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Integrated geochronology and petrogenesis of volcanic suites for tectonic sedimentary studies: Karoo Basin, South Africa

Matthew P. McKay

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**Integrated geochronology and petrogenesis of volcanic suites for
tectonic sedimentary studies: Karoo Basin, South Africa**

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**Dissertation submitted
to the Ebery College of Arts and Sciences
at West Virginia University**

in partial fulfillment of the requirements for the degree of

**Doctor of Philosophy in the
Department of Geology and Geography**

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**Morgantown, West Virginia
2015**

**Keywords: U-Pb zircon, geochronology, petrogenesis, Karoo Basin, Gondwana
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ABSTRACT

Integrated geochronology and petrogenesis of volcanic suites for tectonic sedimentary studies: Karoo Basin, South Africa

Matthew P. McKay

By integrating high-precision, U-Pb zircon geochronology with zircon and whole rock/tuff geochemistry, the tectonic history of an active margin can be assessed independently from strata preserved in sedimentary basins. This approach is particularly useful in regions where subsequent active tectonism has resulted in extensive igneous intrusion, tectonic dissection, or structural deformation of crustal suites, obscuring the record of previous geologic events. In this work I present 603 U-Pb zircon age coupled with zircon geochemical analyses collected from Sensitive High Resolution Ion Microprobe (SHRIMP) microanalyses, 15 U-Pb zircon Thermal Ionization Mass Spectrometry (TIMS) ages, and 109 U-Pb Laser Ablation-Inductively Coupled Plasma Mass Spectrometer (LA-ICPMS), and 41 whole rock geochemical analyses to assess 1) the utility and limitations of U-Pb zircon tuff geochronology when estimating absolute depositional ages of strata for chronostratigraphy, 2) the petrogenesis of volcanic tuffs from zircon U-Pb age and rare earth element (REE) compositions, and whole rock major and trace element concentrations, 3) advantages and limitations of geochronologic techniques (TIMS vs. SHRIMP vs. LAICPMS) and 4) the interaction between plate margin magmatism, orogenic deformation, and sedimentation into a tectonically active basin.

DEDICATION

This work is dedicated to Katie, the letter “z”, Archibald’s BBQ in Northport, AL, and the men and women of the U.S. Coast Guard.

“You’ve gotta go out, but you don’t have to come back.”
Semper Paratus

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Commonly used symbols and abbreviations

Ar	<i>Argon</i>
Ce	<i>Cerium</i>
CFB	<i>Cape Fold Belt</i>
CL	<i>Cathodoluminescence</i>
HREE	<i>Heavy rare earth element</i>
KDE	<i>Kernel density estimate</i>
LA-ICPMS	<i>Laser ablation inductively coupled mass spectrometry</i>
LREE	<i>Light rare earth element</i>
Ma	<i>Megaannus (Million years) before present</i>
m.y.	<i>Million years (indicating durations)</i>
ppm	<i>Parts per million</i>
Pb	<i>Lead</i>
Rb	<i>Rubidium</i>
REE	<i>Rare earth element</i>
SHRIMP	<i>Sensitive high resolution ion microprobe</i>
SIMS	<i>Secondary ion mass spectrometry</i>
Sr	<i>Strontium</i>
Ti	<i>Titanium</i>
TIMS	<i>Thermal ionization mass spectrometry</i>
Th	<i>Thorium</i>
U	<i>Uranium</i>
XRF	<i>X-ray fluorescence (spectrometry)</i>
Y	<i>Yttrium</i>
Yb	<i>Ytterbium</i>
Zr	<i>Zirconium</i>

PROLOGUE

Volcanic tuffs preserved in sedimentary strata are frequently used to provide absolute age controls for the encasing strata, since igneous rocks can be more easily directly dated using radioisotope methods. Tuffs in sedimentary basins may also provide a better record of prolonged magmatism in the deep-time record, since basins are fundamentally dominated by deposition and active igneous provinces are prone to uplift, subsequent magmatic intrusion, deformation, and erosion and may not be preserved. These two motivations have resulted volcanic tuff studies by stratigraphers/sedimentologists and petrologists, with little integration between the two subdisciplines.

In the following work, I integrate the petrologic and stratigraphic study of volcanic tuffs. In this work tuffs not only provide stratigraphic age controls but also yield insight into the tectonic history of a magmatic system that may no longer be represented in the observable rock record. This study focuses on tuffs preserved in the Karoo Basin of South Africa, that are age correlative to volcanic and igneous rocks throughout late Paleozoic-early Mesozoic Gondwana. In **Chapter 1** I address the age of zircon grains in volcanic tuffs and find that the magmatic recycling of zircon can result in older zircon grains in significantly younger (<20 m.y.) volcanic tuffs. The trends in zircon ages can be linked along margin magmatic systems through time. In **Chapter 2** that concept is advanced by investigating the rare-earth element geochemistry of zircon in volcanic tuffs. The zircon geochemistry supports the findings in Chapter 1, and the magmatic system that sourced the volcanic tuffs in the Karoo Basin may have been sourced from a back-arc system that evolved towards lower Zr melts in the latest Permian and Early Triassic, which accounts for the lack of Triassic zircon. The data from Chapters 1 & 2 was collected using microanalytical techniques, which yield spatial precision such that textural domains with zircon grains can be target at the expense of age precision/uncertainty. In **Chapter 3**, these results are contrasted with the higher precision Thermal Ionization Mass Spectrometry (TIMS) technique, which analyses the age of entire grains but returns high-precision/low-uncertainty results. Based on the TIMS results and cathodoluminescence images of zircon grains, zircon grains in Karoo volcanic tuffs are poly-growth grains, with multiple phases of zircon growth, and are therefore unsuitable for TIMS age dating. In fact, this chapter highlights the internal age complexity of zircon grains, which was the original motivation for developing microanalytical techniques. Finally, in **Chapter 4**, I employ the stratigraphic age controls from the previous chapters, and compare/contrast the zircon populations of volcanic tuffs with detrital zircon from clastic units in the Karoo Basin (in part from J. Dean, 2014). The results indicate that turbidite deposition in the Karoo Basin is (a) directly post-dates peak magmatism along the Gondwanan margin, (b) synchronous with uplift of the Cape Fold Belt, and (c) dominated by sediment that is directly sourced from active margin volcanism. Based on these observations, we present a model for sedimentation in the Karoo where high sedimentation rates are controlled by the generation of large volumes of easily erodable volcanic tuffs that was deposited in the Cape Fold Belt and subsequently washed into the basin during initial uplift. This model suggests that increased magmatism may be a factor in turbidite system development.

The integrated techniques in this study were crucial for interpreting not only the age of the sedimentary strata, but also the magmatic history recorded in the Karoo Basin. Therefore, integration of igneous petrology, petrochronology, and radioisotope geochronology should be considered in any stratigraphic study involving volcanic tuffs.

CHAPTER 1: U-Pb ZIRCON TUFF GEOCHRONOLOGY FROM THE KAROO BASIN, SOUTH AFRICA: IMPLICATIONS OF ZIRCON RECYCLING ON STRATIGRAPHIC AGE CONTROLS

ABSTRACT

Along the >650 km long southern margin of the Karoo Basin in South Africa, we traversed 4 evenly spaced stratigraphic transects and collected 22 samples of volcanic, air-fall tuffs thought to be distal deposits derived from the Permian-Triassic Southern Gondwanan volcanic arc. We present 469 new U-Pb zircon ages determined by Sensitive High Resolution Ion Microprobe-Reverse Geometry (SHRIMP-RG) at the Stanford-USGS Microanalytical Center in order to constrain the maximum depositional ages for the southern Karoo Basin strata. Weighted means of these youngest coherent zircon populations were selected to maximize the number of analyses while minimizing the Mean Square Weighted Deviation (MSWD) to increase the robustness and decrease the influence of Pb-loss and inheritance in determining the maximum depositional age. Maximum depositional ages for the marine Ecca Group range from 250-274 Ma whereas in the conformably overlying terrestrial Beaufort Group maximum depositional ages ranged from 257-452 Ma. Across the southern Karoo Basin, the Ecca Group tuffs produce maximum depositional ages that young upward; however, the Beaufort Group tuffs yield maximum depositional ages that are geochronologically out-of-sequence. Furthermore, maximum depositional ages of the Beaufort Group tuffs are consistently older than ash ages within the underlying marine strata. Our results are supported by previously published U-Pb tuff zircon geochronology in the Karoo Basin and demonstrate that the presence of out-of-sequence, older tuff ages are repeatable in Beaufort Group tuffs along the southern margin of the basin. We propose that tuff in Karoo Basin are correlative with tuffs in southern South America, and that the age spectra of these tuffs were influenced by magmatic crustal recycling. We use these data to highlight the complexity of U-Pb zircon datasets from tuffs, address the use of U-Pb zircon ages to provide absolute age controls, and discuss the implications of these new age controls on the Permian-Triassic Karoo strata.

Keywords: Geochronology; zircon; volcanic tuff; Karoo Basin; Gondwanan volcanism

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INTRODUCTION

The depositional age of clastic sedimentary strata is inherently difficult to date directly, since radiometric ages for clastic detritus reflect the age of the sediment source and not the depositional age of the sediment. Biostratigraphic ages can often be used to obtain relative geologic ages by correlating strata of interest to a Global Stratotype Section and Point (GSSP). GSSP's are defined by fossil assemblage, which precludes the direct correlation of sections between marine and terrestrial sediments. Biostratigraphic correlations, therefore, typically rely on lithostratigraphic classification, although sedimentary deposits are commonly time transgressive. Recent advances in sedimentary geochronology have demonstrated the tenuous nature of biostratigraphy-based ages and have shown that correlating strata to global events is tenuous without absolute age controls (*Surpless et al.*, 2006). One approach for resolving the maximum depositional age of sedimentary strata is through radiometric dating of syneruptive minerals found in volcanic tuffs preserved as interbeds in sedimentary basin fill strata. Zircon U-Pb geochronology is the most frequently employed tool for estimating the eruptive age of a volcanic ash, which is a proxy for the depositional age of the encasing strata (*Bowring and Schmitz*, 2003). This method requires the assumption that zircon within the ash are co-eruptive, and do not contain 1) older, inherited magmatic grains, 2) detrital zircon from sedimentary reworking and contamination of the ash, and 3) damaged grains that have undergone alteration and Pb-loss. U-Pb zircon data from tuffs do not always demonstrate a well-defined, single population. This suggests that tuffs might contain multi-age zircon populations. Therefore, the traditional assumption that zircon grains within tuffs are dominantly co-eruptive is at times flawed. Within the Karoo Supergroup of South Africa, multiple U-Pb zircon studies have resolved complex spectra of ages (*Coney et al.*, 2007; *Fildani et al.*, 2007; 2009; *Lanci et al.*, 2013; *Rubidge et al.*, 2013), leading to conflicting age interpretations for the absolute, maximum depositional age of the strata. This problem makes the Karoo strata ideal to test commonly held assumptions that zircon within volcanic tuffs are dominantly co-eruptive and that these ages represent the depositional age of sedimentary strata.

The Karoo Supergroup is in part composed of the marine Eccra Group and the conformably overlying, terrestrial Beaufort Group (*Veevers et al.*, 1994a). The Upper Beaufort Group has long been thought to contain the Permian-Triassic boundary, which was interpreted from biostratigraphic correlations (*Smith and Ward*, 2001). A paucity of fossils, however, limits biostratigraphic controls within the Permian-to-Triassic Eccra and Beaufort Groups (*Smith*, 1995). To circumvent limited biostratigraphic age controls with large uncertainties for the depositional age of the Karoo strata, recent studies have attempted to constrain the absolute age of the vertebrate fossil-defined Permian-Triassic boundary within the Karoo Supergroup strata using U-Pb geochronology on zircon from interbedded volcanic tuffs (*Coney et al.*, 2007; *Fildani et al.*, 2007; 2009), similar to the approach

used to define the age of the GSSP Permian-Triassic boundary from tuffs within fossiliferous marine strata in southern China (252.28 ± 0.08 Ma; *Shen et al.*, 2011). Fourteen volcanic-ash zircon U-Pb ages from the Beaufort Group in the central and southwestern Karoo Basin have yielded wholly Permian maximum depositional ages ranging from 266-252 Ma (*Coney et al.*, 2007; *Rubidge et al.*, 2013; *Lanci et al.*, 2013). Zircon from 16 tuff samples from the underlying Eccca Group exposed in the southwestern Karoo Basin contain 12 Triassic and 193 Permian grains and yield maximum depositional ages ranging from 275-250 Ma (*Fildani et al.*, 2007; 2009). The presence of latest Permian zircon is also documented in detrital zircon ages from sandstones in the Eccca Group from the southwestern Karoo Basin (*Vorster*, 2013). Thus, in spite of the geographically and stratigraphically restricted nature of existing tuff zircon U-Pb ages, it appears that the radiometric ages from interbedded tuffs in the Upper Eccca Group are younger than tuffs in the overlying Beaufort Group, which is not consistent with the upsection younging trend expected for ash deposits.

To address this apparent contradiction of older U-Pb zircon ages in the overlying Beaufort compared to younger ages in the underlying Eccca, we performed a regional study to sample tuffs from both the Eccca and Beaufort Groups across the southern Karoo Basin (**Fig. 1**). We present 469 new U-Pb zircon single-grain ages to determine maximum depositional ages for 22 air-fall tuffs. Our results include the first age controls for deposition of the Eccca Group in the eastern Karoo

Figure 1: **A)** Geology of Southern Gondwanan (modified after Zeigler et al., 1983, Lawver et al., 1992; Lopez-Gamundi and Rossello, 1998; Fildani et al., 2007) showing the relative locations of the Gondwanide Magmatic Province, Fold Thrust Belt, and Foreland Basin (i.e. Karoo Basin). **B)** Geologic map of the Karoo Basin, South Africa (adapted from Catuneanu et al., 2002). Sample localities shown: Tanqua, Laingsburg, Central Basin, and Ripon depocenters.

Basin along with age controls throughout the entire Eccca Group and lower Beaufort Group for 4 stratigraphic sections spaced across the southern Karoo Basin margin. These results demonstrate that tuffs from the Beaufort Group consistently yield zircon with U-Pb ages that overlap or are older than zircon from the tuffs in the underlying Eccca Group. Maximum depositional ages for the Eccca Group range from 274-249 Ma and are coeval across the southern margin of the basin. The maximum depositional ages from the overlying Beaufort Group, however range from 274-255 Ma. In each of the 4 stratigraphic sections, the youngest maximum depositional age of the Beaufort Group tuffs is consistently older than the youngest maximum depositional age of the underlying Eccca Group. This relationship could be satisfied by three interpretations: 1) Eccca Group strata that crop out along the southernmost Karoo Basin are younger than the Beaufort Group strata exposed to the north, which would require a fundamental revision of the regional stratigraphic and/or structural framework, 2) the volcanic tuffs in the Beaufort Group do not contain syneruptive zircon that reflect the true depositional age, or 3) cryptic Pb-loss has selectively affected zircon in tuffs in the uppermost Eccca Group across the 650 km-long southern margin of the basin, while not affecting zircon in lower Eccca or overlying Beaufort Groups. We consider these competing hypotheses and examine the implications to explore the Permian-Triassic evolution of Southern Gondwana.

GEOLOGIC BACKGROUND

The Eccca and Beaufort Groups of the late Carboniferous-Jurassic Karoo Supergroup accumulated as a flysch-to-molasse style succession within the Karoo Basin, a tectonically subsiding basin developed in the Gondwanan cratonic interior (*Catuneanu et al.*, 2002; *Tankard et al.*, 2009; *Holt et al.*, 2015). The northeast-southwest elongate basin is bounded by the Cape Fold Belt to the west and south (**Fig. 1**) that contains three clastic depositional areas: the Tanqua, Laingsburg, and Ripon depocenters. The Karoo Supergroup includes the basal fluvioglacial Dwyka Group (*Crowell*, 1978), the overlying Eccca Group, and Beaufort Group. Following deposition of the Dwyka Group, deep-water basinal environments shoaled upward into shallow-water, marginal marine environments during deposition of the Eccca Group. The lowermost Eccca Group is mudstone-dominated at the base (Prince Albert, Whitehill, Collingham, Vischkuil, and Tierberg formations) and is overlain by basin-floor, sandy turbidite strata (Skoorsteenbergh, Laingsburg, and Ripon formations; *Bouma and Wickens*, 1994; *Catuneanu et al.*, 2002). The upper Eccca Group consists of submarine slope channel/levee systems (Fort Brown Formation; *Hodgson et al.* 2011), shelf-edge and shelf clastics (Kookfontein and Waterford formations; *Wild et al.*, 2009; *Flint et al.*, 2011; *Jones et al.*, 2013) that record diachronous filling of the basin (*Rubidge et al.*, 2000). The Beaufort Group records the transition to terrestrial deposystems and evolution of terrestrial vertebrates and macroflora (*Groenewald and Kitching*, 1995; *Smith*, 1995; *Gastaldo et al.*, 2005).

Interbedded throughout the Eccca and Beaufort strata are numerous air-fall volcanic tuffs thought to have been produced by a late Paleozoic Gondwanan magmatic arc, the remnants of which are locally preserved as the Choiyoi and Puesto Viejo magmatic suites in South America (*Veevers et al.*, 1994a; *Lopez-Gamundi*, 2006; *Kleiman and Japas*, 2009; *Rocha-Campos et al.*, 2011; *Lopez-Gamundi et al.*, 2013). Choiyoi and Puesto Viejo magmatism dates from ~276 to ~234 Ma and is responsible for airfall ash deposits in the Paraná (*Rocha-Campos et al.*, 2011) and Cuyo basins (*Spalletti et al.*, 2008) in South America, in addition to the Karoo Basin in South Africa (**Fig. 1B**), based on paleogeography and geochemistry (*Lopez-Gamundi et al.*, 2006). The Choiyoi and Puesto Viejo magmatic suites, which are separated by a ~251-240 Ma tuff gap (*Veevers et al.*, 1994b; *Veevers*, 2004; *Spalletti et al.*, 2008; *Kleiman and Japas*, 2009), contain distinct zircon populations. The Permian Choiyoi Group contains an abundant Permian zircon population (*Domeier et al.*, 2011; *Rocha-Campos et al.*, 2011) with some mixing of mid-Permian (>260 Ma) and Late Permian (250-260 Ma) zircon in Late Permian tuffs (*Rocha-Campos et al.*, 2006). The Triassic Puesto Viejo Group is dominated by recycled Permian (>260 Ma) zircon with few co-eruptive zircon (*Spalletti et al.*, 2008; *Domeier et al.*, 2011), interpreted to be due to assimilation of Permian country rocks during Triassic magmatic ascent (*Domeier et al.*, 2011). Weighted mean U-Pb ages for the Puesto Viejo Group range from ~260 Ma to ~230 Ma (*Spalletti et al.*, 2008; *Domeier et al.*, 2011; *Ottone et al.*, 2014), even though it is generally accepted that Puesto Viejo magmatism occurred between 241-230 Ma (*Kleiman and Japas*, 2009; *Domeier et al.*, 2011).

U-PB METHODS AND ANALYSES

Twenty-two tuffs were sampled from 4 transects through formations of the Eccca and Beaufort Groups exposed along the southern Karoo Basin (**Fig. 1**; sample locations contained in **Appendix A**). Five samples were collected from the Tanqua depocenter in the western Karoo Basin and were integrated with previously published results from *Fildani et al.* (2007; 2009) and *Lanci et al.* (2013). Four new samples were collected from the southernwestern Laingsburg depocenter to augment previously published data in the Laingsburg area (*Fildani et al.*, 2007; 2009). In the eastern Ripon depocenter, ten samples were collected along a single, continuous north-dipping transect. Three samples were collected from the Eccca Group in a mudstone-dominated, condensed section in the central Karoo Basins between the Laingsburg and Ripon depocenters (~22.5°E; **Fig. 1**). Zircon grains were separated from tuff (**Fig. 2A**) samples using mineral separation techniques, including the use of a Franz magnetic separator to remove high U zircon that may yield discordant results (*Sircombe and Stern*, 2002). Samples yielded between 0 and >200 zircon. Size, morphology, and inclusion density were not considered when selecting zircon for analysis in an effort to characterize the entire zircon population of an ash and not bias results towards prismatic, acicular, euhedral zircon populations. Catholuminescence images (**Fig. 2B**) were used to target

Figure 2: A) Volcanic tuff (hammer for scale) interbedded in mudstones and sandstones in the Karoo Supergroup. B) Catholuminescence image of zircon grain from a tuff in the Eccia Group showing zircon rim and core growths. C) Kernel density estimate of sample 12ZA07. Peaks between 230-300 Ma are identified with an asterisk.

intermediate U (100-1000 ppm), oscillatory zoned grain rims and avoid complex cores, when present. Sensitive High Resolution Ion MicroProbe-Reverse Geometry (SHRIMP-RG) analyses of zircon grains were conducted at the Stanford Microscopic Analytical Center under analytical conditions similar to those of *Barth and Wooden (2006)*. SHRIMP-RG results were calculated with reference to the R33 zircon standard (*Black et al., 2004*) and results were reduced using the SQUID2 software (*Ludwig, 2009*).

Ages reported are from common-Pb corrected $^{206}\text{Pb}/^{238}\text{U}$ ratios. Of the 469 total single-grain analyses, 353 were accepted on the basis of low common-Pb concentrations, low uncertainty (<3%) and concordance. Grains were determined to be concordant if $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ages overlapped within uncertainty. Anomalously old zircon (>300 Ma) are interpreted as inherited, xenocrystic or detrital grains, while anomalously young, high-U or high common-Pb (<<~250 Ma) are dismissed as having been affected by Pb-loss or common-Pb contamination. Kernel density estimate (KDE) plots (**Fig. 2C**) were used to interpret recycled, inherited zircon from likely autocrystic/co-eruptive zircon populations. Zircon age populations were identified to

determine tuff maximum depositional ages, which if zircon are syneruptive autocrysts, should equal the eruption age of the tuff. Population ages were then calculated from the weighted average of a coherent zircon population ($n \geq 3$) using Isoplot 3.75 (Ludwig, 2008). Although calculating maximum depositional ages from coherent age populations commonly produces higher uncertainty compared with using the youngest single-grain age from a sample, it is viewed as a more robust age given the greater reproducibility. A table of analytical results is provided in [Appendix B](#). Maximum depositional age interpretations are reported in their sampled stratigraphic locations with numerical age interpretations ([Fig. 3](#)) and schematically with associated errors ([Fig. 4](#)) to demonstrate stratigraphic trends in tuff ages.

U-PB RESULTS AND INTERPRETATION

Analysis of 22 ash samples from the marine Ecça and terrestrial Beaufort groups of the lower Karoo Supergroup yielded 116 pre-Permian, 223 Permian, and 14 Triassic concordant zircon ages of 469 total analyses. In many samples, zircon produced a dispersed range of ages (> 20 Ma). While this age range could be due to mixing of different age domains within individual zircon grains during analysis, analytical uncertainty, or Pb-loss (Castiñeiras *et al.*, 2010), magma system evolution is complex and commonly recycles older zircon into later eruption/emplacement events and some individual plutons have been resolved to be emplaced over a period of >10 Ma (Coleman *et al.*, 2004; Miller *et al.*, 2007; Schwartz *et al.*, *in press*). The suspected volcanic sources, the Choiyoi and Puesto Viejo igneous suites, are known to have large populations of recycled zircon (Spalletti *et al.*, 2008; Domeier *et al.*, 2011; Ottone *et al.*, 2014). We therefore interpret this range to represent mixing of zircon age population based on A) high mean square weighted deviation (MSWD) (1.6-17) of the weighted mean for Permian/Permo-Triassic zircon populations (Miller *et al.*, 2007; Compston & Gallagher, 2012), B) lack of inherited cores interpreted from cathodoluminescence images, C) the reproducibility of ages between several grains ($n \geq 3$), D) concordance of the analyses, and E) known history of the volcanic system. In order to avoid introducing bias towards inherited/recycled zircon age populations, maximum depositional ages are calculated from the weighted mean of the youngest, concordant zircon population (P_1) of three or more analyses as identified by kernel density plots, to minimize the risk of producing an age affected by Pb-loss (Dickinson and Gehrels, 2008). Inherited zircon population ages (P_2) were interpreted using the same approach on older, concordant zircon populations. This approach decreases the total number of analyses, which could negatively affect the uncertainty in the weighted mean age. The result, however, more likely represents the eruption age of the ash and in most cases produces higher precision ages and a lower MSWD. This approach differs from the method used by Lanci *et al.* (2013) where interpreted ash ages were calculated from all zircons between 300 Ma and 250 Ma and included all ages within a dispersed range of up to 20 m.y. Results from previous geochronology studies on tuffs within

Figure 3: Chronostratigraphic correlation between the Karoo Supergroup and South American Volcaniclastic strata (Puesto Viejo volcanics or equivalents). Karoo Supergroup ages are from Coney et al. (2007), Fildani et al. (2007; 2009), Weislogel et al. (2011), Rubidge et al. (2013), Lanci et al. (2013), and this study. S. American volcanic ages are from Domeier et al. (2011); Spalletti et al. (2008); Rocha-Campos et al. (2011); and Ottone et al. (2014). Maximum depositional ages from this study are reported with the associated 95% confidence uncertainties at the sampled stratigraphic interval. The interval where tuffs were not present is identified by a striped pattern where observed in the Tanqua, Laingsburg, and Ripon depocenters. Sample locations are reported in [Appendix A](#). The individual analyses can be found in the [Appendix B](#). Karoo and S. American Volcanics both show trends upsection where Latest Permian volcanics yield ages that are younger than the overlying volcanic deposits.

the Karoo Supergroup (Coney *et al.*, 2007; Fildani *et al.*, 2007; 2009; Lanci *et al.*, 2013, Rubidge *et al.*, 2013), tuffs within correlative basins (Spalletti *et al.*, 2008; Domeier *et al.*, 2011; Rocha-Campos *et al.*, 2006; 2013; Lopez-Gamundi *et al.* 2011;) and Permo-Triassic crustal plutonic rocks (Pankhurst *et al.*, 2014) in South America contained populations of inherited grains. Based on this known inheritance, indiscriminately including these older zircons in weighted age calculations is not a favorable approach to obtain reasonable maximum depositional ages for the Karoo tuffs. Therefore, our ages are presented as weighted averages of the youngest zircon population to avoid introducing statistical bias towards dominant inherited populations when determining tuff ages. These results are shown in stratigraphic order, with uncertainties reported at a 95% confidence level (Fig. 3). Also provided are previously reported ages for the Karoo strata and reported ages of comparable South American volcanic suites.

Tanqua Depocenter

Ecce Group. Three tuffs were sampled from the Ecce Group to augment the existing 5 tuff ages from Fildani *et al.* (2007; 2009) (Location on Fig 1B). Results from samples collected from the Tanqua depocenter are described in ascending stratigraphic order. While tuffs are common throughout the section and the samples presented here represent only a small fraction of the tuffs in the Karoo strata, no volcanic deposits were found in the interval between sample 12ZA07 in the Ecce Group and 12ZA16 in the Beaufort Group.

Sample 12ZA10. The lowermost sample in the Tanqua depocenter is 12ZA10, which was collected from a ~3 cm thick, green, clay-textured tuff interbedded with mudstones in lower Skoorsteenberg Formation of the Ecce Group. Of 13 total analyses, 4 were rejected based on high discordance. Nine individual zircon analyses yielded concordant U-Pb ages that range from 275-255 Ma. The youngest population consists of 4 grains that range from 264-255 Ma and yield a weighted average of 262.8 ± 3.8 Ma (MSWD=0.49); the older population consists of 5 grains that range from 275-268 Ma and that yield a weighted average of 271.6 ± 3.0 (MSWD=0.40).

Sample 12ZA08. Sample 12ZA08 was collected ~175 meters upsection from 12ZA10, from a ~1 cm thick, light green, clay-textured tuff interbedded in mudstones in the middle Skoorsteenberg Formation of the Ecce Group. Of 16 total analyses, 10 analyses yielded concordant ages. Carboniferous ages (309, 311 Ma) were produced from two discordant analyses, while the youngest ages are concordant and Permian-Triassic in age (270-252 Ma). The youngest population consists of 5 grains that range from 265-253 Ma and yield a weighted averages of 256.5 ± 5.8 Ma (MSWD=1.3). An older population of 5 grains ranges from 270-267 Ma and produces a weighted average of 267.8 ± 2.6 (MSWD=0.22).

Sample 12ZA07. Sample 12ZA07 is from a 5 cm thick, tan-to-green/grey tuff interbedded in mudstones near the base of the Kookfontein Formation of the Eccia Group, which conformably overlies the Skoorsteenberg Formation. Sample 12ZA07 is approximately 225 meters stratigraphically above sample 12ZA08. Of the 18 zircon analyzed, 5 were rejected due to discordance. From the 13 concordant ages, 2 anomalously old ages (539 and 294 Ma) are dismissed as inherited outliers, while 11 Permo-Triassic grains range from 273-237 Ma. The youngest 5 grains form a coherent population ranges from 254-237 Ma that produces a weighted average of 250.3 ± 4.8 Ma (MSWD=1.0). An older population of 6 grains ranges from 273-259 Ma and yields a weighted average of 267.8 ± 5.9 (MSWD=2.9).

Beaufort Group. Two tuffs were sampled from the Adelaide Subgroup of the Beaufort Group to augment 4 tuff ages from *Lanci et al.* (2013).

Sample 12ZA16. Sample 12ZA16 is from a 5-10 cm thick, white, chalky tuff interbedded within mudstones in the lower Abrahamskraal Formation (Adelaide Subgroup) of the Beaufort Group. Of the 16 total analyses, 11 yielded concordant ages ranging from 291-256 Ma. One analysis yielded an age of 291 Ma and is considered to be an outlier, since it is 17 m.y. older than the next youngest age. The youngest coherent population of zircon yields a weighted average of 264.7 ± 2.5 Ma (MSWD=0.86) from 7 grains, with an older >270 Ma population of 3 grains that yields a weighted average of 271.8 ± 2.4 Ma (MSWD=0.25).

Sample 12ZA18. Sample 12ZA18 is from a 45 cm thick, white-to-green tuff in the upper Abrahamskraal Formation (Adelaide Subgroup) of the Beaufort Group, approximately ~50 meters above 12ZA16. From 37 total analyses, 28 concordant ages were produced. Inherited, pre-Permian grains dominate the sample, with 17 concordant analyses ranging from 2607-359 Ma. Permian age grains range from 290-238 Ma. The two oldest Permian grains (286, 290 Ma) are dismissed as inherited outliers. The youngest populations of 4 grains ranges from 267-255, which yields a weighted average of 260.6 ± 8.9 (MSWD=7.4). An older population of 5 grains ranges from 278-272 Ma and produces a weighted average of 274.5 ± 3.9 (MSWD=1.4). Two older, Permian grains (286, 290 Ma) may represent a minor population, but are considered as significantly older, inherited outliers. Two Triassic ages (238, 239 Ma) form a small population, but both analyses have elevated common Pb values.

Laingsburg Depocenter; Southwest Basin

Because the Eccia Group tuffs were well characterized by *Fildani et al.* (2007; 2009), we sampled tuffs in the Adelaide Subgroup of the Beaufort Group from the Laingsburg subbasin (Fig 1B) and report 4 new tuff ages. Like the Tanqua section, tuffs are common throughout the strata,

however, no tuffs were identified between the samples presented by *Fildani et al.* (2007; 2009) and 12ZA05.

Sample 12ZA05. Sample 12ZA05 was collected from a ~30 cm thick, well-lithified, light-brown tuff within the upper Fort Brown Formation of the Ecca Group in the Laingsburg subbasin. Out of 18 total analyses, 14 grains produced concordant ages. Older, >300 Ma grains dominate this sample, since 13 of 14 concordant ages ranged from between 2139-304 Ma. Only 1 analysis yielded a concordant Permian age of 274.3 ± 4.6 Ma.

Sample BLOU. Sample BLOU was collected from a well-lithified tuff interbedded in the Abrahamskraal Formation (Adelaide Subgroup) of the Beaufort Group. Of 26 total analyses, 22 grains produced concordant U-Pb ages. The tuff was dominated by older, >300 Ma grains, with 14 grains between ~3.2 Ga and 372 Ma. Of 8 Permian grains ranging from 289-272 Ma, 6 grains were

Figure 4: Maximum deposition ages, based on U-Pb zircon, from **Figure 3**, shown schematically, with associated error. In all four studied sections, maximum depositional ages young upsection in the Lower and Middle Ecca. Proceeding upsection, an interval is encountered with few to no tuffs. Above this tuff-free interval, U-Pb zircon based maximum depositional ages are chaotic and older than in the underlying strata.

interpreted to form a coherent population ranging between 279-272 Ma that produced a weighted mean of 276.4 ± 2.3 (MSWD=0.69).

Sample SUTH. Sample SUTH was collected from a well-lithified tuff interbedded in the Abrahamskraal Formation (Adelaide Subgroup) of the Beaufort Group. Of 32 total analyses, 22 grains produced concordant ages. An older group of 8 concordant ages ranged between 1750-468 Ma, while 14 concordant Carboniferous-Permian ages ranged from 301-260 Ma. Two populations are interpreted from Permian ages. The youngest coherent population of 6 ages that range from 267-260 Ma and yields a weighted mean of 264.9 ± 1.9 Ma (MSWD=1.17); an older, coherent population of 4 grains range from 276-270 Ma and yields a weighted mean age of 271.7 ± 2.3 Ma (MSWD=1.17).

Sample 13ZA93. Sample 13ZA93 was collected from a ~25 cm thick tuff interbedded between mudstones in the upper Abrahamskraal Formation (Adelaide Subgroup) of the Beaufort Group. Only 8 zircon grains were separated and U-Pb analysis reveals that the zircon grains are largely recycling, since 6 of 8 are >300 Ma. No coherent zircon population was interpreted from the two Permian grains (269, 280 Ma) present and the youngest grain, 269 Ma is reported on [Fig. 4](#).

Prince Albert Transect; South-central basin

Three samples were collected from the lower Eccu Group in the central basin ([Fig 1B](#)), near Prince Albert, Western Cape. This location is located between the Laingsburg and Ripon subbasins. The strata here represent a condensed section, and no tuff gap is reported for this composite section, however this region has not been fully logged or studied in detail. These data augment work by *Rubidge et al.* (2013), who reported ID-TIMS zircon U-Pb ages from tuffs within the Adelaide and Tarkastad Subgroups of the Beaufort Group ~100 kilometers to the north.

Sample 12ZA19. Sample 12ZA19 was collected from a light-green ash approximately 8 m above the base of the Prince Albert Formation of the Eccu Group. Of 19 zircon that were analyzed, 11 concordant ages were produced. Concordant, inherited zircon ages were 526, 542, 642 Ma, while 8 Permian, concordant zircon ages range from 281-272 Ma. Two populations of zircon are interpreted from concordant ages with the youngest population of 6 grains that range from 277-272 Ma and yield a weighted average of 273.7 ± 2.7 Ma (MSWD=0.37), with 2 older ~280 Ma grains (280, 281 Ma) treated as outliers.

Sample 12ZA22. Sample 12ZA22 was collected from a brown, fissile ash near the base of the Ripon Formation of the Eccu Group. This ash yielded zircon that produced 13 concordant ages from 18 total analyses. Concordant, inherited zircon ages ranged from 432-1018 Ma (n=7), while 6 Permian-Triassic, concordant zircon ages range from 266-248 Ma. Two population of zircon are

interpreted from concordant ages; the youngest population of 4 grains ranges from 259-248 Ma and yields a weighted average of 255.1 ± 4.5 (MSWD=0.76) Ma. An older ~265 Ma population is represented by 2 grains (266, 264 Ma) that are treated as outliers.

Sample 12ZA23. Sample 12ZA23 was collected from a soft, green, clay-rich ash in the Ripon Formation of the Eccca Group. Of 34 grains analyzed, 30 analyses yielded concordant, Permian-Triassic ages that range from 249-283 Ma. A single, concordant 470 Ma age was also produced. Based on a histogram of concordant Permo-Triassic ages, age spectra peaks occur at ~282 Ma, ~271 Ma, ~266 Ma, 258 Ma, and 250 Ma. A population of 7 zircon have concordant age ranges from 249-257 Ma and yields a weighted average of 251.1 ± 2.5 Ma (MSWD=1.07). Grouping of the 20 older, Permian analyses results in a weighted average of 267.3 ± 1.3 (MSWD=0.91).

Ripon Depocenter; Eastern Basin

Nine samples were collected from the Ripon Depocenter in the eastern Karoo Basin; 4 from the Eccca Group and 5 from the Adelaide Subgroup of the Beaufort Group. All 9 samples are from a single continuous, north-dipping section exposed in road-side outcrops and represent the first geochronology in the eastern basin ([Fig 1B](#)). No volcanic deposits were found in the interval between sample 12ZA61 in the upper Eccca Group and 12ZA46 in the lower Beaufort Group. The rest of the strata contained numerous tuff beds interbedded throughout the strata.

Sample 12ZA54. Sample 12ZA54 was collected from a brown, clay-rich ash about 1.5 meter below the top of the Collingham Formation of the Eccca Group. Of 16 total zircon analyses, 10 grains yielded concordant ages. The oldest ages (458, 456, 431 Ma) were produced from concordant analyses, while the youngest, concordant, Permian-Triassic ages range from 277-257 Ma). A coherent population of 5 zircon ranges from 269-257 Ma and produces a weighted average of 263.1 ± 6.4 Ma (MSWD=1.4). Two inherited Permian grains of 271 and 277 Ma are treated as outliers.

Sample 12ZA55. Sample 12ZA55 was collected from a green, clay-rich ash approximately 6 m above the base of the Collingham Formation. From 18 total zircon analyses, 9 grains produced concordant ages. A single inherited zircon produced a concordant age of 341 Ma, while 8 grains produced concordant, Permian ages that range from 291-259 Ma. One population of zircon is interpreted from 6 concordant ages that range from 269-259 Ma and yield a weighted average of 268.0 ± 3.2 Ma (MSWD=1.4).

Sample 12ZA60. Sample 12ZA60 was collected from a clay-rich, white-to-tan ash within the Ripon Formation of the Eccca Group. Of 16 total zircon analyses, 14 concordant ages were produced. The oldest ages (450, 351 Ma) were produced from concordant analyses, while the

younger, concordant, Permian ages ($n=12$) range in age from 295-257 Ma. Two populations of zircon are interpreted from concordant ages; the youngest population of 5 grains ranges from 264-257 Ma and yields a weighted average of 262.5 ± 3.0 Ma (MSWD=0.21), while an older population of 6 grains yields a weighted average age of 268.7 ± 1.8 (MSWD=0.92).

Sample 12ZA61. Sample 12ZA61 was collected within a clay-rich ash within the Lower Fort Brown Formation of the Eccu Group. Of 25 total analyses, 21 zircon grains produced concordant ages. Older, inherited ages (516, 520, 1108 Ma) were produced from concordant analyses, while younger, Permian-Triassic, concordant ages range in age from 274-232 Ma. A significant late Permian to middle Triassic population was resolved in this sample, however three of the analyses have high uncertainties, making them less reliable than high-precision analyses, but still meaningful. Two populations of zircon are interpreted from concordant ages; the youngest population of 8 grains ranges from 257-232 Ma and yields a weighted averages of 251.6 ± 3.9 Ma (MSWD=2.8), while an older population of 10 grains ranges from 274-257 produced a weighted average of 264.7 ± 3.2 (MSWD=1.9).

Sample 12ZA46. Sample 12ZA46 was collected from an ash within the Koonap Formation (Adelaide Subgroup) of the Beaufort Group. Only 11 zircon grains were recovered from this sample. All 11 grains were analyzed, however only 9 produced concordant ages. Older, inherited ages (325, 464, 478, 523 Ma) were produced from concordant analyses, while younger, Permian concordant ages range from 285-253 Ma, excluding a concordant 229 Ma analysis with high common-Pb. One population of zircon is interpreted from concordant ages that range from 260-253 Ma and yields a weighted average of 257.3 ± 4.3 Ma ($n=4$), with a single 285 Ma grain treated as a statistical outlier.

Sample 13ZA75A. Sample 13ZA75 was collected from a brown, gritty ash within the Koonap Formation (Adelaide Subgroup) of the Beaufort Group. Of 15 total analyses, only 8 grains yielded concordant ages. Older, inherited ages (431, 469, 505, 584, 1112 Ma) were produced from concordant analyses, while 3 younger, concordant Permian ages are scattered at 265, 270, 278 Ma. No distinct zircon population is interpreted from this sample, and a weighted mean age of the 3 Permian zircon is 270 ± 15 Ma.

Sample 13ZA76. Sample 13ZA76 was collected from a white, chalky ash within the upper Koonap Formation. Of 40 total analyses, 31 grains produced concordant ages. Inherited, pre-Permian grains range from 1721-326 Ma ($n=6$). Two populations are interpreted from Permian ages, with the youngest population of 8 grains producing an age of 260.4 ± 2.8 (MSWD=1.9), while a 267.6 ± 1.5 (MSWD=0.84) is interpreted as an inherited population.

Sample 12ZA45. Sample 12ZA45 was collected from an ash interbedded in a mudstone-rich interval of the uppermost Koonap Formation of the Beaufort Group. Only 9 zircon grains were recovered from this sample. All 9 grains were analysed; 6 grains produced concordant ages. Additional analysis was hampered due to a low abundance of zircon in this sample. Older, inherited concordant ages (445, 454, 455, 457 Ma, 522, 1098) dominate the zircon population, with the only younger age (271 Ma) excluded due to high discordance. The 4 Ordovician zircon form a tight cluster, and yield a 452.5 ± 9.5 Ma (MSWD=2.7) weighted average age.

Sample 13ZA72A. Sample 13ZA72 was collected from a white, chalky-textured ash within the Middleton Formation (Adelaide Subgroup) of the Beaufort Group. Of 32 total analyses, 28 grains produced concordant ages. Concordant, pre-Permian ages ($n=11$) range from 1102-334 Ma, and concordant Permian zircon range between 282-252 Ma ($n=17$). Two coherent populations are interpreted; the youngest population of 4 grains ranges from 258-252 Ma produces a weighted mean age of 255.3 ± 4.0 (MSWD=1.3), and the older, inherited population of 5 grains yields an age of 267.8 ± 3.6 Ma (MSWD=1.4).

DISCUSSION

TUFF DISTRIBUTION AND COMPOSITION-*GONDWANAN TUFF GAP*

The abundant tuffs interbedded throughout the Karoo Supergroup strata provide the opportunity to assess U-Pb zircon ash ages from numerous stratigraphic horizons over a ~2-3 km thick section and offer insight into the Karoo Basin evolution. Based on field observations, the three major depocenters, Tanqua, Laingsburg, and Ripon all contain a stratigraphic interval where tuffs are not present. We note that the textural character of airfall tuffs is, in general, different above and below this observed gap in tuff deposition. Below the gap, tuffs are green, clay-rich, and typically <10 cm. In contrast, above the gap, tuffs are distinctly either A) white and chalky, or B) light brown and gritty/sandy with thicknesses varying between 5 cm up to 40 cm. We speculate here that this “tuff gap” is similar to the “tuff gaps” reported throughout southern Gondwana (New Zealand, Australia, and Antarctica), where volcanic tuffs are rare-to-absent within otherwise ash-rich strata (Veevers *et al.*, 1994b). It remains unclear if those “tuff gaps” are related to a hiatus in volcanic activity or dilution and lack of preservation in a terrestrial depositional environment (Veevers, 2004; Retallack and Krall, 1999); these gaps, however, are thought to be synchronous across Gondwana (Veevers, 2004). We propose herein an unidentified “tuff gap” in the Karoo strata that is present in a variety of depositional environments, recorded in deep-to-marginal marine (Ecca Group) and terrestrial (Beaufort Group) sediments across the basin (Fig. 3, 4). Although the cause of the tuff gap is still poorly understood and the mechanism responsible for the evolution from clay-rich to chalky and gritty/sandy tuffs is unknown, these observations provide a distinct

framework with three distinct ash regimes: green, clay-rich tuffs, ash absent altogether (i.e. tuff gap), and chalky/gritty tuffs.

The appearance and character of the Karoo tuffs might be due to either a 1) change in weathering conditions, 2) dilution of tuffs with clastic detritus, or 3) evolution of the volcanic ejecta from glass-dominated tuffs preserved as clay-rich tuffs, to lithic deposits, manifest as chalky or gritty/sandy tuffs. Since tuffs occur above this tuff gap, in both marginal marine and terrestrial strata deposited in both high and low energy environments, it is unlikely the ash regimes are due to clastic dilution. Additionally, the tuff gap is typically present in deep to marginal marine low-energy depositional environments, where dilution would be unlikely. Tuffs above the gap also generally contain smaller zircon populations (<100 zircon/kg) than tuffs below (>>100 zircon/kg). During mineral separation, the heavy mineral composition of chalky and gritty tuffs were found to commonly contain dark, lithic grains, while clay-rich tuffs yielded few to no lithic grains and were dominated by mineral grains in the heavy mineral separates. This suggests that tuffs below the tuff gap may have been crystal-rich vitric tuffs, while the overlying volcanics are likely zircon-sparse, lithic tuffs.

