupt or gradual and their topography is smooth or wavy. The B horizons are divided into Bw, argillic (Bt, Btk) and calcic (Bk, Bkk). The texture is predominantly sandy, but loamy-sand also occurs, and the colors range from red (10R 4/8) to pink (5YR 8/4) or light pink (7.5R 8/4). Pedogenic structures are fine to medium, angular to subangular, blocky peds and medium to coarse, prismatic partings in which clay coatings sometimes cover the ped faces. The Ck and Cr horizon is 15 to 45 cm thick, sandy in texture, light pink in color (7.5R 8/4) and structureless. The carbonate concentration is heterogeneous among the horizons, being weak in Bw and Bt, medium in Bk, Btk and Ck, and strong in Bkk. Their occurrence is associated mainly with calcareous rhizcretions, invertebrate traces and laminar structures.

The Monte Alto pedotype (Fig. 4B) consists of three compound paleosols, 0.2–2.9 m thick, and shows sequence of Bw/Bt/Btk/Bk/Bkk horizons. The distinctness and topography of the horizons boundaries are clear to abrupt and smooth or wavy, respectively. The texture is loamy-sand on argillic (Bt and Btk) and sandy on Bw and calcic horizons (Bk and Bkk). The paleosol colors are red (2.5YR 4/8) and light reddish brown (2.5YR 7/4) with fine to medium, angular and subangular blocky peds in Bw, Bt and Btk horizons. Clay coatings on grains and peds are less prevalent in Bt horizons. Calcium carbonate concentration varies from weak (<5%) to strong (≥60%) in Bt to Bkk horizons, respectively. Their occurrence is associated with calcareous rhizcretions.

The Garça pedotype (Fig. 4C) consists of a succession of five poly-genetic profiles, 5.5 m thick, and shows a sequence of Bw/Bt/Btk/Bk/Bkk/Bkkm/BC/Ck horizons. The distinctness is clear to abrupt and topography is smooth and wavy. The texture is loamy-sand on argillic (Bt, Btk) and sandy on Bw, calcic (Bk, Bkk) and petrocalcic (Bkkm) horizons. The paleosol colors are red (2.5YR 5/8), pink (2.5YR 8/3), and light pink (2.5YR 7/8) with a fine to medium, angular and subangular blocky, and medium prismatic peds. The Ck and B/C horizon are 25 and 30 m thick, pebbly and sandy in texture, pink (2.5YR 8/3) in color and structureless. The horizon is cemented by calcium carbonate and displays carbonate nodules of 0.8 to 2 cm in diameter, covering up to 10% of the horizon surface. The secondary carbonate varies from weak (<5%) in Bt to very strong (≥80%) in Bkkm horizons, and occur with

nodules, rhizoliths, invertebrate traces and laminar structures.

4.3. Carbonate accumulation in pedogenic horizons

4.3.1. Macromorphological features

Three argillic and five calcic horizons (Fig. 4A, B, C) were selected for detailed analyses of the different forms of calcium carbonate accumulation and distribution: Btk1, 5Btk3, 5Bkk2 and 6Bkk3 from Avencas pedotype; 2Bkk1 and 3Bkk2 from Monte Alto pedotype; and 4Btk2 and 5Bk3 from Garça pedotype (Table 1).

The argillic horizons (Btk1, 5Btk3 and 4Btk2) (Fig. 5A, B, G) are 15–27 cm thick, loamy sand in texture and red (10R 4/8; 2.5YR 5/8) in color. The pedogenic structures are fine to medium, subangular to angular blocky peds and medium prismatic partings with rare clay coatings. The carbonate concentration varies from 20% to 50% in Btk horizons, occurring in calcareous rhizcretions, root calcified laminae and invertebrate burrows (Fig. 6A, B, C), being attributable to the stage II of Machette's (1985) classification. Carbonate in trace fossils show slightly to moderately concentration, composed of powdery micritic or sparry calcite. Horizontal root laminae are comprised of sparry calcite 0.3–0.5 cm in length, in some cases, the intersection of lamination caused distinctive fine interlacing (Fig. 5B). The intensity of bioturbation varies from 50 to 55% and trace diversity is low, represented by *Skolithos*, *Planolites*, *Naktodemasis*, and calcareous rhizcretions.

Calcic horizons (5Bkk2, 6Bkk3, 2Bkk1, 3Bkk2, 5Bk3) (Fig. 5C, E, H) are 10–70 cm thick, pink (7.5YR 7/4), light pink (7.5YR 8/4), and red (2.5YR 5/8) in color. Horizons are structureless or very rarely show medium subangular blocky structure. The carbonate content of the paleosols varies from powdery coatings to micritic masses up to 60% of the total volume in horizons with abundant calcareous rhizcretions and corresponding to stage III of Machette (1985) (Fig. 6D, E, F). The rhizcretions form coalescent structures of 10–30 cm in diameter, with micrite and sparry calcite cementation (Fig. 5F). The bioturbation index is 70% and the ichnofossils are calcareous rhizcretions, *Planolites*, *Skolithos* and *Palaeophycus*.

