Coupled stratigraphic and U-Pb zircon age constraints on the late Paleozoic icehouse-to-greenhouse turnover in south-central Gondwana

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ABSTRACT
The demise of the Late Paleozoic Ice Age has been hypothesized as diachronous, occurring first in western South America and progressing eastward across Africa and culminating in Australia over an ~60 m.y. period, suggesting tectonic forcing mechanisms that operate on time scales of 105 yr or longer. We test this diachronous deglaciation hypothesis for southwestern and south-central Gondwana with new single crystal U-Pb zircon chemical abrasion thermal ionizing mass spectrometry (CA-TIMS) ages from volcaniclastic deposits in the Paraná (Brazil) and Karoo (South Africa) Basins that span the terminal deglaciation through the early postglacial period. Intrabasinal stratigraphic correlations permitted by the new high-resolution radioisotope ages indicate that deglaciation across the S to SE Paraná Basin was synchronous, with glaciation constrained to the Carboniferous. Cross-basin correlation reveals two additional glacial-deglacial cycles in the Karoo Basin after the terminal deglaciation in the Paraná Basin. South African glaciations were penecontemporaneous (within U-Pb age uncertainties) with third-order sequence boundaries (i.e., inferred base-level falls) in the Paraná Basin. Synchrony between early Permian glacial-deglacial events in southwestern to south-central Gondwana and pCO2 fluctuations suggest a primary CO2 control on ice thresholds. The occurrence of renewed glaciation in the Karoo Basin, after terminal deglaciation in the Paraná Basin, reflects the secondary influences of regional paleogeography, topography, and moisture sources.

INTRODUCTION

The Late Paleozoic Ice Age (LPIA), spanning 340–280 Ma, has produced the only known archive of a permanent icehouse-to-greenhouse turnover on a planet populated by complex terrestrial ecosystems and metazoan life (Gastaldo et al., 1996). The spatial and temporal distribution of continental ice throughout southern Gondwana during the LPIA and its ultimate demise have been attributed in large part to the long-term (105 to 106 yr) drift of southern Gondwana away from the South Pole (Crowell, 1983; Limarino et al., 2014) as well as tectonic controls (Visser, 1997). Alternatively, CO2 forcing has been hypothesized as the primary driver of the repeated, discrete glaciations and intervening periods of diminished ice, and the ultimate turnover to permanent greenhouse conditions (Montañez et al., 2007, 2016). Although these two proposed forcing mechanisms (tectonic versus climate) for the late Paleozoic glaciation history are interlinked through the influence of large-scale tectonics on CO2 sources (i.e., volcanism) and sinks and through atmospheric and ocean circulation (McKenzie et al., 2016; Montañez et al., 2016), the two mechanisms differ in their temporal scales of influence on ice distribution and dynamics. Tectonic controls would have operated on 105 to 106 yr time scales and resulted in a diachronous glacial record across high-latitude Gondwana (Isbell et al., 2012; Limarino et al., 2014). Late Paleozoic climate simulations, however, do not support a tectonic drift model for ice initiation thresholds (Lowry et al., 2014). Conversely, a CO2-driven deglaciation (and associated base-level changes) would be expected to have been rapid (105 to 106 yr) and thus broadly synchronous across multiple basins.

The precision and distribution of existing U-Pb age constraints for ice-proximal deposits of southern Gondwana precludes evaluation of the relative influence of hypothesized glaciation-deglaciation drivers and their role in the ultimate turnover to a permanent greenhouse in the middle Permian. Here we present a temporally refined record of glaciation in southwestern to south-central Gondwana across the latest Carboniferous and early Permian, built using high-precision, single-crystal zircon U-Pb chemical abrasion thermal ionizing mass spectrometry (CA-TIMS) dating of volcaniclastic deposits located within the earliest postglacial sediments of the Paraná Basin, Brazil, and two glacial-deglacial cycles (deglaciation sequences DS III and DS IV) in the Karoo Basin, South Africa (Visser, 1997). The new chronostratigraphic framework is used to evaluate the synchrony of ice loss across this region and to evaluate the
base-level response in the Paraná Basin to the higher-latitude ice record (Karoo Basin) during the early Permian.

