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A new stratigraphic framework built on U-Pb single-zircon TIMS ages and implications for the timing of the penultimate icehouse (Paraná Basin, Brazil)

Neil Patrick Griffis[1,†], Roland Mundil[2], Isabel Patricia Montañez[1], John Isbell[3], Nicholas Fedorchuk[3], Fernando Vesely[4], Roberto Iannuzzi[5], and Qing-Zhu Yin[1]

[1]*Department of Earth and Planetary Sciences, University of California, Davis, California 95616, USA*
[2]*Berkeley Geochronology Center, Berkeley, California 94709, USA*
[3]*Department of Geosciences, University of Wisconsin, Milwaukee, Wisconsin 53211, USA*
[4]*Departamento de Geologia, Universidade Federal do Paraná, Curitiba, PR, 80060-000, Brazil*
[5]*Departamento de Paleontologia e Estratigrafia, Universidade Federal Rio Grande do Sul, Porto Alegre, RS, 90040-060, Brazil*

ABSTRACT

The timing of the late Paleozoic glaciation and its terminal deglaciation in the Paraná Basin, Brazil, is unconstrained and prohibits correlation of the Paraná Basin ice record with other high-latitude Gondwanan and low-latitude contemporaneous records. Here, we reexamine the existing U-Pb framework for the Carboniferous–Permian Paraná succession through high-precision, single-crystal chemical abrasion–thermal ionization mass spectrometry (CA-TIMS) analysis of individual zircons from tonsteins and subaerial volcanic ash deposits, which overlie sedimentary deposits with glacial indicators. The new ages document two distinct volcanic intervals and define a substantially new and revised chronostratigraphy for postglacial coal-bearing intervals in the southern Paraná Basin. The new CA-TIMS ages further indicate that glaciation in south-central Gondwana, long considered to be Early Permian, is entirely Carboniferous in age and that terminal deglaciation in this key west-central Gondwanan basin occurred near the Permian-Carboniferous boundary. Single-crystal U-Pb CA-TIMS ages from the ice-proximal high-latitude basins of southern Africa and Australia are needed to test the synchronicity of late Paleozoic glaciation and deglaciation events throughout Gondwana, with implications for empirical- and model-based paleoclimate reconstructions.

†npgriffis@ucdavis.edu

INTRODUCTION

The late Paleozoic ice age, one of two major icehouses of the Phanerozoic Era, was associated with atypical atmospheric composition (very low pCO_2 and high pO_2), large-scale climate changes, and the radiation of Earth's most expansive tropical forests (Montañez et al., 2007; Montañez, 2016; Fielding et al., 2008a; Montañez and Poulsen, 2013; Soreghan et al., 2014). Despite decades of research on geologic archives of the late Paleozoic ice age, the glaciation history for Southern Hemisphere Gondwana remains poorly constrained. This is in large part due to the limited precision and accuracy of existing radioisotopic constraints on glacial and postglacial deposits in Gondwanan basins. One of the main challenges in reconstructing late Paleozoic ice age glaciation history is the ability to accurately correlate geologic records intra- and interbasinally throughout Gondwana and with paleotropical proxy records, from which much of our existing understanding of glacioeustasy and climate has been inferred.

The Paraná succession has yielded a wealth of U-Pb zircon ages derived from simple to complex volcanic deposits, resulting in an extensive single-crystal age inventory. However, previous U-Pb zircon analyses employed multicrystal batch analysis using thermal ionization mass spectrometry (TIMS) or in situ analysis of single crystals by laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) and secondary ion mass spectrometry (SIMS) and presented a stratigraphic framework that is challenging to resolve (Fig. 1). Advances in zircon pretreatment and analysis techniques now yield weighted mean $^{206}Pb/^{238}U$ zircon ages on individual volcanic deposits at a precision of <0.1% through CA-TIMS (Mundil et al., 2004; Mattinson, 2005; Schaltegger et al., 2015). Such ages permit the construction of high-resolution chronostratigraphic frameworks that are ideally suited for studying geologic, climatic, and biologic processes (Schoene et al., 2010; Gulbranson et al., 2010; Eros et al., 2012a, 2012b; Schmitz and Davydov, 2012; Metcalfe et al., 2015). Here, we present the first high-resolution single-crystal CA-TIMS results for zircons recovered from four previously dated Paraná Basin tonstein deposits recovered from coals (Candiota and Faxinal) and one previously undated subaerial volcanic ash-fall deposit (Quitéria, which overlie the late Paleozoic age Itararé Gp.). We further discuss the implications of the new CA-TIMS U-Pb ages in the context of other recently published U-Pb ages for southern Gondwana glaciation.

GEOLOGIC AND STRATIGRAPHIC SETTING

The Paraná Basin of southern Brazil, with extensions into Argentina, Paraguay, and Uruguay, contains one of the thickest successions of Carboniferous–Permian glacial and postglacial strata in the world (Fig. 2). This broad glaciogenic basin (~1.7 million km^2) has long been considered a key geographic location regarding the late Paleozoic ice age because of its climatically sensitive temperate position and proximity to multiple topographic centers from which ice masses may have emanated. The Paraná Basin is considered to be a major depocenter for multiple

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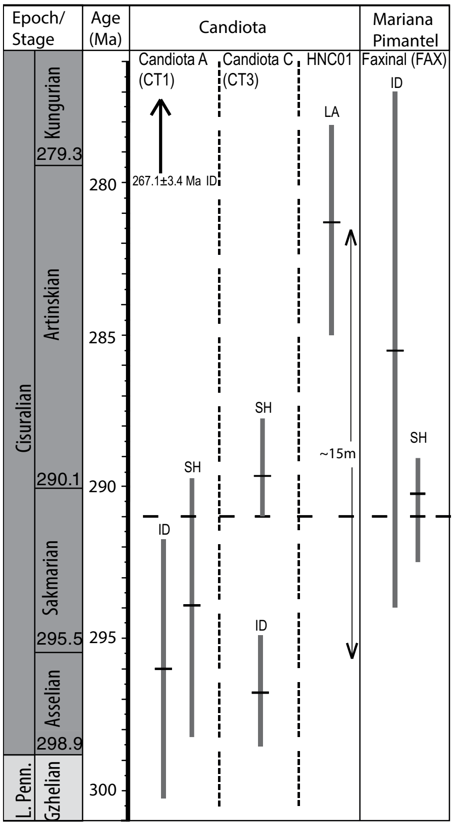

Figure 1. Existing $^{206}Pb/^{238}U$ age constraints for the late Paleozoic Candiota and Faxinal coals in the Paraná Basin (de Matos et al., 2001; Guerra-Sommer et al., 2008a, 2008b, 2008c; Mori et al., 2012). Current framework suggests deposition of Candiota coals spanned over 30 m.y., with black arrow denoting the age of de Matoes et al. (2001). In addition, individual age uncertainties preclude correlation of deposits at substage resolution. The ages of Faxinal ashes are within error of those from Candiota, given their large uncertainties. Dashed line is the average reported U-Pb secondary ion mass spectrometry (SIMS) age for all of the Rio Grande do Sul coal deposits, including Candiota and Faxinal from Simas et al. (2012). SH—SIMS; ID—isotope dilution–thermal ionization mass spectrometry; LA—laser-ablation–inductively coupled plasma–mass spectrometry.

ice sheets, which were possibly continental in scale and advanced into the basin from the east, southeast, and possibly the west (Crowell, 1995; Isbell et al., 2012; Vesely et al., 2015).

