

# Mississippian southern Laurentia tuffs came from a northern Gondwana arc

Hepeng Tian<sup>1</sup>, Majie Fan<sup>1</sup>, Victor A. Valencia<sup>2</sup>, Kevin Chamberlain<sup>3</sup>, Robert J. Stern<sup>4</sup> and Lowell Waite<sup>4</sup>

<sup>1</sup>Department of Earth and Environmental Sciences, University of Texas at Arlington, Arlington, Texas 76019, USA

<sup>2</sup>School of Environment, Washington State University, Pullman, Washington 99164, USA

<sup>3</sup>Department of Geology and Geophysics, University of Wyoming, Laramie, Wyoming 82071, USA

<sup>4</sup>Department of Geosciences, University of Texas at Dallas, Richardson, Texas 75083, USA

## ABSTRACT

**A Paleozoic arc that formed by southward subduction of the Rheic oceanic plate beneath northern Gondwana has long been inferred, but its history and geochemical signatures remain poorly understood. New U-Pb ages, juvenile  $\epsilon_{\text{Hf}}$  signatures, and trace-element composition data of young zircons from tuffs at two southern Laurentia sites indicate their derivation from a continental arc that was active from ca. 328 to ca. 317 Ma and permit correlation of sedimentary sequences 800 km apart in southern Laurentia. These include the Stanley tuffs in the Ouachita Mountains of southeastern Oklahoma and southwestern Arkansas and the newly discovered Barnett tuff in the subsurface of the Midland Basin in west Texas (USA). The Barnett tuff has a zircon chemical abrasion–isotope dilution–thermal ionization mass spectrometry U-Pb date of  $327.8 \pm 0.8$  Ma, similar to the oldest Stanley tuff in the Ouachita Mountains. Zircon Hf isotope depleted mantle model ages further suggest that the source was a continental arc on basement with both Grenville and Pan-African affinities, pointing to northern Gondwana or peri-Gondwana terranes. The new data link the tuffs to granitoids (326 Ma) of the Maya block in southern Mexico, which was part of northern Gondwana. Correlation of the Stanley-Barnett tuffs across southern Laurentia suggests the likely presence of Mississippian tuffs over a broad region in southern Laurentia, and their usefulness for constraining absolute ages of basin fills and characterizing the Gondwanan arc.**

## INTRODUCTION

Assembly of the supercontinent Pangea through Rheic Ocean closure and the subsequent Laurentia-Gondwana collision are among the most important tectonic events in late Paleozoic Earth history (e.g., Nance et al., 2014). It has long been inferred that the southward subduction of the Rheic oceanic plate formed an arc system in the peri-Gondwana realm, including the Carolina, Suwannee, Coahuila, and Maya blocks, originally located in northern Gondwana (e.g., Lopez, 1997; Lawton et al., 2021). However, the history and geochemical signatures of the arc system remain poorly understood because the geologic record has been obscured by younger magmatism related to subduction of the paleo-Pacific oceanic plate, Pangea breakup, deep burial, and erosion (e.g., Kirsch et al., 2012; Ortega-Obregón et al., 2013). The few studies of this arc and its

geochemical signatures have also raised uncertainties about how to distinguish the inferred northern Gondwana arc from the Ordovician arc related to Iapetus Ocean closure (Alemán-Gallardo et al., 2019) and the Permian–Triassic arc related to subduction of the paleo-Pacific oceanic plate (e.g., Torres et al., 1999). Studies of the arc system also have implications for understanding the Laurentia-Gondwana collision; for example, the geochemistry of Late Mississippian granitoids in the Maya block suggests breakoff of the Rheic oceanic slab accompanying collision along the Ouachita suture (Zhao et al., 2020), although Gondwana-derived sediments did not arrive in the Ouachita foreland during this time (Prines, 2020).