Fig. 4. Sedimentary logs and schematic diagram showing the distribution of bioturbation structures in the studied horizons of Avenca (4A), Monte Alto (4B) and Garça (4C) pedotypes.

Fig. 5. Macromorphological features of the argillic and calcic horizons. (A, B) Btk1 horizon displaying loamy-sand texture, red color (10R 4/8) and calcarious rhizcretion (Rh). (C) Calcarious rhizcretion (Rh). (D) General view of 6Btk3 horizon (red dotted lines). (E) General view of 2Btk1 horizons (yellow dotted lines). (F) Coalescent calcarious rhizcretion (Rh). (G) 4Btk2 horizon characterized by loamy-sand texture and carbonate coatings covering pedogenic structures. Bioturbation structures are *Naktodemasis* (Nk) and *Planolites* (Pl). (H) *Planolites* (Pl) and *Skolithos* (Sk; red dotted lines) preserved in the 5Btk3 horizon, showing horizontal and vertical tubes, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4.3.2. Paleosol ichnology

Continental ichnofossils provide important information about depositional environments, paleohydrology, paleoclimate, and ancient soil biodiversity (e.g., Hasiotis, 2002; Hasiotis et al., 2007; Smith et al., 2008a). The calcic horizons of Avenca, Monte Alto and Garça pedotypes contain such continental ichnofossils as calcarious rhizcretions and the actively and passively filled burrows of soil-dwelling invertebrates.

Calcareous rhizcretions (Fig. 4A, B, C): Vertical and subvertical, linear and downward branching accumulations of white to gray, powdery to solid calcite. Calcareous rhizcretions range from 1 to 15 cm in length and 0.2–6 cm in diameter. Rhizcretions are abundant in all argillic and calcic horizons (Fig. 5B, D, F). Moreover, in the Btk1, 5Btk3

and 5Btk3 horizons, they form horizontal, 0.2–1 cm of thick calcite laminae that branch off the rhizoliths and are composed of spar calcite. Calcareous rhizcretions form when carbonate precipitates around a root or cluster of the fine roots (Klappa, 1980; Kraus and Hasiotis, 2006) and occur in alluvial, palustrine, lacustrine and eolian environments (Hasiotis, 2002; Frey et al., 2002; Alonso-Zarza et al., 2008).

Actively filled burrows (Fig. 5H): contain evidence of displacement with internal structure or meniscate sediment packets. They are horizontal to subvertical, unlined, cylindrical tubes, simple, unbranched, up to 8 cm long and 1 cm in diameter. Backfilled sediment is typically the same as the surrounding matrix and arranged in meniscate packets. Burrows composed of tightly-spaced and thick, meniscate backfill

Fig. 6. Computed tomography (CT) images showing the density contrast between carbonate concentrations and paleosol matrix. (A) Vertical and transversal sections of calcareous rhizocretions (yellow arrow) and rhizogenic horizontal laminae (orange arrows) in 4Btk3 horizon of the Garça pedotype. (B, C) Calcium carbonate cementation inside of calcareous rhizocretions (yellow arrow). (D) Vertical and transversal calcareous rhizocretion (yellow arrow) and horizontal tube of invertebrate (orange arrows) in 2Bkk1 horizons of the Monte Alto pedotype. (E, F) Dense carbonate concentration in calcareous rhizocretions (yellow arrow) and horizontal burrow (orange arrows). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

packets are characteristic of the ichnotaxon *Taenidium* isp. (D'Alessandro and Bromley, 1987; Keighley and Pickerill, 1994). Burrows composed of a nested series of overlapping, asymmetrical- and ellipsoid-shaped cells that are themselves filled with thin menisci are assigned to the ichnotaxon *Naktodermasis* isp. (Smith et al., 2008b). Other actively filled burrows showing smooth walls, are unlined and filled with materials different from the host rocks are classified as *Planolites* isp. (Pemberton and Frey, 1982). *Taenidium* isp. and *Planolites* isp. Occur in the Btk1, 5Btk3, 5Bk3 and 4Btk2 horizons, *Naktodermasis* isp. is limited to the 3Btk1 horizon.