**GEOLOGIC SETTING, STRATIGRAPHY, AND EXISTING U-Pb GEOCHRONOLOGY**

The Paraná and Karoo Basins span a collective area of 2.3 × 10^6 km² and were the largest depocenters of LPIA sediment accumulation in southwestern to south-central Gondwana (Fig. 1). The Paraná Basin, located between 40°S and 55°S during the earliest Permian (Franco et al., 2012; Domeier and Torsvik, 2014), records an extensive record of paleo-glaciation within the Itararé Group (Rocha-Campos et al., 2008). Record of the demise of glaciation in the Paraná Basin occurs within the upper Taciba Formation (Itararé Group), composed of diamictite and dropstone-poor mudstones (Fig. 1; Vesely and Assine, 2004). The terrestrial and marginal marine facies assemblage of the Guatá Group, which include the Rio Bonito and Palermo Formations, overlay the Itararé Group and attain a maximum thickness of 300 m (Fig. 1; Rocha-Campos et al., 2008, Holz et al., 2010). In southeastern Paraná Basin, the Rio Bonito Formation is further divided into the Triunfo, Paraguacu, and Siderópolis Members (Schneider et al., 1974), which are not formally recognized in the southern Paraná Basin. However, sequence boundaries SB-2 and SB-3, which bracket these members, are correlated between regions (Fig. 1; Holz et al., 2006; Iannuzzi et al., 2010).

Two third-order depositional sequences, previously suggested to have been controlled by regional tectonic forcing (Holz et al., 2006), occur in the latest Carboniferous through early Permian sedimentary record of the Paraná Basin. The first sequence boundary (SB-2 of Holz et al. [2006]) separates deeper-water glacially influenced diamictites and organic mudstones of the Taciba Formation from fluvial sandstones and coals of the Triunfo Member of the Rio Bonito Formation in the southeastern Paraná Basin (Fig. 1). In regions of the southern Paraná Basin, this sequence boundary locally separates crystaline basement and fluvial sandstones (SB-1 + 2 of Holz et al. [2006]). In the southeastern Paraná Basin, the fluvial sandstones of the Triunfo Member transition into the offshore mudstones of the
Paraguacu Member (T-P1 in Fig. 1). A second third-order sequence boundary (SB-3) separates offshore mudstones of the Paraguacu Member and fluvial to shallow marine sandstones of the Sideropoliis Member (Fig. 1). In southern Brazil, SB-3 separates offshore mudstones from nearshore heterolithic mudstones, fluvial sandstones, and coals (Holz et al., 2006; Iannuzzi et al., 2010). The marine Palermo Formation overlies and interferes laterally with the Rio Bonito Formation and is interpreted as the most widespread transgression of the early Permian (T-P2 in Fig. 1; see Holz et al., 2006). U-Pb zircon laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) ages for volcaniclastic deposits sampled above SB-2 are variable and range from 298.8 ± 1.9 Ma to 281.3 ± 3.4 Ma, providing insufficient temporal resolution for constraining the unconformity (see the GSA Data Repository1; Grifis et al., 2018).

The Karoo Basin of South Africa, located at >60°S during the latest Carboniferous and early Permian (Fig. 1; Domeier and Torsvik, 2014), hosts an up to 800-m-thick glaciogenic succession of that same age, which is divided into four deglaciation sequences (DS I–DS IV). These sequences are defined as clast-rich diamictite deposits overlain by clast-poor organic-rich mudstones and/or diamictite separated by unconformities, and are hypothesized to represent tectonic-eustatic cycles (Visser, 1997). The top of DS III is interpreted to represent the first major marine transgression into the Karoo Basin that can be traced across southern Africa and is dated by a U-Pb zircon secondary ion mass spectrometry (SIMS) age of 297 ± 1.8 Ma (age marker 7 in Fig. 1; Visser, 1997; Bangert et al., 1999; Stollhofen et al., 2008). DS III is overlain by a thick diamictite (100–300 m), which marks the return to glacial conditions in the Karoo Basin prior to terminal deglaciation (DS IV). The final deglaciation in the Karoo Basin is recorded by a thick marine mudstone in the basal Ecca Group (Prince Albert Formation) and culminates with a black shale (Whitehill Formation) (Fig. 1; Visser, 1997; Bangert et al., 1999) and is constrained to 289.6 ± 3.8 to 288.0 ± 3.0 Ma by SIMS U-Pb zircon ages for volcaniclastic deposits in the basal Ecca Group (age marker 8 in Fig. 1).

