Integrating Zircon Trace Element Geochemistry and High-Precision
U-Pb Zircon Geochronology to Resolve Timing and Petrogenesis of
the late Ediacaran-Cambrian Wichita Igneous Province, Southern
Oklahoma Aulacogen, USA

Supplementary Material

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**Analytical Methods and Results**

**Sample preparation**

An abundant population of relatively small (approximately 100-200 µm in long dimension), equant to prismatic zircon crystals was separated from each hand sample by conventional density and magnetic methods. The entire zircon separate was placed in a muffle furnace at 900°C for 60 hours in quartz beakers to anneal minor radiation damage; annealing enhances cathodoluminescence (CL) emission (Nasdala et al., 2002), promotes more reproducible interelement fractionation during laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) (Allen and Campbell, 2012), and prepares the crystals for subsequent chemical abrasion (Mattinson, 2005). Following annealing, individual grains were hand-picked and mounted, polished and imaged by CL on a scanning electron microscope. From these compiled images, the locations of spot analyses for LA-ICP-MS were selected.

**LA-ICPMS analysis**

LA-ICPMS analysis utilized an X-Series II quadrupole ICPMS and New Wave Research UP-213 Nd:YAG UV (213 nm) laser ablation system. In-house analytical protocols, standard materials, and data reduction software were used for acquisition and calibration of U-Pb dates and a suite of high field strength elements (HFSE) and rare earth elements (REE). Zircon was ablated with a laser raster 15 µm wide using fluence and pulse rates of ~5 J/cm² and 20 Hz, during a 45 second analysis (15 sec gas blank, 30 sec ablation) that excavated a line ~5 µm deep. Ablated material was carried by a 1.15 L/min He gas stream to the nebulizer flow of the plasma. Quadrupole dwell times were 5 ms for Si and Zr, 200 ms for $^{49}$Ti and $^{207}$Pb, 80 ms for $^{206}$Pb, 40 ms for $^{202}$Hg, $^{204}$Pb, $^{208}$Pb, $^{232}$Th, and $^{238}$U and 10 ms for all other HFSE and REE; total sweep duration is 950 ms. Background count rates for each analyte were obtained prior to each line analysis and subtracted from the raw count rate for each analyte. For concentration calculations, background-subtracted count rates for each analyte were internally normalized to $^{29}$Si and calibrated with respect to NIST SRM-610 and -612 glasses as the primary standards. Ablation pits that appeared to have intersected glass or mineral inclusions were identified based on Ti and P signal excursions, and data from those analyses were generally discarded. U-Pb dates from these analyses were considered valid if the U-Pb ratios appeared to have been unaffected by the inclusions. Signals at mass 204 were normally indistinguishable from zero following subtraction.
of mercury backgrounds measured during the gas blank (<100 cps $^{202}\text{Hg}$), and thus dates are reported without common Pb correction. Rare analyses that appeared contaminated by common Pb were rejected based on mass 204 greater than baseline. Additionally, elements sensitive to micro-inclusions of apatite, monazite, rutile, oxides, and melt inclusions (e.g., P, Ti, LREE) were monitored if there were excursions in these elements, these analyses were rejected and not included for interpretations in this study. Temperature was calculated from the Ti-in-zircon thermometer (Watson et al., 2006). Because there are no constraints on the activity of TiO$_2$ in the source rocks, an average value in crustal rocks of 0.8 was used and an activity of SiO$_2$ of 1.0 was used based on the presence of quartz in all samples (Hayden and Watson, 2007).

