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Geochronological correlation of the main coal interval in Brazilian Lower Permian: Radiometric dating of tonstein and calibration of biostratigraphic framework

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ABSTRACT

The radiometric age of 291 ± 1.2 Ma obtained through single-crystal zircon U–Pb ages (Sensitive High Resolution Ion MicroProbe – SHRIMP II) of tonsteins from the Leão-Butiá Coalfield, southern Paraná Basin (Rio Grande do Sul state), associated with previous SHRIMP II radiometric data obtained from tonsteins from the western (Candiota Coalfield) and eastern (Faxinal and Leão-Butiá coalfields) borders of the basin indicate that the mean age of the main peat-forming interval is 291.0 ± 1.3 Ma. In a regional context, the mean age represents a consistent geochronological correlation for the uppermost and more important coal seams in southern Brazilian coalfields, but this assumption does not establish an ash fall origin from a single volcanic event. According to the International Stratigraphic Chart, the interval is dated as middle Sakmarian. The coal palynofloras are included in the *Protohaploxypinus goraiensis* Subzone within the palynostratigraphic framework for the Brazilian Paraná Basin. Formal relationships are also established with the *Glossopteris–Rhodeopteridium* Zone within the phytostratigraphic chart for the Lower Permian of southern Brazilian Paraná Basin.

1. Introduction

Tonsteins are volcanic ash falls in coal-bearing sequences that have altered to kaolinite (Spears, 2012) and are recognized as reliable marker beds for stratigraphic analysis (Bouroz, 1972; Lyons et al., 2006). These clay beds can extend over large distances and usually contain relict volcanic minerals that can be dated by radiometric analyses. As the geographical distribution of the marker beds is restricted to sites with favorable preservation potential (such as lacustrine and swamp environments), their occurrence in coal sequences reflects particular sedimentary conditions in peat-forming areas and constitutes possible target of reliable geochronological data (Way et al., 1986; Saylor et al., 2005). Air fall volcanic ash deposited during a short-term eruptive event helps identify tonstein beds as chronostratigraphic markers and, consequently, as useful stratigraphic tools in both regional and global correlations (Huff et al., 1992).

Evidence of Early Permian explosive volcanic activity (Formoso et al., 1999), represented by tonstein beds, is widespread in various coal successions in the Cisuralian of the southern Brazilian Paraná Basin (Fig. 1). These coal-bearing rocks are related to a paralic setting (assigned to the Rio Bonito Formation), that is, adjacent to estuarine, deltaic, backshore, foreshore and shoreface siliciclastic sedimentary facies and most of the peat-forming areas in the basin have been identified as part of a back-barrier lagoonal paleoenvironment (Alves and Ade, 1996; Holz, 1998; Milani et al., 2007).

The resolution of a stratigraphic framework for the coal-bearing interval in southernmost Paraná Basin has presented difficulties due to the discontinuity of strata and the apparently isolated, discontinuous coalfields placed at different tectonic blocks and the distance of approximately 300 km between the coalfields located at the western and eastern borders of the basin (Fig. 1).

Nevertheless, in the last decade, tonstein beds have been used as a geochronological correlation tool for the coal-bearing strata in the southern Paraná Basin (Guerra-Sommer et al., 2008a,b,c; Rocha-Campos et al., 2007; Mori et al., 2012) because they enable high resolution calibration with other paleontological and stratigraphic tools for the study interval.

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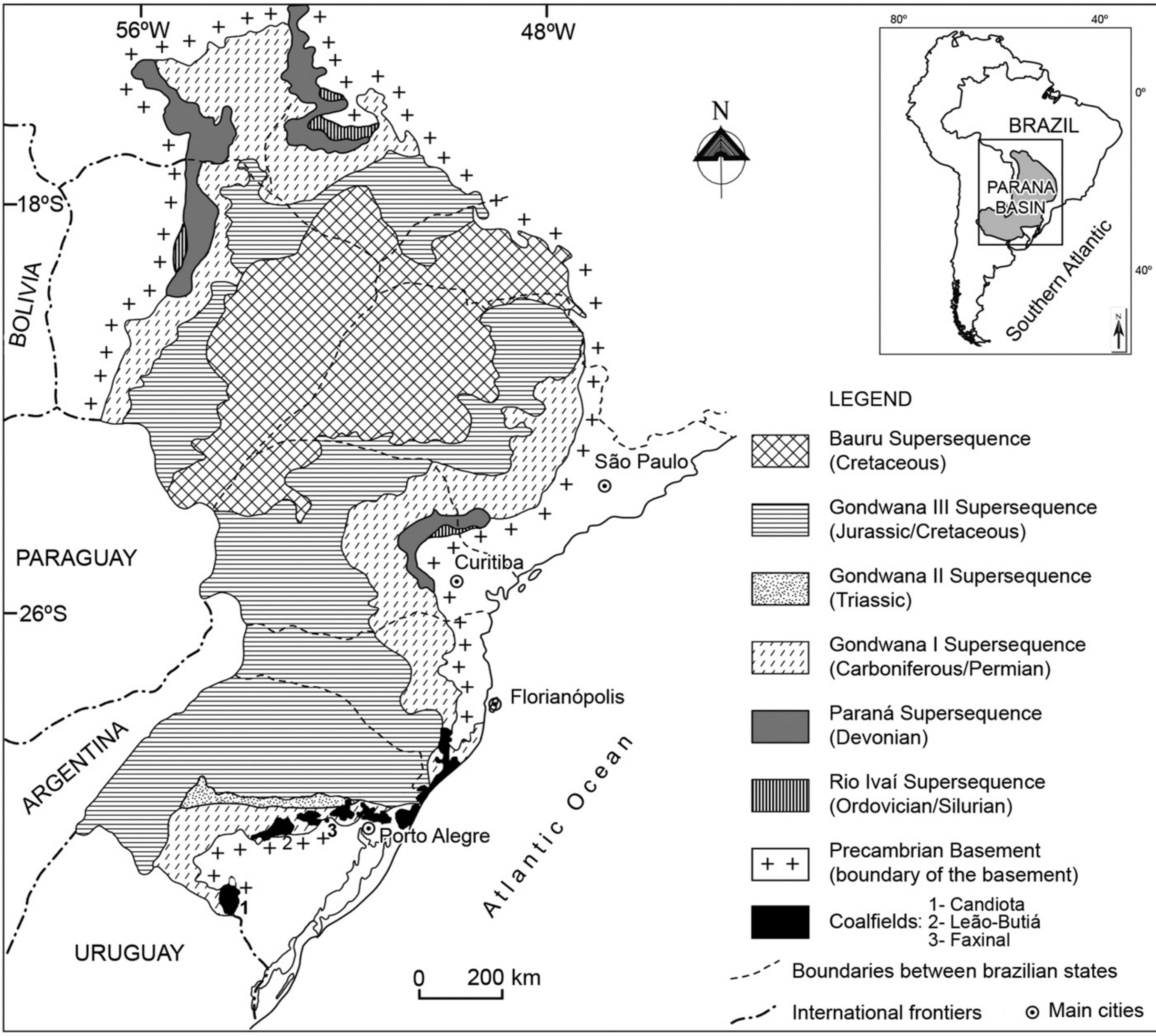

Fig. 1. Simplified geological map of the Paraná Basin in Brazil, with major tectonic elements after Milani et al. (2007); geographic references after Santos et al. (2006); location map of the coalfields of Rio Grande do Sul state including Candiota, Faxinal and Leão-Butiá coalfields after Horbach et al. (1986).

In Candiota Coalfield (western border of the basin), multiple thin tonstein beds (less than 1 cm thickness) are interbedded in different and very thin coal seams. The two most important tonstein beds are interbedded in the uppermost Candiota coal seam; they are the Lower Candiota tonstein (Tonstein A: 1.5 cm thickness) and Upper Candiota (Tonstein C: 2.0 cm thickness). From the basin's eastern region, a single but thick tonstein bed (mean thickness 7.0 cm) is identified at the base of the uppermost coal seam (S) of the Faxinal Coalfield, whereas for the Leão-Butiá very thin tonstein beds are interbedded in the six most evident coal seams. The presence of tonstein beds showing frequent multiple horizontal bedding within single coal seams in different coalfields indicates that ash fall did not interrupt peat accumulation.

Radiometric dating and mean ages of the ash fall beds interbedded in the topmost coal seams in different coalfields have been obtained trying to delimitate the main peat-forming interval in the Permian of the southernmost Brazilian Paraná Basin, even though there are some uncertainties such as (i) the occasional occurrence of episodes of volcanic ash deposition and subsequent localized erosion in some sites, (ii) the occasional reduction of thickness and (iii) the disappearance of a tonstein bed over a distance of some meters (Zhou et al., 2000).

The first attempt to establish radiometric ages for the tonsteins of the southern Brazilian coal succession was made in the Candiota Coalfield by Matos et al. (2001). They used the IDTIMS U–Pb method to date zircon grains of Tonstein A (mean thickness 1.5 cm) interbedded with the Lower Candiota Coal Seam at the uppermost coal interval. The U–Pb age of 267.1 ± 3.4 Ma constrained the interval of deposition to the Cisuralian according to the criteria presently proposed by Ogg and comp, 2010.