**U-Pb ZIRCON CA-TIMS CHRONOSTRATIGRAPHY FOR SOUTHWESTERN TO SOUTH-CENTRAL GONDWANA**

We present a chronostratigraphic framework for the Paraná and Karoo Basins, anchored by new (n = 6) and recently published (n = 5; Grifis et al., 2018) U-Pb single-crystal zircon CA-TIMS ages for volcaniclastic deposits, in order to evaluate the synchronicity of the LPIA demise in South America and southern Africa, respectively (Fig. 1; see the Data Repository). A thorough description of samples, zircon treatments, and analytical techniques, including data tables and concordia and age-ranked plots, are presented in the Data Repository. The newly developed U-Pb zircon CA-TIMS–anchored chronostratigraphic framework indicates that a major deglaciation event occurred in both the Paraná (terminal deglaciation) and Karoo basins proximal to the Carboniferous-Permian boundary (CPB; T-CP in Fig. 1). Subsequent glaciation-deglaciation cycles in the Karoo Basin are synchronous with marine transgressions in the Paraná Basin in the early (ca. 296 Ma) and late early (282 Ma) Permian (T-P1 and T-P2 in Fig. 1).

Volcaniclastic deposits within the lowermost Rio Bonito Formation confirm a pre-CPB deglaciation age (298.9 Ma) for all glacial deposits in the southern to southeastern Paraná Basin (Cagliari et al., 2016; Grifis et al., 2018). U-Pb zircon CA-TIMS ages for volcaniclastic within the Candiotas coal to the south (298.23 ± 0.31 Ma [sample CT1] to 297.77 + 0.35/−0.59 Ma [sample HNC; age marker 1 in Fig. 1), which can be traced into nearby core HV-59 (see the Data Repository for location), and for a volcaniclastic layer in the Triunfo Member in the southeastern Paraná Basin (297.4 ± 1.13/−1.19 Ma [sample AN1]; age marker 5 in Fig. 1) all constrain glacia tion in these regions of the Paraná Basin to >298 Ma (Grifis et al., 2018). These volcaniclastics overlie a regional sequence boundary (SB-2 and SB 1; Fig. 1) by 30–60 m, indicating that inferred base-level fall was synchronous across the south to southeastern Paraná Basin. Glacial conditions in the Karoo Basin in the earliest Permian are recorded by thick (>100 m) diamictites (lower DS III; Fig. 1) and are hypothesized to be synchronous with the base-level fall in the Paraná Basin (SB-2). If confirmed, the terminal deglaciation in the southern Paraná Basin could be contemporaneous with the top of DS II in southern Africa dated at 302.0 ± 3.0 Ma to 299.2 ± 3.2 Ma (Visser, 1997; Bangert et al., 1999). High-resolution U-Pb zircon CA-TIMS ages for the upper Taciba Formation (Paraná Basin) and DS II (Kalabari Basin, southern Africa; Ka in Fig. 1) are now required to test this hypothesis (see the Data Repository).

In the Karoo Basin, subsequent glacial demise is indicated by thick (up to 200 m) glacial diamictites, which transition into glacially influenced transgressive mudstones and sandstones (top of DS III). A volcanic ash, located at the top of DS III, yields a U-Pb zircon CA-TIMS age of 296.41 + 0.27/−0.35 Ma (age marker 7 in Fig. 1). Notably, this major transgression at the top of DS III is traceable across southern Africa (Visser, 1997; Stollhofen et al., 2008) and contemporaneous with the transgressive Paraguacu Member (PG on Fig. 1) in the Paraná Basin. The age for Paraguacu Member is inferred based on the stratigraphic juxtaposition of marine mudstones over terrestrial and nearshore deposits, which are dated at 296.97 + 0.45/−0.72 Ma (age marker 2 in Fig. 1; Grifis et al., 2018). The apparent synchronicity of the aforementioned transgressive surfaces, which record an abrupt shift to marine conditions throughout both depositional basins, is interpreted to record a substantial loss of continental ice at 296 Ma (plus or minus several hundred thousand years) (T-P1 in Fig. 1).

