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Bridging High and Low Temperature Thermal Histories Across the Kaapvaal Craton, Southern Africa from Advances in Titanite and Zircon (U-Th)/He Thermochronology

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BRIDGING HIGH AND LOW TEMPERATURE THERMAL HISTORIES ACROSS THE KAAPVAAL CRATON, SOUTHERN AFRICA FROM ADVANCES IN TITANITE AND ZIRCON (U-TH)/HE THERMOCHRONOLOGY

by

Jaclyn Suzanne Baughman

B.A., Colgate University, 2013

A thesis submitted to the
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This thesis entitled:
Bridging high and low temperature thermal histories across the Kaapvaal craton, southern Africa from advances in titanite and zircon (U-Th)/He thermochronology
written by Jaclyn Suzanne Baughman
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Date________

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
ABSTRACT

Bridging high and low temperature thermal histories across the Kaapvaal craton, southern Africa from advances in titanite and zircon (U-Th)/He thermochronology

Jaclyn S. Baughman (Ph.D, Geological Sciences)

Thesis directed by Associate Professor Rebecca M. Flowers

Cratons are the oldest and most stable portions of continents, but the degree to which they are affected by post-cratonization tectonic and magmatic processes is unclear. Mid-temperature (300-110°C) thermal histories are important for addressing this problem, but these are difficult to resolve due to the paucity of well-developed chronometers sensitive to that temperature window. For example, in the Kaapvaal craton of southern Africa, high temperature (>300°C) geo- and thermochronology constrains Archean craton stabilization, while low temperature (<110°C) thermochronology constrains the Paleozoic-Mesozoic history of craton burial and exhumation, leaving an almost 3 billion year gap in Kaapvaal’s thermal history. The goals of my dissertation are to 1) better resolve titanite He diffusion kinetics to assess its utility as a mid-temperature thermochronometer, and 2) apply titanite and zircon (U-Th)/He (THe, ZHe) thermochronology to decipher the deep-time thermal history of the Kaapvaal craton.

Prior work showed that radiation damage influences the He retentivity and closure temperature (Tc) of apatite and zircon, but this effect was not documented in titanite. I
acquired THe dates, Raman spectra, and He diffusion data for a suite of Kaapvaal craton
titanite that show at low radiation damage the titanite Tc is ~210-150°C, but at higher
damage the Tc drops to <50°C. This damage-diffusivity pattern is similar to zircon, but
because titanite typically has substantially lower U and Th, the data imply that for the same
protracted thermal history titanite will accumulate less damage and record older dates
than zircon.

I applied THe and ZHe dating in a focused study of the Phalaborwa carbonatite, as
well as to a broad suite of samples across the craton from both on- and off- the southern
African Plateau. THe dates are older than ZHe dates and reach a maximum of 1.0-1.2 Ga
from all regions. These data and geologic constraints require a significant, previously
undetected heating (≥150°C) event at this time, most simply explained by burial (>4 km)
coincident with Namaqua-Natal orogenesis. The inferred basin has been removed from the
geologic record, demonstrating the utility of THe and ZHe for detecting such events.
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CHAPTER 1

INTRODUCTION
1. USING (U-TH)/HE THERMOCHRONOLOGY TO DECIPHER DEEP-TIME CRATONIC HISTORIES

Thermochronology is a powerful analytical tool for deciphering thermal histories, but there are few thermochronometers that provide access to temperatures from ~300-120°C. This temperature range is important for connecting deep crustal processes with geomorphic and surface applications and for constraining exhumation histories in a nearly ubiquitous gap in time-temperature reconstructions. In ancient cratonic interior settings, this thermal history gap commonly leads to a several billion year gap in t-T (time-temperature) reconstructions. Accessing it may provide insights on the degree to which documented post-craticentric tectonic and magmatic events affect cratons. Lower temperature thermochronology (<120°C) studies in these settings reveal multiple phases of Phanerozoic heating and cooling (e.g., Lorencak et al., 2004; Kohn et al., 2002; Flowers, 2009; Ault et al., 2009; Gleadow et al., 2002; Weber et al., 2005) that suggest cratons underwent more substantial burial, erosion, and elevation change than previously thought. Evidence for these Phanerozoic burial episodes (1-4 km) has been fully eroded from the rock record like in the Canadian Shield (e.g., Lorencake et al., 2004; Kohn et al., 2005; Flowers et al., 2012; Ault et al., 2013) and Australia (Gleadow et al., 2002; Kohn et al., 2002; Weber et al., 2005) and can only be identified using thermochronometric techniques. This leads to the questions of what other tectonothermal events are missing from the deeper-time rock record of continental interior settings, and can we use thermochronologic tools to identify them?

Recent work on the better-studied apatite and zircon (U-Th)/He thermochronometers (apatite-AHe, zircon-ZHe) has identified a strong influence of
accumulated radiation damage on He retentivity and therefore on the effective closure temperatures ($T_c$) of these minerals (Figure 1.1, Shuster et al., 2006; Flowers et al., 2009; Guenthner et al., 2013). These studies revealed that the temperature sensitivity of apatite varies from >90 to ~30°C depending on damage (Fig. 1.1a, positive correlation between damage and $T_c$), and indicates zircon $T_c$ can vary by >100°C, from 200°C at low damage, down to temperatures lower than AHe at high damage (Fig. 1.1b; Flowers et al., 2009; Guenthner et al., 2013; Johnson et al., 2017). Zircon commonly has high concentrations (100s-1000s ppm) of uranium, which over long timescales like those in cratonic settings, makes it particularly susceptible to radiation damage accumulation and increased He diffusivity, which lowers its $T_c$ (Fig. 1.1b). To access higher temperature portions of cratonic thermal histories this work further develops and applies the less studied mid-temperature titanite (U-Th)/He (THe) thermochronometer. Titanite is a relatively common accessory mineral in igneous and metamorphic rocks, often has substantially lower [U] and [Th] compared to zircon, and past (U-Th)/He studies have shown that this mineral is sensitive to intermediate temperatures of 220-190°C (Reiners and Farley, 1999; Stockli and Farley, 2004).

The Kaapvaal Craton, South Africa, is an excellent location to study the relative temperature sensitivities of the THe, ZHe, and AHe thermochronometric systems at high radiation damage levels as well as access the thermal history gap found in nearly all cratonic and interior settings. Little is known about an ~2.5 byr period of the craton’s history, between its ca. 3.0 Ga stabilization and Mesozoic-Cenozoic uplift and unroofing of
Figure 1. Schematic relationship of apatite (A) and zircon (B) He closure temperature and radiation damage.
the southern African Plateau. The Kaapvaal Craton experienced significant Proterozoic accretion and major episodes of intracontinental magmatism during this interval, but like many cratons, little is known of its erosional response to these events.

The primary goals of this dissertation are 1) to better develop THe thermochronology and improve our understanding of how its temperature sensitivity compares with the more widely applied ZHe and AHe methods, and 2) to decipher the mid-temperature thermal evolution of the Kaapvaal Craton and its implications for missing pieces of its post-cratonization history.

2. GEOLOGIC AND THERMOCRONOLOGIC HISTORY OF SOUTHERN AFRICA

The Kaapvaal Craton, South Africa, is one of the oldest Archean continental bodies, is composed of TTG, greenstone, and gneissic terranes, and likely formed through processes resembling present day plate tectonics (Fig. 2a,b; e.g., de Wit et al., 1992). Archean and Paleoproterozoic sedimentary and volcanic units overlie much of the Archean basement (Fig. 2a; e.g., Poujol et al., 2003), with the 300-183 Ma Karoo basin dominating the Phanerozoic record (Fig. 2a; Catuneanu et al., 2005). The craton is currently a major part of the southern African Plateau; the high elevation, low relief plateau dominates the topography at average elevations of 1000 m and is ringed by the “Great Escarpment” (Fig.2c).

High temperature U-Pb dating (e.g., Schoene and Bowring, 2006) and biotite $^{40}$Ar-$^{39}$Ar dating (Layer, 1992) constrain early lithospheric growth and formation followed by cooling to <300°C by 2.7 Ga. Sustained low temperatures have led to significant radiation damage accumulation of zircon and titanite, making this an excellent location to study the
Figure 2. Simplified maps of southern Africa including A) geologic, B) terrane, and C) topographic.
influence of radiation damage on He diffusion kinetics and temperature sensitivity of these mid-temperature chronometers. Following initial cratonization, Kaapvaal was affected by multiple accretionary events and intracratonic magmatism (Fig. 2a,b) including 1) collision with the Zimbabwe Craton across the ~2.6 Ga high-grade Limpopo Belt (Kreissig et al., 2001), 2) 2.1-1.8 Ga accretion of the Kheis, Okwa, Magondi, and Rehoboth mobile belts to the west (Jacobs et al., 2008), 3) emplacement of the world’s largest layered mafic intrusion, the Bushveld complex and associated Phalaborwa and Shiel complexes at 2.06 Ga (e.g., Cawthorne and Walraven, 1998), 4) alkaline and carbonatite magmatism, with preserved volcanics at 1.4-1.25 Ga (Hanson et al., 2006), 5) Major Namaqua-Natal orogenesis on the modern day southern border of South Africa and emplacement of the Umkondo large igneous province (LIP) at 1.1 Ga, associated with the building of Rodinia (McCourt et al., 2006; Eglington, 2006), 6) Neoproterozoic Pan-African accretion (e.g., Rino et al., 2008), 7) Paleozoic Cape orogeny, 8) Karoo LIP at 183 Ma associated with the breakup of Gondwanaland (e.g., Svenson et al., 2012), and 9) emplacement of numerous kimberlites from the Paleoproterozoic to the Cenozoic (e.g., Jelsma et al., 2004).

Despite the extensive and long-lived accretionary and magmatic history of the Kaapvaal craton and surrounding terranes, little work has been done to constrain the craton’s surface response to these known geologic events. Thermochronologic studies have been focused on resolving the low temperature Mesozoic-Cenozoic history of burial and unroofing, related to uplift of the southern African Plateau to its present elevation usingapatite fission-track and AHe data (e.g., Brown et al., 2002, Tinker et al., 2008, Flowers and Schoene, 2010; Stanley et al., 2013). Thermochronologic constraints on the time-temperature history in the intervening time between Archean craton formation and
stabilization and Mesozoic unroofing are limited. Plagioclase $^{40}$Ar/$^{39}$Ar data for a single sample from the Bushveld complex were interpreted to record initially rapid cooling to $< 300$ °C followed by protracted cooling to temperatures of 150-200 °C by $\sim$1.4 Ga (Cassata et al., 2009). These data include five Neoproterozoic titanite fission-track dates from the southeastern craton (Jacobs and Thomas, 2001), and four Neoproterozoic THe dates from 2 samples within in the Ancient Gneiss Complex (Flowers and Schoene, 2010). This work greatly expands the Proterozoic thermochronologic record using THe and ZHe dating across the Kaapvaal craton.

3. METHODOLOGICAL TOOLS USED

I use a variety of analytical and interpretative tools in this dissertation to address the goals outlined in section 1.1. These include (U-Th)/He data acquisition, Raman spectroscopy to characterize radiation damage accumulation, He diffusion experiments to assess titanite He diffusion kinetics and calculate closure temperatures for individual samples, and HeFTy thermal history modeling to develop geologically reasonable time-temperature histories that adhere to our current understanding of (U-Th)/He diffusion kinetics for a variety of phases.

3.1. (U-Th)/He data acquisition

(U-Th)/He thermochronology takes advantage of the radioactive decay of uranium and thorium to lead. These decay chains include several episodes of alpha decay that release a $^4$He nucleus. A mineral’s He diffusivity is not only a function of crystal lattice structure, but also of grain size (e.g., Reiners and Farley, 1999; Farley, 2000), U and Th
distribution (e.g., Hourigan et al., 2005; Farley et al., 2011; Ault and Flowers, 2012), and to a large extent (in at least some minerals) accumulated radiation damage (Shuster et al., 2006; Flowers et al., 2009; Guenthner et al., 2013).

Radiation damage from U-Th decay has been shown to affect He retentivity and therefore the temperature sensitivity of apatite and zircon (Fig. 1). For samples that experienced the same thermal history, the effective uranium concentration (eU, \([\text{U}]+0.235[\text{Th}];\) Flowers et al., 2007) can be used as a proxy for accumulated radiation damage because grains with higher eU will experience greater self-irradiation than grains with lower eU. In apatite, radiation damage accumulation increases the mineral closure temperature (Fig. 1a; Shuster et al., 2006; Flowers et al., 2009), which can manifest as a positive correlation between date and eU for samples that experienced protracted thermal histories (Shuster et al., 2006, Flowers et al., 2009, Flowers, 2009). In zircon, damage accumulation initially increases the He closure temperature from ~140 to 220 °C, until a damage percolation threshold is reached, at which point He retentivity decreases and the closure temperature is reduced (Fig. 1b; Guenthner et al., 2013; Ketcham et al., 2013). This effect can cause a positive correlation between ZHe date and eU at low damage levels, and a negative date-eU correlation at damage levels greater than the percolation threshold, depending on the thermal history (e.g., Guenthner et al., 2014; Orme et al., 2016).

Radiation damage can be annealed at high temperatures, reversing the effects of damage accumulation on He diffusivity (e.g., Shuster and Farley, 2009; Flowers et al., 2009; Gautheron et al., 2009; Guenthner et al., 2013). Understanding both damage accumulation and annealing systematics is therefore important for interpreting (U-Th)/He data. Parent recoil, alpha particles, and fission events all cause crystal damage. However it remains
unclear which is the dominant control on mineral He retentivity and thus is an area of ongoing investigation. Previous experimental work suggested the zircon fission-track percolation threshold corresponds with the damage level above which zircon He retentivity drops (Ketcham et al., 2013). Because of this, the available zircon radiation damage accumulation and annealing model (ZRDAAM) assumes fission-track damage kinetics for both damage accumulation and removal upon heating. Fission-track annealing in zircon occurs at temperatures of ≥220-310 °C (Yamada et al., 2007). However, recent work suggests that ZRDAAM appears unable to reproduce some high-damage ZHe data, suggesting that fission track kinetics may not be wholly appropriate and that improved calibration of the model is required (Johnson et al., 2017; Anderson et al., 2017; Mackintosh et al., 2017; Powell et al., 2016).

Despite ongoing research to understand the complexity of radiation damage and annealing, date-eU patterns can be used to make first order thermal history interpretations. In the case of zircon, a negative date-eU correlation indicates 1) that the sample accumulated enough damage due to high eU and/or long damage accumulation time to pass the zircon percolation threshold and 2) the sample underwent slow cooling and/or was partially reset by a later reheating event. On the other hand, fast cooling through the temperature sensitivity range of the mineral suite /or reheating and complete resetting will not result in a date-eU correlation even if the mineral suite is characterized by variable Tc (e.g., Flowers et al., 2007, Guenthner et al., 2013). In this work, I use (U-Th)/He data and date-eU correlations to assess the role of radiation damage on He retentivity, and to make thermal history interpretations across the Kaapvaal craton.
Additional considerations in (U-Th)/He date calculation and data interpretation include alpha-ejection corrections, grain size, and U-Th zonation. During alpha decay of U and Th, He atoms can travel up to 20µm, requiring a geometric correction for He lost from the crystal lattice due to alpha-ejection (Farley et al., 1996). Grain size controls the diffusion domain size of individual crystal, by which larger grain sizes lead to greater He retentivity and higher Tc (e.g., Farley, 2000). Parent isotope zonation affects the spatial distribution of 4He and therefore the evolution of the He diffusion profile (Farley, 2000; Meesters and Dunai, 2002; Hourigan et al., 2005), and can lead to intracrystalline damage zones locally affecting He retentivity within a single grain (Farley et al., 2011; Ault and Flowers, 2012; Anderson et al., 2017). Grain-dimension variations can yield size-date correlations (e.g., Reiners and Farley, 2001), while U-Th zonation can contribute to general data scatter (e.g., Flowers and Kelley, 2011; Ault and Flowers, 2012; Anderson et al., 2017).

Much of this dissertation focuses on further developing THe thermochronology. Titanite is a relatively common accessory mineral in igneous and metamorphic rocks, and (U-Th)/He studies have shown that this mineral is sensitive to temperatures of 220-190°C, indicating its potential utility as a mid-temperature thermochronometer (Reiners and Farley, 1999; Stockli and Farley, 2004). Although an early He dating study of titanite suggested that radiation damage enhanced He diffusivity in highly damaged crystals (Hurley, 1954), the more recent studies concluded that radiation damage did not influence titanite He retentivity (Reiners and Farley, 1999; Stockli and Farley, 2004). However, these newer studies did not include highly damaged crystals in their investigations, and the recognition that radiation damage influences both apatite (e.g., Shuster et al., 2006; Flowers et al., 2009) and zircon (Guenthner et al., 2013) He retentivity suggests that the
extent to which damage affects the diffusivity of other U-Th rich accessory minerals should be re-examined.

3.2. Quantification of radiation damage: Alpha dose calculation and Raman spectroscopy

A major component of this research is quantifying the amount of accumulated radiation damage (alpha dose) within individual samples to assess the relationship between titanite damage and He diffusivity and compare damage levels across chronometers and between samples with variable thermal histories. I do this in two ways. First through alpha dose calculation and second using Raman spectroscopy for independent damage assessment.

Alpha dose is the total volume fraction of radiation damage in the crystal, calculated from eU and the damage accumulation time (e.g., Nasdala et al., 2005). Accurate alpha dose estimates require information about the temperature above which radiation damage anneals and how long damage has been accumulating below that temperature. Some experimental work has suggested that the temperatures at which fission tracks anneal in apatite and zircon are reasonable proxies for those required to anneal the damage that matters for apatite and zircon He diffusion (Shuster and Farley, 2009; Ketcham et al., 2013). However, the robustness of the fission-track annealing kinetic assumption and the extent to which damage annealing depends on the degree of accrued damage are active topics of study (e.g., Baughman et al., 2017; Willett et al., 2017; Anderson et al., 2017). As I cannot easily account for these complexities I use the approach of past work and assume damage accumulation times based on published fission-track annealing temperatures for apatite (≥60-110 °C, e.g., Fitzgerald and Gleadow, 1990), zircon (≥220-310 °C, Yamada et
al., 2007), and titanite (≥265-310 °C, Coyle and Wagner, 1998). Specifically, I use estimates for the timing of cooling below ~110 °C, ~250 °C, and ~300 °C as the times at which damage accumulation began for apatite, zircon, and titanite, respectively.

Raman spectroscopy provides an independent assessment of present day radiation damage accumulation, without relying on damage annealing kinetic assumptions or requiring additional thermal history information. Raman spectroscopy uses a laser to irradiate a small area and induces inelastic or “Raman” scattering of the monochromatic laser light. The measured Raman scattering is used to identify the chemistry and bond strength of the sample. Raman spectroscopy is routinely employed to quantitatively evaluate radiation damage in zircon by measuring the width and/or position of a major peak that broadens and shifts with increasing damage due to changing bond strength (e.g., Nasdala et al., 2001; Palenik et al., 2003). In contrast, the approach is more qualitative for titanite. With increasing structural damage, the major titanite Raman peaks undergo spectral broadening, frequency shifts, and merging, making it more difficult to quantitatively assess the effect of damage using a single peak (Beirau et al., 2012; Zhang et al., 2013).