The Itararé Group is the lowermost sedimentary unit of the late Paleozoic ice age in the Paraná Basin (Fig. 2). The overlying Rio Bonito Formation (up to 200 m thick) is characterized by marginal marine and terrestrial facies and hosts intercalated volcanic deposits, which were analyzed in this study (Figs. 2 and 3). Tonsteins are thin (~5–10 cm) clay-rich deposits within coal seams shown to be chemically leached ash falls (Seiders, 1965; Bohor and Pillmore, 1976) and have been identified throughout the Candiota and Faxinal Mines (Guerra-Sommer et al., 2008a, 2008b, 2008c; Mori et al., 2012). In order to constrain the relative stratigraphic position of the coals in the latter to the underlying Itararé Group, tonsteins in the lowermost coal-bearing horizons of the Candiota Mine and immediate surrounding area were traced into a core that contains both the Itararé Group as well as the Rio Bonito Formation (Fig. 3). Whole core was provided by Companhia de Pesquisa de Recursos Minerais (CPRM), Caçapava do Sul, Rio Grande do Sul State (Fig. 2).

EXISTING AGE CONTROL FOR THE RIO BONITO FORMATION, RIO GRANDE DO SUL STATE, BRAZIL

The emphasis over the last decade on placing radioisotopic age constraints on the Carboniferous–Permian succession in the Paraná Basin reflects the importance of these coals for refining the palynological-based biostratigraphy for southwestern Gondwana (Souza, 2006; Mori et al., 2012; Césari et al., 2011) and for correlation of the glacial successions with those in other Gondwanan basins (Fig. 4). Existing multicrystal batch analyses via TIMS and in situ techniques permit depositional relationships to be inferred between coals of the coal-bearing interval in the southern portion of the Paraná Basin. The inferred temporal separation of the different coals ranges from coeval to tens of million years (Fig. 1). A review of the existing U-Pb zircon data for the Paraná Basin coals and the assigned biostratigraphic ages (Figs. 1 and 2) for the Candiota and Faxinal sections is presented in the GSA Data Repository.[1]

NEW CA-TIMS U-Pb ZIRCON AGES

Here, we report CA-TIMS analyses of zircons isolated from the Candiota A (CT1), Candiota C (CT3), Hulha Negra Candiota (HNC01), and Faxinal (FAX) tonsteins, as well as from a newly discovered ash-fall deposit at Quitéria (QUI; Figs. 2 and 3). Samples were collected from outcrop and open-pit mine exposures, and exact coordinates of sample sites are provided in each section. Details of the analytical procedures, including tracer utilization and calibration, as well as the data and concordia plots, can be found in the data repository (see footnote 1). We present the U-Pb zircon dates as eruption ages in the form of a weighted mean of the $^{206}Pb/^{238}U$ ages from the youngest coherent cluster of concordant zircons (Fig. 5) that exhibited no scatter in excess of the analytical uncertainty. In addition, we applied an approach that approximates the youngest age of the population (cf. Schoene et al., 2010; Irmis et al., 2011; Husson et al., 2016) using the "youngest detrital age" algorithm implemented in Isoplot (Ludwig, 2008), which assumes that the errors assigned to each date are normally distributed. The algorithm repeatedly perturbs each date randomly by its assigned error and selects the youngest of the suite of perturbed dates. This latter approach typically yields a robust and accurate depositional age at the expense of slightly elevated uncertainty. It further requires a minimum number of analyses in order to truly capture the youngest age ($n = \geq 6$). We thus argue that the new ages presented here may be more realistic in a geological sense, i.e., a more accurate approximation of the eruption/deposition age. For example, the highly precise weighted mean age of CT3 (<0.06%) may not capture the true depositional age, because it may be biased by the pre-eruptive residence time of zircon (Caricchi et al., 2014; Ickert et al., 2015).

Candiota A and C, Lowermost Coal-Bearing Interval

(Candiota A Locality 31°27′43.69″S, 53°41′33.01″W; Candiota C locality 31°27′43.69″S, 53°41′33.01″W)

Zircon-bearing fine clastic sediments (tonstein) were collected from the Candiota coal seams from fresh-cut surfaces in the Candiota Mine, located within the town of Candiota, Rio Grande do Sul State, Brazil (samples CT1 and CT3 on Fig. 2C). Candiota A (CT1) is a thick (~10 cm), calcite-cemented tonstein. Candiota A and C tonsteins were sampled from the same layer analyzed by de Matos et al. (2001; Candiota A) and Guerra-Sommer et al. (2008a, 2008c; Candiota A and C). Candiota tonstein C (CT3) is a white, thin (~5 cm), clay-rich layer located 0.5 m above Candiota tonstein A (Fig. 3). All zircons from tonsteins A and C are euhedral and exhibit no signs of transport abrasion. Nine zircons were analyzed from Candiota A (CT1; Table DR1 [see footnote 1]), and a weighted mean age of

[1]GSA Data Repository item 2017399, concordia plots and isotopic data for each sample and a discussion of previous U-Pb geochronology for the Paraná Basin coals, is available at http://www.geosociety.org/datarepository/2017 or by request to editing@geosociety.org.