MAXIMUM DEPOSITIONAL AGES FROM U-PB ZIRCON ANALYSES

Based on these new U-Pb zircon SHRIMP results, integrated with previously published data (Coney *et al.*, 2007; Fildani *et al.*, 2007; 2009; Rubidge *et al.*, 2013; Lanci *et al.*, 2013),

Figure 5: Youngest Grain Age (Ma) vs. Weighted Mean Age (Ma) plot (Left) shows a younging upsection of U-Pb zircon tuff ages in the Eccca Group. In the Beaufort Group (Right), no trend is observed. Two samples (13ZA72A-Middleton Fm, 13ZA76-Upper Koonap Fm) in the Middle Beaufort produce ages that are within error one of the lowest stratigraphic samples (12ZA46-an ash located directly above the “tuff gap” in the Lower Koonap Fm). No younging-upward trend, however is observed in the Beaufort Group tuffs.

(Fig. 3, 4) strata of the Eccra Group below the regional tuff gap appear coeval across the southern margin of the basin based on ash ages, with the base of the Eccra Group ~275 Ma, and consistent younging-upward stratigraphically across the basin (Fig. 5A) to the base of the ash gap at ~250 Ma, above which volcanic tuffs become rare to absent for ~300-600 m. Tuffs in the Beaufort Group above this interval consistently yield ages older than the underlying strata and do not display a younging-upward trend (Fig. 5B). *Fildani et al.*, (2007; 2009) and *Lanci et al.* (2011) presented tuff ages based on extensive SHRIMP datasets (N=16, n=205 and N=4, n=111, respectively) to address the absolute age of the strata. *Fildani et al.* (2007; 2009) only presented ages from the Eccra Group, while *Lanci et al.* (2011) only presented data from the overlying Beaufort Group. When compared to limited data that were available at the time (*Coney et al.*, 2007), *Fildani et al.* (2009) observed a discrepancy in the ages of the Eccra and Beaufort Groups and used those ages to present a model for time transgressive filling across the basin. *Lanci et al.* (2013) suggested that the robust single crystal age data presented by *Fildani et al.* (2007; 2009) were erroneously young due to Pb-loss. The ages presented in this study are based on zircon age populations ($n \geq 3$) to estimate ash ages, greatly minimizing the chances of the age being affected by Pb-loss (*Saylor et al.*, 2012), but corroborate, support, and reproduced the ages estimates produced by *Fildani et al.* (2007; 2009), *Coney et al.* (2007), *Weislogel et al.* (2011), *Rubidge et al.* (2013), *Lanci et al.* (2013). Therefore, it is not likely that the zircon ages presented in this study have been affected by Pb-loss because A) only concordant analyses were considered, B) ash ages are based on concordant age populations and weighted averages, C) individual results are repeatable (*Fildani et al.*, 2007; 2009; *Rubidge et al.*, 2013; *Lanci et al.*, 2013) and D) the observed age inversion is present in both this study and previous studies (*Fildani et al.*, 2007; 2009; *Coney et al.*, 2007; *Weislogel et al.*, 2011; *Rubidge et al.*, 2013; *Lanci et al.*, 2013) using a variety of analytical techniques (SHRIMP, TIMS, LA-ICPMS) and consistently occurs across the basin directly above the proposed tuff gap. No relationship between U concentration and age was observed, further suggesting that Pb-loss from U-decay, lattice damage and diffusion has not affected concordant zircon ages (*Kryza et al.*, 2012). If Pb-loss is believed to be the cause of the observed contradictory ages, then Pb-loss must be more significant and pervasive in the Eccra Group than in the Beaufort Group, which would require a stratigraphically selective Pb-loss mechanism that disturbed the isotopic systems of some tuffs, while leaving others in the overlying strata effectively unaltered. Therefore, we interpret the weighted mean U-Pb zircon ages to represent a maximum depositional age of the airfall ash and will explore the implications of these new age controls across the >600km long southern margin of the Karoo Basin.

The abrupt appearance of older ages is restricted to the strata above the observed tuff gap. Possible mechanisms that could cause these older, seemingly anomalous tuff ages include:

1) structural juxtaposition of older strata (fluvial) over younger (marine); 2) time-transgressive facies tracts producing synchronous marine and terrestrial deposition; 3) detrital reworking and contamination in high-energy, terrestrial environments; and 4) lack of co-eruptive zircon in early-to-mid Triassic tuffs.

No field evidence by any workers in the Karoo Basin has been observed or reported to identify tectonic structures that could render older-over-younger strata over 1000's of square kilometers to cause inversion of zircon ages in the tuffs. Tanqua depocenter strata are flat-lying and undeformed and Beaufort and Eccca Group strata in the Laingsburg and Ripon depocenter are deformed by broad, upright folds; any repetition of mapped strata is locally isolated.

Alternately, time-transgressive facies deposition could create the observed age inversion. Previous models for basin infilling based on paleoflow and provenance analysis concluded that sediment was transported into the basin mainly from the south; this model would predict stratigraphic younging of ash beds northward (*Veevers et al.*, 1994a; *Rubidge et al.*, 2000; *Flint et al.*, 2011). However, this scenario appears to conflict with the observed older zircon ages in Beaufort Group tuffs that lie to the north of the younger Eccca Group ash samples. *Fildani et al.* (2009) suggested diachronous filling of the basin from east to west, with terrestrial deposition in the east being coeval with deep marine conditions in the west. The new results from the Ripon depocenter, indicate contemporaneous marine deposition over >600 km across the southern margin of the Karoo Basin and do not support this scenario unless we hypothesize a highly segmented basin. Recent studies of the Beaufort Group (*Lanci et al.*, 2013; *Wilson et al.*, 2014) report consistent paleocurrents to the NE, supporting sediment dispersal pattern for the whole deep water to fluvial section. For diachronous filling to produce the observed age inversion, marine conditions in the southern basin would need to be coeval with or postdate fluvial deposition to the north. While no evidence in the stratigraphic record has been directly identified to support either of these scenarios, more age constraints from across the basin are required to better understand basin-wide sedimentation patterns.

Here, we consider the possibility that some tuffs within the Karoo Supergroup do not contain coherent populations of terminal-phase, co-eruptive zircon. In this scenario, a terminal-phase zircon population may be present, but is diluted by older zircon due to (1) sedimentary reworking of older ash or clastic material within younger ash deposits, (2) inclusion of older xenocrystic or co-magmatic zircon residing within the magmatic system or (3) incorporation of older lithic volcanic material from the volcanic carapace during eruption. One Beaufort Group ash sample (12ZA46) showed signs of detrital contamination, with 5 of 10 zircon grains being significantly older (>280 Ma) than the youngest coherent population (257.3 ± 4.3 Ma; $n=4$). Air-

Figure 6: Correlation of KDE plots from the Puesto Viejo (A, B, C; *Spalletti et al.*, 2008; *Domeier et al.*, 2011) and Choiyoi (D, E, F) volcanic suites to comparable KDE signatures in interbedded tuffs of the Karoo Supergroup. Beaufort Group (G, H, I) samples show similar KDE signatures to the Puesto Viejo volcanics, while the underlying Ecça Group samples (J, K, L) matches the stratigraphic trend observed in the Choiyoi Group. The uppermost Choiyoi samples contain peaks at 253 and 263 Ma, compared to 253 and 264 Ma in the Ecça Group directly below the base of the tuff gap.

fall tuffs deposited in fluvial depositional environments, such as the Beaufort Group depositional system, are particularly prone to reworking and detrital mixing by overland flows, pedogenesis and bioturbation. While it is difficult to assess the role of clastic dilution and terrestrial reworking without resolving the detrital zircon populations of adjacent siliciclastic units, tuffs within the Beaufort Group retain an ash lithology and show no physical signs of detrital reworking. If tuffs were significantly contaminated with detrital zircon, that would require significant reworking with a large volume of clastic material such that the ash lithology would not be retained.

In addition, with 9 ash ages for the Beaufort Group from this study and 4 tuffs from *Lanci et al.* (2013), 113 grains yield a Permian age, yet only 4 moderately concordant Triassic grains have been recovered (12ZA18 shown in Fig.6G), compared to 253 concordant Permian grains and 26 concordant Triassic grains in the 13 ages tuffs within the Eccca Group from this study and 8 tuffs from *Fildani et al.* (2007; 2009). Of the 26 concordant Triassic ages in the Eccca Group, 18 were obtained from tuffs just below the presumed tuff gap (12ZA07, CVX12, 12ZA23, 12ZA61). These four samples all yield ~250-251 Ma weighted mean ages, which coincides with the basal age of the tuff gap (~251 Ma) elsewhere in Gondwana (*Veevers et al.*, 1994b). Since the base of the tuff gap is approximately the boundary between the Permian and Triassic, ages just below this interval would be expected to straddle the boundary, with a range of ~249-254 Ma ages, which is observed in Eccca tuffs and is compatible with our age interpretation. Furthermore, the absence of a large, Triassic zircon population in Beaufort tuffs suggests limited availability of co-eruptive, autocrystic zircons in the Beaufort Group. Magmatic recycling is also compatible with the observation of shared recycled populations within the weighted averages of ash zircon populations, where 7 tuffs in this study contained a ~267-268 Ma tuff population (P_1 of 12ZA16, 12ZA55, SUTH, and P_2 of 12ZA23, 12ZA60, 13ZA72, 13ZA76) and 7 tuffs contained a ~261-264 Ma tuff population (P_1 of 12ZA10, 12ZA18, 12ZA54, 12ZA60, 13ZA67, 13ZA76, and P_2 of 12ZA61). These inherited populations likely represent zircon crystallization events in the magmatic source of the tuffs and may be present in any subsequently erupted ash. A similar observation has been made in proximal volcanic deposits in the Southern Pyrenees, where distinct zircon crystallization events are represented in subsequent eruption events (*Pereira et al.*, 2014). Recycling is further suggested by the dominance of 25 concordant Ordovician xenocrysts in Karoo tuffs from this study alone, which is most evident sample 12ZA45, where the only coherent age population (n=4 of 6 concordant analyses) consisted of ~453 Ma grains.

Recycling of antecrystic and xenocrystic zircon in Late Permian-Triassic volcanics is recognized in correlative volcanics in South American (*Spalletti et al.*, 2008; *Domeier et al.*, 2011). Two, successive magmatic suites in South America, the Permian Choiyoi Group and Triassic Puesto Viejo Group record the same volcanism responsible for tuffs in the Karoo Supergroup. The

Permian Choiyoi Group yields well defined U-Pb zircon age peaks between 280 to 253 Ma (Fig. 6D, E, F) with signs of zircon recycling restricted to the uppermost Upper Choiyoi Group. A tuff from the Upper Choiyoi was found to be dominated by ~276 Ma zircon (SM-1; *Rocha-Campos et al.*, 2006) and also contain a distinct subpopulation of ~253 Ma zircon (n=4; *Rocha-Campos et al.*, 2006). This ~253 Ma age reflects the age of the last phases of Choiyoi volcanism (*Kleiman and Japas*, 2009). Zircon recycling intensifies within the Triassic Puesto Viejo Group, which contain more complex zircon populations (Fig. 6A, B, C). Published U-Pb zircon from the lowest Puesto Viejo Group (PV06 of *Domeier et al.*, 2011; PRT0 of *Spalletti et al.*, 2008 from the Potrerillos Fm, a coeval, stratigraphic equivalent of the Puesto Viejo Group [*Ottone et al.*, 2014]) show that samples contain dominant ~260-280 Ma populations with few to no Triassic grains. $^{40}\text{Ar}/^{39}\text{Ar}$ feldspar ages for the same intervals range between 239 to 235 Ma, suggesting a >20 m.y. discrepancy between U-Pb zircon and $^{40}\text{Ar}/^{39}\text{Ar}$ feldspar geochronology systems. Samples from the mid-to-upper Puesto Viejo Group contained significantly more Triassic grains (PRT1, PRT2 of *Spalletti et al.*, 2008; *Ottone et al.*, 2014), yielding weighted mean ages of 239-230 which are within error of correlative $^{40}\text{Ar}/^{39}\text{Ar}$ feldspar ages. The high proportion of Permian grains and discrepancies between U-Pb zircon and $^{40}\text{Ar}/^{39}\text{Ar}$ ages in the lowest Puesto Viejo Group led *Domeier et al.* (2011) to suggest that these volcanics were dominated by recycled, xenocrystic zircon. These observations were further used to propose that the Puesto Viejo magma chamber was volumetrically too small to generate new zircon grains (*Domeier et al.*, 2011).

When U-Pb zircon spectra from Karoo Supergroup tuffs (Fig. 6G-L) are compared to age equivalent volcanics in South America (Fig. 6A-F), the impact of zircon recycling on tuff geochronology can be observed. Lower Choiyoi volcanic samples (Fig. 6E-F; *Rocha-Campos et al.*, 2011) contain a single, cohesive zircon population, which was resolved in samples from the Lower-Middle Ecça Group. Samples from the uppermost Upper Choiyoi (PV01d from *Domeier et al.*, 2010; CH-05 from *Rocha-Campos et al.*, 2011; SM-1 from *Rocha-Campos et al.*, 2006-data unpublished), however typically contain a Late Permian zircon population (~253 Ma) that is distinct from an older Middle-to-Late Permian populations (~263-273 Ma). The KDE for available data from the uppermost Upper Choiyoi volcanics (Fig. 6D) is remarkably similar to Upper Ecça Group tuffs (Fig. 6J), with local maxima at ~253 and ~263 Ma. Comparison of U-Pb zircon and $^{40}\text{Ar}/^{39}\text{Ar}$ ages (Fig. 6B, C) for the Lower Puesto Viejo volcanics demonstrate that Early to Middle Triassic volcanics do not contain dominant, co-eruptive zircon populations, but are rich in older, mid-Permian zircon (Fig. 6C). This trend is observed in samples from the Lower Beaufort (Fig. 6H, I). In subsequent Puesto Viejo volcanics, small, coherent populations of co-eruptive zircon become observable (Fig. 6A, B), which can also be observed in zircon populations from Lower Beaufort tuffs (Fig. 6G). Based on the similarity of zircon population distributions, weighted mean

ages, and stratigraphic position relative to the overlying magmatic/tuff gap, we propose several age correlations (Fig. 7):

1. Lowest Ecça Group tuffs (within the Prince Albert, Whitehill Fms) are age equivalent to the Early-Middle Permian Lower Choiyoi Group (>265 Ma).
2. Mid-Ecça Group tuffs (within the Collingham, Vischkuil, Skoorsteenberg, Laingsburg, Ripon Fms.) are age equivalent to the upper, Lower Choiyoi and lowest, Upper Choiyoi Group rocks (~265-255).
3. Upper Ecça Group tuffs (Kookfontein, Fort Brown Fms) are age equivalent to the late Upper Choiyoi Group (253 Ma).
4. The overlying Lower Beaufort Group tuffs are dominated by recycled zircon grains, which suggest they are age equivalent with Puesto Viejo volcanism (241-235 Ma).
5. The Tuff Gap proposed in this study (Fig. 3, 4, 7), could represent magmatic quiescence between Choiyoi and Puesto Viejo magmatic activity (252-241 Ma).

IMPLICATIONS FOR MAGMATISM IN SOUTHERN GONDWANA

Zircon is known to be present in variable concentrations in different tectonographic terranes (discussed as “zircon fertility” in *Moecher and Samson*, 2006). Therefore a zircon-rich terrane would be overrepresented in any zircon geochronology study compared to a zircon-sparse or zircon-poor terrane. This is most commonly applied to understand the geologic bias in detrital zircon provenance studies. The same mechanism, however, may create bias in the study of a magmatic system if certain magmatic systems produce few to no zircon, while others generate large volumes of zircon. The Southern Gondwanan magmatic system as recorded in South America and the Karoo Basin appears to have consisted of three distinct pulses of magmatism: 1) zircon-rich, subduction and orogenic collapse drive magmatism that erupted crystalliferous, vitric tuffs prior to ~252 Ma, 2) magmatic and volcanic quiescence from 252-241 Ma, and 3) renewed magmatism driven by extensional rifting that resulted in recycling of older crustal materials and eruption of lithic tuffs. Crystalline basement rocks from the Antarctic Peninsula (*Riley et al.*, 2012), which would have been tectonically adjacent to South Africa within Gondwana (Fig. 1A), provide further insight into zircon crystallization over time (Fig. 8). Permian-Cretaceous basement from the Antarctic Peninsula contain co-emplacement and recycled igneous zircon, as well as metamorphic zircon that record Permian-Triassic metamorphism. When considering only low U/Th (<10; n=62), which likely represents igneous zircon (*Hoskin and Black*, 2000), there is a distinct pattern that is strikingly similar to the zircon trends observed in South America and South Africa. There are two

Figure 8: KDE age distribution of igneous (U/Th<10) Permian-Triassic zircon from Gondwanan crystalline basement in the Antarctic Peninsula (Riley et al., 2012). The peaks of zircon ages represent pulses of igneous zircon crystallization. Two peaks at ~272 and ~255 Ma are coeval with Lower and Upper Choiyoi volcanism, no zircon are found in the time interval of the tuff gap, and few, sparse zircon correlate to Puesto Viejo volcanism, despite known Early Triassic volcanism in Southern Gondwana.

Permian spikes of zircon represented in the Antarctic samples at ~272 and ~255 Ma. The roughly correlate to the Lower (290-265 Ma) and Upper (270-250 Ma) Choiyoi Group volcanic suites and the latter pulse with the tuffs of the Ecce Group. Only one zircon lies within the range of the tuff gap, but this grain also is within error of the ~255 Ma peak, therefore, there are effectively no zircon produced during this interval, which likely reflects magmatic quiescence. The Antarctic Peninsula samples only yield 3 grains that correlate with Puesto Viejo magmatism (240-220 Ma). Despite known volcanism during this time, the sparse presence of such a small population suggests that very few zircon were crystallized during this period. These observations, along with the lack of co-eruptive zircon in South American and Karoo Basin volcanics strongly suggest that zircon production in Southern Gondwanan was subdued in the Early Triassic across the western half of the margin. The lack of co-eruptive zircon, therefore, may be a super-regional phenomenon, that might affect more areas throughout Gondwana, particularly in the Early Triassic, thereby hindering U-Pb zircon geochronology in Early Triassic volcanics.

SUMMARY

Using 469 new single-grain analyses, we used coherent age populations to determine 22 U-Pb zircon tuff ages in 4 stratigraphic sections of the lower Karoo Supergroup across the Karoo Basin. Regionally, tuffs within the terrestrial Beaufort Group consistently produce ages that are older than the underlying marine Ecca Group, which can be observed in multiple studies (*Coney et al.*, 2007; *Fildani et al.*, 2007; 2009; *Rubidge et al.*, 2013; *Lanci et al.*, 2013) using different analytical techniques (SHRIMP, TIMS, LA-ICP-MS). The reproducibility of tuff ages in the marine section and internally consistent age for the base of the tuff gap suggests that ages below a proposed regional tuff gap may provide reliable chronostratigraphic control, while tuffs above the tuff gap yield chaotic ages that pre-date deposition (Fig. 5). We propose that post-depositional reworking combined with a lack of terminal phase, volcanic zircon in distal airfall tuffs within the Beaufort Group may be responsible for the inversion of U-Pb zircon ages. Zircon recycling is observed in correlative proximal volcanic tuffs in Permo-Triassic basins of South America, corroborating this hypothesis. The zircon U-Pb ages from tuffs in the Beaufort Group should therefore be considered as constraints on maximum depositional ages, not as a representation of the actual depositional age (i.e. “golden spike” ages). Our proposed explanation brings together data considered thus far puzzling and contradictory, and is compatible with recent observations in other long-lived arc to post-orogenic systems that show protracted zircon recycling (*Pereira et al.*, 2014). Our observations support recent evidence from South America that the absolute ages assigned to Gondwanan biozones may be erroneously old (*Ottone et al.*, 2014). Our new data are in agreement with all recently published ages (*Fildani et al.*, 2007, 2009; *Rubidge et al.*, 2013; *Lanci et al.*, 2013) and demonstrate the importance of considering the magmatic history of a volcanic source when interpreting U-Pb zircon datasets from tuffs to estimate maximum depositional ages. These new data illustrate how tuff geochronology can, at times, be ambiguous when using a limited dataset. By compiling a regionally extensive study and understanding the nature of volcanism, however, the ambiguity might be reduced, resulting in more competent stratigraphic age controls.

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CHAPTER 2: PETROGENESIS AND PROVENANCE OF DISTAL VOLCANIC TUFFS FROM THE PERMIAN-TRIASSIC KAROO BASIN, SOUTH AFRICA: A WINDOW INTO A DISSECTED, MAGMATIC PROVINCE

ABSTRACT

We present zircon rare-earth element (REE) compositions integrated with U–Pb ages of zircon and whole rock geochemistry from 29 volcanic tuffs preserved in the Karoo Supergroup, South Africa, to investigate the history of magmatism in Southern Gondwana. Whole rock compositions suggest a subduction-driven, magmatic arc source for early (>270 Ma) to middle Permian (270–260 Ma) Karoo tuffs. After ~265 Ma, the magmatic source of the volcanic deposits transitioned toward intraplate, shallow-sourced (<40 km) magmatism. Zircon U–Pb ages and REE chemistry suggest that early to middle Permian magmas were oxidizing, U- and HREE-enriched, melts, while middle Permian to Triassic zircon record HREE-depleted, more reduced magmatism. Middle Permian to Triassic tuffs contain increasingly large volumes of “zircon cargo” derived from assimilated crustal material; therefore magmas may have been zircon undersaturated, resulting in less zircon growth and increased inheritance in late Permian to Triassic, Gondwanan volcanics. Zircon U–Pb ages and REE chemistry suggest a shift from arc magmatism in the early Permian to extensional magmatism by the late Permian, which may be associated with development of a back-arc magmatic system adjacent to Western Antarctica that predates known extensional volcanism elsewhere in Gondwana. Opening of the Southern Ocean in the Jurassic-Cretaceous paralleled this extensional feature, which may be related to reactivation of this Permo-Triassic back arc. This study demonstrates the potential of zircon U–Pb age and REE compositions from volcanic tuffs preserved in sedimentary strata to provide a more complete record of magmatism, when the magmatic province has been largely lost to active tectonism.

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INTRODUCTION

The magmatic history of igneous provinces is often poorly preserved in the rock record due to rifting of continental crust, orogenic uplift and erosion, and successive intrusion by younger, genetically unrelated magmas along long-lived active margins (*Barth et al.*, 2013). Volcanic tuffs preserved in sedimentary basins, however, have been shown to contain a more complete time-series record of volcanism (*Perkins and Nash*, 2002) since syn-tectonic sedimentary basins tend to subside during periods of active magmatism and deformation (*DeCelles*, 2012). Studies of modern volcanism, however, have shown that the composition of volcanic tuffs varies with distance from the volcanic vent during atmospheric transport (*Hinkley et al.*, 1980; *Fruchter et al.*, 1980; *Taylor and Lichte*, 1980) via crystal fractionation through settling of minerals and volcanic glass based on density out of ash clouds with increasing distance (*Hinkley et al.*, 1980). Further convoluting the petrologic link between the distal volcanic deposits and the magmatic source, weathering and diagenetic alteration of chemically unstable glass shards can further alter tuff chemistry and mineralogy (*Dahlgren et al.*, 1993; 1997).

Whole-rock elemental composition continues to be useful in bridging the link between distal volcanic tuffs and their parental magmas (*Tomlinson et al.*, 2014; *Heintz et al.*, 2015), in particular through the use of immobile trace elements (e.g., Rb, Y, Nb, Zr, and REEs) that are less affected by weathering or diagenetic processes in volcanic ashes (*Floyd and Winchester*, 1978; *Hastie et al.*, 2007). However, recent research into the partitioning of trace elements into zircon (*Grimes et al.*, 2007; *Rubatto and Hermann*, 2007; *Schoene et al.*, 2012), a highly refractory and durable mineral phase, has proven the potential of zircon chemical composition to provide insight into deep crustal magmatic processes. Laser Ablation-Inductively Coupled Plasma Mass Spectrometer (LA-ICPMS) (*Li et al.*, 2000; *Kohn and Corrie*, 2011, *Kylander-Clark et al.*, 2013) and Secondary Ion Mass Spectrometer (SIMS) analyses (*McClelland et al.*, 2009) techniques now allow for the simultaneous microanalysis of U–Pb isotopic and trace element compositions on single zircon crystals, leading to the development of the relatively new field of petrochronology, which couples radiometric age with trace element geochemical composition on single mineral crystals (*Kylander-Clark et al.*, 2013). Zircon petrochronology has been employed to investigate a wide range of petrologic processes, including the time scales for pluton construction (*Barboni et al.*, 2013; *Chelle-Michou et al.*, 2014), crustal melting (*Barth et al.*, 2013; *Gordon et al.*, 2013), high-grade metamorphic processes (*Rubatto*, 2002; *Hiess et al.*, 2015), volcanic tuff deposits, and tephrochronology (e.g., *Schmitt et al.*, 2010; *Harvey*, 2014).

In this study we use whole rock major (SiO_2 , TiO_2 , Al_2O_3 , FeO (total), MnO, MgO, CaO, Na_2O , K_2O , P_2O_5) and trace element (Ni, Cr, Sc, V, Ba, Rb, Sr, Zr, Y, Nb, Ga, Cu, Zn, Pb, La, Ce,

Th, Nd, U, Cs) composition combined with single zircon U–Pb isotopic and REE compositions from distal, volcanic tuffs in the Karoo Supergroup of South Africa to investigate the magmatic provenance of volcanic tuffs in the Karoo Basin, characterize the petrogenetic history of Permian–Triassic magmatism along the margin of southern Gondwana, and demonstrate the utility of petrochronology in tephra-based studies. While whole rock geochemistry of Permian Karoo tuffs are comparable to known transitional magmatism in South America, while zircon U–Pb ages and REE compositions in Karoo tuffs record evidence of a transition from hydrous, more evolved magmatism in the early to middle Permian to drier, more primitive magmatism in the middle to late Permian. The timing of this magmatic shift and zircon geochemistry are not compatible with known South American volcanics and requires a reevaluation of the volcanic source. We explore the implications of the zircon U–Pb and REE data when coupled with whole rock data from volcanic tuffs to characterize a volcanic system that has been largely lost to active tectonism.

GEOLOGIC BACKGROUND

The Carboniferous–Triassic Karoo Supergroup of South Africa preserves distal volcanic deposits that were erupted from a continental magmatic arc system along the southern margin of Gondwana (Veever *et al.*, 1994, Bangert *et al.*, 1999; Panhurst *et al.*, 2006; Fildani *et al.*, 2007; Fig. 1). Karoo Supergroup tuffs are fine-grained and grade from green, clay-rich, thin beds (typically <10 cm) in the deep-to-marginal marine Eccu Group, to brown, lithic-rich and white, chalky beds that can be up to ~40 cm (but typically <10 cm) in the overlying terrestrial Beaufort Group (Fildani *et al.*, 2007; McKay *et al.*, 2015). The transition from green-clay-rich tuffs towards more chalky and lithic-rich volcanic deposits is marked by a “tuff-gap” (McKay *et al.*, 2015) that may correlate to decreased volcanism.

Based on stratigraphic correlations, the Karoo tuffs have widely been suggested to be sourced by the same magmatic system responsible for eruption of ignimbrite sequences interbedded with clastic continental strata within the Permian Choiyoi Group and Puesto Viejo Formation in central South America (Fig. 1; Bangert *et al.*, 1999; Cole, 1992; López-Gamundi and Rossello, 1998; Rocha-Campos *et al.*, 2011). Choiyoi Group magmatism can be characterized as two distinct igneous suites generated during different phases of southern Gondwanan tectonic history. The early-to-middle Permian Lower Choiyoi Group (290–265 Ma) contains rocks with a volcanic arc affinity characterized by low Zr (<200 ppm), Nb (<15 ppm), and Y (<80 ppm) with generally higher Sr/Y (>30) compositions and are sourced from active subduction along the southern Gondwana margin (Panhurst *et al.*, 2006; Kleiman and Japas, 2009). In contrast, the middle-to-late Permian (265–251 Ma) Upper Choiyoi Group volcanic rocks indicate a post-orogenic magmatic source and contain elevated Zr (100–700 ppm), Nb (10–35 ppm), and Y (70–90 ppm), and low Sr/Y (<40)

Figure 1: Simplified geologic map of southwestern Gondwana (López-Gamundi and Rossello, 1998; polar projection) shows the approximate locations of the Karoo Basin, Permian-Triassic volcanic suites in South America (Choiyoi and Puesto Viejo), western Antarctic volcanogenic sediments (from Elliott *et al.*, 2015^{ab}) and Antarctic Peninsula igneous suites (Riley *et al.*, 2008). This study looks to compare the volcanic tuffs from the Karoo to potential igneous sources in South American and Antarctica to evaluate volcanic provenance and the implications for Gondwanan tectonism. Note the large area between the African continent and the active margin that has been dissected during opening of the Atlantic and Southern Ocean. Depocenters denoted: Tanqua (T), Laingsburg (L), central (C), and Ripon (R).

(Kleiman and Salvarredi, 2001, Kleiman and Japas, 2009). Following a period of magmatic quiescence from 251-240 Ma, the Triassic Puesto Viejo volcanic rocks (240-230 Ma) were erupted during a phase of continental extension and rifting (Ramos and Kay, 1991, Kleiman and Japas, 2009).

Some workers have questioned this historic correlation of Karoo Supergroup tuffs with South American volcanic centers due to the distance between the southern Karoo Basin and known volcanism along the Gondwanan margin, which would have been >1000 km based on paleogeographic reconstructions (Bangert *et al.*, 1999; Lanci *et al.*, 2013). This long distance is inconsistent with the grain size of Karoo tuffs, which includes casts of pyroclastic grains, suggesting a more proximal volcanic source, possibly as close as 100-300 km from the basin (McLachlan and Jonker, 1990; Bangert *et al.*, 1999). Further complicating correlation efforts is that eruptive age control has been difficult to obtain for the middle Permian through Middle Triassic volcanic rocks in southern Gondwana (Domeier *et al.*, 2011; Ottone *et al.*, 2014, McKay *et al.*, 2015). U–Pb SHRIMP (Sensitive High Resolution Ion MicroProbe) studies of the Choiyoi and Puesto Viejo volcanics have shown that recycled/inherited zircon grains dominate Late Permian to Early Triassic tuffs, with few zircon crystallization ages interpreted to be syneruptive making interpretation of the age of eruption and deposition difficult (Spalletti *et al.*, 2008; Rocha-Campos *et al.*, 2006; Domeier *et al.*, 2011). Ages for volcanic rocks in South America have been obtained through a combination of U–Pb zircon and $^{40}\text{Ar}/^{39}\text{Ar}$ ages (Spalletti *et al.*, 2008; Rocha-Campos *et al.*, 2006; Domeier *et al.*, 2011, Ottone *et al.*, 2014). Volcanic deposits from the Lower Choiyoi yield U–Pb zircon ages that range from 282-265 Ma (Rocha-Campos *et al.*, 2011). Upper Choiyoi Group rocks yield U–Pb zircon ages that range from 265-251 Ma (Rocha-Campos *et al.*, 2011), that are within error of $^{40}\text{Ar}/^{39}\text{Ar}$ plateau ages of 260 (biotite) and 256 (K-spar) Ma from correlative rocks (Domeier *et al.*, 2011). Puesto Viejo volcanic rocks display $^{40}\text{Ar}/^{39}\text{Ar}$ amphibole and potassium feldspar ages that are younger than U–Pb zircon from the same samples (Domeier *et al.*, 2011). While the lower Puesto Viejo Group typically yield ~265 Ma U–Pb zircon ages, $^{40}\text{Ar}/^{39}\text{Ar}$ plateau ages range from 235 (K-spar) to 254 (biotite) Ma, with a number of samples producing ~240 Ma plateau age in amphibole and K-spar (Domeier *et al.*, 2011). These ages are significantly younger than U–Pb zircon ages from the Puesto Viejo Group, suggesting zircon crystallization predates eruption and cooling by > 10 Ma.

Similarly, zircon U–Pb geochronology of Karoo Supergroup tuffs also reveal a scarcity of zircon with syneruptive ages in Permo-Triassic volcanic deposits (McKay *et al.*, 2015). This lack of syneruptive zircon has led to a number of contradictory age results for the Karoo Supergroup (Fildani *et al.*, 2007; 2009; Lanci *et al.*, 2013; Rubidge *et al.*, 2013; McKay *et al.*, 2015). The age “paradox” resolved in South American volcanic suites (Domeier *et al.*, 2011; Ottone *et al.*,

2014) is likely linked to long-term magmatic zircon recycling (*Domeier et al.*, 2011; *Ottone et al.*, 2014; *McKay et al.*, 2015) and similar zircon recycling may be the cause of the age controversy in the Karoo Supergroup strata (*McKay et al.*, 2015). Based on U–Pb zircon age populations and stratigraphic position, tuffs in the Eccia Group are coeval with the Upper Choiyoi Group volcanic rocks (265–250 Ma), while tuffs in the Beaufort Group correlate to the Triassic (<240 Ma) Puesto Viejo Group. This correlation, however, is based entirely on geochronology, and no geochemical evidence has been presented to link the South African and South American volcanic deposits.

Closer candidates for volcanic sources have not been identified, primarily because large portions of the crust where a more proximal volcanic source may have existed has since been tectonically destroyed or buried through rifting and opening of the Atlantic and Indian Oceans. Portions of Antarctica, the Antarctic Peninsula, and other terranes (i.e. Thurston Island and Mary Byrd Land) are thought to have been adjacent to these now missing crustal blocks (*Lawver et al.*, 1992), and could also have hosted the volcanic system that sourced Karoo tuffs. The Antarctic terranes record Cambrian through Jurassic magmatism and metamorphism (*Millar et al.*, 2002). Permian-Triassic granitoids are located in crystalline basement terranes (*Riley et al.*, 2012), and possibly correlative tuffs are present in Permian-Triassic strata in Antarctic sedimentary basins (*Elliot et al.*, 2015^b). Therefore, the Karoo tuffs may have been sourced by more proximal volcanic systems located in the dissected Gondwanan crust adjacent to Antarctic terranes.

WHOLE ROCK GEOCHEMISTRY

Methods

Whole rock geochemistry from 41 volcanic tuff samples (**Fig. 2**) from the Karoo Basin were determined by x-ray fluorescence (XRF) and inductively coupled mass spectrometry (ICPMS) at the Washington State University’s GeoAnalytical Lab. Major element oxide (SiO_2 , TiO_2 , Al_2O_3 , FeO (total), MnO, MgO, CaO, Na_2O , K_2O , P_2O_5) and trace element compositions (Ni, Cr, Sc, V, Ba, Rb, Sr, Zr, Y, Nb, Ga, Cu, Zn, Pb, La, Ce, Th, Nd, U, Cs), along with volatile content (loss on ignition [LOI]) were collected using XRF methods described by *Johnson et al.* (1999). For ICPMS analyses, samples were analyzed for trace and rare earth element concentrations (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ba, Th, Nb, Y, Hf, Ta, U, Pb, Rb, Cs, Sr, Sc, Zr), as described by *Lichte et al.* (1987), *Jarvis* (1988), *Jenner et al.* (1990), and *Longerich et al.* (1990). Elemental concentrations were collected by both XRF and ICPMS for Sc, Ba, Rb, Sr, Zr, Y, Nb, La, Ce, Th, Nd, U, Cs, with 90% XRF measured concentrations are within $\pm 10\%$ of the ICPMS results ($\sim 70\%$ of XRF results are within $\pm 5\%$ of ICPMS values), suggesting good agreement between both analytical techniques. Four samples were analyzed 2–3 times to assess instrumental drift and reproducibility; multiple analyses showed no significant instrumental bias or analytical variability.

Figure 2: Chronostratigraphic constraints on the Karoo Supergroup strata based on U-Pb zircon geochronology of volcanic tuffs. Ecga Group tuffs young upward and tuffs in the uppermost Ecga Group are reproducibly younger than in the zircon-poor tuffs of the Beaufort Group (*McKay et al.*, 2015). A tuff gap is regionally present, typically found directly above tuffs that yield

a ~251 Ma age, which would correspond to the Permian-Triassic boundary. Tuffs maximum depositional ages reported in this study have boxes around them and corroborate previously published age controls. Geochemistry samples marked with a star to the right of the sample ID, ±age if determined.

Results

Major element concentrations for 41 volcanic tuffs ([Appendix C](#)) show variability in SiO_2 , Al_2O_3 , and CaO . Six samples with high CaO (>5% weight), low SiO_2 (<50%), high LOI (>10%) are likely to contain minor secondary calcite and are excluded from further discussion (09TBT01, SUTHER, 12ZA61, 14ZA121, 14ZA128, 14ZA129) since their composition may have been affected by secondary diagenetic alteration. The remaining analyses (N=35) were normalized to oxide totals (LOI excluded). Samples containing no significant calcite have SiO_2 that range from 47 to 73%, Al_2O_3 between 12 and 30%, CaO < 5%, NaO <5%, K_2O from 1 to 7%, and P_2O_5 typically <1%. FeO values are reported as total Fe and range between 1 and 7%. MnO content is less than 0.3% and MgO varies slightly between 0.5 and 2.5, with most values between 1 and 2%. TiO_2 is between 0.2 and 0.9% for all samples. Little variation is observed between the geochemistry of samples from the Beaufort and Eccca Groups in major element geochemistry. Trace elements results, including REEs, ([Fig. 3A-H](#)) also shows no distinguishing characteristics between the Eccca and Beaufort Group tuffs. Eccca Group tuffs show more compositional variability than the overlying Beaufort Group tuffs in Nb (ppm), Zr (ppm), Y (ppm), and Rb (ppm), Yb (ppm), and Ce (ppm). Both the Eccca and Beaufort tuffs have negative sloped REE patterns with minor negative Eu anomalies. The most prominent Eu anomalies are two positive Eu anomalies, both found in Eccca tuffs. Five Beaufort tuffs also contain negative Ce anomalies and 1 Beaufort tuff contained a positive Ce anomaly, while no Ce anomalies were observed in Eccca tuffs.

ZIRCON U-Pb AGES AND REE COMPOSITION

Methods

Twenty-nine tuffs were sampled from 4 transects through formations of the Eccca and Beaufort Groups exposed along the southern Karoo Basin ([Fig. 1](#)). Zircon grains were separated from samples using mineral separation techniques, including the use of a Franz magnetic separator to remove magnetically susceptible zircon that may have high U and yield discordant results (*Sircombe and Stern, 2002*). Zircon yields were variable for different sample; ranging between 0 and >200 zircon. Size, morphology, and inclusion density were not considered when selecting zircon for analysis in an effort to characterize the entire zircon population of a tuff and not bias results towards prismatic, acicular, euhedral zircon populations. Zircon grains were mounted in epoxy and polished to expose an interior cross-section of the grain. Catholuminescence images were used to avoid inclusions and complex cores, and to target intermediate grey (corresponding to U concentration between 100-1000 ppm), oscillatory-zoned, rim domains near for *in-situ* zircon analyses. In-situ zircon analyses were performed on the SHRIMP-RG (sensitive high resolution ion microprobe - reverse geometry) ion microprobe at the Stanford University Microscopic Analytical

Figure 3: Whole rock geochemistry of Karoo tuffs plotted with geochemistry from the Choiyoi Group (Kleiman and Salvarredi, 2001; Kleiman and Japas, 2009) and Puesto Viejo (Kleiman and Salvarredi, 2001) volcanic deposits in South America. (A) Zr/TiO₂ vs. Nb/Y with geochemical discrimination diagram of Winchester and Floyd (1977), (B) Rb vs. Y+Nb, (C) Nb vs. Y with discrimination diagram of Pearce et al. (1984) COLG-collisional granitoid; WPG-within plate granitoid; VAG-volcanic arc granitoid; ORG-orogenic granitoid, (D) Nb vs. Zr, (E) Sr/Y vs. La/Yb, (F) Ce/Y vs. Approx. age (Ma), (G) chondrite normalized REE spider diagrams.

Center (SUMAC) under analytical conditions similar to those of *Barth and Wooden* (2010). The primary ion beam (O_2^-) was focused to a spot diameter between 18 to 22 microns in diameter, a depth of ~1.5 microns for analyses performed in this study. U–Pb ages were calculated with reference to the R33 and Temora zircon standards (419.3 and 416.8 Ma; *Black et al.*, 2004). Zircon trace elements, including U, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Er, Yb, Lu, Hf, Th, and U were measured concurrently with U–Pb analyses and calibrated with the compositional zircon standard MADDER (*Barth and Wooden*, 2010). Model ages and trace element concentrations were calculated using the SQUID 2.51 (*Ludwig*, 2009) and ISOPLOT 3.76 software (*Ludwig* (2012)). $^{206}Pb/^{238}U$ ages are corrected for common Pb using ^{207}Pb (assuming $^{206}Pb/^{238}U$ – $^{207}Pb/^{235}U$ age-concordance) and a model Pb composition from *Stacey and Kramers* (1975) with no additional error propagated from the uncertainty in the model common-Pb composition. On average, zircon analyses contained >99.5% radiogenic Pb and the common-Pb correction was negligible for accepted analyses.

Of the 590 total individual grain analyses, 520 were accepted ranging from 226 to 2607 Ma on the basis of low common-Pb concentrations, low analytical uncertainty (<3%) and concordance. Grains were determined to be concordant if $^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ages overlapped within 2σ uncertainty. To determine maximum depositional ages, anomalously old zircon ages (>300 Ma) are interpreted as inherited, xenocrystic or detrital in origin, while anomalously young (<<~250 Ma), high-U (>1000 ppm) or high common-Pb are dismissed as having been affected by Pb-loss or common-Pb contamination (resulting in an anomalous common Pb correction). Zircon age populations that were identified using kernel density estimate (KDE) plots to interpret the youngest, coherent population within a tuff. A weighted mean age was calculated from the youngest, coherent population of concordant grains (>3 grains) to determine maximum depositional ages for 6 of 7 tuffs. One, zircon-poor tuff contained only anomalously old, Cambrian or older age grains, with no coherent population. Uncertainties for weighted mean ages are presented as 2σ , including internal and external error. We report REE compositions for the 469 U–Pb zircon ages from 22 volcanic tuffs reported by *McKay et al.* (2015) and an additional 121 U–Pb zircon ages and REE compositions from 7 new tuff samples ([Appendix D](#)). There is no geographic relationship observed in U–Pb ages or REE zircon compositions. Zircon U–Pb ages, however, do show stratigraphic trends, and, therefore, samples will be presented based on stratigraphic position.

U–Pb zircon maximum depositional ages

The 121 newly obtained U–Pb zircon ages provide estimates for the maximum depositional age of 7 volcanic tuffs from the Karoo Basin are reported based on stratigraphic order: 1 sample from the southwestern Karoo near Robertson, Western Cape, 2 tuffs from the Laingsburg depocenter in the western Karoo Basin, 2 tuffs from the Central Karoo Basin, and 2 tuffs from the Ripon depocenter in the eastern Karoo Basin (UTM locations in Electronic Appendix).

ECCA GROUP

Four tuff samples were collected from within the Eccca Group: 1 from the Tanqua depocenter, 2 from Laingsburg depocenter, and 1 from Ripon depocenter (Fig. 2). Sample, 14ZA142, was collected from the lower Eccca Group within a structural inlier of Karoo Supergroup strata correlated with the Tanqua depocenter within the Cape fold belt near Robertson, Western Cape. The two youngest individual zircon ages are 226 ± 6 and 256 ± 9 Ma, but were rejected on the basis of relatively high analytical uncertainties ($\sim 3\%$, 1σ) and do not define a population. Therefore, the youngest, coherent population yields an age of 270.4 ± 2.7 (2σ , $n=5$, MSWD=2.1). Sample 14ZA154 was collected from a clay-rich tuff in the middle Ripon Formation of the Eccca Group near Grahamstown, Eastern Cape and contained zircon ranging in age from 230-1596 Ma. The weighted mean age of the youngest coherent zircon population is 264.3 ± 9.8 ($n = 5$, MSWD=3.5). Sample 14ZA121 was collected from a green, clay-rich tuff near Laingsburg, Western Cape from the middle-to-upper Laingsburg Formation and contained zircon that ranged in age between 220-1036 Ma. A subpopulation of 6 grains yielded a weighted mean age of 257.7 ± 4.6 Ma, with an MSWD of 3.7. Zircon from 14ZA116, sampled from a clay-rich tuff in the upper Laingsburg Formation, ranged in age from 228-1888 Ma. From 40 total analyses, 31 were Permian-Triassic in age. A population of 10 grains yield a weighted mean age of 250.0 ± 2.1 Ma with an MSWD=3.7. Ages from samples 14ZA121 and 14ZA116 strongly suggest a late Permian to Early Triassic maximum depositional age for the upper Laingsburg.