3.3. He diffusion experiments

He diffusion kinetics are routinely assessed using stepwise degassing ⁴He diffusion experiments. Individual samples are step-heated and the fraction of He gas released is precisely measured at each temperature step. Samples are regularly subjected to prograde and retrograde heating, with results plotted on Arrhenius arrays in order to derive kinetic
parameters and calculate a closure temperature for the individual samples. The rate of diffusion is strongly temperature dependent and follows an Arrhenius relationship:

\[ D = D_0 e^{-\frac{E_a}{RT}} \]

Rearranged into \( y = b + mx \) form:

\[ \ln D = \ln D_0 - \frac{E_a}{R \left( \frac{1}{T} \right)} \]

where \( D \) is the diffusivity, \( D_0 \) is the \( y \) intercept and represents diffusivity at infinite temperature, \( E_a \) is the activation energy, \( R \) is the gas constant, and \( T \) is temperature (K).

Therefore to construct an Arrhenius array, the x-coordinate is defined by the heating step temperature, and the y-coordinate is diffusivity, which can be experimentally determined using the time of the heating step, temperature, and fraction of gas released. A linear array suggests a single major diffusion domain and enables determination of diffusive parameters. By determining the diffusivity of a material at a variety of temperatures, we can construct an Arrhenius plot in which the slope of the line produced yields \( E_a \) and the \( y \)-intercept contains \( D_0 \).

After acquiring diffusion kinetic information one can solve for closure temperature (\( T_c \)) using the following equation (Dodson, 1973):

\[ T_c = \frac{E_a}{R ln \left[ \frac{ARTe^2D_0}{\alpha^2E_a \left( \frac{dT}{dt} \right)} \right]} \]
To solve this equation requires a few additional assumptions. $A$ is the domain geometry (slab, cylinder, sphere) and $a$ is the domain size. $T_c$ calculations assume equal volume diffusion in all directions and that the grain itself is the domain size. The equation also requires a prescribed cooling rate ($dT/dt$). For consistency with previous work on noble gas diffusivity, including titanite He diffusion studies (Reiners and Farley, 1999; Cherniak and Watson, 2011), my calculations of diffusivity ($D/r^2$, where $r$ is grain radius; Fechtig and Kalbitzer, 1966) and closure temperature ($T_c$, Dodson, 1973) assume spherical geometry of diffusion domains.

3.4. HeFTy thermal modeling

HeFTy thermal history modeling software is useful for constraining possible time-temperature ($tT$) histories that satisfy (U-Th)/He results while honoring geologic constraints and using current He diffusion kinetic information. My simulations employ radiation damage He diffusion kinetic models for apatite (RDAAM, Flowers et al., 2009) and zircon (ZRDAAM, Guenthner et al., 2013). Both assume fission-track annealing kinetics to account for the damage that influences He diffusion. No such radiation damage accumulation and annealing He diffusion model is available for titanite. Ongoing work continues to test these models and highlights that the use of fission-track annealing kinetics may not be entirely appropriate (e.g., Willett et al., 2017), that annealing rates in zircon may be somewhat dependent on the level of accumulated damage (e.g., Zhang et al., 2000, 2013; Geisler et al., 2001), and that additional calibration of the high-damage end of the ZRDAAM is required (e.g., Johnson et al., 2017; Anderson et al., 2017). However, RDAAM and ZRDAAM are useful in constraining thermal histories that fit observed data.
patterns to first order and I take care to not over interpret model results due to known uncertainties.

I performed both forward and inverse thermal history modeling. The forward model approach requires the input of a particular tT path, grain size and eU concentration information for modeled grains and can be used to generate a date-eU curve for comparison against measured date-eU results. I use this approach to test a variety of geologically reasonable thermal histories and assess if different tT paths can be used to explain spatially variable date-eU patterns. Alternatively, inverse thermal history models acquire synthetic data for many random tT paths (I test 10,000 minimum) that are forced through user defined t-T constraints based on geologic information. HeFTy identifies “acceptable-” and “good-fit” thermal histories that satisfy the He date, eU, and grain size of modeled (U-Th)/He data based on goodness-of-fit statistics (Ketcham, 2005; Ketcham et al., 2009). As a variety of tT paths can generally satisfy a given (U-Th)/He date our results yield non-unique solutions.

4. DISSERTATION OUTLINE

Chapters 2-4 comprise the core of this dissertation. Each chapter is presented as a stand-alone manuscript for journal publication, including tables, figures, references, and supplemental information. The dissertation concludes with an extended 5 part appendix including a) a coupled (U-Th)/He thermochronology and Raman spectroscopy study from the Ancient Gneiss Complex, southern Africa, b) an assessment of off-Kaapvaal craton titanite (U-Th)/He data, c) maps and tables for additional samples collected in southern Africa, d) an AHe dataset from the Phanerozoic Cape Fold Belt, and finally e) education
Chapter 2, entitled *Influence of radiation damage on titanite He diffusion kinetics*, focuses on the grain-scale. Titanite samples were analyzed from Archean basement from across the Kaapvaal craton, which yielded a strong negative correlation between He date (~20-1200 Ma) and eU (10-970 ppm), indicative of radiation damage decreasing the He retentivity of the titanite-He system. This relationship was further explored using 1) Raman spectroscopy to independently assess radiation damage accumulation, 2) He diffusion experiments to obtain He diffusion kinetic information and estimate closure temperature, and 3) titanite heating experiments to assess if radiation damage was annealed during the diffusion experiments. My work reveals that radiation damage decreases the He retentivity and closure temperature of titanite once a damage threshold is reached. In addition I compare the THe system to the ZHe system and predict that in most settings zircon will more quickly reach its damage percolation threshold and record cooling through lower temperatures due to higher eU.

Chapter 3, entitled *Deciphering a 2 Gyr-long thermal history from a multichronometer (U-Th)/He study of the Phalaborwa carbonatite, Kaapvaal craton, South Africa*, takes a grain-scale understanding of titanite and other dating tools to learn about the local-scale geology. I collected (U-Th)/He data for titanite (THe), zircon (ZHe), apatite (AHe), and baddeleyite (BHe) from the 2.06 Ga Phalaborwa carbonatite complex and nearby Archean basement within the Kaapvaal craton. From this dataset, I evaluate the relative temperature sensitivities of the dated minerals based on age relationships and how radiation damage affects them based on date-eU correlations. BHe dates overlap with Phalaborwa
emplacement and record the highest temperatures of the dated phases. THe dates are older than ZHe and both have negative date-eU correlations indicative of radiation damage lowering the He retentivity and Tc of the systems. AHe dates are reproducible with a mean date of ~100 Ma consistent with Karoo burial and subsequent unroofing at that time. Thermal history modeling of our data yields time-temperature paths that 1) explain the AHe, ZHe, and THe data while honoring existing geologic constraints, thus demonstrating the internal consistency of the dataset, 2) imply possible reheating at 1.1 Ga during Namaqua-Natal orogenesis, and 3) limit maximum probable temperatures to ~180 °C during the 300-183 Ma Karoo basin burial. The results show that exploiting multiple (U-Th)/He thermochronometers and radiation damage effects can provide new insights into long-term craton evolution.

Chapter 4, entitled Bridging high and low temperature thermal histories: Titanite and zircon (U-Th)/He thermochronology constrain substantial ~1.1 Ga burial and exhumation of the Kaapvaal craton, southern Africa, uses what was learned in Chapters 2 and 3 and applies THe and ZHe dating to a broad suite of samples across the craton from both on- and off- the southern African Plateau. THe dates are older than ZHe dates, reach a maximum of 1.0-1.2 Ga in all regions, and display negative date-eU correlations. ZHe data define date-eU patterns that vary spatially. Inverse and forward thermal history modeling suggest that variable burial depths by the Phanerozoic Karoo basin can reproduce the observed spatial differences in ZHe date-eU patterns. The oldest THe dates of ~1.1 Ga, combined with geologic constraints, require a significant, previously undetected heating (≥150°C) event at this time. This heating is most simply explained by burial (>4 km) coincident with
Namaqua-Natal orogenesis. The inferred basin has been removed from the geologic record, demonstrating the utility of THe and ZHe for detecting such missing events.

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CHAPTER 2

Influence of radiation damage on titanite He diffusion kinetics

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ABSTRACT

Titanite (U-Th)/He (THe) dating is a little-utilized thermochronometer that previous study showed is sensitive to temperatures of 210-175 °C. Although it has been recognized that radiation damage influences the He retentivity of apatite and zircon, this effect has not been documented in titanite. We acquired 51 THe analyses from 11 Archean basement samples across the Kaapvaal craton, South Africa. The THe dates range from ~20-1200 Ma and are negatively correlated with their ~10-970 ppm span of effective U concentration (eU). Raman spectra acquired for 4 of these samples display peak broadening with increasing eU. 4He diffusion experiments on the same 4 samples suggest bulk closure temperatures (Tc) that vary by ~175°C. Estimated alpha dose versus Tc for our results and published THe diffusion data document Tc values of ~150-210 °C at alpha doses <50x10^16 alpha/g, with a sharp decrease in He retentivity above this threshold. This damage-diffusivity pattern is similar to zircon, but the damage level at which the reduction in retentivity occurs appears to be lower for titanite. Because titanite typically has substantially lower eU than zircon, for the same protracted thermal history THe dates are likely to record higher temperature portions of the history than zircon (U-Th)/He dates. The results demonstrate that THe dating can access a much larger temperature range and potentially be used to decipher more detailed time-temperature paths than previously thought.

1. INTRODUCTION

(U-Th)/He thermochronometry is a powerful tool for deciphering thermal histories and therefore is applied to help understand diverse temperature-dependent processes. The
vast majority of published (U-Th)/He studies have focused on just two minerals, apatite and zircon. Radiation damage can cause the closure temperatures of these two phases to vary by 10’s of °C (Shuster et al., 2006; Flowers et al., 2009; Guenthner et al., 2013). The recognition of this phenomenon has expanded the temperature range that can be deciphered using these two minerals alone (e.g., Flowers et al., 2007, 2009; Flowers, 2009; Ault et al., 2013; Guenthner et al., 2014; Orme et al., 2016). Better understanding the extent to which radiation damage affects the He retentivity of other U-Th rich accessory minerals may open new opportunities to further exploit this phenomenon to improve thermal history interpretation.

Like apatite and zircon, titanite is a relatively common U- and Th-bearing accessory phase in igneous and metamorphic rocks. Titanite is regularly used as a U-Pb chronometer (e.g., Corfu, 1988; Cherniak, 1993; Schoene and Bowring, 2007), geochemical tracer (e.g., von Blanckenburg, 1992; Cherniak, 2015) and geothermometer (e.g., Hayden et al., 2008; Kohn and Corrie, 2011). However, only a handful of studies have applied it as a He thermochronometer (Bauer et al., 2016; Duebendorfer et al., 2010; Pik et al., 2003; Reiners, 2000). (U-Th)/He dating and 4He diffusion experiments on titanites from different geologic settings previously documented grain-size dependent He closure temperatures from 210-175°C (Reiners and Farley, 1999). This finding was corroborated with (U-Th)/He data and diffusion experiments on titanites from the well-studied KTB borehole (Stockli and Farley, 2004). 4He/3He outgassing and implantation studies also supported this conclusion (Shuster et al., 2004, Cherniak and Watson, 2011), and further showed that titanite He diffusion is isotropic (Cherniak and Watson, 2011). Although an early He dating study of titanite had suggested that radiation damage enhanced He diffusivity in highly damaged
crystals (Hurley, 1954), the later work did not observe a radiation damage effect. However, the recognition that radiation damage influences apatite and zircon retentivity suggests that its role in titanite He diffusion kinetics should be re-examined.

Here we present (U-Th)/He, Raman, heating experiment, and ⁴He diffusion experiment data for titanite from basement samples across the Kaapvaal craton in South Africa (Fig. 1A). The initial goal of our study was to use THe dating to decipher the ~200 °C cooling history of the region, but our results instead documented the strong influence of radiation damage on the THe thermochronometer. We combine our results with previously published THe kinetic data to evaluate the titanite radiation damage-He diffusivity relationship, and compare this pattern with that of the zircon (U-Th)/He (ZHe) system.

2. BACKGROUND

2.1. (U-Th)/He Thermochronology

(U-Th)/He thermochronology takes advantage of the radioactive decay of uranium and thorium to lead. These decay chains include several episodes of alpha decay that release a ⁴He nucleus. A mineral’s He diffusivity is not only a function of crystal lattice structure, but also of grain size (e.g., Reiners and Farley, 1999; Farley, 2000), U and Th distribution (e.g., Hourigan et al., 2005; Farley et al., 2011; Ault and Flowers, 2012), and to a large extent (in at least some minerals) accumulated radiation damage (Shuster et al., 2006; Flowers et al., 2009; Guenthner et al., 2013).

Radiation damage has been shown to affect He retentivity and therefore the temperature sensitivity of apatite and zircon. For samples that experienced the same thermal history, the effective uranium concentration [eU, [U]+0.235[Th]; Flowers et al.,
Figure 1. (A) Simplified geologic map of the Kaapvaal craton showing sample locations. Inset shows location of Kaapvaal craton in southern Africa. (B) TH_e date versus eU for Kaapvaal craton titanites with <400 ppm eU. Sample symbols as in (A). The TH_e dates and eU values for the titanite grains on which diffusion experiments were conducted are shown as orange triangles. The 1sigma uncertainties on the TH_e dates are smaller than the symbols. eU uncertainties are 20%. (C) Same plot as (B) but x-axis extends to 1000 ppm eU and therefore includes the three analyses with eU > 400 ppm not shown in (B).
2007) can be used as a proxy for accumulated radiation damage because grains with higher eU will experience greater self-irradiation than grains with lower eU. In apatite, radiation damage accumulation increases the mineral closure temperature (Shuster et al., 2006; Flowers et al., 2009), which can manifest as a positive correlation between date and eU for samples that experienced protracted thermal histories (Shuster et al., 2006, Flowers et al., 2009, Flowers, 2009). In zircon, damage accumulation initially increases the He closure temperature from ~140 to 220 °C, until a damage percolation threshold at an alpha dose of ~150x10^{16} alpha/g is reached, at which point He retentivity decreases and the closure temperature is reduced (Guenthner et al., 2013; Ketcham et al., 2013). This effect can cause a positive correlation between ZHe date and eU at low damage levels, and a negative date-eU correlation at damage levels greater than the percolation threshold, depending on the thermal history (e.g. Guenthner et al., 2014; Orme et al., 2016). Radiation damage can be annealed at high temperatures, reversing the effects of damage accumulation on He diffusivity (e.g., Shuster and Farley, 2009; Flowers et al., 2009; Gautheron et al., 2009; Guenthner et al., 2013). Understanding both damage accumulation and annealing systematics is therefore important for interpreting (U-Th)/He data.

Additional considerations in (U-Th)/He date calculation and data interpretation include alpha-ejection corrections and U-Th zonation. During alpha decay of U and Th, He atoms can travel up to 20µm, requiring a geometric correction for He lost from the crystal lattice due to alpha-ejection (Farley et al., 1996). Parent isotope zonation influences the alpha-ejection correction and ^4He concentration gradient, and may lead to variable intracrystalline damage and He retentivity (e.g., Hourigan et al., 2005; Farley et al., 2011; Ault and Flowers, 2012; Johnstone et al., 2013). U-Th zoning may also produce a
heterogeneous distribution of He, which can cause apparent non-Arrhenius diffusive behavior (e.g., Farley et al., 2011).

2.2. Raman Spectroscopy and Titanite Characterization

Raman spectroscopy uses a laser to irradiate a small area and induce inelastic or “Raman” scattering of the monochromatic laser light. The measured Raman scattering is used to identify the chemistry and bond strength of the sample. Raman spectroscopy is routinely employed to quantitatively evaluate radiation damage in zircon by measuring the width and/or position of a major peak that broadens and shifts with increasing damage due to changing bond strength (e.g., Nasdala et al., 2001, Palenik et al., 2003). In contrast, the approach is more qualitative for titanite. With increasing structural damage, the major titanite Raman peaks undergo spectral broadening, frequency shifts, and merging, making it more difficult to quantitatively assess the effect of damage using a single peak (Beirau et al., 2012; Zhang et al., 2013).

Backscattered electrons (BSE) consist of high energy electrons that reflect off of the sample as a function of atomic number. High atomic numbers, or denser material, backscatter electrons more strongly than less dense material. Studies have taken advantage of this phenomenon and used BSE imaging to identify titanite REE zonation, which commonly is correlated with titanite U-Th zonation (e.g., Aleinikoff, et al., 2002).

2.3. Geologic Setting

The Kaapvaal craton of southern Africa is an archetypal Archean craton bounded by Proterozoic mobile belts (Fig. 1). Younger terranes were accreted during the
Neoproterozoic Pan-African and Paleozoic Cape orogenies. The ∼300-183 Ma Karoo Basin sedimentary rocks, 183 Ma Karoo volcanics, and Cenozoic Kalahari Basin deposits cover much of the Kaapvaal craton today (e.g., Catuneanu et al., 2005). The craton was affected by repeated episodes of intracontinental magmatism, including emplacement of the 2.06 Ga mafic Bushveld complex (e.g., Cawthorn and Walraven, 1998), ca. 1.4-1.35 Ga alkaline and carbonatite magmatism (Hanson et al., 2006), ∼1.1 Ga Umkondo large igneous province activity (e.g., Hanson et al., 2004), and episodic kimberlite emplacement (e.g., Jelsma et al., 2004).

A variety of thermochronologic data exist to constrain the <300 °C thermal history of the Kaapvaal craton. Muscovite and phlogopite Rb-Sr data indicate cooling of the northern craton to <300 °C by 2.0 Ga (Barton and van Reenen, 1992), while biotite \(^{40}\)Ar-\(^{39}\)Ar results constrain cooling of the eastern craton to <300 °C by 2.7 Ga (Layer et al., 1992). A handful of titanite fission-track dates from the southeastern craton and THc dates from the eastern craton are Neoproterozoic (Jacobs and Thomas, 2001; Flowers and Schoene, 2010). Plagioclase \(^{40}\)Ar/\(^{39}\)Ar data for a single Bushveld complex sample is interpreted to record initially rapid cooling to <300 °C followed by protracted cooling to ambient temperatures of 150-200 °C by ∼1.4 Ga (Cassata et al., 2009). Apatite fission-track and AHe data resolve the craton’s low temperature (∼120-40 °C) erosion history associated with Mesozoic plateau uplift (e.g., Brown et al., 2002; Flowers and Schoene, 2010; Beucher et al., 2013; Stanley et al., 2015).

3. SAMPLES AND METHODS

3.1. Samples
The studied titanites are from 11 Archean basement samples across the central and eastern Kaapvaal craton (Fig. 1A). Titanite separates for 9 of these samples were obtained from the South African Council for Geoscience. We also acquired additional THe data for two samples from which THe and AHe results were published previously by Flowers and Schoene (2010). Titanites from four of these samples were selected for Raman spectroscopy and 4He stepwise diffusion experiments. We also obtained Raman spectra and 4He diffusion data for the Fish Canyon Tuff (FCT) titanite standard for which diffusion kinetic data were published by Reiners and Farley (1999). Titanites from FCT, as well as two of the African titanite samples for which diffusion experiment data were acquired, were additionally subjected to heating and secondary Raman analysis.