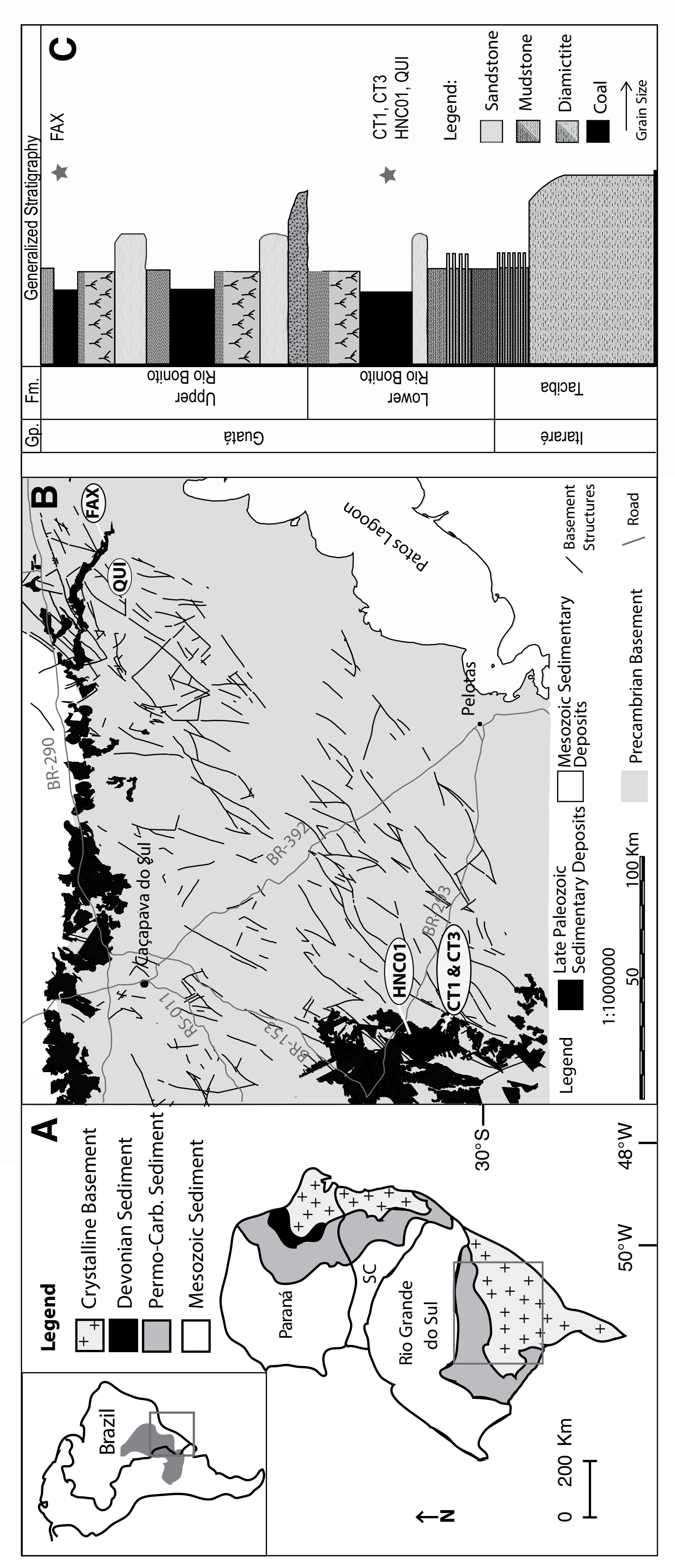

Figure 2. (A) Generalized map –of the study area in the southern Paraná Basin and location within South America, showing the Paraná Basin in outline (inset map); SC—Santa Catarina State. (B) Geologic map of part of Rio Grande do Sul State (box in A) showing distribution of Carboniferous–Permian deposits in black. Note prevalence of Precambrian basement structures, which strongly influenced local thicknesses of Carboniferous–Permian deposits. Sampling locations for isotopic dating are: QUI—Quitéria; FAX—Faxinal; HNC—Hulha Negra Candiota; CT1 and CT3—Candiota Mine. (C) General stratigraphy of the Carboniferous–Permian succession of the Paraná Basin, including the coals and diamictites. Stars show the general stratigraphic location of tonsteins.

298.23 ± 0.31 Ma (mean square of weighted deviates [MSWD] = 0.43) was calculated from a coherent group of five analytically concordant grains (Fig. 5). Four grains were excluded from the calculation of the mean because they were discordant. Inclusion of the $^{206}Pb/^{238}U$ ages from the discordant analyses results in an insignificant change of mean age (weighted $^{206}Pb/^{238}U$ of 298.32 ± 0.28 Ma, youngest zircon age of 297.81 +0.48/–1.3 Ma). Th/U for the Candiota A sample ranges between 0.7 and 0.8.

In total, 15 zircons were analyzed from the Candiota C (CT3) tonstein (Table DR1 [see footnote 1]). The ages for the analytically concordant crystals range from 310 to 297 Ma. A weighted mean $^{206}Pb/^{238}U$ age of 298.64 ± 0.17 Ma (MSWD = 1.0) was calculated from the 12 youngest coherent grains, as well as a youngest zircon age of 297.58 +0.68/–1.40 Ma (Fig. 5). Th/U for the Candiota C zircons ranges from 0.5 to 0.8.

Hulha Negra Candiota

(Locality 31°23′41.50″S, 53°47′16.12″W)

The Hulha Negra tonstein (HNCO1) in the Candiota coal-bearing interval was collected from a road cut at national highway BR-293 8 km east of the town of Hulha Negra, Rio Grande do Sul State, Brazil, and was sampled from the same tonstein layer that was analyzed by Mori et al. (2012; see also Figs. 2 and 3). The Hulha Negra Candiota (HNC01) tonstein is recognized as a thin (~5 cm) yellowish to white mudstone within the C4 coal seam of the Candiota interval (Mori et al., 2012). In total, 17 zircons were analyzed from this sample (Table DR1 [see footnote 1]). Three analyses were discordant and were excluded from the calculation of the age. A weighted mean $^{206}Pb/^{238}U$ age of 298.03 ± 0.25 Ma (MSWD = 0.33) was calculated using the youngest four coherent grains and yielded a "youngest zircon age" of 297.77 +0.35/–0.59 Ma (Fig. 5). The HNC01 tonstein, which contains plant material, is interpreted as a primary volcanic ash fall, and the dispersion in $^{206}Pb/^{238}U$ ages is due to inheritance (Fig. 5). The oldest zircon (535 Ma) in the data set displays a Th/U ratio of 0.7, whereas the younger crystals, with the exception of one, have unusually high Th/U ratios (>2 and up to 7.8). One discordant analysis yielded a Devonian age of 411 Ma and an elevated Th/U ratio (Fig. 6). We therefore infer mixing between the young volcanic component (298 Ma) and old inheritance, resulting in the suite of slightly older ages (both concordant and discordant) between 299 Ma and 326 Ma (Fig. 6). Uncertainties are elevated for the older analyses because the samples were not run to exhaustion.