Santos et al. (2006) challenged the results obtained by Matos et al. (2001) by performing SHRIMP U–Pb dating on zircon grains from bentonitic ash fall beds in the Irati Formation, which

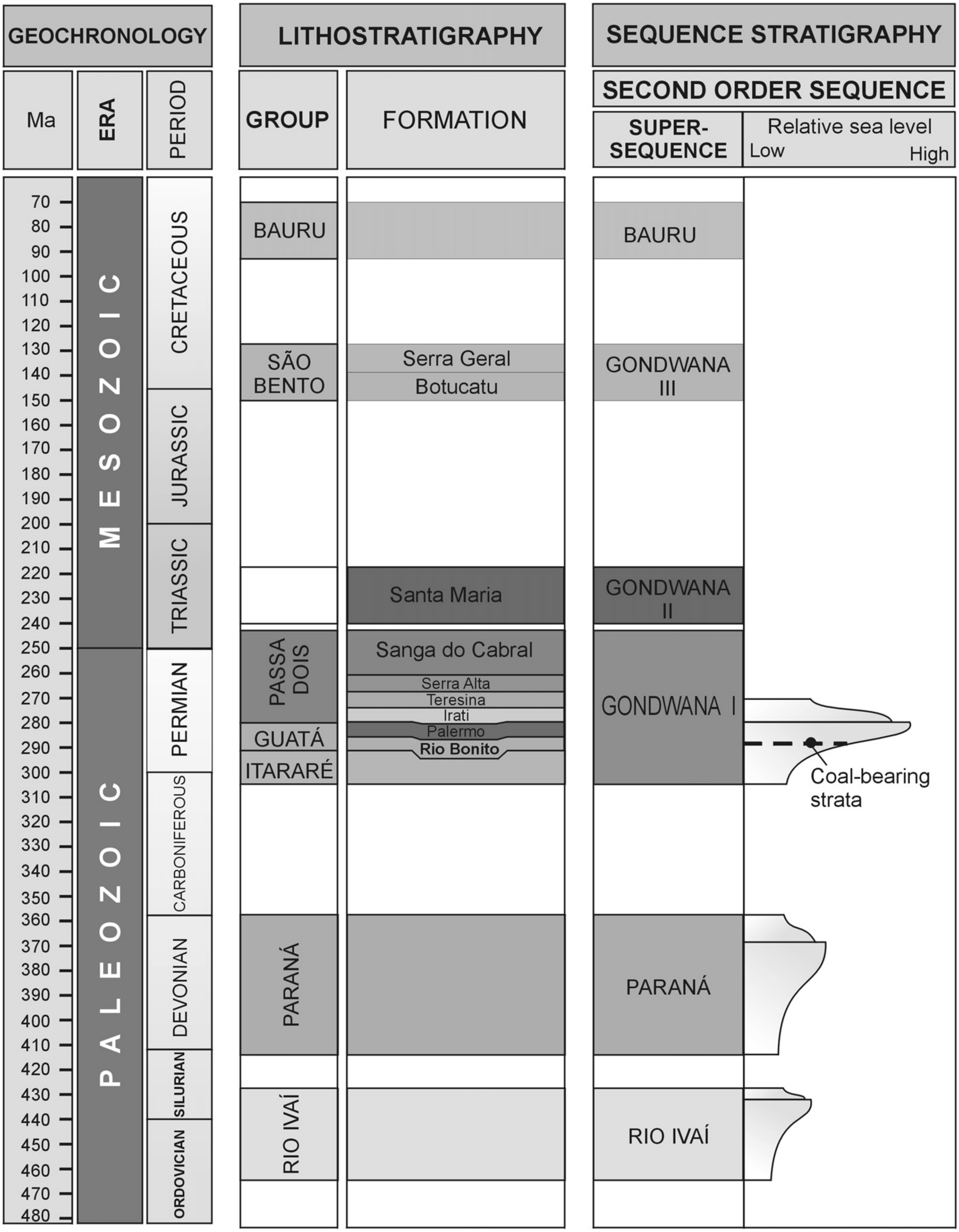

Fig. 2. Stratigraphic framework of the Early Permian of the southern Paraná Basin. Numerical ages from Ogg (2010). (*) Mean age for the southern Brazilian coal-bearing strata.

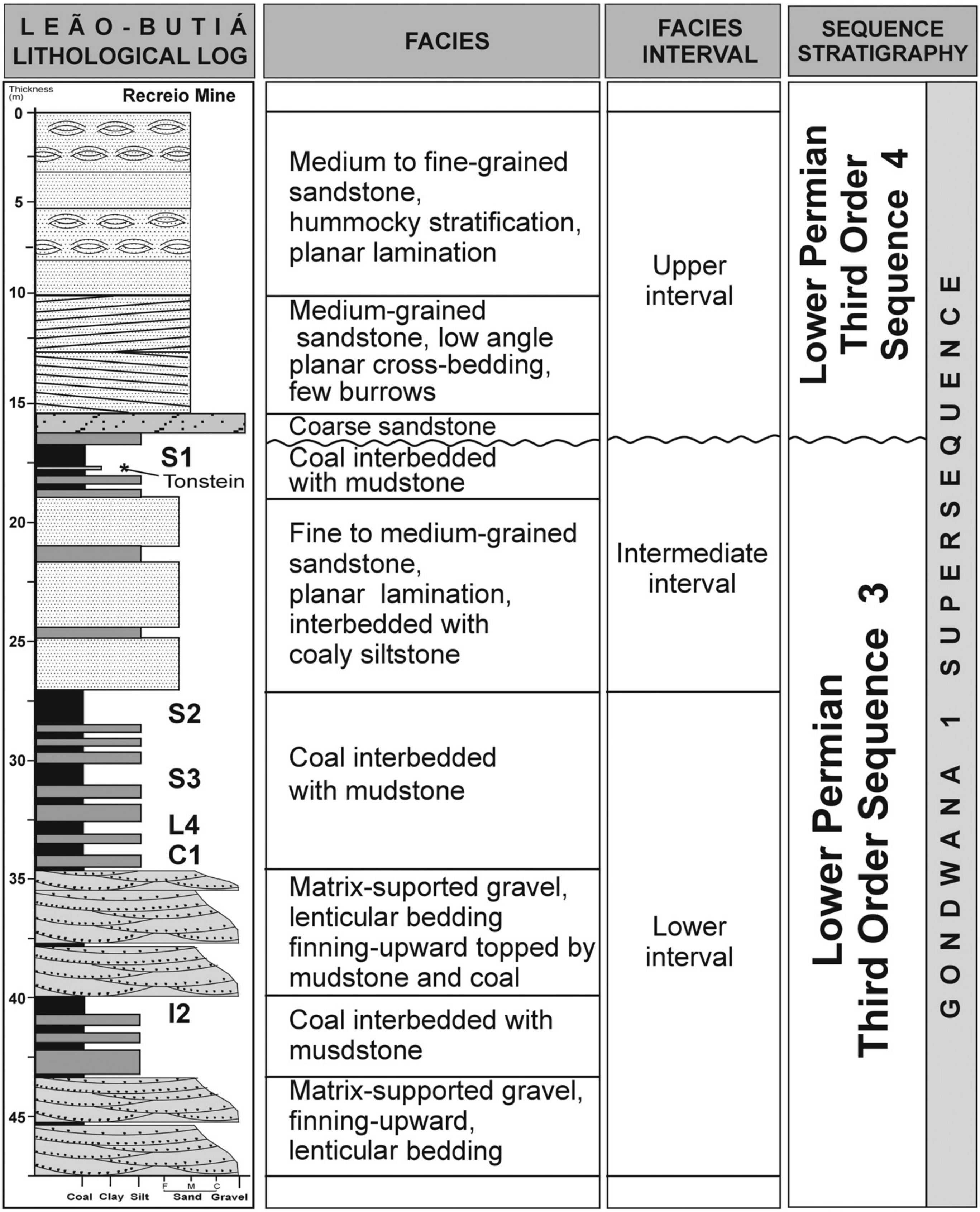

Fig. 3. Stratigraphic log of Recreio Mine (Leão-Butiá Coalfield). (*) Tonstein sampling.

overlies the Rio Bonito Formation. The minimum age obtained by Santos et al. (2006) for the Irati Formation was 278.4 ± 2.2 Ma, approximately 11 Ma older than the sample dated by Matos et al. (2001).

To refine the chronostratigraphic framework for coal succession in the southern Paraná Basin, Guerra-Sommer et al. (2008a) conducted radiometric analyses in tonstein beds interbedded with the uppermost coal seams at the Candiota Coalfield. The ages obtained by these authors through U–Pb zircon dating (IDTIMS) were 296.9 ± 1.65 Ma (Lower Candiota Coal Seam – Tonstein A) and 296 ± 4.2 Ma (Upper Candiota Coal Seam – Tonstein C, mean thickness 2 cm).

A radiometric age of 285.4 ± 8.6 Ma was obtained at the Faxinal Coalfield (eastern border of the Paraná Basin) by Guerra-Sommer et al. (2008b) through U–Pb zircon dating (IDTIMS) of the tonstein bed interbedded with the upper Coal Seam S.

After determining the zircon ages of two tonstein beds from Candiota and one tonstein bed from Faxinal by IDTIMS, a larger number of zircon grains was investigated by Guerra-Sommer et al. (2008c) using the ion microprobe SHRIMP U–Pb method. This allowed them to calculate the pooled and TuffZir ages (Ludwig, 2003), which in turn increased the precision of these ages. The more precise age was particularly important for the Faxinal tonstein, where the IDTIMS age has a relatively large error interval of 8.6 Ma. The dating of zircon grains by Guerra-Sommer et al. (2008c) yielded a mean age of 290.6 ± 1.5 Ma. Correlation with the International Stratigraphic Chart (Ogg and comp, 2010) constrained the peat-forming areas of Faxinal and Candiota to the Sakmarian (Fig. 2).

Mori et al. (2012) obtained an absolute age of 281.4 ± 3.4 Ma from a tonstein bed located at the base of a thin coal seam (Candiota 4 Coal Seam) using Laser Ablation Microprobe, Multicollector, Inductively Coupled Plasma, Mass Spectrography (LAM-MC-ICP-MS U–Pb) zircon analyses. The tonstein bed is stratigraphically above the tonstein beds A and C interbedded with the Lower Candiota and the Upper Candiota coal seams analyzed by Guerra-Sommer et al. (2008a, c).