BEAUFORT GROUP

Three samples were collected from the Beaufort Group. Sample 14ZA130 was collected from a light-brown tuff in the upper Abrahamskraal/Koonap Formation within the Beaufort Group (Fig. 2) about 25 km SE of Fraserburg, in the central part of the basin. This tuff yielded only 8 zircon, none of which were Permian-Triassic in age. The youngest grain within 14ZA130 was Late Cambrian with age of 497 ± 6 Ma (1σ), which is an age that has been reported for Permian-Triassic tuffs in the Karoo Supergroup (*McKay et al.*, 2015) as well as in coeval volcanics in South America (*Domeier et al.*, 2011). Sample 14ZA168, collected 10 miles north of Graaff-Reinet, Eastern Cape, in the middle Balfour Formation within the central basin yielded zircon that ranged in age between 252 and 1620 Ma. Permian grains dominate this sample ($n=19$ of 30; 63%). A coherent population of 11 grains produce a weighted mean age of 257.5 ± 2.5 Ma (MSWD=1.43), which serves as the maximum deposition age for the Balfour Formation. Sample 14ZA161 was collected ~ 10 km NE of Seymour, Eastern Cape from the Balfour Formation of the Beaufort Group and contained zircon ranging in age from 219 to 2655 Ma. A small population of 5 low common Pb, concordant zircon produce a weighted mean age of 255.4 ± 3.1 Ma with an MSWD = 1.8.

Trace elements in zircon

To understand Permian-Triassic magmatism, we focus on the geochemical composition of 364 zircon that produced U–Pb ages < 300 Ma. Zircon data are subdivided into four age groups: early Permian (300–270 Ma), middle Permian (270–260 Ma), late Permian (260–251 Ma), and Triassic (<251 Ma) (Fig. 4). Mean $\text{Hf}_{\text{zircon}}$ concentration decreases from ~9300 ppm in the early Permian to 7000 ppm in the Early Triassic (Fig. 4A). Mean chondrite normalized $\text{Yb/La}_{\text{zircon}}$ decreases (Fig. 4B) from 13,200 in the early Permian to ~4700 in the late Permian and ~3400 in the Early Triassic. Mean $\text{Ce/Ce}^*_{\text{zircon}}$ also systematically decreases (Fig. 4C) from 67 in the early Permian, to 48 in the middle Permian, to 43 in the late Permian, and finally to 12 in the Early Triassic. Mean $\text{Hf/Lu}_{\text{zircon}}$ decreases from 160 in the early Permian to ~110 in the middle and late Permian, to 44 in the Early Triassic. Chondrite normalized $\text{Eu/Eu}^*_{\text{zircon}}$ (Fig. 4E) does not vary significantly through time, with early, middle, late Permian and Early Triassic grains producing mean values of ~0.37. $\text{Th/U}_{\text{zircon}}$ increases slightly through time from 0.64 in the early Permian to 0.77 in the late Permian (Fig. 4G). The Eccra and Beaufort Group tuffs contain elevated Th/U (>1.0) zircon (Fig. 5). Beaufort Group tuffs, however, contain a larger population of higher Th/U (>1.5) zircon, while few Eccra Group tuff zircon exceed $\text{Th/U} \geq 1.5$ (Fig 5?).

Ti in zircon

The incorporation of Ti into zircon has been shown to be controlled by the temperature during crystallization (Watson and Harrison, 2005; Watson *et al.*, 2006; Hiess *et al.*, 2008). Concentrations of Ti in zircon were collected for 77 zircons from 6 tuffs (12ZA07, 12ZA22, 12ZA23, 12ZA46, 12ZA54, 12ZA61; Appendix E) concurrent with U–Pb and REE analyses. Twenty-six zircon analyses yielded high Fe concentrations (>300 ppm) were excluded, leaving 51 Permo-Triassic $\text{Ti}_{\text{zircon}}$ analyses. $\text{Ti}_{\text{zircon}}$ model temperatures were calculated based on Si and Ti activities from Claiborne *et al.* (2010) and range from ~620° C to greater than 800° C, with $\pm \sim 10\%$ uncertainty in each analysis. As a whole, the variability observed in $\text{Ti}_{\text{zircon}}$ model temperatures is minor throughout the Permian and Early Triassic, and all the Permian to Triassic average model temperatures are within uncertainty of one another (Fig. 4I). $\text{Ti}_{\text{zircon}}$ indicates temperatures ~800°C for 285–276 Ma zircon. Temperatures decreases to below 800°C into the middle Permian, when $\text{Ti}_{\text{zircon}}$ model temperatures indicate an average of $747 \pm 43^\circ\text{C}$ (1σ). Late Permian $\text{Ti}_{\text{zircon}}$ model temperatures are slightly higher with an average $757 \pm 37^\circ\text{C}$ (1σ). Only 5 measurements were made on Early Triassic zircon and these temperature estimates are approximately equivalent with Late Permian temperature estimates, with an average $\text{Ti}_{\text{zircon}}$ temperature $760 \pm 19^\circ\text{C}$ (1σ).

Figure 4: Zircon geochemistry and U-Pb ages show temporal trends in chemistry from Permian-Triassic age zircon within Karoo Supergroup tuffs. (A) Hf (ppm), (B) Yb/La, (C) Ce/Ce*, and (D) Hf/Lu decrease through time. (E) No trend exists between Ce/Ce* and Eu/Eu*, while (F) Hf and Ce/Ce* are lower and less variable in late Permian and Early Triassic zircon. (G) T_{Ti} increases through time, with high Th/U (>1.0) zircon only occurring after the middle Permian (<270 Ma). T_{Ti} temperatures are all within error and show no trends with Ce/Ce* (H) or Th/U (I).

DISCUSSION

Zircon geochemistry can record the prolonged petrogenetic history of a magmatic system (Claiborne *et al.*, 2010; Schoene *et al.*, 2012) that may differ from the whole rock chemistry of volcanic tuffs, which is susceptible to post-eruptive alteration by hydrothermal fluids, diagenesis, and weathering processes (Hastie *et al.*, 2007; Gatti *et al.*, 2014), whereas zircon may preserve a more robust record of magmatic composition. Therefore, whole rock and zircon geochemistry will be discussed separately.

Petrogenesis of Karoo tuffs from whole rock geochemistry

A traditional technique to determine the tectonic source of igneous rocks is by using geochemical discrimination diagrams, in which igneous suites from well characterized tectonic settings are used to defined geochemical “fields”. These fields commonly overlap and the results can be ambiguous or misleading in complex magmatic systems (Förster *et al.*, 1997); however, since this approach has been used to classify volcanic igneous suites in age equivalent rocks from elsewhere in Gondwana (Kleiman and Japas, 2009), we compare Karoo Supergroup tuff whole rock geochemical composition with granitoid discrimination diagrams from Pearce *et al.* (1984) to attempt to distinguish the nature of the magmatic system that sourced the distal ashes of the Karoo Basin. Tuffs from the Eccca and Beaufort Groups in the Karoo Supergroup are nearly indistinguishable from one another based on whole rock geochemical signatures. Since major element composition may be easily altered (Hastie *et al.*, 2007), immobile trace elements may better reflect the tectonic affinity of the tuff (Floyd and Winchester, 1978). Using a discrimination diagram based on Zr/TiO₂ (Fig. 3A; Winchester and Floyd, 1977) the Eccca tuffs ranged between dacitic and basaltic compositions, whereas Beaufort tuffs are basaltic to andesitic in composition. Low Nb/Y (<1) may reflect sub-alkaline compositions for both Eccca and Beaufort tuffs. Beaufort Group tuffs show less geochemical variability in Nb, Zr, Y, and Rb compared to Eccca Group tuffs, but tuffs from both Eccca and Beaufort Groups plot between Volcanic Arc (VAG) and intraplate (Within Plate Granites-WPG) granitoid fields of Pearce *et al.* (1984) (Fig. 3B, 3C). This is distinct from the arc driven magmatism of the Lower Choiyoi Group in South America (Kleiman and Japas, 2009), which have lower Nb, Zr, Rb, and Y concentrations that plot (Fig. 3B, C) in the Volcanic Arc and syn-collisional granitoid fields of Pearce *et al.* (1984).

Karoo tuffs generally are characterized by low Sr/Y (<20), La/Yb (<25), and Ce/Y (<4) values. Based on similar Nb (>10 ppm), Zr (>100 ppm), Rb (>100 ppm), Y (>60), Sr/Y (<25), La/Yb (<25), and Ce/Y (<4) values, Karoo Supergroup tuffs are most similar to Upper Choiyoi volcanics, which are interpreted to be produced by post-orogenic collapse magmatism (Kleiman and Japas, 2009). Karoo Supergroup tuffs, similar to Upper Choiyoi and Puesto Viejo volcanics,

contain low Sr/Y (<40) (Fig. 3E), which indicates sourcing by primitive melt that evolved in the absence of garnet, suggesting shallow, low-pressure magmatic sources (Moyen, 2009). Ce/Y serves as proxy for the ratio of light rare earth elements (LREE) to heavy rare earth elements (HREE) (Mantle and Collins, 2008), which can be controlled by the depth of crustal melting. The majority of Karoo tuffs, like the Upper Choiyoi, and Puesto Viejo volcanics have lower Ce/Y (<3.5). Several early Permian (>260 Ma) tuffs from the Eccca Group have elevated Ce/Y (>3.5), which is similar to early Permian Lower Choiyoi volcanism (Fig. 3F). The transition from high Sr/Y (>40), high Ce/Y (>3.5) magmatism in the early Permian to lower Sr/Y (<20), lower Ce/Y (<3.5) magmatism observed in later Permian-Triassic Karoo, Upper Choiyoi, and Puesto Viejo volcanic suites could suggest that primitive melt sources that fed Permian-Triassic volcanism in western Gondwana were sourced increasingly shallower depths beneath possibly thinner crust. The observed transition from high Sr/Y, high Ce/Y melts in the early Permian to lower Sr/Y, Ce/Y melts in the middle Permian through Early Triassic in South American igneous suites coincides with an interpreted shift from arc to extensional magmatism (Kleiman and Japas, 2009). Although no high Sr/Y tuffs were identified in the Karoo Supergroup, both Karoo tuffs and Choiyoi volcanics show a similar transition from high Ce/Y melts in the early Permian (Eccca Group) to low Ce/Y in the late Permian (Eccca) and Early Triassic (Beaufort) Karoo Supergroup.

Negative Eu anomalies in Upper Choiyoi and negative and positive Eu anomalies in Karoo tuffs (Fig. 3G) suggest the presence of plagioclase in a crustal melt source (Gao and Wedepohl, 1995). This geochemical shift might represent an increasingly shallower melt source for the Karoo tuffs, similar to the transition from deep-sourced, arc driven melting towards extensional magmatism that has been interpreted for South American volcanics. Although the similarity between South American and Karoo Supergroup tuffs could be used to support a similar parent volcanic center, a major shift to extensional magmatism likely occurred along the entire southern Gondwanan margin. Geochemistry from Permian-Triassic basalts in southeastern Gondwana has suggested coeval, Permian-Triassic crustal thinning associated with a shift towards extensional magmatism (Mantle and Collins, 2008). Therefore, a transition from subduction-driven arc magmatism towards extensional magmatism is not distinctive in identifying a specific volcanic center as the source of Permo-Triassic volcanic suites throughout southern Gondwana, but rather a transition from convergent towards extensional magmatism may have been margin-wide.

Zircon petrochronology of Karoo tuffs

Zircon trace element chemistry has been widely applied to characterize magma-chamber processes because zircon chemistry reflects the equilibrium melt composition from which it crystallized (e.g., Barth and Wooden et al., 2010; Claiborne et al., 2010). Since zircon is much

more resistant to weathering, reworking/detrital mixing, and post-depositional alteration than other mineral phases in a tuff, it may retain the most accurate information about the magmatic source composition of a tuff. Thus, zircon geochemistry from the Permian-Triassic tuffs in the Karoo Supergroup provides an opportunity to explore the temporal history of magmatism in southern Gondwana.

The decreasing Hf concentration in zircon ($\text{Hf}_{\text{zircon}}$) from an average of ~9300 ppm in the early Permian to ~7000 ppm in the Triassic suggests melts became increasingly primitive and less fractionated through time (Fig. 4A). The decrease in Ce/Ce* from an average of 67 in the early Permian to an average of 12 in the Triassic (Fig. 4C), with no clear major change in $\text{Ti}_{\text{zircon}}$ model temperatures (Fig. 4I) suggests a decrease in $f\text{O}_2$ to more reducing magma conditions. This may represent a transition from subduction-driven arc magmatism to extensional back-arc (e.g., intraplate) magmatism, since intraplate melts are more reduced than arc magmas (e.g., *Kelley and Cottrell, 2009*). Hf concentration and Ce/Ce*, proxies for melt evolution and $f\text{O}_2$ respectively, generally show a direct relationship (Fig. 4F), with lowest values reflecting chemically primitive melts present in the youngest Triassic zircon. Average Th/U in zircon increases from ~0.6 in the early Permian to 0.8 in the middle Permian through the Early Triassic, with an increasing number of high Th/U (>1.0) <~275 Ma grains. With little change in $\text{Ti}_{\text{zircon}}$ model temperatures, this suggests that middle-to-late Permian melts became less evolved, indicating derivation from a more mafic source (*Kirkland et al., 2015*).

Zr saturation and inheritance

More primitive, less evolved melts tend to have lower Si activity (i.e., quartz not present as a crystallizing phase) and generally have lower Zr concentration, as Zr is an incompatible trace element which generally increases with increasing melt evolution or differentiation. A shift towards more primitive melts (i.e., lower whole rock Zr, increase in $\text{Th/U}_{\text{zircon}}$, and decreasing Hf and Ce/Ce* in zircon) may explain the high occurrence of recycled zircon (i.e., zircon older than 260 Ma) in Beaufort tuffs compared to the underlying Eccra tuffs. Eccra tuffs display a wide range of whole rock Zr concentrations (129-453 ppm, mean: 292 ppm) that are on average higher than in the overlying Beaufort tuffs (118-258 ppm; mean= 205 ppm). Lower Zr abundance would lead to melts that are less likely to achieve Zr saturation, resulting in decreasing zircon crystallization. $\text{Ti}_{\text{zircon}}$ model temperature suggest that zircon from Karoo tuffs crystallized in melts between ~700-800°C, a temperature range where inheritance-rich magmas are common (*Miller et al., 2003*). The Zr saturation models of *Watson and Harrison (1983)* estimate that the minimum whole-rock concentration of Zr required to crystallize zircon in a sub-alkaline basaltic andesite is ~115 ppm at ~750°C and ~225 ppm at 800°C. Eccra Group tuffs contain a wide range of Zr, with a low Zr

population ranging from 130-347 ppm and a higher Zr population with concentrations between Zr 400-500 ppm. The bimodal nature of whole rock Zr concentrations (**Fig. 3D**) in Eccatuffs suggest that while some Permian magmatism may have been Zr-poor, periodic, high Zr magmatism may have driven zircon crystallization during Eccat time. Zr whole-rock composition of Beaufort tuffs (118-257 ppm) are all near the lower limit for zircon saturation concentrations at 700-800° C with no evidence for episodic high Zr magmatism, which suggest that little to no new zircon would crystallize in the magmatic source of the tuffs deposited in the Beaufort Group, particularly within melts above >750° C. New zircon growth may have been restricted (or absent altogether) during Beaufort-age magmatism, which would promote the occurrence of inherited grains in volcanic tuffs, as has been observed in Beaufort tuffs (*McKay et al.*, 2015). Increased inheritance of zircon would also account for the difficulty in obtaining reliable U-Pb zircon depositional age constraints in Beaufort tuffs.

Zircon correlation between South Africa and Gondwanan suites

Zircon REE data is not available in the published literature for potential correlative magmatic and volcanic suites from South American and Antarctica, therefore, correlations based on zircon chemistry are restricted to Th and U, since these elements are collected for all U-Pb zircon analyses. Since magmatic temperature, composition, and fractionation control Th/U in zircon ($\text{Th}/\text{U}_{\text{zircon}}$; *Kirkland et al.*, 2015), volcanic deposits that share a magmatic source should contain zircon that display comparable $\text{Th}/\text{U}_{\text{zircon}}$ trends with time (i.e. $^{238}\text{U}/^{206}\text{Pb}$ age). In Karoo tuffs, $\text{Th}/\text{U}_{\text{zircon}}$ evolved from exclusively low Th/U (<1.0) in the early Permian (300-270 Ma) to highly variable Th/U that range from >1.5 to 0.2 from the middle Permian to Triassic (<270 Ma). $\text{Th}/\text{U}_{\text{zircon}}$ from South America volcanic suites (*Spalletti et al.*, 2008; *Rocha-Campos et al.*, 2011; *Domeier et al.*, 2011; *Barredo et al.*, 2012; *Ottone et al.*, 2014) increases from low variability, dominantly low $\text{Th}/\text{U}_{\text{zircon}}$ (<1.0) in the Permian to high variability, high $\text{Th}/\text{U}_{\text{zircon}}$ (>1.0) during Triassic rifting (**Fig. 5**). High $\text{Th}/\text{U}_{\text{zircon}}$ (>1) may occur in zircon that crystallized from less evolved melts (*Kirkland et al.*, 2015), and the occurrence of a wide range of $\text{Th}/\text{U}_{\text{zircon}}$ compositions likely represents spatially and/or temporally dynamic variable magmatic source chemistry or temperatures (*Barth et al.*, 2013; *Kirkland et al.*, 2015).

Zircon from Karoo tuffs that contain high $\text{Th}/\text{U}_{\text{zircon}}$ (>1.0) range in age from 280–240 Ma (n = 45 of 364; ~12%). This contrasts with $\text{Th}/\text{U}_{\text{zircon}}$ from South American volcanic rocks, where high $\text{Th}/\text{U}_{\text{zircon}}$ (>1.0) is mostly restricted to Triassic (< 245 Ma) grains (n = 17 of 186; ~9%) that are associated with Puesto Viejo and Rincón rift volcanic rocks. Puesto Viejo volcanism also recycled older Permian [280-250 Ma] Choiyoi-age zircon “cargo” (**Fig. 5A**) resulting in a bimodal population of older, low $\text{Th}/\text{U}_{\text{zircon}}$ zircon between 0.3-0.5 and younger, high $\text{Th}/\text{U}_{\text{zircon}}$

Figure 5: Th/U vs U-Pb age (Ma) for Permian-Triassic zircon from (A) South America (*Spalletti et al., 2008; Rocha-Campos et al., 2011; Domeier et al., 2011; Barredo et al., 2012; Ottone et al., 2014*), (B) Karoo Supergroup-South Africa (*this study*), and (C) Antarctica (*Riley et al., 2012; Elliot et al., in press^a; Elliot et al., in press^b*). (A) High Th/U zircon (>1.0) in South America are related to Puesto Viejo and Rincón rift volcanism between <245 Ma. (B) Karoo tuffs also contain high Th/U zircon, but high $\text{Th}/\text{U}_{\text{zircon}}$ are significantly older (275–255 Ma) than those in South America. (C) Antarctic volcanogenic sediments also contain high Th/U Permian zircon suggesting a correlation between Karoo tuffs and volcanism adjacent to Antarctica. The presence of higher (>1.0) zircons, which are present in extensional magmatism in South America, might reflect an early phase of extensional magmatism near Antarctica.

zircon between 0.8–2.5. Similar high (>1.0) $\text{Th}/\text{U}_{\text{zircon}}$ is observed in 280–250 Ma zircon recovered from Beaufort and Eccca Group tuffs (*Fig. 5B*), which is not compatible with it being sourced from South America, where 280–250 Ma zircon are almost entirely devoid of high $\text{Th}/\text{U}_{\text{zircon}}$ (>1.0). We, therefore, propose that high $\text{Th}/\text{U}_{\text{zircon}}$ (>1.0) might record 270–250 Ma extensional magmatism elsewhere in Gondwana that is either not yet identified or is buried in the subsurface.

Permian zircon with high $\text{Th}/\text{U}_{\text{zircon}}$ are, however, present in volcanoclastic suites from Antarctica (*Fig. 5C*) are geochemically and temporally compatible with sharing a magmatic source with Karoo Supergroup tuffs. Mid-crustal plutons in the Antarctic peninsula (*Riley et al., 2012*) and volcanoclastic strata in the Central Transantarctic (*Elliot et al., in press^a*) and Ellsworth

Mountains (*Elliot et al.*, in press^b) contain zircon with variable $\text{Th}/\text{U}_{\text{zircon}}$ ranging from <0.01 to 1.7 . High Th/U , Permian-Triassic zircon (>1.0) from Antarctica comprise a similar proportion of the Permian-Triassic zircon population ($n=41$ of 428 ; $\sim 10\%$) with most high $\text{Th}/\text{U}_{\text{zircon}}$ (>1) occurring between 280 - 250 Ma, similar to Karoo tuff zircon. Based on this comparison, mid-crustal and volcanogenic sediment/tuffs from Antarctica most closely match the U-Pb age and Th/U composition of zircon in the Karoo Basin, suggesting that volcanic tuffs were sourced from Antarctica or elsewhere in Gondwana. Therefore, although the whole rock geochemistry of South American and Karoo Supergroup volcanic suites are comparable, the $\text{Th}/\text{U}_{\text{zircon}}$ of coeval zircon composition is not.

Implications for Gondwanan tectonism

The geochemistry of volcanic tuffs from the Karoo Supergroup suggests that the magmatic source for Karoo ashes was not a subduction-driven, continental volcanic arc sourced from beneath the middle to lower crust (>40 km). In contrast, geochemistry suggests that the tuffs were sourced from a system transitioning towards intraplate volcanism which is characterized by high Nb, Zr, Y, and lower Sr/Y, La/Yb, and Ce/Y. Intraplate, post-orogenic to rift related magmatism like began by ~ 270 Ma within southwestern Gondwana, ~ 30 Ma earlier than previously thought. Tuff whole-rock geochemistry records low Sr/Y (<20) and Ce/Y (decreasing from up to 5 in the middle Permian to <3 in the late Permian to Early Triassic), which suggests a lack of garnet and melts less enriched in LREE, respectively. This interpretation suggests a shallowing origin of melt (Fig. 4G, H) that is geochemically compatible with back-arc extensional volcanism (Fig. 4E). Zircon geochemistry further corroborates this hypothesis, with decreasing Hf (ppm) (Fig. 4A) suggesting more primitive, lower $f\text{O}_2$, less-hydrous melts (Fig. 4C), which would be expected during a transition from convergent arc to extensional magmatism. High $\text{Th}/\text{U}_{\text{zircon}}$ in Permian zircon may share a similar genetic history to Triassic rift-related zircon in the Puesto Viejo volcanics of South America, but temporally predate Puesto Viejo magmatism. Therefore, a poorly understood backarc magmatic zone may rest in the basement rocks of the extended, buried margins of the South American, Antarctic, or African continental shelf. Recent research in the Antarctic has inferred back-arc extension between the Antarctic Peninsula and other, outboard fragmented terranes of southern Gondwana and east Antarctica (Fig. 6; *Elliot et al.*, in press^b). *Elliot et al.* (in press^b) suggested the presence of Permo-Triassic back-arc basins along the boundaries between 1.) the Antarctic Peninsula and South Africa/Eastern Antarctica and 2) Mary Byrd Land and Eastern Antarctica. The geochemical and geochronological data presented here supports the presence of this hypothetical back-arc magmatism in western Gondwana, although little, direct physical evidence of this system remains exposed, nor has it been identified in the subsurface through borehole or geophysical data. Extensional magmatism in the Permian Antarctic-Karoo back-

Figure 6: Paleogeographic schematic map of southern Gondwana with the location of possible back arc magmatism (Elliot *et al.*, 2015^b) inboard of the Gondwanide magmatic arc.

arc appears to predate Triassic extensional magmatism in South America, indicating Permian-Triassic rifting may have migrated westward over time. The development of a Permian-Triassic age crustal weakness in the now-dissected crust of Gondwana may have ultimately played a role in the subsequent Jurassic rifting and break-up of the Gondwanan supercontinent along those pre-existing crustal boundaries. The break-up of Gondwana is typically considered to have begun along the boundary between Africa and Antarctica, just to the east of the Karoo Basin. The Karoo Igneous Province, located in the central Karoo Basin (Fig. 1) may be related to initial rifting of Gondwana (Encarnación *et al.*, 1996; Jourdan *et al.*, 2005). Jurassic rifting of western Gondwana would parallel the trend of the Permian-Triassic extensional feature with the southern Atlantic and Southern oceans opening along the same crustal boundary in a similar southeast to northwest trend. The hypothesized Permian-Triassic back-arc was located at the triple junction along which South America, Africa, and Antarctica rift apart, which suggests this missing tectonic feature may have played a pivotal role in Mesozoic rifting of Gondwana and morphology the tectonic plates generated from the break-up of Gondwana.

CONCLUSIONS

Based on tuff whole rock and zircon geochemistry and U-Pb geochronology, we propose that volcanic tuffs in the Karoo Basin may have been sourced by a post-orogenic to rift extensional magmatic system. Although Karoo tuffs have been linked to age-correlative South American

volcanism, zircon REE and Th/U geochemistry suggests that Karoo tuffs are genetically more similar to volcanic tuffs and volcanogenic sediment in Antarctica. Zircon geochemistry suggests that volcanism was sourced from increasingly reduced, primitive magmas in the middle to late Permian, while whole rock geochemistry shallower-sourced melts in an intraplate setting. We interpret these observations to be consistent with back arc magmatism. With the intense tectonic dissection of southern Gondwana during Mesozoic opening of the Indian and Atlantic oceans, large portions of the Gondwanan rock record are not accessible for field study and high detail geochemical-geochronology analyses, and no evidence for this possible back arc remains. Integrating U–Pb zircon and zircon REE geochemistry with whole rock tuff geochemistry allows us to reconstruct the magmatic history of Gondwana and missing tectonographic provinces. This study demonstrates the utility of zircon U–Pb and REE analyses for U–Pb zircon provenance of volcanic tuffs to provide insight beyond whole rock chemistry, which may be altered by post-eruptive processes. Currently, the global lack of zircon geochemistry datasets hinders wide-spread use of integrated zircon U–Pb and geochemistry as a correlation tool. Advances in microanalysis in the near future may facilitate a proliferation of zircon geochemistry, greatly enhancing provenance techniques in sedimentology, petrology, and tephrochronology.

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CHAPTER 3: TIMS, LA-ICPMS, AND SHRIMP PROVIDE DIFFERENT AGES FOR COMPLEX, POLYSTAGE ZIRCON: INHERITANCE OR Pb-LOSS?

ABSTRACT

Absolute ages for geologic strata are increasingly based on U-Pb isotope analysis of the mineral zircon using three commonly applied techniques: Chemical Abrasion Thermal Ionization Mass Spectrometry (CA-TIMS), Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICPMS), and Sensitive High Resolution Ion Microprobe (SHRIMP). We present 15 TIMS and 109 LA-ICPMS ages in addition to 13 depth profiled SHRIMP U-Pb ages for zircon grains from volcanic tuffs interbedded in sedimentary strata of the Permian-Triassic Karoo Supergroup in South Africa. Zircon selected for CA-TIMS analyses were chemically abraded prior to analysis, significantly reducing the effects of Pb-loss, while grains for LA-ICPMS and SHRIMP analyses were not treated. CA-TIMS results from the Upper Ecca Group are 264.7 to 274.5 Ma with a population of 10 (of 12) at ~268 Ma. These ages are comparable to 255 to 295 Ma LA-ICPMS results with a weighted mean age of 272.3 ± 1.2 Ma (MSWD=1.9; n=68) from the same stratigraphic interval. SHRIMP results from the same stratigraphic interval, however contain a significant population of <260 Ma (weighted mean= 253.7 ± 1.0 ; MSWD=1.7; n=53) grains in addition to a middle Permian population with a weighted mean= 267.9 ± 0.98 (MSWD=2.5; n=88) Ma. Three zircon from volcanic tuffs in the overlying Beaufort Group fluvial strata yielded TIMS ages of 256.3, 262.5, 267.6 Ma; the 256.3 Ma grain is younger than 100% of LA-ICPMS and 95% of SHRIMP ages from the same stratigraphic group. Cathodoluminescence (CL) images of zircon grains suggest polyphase zircon growth and Ti-in-zircon temperature estimates and Zr saturation temperatures are compatible with “cold, inheritance-rich” magmatism. Since LA-ICPMS and CA-TIMS require analyzing exponentially larger aliquots and SHRIMP microanalyses provide increased spatial resolution, SHRIMP analyses may resolve the age of thin, highly complex zircon overgrowths that are unresolvable by LA-ICPMS and CA-TIMS approaches.

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INTRODUCTION

U–Pb zircon geochronology has become one of the most widely used approaches to date magmatism, metamorphism, and sediment deposition (*Harley et al.*, 2007; *Lawton*, 2014; *Kirkland et al.*, 2015). Since zircon is chemically and mechanically robust it resists mechanical abrasion during magmatic and sedimentary transport and dissolution that may occur during surficial weathering or within long-lived magma systems. The durability of zircon results in grains being recycled through many generations of magmatism, erosion, and sedimentation (*Belousova et al.*, 2006; *Thomas*, 2011). Magmatic systems frequently recycle older, inherited grains over millions of years, which may provide misleading ages for magmatism in inheritance rich igneous rocks (*Compston*, 2000; *Compston and Gallagher*, 2012). Additionally, the high U content of zircon grains can result in radiation damage to the crystal lattice of the mineral. This damaged lattice can lead to loss of Pb through diffusion (*Mattinson*, 2005). Zircon grains may also have multiple stages of crystal growth during the complex evolution of a magmatic system, resulting in older cores with younger rims (*Belousova et al.*, 2006). This complexity is frequently encountered in zircon geochronology studies and can be addressed by (1) eliminating analyses that are interpreted as “too old”, (2) discounting high U, possibly discordant analyses that are “too young” and may be due to Pb loss, (3) removal of zircon through chemical or mechanical processes that are likely to be affected by Pb loss, and (4) employing microanalysis to target specific zones within zircon to avoid mixing different age domains within single grains.

Approaches to minimize the effects of inheritance, Pb loss, and age domain mixing are used differently depending on the analytical technique used to collect U–Pb isotope data: (1) Isotope dilution-thermal ionization mass spectrometry (ID-TIMS), (2) Laser ablation-inductively coupled mass spectrometry (LA-ICPMS), and (3) Secondary ion mass spectrometry (SIMS; this study and previously published SIMS ages are from the Sensitive High Resolution Ion Microprobe [SHRIMP], a SIMS instrument, at the Stanford Univ. Microanalytical Center). ID-TIMS analysis requires complete dissolution of the zircon grain by HF acid digestion, which precludes any spatial resolution of age domains within a grain. It is therefore crucial to analyze grains that show no evidence for complex zoning (*Parrish and Noble*, 2003). To avoid the potential effects of Pb-loss in ID-TIMS analyses, grains are commonly abraded mechanically using the air abrasion technique (*Goldich and Fischer*, 1986) or chemically using HF leaching steps and high temperature annealing (Chemical abrasion-CA-ID-TIMS; *Mattinson*, 2005).

Chemical abrasion can be applied to samples prior to SHRIMP and LA-ICPMS analyses (*Kryza et al.*, 2012). However, SHRIMP and LA-ICPMS microanalyses can be collected more rapidly and the effects of Pb-loss are commonly mitigated by eliminating high U, younger analyses

that do not form coherent age populations. For complex zircon grains, microanalytical techniques are preferred (*Parrish and Noble, 2003*) to avoid mixing of age domains yielding a misleading or erroneous result. LA-ICPMS and SHRIMP techniques allow for the analyses of exponentially smaller aliquots that are spatially sampled using laser ablation or secondary ion microprobe, respectively, to bombard selected domains. LA-ICPMS typically analyses a spot of ~30 μm wide and ~15 μm deep, while SHRIMP provides greater resolution in the form of a shallower analytical pit that is commonly ~25 μm wide but only ~2 μm deep. Spatial resolution during microanalyses comes at the expense of precision. TIMS analyses can yield ages with 1σ uncertainties as low as 0.025%. SHRIMP and LA-ICPMS analyses uncertainties can be an order of magnitude larger and generally range from an uncertainty of <1-4% (1σ). Typically, SHRIMP provides lower uncertainties; in this study SHRIMP analyses for the same suite of tuffs yielded an average 1σ uncertainty of 1.5%; while the average uncertainty for LA-ICPMS analyses is 2%. For rocks of Permo-Triassic age, that equates to LA-ICPMS analyses providing 1σ uncertainty ranges that are >2.5 m.y. greater than that of SHRIMP results.

To test the variability that can be observed within each analytical approach, we present LA-ICPMS, and TIMS ages for zircon from volcanic tuffs in the Karoo Supergroup strata of South Africa. Tuffs in the Karoo Supergroup are of Gondwanan affinity and commonly contain complex zircon populations. While some suggest that Permian-Triassic volcanic rocks from Gondwana contain large populations of recycled zircon (*Domeier et al., 2010; Ottone et al., 2014; McKay et al., 2015*) in younger Permian-Triassic tuffs, Pb-loss has also been ‘blamed’ to account for late Permian and Triassic zircon population in strata that is thought to be significantly older (>15 Ma) (*Lanci et al., 2013*). No evidence for Pb-loss, however, can be documented since younger ages do not correlate to higher U concentrations and age results are repeatable. To address the relationship of Pb-loss and inheritance in Gondwana tuffs, we compare TIMS and LA-ICPMS results to previously published SHRIMP U–Pb results from the same suite of tuffs (*McKay et al., 2015; in review*) and discuss the disparity in U–Pb ages from SHRIMP, LA-ICPMS, and TIMS ages, and note an increasingly likely of age component mixing with increased sample aliquot volume relative to decreasing spatial resolution.

GEOLOGIC BACKGROUND

The Karoo Basin of South African is composed of clastic strata deposited in the Gondwanide foreland basin that contain numerous interbedded tuff horizons. Tuff geochronology studies have focused on intervals in the marine Ecca Group and overlying, fluvial Beaufort Group. The results, however, have been paradoxical. Ecca Group tuffs record a younging upward sequence of U–Pb zircon ages that range from ~275 to ~250 Ma, as resolved by SHRIMP (*Fildani et al., 2007; 2009;*

McKay *et al.*, 2015). Overlying Beaufort Group tuffs, however, contain the same age range from ~268-252 Ma even though Beaufort strata postdate the underlying Eccia Group (Veevers *et al.*, 1994). Zircon from Beaufort Group tuffs have been dated using both TIMS and SHRIMP (TIMS: Coney *et al.*, 2007; Rubdige *et al.*, 2013; SHRIMP: Lanci *et al.*, 2013; McKay *et al.*, 2015; *in review*) and the results are complimentary. $^{40}\text{Ar}/^{39}\text{Ar}$ ages of detrital mica of <250 Ma from the lower Beaufort Group suggest, however that the Beaufort Group is likely Triassic (Hälbich *et al.*, 1983; Arosio, 2012), which supports the age interpretation of the underlying Eccia as early to late Permian (Fildani *et al.*, 2009; McKay *et al.*, 2015) and the zircon in Beaufort tuffs may be recycled and not represent absolute depositional ages (McKay *et al.*, 2015).

METHODS

TIMS

Of the 590 total SHRIMP analyses (presented by McKay *et al.*, 2015, *in review*), 16 grains ranging from 237 to 258 Ma were selected for TIMS analyses (Fig. 1). Grains were (1) picked from epoxy SHRIMP mounts and (2) pre-pretreated using chemical abrasion and thermal annealing as described by Mattingson (2005). Sample preparation and analyses was conducted by the ACTLABS Geochronology and Isotopic Geochemistry team. Grains were then (3) placed in Teflon vials along with the EARTHTIME ET535 ^{205}Pb - ^{233}U - ^{235}U -spike (Condon *et al.*, 2015) and (4) dissolved in HF at 220°C in a pressure vessel for 48-60 hours. (5) U and Pb ions were then separated using ion-exchange chromatography (Parrish and Noble, 2003) and (6) measured using a VG Sector 54 multi-collector TIMS. Due to the small grain size, 2 grains were completely dissolved or lost during chemical abrasion.

LA-ICPMS

Four samples were selected for U–Pb zircon analyses using the University of Arizona Laserchron Center LA-ICPMS. Zircon grains were mounted in epoxy and polished to expose a cross section of the grain. Samples were ablated using a Photon Machines Analyte G2 Excimer laser with a spot size of ~30µm (Gehrels *et al.*, 2008). Isotope ratios were corrected to the University of Arizona Sri Lanka zircon standard (Gehrels *et al.*, 2008). Analyses, like SHRIMP results, that are discordant, >>300 Ma, high common Pb, or high U are disregarded for further analysis.

SHRIMP

Grains that were interpreted to have multiple zircon domains were extracted from epoxy mounts and placed in an iridium mounts, with the external crystal face exposed. The grain was then bombarded by the SHRIMP ion-beam (under analytical conditions described in McKay

Figure 1: CL images of analyzed zircon grains reveals complex grains, which could correlate to polygrowth zircon, affecting higher volume sampling techniques.

et al., 2015) to obtain U-Pb isotopic ratios for small rims of Karoo tuff zircon. High common Pb or high U analyses, like LA-ICPMS results, were disregarded.

RESULTS

Results are grouped into three stratigraphic intervals to present a more representative dataset: (1) the Lower Ecca Group marine sediments, (2) Upper Ecca marine to marginal marine strata, and (3) Beaufort Group fluvial strata. While these units were likely deposited diachronously (Rubidge *et al.*, 2000), geochronology and the distribution of tuffs stratigraphically suggest only minor age variability (Fildani *et al.*, 2009; McKay *et al.*, 2015) across the field area.

TIMS

Zircon from tuffs in the Upper Ecca Group (N=3; n=11) yielded 9 of 11 Permian ages are within 1 m.y. of 268 Ma (Fig. 2B), with two outliers with ages of 264.74 and 274.55 Ma. While only a limited number of analyses were collected, zircon from tuffs in the Beaufort Group (N=2, n=3; Fig. 2C) produced a range of ages with no populations, with ages of 256.30, 262.50, 267.63 Ma; the uncertainties for these three ages are low 0.13, 0.13, and 0.47 m.y respectively, with no ages overlapping within uncertainty (Table 1).

Figure 2: A-C Kernel density estimate (KDE-light blue) and values (diamond with 1 sigma error bars) for TIMS ages for Lower Ecça, Upper Ecça, and Beaufort Group; D-F: KDE of LA-ICPMS ages for Lower Ecça (no data), Upper Ecça, and Beaufort Group; and G-I: KDE of SHRIMP ages for Lower Ecça, Upper Ecça, and Beaufort Groups. Relative sample volume, spatial resolution, and chemical abrasion treatment noted on y-axis; relative stratigraphic position on x-axis.

TABLE 1-TIMS U-Pb ages

Grain	Th/U	206Pb/238U	2 σ %	207Pb/235U	2 σ %	207Pb/206Pb	2 σ %	Corr. Coef.	206/238 Age (Ma)	2 σ
12ZA07-6				Dissolved during chemical abrasion						
12ZA07-8	0.66	0.042557	0.59	0.30720	7.43	0.05238	7.28	0.293	268.66	1.56
12ZA07-9	0.8	0.042454	0.05	0.30297	0.28	0.05178	0.26	0.407	268.03	0.14
13ZA72A-6	0.66	0.040560	0.05	0.28758	0.17	0.05145	0.14	0.522	256.3	0.13
13ZA72A-17	0.66	0.041560	0.05	0.29542	0.19	0.05158	0.17	0.456	262.5	0.13
14ZA116-1	0.66	0.041922	0.35	0.30556	4.35	0.05289	4.26	0.297	264.7	0.91
14ZA116-2	0.5	0.042758	0.87	0.33327	10.80	0.05655	10.59	0.281	269.9	2.31
14ZA116-6	0.78	0.042490	0.34	0.30925	3.41	0.05281	3.34	0.275	268.25	0.88
14ZA116-14	0.66	0.042526	0.08	0.30361	0.61	0.05180	0.59	0.322	268.47	0.20
14ZA116-24	1.25	0.043509	0.18	0.31853	2.08	0.05312	2.03	0.295	274.55	0.49
14ZA116-26	0.78	0.042534	0.16	0.30478	1.81	0.05199	1.77	0.295	268.52	0.42
14ZA116-29	0.78	0.042500	0.11	0.30389	1.07	0.05188	1.05	0.285	268.31	0.28
14ZA116-31	0.63	0.042544	0.1	0.30556	0.96	0.05211	0.93	0.312	268.58	0.27
14ZA116-37	0.70	0.042514	0.08	0.30410	0.82	0.05190	0.80	0.210	268.39	0.21
12ZA18-6	0.35	0.042390	0.18	0.30625	2.17	0.05242	2.14	0.284	267.63	0.47
12ZA23-11				Dissolved during chemical abrasion						
14ZA142-41	1.1	0.042734	2.93	0.38998	24.04	0.06622	23.08	0.38	269.76	7.75

Extended dataset available in Electronic Appendix.

LA-ICPMS

While no samples from the Lower Eccla Group were analyzed via LA-ICPMS, tuffs that were erupted during Lower Eccla deposition have tightly coherent zircon populations and, as such, do not show evidence of zircon recycling (*McKay et al.*, 2015). LA-ICPMS U–Pb zircon ages from the Upper Eccla Group (**Fig. 2E**; analytical results in **Appendix F**) range from 255–1070 Ma (N=3; n=73 concordant analyses). LA-ICPMS analyses fall into one coherent population that ranges from 260–283 Ma, with a weighted average of 272.3 Ma $\pm$ 1.2 (MSWD=1.9; n=68). A histogram of U–Pb of LA-ICPMS ages suggest two subpopulations at ~269 and ~279 Ma, however uncertainties on LA-ICPMS analyses preclude definitely splitting these populations. Two outlying ages of 255 and 257 Ma may represent minor Pb-loss or a geologically meaningful, albeit small population; these analyses, however, have 1 σ uncertainties of 8 and 5 Ma, respectively, that significantly overlap with 1 σ uncertainties of zircon analyses within the 260–283 Ma population.

Beaufort Group tuff zircon (**Fig. 2F**) yielded LA-ICPMS ages that range from 422 to 261 Ma (N=1; n=34 concordant analyses). Permian-Triassic grains form one population that falls between 261–282 Ma that forms a statistical peak around 271 Ma, with three, older outliers at 291, 300, and 422 Ma. No anomalously young grains were excluded and no observed Pb-loss ages were interpreted.

TABLE 2-SHRIMP Depth Profiled U-Pb ages

Spot	Comm Pb %206	U (ppm)	Th (ppm)	206/238 Age (Ma)	1 σ	207/206 Age (Ma)	1 σ	Disc%
12ZA18-13.1	9.8	873	244	207	4	-6	1362	3469
12ZA18-6.1	-0.1	410	149	250	1	211	102	-19
12ZA18-6.1	-0.1	374	121	254	2	-125	252	+307
12ZA18-6.1	0.0	363	136	234	3	225	48	-4
12ZA18-6.2	0.3	420	145	261	3	161	136	-62
13ZA72-1.1	0.6	183	181	235	3	41	334	-476
13ZA72-1.1	0.1	272	315	223	2	243	69	+8
12ZA23-10.1	53.5	244	478	464	7	2535	492	+94
12ZA23-11.1	13.9	258	196	246	2	1984	159	+88
12ZA23-9.1	42.9	436	492	474	15			
12ZA23-9.2	49.0	425	223	438	7	4584	1332	+92
12ZA23-9.3	33.7	425	458	492	9	4925	704	+90
12ZA61-4.1	2.8	491	359	264	4	1428	143	+82

Extended dataset available in Electronic Appendix.

SHRIMP

SHRIMP depth profiles of 7 grains from the Beaufort Group and 6 grains from the Eccia Group produced 6 high common Pb (>20% ^{208}Pb) and 7 low common Pb ages. The only low common Pb age from the Eccia Group was ~264 Ma, while low common Pb analyses from the Beaufort Group tuff zircon were, 223, 234, 235, 250, 254, 261 Ma (Table 2). Low common Pb analyses yielded moderate to low U concentrations less than 500 ppm.

DISCUSSION

TIMS and LA-ICPMS ages for tuff zircon in the Upper Eccia suggest early to middle Permian ages, while SHRIMP ages record late Permian to Early Triassic ages (Fig 2). The disparity in ages obtained using different instruments (TIMS, LA-ICPMS, SHRIMP-RG) appears to be restricted to zircon from tuffs in the Upper Eccia Group. While early and middle Permian ages are common throughout the stratigraphic section, late Permian zircon ages are restricted to Upper Eccia (Fildani *et al.*, 2009; McKay *et al.*, 2015) and upper-most Beaufort tuffs (Coney *et al.*, 2007; Rubidge *et al.*, 2013). The possible mechanisms responsible for the observed discrepancies between SHRIMP and TIMS/LA-ICPMS U–Pb age are: (1) instrumental bias (2) common Pb contamination (3) non-zircon inclusions within zircon grains (4) Pb-loss in Upper Eccia tuff zircon and (5) recycling and inheritance of older grains with small, micron-scale zircon overgrowths.

