

# Geochemical study of the vertebrate assemblage zones of the Santa Maria Supersequence (Middle to Late Triassic), Paraná Basin, Brazil

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## Abstract

The Middle-Upper Triassic section of the Paraná Basin is included in the Santa Maria Supersequence. This stratigraphic unit is classified as a second-order Supersequence, being subdivided into three third-order sequences in which four Assemblage Zones (AZ) based on tetrapods are recognized. In this work, chemical analyses of fossils and hosting rocks of each AZ were performed in order to verify whether the geochemical patterns of the rocks could serve to distinguish them even in the absence of fossils. For this purpose, nine samples of fossils and their sedimentary matrices were analyzed, by ICP-MS. The results show that there were changes in the chemical parameters in force at the depositional time of each sequence (and corresponding AZ). In general, the lower portion of the package was deposited under more basic and dry environmental conditions, indicated by the Ca and Ba concentrations found in the rocks and bones that contains them. By its turn, the top of the section is characterized by more acid and humid conditions, evidenced by Al, Si, and Sr increase. Such a geochemical shift from dry to humid conditions occurred just at the beginning of the Late Triassic and is probably related to the Carnian Pluvial Episode.

**KEYWORDS:** biostratigraphy; paleoclimatology; Gondwana; Carnian Pluvial Episode.

## INTRODUCTION

The Paraná Basin (PB) is filled with an 8,000 m thick sedimentary package. This package does not display a depositional continuity, but polycyclic events resulting from successive sedimentation episodes related to the tectonic events that hit the SW portion of the Gondwana (Milani 1997, Milani *et al.* 1998). The Middle-Upper Triassic strata (Santa Maria Supersequence — SMS *sensu* Zeffass *et al.* 2003, Horn *et al.* 2014, Horn *et al.* 2018a, 2018b) that occurs only in Rio Grande do Sul State (Fig. 1) are worldwide recognized by their vertebrate fossil content. It includes Synapsida — dicynodonts and cynodonts (taxa containing the sister-group of mammals) — and Diapsida — rhynchosaurs and archosaurs, including the first dinosaur representatives (Schultz *et al.* 2000, Langer *et al.* 2007).

These vertebrates are distributed across the sedimentary package in four Assemblage Zones (AZ) named, base-to-top, *Dinodontosaurus*, *Santacruzodon*, *Hyperodapedon*, and *Riograndia*. Each AZ has its own particular fossiliferous content which has been used to stratigraphically distinguish them in the field (Zeffass *et al.* 2003, Soares *et al.* 2011, Langer *et al.* 2018). Pavanatto *et al.* (2018) synthesized the main fossil species of each AZ, namely: *Dinodontosaurus* AZ — dicynodonts (*e.g.*, *Dinodontosaurus* sp.), Traversodontidae cynodonts (*e.g.*, *Massetognathus ochagaviae*, Schmitt *et al.* 2019) and rauisuchians (*Prestosuchus chiniquensis*); *Santacruzodon* AZ — almost exclusively composed of Traversodontidae cynodonts (*e.g.*, *Menadon besairei* and *Santacruzodon hopsoni*); *Hyperodapedon* AZ — predominantly rhynchosaurs (*e.g.*, *Hyperodapedon* sp.), as well as, Traversodontidae (*e.g.*, *Exaeretodon riograndensis*), probainognathian cynodonts (*e.g.*, *Prozostrodon brasiliensis*), and sauropodomorph dinosaur (*e.g.*, *Saturnalia tupiniquim*); *Riograndia* AZ — small probainognathian cynodonts (*e.g.*, *Riograndia guai-bensis*, *Brasilodon quadrangularis*), dicynodonts (*Jachaleria candelariensis*), as well as, theropod (*Guaiibasaurus candelariensis*) and “prosauropod” (*e.g.*, *Unaysaurus tolentinoi*) dinosaurs. On the other hand, many outcrops of the Santa Maria Supersequence that occur near the fossiliferous localities do not contain fossils, being tentatively associated to a biozone due to its geographical proximity or lithological similarities.

In this context, chemical analyses of the fossils and their sedimentary matrices were carried out, in each biozone, aiming to get geochemical patterns that allow us to characterize and individualize these AZ, even without their particular fossil content. Furthermore, these analyses also sought to obtain some paleoclimatic and paleoenvironmental conditions that