The main goals of this paper are to (i) obtain a radiometric age of the tonstein bed of the Leão-Butiá Coalfield, located between the Candiota (western basin) and Faxinal (eastern basin) coalfields through single-crystal zircon U–Pb age (U–Pb SHRIMP), (ii) establish mean age for the Leão-Butiá, Candiota and Faxinal coalfields, (iii) define the time interval for the main coal formation in the southern Paraná Basin, (iv) compare previous calibration of biostratigraphic data with radiometric dating from the main coal-bearing strata in southern Paraná basin and (v) confirm the

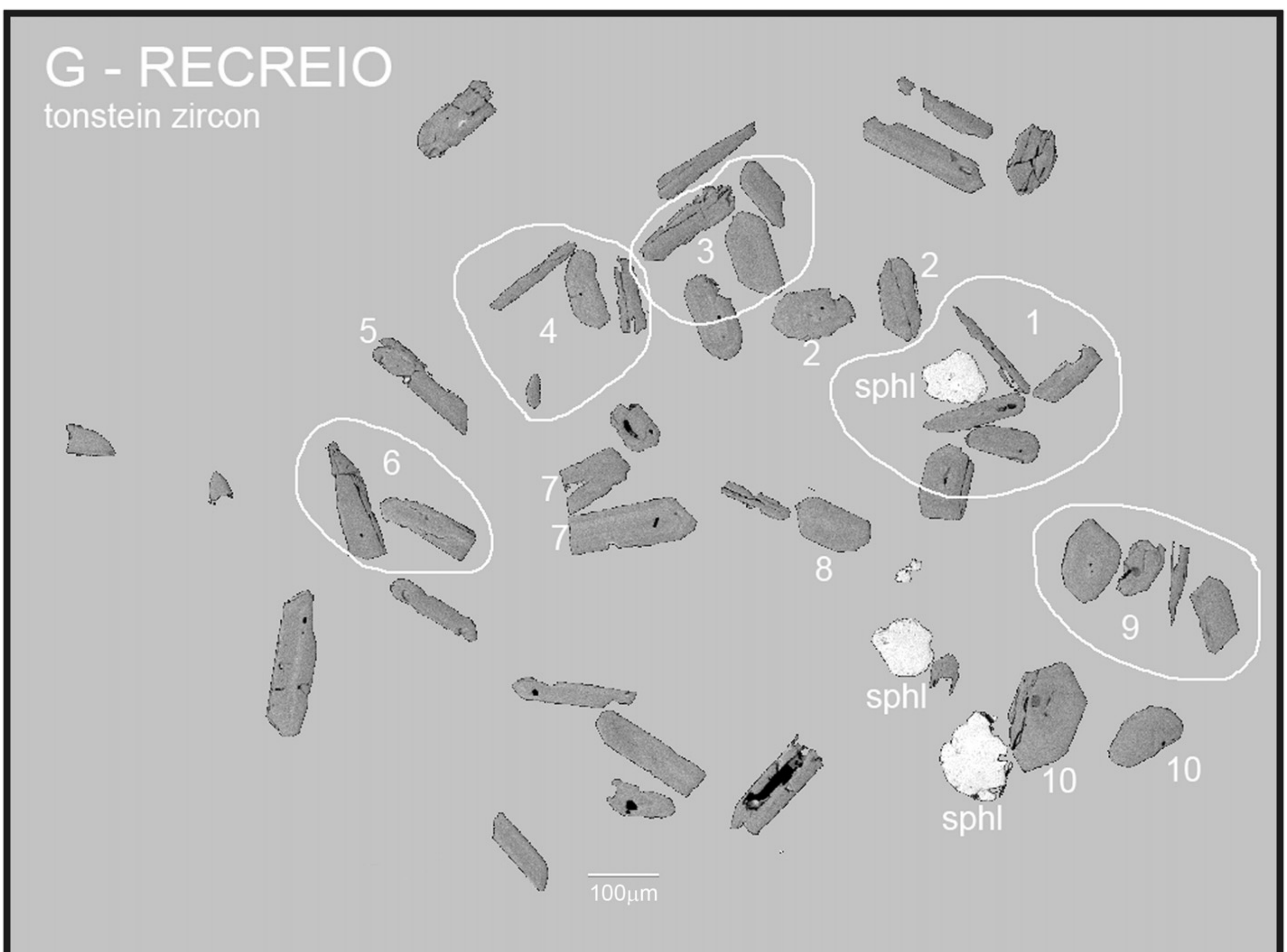

Fig. 4. BSE image of zircon grains of Recreio tonstein for single-crystal zircon U–Pb age (U–Pb SHRIMP) analyses. The grains with detailed BSE images and analyses are numbered from 1 to 10. The sample also contains grains of ZnS–sphalerite (initially suspected to be titanite), indicated above. Sphalerite includes thorite ($ThSiO_4$).

biostratigraphic interval for the main coal formation interval in the southern part of Paraná Basin.

2. Geologic and stratigraphic setting

The Paraná Basin (1,700,000 km^2) is an intracratonic basin spanning southern Brazil, southeastern Paraguay, northeastern Argentina and northern Uruguay. The basin's basement consists of Paleoproterozoic and Mesoproterozoic rocks of the La Plata Craton and Neoproterozoic mobile belts, which were amalgamated during the Brasiliano/Pan-African orogeny (900–543 Ma) as part of the assembly of Gondwana.

A novel stratigraphic framework for the Paraná Basin was created through the pioneering work of Milani and Ramos (1998). According to Milani et al. (2007), six supersequences have been identified (from base to top): Rio Ivaí (Ordovician/Silurian), Paraná (Devonian), Gondwana I (Carboniferous/Early Triassic), Gondwana II (Late Triassic), Gondwana III (Jurassic – Early Cretaceous) and Bauru (Late Cretaceous).

The Gondwana I Supersequence, which includes the coal-bearing strata assigned to the Rio Bonito Formation, is a second-order transgressive–regressive cycle and the thickest part of the Paraná Basin (up to 2800 m) identified in the basin's depocenter in the states of São Paulo and Mato Grosso (Holz et al., 2006). The Gondwana I Supersequence includes seven third-order sequences, called the Lower Permian Third-Order Sequence 1 to 7 (LPTS 1 to 7 according to Holz et al., 2010), ascribed to the Sakmarian. The basal transgressive interval corresponds to diamictites, sandstones and siltstones/mudstones of periglacial facies association (previously related to the lithostratigraphic units known as the Itararé Group), fluvio-paralic and lagoon back-barrier models to marine facies association (related to the Rio Bonito Formation) and the maximum flooding interval (corresponding to the Palermo Formation). The overlying regressive package represents a continental trend (Irati, Serra Alta, Teresina and Rio do Rasto formations), topped by fluvio-eolian deposits, assigned to the Sanga do Cabral Formation (Menezes, 2000; Milani et al., 2007).

The main coalfields in Rio Grande do Sul, such as Candiota, Faxinal and Leão-Butiá, are located on the southernmost portion of the Brazilian Paraná Basin.

The coal-bearing succession of Leão-Butiá has a similar sequential stratigraphic context as that of Candiota: most of Leão-Butiá is included in the transgressive system tract of the LPTS-3. Three interval facies are recognized from the base to the top of the coal seam package. As depicted in Fig. 3, the lower interval comprises two fining-upward conglomeratic facies successions, each one topped by thin coal beds interbedded with mudstone. This interval comprises the most important coal-bearing succession of the Candiota Coalfield and corresponds to mudstone facies with coaly mudstone lenses, paleosoils and coal beds that are as much as 0.40 cm thick. The most evident coal seams of this interval, which outcrop along the cutbanks of the Recreio open pit, are locally named I2, CI, L4, S3, S2 and the uppermost, S1. The samples analyzed herein were collected from a thin clay bed (mean thickness 2 cm) interbedded with the