For U-Pb and $^{207}\text{Pb}/^{206}\text{Pb}$ dates, instrumental fractionation of the background-subtracted ratios was corrected and dates were calibrated with respect to interspersed measurements of zircon standards and reference materials. The primary standard Plešovice zircon (Sláma et al., 2008) was used to monitor time-dependent instrumental fractionation based on two analyses for every 10 analyses of unknown zircon. A polynomial fit to the primary standard analyses versus time yields each sample-specific fractionation factor. A secondary bias correction was subsequently applied to unknowns on the basis of the residual age bias as a function of radiogenic Pb count rate in standard materials, including Seiland, Zirconia, and Plesovice zircon, or similar materials of known age and variable Pb content. A polynomial fit to the secondary standard analyses with Pb count rate yields each sample-specific bias correction. Radiogenic isotope ratio and age error propagation for all analyses includes uncertainty contributions from counting statistics and background subtraction. Because the detrital zircon analyses are interpreted individually, uncertainties from the standard calibrations are propagated into the errors on each date. These uncertainties are the local standard deviations of the polynomial fits to the interspersed primary standard measurements versus time for the time-dependent, relatively larger U/Pb fractionation factor, and the standard errors of the means of the consistently time-invariant and smaller $^{207}\text{Pb}/^{206}\text{Pb}$ fractionation factor. These uncertainties are ~2% ($2\sigma$) for $^{206}\text{Pb}^{238}\text{U}$ and ~1% ($2\sigma$) for $^{207}\text{Pb}/^{206}\text{Pb}$. Additional details of methodology and reproducibility are reported in Rivera et al. (2013).

**ID-TIMS analysis**
U-Pb geochronology methods for isotope dilution thermal ionization mass spectrometry follow those previously published by Davydov et al. (2010) and Schmitz and Davydov (2012). All analyses were undertaken on crystals previously mounted, polished and imaged by cathodoluminescence (CL), and analyzed by LA-ICPMS. Zircon crystals were subjected to a modified version of the chemical abrasion method of Mattinson (2005), whereby single crystal fragments plucked from grain mounts were individually abraded in a single step with concentrated HF at 190°C for 12 hours. Zircon fragments were dissolved in Parr bombs at 220 °C for 48 h. Dissolved zircon solutions were subsequently dried down, redissolved in 100 µl 6 N HCl and converted to chlorides in Parr bombs at 180 °C for 12 h, after which solutions were dried again and brought up in 50 µl 3 N HCl. U and Pb were isolated by anion exchange column chromatography using 50 µl columns and AG-1 X8 resin [200–400 mesh, chloride form (Eichrom); Krogh, 1973].

The U-Pb aliquot was loaded in a silica gel emitter (Gerstenberger & Haase, 1997) to an outgassed, zone-refined Re filament. Isotopic determinations were performed using an IsotopX PhoeniX-62 TIMS. A correction for mass-dependent Pb fractionation was applied based on repeated measurements of NBS 982 (Catanzaro et al., 1968) Pb on both the Daly ion counter [0.16 ± 0.03 %) amu⁻¹; 1s] and the Faraday cups [0.10 × (1 ± 0.02 %) amu⁻¹; 1s]. Uranium was run as an oxide (UO₂) and measured in static mode on Faraday detectors equipped with 10¹² Ω resistors. The U mass fractionation for the same analyses was calculated using the \(^{233}\text{U}/^{235}\text{U}\) ratio of the double spike solution (0.99506 % ± 0.01 %, 1s).

U-Pb dates and uncertainties for each analysis were calculated using the algorithms of Schmitz and Schoene (2007), the U decay constants of Jaffey et al. (1971), and a value of \(^{238}\text{U}/^{235}\text{U} = 137.88\). Uranium oxide measurements were corrected for isobaric interferences using an \(^{18}\text{O}/^{16}\text{O}\) value of 0.00206. Uncertainties are based upon non-systematic analytical errors, including counting statistics, instrumental fractionation, tracer subtraction, and blank subtraction. All non-radiogenic Pb was attributed to laboratory blank with a mean isotopic composition determined by total procedural blank measurements. These error estimates should be considered when comparing our \(^{206}\text{Pb}/^{238}\text{U}\) dates with those from other laboratories that used tracer solutions calibrated against the EARTHTIME gravimetric standards. When comparing our dates with those derived from other decay schemes (e.g., \(^{40}\text{Ar}/^{39}\text{Ar}, ^{187}\text{Re}/^{187}\text{Os}\)), the uncertainties in tracer calibration (0.05%; Condon et al., 2015; McLean et al., 2015) and U decay constants (0.108%;
should be added to the internal error in quadrature. Quoted errors for calculated weighted means are thus of the form ±X(Y)[Z], where X is solely analytical uncertainty, Y is the combined analytical and tracer uncertainty, and Z is the combined analytical, tracer and $^{238}$U decay constant uncertainty.