Passively filled burrows (Fig. 5G): are characterized by homogenous fill or crystalline spar fill and are 4–20 cm long and 0.5–2 cm wide. Two ichnogenera were recognized based on differences in their orientation, differential weathering and the presence or absence of linings. Lined, straight to slightly curved, horizontal to subvertical and unbranched burrows were assigned to *Palaeophycus* isp. (Pemberton and Frey, 1982; Keighley and Pickerill, 1995), whereas *Skolithos* isp. (Alpert, 1974) is characterized by unlined, subvertical to vertical, and unbranched burrows. Both *Palaeophycus* isp. and *Skolithos* isp. Occur in the 5Bk3 and 4Btk2 horizons.

4.3.3. Micromorphological features

Fifteen representative thin sections of argillic (Btk1, 5Btk3 and 4Btk2) and calcic (5Bkk2, 6Bkk3, 2Bkk1, 3Bkk2 and 5Bk3) horizons were described in detail regarding their aspects of pedality, coarse/fine (c/f) ratio, b-fabric, clay coatings, pedogenic calcium carbonate and biogenic structures. The argillic horizons exhibit weakly to strongly developed, enaulic c/f related distribution, parallel-striated, granostriated and calcitic crystallitic b-fabric, angular and subangular blocky structures, simple to complex voids and a coarse texture of fine- to medium-grained sand (Fig. 7A, B). The parental material is classified as lithic sub-arkose, according to McBride (1963) and the patterns of alteration of lithic fragments, K-feldspar, plagioclase and muscovite vary from 0 (0–2.5%) to 3 (75–97.5%) (Stoops et al., 1979). The argillaceous material is organized as clay coatings, with parallel orientation and extinction and having capping, pendant and link capping morphologies. Furthermore, two biogenic features are observed in the argillic horizons: a) rhizocretions, 3–20 mm, circular to sub-circular in diameters; and b) *Taenidium*, characterized by simple tubes filled with sandy menisci in longitudinal sections. Pedogenic carbonate occurs as micritic, microsparitic or sparry calcite concentrated within and adjacent to rhizocretions, engulfing quartz, feldspar and mica grains, and in fractures (Fig. 7A).

Fig. 7. Micromorphology of the studied horizons. (A) Void of the 6Bkk3 horizon filled with coarsely crystalline calcite and fractured rounded quartz grain (left side) filled with micrite. Plane-polarized light. (B) Subangular blocky structures cut by rhizogenic laminae (yellow arrows) within 4Btk3 horizon. Cross polarized light. (C) Cross section of calcareous rhizocretion of the 2Bkk1 horizon. Plane-polarized light. (D) Cross section of *Planolites* isp. (yellow dotted lines) showing clay fill (orange arrows) in the Btk1 horizon. Plane-polarized light. (E) Calcareous rhizocretion of the 2Bkk1 horizon showing four internal zones: a, central hollow filled by sparry calcite; b, alveolar-septal micrite; c, sand grains cemented by micrite; d, sparry and microsparitic calcite bordering rhizocretions. Cross polarized light. (F) Aggregates of grains attributed to calcified cortical cells developed within rhizocretions of the 2Bkk1 horizon. Plane-polarized light. (G) Corn-cob *Microcodium* within 5Bkk2 horizon. Plane-polarized light. (H) Obtuse rhombohedra forming bladed calcite surrounding lithic fragment and quartz grains in the 6Bkk3 horizon. Cross polarized light. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Calci horizons show weakly developed, enaulic c/f-related distribution, calcitic crystallitic b-fabric, angular blocky structures, simple and complex voids, and a texture of fine- to medium-grained sand. The parent material is lithic sub-arkose following McBride (1963), and the patterns of alteration of minerals and rock fragments vary from 0 (0–2.5%) to 3 (75–97.5%) (Stoops et al., 1979). The argillaceous material is organized in two types of coatings: capping and link capping. In comparison to argillic horizons, the calci horizons present an increase of biogenic activity (Fig. 7C). The ichnofossils are: a) rhizocretions with 2–15 mm, circular to sub-circular in diameters; and b) *Planolites*, distinguished by simple tubes in transversal section partially filled with clay minerals (Fig. 7D). The 5Bkk2, 6Bk3k, 2Bkk1, 3Bkk2 and 5Bk3 horizons present 50–80% of pedogenic carbonate. The pedogenic

carbonate occurs as micritic, microsparitic and sparry calcite concentrated within and nearby of the rhizocretions, sometimes engulfing clasts, and within fractures.

4.3.4. *Rhizoliths* petrography

In transverse view, the rhizocretions exhibit circular to sub-circular morphology, 2–20 mm in diameter, and formed of concentric layers of micritic, microsparitic and sparry calcite that engulfed siliciclastic grains. Internal structures are poorly preserved in most observed rhizoliths, but in some, four different micromorphological zones can be identified: a) central pore; b) alveolar structures; c) sand grains with micrite coating; and d) sparry and microsparitic calcite bordering rhizocretions (Fig. 7E). The central hollow (a) located in the central part of

the rhizoliths, is 0.5–1.5 mm in diameter, and is often filled with sparry calcite. The alveolar septal micrite (b) cover the central pore, defined by irregular and discontinuous laminae, 0.1–0.2 mm thick, and composed of micrite or microspar. The external part (c) is formed of cemented sand grains by micrite. The accumulation of calcium carbonate in the adjacent area of the rhizocretion is composed of sparry and microsparitic calcite (d). Sparry calcite occur filling pores that are located between two or more rhizocretions.