Instrumentational bias is unlikely since SHRIMP analyses corroborate Beaufort TIMS U–Pb ages, not only in this study, but in previous geochronology efforts (Coney *et al.*, 2007; Lanci *et al.*, 2013; McKay *et al.*, 2015). SHRIMP ages could be anomalously young (1) if the samples were contaminated with common Pb resulting in an anomalous common Pb correction, or (2) if the SHRIMP analyses hit a small inclusion, which are known to exist in volcanic zircon (Hoskin and Schaltegger, 2003). In contrast, LA-ICPMS and TIMS analyses would be less likely to be effected by small inclusions due to the increased volume of material sampled. During SHRIMP analyses, however, non-radiogenic ^{204}Pb and ^{208}Pb isotopes are measured, which provides a tool for quantitative assessment of common Pb contamination or the presence of non-zircon inclusions.

Cryptic Pb-loss could also account for younger, but still concordant ages from grains that have not been treated to remove damaged zones using chemical abrasion. In this case, LA-ICPMS and SHRIMP ages should both produce younger, Pb-loss effected ages, since both datasets were collected from untreated zircon grains. LA-ICPMS ages, however, did not yield the young ages observed using SHRIMP. Although Pb-loss can affect grains with a wide range of U concentrations (Mattinson, 2005), zircon from Karoo tuffs have relatively low U concentration (<1000 ppm) and no relationship was observed between U content and age. SHRIMP ages collected by depth profiling record low U (<1000 ppm), low common Pb zircon domains from a single crystal from the Beaufort Group tuff (12ZA18), become older with increasing age (Fig 2). This suggests multiple stages of successive zircon growth and that zircon age ranges may be due to protracted magmatism and recycling of zircon grains in increasingly younger, more evolved magmas. If Pb-loss were the controlling factor, age should decrease with increasing U concentration, and the three depth profiled ages from grain 12ZA18-6 all exhibit a spread of ages at similar U concentrations ~375–425 ppm).

Figure 3: TIMS, LA-ICPMS, and SHRIMP analyses of zircon from tuffs in the Lower Beaufort Group show a discrepancies between the results from each technique. LA-ICPMS ages (12ZA16) are generally older than TIMS ages from the same stratigraphic interval. SHRIMP analyses from 12ZA18 suggests a ~270 Ma population that correlates to LAICPMS ages and a smaller, ~238 Ma population while zircons from 12ZA16 yield ~265 Ma ages only, slightly younger than LA-ICPMS ages. SHRIMP depth profiled analyses (circles) of grains from 12ZA18 yielded domains younger than observed via TIMS, LA-ICPMS, or SHRIMP.

Figure 4: SHRIMP (yellow KDE) and TIMS (diamonds with error bars) analyses of zircons from 14ZA116 indicate that few SHRIMP analyses are within error of TIMS analyses. The lack of comparable age grains and scatter observed in both SHRIMP and higher precision TIMS suggest geologic age variability, i.e. multiple age populations.

SHRIMP analyses of sample 14ZA116 resulted in only a single grain at ~268 Ma that is compatible with its dominant TIMS age population of ~268 Ma. If Pb-loss were the culprit behind the age discrepancies between methods, then 14ZA116 would predictably contain a large population of ~268 ($\pm$ unspecified error) Ma SHRIMP ages, with a bell-shaped curve representing minor inheritance and Pb-loss. This distribution in ages, however, is entirely missing from the SHRIMP data for this sample (Fig. 4). In fact, the ~268 Ma TIMS age population corresponds to a statistical low in the SHRIMP U-Pb age distribution. The lack of TIMS age populations in SHRIMP age data is not consistent with Pb-loss in Karoo tuff zircon.

Zircon populations in igneous rocks can record multiple generations of growth, and significantly older grains (>5 m.y.) can be recycled in younger melts if (A) magmatic activity occurs rapidly or (B) if later stage magmatism remains near Zr saturation. The geochemistry of Karoo tuffs (McKay *et al.*, in review), suggests that magmatism responsible for volcanism recorded in the Karoo Supergroup contained intermediate to low Zr concentrations (<500 ppm), particularly in the Upper Eccia and Beaufort groups, where significant age discrepancies occur between SHRIMP and TIMS results. Zr saturation estimates (McKay *et al.*, in review; based on Watson and Harrison, 1983) suggest Zr saturation and therefore zircon crystallization would occur at Zr >115 ppm at 750°C and Zr >225 ppm at 800°C. Lower Eccia Group tuffs have Zr concentrations of 129-453 ppm, with more than 50% of tuffs having Zr >~225 ppm. At ~750°C, all Lower Eccia Group tuffs contain sufficient Zr to crystallize zircon, and over half contain >225 ppm and zircon growth would be predicted above 800°C (Fig. 5). Upper Eccia Group tuffs contain Zr ranging from 129-453 ppm, with 6 of 8 tuffs having Zr > 225 ppm, with only one sample with Zr concentrations <115ppm that would not predictably crystallize zircon. Beaufort Group tuffs Zr ranges from 118-258 ppm, and Ti-in-zircon suggest temperatures of no zircon crystallization and dissolution would dominate Beaufort tuffs at 800°C, while little zircon would form at the cooler magmatic temperatures of

Figure 5: Ti-in-zircon and whole rock Zr concentrations (from McKay et al., in review) suggest that Beaufort Group tuffs were sourced from Zr-depleted, cooler magmas and may have been unable to generate coeruptive zircon resulting in increased inheritance.

~750°C. Therefore, Beaufort Group tuffs would have been just at or well below Zr saturation levels. The observed Ti-in-zircon temperatures of ~750° C from the entire Karoo Supergroup suite of tuffs is comparable with a mean temperature for “cold, inheritance-rich” magmas of ~760° C (Miller *et al.*, 2003). Rapid magma generation and ascent would be required to prevent the dissolution and resorption of older, inherited zircon grains (Bea *et al.*, 2007). This phenomenon would account for Beaufort Group tuffs containing grains that are significantly older than zircon in the underlying Ecca Group. Only larger, inherited grains would persist in Beaufort age melts, smaller, young grains either failing to grow or being consumed during Zr-poor magmatic pulses. The low zircon yields reported in Beaufort samples (McKay *et al.*, 2015) further supports this hypothesis.

Discrepancies between SHRIMP and ID-TIMS ages have been resolved by other studies, albeit in rocks with drastically different zircon age populations. In the Humbolt Range, NV, Premo *et al.* (2008) resolved Cretaceous, 70-90 Ma igneous overgrowths on ~1500 and 2200 Ma cores in an deformed monzogranite that was previously dated at ~2500 Ma using ID-TIMS. Compston (2000) found multiple populations of U-Pb zircon ages via SHRIMP at 476, 450, 436, and 418 Ma. While ID-TIMS ages corroborate the older, ~450 and 476 Ma populations, Rb-Sr whole rock and K-Ar ages suggest late stage volcanism at ~420 Ma which is within error of the ~417 Ma populations, which made up ~30% of zircon from the sampled tuffs, suggesting small µm scale zircon rims were analyzed via SHRIMP but would have been removed during pre-TIMS abrasion (Compston, 2000). Cathodoluminescence (CL) of Karoo tuff zircon (Fig. 1 and 6) show complex, oscillatory zoned zircon, which commonly have discontinuities between cores and irregular rim

overgrowths (Fig. 6). These distinct breaks suggest periods of subdued zircon growth. CL imagery of zircon 14ZA116-2 (Fig. 6A) from an Upper Eccra tuff shows that the high uncertainty SHRIMP analysis of 243 ± 10 is fact mixed material between a low U (bright) and low U (dark) zone that are separated by an intra-grain discontinuity (red dashed line). TIMS analyses of the same grain also has a high uncertainty (for TIMS) of 2.31 m.y. These high uncertainties, along with CL images strongly suggest polyphase growth of zircon.

The Upper Eccra Group displays a significant population of SHRIMP ~ 268 Ma zircon ages, with a large component (27 of 205 concordant analyses) of pre-Permian grains and a significant population of late Permian-early Triassic grains ($n=53$). A group of 88 grains forms a population of 267.9 ± 0.98 Ma that coincides with the major peaks observed in LA-ICPMS and SHRIMP analyses (Fig. 2). Tuff 14ZA116, which contains a large population of 7 grains with a weighted mean of 268.5 ± 0.1 Ma (2σ ; MSWD=0.71) only contains 6 SHRIMP analyses (of 39) that are within 1σ error of this age population, with 23/30 Permian-Triassic grains younger than, outside of 1σ , 268.5 Ma. If cryptic Pb-loss were responsible for the age discrepancies, a bell-shaped population centered at ~ 268 Ma would be expected, with minor Pb-loss and inheritance forming the outliers. Instead, Upper Eccra Group tuffs contain a distinct population of late Permian (~ 252 -257 Ma) grains, which are not likely due to Pb-loss but may represent late Permian magmatic overgrowths on middle Permian zircon during subsequent magmatism. In addition to an abundance of Ordovician and older SHRIMP ages (McKay *et al.*, 2015), the presence of 256.3, 262.5, and 267.6 Ma grains as determined by TIMS in Beaufort tuffs, with uncertainties < 0.5 m.y. all but confirms zircon recycling in the Beaufort tuffs. The presence of Late Permian and Triassic detrital mica (246 and 228 Ma; Hälbig *et al.*, 1983; 252-254 Ma; Arosio, 2012) and detrital zircon (52% of Permian-Triassic detrital zircon reported were < 268 Ma; Arosio, 2012) in the lower Beaufort stratigraphically approximate to sample 12ZA18, precludes a middle Permian (267.6 Ma) age for this strata, as suggested by CA-TIMS zircon geochronology. Detrital mica ages, however, may provide more reliable age constraints, since mica crystallization would be entirely independent from zircon recycling systematics. To further test this hypothesis, chemical abrasion (CA) SHRIMP analyses could be performed, however, CA-SHRIMP has been shown to possibly yield erroneously old results compared not only to CA-ID-TIMS but also Rb-Sr isochron ages (Kryza *et al.*, 2014). Additional $^{40}\text{Ar}/^{39}\text{Ar}$ and Rb-Sr whole rock ages, however should be impervious to the effects of crustal recycling/inheritance and Pb-loss and may unravel to complexity of zircon-based, Karoo chronostratigraphy.

Figure 6: CL images, SHRIMP analyses (red circles), SHRIMP, and TIMS ages for selected zircon, with interpreted growth domains within the zircon grains (dashed red line). SHRIMP analyses from 12ZA18-6 are depth profiled ages and not visible in this CL.

CONCLUSION

Magmatic recycling, inheritance, and Pb-loss in zircon populations can obscure geologically meaningful geochronology results. Since only grains selected for TIMS analyses were treated to remove Pb-loss domains, younger ages that are exclusive to SHRIMP analyses and completely absent from LA-ICPMS and TIMS datasets suggest that the age discrepancies are controlled by spatial resolution and aliquot volume, with the SHRIMP analyses requiring the least amount of sample (by an order of magnitude) with the highest spatial resolution. By coupling CL imagery, microanalysis, with a characterization of the magmatic system, U-Pb zircon SHRIMP, LA-ICPMS, and TIMS ages record a story of significant crustal recycling and inheritance in the magmatic source of tuffs in the Karoo Supergroup, South Africa. Although cryptic Pb-loss cannot be ruled out, Ti-in-zircon and Zr saturation temperatures suggest the magmatic source was near Zr-undersaturation during the late Permian and Early Triassic (McKay et al., in review). This evidence suggests that inheritance may have strongly influenced the U-Pb age results.

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CHAPTER 4: STRUCTURAL AND MAGMATIC CONTROLS ON TURBIDITE SYSTEM DEVELOPMENT: KAROO BASIN, SOUTH AFRICA

ABSTRACT

We investigate the relationship between tectonism and sedimentation by integrating 587 new U-Pb detrital zircon analyses from 6 sandstones in the Karoo Basin with stratigraphic age controls from 590 U-Pb tuff zircon analyses from 23 volcanic tuffs. U-Pb detrital zircon from the Karoo Supergroup indicates that the source of the turbiditic, deltaic, and fluvial sediments was an active volcanic province, with lesser contribution from the nearby Cape Fold Belt. The depositional ages obtained from the turbidites of the Karoo Basin, based on U-Pb zircon tuff ages, and the published ages for Cape Fold Belt, suggest that influx of coarse clastic sediment is synchronous with deformation in the adjacent Cape Fold Belt during the Gondwanan Orogeny. Deformational age estimates from the Cape Fold Belt are comparable to age estimates for orogenic deformation and metamorphism around the southern margin of Gondwana, suggesting a wide-spread, synchronous, regional orogenic event. U-Pb zircon from volcanic suites in South Africa and South America coupled with U-Pb zircon from midcrustal plutonic rocks indicate that peak magmatism occurs between deformation events and predates turbidite deposition. Along this convergent margin, turbidite sedimentation appears to coincide with a major deformational phase, while magmatism is out-of-phase with deformation and turbidite sedimentation. While structural development of the Cape Fold Belt likely controlled the entry point of sediment into the basin, the main control on the influx of clastic sediment into the Karoo Basin may be increased volcanism along the Gondwanan margin. The large volume of volcanic detritus suggest synchronous sediment routes into the basin that could by-pass the emerging Cape Fold Belt. Ejecta could be transported via atmospheric transport independently from aqueous transport pathways and continental drainage divides to the

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leeward side of an orogenic belt. This easily eroded, volcanic-sourced sediment may have been focused along structures, controlling post-peak magmatic, syn-deformational turbidite deposition early in the basins history. Once erosion had removed the majority of air-fall ash material in the fold and thrust belt, sedimentation including increasing amounts of recycled orogen sediment.

INTRODUCTION

The Carboniferous-Jurassic Karoo Supergroup of southern Africa records shallowing-upward, deep-water to continental sedimentation in a tectonically controlled Gondwanan basin. The deep-water strata of the Eccu Group contains fine-grained turbidite systems that have been heavily studied to develop models for turbidite system evolution and commonly serve as outcrop analogues for turbidite petroleum reservoir studies (*Wickens and Bouma, 2000*). The development of these turbidites has been suggested to be controlled by many factors, including increased erosion in response to tectonic uplift, climatic variation, and eustatic fluctuation (*Bouma, 2000; Flint et al., 2011*). We present volcanic and detrital U-Pb zircon age constraints for turbidite systems and marginal marine sediments in the Eccu Group, U-Pb detrital zircon ages, integrated with previously published geo-thermochronology from the Cape Fold Belt (South Africa), Patagonia (South America), and the Antarctic Peninsula to investigate the relationship between sedimentation, the Gondwanide Orogeny, and active magmatism. From these data we observe a temporal and spatial correlation between initiation of turbidite systems in the Karoo Basin and deformation in the Cape Fold Belt, as part of the Gondwanide Orogeny. While the Cape Fold Belt likely controlled sediment entry point into the basin, the dominance of volcanic sediment in the detrital zircon record requires far-fetched transport from the continent margin, through an emerging metamorphic hinterland and fold belt into the basin. Based on these data, we suggest that the initiation of turbiditic deposition in the Karoo Basin may have been controlled by increased volcanism and the ensuing deposition of easily eroded volcanic ash in addition to structural development of the Cape Fold Belt, thereby providing a model for transporting active margin sediments across an active deformation belt.

Figure 1: Paleogeographic reconstruction of southern Gondwana (from McKay et al., 2015 and references therein) with margin-wide basins, fold and thrust belts, and magmatic provinces. Inset: Figure 2 Karoo Basin and Cape Fold Belt.

GEOLOGIC BACKGROUND

2.1 Tectonic setting

The Karoo Basin formed in response to Carboniferous-Triassic subduction along the active, Gondwanan margin (Veevers et al., 1994; Tankard et al., 2009), as part of a continent-wide foreland basin system (López-Gamundi and Rossello, 1998), extending across South America (Paraná and San Rafael basins), southern Africa (Karoo basins), Antarctica (Transantarctic basin), and Australia (Sydney basin) (Fig. 1). Basin subsidence was mechanically driven by a combination of orogenic, flexural loading driven by development of the Cape Fold Belt during the Gondwanide Orogeny (Cole, 1992; Catuneanu et al., 1998) and epeirogenic, dynamic topography (Pysklywec and Mitrovica, 1999; Catuneanu et al., 2002; Tankard et al., 2009), which is typical of a retroarc foreland basin.

2.2 Cape Fold Belt

The Cape Fold Belt deformed Paleozoic-early Mesozoic strata during the Cape Orogeny, as part of the more extensive Gondwanide Orogeny, along the southern and southwestern margin of the Cape of Good Hope (Fig. 2). The fold belt is comprised of a north-south trend, the Cedarberg

Figure 2

Figure 2: Schematic geologic map of South Africa with the Karoo Supergroup (greens; with turbidite depocenters in yellow), Cape Supergroup (blues and grays), crystalline basement, with generalized structural elements. After De. V. Wickens, 1992; Veevers et al., 1994; Johnston, 2002; Catuneanu et al., 2002.

arm, and an east-west trend represented by the Outeniqua and Swartberg arms. The east-west and north-south trends converge into the Ceres/Cape syntaxis (synformal oroclinal bend), which is structurally manifest by a northeast plunging anticlinorium. Along the eastern coast of the Cape of Good Hope, the foldbelt takes a cryptic, antitaxial (antiformal oroclinal) bend near Port Elizabeth (Johnston, 2000). Cape Orogeny, part of the larger Gondwanide Orogeny, occurred in sporadic pulses with deformation in the Cape Fold belt focused at ~278, ~259, ~247, ~230, ~215 Ma (Hälbich et al., 1983). Basement exhumation was further constrained at ~294, ~276, ~259, ~239, ~223 Ma (Gresse et al., 1992), in the western Cape Fold Belt and 260 ± 1 Ma in Cape Supergroup equivalents in eastern South Africa (Thomas et al., 1992). More recent age constraints on deformation pin the Cape Orogeny between 276-248 Ma (Hansma et al., in press). Correlative deformation belts in Patagonia and the Antarctic Peninsula also record deformation associated with the Cape/Gondwanide Orogeny; comparing more robust age constraints from throughout western Gondwana to contentious age controls in South Africa may therefore provide insight into timing of the Cape Orogeny. Late Paleozoic-Early Mesozoic metamorphism and syndeformation magmatism are also recorded in the Antarctic Peninsula, and thought to be related to the Gondwanide Orogeny. The

Figure 3: Outcrop photographs of (A.) turbidites within the Eccca Group in the Laingsburg subbasin, (B.) volcanic tuffs in the lower Eccca Group (tuffs marked with yellow arrows), (C.) chevron folds in quartzites within the Cape Fold Belt. Scales are approximate on A. & C.

oldest event associated with the Gondwanide Orogeny in the Antarctic Peninsula is an Rb/Sr whole rock age of 297 ± 3 Ma for a synmetamorphic pegmatite (Milne, 1990). U-Pb zircon ages for high U, metamorphic zircon overgrowth recording ~ 280 Ma (Riley *et al.*, 2012), 258 Ma (258 ± 5 Ma, Riley *et al.*, 2012; 258 ± 3 ; Millar *et al.*, 2002), and 206 ± 4 Ma (Millar *et al.*, 2002) metamorphism, providing direct age controls for the Gondwanide Orogeny. Syndeformational plutons were also emplaced at 272 ± 2 and 255 ± 5 (Riley *et al.*, 2012), further constraining the Gondwanide Orogeny. Granitic orthogneisses from the Antarctic Peninsula yielded hornblende K/Ar ages of 237 ± 9 and 243 ± 10 Ma (Rex, 1976), that may represent exhumation and cooling. Ordovician plutons underwent migmatization around ~ 228 (229 ± 3 , 227 ± 1), further suggesting that the Gondwanide Orogeny persisted until at least the Mid-Triassic (Millar *et al.*, 2002). Based on these age controls, deformation and metamorphism in the Antarctic Peninsula were active from 297-206 Ma, with pulses of deformation at 297, ~ 278 , ~ 258 , and 228 Ma, suggesting contemporaneous deformation throughout the western Gondwanan active margin.

2.3 Karoo Basin

The basin fill of the Karoo Basin is the Karoo Supergroup, which is comprised of a flysch to molasse style, shallowing upward sequence. Deposition in the Permian-Jurassic Karoo Basin initiated with glacial sedimentation of the Dwyka Group of the Karoo Supergroup during the late Paleozoic Gondwanan glaciation and the subsequent glacial retreat (*Veever et al.*, 1994; *Bangert et al.*, 1999). Following ice retreat the marine Ecca Group was deposited in an already deepwater environment, suggesting initial subsidence of the basin predates deglaciation. The basal units of the Ecca Group are deepwater mudstones of the Prince Albert, Whitehill, and Collingham Formations that are ubiquitous across the southern Karoo basin, with minor thinning of the Whitehill and Collingham formations over the Ceres syntaxis of the Cape Fold Belt (*de Beer*, 1992; *Scott et al.*, 2000), suggested syntectonic deposition. Above the Collingham Formation, lithostratigraphic successions within the Ecca Group are unique between three, distinct depocenters, the Tanqua, Laingsburg, and Ripon depocenters along the southern basin. Sediment supply into the basin can be described by two phases, where deposition of the Ecca Group and lower Beaufort (Adelaide and Tarkastad subgroups) is dominated by lithic-rich sediment, where lithic components decrease and quartz components increase in the upper Beaufort (*Johnson*, 1991). The compositional immaturity of the Ecca and lower Beaufort was interpreted to reflect a transitional/dissected arc source, while the compositionally more mature upper Beaufort was likely sourced from the nearby Cape Supergroup (*Johnson*, 1991; *Scott*, 1999). This is atypical of a traditional foreland basin, where the dominate sediment source is the adjacent fold belt (*Scott*, 1997). Several explanations have been proposed to explain the lack of Cape Supergroup sediments within the Ecca and lower Beaufort, including a lack of subaerial exposure of the early Cape Fold Belt, decreased erosion of the Cape Fold Belt in response to an orogenic rainshadow (*Scott*, 1997), and absence of the Cape Fold Belt during Ecca and lower Beaufort time (*Tankard et al.*, 2009). Recent U-Pb detrital zircon from the Ecca and Beaufort Groups, however record a major population of Cape Supergroup sourced zircon within the Ecca Group, previously interpreted to be devoid of Cape Supergroup sediments (*Vorster*, 2013; *Dean*, 2014.), suggesting that the Cape Fold Belt was subaerial exposed

Figure 4: Chronostratigraphic ages from Fildani et al., 2007; 2009; Lanci et al., 2013; McKay et al., 2015; in press. A tuff free interval is denoted where no tuffs were found (McKay et al., 2015).

and eroded. This fold belt sourced material was then transported into the Karoo Basin, but diluted with an overwhelming influx of immature, active margin sediment, masking the compositional signal of the adjacent, compositionally mature fold belt.

2.2.1 Tanqua Subbasin

The Tanqua subbasin in the west contains undeformed, shallow dipping strata is bound by the Ceres syntaxis to the east and by the Cedarberg Range of the Cape Fold Belt to the west. The

Collingham Formation is overlain by the mudstone dominated Tierberg Formation. Deposition of the Tierberg muds was followed by development of 5 distinct, very fine-to-fine grained turbidite systems, defined as Fans 1-5 (*Hodgson et al.*, 2006) within the Skoorsteenberg Formation, which is comprised of fine-grained sand turbidites and interfan mud sediments (*Hodgson et al.*, 2006; *Wild et al.*, 2009) which onlap onto the Ceres syntaxis to the southeast. Marginal marine and deltaic sediments of the Kookfontein and Waterford formations overly the Skoorsteenberg turbidites, followed by the conformable deposition of the fluvial Abrahamskraal Formation of the terrestrial Beaufort Group, representing the transition of the basin from underfilled to overfilled.

2.2.2 Laingsburg Subbasin

The Laingsburg subbasin in the southwest contains broad to tightly folded Karoo strata that are bound to the northwest by the Ceres syntaxis and to the south by the Swartberg Range of the Cape Fold Belt. The Collingham formation is overlain by mudstones and mass-transport complexes within the Vischkail formation. The Vischkail formation is overlain by multiple very fine-to-fine grained turbidite systems, defined as Fans A-G (*Flint et al.*, 2011) within the Laingsburg and Fort Brown formations, which are comprised of fine-grained sand turbidites and interfan mud sediments (*Sixsmith et al.*, 2004) which onlap onto the Ceres syntaxis to the northwest. Transition from marine to terrestrial occurs in the overlying marginal marine and deltaic sediments of the Waterford formation and fluvial Abrahamskraal Formation of the terrestrial Beaufort Group.

2.2.3 Ripon Subbasin

In the Ripon subbasin, the stratigraphy of the lower Eccia Group is comparable to the Laingsburg and Tanqua subbasins, with the Dwyka Group overlain by the Prince Albert, overlying Whitehill, and ash-rich Collingham formations. The basal Ripon Formation is characterized by fine to medium grained turbidite fans with associated interfan muds. The first turbidite fan appears to have been deposited directly upon, perhaps unconformably, the Collingham (*Veevers et al.*, 1994). The muds sequences observed above the lower Eccia Group in Tanqua and Laingsburg

(Tierberg and Vischkail fms.) are distinctly absent from the Ripon area, which may suggest that Ripon turbidite systems developed prior to turbidite development in the western Karoo Basin (Catuneanu et al., 2002).

3.2 Chronostratigraphic controls from U-Pb zircon ash ages

3.2.1 Tanqua Subbasin

U-Pb zircon ages from tuffs in the Eccra Group within the Tanqua subbasin (Fig. 4) range from 267 to 250 Ma (Fildani et al., 2007; 2009; Lanci et al., 2011; McKay et al., 2015) and young upward, suggesting that these ages may, at best, represent near-synchronous depositional ages of the tuffs, and by proxy the host strata. Above the younging upward series of tuffs in the Eccra Group lies a stratigraphic interval that does not contain any recognized volcanic tuffs that may correlate to a decrease in 250-241 Ma volcanism in Gondwana (Veevers, 2004; McKay et al., 2015). Air-fall tuffs are again recognized above this interval in the Beaufort Group, although these ages are chaotic (McKay et al., 2015) and may relate to increased volcanic recycling (McKay et al., 2015), which can be observed in South American correlative volcanic deposits (Domeier et al., 2011). Ages in the Beaufort Group tuffs are, therefore considered maximum depositional ages, although one tuff contained 3 grains (McKay et al., 2015; McKay et al., *in press*) that are ~236 Ma, which may form the most reliable age constraint for lower Beaufort deposition. This age is compatible with $^{40}\text{Ar}/^{39}\text{Ar}$ ages of detrital mica in the lower Beaufort Group of 250, 246, and 228 Ma (Hälbich et al., 1983; Arosio, 2012), that suggests a Triassic age for the lower Beaufort Group.

3.2.2 Laingsburg Subbasin

Tuffs within the Eccra Group in the Laingsburg subbasin, similar to Tanqua subbasin, range from 265 to 249 Ma based on U-Pb zircon ages (Fildani et al., 2007; 2009; McKay et al., 2015). A tuff-free interval was also observed above a ~249 Ma tuff, which correlates to the tuff-free interval in the Tanqua subbasin. Above this interval U-Pb ages are ~274-260 Ma and contain increased number of older, xenocrystic grains, suggesting the age controls for the upper Eccra and Beaufort

Figure 5. Kernel density estimate plots and pie charts for U-Pb detrital zircon ages for the (a) Beaufort Group sandstones <240 Ma, (b) Waterford Formation and upper Eccca Group strata interpreted to be ~240-250 Ma based on the location of the tuff gap, (c) Eccca Group strata below the tuff gap (>250 Ma), (d) the Cape Fold Belt, and U-Pb zircon from tuffs in the (e) Beaufort and (f) Eccca Groups. There is an increase in Cape Fold Belt sourced zircon inversely proportional to a decrease in volcanic sourced grains through time/up-section. Zircons <300 Ma are dominantly ~270 Ma in age, coincident with a peak in volcanism in southern Gondwana.

groups should be considered maximum depositional ages, while tuffs below the tuff gap contain more coherent zircon populations, which are more indicative of representing depositional ages of the host strata.

3.3.3 Ripon Subbasin

Eccca Group deposition in the Ripon subbasin is between ~269 Ma and 251 Ma. The lowest age constraints from the Eccca Group are from the Ripon Subbasin and include ages from the interbedded tuffs and mudstones of the Collingham Formation and range from 268-262 Ma.

Figure 6: Chronostratigraphic schematic crosssection across the Karoo Basin, with deformation events of the Cape Orogeny, structural trends (at bottom), and margin magmatism (zircon kernel density plot-red; individual analyses-yellow plotted against relative Th/U). Tuff deposition (indicated by black bars) are most common during peak magmatism. Following peak magmatism, the D3 deformation event of the Cape Orogeny is coeval with the initiation of turbidite deposition in the Tanqua, Laingsburg, and Ripon depocenters.

Turbidite deposition in the Ripon subbasin appears to be coeval with turbidite deposition elsewhere in the Karoo basin and began ~262 Ma and continued through ~251 Ma. Above 251 Ma strata, a tuff gap is present. Above this gap, recycled zircon ages are present, although Triassic ages (~235, 223 Ma) were obtained from 2, low common Pb, low U, depth profiled analyses on grains from the upper Koonap Formation.

4. Discussion

4.1 Sediment source for the Karoo turbidites

The source of the Karoo turbidite sediment may hold clues as to the genetic history and influence of tectonism on the submarine fan systems as well as offer insights on the evolution of the Gondwanan margin. Sandstone petrography reveals that the Eccu Group and lower Beaufort Group are significantly rich in lithics compared to the Cape Fold Belt (*Johnson, 1991*) and include heavy minerals such as garnet, biotite, and tourmaline, which suggests that sediment was supplied from both the active margin magmatic province and the Gondwanide fold-thrust belt (i., 2003). Sm-Nd isotopic analysis (Nd model ages and ϵ_{Nd} values; *Andersson et al., 2003*) also suggest a mixed provenance between juvenile, Permian sediment and older, Paleozoic, Proterozoic, and Archean sediment sources. Detrital zircon U-Pb ages from submarine fans within the Laingsburg and Ripon formations corroborate this model, with ~25-65% of zircon populations consisting of Carboniferous-Triassic grains, likely from margin volcanic sources, and 35-75% of zircon representing recycling of pre-Carboniferous material, likely from the erosion of Paleozoic strata exposed during the Cape/Gondwanide Orogeny (*Vorster, 2013; Dean, 2014*). While the percentage of zircon should not be confused as a proxy for relative proportions of sediment from each source (*Moecher and Samson, 2006*), these data suggest that A) the Cape Fold Belt/Gondwanide foldbelt was subaerially exposed and constituted a significant sediment source for the Karoo turbidites, and B) large volumes of volcanic sediment were capable of being transported from the margin to the basin. Previous work has suggested that the abundance of volcanoclastic sediments requires a sediment transport pathway through the Cape Fold Belt (*Scott et al., 2000*). However, volcanic

grains are, by nature, explosively erupted, allowing transport over topographic features. Western Cordillera U.S. volcanic grains have been observed in modern Gulf of Mexico strata, even though they must have been sourced from west of the US continental divide (*Fildani et al., in prep.*). Therefore, the provenance of volcanic grains is not restrained by aqueous transport and does not require sediment transport pathways. The volcanic grains observed in the Karoo basin may have been erupted, transported, and deposited on the emerging Cape Fold Belt. These easily erodable volcanic sediments would then be preferentially swept into the basin. The abundance of volcanic tuffs in the lower Ecca (~270-265 Ma) and an increase in volcanic zircon 270-260 Ma (**Fig. 6**) confirms increased just prior to turbidite deposition in the Karoo basin. The evolution of Karoo sediments from (A) Permian, volcanic margin dominated to (B) Permian-Triassic, fold belt dominated may be, in part, related to the flushing of 270-260 Ma grains out of the early Cape Fold Belt in late Permian turbidites. Volcanic grains in later fluvial deposition may be recycled from earlier >260 Ma volcanic sediments, with increased proportions of Cape Supergroup-sourced sediments.

The relationship between deformation and sedimentation has been previously explored, but without absolute age controls for the Karoo strata. The strata below (Whitehill & Collingham formations; *de Beer, 1990; 1992*) and above (Waterford Fm; *Wickens and Bouma, 2000*) over the Ceres syntaxis suggests that syntaxial development persisted through multiple deformational phases, likely ~276 to post-245 Ma. The partitioning of the turbidite strata in both the Tanqua and Laingsburg subbasins by the syntaxis suggests major topographic relief that must have developed following after deposition of the underlying strata, and likely during the deposition of Karoo turbidite fans (*Scott et al., 2000*), which would coincide with the largest deformation event within the syntaxis. Based on this link with tectonism, turbidite initiation throughout the Karoo Basin has been suggested to be caused by: A) increase in sediment supply through orogenic uplift and erosion (*Visser, 1992*), B) increased basin subsidence and accommodation (*Cole, 1992*), C) increased paleoslope during deformation (*Visser, 1992*). Within the western basin, turbidites in the Tanqua and Laingsburg subbasins are partitioned by the Ceres syntaxis that bounds each subbasin

to the southeast and northwest respectively, suggesting development of the turbidite fan systems is during or after initial deformation and uplift in the Cape Fold Belt (*de Beer, 1992; Scott et al., 2000*). At a much smaller scale, individual submarine fan deposition may have been controlled by Cape Fold Belt structural trends within the Laingsburg subbasin. Within the deformed Laingsburg strata, the areal extent of submarine fans along with the paleoflow trends and facies distribution suggest that subtle, emerging Cape Fold Belt structures created basin floor topography that routed fans within the basin (*Sixsmith et al., 2004*).

4.3 Deformation and Sedimentation

Scott (1997) suggested that immersing structures of the Cape Fold Belt may have acted as pathways for sediment into the subbasins based on the spatial relationship and paleoflow directions in the western Karoo Basin. This hypothesis would require a pathway 100's of km's in length, however volcanic transport could deposit large volumes of volcanoclastic sediment across a region. Since turbidite deposition is associated with oroclinal bends, it is possible that these structures may have acted to focus volcanic sediment that previously accumulated elsewhere in the foldbelt and hinterland (**Fig. 2; 6**). Furthermore, prior to development of the antitaxial and syntaxial structures, the foldbelt may have acted as a barrier to coarser sediment entering the basin.

If deformation is synchronous, each deformation phase may have resulted in different effects upon subsidence and sediment influx. The first deformation phase (D1 at 296 Ma or earlier?) would have resulted in crustal loading and subsidence in the Karoo basin prior to early Permian deglaciation of Gondwana. Additional subsidence would have occurred during the second orogenic episode (D2 at 276 Ma), which is roughly coeval with final retreat of Gondwanan glaciers, as recorded by initial Prince Albert formation deposition. Following D2, the Cape Fold Belt may have acted as a sediment barrier, restricting sediment influx to muds, as observed in the mudstones of the Prince Albert, Whitehill, and Collingham formations. The earliest development of the Ceres

syntaxis occurred in the form of minor deformation and uplift during this event, creating the basin floor topography recorded by minor thinning of the Whitehill and Collingham formations (*de Beer, 1992; Scott et al., 2000*). At the onset of the D3 event, the Ceres syntaxial and Port Elizabeth antitaxial bends in the Cape Fold Belt experienced major syndeformational metamorphism, recorded as pervasive development of cleavage mica and crystalline basement exhumation dated at ~259 Ma (*Hälbich et al., 1983; Gresse et al., 1992*). The initial development of turbidites in the Tanqua (263 Ma), Laingsburg (~263 Ma), and Ripon (~262 Ma) depocenters coincides with (or slightly predate, within error) this deformation event. The distribution of turbidites approximate to, and structurally confined by major oroclinal bends suggests that high sedimentation rates associated with turbidite development may in fact be related to sediment channeling and focusing instead of increased erosion associated with uplift or climatic factors, potentially representing a previously unexplored tectonic control on turbidite development.

Deformation associated with D4-D5 are indistinguishable based on age, and this period in the Cape Orogeny is dominated by thrust fault development within the Cape Fold Belt and folding of the Ecca and lower Beaufort Groups (*Hälbich, 1992*). The chaotic nature of ages for deformation in the Cape Fold Belt are echoed in the age constraints for the Gondwanide Orogeny in correlative deformation belts throughout Gondwana (**Fig. 6**), suggesting that the nature and timing of Triassic deformation associated with the Gondwanide Orogeny may be comparable along the Panthalassan margin, unlike Permian deformation that appears to be isolated to distinct events throughout Gondwana.

Even within the Permo-Triassic basins of Gondwana, deformation focusing and channeling may not be isolated. Oroclinal bends have been recognized elsewhere along the Gondwanide foldbelt, as have Permo-Triassic marine and lacustrine turbidite sequences. The Ventana Fold Belt in northern Argentina is a western correlative of the Cape Fold Belt and contains a syntaxis that may be the western edge of a crustal salient possibly controlled by inherited basement structure (*Pangaro and Ramos, 2012*). If oblique structure development did control turbidite system initiation

in the Karoo Basin, it is likely that sediment influx into basins north of the Ventana Fold Belt would have also been controlled by syntaxial sediment focusing and channeling. Further studies, however, are required to test that hypothesis in the Sauce Grande, Cuyo, and Parana basins that are adjacent to the Ventana Fold Belt. Likewise, turbidites throughout Permo-Triassic Gondwanan basins may share a spatial and relationship with active structures in the adjacent deformation belts, which requires continued investigation.

CONCLUSION

Although there is significant error in age controls on sedimentation and deformation, a temporal relationship is apparent between deformation associated with the Gondwanide Orogeny and initiation of turbidite systems within the Karoo Basin. Based on the age controls of deformation early basin subsidence occurred in response to early deformation and crustal loading associated with the D1 event at ~294 and D2 event at ~276 Ma creating an underfilled foredeep. Turbidite systems development in the Tanqua, Laingsburg, and Ripon depocenters coincides with the D3 deformation event at ~259 Ma, which is following a period of increased volcanism. Given the spatial relationships between the Tanqua and Laingsburg depocenters with the Ceres syntaxis and Ripon depocenter with the Port Elizabeth antitaxis, major development of oroclinal bends in the Gondwanide Fold Belt occurred during the ~259 Ma, D3 deformation, with the syntaxial/antitaxial structures focusing and channeling sediment from the magmatic arc into the basin, with only minor detrital input from the emerging Cape Fold Belt. Increased volcanism ~265 Ma would have dispersed large volumes of easily transportable volcanic material across the fold-belt and other hinterland areas. Therefore, the high sedimentation rates thought to control turbidite development may not have been directly linked to increased erosion of the adjacent orogenic belt, but instead may be a result of an increased volume of poorly lithified volcanic-source sediment focused by a structurally confined sediment pathway. This model is consistent with the minor presence of Cape Supergroup sediments in the marine Eccu Group of the Karoo Supergroup, the age constraints for deformation along the Panthalassic margin of Gondwana, chronostratigraphic constraints

on turbidite deposition, and field observations within the sedimentary strata. If applicable in other tectonically-influence foreland basins, our model predicts 1) early sedimentation may be dominated by organic-rich, deepwater mudstones and shales, with the fold belt acting as a barrier to coarse, clastic sediment, 2) increased volcanism may correlate to increased turbidite frequency, and 3) syndeformational turbidite deposition may record distinct deformational events, including oroclinal bend development, which may be difficult to constrain using traditional geo/thermochronology techniques. This demonstrates that the temporal and spatial extent of sedimentation might reveal a more complete tectonic history of adjacent tectonically active margins.

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SUMMARY

U-Pb zircon geochronology coupled with zircon and whole rock/tuff geochemistry from volcanic tuffs in the Karoo Basin provide insight into the tectonic history of southern Gondwana. While there is a discrepancy between age results from different geochronology techniques, new SHRIMP age controls challenge the interpretation of the Permian-Triassic boundary in the Karoo. Whole rock and zircon geochemistry suggest that these tuffs record a transition from subduction driven to extensional, back arc magmatism. Based on zircon geochemical correlations, the tuffs in South Africa were likely sourced from magmatism in or near western Antarctica. Increased eruptivity and deformation along the active margin of Gondwana may have influenced the development of turbidites which were sourced heavily from volcanic material.

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Tectonics • Field Geology • Geochronology • Petrology • Stratigraphy • Structure • Microanalysis

EDUCATION

West Virginia University (WVU), Morgantown, WV

Fall 2011-December 2015

Doctor of Philosophy (Ph.D.), Geology, Advisor: Dr. Amy Weislogel

Cumulative WVU GPA: 4.00

A.B.D.

Specialty: Tectonics, petrology, geochronology, volcanic stratigraphy, geochemistry, structural geology, volcanology

University of Alabama (UA), Tuscaloosa, AL

Jun 2007-Aug 2011

Master of Science (M.S.), Geology, Advisor: Dr. Harold H. Stowell

August 2011

Graduate GPA: 3.89

Metamorphic and igneous petrology, geochemistry, geochronology, structural geology

Bachelors of Science in Geology (B.S.G)

August 2009

Cumulative UA GPA: 3.69

Cumulative Major GPA: 3.759

PROFESSIONAL EXPERIENCE

Geological Survey of Alabama

October 2014-Present

Geologist-Geologic Investigations Division

National Cooperative Geologic Mapping Program-STATEMAP

Focus on Southern Appalachian Valley and Ridge & Piedmont

Mineral resources

External Research Internship:

StatOil *in residence* at Univ. Texas at Austin w./ Dr. A Fildani and Dr. D. Stockli Summer 2014

Zircon U-Pb and (U-Th)/He geo/thermochronology as an advanced provenance tool

Tectonic controls on continental drainages: Gulf of Mexico, Eastern Canada, Pyrenees

Laser-Ablation ICPMS Split Stream U-Pb and REE data collection technique

Internships:

Chevron Energy Technology Company-Hydrocarbon Charge Team

Summer 2013

Petroleum system modeling: West of Shetlands, offshore U.K.

Chevron Energy Technology Company-Hydrocarbon Charge Team

Summer 2012

Integrating seismic attributes, geochemistry, and basin modeling

Teaching/Research experience:

Research assistant, WVU

Spring 2013 to Fall 2014

Sedimentology & Stratigraphy (GEOL311) lab instructor, WVU

Spring 2012, Spring 2013

Field Course (GEOL404) graduate instructor, WVU

Summer 2013

Planet Earth (GEOL102) lab instructor, WVU

Fall 2011, Spring 2012

Earth Through Time (GEOL102/104) lab instructor, WVU

Fall 2012, Spring 2013

Mineralogy (GEO210) lab instructor, UA

Fall 2009, Fall 2010

Field Course (GEO495) graduate instructor, UA	Summer 2010
Research assistant/isotope lab manager, UA	Spring 2010 & 2011, Summer 2011
Undergraduate research assistant/field assistant, UA	Spring 2008-Summer 2009

AWARDS, GRANTS, AND PROFESSIONAL SERVICE

AAPG Foundation U.S. Military Veterans Scholarship Committee Member	2015
Convener/Chair: Techniques in Geochronology & Microanalysis (V33D, 34A, 41A)	A.G.U. 2014
Chesapeake Energy Fellow	2011-2012; 2013-2014
Session Chair: Contractual Tectonics and Fold-Thrust Belts	AAPG ACE Pittsburgh 2013
West. Virg. Univ. Milton T. & Doris E. Heald Promising Researcher Award	2013
Society for Sedimentary Geology Foundation Research Grant recipient	2012-2013; 2013-2014
Richard W. Beardsley Research Grant recipient (A.A.P.G.)	2013-2014
SEPM Wilson Medal Selection Committee Member	2013
Geological Society of America Research Grant recipient	2012-2013
Arthur A. Meyerhoff Memorial Grant recipient (A.A.P.G.)	2012-2013
Graduate Student Recruitment Coordinator, W.V.U. Dept. of Geology and Geography	2012
Outstanding teaching award, Univ. Alabama Dept. of Geological Sciences	2009-2010

PUBLICATIONS (1 published, 1 in review, 3 in final prep/coauthor review, and 3 in prep):

- **McKay, M.P.**, Weislogel, A.L., Fildani, A., Brunt, R., Hodgson, D., Flint, S. (2015), U-PB zircon tuff geochronology from the Karoo Basin, South Africa: implications of zircon recycling on stratigraphic age controls, *International Geology Review*, .
- **McKay, M.P.**, Coble, M., Hessler, A.M., Weislogel, A.L., Fildani, A. (*in review*), Petrogenesis and provenance of distal, airfall tuffs in the Permian-Triassic Karoo Basin, South Africa: a window into a dissected, magmatic province, *Geosphere*
- **McKay, M.P.** & Jackson, W.T., Jr., (*in final prep*), Tectonic stress regime recorded in zircon geochemistry, *Lithosphere*.
- Fildani, A., **McKay, M.P.**, Stockli, D.F., Clark, J.D., Weislogel, A.L., Dykstra, M., Hessler, A.M., (*in final prep/coauthor review*) Insights into the ancient Mississippi drainage system from detrital zircons analyses of the modern Mississippi deep-sea fan, *Geology*.
- **McKay, M.P.**, Stowell, H.H., Gray, K.D., Schwartz, J.J. (*in coauthor review*) Sm-Nd garnet, U-Pb zircon geochronology, and P-T paths from the Salmon R. suture zone, west-central Idaho: Constraining terrane accretion events?, *Tectonics*.
- **McKay, M.P.**, Osborne, W.E., (*in prep*), Geology of the Howelton 7.5 minute quadrangle, Etowah County, Alabama, Geological Survey of Alabama 7.5 minute quadrangle series.
- **McKay, M.P.**, Fildani, A., Weislogel, A., Dean, J. (*in prep*), Structural and magmatic controls on turbidite system development: Karoo Basin, South Africa, *Basin Research*.
- **McKay, M.P.**, Weislogel, A., Fildani, A., (*in prep*) TIMS, LA-ICPMS, and SHRIMP provide different ages for complex, polystage zircon: Inheritance of Pb-loss?, *Terra Nova*.