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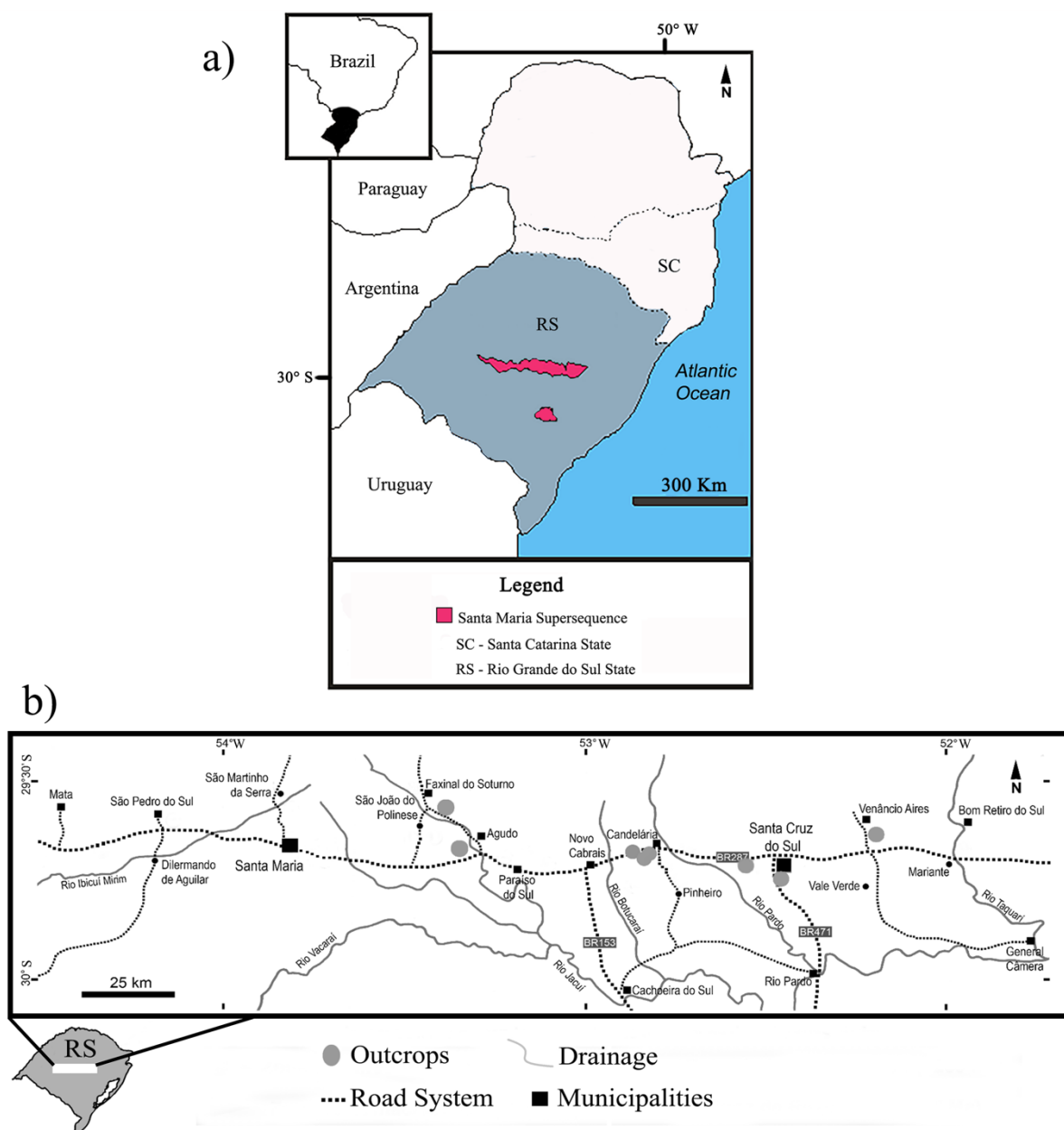
prevailed at the time of deposition of the rocks that encompass each of the AZ.

### GEOLOGICAL SETTING

The Santa Maria Supersequence (SMS) was defined and subdivided by Zeffass *et al.* (2003), from base-to-top, in the third-order sequences Santa Maria I, II, and III. Within the first two, four biozones were defined based on its tetrapod occurrences, *Dinodontosaurus* AZ and *Santacruzodon* AZ, in SMS I, in addition to *Hyperodapedon* AZ and *Riograndia* AZ, in SMS II (Soares *et al.* 2011). Then, Horn *et al.* (2014) dismembered the SMS I into two sequences, so that the younger *Santacruzodon* AZ (Early Carnian age) became incorporated into a fourth third-order sequence, named Santa Cruz. In this context (the presence of a new sequence included between the SMS I and SMS II sequences by Zeffass *et al.* 2003), Horn *et al.*

(2014) renamed all the previous sequences from base-to-top as Pinheiros-Chiniquá Sequence (including the *Dinodontosaurus* AZ — Ladinian), Santa Cruz Sequence (encompassing the *Santacruzodon* AZ — Early Carnian), Candelária Sequence (encompassing the *Hyperodapedon* and *Riograndia* AZ — Carnian to Norian), and Mata Sequence (Rhaetian). This latter corresponding to the Santa Maria III Sequence from Zeffass *et al.* (2003) and the only one devoid of fossil vertebrates.

The vertebrate biozones relative ordering is corroborated via biostratigraphic correlation with similar faunas found in Argentina and Africa. In addition, some absolute ages were obtained from fossiliferous outcrops of the SMS by the U-Pb method in dating detrital zircons (Langer *et al.* 2018, Philipp *et al.* 2018), indicating ages of 236.1 (Santa Cruz Sequence), 233.23 (*Hyperodapedon* AZ), and 225.42 Ma (*Riograndia* AZ). The AZ stratigraphic framework and their respective dating are presented in Figure 2.

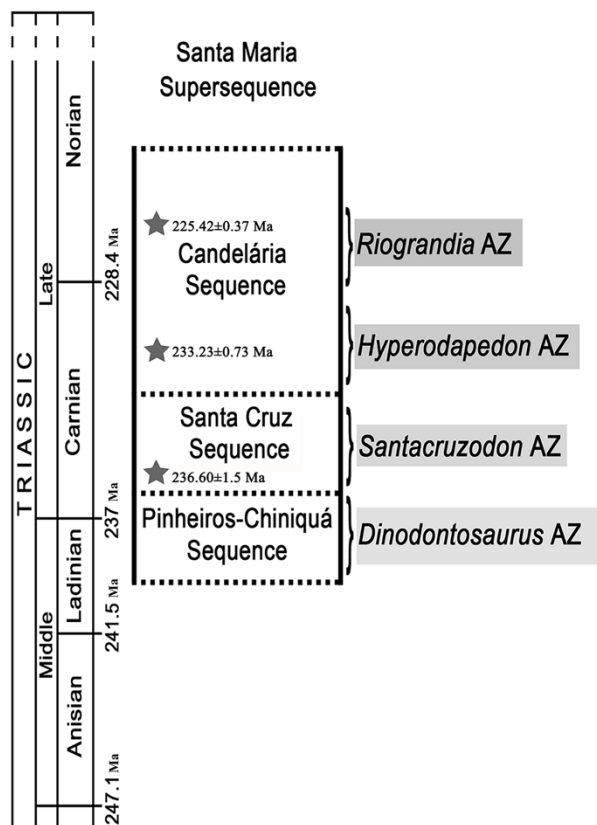


Source: adapted from Martinelli *et al.* (2017) and Paim (2020).

**Figure 1.** (A) Geographic map of southern Brazil showing the outcrop belt of the Santa Maria Supersequence from where the studied rocks and fossils were collected (in pink). (B) Localization of the studied outcrops and their Municipalities.

## MATERIALS AND METHODS

Nine fossil samples and their respective matrices were analyzed by inductively coupled plasma — mass spectrometry (ICP-MS) at Acme Analytical Labs Ltd., located in Vancouver, Canada.



AZ: assemblage zone.

From: adapted from Martinelli *et al.* (2017), Langer *et al.* (2018) and Philipp *et al.* (2018).