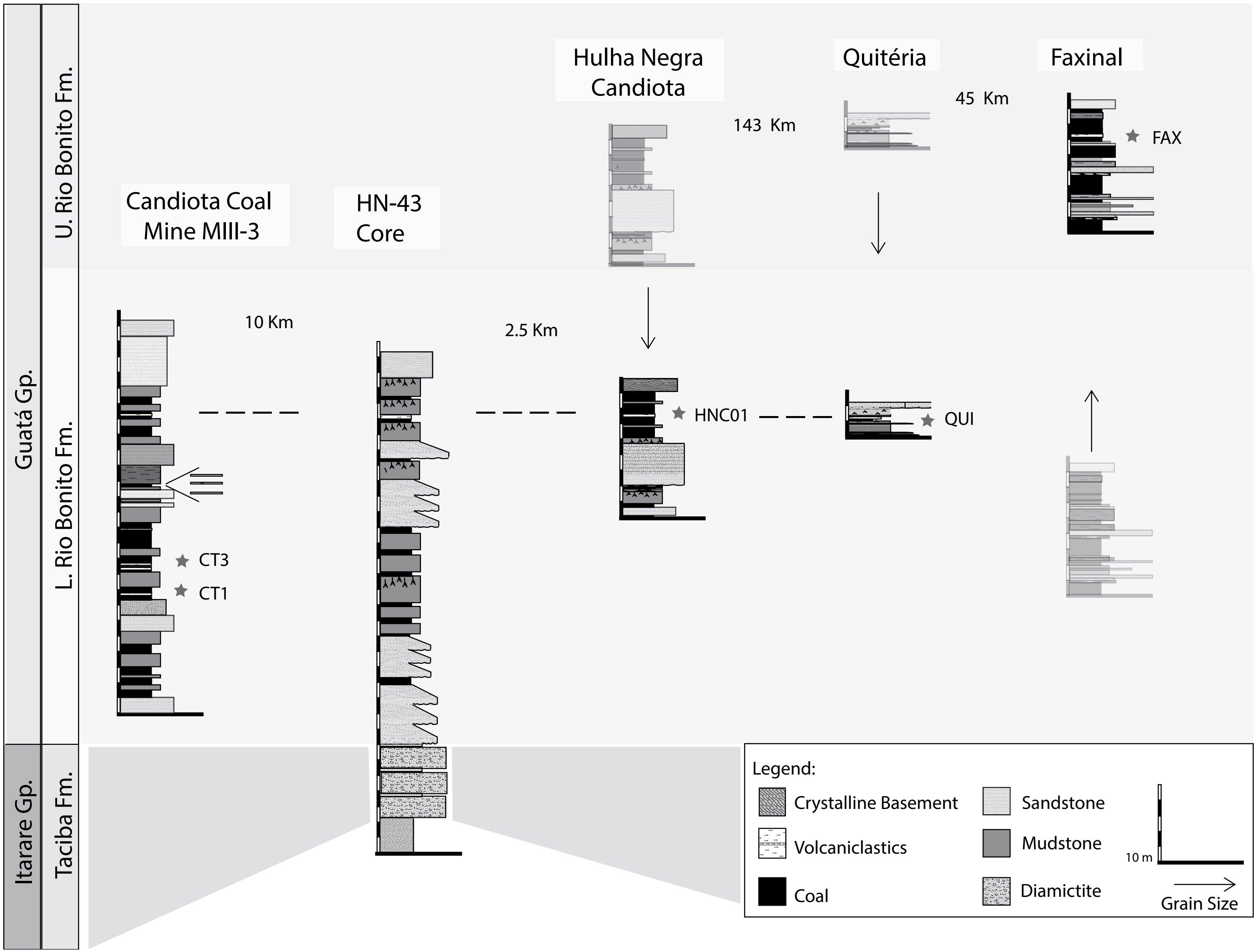

Figure 3. Lithostratigraphy of sections that host volcanic samples (stars) analyzed in this study. Core HN-43 permits correlation of Candiota Mine and Hulha Negra Candiota (HNC) outcrops in the Rio Bonito Formation, as well as brackets the upper age of the Itararé Group. Dashed line is the stratigraphic datum defined by the uppermost tonstein observed in coal deposits of the Candiota region; similar measured $^{206}Pb/^{238}U$ ages of these tonsteins permit correlation between core and outcrops in the Candiota region and extension into the Quitéria region. Geographic distance between samples is noted at top. The $^{206}Pb/^{238}U$ ages reported here place the Candiota coal-bearing interval fully in the lowermost Rio Bonito Formation and the Faxinal coal-bearing interval in the upper Rio Bonito Formation. Stratigraphy for the Faxinal mine is from Guerra-Sommer et al. (2008c). Dark black arrows point to the new stratigraphic locations of the Hulha Negra Candiota, Quitéria, and Faxinal sections; previously assigned stratigraphic location of the outcrops is faded. Small lines next to Candiota Coal Mine Candiota MIII-3 section are additional volcanic ashes identified in the field.

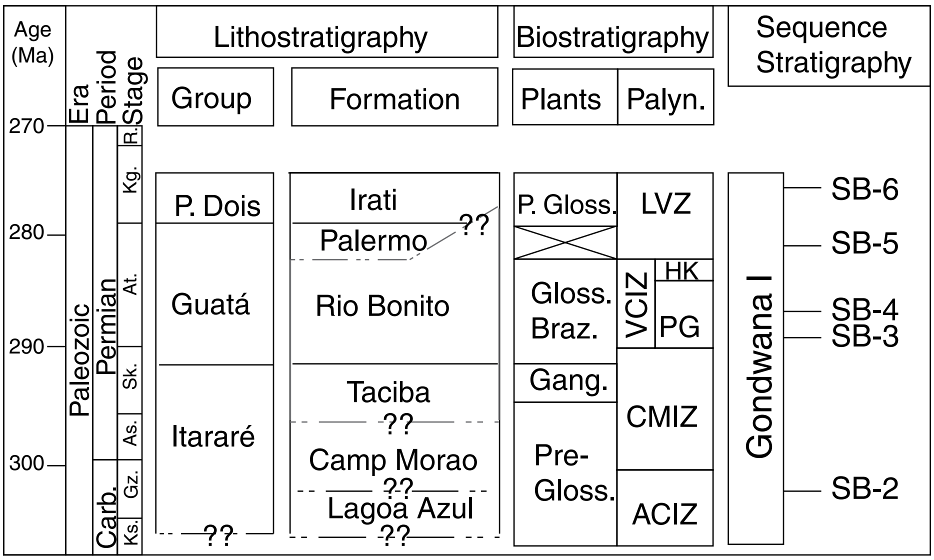

Figure 4. Existing stratigraphic framework for late Paleozoic deposits of the Paraná Basin, modified after Holz et al. (2010). Era, periods, and stages are based on Gradstein et al. (2012). Lithostratigraphy and sequence stratigraphic boundaries are modified to incorporate the ages of Mori et al. (2012). Biostratigraphy is after Mori et al. (2012) and Simas et al. (2012). P. Gloss—*Polysolenoxylon-Glossopteris flora*; Gloss Bras.—*Glossopteris-Brasilodendron* flora; Gang—*Phyllotheca-Gangamopteris flora*; Pre-Gloss.—*Pre-Glossopteris flora*; Palyn—palynomorphs; LVZ—*Lueckisporites virkkiae* palynozone; VCIZ—*Vittatina costabiliz* palynozone; PG—*Protohaploxypinus goraiensis* subzone; HK—*Hamiapollenites karrooensis* subzone; ACIZ—*Ahrensisporites cristatus* interval zone; CMIZ—*Crucisaccites monoletus* interval zone; SB—sequence boundary; Ks.—Kasimovian; Gz. —Gzhelian; As. —Asselian; Sk. —Sakmarian; At. —Artinskian; Kg. —Kungarian; R. —Roadian.

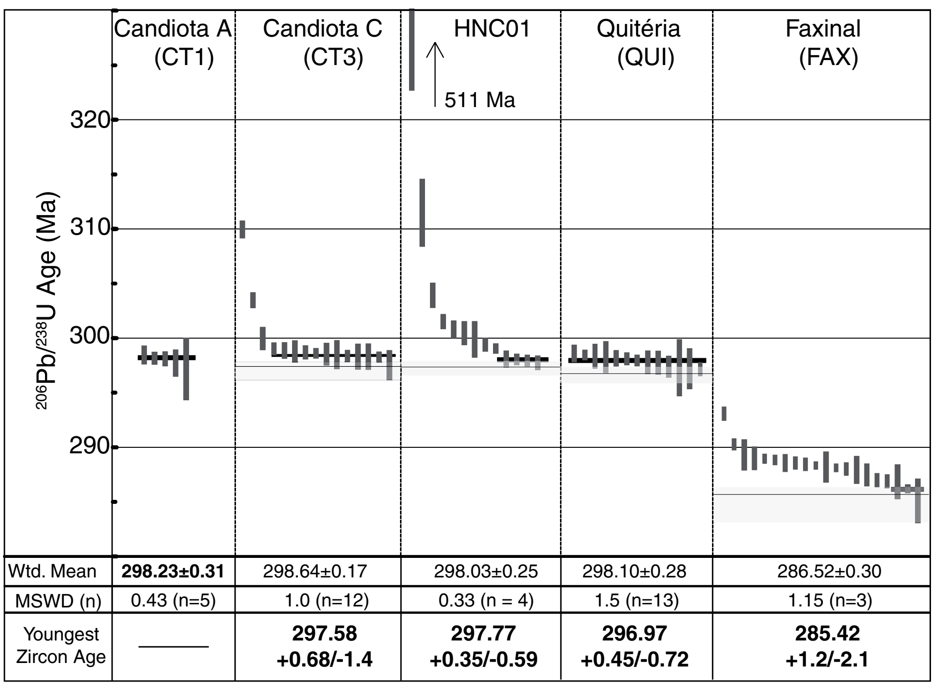

Figure 5. $^{206}Pb/^{238}U$ ages for Paraná deposits determined in this study. Weighted mean ages were calculated from the youngest coherent grouping. A youngest zircon age was also calculated. Thick black lines through the data indicate the weighted mean age and uncertainty. Gray bands denote age of the youngest zircon as estimated in Isoplot (Ludwig, 2008). A youngest zircon age could not be calculated for Candiota A because the algorithm requires more than 5 concordant analyses. MSWD—mean square of weighted deviates; *n*—number of zircons used in the weighted mean age calculation.