We describe a newly discovered Late Mississippian tuff in the Barnett Shale in the subsurface of the Midland Basin of west Texas and use zircon geochemistry and geochronology to

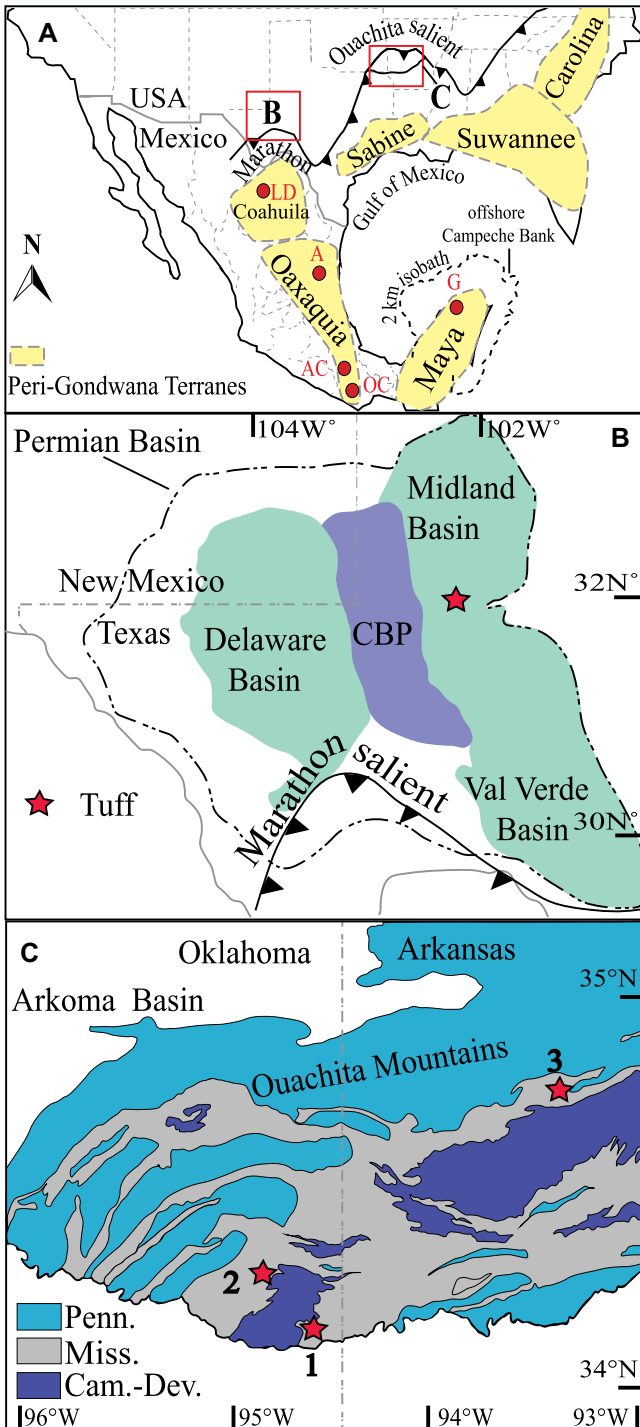
show that this tuff correlates with Late Mississippian Stanley tuffs exposed in the Ouachita Mountains (Shaulis et al., 2012). We infer that these tuffs were likely derived from volcanoes in the northern Gondwana arc, with the Ouachita Mountains being closer to the source than the Midland Basin. These tuffs are useful for chronostratigraphy and stratigraphic correlations, and their geochemical and isotopic attributes provide important insights into the Gondwana arc.

## GEOLOGIC BACKGROUND

A diachronous collision between Laurentia and Gondwana formed the Ouachita-Marathon fold-and-thrust belt in southern Laurentia (Fig. 1A). Although the orogen has been eroded and mostly buried, the Ouachita Mountains in Oklahoma and Arkansas expose rocks deposited during Rheic Ocean closure (Fig. 1B). The Ouachita Mountains contain thick Carboniferous clastic rocks deposited in a deep-marine fan system, which was later deformed in an accretionary prism and incorporated into the orogen during collision (Morris, 1989). The Mississippian Stanley Group is ~4 km thick and contains mostly shale and some interbedded sandstone. The group contains five major, widespread tuffs, including, from bottom to top, the Beavers Bend, Hatton, lower and upper Mud Creek, and Chickasaw Creek tuffs (Fig. S1 in the Supplemental Material<sup>1</sup>; Niem, 1977; Shaulis et al., 2012). The Stanley tuffs generally thin from south to north, with the lower four tuffs ranging up to 40 m thick in southern areas (Niem, 1977).