**Figure 2.** The assemblage zones from Santa Maria Supersequence in a schematic view with some detrital zircons dating made by Langer *et al.* (2018) and Philipp *et al.* (2018).

The analyzed fossils belong to the Paleovertebrate Section of the Geosciences Institute of the Universidade Federal do Rio Grande do Sul collection (UFRGS-PV-T), as well as, to the Museu Municipal Aristides Carlos Rodrigues collection (MMACR-PV-T), from Candelária, Rio Grande do Sul. The fossils' description and their provenance are presented in Table 1.

For the correlation between the chemical elements (Pearson's Correlation), Excel Software (2010) was used. The results with positive (direct correlation) or negative values (inverse correlation), higher than 0.7, were considered significant and made it possible to group chemical elements with similar geochemical behavior.

## RESULTS

Here were considered the chemical analysis results of the major and trace elements that have relatively high contents and were contained in the sedimentary matrices and the fossil bones. Despite the number of samples for each AZ not being expressive, it was possible to identify and differentiate the different biostratigraphic units according to their geochemical data. It suggests that the same result can be obtained in the outcrops that do not present the characteristic fossil content of any biozone. The distinction of the AZ sediments composition, from arithmetic means, is synthesized in Table 2.

The distinct composition of the AZ bones, from arithmetic means, is synthesized in Table 3.

The most relevant data analyses that allow to individualize each AZ are described below. The sedimentary rock results are described first, followed by fossil bones.

### Chemical elements analyses in sedimentary rocks

#### *Dinodontosaurus* AZ

We analyzed rock matrices of this biozone associated with one raiusuchian (*Prestosuchus chiniquensis*) rib and one

**Table 1.** Description and provenience of the sampling used for geochemical analyses by ICP-MS.

Sample	Fossil	Bone	Seq.	AZ	Age	Sed.	Locality	Catalog no.
O1A, S1A	Raiusuchia <i>Prestosuchus</i>	Rib	Pinheiros-Chiniquá	<i>Dinodontosaurus</i>	Ladinian	Clayey siltite; Pelite	Dona Francisca	UFRGS-PV-0629-T
O1B, S1B	Dicynodontia <i>Dinodontosaurus</i>	Vertebra					Venâncio Aires	UFRGS-PV-0300-T
O2A, S2A	Cynodontia <i>Menadon</i>	Lower jaw	Santa Cruz	<i>Santacruzodon</i>	Carnian (Base)	Clayey siltite; Pelite	Santa Cruz do Sul	UFRGS-PV-1165-T
O2B, S2B	Undetermined Cynodontia	Skull					Venâncio Aires	UFRGS-PV0457-T
O3A, S3A	Cynodont <i>Exaeretodon</i>	Lower jaw					Agudo	UFRGS-PV-1226-T
O3B, S3B	Rhynchosauria <i>Hyperodapedon</i>	Rib	Candelária (Lower)	<i>Hyperodapedon</i>	Carnian (Top)	Clayey siltite; Pelite	Vale do Sol	UFRGS-PV-1206-T
O3C, S3C	Rhynchosauria <i>Hyperodapedon</i>	Skull					Santana da Boa Vista	UFRGS-PV-1248-T
O4A, S4A	Dicynodontia <i>Jachaleria</i>	Rib	Candelária (Upper)	<i>Riograndia</i>	Norian	Clayey siltite; Pelite	Candelária	UFRGS-PV-0540-T
O4B, S4B	Undetermined Archosaur	Post-cranial fragments					Candelária	MMACRPV012T

ICP-MS: inductively coupled plasma – mass spectrometry; Seq.: sequences; AZ: assemblage zone; Sed.: sediment/matrices.

dicynodont (*Dinodontosaurus* sp.) vertebra (see Tab. 1 for details). The geochemical analyses results (Tab. 2) indicated that these rocks have the highest mean values of Ba (1,569 ppm) and the lowest of P (0.06%).

### Santacruzodon AZ

The host sediment associated with a cynodont jaw (*Menadon besairiei*) and also a skull of an undetermined species of cynodont enabled us to conclude that the *Santacruzodon* AZ has the highest average of Ca (17.38%) and Sn (2 ppm). It also has the lowest values of Al (5.54%), Si (17.84%), V (30 ppm), Zn (7 ppm), Rb (70 ppm), Sr (150 ppm), Zr (187 ppm), and Pb (7 ppm).

### Hyperodapedon AZ

For this AZ, the rock matrices around a cynodont lower jaw (*Exaeretodon riograndensis*) and a rib and a skull of a rhy-chosaur (*Hyperodapedon* sp.) were analyzed (see Tab. 1 for details). These samples presented a significant number of elements with high average contents (Na, Mg, Al, Si, K, Sc, Ti, Mn, Fe, Co, Ni, Cu, Ga, Rb, Sr, Zr, Nb, and Pb). The most relevant contents are Al (9.18%), Si (31.84%), Fe (2.28%), Rb (115 ppm), Sr (889 ppm), Zr (392 ppm), and Pb (46 ppm), as showed in Table 2. A relative high content of Nb (12 ppm) was detected. According to Nagarajan *et al.* (2007), Nb's average in sedimentary rocks is 1.90 ppm. On the other hand, the associated rocks of this biozone have the lowest contents of F (0.05%) and Ca (1.05%).

### Riograndia AZ

We analyzed the host sediments of a dicynodont rib (*Jachalera candelariensis*) and an undetermined archosaur post-cranial fragment (see Tab. 1 for details). The results of this AZ indicated the highest content of F (0.41%), P (2.18%),

V (271 ppm), and Y (585 ppm). The Y anomaly is highly surprising when compared to the Anders and Grevesse (1989) chondrites average (1.56 ppm). The high values of Nb (7 ppm) are also anomalous both in relation to the chondrites (246 ppb) and Post-Archean Australian Average Shale (PAAS) (1.90 ppm, Nagarajan *et al.* 2007) standards. Despite the fact that Nb can be relatively concentrated in comparison to the PAAS pattern, this biozone has the lowest contents of this element. In addition, the *Riograndia* AZ has the lowest values of Fe (1.14%) and Ba (573 ppm).

The characteristic elements of each AZ, in the host rocks around the fossils, are presented in Table 4.