Faxinal

(Locality 30°15′58.22″S, 51°42′13.36″W)

The Faxinal tonstein (FAX) of the Upper Rio Bonito Formation was collected from a freshly cut mine surface in the Faxinal coal mine, which is 25 km south of the town of Arroio dos Ratos in the Mariana Pimentel paleovalley in Rio Grande do Sul State, Brazil, and it was sampled from the same tonstein layer analyzed by Guerra-Sommer et al. (2008b; see also Figs. 2 and 3). The Faxinal tonstein is a thin (~5–10 cm) gray mudstone with abundant plant debris. In total, 20 zircons were analyzed from this sample (Table DR1 [see footnote 1]). A weighted mean age of 286.52 ± 0.30 Ma (MSWD = 1.15) was calculated from the youngest three zircons. However, given the limited number of zircons that reproduce toward the young end-member age, we report a youngest and more robust zircon age of 285.42 +1.2/–2.1 Ma (Fig. 5). Th/U ratios for the Faxinal zircons range between 0.4 and 0.8.

Quitéria

(Locality 30°20′16.90″S, 52°10′14.50″W)

The Quitéria ash fall (QUI) was sampled from a fresh outcrop exposure located 25 km southwest of the town of Minas do Leão in Rio Grande do Sul State, Brazil and is not associated with a known "coal-bearing interval." Quitéria is a thick (~20 cm) white ash-fall deposit, which contains large lycophyte stumps preserved in upright living position, corroborating the interpretation of this deposit as a primary ash fall. Zircons isolated from the Quitéria ash are long and prismatic with aspect ratios of 2:1 or greater. In total, 13 zircons were analyzed (Table DR1 [see footnote 1]). A weighted mean age of 298.10 ± 0.28 Ma (MSWD = 1.5) was calculated from 13 concordant zircons (Fig. 5). The "youngest zircon age" algorithm yielded an age of 296.97 +0.45/–0.72 Ma. Th/U ratios for the Quitéria zircons range between 0.7 and 0.9. A subset of an additional six zircons of the Quitéria sample was analyzed using the newly acquired EarthTime 535 tracer solution. The resulting mean age of 298.53 ± 0.63 Ma (MSWD = 3.4) from this batch is slightly older, but within uncertainty with the former age of 298.10 ± 0.28 Ma, even without taking into account an augmented error resulting from uncertainty in U/Pb in the tracer solutions. The elevated MSWD may be the result of excess scatter from the occurrence of subtle inheritance and/or Pb loss. Also, the common Pb concentration of some of the six ages was slightly elevated due to the use of a new dissolution assembly, making the ages more susceptible to the $^{206}Pb/^{204}Pb$ ratio of the common Pb correction. The ages of the respective youngest and oldest analyzed zircons from both batches agree within uncertainty.

DISCUSSION

Reevaluation of several of the previously dated volcanic deposits in the southern Paraná Basin reveals large discrepancies in the radioisotopic ages, which have fundamental implications for development of a chronostratigraphic framework of sedimentary successions in general and for constraining the history of deglaciation, specifically, in the southern part of the Paraná Basin. Notably, the previously reported ages for the Candiota A (296 ± 4.2 Ma to 267 ± 3.4; de Matos et al., 2001; Guerra-Sommer et al., 2008a) and C deposits (296.9 ± 1.6 to 289.36 +1.84/–1.58 Ma; Guerra-Sommer et al., 2008a, 2008c), and Hulha Negra Candiota (281.4 ± 3.4 Ma; Mori et al., 2012) are largely in disagreement with the ages obtained in this study by CA-TIMS analysis of zircons from the same deposit (cf. Figs. 1 and 5 and Fig. 3). It is not possible to attribute this degree of disparity in the ages to a single process. In other studies, laser-ablation analysis of untreated zircons of Paleozoic age have been observed to be 4%–6% younger than CA-treated zircons measured via laser ablation, a degree well beyond the typical 1%–2% analytical uncertainty (von Quadt et al., 2014). Furthermore, an ~3% bias between CA-treated and untreated zircons for SIMS analysis has been documented (Watts et al., 2016). One source of this offset in U-Pb ages may be Pb loss that results in a younger age for untreated zircons, whereas chemically abraded zircons are expected to remove open-system domains and yield an accurate age. Thus, it is possible that some of the offset between untreated and chemically abraded analyses from the Paraná Basin succession reflects posteruptive Pb loss.

In contrast, our younger age (285.42 +1.2/–2.1 Ma) for the Faxinal tonstein in comparison to the previously published SIMS value (290.15 +2.45/–0.85 Ma; Guerra-Sommer et al., 2008c) suggests that Pb loss may not be a significant issue for Faxinal zircons. Ages measured by CA-TIMS that are younger than SIMS ages have been attributed to the use of heterogeneous standards in SIMS and laser-ablation analysis (Metcalfe et al., 2015). This source of discrepancy is difficult to evaluate for previously analyzed Paraná Basin deposits as no information on the use of the zircon standard(s) for the LA-ICP-MS or ion microprobe data is provided in the literature (cf. Black et al., 2003). We suggest that the age differences between the CA-TIMS–derived and ion microprobe–derived values for the Faxinal samples may be attributed to the large individual errors on single spot analyses by ion microprobe (Schoene, 2014). Furthermore, when individual microprobe ages are dispersed, subjective and inconsistent selection of subsets that appear coherent can lead to erroneous data interpretation, resulting in inaccurate ages.

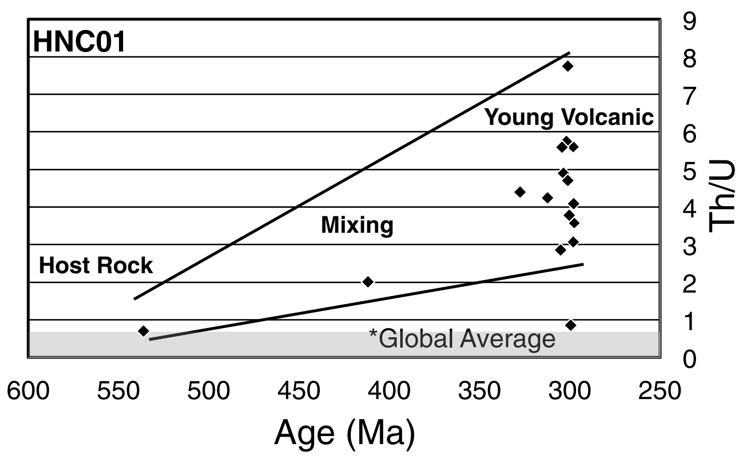

Figure 6. Th/U concentrations for the Hulha Negra Candiota (HNC) tonstein. Black bars delineate a mixing trend between the older low-Th/U component and the younger, more-radiogenic component. Gray bar highlights global average Th/U ratio in zircons (Bindeman et al., 2006).