Two distinctive rhizogenic microfabrics are identified in the thin sections: calcified cortical cell and *Microcodium*. These features are well preserved and occur nearby or within the rhizocretions. Root cells are completely calcified, with circular to sub-circular shapes and diameters varying from 0.25–0.5 mm (Fig. 7F). Under crossed polarizers, the root cells exhibit a calcite aggregate pattern with uniform extinction. *Microcodium* is present as cylindrical grain aggregates, 0.4–1 mm in length, composed of elongated calcite crystals, prismatic in shape and with monocrystalline structure (Fig. 7G). Under crossed polarizers, *Microcodium* presents sweeping extinction patterns, sometimes, observed within the rhizocretions.

In addition, clay pedofeatures and bladed or columnar calcite crystals also occur within rhizocretions. The clay pedofeatures coat grains and voids and exhibit parallel orientation and birefringence. Bladed and columnar textures are arranged in a ring of sparry calcite surrounding quartz and feldspar grains, and igneous rock fragments (Fig. 7H). The calcite crystals can be acute rhombohedra that show form of columnar

crystals, or obtuse rhombohedra, which exhibit form of bladed crystals. The crystals occur around quartz or feldspar grains within rhizocretions, 0.05–0.2 mm in length, and are disposed perpendicular to the nucleation surface.

4.3.5. Calcite stages under CL

Seven stages of calcite are recognized in the argillic and calcic horizons based on observations of thin sections under CL (Table 2 and Fig. 8). The stages are distinguished by luminescence intensity, paragenetic relationships, and thickness of distinct phases of carbonate cementation (Kaufman et al., 1988). Based on cross-cutting relationships observed in thin section, the stages appear to represent a mostly stepwise and consecutive formation of calcite from stage 1 to 7.

The first stage (S1) consists of thin micritic continuous coating in individual quartz and feldspar grains, with brightly orange luminescence. The second stage (S2) is gradational to S1, with dull-luminescent bladed calcite that grew perpendicular to surface of the sand grains. The third stage (S3) is distinguished by brown-orange luminescent micrite, which occurs filling intergranular pores and grain fractures. Stage 3 cuts the previous first and second stages and all three (S1, S2, and S3) appear to be associated with and forming rhizocretions.

The fourth stage (S4) shows an abrupt transition of bright luminescent microspar that cross-cuts and overlaps S3. The fifth stage (S5) is composed of non-luminescent sparry calcite that cements small voids inside of rhizocretion (cutting S3) or filling large voids in groundmass.

Fig. 8. Cathodoluminescence (CL) photomicrographs of different stages of calcite precipitation. (A) Brightly luminescent micrite (S1) and dull-luminescent bladed calcite (S2) within rhizocretions in the 6Bkk3 horizon. (B) Dull-luminescent bladed calcite (S2), dull-luminescent micrite (S3) and brightly luminescent microspar (S4) inside and nearby of calcareous rhizocretion in the 3Bkk2 horizon. (C) Dull-luminescent micrite (S3) as filled of rhizocretion and zoned sparry calcite (S5) inside voids in the 4Btk2 horizon. (D) Two stages of filled voids composed of zoned sparry calcite (S5) and (S6) in the 2Bkk1 horizon. (E, F) Sequence of calcite precipitation from dull-luminescent bladed calcite (S2) to brightly luminescent sparry (S7) in the 6Bkk3 and 2Bkk1 horizons, respectively.

The sixth stage (S6) consists of acute and obtuse rhombohedral calcite, with bright or non-luminescent zoning that appears adjacent to S5 in the large voids. The seventh stage (S7) is formed of rhombohedral sparry calcite of bright luminescence, which appears filling the remainder of the large voids.

The argillic and calcic horizons of the three study areas present variations in relation to occurrence of the stages. The calcic horizons from Avenças and Monte Alto pedotypes all show the seven stages of calcite, but the fourth stage (S4) of calcite is absent in the argillic horizons from Avenças pedotype. The same case is observed in the horizons from Garça pedotype that also exhibit an incomplete sequence without fourth (S4) and sixth (S6) stages. Other important fact, the organization of the different calcite stages in the study horizons represents specific interpretations. Complete sequence composed of S1 to S7 that fill macropores by multiple phases of calcite growth are interpreted as α -type fabric. Conversely, pores filled by S3 and S4 stages that show biogenic structures as *Microcodium*, calcified root cell and alveolar structure are interpreted as β -type fabric.