## Chemical elements analyses in bones

### *Dinodontosaurus* AZ

The fossil bones of this biozone presented the highest average contents of Ca (36%). Otherwise, they have the lowest contents of F, Na, Al, Si, P, Sc, Ti, V, Cr, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, W, and Pb. The most relevant values are those of Si (2.28%), P (2.91%), Sr (735 ppm), and Y (396 ppm).

### *Santacruzodon* AZ

In this biozone, the bones registered high contents of Be, Cr, Mn, Fe, Co, Ga, As, Y, Ba, W, and Pb. The most relevant values are those of Cr (0.01%), Mn (2.05%), As (364 ppm), Y (2,358 ppm), and Ba (27,466 ppm). On the other hand, this AZ has the lowest contents of K (0.1%).

### *Hyperodapedon* AZ

The fossils of this AZ had the highest average contents of Na, Al, Sc, Ti, Ni, Rb, and Sr. The most relevant values are those of Al (0.91%) and Sr (5,939 ppm). This AZ presented the lowest average values of Be (2 ppm), Ca (31.14%), and Mn (0.34%).

**Table 2.** Average contents of the main elements analyzed on rock matrices for each AZ\*.

AZ	(% )				(ppm)							
	Al	Si	P	Ca	Rb	Sr	Y	Zr	Nb	Ba	Pb	
Top	<i>Riograndia</i>	6.59	29.41	<b>2.18</b>	6.49	77.05	617.30	<b>584.90</b>	386.90	7.45	573.00	22.20
↑	<i>Hyperodapedon</i>	<b>9.18</b>	<b>31.84</b>	0.10	1.05	<b>115.37</b>	<b>889.47</b>	<b>34.20</b>	<b>392.57</b>	<b>12.50</b>	795.00	<b>46.03</b>
↑	<i>Santacruzodon</i>	5.54	17.84	0.095	<b>17.38</b>	70.75	150.80	64.00	187.00	7.60	1,367.50	7.65
Base	<i>Dinodontosaurus</i>	7.42	24.78	0.06	9.00	93.65	197.10	38.90	294.50	11.05	<b>1,569.50</b>	10.00

\*The highest contents are in bold and the lowest, in italics; AZ: assemblage zone.

**Table 3.** Average contents of the main elements of bone fragments analyzed for each AZ\*.

AZ	(% )				(ppm)								
	Al	Si	P	Ca	V	Zn	As	Sr	Y	Zr	Ba	Pb	
Top	<i>Riograndia</i>	0.75	<b>2.79</b>	<b>10.33</b>	34.78	683.00	32.00	265.50	1,923.60	1,756.35	<b>130.45</b>	1,537.50	115.20
↑	<i>Hyperodapedon</i>	<b>0.91</b>	2.30	7.67	31.14	141.00	29.33	292.10	<b>5,939.33</b>	1,104.67	115.37	17,193.67	111.33
↑	<i>Santacruzodon</i>	0.80	2.44	7.35	31.25	410.00	24.00	<b>364.30</b>	1,449.55	<b>2,358.25</b>	80.05	<b>27,466.00</b>	<b>203.05</b>
Base	<i>Dinodontosaurus</i>	0.62	2.28	2.91	35.83	95.50	14.00	80.65	735.35	396.90	33.35	19,301.00	32.40

\*The highest contents are in bold and the lowest, in italics; AZ: assemblage zone.



## Riograndia AZ

It is possible to stand out, for this AZ, the highest average contents of Si, P, K, V, Cu, Zn, and Nb, highlighting the expressive absolute values of Si (2.79%), P (10%), and V (683 ppm). However, this AZ has the lowest average contents of Mg (0.14%), Fe (0.18%), and Ba (1,537 ppm).

The characteristic elements of each AZ in the fossil bones are presented in Table 5.

## DISCUSSION

Some of the analyzed elements could be used to differentiate AZ hosting rocks, not by their high or low contents, but by their standard deviation (SD;  $\sigma$ ). The SD represents the sample group homogeneity (Bland and Altman 1996), e.g., the F ( $\sigma = 0.0007$ ) and the P ( $\sigma = 0.03$ ) in the *Dinodontosaurus* AZ; the K ( $\sigma = 0.20$ ) in the *Hyperodapedon* AZ, and Fe ( $\sigma = 0.0$ ) in the *Riograndia* AZ. High standard deviation values indicate that the sample group is heterogeneous or inconstant (Bland and Altman 1996, Walker 1931), e.g., the Ba SD ( $\sigma = 1,447.45$ ) and Sr ( $\sigma = 1,283.83$ ) in *Hyperodapedon* AZ. Thus, when analyzing other outcrops

in future works and encountering those high SD results, the researcher may have some notion from which AZ the samples came through. So, those SD values (high — heterogeneity and low — homogeneity) could also be used as an identification criterion for these biozones. It is applicable provided that the sample  $n$  is representative, since their values are associated to the number of samples analyzed. The SD significance increases as sampling increases and vary according to the analyses results.

Tables 6 and 7 contain, in bold, the lowest (sample homogeneity) and the highest SD values (sample heterogeneity), in red.

P and the K are relatively depleted, in relation to the average values, in both, sediments and bones of the lowermost AZ (*Dinodontosaurus* and *Santacruzodon*). P is more depleted in *Dinodontosaurus* AZ and K in *Santacruzodon*. In the *Hyperodapedon* AZ, Na, Al, Sc, Ti, Ni, Rb, and Sr have high average contents, but Ca values are low. This behavior occurs in both sediments and bones. *Riograndia* AZ has high average contents (in both matrices and bones) of F, P, V, and Zn. However, Mg, Fe, and Ba have low values compared to the other biozones.

The high contents of Al, Si, Ti, Fe, Ni, Rb, Zr, and Nb allowed to individualize solely the *Hyperodapedon* AZ sediments. This AZ can also be differentiated by the lowest contents of F, P, and Ca. This particular composition from *Hyperodapedon* AZ can be observed in Tables 4 and 8.

The *Riograndia's* AZ sediments can be differentiated by the low content of Mg, meanwhile, those from *Santacruzodon* AZ, by the low content of As (Tabs. 4 and 8).