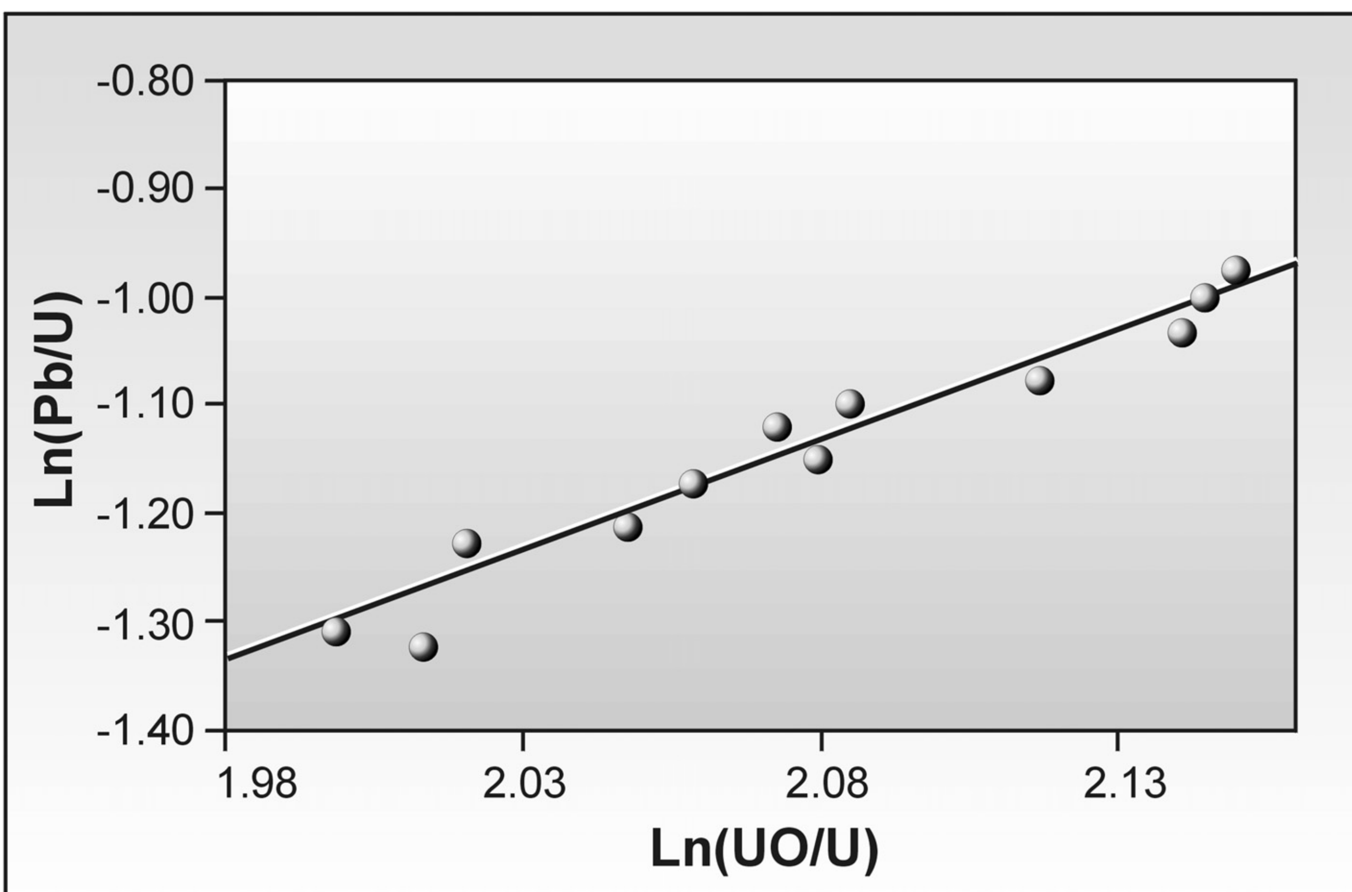

Fig. 5. Slope of 2 was used for Pb–U calibration using 12 analyses of standard BR266. Note that the observed slope of the robust fit line (2.03) is almost identical to the standard slope of zircon (2.00).

base of the S1 Coal Seam, which was identified through petrographic analysis as ash fall of volcanic origin. The lower interval corresponds to a distal alluvial fan and peat-forming facies associations.

The intermediate interval corresponds to fine- to medium-grained sandstones interbedded with coaly siltstones and topped by coal (S1 bed) interbedded with mudstone. This interval comprises back-barrier lagoon and peat-forming facies associations. The upper interval is identified by fine- to medium-grained sandstone facies and indicates the transgression of a foreshore and shoreface facies association.

3. Zircon dating

3.1. Methodology

In situ U–Pb analyses of zircon were conducted using a Sensitive High-mass Resolution Ion Microprobe (SHRIMP II) located at Curtin University of Technology in Perth, Western Australia and operated by a Western Australia University-government consortium with the Australia Research Council (ARC).

The sample was zircon-rich; less than 1 kg of tonstein produced approximately 2500 zircon grains. The sample was prepared using standard procedures for crushing, milling, sieving at 60 mesh, washing, drying and extracting the heavy concentrate using tetrabromoethane (TBE, density = 3). The concentrate was separated into three non-magnetic fractions and zircon grains were extracted from those fractions at 1.2 A and 3° lateral slope. Most zircon grains are long prisms (aspect ratio 4:1 to 10:1) that are too narrow to place in an analytical spot of approximately 20 micra in diameter. Therefore, only the larger grains (approximately 40 grains) were selected and placed in a 25-mm-epoxy mount for analyses. The mount was polished and coated with carbon for back-scattered electron (BSE) imaging using a JEOL JSM-6400 (SEM) fitted with a Link ISIS energy dispersive spectrometer (EDS) located at the Centre for Microscopy, Characterization and Analysis at the University of Western Australia.

The BSE images permitted interpretation of the internal structure of the grains; no possible older core was detected. Most of the grains had large length-to-width ratios, which is typical of rapid grain crystallization in a volcanic setting (Hoskin and Schaltegger, 2003). Some grains have narrow and long melt inclusion along the *c*-axis, which are glassy and characteristic of fast cooling zircon, typical of volcanic environment (Thomas et al., 2003). The images were also used to select the best areas to place the analytical spot, avoiding fractures, altered zones and inclusions. The group of selected zircon grains ranged in size from 80 μm to 250 μm (Fig. 4).

Analyses were performed using a ≤2.35 nA O_2^- primary beam focused on 20–25 μm spots. Sixteen analyses were performed during two analytical sessions on 02/10/2010 and 02/15/2010. Zircon BR266 (559 Ma, 903 ppm U) was used as the primary Pb–U standard and as the U content calibration. Zircon OGC1 was used to monitor the $^{207}Pb/^{206}Pb$ ratio. Twelve analyses on BR266 were performed; the error spot to spot used for sample calibration was

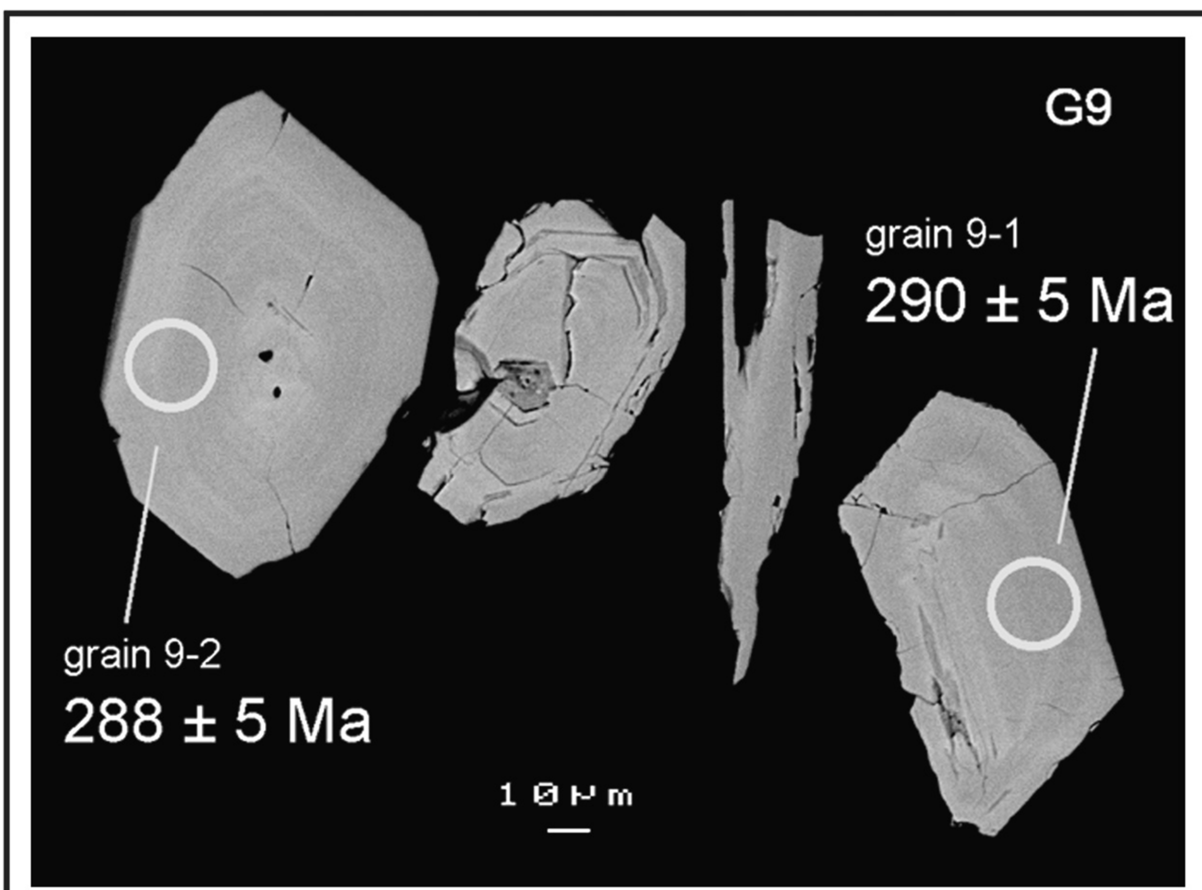

Fig. 6. BSE image of grains 9-1 and 9-2, showing ages ($^{206}Pb/^{238}U$) and spot location.

2.03% (2σ) and the 2σ error of the mean age of the standards at 559 Ma was 0.99% (Figs. 5 and 6).

3.2. Results

Zircon is relatively rich in U (average 625 ppm) and Th (average 362 ppm) and poor in radiogenic lead (average 25 ppm for ^{206}Pb), as expected for relatively young zircon. The analyzed internal areas of zircon had a very low to nonexistent non-radiogenic lead content (calculated from analyses of ^{204}Pb) and the highest content of common lead was 0.31%. Because the content of ^{207}Pb is very low (less than 1 ppm), the $^{207}Pb/^{206}Pb$ and $^{207}Pb/^{235}U$ ages are not used and the $^{206}Pb/^{238}U$ age is preferred because it is within a lower relative error. Three different ages were calculated: the inverse concordia (using $^{207}Pb/^{206}Pb$ and $^{238}U/^{206}Pb$ ratios), the mean and the TuffZirc algorithm (Ludwig and Mundil, 2002), proposed as a tool for obtaining the U–Pb ages of zircon grains from Phanerozoic tuffs, which uses the $^{206}Pb/^{238}U$ ages. The inverse concordia age using all 16 analyses (MSWD = 0.98 and probability = 0.32) was 291 ± 1.2 Ma, whereas the TuffZir age was 289 + 2.41/−0.90 Ma at a confidence level of 97.8%. The two ages are equivalent, that is, they are within errors (Figs. 7–9; Table 1).

4. Stratigraphic implication of zircon dating

The single-crystal U–Pb age of 291 ± 1.2 Ma, obtained from the tonstein bed of the Leão-Butiá Coalfield using SHRIMP II, is significant for the integration of geochronology into the stratigraphic framework. As summarized in Fig. 10, radiometric dating facilitates the geochronological calibration of the coal succession in the southern Paraná Basin.