4.4. Stable isotope of pedogenic carbonate

Carbon and oxygen isotope values of ten pedogenic carbonate samples from argillic and calcic horizons are summarized in Table 3. The $\delta^{13}\text{C}$ composition of Btk1/6Bkk3 horizons from Avenças pedotype range from -7.7 to -7.8 ‰ with standard deviation of 0.017 ‰ and $\delta^{18}\text{O}$ composition range from -5.88 to -6.52 ‰ with standard deviation of 0.022 ‰. The average values are -7.7 ‰ to $\delta^{13}\text{C}$ isotope and -6.0 ‰ to $\delta^{18}\text{O}$ isotope. 2Bkk1/3Bkk2 horizons from Monte Alto pedotype shows $\delta^{13}\text{C}$ values from -7.9 to -8.1 ‰ and $\delta^{18}\text{O}$ values range from -5.7 to -6.9 ‰, with standard deviation of 0.010 ‰ and 0.022 ‰, respectively. Their average values are -8.0 ‰ to $\delta^{13}\text{C}$ and -6.5 ‰ to $\delta^{18}\text{O}$. Pedogenic carbonate of the 5Bk3 horizon from Garça pedotype presents $\delta^{13}\text{C}$ isotope values of -7.8 to -7.6 ‰, with standard deviation and average values of 0.010 ‰ and -7.7 ‰. The $\delta^{18}\text{O}$ ranges from -6.4 to -6.6 ‰, and show standard deviation and average values of 0.09 ‰ and -6.5 ‰. (Fig. 9).

5. Discussion

5.1. Soil biota and paleoproductivity relationship

The CO_2 content of the soil is an important indicator of different biotic and abiotic processes distributed along the soil profile (Cerling, 1991). The general physical properties that alter the CO_2 dynamics are porosity, temperature and moisture levels (Buyanovsky and Wagner, 1983). Biological CO_2 is produced by plant and animal respiration, and microbial oxidation of organic matter in the soil (Cerling, 1999). The

relationship between soil biota and $p\text{CO}_2$ in the soil provides the basis for paleoproductivity estimates (Cerling, 1999; Waide et al., 1999; Myers et al., 2012). The studied horizons from Avenças, Monte Alto and Garça pedotypes exhibit paleosol biota characterized by low ichnodiversity, composed of *Planolites*, *Taenidium*, *Naktodemasis*, *Skolithos*, *Palaeophycus*, and calcareous rhizocretions. Considering that the invertebrate traces represent feeding and dwelling behaviors of annelids and arthropods, and calcareous rhizocretions were likely produced by plant absorption and respiration, it is possible to assign these ichnofossils to two groups (Hasiotis, 2002; Hasiotis et al., 2007): 1) Terraphillic, produced by organisms that inhabit superficial zones with low humidity; and 2) Hygrophillic, produced by organisms that lived within the vadose zone. The bioturbation index varies from moderate (argillic and calcic horizons) to high (calcic horizons), controlled by the abundance of rhizocretions. Considering this data set, the soil biota is interpreted as formed by organisms adapted to water and nutrient deficits (Hasiotis et al., 2007; Smith et al., 2008a).

The dominant photosynthetic pathway of paleovegetation living in the studied paleosols can be inferred from the $\delta^{13}\text{C}$ values of pedogenic carbonate following Romanek et al. (1992), assuming that soil CO_2 is 4.4 ‰ enriched in ^{13}C relative to soil respired CO_2 at all soil depths (Cerling, 1984; Cerling, 1991). Calculated $\delta^{13}\text{C}$ values of plant CO_2 for the studied horizons show a range of -22.2 to -23.4 ‰ (Table 3). The average values of plant CO_2 are -22.6 ‰, -23.3 ‰ and -22.6 ‰ in the Avenças, Monte Alto and Garça pedotypes, respectively. These values fall within the large range of isotopic values reported for C_3 plants (-35 ‰ to -20 ‰, -26 ‰ on average) (Farquhar et al., 1982; Cerling, 1984, 1991; Ehleringer, 1989; Lee, 1999). It must also be noted that the values of $\delta^{13}\text{C}$ of atmospheric CO_2 vary along to geological time, resulting in a change in the global carbon cycle. The pre-industrial atmosphere exhibits isotope composition of -6.5 ‰ unlike of current values that is about -8 ‰ (Friedli et al., 1986). With this, in the Cretaceous, the $\delta^{13}\text{C}$ of atmospheric CO_2 show values 1.5 ‰ higher than that it is today modifying $\delta^{13}\text{C}$ of C_3 plants to values of -28 to -20 ‰ (Gröcke, 2002; Tütken, 2011; Owocki et al., 2019). The C_3 plants that include most trees, shrubs, herbs, bushes and grasses are the most primitive photosynthetic terrestrial plants that convert inorganic carbon to three-carbon sugar via the Calvin-Benson-Bassham (CBB) cycle in the stoma of their chloroplasts (Cerling, 1984; Cerling and Quade, 1993; Tipler and Pagani, 2007; Kohn, 2010). Furthermore, biochemical properties of the CO_2 -fixing enzymes and the diffusion of CO_2 in the leaf during photosynthesis lead to depletion in ^{13}C in the C_3 plant-respired CO_2 in soil (O'Leary, 1988; Tipler and Pagani, 2007). (Ehleringer, 1989) attributed the low content of ^{13}C (among -22 to -26 ‰) in drylands to plants growing in water stressed conditions, similar to the values described in this study.