3.2. *Titanite (U-Th)/He thermochronologic methods*

Individual titanite crystals were handpicked for (U-Th)/He analysis based on size, morphology, and clarity using a Leica M165 binocular microscope. Grains were photographed and measured using a calibrated digital camera. After characterization, single titanite grains were placed in Nb packets for analysis and loaded into an ASI Alphachron He extraction and measurement line at the University of Colorado Boulder Thermochronology Research and Instrumentation Lab (CU TRaIL). The packets containing the grains were placed in an ultra-high vacuum (~3x10^-8 torr) chamber and heated with a diode laser to ~800-1100°C for 5-10 minutes to extract the radiogenic 4He. Gas was spiked with 3He, purified using SAES getters methods, and measured on a Balzers PrismaPlus QMG 220 quadrupole mass spectrometer. This procedure was repeated at least once per grain to ensure all gas from the crystal was released and measured. The packets containing the
titanites were retrieved and dissolved using Parr large-capacity dissolution vessels in a multi-step acid-vapor dissolution process. Grains (including the Nb tube) were placed in Ludwig-style Savillex vials, spiked with a $^{235}$U and $^{230}$Th tracer, and dissolved in 29 M HF at 220 °C for 72 hours. Samples were then dried down on a hot-plate, dissolved in 6 M HCl at 200 °C for 24 hours, again dried down, taken up in 200 µL of a 7:1 HNO$_3$:HF mixture, heated on a warm hotplate for 1 hour, and finally diluted with 2.8 mL or more of doubly-deionized water. Dissolved samples were measured for U and Th on a Thermo-Finnigan Element2 magnetic sector ICPMS at the University of Colorado Boulder. More recently analyzed titanites were spiked with a tracer that also included $^{145}$Nd, and Sm was additionally measured in the sample solutions. (U-Th)/He dates and all associated data were calculated on a custom spreadsheet. The reported 1 sigma uncertainty on the single-grain dates includes the propagated uncertainty from the U, Th, and He measurements.

No alpha-ejection correction was applied to the dates because all analyzed titanites are fragments and fragmentation likely occurred during sample processing (Fig. S1). Applying no correction assumes that none of the fragment surfaces were close enough to the original crystal face to undergo He loss. BS size of the dated fragments, even if this assumption is inappropriate then the reported dates would not be greatly underestimated. For example, if 50% of original faces remained then the reported THe dates would be “too young” by only 4-10%.

Determination of accurate U, Th, and eU concentrations depend on accurate grain volume estimates. Dated fragment morphologies include rectangular prism, capsule, and ellipsoid geometries. U and Th concentrations were calculated from grain volumes assuming one of these geometries modified after Ketcham et al. (2011), or an average of
two of the three of them as the best fragment morphology approximation (Fig. S1). We conservatively apply a 20% uncertainty to all eU values. This uncertainty estimate is based on the maximum eU difference calculated from grain volumes assuming two different morphologies that most closely approximate the grain geometry. A 20% uncertainty is also consistent with a recent study comparing stoichiometric and morphologic methods for volume estimates of apatite and zircon that found average percent differences of 15% and 25% for eU, respectively (Guenthner et al., 2016).

3.3. Raman spectroscopy and titanite characterization methods

To independently assess the relative magnitude of radiation damage of our titanites we acquired Raman spectra for 4 samples that encompass the full eU span of our dataset. We also acquired data for the FCT titanite standard (eU ~ 60 ppm) as a control, which we expect to be characterized by lower damage than the Kaapvaal craton titanites due to its modest U and Th abundances and much younger age (~28 Ma).

Twelve titanites were handpicked from each sample to include grains with a range of clarity and color and to exclude those with inclusions and internal fractures. The selected grains were placed on double-sided tape on a square of plexiglass. Epoxy was poured on top of the grains in a ring-shaped mold. After epoxy hardening the grain mount was polished to expose the crystal interiors. Titanite spectra were acquired using the 532 nm laser at room temperature from the 100 cm⁻¹-1200 cm⁻¹ bandwidth range on a Horiba LabRAM HR Evolution Raman microscope-spectrometer at the University of Colorado Boulder. For each sample we obtained point (~2 µm wide, ~4µm deep) spectra for 8-12 titanites and acquired 3-4 point transects on at least 3 titanite grains per sample. A baseline
correction was applied to all data to account for potential photoluminescence. We also acquired electron backscatter (BSE) images for these same titanites to evaluate whether they show zoning, which could imply zonation in U and/or Th.

3.4. Heating experiment methods

To determine whether radiation damage was annealed during the diffusion experiments, we selected 2 African titanites and the FCT titanite standard for heating experiments and additional Raman study. These samples were chosen to include the lowest (FCT), intermediate (sample FW82-038), and highest (sample GB397) damage levels of our samples suite. After the Raman analysis described above, titanites were extracted from the original mount (two each for samples FCT and FW82-038, and four for sample GB397), packed in Nb tubes, placed in the diffusion cell of the ASI Alphachron and subjected to the identical diffusion experiment heating schedule as titanites from that same sample (Table S1; diffusion experiments described below). The titanites were then removed from the Nb packet, remounted, and final Raman spectra were collected following the same procedures described above. Five of these titanites were successfully re-imaged by Raman, while three were lost in different stages of the analytical process.

3.5. ²⁴He stepwise diffusion experiments methods

Accurate interpretation of THe dates and understanding the extent to which radiation damage plays a role requires characterization of He diffusivity. We conducted stepwise degassing ²⁴He diffusion experiments on the same 4 samples characterized by Raman spectroscopy, as well as on the FCT titanite. For each experiment an individual
titanite fragment was packed in a Nb tube and placed in the diffusion cell of the ASI Alphachron at the University of Colorado Boulder. Each sample was cycled through a series of prograde, retrograde, and final prograde isothermal heating steps ranging from 130 to 600 °C for 20 to 240 minutes. Temperature and duration schedules were modified based on damage and diffusivity of each sample to ensure appropriate percentage of gas extraction throughout the experiment (Table S2). Samples were heated via projector bulb and temperatures were precisely measured using a K-type thermocouple in direct contact with the sample. Gas released during each step was spiked with \(^3\)He, purified by gettering methods, and analyzed using a quadrupole mass spectrometer. After the heating schedule was complete, samples were fully degassed by laser heating to measure the remaining fraction of gas. The packets were then retrieved, spiked, dissolved, and measured for U and Th for (U-Th)/He date determination following the same procedures described in section 3.2.

4. RESULTS

4.1. Titanite (U-Th)/He dates

We acquired (U-Th)/He dates for 51 single titanite fragments from the 11 samples. All data are reported in Table 1. The THe dates vary from 20.2 ± 0.2 Ma to 1187.4 ± 12.9 Ma and are negatively correlated with their ~10-970 ppm span of eU (Fig. 1B,C). Figure 1 color-codes the samples by their location in the northern (green), eastern (blue), southeastern (purple), and central (maroon) Kaapvaal craton. There are no obvious differences in the results from these sub-regions. All the THe data fall on the same general
Table 1. Titanite (U-Th)/He data from Archean basement rock of the Kaapvaal craton

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<th>Samplea</th>
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<th>I (µm)c</th>
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<th>Th (ppm)</th>
<th>Sm (ppm)c</th>
<th>eU (ppm)c</th>
<th>1σ (ppm)c</th>
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\(^a\) diff-1 are the results for the titanites on which diffusion experiments were conducted

\(^b\) Morphology used for volume and concentration estimates. Where two morphologies noted, the average volume and concentration results were used. rec-rectangular prism, cap-capsule, ellip-ellipsoid

\(^c\) equivalent spherical radius

\(^d\) mean length measurement

\(^e\) NA-Note available

\(^f\) eU - effective uranium concentration, weights U and Th for their alpha productivity, computed as [U] + 0.235 * [Th]

\(^g\) eU uncertainty is assumed to be 20%

\(^h\) Analyzed titanites are fragments, so no alpha-ejection correction was applied to the dates

\(^i\) Analytical uncertainty based on U, Th, and He measurements
date-eU trend despite the large area (~200,000 km²) from which the samples were collected (Fig. 1).

4.2. *Raman spectroscopy and titanite characterization results*

A representative Raman spectrum from each sample is presented in Figure 2, with FCT titanite standard as the bottom spectrum and the Kaapvaal craton titanites arranged in order of increasing eU from bottom to top. All Raman spectra are plotted in Fig. S2. Spectra are normalized to the largest peak because Raman intensity depends on a variety of factors including laser beam intensity and frequency, thus for all spectra the y-axis of intensity is relative. Our results show a general trend of Raman peak broadening from the lowest to highest eU titanites, which is consistent with the pattern expected for increasing radiation damage (Zhang et al., 2013). This result supports using eU as a proxy for damage in the Kaapvaal craton sample suite.

Raman spectra transect results and BSE images can be used to evaluate if the African titanites are strongly zoned in U and Th. Figure S2 shows that the variability of Raman spectra within single grains is minimal in all four samples, and is far less than the inter-sample differences in spectra (Fig. 2, S2). These observations suggest that the studied titanites lack strong U-Th zonation that would lead to heterogeneous damage and variable intragrain Raman spectra results. All titanite BSE images are unzoned, which implies a relatively homogeneous distribution of major elements and REEs (representative BSE images in Fig. S2). Titanite REE and U-Th zonation are commonly correlated (e.g. Aleinikoff, et al., 2002), so these results also suggest a lack of U-Th zonation.
Figure 2. Representative Raman spectra for titanites from four Kaapvaal craton samples arranged in order of increasing eU from bottom to top. A representative spectrum for the FCT titanite standard, expected to be more crystalline than the Kaapvaal craton titanites, is shown for reference at the bottom. All spectra are shown in Figure S2.
4.3. **Heating experiments results**

The extent of radiation damage annealing during the diffusion experiments can be assessed by comparing the Raman spectra collected before and after the heating experiments on the same grains (Fig. 3, S3). No change in the spectra would suggest that no damage annealing occurred during the experiment, and thus indicate that the diffusive behavior of the titanite was not modified by the heating. In contrast, a tightening of the spectra would imply some damage annealing and recovery of crystallinity, which might be manifested as a change in the titanite He diffusion kinetics over the course of the experiment and a deviation from linearity on the Arrhenius array.

For the most crystalline sample, FCT, there is no obvious change between Raman spectra pre- and post-heating to the maximum diffusion experiment temperature of 520 °C (Fig. 3, S3A). The intermediate damage sample, FW82-038, shows only minor spectral change after heating to temperatures of 600 °C (Fig. 3, S3B). We performed two experiments on the most damaged sample, GB397. Grain 01 was heated to a maximum temperature of 350 °C, and shows no evidence of crystal recovery (Fig. 3, S3C). In contrast, Grains 03 and 09 were heated to a maximum temperature of 420 °C and peaks at all Raman shift values are better defined and tighter after heating (Fig. 3, S3D, E). This result indicates that some damage annealing occurred at temperatures between 350 °C (Grain 01 no change in spectra) and 420 °C (Grains 03, 09 modified spectra).

4.4. **^4 He stepwise diffusion experiment results**

Figure 4 shows the Arrhenius arrays for all five diffusion experiments. For consistency with previous work on noble gas diffusivity, including titanite He diffusion
Figure 3. Representative Raman spectra collected before and after heating experiments, arranged with the least damaged sample (FCT) at bottom, intermediate damage sample (FW82-038) in middle, and highest damage sample (GB397) at top. The GB397 titanites were heated to two different maximum temperatures of 350 °C and 420 °C, and results for both are shown. All heating experiment results are displayed in Figure S3.
studies (Reiners and Farley, 1999; Cherniak and Watson, 2011), our calculations of diffusivity ($D/r^2$, where $r$ is grain radius, Fechtig and Kalbitzer, 1966) and closure temperature ($T_c$, Dodson, 1973) assume spherical geometry of diffusion domains. This assumption is reasonable owing to the blocky morphology of the analyzed titanite fragments and isotropic nature of titanite He diffusion (Cherniak and Watson, 2011). Prior study of isotropic diffusion in apatite found that use of a spherical diffusion domain yields nearly identical results to a finite cylinder, indicating that the simpler spherical assumption is appropriate (Farley et al., 2010).

We explored multiple methods for regressing the data for kinetic parameter calculations. Analytical uncertainties associated with the gas released at each step are smaller than the points on the Arrhenius arrays in Figure 4, and were propagated through the kinetic parameter calculations. Figure 4 shows our preferred regression approach, in which we performed a least squares linear regression on all continuous experiment steps where the difference between the expected diffusivity based on the regression and the calculated diffusivity from the diffusion experiment was less than 1 ln (s$^{-1}$). Plots of these residuals versus cumulative release fraction are also shown to display how much of the extracted gas was included in each regression (Figure 4). This approach is the same as that of Tremblay et al. (2014), except for additionally requiring that the included steps form part of a continuous sequence. Figure S4 compares the results of this regression approach with an alternative and commonly used method of excluding the first prograde sequence and obviously anomalous points at high temperatures. The kinetic parameters that are derived from these two approaches are indistinguishable. We therefore favor the approach
Figure 4. Arrhenius plots for Kaapvaal craton and FCT titanites. Linear regression for kinetic parameters include all dark gray points, which consist of all continuous heating steps where the difference between the expected diffusivity based on the regression and the calculated diffusivity from the diffusion experiment is less than 1 ln (s⁻¹). Light grey points are those excluded from the regression. Initial prograde steps are indicated by diamonds, subsequent retrograde and prograde steps are shown as circles. Calculated 1σ errors on ln(D/r²) are smaller than the symbols. Residual ln plots versus cumulative release fraction are also shown to display how much gas was included in each linear regression.
in Figure 4 because it maximizes the gas and number of temperature steps included in the regressions.

Linear Arrhenius behavior was displayed by the majority (52.5-99.5%) of gas released during the African titanite experiments, and by all of the gas in the FCT experiment (Fig. 4). These results suggest a single major diffusion domain in the samples. The early steps of the African titanite experiments fall off the linear trend (Fig. 4). The gas in these initial steps comprises only 1-10% of the total gas in three of the titanites (Fig. 4a,b,d), and ~20% in the fourth (Fig. 4c). Similar nonlinear initial prograde patterns have been observed in published apatite, zircon, and titanite He diffusion experiments and attributed to U-Th zonation, alpha ejection, diffusive rounding, and/or fast pathways induced by radiation damage at the grain surface (e.g., Reiners and Farley, 1999; Farley, 2000; Reiners et al., 2002, Guenthner et al., 2013). However, these explanations cannot account for our data because our analyzed titanites are fragments and appear to lack strong U-Th zonation. Anisotropic accumulation of radiation damage within titanite (Beirau et al., 2012) leading to multiple diffusion domains and faster lattice pathways, or titanite structural phase changes at increased damage (Zhang et al., 2013) might also lead to non-Arrhenius behavior. Regardless, exclusion of these initial points from our regression appears appropriate.

The Raman spectra results from the heating experiments (section 4.3) suggest that substantial damage annealing did not occur during diffusion experiments on the low to intermediate damage titanites. The linearity of the Arrhenius arrays up through the highest temperatures of the diffusion experiment (up to 455-600 °C) for FCT and 3 of the African titanites support this conclusion (Fig. 4A-C,E). In contrast, the Raman spectra results for the
most damaged sample (GB397) suggest some annealing of damage over the 350-420 °C temperature range. The Arrhenius array for this sample aligns well with that conclusion, showing an abrupt deviation from linearity that begins at 360 °C and continues to the experiment’s maximum temperature of 420 °C (Fig. 3D). This rollover pattern can be explained by healing of damage that leads to a more He retentive crystal lattice, and justifies exclusion of the >350°C points from the linear regression of this sample’s Arrhenius array.

Table 2 reports diffusive parameters and uncertainties for all 5 experiments, along with a Tc for each sample calculated from the derived kinetic parameters. Tc calculations assume a 10 °C/Ma cooling rate and spherical geometry, no uncertainty is given as assumptions implicit to Tc calculation are difficult to quantify. The activation energies (Ea) and frequency factor/diffusion dimension (D₀/r²) calculated for our Kaapvaal craton titanites are negatively correlated with eU (Fig. 5A,B). The diffusivity calculated at geologically reasonable temperatures of 150 °C displays a positive relationship with eU (Fig. 5C). Figure 5D shows that the Tc values estimated from these kinetic parameters vary by ~175 °C and are negatively correlated with eU. Our estimated FCT titanite Tc of 155 °C is lower than that reported by Reiners and Farley (1999), and may be due to our analysis of a smaller grain size, as suggested by the similar Ea but lower D₀/r² values when compared with their results.

5. DISCUSSION
Table 2. Diffusion kinetic parameters from titanite $^4$He step-heating experiments

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>eU (ppm)$^a$</th>
<th>$1\sigma^b$</th>
<th>ln ($D_0/r^2$) (s$^{-1}$)</th>
<th>$1\sigma^c$</th>
<th>Ea (kJ/mol)</th>
<th>$1\sigma^c$</th>
<th>Tc (°C)$^d$</th>
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<tr>
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<td>24.9</td>
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<td>13.3</td>
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<td>0.30</td>
<td>161.1</td>
<td>1.7</td>
<td>155</td>
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</tbody>
</table>

$^a$ eU for the African titanites is based on measurements of the titanite used in the diffusion experiment. For FCT, it is the mean of 15 FCT titanites analyzed in the CU He lab

$^b$ eU uncertainty assumed to be 20%

$^c$ 1σ uncertainties are calculated only from steps used for the linear regression

$^d$ Closure temperatures are calculated assuming a 55 µm spherical geometry and a 10 °C/myr cooling rate
Figure 5. (A) $E_a$ (kJ/mol), (B) $\ln(D_0/r^2)$ (s$^{-1}$), (C) $\ln(D/r^2)$ (s$^{-1}$) at 150 °C, and (D) $T_c$ versus $eU$ for the Kaapvaal craton samples. 1 sigma uncertainties on $E_a$ and $\ln(D/r^2)$ in A) and B) are smaller than the symbols. $eU$ uncertainties are 20%.
5.1. Evidence from African titanite data for influence of radiation damage on titanite He diffusion kinetics

In the discussion below we assume that the Kaapvaal craton titanites share a broadly similar post-1200 Ma thermal history, which is necessary to use eU as a damage proxy in a sample suite. This interpretation is supported by the observation that their THe data define the same general date-eU trend with maximum dates of 1200 Ma, and is consistent with the structural coherency and cratonic character of the study region since that time. The first-order post-300 Ma history of this region is known to be characterized by 300-183 Ma Karoo Basin burial (e.g., Catuneanu et al., 2005) and subsequent Cretaceous erosion (e.g., Flowers and Schoene, 2010; Beucher et al., 2013).

The negative THe date-eU correlation, Raman spectroscopy data, and diffusion experiment results for our Kaapvaal craton samples show that the He retentivity of titanite decreases dramatically with increasing radiation damage at high damage levels. The negative THe date-eU pattern (Fig. 1B,C) is similar to that observed in ZHe datasets, which can be explained by radiation damage decreasing ZHe retentivity (Guenthner et al., 2013). The broadening of the titanite spectra with increasing eU corroborates that the higher eU African titanites are more damaged (Figure 2). And the diffusion experiment results document that the higher eU and more damaged titanites are less retentive to He than the lower eU and less damaged grains (Figure 4). We note that the negative closure temperature estimated for our most damaged titanite (GB397) is incompatible with the fact that it does indeed contain substantial He. This relationship was similarly observed for the most damaged zircon sample of Guenthner et al. (2013), and suggests that processes in
addition to simple thermally-activated volume diffusion from a single diffusion domain are operative.