The Midland Basin, which contains the newly discovered Barnett tuff described herein (Fig. S1), is a major subbasin of the Permian Basin formed north of the Marathon salient, which is

<sup>1</sup>Supplemental Material. Description of tuffs, analytical methods, and results, Figures S1–S7, and Tables S1–S5. Please visit <https://doi.org/10.1130/GEOL.S.16906879> to access the supplemental material, and contact editing@geosociety.org with any questions.



**Figure 1.** Simplified geologic maps of the study area. (A) Southern North America showing locations of peri-Gondwana terranes, the Ouachita-Marathon fold-and-thrust belt, and study areas. A—Aserradero Rhyolite; AC—Acatlan Complex; G—granitoids in Maya block; LD—Las Delicias arc; OC—Oaxacan Complex. Offshore Campeche Bank was modified after Dickinson and Lawton (2001). (B) Permian Basin showing location of the Midland Basin, which contains the Barnett tuff. CBP—Central Basin Platform. (C) Ouachita Mountains showing locations of five Stanley tuffs (modified after Shaulis et al., 2012): 1—Beavers Bend and Hatton tuffs; 2—Lower and Upper Mud Creek tuffs; 3—Chickasaw Creek tuff. Penn.—Pennsylvanian; Miss.—Mississippian; Cam-Dev.—Cambrian-Devonian.

the western continuation of the Ouachita belt (Fig. 1A). The Permian Basin region was part of a passive margin from the Early Ordovician to Late Mississippian, and it achieved its current configuration during the Pennsylvanian–early Permian Laurentia-Gondwana collision and the Ancestral Rocky Mountain orogeny (Leary et al., 2017). The Mississippian, deep-marine Barnett Shale in the Midland Basin is ~240 m thick (Mauck et al., 2018). The Barnett tuff, discovered in a core from the basin center (Fig. S2), is the first reported tuff in the Midland Basin.

#### MATERIALS AND METHOD

Zircons were extracted from one Barnett tuff and five Stanley tuff beds. Scanning electron microscope (SEM) images of individual grains were taken to characterize roundness. Zircon U-Pb dates, Lu-Hf isotopes, and trace-element (TE) compositions were analyzed by laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS). Young grains of the Barnett tuff were plucked from the mount for chemical abrasion–isotope dilution–thermal ionization mass spectrometry (CA-ID-TIMS) dating

following Mattinson (2005). Details about zircon separation, SEM imaging, analytical procedures, data reduction, and filtering are described in the Supplemental Material. In total, we report 741 zircon LA-ICP-MS and 7 TIMS U-Pb dates, and 65 Lu-Hf and 44 TE analyses (Tables S1–S4). Zircon Hf isotope two-stage depleted mantle model ages ( $T_{DM2}$ ) were calculated using an average crustal value of  $^{176}\text{Lu}/^{177}\text{Hf} = 0.0113$  following Rudnick and Gao (2003). Errors of zircon U-Pb and Hf analyses and U-Pb ages are reported as  $2\sigma$  standard deviation.

The age of each tuff was calculated from the mode of the youngest dominant LA-ICP-MS population in the kernel density estimation (KDE) plot (Fig. 2). The age was calculated as the weighted mean of more than three grains overlapping at  $2\sigma$ , for which values had a mean square of weighted deviation (MSWD) near 1. See the Supplemental Material for more details.