Correlation with the International Stratigraphic Chart (Ogg and comp, 2010) constrains the age of the Leão-Butiá coal seams (291 ± 1.2 Ma) to the Sakmarian. Considering that the Leão-Butiá Coalfield is positioned between the Candiota (west) and Faxinal (east) geological cross-section, the integration of results from tonstein beds interbedded with the upper interval of these coalfields corroborates the sequence stratigraphy framework, which includes the coal-bearing strata in the Lower Permian Third-Order Sequence 3 (LPTS-3). The mean U–Pb age obtained through 103 analyses of six samples (Candiota, Faxinal and Recreio) was 291 ± 1.3 Ma (95% confidence, MSWD = 1.4). These results support inferences about the time interval for main coal generation in different coalfields in the southern Paraná Basin, that is, it is constrained to the middle Sakmarian. Thus, a consistent geochronological correlation was provided for

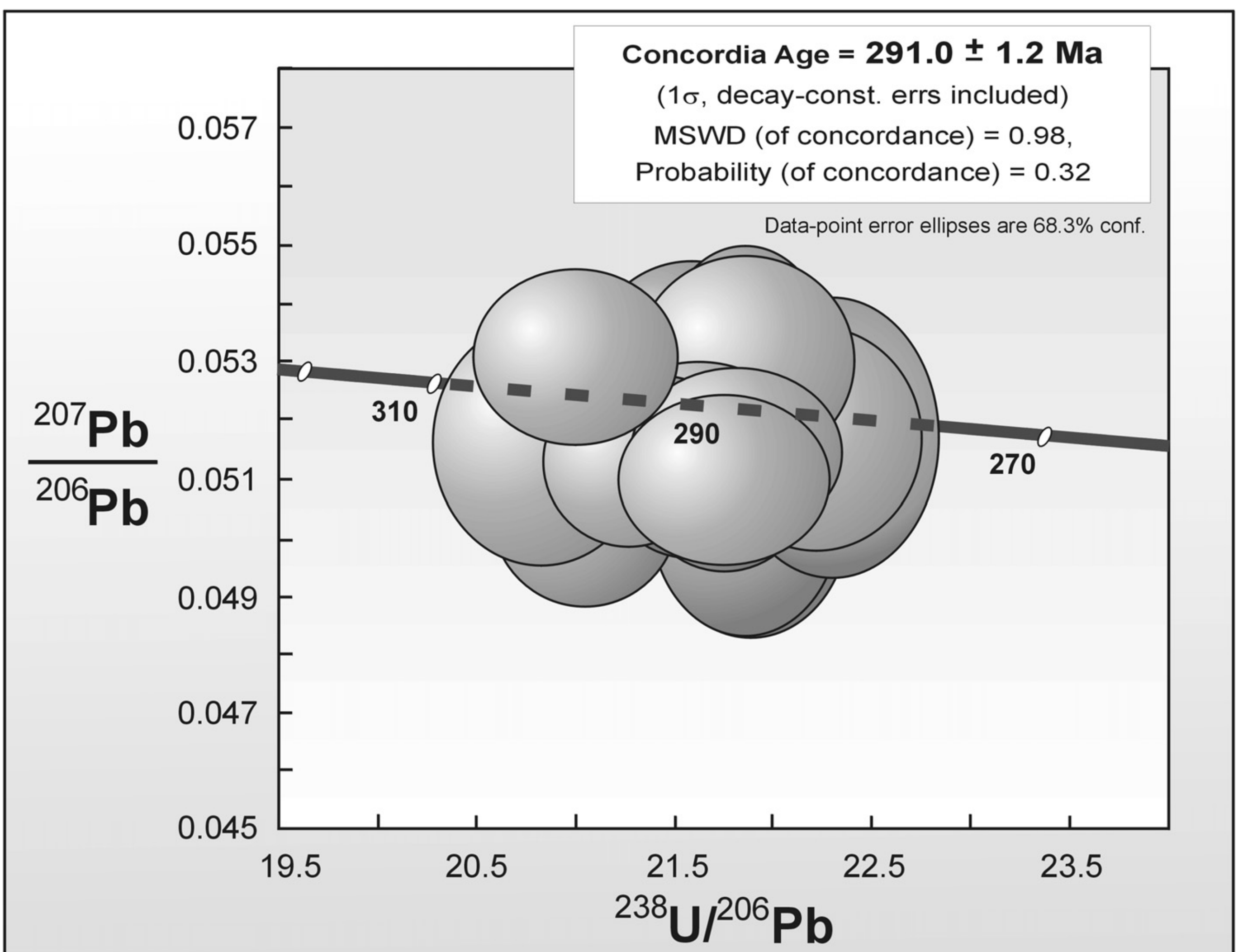

Fig. 7. Concordia age of 291 ± 1.2 Ma using all 16 analyses. Agebox heights are 2σ. TuffZirc age = 288.96 + 2.41 − 0.90 Ma (97.8% conf., from coherent group of 13).

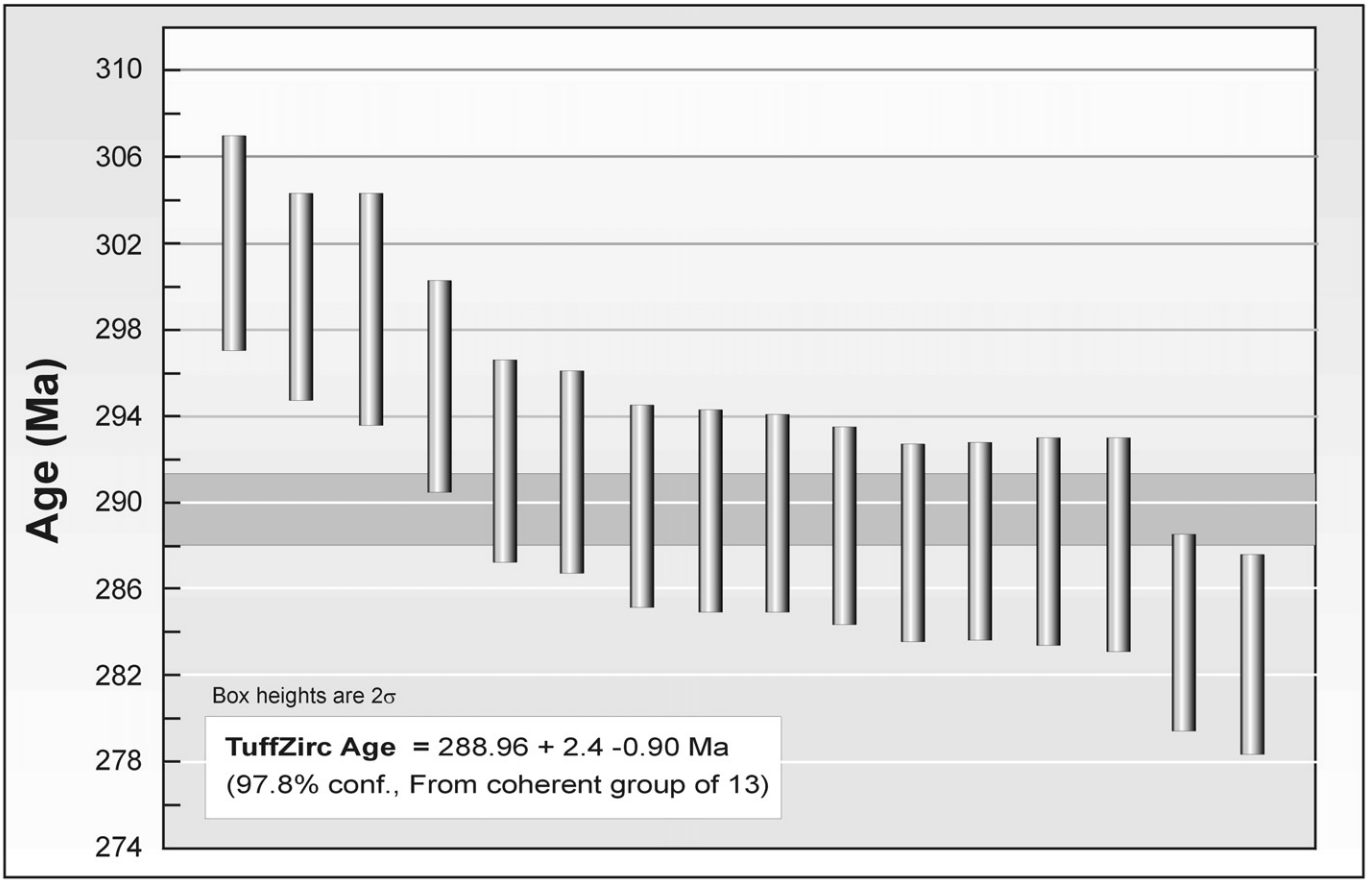

Fig. 8. TuffZir $^{206}Pb/^{238}U$ age using 13 out of 16 analyses. See Table 1 for the data.

regional coal seams in southern Brazilian coalfields. Nevertheless, this assumption does not imply a common origin for the different tonstein beds that is, an ash fall origin from a single volcanic event. Correlation between the studied tonstein beds must be ratified by future mineralogic and chemical bases as recommended by Burger (1985), Triplehorn et al. (1991) and Spears (2012).

Various authors, as summarized in Fig. 11, proposed correlation charts between radiometric dating and palynostratigraphic and plant stratigraphy for the Upper Paleozoic in the southern portion of the Paraná Basin. The correlations were based on the charts of Marques-Toigo (1991) and Guerra-Sommer and Cazzulo-Klepzig (1993), which were later refined by Souza and Marques-Toigo (2003, 2005) and Iannuzzi et al. (2010).