Our heating experiment results imply that annealing of the radiation damage relevant to titanite He diffusion occurs more readily in highly damaged samples. While the Raman spectra of the most crystalline (FCT) and moderate damage (FW82-038) samples indicate little or no damage healing even after attainment of ≥520°C temperatures, Raman results for the most damaged sample (GB397) show evidence of annealing at temperatures of 350-420 °C. This interpretation is further supported by the rollover of the GB397 Arrhenius array in this 350-420 °C temperature range, but no deviation from linearity in the Arrhenius arrays of the lower damage samples (FCT, FW82-038) even at the ≥520°C temperatures. These results are in accordance with previous work on titanite that suggests high damage samples start to anneal at lower temperatures than less damaged samples (Zhang et al., 2013; Hawthorne et al., 1991; Zhang, 2013; Beirau et al., 2012). At these high levels of damage, both titanite (at ~150 x 10^{16} alpha/gram) and zircon (at ~1250 x 10^{16} alpha/gram, at an order of magnitude higher than titanite) are unable to recover to a crystalline state via traditional, moderate temperature (e.g. epitaxial) damage annealing processes (Beirau et al., 2012; Zhang et al., 2000) due to the amorphous state of the crystal.

5.2. Influence of radiation damage on titanite He diffusion kinetics from a broader data compilation

We can additionally consider the previously published titanite diffusion data (Reiners and Farley, 1999; Stockli et al., 2004) to better constrain how titanite He diffusivity is affected across a broader damage range than represented by our titanite
samples alone. Comparison of the He diffusion kinetic results for samples that underwent different thermal histories requires an estimate of alpha dose. Alpha dose is the total fraction of radiation damage in the crystal and is a function of both eU and the time that damage has been accumulating. Accurate alpha dose calculations require knowledge of both the mineral-specific annealing temperature and how long the sample has been below that temperature.

Parent recoil during alpha emission is the dominant cause of crystal damage, with a smaller contribution of damage due to the alpha particle itself and rare fission events. In apatite, the temperatures at which fission tracks anneal appear to be a reasonable estimate for alpha damage annealing (Shuster and Farley, 2009). In zircon, the correlation between the fission track percolation threshold and the dosage at which He diffusivity abruptly increases suggests that fission tracks exert a primary influence on zircon’s He retentivity (Ketcham et al., 2013). Fission-track annealing kinetics were therefore used for the kinetics that govern damage annealing in both the apatite (Flowers et al., 2009) and zircon (Guenthner et al., 2013) radiation damage accumulation and annealing He diffusion kinetic models. As an initial step we assume that to first order titanite fission track and alpha damage annealing temperatures are similar and independent of the degree of accumulated damage (although the latter is not entirely correct for highly damaged titanites based on our heating experiment results). The most recent estimate of the titanite fission-track partial annealing zone is 265-310 °C (Coyle and Wagner, 1998.), implying ~300 °C as the temperature at which titanites begin to accumulate damage.

Table S3 lists all assumptions associated with our alpha dose calculations for both our samples and previously published data. The computations use our own or published U-
Th concentration data, except for newly acquired U-Th concentration data for two grains each from the four samples of Reiners and Farley (1999), as reported in Table S4. Alpha doses for the Kaapvaal craton titanites assumed an accumulation time of 2 Byr based on regional muscovite and phlogopite Rb-Sr data from the northern craton ($T_c \sim 300 ^\circ C$, Barton and van Reenen, 1992). For the rapidly cooled FCT titanite we used its 28 Ma crystallization age as the accumulation time. For the four Reiners and Farley (1999) titanites from Gold Butte block in Nevada, Chain of Ponds pluton in Maine, and the Sierra Nevada batholith in California we assumed damage accumulation times based on muscovite or biotite $^{40}\text{Ar}/^{39}\text{Ar}$ data ($T_c \sim 300-350 ^\circ C$) from the same or nearby samples. For the two Stockli and Farley (2004) titanites from the KTB drillhole we used accumulation times based on TFT dates from the same samples (Coyle and Wagner, 1998).

Figures 6A and 6B plot the kinetic parameters versus alpha dose for our titanites, and those of Reiners and Farley (1999) and Stockli and Farley, (2004) discussed above. $E_a$ is fairly consistent (152-198 kJ/mol) with increasing alpha dose until $E_a$ steeply drops off at a damage threshold of $\sim 50 \times 10^{16}$ alpha/g (Fig. 6A). The $E_a$ values for two titanites determined by ion implantation experiments and nuclear reaction analysis are 135-148 kJ/mol (Cherniak and Watson, 2011) and therefore fall within the range of our Kaapvaal titanite $E_a$ results, but the alpha doses of these titanites are unknown so we cannot plot them on Figure 6. The $\ln(D/r^2)$ values at 150°C (~34.9 to ~41.2 sec$^{-1}$) show some variability but no consistent trend up to this same damage threshold, at which point the diffusivity sharply increases (Fig. 6B). Previous work has shown that the titanite diffusion domain is the crystal itself (Reiners and Farley, 1999). We have limited grain size information for the
Figure 6. (A) $E_a$ (kJ/mol) versus estimated alpha dose and (B) \( \ln(D/r^2) \) (s\(^{-1}\)) calculated at 150 °C versus estimated alpha dose. 1 sigma uncertainties on $E_a$ and \( \ln(D/r^2) \), and eU uncertainty on the African titanites used to calculate alpha dose are smaller than the symbols. (C) $T_c$ versus estimated alpha dose for titanites from this study, and those for which THe diffusion data were published by Reiners and Farley (1999) and Stockli and Farley (2004). Compilation of zircon $T_c$ versus estimated alpha dose from Guenthner et al. (2013) shown in light gray circles. All assumptions for titanite alpha dose calculations are reported in Table S3. Vertical dashed lines represent approximate alpha damage level at which He retentivity begins to dramatically decrease. (D) Accumulation time versus alpha dose for titanite and zircon of variable eU. Vertical dashed lines are the same as in (C). Black curves are computed for typical titanite eU values of 10, 100, and 200 ppm eU, assuming Th/U = 2, the mean of the Kaapvaal craton titanites analyzed in this study. Grey curves are for typical zircon eU values of 500, 1000, and 2000 ppm eU, assuming a typical zircon Th/U ratio of 0.5 as reported by Reiners et al. (2005). The curves are solid where accumulation hasn’t reached the titanite and zircon damage thresholds at which He retentivity decreases, and dotted after crossing the threshold. The horizontal black lines mark the 600 and 1200 myr accumulation times as discussed in the text.
titanites with published kinetic data, and so cannot fully disentangle whether grain size variability can explain the dispersion in \( \ln(D/r^2) \) at alpha doses <50x10^{16} \text{alpha/g}.

Figure 6C shows titanite \( T_c \) versus alpha dose for these same samples. Titanite \( T_c \) varies from \(~150-210 \text{ °C} \) at alpha doses up to \(~50x10^{16} \text{alpha/g} \) (Fig. 6C). Owing to this \( T_c \) variation, incomplete grain size knowledge, and uncertainties in the alpha dose estimates it is unclear whether titanite undergoes an initial increase in He retentivity associated with increasing damage at low alpha dose levels as observed in apatite (Shuster et al., 2006; Flowers et al., 2009) and zircon (Guenthner et al., 2013), or if He retentivity is generally invariant over this damage range. However, the results clearly show a steep decrease in He retentivity at alpha doses greater than \(~50x10^{16} \text{alpha/g} \). To confirm that the overall \( T_c \) versus alpha dose pattern does not dramatically change using a different annealing temperature assumption we also computed minimum alpha dose values using an accumulation time based on the THe dates (Table S3) and plot these on Figure S5. The main effect of using these minimum estimates is to lower the damage threshold at which titanite He retentivity decreases to \(~35x10^{16} \text{alpha/g} \), however the general pattern of the data does not change.

5.3. **Comparison of the titanite and zircon radiation damage-He diffusivity relationships**

The dramatic decrease in titanite He retentivity above a certain alpha dose threshold is similar to the behavior in zircon. Our alpha dose estimates allow us to more directly compare the titanite and zircon radiation damage-He diffusivity relationships. Figure 6C includes the compilation of zircon \( T_c \) vs. alpha dose from Guenthner et al. (2013) (light gray circles). Both titanite and zircon are characterized by \( T_c \) values of \(~150-210 \text{ °C} \)
at lower alpha dose and a rapid decrease in $T_c$ at higher damage levels. However, the damage threshold at which the reduction in He retentivity occurs appears to be lower for titanite ($\sim 50 \times 10^{16}$ alpha/g; vertical black dashed line in Fig. 6C) than zircon ($\sim 150 \times 10^{16}$ alpha/g; vertical dashed grey line in Fig. 6C).

The observation that the damage threshold at which He retentivity decreases is lower for titanite than zircon may be caused by the generation of larger damage zones in titanite than zircon during alpha recoil and/or fission-track decay. The attainment of sufficient damage in zircon to reach interconnectedness or “percolation” has been proposed as a mechanism to enhance diffusivity at high damage levels (Ketcham et al., 2013; Guenthner et al., 2013). A mean energy of 95 keV for the $^{238}\text{U}$ and $^{232}\text{Th}$ decay chains yields a larger average ion alpha recoil stopping distance in titanite ($\sim 29$ nm) than zircon ($\sim 25$ nm; using the Stopping and Range of Ions in Matter software, SRIM, Ziegler et al., 2008). Similarly, titanite fission tracks are longer (19.6 µm) than those in zircon (16.7 µm; Jonckheere, 2003). The larger damage zones within titanite suggest that titanite will reach its percolation threshold, and its associated increase in He diffusivity, at lower total damage levels than zircon. This interpretation is further supported by evidence for titanite reaching a higher level of metamictization at lower alpha dose when compared with zircon (e.g. Ewing et al., 2000).

5.4. **Evaluating which portions of the thermal history titanite and zircon will record**

Despite the similarity of the damage-diffusivity patterns for titanite and zircon, consideration of the typical eU of these minerals is necessary to evaluate whether they are likely to record the same portion of a thermal history. Figure 6D shows accumulation time
versus alpha dose for a range of typical titanite eU values (black curves; 10, 100, and 200 ppm eU). The approximate damage threshold at which the He retentivity drops for titanite is marked by the vertical dashed black line (see also Figure 6C for position of this line). Thus, if a rock contains typical 100 ppm eU titanites, after 600 myr the titanites will still retain a Tc of ~150-200 °C because of insufficient damage accumulation (in Figure 6D, after 600 myr the 100 ppm eU curve has not yet crossed the vertical dashed black line). Nearly 1200 Myr of accumulation time is required for the 100 ppm titanite to acquire enough damage to cross the titanite alpha dose threshold at which He retentivity drops (in Figure 6D, after 1200 myr the 100 ppm eU curve intersects the vertical dashed black line).

Zircon commonly has an order of magnitude higher eU than titanite. Figure 6D also shows accumulation times for typical zircon eU values (gray curves; 500, 1000, and 2000 ppm eU). The approximate damage threshold where ZHe retentivity is reduced is marked by the vertical dashed gray line. If a rock contains typical 1000 ppm eU zircons, after 600 Myr the zircons will have crossed their damage threshold and be characterized by a reduced Tc of <150 °C. In contrast, as noted above, 100 ppm eU titanites in the same rock will still retain a higher Tc (~150-200 °C) because of less damage accumulation.

For titanite and zircon with typical eU, the results displayed in Figure 6D suggest that for accumulation times of no more than a few 100 Myr, the THε and ZHe dates will both access temperatures of 150-210 °C. For more protracted thermal histories with longer accumulation times, THε dates are more likely to record higher (150-210 °C) temperatures and thus older portions of the time-temperature path than zircon. This behavior is a consequence of the generally lower eU and thus less damaged character of titanite, which makes it less likely to surpass its percolation threshold. In contrast, even though the zircon
percolation threshold occurs at higher damage levels than in titanite, higher zircon eU and thus much greater damage accumulation rates predict that in most circumstances it will cross its percolation threshold and experience a reduction in He retentivity sooner than titanite.

6. CONCLUSIONS

Our THe dates, Raman spectra, and \(^4\)He diffusion kinetic data document the substantial reduction in titanite He retentivity at alpha doses >50x10\(^{16}\) alpha/g. Damage accumulation times of >600-1200 Myr are required to attain this damage threshold for titanites of typical eU (10-200 ppm). The protracted cooling history of the Kaapvaal craton provided sufficient accumulation time for this threshold damage level to be crossed, such that the effect of radiation damage was manifested as a negative THe date-eU correlation. Previous THe studies involved analysis of grains with lower alpha dose for which the effect of radiation damage on the He retentivity was not substantial. Because titanite typically has an order of magnitude lower eU than zircon (500-2000 ppm), for the same protracted thermal history a titanite of typical composition is less likely to cross its damage threshold than a typical zircon. Titanite is therefore more likely to access higher temperature portions of a protracted time-temperature path than zircon.

Given that extended (>600 Myr) accumulation times are required to attain the alpha dose necessary to strongly affect the He retentivity of typical titanites, in many circumstances the He diffusion kinetic parameters of Reiners and Farley (1999) will be appropriate for interpreting the significance of a THe dataset. However, for longer accumulation times, like those of the Kaapvaal craton titanites in our study, a titanite
radiation damage accumulation and annealing He diffusion kinetic model would be necessary for full quantitative interpretation of the time-temperature path. With such a model it would be possible to exploit radiation damage to decipher high-resolution thermal histories in the same manner as done for the AHe (e.g., Flowers et al., 2007, 2009) and ZHe (e.g., Guenthner et al., 2014; Orme et al., 2016) systems.

ACKNOWLEDGEMENTS

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Figure S1. Representative images of dated titanites with the morphologies used to calculate their volumes listed. Grains were assigned a rectangular prism, capsule, or ellipsoid morphology, or two of these morphologies. The volume was used for the U, Th, and eU concentration calculation, as shown. For grains with two geometries noted, the mean of the concentrations yielded by the two morphologies was used.
Figure S2. All Raman spectra for Kaapvaal craton titanites from samples (A) FW82-037, (B) FW82-038, (C) GB500, (D) GB397, (E) FCT. Multiple spots forming a transect within a single titanite are marked as grain 1a, 1b, etc. Representative BSE images are included for each sample.
Figure S3. Arrhenius plots for Kaapvaal craton and FCT titanites showing two different linear regression approaches for kinetic parameters. (A=E are same as in Fig. 4, but are included here to facilitate comparison with the alternative regression approach for the same data in F-J). See full explanation of the two approaches in text. Regressions for kinetic parameters include all dark grey points. Light grey points are excluded. Initial prograde steps are indicated by diamonds, subsequent retrograde and prograde steps are shown as circles. Calculated 1σ errors on ln(D/r²) are smaller than the symbols. Residual ln plots versus cumulative release fraction are also shown to display how much gas was included in each linear regression. Results of the two regression approaches are indistinguishable, but A=E include a greater amount of the extracted gas in the regression.
Figure S4. All Raman spectra collected before and after heating experiments. All samples were originally analyzed using Raman spectroscopy (Fig. S2), subjected to the same step-heating schedule as the equivalent diffusion experiment (Table S1, S2), then re-mounted and new Raman spectra acquired after-heating. The GB397 titanites were heated to two different maximum temperatures of 350 °C and 420 °C.
Figure S5. Tc versus estimated alpha dose for titanites from this study, Farley (1999), and Stockli and Farley (2004). Bolded symbols represent our favored alpha dose estimates, which are also plotted in Fig. 5c. Non-bolded symbols mark our minimum alpha dose estimates. All assumptions for titanite alpha dose calculations are reported in Table S3. Compilation of zircon Tc versus estimated alpha dose from Guenthner et al. (2013)shown in light gray circles.
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\(^a\) Bolded steps included in regression of data for kinetic parameters

\(^b\) Values for ln(D/r²) calculated from equations described in Fechtig and Kalbitzer (1966) assuming a spherical geometry
Table S3. Titanite alpha dose assumptions and estimates

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<th>Tc (°C)</th>
<th>eU (ppm)</th>
<th>U (ppm)</th>
<th>Th (ppm)</th>
<th>Source of U and Th concentration data</th>
<th>Accum. time (Ma)</th>
<th>Source of accum. time constraint</th>
<th>alpha dose (alpha x 10^{16}/g)</th>
<th>Min accum. time (Ma)</th>
<th>Source of min accum. time constraint</th>
<th>Min alpha dose (alpha x 10^{16}/g)</th>
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<td>29.2</td>
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<td>28</td>
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<td>29.2</td>
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<td>FW82-037</td>
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<td>Regional muscovite and phlogopite Rb-Sr dates from Barton and van Reenen (1992)</td>
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Reiners and Farley (1999) samples
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<th>Ti (ppm)</th>
<th>Zr (ppm)</th>
<th>Hf (ppm)</th>
<th>Notes</th>
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<td>53.9</td>
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<td></td>
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<td>Muscovite $^{40}$Ar/$^{39}$Ar date on same sample from Reiners et al. (2000)</td>
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*Closure temperatures are this study, Reiners and Farley (1999), and Stockli and Farley (2004) as noted in the "sample" column.

bAccumulation time is based on the best estimate of cooling through ~300 °C.

*These alpha doses are plotted in Figures 5 and S3.

*Minimum accumulation times is based on the THe date for the same sample.

*These alpha doses are the minimum values plotted in Figure S3.
### Table S4. Concentration information for Reiners and Farley (1999) samples

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<tr>
<th>Sample</th>
<th>Location</th>
<th>I (µm)(^a)</th>
<th>(w_1) (µm)(^b)</th>
<th>(w_2) (µm)(^b)</th>
<th>U (ppm)(^c)</th>
<th>Th (ppm)(^c)</th>
<th>eU (ppm)(^d)</th>
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<td>230</td>
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\(^a\) average measured length of two sides  
\(^b\) measured width  
\(^c\) concentration information using a rectangular prism volume geometry  
\(^d\) eU - effective uranium concentration, weights U and Th for their alpha productivity, computed as \([U] + 0.235 \times [Th]\)
CHAPTER 3

Deciphering a 2 Gyr-long thermal history from a multichronometer (U-Th)/He study of the Phalaborwa carbonatite, Kaapvaal craton, South Africa

Published in: Geochemistry, Geophysics, Geosystems

Coauthors: Rebecca M. Flowers¹

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ABSTRACT

(U-Th)/He data were obtained for four minerals (baddeleyite-BHe, titanite-THe, zircon-ZHe, apatite-AHe) from the 2.06 Ga Phalaborwa carbonatite complex and nearby Archean basement of the Kaapvaal craton, South Africa. Our goals are to evaluate the relative He temperature sensitivities of these phases, better understand how radiation damage and other factors affect them, and inform aspects of the craton’s thermal history. BHe dates overlap with Phalaborwa emplacement and record the highest temperatures of the dated phases. THe dates are 700-1100 Ma and display a limited negative date-eU correlation. ZHe dates are negatively correlated with eU, are younger (561-32 Ma) and have higher eU than the THe data, with the highest-eU grains younger than the AHe dates. AHe dates are reproducible with a mean of 107 ± 7 Ma. The THe and ZHe data show radiation damage reduction of their He retentivities manifested as the negative date-eU correlations. Alpha dose estimates for zircon are several orders of magnitude higher than for titanite, consistent with the ZHe dates recording lower temperatures and a younger portion of the history than the THe dates. Thermal history modeling yields time-temperature paths that 1) explain the AHe, ZHe, and THe data while honoring existing geologic constraints, thus demonstrating the internal consistency of the dataset, 2) imply possible reheating during Namaqua-Natal orogenesis, and 3) limit maximum probable temperatures to ~180 °C during 300-183 Ma Karoo basin burial. The results show that exploiting multiple (U-Th)/He thermochronometers and radiation damage effects can provide new insights into long-term craton evolution.