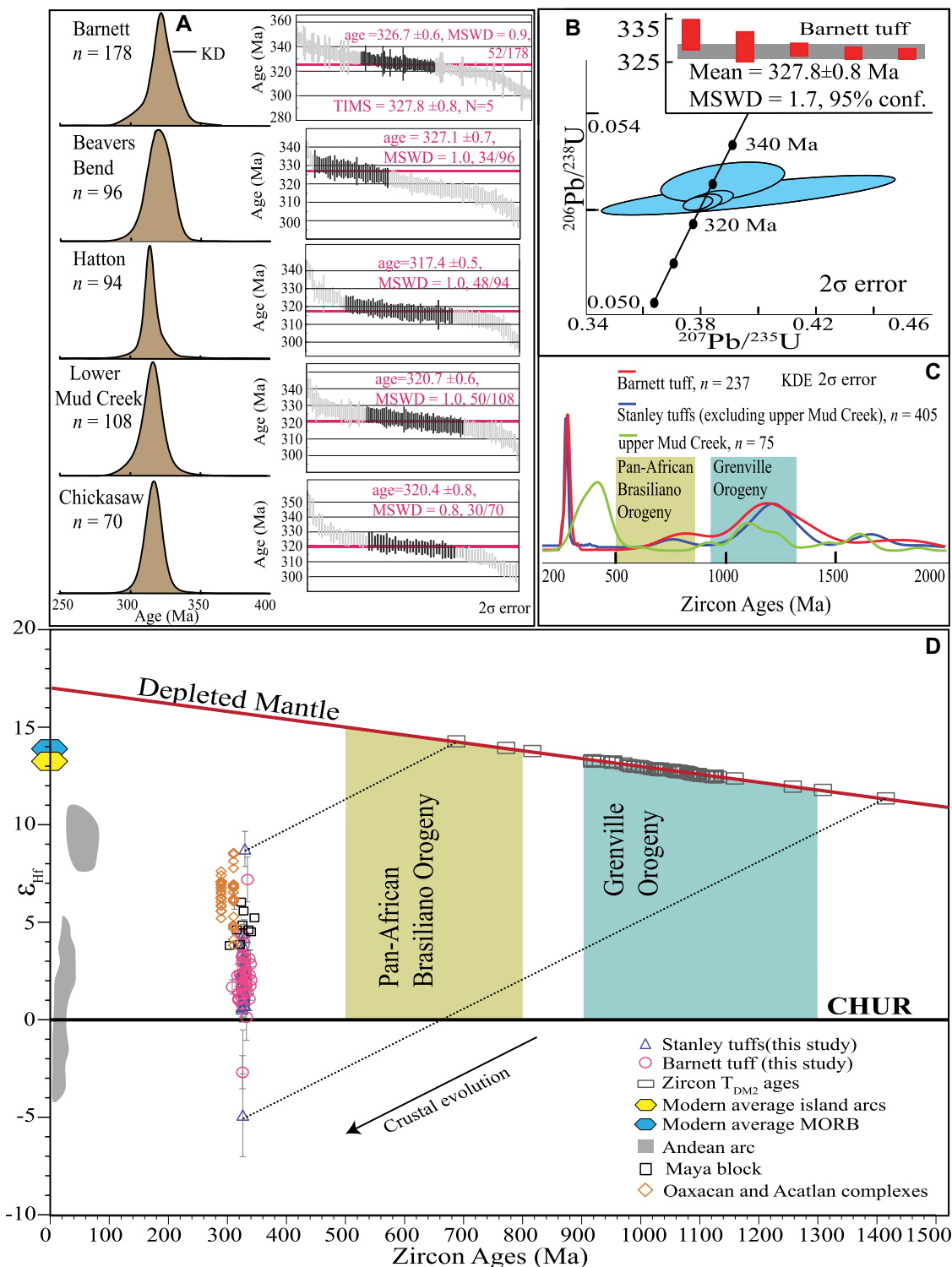
#### RESULTS

Zircons from four of the Stanley tuffs and the Barnett tuff were mostly elongated and euhedral and interpreted to be air-fall grains with minimal abrasion during transport (Figs. S3 and S4). The youngest mode date of the Barnett tuff was  $326.6 \pm 0.6$  Ma (Fig. 2A), which matches well with the CA-ID-TIMS date of  $327.8 \pm 0.8$  Ma (Fig. 2B; Fig. S5), suggesting that our method of calculating tuff age from LA-ICP-MS dates was accurate. Four of five Stanley tuffs yielded dates of  $327.1 \pm 0.7$ ,  $320.7 \pm 0.6$ ,  $320.4 \pm 0.8$ , and  $317.4 \pm 0.5$  Ma, respectively (Fig. 2A). The upper Mud Creek tuff did not have enough young grains for age determination. The Barnett tuff and the oldest Stanley tuff, Beavers Bend tuff, could be correlated based on overlapping ages.