Stratigraphic Implications of the CA-TIMS Ages

The new CA-TIMS ages for the Rio Bonito Formation redefine and refine the chrono stratigraphic and sequence-stratigraphic framework for the Paraná Basin (Figs. 3 and 4). The existing age control for this framework suggests that glaciation in SW Gondwana ceased in the Early Permian (ca. 291 Ma), followed by a near-synchronous but protracted period (~2 m.y.) of coal deposition in response to climatic amelioration with deglaciation (Milani et al., 1998; Guerra-Sommer et al., 2008c; Simas et al., 2012; Cagliari et al., 2014). A recent study by Cagliari et al. (2016), which amended the previous finding from Cagliari et al. (2014), is in agreement with our CA-TIMS analysis and suggests that Rio Bonito coal deposition began proximal to the Carboniferous-Permian boundary in the southern part of the Paraná Basin. The ages for the oldest coal-bearing deposits in the southern Paraná Basin reported by Cagliari et al. (2014, 2016), however, must be used cautiously, because zircon crystals from these studies were untreated with respect to Pb loss. Furthermore, the age selection criteria used in the two studies (Cagliari et al., 2014, 2016) were inconsistent for the age calculations despite the near-identical nature of the data sets. The age reported in Cagliari et al. (2014) was calculated from the six youngest coherent grouping of zircons, two of which were discordant, resulting in a weighted mean age of 290.6 ± 2.8 Ma. In contrast, Cagliari et al. (2016) selected an age of 298.8 ± 1.9 Ma from a coherent cluster of zircons chosen near the middle of the data set with no criteria provided as to why both younger and older ages were omitted for the calculation of the mean. Importantly, recalculation of the Cagliari et al. (2016) data for the uppermost ash, using a coherent grouping of the 9 youngest zircons is equally valid and would yield an age that is in agreement with our new CA-TIMS age (ca. 287 Ma) for the youngest tonstein (Faxinal), highlighting the large uncertainty in the previously published U-Pb ages (Figs. 5 and 7). In summary, the new CA-TIMS U-Pb ages indicate at least two distinct periods of coal formation separated by minimally 12 m.y. This finding highlights the fact that the Rio Bonito coal interval is not an isochronous stratigraphic marker throughout the basin, as has been previously suggested and subsequently utilized for correlation (Fig. 3; Guerra-Sommer et al., 2008c; Simas et al., 2012).

The new radioisotopic ages presented here further significantly change the palynological framework for the Paraná Basin. The Permian succession of the Paraná Basin is composed of two palynozones, the *Vittatina costabiliz* and *Lueckisporites virkkiae* zones. The *V. costabiliz* palynozone extends from the top of the Itararé Group to the uppermost Rio Bonito Formation. The *V. costabiliz* palynozone consists of two subzones, the lower *Protohaploxypinus goraiensis* and upper *Hamiapollenites karrooensis* subzones. The *L. virkkiae* palynozone occurs from the uppermost levels of Rio Bonito Formation or from the basal levels of Palermo Formation and extends to the lowermost Rio do Rasto Formation (Fig. 4; Souza, 2006; Mori et al., 2012).

The first radioisotopic age for an important fossil-plant–bearing interval (Quitéria) in the southern Paraná Basin, presented here, indicates an earliest Permian age (296.97 +0.45/–0.72; Asselian), which is substantially older than the middle-to-late Early Permian age (Artinskian; 290.1–279.3 Ma) inferred for this interval from the palynostratigraphy (Souza, 2006; Holz et al., 2010). The Quitéria outcrop was originally assigned to the *H. karrooensis* subzone of the *V. costabiliz* palynozone (Figs. 3 and 4; Jasper et al., 2006), though a subsequent paleontological study suggested that the Quitéria interval belongs to the *P. goraiensis* subzone and is therefore older than previously assumed (Fig. 4; Boardman et al., 2012a). The weighted mean CA-TIMS age presented in this study for the Quitéria outcrop is similar to those calculated for the Candiota A and C and Hulha Negra Candiota deposits (ca. 297–298 Ma). This indicates that the Quitéria and Candiota deposits were contemporaneous.

The new U-Pb CA-TIMS ages reveal discrepancies in the stratigraphic positioning of the Rio Bonito Formation outcrops based on palynomorphs and highlight the need for re-evaluation of the Paraná Basin palynomorph-based stratigraphic ranges currently used for correlation throughout greater southern Gondwana. It is difficult to reconcile the presence of the *L. virkkiae* palynozone in the Hulha Negra Candiota outcrop given the new radioisotopic ages for the HNC01 tonstein (297.77 +0.35/–0.59 Ma). Originally, the lower limit of the *L. virkkiae* palynozone was assigned to the basal-most levels of the Palermo Formation (Souza, 2006; Fig. 4). The U-Pb CA-TIMS age (297.77 +0.35/–0.59 Ma) is consistent with the presence of the *P. goraiensis* subzone (lower *V. costabiliz* palynozone), but not the presence of *L. virkkiae* palynozone in the Hulha Negra outcrop, as the latter is considered Artinskian. An alternative interpretation, which assumes that certain elements of the *L. virkkiae* palynozone extend down into the *V. costabiliz* palynozone deposits of the Rio Bonito Formation in Rio Grande do Sul State, would be compatible with the new radioisotope ages and would confirm a previously proposed hypothesis (see Mori et al., 2012; Boardman et al., 2012a, 2012b). Additionally, the new age for the Faxinal deposit (285.42 +1.2/–2.1 Ma) would confirm a previously proposed assignment to the *H. karrooensis* subzone (Guerra-Sommer et al., 2008b), but it does not support the more recent assignment of the Faxinal deposit to the older *P. goraiensis* subzone (Guerra-Sommer et al., 2008c; Simas et al., 2012). Notably, our results document that some key taxa (Fig. 4; including those of the *L. virkkiae* palynozones in the Hulha Negra Candiota and Faxinal deposits) first appeared in the Paraná Basin in the earliest Permian (Asselian; 298.9–295.5 Ma), analogous to that documented in Bolivia (DiPasquo et al., 2015). The CA-TIMS U-Pb ages presented here indicate that deposition of the Rio Bonito Formation started proximal to the Carboniferous-Permian boundary (298.9 Ma), and because the *V. costabiliz* palynozone extends down into the underlying Itararé Group, it is possible that key taxa from that palynozone, (i.e., *V. costabiliz*) may