1. INTRODUCTION
Cratons are the oldest and most stable portions of continents, but the degree to which they are affected by post-cratonization tectonic and magmatic processes is unclear. This is partly because deciphering extended cratonic time-temperature \((tT)\) histories is difficult, owing to incomplete stratigraphic records and challenges with accessing the appropriate thermal history range with conventional thermochronometers. Advances in \((U-\text{Th})/\text{He}\) thermochronology provide new potential to address this problem. The strong influence of radiation damage on the He retentivity of apatite, zircon, and titanite means that \((U-\text{Th})/\text{He}\) data for these phases can be used to decipher cooling through wide temperature ranges (e.g., Shuster et al., 2006; Flowers et al., 2009; Gautheron et al., 2009; Guenthner et al., 2013; Orme et al., 2016; Powell et al., 2016; Baughman et al., 2017). For example, zircon and titanite \((U-\text{Th})/\text{He} (Z\text{He}, T\text{He})\) closure temperatures \((T_c)\) can vary by up to 180 °C owing to this effect (Guenthner et al., 2013; Baughman et al., 2017). He diffusion kinetics can also be influenced by grain size, which controls the diffusion domain size of the individual crystal (e.g., Farley, 2000), as well as by U-Th zonation, which affects the He diffusion profile and can lead to zones of variable radiation damage (e.g., Farley, 2000; Meesters and Dunai, 2002; Farley et al., 2011; Ault and Flowers, 2012). The differences in He diffusion kinetics between and within different He thermochronometers are amplified by protracted thermal histories like those common in cratonic regions. In such settings, radiation damage effects can lead to spans of He dates correlated with effective U concentration \((eU, (U) + 0.235 \times (\text{Th}); \text{Shuster et al., 2006; Flowers et al., 2007})\), grain-dimension variations can yield size-date correlations (e.g., Reiners and Farley, 2001), and U-Th zonation can contribute to more general data scatter (e.g., Flowers and Kelley, 2011; Ault and Flowers, 2012; Anderson et al., 2017). With improved understanding of the
various factors that contribute to (U-Th)/He data dispersion comes the possibility to accurately reconstruct deep-time thermal histories (e.g., Flowers and Kelley, 2011).

The Kaapvaal craton of southern Africa is a classic example of a craton that initially stabilized in the Archean and was subsequently affected by repeated accretionary and intracratonic magmatic events. A variety of geochronologic and thermochronologic data inform the history of Kaapvaal growth, stabilization, and cooling through temperatures of ~300 °C (e.g., Layer et al., 1992; Schoene et al., 2008), as well as the Mesozoic to Cenozoic history of southern African Plateau erosion and cooling through temperatures <120 °C (e.g., Brown et al., 2002; Flowers and Schoene, 2010; Beucher et al., 2013; Stanley et al., 2013, 2015). However, thermochronologic constraints on the tT history of the Kaapvaal craton between Precambrian and Mesozoic time are more limited (Jacobs and Thomas, 2001; Cassata et al., 2009; Flowers and Schoene, 2010). Such data are needed to better constrain cryptic portions of the craton’s history during this interval.

Here we present a multi-thermochronometer (U-Th)/He study of the 2.06 Ga Phalaborwa carbonatite complex in the northeastern Archean Kaapvaal craton to address these questions. The plethora of U-Th bearing accessory minerals in the Phalaborwa complex, together with the region’s protracted thermal history, make it an excellent target for this work. We use the results, which span 2 Gyr, to compare the relative temperature sensitivities of the four dated phases, evaluate how radiation damage and other factors influence the dataset, and consider the significance of the broad data patterns for the tT history. We then carry out thermal history modeling both to determine if available radiation damage models can reasonably reproduce the results and to gain new insights into the craton’s evolution.
2. BACKGROUND

2.1. (U-Th)/He thermochronology

(U-Th)/He thermochronology takes advantage of the radioactive decay of U and Th to Pb, during which alpha decay releases $^4$He atoms. He is retained within the crystal lattice after cooling below a temperature threshold. A mineral’s He diffusion kinetics are primarily dependent on crystal structure, grain size (e.g., Reiners and Farley, 1999), to a lesser extent U-Th zonation (e.g., Farley, 2000), and in some minerals radiation damage (Shuster et al., 2006; Flowers et al., 2009; Guenthner et al., 2013; Baughman et al., 2017).

The dependence of He diffusion on grain size has been shown by positive correlations between date and grain dimension (Reiners and Farley, 2001), as well as by laboratory He diffusion experiments (Farley, 2000). For typical grain sizes and cooling rates, variable grain dimension can cause closure temperature variations of ~10 °C, but the magnitude of this effect increases for slower cooling and greater grain size variability (Farley, 2000). Parent isotope zonation affects the spatial distribution of $^4$He and therefore the evolution of the He diffusion profile (Farley, 2000; Meesters and Dunai, 2002; Hourigan et al., 2005), and can lead to variable intracrystalline damage and thus spatially variable He retentivity (Farley et al., 2011; Ault and Flowers, 2012; Anderson et al., 2017). U-Th zonation also can affect the alpha-ejection correction, which is computed using a no-zonation assumption.

Radiation damage has an especially strong influence on He diffusivity. Accumulated radiation damage can cause a mineral’s He $T_c$ to vary by 10’s to >100 °C. In apatite, damage accumulation can increase the $T_c$ from ~50 to 110 °C (Farley, 2000; Shuster et al., 2009; Flowers et al., 2009). In zircon, the addition of damage causes the $T_c$ to initially increase...
from 150 to 200 °C until a percolation threshold is reached at which point the $T_c$ can drop to <50 °C (Guenthner et al., 2013; Ketcham et al., 2013). The radiation damage effect on titanite is similar to zircon, with a $T_c$ of ~180 °C at low damage and a dramatic reduction in He retentivity above a damage percolation threshold (Baughman et al., 2017). Radiation damage can be annealed by heating, which can partly or fully reverse the effects of radiation damage on He retentivity (e.g., Shuster and Farley, 2009; Ketcham et al., 2013). Radiation damage accumulation and annealing He diffusion kinetic models are available for apatite (RDAAM, Flowers et al., 2009; and an alternative model by Gautheron et al., 2009) and zircon (ZRDAAM, Guenthner et al., 2013).

Parent recoil, alpha particle damage, and fission events can all cause crystal damage, but which type of damage primarily governs the mineral He diffusion kinetics is a topic of ongoing investigation. Previous experimental work suggested that apatite fission-track annealing occurs at similar temperatures to apatite alpha damage annealing, which is the damage thought to trap He (Shuster and Farley, 2009), and that the zircon fission-track percolation threshold corresponds with the damage level at where zircon He retentivity drops (Ketcham et al., 2013). Based on this evidence, the available apatite and zircon radiation damage models assume fission-track annealing kinetics to remove the damage that influences He diffusion. Fission-track annealing in apatite, zircon, and titanite occurs at temperatures of ≥60-110 °C (e.g., Fitzgerald and Gleadow, 1990), ≥220-310 °C (Yamada et al., 2007), and ≥265-310 °C (Coyle and Wagner, 1998), respectively. However, more recent work highlights that the use of such fission-track annealing kinetics may not be entirely appropriate (e.g., Willett et al., 2017), that annealing rates in zircon and titanite may be somewhat dependent on the level of accumulated damage (e.g., Zhang et al., 2000, 2013;
Geisler et al., 2001), and that ZRDAAM appears unable to reproduce some high-damage ZHe data, suggesting a need to improve calibration of the high-damage end of the model (e.g., Johnson et al., 2017; Anderson et al., 2017). No radiation damage He diffusion kinetic model yet exists for titanite, however, the generally low U-Th concentrations of this mineral makes it less likely to surpass its damage percolation threshold (Baughman et al., 2017), such that in many cases use of uniform diffusion kinetics (e.g., Reiners and Farley, 1999; Stockli and Farley, 2004) may suffice for understanding titanite datasets.

Radiation damage effects can lead to spans of He dates correlated with eU (Shuster et al., 2006; Flowers et al., 2007). eU can be used as a damage proxy for a single mineral for samples with a shared thermal history. Positive (for apatite and zircon) or negative (for zircon and titanite) date-eU correlations can arise depending on the mineral, the eU span of the dated phases, and the time-temperature (tT) history (e.g., Flowers et al., 2009; Guenthner et al., 2013; Baughman et al., 2017). A mineral suite with an eU span that undergoes a protracted thermal history characterized by sufficient time for damage to accumulate and variable He retentivites to develop can yield date-eU correlations in circumstances of protracted cooling through the mineral’s partial retention zone or reheating and partial resetting (see examples in Flowers et al., 2007; 2009, Flowers, 2009). These same protracted thermal histories also magnify the effects of grain-size and U-Th zonation on the results, which can cause additional data dispersion. Conversely, even if variable $T_c$ values exist in a mineral suite, circumstances of fast cooling through the $T_c$ range or reheating and complete resetting of the dated grains may not result in a date-eU pattern (e.g., see examples in Flowers et al., 2009; Ault et al., 2009). In some cases, the competing effects of radiation damage in different phases can yield patterns “inverted”
from those conventionally expected, such as He dates for high damage zircon that are younger than apatite (U-Th)/He (AHe) dates from the same sample (Johnson et al., 2017).

Alpha ejection (Farley et al., 1996; Hourigan et al., 2005; Ketcham et al., 2011; Gautheron et al., 2012), He injection (e.g., Spiegel et al., 2009; Murray et al., 2014), and grain fragmentation (Beucher et al. 2013; Brown et al., 2013) are additional considerations in (U-Th)/He thermochronology. He atoms can travel up to 20 µm during alpha decay, so alpha-ejection corrections must be made for whole crystals to account for He lost by this effect, which requires an accurate estimate of the grain’s surface area to volume ratio (Farley et al., 1996). Low eU minerals are especially vulnerable to bias from He injection from nearby higher eU phases or grain-boundary coatings (e.g., Spiegel et al., 2009; Murray et al., 2014). Grain fragmentation during mineral separation can also contribute to data scatter if the fragments capture different portions of the mineral’s natural He diffusion profile (Beucher et al. 2013; Brown et al., 2013).

Compared to apatite, zircon, and titanite, little is known about the He retentivity of baddeleyite. Baddeleyite is a rare zirconium oxide found in silica-poor systems, and has been applied as a U-Pb geochronometer (e.g., Eriksson, 1984; Heaman, 2009; Wu et al., 2011). We are aware of no published BHe data.

2.2. **Geologic setting and Phalaborwa carbonatite complex**

The Kaapvaal craton of southern Africa is an archetypal Archean craton that formed and initially stabilized between 3.6 and 2.7 Ga (Fig. 1a; de Wit et al., 1992). The Archean basement rocks of the Kaapvaal and Zimbabwe cratons are sutured across the high-grade
Figure 1. (a) Simplified geologic map of southern Africa displaying the extent of the Kaapvaal craton, younger accretionary belts, and major Proterozoic magmatic activity. Inset map shows location of Kaapvaal craton in Africa. (b) Geologic map of the Phalaborwa carbonatite complex, modified after Eriksson (1984), with sample locations. See text for additional sample information.
The Kaapvaal craton was affected by repeated episodes of intracontinental magmatism. These include the emplacement of the Phalaborwa carbonatite, the extensive layered Bushveld complex, and other nearby alkaline and carbonatite complexes at 2.06 Ga (e.g., Yuhara et al., 2003; Cawthorne and Walraven, 1998), alkaline and carbonatite magmatism at ca. 1.4-1.35 Ga (Hanson et al., 2006), and intrusion of the extensive Umkondo large igneous province (LIP) at ~1.1 Ga (e.g., Hanson et al., 2004). Other LIPs affected the craton during the Phanerozoic, including the 183 Ma Karoo LIP associated with Gondwana breakup (e.g., Svenson et al., 2012). Numerous kimberlites were episodically emplaced in the Kaapvaal craton from the Paleoproterozoic to the Cenozoic (e.g., Jelsma et al., 2004).
Emplacement of the Phalaborwa complex occurred by multiple magma pulses (e.g., Eriksson, 1989). The complex is dominated by pyroxenite, phoscorite, banded carbonatite, and transgressive carbonatite, and includes satellite syenite plugs such as the Spitskop syenite (e.g., Eriksson, 1984; Yuhara et al., 2003; Fig. 1b). We could find no published information regarding the probable emplacement depth or exposure level of the complex. Phalaborwa's age of 2.06 Ga is constrained by baddeleyite, zircon, uranothorianite, and thorianite U-Pb dates (Eriksson, 1984; Heaman and LeCheminant, 1993; Reischmann, 1995; Heaman et al., 2009; Wu et al., 2011). Phalaborwa baddeleyite is used as a U-Pb standard due to its abundance, reproducibility, and concordance, and yields a precise $^{207}\text{Pb}/^{206}\text{Pb}$ date of 2059.60 ± 0.35 Ma; (Heaman et al., 2009).

Although no thermochronologic data are available for the Phalaborwa complex itself, a variety of geochronologic and thermochronologic data exist for the broader region. Zircon and apatite U-Pb (e.g., Schoene and Bowring, 2006; Schoene et al., 2008) and biotite $^{40}\text{Ar}-^{39}\text{Ar}$ (Layer et al., 1992) dates constrain the Mesoarchean assembly of the eastern craton and its subsequent cooling to < 300 °C by 2.7 Ga, while muscovite and phlogopite Rb-Sr data indicate cooling of the northern craton to < 300 °C by 2.0 Ga (Barton and van Reenen, 1992). Apatite fission-track (AFT) and AHe data resolve the low temperature (~120-40 °C) erosion history likely associated with Mesozoic uplift of the present southern African Plateau (e.g., Brown et al., 2002; Flowers and Schoene, 2010; Beucher et al., 2013; Stanley et al., 2013, 2015). Thermochronologic constraints on the $t_T$ history in the intervening time are limited. These data include five Neoproterozoic titanite fission-track dates from the southeastern craton (Jacobs and Thomas, 2001), a suite of 1200 to 20 Ma THe dates negatively correlated with eU from Archean basement samples across the central, eastern
and northern craton (Flowers and Schoene, 2010; Baughman et al., 2017), and plagioclase

$^{40}\text{Ar}/^{39}\text{Ar}$ data for a single sample from the Bushveld complex interpreted to record initially rapid cooling to $< 300$ °C followed by protracted cooling to temperatures of 150-200 °C by $\sim 1.4$ Ga (Cassata et al., 2009).

3. (U-TH)/HE THERMOCHRONOLOGY

3.1. Samples

We acquired (U-Th)/He data for four different minerals from a Phalaborwa phoscorite sample, two Phalaborwa mineral megacrysts, and a nearby Archean basement sample. Sample locations are shown in Figure 1B. Specifically, we collected and performed mineral separation on phoscorite sample SA14-2D, from which we dated large apatite fragments. We obtained (U-Th)/He data for fragments of the same Phalaborwa baddeleyite megacryst (sample IN-1) dated by U-Pb TIMS in Heaman (2009). We also dated zircon fragments from a single 2 cm Phalaborwa zircon megacryst (here designated sample VT-Phal) on loan from the Virginia Tech Mineralogical Collection. Titanite fragments and euhedral zircon crystals were analyzed from nearby Archean gneiss sample GJ1012 for which separates were obtained from the South African Council for Geoscience. A subset of the THe data from the Archean gneiss were published by Baughman et al. (2017). There are no major geologic structures between the Phalaborwa carbonatite complex and the
Archean basement, suggesting a shared thermal history since Phalaborwa emplacement at 2.06 Ga.

3.2. Methods

Single crystals of apatite, zircon, titanite, and baddeleyite were handpicked based on size, morphology, and clarity using a Leica M165 binocular microscope. Grains were then photographed and dimensions measured using a calibrated digital camera. Following characterization, single grains were placed in Nb packets for analysis and loaded into an ASI Alphachron He extraction and measurement line at the University of Colorado Boulder. The packets containing the grains were placed under vacuum (~3x10^{-8} torr) and heated with a diode laser to ~800-1100 °C to extract the radiogenic $^4$He. Gas was spiked with $^3$He, purified using SAES getter methods, and measured on a Balzers PrismaPlus QMG 220 quadrupole mass spectrometer. Packets were lased at minimum twice to guarantee all He was released and measured. Baddeleyite fragments required repeated lasing (6-26 times for durations of 10 minutes at 15 A) to fully extract all He.

Dissolution methods varied based on the mineral’s resistance to dissolution. Titanite, baddeleyite, and zircon grains were spiked with a mixed $^{235}$U-$^{230}$Th or $^{235}$U-$^{230}$Th-$^{145}$Nd tracer, and then dissolved using Parr large-capacity dissolution vessels via a multi-step acid-vapor HF and HCl dissolution process as described in Baughman et al. (2017). Apatite samples were spiked with a $^{235}$U-$^{230}$Th-$^{145}$Nd tracer, then dissolved in HNO$_3$ for 2 hours at 80 °C. Dissolved samples were measured for U and Th on a Thermo-Finnigan Element2 magnetic sector ICPMS at the University of Colorado Boulder.

Standard alpha-ejection corrections and volume estimates based on an
orthorhombic prism geometry with pyramid terminations (from Ketcham et al. 2011) were applied to the euhedral zircon grains from the Archean basement sample. No correction was applied to the other dated grains, because they were fragments. Applying no correction assumes that the fragments have no or minimal original crystal faces remaining. This assumption is clearly robust for the fragments from the Phalaborwa zircon and baddeleyite megacrysts, and the large size of the other dated fragments minimizes the potential effect of any captured faces on the date. Mass and U and Th concentrations were calculated from grain volumes that assume a geometry closely representing that of individual grains using the approach described in detail in Baughman et al., (2017). The geometries include rectangular prism, ellipsoid and capsule shapes modified after Ketcham et al. (2011). We conservatively apply a 20% uncertainty in eU to account for uncertainties in morphologies assumed for volume calculations as described in Baughman et al. (2017).

3.3. Results

Single-grain and grain fragment (U-Th)/He data collected for this study are reported in Table 1. Figure 2a is a plot of (U-Th)/He date versus eU for all results. Figure 2b and 2c show the results for the 2.06 Ga Phalaborwa samples and the ~3.2 Ga Archean basement sample separately, because the different crystallization ages could lead to variable accumulated radiation damage that might influence the (U-Th)/He dates. The uncertainty of each date is reported at 2σ, includes propagated U, Th, Sm and He analytical error, and is smaller than the symbols in Figure 2.