In all tuffs, grains older than 500 Ma, which accounted for 16% of all grains, clustered at 850–500 Ma and 1300–900 Ma (Fig. 2C; Fig. S6). The Hf isotope signatures of ca. 325 Ma zircons from all tuffs were juvenile, with most  $\epsilon_{\text{HF}}$  values between 0 and 5 (Fig. 2D). These values are in the range of the Andean continental arc (e.g., Jones et al., 2015) but lower than those from intra-oceanic arcs and mid-oceanic ridge basalts (Workman and Hart, 2005; Dhuime et al., 2011). Zircon  $T_{DM2}$  ages ranged between ca. 700 and ca. 1400 Ma (Fig. 2D). Zircons from all units showed high total rare earth element ( $\Sigma\text{REE}$ ) contents, enrichment of heavy (H) REEs, negative Eu anomalies, and positive Ce anomalies (Fig. 3; Fig. S7). Discrimination diagrams following Belousova et al. (2002) and Grimes et al. (2015) project these tuffs to the granitoid parent rock composition and arc setting (Fig. 3).

#### CONTINENTAL ARC AFFINITY AND LOCATION

Our ages indicate that the Barnett and Beavers Bend tuffs resulted from the same or semi-

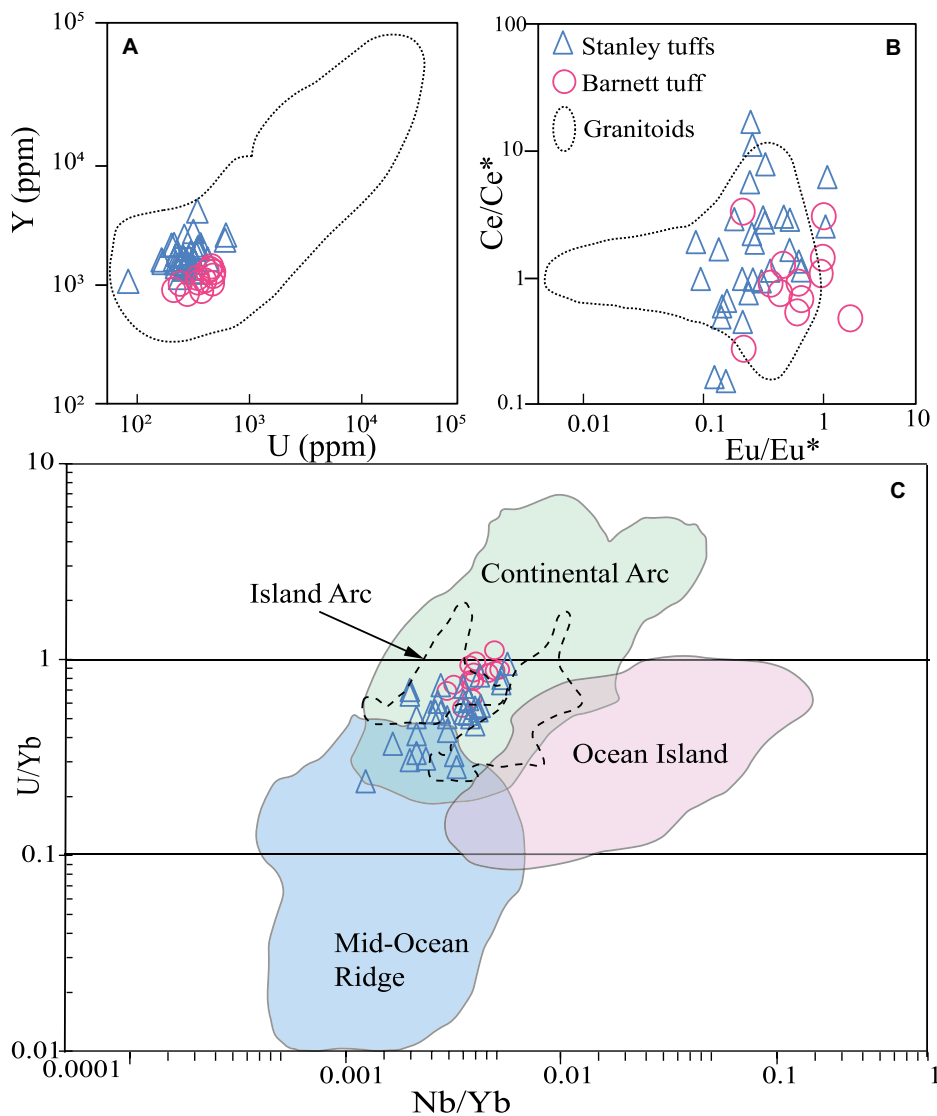


**Figure 2.** (A) Adaptive kernel density estimate (KDE) plots of the youngest statistical population and ranked data plot showing the youngest mode date calculations for the Barnett and four Stanley (Beavers Bend, Hatton, Lower Mud Creek, and Chicksaw) tuffs. Note that only grains shown in black were used for our calculations. Ages are given in Ma. MSWD—mean square of weighted deviates. (B) Concordia plot showing chemical abrasion–isotope dilution–thermal ionization mass spectrometry (CA-ID-TIMS) dates of the Barnett tuff. (C) KDE of all inductively coupled plasma–mass spectrometry (ICP-MS) dates. (D) Zircon U-Pb dates and  $\epsilon_{\text{Hf}}$  values of the Barnett and Stanley tuffs compared with those of Andean continental arc (Jones et al., 2015), average island arc (Dhuime et al., 2011), mid-oceanic ridge basalt (MORB; Workman and Hart, 2005), and Mississippian magmatic rocks in the Maya block (Zhao et al., 2020) and Oaxaquia block (Oaxacan and Acatlan complexes) (Ortega-Obregón et al., 2013) of Mexico. CHUR—chondritic uniform reservoir;  $T_{\text{DM2}}$ —two-stage depleted mantle model ages.

contemporary volcanic eruptions at ca. 328 Ma. Zircon  $T_{\text{DM2}}$  ages and TE signatures (Figs. 2 and 3; Fig. S7) further suggest that both were sourced from a continental arc with felsic parent magma composition, consistent with the interpretation of whole-rock geochemistry of the Stanley tuffs (Loomis et al., 1994). Melts of continental crust have low positive or negative  $\epsilon_{\text{Hf}}$  values because continental crust has low Lu/Hf and less radiogenic Hf than depleted mantle