All the analyzed samples, regardless of the Sequence/AZ they belong to, correspond to red silt-clay sedimentary rocks. The sedimentary facies analyses made by Horn *et al.* (2018a) at SMS enabled these authors to identify two dominant associations across the package:

- dry mudflat facies (loess deposits);
- sheet delta facies (underwater deposits).

A dry mudflat association characterizes the Pinheiros-Chiniquá (*Dinodontosaurus* AZ) and the Santa Cruz (*Santacruzodon* AZ) Sequences. A sheet delta association, on the other hand, characterizes the Candelária Sequence (*Hyperodapedon* and *Riograndia* AZs). In this context, the faciological variation of the lowermost portion of the Candelária Sequence indicates a change from arid to humid conditions. Similar climatic changes were described by Zeng *et al.* (2019) for the Mungaroo Formation (Middle-Upper Triassic, Australia), where the climate changed from temperate and warm to humid and monsoonal. Thus, the existence of contemporary higher humidity events, in opposite portions of Gondwana, was found. Besides, the paleontological and sedimentological studies carried out by Zeng *et al.* (2019) detected different intensities in the megamonsoon events that hit the Northwest Shelf of Australia, during the Middle Triassic. The Mungaroo Formation records higher humidity and the Brigadier Formation, overlapping, would mark a decrease in those monsoonal effects (Zeng *et al.* 2019). Something similar was recorded in the passage from *Hyperodapedon* AZ to

**Table 4.** Differences in the composition of the sedimentary matrices of each assemblage zone. The concentrations of elements (major and trace) of certain biozones when compared to the others are highlighted.

AZ	Sedimentary matrices	
	Maximum	Minimum
<i>Riograndia</i> AZ	Be, F, P, V, Zn, As, Y	<b>Mg</b> , Mn, Fe, Co, Nb, Sn, Ba
<i>Hyperodapedon</i> AZ	Na, Mg, <b>Al</b> , <b>Si</b> , K, Sc, Ti, Mn, <b>Fe</b> , Co, <b>Ni</b> , Cu, Ga, <b>Rb</b> , Sr, <b>Zr</b> , <b>Nb</b> , W, Pb	<b>F</b> , <b>P</b> , <b>Ca</b> , Y
<i>Santacruzodon</i> AZ	Ca, Sn	Be, Na, Al, Si, K, Sc, Ti, V, Cr, Ni, Cu, Zn, <b>As</b> , Rb, Sr, Zr, W, Pb
<i>Dinodontosaurus</i> AZ	Ba	Be, P, Sn

\*In bold the elements that make it possible to individualize each biostratigraphic units; AZ: assemblage zone.

**Table 5.** Differences in fossil bones fragments compositions (major and trace concentrations) of each assemblage zone when compared to the others.

AZ	Bones	
	Maximum	Minimum
<i>Riograndia</i> AZ	F, Si, P, K, V, Cu, Zn, Nb	Mg, Fe, Ba
<i>Hyperodapedon</i> AZ	Na, Al, Sc, Ti, Ni, Rb, Sr	Be, Ca, Mn
<i>Santacruzodon</i> AZ	Be, Cr, Mn, Fe, Co, Ga, As, Y, Ba, W, Pb	K
<i>Dinodontosaurus</i> AZ	Mg, Ca	F, Na, Al, Si, P, Sc, Ti, V, Cr, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, W, Pb

AZ: assemblage zone.

*Riograndia* AZ, in Brazil. Corroborating the sedimentological data by Horn *et al.* (2018a, 2018b), the high contents of Al, Si, and Fe recorded on *Hyperodapedon's* AZ sediments (Carnian) indicate a humidity peak. This peak, according to

the dating (233.23 Ma.), could be related to the global event named “Wet Intermezzo” or Carnian Pluvial Episode (CPE), whose stipulated age is between 230 and 232 Ma. (Furin *et al.* 2006, Ogg 2015, Benton *et al.* 2018). In the *Riograndia's* AZ

**Table 6.** Standard deviation (major elements) obtained by ICP-MS analyses in sediment samples of assemblage zones from Santa Maria Supersequence.

Elements(%)	Base → Top			
	AZ (σ)			
	<i>Dinodontosaurus</i>	<i>Santacruzodon</i>	<i>Hyperodapedon</i>	<i>Riograndia</i>
F	σ = 0.0007	σ = 0.016	σ = 0.01	σ = <b>0.46</b>
Mg	σ = 0.11	σ = <b>0.53</b>	σ = 0.09	σ = 0.05
Al	σ = 2.52	σ = <b>5.79</b>	σ = 0.37	σ = 1.10
Si	σ = 9.97	σ = <b>18.84</b>	σ = 1.63	σ = 6.49
P	σ = 0.03	σ = 0.06	σ = 0.06	σ = <b>2.56</b>
K	σ = 0.58	σ = <b>1.35</b>	σ = 0.20	σ = 0.38
Ca	σ = 11.29	σ = <b>23.41</b>	σ = 0.45	σ = 6.08
Ti	σ = 0.13	σ = <b>0.28</b>	σ = 0.02	σ = 0.05
Fe	σ = 0.49	σ = <b>1.43</b>	σ = 0.26	σ = 0.00

\*The highest contents are in bold and the lowest, in italic; ICP-MS: inductively coupled plasma – mass spectrometry; AZ: Assemblage Zones.

**Table 7.** Standard deviation (trace elements) obtained by ICP-MS analyses in sediment samples of Assemblage Zones from Santa Maria Supersequence.

Elements (ppm)	Base → Top			
	AZ (σ)			
	<i>Dinodontosaurus</i>	<i>Santacruzodon</i>	<i>Hyperodapedon</i>	<i>Riograndia</i>
V	σ = 0.71	σ = 20.51	σ = 18.33	σ = <b>323.34</b>
Zn	σ = 1.41	σ = 6.36	σ = 3.79	σ = <b>17.68</b>
Ga	σ = 4.17	σ = 9.12	σ = 1.08	σ = 0.35
As	σ = 1.63	σ = 0.21	σ = 2.51	σ = <b>51.69</b>
Rb	σ = 29.63	σ = <b>73.47</b>	σ = 14.89	σ = 8.41
Sr	σ = 31.40	σ = 10.47	σ = <b>1,283.83</b>	σ = 507.42
Y	σ = 25.17	σ = 46.10	σ = 5.57	σ = <b>704.42</b>
Zr	σ = 149.62	σ = <b>192.90</b>	σ = 64.73	σ = 102.11
Nb	σ = 3.61	σ = <b>7.92</b>	σ = 0.53	σ = 0.92
Ba	σ = <b>1,447.45</b>	σ = 1,117.94	σ = 548.51	σ = 41.01
Pb	σ = 3.68	σ = 4.88	σ = <b>59.73</b>	σ = 23.48

\*The highest contents are in bold and the lowest, in italic; ICP-MS: inductively coupled plasma – mass spectrometry; AZ: Assemblage Zones.