Baddeleyite fragments yield dates of 2034 ± 324 Ma and 2124 ± 132 Ma (eU of 302 and 235 ppm, respectively) that are within error of the Phalaborwa emplacement age
98


| Z08 | intact | ortho | 393.2 | 120.5 | 53.8 | 6.2 | 234.2 | 3.3 | 78.4 | 1.2 | 5.1 | 4.6 | 252.6 | 50.5 | 280.1 | 0.6 | 0.33 | 194.2 | 5.0 | 0.85 | 244.9 | 5.0 |
| Z09 | intact | ortho | 257.6 | 108.8 | 68.1 | 20.8 | 461.3 | 7.8 | 152.6 | 2.4 | 10.8 | 0.9 | 497.2 | 99.4 | 414.4 | 0.8 | 0.33 | 152.6 | 4.7 | 0.83 | 178.5 | 4.7 |
| Z10 | intact | ortho | 422.3 | 135.3 | 66.0 | 9.3 | 435.4 | 5.0 | 90.4 | 2.5 | 11.6 | 2.0 | 456.6 | 91.3 | 301.6 | 0.6 | 0.21 | 121.3 | 2.7 | 0.87 | 146.3 | 2.7 |

2. Morphology used for volume and concentration estimates. Where two morphologies noted, the average volume and concentration results were used. rec-rectangular prism, cap-capsule, ellip-ellipsoid, ortho-orthorhombic prism with 2 pyramidal terminations
3. mean length measurement
4. mean width measurement
5. equivalent spherical radius
6. ND-Nc data
7. $\alpha$U - effective uranium concentration, weights U and Th for their alpha productivity, computed as $[U] = 0.235 \times [\text{Th}]$
8. $\sigma$U uncertainty conservatively assumed to be 20%
9. Double analytical uncertainty based on uncertainties in U, Th, and He measurements
10. It is alpha-ejection correction of Ketcham et al (2011) assuming an orthorhombic prism geometry. NA- not applicable because analyzed grain is a fragment.
11. Only whole crystals are corrected for alpha ejection.
Figure 2. (U-Th)/He date vs. eU for (a) All data, (b) data from the 2.06 Ga Phalaborwa samples only, (c) Archean basement samples only. eU uncertainties are 20%. Date uncertainties are plotted at 2σ, and include uncertainties on U, Th, Sm, and He measurements. Data for the two interior and two exterior Phalaborwa zircon fragment data are stippled with black and white dots, respectively. Grey bands in (a) represent timing of geologic events in and surrounding the Kaapvaal craton.
(purple circles, Fig. 2a,b). Phalaborwa apatite are characterized by an unusually high eU for apatite (70-185 ppm). Five analyses yield reproducible dates with a mean and 1sigma standard deviation of 107 ± 7 Ma (yellow circles, Fig. 2a,b). Sixteen ZHe dates for fragments from the Phalaborwa zircon megacryst range from ~561-190 Ma, have a relatively large eU span from ~130-480 ppm, are dispersed, and display a weak negative date-eU correlation (blue circles, Fig. 2a,b). We specifically targeted two fragments from the grain interior and two from the exterior to evaluate potential effects of He diffusion profile development in this large crystal on the ZHe dates. The interior fragments yield older dates (391 ± 7 Ma and 253 ± 5 Ma) than the exterior fragments (226 ± 7 Ma and 190 ± 13 Ma) despite similar eU (~195-280 ppm, 220-230 ppm, respectively).

For the Archean basement sample, THe data (N=7) vary from 1100-700 Ma and are negatively correlated with a 20-110 ppm span of eU (orange triangles, Fig. 2a,c). The basement ZHe dates (N=8), range from 245-32 Ma and are negatively correlated with an eU range from ~250-1470 Ma (blue triangles, Fig. 2a,c).

4. DISCUSSION

The (U-Th)/He data for four different minerals from the Phalaborwa sample suite span ~2.0 Ga. Several of the mineral chronometers yield overlapping dates and display date-eU correlations manifesting the control of radiation damage on the results. Below we first use these results to gain insight into the He diffusion kinetics of the dated phases by assessing their relative temperature sensitivities, the effects of radiation damage and other factors on them (section 4.1), and how the data bear on the current He diffusion kinetic models (4.2). We then show the utility of the overall data patterns for qualitatively
understanding aspects of the thermal history (section 4.3). Finally, we perform thermal history modeling to test if available He diffusion kinetic models can reproduce the dataset and demonstrate how the results can be used to obtain new insights portions of the eastern Kaapvaal craton’s tT path (section 4.4).

4.1. Relative temperature sensitivities and radiation damage effects

Our data for four different He chronometers from samples with a shared thermal history since 2.06 Ga allow us to interpret the relative temperature sensitivities of the dated phases based on their age relationships. Baddeleyite yields the oldest (U-Th)/He dates of the analyzed minerals, recording Phalaborwa emplacement at 2.06 Ga (Fig. 2a,b). Baddeleyite thus records cooling through the highest temperatures of the four minerals dated in this study. Previous diffusion experiment studies on the other dated phases, including zircon and titanite, suggest maximum \( T_c \) values of \( \sim 200 \) °C for crystals with relatively little damage accumulation (e.g., Baughman et al., 2017; Reiners and Farley, 1999; Guenthner et al., 2013). However, we suspect that baddeleyite has a substantially higher closure temperature than this minimum limit because the laboratory heating durations required to fully extract He from the baddeleyite crystals were far greater than those needed to completely degas our other analyzed phases.

The THe dates from the Archean basement sample, ranging from 700-1100 Ma, are all older than those for zircon and apatite and younger than those for baddeleyite (Fig 2). The three higher eU (82-110 ppm) titanite yield younger dates than the lower eU (<63 ppm eU) titanite and together define a limited negative correlation between date and eU. This pattern is part of a broader strong negative correlation between THe date (20-1200 Ma)
and eU (10-970 ppm) yielded by basement samples across a larger region of the Kaapvaal craton (Baughman et al., 2017). This negative relationship suggests that at least the three higher eU titanite crystals accumulated sufficient damage for enhanced He diffusion and a reduction of their $T_c$ to <200 °C.

Dated zircon from the Phalaborwa and Archean gneiss samples have higher eU (>150 ppm) and yield younger dates than titanite (Fig 2a). The ZHe dates thus reflect cooling through lower temperatures than the THe dates. The two highest eU (>1200 ppm) zircon grains record dates of 84 and 32 Ma, younger than the reproducible AHe dates at 107 ± 7 Ma. This pattern implies that the most heavily damaged zircon have a lower temperature sensitivity than the AHe system. This “inversion” of AHe and ZHe dates, with ZHe younger than co-existing AHe dates, has been observed previously (Johnson et al., 2017). The overall negative ZHe date-eU trend reflects reduced ZHe retentivity with increasing damage.

The Phalaborwa zircon dataset is characterized by substantial scatter despite derivation of the dated fragments from the same ~2 cm-diameter zircon megacryst. The spatially variable age distribution can be explained by the combined effects of a $^4$He diffusion profile and eU zonation. Older ZHe dates for two interior fragments than two exterior fragments are consistent with sampling from a diffusion profile caused by a more retentive grain interior that did not undergo the same level of He loss from diffusion as the grain exterior. Additionally, the large eU span (~130-480 ppm) of the dataset indicates that some of the ZHe date dispersion is attributable to eU zonation. He redistribution by ejection of He between zones can induce aberrations in what otherwise might be a
smoothly varying core-rim He diffusion profile (e.g., Boyce and Hodges, 2005; Farley et al., 2010).

4.2. **Alpha dose estimates and He retentivities**

Alpha dose estimates enable us to assess the probable mineral He retentivities at the time of their recorded dates by comparison with independent alpha dose versus closure temperature information for the dated phases. While eU can be used as a damage proxy for a single chronometer with a shared thermal history, alpha dose estimates allow comparison across chronometers and variable tT paths. Alpha dose is the total volume fraction of radiation damage in the crystal, calculated from eU and the damage accumulation time (e.g., Nasdala et al., 2005). Accurate alpha dose estimates require information about the temperature above which alpha damage anneals and how long damage has been accumulating below that temperature. Parent recoil caused by alpha emission is responsible for most crystal damage, with much less caused by fission-tracks and damage from the alpha particle itself. As described in section 2.1, experimental work has suggested that the temperatures at which fission tracks anneal in apatite and zircon are reasonable proxies for annealing of the damage that matters for apatite and zircon He diffusion (Shuster and Farley, 2009; Ketcham et al., 2013). The apatite RDAAM (Flowers et al., 2009) and zircon ZRDAAM (Guenthner et al., 2013) radiation damage models therefore utilize fission-track annealing kinetics as the damage annealing models. However, the robustness of the fission-track annealing kinetic assumption and the extent to which damage annealing depends on the degree of accrued damage are active topics of study (e.g., Baughman et al., 2017; Willett et al., 2017; Anderson et al., 2017). We cannot easily account
for these complexities here based on the available information, so we assume damage accumulation times based on published fission-track annealing temperatures for apatite (≥60-110 °C, e.g., Fitzgerald and Gleadow, 1990), zircon (≥220-310 °C, Yamada et al., 2007), and titanite (≥265-310 °C, Coyle and Wagner, 1998). Specifically, we use estimates for the timing of cooling below ~110 °C, ~250 °C, and ~300 °C as the times at which damage accumulation began for apatite, zircon, and titanite, respectively.

We estimated alpha doses for the Phalaborwa apatite and Archean basement zircon and titanite. We excluded the Phalaborwa zircon owing to its data dispersion, and did not consider the baddeleyite results because no information is available on how radiation damage may affect its He retentivity. Table S1 lists the assumptions associated with our alpha dose calculations. All estimates use grain-specific U and Th data. We use 2060 Ma as the time of cooling below ~300 °C and ~250 °C for zircon and titanite, which is consistent with mica Rb-Sr dates of ~2 Ga that constrain cooling to <300 °C (Barton and van Reenen, 1992) and with 2.06 Ga emplacement of the Phalaborwa carbonatite (Heaman et al., 2009). We use 150 Ma as the time of cooling below ~120 °C based on nearby AFT dates of that age (Gallagher et al., 1998). For each grain, we took the difference between the onset of damage accumulation (2060 Ma for titanite and zircon, 150 Ma for apatite) and its He date, to obtain an alpha dose estimate at the time of each grain’s recorded He date.

Figure 3 is a plot of alpha dose vs. He date for the Phalaborwa apatite and Archean basement zircon and titanite. The Phalaborwa apatite is characterized by alpha dose estimates that are one to three orders of magnitude lower than those for zircon and titanite. This is true despite the apatite being unusually high in eU (up to 119 ppm, in contrast with more typical 25-30 ppm apatite eU values) and overlapping the titanite eU
Figure 3. (U-Th)/He date vs. estimated alpha dose for Phalaborwa apatite, basement titanite, and basement zircon data. The alpha doses are estimated at the time of the recorded He dates. See text and Table S1 for full details of these calculations. Vertical dashed black and grey lines mark the approximate titanite and zircon damage percolation thresholds at which the mineral He retentivity rapidly declines from Baughman et al. (2017) and Guenthner et al. (2013), respectively.
range. The lower estimated alpha dose for the apatite than titanite is due to the lower apatite damage annealing temperature. Prior work showed that radiation damage accumulation in apatite initially increases the AHe retentivity, which can lead to positive correlations between date and eU (e.g., Shuster et al., 2006; Flowers et al., 2009). Although an apatite damage percolation threshold at which He retentivity declines may exist, which could be manifested as a negative date-eU correlation in an AHe dataset, such a threshold has not yet been documented. For most thermal histories apatite will acquire a lower alpha dose than zircon and titanite, owing both to its lower annealing temperatures and typically lower eU than those phases, such that apatite is less likely to cross that hypothetical threshold even if it exists.

The titanite have alpha doses an order of magnitude higher than the apatite, but still one to two order of magnitudes lower than the zircon. In our dataset, the three youngest titanite grains have alpha doses at or near the titanite alpha dose percolation threshold where the titanite He retentivity abruptly declines (vertical dashed black line on Fig. 3; Baughman et al., 2017). This relationship is consistent with the negative THe date-eU correlation defined by these three data points. The titanite alpha dose vs. Tc relationship of Baughman et al. (2017) suggests that the four older THe dates with alpha doses lower than the percolation threshold were likely characterized by THe Tc values of 150-200 °C at the time of their recorded dates.

The zircon have the highest alpha doses of the dataset, with all surpassing the zircon percolation threshold where the He retentivity drops from ~ 150 °C to <50 °C (vertical dashed grey line on Fig. 3; Guenthner et al., 2013). The ZHe dates are significantly younger than the THe dates, consistent with their recording cooling through temperatures less than
the titanite owing to their greater damage accumulation. Moreover, the highest alpha dose zircon yield ZHe dates younger than the apatite, owing to ZHe retentivity reduction even below the apatite $T_c$.

The dated titanite, and zircon have typical eU ranges, such that their relative He retentivities may be representative of those from cratonic settings. Our THe and ZHe results are consistent with the suggestion of Baughman et al. (2017) that THe dates are more likely to record higher (150–210 °C) temperatures and thus older portions of the thermal history than ZHe dates despite the position of the titanite percolation threshold at a lower alpha dose than the threshold for zircon. This is due to the far higher eU and therefore greater damage accumulation rate of typical zircon than titanite, making zircon more likely to surpass its percolation threshold and undergo a reduction in He retentivity. Thus, to first order our data patterns make sense with previously defined percolation thresholds for these phases. We use these outcomes below to aid in interpreting the thermal and geologic significance of the results.

4.3. Geologic implications from data patterns

The distribution of (U-Th)/He dates over a 2 Gyr interval of the eastern Kaapvaal craton’s history provides the opportunity to better decipher key elements of cryptic portions of the regional thermal evolution. Here we first describe the qualitative insights that can be gained by considering the oldest (U-Th)/He dates, the negative date-eU correlations, and the youngest dates in the context of regional geologic constraints. In the next section, we present tT simulations of the apatite, titanite, and zircon (U-Th)/He data with the primary aims of testing the internal consistency of the results using the available
He diffusion kinetic models, and more quantitatively constraining specific aspects of this history.

Our oldest (U-Th)/He dates are for the baddeleyite, which record cooling following Phalaborwa emplacement at 2.06 Ga, as constrained by previous geochronologic data (Eriksson, 1984; Heaman and LeCheminant, 1993; Reischmann, 1995; Heaman, 2009; Wu et al., 2011). The oldest titanite date is ~1.1 Ga. The emplacement of 1.4-1.35 Ga alkaline and carbonatite complexes in the central craton, some of which preserve original volcanic structures, indicate that the central cratonic basement was at the surface by ~1.35 Ga (Hanson et al., 2006). Plagioclase $^{40}$Ar/$^{39}$Ar data for a Bushveld complex sample in the central craton suggest cooling through temperatures of 150-200 °C by 1.4 Ga (Cassata et al., 2009). However, both of these constraints are relatively distal from the Phalaborwa carbonatite (~300-350 km), and the extent to which they are applicable to our dataset is unclear. If Phalaborwa initially cooled to near surface temperatures by 1.35 Ga as implied by the central craton magmatic bodies, then one or more later reheating events would be required to reset the THe dates to ~1.1 Ga. This 1.1 Ga timing is coincident with the large-scale high-temperature Namaqua-Natal orogenesis that affected the eastern and southern craton (e.g., Jacobs et al., 2008; Eglington, 2006) and with Umkondo LIP emplacement (e.g., Hanson et al., 2004). The THe data thus may record thermal resetting due to crustal heating and/or burial associated with these events.

The negative date-eU patterns for the THe and ZHe data that together span ~1100 Ma require slow cooling and/or partial resetting during one or more post-1100 Ma reheating event(s). In contrast, a single phase of fast cooling over the entire temperature sensitivity range of these minerals would generate uniform dates regardless of eU, which is
not observed (see Flowers et al., 2009 and Guenthner et al., 2013 for discussion of AHe and ZHe date-eU patterns). Protracted cooling from ~1150-600 Ma is a possible contributor to the ~1150-600 Ma negative date-eU patterns. Reheating during subsequent events, including during deposition of the 300-183 Ma Karoo basin over this region to partially or fully reset the higher damage titanite and zircon, might also account for some or all of the negative date-eU correlation.

The youngest reproducible dates are for apatite, with a mean of 107 ± 7 Ma that is consistent with ~100 Ma AHe dates from the eastern Kaapvaal craton interpreted to record several kilometers of mid-Cretaceous erosion (Flowers and Schoene, 2010). The absence of a date-eU correlation despite the relatively broad eU span of the dated Phalaborwa apatite suggests fast cooling following complete resetting of all apatite during Karoo basin burial. Full resetting of the AHe dates during the Mesozoic means that these data do not constrain the pre-Mesozoic thermal history of the inverse model below, which is instead driven by the THe and ZHe results.

4.4. Geologic implications from thermal history modeling

Our qualitative analysis above provides some first order insights into the geologic significance of our dataset. However, we can acquire more quantitative constraints on the tT history by using thermal history modeling. In this section, our primary goals are to utilize this approach to better evaluate 1) if reheating at ca. 1.2-1.1 Ga can explain the ~1.1 Ga THe dates, and 2) if the data can limit maximum probable Karoo basin burial temperatures. A related purpose of the modeling is to consider if the apatite, zircon and titanite (U-Th)/He data are internally consistent and can be explained by the available He
diffusion kinetic models.

A variety of tT paths can generally satisfy a given (U-Th)/He date and therefore our results yield non-unique solutions. Data for multiple minerals spanning a broad eU range as in our Phalaborwa dataset have the potential to limit viable thermal histories. We carried out inverse thermal history modeling of the Phalaborwa apatite, basement zircon, and basement titanite (U-Th)/He data using the HeFTy modeling software to constrain possible tT histories that satisfy these results while honoring geologic information (Ketcham, 2005; Ketcham et al, 2009). We did not include the Phalaborwa ZHe data in the simulations due to their dispersion, nor the baddeleyite (U-Th)/He data owing to the lack of a baddeleyite He diffusion kinetic model that is required for the tT modeling. Our simulations employed radiation damage He diffusion kinetic models for apatite (RDAAM, Flowers et al., 2009) and zircon (ZRDAAM, Guenthner et al., 2013). No such radiation damage accumulation and annealing He diffusion model is available for titanite. We therefore only simulated our four oldest titanite dates that our alpha dose calculations suggest did not surpass the titanite alpha dose damage threshold and therefore had not undergone a substantial decline in He retentivity at the time of their recorded He date. We used the titanite He diffusion model of Reiners and Farley (1999) that assumes uniform diffusion kinetics regardless of radiation damage. A shortcoming of this approach is that titanite alpha doses may have been higher, and thus the titanite He retentivities lower, during post-1.1 Ga reheating events than our estimated alpha doses at 1.1-0.9 Ga would imply. This issue of evolving He retentivities would be accounted for by development and use of a radiation damage model for titanite.

We tested 25,000 random tT paths forced through defined tT constraints based on geologic information. HeFTy identifies “acceptable-” and “good-fit” thermal histories that
satisfy the He date, eU and grain size of modeled U-Th/He data based on goodness-of-fit statistics, (Ketcham, 2005; Ketcham et al., 2009). The constraints applied to our thermal history simulations include 1) cooling to <300 °C by 2.0 Ga based on regional Rb-Sr and $^{40}$Ar-$^{39}$Ar dates and the Phalaborwa emplacement age (we are aware of no published emplacement depth estimates with which to further refine this tT constraint at the start of the model), 2) allowing (but not requiring) cooling to near-surface temperatures between 1.45-1.35 Ga based on preserved volcanics of that age in the central craton 300-350 km distal from Phalaborwa, 3) allowing reheating from 1.2-0.9 Ga during Namaqua-Natal orogenesis, 4) cooling to <60 °C at ~300 Ma based on the regional unconformity between the oldest Karoo sedimentary rocks and Archean basement that suggests the basement was within several kilometers of the surface at this time, 5) allowing reheating from 300-150 Ma due to Karoo burial, 6) cooling to <120 °C by 150 Ma based on nearby AFT dates, and 7) present-day surface temperature conditions. Table S2 is a model input table following the approach of Flowers et al. (2015) that reports additional details of how the data were treated in the tT simulation.