of similar ages (Kinny and Maas, 2003). However, zircons from a continental arc could yield a large range of  $\epsilon_{\text{Hf}}$  values where the melts have different degrees of mixing between mantle-derived mafic melts and partial melts of old continental crust (Kemp et al., 2007). Zircon Hf model ages provide further constraints on the continental crust on which the arc was built (Dhuime et al., 2011). Our zircon  $T_{\text{DM2}}$  ages fall between the ages of the Grenville orogeny

(1300–900 Ma) and the Pan-African orogeny (850–500 Ma) (Fig. 2D), suggesting that the parent melt was mostly derived from continental crust with both basement types, consistent with a northern Gondwana source. This interpretation is also supported by subordinate zircon U-Pb age modes at 850–500 Ma and 1300–900 Ma (Fig. 2C). These grains were most likely inherited from Gondwana Pan-African and Grenville basement.



**Figure 3.** (A) Discrimination diagrams of (A) Y versus U abundances and (B) Ce/Ce\* versus Eu/Eu\* ratios, where granitoid parent rock compositions follow Belousova et al. (2002) and Eu\* and Ce\* were calculated as  $\sqrt{(Sm_N \times Gd_N)}$  and  $Nd_N^2/Sm_N$ , respectively (where N indicates chondrite-normalized abundances following McDonough and Sun [1995]). (C) U/Yb versus Nb/Yb, following Grimes et al. (2015).

Mississippian magmatism coeval with our reported Laurentia tuffs (ca. 328–317 Ma) has been reported from several Gondwanan or peri-Gondwanan blocks that lie in the Alleghanian-Ouachita hinterland. The magmatism includes, from east to west: Alleghanian granites (326–285 Ma) in the Carolina terrane of the southern Appalachians (Hibbard and Samson, 1995), granitoids ( $326 \pm 5$  Ma) in the Maya block (Zhao et al., 2020), Las Delicias arc (331–270 Ma) in the Coahuila block (Lopez, 1997), and the Aserradero Rhyolite ( $341 \pm 4$  Ma) (Ramírez-Fernández et al., 2021) in the Oaxaquia block of Mexico (Fig. 4A). All of these are Gondwanan or peri-Gondwanan terranes that accreted to southeastern and southern Laurentia during Rheic Ocean closure. The reconstructed distribution of these terranes suggests an elongated continental arc that developed on northern