**G8 (Anorthosite from Glen Mountains Layered Complex):** CL-imaging of the 50 largest zircon crystals from this sample revealed a homogenous population of moderately luminescent, oscillatory to sector zoned crystals. Nine grains were selected for CA-TIMS analysis on the basis of the uniform, predominant CL pattern. Chemical abrasion in concentrated HF at 190°C for 12 hours resulted in moderate dissolution of the zircon crystals. All eight analyses are concordant and equivalent, with a weighted mean $^{206}$Pb/$^{238}$U date of 532.49 ± 0.12(0.28)[0.62] Ma (MSWD = 0.93), which is interpreted as dating the crystallization of this anorthosite.

**AE-389 (Rhyolite from the Arbuckle Mountains):** CL-imaging of the 100 largest zircon crystals from this sample revealed a homogenous population of moderately luminescent, oscillatory to sector zoned crystals. A lesser number of crystals have irregularly shaped, relatively non-luminescent cores overgrown by aforementioned luminescent, oscillatory rims. There are also a few zircon crystals that are poorly luminescent but are oscillatory zoned and are considered to be xenocrysts. Eight grains were selected for CA-TIMS analysis on the basis of the uniform, predominant CL pattern. Chemical abrasion in concentrated HF at 190°C for 12 hours resulted in moderate dissolution of the zircon crystals. All eight analyses are concordant and equivalent, with a weighted mean $^{206}$Pb/$^{238}$U date of 539.20 ± 0.15(0.30)[0.64] Ma (MSWD = 0.54), which is interpreted as dating the eruption age of this rhyolite.

**JP-22 (Rhyolite flow from base of volcanic succession at Bally Mountain):** CL-imaging of the 100 largest zircon crystals from this sample revealed a homogenous population of moderately luminescent, oscillatory to sector zoned crystals. A lesser number of crystals have irregularly shaped, relatively non-luminescent cores overgrown by aforementioned luminescent, oscillatory rims. There are also a few zircon crystals that are poorly luminescent but are oscillatory zoned and are considered to be xenocrysts. Eight grains were selected for CA-TIMS analysis on the basis of the uniform, predominant CL pattern. Chemical abrasion in concentrated HF at 190°C for 12 hours resulted in moderate dissolution of the zircon crystals. All eight analyses are concordant and equivalent, with a weighted mean $^{206}$Pb/$^{238}$U date of
530.98 ± 0.14 Ma(0.29)[0.62] Ma (MSWD = 0.94), which is interpreted as dating the eruption age of this rhyolite.

**JP-120 (Rhyolite flow from top of volcanic succession at Bally Mountain):**

CL-imaging of the 100 largest zircon crystals from this sample revealed a homogenous population of moderately luminescent, oscillatory to sector zoned crystals. A lesser number of crystals have irregularly shaped, relatively non-luminescent cores overgrown by aforementioned luminescent, oscillatory rims. There are also a few zircon crystals that are poorly luminescent but are oscillatory zoned and are considered to be xenocrysts. Thirteen grains were selected for CA-TIMS analysis on the basis of the uniform, predominant CL pattern. Chemical abrasion in concentrated HF at 190°C for 12 hours resulted in moderate dissolution of the zircon crystals. All thirteen analyses are concordant and equivalent, with a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date of 530.70 ± 0.12 Ma(0.28)[0.62] Ma (MSWD = 0.81), which is interpreted as dating the eruption age of this rhyolite.