A final phase of glaciation in the Karoo Basin expressed by thick (200 m) diamictites (lower DS IV), which overlie transgressive mudstones (top of DS III), occurred in the early Permian (Visser, 1997). In the Paraná Basin, an erosional unconformity (SB-3 in Fig. 1) separates marine deposits of the Paraguacu Member from fluvial deposits of the overlying Siderópolis Member. The SB-3 unconformity has been interpreted as representing a forced regression, driven by major base-level fall (Holz et al., 2006). A U-Pb zircon CA-TIMS age for a volcaniclastic layer sampled between two fluvial sandstones (Alfredo Wagner locality), which overlie marginal marine mudstones that can be traced into nearby core 7-RL-04-SC, provides a minimum age for the onset of SB-3 of 294.82 ± 0.59/−0.83 Ma (age marker 6 in Fig. 1). In the southern Paraná Basin, volcaniclastic layers sampled from terrestrial coal deposits above SB-3 from the Recreo (age marker 4 in Fig. 1) and Faxonial (age marker 3 in Fig. 1) mines yield ages of 290.36 + 0.4/−0.32 Ma and 285.42 ± 1.2/−2.1 Ma, respectively, indicating that low base level persisted in this region of the Paraná Basin into the Permian. (For location information, see the Data Repository.)

Terminal deglaciation (DS IV) in the Karoo Basin is recorded by a thick (100 m) interval of turbidite deposits of the Prince Albert Formation that is capped by black shales of the Whitehill Formation (T-P2 in Fig. 1; Visser, 1997). Volcanic ash layers sampled from the lower (age marker 8 in Fig. 1) and middle (age marker 9 in Fig. 1) Prince Albert Formation yield new U-Pb zircon CA-TIMS ages of 282.17 Ma ± 0.32/−0.44 and 281.15 ± 0.72/−1.12 Ma, respectively, indicating that this region of south-central Gondwana was fully deglaciated by 282 Ma. In the Paraná Basin, marine mudstones and sandstones of the Palermo Formation (PL in Fig. 1) overlie fluvial and shallow marine sandstones of the Siderópolis Member (eastern Paraná Basin) and the Faxonial and Recreo mine coals (southern Paraná Basin). The Palermo marine deposits are interpreted as recording a major transgression, consistent with ice loss in southwestern and south-central Gondwana (T-P2 in Fig. 1; Holz et al., 2010).

1GSA Data Repository item 2019387, sample location and descriptions, laboratory and analytical techniques, data tables, concordia diagrams, and age ranked plots, is available online at http://www.geosociety.org/datarepository/2019/, or on request from editing@geosociety.org.
**CO₂-FORCED DEGLACIATION**

Reconstructed atmospheric pCO₂ for the latest Pennsylvanian and early Permian indicates a stepped rise from a minimum across the CPB to maximum concentrations (<2× present atmospheric level [PAL]) toward the end of the early Permian, which is consistent with the presented stepwise deglaciation history (Fig. 2; Montañez et al., 2007; revised in Richey et al., 2017). Terminal deglaciation in the Paraná Basin, which occurred proximal to but before the CPB, coincides with overall high pCO₂ (>1×PAL) through the latest Carboniferous (Fig. 2). Return to glacial conditions in the Karoo Basin in the earliest Permian (DS III), which coincides with regional base-level fall (SB-2) in the Paraná Basin, is synchronous with a drop in pCO₂ (0.5×PAL). The demise of DS III in the Karoo Basin, synchronous with the Paraguacu transgression, is coincident with a renewed rise in pCO₂ to PAL (296 Ma). A return of ice in the Karoo Basin, coincident with a base-level fall (SB-3) in the Paraná Basin, is synchronous with a second CO₂ fall to 0.5×PAL at 295 Ma. Terminal demise of glaciation in the Karoo Basin occurred during a protracted CO₂ rise through the remainder of the early Permian (Fig. 2). Overlap in timing of inferred deglaciations and base-level rises with stepwise increases in pCO₂ suggests that stepwise and near-synchronous deglaciation across southwestern and south-central Gondwana was likely greenhouse-gas forced. Notably, the repeated return to glacial conditions in the higher-latitude (>60°S) Karoo Basin, while the lower-latitude Paraná Basin (<55°S) remained ice free, indicates the superimposed influence of additional regional drivers (e.g., paleogeography, topography, and atmospheric moisture) on local to regional thresholds for ice accumulation in southern Gondwana (Isbell et al., 2012; Montañez and Poulsen, 2013).

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