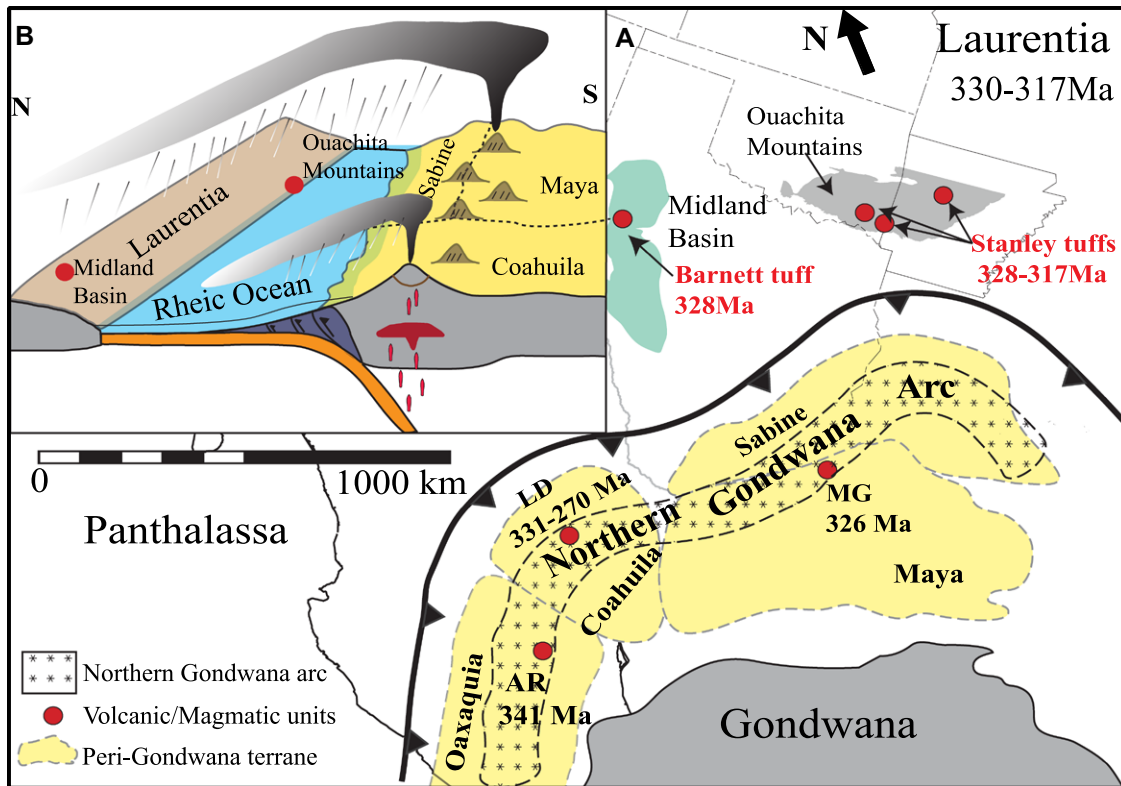
Gondwana caused by subduction of the Rheic oceanic plate (Fig. 4A). The Carolina terrane is predominantly composed of Neoproterozoic to early Paleozoic rocks with juvenile bulk-rock  $\epsilon_{Nd}$  signatures, and the Alleghanian granites also contain inherited Grenvillian zircons (Mueller et al., 2011). However, it is generally agreed that the terrane was accreted to Laurentia during the Late Ordovician–Silurian (e.g., Hibbard et al., 2002), and reinterpretation of petrology and geochemistry data suggests that the granites were related to postcollision slab break-off or delamination rather than continental arc magmatism (Zhao et al., 2020). In addition, the Carolina terrane is too distant to have provided proximal subaqueous pyroclastic flows to the Stanley tuffs.