TECHNICAL PRESENTATIONS:

- **McKay, M.P.**, Weislogel, A.L., Fildani, A. (2014), Permian-Triassic Magmatism Along the Southern Gondwana Margin: Correlating Proximal and Distal Volcanic Deposits, *AGU 2014 Abstract #27627*.
- Fildani, A., **McKay, M.P.**, Stockli, D.F., Clark, J.D., Weislogel, A.L., Dykstra, M., Hessler, A.M., (2014), Insights into the ancient Mississippi drainage system from detrital zircons analyses of the modern Mississippi deep-sea fan, *AGU 2014 Abstract #24921*.
- Clark, J.D., Stockli, D.F., **McKay, M.P.**, Thomson, K., Puigdefabregas, C., Castelltort, S., Dykstra, M., Fildani, A. (2014), Using U-Pb Detrital Zircon to Identify Evolution of Sediment Drainage in the South Central Pyrenean Foreland Basin, Spain, *AGU 2014 Abstract #30546*.
- Bollen, E. M., Stowell, H. H., Schwartz, J. J., **McKay, M. P.** (2014), New P-T Paths for Metamorphism of Amphibolite from the Salmon River Suture Zone, Idaho, *GSA 2014 Abstract # 249883*.
- **McKay, M.P.**, Weislogel, A.L., Fildani, A. (2014^a), Using zircon REE compositions to aid in U-Pb zircon volcanic ash age interpretation in the Karoo Supergroup of South Africa, *Goldschmidt 2014*.
- **McKay, M.P.** (2014^b), Sedimentary perspectives on orogenesis: magmatism and deformation recorded in the Karoo Basin, South Africa, *GSA 2014 Penrose Conference: Linkages and feedbacks in orogenic processes – a conference honoring the career of Robert D. Hatcher, Jr., Ashville, NC*.
- Weislogel, A.L., **McKay, M.P.**, Dean, J., Fildani, A. (2013), Perspectives and perils of using U-Pb zircon geochronology to constrain stratigraphic age: lessons from the Permian-Triassic Karoo basin, South Africa, *A.G.U. Fall Meeting 2013*, abstract #V13D-2646.
- **McKay, M.P.** (2013), Tectonic controls on turbidite distribution, Invited technical presentation given to: 1) Shell-Clastic Research Team, 2) Chevron-Clastic Stratigraphy R&D, 3) Chevron-Energy Tech. Company Geosciences Division Technical Talk
- **McKay, M.P.**, Dean, J., Weislogel, A.L. (2013), The impact of high precision age controls in basin modeling for tectonic studies: Karoo Basin, South Africa, *2013 AAPG ACE Presentation*.
- **McKay, M.P.** (2012), Resolving tectonic subsidence from quantitative basin modeling: Karoo Basin, South Africa, *AAPG Search and Discovery article #90157*.
- **McKay, M.P.**, Weislogel, A.L., Dean, J., Fildani, A. (2012), Integrating burial history and isostatic models to evaluate tectonic subsidence models: Karoo Basin, South Africa, *GSA Abstracts with Programs*, 44 (7).
- Stowell, H.H., **McKay, M.P.**, Schwartz, J.J., Gray, K.D. (2011), Loading and metamorphism within the Salmon River suture zone, west-central Idaho. *GSA Abstracts with Programs*, Vol. 43, No. 5.
- **McKay, M.P.**, Weislogel, A.L., 4 others (2011^a), Evolution and petrogenesis of Gondwanan volcanism from ashes within the Eccu & Beaufort Grps: Karoo Basin, S. Afr., *A.G.U. Fall Meeting 2011*, #V31F-2597.
- **McKay, M.P.**, Stowell, H.H., Schwartz, J.J. (2011^b), P-T-t paths from the Salmon River suture zone, west-central Idaho: Continental growth by arc accretion, *GSA Abstracts with Programs*, Vol. 43, No. 4, p. 76.

Short Courses/Field Trips:

GSA Penrose Field Conference: Linkages and feedbacks in orogenic processes	2014
Chevron ETC Turbidite Field Course: Karoo Basin, S. Africa (as a graduate instructor)	2012
UCLA-NSF Secondary Ion Probe Microanalysis Workshop	2012
SEPM and UL-Lafayette 3-D seismic interpretation, Lafayette, La	2011

Short Courses/Field Trips (cont.):

GSA Rocky Mtn/Cordilleran Meeting field trip, Evolution of the Blue Mtns, OR and ID	2011
AAPG Imperial Barrel Award workshop, San Antonio, TX	2010
GSA Annual Meeting field trip, Transect through the Salmon River suture zone, Idaho	2009

Selected Field Experience/Study Areas:

Appalachian Mountains	Geol. Survey of Alabama
South Africa (western Gondwana remnants)	WVU Ph.D. research
Western Cordillera	
Idaho, Oregon, Washington	Univ. of Ala. M.S. research, field assistant
New Mexico and Colorado	Univ. of Ala. field course graduate instructor
South Dakota and Montana	WVU field course graduate instructor
Atlantic Canada and Liberia	Chevron, seismic attribute analysis, basin modeling
West of Shetlands and North Sea	Chevron, petroleum exploration, basin modeling
Gulf of Mexico, Atl. Canada, Pyrenees	StatOil, detrital geochronology for provenance

RESEARCH:

Ph.D. (2011-Present), West Virginia Univ.: Geochronology and petrogenesis of volcanic tuffs from the Karoo Basin, South Africa: Implications on basin evolution, Gondwanan magmatism, and deformation

- Secondary Ion Microprobe (SIMS/SHRIMP) U-Pb zircon geochronology of ashes used for age controls
- Geochronology-defined Permian-Triassic boundary lies stratigraphically >1 km below the biostratigraphically-defined P-Tr boundary (strata is >10 m.y. younger than thought).
- Zircon geochemistry used to interpret petrogenetic history of the Gondwanan margin
- Results demonstrate that REE composition can be used to identify subpopulations of zircon for data interpretation; may have implications on interpretation methods for ash geochronology.
- Chemical mapping using Electron Probe Microanalysis (EPMA) Wave-Length Dispersive (WDS) and Energy Dispersive (EDS) mapping/imaging of zircon grains has led to more precise U-Pb analyses by eliminating analysis of grains with potential Pb-loss and focusing on chemical populations of interest.
- Karoo Basin Invited Petroleum Industry Presentations: Chevron Energy Technology Company, Chevron Clastic Stratigraphy R & D Team, Shell Clastic Stratigraphy Research Group

M.S. (2009-2011), Univ. of Alabama: Constraining metamorphic events in a polydeformational, polymetamorphic accreted island-arc terrane, Salmon River Suture Zone, West Central Idaho.

- Integrated study: EPMA, X-ray Fluorescence (XRF) Spectrometry, Inductively Coupled Plasma Mass Spectrometry (ICPMS), Thermal Ionization Mass Spectrometry (TIMS) Sm-Nd geochronology, and field mapping/surveying
- Results suggest thrust loading controls metamorphic pulses, not accretion events.
- Resolved long-lived orogenic events (>30 m.y.) associated with assembly of the western Laurentia.

PROFESSIONAL MEMBERSHIPS:

Geological Society of America
American Association of Petroleum Geologists
Society for Sedimentary Geology (SEPM)
American Geophysical Union
Mineralogical Society of America
Deep Time Institute, Board Member
Alabama Geological Society

CERTIFICATIONS AND TRAINING

National Association of Underwater Instructors (NAUI) Certified Scuba Diver (Open Water)
High Ropes Course/Repelling/Mountaineering experience

MILITARY OPERATIONS/LOGISTICS/MANAGEMENT

During a four-year enlistment (May 2003-May 2007) in the United States Coast Guard I honorably attained the rank of Petty Officer Second-Class (E-5) in the Yeoman rating. Duties as an active duty NCO included:

- Deck Seaman (E-3), USCGC Decisive (Aug. 2003-Mar. 2004); Duties/qualifications included: deck, heavy machinery & small boat operation/maintenance, damage control & weapons qualified, helm/lookout, quartermaster, battle medic.
- Yeoman (E-4; E-5), PSC Topeka (April 2004-May 2007); Auditor; Travel Support Team Assistant Team Leader, meritorious service supporting personnel throughout the field, fleet, and in-theatre operations.

Selected Awards & Commendations (individual awards in **BOLD**):

- Armed Forces Service Medal for meritorious service during Hurricane Katrina response
- **Commandants Letter of Commendation** for outstanding performance of duty
- Presidential Unit Citation for Hurricane Katrina preparation, response, and recovery
- **Good Conduct Medal**
- Meritorious Unit Citation-Operations
- Coast Guard "E" Ribbon
- **Pistol Marksmanship**
- Global War on Terrorism Medal
- National Defense Medal

REFERENCES

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Dr. Harold Stowell, Professor, M.S. advisor University of Alabama hstowell@geo.ua.edu

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Further References and Supporting Documentation Furnished Upon Request

Appendix A: UTM locations for samples

WGS1984 Datum		(E)	(S)
Sample ID	Zone	Easting	Northing
09LGC-01	34H	499591	6321783
09LGC-04	34H	499614	6321821
09LGV-01	34H	499653	6321854
09LGV-02	34H	499631	6321986
09LGV-04	34H	499587	6322155
09TBT-01	34J	381726	6493248
09TBT-04	34J	382146	6494390
12ZA05B	34H	468362	6339683
12ZA07	34H	405027	6393983
12ZA08	34H	404351	6394562
12ZA10	34H	404352	6349738
12ZA12	34H	436541	6414097
12ZA16	34H	438007	6414177
12ZA18	34H	443935	6419135
12ZA19	34H	643534	6333624
12ZA22A&B	34H	643542	6334491
12ZA23	34H	643558	6334551
12ZA45	35H	467444	6345581
12ZA46	35H	466973	6345303
12ZA54	35H	465066	6324815
12ZA55	35H	465184	6324766
12ZA60	35H	464923	6325655
12ZA61	35H	463796	6328315
13ZA67	35H	464802	6325212
13ZA72A	35H	465441	6361597
13ZA75B	35H	466981	6345320
13ZA76	35H	467384	6345555
13ZA77	35H	463485	6335583
13ZA78A	35H	464393	6327210
13ZA79	35H	464762	6325361
13ZA93A	34H	456880	6397502
14ZA116A	34H	498466	6322788
14ZA121	34H	461573	6331369
14ZA128A	34H	443811	6418968
14ZA129A	34H	568541	6447715
14ZA130A	34H	560632	6428940
14ZA141	34H	373943	6266659
14ZA142	34H	373774	6265469
14ZA154	35H	464299	6326517
14ZA161A	35H	484158	6404712
14ZA162A	35H	481244	6401608
14ZA168A	35H	271276	6441037
BLOUKRANS	34H	492420	6343593
SUTHER	34H	465375	6412116

Appendix B: U-Pb zircon SHRIMP analyses

Spot name	U (ppm)	Th (ppm)	²⁰⁷ Pb corrected			²⁰⁴ Pb corrected								
			²⁰⁶ Pb/ ²³⁸ U Age (Ma)	1σ		²⁰⁷ Pb/ ²⁰⁶ Pb Age (Ma)	1σ	% Disc	²⁰⁷ Pb*/ ²³⁵ U	% error	²⁰⁶ Pb*/ ²³⁸ U	% error	error corre.	
12ZA23-13.1	251	184		2	249		357	68	+31	0.292	3.1	0.0395	0.7	0.2
12ZA23-32.1	235	173		4	249		172	150	-46	0.269	6.6	0.0394	1.5	0.2
12ZA23-12.1	96	39		7	250		437	195	+43	0.305	9.2	0.0398	2.7	0.3
12ZA23-5.1	77	42		3	254		580	483	+57	0.332	22.3	0.0406	1.9	0.1
12ZA23-9.1	207	136		8	257		208	120	-24	0.281	6.0	0.0406	3.1	0.5
12ZA23-38.1	231	142		2	257		163	206	-58	0.276	8.9	0.0405	0.9	0.1
12ZA23-1.1	605	886		4	257		317	37	+19	0.297	2.4	0.0408	1.7	0.7
12ZA23-7.1	708	697		8	257		239	40	-8	0.286	3.5	0.0407	3.1	0.9
12ZA23-25.1	73	38		5	260		214	337	-21	0.285	14.7	0.0410	2.2	0.1
12ZA23-11.1	625	239		6	260		282	34	+8	0.295	2.9	0.0412	2.5	0.9
12ZA23-4.1	420	384		6	260		290	58	+10	0.296	3.4	0.0413	2.3	0.7
12ZA23-16.1	705	381		5	262		287	32	+9	0.298	2.4	0.0415	1.9	0.8
12ZA23-29.1	454	469		11	262		-	-	-	0.078	198.6	0.0397	3.0	0.0
12ZA23-24.1	718	704		8	263		331	43	+21	0.305	3.5	0.0417	3.0	0.8
12ZA23-6.1	649	413		4	264		207	43	-28	0.289	2.5	0.0417	1.7	0.7
12ZA23-8.1	853	714		4	264		249	33	-6	0.295	2.1	0.0419	1.6	0.7
12ZA23-14.1	494	486		4	264		255	61	-4	0.296	3.1	0.0419	1.6	0.5
12ZA23-3.1	1162	812		5	265		286	25	+7	0.301	2.0	0.0420	1.7	0.8
12ZA23-10.1	588	243		4	265		283	48	+6	0.301	2.5	0.0420	1.4	0.6
12ZA23-2.1	230	181		4	265		246	130	-8	0.296	5.9	0.0420	1.6	0.3
12ZA23-22.1	291	227		5	266		315	67	+16	0.306	3.5	0.0421	2.0	0.6
12ZA23-21.1	771	1135		2	266		266	38	-0	0.300	1.8	0.0422	0.8	0.5
12ZA23-31.1	1302	1156		1	267		346	85	+23	0.312	3.8	0.0424	0.6	0.2
12ZA23-33.1	621	341		2	268		311	41	+14	0.308	1.9	0.0425	0.6	0.3
12ZA23-36.1	461	423		2	269		265	68	-1	0.303	3.1	0.0426	0.9	0.3
12ZA23-15.1	203	127		5	269		297	71	+10	0.308	3.7	0.0427	2.0	0.5
12ZA23-34.1	793	644		5	270		311	38	+13	0.310	2.5	0.0428	1.9	0.8
12ZA23-30.1	279	199		2	270		350	119	+23	0.316	5.3	0.0429	0.8	0.2
12ZA23-26.1	403	373		2	271		84.5	183	-224	0.281	7.7	0.0428	0.8	0.1
12ZA23-23.1	264	222		3	274		261	105	-5	0.308	4.7	0.0434	1.1	0.2
12ZA23-27.1	836	322		2	276		278	34	+0	0.313	1.6	0.0438	0.6	0.4

Spot name	U (ppm)	Th (ppm)	²⁰⁷ Pb corrected				²⁰⁴ Pb corrected						
			²⁰⁶ Pb com %	²⁰⁶ Pb/ ²³⁸ U Age (Ma)	1σ	²⁰⁷ Pb/ ²⁰⁶ Pb Age (Ma)	1σ	% Disc	²⁰⁷ Pb*/ ²³⁵ U	% error	²⁰⁶ Pb*/ ²³⁸ U	% error	error corre.
12ZA23-28.1	565	397	-0.13	282	3	245	52	-16	0.315	2.5	0.0447	1.1	0.4
12ZA23-37.1	256	190	0.63	283	2	420	115	+33	0.343	5.2	0.0451	0.9	0.2
12ZA23-35.1	411	425	0.06	470	3	482	38	+3	0.592	1.9	0.0756	0.7	0.4
12ZA54-7.1	238	159	2.979	215	8	294	221	+27	0.245	10.4	0.0340	3.7	0.4
12ZA54-5.1	613	981	0.181	241	9	301	46	+20	0.276	4.1	0.0382	3.6	0.9
12ZA54-12.1	339	391	0.101	257	7	305	73	+16	0.294	4.2	0.0407	2.7	0.6
12ZA54-6.1	449	412	0.325	258	4	295	60	+13	0.295	3.1	0.0409	1.6	0.5
12ZA54-14.1	479	527	0.260	260	5	346	54	+25	0.304	3.1	0.0413	2.0	0.6
12ZA54-8.1	764	609	0.038	261	2	324	47	+20	0.302	2.2	0.0414	0.6	0.3
12ZA54-11.1	254	168	-0.242	262	5	221	96	-19	0.289	4.6	0.0414	1.9	0.4
12ZA54-15.1	707	937	0.045	263	3	285	38	+8	0.299	2.1	0.0417	1.3	0.6
12ZA54-16.1	362	422	0.148	266	3	348	58	+24	0.312	2.9	0.0423	1.3	0.4
12ZA54-9.1	616	798	0.137	269	3	302	43	+11	0.308	2.2	0.0427	1.2	0.5
12ZA54-4.1	483	374	-0.103	270	3	210	52	-29	0.296	2.6	0.0426	1.3	0.5
12ZA54-1.1	497	381	-0.126	271	5	253	58	-8	0.304	3.1	0.0430	1.8	0.6
12ZA54-13.1	471	539	0.027	277	2	323	42	+15	0.320	1.9	0.0439	0.6	0.3
12ZA54-3.1	682	372	0.626	431	12	479	91	+10	0.541	5.0	0.0692	2.9	0.6
12ZA54-10.1	330	77	-0.010	456	3	459	38	+1	0.567	1.9	0.0732	0.7	0.4
12ZA54-2.1	488	110	0.119	458	10	455	31	-1	0.570	2.7	0.0736	2.3	0.9
12ZA61-7.1	733	510	1.099	232	10	248	130	+7	0.259	7.0	0.0366	4.2	0.6
12ZA61-9.1	860	679	1.399	234	8	285	80	+18	0.265	5.0	0.0370	3.6	0.7
12ZA61-14.1	993	745	0.645	246	7	306	81	+20	0.282	4.5	0.0390	2.7	0.6
12ZA61-25.1	1067	941	2.52	249	1	340	90	+27	0.290	4.0	0.0395	0.6	0.2
12ZA61-12.1	588	405	0.108	253	4	249	44	-2	0.282	2.6	0.0399	1.8	0.7
12ZA61-22.1	772	681	1.93	253	4	178	305	-43	0.274	13.1	0.0400	1.4	0.1
12ZA61-29.1	407	189	0.57	256	2	345	78	+26	0.299	3.5	0.0406	0.7	0.2
12ZA61-10.1	403	217	0.682	257	5	376	82	+32	0.304	4.2	0.0408	2.0	0.5
12ZA61-24.1	754	739	0.59	259	2	297	60	+13	0.296	2.7	0.0411	0.8	0.3
12ZA61-11.1	579	538	-0.075	261	6	189	39	-38	0.284	2.8	0.0412	2.2	0.8

Spot name	U (ppm)	Th (ppm)	²⁰⁷ Pb corrected				²⁰⁴ Pb corrected						
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12ZA61-8.1	371	292	-0.094	264	4	208	55	-27	0.289	2.8	0.0417	1.5	0.5
12ZA61-15.1	847	606	0.035	264	4	238	36	-11	0.293	2.3	0.0417	1.7	0.7
12ZA61-30.1	267	166	-0.14	264	2	74.2	119	-260	0.273	5.1	0.0416	0.9	0.2
12ZA61-4.1	476	279	0.036	264	5	299	57	+12	0.302	3.3	0.0419	2.1	0.6
12ZA61-28.1	756	518	0.22	265	2	299	50	+12	0.303	2.3	0.0420	0.8	0.4
12ZA61-1.1	485	315	0.276	266	5	287	46	+7	0.302	2.7	0.0421	1.8	0.7
12ZA61-26.1	578	141	-0.21	266	2	164	49	-63	0.286	2.2	0.0420	0.7	0.3
12ZA61-6.1	453	277	0.070	267	4	194	57	-38	0.291	3.0	0.0422	1.7	0.6
12ZA61-23.1	775	746	-0.05	268	3	168	56	-61	0.289	2.7	0.0424	1.2	0.4
12ZA61-5.1	309	213	-0.043	269	3	202	69	-33	0.294	3.2	0.0425	1.3	0.4
12ZA61-27.1	508	459	0.23	271	3	323	52	+16	0.314	2.6	0.0430	1.3	0.5
12ZA61-13.1	721	194	-0.045	274	4	276	31	+1	0.310	2.1	0.0434	1.6	0.8
12ZA61-21.1	109	122	-0.16	516	5	394	112	-31	0.624	5.1	0.0830	1.1	0.2
12ZA61-2.1	166	152	-0.048	520	10	564	62	+8	0.684	3.5	0.0841	2.0	0.6
12ZA61-3.1	216	130	0.041	1108	18	1102	20	-1	1.972	1.9	0.1875	1.7	0.9
12ZA07-11.1	686	947	7.427	181	7	606	377	+71	0.240	17.9	0.0289	3.9	0.2
12ZA07-25.1	422	289	0.068	237	8	197	68	-21	0.259	4.4	0.0375	3.2	0.7
12ZA07-9.1	368	207	0.128	246	8	225	73	-9	0.271	4.6	0.0388	3.4	0.7
12ZA07-6.1	501	233	0.136	251	5	265	61	+6	0.282	3.3	0.0397	2.0	0.6
12ZA07-7.1	239	113	0.040	252	5	286	98	+12	0.287	4.7	0.0399	2.0	0.4
12ZA07-20.1	435	304	-0.080	253	5	176	44	-45	0.273	2.8	0.0399	2.0	0.7
12ZA07-8.1	263	99	0.268	254	4	247	111	-3	0.283	5.1	0.0402	1.7	0.3
12ZA07-3.1	391	188	0.133	259	4	299	73	+13	0.296	3.6	0.0411	1.6	0.4
12ZA07-24.1	325	161	0.151	262	2	328	1263	+20	0.303	55.8	0.0415	3.8	0.1
12ZA07-5.1	296	173	-0.003	263	4	274	71	+4	0.297	3.5	0.0416	1.6	0.5
12ZA07-21.1	275	113	0.038	263	3	317	60	+17	0.304	3.0	0.0418	1.3	0.4
12ZA07-10.1	800	735	-0.005	266	4	284	32	+6	0.303	2.1	0.0422	1.6	0.7
12ZA07-4.1	482	214	0.046	267	4	291	49	+8	0.305	2.7	0.0424	1.6	0.6
12ZA07-22.1	1110	1238	0.377	273	2	283	66	+3	0.310	3.0	0.0433	0.7	0.2
12ZA07-23.1	539	355	-0.087	276	2	216	37	-28	0.304	1.8	0.0437	0.8	0.4

Spot name	U (ppm)	Th (ppm)	²⁰⁷ Pb corrected				²⁰⁴ Pb corrected						
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12ZA07-26.1	460	267	1.670	294	2	433	84	+32	0.359	3.9	0.0469	0.8	0.2
12ZA07-2.1	214	75	0.394	539	10	663	49	+19	0.746	3.0	0.0876	1.9	0.6
12ZA07-1.1	113	75	-0.266	745	11	581	65	-29	0.998	3.4	0.1219	1.6	0.5
12ZA46-4.1	602	776	7.980	229	11	272	777	+16	0.259	34.2	0.0363	4.3	0.1
12ZA46-10.1	240	311	0.121	253	5	217	98	-17	0.278	4.6	0.0399	1.8	0.4
12ZA46-1.1	123	89	0.481	257	5	315	203	+19	0.296	9.2	0.0408	2.1	0.2
12ZA46-5.1	300	230	-0.087	258	4	264	70	+2	0.290	3.5	0.0408	1.7	0.5
12ZA46-3.1	474	385	-0.104	260	4	247	58	-6	0.290	2.9	0.0411	1.5	0.5
12ZA46-7.1	211	149	0.144	276	4	184	97	-51	0.299	4.5	0.0436	1.5	0.3
12ZA46-6.1	148	110	-0.165	285	7	250	147	-15	0.319	6.9	0.0452	2.6	0.4
12ZA46-2.1	945	514	0.145	325	11	365	22	+11	0.385	3.6	0.0518	3.4	1.0
12ZA46-9.1	664	412	0.105	464	9	495	22	+7	0.588	2.1	0.0747	1.9	0.9
12ZA46-8.1	412	51	-0.104	478	3	442	31	-8	0.591	1.5	0.0768	0.7	0.4
12ZA46-11.1	146	84	-0.070	523	9	512	53	-2	0.671	3.0	0.0846	1.8	0.6
12ZA22B-4.1	988	404	5.519	244	5	353	129	+31	0.286	6.0	0.0387	1.9	0.3
12ZA22B-7.1	231	79	1.355	248	8	291	164	+15	0.282	8.0	0.0392	3.5	0.4
12ZA22B-6.2	474	196	0.140	258	4	284	58	+9	0.293	3.0	0.0408	1.6	0.5
12ZA22B-5.1	1113	508	1.396	259	5	389	51	+34	0.308	3.0	0.0411	1.9	0.6
12ZA22B-1.1	115	61	0.919	261	3	-189	432	+241	0.240	17.3	0.0408	1.4	0.1
12ZA22B-2.1	480	202	0.086	264	4	274	50	+3	0.299	2.6	0.0418	1.4	0.5
12ZA22B-6.1	414	243	-0.188	265	5	127	82	-111	0.280	3.9	0.0418	1.8	0.5
12ZA22B-3.1	593	264	0.148	266	3	219	78	-22	0.293	3.6	0.0421	1.2	0.3
12ZA22A-10.1	495	385	1.88	253	3	395	120	+37	0.302	5.5	0.0401	1.4	0.2
12ZA22A-6.1	560	215	0.20	259	5	306	37	+15	0.297	2.6	0.0411	2.1	0.8
12ZA22A-5.1	290	210	33.39	265	5	-	-	-	0.147	93.8	0.0407	2.4	0.0
12ZA22A-1.1	672	308	0.76	432	9	558	30	+23	0.564	2.5	0.0695	2.0	0.8
12ZA22A-7.1	1330	568	0.07	482	5	469	17	-3	0.605	1.3	0.0777	1.0	0.8
12ZA22A-9.1	382	22	0.06	495	8	516	28	+4	0.635	2.0	0.0799	1.6	0.8

Spot name	U (ppm)	Th (ppm)	²⁰⁷ Pb corrected				²⁰⁴ Pb corrected						
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12ZA22A-2.1	639	105	1.07	536	5	575	39	+7	0.708	2.0	0.0867	1.0	0.5
12ZA22A-8.1	384	21	-0.16	926	13	867	83	-7	1.444	4.3	0.1540	1.5	0.3
12ZA22A-3.1	296	181	0.19	976	20	1015	19	+4	1.650	2.3	0.1638	2.1	0.9
12ZA22A-4.1	157	102	0.20	1018	8	1049	27	+3	1.755	1.5	0.1713	0.8	0.5
12ZA10-14.1	421	245	0.76	255	7	231	75	-11	0.283	4.3	0.0403	2.9	0.7
12ZA10-13.1	467	156	0.16	262	3	311	47	+16	0.302	2.3	0.0416	1.1	0.5
12ZA10-12.1	771	579	2.76	264	7	281	543	+6	0.299	23.8	0.0418	2.3	0.1
12ZA10-3.1	538	285	0.05	264	3	253	46	-5	0.296	2.3	0.0419	1.2	0.5
12ZA10-2.1	339	173	-0.04	264	6	146	77	-82	0.282	4.0	0.0417	2.3	0.6
12ZA10-8.1	1110	935	0.02	268	4	263	26	-2	0.302	2.0	0.0425	1.7	0.8
12ZA10-11.1	888	565	-0.04	270	3	244	28	-11	0.301	1.8	0.0427	1.3	0.7
12ZA10-6.1	199	92	-0.30	271	6	145	91	-89	0.289	4.5	0.0428	2.3	0.5
12ZA10-5.1	634	457	0.51	272	2	293	53	+7	0.310	2.5	0.0431	0.9	0.3
12ZA10-10.1	515	388	0.24	273	5	245	49	-12	0.304	2.7	0.0432	1.7	0.6
12ZA10-9.1	526	316	0.56	273	3	45.0	90	-513	0.278	3.9	0.0430	1.1	0.3
12ZA10-15.1	206	99	20.84	274	13	-	-	-	0.143	85.9	0.0420	4.8	0.1
12ZA10-4.1	669	421	0.17	275	4	289	36	+5	0.313	2.1	0.0436	1.4	0.7
12ZA16-2.1	270	204	0.10	256	11	278	66	+8	0.290	5.1	0.0405	4.2	0.8
12ZA16-3.1	658	622	0.41	260	4	276	47	+6	0.294	2.5	0.0411	1.5	0.6
12ZA16-7.1	374	326	0.14	261	4	272	54	+4	0.294	2.8	0.0413	1.5	0.5
12ZA16-6.1	175	143	2.44	262	10	-790	1438	+135	0.190	50.9	0.0406	3.5	0.1
12ZA16-15.1	247	222	5.63	263	4	184	422	-43	0.285	18.2	0.0415	1.4	0.1
12ZA16-13.1	543	664	0.26	264	5	177	60	-50	0.285	3.2	0.0417	1.9	0.6
12ZA16-10.1	388	473	0.25	265	5	260	55	-2	0.297	3.0	0.0419	1.8	0.6
12ZA16-9.1	251	201	0.04	267	2	293	78	+9	0.304	3.5	0.0422	0.7	0.2
12ZA16-21.1	366	227	0.08	267	4	186	65	-44	0.290	3.1	0.0422	1.5	0.5
12ZA16-12.1	709	1067	0.08	268	4	275	30	+3	0.303	1.9	0.0424	1.3	0.7
12ZA16-5.1	529	780	0.22	268	4	207	51	-30	0.293	2.7	0.0423	1.5	0.6
12ZA16-11.1	392	300	2.03	271	3	406	257	+34	0.326	11.5	0.0431	0.7	0.1

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12ZA16-16.1	764	419	0.03	272	2	242	34	-12	0.303	1.6	0.0430	0.6	0.4
12ZA16-17.1	307	348	22.68	272	10	955	628	+72	0.432	30.8	0.0442	2.8	0.1
12ZA16-19.1	410	269	0.03	274	3	264	49	-4	0.308	2.4	0.0433	1.1	0.5
12ZA16-14.1	119	87	56.37	291	20	976	1520	+71	0.467	74.9	0.0473	6.9	0.1
12ZA19-7.1	792	1113	2.99	221	5	354	87	+38	0.259	4.5	0.0350	2.4	0.5
12ZA19-14.1	252	108	0.37	271	2	425	62	+37	0.329	2.9	0.0432	0.8	0.3
12ZA19-16.1	305	171	0.13	272	2	307	63	+11	0.313	2.9	0.0432	0.7	0.3
12ZA19-12.1	633	260	-0.03	274	4	240	58	-14	0.305	3.0	0.0433	1.6	0.5
12ZA19-17.1	288	120	0.05	274	4	301	53	+9	0.314	2.7	0.0435	1.4	0.5
12ZA19-22.1	446	152	0.18	275	4	287	41	+5	0.312	2.4	0.0435	1.6	0.7
12ZA19-9.1	255	118	0.14	277	4	335	67	+18	0.322	3.3	0.0439	1.5	0.5
12ZA19-2.1	271	151	0.05	277	5	238	72	-17	0.309	3.5	0.0439	1.7	0.5
12ZA19-18.1	382	137	0.19	278	2	349	40	+21	0.326	2.0	0.0441	0.9	0.4
12ZA19-4.1	422	165	0.48	278	2	392	50	+29	0.333	2.3	0.0443	0.7	0.3
12ZA19-15.1	576	266	-0.05	279	3	216	41	-29	0.308	2.0	0.0442	1.0	0.5
12ZA19-3.1	536	259	-0.21	280	6	177	38	-59	0.303	2.7	0.0443	2.1	0.8
12ZA19-19.1	312	147	0.04	280	5	285	53	+2	0.319	2.9	0.0444	1.7	0.6
12ZA19-13.1	310	134	0.11	281	4	278	56	-1	0.318	2.8	0.0445	1.3	0.5
12ZA19-10.1	383	308	0.20	282	3	344	49	+18	0.330	2.4	0.0448	1.1	0.5
12ZA19-11.1	394	169	-0.12	289	5	197	48	-47	0.316	2.6	0.0458	1.6	0.6
12ZA19-8.1	201	112	0.06	526	7	499	51	-6	0.670	2.7	0.0849	1.3	0.5
12ZA19-5.1	325	40	0.08	542	8	546	32	+1	0.708	2.1	0.0878	1.6	0.7
12ZA19-6.1	502	142	0.35	642	10	735	65	+13	0.925	3.4	0.1051	1.5	0.4
12ZA55-6.1	881	787	2.40	205	5	170	177	-21	0.2201	7.9	0.03226	2.2	0.3
12ZA55-2.1	208	176	1.35	245	4	-184	276	+236	0.2257	11.2	0.03830	1.9	0.2
12ZA55-17.1	425	281	1.17	259	4	244	77	-6	0.2885	3.7	0.04095	1.5	0.4
12ZA55-3.1	420	213	0.29	264	3	366	49	+28	0.3120	2.5	0.04198	1.2	0.5
12ZA55-12.1	129	88	0.22	265	4	350	93	+25	0.3105	4.4	0.04208	1.6	0.4
12ZA55-14.1	482	279	0.05	268	3	265	38	-1	0.3022	2.1	0.04250	1.3	0.6

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12ZA55-16.1	452	371	0.02	269	2	268	42	-0	0.3033	2.0	0.04260	0.6	0.3
12ZA55-18.1	435	313	0.04	269	2	202	59	-34	0.2944	2.6	0.04255	0.6	0.2
12ZA55-8.1	337	199	-0.02	269	5	298	46	+10	0.3078	2.8	0.04268	2.0	0.7
12ZA55-5.1	472	240	0.16	270	4	-45	99	+712	0.2646	4.3	0.04244	1.5	0.3
12ZA55-10.1	362	290	0.05	271	2	276	58	+2	0.3066	2.6	0.04292	0.6	0.2
12ZA55-11.1	463	455	0.08	272	4	204	51	-34	0.2983	2.7	0.04308	1.5	0.6
12ZA55-15.1	243	129	-0.05	274	4	217	93	-27	0.3019	4.3	0.04336	1.6	0.4
12ZA55-4.1	273	186	0.30	276	4	-133	186	+312	0.2601	7.6	0.04324	1.4	0.2
12ZA55-7.1	829	1033	0.00	276	4	209	37	-33	0.3025	2.2	0.04361	1.5	0.7
12ZA55-9.1	859	905	0.12	276	3	173	45	-61	0.2982	2.3	0.04364	1.2	0.5
12ZA55-1.1	428	318	0.72	291	4	373	101	+22	0.3453	4.7	0.04632	1.5	0.3
12ZA55-13.1	668	891	5.06	341	3	-	-	-	0.0694	102.5	0.05148	1.4	0.0
12ZA08-15.1	311	268	0.27	252	4	368	65	+32	0.2979	3.4	0.04005	1.8	0.5
12ZA08-2.1	72	49	0.44	254	3	341	231	+26	0.2966	10.3	0.04036	1.2	0.1
12ZA08-14.1	217	213	-0.01	258	7	258	85	-0	0.2898	4.7	0.04088	2.9	0.6
12ZA08-5.1	134	136	4.00	261	7	259	384	-1	0.2925	16.9	0.04126	2.8	0.2
12ZA08-6.1	149	82	0.02	263	2	-27	169	+1084	0.2601	7.0	0.04141	0.9	0.1
12ZA08-16.1	155	155	1.03	265	5	300	145	+12	0.3027	6.6	0.04193	1.8	0.3
12ZA08-4.1	164	155	0.41	267	4	209	138	-28	0.2925	6.2	0.04215	1.6	0.3
12ZA08-13.1	292	223	0.02	267	3	157	67	-71	0.2860	3.1	0.04214	1.3	0.4
12ZA08-12.1	344	356	-0.19	268	2	138	89	-96	0.2844	3.8	0.04227	0.7	0.2
12ZA08-9.1	152	122	-0.06	268	2	335	107	+20	0.3121	4.8	0.04257	0.8	0.2
12ZA08-11.1	166	96	0.10	269	4	73.1	160	-272	0.2775	6.9	0.04237	1.4	0.2
12ZA08-7.1	172	168	-0.02	269	3	299	70	+10	0.3081	3.3	0.04270	1.1	0.3
12ZA08-10.1	148	107	-0.09	270	5	313	104	+14	0.3106	5.0	0.04278	2.0	0.4
12ZA08-8.1	137	134	1.35	277	6	16.7	278	-1582	0.2784	11.8	0.04354	2.3	0.2
12ZA08-3.1	90	82	1.70	309	7	-936	991	+135	0.2133	34.0	0.04784	2.5	0.1
12ZA08-1.1	259	56	2.18	311	5	921	46	+67	0.4864	2.8	0.05056	1.7	0.6
12ZA60-4.1	305	258	5.65	257	10	259	388	+0	0.2887	17.3	0.04072	4.0	0.2

Spot name	U (ppm)	Th (ppm)	²⁰⁷ Pb corrected				²⁰⁴ Pb corrected						
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12ZA60-3.1	462	274	0.06	261	3	249	50	-5	0.2919	2.5	0.04134	1.2	0.5
12ZA60-8.1	332	308	0.87	262	4	279	147	+6	0.2963	6.6	0.04142	1.4	0.2
12ZA60-5.1	985	1336	0.16	263	3	331	27	+21	0.3056	1.7	0.04176	1.2	0.7
12ZA60-11.1	212	105	0.20	264	3	241	91	-10	0.2938	4.1	0.04177	1.1	0.3
12ZA60-1.1	677	120	0.11	267	2	265	36	-1	0.3002	1.7	0.04224	0.7	0.4
12ZA60-14.1	381	239	0.06	268	4	280	43	+5	0.3034	2.5	0.04240	1.6	0.7
12ZA60-6.1	275	113	0.06	268	2	255	63	-5	0.3000	2.8	0.04239	0.7	0.2
12ZA60-13.1	502	455	0.23	269	2	295	44	+9	0.3072	2.0	0.04266	0.6	0.3
12ZA60-15.1	432	350	0.13	272	4	276	61	+2	0.3076	3.0	0.04306	1.3	0.5
12ZA60-7.1	429	335	0.15	273	3	277	48	+1	0.3095	2.3	0.04331	1.1	0.5
12ZA60-16.1	369	201	-0.02	275	5	195	48	-42	0.3004	2.7	0.04355	1.7	0.6
12ZA60-2.1	573	508	3.25	285	5	519	107	+46	0.3625	5.2	0.04554	1.7	0.3
12ZA60-12.1	455	294	0.13	295	2	295	66	-0	0.3378	3.0	0.04690	0.6	0.2
12ZA60-10.1	419	170	0.52	351	8	333	56	-6	0.4096	3.4	0.05593	2.4	0.7
12ZA60-9.1	152	47	0.12	450	4	493	50	+9	0.5697	2.4	0.07241	0.9	0.3
BLOU-2.1	177	112	-0.12	270	4	64.9	106	-320	0.277	4.7	0.0425	1.4	0.3
BLOU-3.1	539	370	-0.04	271	2	229	39	-18	0.300	1.9	0.0429	0.8	0.4
BLOU-7.1	448	142	0.18	272	3	321	39	+16	0.314	2.0	0.0431	1.1	0.5
BLOU-13.1	169	109	-0.12	275	5	322	88	+15	0.318	4.3	0.0437	2.0	0.5
BLOU-9.1	501	379	0.01	276	2	265	37	-4	0.311	1.8	0.0437	0.8	0.4
BLOU-14.1	271	286	2.23	277	7	568	289	+52	0.360	13.5	0.0442	2.3	0.2
BLOU-8.1	290	157	0.13	278	2	344	48	+20	0.325	2.3	0.0441	0.8	0.4
BLOU-5.1	265	171	-0.06	279	2	203	100	-38	0.305	4.4	0.0441	0.9	0.2
BLOU-6.1	351	126	0.15	284	2	54.4	93	-429	0.291	4.0	0.0448	0.8	0.2
BLOU-15.1	208	130	0.18	289	9	352	150	+18	0.339	7.4	0.0459	3.3	0.4
BLOU-17.1	82	55	-0.05	289	5	271	86	-7	0.327	4.2	0.0458	1.9	0.4
BLOU-16.1	142	98	-0.04	302	3	198	93	-53	0.330	4.1	0.0478	1.0	0.2
BLOU-19.1	256	146	0.18	372	4	317	65	-18	0.431	3.1	0.0593	1.1	0.4
BLOU-24.1	128	71	1.94	376	4	212	219	-79	0.415	9.5	0.0598	1.2	0.1
BLOU-1.1	474	10	0.02	411	5	401	30	-2	0.496	1.9	0.0657	1.3	0.7

Spot name	U (ppm)	Th (ppm)	²⁰⁷ Pb corrected				²⁰⁴ Pb corrected						
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BLOU-10.1	431	9	0.25	479	4	547	27	+13	0.623	1.5	0.0773	0.8	0.5
BLOU-20.1	350	90	-0.04	493	4	445	38	-11	0.611	1.9	0.0793	0.8	0.4
BLOU-4.1	385	169	1.26	510	7	482	104	-6	0.644	4.9	0.0822	1.5	0.3
BLOU-21.1	202	48	0.07	529	10	462	58	-15	0.662	3.2	0.0854	1.8	0.6
BLOU-25.1	357	112	0.71	542	10	482	96	-13	0.685	4.7	0.0875	1.8	0.4
BLOU-12.1	307	96	0.06	544	4	545	30	+0	0.710	1.6	0.0881	0.8	0.5
BLOU-26.1	209	175	0.10	562	8	575	42	+2	0.744	2.4	0.0911	1.4	0.6
BLOU-18.1	54	28	-0.25	798	10	831	74	+4	1.216	3.8	0.1320	1.4	0.4
BLOU-23.1	171	53	-0.10	1125	11	1098	23	-3	2.000	1.5	0.1905	1.0	0.6
BLOU-11.1	409	217	7.84	3123	51	3412	7	+3	26.951	0.9	0.6760	0.8	0.9
BLOU-22.1	65	20	9.43	3132	84	3471	8	+3	28.573	1.4	0.6903	1.3	0.9
13ZA93A-7.1	594	283	0.644	269	2	277	65	+3	0.304	2.9	0.0426	0.8	0.3
13ZA93A-4.1	617	513	0.020	280	3	295	745	+5	0.320	32.7	0.0444	2.4	0.1
13ZA93A-6.1	290	153	-0.109	483	4	457	873	-6	0.601	39.4	0.0777	2.8	0.1
13ZA93A-5.1	756	54	-0.061	488	4	472	323	-3	0.613	14.7	0.0787	1.3	0.1
13ZA93A-1.1	292	123	0.094	515	6	507	36	-1	0.658	2.0	0.0831	1.2	0.6
13ZA93A-2.1	134	12	0.261	571	6	641	41	+11	0.782	2.2	0.0929	1.0	0.5
13ZA93A-3.1	124	68	0.023	590	6	609	1242	+3	0.796	57.6	0.0959	4.3	0.1
13ZA93A-8.1	280	78	0.328	794	13	876	22	+10	1.237	2.0	0.1314	1.7	0.9
13ZA72A-14.1	193	99	0.193	252	2	308	58	+18	0.290	2.7	0.0400	0.9	0.3
13ZA72A-21.1	207	203	0.333	254	2	321	67	+21	0.293	3.1	0.0402	0.9	0.3
13ZA72A-8.1	517	478	0.056	256	2	272	34	+6	0.289	1.7	0.0406	0.8	0.5
13ZA72A-6.1	338	231	-0.186	257	3	157	52	-64	0.275	2.4	0.0405	1.1	0.4
13ZA72A-17.1	318	150	0.316	258	2	291	60	+12	0.294	2.8	0.0409	0.8	0.3
13ZA72A-12.1	506	221	0.198	264	2	284	65	+7	0.300	3.0	0.0418	0.8	0.3
13ZA72A-27.1	328	243	-0.162	265	2	171	55	-56	0.286	2.5	0.0419	0.8	0.3
13ZA72A-23.1	270	159	-0.037	268	2	273	53	+2	0.303	2.4	0.0424	0.9	0.3
13ZA72A-9.1	206	70	0.138	270	2	375	78	+29	0.320	3.6	0.0429	0.9	0.3
13ZA72A-24.1	270	146	-0.017	270	2	254	51	-6	0.302	2.4	0.0428	0.9	0.4