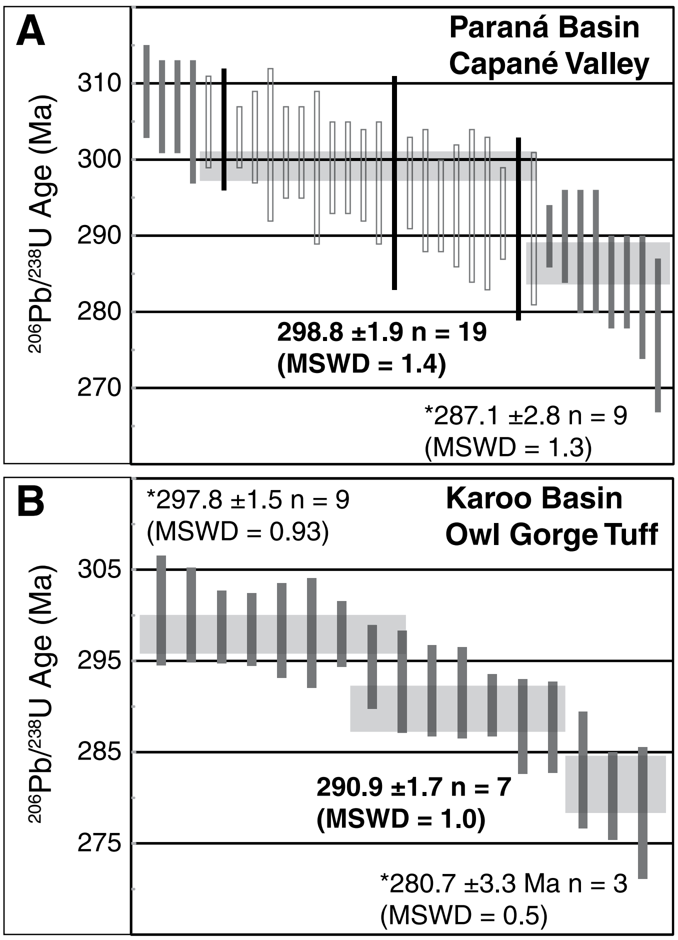

Figure 7. Distribution of individual zircon ^{206}Pb/^{238}U ages from (A) Capané Valley (Cagliari et al., 2016) and (B) Owl Gorge Tuff in southern Africa (Werner, 2006). The bolded age is that reported in the literature. Ages with asterisk are alternative interpretations of the data reported in the literature (see text for details). For the Capané Valley sample, unfilled bars indicate ages used to determine the ^{206}Pb/^{238}U age in this study; dark bars are individual analyses rejected in the age calculation. Individual error bars from the Owl Gorge Tuff were doubled in order to plot the values at the 2σ level. MSWD—mean square of weighted deviates.

have first appeared in the latest Carboniferous (Césari et al., 2011). Independent evidence of this hypothesis exists; earlier appearances of some common palynomorphs found in the *V. costabiliz* palynozone have been documented in the latest Carboniferous, upper Dwyka Group of Namibia (Stephenson, 2009), though more robust radioisotopic age constraints are needed to confirm the absolute age of the Dwyka Group (see following).

Timing of Glaciation in South-Central Gondwana

The apex of late Paleozoic glaciation is hypothesized to have occurred during the Early Permian (Asselian through mid-Sakmarian; 298.9 to ca. 292.5 Ma) based on the inferred distribution of higher-latitude glacial or glacially associated deposits, stratigraphic relationships, and paleotropical stable isotope and stratigraphic archives (Rygel et al., 2008; Fielding et al., 2008a, 2008b; Isbell et al., 2003, 2008, 2012; Koch and Frank, 2011). Terminal deglaciation, with the exception of alpine glaciation in eastern Australia (Fielding et al., 2008a), is inferred to have been asynchronous, initiating in western Gondwana in the middle Pennsylvanian (Gulbranson et al., 2010; Henry et al., 2010) and progressing eastward in southern Gondwana through the Pennsylvanian and Early Permian (Caputo and Crowell, 1985; Isbell et al., 2012; Cagliari et al., 2016). The glacial succession of the Paraná Basin has factored largely in this hypothesized glaciation-deglaciation history, given a proposed Early Permian age for most glacial deposits (Guerra-Sommer et al., 2008a, 2008c; Simas et al., 2012; Holz et al., 2008, 2010), the geographic extent of Paraná glacial deposits (1.0×10^6 km^2), and proposed correlation with regionally widespread Early Permian deglaciation cycles in southern Africa (Fielding et al., 2008a, 2008b; Isbell et al., 2003, 2008, 2012; Rocha-Campos et al., 2008; summarized in Montañez and Poulsen, 2013). Furthermore, glacial-marine diamictites and coals of the Paraná succession (Figs. 2C and 3) have long been recognized as important lithostratigraphic markers for cross-Gondwana correlation of the Carboniferous–Permian glacial to deglacial successions (Du Toit, 1937; Isbell et al., 2003; Milani and De Wit, 2008; Linol et al., 2015).

In contrast, integration of the new CA-TIMS U-Pb zircon ages from the Paraná succession with published high-precision CA-TIMS U-Pb zircon ages from Argentina (Gulbranson et al., 2010) indicates that glaciation in at least these regions of western to west-central Gondwana was entirely Carboniferous (older than 298.9 Ma). The onset of glaciation in western Gondwana (Argentina) is well constrained by CA-TIMS U-Pb zircon ages to 335.99 ± 0.06 Ma (Fig. 8). The subsequent collapse of glaciers in this region occurred in the latest Bashkirian to early Moscovian (315.2 Ma; Gulbranson et al., 2010). In the southern Paraná Basin, the coal facies directly overlie the glacial deposits, and based on the oldest age of the lower coal-bearing interval (Candiota A, 298.23 ± 0.31 Ma), deglaciation occurred ~17 m.y. later, proximal to the Permian-Carboniferous boundary (Fig. 8).

The coal-hosted tonsteins in the Paraná Basin provide the only absolute age constraints for deglaciation in this region of Gondwana, as no reliable radioisotope ages exist for the glacial deposits of the Itararé Group. A recent, late Carboniferous age for the top of the uppermost glacial interval (Taciba Formation) of the Itararé Group was suggested based on LA-ICP-MS analysis of untreated zircons from a purported ash in the Itararé Group (Cagliari et al., 2016). The volcaniclastic deposit, which was sampled in a coal facies and not in glacial material, yielded an age of 307.7 ± 3.1 Ma. Notably, the 10 youngest concordant zircon grains, however, produce a recalculated age (302.0 ± 4.9 Ma) that overlaps with the CA-TIMS age of the Candiota coal deposits (298.23 ± 0.31 Ma). The selection of the youngest grouping is the typical approach for defining an age of a volcaniclastic unit using U-Pb geochronology (cf. Gulbranson et al., 2010; Cagliari et al., 2014), though, as discussed earlier, this can be problematic if the sample is not chemically abraded and the sample has lost radiogenic Pb. Given the radioisotope constraints on coal deposition to the Carboniferous-Permian boundary and the stratigraphic proximity of the uppermost Taciba Formation and the Candiota coal-bearing interval, we hypothesize that the Itararé Group tonstein deposit from Cagliari et al. (2016) may be near contemporaneous with the postglacial Candiota coal deposits. Additional CA-TIMS analyses of zircons from this deposit are needed to confirm this proposed correlation. Last, all U-Pb ages that constrain the glaciation to the Carboniferous are from the southern margin of the Paraná Basin, and so an understanding of the degree to which the glacial deposits in the northern Paraná Basin are coeval awaits future high-precision CA-TIMS U-Pb zircon dating.