The studied tuffs are most like Maya block granitoids, although a source in the poorly

known Sabine terrane cannot be precluded. The Maya block lay south of the Ouachita Mountains, and the Coahuila block was adjacent to the Marathon thrust belt before the Gulf of Mexico opened in Jurassic time (Fig. 4). The Maya and Coahuila blocks both have Grenvillian and Pan-African basement, based on studies of igneous rocks and detrital zircons in their late Paleozoic strata (e.g., Martens et al., 2010; Lopez et al., 2001). Las Delicias arc volcanic rocks have juvenile  $\epsilon_{Nd}$  signatures (Lopez, 1997). However, zircons from these rocks have low Rb/Sr ( $<0.05$ ) and La/Yb ( $<3.7$ ) ratios and large ion lithophile elements (LILE) contents, including REEs, U, and Th, suggesting that the arc was developed on a thin continental crust with limited crustal contamination (Lopez, 1997). This signature is different from that of the bulk Stanley tuffs, which have high LILEs, Rb/Sr (average 3.2), and La/Yb ( $>10$ ) (Loomis et al., 1994). The geochemical signatures, juvenile zircon  $\epsilon_{Hf}$  signatures (4–6), and  $T_{DM2}$  ages (1080–950 Ma) of Maya block granitoids (Zhao et al., 2020) are consistent with those of our studied tuffs (Fig. 2). The significantly older (ca. 341 Ma) Aserradero Rhyolite in the Oaxaquia block has an upper-crust source without evidence of mantle input, and the inherited zircons are all Grenvillian (Ramírez-Fernández et al., 2021). Carboniferous magmatism (ca. 311 Ma) documented in the Oaxacan and Acatlan metamorphic complexes in the Oaxaquia block are much younger than the Stanley and Barnett tuffs, and their oldest zircons have higher  $\epsilon_{Hf}$  values than those of our tuffs (Fig. 2D; Ortega-Obregón, 2013). In addition, the geochemical signatures of the complexes were interpreted to be related to the subduction of the paleo-Pacific oceanic plate beneath western Gondwana (Ortega-Obregón, 2013).

## IMPLICATIONS

Our CA-ID-TIMS U-Pb zircon date of the Barnett tuff is the first absolute age of the Permian Basin sedimentary sequence. The previous apparent lack of datable tuff beds in the Permian Basin and diachronous nature of microfossil biozones raised uncertainty about the absolute ages of these important strata. In the Permian Basin, the lower Barnett Shale was correlated to the international Viséan (346.7–330.9 Ma) Stage based on conodont biostratigraphy (Mauck et al., 2018). Our zircon U-Pb date ( $327.8 \pm 0.8$  Ma) of the Barnett tuff places some of the lower Barnett Shale into the international Serpukhovian (330.9–323.2 Ma) Stage. The correlation between the Barnett and Beavers Bend tuffs across  $\sim 800$  km further suggests that tuffs of this age may be widespread along the southern Laurentia margin and might provide a means to constrain the absolute ages of other basin fill, such as that in the Fort Worth Basin.



**Figure 4. (A)** Paleogeographic reconstruction at 330–317 Ma showing location of the Gondwana arc and rock units described in this paper, modified after Lawton et al. (2021). **(B)** Tectonic model for Late Mississippian magmatic activity in northern Gondwana. AR—Aseradero Rhyolite; LD—Las Delicias arc; MG—granitoids from the Chicxulub Scientific Drilling Project (<https://www.icdp-online.org/projects/world/north-and-central-america/chicxulub-2-mexico/>) in the Maya block.

Our results suggest that Gondwana-Laurentia collision did not occur until after the youngest arc magmatism at ca. 317 Ma, which is consistent with the results of sediment provenance studies (Fig. S6). Neoproterozoic zircons sourced from the Pan-African orogen of Gondwana did not arrive in Laurentia during the Late Mississippian deposition of the Stanley Group (Prines, 2020), but they are present in Pennsylvanian strata of the Fort Worth Basin (Alsalem et al., 2018; Fig. S6), indicating that the collision in the Ouachita salient happened during the Pennsylvanian.

## CONCLUSIONS

Our new zircon U-Pb dates,  $\epsilon_{\text{HF}}$  signatures, and trace-element compositions of tuffs from the Ouachita Mountains and the Midland Basin imply that a continental arc was active from ca. 328 to ca. 317 Ma due to subduction of the Rheic oceanic plate beneath northern Gondwana. During the Late Mississippian, eruptions of arc volcanoes delivered tuffs northward into the adjacent deep-water basin between the arc and Laurentia and further north to southern Laurentia. The deep-water deposits were then incorporated in the Ouachita orogen during the subsequent Laurentia-Gondwana collision. Our results have implications for chronostratigraphy in southern Laurentia as well as the timing of Laurentia-Gondwana collision.

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