Spot name	U (ppm)	Th (ppm)	²⁰⁷ Pb corrected				²⁰⁴ Pb corrected						
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13ZA72A-10.1	342	217	-0.158	270	3	165	52	-64	0.291	2.4	0.0427	1.0	0.4
13ZA72A-5.1	1023	778	-0.006	271	3	228	31	-19	0.300	1.9	0.0428	1.3	0.7
13ZA72A-19.1	559	408	-0.129	272	2	247	40	-10	0.304	1.9	0.0431	0.8	0.4
13ZA72A-4.1	915	251	0.077	273	2	297	26	+8	0.312	1.3	0.0432	0.7	0.5
13ZA72A-16.1	551	336	0.687	273	3	211	72	-30	0.300	3.3	0.0432	1.0	0.3
13ZA72A-30.1	678	298	-0.125	274	3	250	39	-10	0.306	2.0	0.0433	1.2	0.6
13ZA72A-18.1	403	208	0.080	278	2	267	45	-4	0.314	2.1	0.0441	0.8	0.4
13ZA72A-15.1	646	281	0.150	279	3	338	658	+18	0.325	29.1	0.0443	2.2	0.1
13ZA72A-2.1	999	232	-0.129	280	3	247	29	-14	0.313	1.6	0.0444	1.0	0.6
13ZA72A-28.1	289	128	0.078	282	2	327	1697	+14	0.328	74.9	0.0449	5.0	0.1
13ZA72A-29.1	212	88	0.020	334	5	331	52	-1	0.389	2.8	0.0532	1.6	0.6
13ZA72A-25.1	564	469	0.006	369	3	368	28	-0	0.438	1.5	0.0589	0.9	0.6
13ZA72A-20.1	411	50	1.445	439	5	500	74	+12	0.558	3.5	0.0706	1.1	0.3
13ZA72A-11.1	166	50	-0.127	467	4	441	1540	-6	0.577	69.4	0.0751	4.8	0.1
13ZA72A-1.1	460	79	-0.106	516	6	479	28	-8	0.650	1.8	0.0832	1.2	0.7
13ZA72A-22.1	299	55	0.020	528	4	498	35	-6	0.672	1.8	0.0852	0.9	0.5
13ZA72A-7.1	630	301	2.359	709	5	988	40	+29	1.168	2.1	0.1175	0.8	0.4
13ZA72A-3.1	158	13	0.414	746	11	874	36	+15	1.160	2.3	0.1233	1.5	0.6
13ZA72A-18.1d	720	315	1.297	886	7	1008	39	+13	1.487	2.1	0.1481	0.9	0.4
13ZA72A-13.1	422	76	0.102	918	9	954	16	+4	1.499	1.3	0.1533	1.0	0.8
13ZA72A-17.1d	528	11	0.188	1048	10	1088	12	+4	1.847	1.2	0.1769	1.0	0.9
13ZA72A-26.1	341	12	-0.211	1102	9	1056	16	-4	1.913	1.1	0.1860	0.8	0.7
12ZA18-6.1	1165	2867	8.671	115	4	282	48	+60	0.129	15.6	0.0180	3.3	0.2
12ZA18-2.1	809	519	3.292	238	4	461	118	+49	0.293	5.5	0.0378	1.5	0.3
12ZA18-11.1	712	753	7.456	239	5	33.1	225	-630	0.242	9.6	0.0375	2.2	0.2
12ZA18-32.1	1233	513	1.538	255	2	258	108	+1	0.286	4.8	0.0403	0.8	0.2
12ZA18-16.1	522	927	0.049	260	2	245	40	-6	0.290	1.9	0.0412	0.8	0.4
12ZA18-24.1	353	411	0.112	262	3	234	86	-12	0.291	3.9	0.0414	1.0	0.3
12ZA18-22.1	136	104	-0.272	265	3	34.5	113	-676	0.268	4.8	0.0417	1.0	0.2
12ZA18-31.1	669	132	0.406	267	2	248	51	-8	0.299	2.3	0.0423	0.8	0.3

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12ZA18-14.1	411	229	3.815	269	20	-195	1321	+242	0.247	53.3	0.0422	7.5	0.1
12ZA18-20.1	147	122	-0.251	271	3	49.0	108	-459	0.276	4.6	0.0427	1.0	0.2
12ZA18-12.1	210	211	0.239	272	2	238	84	-14	0.302	3.7	0.0430	0.9	0.2
12ZA18-18.1	450	244	0.014	272	3	272	38	-0	0.307	1.9	0.0431	1.0	0.5
12ZA18-30.1	261	339	-0.346	274	3	226	74	-22	0.303	3.4	0.0434	1.3	0.4
12ZA18-29.1	212	252	-0.079	276	4	300	73	+8	0.315	3.5	0.0437	1.4	0.4
12ZA18-23.1	491	17	-0.034	278	2	262	35	-6	0.313	1.7	0.0441	0.8	0.5
12ZA18-28.1	553	190	1.527	286	2	170	114	-70	0.309	4.9	0.0452	0.8	0.2
12ZA18-13.1	197	200	27.160	290	6	742	1232	+62	0.412	58.4	0.0467	4.5	0.1
12ZA18-10.1	603	305	1.115	326	4	660	26	+51	0.445	1.8	0.0524	1.3	0.7
12ZA18-17.1	709	433	1.291	359	3	425	57	+16	0.437	2.7	0.0573	0.9	0.3
12ZA18-26.1	641	691	0.129	366	8	-98	151	+483	0.353	6.6	0.0578	2.3	0.4
12ZA18-7.1	422	78	0.228	469	4	537	27	+13	0.608	1.5	0.0757	0.8	0.5
12ZA18-21.1	259	320	0.194	471	4	467	43	-1	0.590	2.1	0.0758	0.9	0.4
12ZA18-15.1	344	252	0.086	474	4	507	29	+7	0.605	1.6	0.0764	0.8	0.5
12ZA18-27.1	363	234	0.009	475	4	466	28	-2	0.594	1.5	0.0765	0.8	0.5
12ZA18-25.1	440	112	-0.054	477	4	443	27	-8	0.591	1.4	0.0768	0.8	0.6
12ZA18-36.1	551	246	1.979	492	6	567	75	+14	0.647	3.7	0.0795	1.2	0.3
12ZA18-19.1	465	267	0.107	528	4	570	25	+8	0.696	1.4	0.0854	0.8	0.6
12ZA18-35.1	118	105	-0.104	546	5	457	57	-20	0.682	2.8	0.0881	1.0	0.4
12ZA18-4.1	270	145	0.147	557	18	290	94	-95	0.644	5.3	0.0896	3.4	0.6
12ZA18-37.1	278	252	1.444	559	8	655	95	+15	0.771	4.6	0.0910	1.4	0.3
12ZA18-8.1	462	100	0.738	644	7	747	29	+14	0.933	1.8	0.1054	1.2	0.6
12ZA18-5.1	350	48	-0.229	714	10	569	56	-26	0.949	3.0	0.1165	1.4	0.5
12ZA18-34.1	175	38	0.723	770	14	958	538	+20	1.253	26.5	0.1279	3.0	0.1
12ZA18-33.1	586	287	3.348	777	6	944	126	+18	1.255	6.2	0.1290	0.9	0.1
12ZA18-9.1	691	614	0.701	998	14	1095	23	+9	1.764	1.9	0.1682	1.5	0.8
12ZA18-1.1	347	101	-0.135	1079	8	1025	18	-5	1.840	1.2	0.1817	0.8	0.7
12ZA18-3.1	191	251	-0.031	2607	26	2605	7	-0	12.025	1.0	0.4984	0.9	0.9
13ZA76A-27.1	234	161	0.390	253	2	346	61	+27	0.296	2.8	0.0402	0.9	0.3

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13ZA76A-30.1	265	134	0.424	256	2	394	43	+36	0.306	2.1	0.0406	0.8	0.4
13ZA76A-31.1	252	217	-0.194	256	3	173	56	-49	0.276	2.7	0.0404	1.1	0.4
13ZA76A-34.1	230	111	-0.024	260	3	239	137	-9	0.289	6.1	0.0411	1.3	0.2
13ZA76A-11.1	310	259	3.300	260	3	-228	329	+217	0.235	13.1	0.0406	1.3	0.1
13ZA76A-37.1	415	194	0.467	260	2	179	80	-46	0.281	3.5	0.0411	0.8	0.2
13ZA76A-20.1	379	224	1.074	260	2	153	171	-72	0.278	7.4	0.0411	0.9	0.1
13ZA76A-26.1	175	40	-0.038	261	2	183	82	-43	0.283	3.6	0.0412	0.9	0.3
13ZA76A-14.1	454	401	0.674	261	2	286	72	+9	0.297	3.3	0.0414	0.8	0.2
13ZA76A-35.1	294	231	0.113	262	2	293	48	+11	0.298	2.3	0.0415	0.8	0.4
13ZA76A-22.1	523	232	0.766	262	3	236	115	-11	0.291	5.1	0.0414	1.2	0.2
13ZA76A-19.1	273	195	14.442	261	5	-416	1649	+165	0.219	63.1	0.0408	2.9	0.0
13ZA76A-2.1	273	182	-0.135	263	2	231	1730	-14	0.291	75.1	0.0416	4.8	0.1
13ZA76A-33.1	593	226	0.107	264	3	284	37	+7	0.300	2.0	0.0418	1.2	0.6
13ZA76A-16.1	711	491	-0.032	265	2	238	34	-11	0.294	1.6	0.0419	0.8	0.5
13ZA76A-18.1	451	324	-0.059	266	2	205	71	-30	0.291	3.2	0.0420	0.8	0.3
13ZA76A-32.1	218	113	-0.100	266	2	253	61	-5	0.298	2.8	0.0421	0.9	0.3
13ZA76A-39.1	88	71	1.964	266	8	438	411	+40	0.325	18.7	0.0423	2.9	0.2
13ZA76A-6.1	456	379	-0.017	267	2	237	43	-12	0.296	2.0	0.0422	0.8	0.4
13ZA76A-9.1	578	1027	0.109	267	3	301	34	+11	0.305	1.8	0.0423	1.0	0.6
13ZA76A-1.1	226	309	-0.019	268	2	248	58	-8	0.299	2.7	0.0424	0.9	0.3
13ZA76A-7.1	199	219	0.000	269	3	373	122	+28	0.319	5.5	0.0427	0.9	0.2
13ZA76A-8.1	469	461	0.063	269	3	251	47	-7	0.301	2.4	0.0426	1.2	0.5
13ZA76A-10.1	184	128	-0.218	270	5	127	82	-114	0.285	3.9	0.0425	1.7	0.4
13ZA76A-21.1	203	114	-0.240	270	4	124	76	-119	0.285	3.6	0.0426	1.6	0.4
13ZA76A-29.1	353	249	8.247	271	3	371	318	+27	0.321	14.2	0.0430	1.1	0.1
13ZA76A-15.1	381	196	0.018	273	2	146	70	-88	0.292	3.1	0.0432	0.8	0.3
13ZA76A-25.1	302	262	9.898	273	10	97.6	996	-183	0.285	42.2	0.0431	2.8	0.1
13ZA76A-12.1	362	127	0.211	274	3	361	44	+24	0.323	2.3	0.0436	1.2	0.5
13ZA76A-5.1	207	116	-0.392	274	2	116	61	-139	0.289	2.7	0.0433	0.9	0.3
13ZA76A-4.1	595	189	-0.026	275	3	274	33	-1	0.311	1.9	0.0436	1.2	0.6
13ZA76A-36.1	510	377	0.188	277	4	325	35	+15	0.320	2.1	0.0439	1.4	0.7

Spot name	U (ppm)	Th (ppm)	²⁰⁷ Pb corrected				²⁰⁴ Pb corrected						
			²⁰⁶ Pb com %	²⁰⁶ Pb/ ²³⁸ U Age (Ma)	1σ	²⁰⁷ Pb/ ²⁰⁶ Pb Age (Ma)	1σ	% Disc	²⁰⁷ Pb*/ ²³⁵ U	% error	²⁰⁶ Pb*/ ²³⁸ U	% error	error corre.
13ZA76A-17.1	211	99	6.558	278	3	20.3	486	-1288	0.280	20.3	0.0438	1.4	0.1
13ZA76A-40.1	541	473	0.837	283	2	276	71	-2	0.320	3.2	0.0448	0.8	0.2
13ZA76A-3.1	223	84	0.074	326	4	240	71	-36	0.364	3.3	0.0518	1.2	0.4
13ZA76A-13.1	298	83	0.049	466	4	436	42	-7	0.574	2.1	0.0749	0.8	0.4
13ZA76A-23.1	618	54	0.043	489	4	494	24	+1	0.620	1.4	0.0788	0.8	0.6
13ZA76A-38.1	305	135	0.582	497	6	484	71	-3	0.628	3.5	0.0802	1.3	0.4
13ZA76A-24.1	119	72	4.807	531	6	659	244	+20	0.733	11.5	0.0863	1.3	0.1
13ZA76A-28.1	139	50	1.724	1721	26	1956	36	+12	5.151	2.5	0.3112	1.5	0.6
12ZA05B-13.1	769	797	4.368	232	4	601	129	+62	0.307	6.3	0.0371	2.0	0.3
12ZA05B-5.1	374	235	1.232	269	4	17.2	223	-1489	0.271	9.4	0.0424	1.7	0.2
12ZA05B-3.1	740	402	0.678	272	2	115	109	-138	0.286	4.7	0.0429	0.7	0.1
12ZA05B-18.1	372	283	0.041	274	5	321	59	+15	0.317	3.1	0.0435	1.7	0.5
12ZA05B-16.1	236	145	0.220	304	2	386	85	+21	0.363	3.9	0.0485	0.8	0.2
12ZA05B-14.1	1854	4221	13.119	326	6	739	178	+57	0.464	8.6	0.0526	1.9	0.2
12ZA05B-8.1	126	114	0.250	367	4	522	134	+30	0.470	6.2	0.0589	1.1	0.2
12ZA05B-9.1	156	81	-0.295	379	4	340	93	-12	0.444	4.2	0.0605	1.0	0.2
12ZA05B-10.1	835	1056	0.086	401	4	421	35	+5	0.489	1.9	0.0642	1.1	0.6
12ZA05B-12.1	305	128	0.197	467	8	465	70	-0	0.584	3.6	0.0751	1.7	0.5
12ZA05B-15.1	1189	674	0.065	476	9	455	27	-5	0.592	2.3	0.0765	1.9	0.8
12ZA05B-1.1	135	140	0.194	499	6	670	99	+26	0.691	4.8	0.0809	1.2	0.2
12ZA05B-4.1	230	96	0.014	528	5	588	60	+10	0.703	2.9	0.0855	0.9	0.3
12ZA05B-6.1	529	132	-0.008	773	5	771	24	-0	1.140	1.3	0.1273	0.7	0.5
12ZA05B-17.1	210	93	1.383	795	13	941	106	+16	1.284	5.4	0.1321	1.7	0.3
12ZA05B-11.1	176	49	-0.011	1067	15	1076	31	+1	1.869	2.2	0.1800	1.5	0.7
12ZA05B-7.1	266	117	-0.400	1346	11	1274	23	-6	2.656	1.5	0.2314	0.8	0.6
12ZA05B-2.1	119	79	5.875	2139	12	2695	22	+19	10.640	1.4	0.4178	0.5	0.4
13ZA67-16.1	746	375	0.890	258	2	298	110	+14	0.295	4.9	0.0408	0.9	0.2
13ZA67-13.1	507	160	0.223	264	2	346	63	+24	0.308	2.9	0.0419	0.7	0.2
13ZA67-32.1	267	136	-0.145	267	2	175	109	-53	0.288	4.7	0.0421	0.8	0.2

Spot name	U (ppm)	Th (ppm)	²⁰⁷ Pb corrected				²⁰⁴ Pb corrected						
			²⁰⁶ Pb com %	²⁰⁶ Pb/ ²³⁸ U Age (Ma)	1σ	²⁰⁷ Pb/ ²⁰⁶ Pb Age (Ma)	1σ	% Disc	²⁰⁷ Pb*/ ²³⁵ U	% error	²⁰⁶ Pb*/ ²³⁸ U	% error	error corre.
13ZA67-3.1	294	219	0.286	267	4	326	110	+18	0.309	5.1	0.0423	1.5	0.3
13ZA67-6.1	327	300	-0.208	269	2	200	128	-35	0.294	5.6	0.0425	0.8	0.1
13ZA67-11.1	364	236	-0.208	269	2	233	96	-16	0.299	4.2	0.0426	0.8	0.2
13ZA67-15.1	361	175	2.783	269	5	159	241	-71	0.289	10.5	0.0425	1.9	0.2
13ZA67-27.1	537	289	-0.151	270	6	219	64	-24	0.298	3.6	0.0428	2.3	0.6
13ZA67-20.1	459	147	-0.043	271	2	287	107	+6	0.308	4.7	0.0429	0.8	0.2
13ZA67-19.1	522	227	0.478	271	5	283	91	+4	0.308	4.4	0.0429	1.8	0.4
13ZA67-24.1	184	116	17.207	273	10	722	899	+63	0.383	42.5	0.0438	3.4	0.1
13ZA67-7.1	770	717	5.565	274	3	221	328	-24	0.302	14.2	0.0433	0.9	0.1
13ZA67-2.1	378	205	-0.121	274	2	275	123	+0	0.310	5.4	0.0434	0.8	0.1
13ZA67-17.1	449	180	0.162	275	2	259	136	-7	0.309	6.0	0.0436	0.7	0.1
13ZA67-37.1	269	222	0.312	276	4	469	100	+42	0.342	4.7	0.0439	1.3	0.3
13ZA67-14.1	330	169	-0.082	277	2	293	73	+5	0.316	3.3	0.0439	0.8	0.2
13ZA67-8.1	567	270	0.028	278	2	313	57	+11	0.321	2.6	0.0442	0.7	0.3
13ZA67-9.1	821	437	0.009	279	3	299	48	+7	0.319	2.4	0.0442	1.1	0.5
13ZA67-10.1	535	481	-0.112	279	2	192	74	-46	0.304	3.2	0.0442	0.7	0.2
13ZA67-35.1	182	96	-0.091	280	3	129	160	-118	0.296	6.9	0.0442	1.0	0.1
13ZA67-25.1	479	292	-0.092	280	4	302	70	+7	0.321	3.4	0.0444	1.5	0.4
13ZA67-26.1	733	327	0.269	280	5	206	100	-37	0.307	4.7	0.0443	1.7	0.4
13ZA67-18.1	1358	1137	6.532	280	3	127	281	-123	0.296	12.0	0.0442	0.9	0.1
13ZA67-36.1	423	425	0.025	292	3	138	101	-113	0.310	4.4	0.0461	1.1	0.3
13ZA67-1.1	465	424	-0.179	300	5	210	79	-44	0.330	3.8	0.0475	1.6	0.4
13ZA67-28.1	221	86	-0.007	301	3	390	104	+23	0.360	4.7	0.0479	1.0	0.2
13ZA67-4.1	486	325	-0.073	301	3	69.2	123	-341	0.311	5.3	0.0476	1.2	0.2
13ZA67-31.1	401	192	0.221	363	3	439	96	+18	0.446	4.4	0.0581	0.7	0.2
13ZA67-29.1	313	130	-0.160	371	5	345	55	-8	0.436	2.8	0.0591	1.4	0.5
13ZA67-5.1	179	82	-0.432	486	5	308	119	-59	0.565	5.3	0.0780	1.0	0.2
13ZA67-12.1	188	89	-0.312	492	5	433	69	-14	0.606	3.3	0.0792	1.0	0.3
13ZA67-33.1	249	96	0.512	1749	39	1825	14	+4	4.821	2.4	0.3132	2.3	0.9

Spot name	U (ppm)	Th (ppm)	²⁰⁷ Pb corrected			²⁰⁴ Pb corrected							error corre.
			²⁰⁶ Pb com %	²⁰⁶ Pb/ ²³⁸ U Age (Ma)	1σ	²⁰⁷ Pb/ ²⁰⁶ Pb Age (Ma)	1σ	% Disc	²⁰⁷ Pb*/ ²³⁵ U	% error	²⁰⁶ Pb*/ ²³⁸ U	% error	
SUTH-5.1	417	337	0.001	256	2	110	85	-134	0.268	3.7	0.0403	0.7	0.2
SUTH-40.1	213	139	-0.114	259	3	134	88	-95	0.275	3.9	0.0409	1.3	0.3
SUTH-7.1	454	504	0.236	260	3	260	67	+0	0.291	3.1	0.0411	1.0	0.3
SUTH-9.1	288	251	0.288	261	2	7.8	141	-3277	0.262	5.9	0.0411	0.8	0.1
SUTH-19.1	365	453	-0.173	262	2	83.2	101	-218	0.271	4.3	0.0412	0.7	0.2
SUTH-31.1	386	410	0.157	262	4	193	65	-36	0.285	3.1	0.0414	1.4	0.4
SUTH-11.1	299	144	-0.111	263	5	203	71	-30	0.288	3.6	0.0416	2.0	0.5
SUTH-1.1	367	362	-0.176	265	2	215	79	-23	0.292	3.5	0.0419	0.7	0.2
SUTH-18.1	223	148	-0.007	265	2	182	104	-46	0.288	4.6	0.0419	0.9	0.2
SUTH-3.1	489	430	0.141	266	3	304	106	+13	0.304	4.7	0.0421	1.0	0.2
SUTH-2.1	364	301	0.133	267	2	270	65	+1	0.302	2.9	0.0423	0.7	0.2
SUTH-30.1	634	1239	-0.082	270	3	251	33	-7	0.302	1.9	0.0427	1.2	0.7
SUTH-13.1	93	111	2.648	270	4	-	-	-	0.153	56.4	0.0415	1.9	0.0
SUTH-10.1	379	120	0.121	270	2	271	63	+0	0.305	2.9	0.0428	0.7	0.2
SUTH-14.1	341	248	-0.056	271	2	76.9	110	-255	0.280	4.7	0.0427	0.8	0.2
SUTH-15.1	381	374	-0.291	271	2	146	66	-87	0.289	2.9	0.0428	0.7	0.3
SUTH-35.1	377	103	0.007	271	2	254	79	-7	0.304	3.5	0.0430	0.8	0.2
SUTH-26.1	39	36	0.258	272	5	-525	1090	+154	0.219	40.8	0.0424	2.5	0.1
SUTH-36.1	218	180	-0.106	276	2	237	52	-17	0.306	2.4	0.0436	0.9	0.4
SUTH-41.1	264	207	0.444	282	3	247	106	-14	0.315	4.7	0.0446	1.1	0.2
SUTH-32.1	332	202	0.246	294	2	379	39	+23	0.349	1.9	0.0467	0.8	0.4
SUTH-4.1	161	136	-0.174	299	3	160	101	-88	0.322	4.4	0.0474	0.9	0.2
SUTH-17.1	689	286	-0.036	301	2	281	44	-7	0.342	2.0	0.0478	0.6	0.3
SUTH-38.1	512	400	0.270	468	4	523	28	+11	0.601	1.5	0.0754	0.8	0.5
SUTH-39.1	393	197	-0.111	475	4	460	32	-3	0.592	1.7	0.0764	0.8	0.5
SUTH-12.1	791	220	0.239	556	3	571	29	+3	0.735	1.5	0.0901	0.6	0.4
SUTH-34.1	580	168	0.017	573	4	556	22	-3	0.752	1.2	0.0929	0.8	0.6
SUTH-6.1	110	49	-0.255	575	10	382	105	-52	0.694	5.0	0.0927	1.7	0.3
SUTH-16.1	218	69	0.453	917	8	1020	31	+10	1.551	1.8	0.1535	0.9	0.5
SUTH-8.1	135	50	-0.270	1058	10	980	33	-8	1.760	1.9	0.1777	0.9	0.5
SUTH-37.1	245	93	0.098	1092	9	1104	36	+1	1.944	2.0	0.1846	0.9	0.4

Spot name	U (ppm)	Th (ppm)	²⁰⁷ Pb corrected				²⁰⁴ Pb corrected						
			²⁰⁶ Pb com %	²⁰⁶ Pb/ ²³⁸ U Age (Ma)	1σ	²⁰⁷ Pb/ ²⁰⁶ Pb Age (Ma)	1σ	% Disc	²⁰⁷ Pb*/ ²³⁵ U	% error	²⁰⁶ Pb*/ ²³⁸ U	% error	error corre.
SUTH-33.1	85	80	0.906	1750	29	1845	17	+5	4.889	1.9	0.3143	1.6	0.9
12ZA45-1.1	645	294	-0.181	271	2	121	57	-126	0.285	2.5	0.0427	0.8	0.3
12ZA45-4.1	256	83	0.036	445	3	430	72	-3	0.546	3.3	0.0714	0.7	0.2
12ZA45-5.1	453	236	1.463	454	4	521	102	+13	0.582	4.8	0.0731	1.0	0.2
12ZA45-6.1	301	58	0.489	455	3	597	49	+24	0.607	2.4	0.0735	0.7	0.3
12ZA45-2.1	207	76	0.049	457	4	461	54	+1	0.570	2.6	0.0735	0.8	0.3
12ZA45-4.2	296	168	-0.066	462	5	383	56	-21	0.555	2.7	0.0741	1.1	0.4
12ZA45-7.2	604	269	1.425	516	14	383	102	-36	0.622	5.3	0.0830	2.8	0.5
12ZA45-7.1	461	207	0.756	522	4	597	65	+13	0.698	3.1	0.0846	0.7	0.2
12ZA45-3.1	237	82	0.245	1098	8	1154	37	+5	2.010	2.0	0.1862	0.8	0.4
13ZA75A-9.1	1655	3253	15.723	182	3	7.6	425	-2313	0.182	17.7	0.0285	1.5	0.1
13ZA75A-13.1	193	149	1.681	263	2	471	134	+45	0.327	6.1	0.0419	0.9	0.2
13ZA75A-6.1	206	356	0.316	265	2	308	89	+14	0.304	4.0	0.0420	0.9	0.2
13ZA75A-3.1	271	469	0.020	269	2	186	87	-45	0.293	3.8	0.0426	0.8	0.2
13ZA75A-2.1	790	858	0.327	270	2	339	45	+21	0.314	2.2	0.0428	0.8	0.4
13ZA75A-7.1	172	396	-0.084	271	4	154	111	-77	0.290	4.9	0.0427	1.4	0.3
13ZA75A-10.1	521	287	-0.174	272	2	181	49	-51	0.295	2.2	0.0430	0.6	0.3
13ZA75A-8.1	534	15	0.034	278	3	263	47	-6	0.313	2.3	0.0441	1.1	0.5
13ZA75A-11.1	300	260	0.049	285	3	72.9	139	-296	0.295	6.0	0.0450	1.1	0.2
13ZA75A-4.1	712	218	-0.057	431	4	385	32	-12	0.517	1.7	0.0690	0.8	0.5
13ZA75A-5.1	247	81	0.121	469	5	435	60	-8	0.578	2.9	0.0754	1.1	0.4
13ZA75A-14.1	910	107	0.032	505	4	462	30	-10	0.631	1.6	0.0814	0.8	0.5
13ZA75A-1.1	139	107	-0.174	530	5	391	82	-37	0.641	3.8	0.0854	1.0	0.3
13ZA75A-12.1	343	1	0.080	584	4	560	39	-4	0.769	1.9	0.0948	0.7	0.4
13ZA75A-15.1	311	134	1.823	1112	12	1450	20	+24	2.410	1.5	0.1916	1.1	0.7

An electronic version of this appendix is available to improve data access.

Appendix C-part 1: XRF Whole Rock Major Element Geochemistry

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	K ₂ O	Na ₂ O	P ₂ O ₅	LOI (%)	Sum
14ZA161A	68.38	0.595	15.72	3.67	0.046	1.02	0.24	3.39	0.66	0.025	5.71	99.46
14ZA162A	63.59	0.597	16.62	3.92	0.062	1.47	1.20	3.62	0.90	0.129	7.45	99.56
14ZA168A	62.67	0.735	17.14	5.22	0.049	1.40	0.47	4.55	1.40	0.086	5.45	99.16
13ZA93A	60.12	0.880	17.02	7.35	0.078	2.04	0.87	4.47	1.76	0.094	4.96	99.66
14ZA130A	62.72	0.789	17.14	4.78	0.046	1.68	0.65	4.44	0.98	0.229	6.03	99.47
14ZA130AR	62.47	0.788	17.01	4.75	0.046	1.67	0.71	4.42	0.98	0.229	6.03	99.10
14ZA130A	62.72	0.789	17.14	4.78	0.046	1.68	0.65	4.44	0.98	0.229	6.03	99.47
14ZA130A	62.20	0.801	17.34	5.11	0.056	1.71	0.66	4.51	0.92	0.239	6.07	99.62
SUTHER	38.06	0.329	16.38	3.45	0.603	1.67	14.90	3.67	1.11	0.128	18.54	98.83
13ZA72A	8.17	0.113	3.01	0.98	0.012	1.53	46.17	0.61	0.11	0.082	38.25	99.03
14ZA129A	50.32	0.573	14.08	3.77	0.106	1.70	11.44	3.40	0.58	0.127	13.56	99.65
BLOUKRANS	58.43	0.557	16.56	3.59	0.141	1.79	5.23	3.98	2.07	0.312	7.24	99.91
14ZA129A	56.50	0.661	16.54	4.47	0.096	2.00	5.12	4.11	0.54	0.133	9.33	99.49
12ZA45	63.41	0.524	17.13	3.39	0.024	1.64	0.82	3.50	1.22	0.107	7.46	99.22
14ZA128A	53.95	0.531	12.23	2.88	0.080	2.23	10.90	3.18	1.69	0.335	11.74	99.76
14ZA128A	54.43	0.547	12.53	3.08	0.079	2.32	9.76	3.23	1.68	0.334	11.14	99.13
12ZA46	63.21	0.625	16.67	5.59	0.046	1.66	1.41	4.48	0.94	0.157	5.19	99.98
13ZA75B	65.20	0.566	16.89	3.83	0.099	1.25	1.48	2.84	1.63	0.165	5.81	99.75
12ZA16	42.69	0.402	11.76	2.26	0.055	1.67	17.82	2.92	1.16	0.741	17.66	99.14
13ZA76	60.96	0.666	17.76	4.10	0.038	1.99	1.23	4.63	1.81	0.109	6.56	99.86
12ZA12	23.45	0.289	5.98	1.90	0.281	0.96	35.14	1.43	0.71	0.124	29.02	99.28
13ZA77-PWD	69.29	0.641	13.57	3.05	0.230	1.08	2.58	2.31	2.37	0.213	4.92	100.25
12ZA07	56.05	0.686	20.89	4.71	0.081	1.90	1.29	4.88	1.21	0.187	7.90	99.79
12ZA23	50.90	0.210	26.33	2.78	0.024	2.21	0.43	7.95	0.21	0.037	7.91	98.98
14ZA116A	48.52	0.374	26.46	2.10	0.051	1.77	2.24	7.53	0.41	0.057	9.21	98.72
12ZA22A	53.42	0.615	21.71	6.24	0.059	2.48	0.97	5.35	1.56	0.135	7.35	99.89
12ZA22B	52.56	0.260	23.05	3.40	0.234	2.16	2.06	7.15	0.35	0.052	8.25	99.53
13ZA78A	50.43	0.451	13.72	2.25	0.238	1.04	13.68	2.77	2.57	0.135	12.79	100.08
12ZA08	22.15	0.361	11.80	1.19	0.531	1.04	30.89	3.58	0.06	0.023	27.68	99.30

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	K ₂ O	Na ₂ O	P ₂ O ₅	LOI (%)	Sum
14ZA121	44.70	0.323	23.04	32.73	0.244	1.80	7.10	6.82	0.33	0.091	11.43	98.60
14ZA141	14.43	0.164	5.65	1.68	0.546	1.40	39.81	1.16	0.35	0.164	33.90	99.25
12ZA54	47.55	0.697	26.44	4.37	0.109	2.04	2.09	6.74	0.39	0.305	8.89	99.61
12ZA61	52.75	0.696	18.62	8.52	0.307	1.39	1.50	2.64	1.05	0.225	11.55	99.25
09LGV-04	49.93	0.722	24.93	4.73	0.068	2.22	1.29	6.24	1.27	0.306	6.97	98.68
12ZA10	47.92	0.269	25.00	2.74	0.138	1.96	3.67	6.79	0.83	0.077	9.77	99.17
09LGV-01	58.26	0.414	22.36	1.97	0.016	1.56	1.44	6.20	0.66	0.190	6.26	99.32
13ZA79	73.17	0.483	14.57	1.67	0.011	0.67	0.68	2.10	3.77	0.124	3.10	100.34
09TBT-04	35.22	0.417	19.86	2.06	0.618	1.06	16.39	5.17	0.16	0.060	17.65	98.66
09LGV-02	51.69	0.656	25.59	3.60	0.022	1.93	0.70	6.82	1.24	0.157	7.02	99.44
14ZA154	58.89	0.683	18.58	6.26	0.026	1.56	0.39	3.93	0.38	0.162	9.06	99.91
14ZA154	61.12	0.620	17.02	6.35	0.030	1.46	0.39	3.82	0.56	0.156	7.49	99.03
09TBT-01	44.04	0.369	23.69	2.16	0.080	1.45	9.23	5.26	0.92	0.108	13.01	100.31
14ZA142	71.43	0.272	13.01	3.55	0.071	0.44	1.15	1.09	4.18	1.033	3.89	100.11
14ZA142 R	71.83	0.273	13.13	3.58	0.072	0.43	1.15	1.09	4.22	1.040	3.89	100.72
14ZA142	71.43	0.272	13.01	3.55	0.071	0.44	1.15	1.09	4.18	1.033	3.89	100.11
14ZA142	69.57	0.287	13.22	4.03	0.054	0.53	1.65	1.35	3.66	1.364	4.31	100.03
09LGC-04	50.52	0.490	24.56	3.23	0.125	1.64	2.60	6.32	1.69	0.291	7.22	98.67
09LGC-01	53.69	0.482	26.80	1.94	0.030	1.29	0.45	6.25	2.05	0.198	5.55	98.73
12ZA55	57.56	0.431	23.70	2.06	0.077	1.47	1.27	6.05	0.21	0.184	6.88	99.88
12ZA19	46.76	0.543	29.77	0.88	0.044	0.55	2.84	5.17	0.87	0.686	9.33	97.43

An electronic version of this appendix is available to improve data access.

Appendix C-part 2: ICPMS Whole Rock Trace Element Geochemistry (in ppm)

Sample	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Er ppm	Yb ppm	Lu ppm	Ba ppm	Th ppm	Nb ppm	Y ppm	Hf ppm	U ppm	Pb ppm	Rb ppm	Sr ppm	Zr ppm
14ZA161A	33.18	28.88	6.41	22.31	3.45	0.63	2.40	0.35	1.33	1.53	0.26	766	16.09	12.25	12.15	5.78	2.77	25.78	142.3	95	208
14ZA162A	25.81	101.84	6.89	27.48	6.73	1.28	6.36	1.07	3.45	3.23	0.47	771	22.33	15.14	34.57	5.68	2.72	39.22	163.9	287	190
14ZA168A	52.07	50.48	9.31	31.47	5.37	0.95	3.98	0.62	2.12	2.16	0.35	849	17.68	14.46	20.16	4.56	4.32	28.39	217.2	153	155
13ZA93A	55.57	93.34	11.85	43.05	7.87	1.47	6.14	0.97	3.23	3.09	0.48	519	18.80	17.29	31.11	4.47	12.17	32.74	206.2	106	151
14ZA130A	67.05	40.86	19.09	74.07	15.12	2.68	11.51	1.68	4.52	3.94	0.59	546	18.71	15.23	41.24	5.67	5.06	27.84	209.1	139	193
14ZA130A	66.84	40.96	19.13	74.51	15.53	2.71	11.47	1.69	4.59	3.91	0.60	550	18.59	15.20	41.40	5.67	4.97	27.75	211.1	141	192
14ZA130A	76.28	54.76	20.99	82.17	17.32	3.02	13.02	1.92	4.99	4.27	0.65	570	18.56	15.54	46.98	5.41	5.09	29.24	218.3	138	185
SUTHER	30.18	54.81	6.43	24.62	4.85	1.00	4.16	0.62	2.15	2.11	0.34	1192	22.59	6.54	24.09	4.27	1.53	20.17	148.4	270	134
13ZA72A	38.57	16.67	6.89	26.13	5.04	0.97	4.93	0.74	2.39	1.79	0.27	199	2.62	2.40	31.90	0.68	2.69	4.76	33.3	340	25
14ZA129A	38.37	68.47	8.38	31.92	6.70	1.36	6.04	0.99	3.80	3.50	0.56	487	14.70	12.18	38.89	3.78	3.25	23.59	161.4	75	129
BLOUKRANS	41.17	91.54	11.19	42.19	9.32	1.30	8.07	1.35	4.59	4.36	0.68	1157	17.82	17.08	43.77	7.21	5.21	58.62	169.1	199	241
14ZA129A	36.18	71.85	8.25	31.44	6.67	1.33	5.92	0.97	3.38	3.25	0.52	522	16.49	13.89	34.10	4.08	3.48	25.62	196.1	67	137
12ZA45	65.63	83.28	13.26	44.75	7.52	1.23	5.38	0.78	2.64	2.57	0.41	628	21.49	19.10	24.12	7.06	5.15	22.59	156.2	157	238
14ZA128A	42.81	79.16	10.63	40.57	8.18	1.42	7.19	1.12	3.64	3.29	0.51	461	12.75	11.73	36.91	5.29	3.77	21.86	140.9	288	192
14ZA128A	43.88	80.97	11.03	41.82	8.27	1.43	7.15	1.12	3.64	3.33	0.52	473	13.03	11.79	37.04	5.42	3.71	21.97	144.8	274	196
12ZA46	36.85	66.47	8.51	32.68	6.87	1.33	6.09	0.95	3.32	3.25	0.53	792	16.27	12.96	32.20	3.45	4.30	26.08	225.0	461	118
13ZA75B	60.15	88.81	14.47	52.86	9.84	1.66	7.29	1.07	3.07	2.72	0.41	579	23.63	15.40	29.53	6.06	5.71	51.52	129.0	575	213
12ZA16	57.49	96.71	12.46	49.47	9.43	1.35	8.41	1.20	3.88	3.52	0.56	778	13.56	10.88	43.15	4.80	8.33	34.17	117.6	389	165
13ZA76	23.85	63.94	6.18	23.08	4.93	0.92	4.13	0.69	2.74	2.83	0.45	1226	23.66	17.05	23.59	7.27	4.70	33.96	185.8	132	258
12ZA12	51.45	49.99	8.51	28.80	4.40	0.81	3.78	0.58	1.86	1.60	0.25	199	6.42	6.05	20.21	1.97	1.64	11.14	68.2	153	71
13ZA77	60.07	101.29	12.93	47.10	9.02	1.92	7.93	1.24	3.75	3.25	0.49	481	14.29	11.49	37.39	7.16	3.23	16.31	100.9	170	257
12ZA07	39.46	99.32	11.58	45.23	10.28	1.64	9.07	1.52	4.83	4.18	0.62	728	33.26	18.21	50.18	7.96	10.49	37.83	230.1	158	264
12ZA23	98.09	184.77	21.80	78.84	14.16	1.42	11.05	1.77	6.60	5.68	0.82	768	51.45	27.38	64.42	13.68	11.89	33.80	351.5	58	407
14ZA116A	53.34	54.20	10.12	33.76	5.72	0.91	6.28	1.25	6.69	6.33	0.98	1190	54.05	27.49	61.99	14.53	12.36	34.57	317.3	110	453
12ZA22A	32.60	63.79	8.43	31.51	6.56	1.60	5.47	0.84	2.39	2.16	0.33	759	25.11	15.87	26.51	4.54	8.56	40.45	244.1	182	129
12ZA22B	84.49	163.91	19.57	72.03	15.47	1.18	12.84	2.14	6.16	5.69	0.87	860	37.17	29.13	57.10	11.74	10.74	38.50	352.8	89	387
13ZA78A	32.34	55.51	7.28	28.43	6.24	1.31	5.52	0.84	2.59	2.28	0.35	615	12.84	9.34	27.18	4.42	2.99	16.27	119.3	303	164
12ZA08	18.38	31.90	4.04	18.09	4.84	3.06	7.08	1.48	7.97	6.81	1.00	413	35.81	20.33	87.32	12.20	9.34	35.55	164.6	1231	429
14ZA121	126.07	103.03	17.24	54.54	6.88	1.06	6.16	1.14	6.51	6.21	0.99	983	49.73	30.14	65.21	12.92	13.32	39.59	290.4	193	412
14ZA141	28.67	43.94	5.51	20.61	4.25	0.86	4.23	0.63	1.92	1.64	0.25	923	5.80	3.16	21.98	1.69	2.17	18.10	57.4	563	60
12ZA54	33.18	74.79	9.73	37.03	7.99	1.47	6.85	1.08	3.19	3.07	0.47	1095	48.09	19.02	32.36	8.44	10.32	23.61	263.0	69	262
12ZA61	51.57	99.41	12.70	48.87	10.75	2.24	10.25	1.69	5.14	4.28	0.65	581	18.65	12.18	52.43	5.82	5.43	50.03	142.2	86	201
09LGV-04	77.69	148.49	15.93	53.13	8.45	1.51	5.49	0.84	2.42	2.08	0.32	1008	50.59	18.72	25.01	6.89	10.02	30.14	269.1	189	202
12ZA10	28.38	58.77	7.03	27.04	5.82	0.89	5.56	1.14	6.15	5.85	0.88	1502	59.42	28.98	54.66	12.33	13.81	64.26	279.6	143	347

Sample	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Er ppm	Yb ppm	Lu ppm	Ba ppm	Th ppm	Nb ppm	Y ppm	Hf ppm	U ppm	Pb ppm	Rb ppm	Sr ppm	Zr ppm
09LGV-01	63.24	123.76	13.47	45.14	8.38	1.50	6.42	0.93	2.92	2.96	0.48	853	38.12	20.25	29.27	8.23	11.44	21.82	229.4	64	265
13ZA79	28.57	67.05	7.36	27.72	5.50	1.07	4.47	0.66	2.13	1.95	0.30	378	12.25	9.04	19.75	4.36	2.79	13.61	82.5	148	158
09TBT-04	98.71	227.10	28.33	113.72	27.48	4.44	21.92	3.27	8.02	6.05	0.89	852	58.34	21.02	97.92	14.33	15.56	45.79	211.0	179	534
09LGV-02	57.89	120.23	14.24	50.67	9.88	1.69	6.82	0.98	2.74	2.44	0.37	896	51.94	15.15	27.71	6.36	9.40	19.57	280.9	98	190
14ZA154	287.79	353.57	44.13	149.20	23.81	5.15	17.18	2.36	6.22	5.19	0.80	447	41.76	15.79	62.32	9.29	17.83	37.40	219.6	54	278
14ZA154	183.06	234.72	30.40	103.85	16.75	3.77	12.48	1.72	4.89	4.06	0.64	475	33.38	14.30	47.91	7.35	14.19	45.82	210.1	55	224
09TBT-01	11.84	18.47	2.49	10.11	2.81	0.67	3.46	0.71	2.74	2.50	0.39	438	35.47	6.08	27.07	6.08	7.74	81.01	154.7	154	166
14ZA142	29.62	59.52	6.72	25.13	5.96	3.22	4.96	0.76	2.13	2.27	0.36	241	16.24	9.58	23.74	3.99	3.74	67.32	56.4	423	159
14ZA142	29.04	58.66	6.66	25.03	5.80	3.23	4.92	0.75	2.13	2.22	0.36	240	16.08	9.73	24.00	3.88	3.70	65.58	57.1	428	159
14ZA142	28.90	63.52	7.83	31.13	8.08	4.32	6.77	1.08	2.68	2.73	0.45	257	16.86	10.06	31.08	4.02	4.05	67.48	70.4	372	171
09LGC-04	30.21	66.09	7.13	24.80	4.18	0.86	2.92	0.44	1.56	1.53	0.24	1079	46.87	13.79	15.07	6.32	6.89	35.96	255.7	147	183
09LGC-01	48.88	129.42	17.63	76.12	24.84	3.46	23.09	3.41	8.56	7.34	1.11	1038	42.08	22.10	89.19	13.19	12.55	18.82	230.1	80	418
12ZA55	43.35	95.33	11.93	44.47	9.10	1.40	6.86	1.05	3.24	3.10	0.50	880	39.68	22.48	33.20	8.63	7.96	11.40	219.2	52	283
12ZA19	121.50	263.04	27.92	101.89	21.23	2.78	16.89	2.61	8.74	8.42	1.34	878	55.26	34.84	80.80	12.16	15.45	32.95	240.7	257	407

An electronic version of this appendix is available to improve data access.