Figure 4 shows the thermal history simulation results, where good- and acceptable-fit thermal histories are in pink and green, respectively, the “best”-fit path is in black, and the imposed tT constraints are labelled and marked by the grey boxes. Several key results emerge from our modeling exercise. First, numerous tT paths can simultaneously satisfy the AHe, ZHe and THe data and geologic constraints, thus demonstrating the internal consistency of the results when using current He diffusion kinetic models. Second, most good-fit tT paths show reheating between 1.2 and 0.9 Ga (to account for 1.1 Ga THe dates), although the reheating magnitude need not have been substantial. Some results show near-
Figure 4. HeFTy inverse thermal history simulation results for the Phalaborwa AHe, basement THe, and basement ZHe data. Grey boxes show applied thermal history constraints, with labels above marking the rationale for the applied constraint. Green and pink lines denote “acceptable” and “good” fit tT paths, respectively, while the solid black line is the “best”-fit result. Refer to the text and Table S2 for additional details about model inputs.
surface temperatures since 1.4 Ga and require later greater Karoo reburial to partially reset all dates to varying degrees. We note that our model does not consider additional reheating events between ca. 1.1 Ga and Karoo basin time that may have affected the data patterns because there is no geologic evidence to imply that such events occurred. This aspect will be more fully considered in ongoing work. We currently favor Namaqua-Natal orogenesis along the eastern and southern Kaapvaal craton margins as the cause of this possible Proterozoic heating phase due to this orogen’s high temperatures and significant extent. Third, the good-fit tT paths suggest temperatures of ~150-180 °C during 300-183 Ma Karoo burial, to account for complete He loss from the apatite and to generate the ZHe date-eU pattern, while not resetting the THe dates to Karoo-age. If a radiation damage He diffusion kinetic model for titanite was available to use, it might lower the maximum Karoo burial temperature constraint to <180 °C. This is because additional alpha dose accumulation between 1.1 Ga and Karoo burial time may have lowered the He retentivity to less than what the uniform kinetic model imposes in this simulation. Finally, the thermal history simulation results require a Mesozoic cooling phase to reproduce the ~107 Ma AHe dates, consistent with previous AHe data from the eastern craton interpreted to record several kilometers of erosion at this time (Flowers and Schoene, 2010).

5. CONCLUSIONS

Our multi-chronometer (U-Th)/He dataset from the Phalaborwa carbonatite allows us to better decipher the last ~2.0 Gyr of the eastern Kaapvaal craton’s history. Baddeleyite data record Phalaborwa emplacement and require the highest Tc values of the studied minerals. The THe and ZHe data display negative date-eU correlations, with older THe than
ZHe dates. The THe data thus access an older portion of the thermal history than the ZHe data, consistent with alpha dose estimates for titanite that are 1-2 orders of magnitude lower than those for zircon. This is a consequence of the far lower eU and thus lower radiation damage accumulation rate for titanite than zircon, which makes titanite less likely to surpass the alpha dose percolation threshold at which the He retentivity dramatically declines. Although the Phalaborwa apatite have higher eU than typical apatite, and overlap with the eU values of our analyzed titanite, the lower damage annealing temperature of apatite (≥120 °C) than titanite (≥300 °C) result in an apatite alpha dose estimate an order of magnitude lower than for titanite. The highest alpha dose zircon yield He dates younger than the reproducible AHe results at 107 ± 7 Ma.

Examination of the general data patterns and consideration of geologic constraints provide important insights into the thermal and geologic significance of the results. We additionally carried out thermal history modeling to test the internal consistency of our dataset and to more quantitatively constrain parts of the northeastern Kaapvaal craton’s tT path. The models can simultaneously reproduce the AHe, ZHe, and THe data while honoring available geologic constraints using current He diffusion kinetic models for these systems. The results suggest that a previously unidentified reheating event possibly associated with Namaqua-Natal orogenesis may have affected the region, and also limit maximum basement temperatures during 300-183 Ma Karoo basin burial to <180 °C. This study thus shows how multiple (U-Th)/He thermochronometers and radiation damage effects can be exploited to better decipher complex and protracted thermal histories in geologic settings like this one.
ACKNOWLEDGMENTS

This work was supported by NSF grants EAR-0951518 and EAR-1126991 to R.M.F. We thank Kevin Chamberlain for providing Phalaborwa baddeleyite standard IN-1, Robert Tracy and Llyn Sharp of Virginia Tech University and Susan Eriksson for access to the Phalaborwa zircon megacryst, the South African Council for Geoscience for titanite and zircon separates from Archean basement sample GJ102, and Johan van Tonder and the Palabora Mining Company for providing us with direct access to collect Phalaborwa samples. Supporting data can be accessed in the supplemental material. We thank two anonymous reviewers for comments that helped improve the manuscript.

REFERENCES


Table S1: Alpha dose estimates at the time of the recorded date

<table>
<thead>
<tr>
<th>Sample</th>
<th>He date (Ma)</th>
<th>eU (ppm)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>U (ppm)</th>
<th>Th (ppm)</th>
<th>Accum. time (Ma)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>alpha dose (alpha x 10&lt;sup&gt;16&lt;/sup&gt;/g)</th>
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<tr>
<td><strong>Phalaborwa apatite, SA14-2D, 2.06 Ga crystallization age (-23.98999, 31.13001)</strong></td>
<td></td>
<td></td>
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<td>A01</td>
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<td>19</td>
<td>374</td>
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<td>14</td>
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<td>47*</td>
<td>1.8</td>
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<td><strong>Archean titanite, GJ1012 (-24.11667, 30.95)</strong></td>
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<td></td>
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<td>63</td>
<td>33</td>
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<td>33</td>
<td>31</td>
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<td>1914&lt;sup&gt;+&lt;/sup&gt;</td>
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<td>527</td>
<td>177</td>
<td>1883&lt;sup&gt;+&lt;/sup&gt;</td>
<td>422.7</td>
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</table>

<sup>a</sup>eU - effective uranium concentration, weights U and Th for their alpha productivity, computed as [U] + 0.235 * [Th]

<sup>b</sup>Accumulation time when (U-Th)/He date recorded. * apatite damage accumulation time calculated by 150 Ma minus the He date. 150 Ma is estimated time of cooling to <120 °C based on nearby AFT date (Gallagher et al., 1998) * zircon and titanite damage accumulation time calculated by 2.06 Ga minus the ZHe or THe date. 2.06 Ga is the time of cooling to <300 °C and <250 °C for zircon and titanite, respectively, based on Rb-Sr dates of ~2 Ga that constrain cooling to <300 °C (Barton and van Reenen, 1992) and Phalaborwa emplacement at 2.06 Ga (e.g., Heaman et al., 2009).
Table S2. Thermal history model input table for inverse simulation of Phalaborwa apatite, basement zircon, and basement titanite (U-Th)/He data

1. Thermochronologic data

**Samples and data* used in simulations**

Phalaborwa simulation - output in Figure 4
- AHe data, 1 sample: SA14-2D
- ZHe data, 1 sample: GJ1012
- THe data, 1 sample: GJ1012

Data necessary for modeling the above samples are reported in Table 1

**Data treatment, uncertainties, and other relevant constraints**

**AHe data**
- **Treatment**: AHe data for SA14-2D binned based on eU values (<50 ppm, 50-100 ppm, 100-150 ppm), with the mean of each bin modeled as a separate constraint.
- **He dates (Ma)**: Mean uncorrected He date of each eU bin. All grains are fragments and not corrected for alpha ejection.
- **Error (Ma) applied in modeling**: 15% of mean raw date for each eU bin.
- **r (um)**: Mean equivalent spherical radius of each eU bin
- **eU (ppm)**: Mean eU of each eU bin

**ZHe data**
- **Treatment**: ZHe data for GJ1012 binned based on eU values (<400 ppm, 400-1000 ppm, 1000-1800 ppm), with the mean of each bin modeled as a separate constraint.
- **He dates (Ma)**: Mean uncorrected He date of each eU bin. Uncorrected date corrected for a-ejection in HeFTy using Ketcham et al. (2011).
- **Error (Ma) applied in modeling**: 1s standard deviation or 15% (whichever was larger) of mean raw date for each eU bin.
- **r (um)**: Mean equivalent spherical radius of each eU bin
- **eU (ppm)**: Mean eU of each eU bin

**THe data**
- **Treatment**: THe data for 4 oldest, lowest eU GJ1012 grains modeled together.
- **He dates (Ma)**: Mean uncorrected He date of all individual grains. All grains are fragments and are not corrected for alpha ejections.
- **Error (Ma) applied in modeling**: 15% of mean raw date for sample.
- **r (um)**: Mean equivalent spherical radius of the 4 simulated grains
- **eU (ppm)**: Mean eU of the 4 simulated grains

2. Additional geologic information

**Phalaborwa complex and Kaapvaal craton**

<table>
<thead>
<tr>
<th>Assumption</th>
<th>Explanation and data source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling &lt;300 °C at ~2000 Ma</td>
<td>Based on regional Kaapvaal craton Rb-Sr and Ar-Ar dates (Layer et al., 1992), and Phalaborwa emplacement age of 2060 Ma (e.g., Heaman, 2009).</td>
</tr>
<tr>
<td>300-0 °C between 1450-1350 Ma</td>
<td>Preserved volcanics of this age in central craton shows basement exposed at surface (Hanson et al., 2006). Box allows for cooling to near surface temperatures but does not require it, because this constraint is 300-350 km distal from Phalaborwa and unclear if applicable to our study area.</td>
</tr>
<tr>
<td>300-0 °C between 1200-900 Ma</td>
<td>Timing of Namaqua-Natal orogenesis (e.g., Jacobs et al., 2008). Box allows for reheating.</td>
</tr>
<tr>
<td>60-0 °C at ~300 Ma</td>
<td>Unconformity between oldest Karoo supergroup units and Archean basement, implies basement is within several km of surface at start of Karoo Basin burial (e.g., Catuneanu et al., 2005).</td>
</tr>
<tr>
<td>300-0 °C at 300-150 Ma</td>
<td>Timing of Karoo Basin burial 300-183 Ma (e.g., Catuneanu et al., 2005). Box allows for reheating.</td>
</tr>
<tr>
<td>120-0 °C at 180-150 Ma</td>
<td>Nearby AFT data indicate cooling to &lt;120 °C by ~150 Ma (Gallagher et al., 1998).</td>
</tr>
</tbody>
</table>
3. System- and model-specific parameters

*He kinetic model:* RDAAM (Flowers et al., 2009) for AHe data; ZRDAAM (Guenthner et al., 2013) for ZHe data; Uniform

*Statistical fitting criteria:* “Good” fits are defined as those for which the mean of the GOF statistics assessed is 0.5, and the minimum is $1/(N+1)$, where $N$ is the number of statistics used (Ketcham et al., 2009). Those thermal histories that fit all data a

*Modeling code:* HeFTy v1.9.1

*Number of tT paths attempted:* 25,000

*tT path characteristics:* Gradual, 18 linear segment
CHAPTER 4

Bridging high and low temperature thermal histories: Titanite and zircon (U-Th)/He thermochronology constrain substantial ~1.1 Ga burial and exhumation of the Kaapvaal craton, southern Africa

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ABSTRACT

Titanite and zircon (U-Th)/He (THe, ZHe) data are presented for 11 samples across the Kaapvaal craton from both on- and off- the southern African Plateau to decipher the mid-temperature (~220-120°C) history for which there are few available constraints. The craton was buried during Phanerozoic time owing to off-craton orogenic activity, but the degree to which the cratonic surface history was affected by earlier tectonic and magmatic events is poorly known. THe and ZHe dates are negatively correlated with eU, reflecting decreased He retentivity with increasing radiation damage. THe dates span from 1187 to 135 Ma over a limited eU range (10-200 ppm), while ZHe results vary from 997 to 32 Ma over a broader eU span (67-1780 ppm). For all samples THe dates are older than ZHe dates, such that titanite records a higher temperature portion of the thermal history than zircon. ZHe data patterns vary spatially and can be explained by variable magnitudes of burial by the Phanerozoic Karoo Supergroup. The maximum THe and ZHe dates, combined with central craton volcanics that document the basement was at the surface at 1.4 Ga, require heating to >150°C at ~1.0-1.2 Ga. This heating may be most simply explained by major burial (>4km) by sediments shed from the Namaqua-Natal orogenic belt on the craton's margin. This inferred basin has been removed from the rock record, showing the value of THe and ZHe thermochronology for detecting such events.

1. INTRODUCTION

Cratons are generally considered regions of long-term continental stability, but they were repeatedly affected by younger magmatic and peripheral tectonic events following their initial formation. Low temperature thermochronologic (<120°C) studies increasingly
reveal substantial Phanerozoic burial and erosion episodes (1-4 km) for which the
stratigraphic evidence has been removed (e.g., Gleadow et al., 2002; Kohn et al., 2002,
2005; Flowers, 2009; Flowers et al., 2012; Ault et al., 2013). However, in deeper time, the
paucity of mid-temperature thermochronometers (120-300°C) commonly leads to a
several billion year gap in tT (time-temperature) reconstructions between initial craton
formation constrained by high temperature geo- and thermochronology (>300°C), and
Phanerozoic burial and unroofing episodes constrained by low temperature
thermochronology (<120°C) (e.g., Baughman and Flowers, 2018; McDannell et al., 2018).
Accessing this thermal history gap is key to deciphering earlier burial and erosion events
that may be missing from cratonic stratigraphic records. New advances in our
understanding of titanite and zircon (U-Th)/He thermochronology (THe, ZHe) (e.g.,
Guenthner et al., 2013; Baughman et al., 2017) hold the promise of dramatically improving
our understanding of these deep-time thermal histories in these ancient settings (e.g.,
Orme et al. 2016, Guenthner et al., 2017; Baughman et al., 2017; Baughman and Flowers,
2018).

The Kaapvaal craton of southern Africa is one such ancient region that initially
formed and stabilized during the Archean (e.g., de Wit et al., 1992) and was later buried in
the Phanerozoic (the 300-183 Ma Karoo basin; e.g., Catuneanu et al., 2005). Although the
craton was repeatedly affected by accretionary tectonic events and intracratonic
magmatism between Archean and Phanerozoic time (e.g., Jacobs et al., 2008), there is
limited information about the response of the craton to these events, in part owing to a
thermal history gap of several billion years that coincides with this interval. Here we
present THe and ZHe data from a suite of basement samples from on- and off- the southern
African Plateau to decipher the deep-time thermal history across the Kaapvaal craton. The results constrain a previously unrecognized, Proterozoic reheating event that affected much of the craton, and imply that the craton was once buried by a Proterozoic basin that was later removed from the stratigraphic record.

2. GEOLOGIC BACKGROUND

2.1. Geologic history

The Archean Kaapvaal craton of southern Africa encompasses a large area ($1.2 \times 10^6$ km$^2$). It and the surrounding terranes record a complex and protracted 3.6 byr accretionary and magmatic history (Fig. 1; e.g. de Wit et al., 1992). The craton itself is composed of a series of Archean TTG, greenstone, and gneissic terranes (Fig. 1). Basement rocks of the Kaapvaal and Zimbabwe cratons are sutured across the high-grade Neoarchean Limpopo Belt (e.g., Kreissig et al., 2001). Archean and Paleoproterozoic sedimentary and volcanic units overlie much of the craton including the Witwaterand Basin and Transvaal sequence in the central craton and Pongola Basin to the south (Fig. 1; e.g., Poujol, 2003). The Kaapvaal craton is bounded on the west (present-day coordinates) by the Paleoproterozoic Kheis-Okwa-Magondi belt and Rehoboth provinces, and on the south by the 1,500 km-long 1.0-1.2 Ga Namaqua-Natal metamorphic province (Fig. 1b, e.g., Jacobs et al., 2008). The Natal belt to the east of the larger province, is composed entirely of 1.25-1.03 Ga juvenile crust and underwent high-temperature granulite facies metamorphism of $\sim 800^\circ$C at 1.05 Ga (McCourt et al., 2006; Eglington, 2006). Subsequently, Pan-African belts were accreted to the continent in Neoproterozoic – Early Paleozoic time during the initial building of Gondwana, followed closely by the Paleozoic Cape orogeny along the craton's
Figure 1. A) Geologic map, B) terrane boundary map, C) topographic map. Boxes in (A) and (C) represent area shown in Figure 2a and 2d respectively.
southern margin (current coordinates, Fig. 1b, e.g., Rino et al., 2008, Catuneanu et al., 2005). The ~300-183 Ma Karoo Basin sedimentary rocks were deposited in a retroarc foreland system to the Cape Fold Belt (Fig. 1). The Karoo Supergroup is topped by the 183 Ma Drakensberg Group Lavas of the Karoo LIP associated with Gondwana breakup and opening of the Indian Ocean (Fig. 1b, e.g., Svenson et al., 2012).

The Kaapvaal craton was repeatedly affected by intracontinental magmatism. Such events include emplacement of the Bushveld complex and other nearby alkaline and carbonatite complexes at 2.06 Ga (Fig. 1a; e.g., Yuhara et al., 2003; Cawthorne and Walraven, 1998), alkaline and carbonatite magmatism at ca. 1.4-1.3 Ga in the central craton (Fig. 2a; Hanson et al., 2006), and intrusion of the extensive Umkondo large igneous province (LIP) at 1112-1106 Ma coincident with Namaqua-Natal orogenesis and Rodinia assembly (Fig. 1a, e.g., Hanson et al., 2004). Numerous kimberlites were episodically emplaced in the Kaapvaal craton from the Paleoproterozoic to the Cenozoic (e.g., Jelsma et al., 2004).

Most of the Kaapvaal craton is now part of the southern African Plateau, with average elevations of >1000 m (Fig. 1c). The plateau is ringed by the Great Escarpment, which cuts across the eastern Kaapvaal craton. This results in substantial topographic relief (>1000 m) across a short distance (10s km).

2.2. *Thermochronometric and geologic time-temperature constraints*

Geo- and thermochronometric data and geologic constraints can be used to reconstruct the time-temperature history of the Kaapvaal craton. Zircon U-Pb geochronology indicates initial craton formation at 3.6-3.0 Ga (e.g., Poujol et al., 2003). High
temperature thermochronometers, including titanite and apatite U-Pb (Fig. 2a; e.g., Schoene and Bowring, 2006; Schoene et al., 2008) and biotite $^{40}$Ar-$^{39}$Ar (Fig. 2a; Layer et al., 1992) dates constrain the Mesoarchean assembly of the eastern craton and its subsequent stabilization and cooling to $< 300^\circ$C by 2.7 Ga. Muscovite and phlogopite Rb-Sr data record cooling of the northern craton to $< 300^\circ$C by 2.0 Ga (Fig. 2a, Barton and van Reenen, 1992).

Low temperature thermochronometers, including AFT and AHe data resolve the low temperature ($\sim 120-40^\circ$C, Fitzgerald and Gleadow, 1990; Farley, 2000; Flowers et al., 2009) erosion history likely associated with Mesozoic uplift of the present southern African Plateau. Most of the AFT data were acquired for samples seaward of the escarpment and record two pulses of rapid cooling and exhumation at 140-120 Ma and 100-80 Ma (Fig. 2a; Brown et al., 2002; Tinker et al., 2008; Kounov et al., 2009). Off-plateau AHe data record the second exhumation pulse with dates of 110-80 Ma (Fig. 2a, Flowers and Schoene, 2010, Kounov et al., 2013). These intervals are coincident with increased deposition in offshore basins (Guillocheau et al., 2012). The on-craton thermochronologic data suggests a more complicated history. AFT results in the central craton record dates $> 350$ Ma (Fig. 2a; Gallagher et al., 1998), while on-plateau AHe data from the southern craton are 120-$< 60$ Ma and document eastward scarp retreat in Mesozoic time (Stanley et al., 2015).