In the correlation chart of Iannuzzi et al. (2007) for Lower Permian post-glacial succession in the southernmost Brazilian Paraná Basin, the SHRIMP U–Pb age of 279 ± 1.8 Ma obtained by Santos et al. (2006) from tuff beds in the Irati Formation in the northern area of the basin was used as a chronostratigraphic parameter. Considering the regional focus of the present work, restricted to the southernmost Brazilian coalfields, that chart is not discussed here.

Calibrations of palynostratigraphic data with numerical ages obtained by the IDTIMS U–Pb method in different tonstein beds in the Candiota Coalfield (Tonstein C: 296.9 ± 1.65 Ma; Tonstein A: 296 ± 4.2 Ma) led Guerra-Sommer et al. (2008a) to constrain to the Asselian the *Protohaploxipinus goraiensis* Subzone defined by Souza and Marques-Toigo (2003), which includes the coal-bearing strata (Fig. 11A).

The palynoflora preserved in Coal Seam S and also in the interbedded tonstein bed in the Faxinal Coalfield, (radiometric age of 285.4 ± 8.6 Ma), attributed to the Sakmarian, was assigned by Guerra-Sommer et al. (2008b) in a regional context to the uppermost portion of the *P. goraiensis*/base of the *Hamiapollenittes karooensis* Subzone of Souza and Marques-Toigo (2003) (Fig. 11B). The palynostratigraphic assignment was based mainly on the presence of *Maculatasporites gondwanensis* and *Maculatasporites minimus*, as mentioned by Guerra-Sommer and Dias-Fabrício (1993). Nevertheless, this assignment is not adequate, because the genus was considered by Cazzulo-Klepzig et al. (2007) as a palynomorph of doubtful botanical affinity which has been commonly identified in coal palynoassemblages described for southern Brazilian coal seams and associated tonstein beds (Cazzulo-Klepzig et al., 2009), typically included in the *P. goraiensis* Subzone of Souza and Marques-Toigo (2003).

The calibration of the palynostratigraphic framework for the Brazilian Paraná Basin (Souza and Marques-Toigo, 2005) with the mean age of 290.6 ± 1.5 Ma obtained by Guerra-Sommer et al. (2008c) from tonsteins interbedded with coal seams from the Candiota and Faxinal coalfields using SHRIMP II dating of zircon grains showed that, in a broader concept, the coal palynofloras were included in the *P. goraiensis* Subzone (Fig. 11C). The radiometric dating is more precise than previously published intervals, showing that the main coal succession from the southern basin is constrained to the middle Sakmarian.

In the correlation chart of chrono- and biostratigraphic data for the Permian of Paraná Basin of Iannuzzi et al. (2010) the ages of 288.4 ± 1.2 Ma obtained by Guerra-Sommer et al. (2008c) using

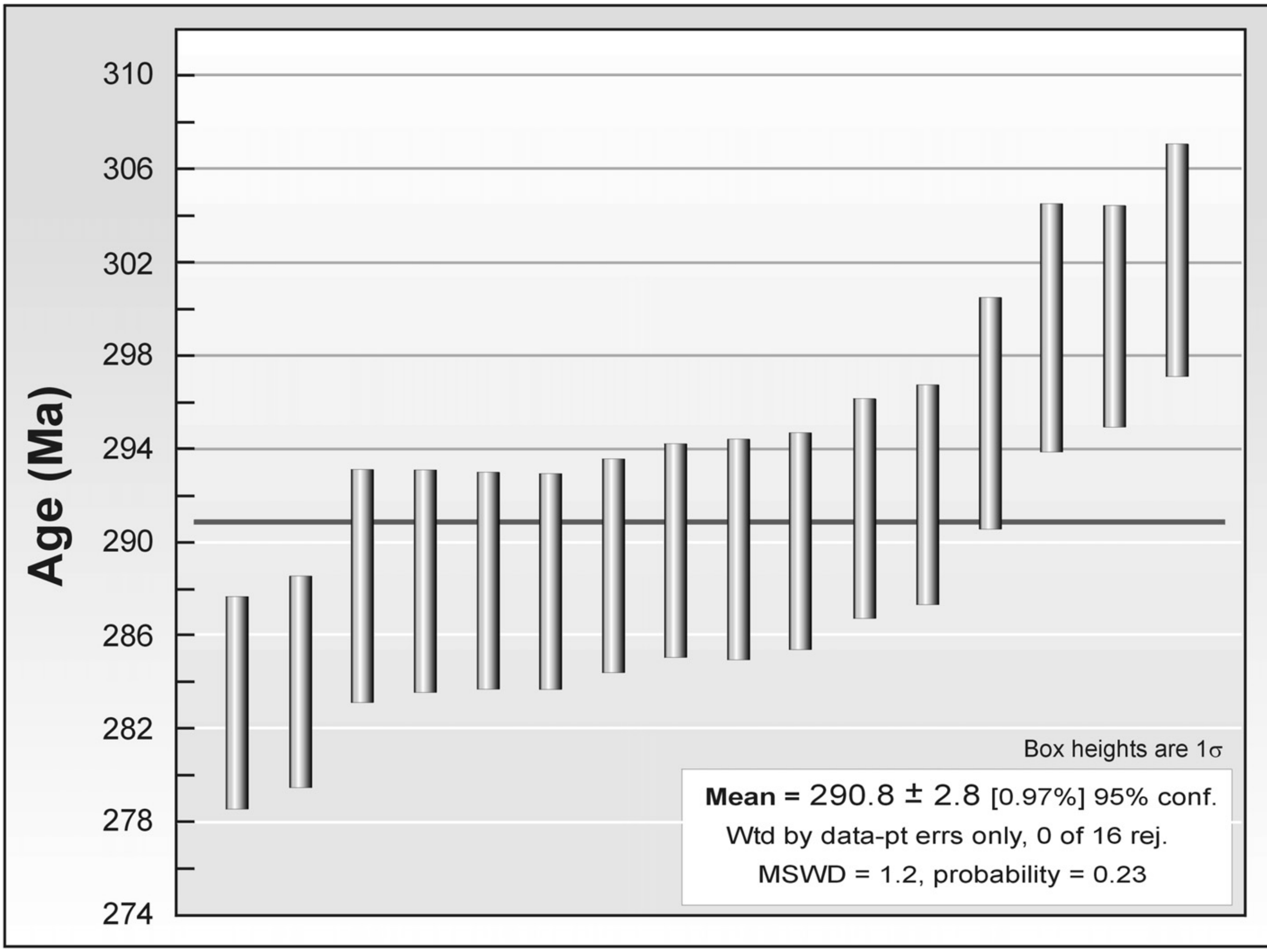

Fig. 9. Mean average age ($^{206}Pb/^{238}U$) of all 16 analyses. See Table 1 for the data. Data reduction was carried out using Squid 1.03 (Ludwig, 2001) and plots were produced using Isoplot 3.0 (Ludwig, 2003).

U–Pb SHRIMP II method from tonstein interbedded with the Upper Candiota Coal Seam are considered as chronostratigraphic markers for the boundary between the *Botrychiopsis plantiana*/*Glossopteris–Rhodeopteridium* Zones. Despite the scarcity of floral evidence in Candiota, from where only *Buriadia isophylla* (Guerra-Sommer and Bortoluzzi, 1982) and *Brasilodendron pedroanum* (Chaloner et al., 1979) have been described, the stratigraphic assignment is possible because they constitute diagnostic taxa.

Additionally, the ages of 285.4 ± 8.6 Ma for a tonstein bed interbedded with the upper coal seam of Faxinal Coal Seam using IDTIMS U–Pb method (Guerra-Sommer et al., 2008b) are considered by Iannuzzi et al. (2010) as chronostratigraphic marker for the top of the *Glossopteris*/*Rhodeopteridium* Zone (Fig. 11D). The presence of rich parautochthonous taphoflora hosted by the Faxinal tonstein (Guerra-Sommer et al., 2008b) enables correlation with this zone, but the absence of identifiable plant fossils in the Leão-Butiá Coalfield (Recreio mine) prevents phytostratigraphic correlations.

The framework synthesized by Holz et al. (2010) for Brazilian Paraná Basin will not be discussed here because those authors have not considered any radiometric ages previously obtained from the coal-bearing strata in southern Paraná Basin.

For the Leão-Butiá Coalfield, object of the present study, previous palynological results obtained by Picarelli and Marques-Toigo (1985) from the S2 and C1 coal seams in the coalfield indicated that pteridophytic trilete spores dominated the palynological content; monosaccate pollen grains were rare and not well preserved and some elements were related to the algae group. The palynological assemblage was dominated by *Puntactisporites gretensis* forma minor, *Lundbladispora braziliensis*, *Cristatisporites* cf. *Cyclogranisporites microvacuolatus*, *Vallatisporites arcuatus*, *Calamospora liquida*, *Cyclogranisporites* sp. and *Horriditriletes* sp. Zygnematacean-like algae (*Tetraporina*) were also important forms. *Quadrisporite*s, vinculated to chlorophyte and *Portalites gondwanensis*, vinculated to fungi, were also recorded. The abundance of pteridophytic spores and elements related to algae suggested a hydrophylous–hygrophylous depositional environment. Biostratigraphic implications were not established.

Palynological investigations essentially on the S1 Coal Seam at Recreio Mine in the Leão-Butiá Coalfield, developed in the present study, have identified palynoassemblages demonstrating a similar composition to that identified in the S2 and C1 coal seams by Picarelli and Marques-Toigo (1985). The palynoassociation is characterized by the dominance of pteridophytic spores associated to zygnematacean-like algae and the rare occurrence of monosaccate pollen grains. These characteristics facilitated the identification of the *P. goraiensis* Subzone according to the palynostratigraphic chart of Souza and Marques-Toigo (2005).

Table 1
U–Pb Shrimp isotopic data of zircon of Recreio tonstein, Rio Bonito Formation.