Appendix D: SHRIMP Zircon Rare Earth Element Geochemistry (in ppm)

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
14ZA168-15.1	860	0.051	34	0.91	2.5	0.76	21	271	464	11298
14ZA168-16.1	1259	0.186	29	4.66	8.2	3.28	47	340	570	7460
14ZA168-2.1	790	0.045	20	1.54	3.0	1.25	21	269	483	8718
14ZA168-18.1	669	0.021	21	0.89	2.5	0.71	18	243	439	9749
14ZA168-14.1	909	0.101	53	0.60	1.8	1.01	16	362	677	10626
14ZA168-3.1	687	5.195	33	6.50	3.7	0.90	15	276	497	12109
14ZA168-6.1	340	0.207	18	0.28	0.8	0.28	7	120	221	11541
14ZA168-19.1	2108	0.264	49	4.61	6.8	4.49	60	690	1178	8436
14ZA168-21.1	170	0.008	14	0.07	0.2	0.13	2	80	160	12535
14ZA168-25.1	700	1.588	33	2.96	2.4	0.57	12	303	589	12213
14ZA168-8.1	1947	16.624	44	18.96	11.6	2.14	53	609	1033	10723
14ZA168-1.1	1166	1.971	23	1.29	2.7	0.28	26	352	578	11797
14ZA168-20.1	781	1.785	42	1.30	2.0	0.56	15	325	612	11288
14ZA168-29.1	801	0.031	49	1.35	3.0	1.11	21	276	482	10801
14ZA168-24.1	662	0.220	33	1.27	2.8	1.30	19	230	412	9297
14ZA168-10.1	786	0.326	8	0.83	0.9	0.23	9	486	912	13816
14ZA168-17.1	1516	0.118	18	4.73	8.7	1.98	53	420	717	8851
14ZA168-22.1	881	0.036	23	1.57	3.1	1.32	21	308	562	10163
14ZA168-4.1	1091	0.283	17	1.39	3.2	0.74	28	336	575	10103
14ZA168-7.1	1433	0.060	6	2.62	6.0	1.38	46	380	616	7793
14ZA168-27.1	782	0.031	19	1.04	2.3	0.39	21	238	384	10205
14ZA168-23.1	759	0.008	17	0.16	0.9	0.11	11	316	577	11937
14ZA168-9.1	723	0.017	8	0.21	1.1	0.32	11	289	555	10840
14ZA168-5.1	2465	0.115	7	1.80	6.4	0.75	65	675	1100	11329
14ZA168-13.1	1267	6.334	30	8.60	7.7	1.22	43	310	503	10838
14ZA168-26.1	1572	0.025	4	1.70	5.5	0.28	46	414	669	10083
14ZA168-11.1	2656	0.016	1	0.37	2.4	0.10	41	640	960	13827
14ZA168-28.1	966	0.505	18	1.03	1.7	0.26	14	403	701	12726

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
14ZA168-12.1	2364	23.953	135	19.58	13.0	3.79	53	870	1535	12011
14ZA168-30.1	1264	1.177	24	2.75	4.0	0.30	30	395	655	9100
14ZA161-25.1	2586	53.384	305	47.95	29.5	10.62	115	591	942	8086
14ZA161-24.1	1445	60.105	395	73.63	30.3	6.49	63	480	833	9879
14ZA161-13.1	1514	0.266	46	4.48	7.8	3.93	49	487	862	8076
14ZA161-9.1	426	0.076	21	0.75	1.6	0.61	11	160	307	9329
14ZA161-7.1	469	0.090	14	0.55	1.1	0.70	8	205	410	8121
14ZA161-2.1	318	0.032	23	0.32	0.9	0.34	9	106	184	9894
14ZA161-15.1	242	0.235	16	0.30	0.6	0.34	5	105	213	9722
14ZA161-10.1	788	0.049	77	1.17	2.8	0.87	22	277	467	10409
14ZA161-23.1	2998	0.346	88	9.36	18.3	4.80	119	745	1201	9399
14ZA161-28.1	596	0.073	23	0.65	1.5	0.38	13	205	366	11043
14ZA161-14.1	820	0.040	45	0.92	2.6	0.83	21	277	491	9265
14ZA161-12.1	367	0.030	21	0.64	1.6	0.47	11	115	195	9598
14ZA161-21.1	1253	0.840	9	4.66	9.3	0.96	63	277	429	9294
14ZA161-30.1	394	0.074	22	0.37	1.1	0.29	9	141	244	11203
14ZA161-11.1	405	0.003	31	0.53	1.4	0.73	11	139	249	10530
14ZA161-26.1	566	0.104	15	0.50	1.1	0.46	10	246	494	8583
14ZA161-6.1	460	1.554	18	2.27	0.9	0.24	5	230	462	14772
14ZA161-20.1	822	0.856	56	1.05	2.3	0.78	17	303	536	9848
14ZA161-3.1	1097	0.092	14	0.55	1.9	0.34	20	396	718	9507
14ZA161-18.1	538	0.026	15	0.26	0.9	0.25	10	211	390	11047
14ZA161-16.1	572	0.012	1	0.43	1.2	0.20	13	191	337	9327
14ZA161-5.1	344	0.009	14	0.21	0.5	0.15	6	120	214	11282
14ZA161-8.1	774	0.014	19	0.66	1.6	0.42	18	253	425	9452
14ZA161-17.1	3251	0.056	1	1.72	5.3	0.12	58	893	1435	11929
14ZA161-29.1	695	0.286	1	0.54	2.2	0.22	22	125	189	12617
14ZA161-22.1	234	0.016	5	0.13	0.4	0.17	4	93	183	11857
14ZA161-27.1	2633	0.052	6	2.95	7.2	0.38	67	730	1177	11387

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
14ZA161-4.1	716	0.036	19	0.55	1.1	0.65	13	273	536	8099
14ZA161-19.1	984	0.036	4	0.76	2.5	0.09	19	322	547	12136
14ZA161-1.1	601	0.022	14	0.38	1.5	0.35	14	247	476	12694
14ZA154-9.1	1026	7.279	66	11.97	10.3	2.94	40	306	540	8208
14ZA154-10.1	809	0.035	23	1.70	3.0	1.07	20	288	523	9033
14ZA154-3.1	2536	1.490	54	6.41	9.2	3.05	65	844	1469	8185
14ZA154-4.1	625	0.025	26	0.79	1.9	0.36	16	178	307	10118
14ZA154-11.1	1237	0.444	18	2.53	4.7	1.59	34	398	681	8871
14ZA154-1.1	1173	8.660	33	7.45	5.7	2.17	32	386	696	11222
14ZA154-7.1	1204	1.765	31	3.08	3.4	0.53	26	371	630	8743
14ZA154-2.1	2403	0.113	8	3.56	7.9	0.75	73	590	936	8442
14ZA154-6.1	1047	0.068	14	4.79	8.5	0.82	49	228	350	7879
14ZA154-8.1	2160	0.011	11	0.76	3.4	0.60	38	745	1229	11409
14ZA154-13.1	3481	88.840	186	82.40	47.9	30.94	152	873	1440	11264
14ZA154-5.1	629	0.939	3	1.54	2.9	0.37	29	79	120	14043
14ZA154-12.1	1465	0.138	30	1.10	3.4	0.18	31	464	781	10596
14ZA130-3.1	198	0.007	1	0.01	0.0	0.02	1	151	399	13248
14ZA130-5.1	498	0.008	4	0.18	0.6	0.05	8	217	454	12874
14ZA130-2.1	518	0.021	11	0.50	1.5	0.41	13	168	286	8819
14ZA130-4.1	473	4.592	15	6.56	7.9	1.17	42	64	100	9272
14ZA130-6.1	904	0.044	7	2.58	5.1	0.68	35	234	376	8615
14ZA130-1.1	1025	0.047	4	2.46	5.1	1.43	33	278	462	7846
14ZA130-8.1	776	21.039	70	4.25	3.3	0.93	20	271	470	7671
14ZA130-7.1	135	0.014	2	0.03	0.2	0.09	2	61	114	8768
14ZA116-10.1	2234	85.959	160.3	86.6	33.7	6.60	109	546	884	7666
14ZA116-15.1	1183	0.287	22.4	4.6	7.8	3.08	47	330	578	6637
14ZA116-25.1	1213	0.047	10.4	1.1	3.2	0.97	34	374	672	7324

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
14ZA116-1.1	910	0.217	13.3	1.2	2.9	0.70	26	252	441	6788
14ZA116-26.1	1127	0.059	11.4	1.3	3.5	1.30	30	363	657	7290
14ZA116-2.1	645	0.023	5.9	0.7	2.1	0.55	18	205	358	7556
14ZA116-28.1	742	0.736	10.1	0.9	2.1	0.26	17	238	417	8225
14ZA116-38.1	1924	0.091	23.2	3.2	8.1	2.28	64	503	840	7606
14ZA116-17.1	1463	1.519	19.0	2.5	3.9	1.08	33	460	827	7186
14ZA116-24.1	583	0.036	38.2	0.9	2.7	1.22	19	223	422	9824
14ZA116-14.1	1375	0.487	15.7	1.9	4.2	1.16	41	382	655	6978
14ZA116-31.1	2468	1.435	21.6	5.6	10.9	2.53	86	685	1141	8845
14ZA116-10.3	3048	63.045	179.2	71.0	30.2	4.78	140	787	1312	8541
14ZA116-37.1	1439	0.079	13.9	3.7	8.4	2.68	55	409	699	8965
14ZA116-21.1	1068	10.120	20.7	3.7	4.6	1.42	32	304	529	7953
14ZA116-6.1	1423	0.108	20.5	1.4	3.6	1.28	35	429	755	7766
14ZA116-29.1	1176	0.369	11.5	4.2	7.2	2.59	46	334	586	8237
14ZA116-39.1	1433	0.153	8.4	3.3	7.2	1.66	51	405	671	8378
14ZA116-4.1	874	0.427	17.6	1.2	2.9	0.63	23	267	460	8312
14ZA116-16.1	2434	0.110	11.7	4.7	11.5	3.01	88	676	1145	7630
14ZA116-8.1	1915	0.149	11.0	4.9	11.3	4.30	80	503	835	8904
14ZA116-9.1	1703	0.045	7.4	3.2	7.6	1.90	57	484	817	8611
14ZA116-32.1	1891	0.064	19.7	4.2	7.6	1.89	61	527	886	10140
14ZA116-20.1	4007	0.799	26.5	9.7	23.0	5.51	152	1033	1691	8005
14ZA116-19.1	3097	0.709	22.5	6.5	15.3	3.56	115	826	1378	8456
14ZA116-33.1	1461	0.037	15.5	1.5	3.9	1.06	39	432	732	8629
14ZA116-13.1	1414	0.067	5.7	2.3	6.0	1.94	43	411	726	7476
14ZA116-18.1	959	0.042	13.5	1.1	2.2	1.02	22	308	559	7919
14ZA116-36.1	2021	7.032	28.4	8.6	10.9	2.93	68	558	948	8779
14ZA116-23.1	2151	0.074	15.2	4.5	10.7	2.62	74	590	985	7754
14ZA116-3.1	1027	0.029	13.3	0.8	2.6	0.95	22	335	615	8332
14ZA116-7.1	1161	19.522	47.9	13.0	9.8	3.25	50	272	464	5889
14ZA116-34.1	1767	65.751	682.9	72.3	34.4	8.23	90	542	912	13413

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
14ZA116-35.1	710	0.062	36.3	0.9	2.3	0.60	16	257	471	11051
14ZA116-11.1	915	0.029	11.3	0.2	0.9	0.17	12	400	768	12334
14ZA116-12.1	1900	0.012	9.1	0.6	2.6	0.45	33	632	1106	11531
14ZA116-27.1	251	0.020	16.3	0.2	0.5	0.27	4	108	225	14276
14ZA116-30.1	818	0.798	17.3	1.3	2.2	0.35	18	292	518	10191
14ZA116-5.1	1639	0.838	28.0	1.2	1.6	0.89	12	485	812	13354
14ZA116-22.1	1501	0.029	50.9	2.1	5.3	0.74	43	435	728	11164
14ZA142-41.1	928	11.431	76.4	13.4	8.7	2.24	28	309	543	10423
14ZA142-3.1	1335	8.405	86.2	17.7	12.4	5.62	45	475	842	13602
14ZA142-40.1	1789	0.429	51.7	3.5	6.8	2.12	46	590	1026	12390
14ZA142-37.1	977	0.194	48.9	1.4	3.3	1.54	25	314	550	7700
14ZA142-34.1	1631	0.071	72.5	1.0	3.6	1.48	36	559	969	11874
14ZA142-35.1	1190	0.536	40.1	2.8	4.5	1.85	31	417	755	10753
14ZA142-25.1	765	0.029	12.4	0.3	1.3	0.25	14	336	620	11001
14ZA142-1.1	1661	0.100	48.5	1.9	4.8	1.51	38	590	1033	12375
14ZA142-7.1	1131	0.049	33.7	1.1	3.4	1.23	28	407	750	10960
14ZA142-20.1	813	0.047	21.5	1.6	3.4	1.17	24	284	541	10821
14ZA142-4.1	945	0.907	18.9	2.4	2.6	0.96	19	362	641	12355
14ZA142-19.1	1553	0.018	17.1	1.3	4.0	0.99	36	577	1044	12454
14ZA142-8.1	618	0.303	19.2	1.0	1.7	0.84	10	322	590	11348
14ZA142-9.1	2610	0.065	5.5	1.3	5.7	0.99	62	710	1139	10154
14ZA142-24.1	2409	1.215	32.6	6.1	10.7	2.49	70	753	1260	10903
14ZA142-13.1	528	1.226	24.5	3.3	2.5	1.14	10	340	731	13314
14ZA142-16.1	1102	0.048	7.8	0.3	1.5	0.09	15	424	751	13956
14ZA142-10.1	713	0.018	20.2	0.4	1.4	0.72	14	246	433	10764
14ZA142-5.1	333	0.012	2.8	0.2	1.7	0.03	18	25	38	13658
14ZA142-14.1	1101	0.342	58.2	3.1	6.1	1.49	40	301	495	9536
14ZA142-30.1	2049	0.079	62.9	2.3	5.7	2.07	51	640	1128	7227
14ZA142-6.1	890	0.101	14.1	0.7	2.4	0.15	21	265	465	11196

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
14ZA142-31.1	2631	2.129	16.2	7.3	12.2	3.25	67	1094	2024	11345
14ZA142-26.1	1421	0.021	4.9	1.1	3.9	0.22	36	422	707	11554
14ZA142-32.1	771	0.052	31.5	0.6	1.7	0.27	17	282	510	11881
14ZA121-9.1	1626	11.675	62.8	12.2	9.4	1.82	51	418	711	8826
14ZA121-18.1	2141	59.687	183.6	66.1	28.0	8.42	81	687	1236	10966
14ZA121-3.1	922	0.700	19.8	1.1	2.8	0.31	23	285	494	9865
14ZA121-11.1	1058	11.961	68.5	19.3	12.9	4.00	39	441	912	12569
14ZA121-2.1	916	0.053	69.7	0.8	2.2	0.68	21	308	529	11008
14ZA121-12.1	1711	0.174	19.5	2.7	6.0	1.25	46	496	856	9370
14ZA121-17.1	1434	0.028	15.2	1.4	3.4	0.88	29	503	911	9064
14ZA121-10.1	1224	0.048	67.6	1.6	4.8	1.45	38	372	627	9590
14ZA121-4.1	1883	0.042	55.9	1.8	4.8	2.08	42	641	1134	9763
14ZA121-8.1	642	1.203	38.8	1.7	2.3	0.84	12	287	570	12015
14ZA121-14.1	1048	0.138	78.5	1.0	2.3	1.13	20	430	799	11346
14ZA121-16.1	217	0.756	2.5	0.5	0.5	0.26	3	111	225	12250
14ZA121-6.1	966	0.022	9.3	0.8	2.6	0.09	23	295	491	13588
14ZA121-15.1	568	0.721	41.7	1.0	1.3	0.53	10	259	465	12675
14ZA121-13.1	1066	1.198	15.3	1.6	2.4	1.04	19	488	1004	9532
14ZA121-7.1	3062	93.225	199.6	90.7	68.3	55.24	260	919	1518	10784
14ZA121-19.1	1177	0.065	6.0	2.8	6.5	0.62	48	274	447	9305
14ZA121-1.1	3915	0.800	4.7	4.6	11.0	0.41	99	1240	2069	11826
14ZA121-5.1	644	0.009	27.7	0.4	1.4	0.17	13	242	421	12856
12ZA23-13.1	1908	5.65	24	11.3	14.8	5.37	84	469	84	4829
12ZA23-32.1	1561	1.41	18	8.6	13.0	4.9	73	390	69	3906
12ZA23-12.1	502	0.93	4	1.2	2.0	0.49	15	148	28	7351
12ZA23-5.1	613	1.11	9	3.0	3.9	1.34	23	177	33	8157
12ZA23-9.1	1425	0.06	13	5.2	8.0	1.88	57	371	67	6295
12ZA23-38.1	626	1.47	17	3.4	4.3	1.2	23	179	32	6068

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
12ZA23-1.1	1646	0.11	60	5.4	9.6	1.68	69	397	70	6734
12ZA23-7.1	2911	0.72	72	10.6	18.0	3.30	118	713	123	6092
12ZA23-25.1	526	0.06	6	1.7	3.2	1.2	20	162	30	6658
12ZA23-11.1	1135	0.18	15	1.0	2.6	0.22	24	362	66	10405
12ZA23-4.1	1061	0.09	33	3.6	5.9	0.28	40	287	52	6225
12ZA23-16.1	2404	0.31	20	3.9	8.2	0.84	64	669	117	8569
12ZA23-29.1	1938	18.70	64	15.2	14.8	3.0	80	527	92	6005
12ZA23-24.1	2577	0.33	111	9.7	18.3	0.9	117	671	119	5744
12ZA23-6.1	3723	1.17	26	8.5	16.7	3.35	122	915	156	7932
12ZA23-8.1	4515	1.32	31	9.9	22.1	4.38	164	1061	181	8275
12ZA23-14.1	2349	2.08	28	7.4	13.2	3.54	90	584	104	6774
12ZA23-3.1	3541	0.08	70	6.2	14.0	1.49	116	911	153	9460
12ZA23-10.1	1594	0.21	21	1.4	3.5	0.57	32	518	96	9036
12ZA23-2.1	1357	0.26	19	6.1	8.8	2.70	58	364	66	7042
12ZA23-22.1	771	0.40	23	2.5	4.1	0.9	27	222	41	5690
12ZA23-21.1	1732	0.07	67	4.3	9.1	1.5	70	437	75	6960
12ZA23-31.1	4875	7.24	146	25.2	35.9	5.6	207	1186	195	6632
12ZA23-33.1	1231	0.07	30	1.7	4.0	0.3	35	336	58	7277
12ZA23-36.1	1923	0.19	36	6.2	12.1	2.3	77	505	86	6526
12ZA23-15.1	1762	0.17	11	6.9	11.8	4.36	71	462	84	6720
12ZA23-34.1	3102	0.09	23	5.5	14.0	2.5	103	812	139	7342
12ZA23-30.1	2100	0.96	22	11.1	16.9	6.1	93	573	100	6163
12ZA23-26.1	2055	30.67	64	14.9	16.8	3.8	93	520	89	5439
12ZA23-23.1	2482	0.43	23	13.6	22.4	9.2	121	635	108	6057
12ZA23-27.1	708	0.02	19	0.5	1.5	0.2	13	284	53	10310
12ZA23-28.1	3104	0.12	19	6.9	14.3	3.5	104	782	134	7397
12ZA23-37.1	2002	43.21	63	19.5	17.2	8.0	94	524	93	5378
12ZA23-35.1	2110	0.10	45	5.1	11.4	3.7	67	608	104	8039
12ZA54-7.1	675	0.96	27	2.2	3.0	0.83	17	202	38	9191

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
12ZA54-5.1	1745	2.61	88	9.0	12.6	5.18	64	525	99	7133
12ZA54-12.1	1624	1.16	39	5.1	8.1	2.87	54	450	82	7914
12ZA54-6.1	1745	2.36	63	8.6	11.1	4.25	60	530	99	10290
12ZA54-14.1	1968	0.35	56	7.2	11.1	4.14	65	601	111	8280
12ZA54-8.1	1997	0.33	71	3.6	7.3	2.17	54	631	115	11357
12ZA54-11.1	625	0.01	34	0.6	1.7	0.50	15	207	39	11061
12ZA54-15.1	2381	0.34	62	6.3	11.0	4.46	72	715	136	8577
12ZA54-16.1	1962	0.15	53	4.7	8.6	3.04	57	584	109	9004
12ZA54-9.1	3517	0.36	137	14.7	25.6	11.45	147	885	153	8762
12ZA54-4.1	1299	0.08	46	2.4	4.2	1.46	29	466	94	10115
12ZA54-1.1	973	0.04	54	1.0	2.7	0.69	22	325	60	11805
12ZA54-13.1	2467	0.15	45	5.7	9.5	3.45	67	760	137	9461
12ZA54-3.1	2583	12.73	58	22.5	15.9	5.68	69	851	156	11324
12ZA54-10.1	1193	0.00	8	0.3	1.3	0.12	18	436	80	12968
12ZA54-2.1	4743	1.55	6	3.1	7.8	0.74	75	1429	240	11672
12ZA61-7.1	1763	13.44	79	17.2	14.9	5.89	59	544	103	8035
12ZA61-9.1	1475	11.62	88	14.3	12.6	5.14	53	416	77	7945
12ZA61-14.1	2289	11.09	85	22.0	18.2	6.61	75	696	129	8820
12ZA61-25.1	2043	22.12	140	28.2	21.2	10.0	87	581	102	8714
12ZA61-12.1	1550	2.36	52	4.4	6.1	2.27	38	524	99	9399
12ZA61-22.1	1629	7.78	73	10.2	10.3	3.7	53	486	87	8932
12ZA61-29.1	1012	0.46	27	1.4	2.5	0.9	19	387	76	8408
12ZA61-10.1	1129	4.23	31	4.6	4.3	1.46	26	385	75	8504
12ZA61-24.1	2694	3.41	70	7.2	9.8	3.6	72	804	140	7698
12ZA61-11.1	1719	0.10	42	2.1	4.4	1.66	38	589	111	8285
12ZA61-8.1	2804	0.11	28	4.0	9.5	3.36	77	812	147	8147
12ZA61-15.1	1242	0.61	42	1.7	2.9	1.07	24	461	90	10112
12ZA61-30.1	858	0.08	18	1.1	2.9	1.0	21	297	56	8387

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
12ZA61-4.1	1190	0.30	26	1.8	3.7	1.19	27	425	83	9916
12ZA61-28.1	831	2.66	47	5.5	5.1	1.9	21	324	64	9470
12ZA61-1.1	1190	0.43	26	3.5	6.0	2.09	39	380	71	10160
12ZA61-26.1	783	0.01	13	0.4	1.3	0.2	14	339	65	10836
12ZA61-6.1	1194	0.78	24	1.9	3.7	1.15	28	418	80	9778
12ZA61-23.1	1494	0.43	47	1.7	3.5	1.6	33	544	101	8267
12ZA61-5.1	2829	0.09	16	5.6	11.9	3.49	93	764	135	8941
12ZA61-27.1	1700	0.12	39	3.9	7.9	3.3	50	549	100	7989
12ZA61-13.1	1258	0.02	18	0.7	2.0	0.49	20	519	102	10382
12ZA61-21.1	2407	0.05	11	2.9	8.7	0.9	72	627	110	9596
12ZA61-2.1	3461	0.03	9	2.8	9.2	0.94	92	872	149	11103
12ZA61-3.1	2119	0.09	23	5.7	9.9	0.27	69	535	92	9069
12ZA07-11.1	1832	28.93	126	39.3	21.8	7.15	79	481	89	6642
12ZA07-25.1	550	3.416	19	2.10	1.9	0.30	13.1	171	31	5339
12ZA07-9.1	1237	1.39	19	2.3	4.2	0.43	32	366	66	8311
12ZA07-6.1	721	0.58	23	1.3	1.8	0.28	14	249	47	9423
12ZA07-7.1	978	0.21	10	1.7	3.2	0.74	25	302	57	7153
12ZA07-20.1	885	0.645	21	1.26	2.9	0.31	22.4	268	48	6995
12ZA07-8.1	762	1.48	17	2.7	2.7	0.40	19	246	45	9305
12ZA07-3.1	849	0.52	22	1.6	2.5	0.35	19	282	52	10809
12ZA07-24.1	665	1.963	19	1.82	2.2	0.24	14.3	209	39	7928
12ZA07-5.1	1563	0.07	12	2.7	5.6	1.09	44	460	82	9053
12ZA07-21.1	648	3.140	16	2.32	2.5	0.32	15.8	212	39	7928
12ZA07-10.1	3855	0.82	49	8.7	16.5	2.40	116	1059	185	7964
12ZA07-4.1	1624	0.03	22	1.6	3.9	0.65	33	559	104	9301
12ZA07-22.1	3098	1.410	61	6.90	12.6	1.72	94.2	796	136	7755
12ZA07-23.1	1530	0.038	28	2.17	5.2	0.53	41.6	453	81	9120
12ZA07-26.1	1346	15.178	52	16.19	9.6	1.84	45.2	366	65	8549
12ZA07-2.1	2754	0.01	7	1.5	5.1	0.68	50	845	147	11832

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
12ZA07-1.1	1368	0.10	5	3.5	6.5	0.94	48	322	57	7884
12ZA46-4.1	2177	25.38	221	37.8	25.5	8.03	81	562	99	8741
12ZA46-10.1	1182	0.20	102	2.4	5.3	2.19	35	340	63	8356
12ZA46-1.1	1046	0.11	15	1.8	4.2	1.53	29	315	56	8924
12ZA46-5.1	785	0.02	41	0.9	2.4	0.67	18	284	54	12092
12ZA46-3.1	1310	0.02	49	1.6	3.7	1.15	30	446	84	9868
12ZA46-7.1	626	1.50	45	4.7	3.4	0.84	15	210	40	10408
12ZA46-6.1	1581	0.06	8	3.6	7.8	2.43	52	453	82	7569
12ZA46-2.1	1319	0.17	26	1.7	4.4	0.42	37	412	75	8359
12ZA46-9.1	4977	0.16	13	8.3	18.7	2.55	149	1221	205	7742
12ZA46-8.1	3261	0.01	1	1.0	4.8	0.24	59	936	161	10756
12ZA46-11.1	697	0.12	16	3.0	5.2	0.78	32	151	26	8952
12ZA22B-4.1	2126	26.83	90	41.7	32.2	4.63	112	622	112	10206
12ZA22B-7.1	781	0.20	7	0.7	2.1	0.17	19	241	44	8821
12ZA22B-6.2	914	0.16	13	0.9	2.6	0.28	22	275	49	9627
12ZA22B-5.1	2897	17.26	35	22.0	18.5	2.14	88	827	144	10864
12ZA22B-1.1	949	0.37	4	2.4	3.8	1.15	32	256	46	7952
12ZA22B-2.1	1396	0.08	15	1.1	3.3	0.28	32	426	76	10851
12ZA22B-6.1	1696	0.11	12	3.3	6.8	1.81	54	494	90	8922
12ZA22B-3.1	1427	0.24	28	1.5	3.4	0.45	27	490	92	10227
12ZA22A-10.1	537	24.52	74	16.4	8.6	3.48	25	171	35	10567
12ZA22A-6.1	1121	0.53	23	1.0	2.4	0.24	23	383	70	10227
12ZA22A-5.1	412	38.45	44	6.7	3.5	0.93	12	138	27	10569
12ZA22A-1.1	783	5.59	43	4.0	3.1	1.41	21	282	54	11824
12ZA22A-7.1	4368	8.44	21	5.9	8.4	0.65	74	1208	199	12779
12ZA22A-9.1	292	0.05	2	0.8	2.8	0.10	18	97	19	10093
12ZA22A-2.1	536	14.15	39	9.9	8.1	2.83	24	164	30	11991

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
12ZA22A-8.1	732	3.45	6	2.2	2.7	0.30	26	117	18	12959
12ZA22A-3.1	1097	0.05	21	0.8	2.5	0.60	25	348	63	10129
12ZA22A-4.1	3001	0.84	175	3.0	8.4	3.45	75	778	131	7179
12ZA10-14.1	1591	0.66	12	3.4	6.4	1.41	47	439	78	6858
12ZA10-13.1	1109	0.07	15	0.9	2.4	0.51	23	403	76	8988
12ZA10-12.1	3375	1.04	26	10.5	18.5	4.43	122	868	147	8284
12ZA10-3.1	1366	0.04	10	1.3	4.1	0.42	34	392	68	10113
12ZA10-2.1	1532	0.12	11	2.5	5.4	1.14	43	444	78	8741
12ZA10-8.1	5448	0.43	37	14.5	28.6	6.06	185	1412	242	7681
12ZA10-11.1	3088	0.17	18	5.1	12.0	2.66	96	862	148	9152
12ZA10-6.1	1217	0.04	3	2.0	5.3	0.55	41	329	57	9104
12ZA10-5.1	2700	0.52	23	6.5	12.9	2.77	85	746	129	8412
12ZA10-10.1	2513	0.26	13	5.3	11.8	2.83	82	678	116	7771
12ZA10-9.1	1970	2.91	14	2.6	5.3	1.77	47	562	101	7804
12ZA10-15.1	891	61.38	41	8.0	4.9	0.98	25	278	50	7296
12ZA10-4.1	2412	0.36	18	5.6	11.6	2.82	81	667	114	9976
12ZA16-2.1	857	0.09	41	2.2	4.3	1.87	27	253	47	9276
12ZA16-3.1	1112	0.26	101	1.8	3.7	2.10	33	327	58	10462
12ZA16-7.1	1602	0.29	39	6.5	10.9	4.94	68	415	72	8487
12ZA16-6.1	596	5.29	37	2.2	3.4	1.63	22	163	29	7581
12ZA16-15.1	837	4.87	49	3.6	5.2	2.54	31	242	43	8371
12ZA16-13.1	1813	1.29	93	9.3	15.7	6.85	86	449	76	7766
12ZA16-10.1	1933	0.57	86	7.9	14.4	6.49	83	485	83	8279
12ZA16-9.1	460	0.05	43	1.1	2.3	1.04	15	142	26	8373
12ZA16-21.1	831	0.48	50	1.2	2.7	1.20	21	257	47	9031
12ZA16-12.1	3220	0.48	83	10.2	21.0	10.88	132	848	146	8202
12ZA16-5.1	2357	0.95	89	9.8	17.2	8.82	101	651	112	8649
12ZA16-11.1	810	0.42	39	3.0	5.3	2.27	28	326	67	7770

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
12ZA16-16.1	1057	0.22	46	1.5	3.3	1.14	28	307	54	11149
12ZA16-17.1	1396	9.65	56	7.5	11.5	4.60	59	373	64	7749
12ZA16-19.1	1246	0.12	45	3.1	5.8	2.59	42	348	61	9319
12ZA16-14.1	277	41.60	58	6.0	2.7	0.73	9	89	17	8971
12ZA19-7.1	1904	6.82	100	25.6	21.3	8.43	85	531	866	7860
12ZA19-14.1	726	0.11	19	0.4	1.5	0.29	14	274	484	10094
12ZA19-16.1	1305	0.03	20	1.0	2.7	1.18	26	456	822	8286
12ZA19-12.1	1278	0.37	27	1.0	3.1	0.36	28	399	70	10138
12ZA19-17.1	846	0.54	20	0.5	1.4	0.27	15	312	58	10683
12ZA19-22.1	917	0.03	21	0.4	1.3	0.23	14	408	82	10597
12ZA19-9.1	773	0.03	21	0.5	1.6	0.35	15	286	54	9635
12ZA19-2.1	1157	0.04	23	0.7	2.6	0.50	24	393	72	10510
12ZA19-18.1	1055	0.20	18	0.6	1.9	0.61	19	411	77	10329
12ZA19-4.1	734	0.01	17	0.3	1.3	0.22	12	283	54	11127
12ZA19-15.1	1718	0.05	35	1.6	4.5	0.67	43	486	84	8983
12ZA19-3.1	1095	0.68	30	1.0	2.1	0.36	20	429	82	9581
12ZA19-19.1	738	0.04	23	0.5	1.4	0.33	15	275	52	9801
12ZA19-13.1	757	0.01	22	0.4	1.4	0.32	15	287	54	10249
12ZA19-10.1	3223	0.60	34	12.5	21.9	10.68	138	817	144	6829
12ZA19-11.1	673	0.04	19	0.4	1.2	0.20	11	267	52	10406
12ZA19-8.1	1173	0.11	14	1.1	2.9	0.76	28	362	65	9724
12ZA19-5.1	1525	0.01	1	0.4	1.9	0.08	26	479	83	12554
12ZA19-6.1	600	0.06	4	0.8	2.8	0.11	20	138	23	12855
12ZA55-6.1	2848	48.08	125	54.6	30.7	13.33	134	821	144	10152
12ZA55-2.1	803	5.29	25	7.0	5.9	2.22	25	285	53	9440
12ZA55-17.1	918	6.28	56	8.0	7.0	2.01	28	307	56	9399
12ZA55-3.1	1255	0.52	23	1.3	2.9	1.04	22	491	97	7202
12ZA55-12.1	743	0.08	12	1.5	2.8	0.89	20	241	44	7494

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
12ZA55-14.1	843	0.39	40	0.8	2.1	0.59	18	301	56	10132
12ZA55-16.1	1851	0.74	30	4.0	7.5	2.59	51	596	111	8840
12ZA55-18.1	1770	0.12	35	2.0	4.3	1.59	36	602	114	8158
12ZA55-8.1	748	0.04	21	0.8	1.7	0.62	13	322	64	9254
12ZA55-5.1	1806	0.31	32	2.1	4.3	1.06	38	628	113	12077
12ZA55-10.1	1163	1.19	31	2.3	3.8	1.28	28	401	75	8608
12ZA55-11.1	2346	0.26	34	4.3	9.2	3.16	71	716	128	7488
12ZA55-15.1	539	0.45	22	0.6	1.5	0.32	12	180	34	10027
12ZA55-4.1	702	5.11	24	3.4	0.7	1.38	19	273	54	10582
12ZA55-7.1	3796	0.50	82	12.7	21.5	7.20	125	1165	207	8658
12ZA55-9.1	4062	0.88	75	9.6	18.7	6.40	129	1241	222	9097
12ZA55-1.1	1267	16.88	46	13.8	1.9	3.56	46	435	83	11161
12ZA55-13.1	1145	53.09	79	39.6	15.0	8.02	73	279	54	9736
12ZA08-15.1	1039	12.65	29	4.8	4.6	1.03	31	287	50	7686
12ZA08-2.1	694	0.14	8	1.1	2.6	1.46	19	206	39	6413
12ZA08-14.1	1836	1.83	23	3.8	8.0	3.62	61	466	79	7001
12ZA08-5.1	765	4.87	17	3.9	4.0	2.44	26	186	33	7327
12ZA08-6.1	833	0.17	12	0.7	2.2	0.73	21	241	42	8690
12ZA08-16.1	1533	0.50	19	1.8	3.7	2.29	36	432	77	7082
12ZA08-4.1	1751	0.40	19	4.2	8.6	4.32	63	464	81	7240
12ZA08-13.1	1785	11.49	35	5.0	4.2	2.66	42	507	92	6731
12ZA08-12.1	2791	1.26	33	4.6	10.1	5.21	87	719	124	7431
12ZA08-9.1	1178	0.03	18	1.3	3.1	1.73	30	343	63	7231
12ZA08-11.1	874	0.68	14	1.1	2.5	0.91	22	258	47	9310
12ZA08-7.1	2061	0.15	20	4.9	11.2	5.49	73	543	94	7701
12ZA08-10.1	1215	0.04	17	1.2	2.9	1.57	26	375	68	7211
12ZA08-8.1	1218	123.66	84	29.1	4.2	4.05	51	311	55	6697
12ZA08-3.1	955	7.19	13	3.3	3.8	2.97	33	248	44	6924
12ZA08-1.1	614	0.18	18	0.2	0.9	0.22	9	207	35	10648

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
12ZA60-4.1	935	26.33	70	23.9	3.0	4.03	43	256	49	10793
12ZA60-3.1	1375	0.19	21	1.7	3.4	1.16	27	479	92	8015
12ZA60-8.1	860	2.07	34	4.4	5.0	1.57	26	294	57	9937
12ZA60-5.1	3360	0.86	156	11.7	21.3	9.90	127	979	172	8267
12ZA60-11.1	1417	0.10	9	1.0	2.7	1.38	28	483	91	6658
12ZA60-1.1	2726	0.12	7	0.3	1.9	0.41	29	1122	210	13482
12ZA60-14.1	921	0.09	11	1.1	2.4	0.67	19	314	57	7704
12ZA60-6.1	288	0.02	16	0.3	0.6	0.36	6	125	26	9712
12ZA60-13.1	3412	2.36	21	10.1	17.8	2.80	130	907	156	9932
12ZA60-15.1	1692	0.30	22	4.1	8.1	2.43	54	499	89	8789
12ZA60-7.1	904	0.46	45	1.3	2.9	0.80	22	305	57	11115
12ZA60-16.1	1274	0.05	32	1.1	2.9	1.71	26	467	90	8405
12ZA60-2.1	774	52.86	214	38.5	11.2	6.83	51	257	53	12414
12ZA60-12.1	1109	0.57	45	2.9	5.4	2.67	35	368	65	12165
12ZA60-10.1	951	4.12	26	3.7	3.4	1.04	19	499	109	11563
12ZA60-9.1	1778	0.04	2	1.4	3.9	0.26	41	556	98	10124
BLOU-2.1	204	0.007	18	0.18	0.4	0.22	4.9	83	18	10463
BLOU-3.1	1624	0.038	36	2.17	5.6	0.52	48.6	444	75	9009
BLOU-7.1	568	0.670	27	2.51	1.9	0.63	10.9	243	47	11199
BLOU-13.1	480	0.016	26	0.52	1.6	0.35	13.0	151	28	10116
BLOU-9.1	956	0.020	56	0.61	2.1	0.82	19.6	357	69	10542
BLOU-14.1	1552	0.347	55	3.18	6.6	2.51	46.2	503	92	8680
BLOU-8.1	486	0.022	33	0.46	1.1	0.65	10.2	208	42	9671
BLOU-5.1	455	0.408	27	0.54	1.0	0.31	8.9	186	37	9936
BLOU-6.1	634	0.667	28	1.70	1.9	0.67	12.2	272	54	8476
BLOU-15.1	387	0.028	22	0.38	1.0	0.54	7.2	165	35	9476
BLOU-17.1	203	0.011	15	0.47	0.9	0.49	5.7	77	15	8788
BLOU-16.1	656	0.014	15	1.23	2.5	0.77	18.0	206	38	9402
BLOU-19.1	701	0.749	21	1.97	2.5	0.66	16.2	250	47	7207

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
BLOU-24.1	488	2.022	13	1.24	2.0	0.58	14.7	155	28	7599
BLOU-1.1	550	0.274	2	0.58	0.6	0.23	6.5	363	75	12478
BLOU-10.1	1373	0.040	1	0.13	0.7	0.16	10.1	640	113	12940
BLOU-20.1	2249	0.022	9	1.17	3.7	0.58	43.1	749	132	10185
BLOU-4.1	1510	28.264	177	46.95	23.2	4.93	55.5	479	84	10257
BLOU-21.1	1266	0.243	10	0.88	2.6	0.32	23.3	432	77	10057
BLOU-25.1	808	0.750	11	1.82	2.0	0.42	14.5	305	59	10280
BLOU-12.1	605	0.018	12	0.29	1.0	0.07	10.3	224	41	10743
BLOU-26.1	943	0.092	31	2.61	4.3	2.36	35.1	262	47	7871
BLOU-18.1	513	0.022	11	0.49	1.4	0.25	11.6	167	30	8907
BLOU-23.1	607	0.045	16	0.46	1.5	0.47	10.6	274	58	9364
BLOU-11.1	1090	0.280	28	1.81	3.1	0.57	25.4	350	64	9482
BLOU-22.1	622	0.015	21	0.35	1.3	0.50	12.9	219	40	9819
13ZA93A-7.1	799	13.998	97	19.88	12.1	3.23	24.4	283	55	11566
13ZA93A-4.1	680	0.207	61	1.20	2.3	1.10	16.9	242	48	10739
13ZA93A-6.1	1605	0.029	10	1.60	4.4	0.62	39.6	449	80	8976
13ZA93A-5.1	3488	0.004	2	0.35	2.2	0.20	32.4	1498	273	12641
13ZA93A-1.1	1720	4.553	11	3.43	4.9	1.02	41.0	516	93	7662
13ZA93A-2.1	489	0.009	24	0.23	1.0	0.27	8.8	301	60	9381
13ZA93A-3.1	343	0.016	20	0.82	1.8	0.38	11.6	91	16	8406
13ZA93A-8.1	1758	0.082	12	1.01	3.4	1.78	38.3	524	92	10476
13ZA72A-14.1	484	0.160	25	0.61	1.4	0.67	11.1	191	40	8658
13ZA72A-21.1	427	0.063	36	0.50	1.5	0.72	10.5	155	32	9995
13ZA72A-8.1	886	0.329	67	1.61	3.1	1.03	22.9	288	55	9976
13ZA72A-6.1	622	0.016	50	0.95	2.1	0.90	15.2	225	44	9661
13ZA72A-17.1	488	0.011	20	0.53	1.4	0.36	11.8	164	32	9897
13ZA72A-12.1	1336	0.044	32	1.19	3.4	0.76	29.0	436	80	10799
13ZA72A-27.1	1954	0.101	14	4.67	9.7	4.13	72.8	530	94	7605

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
13ZA72A-23.1	575	0.119	28	0.56	1.4	0.36	12.7	198	38	10580
13ZA72A-9.1	1087	0.012	7	0.94	2.8	0.71	24.3	353	66	8616
13ZA72A-24.1	533	0.007	30	0.44	1.4	0.44	11.4	191	36	10989
13ZA72A-10.1	423	0.462	42	1.71	1.8	0.90	12.4	155	33	9107
13ZA72A-5.1	2705	0.480	40	4.58	8.9	2.18	86.8	685	119	8381
13ZA72A-19.1	1360	0.022	36	1.47	4.9	0.91	36.9	423	74	10618
13ZA72A-4.1	906	1.198	31	4.52	4.6	1.68	18.2	399	83	10256
13ZA72A-16.1	935	4.422	56	11.41	9.8	3.04	29.2	313	59	8451
13ZA72A-30.1	616	0.003	21	0.36	1.4	0.24	13.2	227	43	10902
13ZA72A-18.1	1524	0.014	23	1.23	3.3	0.99	29.0	526	98	8130
13ZA72A-15.1	2492	0.026	21	2.21	7.3	0.80	68.1	664	113	9890
13ZA72A-2.1	1682	0.011	21	0.42	1.8	0.29	22.2	651	122	11938
13ZA72A-28.1	992	0.012	17	0.88	2.7	0.46	24.3	304	56	9243
13ZA72A-29.1	798	0.013	6	0.70	2.1	0.15	16.8	311	58	9712
13ZA72A-25.1	2047	0.023	36	1.75	4.6	1.61	44.7	613	111	7257
13ZA72A-20.1	371	6.906	45	11.83	6.7	2.04	15.8	212	48	10194
13ZA72A-11.1	346	0.007	8	0.17	0.6	0.32	6.6	164	38	10305
13ZA72A-1.1	1345	0.002	2	0.25	1.5	0.07	21.6	412	74	11851
13ZA72A-22.1	1604	0.049	7	0.35	1.7	0.26	20.7	576	105	9551
13ZA72A-7.1	1360	52.060	276	84.99	51.6	19.11	113.8	307	58	10008
13ZA72A-3.1	919	0.345	5	0.59	1.6	0.42	13.9	336	66	11203
13ZA72-18.1d	1502	91.860	479	130.92	69.6	14.53	105.6	423	76	10439
13ZA72A-13.1	838	0.019	8	0.36	1.4	0.11	13.7	343	68	15595
13ZA72-17.1d	243	0.081	1	0.12	0.1	0.04	0.9	227	56	8763
13ZA72A-26.1	623	0.005	1	0.06	0.4	0.04	7.7	188	31	12968
12ZA18-6.1	3270	246.157	802	476.83	353.3	94.62	504.1	716	127	7111
12ZA18-2.1	2425	98.110	478	147.67	65.8	15.67	137.1	673	119	11535
12ZA18-11.1	1965	39.750	775	62.75	28.8	7.85	84.0	546	101	8757
12ZA18-32.1	2873	19.259	66	29.25	15.8	4.47	59.4	899	159	12861