**Table 8.** ICP-MS results for sediment samples of assemblage zones from Santa Maria Supersequence, based on calculated standard deviation.

AZ	(%)								(ppm)					
	F	Mg	Al	Si	P	Ca	Ti	Fe	Ni	As	Rb	Zr	Nb	
Top	<i>Riograndia</i>	0.740	0.58	5.81	24.82	3.99	10.79	0.26	1.14	4.8	82.2	71.1	314.7	6.8
		0.086	0.52	7.37	34.00	0.36	2.19	0.32	1.14	3.7	9.1	83.0	459.1	8.1
↑	<i>Hyperodapedon</i>	0.048	0.84	<b>9.03</b>	<b>32.68</b>	0.06	<b>0.77</b>	<b>0.44</b>	<b>2.10</b>	<b>5.7</b>	3.7	<b>113.0</b>	<b>436.2</b>	<b>12.9</b>
		0.045	0.80	<b>8.91</b>	<b>32.87</b>	0.07	<b>0.81</b>	<b>0.45</b>	<b>2.15</b>	<b>9.0</b>	7.1	<b>101.8</b>	<b>423.3</b>	<b>11.9</b>
	<i>Santacruzodon</i>	0.063	0.97	<b>9.60</b>	<b>29.96</b>	0.17	<b>1.57</b>	<b>0.47</b>	<b>2.58</b>	<b>7.4</b>	2.2	<b>131.3</b>	<b>318.2</b>	<b>12.7</b>
		0.033	0.27	1.44	4.52	0.14	33.93	0.07	0.42	1.4	1.9	18.8	50.6	2.0
Base	<i>Dinodontosaurus</i>	0.055	1.02	9.63	31.16	0.05	0.82	0.46	2.44	5.0	1.6	122.7	323.4	13.2
		0.054	0.84	9.20	31.83	<b>0.04</b>	1.02	0.46	2.27	4.4	1.4	114.6	400.3	13.6
		0.055	0.68	5.64	17.73	<b>0.08</b>	16.98	0.28	1.58	2.6	3.7	72.7	188.7	8.5

\*The highest contents are in bold and the lowest, in italic; ICP-MS: inductively coupled plasma – mass spectrometry; AZ: Assemblage Zones.

sediments, there is a reduction in these elements content, although they remain relatively high. It could indicate that the CPE decreased its intensity.

The rock matrices of the *Dinodontosaurus* and *Santacruzodon* AZ are enriched in Ca, Sn, and Ba. According to Brookings (1988), these elements are concentrated in more basic pH conditions ( $\approx 7.83$  and 14), indicating more arid environmental conditions. The sediments of *Hyperodapedon* and *Riograndia*, on the other hand, are enriched in Al, Si, and Sr. The first two elements are characteristic of minerals that crystallized under broad pH conditions ( $\approx 1$  to 12.5). Meantime, also according to Brookings (1988), minerals that contain Sr are generally formed under acid to slightly basic conditions ( $\approx 1$  to 7.32). It could indicate an acidification followed by a humidity increase across the SMS depositional evolution.

The highest levels of Si in studied bones are recorded in *Riograndia* AZ (2.79%) and not in *Hyperodapedon* (2.3%). This contradicts the previous observations made by Reichel *et al.* (2005) and Horn (2013) that detected chalcedony (with diagenetic particularity) only in *Santacruzodon*'s sediment. These authors used thin sections to carry these observations. The relatively high levels of Si in *Riograndia* AZ indicate more acid conditions in weather profiles. It could be associated to many factors, including, in this case, leaching by acid rains. Acid rains at that moment would be an effect of the Large Igneous Provinces (LIPs) volcanism related to the climatic changes, as described by Benton (2018), Benton *et al.* (2018) and Zeng *et al.* (2019). Preto *et al.* (2010), Benton and Newell (2014), and Benton *et al.* (2018), specially associated to the warming and increased rainfall, to the end Triassic mass extinctions. For Benton (1986), there was more than one extinction event during the end of the Triassic period. The first one would have occurred during the Carnian and the second, in Norian (around 17 to 20 Ma. after the first). The first extinction event, although smaller, was subdivided into two sub events. One with low intensity that affects the ammonites (at the beginning of Carnian) and the second one, larger, that affects some tetrapod groups (at the end of Carnian).

A Wrangellian large igneous province (WLIP), associated with rifting at the beginning of Pangea's breaking up and to megamonsoon events, would have been responsible for triggering the CPE (Zeng *et al.* 2019). Initially, the CPE was interpreted as a high humidity episode, though short-lived (Preto and Hinnov 2003, Rigo *et al.* 2007), in regional scale, restricted only to the European plate and the Tethys Ocean (Simms and Ruffell 1989, 1990, Simms *et al.* 1995). Meantime, recent studies (Preto *et al.* 2010, Benton and Newell 2014, Cheng *et al.* 2019, Horn *et al.* 2018a, 2018b, Zeng *et al.* 2019) have been demonstrating that its occurrence was in global scale. The CPE was detected in sediments from many different places around the world, such as, in the SW of the United States (Prochnow *et al.* 2006, Lucas and Tanner 2018), Australia (Zeng *et al.* 2019), and Brazil (Horn *et al.* 2018a). Thus, it covers both the northern and the southern hemispheres. Benton *et al.* (2018) correlate a rapidly climatic changing event (dry-wet-dry) that

supposedly happened in the Carnian, with the dinosaur's diversification. The analyzed sediments of Zeng *et al.* (2019), in Mungaroo Formation (Australia), reflects relatively rapid deposition associated to a strong hydrodynamic condition. This suggests that the megamonsoon would have happened in a relatively short, though expressive, time, at least in that region. Although these evidences point to a rapid great humidity event in the Carnian, Ogg (2015) suggests that biostratigraphic calibrations (in both marine and continental environments) and radioisotopic dating should be made to delimitate the real duration of this episode.