Studies using pedogenic carbonates to reconstruct paleovegetation communities have never been performed in the Upper Cretaceous paleosols of the Marília Formation. However, the application of stable isotopes for paleovegetation reconstruction is relatively common to other Cretaceous successions (e.g., Ghosh et al., 1995; Nordt et al., 2002, 2003). Comparing the $\delta^{13}\text{C}$ of C_3 values of -21 to -26 ‰ from cited works with -22.2 to -23.4 ‰ obtained in this study, it is possible to indicate that C_3 plants formed the vegetation cover of the studied paleosols.

The productivity-biota relationship can be classified into four types: linear positive, linear negative, unimodal, or no relationship (Waide et al., 1999; Mittelbach et al., 2001). Each classification is estimated according with relation among ecological diversity and soil respiration rates under a spatial scale (Waide et al., 1999; Mittelbach et al., 2001; Myers et al., 2012). Linear positive pattern occurs with an increase of diversity and soil respiration, linear negative is the reduction of diversity as soil respiration increase, and unimodal is the equilibrium (Waide et al., 1999). The $p\text{CO}_2$ levels in soils generally show values between 5000 to 9000 ppmv at depth ≥ 50 cm in high productivity and between 3000 to 5000 ppmv in low productivity soils (Cerling, 1999).

Fig. 9. Relationship between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ for the studied horizons.

Productivity values formulated by Retallack (2008, 2009) were used to infer relative levels of primary productivity in the study areas (Myers et al., 2012). The soil pCO_2 of argillic horizons show values from 2270 to 3604 ppmv, suggesting low paleoproductivity levels; and calcic horizons display high paleoproductivity levels, with values ranging from 5952 to 7645 ppmv (Table 3). The relationship between paleosols biota and paleoproductivity shows a positive linear pattern, in which calcic horizons characterized by higher abundance of traces exhibit more paleoproductivity levels than argillic horizons that present moderate abundance of traces (Fig. 10). This positive relation is likely linked to short moisture conditions as is currently observed in modern terrestrial ecosystems (Myers et al., 2012).

Climate determines the distribution, diversity and productivity of terrestrial organisms, water input and temperature in the soil (Hasiotis, 2002). The paleosols of the Echaporã Member were developed in a general dry condition (Basilici et al., 2009; Dal' Bó et al., 2009; Fernandes, 2010). In contrast, Basilici et al. (2009), Dal' Bó et al. (2009) and Dal' Bó et al. (2010), identified important moisture intervals during soil formation, and interpreted the paleoclimate as semi-arid with periodical rainfall. The formation of Bk and Bkk horizons in studied paleosols represent evaporative conditions in a warm climate. Nevertheless, the thickness and depth of calcic horizons, features of clay translocation, positive relation of soil biota and productivity, besides of substrate colonization by hygrophilic organisms are evidence of moisture conditions during soil formation, thus corroborating the previous interpretations of Basilici et al. (2009), Dal' Bó et al. (2009) and Dal' Bó et al. (2010).

5.2. Genesis of pedogenic carbonate in argillic and calcic horizons

The studied argillic and calcic horizons contain heterogeneous concentrations of pedogenic carbonate ranging from 20 to 60% of the of the total volume and correlating with stages II and III of Gile et al. (1966) and Machette (1985). The distribution of calcium carbonate is attributed to variations in bioturbation and differences in permeability and primary porosity between the horizons. Calcic horizons with sandy textures show higher permeability and porosity than argillic horizons with loamy-sand texture. The source of Ca^{2+} is varied and probably originated from weathering of igneous rock fragments of the parent material and rainwater enriched in Ca^{2+} ions. However, local dust input cannot be ruled out as a source, as pointed out by Dal' Bó et al. (2010). The carbon source is introduced to the soil via productivity, which is controlled by organism's respiration (invertebrate, microbial and roots) (Cerling, 1999; Myers et al., 2012). In the studied horizons, high rates of productivity found in calcic horizons increased dissolution of minerals, removing mobile cations, such as Ca^{2+} , and thus saturating the soil solution (Gocke et al., 2011), whereas in argillic horizons the lesser intensity of this process was associated to low productivity of the organisms.