Spot	U (ppm)	Th (ppm)	Th U	Pb (ppm)	f206[a] (%)	Isotopic ratios				Ages			
						$^{207}Pb^c/^{206}Pb^c$ Error[b]	$^{207}Pb^c/^{235}U$ error[b]	$^{206}Pb^c/^{238}U$ Error[b]	$^{238}U^c/^{206}Pb$ er[b]	$^{207}Pb/^{206}Pb$[e]	$^{206}Pb/^{238}U$[e]	Correl. coefic.	Disc.[d] (%)
Recreio, tonstein													
g.1-1	742	616	0.86	29.9	0.05	0.05133 ± 1.92	0.3320 ± 2.58	0.0469 ± 1.72	21.3185 ± 1.72	256 ± 44	296 ± 5.0	0.667	−16
g.1-2	399	183	0.47	16.3	0.05	0.05149 ± 3.46	0.3373 ± 3.90	0.0475 ± 1.82	21.0502 ± 1.82	263 ± 79	299 ± 5.3	0.465	−14
g.2-1	689	365	0.55	13.2	0.31	0.05165 ± 2.47	0.3207 ± 2.96	0.0450 ± 1.64	22.2063 ± 1.64	270 ± 57	284 ± 4.6	0.553	−5
g.3-1	334	176	0.55	26.4	0.50	0.05156 ± 4.27	0.3249 ± 4.62	0.0457 ± 1.77	21.8823 ± 1.77	266 ± 98	288 ± 5.0	0.384	−8
g.3-2	662	390	0.61	26.8	0.19	0.05273 ± 2.44	0.3368 ± 2.94	0.0463 ± 1.64	21.5854 ± 1.64	317 ± 55	292 ± 4.7	0.559	8
g.4-1	719	326	0.47	28.5	0.16	0.05155 ± 2.33	0.3270 ± 2.85	0.0460 ± 1.64	21.7385 ± 1.64	266 ± 54	290 ± 4.6	0.574	−9
g.5-1	362	215	0.61	18.9	0.00	0.05162 ± 2.76	0.3415 ± 3.24	0.0480 ± 1.70	20.8412 ± 1.70	269 ± 63	302 ± 5.0	0.525	−12
g.6-1	827	444	0.56	22.5	0.00	0.05303 ± 1.89	0.3479 ± 2.49	0.0476 ± 1.63	21.0149 ± 1.63	330 ± 43	300 ± 4.8	0.653	9
g.7-1	479	191	0.41	14.9	0.30	0.05161 ± 4.30	0.3254 ± 4.62	0.0457 ± 1.69	21.8681 ± 1.69	268 ± 99	288 ± 4.8	0.367	−8
g.7-2	583	345	0.61	33.8	0.30	0.05171 ± 3.10	0.3200 ± 3.52	0.0449 ± 1.66	22.2790 ± 1.66	273 ± 71	283 ± 4.6	0.472	−4
g.8-1	870	407	0.48	34.4	0.00	0.05097 ± 1.86	0.3229 ± 2.46	0.0460 ± 1.62	21.7626 ± 1.62	239 ± 43	290 ± 4.6	0.658	−21
g.9-1	474	179	0.39	18.8	0.23	0.05178 ± 3.04	0.3281 ± 3.47	0.0460 ± 1.67	21.7590 ± 1.67	276 ± 70	290 ± 4.7	0.483	−5
g.9-2	544	232	0.44	21.4	0.02	0.05241 ± 2.80	0.3304 ± 3.25	0.0457 ± 1.65	21.8680 ± 1.65	303 ± 64	288 ± 4.7	0.508	5
g.10-1	800	495	0.64	31.5	0.00	0.05135 ± 1.94	0.3246 ± 2.53	0.0458 ± 1.63	21.8127 ± 1.63	256 ± 45	289 ± 4.6	0.642	−13
g.10-2	671	282	0.43	26.3	0.00	0.05303 ± 2.19	0.3344 ± 2.73	0.0457 ± 1.64	21.8668 ± 1.64	330 ± 50	288 ± 4.6	0.600	13
g.11-1	851	945	1.15	33.9	0.17	0.05128 ± 2.15	0.3269 ± 2.71	0.0462 ± 1.64	21.6284 ± 1.64	254 ± 50	291 ± 4.7	0.607	−15

[a] f206 = (common ^{206}Pb)/(total measured ^{206}Pb) based on measured ^{204}Pb.
[b] Isotopic ratios errors in %.
[c] All Pb in ratios are radiogenic component corrected for ^{204}Pb.
[d] disc. = discordance, as $100 - 100\{t[^{206}Pb/^{238}U]/t[^{207}Pb/^{206}Pb]\}$.
[e] Uncertainities are 1σ.

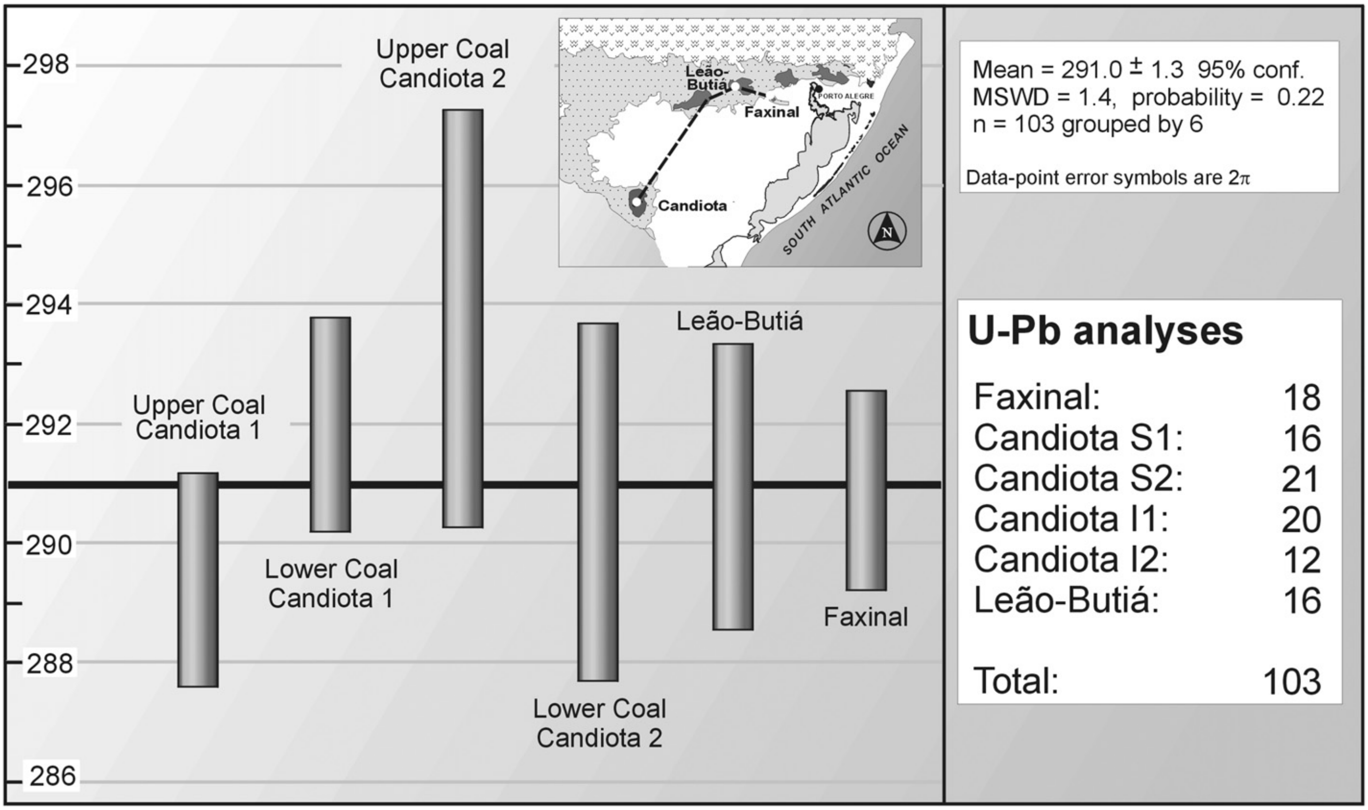

Fig. 10. Mean average age of all 103 U–Pb analyses from tonstein from Leão-Butiá and correlation with data from the Candiota and Faxinal coalfields. Data from this work and from Guerra-Sommer et al. (2008c).

Distinct compositional features identified in Candiota, Faxinal and Leão-Butiá palynofloras are interpreted as representing local paleoenvironmental conditions without significant stratigraphic constraints. These inferences agree with the chronostratigraphic chart of Holz et al. (2010) based on sequence stratigraphy, which has linked the coal seams in Rio Grande do Sul to a single third-order sequence, the LPTS-3 (Sakmarian).

The age of 281.4 $\pm$ 3.4 Ma obtained by Mori et al. (2012) from a tonstein level at the base of the Coal seam 4 (uppermost Rio Bonito) evidenced the oldest age (Sakmarian–Artinskian) for the *Lueckisporites virkkiae* Zone in the Paraná Basin (Fig. 11E). The mean age of 291 $\pm$ 1.3 Ma obtained in the present study for Candiota, Leão-Butiá and Faxinal tonsteins (Fig. 11F) interbedded in main coal seams does not conflict with the results of Mori et al. (2012). An overall change in floristic composition is marked by the transition from the *Vitattina costabilis* Zone (*P. goraiensis* Subzone) to the *L. virkkiae* Zone, right at the Sakmarian–Artinskian boundary during the deposition of the uppermost thin coal seams in the Candiota Coalfield. It demonstrates changes in composition of the peat-forming floras at the end of the coal interval, when gymnosperms become common elements represented by dominant bisaccate (non-taeniate and taeniate) and polyplicate pollen grains (Mori et al., 2012). The composition change can be attributed to tectonic activities and also to climatically driven changes in paleofloras. The peat-forming areas would be distributed in restricted niches at the coastal areas, probably distinct from the back-barrier lagoonal environment that prevailed during the main coal interval.