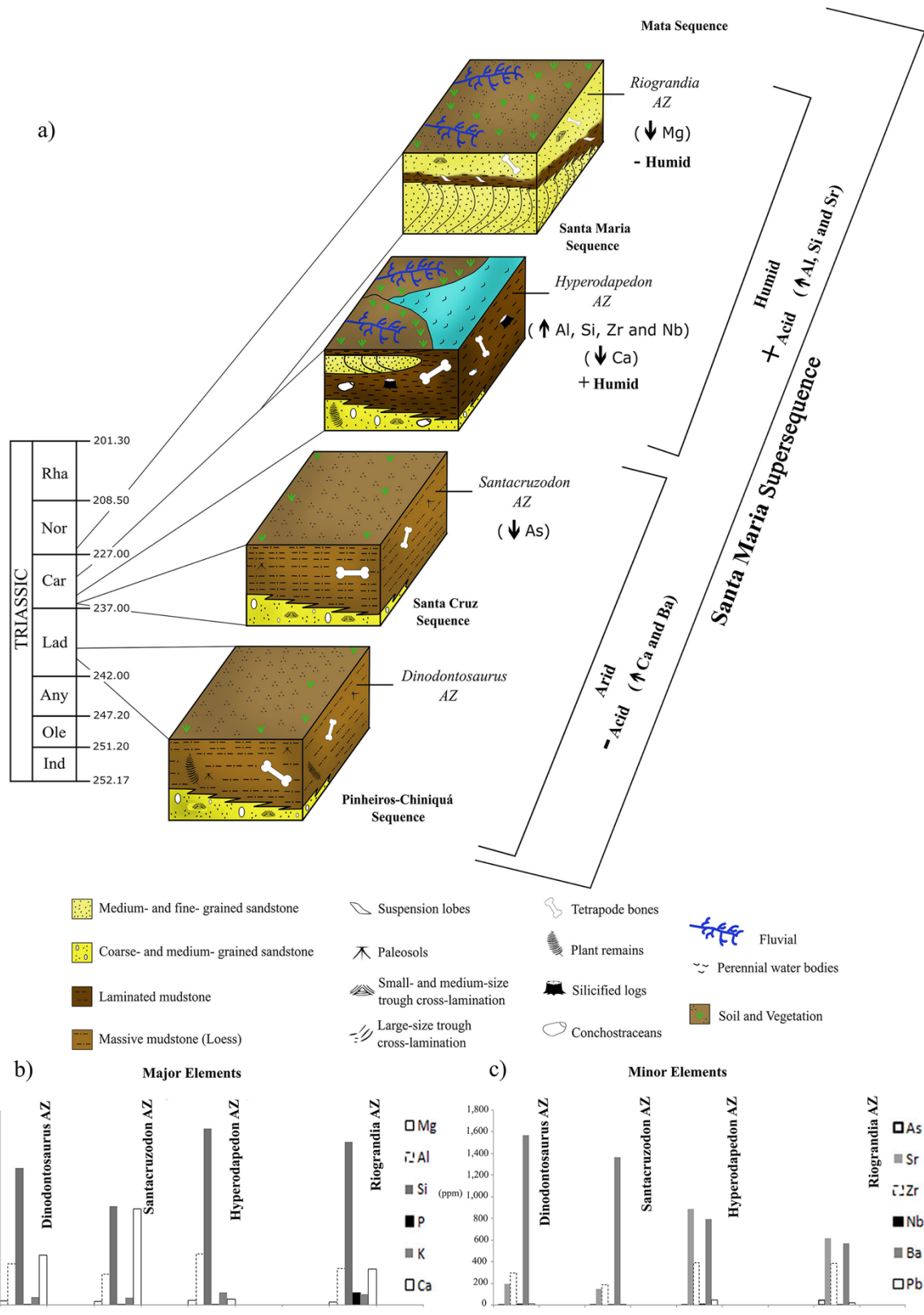
In relation to the variations in the Mg and Al contents, Mg is characterized by its high mobility, meanwhile Al, by its low mobility, both in weather profiles (White 2013). In sediments under Standard Ambient Temperature and Pressure (SATP), lower values of Mg (in comparison to Al) are expected. If the Al contents also quickly decrease, in comparison to the sediments average values (as the North American Shale Composite – NASC pattern of Gromet *et al.* (1984); 2.86% Mg and 16.90% Al), it indicates that the weathering processes were very intense (Sheldon and Tabor 2009). In the studied samples, the Mg (0.87%) and Al (9.18%) contents found in *Hyperodapedon*'s AZ sediments are low, in comparison to the average contents of the NASC pattern. This suggests a very intense weathering process (Benton and Newell 2014) that can be associated with higher humidity episodes.

A synthetic model with the most relevant changes (faciological and geochemical) that occurs across the SMS assemblage zone depositions is illustrated in Figure 3. This model helps to identify the facies (dry mudflat — *Dinodontosaurus* and *Santacruzodon* AZ and sheet delta — *Hyperodapedon* and *Riograndia* AZ) and presents a geochemical synthesis of each particular biozone across the SMS.

Another data that could reinforce the environmental changes discussed here came from the fossil plants of the Cuyo basin, in Argentina. The Potrerillos Formation was deposited between 239 and 230.3 Ma. It is basically composed by an interleaving of peat and pyroclastic sediments reworked in conglomerates, sandstones and shales (Spalletti *et al.* 2008). This formation had its paleoflora analyzed by Artabe *et al.* (2007). They subdivided it into two Triassic biozones, the *Yabeiella mereyesiaci* - *Scytophyllum bonettiae* - *Protophylladoxylon cortaderitaensis* assemblage biozone (MBC) (Middle Triassic) and the *Yabeiella brackebuschiana* - *Scytophyllum neuburgianum* - *Rhexoxylon piatnitzkyi* assemblage biozone (BNP) (Upper Triassic). According to Artabe *et al.* (2007), the paleofloristic associations of Potrerillos (MBC and BNP) would be inserted in a dry subtropical zone of the southeast extratropical area of the Gondwana. This area should be exposed to megamonsoon regimes. This is corroborated by the presence of plant groups with seasonality adaptations and xeromorphic characteristics. According to Spalletti *et al.* (2005), the MBC and BNP paleofloras share species of *Yabeiella* and *Scytophyllum* genus. However, they differ in the occurrence of the genera *Protophylladoxylon* (MBC) and *Rhexoxylon* (BNP), being the latter attributed to conifers, a group not closely related to the Corystosperms (Bodnar 2008).