**WP16-2 (Mt. Scott Granite):**

CL-imaging of the 100 largest zircon crystals from this sample revealed a homogenous population of moderately luminescent, oscillatory to sector zoned crystals. A lesser number of crystals have irregularly shaped, relatively non-luminescent cores overgrown by aforementioned luminescent, oscillatory rims. There are also a few zircon crystals that are poorly luminescent but are oscillatory zoned and are considered to be xenocrysts. Eight grains were selected for CA-TIMS analysis on the basis of the uniform, predominant CL pattern. Chemical abrasion in concentrated HF at 190°C for 12 hours resulted in moderate dissolution of the zircon crystals. All eight analyses are concordant and equivalent, with a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date of 530.45 ± 0.14 Ma(0.29)[0.62] Ma (MSWD = 0.69), which is interpreted as dating the crystallization of this granite.

**WP18-1 (Cache Granite):**

CL-imaging of the 55 largest zircon crystals from this sample revealed a homogenous population of moderately luminescent, oscillatory to sector zoned crystals. A lesser number of crystals have irregularly shaped, relatively non-luminescent cores overgrown by aforementioned luminescent, oscillatory rims. There are also a few zircon crystals that are poorly luminescent but are oscillatory zoned and are considered to be xenocrysts. Seven grains were selected for CA-TIMS analysis on the basis of the uniform, predominant CL pattern. Chemical abrasion in
concentrated HF at 190°C for 12 hours resulted in moderate dissolution of the zircon crystals. All seven analyses are concordant and equivalent, with a weighted mean \(^{206}\text{Pb}^{238}\text{U}\) date of \(530.61 \pm 0.13\) Ma(0.29)[0.62] Ma (MSWD = 0.12), which is interpreted as dating the crystallization of this granite.

**JPQ-71797 (Quanah Granite):**

CL-imaging of the 60 largest zircon crystals from this sample revealed a homogenous population of moderately luminescent, oscillatory to sector zoned crystals. A lesser number of crystals have irregularly shaped, relatively non-luminescent cores overgrown by aforementioned luminescent, oscillatory rims. There are also a few zircon crystals that are poorly luminescent but are oscillatory zoned and are considered to be xenocrysts. Eight grains were selected for CA-TIMS analysis on the basis of the uniform, predominant CL pattern. Chemical abrasion in concentrated HF at 190°C for 12 hours resulted in moderate dissolution of the zircon crystals. Six of the eight analyses are concordant and equivalent, with a weighted mean \(^{206}\text{Pb}^{238}\text{U}\) date of \(530.23 \pm 0.14\) Ma(0.29)[0.62] Ma (MSWD = 0.12), which is interpreted as dating the crystallization of this granite.

**REFERENCES**


Rivera, T.A., Storey, M., Schmitz, M.D., Crowley, J.L., 2013. Age intercalibration of $^{40}$Ar/$^{39}$Ar sanidine and chemically distinct U/Pb zircon populations from the Alder Creek Rhyolite Quaternary geochronology standard: Chemical Geology 345, 87–98.


Fig. DR1: Geological setting of Arbuckle rhyolite samples. (A) Geological map of Arbuckle Mountains, modified from Ham (1973). WTH = West Timbered Hills, ETH = East Timbered Hills. Location of map is shown in inset. (B) Geological map and cross-section of igneous exposures in East Timbered Hills, modified from Eschberger et al. (2014). Location of dated rhyolite sample AE389 is indicated, along with location of hypabyssal felsic intrusion dated by Thomas et al. (2012). Faults are from Johnson (1990). (C) Geological map of igneous exposures in West Timbered Hills, modified from Boro (2015) and Toews (2015). Location of dated rhyolite sample JP-118 is indicated. Faults are generally taken from Johnson (1990).

References:

Boro, J.R., 2015, Volcanic lithofacies and geochemistry of Cambrian rift-related rhyolites in the West Timbered Hills, Arbuckle Mountains, southern Oklahoma [M.S. thesis]: Fort Worth, Texas, Texas Christian University, 101 p.