Fig. 10. Paleosol paleoproductivity expressed by the relationship between bioturbation indexes and soil respiration.

The isotopic carbon data of the pedogenic carbonate and the ichnopedologic associations of the studied profiles provided evidence for C_3 plants, adapted to dry conditions that prevailed during soil formation. Calcified root cells and crystallitic b-fabric are observed within the rhizcretions, and the precipitation of calcium carbonate is interpreted as forming in two different stages: a) After the decay of roots, represented by stages S1 to S7; and b) during the life span of roots, characterized by stages S3 to S4. The decay of deceased roots may have triggered calcareous rhizcretion formation due to the release of CO_2 during respiration of soil and by the root degradation forming acidic conditions that quickly dissolved primary constituents and created a supersaturated condition favoring carbonate precipitation (Wang et al., 2015; Fa et al., 2016;). Furthermore, supersaturated conditions may be explained by the negative values of oxygen isotopes of the pedogenic carbonate (Fig. 9), formed due to high rates of soil water evaporation. Abiotic processes, such as seasonal temperature and moisture variation as well as pCO_2 degassing, dominate the carbonate production after root decomposition (Platt and Wright, 1991; Sun et al., 2020).

The first three stages of calcite precipitation inferred from the CL analysis of thin sections are likely related to abiotic processes. The S1 represents low quantities of Ca^{2+} available in soil solution and a decreased pH due to root decomposition, resulting in the precipitation of a thin micrite layer around the quartz and feldspar grains and igneous rock fragment (Wang et al., 2015). The S2 is characterized by bladed calcite, which developed when the macropores, originated after the decay of roots, were filled by soil solution enriched of Ca^{2+} (Rasbury et al., 2006; Hameed et al., 2018). The S3 was originated by rapid precipitation of calcium carbonate due to alternation of temperature and short pluvial events. In this case, the force of micrite crystallization created a pressure that reorganized silicate grains inside the calcite matrix (Monger and Daugherty, 1991; Sun et al., 2020). Microsparitic and coarse calcite pore fill textures are characteristic of S4 to S7 stages. In these stages, moister conditions and slower evaporation of soil solution favored precipitation of coarse grains in voids, neomorphism and replacement of previous stages. These multiple phases of inorganic calcite growth as the result of supersaturated soil solutions is characteristic of α -type fabric (Wright, 1990). Furthermore, the stages suggest that carbonate precipitation occurred in the upper vadose zone, as effect of 'per descensum' model (Goudie, 1983), whereby carbonate is moved in solution from upper horizons to precipitate at lower levels (Wright, 2007).

Biogenic activity during the formation of pedogenic carbonate in the studied horizons are marked by different process during the life span of roots. Some calcareous rhizcretions exhibit S3 to S5 stages, which are represented by central pores (a), alveolar structures (b), sand grains cemented by micrite (c) and neomorphic microsparitic calcite (d) (Fig. 7E). The microsparitic calcite and sand grains cemented by micrite coating consist of S3 and S4 stages, and are promoted by the process of high transpiration rates of plants, leading to an increase of Ca^{2+} and carbon acid in soil solution, and an oversaturation close to the roots surface (Gocke and Kuzyakov, 2011). Cramer and Hawkins (2009) and Gocke and Kuzyakov (2011) recognized the stronger influence of plant transpiration on precipitation and neomorphism of carbonate, leading to rhizcretion formation. Stage S5 precipitation is characterized by filling of central pores with coarse calcite. This stage was formed during the decay of root and water saturation of horizons. The preservation of alveolar structure without laminated micrite on S3 stage is interpreted as an interplay between the microorganisms in the rhizosphere and decomposition of the root (Alonso-Zarza et al., 2008). The cellular biomineralizations, such as *Microcodium* and calcified cortical cell that occur within calcareous rhizcretions, is a special adaptation of the plant in nutrient poor substrates that enhance displacement of elements into the rhizosphere (Kosir, 2004). The stages and biogenic structures suggest that carbonate precipitation occurred in the surficial zone, and correspond to β -type fabric (Wright, 1990) that together with α -type fabric suggests a mixture of biogenic and abiogenic process during the

Fig. 11. Schematic reconstruction of the abiotic and biotic processes of carbonate precipitation in the studied horizons. During living of root: (A) Water uptake by plant roots and supersaturation in calcium carbonate nearby root surface. (B) Calcification of cortical cells. After the decay of root: (C) 'per descensum' process of water and ions and precipitation of coarse crystals in voids. (D) Different types of calcite precipitation stages, filling macropores after burial.

pedogenic carbonate formation in argillic and calcic horizons of Avenca, Monte Alto and Garça pedotypes (Fig. 11).