Shi *et al.* (2016) suggest that there is a correlation between *Corystosperms* and *Ginkgo*, a genus that continues until today. This similarity with living species allows to presume that, as in the actual *Ginkgos*, the *Corystosperms* (*R. cortaderitaense*) should be adapted to well-drained and high-recharging environments, like streams and river dikes (Royer *et al.* 2003). Fu

*et al.* (1999) registered some *Ginkgo* occurrences in deciduous forests and loess deposits (well drained), whose soil's pH is around 5.0 to 5.5. Such favorable characteristics that allow the *R. cortaderitaense*'s occurrence (acidity and well-drained soils) allow associating the BNP biozone (*Cuyo's* basin, Argentina) climate to the uppermost AZ from SMS,



AZ: assemblage zone.

**Figure 3.** (A) A synthetic model with the most relevant changes (faciological and geochemical) that occurs across Santa Maria Supersequence AZ depositions. (B) Graphic with the major element's variation across the AZ. (C) Graphic with the trace element's variation across the AZ.



particularly the *Hyperodapedon* AZ. These enlarge the influence zone of the biggest humidity event of the Carnian period (CPE) until the Argentine soils. This paleoclimatic condition of megamonsoon regimes is similar to that observed in the SMS region. Horn *et al.* (2018b) identified some climatic changes between the SMS biozones, from driest to wetter, in particular between the lowermost (*Dinodontosaurus* and *Santacruzodon*) and the uppermost (*Hyperodapedon* and *Riograndia*). Guerra-Sommer and Klepzig (2000) and Barboni and Dutra (2015) reported occurrences of leaves, Cuticle fragments and *ex situ* fossil woods, with a predominance of the genus *Dicroidium*, in the Middle-Upper Triassic package (Passo das Tropas Member) paleoflora. This genus includes the Division *Ginkgophyta*. Such occurrences were first assigned to the Anisian-Ladinian age (Guerra-Sommer and Klepzig 2000), but recent studies comparing these ginkgophytes with those from different Gondwanan assemblages attributed a Carnian age for these Brazilian deposits (Barboni and Dutra 2015). This age is correlated to the *Hyperodapedon*'s AZ dating. The occurrences of *ex situ* fossil woods can be interpreted as episodic flooding events, which corroborate with our hypothesis of a high humidity episode during the *Hyperodapedon*'s AZ deposition. This work uses geochemical data obtained from vertebrate fossils and their sedimentary matrices to verify the climatic changes, unlike the Potrerillos Formation observations that used the conglomerate deposition as a criterion for the biozones (MBC and BNP) delimitation (indicating high energy flows, maybe related to a humidity peak). Subtle climatic changes are also recorded in SMS from faciological studies (gradation from loess deposits to underwater deposits) carried out by Horn *et al.* (2018a, 2018b).

Another data source that indicates a rise in humidity at the beginning of the Upper Triassic came from the particle size analysis made by the authors with rock samples from the analyzed biozones. It was observed an increase in the clay and sand percentages toward the top of the SMS package. This reinforces the idea that the uppermost AZ of this sequence were wetter than the basal ones. Besides the clay and sand content increase, the permanence of high silt percentages (above 80%) are highlighted, especially in the thicker fractions, even in the wetter biozones. Thus, it suggests that the leading sediment supplier, in all biozones, was the wind, in a peridesertic context. In the lowermost AZ (*Dinodontosaurus* and *Santacruzodon*), the silt was deposited under massive layers (loess). On the other hand, the uppermost's (*Hyperodapedon* and *Riograndia*), the dust brought by the wind was reworked by the water, generating laminated deposits.

## CONCLUSIONS

Throughout depositional evolution of the SMS, there was a change in the facies association, from dry mudflat facies (Pinheiros-Chiniquá and Santa Cruz Sequences) to sheet delta facies (Candelária Sequence). This facies change followed by geochemical variations record the passage from more basic conditions (characterized by the highest values

of Ca and Ba of the *Dinodontosaurus* and *Santacruzodon* AZ) to a more acid environment (characterized by the highest percentages of Al, Si, and Sr of the *Hyperodapedon* and *Riograndia* AZ). This set of evidence points to a record of the CPE also for the SW portion of the Gondwana. The sedimentary matrices of the *Santacruzodon* AZ can be diagnosed by the low contents of As. The sediments of the *Hyperodapedon* AZ, in their turn, are differentiated by the high contents of Al, Si, Ti, Fe, Ni, Rb, Zr, and Nb and the low values of F, P, and Ca. The *Riograndia* AZ's sediments can be individualized by their low content of Mg. The low contents of Mg and Al observed in *Riograndia* AZ attest a wetter period in this SMS biozone. However, if compared with the high contents of Al, Si, and Fe recorded in the *Hyperodapedon* AZ's sediments, it is possible to conclude that the highest humidity peak of the SMS is associated to this AZ. This hypothesis is more plausible, since sediments that are relatively enriched in Si, Al, and Fe used to be more mature (sediments exposed for very long periods of intense weathering, could be their soil profile leaching) than those with Mg and Al. Therefore, the studied section records a high humidity episode, in the uppermost AZ of the SMS (Carnian) that could be related to the global event named CPE.

In addition, the geochemical study of the assemblage zones of the SMS shows that these biozones could be used as a stratigraphic element of correlation due to their characteristic geochemical compositions. However, due to the chemical heterogeneity observed in the studied samples, it is considered important to continue the studies in this area. More samples need to be analyzed in order to precisely determine the content variations of these elements across the AZ.

More detailed studies of geochemical variations of the fossiliferous of the studied AZ are needed. A paleofloristic study, similar to those made in Argentina, can also be performed. The particle size studies also need a refinement, in order to verify how the global paleoclimatic variations can influence the facies and AZ genesis in the Santa Maria Supersequence.

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