It is important to emphasize that the mean age of 291 $\pm$ 1.3 Ma obtained for the Candiota, Faxinal and Leão-Butiá (Recreio mine) coalfields is here considered as the climax of the *Glossopteris* flora in southern Paraná Basin, rather than the top of the *Glossopteris–Rhodeopteridium* Zone. The upper limit of the zone was placed just below the limit *P. goraiensis* Subzone/*L. virkkiae* Zone defined by Mori et al. (2012). The phytostratigraphic assignment was based on the presence of fragmentary but identifiable *Glossopteris*, *Buriadia*, and *Brasilodendron* fragments found in siltstones underlying the tonstein bed analyzed by those authors (Fig. 11F).

The source of the air fall volcanic ash bed in the southern Paraná Basin, the Karoo Basin, in South Africa and in Argentinean basins was believed by several authors (López-Gamundi, 1994; Limarino et al., 1996; Stollhofen et al., 2000; Matos et al., 2001; Coutinho and Hachiro, 2005) to be located in Patagonia and West Antarctica, forming an extensive volcanic arc situated to the south and west in the pre-breakup Gondwana configuration. Guerra-Sommer et al. (2008a, b, c) accepted this inference as the probable origin for the air fall volcanic ash kaolinized deposits in the Candiota and Faxinal coalfields. Nevertheless, Rocha-Campos et al. (2011) have a different interpretation about the source of the volcanic ash bed. These authors have concluded that the SHRIMP U/Pb zircon ages of 251 Ma, 264 Ma and 281 Ma of Choiyoi igneous province, from the San Rafael Block in central-western Argentina, imply long-lasting (albeit episodic) igneous activity of approximately 30 Ma during the Late Paleozoic. These three ages correspond to the upper, middle and lower Choiyoi volcanic phases, respectively. The authors analyzed eleven stratigraphically controlled samples of the Choiyoi volcanic section. Of these, four samples representative of the basal, middle and upper portions of the Choiyoi succession were selected for dating. Investigation of geochemical features demonstrated the congruence of composition, evolution and tectonic setting between the Choiyoi succession volcanic rocks and time-correlatable Late

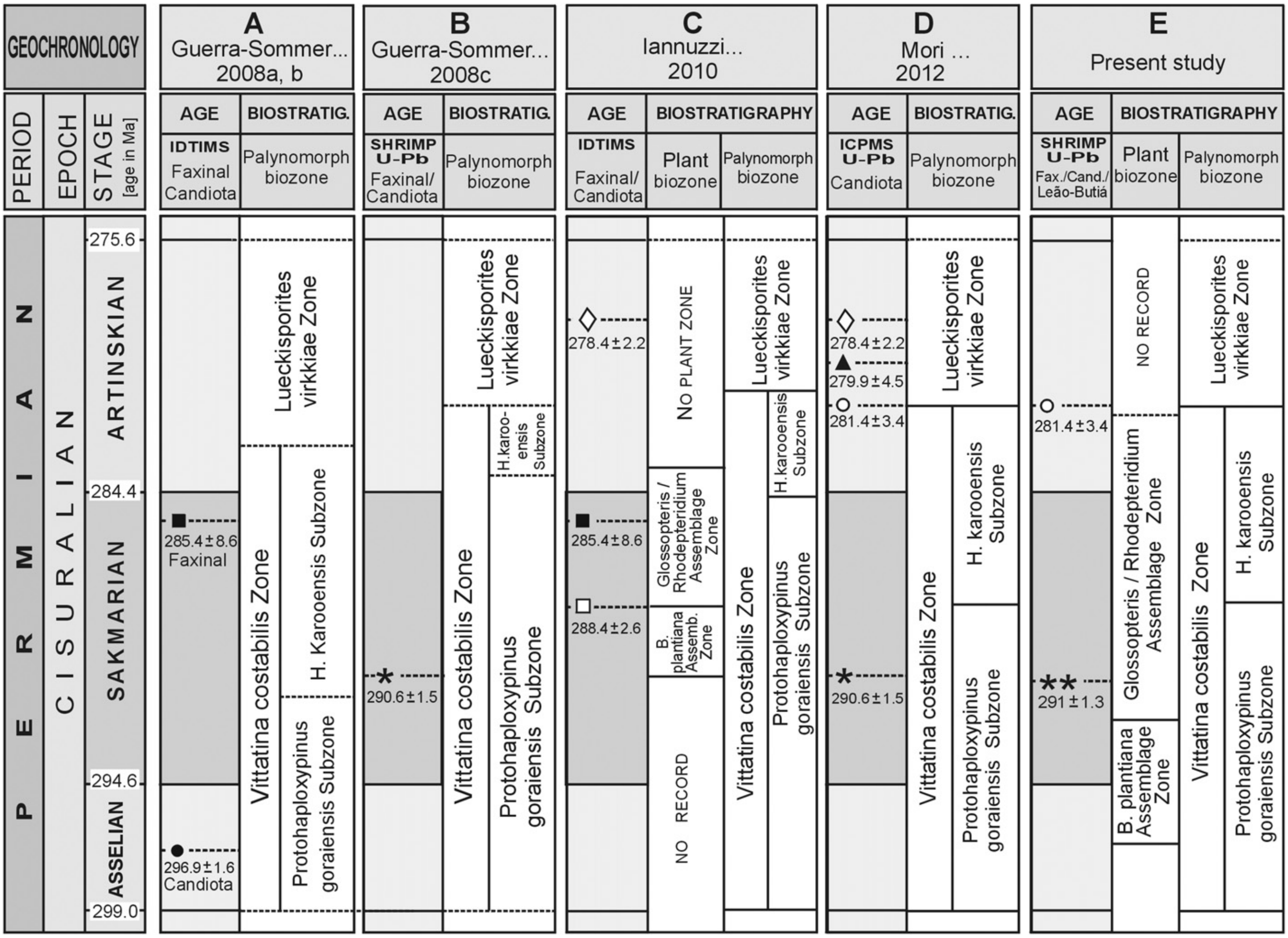

Fig. 11. Comparison between different correlation charts of radiometric and biostratigraphic data for the Lower Permian of Paraná Basin. ● Radiometric age (IDTIMS U–Pb) from tonstein interbedded in the Upper Candiota Coal Seam obtained by Guerra-Sommer et al. (2008a) ■ IDTIMS U–Pb age for Faxinal Coalfield by Guerra-Sommer et al. (2008b); * Mean age (U–Pb SHRIMP II) obtained for Candiota and Faxinal by Guerra-Sommer et al. (2008c); □ U–Pb SHRIMP II age obtained from tonstein interbedded with the Upper Candiota coal seam by Guerra-Sommer et al. (2008c); ◇ radiometric age (U–Pb SHRIMP) obtained by Santos et al. (2006) for Irati Formation; ▲ radiometric age (U–Pb SHRIMP) obtained by Rocha-Campos et al. (2007) for Irati Formation; ○ radiometric age (LAM-MC-ICP-MS U–Pb) obtained by Mori et al. (2012); ** mean age (U–Pb SHRIMP) of the Candiota, Faxinal and Leão-Butiá coalfields obtained in the present study. Stage limits according to Ogg (2010).

Paleozoic ash fall beds from the Paraná Basin. Considering the new geochronological framework, the Choiyoi volcanism in the San Rafael Basin was synchronous with the upper interval of the Late Paleozoic ash bed-bearing package of the Paraná Basin which comprises the deposition of the Irati and the Rio do Rasto Formations. Sources of older ash fall beds (Cisuralian and Pennsylvanian) from areas in the north and south of the San Rafael Basin have the distance between them and the Paraná Basin as a limiting factor. Two hypotheses are considered by Rocha-Campos et al. (2011) for the source of the air fall volcanic ash bed during the Cisuralian and Pennsylvanian: (a) a partial local origin from volcanic terrains close to the southern margin of the Paraná Basin (Coutinho and Hachiro, 2005); (b) an origin from volcanic belts formed along a Permian protorift during the initial opening of the South Atlantic (Stollhofen et al., 2000; Santos et al., 2006). Taking into account these data, the explosive source for the distal ash fall precipitation in southern Paraná Basin during the Sakmarian remains an open question.

5. Conclusions

On the basis of the radiometric age of 291 ± 1.2 Ma obtained through single-crystal zircon U–Pb ages (Ion Microprobe SHRIMP II) of the tonstein bed from the Leão-Butiá Coalfield and data provided by the sequence stratigraphy framework for the Carboniferous/Permian of the Paraná Basin, the following conclusions are here presented:

- The main coal seams in different coalfields (Candiota, Leão-Butiá and Faxinal) from the western to the eastern borders of the southern Paraná Basin have a mean age of 291.0 ± 1.3 Ma. According to the International Stratigraphic Chart, the main peat-forming interval in southernmost Brazilian Paraná Basin is dated as middle Sakmarian.
- The coal palynofloras, in a broader concept, are included in the *P. goraiensis* Subzone within the palynostratigraphic framework for the Brazilian Paraná Basin.
- Differences in palynological content in the various coalfields reflect paleoecological conditions rather than expressive stratigraphic signatures.
- Formal relationships of the main coal interval in southern Paraná Basin with the *Glossopteris–Rhodeopteridium* floral zone are established for Faxinal and Candiota coalfields. The absence of identifiable plant fossils in the Leão-Butiá Coalfield (Recreio mine) prevents phytostratigraphic correlations.

- The mean U–Pb age of 291 ± 1.3 Ma obtained for Candiota, Faxinal and Leão-Butiá coalfields represents a consistent geochronological correlation in a regional context for the main coal interval in southern Brazilian coalfields.
- Petrographic, mineralogical and geochemical analyses of the tonstein layers associated with the uppermost coal seams of Faxinal, Leão-Butiá and Candiota are needed in order to define an origin of a single or of multiple volcanic eruptive events and to refine stratigraphic data from the coal-bearing interval.

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