The glaciation history in the southern Paraná Basin restricted to the late Carboniferous has major implications for correlation with other Gondwanan basins and, in turn, for constraining the geographic extent of ice sheets through time and the timing of terminal deglaciation. Radioisotopic ages constraining late Paleozoic

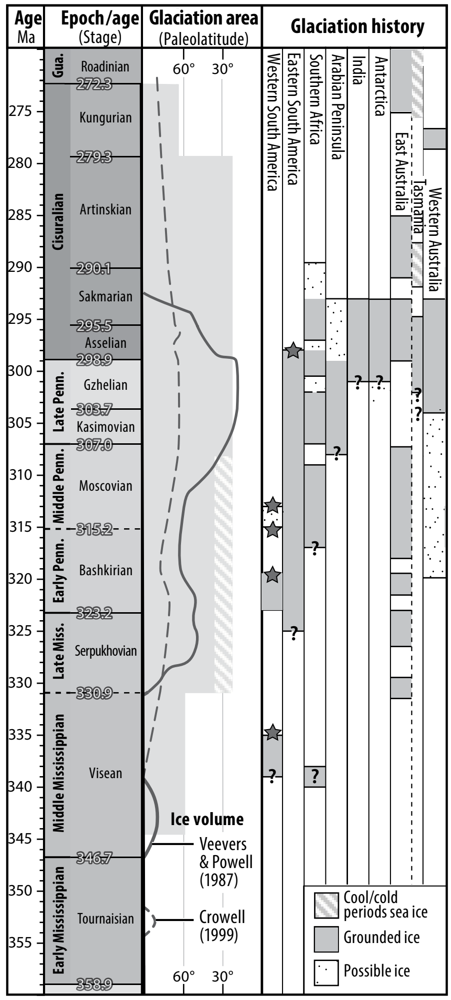

Figure 8. Record of ice distribution through time for Gondwana. Glaciation area is modified after Frakes and Francis (1988) and Crowley and Baum (1992) and after Montañez and Poulsen (2013). Superimposed on glaciation area are relative ice-volume curves through time from Veevers and Powell (1987; solid line) and Crowell (1999; dashed line). Glaciation history is modified from Isbell et al. (2003, 20012), Fielding et al. (2008a), and Montañez and Poulsen (2013). Stars indicate areas where age control is provided by chemical abrasion–thermal ionization mass spectrometry (CA-TIMS) analyses. All other age control for high-latitude Gondwana glaciation is provided by secondary ion mass spectrometry (SIMS) analysis of zircon or biostratigraphy. Question marks denote areas where the onset of glaciation is ambiguous. Gua.—Guadalupian; Penn.—Pennsylvanian.

glacial deposits outside of South American basins are limited to southern Africa and eastern Australia (Werner, 2006; Stollhofen et al., 2008; see Fielding et al., 2008b). All of these age constraints were obtained by in situ SIMS analysis of untreated zircons, and for the Australian successions, they were normalized to standards that are heterogeneous (Black et al., 2003; Metcalfe et al., 2015). A ca. 290 Ma age (Artinskian-Sakmarian boundary) for the end of late Paleozoic ice age glaciation in southern Africa is based on one U-Pb zircon age of 290.9 ± 1.7 Ma from the Owl Gorge Tuff in the Ecca Group, which overlies the glacial deposits of the Dwyka Group (Stollhofen et al., 2008; Isbell et al., 2012). This radioisotopic age was determined using a probability density plot populated by zircons measured by ion microprobe. The weighted mean of coherent groups produces three distinct ages, which include a young subset 280.7 ± 3.3 Ma, the selected age of 290.9 ± 1.7 Ma, and an older subset at 297.8 ± 1.5 Ma (Fig. 7; Werner, 2006). The author did not present the rejection criteria for the youngest group of zircons. The oldest coherent group of zircons, which yielded an age (297.8 ± 1.5 Ma) proximal to the Carboniferous-Permian boundary, was interpreted as recording xenocryst inheritance from previous crystallization events and therefore rejected as the age of eruption. Notably, the Owl Gorge Tuff zircons were not chemically abraded, and based on our observation of the discrepancies between CA-treated and untreated zircons in the Paraná Basin, it is reasonable to question whether some of the Dwyka and Ecca Group zircons may have undergone postdepositional Pb loss (cf. Watts et al., 2016). If this is the case, then the youngest glacial deposits could be Carboniferous (older than 297.8 ± 1.5 Ma). This hypothesis is further supported by the slightly elevated Th/U ratios (0.5–2.8) of the 297.8 ± 1.5 Ma age fraction of the Owl Gorge Tuff, suggesting a possible shared volcanic source with the Candiota (HNC01) volcanic deposits (297.77 +0.35/–0.59 Ma) of the Paraná Basin. The latter contain similarly elevated U-Th zircon values (0.9–7.8).

In eastern Australia, continental ice and/or cool periods of sea ice are hypothesized to have persisted through the late Carboniferous, with alpine ice and cool periods of sea ice continuing through much of the Permian (Fig. 8; Fielding et al., 2008a, 2008b; Metcalfe et al., 2015). Pennsylvanian periods of glaciation (during 313–308 Ma) and the Early Permian glaciation (299–291 Ma) are anchored by U-Pb zircon ages measured by SIMS (Fielding et al., 2008b). Two issues could compromise the chronostratigraphic framework for eastern Australia. First, it is based on heterogeneous standards (Black et al., 2003; Metcalfe et al., 2015). Second, whether or not the chemically unabraded zircons from the volcanic deposits of the eastern Australian succession suffered Pb loss has not been addressed. Therefore, similar issues associated with the U-Pb zircon stratigraphic record observed in the Paraná Basin may hamper the stratigraphic record of the late Paleozoic from southern Africa and Australia. The existing chronostratigraphic frameworks for the Carboniferous–Permian successions of southern Africa and eastern Australia need to be revisited using single-crystal analysis of individual grains by high-precision CA-TIMS of individual zircons.

CONCLUSIONS

Comparison of single-zircon CA-TIMS ages obtained in this study with previously published in situ zircon U-Pb ages for the same volcanic deposits from the Carboniferous–Permian succession of the Paraná Basin reveals discrepancies of up to 15 m.y. The disparity in ages reflects previously unrecognized open-system behavior, likely complications from the occurrence of inheritance problems, and inconsistent data treatment.

Reanalysis of previously dated tonsteins indicates two distinct coal-bearing intervals in the Early Permian of the Paraná succession, including evidence that coals of the lower interval, previously dated to span from 296 ± 4.2 to 267 ± 3.4 Ma (2σ), are contemporaneous throughout the southern part of the Paraná Basin. This subdivision of the coal-bearing deposits of the Rio Bonito Formation into distinct intervals highlights the need for more precise CA-TIMS U-Pb ages throughout the basin. The long age range of existing Permian palynozones for southern Gondwana limits their chronostratigraphic utility in the Rio Bonito Formation of the Paraná Basin. Ultimately, the limits of using palynomorphs in this key Gondwanan basin may have implications for intra- and interbasinal correlation throughout southern Gondwana, an issue that warrants further study.

The CA-TIMS U-Pb ages presented in this study indicate terminal deglaciation occurred in southwestern and south-central Gondwana prior to and proximal to the Carboniferous-Permian boundary, respectively. Future assessments of volcanic deposits from the northern part of the Paraná Basin are required to further test whether the demise of the late Paleozoic ice age in west-central Gondwana occurred synchronously or not, with clear implication for the magnitude of the hypothesized Early Permian apex of glaciation.

New robust high-resolution radioisotope age control in several Gondwanan basins is needed to test the synchronicity of deglaciation across high-latitude Pangea. The discrepancy in ages between the high-precision CA-TIMS U-Pb ages of single zircons and those ages obtained by in situ analysis of zircons from the same deposits revealed by this study highlights the need for reevaluation of other key high-latitude glacigenic successions in central and eastern Gondwana.

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