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
12ZA18-16.1	1045	0.251	79	1.80	4.5	2.27	37.4	279	49	8725
12ZA18-24.1	1809	0.211	85	2.56	6.3	3.39	55.2	515	92	8189
12ZA18-22.1	709	0.164	32	0.70	1.6	0.88	16.4	228	42	9543
12ZA18-31.1	508	0.319	17	0.61	1.0	0.40	7.0	234	49	12014
12ZA18-14.1	1456	8.091	66	12.16	8.7	3.10	49.6	444	82	8463
12ZA18-20.1	829	0.112	25	1.11	2.6	1.56	22.8	267	52	7510
12ZA18-12.1	1335	5.646	39	15.30	20.1	8.54	96.5	278	47	8777
12ZA18-18.1	862	0.139	39	0.97	2.0	0.64	16.9	318	61	11124
12ZA18-30.1	1834	0.054	61	4.19	9.4	4.81	62.5	512	93	7782
12ZA18-29.1	1364	0.075	50	4.00	8.2	3.96	50.1	384	70	8035
12ZA18-23.1	211	0.014	3	0.56	2.1	0.68	19.2	27	5	11740
12ZA18-28.1	854	4.737	144	8.05	5.1	1.51	20.5	320	65	10433
12ZA18-13.1	938	32.119	60	7.30	5.7	2.57	32.8	292	56	8419
12ZA18-10.1	845	0.141	42	0.72	1.9	0.83	19.1	300	57	10410
12ZA18-17.1	1792	35.402	143	48.31	28.6	7.43	71.0	577	111	10949
12ZA18-26.1	964	8.870	82	13.70	8.7	3.07	30.9	258	49	6463
12ZA18-7.1	3303	0.457	5	1.75	4.5	0.21	53.8	961	167	11308
12ZA18-21.1	2039	0.753	24	3.98	8.3	0.76	62.1	571	100	8405
12ZA18-15.1	3372	0.059	5	4.09	10.0	0.59	89.8	881	151	9818
12ZA18-27.1	2235	0.097	46	1.18	3.9	1.26	41.3	756	138	9667
12ZA18-25.1	1324	0.008	10	0.51	1.9	0.38	22.6	468	85	10646
12ZA18-36.1	1085	6.231	151	6.19	4.3	0.99	26.7	359	68	9724
12ZA18-19.1	415	0.020	26	0.30	0.9	0.48	7.2	185	38	11196
12ZA18-35.1	162	0.027	3	1.74	4.8	0.14	20.4	20	3	10807
12ZA18-4.1	1243	2.550	27	2.74	2.8	0.72	24.2	412	75	8617
12ZA18-37.1	988	13.553	91	24.31	12.4	3.10	32.6	358	74	8136
12ZA18-8.1	535	1.500	45	2.13	2.3	0.40	16.2	166	31	9309
12ZA18-5.1	592	0.679	4	1.08	2.0	0.15	15.6	185	34	8181
12ZA18-34.1	938	0.030	4	1.90	4.5	1.37	32.3	283	52	8136
12ZA18-33.1	3655	30.655	525	29.39	18.9	2.53	98.9	967	171	9223

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
12ZA18-9.1	1228	4.379	27	13.48	19.4	5.53	59.9	375	67	9414
12ZA18-1.1	450	0.775	18	2.15	2.0	0.30	10.5	148	27	10879
12ZA18-3.1	660	0.048	87	1.95	4.1	1.45	26.3	175	32	9048
13ZA76A-27.1	871	0.032	15	1.50	3.5	1.27	25.1	274	53	7265
13ZA76A-30.1	530	0.031	17	0.60	1.4	0.47	11.7	198	39	8634
13ZA76A-31.1	1232	0.134	44	2.45	5.3	2.12	38.9	361	65	7464
13ZA76A-34.1	718	0.008	20	0.63	1.8	0.36	16.5	236	43	9473
13ZA76A-11.1	918	6.213	84	8.30	6.0	1.81	28.4	275	49	10390
13ZA76A-37.1	783	0.322	39	1.60	2.0	0.96	16.3	286	58	10200
13ZA76A-20.1	610	1.560	32	4.19	3.7	1.08	16.2	193	37	7550
13ZA76A-26.1	1123	0.008	5	0.17	1.2	0.44	13.1	497	94	12820
13ZA76A-14.1	750	4.658	76	9.71	6.7	2.04	29.2	236	44	9518
13ZA76A-35.1	533	0.009	40	0.49	1.4	0.68	10.9	199	44	10300
13ZA76A-22.1	713	49.520	171	37.44	14.4	2.40	27.1	267	52	8662
13ZA76A-19.1	780	16.621	35	4.28	3.9	1.37	25.9	232	44	8770
13ZA76A-2.1	972	0.053	15	2.63	4.4	1.43	28.8	323	61	8351
13ZA76A-33.1	1825	0.095	13	0.76	2.3	0.54	21.9	860	172	12575
13ZA76A-16.1	1338	0.117	34	3.14	6.8	2.17	40.4	441	83	9323
13ZA76A-18.1	972	0.066	52	1.11	2.9	0.52	25.2	301	55	10142
13ZA76A-32.1	511	0.015	20	0.51	1.3	0.58	11.3	224	48	8867
13ZA76A-39.1	426	0.306	15	1.33	2.3	0.57	16.2	118	21	6904
13ZA76A-6.1	1631	0.201	22	4.29	8.0	2.92	57.7	486	89	8020
13ZA76A-9.1	995	0.028	115	1.45	4.3	1.55	34.5	281	51	10213
13ZA76A-1.1	2255	0.072	47	5.38	13.2	6.07	91.2	529	91	9297
13ZA76A-7.1	1549	0.133	27	4.47	8.6	4.50	57.6	425	77	6959
13ZA76A-8.1	1891	0.151	28	6.56	10.6	4.20	73.3	532	96	7814
13ZA76A-10.1	529	0.011	30	0.37	1.4	0.54	10.9	196	38	10426
13ZA76A-21.1	697	0.020	16	0.93	1.9	0.71	14.6	240	46	7709
13ZA76A-29.1	1321	1.237	22	2.64	5.0	1.35	34.5	388	70	7551

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
13ZA76A-15.1	452	1.255	36	3.86	3.2	1.17	12.9	154	31	8831
13ZA76A-25.1	875	0.328	72	1.02	2.6	1.03	21.5	282	51	10432
13ZA76A-12.1	245	0.105	14	0.33	0.4	0.26	3.9	127	30	11458
13ZA76A-5.1	1241	0.103	14	2.36	5.0	0.88	34.6	328	59	8436
13ZA76A-4.1	681	0.032	9	0.50	1.5	0.17	15.1	224	40	9923
13ZA76A-36.1	1197	0.086	51	1.84	3.4	1.35	22.7	492	98	9627
13ZA76A-17.1	910	0.633	26	1.24	1.9	0.68	16.5	309	57	11486
13ZA76A-40.1	1438	0.925	49	3.11	5.2	1.12	35.4	442	83	9208
13ZA76A-3.1	801	0.027	7	1.21	2.6	0.13	21.4	278	52	10552
13ZA76A-13.1	723	0.192	7	0.58	1.4	0.21	13.4	263	51	10140
13ZA76A-23.1	2382	0.046	1	0.62	3.2	0.22	37.5	795	143	11659
13ZA76A-38.1	1101	7.054	66	23.87	17.2	2.88	57.3	226	38	8001
13ZA76A-24.1	469	0.287	16	1.48	2.8	0.25	18.4	111	19	9312
13ZA76A-28.1	828	0.013	7	0.35	1.5	0.20	16.6	273	50	10532
12ZA05B-13.1	1915	121.12	579	180.9	81.4	16.67	156.7	498	92	11016
12ZA05B-5.1	1023	16.31	94	43.5	22.3	3.65	49.8	344	67	10608
12ZA05B-3.1	1294	16.01	78	24.3	11.8	3.91	38.8	425	82	10838
12ZA05B-18.1	886	0.30	46	1.7	2.9	1.17	21.7	259	49	7916
12ZA05B-16.1	520	0.02	15	0.8	1.7	0.79	11.6	203	44	8878
12ZA05B-14.1	7191	135.24	2543	467.3	295.1	93.69	817.4	2171	361	15673
12ZA05B-8.1	907	0.02	64	1.4	3.5	1.11	23.5	301	57	9052
12ZA05B-9.1	2237	0.06	3	3.7	8.2	0.54	64.0	566	99	8842
12ZA05B-10.1	4057	0.42	110	9.8	17.4	3.94	109.0	1184	216	7649
12ZA05B-12.1	904	1.47	26	3.4	3.5	0.68	18.1	292	53	11595
12ZA05B-15.1	8460	1.06	21	5.1	14.9	1.88	156.9	2390	410	10466
12ZA05B-1.1	1815	0.03	36	2.2	4.8	2.01	45.6	535	100	8530
12ZA05B-4.1	294	0.02	27	0.4	1.1	0.21	7.1	101	19	10597
12ZA05B-6.1	1926	0.44	9	1.1	3.2	0.35	36.8	557	99	12527
12ZA05B-17.1	943	2.92	17	4.6	4.6	0.73	25.8	302	56	9292

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
12ZA05B-11.1	521	0.01	8	0.4	1.4	0.16	11.2	172	33	11190
12ZA05B-7.1	2695	0.02	6	1.4	4.5	0.30	48.1	773	132	10614
12ZA05B-2.1	840	0.29	19	1.8	2.8	0.64	24.0	230	44	10994
13ZA67-16.1	1444	10.59	66	24.1	15.0	3.65	48.8	411	77	9973
13ZA67-13.1	1381	0.78	23	2.2	3.9	1.58	32.1	429	79	10050
13ZA67-32.1	351	0.00	16	0.5	0.9	0.30	6.7	162	36	4518
13ZA67-3.1	1682	0.31	42	2.9	5.3	1.90	43.0	482	90	8929
13ZA67-6.1	681	0.31	60	1.7	2.6	1.22	17.0	238	48	9437
13ZA67-11.1	2501	3.83	37	7.9	13.3	3.53	87.5	558	99	6765
13ZA67-15.1	379	18.17	46	12.4	5.6	1.34	14.0	130	27	10091
13ZA67-27.1	1079	0.48	64	1.5	2.9	1.15	20.9	378	76	4202
13ZA67-20.1	1331	0.01	13	1.0	3.2	0.78	27.4	452	82	9455
13ZA67-19.1	550	1.67	41	2.5	2.2	0.77	11.1	214	42	10845
13ZA67-24.1	233	2.80	12	2.1	1.9	1.54	7.1	97	23	3357
13ZA67-7.1	1701	35.79	228	60.3	37.7	14.74	100.1	463	86	9365
13ZA67-2.1	723	0.01	34	0.6	1.6	0.39	13.5	268	54	11056
13ZA67-17.1	537	0.97	28	3.2	3.4	0.92	15.2	204	41	11223
13ZA67-37.1	614	0.35	26	1.6	2.5	1.18	17.4	204	43	4615
13ZA67-14.1	451	-	37	0.4	1.0	0.41	8.5	196	43	10025
13ZA67-8.1	907	0.05	25	0.5	1.9	0.45	16.8	334	67	10244
13ZA67-9.1	1199	0.00	52	0.8	2.9	0.36	23.1	393	75	11258
13ZA67-10.1	759	0.30	37	1.3	2.2	0.82	15.0	267	53	8995
13ZA67-35.1	887	0.01	38	0.5	1.8	0.49	15.9	294	55	4908
13ZA67-25.1	1974	0.18	23	3.4	6.9	2.04	51.8	579	109	3923
13ZA67-26.1	1232	4.79	89	12.2	9.7	2.95	34.5	390	73	4941
13ZA67-18.1	3277	60.43	440	48.8	29.0	12.49	122.3	941	170	10340
13ZA67-36.1	1075	1.97	42	4.8	5.4	2.14	33.9	356	75	4081
13ZA67-1.1	692	0.01	43	0.8	1.8	0.67	15.1	261	53	9955
13ZA67-28.1	604	0.01	15	0.2	1.0	0.45	9.5	278	63	4388

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
13ZA67-4.1	645	2.21	51	4.2	4.0	1.34	17.4	225	45	10705
13ZA67-31.1	751	1.98	28	7.4	5.9	1.27	22.6	252	50	4216
13ZA67-29.1	855	0.01	38	0.3	1.0	0.33	11.1	327	64	4167
13ZA67-5.1	1527	0.04	7	1.2	3.9	0.47	33.9	427	73	9754
13ZA67-12.1	1828	0.01	3	1.7	5.7	0.33	51.3	484	87	9252
13ZA67-33.1	770	0.02	19	0.4	1.2	0.16	12.0	295	57	4658
SUTH-5.1	1085	0.57	71	1.9	4.5	2.14	32	336	60	8424
SUTH-40.1	341	0.06	25	0.3	0.8	0.49	7	147	33	9986
SUTH-7.1	699	0.16	77	1.1	2.6	1.16	19	223	43	9354
SUTH-9.1	497	0.34	45	1.2	1.6	0.85	12	186	38	8169
SUTH-19.1	1365	0.31	73	6.9	11.7	5.53	59	391	73	8012
SUTH-31.1	617	8.39	64	3.4	2.9	1.29	19	217	44	9469
SUTH-11.1	332	0.11	22	0.3	0.9	0.46	7	145	32	9411
SUTH-1.1	916	0.15	70	1.6	3.8	1.42	26	300	57	9284
SUTH-18.1	905	0.01	42	0.5	1.9	0.73	16	345	63	10198
SUTH-3.1	345	0.20	37	0.5	1.1	0.54	8	134	29	9200
SUTH-2.1	1324	0.35	37	2.2	5.7	1.79	44	345	59	9767
SUTH-30.1	1239	0.02	99	2.3	5.8	2.33	40	354	63	9294
SUTH-13.1	543	0.74	24	0.9	1.7	0.82	14	176	33	8476
SUTH-10.1	451	0.02	15	0.2	1.0	0.15	9	151	28	11214
SUTH-14.1	669	1.00	42	1.9	3.6	1.22	18	221	40	8666
SUTH-15.1	535	0.05	49	0.9	1.9	0.80	14	193	36	10002
SUTH-35.1	350	0.03	14	0.2	0.6	0.13	6	147	29	10689
SUTH-26.1	365	0.01	11	0.6	1.5	0.61	11	125	23	8638
SUTH-36.1	873	0.02	18	2.4	4.1	1.49	26	288	52	8485
SUTH-41.1	457	0.14	19	0.7	1.1	0.47	8	206	43	9143
SUTH-32.1	635	0.01	36	0.5	1.4	0.45	12	257	51	9272
SUTH-4.1	868	0.12	31	0.8	2.0	0.99	17	334	64	9531
SUTH-17.1	1392	0.24	50	0.6	1.8	0.56	19	577	108	11000

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
SUTH-38.1	2023	0.34	23	2.3	5.3	0.56	48	559	97	9357
SUTH-39.1	1711	0.17	23	1.2	2.3	0.83	29	605	114	10179
SUTH-12.1	342	1.94	50	5.4	3.6	1.60	14	92	17	8339
SUTH-34.1	1305	0.05	7	0.6	2.0	0.17	23	453	81	11689
SUTH-6.1	1090	0.02	3	0.7	2.4	0.27	23	327	58	9622
SUTH-16.1	1356	0.06	17	2.8	6.3	0.07	45	352	59	8355
SUTH-8.1	559	0.38	10	1.1	1.6	0.18	13	172	30	9345
SUTH-37.1	338	0.26	22	1.6	1.3	0.41	9	147	29	9472
SUTH-33.1	655	0.26	45	1.1	2.5	0.83	18	211	39	6476
12ZA45-1.1	1347	0.14	17	1.8	3.7	0.88	30	451	81	8044
12ZA45-4.1	1094	0.03	4	0.7	2.3	0.13	23	378	66	8501
12ZA45-5.1	1757	1.33	20	9.5	10.6	1.25	54	534	90	10102
12ZA45-6.1	1534	0.05	2	0.5	2.3	0.11	27	527	95	10625
12ZA45-2.1	1561	0.02	2	1.8	4.6	0.27	37	515	92	8200
12ZA45-4.2	1860	0.14	6	3.7	7.1	0.64	55	547	94	8410
12ZA45-7.2	1435	2.17	25	12.7	9.6	1.50	38	427	72	9136
12ZA45-7.1	993	1.15	20	8.8	6.1	1.11	27	300	53	9529
12ZA45-3.1	1432	0.04	5	2.0	5.0	0.44	38	421	71	8809
13ZA75A-9.1	6556	233.04	1228	447.9	124.0	61.80	467	1546	250	9284
13ZA75A-13.1	771	6.71	54	22.2	10.8	2.78	30	225	39	7747
13ZA75A-6.1	1652	0.12	78	6.7	12.7	4.94	71	438	74	8148
13ZA75A-3.1	1841	0.81	102	10.5	16.7	7.86	85	495	86	7008
13ZA75A-2.1	1658	0.38	24	3.1	7.3	1.49	57	441	74	7821
13ZA75A-7.1	1838	0.19	50	7.4	13.7	8.07	79	526	95	6771
13ZA75A-10.1	681	0.02	34	0.7	2.1	0.64	17	248	45	9807
13ZA75A-8.1	793	0.04	0	0.3	1.8	0.06	21	157	25	11759
13ZA75A-11.1	2538	0.28	17	8.1	16.1	4.37	102	661	112	6212
13ZA75A-4.1	1635	0.01	11	1.0	4.1	0.48	38	540	97	10654

Spot name	Y (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)
13ZA75A-5.1	1037	0.08	15	0.3	1.3	0.34	15	417	77	10645
13ZA75A-14.1	2495	4.05	40	9.4	7.1	0.99	54	741	120	9997
13ZA75A-1.1	1651	0.22	15	3.8	7.3	2.65	51	468	81	7685
13ZA75A-12.1	197	0.02	1	0.0	0.2	0.29	4	31	5	9567
13ZA75A-15.1	995	0.08	13	1.8	3.6	0.61	27	299	53	7663

An electronic version of this appendix is available to improve data access.

Appendix E: SHRIMP Ti-in-zircon temperature analyses

Spot name	⁴⁸ Ti (ppm)	⁴⁸ Ti/ ⁴⁹ Ti	Fe (ppm)	Temp (⁴⁸ Ti) °C
12ZA23-13.1	12.3	13.5	28.3	758
12ZA23-12.1	27.7	13.8	339.8	843
12ZA23-5.1	22.8	13.3	79.5	821
12ZA23-9.1	8.1	13.3	0.3	719
12ZA23-1.1	13.1	13.3	0.1	764
12ZA23-7.1	9.1	13.4	4.2	729
12ZA23-11.1	3.9	13.1	2.1	657
12ZA23-4.1	10.2	13.6	1.1	741
12ZA23-16.1	3.6	14.5	1.7	652
12ZA23-6.1	8.2	13.8	2.4	721
12ZA23-8.1	14.9	13.5	7.7	777
12ZA23-14.1	11.7	13.3	4.4	753
12ZA23-3.1	5.8	13.3	0.6	691
12ZA23-10.1	7.9	13.6	21.1	717
12ZA23-2.1	9.8	13.2	1.6	736
12ZA23-15.1	15.6	13.9	0.3	781
12ZA54-7.1	12.4	13.5	1109.4	759
12ZA54-5.1	13.5	13.3	38.3	767
12ZA54-12.1	22.1	12.7	34.1	818
12ZA54-6.1	12.9	13.8	17.1	763
12ZA54-14.1	13.0	12.9	3.7	764
12ZA54-8.1	7.1	14.9	9.1	708
12ZA54-11.1	14.7	13.3	0.1	776
12ZA54-15.1	18.6	13.3	1.2	800
12ZA54-16.1	20.4	13.1	2.3	809
12ZA54-9.1	15.0	13.5	3.7	778
12ZA54-4.1	14.9	13.2	0.4	777
12ZA54-1.1	11.4	13.0	0.1	751
12ZA54-13.1	18.8	13.0	0.0	801
12ZA54-3.1	8.5	13.1	105.4	724
12ZA54-10.1	5.7	13.5	4.7	689
12ZA54-2.1	13.5	14.3	31.0	768
12ZA61-7.1	9.4	13.1	250.0	741
12ZA61-9.1	16.2	13.1	228.5	794
12ZA61-14.1	9.2	12.9	107.8	738
12ZA61-12.1	9.0	14.3	28.6	736
12ZA61-10.1	16.9	13.5	168.6	798
12ZA61-11.1	9.9	13.0	1.9	745

Spot name	⁴⁸ Ti (ppm)	⁴⁸ Ti/ ⁴⁹ Ti	Fe (ppm)	Temp (⁴⁸ Ti) °C
12ZA61-8.1	19.4	13.3	1.0	812
12ZA61-15.1	7.1	13.5	12.3	715
12ZA61-4.1	6.1	13.3	3.1	702
12ZA61-1.1	7.9	12.8	253.1	724
12ZA61-6.1	11.9	13.2	689.1	763
12ZA61-5.1	12.9	13.9	0.0	771
12ZA61-13.1	5.1	13.8	0.3	687
12ZA61-2.1	27.3	13.3	2.1	850
12ZA61-3.1	5.3	13.8	22.1	690
12ZA07-11.1	44.5	13.6	3497.5	932
12ZA07-25.1	-	-	-	-
12ZA07-9.1	6.9	14.0	7.5	728
12ZA07-6.1	11.5	13.1	2.4	777
12ZA07-7.1	10.8	13.7	4.6	771
12ZA07-8.1	8.3	13.3	26.8	746
12ZA07-3.1	8.9	13.7	6.7	753
12ZA07-5.1	9.5	12.7	0.2	758
12ZA07-10.1	11.0	13.5	5.3	773
12ZA07-4.1	12.2	13.5	0.3	783
12ZA07-2.1	14.1	13.3	50.3	798
12ZA07-1.1	34.1	13.2	28.9	898
12ZA46-4.1	52.4	13.5	281.7	947
12ZA46-10.1	10.4	12.7	6.7	762
12ZA46-1.1	20.0	13.0	3.6	830
12ZA46-5.1	10.6	13.5	0.4	764
12ZA46-3.1	15.4	13.2	0.2	802
12ZA46-7.1	14.0	13.8	4.3	792
12ZA46-6.1	14.5	13.0	4.9	795
12ZA46-2.1	8.5	13.2	12.2	743
12ZA46-9.1	14.6	13.2	2.3	796
12ZA46-8.1	11.6	13.8	4.2	773
12ZA46-11.1	32.6	13.1	11.6	886
12ZA22B-4.1	35.7	13.2	175.8	914
12ZA22B-7.1	4.7	13.5	14.5	702
12ZA22B-6.2	4.8	14.0	0.9	703
12ZA22B-5.1	9.3	13.4	64.4	764
12ZA22B-1.1	17.5	13.7	152.8	830
12ZA22B-2.1	4.3	12.4	1.8	694
12ZA22B-6.1	9.4	13.4	0.4	765

Spot name	^{48}Ti (ppm)	$^{48}\text{Ti}/^{49}\text{Ti}$	Fe (ppm)	Temp (^{48}Ti) °C
12ZA22B-3.1	7.5	13.4	34.0	743

An electronic version of this appendix is available to improve data access.

Appendix F: U-Pb zircon LA-ICPMS analyses

			Isotopic Ratios						Apparent Ages (Ma)								
Spot name	U (ppm)	U/Th	²⁰⁷ Pb*/ ²⁰⁶ Pb*	± (%)	²⁰⁷ Pb*/ ²³⁵ U	± (%)	²⁰⁶ Pb/ ²³⁸ U	± (%)	error corr.	²⁰⁶ Pb/ ²³⁸ U	± (Ma)	²⁰⁷ Pb/ ²³⁵ U	± (Ma)	²⁰⁶ Pb/ ²⁰⁷ Pb	± (Ma)	Best Age	± (Ma)
12ZA16-20.1	416	0.7	18.8342	4.6	0.3034	4.8	0.0414	1.2	0.25	261.8	3.1	269.1	11.3	332.8	105.3	261.8	3.1
12ZA16-17.2	271	0.7	17.9828	13.2	0.3192	14.0	0.0416	4.7	0.34	262.9	12.1	281.3	34.4	436.8	294.3	262.9	12.1
12ZA16-19	327	0.7	19.5344	4.1	0.2964	7.7	0.0420	6.5	0.84	265.2	16.8	263.6	17.8	249.5	95.4	265.2	16.8
12ZA16-28	227	1.1	19.2507	4.4	0.3018	4.9	0.0421	2.2	0.46	266.0	5.8	267.8	11.6	283.1	100.3	266.0	5.8
12ZA16-5	255	1.3	19.3190	5.2	0.3018	5.8	0.0423	2.6	0.45	267.0	6.9	267.8	13.7	274.9	118.9	267.0	6.9
12ZA16-15.2	283	0.9	20.1141	4.7	0.2901	5.2	0.0423	2.2	0.43	267.2	5.9	258.7	11.9	181.7	110.2	267.2	5.9
12ZA16-26	395	1.2	19.2388	3.6	0.3044	4.0	0.0425	1.6	0.41	268.2	4.3	269.8	9.4	284.5	82.8	268.2	4.3
12ZA16-17.3	371	1.1	19.8393	3.7	0.2955	4.2	0.0425	1.9	0.45	268.4	5.0	262.9	9.7	213.7	86.9	268.4	5.0
12ZA16-29	265	0.8	19.9325	4.4	0.2944	4.4	0.0426	0.7	0.16	268.7	1.9	262.0	10.2	202.8	101.1	268.7	1.9
12ZA16-23.2	207	1.5	18.5833	8.8	0.3162	9.2	0.0426	2.4	0.27	269.1	6.4	279.0	22.3	363.2	199.5	269.1	6.4
12ZA16-10	459	1.3	18.9732	6.7	0.3110	6.9	0.0428	1.5	0.22	270.1	4.0	274.9	16.5	316.1	152.6	270.1	4.0
12ZA16-25	498	0.8	19.4056	5.8	0.3042	6.0	0.0428	1.5	0.25	270.3	4.0	269.7	14.1	264.7	132.2	270.3	4.0
12ZA16-4	369	1.0	19.8649	8.4	0.2975	8.5	0.0429	1.3	0.15	270.5	3.4	264.4	19.9	210.7	196.0	270.5	3.4
12ZA16-18	282	0.6	15.2712	28.8	0.3869	29.1	0.0429	4.0	0.14	270.5	10.7	332.1	82.6	789.9	616.9	270.5	10.7
12ZA16-32	194	0.9	18.2229	20.4	0.3250	22.4	0.0430	9.2	0.41	271.1	24.3	285.7	55.8	407.2	461.2	271.1	24.3
12ZA16-8	294	0.8	18.2844	10.1	0.3244	10.5	0.0430	2.8	0.27	271.5	7.5	285.3	26.2	399.6	227.8	271.5	7.5
12ZA16-27	348	1.5	19.4856	3.6	0.3047	4.8	0.0431	3.1	0.65	271.7	8.3	270.0	11.4	255.2	83.5	271.7	8.3
12ZA16-23	319	1.0	19.4646	3.2	0.3050	3.4	0.0431	1.2	0.36	271.8	3.3	270.3	8.1	257.7	73.4	271.8	3.3
12ZA16-24	400	1.3	19.7851	2.3	0.3003	2.8	0.0431	1.6	0.56	271.9	4.1	266.6	6.5	220.1	52.9	271.9	4.1
12ZA16-6	301	1.4	18.8084	2.6	0.3160	3.7	0.0431	2.5	0.69	272.0	6.8	278.8	8.9	336.0	59.9	272.0	6.8
12ZA16-30	241	0.6	19.5584	11.6	0.3052	11.7	0.0433	1.7	0.14	273.2	4.5	270.5	27.9	246.6	268.2	273.2	4.5
12ZA16-1.2	243	1.2	20.0314	6.0	0.2981	8.5	0.0433	6.1	0.72	273.3	16.3	264.9	19.9	191.4	138.5	273.3	16.3
12ZA16-20	275	1.3	19.5457	5.6	0.3056	5.7	0.0433	1.4	0.25	273.4	3.8	270.7	13.7	248.2	128.2	273.4	3.8
12ZA16-16	299	0.7	19.7350	7.3	0.3028	7.5	0.0433	1.7	0.23	273.5	4.6	268.6	17.6	225.9	167.8	273.5	4.6
12ZA16-17.1	319	0.8	19.1054	8.6	0.3140	8.8	0.0435	1.9	0.21	274.6	5.1	277.3	21.3	300.4	195.5	274.6	5.1
12ZA16-31	273	1.3	20.1678	4.4	0.2975	4.6	0.0435	1.4	0.30	274.6	3.6	264.4	10.6	175.5	101.6	274.6	3.6
12ZA16-11	125	1.1	21.9961	10.2	0.2742	10.6	0.0438	2.7	0.26	276.0	7.4	246.1	23.2	-30.8	248.7	276.0	7.4

			Isotopic Ratios						Apparent Ages (Ma)								
Spot name	U (ppm)	U/Th	²⁰⁷ Pb*/ ²⁰⁶ Pb*	± (%)	²⁰⁷ Pb*/ ²³⁵ U	± (%)	²⁰⁶ Pb/ ²³⁸ U	± (%)	error corr.	²⁰⁶ Pb/ ²³⁸ U	± (Ma)	²⁰⁷ Pb/ ²³⁵ U	± (Ma)	²⁰⁶ Pb/ ²⁰⁷ Pb	± (Ma)	Best Age	± (Ma)
12ZA16-12	443	1.4	19.7658	4.0	0.3057	4.2	0.0438	1.2	0.28	276.5	3.2	270.9	9.9	222.3	92.3	276.5	3.2
12ZA16-16.2	487	0.5	19.4401	2.8	0.3110	3.0	0.0438	1.2	0.40	276.6	3.3	274.9	7.3	260.6	64.1	276.6	3.3
12ZA16-22	182	1.2	18.6859	5.8	0.3252	6.0	0.0441	1.3	0.22	278.0	3.5	285.9	14.9	350.7	132.1	278.0	3.5
12ZA16-21	215	1.1	19.2414	6.7	0.3160	7.1	0.0441	2.4	0.34	278.2	6.6	278.8	17.3	284.1	152.5	278.2	6.6
12ZA16-15	406	1.4	19.9593	3.1	0.3060	3.5	0.0443	1.6	0.45	279.4	4.3	271.1	8.3	199.7	71.9	279.4	4.3
12ZA16-9	539	0.8	15.9716	17.3	0.3858	17.3	0.0447	1.0	0.06	281.8	2.7	331.3	48.9	695.1	370.3	281.8	2.7
12ZA16-14	178	0.9	20.4563	8.5	0.3114	8.8	0.0462	2.2	0.25	291.1	6.2	275.2	21.2	142.3	200.5	291.1	6.2
12ZA16-7	309	1.0	19.3335	2.2	0.3400	2.8	0.0477	1.7	0.60	300.3	4.9	297.2	7.1	273.2	50.6	300.3	4.9
12ZA16-13	550	2.1	17.6358	6.5	0.5290	6.6	0.0677	0.9	0.14	422.0	3.8	431.1	23.1	480.0	144.0	422.0	3.8
12ZA10-16	681	1.0	18.5698	8.5	0.3057	9.9	0.0412	5.1	0.52	260.1	13.0	270.8	23.5	364.8	191.0	260.1	13.0
12ZA10-18	580	0.9	19.4665	3.7	0.2932	4.0	0.0414	1.4	0.34	261.5	3.5	261.1	9.1	257.5	85.5	261.5	3.5
12ZA10-1	199	1.3	20.3310	8.4	0.2871	8.9	0.0423	2.8	0.31	267.3	7.3	256.3	20.2	156.7	198.0	267.3	7.3
12ZA10-25	278	1.4	19.1134	4.7	0.3060	6.1	0.0424	3.9	0.64	267.8	10.2	271.1	14.4	299.4	106.5	267.8	10.2
12ZA10-24.1	557	1.2	19.9083	3.4	0.2942	3.6	0.0425	1.2	0.34	268.1	3.2	261.8	8.3	205.7	78.7	268.1	3.2
12ZA10-18.2	439	0.7	17.7879	13.6	0.3294	14.1	0.0425	3.4	0.24	268.3	9.0	289.1	35.4	461.0	303.8	268.3	9.0
12ZA10-24.2	512	1.3	19.0157	2.8	0.3085	2.9	0.0426	0.6	0.22	268.6	1.7	273.1	6.8	311.1	63.4	268.6	1.7
12ZA10-23	772	0.9	18.9123	2.3	0.3124	2.3	0.0429	0.5	0.22	270.5	1.4	276.1	5.6	323.4	51.4	270.5	1.4
12ZA10-21	556	1.0	18.3846	8.0	0.3219	8.1	0.0429	0.8	0.10	270.9	2.2	283.4	20.0	387.4	180.6	270.9	2.2
12ZA10-14.2	811	1.0	19.5863	2.5	0.3025	2.7	0.0430	1.1	0.42	271.2	3.0	268.3	6.4	243.4	56.7	271.2	3.0
12ZA10-9	382	1.1	18.7051	8.2	0.3169	8.3	0.0430	1.6	0.19	271.4	4.3	279.5	20.4	348.4	185.5	271.4	4.3
12ZA10-22	974	1.8	18.9363	2.1	0.3135	2.3	0.0430	1.0	0.42	271.7	2.6	276.9	5.7	320.6	48.2	271.7	2.6
12ZA10-28	673	1.0	17.5554	14.1	0.3382	14.2	0.0431	1.0	0.07	271.8	2.6	295.8	36.4	490.1	313.3	271.8	2.6
12ZA10-8.2	424	1.5	20.1320	3.8	0.2969	4.0	0.0433	1.2	0.31	273.5	3.3	263.9	9.2	179.7	87.5	273.5	3.3
12ZA10-18.2	767	1.2	19.3600	2.1	0.3089	2.3	0.0434	0.9	0.40	273.7	2.4	273.3	5.4	270.0	47.7	273.7	2.4
12ZA10-4.1	706	0.8	19.3048	3.1	0.3108	3.3	0.0435	1.2	0.37	274.6	3.3	274.8	8.0	276.6	70.7	274.6	3.3
12ZA10-6	336	1.3	18.9036	6.6	0.3181	6.8	0.0436	1.3	0.20	275.2	3.6	280.4	16.6	324.5	150.9	275.2	3.6
12ZA10-17	338	1.3	19.2846	6.2	0.3119	6.5	0.0436	1.9	0.29	275.3	5.0	275.7	15.6	279.0	141.9	275.3	5.0
12ZA10-14	693	1.0	19.3242	1.9	0.3118	2.8	0.0437	2.1	0.73	275.8	5.6	275.6	6.8	274.3	43.5	275.8	5.6

Spot name			Isotopic Ratios										Apparent Ages (Ma)							
			U (ppm)	U/Th	$^{207}\text{Pb}^*/^{206}\text{Pb}^*$	$\pm$ (%)	$^{207}\text{Pb}^*/^{235}\text{U}$	$\pm$ (%)	$^{206}\text{Pb}/^{238}\text{U}$	$\pm$ (%)	error corr.	$^{206}\text{Pb}/^{238}\text{U}$	$\pm$ (Ma)	$^{207}\text{Pb}/^{235}\text{U}$	$\pm$ (Ma)	$^{206}\text{Pb}/^{207}\text{Pb}$	$\pm$ (Ma)	Best Age	$\pm$ (Ma)	
12ZA10-26	783	1.8	19.2467	1.0	0.3133	1.8	0.0437	1.5	0.82	275.9	4.0	276.7	4.4	283.5	23.8	275.9	4.0			
12ZA10-8.1	631	1.2	19.4033	1.9	0.3113	2.2	0.0438	1.1	0.49	276.4	3.0	275.2	5.3	264.9	44.1	276.4	3.0			
12ZA10-11	306	1.2	20.4197	3.7	0.2964	4.8	0.0439	3.1	0.65	276.9	8.5	263.6	11.2	146.5	85.8	276.9	8.5			
12ZA10-13	516	1.0	19.5314	1.8	0.3103	2.0	0.0440	0.8	0.40	277.3	2.1	274.4	4.8	249.8	42.2	277.3	2.1			
12ZA10-5.1	552	1.2	19.0138	3.9	0.3188	4.3	0.0440	1.8	0.41	277.3	4.8	281.0	10.6	311.3	89.6	277.3	4.8			
12ZA10-5.2	591	1.3	19.3559	2.2	0.3142	2.8	0.0441	1.8	0.64	278.2	5.0	277.4	6.9	270.5	49.9	278.2	5.0			
12ZA10-12.1	797	0.9	17.9923	12.2	0.3380	12.3	0.0441	1.5	0.12	278.2	4.0	295.7	31.5	435.6	272.3	278.2	4.0			
12ZA10-29.1	814	1.0	18.1613	4.6	0.3358	4.8	0.0442	1.4	0.28	279.0	3.7	294.0	12.4	414.7	103.8	279.0	3.7			
12ZA10-27	382	1.3	19.2410	2.7	0.3175	3.2	0.0443	1.7	0.54	279.5	4.7	280.0	7.9	284.2	62.5	279.5	4.7			
12ZA10-29.2	268	1.6	18.4947	6.7	0.3306	7.0	0.0443	1.7	0.25	279.7	4.8	290.0	17.5	373.9	151.7	279.7	4.8			
12ZA10-12.2	290	1.5	19.2497	4.6	0.3176	5.8	0.0443	3.5	0.60	279.7	9.5	280.1	14.2	283.2	106.4	279.7	9.5			
12ZA10-10.3	392	0.9	19.7581	7.6	0.3098	7.7	0.0444	1.4	0.18	280.0	3.8	274.0	18.5	223.2	175.0	280.0	3.8			
12ZA10-4.2	218	1.4	19.8319	7.5	0.3090	7.6	0.0444	1.4	0.19	280.3	4.0	273.4	18.2	214.6	172.9	280.3	4.0			
12ZA10-10.2	296	0.6	19.6965	3.8	0.3113	4.3	0.0445	2.1	0.49	280.5	5.9	275.2	10.4	230.4	86.7	280.5	5.9			
12ZA10-2	398	0.9	19.4243	4.2	0.3158	4.4	0.0445	1.3	0.30	280.6	3.6	278.7	10.8	262.5	96.7	280.6	3.6			
12ZA10-20	366	1.4	19.5999	4.0	0.3132	4.2	0.0445	1.3	0.31	280.8	3.6	276.7	10.2	241.8	92.3	280.8	3.6			
12ZA10-3	298	2.0	19.8908	3.8	0.3093	4.1	0.0446	1.7	0.42	281.4	4.8	273.7	9.9	207.7	87.0	281.4	4.8			
12ZA10-10	317	0.7	17.3157	19.7	0.3573	20.7	0.0449	6.4	0.31	282.9	17.8	310.2	55.4	520.3	435.9	282.9	17.8			
12ZA10-7	545	1.2	19.0001	4.0	0.3307	5.0	0.0456	3.1	0.61	287.3	8.6	290.1	12.7	312.9	91.3	287.3	8.6			
12ZA08-6	78	1.1	20.2931	14.4	0.2827	14.7	0.0416	3.1	0.21	262.7	8.0	252.8	33.0	161.1	338.7	262.7	8.0			
12ZA08-3	164	0.9	19.3600	4.8	0.3044	4.9	0.0427	0.9	0.19	269.8	2.5	269.8	11.5	270.0	109.5	269.8	2.5			
12ZA08-2	116	0.9	18.6172	9.5	0.3262	9.8	0.0440	2.4	0.24	277.8	6.4	286.6	24.4	359.1	214.4	277.8	6.4			
12ZA08-5.2	144	1.0	20.1079	11.5	0.3026	11.9	0.0441	3.3	0.27	278.4	8.9	268.4	28.1	182.4	268.0	278.4	8.9			
12ZA08-7	60	1.0	23.4130	18.7	0.2954	20.1	0.0502	7.4	0.37	315.5	22.6	262.8	46.5	-184.4	470.3	315.5	22.6			
12ZA08-5.1	42	0.4	18.5335	9.8	0.4391	10.3	0.0590	3.3	0.32	369.7	12.0	369.6	32.0	369.2	220.4	369.7	12.0			
12ZA60-12.1	236	1.0	19.2396	4.6	0.2891	5.5	0.0403	3.1	0.56	255.0	7.7	257.9	12.6	284.3	105.3	255.0	7.7			
12ZA60-12.3	190	1.0	19.5487	9.3	0.2869	9.5	0.0407	1.9	0.20	257.0	4.7	256.1	21.4	247.8	213.6	257.0	4.7			

Spot name	U (ppm)	U/Th	Isotopic Ratios					Apparent Ages (Ma)									
			$\frac{^{207}\text{Pb}^*}{^{206}\text{Pb}^*}$	$\pm$ (%)	$\frac{^{207}\text{Pb}^*}{^{235}\text{U}}$	$\pm$ (%)	$\frac{^{206}\text{Pb}}{^{238}\text{U}}$	$\pm$ (%)	error corr.	$\frac{^{206}\text{Pb}}{^{238}\text{U}}$	$\pm$ (Ma)	$\frac{^{207}\text{Pb}}{^{235}\text{U}}$	$\pm$ (Ma)	$\frac{^{206}\text{Pb}}{^{207}\text{Pb}}$	$\pm$ (Ma)	Best Age (Ma)	$\pm$ (Ma)
12ZA60-12.2	267	0.7	18.9856	5.0	0.2989	6.6	0.0412	4.2	0.64	260.0	10.7	265.5	15.3	314.7	114.8	260.0	10.7
12ZA60-11	593	0.7	18.3283	6.7	0.3125	7.0	0.0415	2.0	0.29	262.4	5.3	276.1	16.9	394.2	150.2	262.4	5.3
12ZA60-17	289	1.1	18.9855	3.9	0.3032	4.2	0.0417	1.4	0.34	263.6	3.7	268.9	9.8	314.7	89.1	263.6	3.7
12ZA60-3	254	1.2	19.9502	4.5	0.2910	4.9	0.0421	2.0	0.40	265.9	5.1	259.4	11.3	200.8	104.8	265.9	5.1
12ZA60-16	232	1.1	19.6039	5.3	0.2965	5.7	0.0422	2.2	0.39	266.2	5.8	263.7	13.3	241.3	121.5	266.2	5.8
12ZA60-2.2	249	1.4	19.6612	4.5	0.2960	4.6	0.0422	0.8	0.17	266.5	2.0	263.3	10.7	234.6	104.5	266.5	2.0
12ZA60-24	411	1.2	19.6361	3.8	0.2981	4.1	0.0425	1.4	0.34	268.0	3.7	264.9	9.5	237.5	88.7	268.0	3.7
12ZA60-17.2	261	1.2	19.5532	5.5	0.3021	5.6	0.0428	1.3	0.23	270.4	3.4	268.0	13.3	247.3	126.4	270.4	3.4
12ZA60-8	410	1.0	19.4978	3.0	0.3032	3.5	0.0429	1.8	0.52	270.6	4.7	268.9	8.2	253.8	68.4	270.6	4.7
12ZA60-13	397	0.9	19.6875	3.6	0.3007	3.9	0.0429	1.4	0.37	271.0	3.8	266.9	9.1	231.5	83.0	271.0	3.8
12ZA60-10	289	1.3	19.1383	3.8	0.3100	4.0	0.0430	1.4	0.35	271.6	3.8	274.2	9.7	296.4	85.9	271.6	3.8
12ZA60-15	295	0.8	19.7633	4.2	0.3003	4.2	0.0430	0.6	0.15	271.6	1.7	266.6	9.9	222.6	96.9	271.6	1.7
12ZA60-20	384	1.5	19.1764	3.1	0.3097	3.5	0.0431	1.5	0.42	271.9	3.9	274.0	8.3	291.9	71.6	271.9	3.9
12ZA60-27	287	1.4	19.3438	5.1	0.3078	5.3	0.0432	1.4	0.27	272.5	3.9	272.5	12.7	272.0	117.0	272.5	3.9
12ZA60-7	185	1.3	19.3578	4.0	0.3076	4.7	0.0432	2.5	0.53	272.6	6.6	272.3	11.1	270.3	90.8	272.6	6.6
12ZA60-24.2	281	1.2	20.1481	2.7	0.2982	3.4	0.0436	2.0	0.61	275.0	5.5	265.0	7.8	177.8	62.3	275.0	5.5
12ZA60-9	159	1.5	18.4785	7.9	0.3256	8.0	0.0436	1.3	0.16	275.4	3.5	286.2	19.9	375.9	177.8	275.4	3.5
12ZA60-23	397	1.2	20.2984	2.0	0.2969	3.1	0.0437	2.3	0.75	275.8	6.2	264.0	7.1	160.5	47.3	275.8	6.2
12ZA60-3.2	247	1.2	19.5606	5.5	0.3100	5.7	0.0440	1.3	0.23	277.4	3.6	274.2	13.7	246.4	127.6	277.4	3.6
12ZA60-19	342	1.5	18.6886	3.3	0.3250	5.3	0.0441	4.2	0.78	277.9	11.4	285.7	13.3	350.4	75.5	277.9	11.4
12ZA60-5	111	1.2	21.1077	15.7	0.2882	15.9	0.0441	2.6	0.16	278.3	7.1	257.1	36.1	68.2	374.8	278.3	7.1
12ZA60-2	141	1.5	20.5782	10.8	0.2983	11.1	0.0445	2.3	0.21	280.8	6.3	265.0	25.9	128.4	255.8	280.8	6.3
12ZA60-4	187	1.4	19.8400	6.5	0.3176	7.2	0.0457	3.2	0.44	288.0	9.1	280.0	17.7	213.7	150.5	288.0	9.1
12ZA60-24.3	180	0.9	20.6999	4.4	0.3128	4.8	0.0470	2.0	0.42	295.8	5.8	276.4	11.6	114.5	103.2	295.8	5.8
12ZA60-14	249	2.7	17.8341	2.1	0.5803	2.4	0.0751	1.1	0.44	466.6	4.8	464.7	8.9	455.3	47.5	466.6	4.8
12ZA60-18	150	2.3	17.7018	4.5	0.6143	4.8	0.0789	1.6	0.34	489.4	7.5	486.3	18.4	471.7	99.1	489.4	7.5
12ZA60-26	509	2.5	13.3223	0.7	1.6973	3.0	0.1640	3.0	0.97	979.0	26.8	1007.5	19.4	1070.2	14.4	1070.2	14.4

An electronic version of this appendix is available to improve data access.