Toews, C.E., 2015, Cambrian phreatomagmatic igneous breccia and associated bimodal hypabyssal intrusion3 in the West Timbered Hills, Arbuckle Mountains, southern Oklahoma [M.S. thesis]: Fort Worth, Texas, Texas Christian University, 103 p.
**206Pb/238U Weighted Mean**

- **G8 Anorthosite GMLC**
  - $533.49 \pm 0.12/0.28/0.62$ Ma
  - $n = 9$, MSWD = 0.91

- **AE-389 Rhyolite Flow Arbuckle Mountains**
  - $539.46 \pm 0.13/0.29/0.64$ Ma
  - $n = 8$, MSWD = 0.87

- **JP-118 Rhyolite Flow Arbuckle Mountains**
  - $539.20 \pm 0.15/0.30/0.64$ Ma
  - $n = 8$, MSWD = 0.54
**206/Pb/238U Weighted Mean**

- **JP-120**, Upper Rhyolite Flow, Bally Mountain
  - $530.70 \pm 0.12/0.28/0.62$ Ma
  - $n = 13, MSWD = 0.81$

- **JP-22**, Lower Rhyolite Flow, Bally Mountain
  - $530.98 \pm 0.15/0.29/0.62$ Ma
  - $n = 8, MSWD = 0.94$

- **PEG**, Gabbro, Roosevelt Gabbro
  - $532.05 \pm 0.12/0.29/0.63$ Ma
  - $n = 8, MSWD = 0.89$
WP16-2
Mt. Scott Granite

WP18-1
Cache Granite

JPQ-71797
Quanah Granite

$^{206}\text{Pb}/^{238}\text{U}$ Weighted Mean
$530.45 \pm 0.13/0.29/0.62 \text{ Ma}$
$n = 8, \text{MSWD} = 0.69$

$^{206}\text{Pb}/^{238}\text{U}$ Weighted Mean
$530.61 \pm 0.13/0.29/0.62 \text{ Ma}$
$n = 7, \text{MSWD} = 0.12$

$^{206}\text{Pb}/^{238}\text{U}$ Weighted Mean
$530.23 \pm 0.14/0.29/0.62 \text{ Ma}$
$n = 6, \text{MSWD} = 0.28$
Quoted errors for calculated $^{206}\text{Pb}/^{238}\text{U}$ weighted means are of the form $\pm X/Y/Z$, where $X$ is solely analytical uncertainty, $Y$ is the combined analytical and tracer uncertainty, and $Z$ is the combined analytical, tracer and $^{238}\text{U}$ decay constant uncertainty. Each ellipse indicates the analysis of a single zircon grain. Dashed lines show the error bounds of the concordia curve due to the uncertainty in the decay constants of $\text{U}$. MSWD refers to the mean square of the weighted deviates. Horizontal black in the the weighted mean panel indicates the weighted mean date and the grey band reflects the internal uncertainty. Colors of the ellipses and individual $^{206}\text{Pb}/^{238}\text{U}$ bars correspond to the color of the mapped unit from Figure 2 in the manuscript.
Sr and Nd Isotopic Data for the Wichita Igneous Province

Granites and rhyolites: $\varepsilon_{\text{Nd}} = +1.9$ to $+4.5$ (Wright et al., 1996; Gilbert and Weaver, 2010).
Basalts: $\varepsilon_{\text{Nd}} = +1.9$ to $+4.1$, $^{87}\text{Sr} / ^{86}\text{Sr} = 0.70319$ (Brueseke et al., 2016).
Diabase intrusions: $\varepsilon_{\text{Nd}} = +1.6$ to $+5.1$, $^{87}\text{Sr} / ^{86}\text{Sr} = 0.70387$ to 0.70484 (Hogan et al., 1995; Gilbert and Weaver, 2010; Lidiak et al., 2014).
Roosevelt Gabbro: $\varepsilon_{\text{Nd}} = +3.3$ to $+5.1$ (Gilbert and Weaver, 2010).
Glen Mountains Layered Complex: $\varepsilon_{\text{Nd}} = +3.6$ to $+5.4$, $^{87}\text{Sr} / ^{86}\text{Sr} = 0.70359$ (Lambert et al., 1988).

References