The relative luminescence intensity and nonluminescence of CaCO₃ suggests conditions of reduction or oxidation in soil pore fluids during precipitation (Hiatt and Pufahl, 2014). The most common activator causing bright luminescence in carbonate is Mn²⁺, while a prevalence of Fe²⁺ tends to quench luminescence (Hemming et al., 1989). Differences in the concentrations of these cations in pedogenic carbonates is due primarily to changes in redox conditions; which in soils is a function mostly of water availability and the presence of decaying organic matter (Mintz et al., 2011; Michel et al., 2016). The alpha fabric cements contain seven luminescent and nonluminescent stages (S1 to S7) that represent the periodic input of meteoric fluid into the soil enriched by iron and manganese cations produced during dissolution of minerals (Fig. 11). The first three calcite stages characterized by bright and dull luminescence represent elevated concentrations of Mn²⁺ and Fe²⁺. This effect is caused by a decrease of oxygen levels during decaying root matter by metabolic processes of microorganisms, creating reduction conditions (Vepraskas, 2001). Nonluminescent sparry calcite (fifth stage) characterized by Fe and Mn-poor cement is interpreted to have precipitated by oxidizing fluids in voids filled with meteoric waters during shallow burial conditions (Barnaby and Rimstidt, 1989; Michel et al., 2016). The two last stages of void fill are identified as: CL zonation (sixth stage) which is the result of a variation of salinity gradients

controlled by the rates of precipitation, dissolution and evaporation from soil solution (Machel and Burton, 1991; Vuillemin et al., 2011); and brightly luminescent sparry calcite (seventh stages) that is the maximal Mn²⁺ detection in the center of the voids that represent a chemical change in pore fluid under low-Eh (Barnaby and Rimstidt, 1989). In beta fabric, the calcite of S3 and S4 stages are precipitated in surficial zones under reducing conditions because of respiration rates variation in rhizosphere produced by interaction roots and microorganisms (Pezeshki and DeLaune, 2012; Gocke et al., 2010).

The genesis of the carbonate accumulations in the studied horizons is related directly or indirectly to the activities of organisms, mainly roots. Nonetheless, the complex development of horizons relates directly to the morphological carbonate sequence proposed by Gile et al. (1966) and Machette (1985). Esteban and Klappa (1983), based on an idealized pedogenic profile, proposed that organism activity is an important agent of weathering and carbonate accumulation. In addition, Alonso-Zarza and Wright (2010) reviewed the pedogenic profile descriptions of Esteban and Klappa (1983) and compared the calcium carbonate accumulations and distinct structures with the six stages of Gile et al. (1966) and Machette (1985). In general, argillic and calcic horizons of Avenca, Monte Alto and Garça pedotypes can be compared to the stages 2 and 3 of the idealized pedogenic profile by Esteban and Klappa (1983) and Alonso-Zarza and Wright (2010) with strong similarities concerning to the quantities of carbonate and biogenic components.

6. Conclusions

The use of macro- and microscopic descriptions and geochemical data of pedogenic carbonate accumulated in argillic and calcic horizons from three pedotypes of the Echaporã Member (Marília Formation, Bauru Basin), helped to unravel the complicated genetic history of these horizons formed by multiple phases of calcite precipitation. In the study areas, the pedotypes formed on fluvial lithic sub-arkose deposits and comprise polygenetic and compound paleosols. Eight argillic and calcic horizons were selected; each with carbonate concentrations of 20 to 60% and exhibiting stages II and III of morphogenetic development. The distribution and different accumulations of calcium carbonate in the profiles were strongly influenced by differences in the bioturbation intensity and textures in the argillic and calcic horizons. The role of biogenic processes in the fixation and accumulation of calcium carbonate is much more important than previously thought. The paleosols are characterized by low ichnodiversity composed by terraphillic and hygorphillic organisms.

Based on isotopic data of in situ pedogenic carbonates, the paleo-vegetation was composed dominantly of C_3 plants, and the invertebrate traces suggest low to medium moisture conditions. The productivity pattern displays a positive linear pattern of productivity. The horizons that show an increase of productivity developed more acidic soil solutions, leading to a higher weathering of primary minerals and igneous fragments. The dissolution of primary constituents and the ionic composition of rainwaters were the sources of Ca^{2+} for pedogenic carbonates. With Ca^{2+} free in the soil solution, different stages of carbonate precipitation formed by abiotic and mainly biotic processes acting to fill soil pores and produced α -type and β -type fabrics during pedogenesis in surficial and vadose zones.

Declaration of Competing Interest

The authors declare no conflict of interest with any research or institution.

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