Thermochronologic constraints on the tT history in the intervening time between Archean craton formation and stabilization and Mesozoic unroofing are limited. Plagioclase $^{40}$Ar/$^{39}$Ar data for a single sample from the Bushveld complex were interpreted to record initially rapid cooling to $< 300^\circ$C followed by protracted cooling to temperatures of 150-200$^\circ$C by $\sim 1.4$ Ga (Fig. 2a, Cassata et al., 2009). These data include five Neoproterozoic titanite fission-track dates from the southeastern craton (Fig. 2a; Jacobs and Thomas,
Figure 2. Thermal and geologic surface constraints. A) Map with location of thermochronometric and geologic surface constraints. Sample locations marked by colored squares. Black symbols represent surface constraints for on-plateau area, grey symbols give locations of surface constraints for off-plateau. B) Time-temperature plot for central craton on-plateau region and C) time-temperature plot for eastern off-plateau region based on regional thermal and geologic constraints. D) Topographic map inset with sample names and locations based on region and location on- and off-plateau.
2001), and four Neoproterozoic THe dates from 2 samples within in the Ancient Gneiss Complex (Flowers and Schoene, 2010). A multi-chronometer study from the Phalaborwa complex in the eastern craton records THe dates of 1100-700 Ma, interpreted to record Namaqua-Natal thermal resetting, and ZHe dates of 561-32 Ma and is interpreted to record partial to full resetting due to Karoo burial and subsequent unroofing (Baughman and Flowers, 2018). Baughman et al. (2017) published a suite of 1200 to 20 Ma THe dates negatively correlated with eU from Archean basement samples across the Kaapvaal craton, which will be further interpreted within this contribution.

The preserved rock record can be used to constrain times when the Archean basement was exposed at the surface. Volcanics of the 1.4-1.2 Ga carbonatite and alkaline complexes that locally sit within the Bushveld complex and Archean basement in the central craton indicate that the basement was at the surface at that time (Fig. 2a; Hanson, 2006). The base of the Karoo Supergroup where it unconformably overlies older rocks of the craton requires that the basement was again at the surface at 300 Ma.

3. (U-TH)/HE THERMOCHRONOLOGY BACKGROUND

(U-Th)/He thermochronology is based on the thermally controlled retention of He, a secondary daughter product of U, Th, and Sm decay to lead, in a mineral system. He retentivity is function of crystal lattice structure, grain size (e.g., Farley, 2000), parent U and Th distribution (e.g., Ault and Flowers, 2012; Farley et al., 2011; Hourigan et al., 2005; Meesters and Dunai, 2002), and in several phases radiation damage (Shuster et al., 2006; Flowers et al., 2009; Guenthner et al., 2013; Baughman et al., 2017).
Zircon and titanite He retentivity is strongly influenced by the accumulation of radiation, which subsequently impacts the temperature sensitivity of the systems. In zircon, the addition of damage causes the closure temperature \( T_c \) to initially increase from 150 to 200°C until that damage percolation threshold is reached at which point the \( T_c \) can drop to <50°C (Guenthner et al., 2013; Ketcham et al., 2013). Similarly, titanite has a \( T_c \) of ~180°C at low damage followed by a dramatic reduction in He retentivity and \( T_c \) above a damage percolation threshold, but the titanite threshold occurs at a lower damage level than zircon (Baughman et al., 2017). However, because zircon often has an order of magnitude greater effective U concentration (eU, [U] + 0.235[Th]) and thus greater damage accumulation rates than titanite, in most circumstances it will cross its percolation threshold and experience a reduction in He retentivity and closure temperature sooner than titanite. ZHe and THe data from settings with known protracted thermal histories such as cratons are most likely to record these damage effects because zircon and titanite have had sufficient time to accumulate enough damage to cross their respective damage percolation thresholds. At low radiation damage, caused by low eU and/or minimal damage accumulation time, titanite and zircon are both expected to record cooling through temperatures of 150-200°C (Reiners and Farley, 1999; Guenthner et al., 2013; Baughman et al., 2017).

Parent recoil, alpha particles, and fission events all cause crystal damage, however it remains unclear which is the dominant control on mineral He retentivity and thus is an area of ongoing investigation. Previous experimental work suggested the zircon fission-track percolation threshold corresponds with the damage level at where zircon He retentivity drops (Ketcham et al., 2013). Because of this, the available zircon radiation
damage accumulation and annealing model assumes fission-track damage kinetics for both
damage accumulation and removal upon heating. Fission-track annealing in zircon occurs
at temperatures of ≥220-310°C (Yamada et al., 2007). However, recent work suggests that
ZRDAAM appears unable to reproduce some high-damage ZHe data, suggesting fission
track kinetics may not be wholly appropriate and improved calibration of the model is
required (Johnson et al., 2017; Anderson et al., 2017; Mackintosh et al., 2017; Powell et al.,
2016). No quantitative radiation damage model is available for titanite.

Radiation damage effects can manifest as spans of (U-Th)/He dates correlated with
eU (e.g., Flowers et al. 2007; Shuster et al., 2006). eU is a useful damage proxy for a single
mineral and for samples with a shared thermal history as increasing damage should
correlate with increasing U and Th. If sufficient damage has accumulated for titanite and
zircon to cross their damage percolation thresholds, then in instances of slow cooling
through the partial He retention zone and/or reheating and partial resetting a negative
date-eU correlation may be generated (e.g., Guenthner et al., 2013; Guenthner et al., 2017;
Baughman et al., 2018). Highly damaged grains are more likely to have lower He
retentivity, and therefore are most susceptible thermal resetting. On the other hand, fast
cooling through the sample’s T_c window and/or reheating and complete resetting will not
result in a date-eU correlation even if the mineral suite is characterized by variable T_c (e.g.,
Flowers et al., 2007, 2009).

The mineral Tc and therefore the (U-Th)/He dates are additionally affected by grain
size (e.g., Reiners and Farley, 2001; Farley, 2000) and U-Th zonation (e.g., Ault and Flowers,
2012; Farley et al., 2011; Hourigan et al., 2005; Meesters and Dunai, 2002). Protracted
thermal histories magnify these effects as they do radiation damage effects. Grain size
controls the diffusion domain size of individual crystal, by which larger grain sizes lead to
greater He retentivity and higher $T_c$ (e.g., Farley, 2000). Parent isotope zonation affects the
spatial distribution of $^4$He and therefore the evolution of the He diffusion profile (Meesters
and Dunai, 2002; Hourigan et al., 2005), and can lead to intracrystalline damage zones
locally affecting He retentivity within a single grain (Farley et al., 2011; Ault and Flowers,
2012; Anderson et al., 2017). Grain-dimension variations can yield size-date correlations
(e.g., Reiners and Farley, 2001), while U-Th zonation can contribute to general data scatter
(e.g., Flowers and Kelley, 2011; Ault and Flowers, 2012; Anderson et al., 2017).

4. SAMPLES, METHODS, AND RESULTS

4.1. Samples

We acquired new ZHe data for eight basement samples from the Kaapvaal craton. We also obtained new THe data for one Proterozoic diabase sill, and consider the data patterns and geologic significance of THe data from seven samples previously reported in Baughman et al. (2017). Both ZHe and THe data are reported for 6 of the 11 samples.

Samples are subdivided into central on-plateau, southeastern on-plateau, southeastern off-plateau and eastern off-plateau (Fig. 2d). The subdivision is based on spatial location and elevation variability between sampling sites. Ten samples (and all zircon samples) are from Archean gneissic basement, while a single titanite sample is sourced from a Proterozoic diabase sill in the central craton. Table 1 reports additional location and rock type information.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Morphology</th>
<th>Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>T02</td>
<td>intact</td>
<td>337.9 248.3 134.2 56.2 11.4 1.5 110.4 12.5 ND ND 37.3 7.5 205.5 0.4 9.71 97.14 24.2 NA NA NA</td>
</tr>
<tr>
<td>T03</td>
<td>rec prism</td>
<td>329.8 235.4 133.4 71.0 14.4 0.2 132.3 1.0 ND ND 45.4 9.1 282.8 0.1 9.21 108.9 13.4 NA NA NA</td>
</tr>
<tr>
<td>T04</td>
<td>capsule</td>
<td>321.6 209.4 124.8 33.8 79.2 10.6 456.6 49.0 ND ND 166.5 37.3 213.4 0.1 5.77 208.8 4.2 NA NA NA</td>
</tr>
<tr>
<td>T05</td>
<td>rec cap</td>
<td>231.5 174.3 96.8 20.6 19.7 0.9 73.9 1.4 ND ND 37.1 7.4 209.1 0.1 3.76 981.6 17.4 NA NA NA</td>
</tr>
<tr>
<td>Z01</td>
<td>ortho</td>
<td>201.3 73.3 46.4 3.8 868.1 11.6 289.4 4.1 3.4 4.3 936.1 187.2 430.7 0.9 0.33 84.7 2.1 0.76 111.6 2.1</td>
</tr>
<tr>
<td>Z02</td>
<td>ortho</td>
<td>208.4 74.9 47.7 4.1 752.0 14.1 317.5 4.7 6.1 4.3 826.6 168.3 509.7 1.7 0.42 113.3 3.8 0.76 147.9 3.8</td>
</tr>
<tr>
<td>Z04</td>
<td>ortho</td>
<td>238.4 90.8 57.5 6.6 621.8 8.2 212.9 3.3 8.5 2.8 671.8 134.4 966.7 2.3 0.34 245.0 6.0 0.80 303.7 6.0</td>
</tr>
<tr>
<td>Z05</td>
<td>ortho</td>
<td>374.3 106.4 70.5 15.9 790.6 14.2 226.2 3.5 6.8 1.7 833.7 166.7 391.9 0.9 0.29 86.6 2.9 0.84 103.2 2.9</td>
</tr>
<tr>
<td>Z07</td>
<td>ortho</td>
<td>285.8 133.9 79.8 16.3 951.8 12.8 244.7 4.0 7.1 1.2 1099.3 201.9 543.8 1.3 0.26 99.1 2.5 0.86 115.6 2.5</td>
</tr>
<tr>
<td>Z08</td>
<td>ortho</td>
<td>279.6 97.2 61.7 9.3 569.6 7.4 133.9 2.6 11.2 4.9 601.0 120.2 678.8 1.8 0.24 206.7 5.0 0.82 251.1 5.0</td>
</tr>
<tr>
<td>Z09</td>
<td>ortho</td>
<td>289.6 90.3 58.5 8.7 559.7 14.2 347.5 5.2 13.8 2.9 1041.3 208.3 331.9 1.0 0.36 58.8 1.6 0.81 72.8 1.6</td>
</tr>
<tr>
<td>Z10</td>
<td>ortho</td>
<td>247.7 110.4 66.6 9.8 617.7 6.0 222.4 2.9 7.0 1.0 670.0 134.0 476.7 2.3 0.36 130.5 2.6 0.83 157.0 2.6</td>
</tr>
<tr>
<td>Z11*</td>
<td>ortho</td>
<td>270.8 96.4 61.5 8.9 1074.6 19.0 306.9 3.9 7.5 2.0 1146.7 229.3 313.4 1.0 0.29 50.5 1.7 0.81 61.9 1.7</td>
</tr>
</tbody>
</table>


**Morphology used for volume and concentration estimates. Where two morphologies noted, the average volume and concentration results were used. rec-rectangular prism, cap-capsule, ellip-ellipsoid, ortho-orthorhombic prism
with 2 pyramidal terminations

1. mean length measurement
2. mean width measurement
3. equivalent spherical radius
4. ND - No data
5. eU - effective uranium concentration, weights U and Th for their alpha productivity, computed as [U] + 0.235 * [Th]
6. eU uncertainty conservatively assumed to be 20%
7. Analytical uncertainty based on uncertainties in U, Th, and Hf measurements
8. PT is alpha-ejection correction of Kebekum et al (2011) assuming an orthorhombic prism geometry. NA- not applicable because analyzed grain is a fragment.
9. Only whole crystals are corrected for alpha ejection.
4.2. Methods

Standard zircon and titanite picking, degassing, and dissolving (U-Th)/He methods were used (Baughman et al., 2017). All analyzed zircon grains were single, euhedral crystals, while all dated titanite were large fragments. Fragmentation likely occurred during sample processing. Standard alpha-ejection corrections and volume estimates based on an orthorhombic prism geometry with pyramid terminations (from Ketcham et al., 2011) were applied to all zircon. No correction was applied to titanite, because they were fragments. Applying no correction assumes that the fragments have no or minimal original crystal faces remaining. This assumption is robust based on the large size of the dated fragments, which minimizes the potential effect of any captured faces on the date (Table 1). Mass and U and Th concentrations were calculated from grain volumes that assume a geometry closely representing that of individual grains using the approach described in detail in Baughman et al., (2017). The geometries include rectangular prism, ellipsoid and capsule shapes modified after Ketcham et al. (2011). We conservatively apply a 20% uncertainty in titanite eU to account for uncertainties in morphologies assumed for volume calculations as described in Baughman et al. (2017), and a standard 15% uncertainty to zircon eU.

4.3. Results

4.3.1. Full dataset

New (U-Th)/He data collected in this study are reported in Table 1. THe and ZHe date-eU plots for all 37 titanite and 43 zircon analyses, color-coded by sub-region, are shown in figure 3a,b. The same plots are shown in figure S1, but with results additionally
Figure 3. A) THe date-eU plot and B) ZHe date-eU plot for all Kaapvaal craton samples color-coded by region. For reference, ZHe and THe dates shown in grey in (A) and (B), respectively. The 2 sigma analytical uncertainty of the dates are encompassed by the symbols. A conservative 20% uncertainty is plotted for titanite and 15% for zircon, pp=previously published in Baughman et al. (2017). All samples are from Archean rock unless noted in the legend.
distinguished by individual sample.

Titanites yield dates from $135 \pm 2.4$ Ma to $1187.4 \pm 32.4$ Ma and are negatively correlated with their $\sim 10$-200 ppm span of eU (Fig. 3a). All subgroups show similar THe date-eU patterns. Zircons yield dates between $32.2 \pm 0.6$ Ma and $997.3 \pm 27.2$ Ma and are, in general, negatively correlated with their 67-1780 ppm span of eU (Fig. 3b). ZHe results are more variable between regions than the THe data (Fig. 3b). Zircon grains on average have significantly higher eU than titanite (mean values of 565 ppm and 65 ppm for zircon and titanite, respectively). ZHe dates are on average younger than THe dates in all regions. For example, 5 of 8 zircon samples yield dates all younger than 400 Ma (Fig. 3b), whereas no titanite samples show this pattern (Fig. 3a).

4.3.2. Subregions

Date-eU plots that include both titanite and zircon data for each subregion are shown in figure 4a-d. All regions share similar negative THe date-eU correlations, with THe results yielding a maximum date of $\sim 900$ Ma in the central, southeastern, and eastern craton. However, ZHe data show more variable patterns between subregions, with higher elevation (on-plateau samples) yielding older ZHe dates than lower elevation (off-plateau samples) at the same eU.

The four central craton samples are from higher elevations (>900 m) on the southern African Plateau (Fig. 2d). THe results yield maximum dates of 1100 Ma, with 7 of 13 analyses yielding dates > 950 Ma (eU < 28 ppm, Fig. 4a). ZHe dates are significantly older here compared with other regions at the same eU. THe and ZHe date-eU patterns are
Figure 4. THe and ZHe date-eU plots for the A) central on-plateau, B) southeastern on-plateau, C) southeastern off-plateau, and D) eastern off-plateau regions. Grey bands on each plot highlight the timing of major known geologic events. Elevation for each sample is given in meters. Uncertainties and other annotation same as Figure 3.
offset from each other. For example, THe dates are \( \sim 800 \) Ma at \( \sim 50 \) ppm eU, while ZHe dates yield \( \sim 800 \) Ma dates at higher eU values of \( \sim 190 \) ppm (Fig 4a).

Data from the southeastern craton are for four samples that encompass an \( \sim 1300 \) m elevation span across the Great Escarpment, with two samples from higher elevations (1490-1800 m) on the southern African Plateau (Fig. 4b) and two from lower elevations (550-650 m) seaward of the Great Escarpment (Fig. 4c). THe results yield a max date of 889.4 ± 31.6 Ma (eU – 38 ppm), compared to a max ZHe date of 340.1 ± 4.7 Ma (eU – 311 ppm) from on the plateau. The THe date-eU pattern is similar on- and off-plateau and covers the same span of eU. ZHe results, however yield different date-eU patterns on- and off-plateau, with older ZHe dates when compared with zircon of the same eU at lower elevation. The high elevation samples flat-line at \( \sim 200 \) Ma (Fig. 4b), older than the low elevation samples. Sample AGC01-4 yields an average date of \( \sim 118 \pm 15 \) Ma for all dates except the lowest eU date, which gives a slightly older date of 174.4 ± 4.2 Ma , defining a limited negative date-eU correlation (Fig. 4c). Low elevation sample SA16-24, shows a different pattern with an average date of 232 ± 25 Ma over a limited eU of 368-384 ppm. The on-plateau ZHe date-eU pattern is overall similar to the on-plateau central craton results.

The three samples from the eastern craton are from lower elevations (<683 m) off of the southern African Plateau. THe and ZHe data patterns resemble those off-plateau in the southeastern craton. The data include the oldest THe and ZHe dates in the study at 1187.4 ± 32.4 Ma (25 ppm eU) and 997.3 ± 27.2 Ma (79 ppm eU), respectively (Fig 4d). THe and ZHe results define a single overlapping negative date-eU trend.
Regional THe and ZHe dates are also plotted against grain size, denoted as the equivalent spherical radius \((r \sim \mu m)\) and color coded by eU (Fig. S2 – titanite, Fig. S3 - zircon). THe dates show a positive correlation with grain size at low eU within samples from the central and eastern craton (Fig. S2a,d). ZHe dates are not correlated with grain size within individual samples (Fig. S3). However, southeast off-plateau ZHe results show a positive correlation between samples AGC01-4 and SA16-24. The smaller grain size \((r = \sim 30 \mu m)\) sample, AGC01-4 yields reproducibly younger dates compared to sample SA16-24 which has a grain size 3X larger \((r = \sim 95 \mu m)\) AGC01-4 (Fig. S3c).

5. DISCUSSION

THe and ZHe data for four regions across the Kaapvaal craton from on- and off- the southern African Plateau span 1200 Ma and record similar titanite date-eU patterns and variable zircon date-eU patterns. Below we first compare the THe and ZHe data patterns using our current understanding of titanite and zircon He diffusion kinetics to assess their relative temperature sensitivities and the effects of radiation damage on them (section 4.1). We then use the overall data patterns, including the oldest dates, negative date-eU patterns, and youngest dates in conjunction with regional geologic constraints to qualitatively decipher aspects of the thermal history (section 4.2). This is followed by inverse and simple forward modeling of a subset of the ZHe data to quantitatively assess if regional differences in the ZHe data patterns can be reasonably explained by spatial variability in the thermal history (section 4.3). Finally, we address the geologic significance of a previously unidentified 1.1 Ga reheating event across the entire craton, likely associated with major
Namaqua-Natal orogenesis, and link it to a larger pattern of collision, burial, and sediment removal within the craton (section 4.4).

5.1. **Complementary THe and ZHe date-eU patterns**

THe and ZHe dates from all regions are negatively correlated with eU, consistent with radiation damage reduction of titanite and zircon He retentivity (Fig. 3, 5; Baughman et al., 2017; Guenthner et al. 2013). Figure 5 highlights previously published zircon (Guenthner et al., 2013) and titanite (Baughman et al., 2017) data showing the correlation between increasing damage and decreasing closure temperature once a damage percolation threshold is crossed (grey dashed line – zircon, black dashed line – titanite). Both mineral systems likely surpassed their damage percolation thresholds due to protracted time spent at low temperatures (below fission track annealing temperatures) as indicated by Ar-Ar and Rb-Sr data that constrain cooling to <300°C by 2.0 Ga across the craton (Fig. 2a; Barton and van Reenen, 1992; Layer, 1992). Therefore the negative date-eU correlation is indicative of higher eU (higher damage) grains accessing lower temperature portions of the thermal history. The zircon pattern is offset to higher eU (and greater damage) compared to titanite, consistent with zircon crossing its damage percolation threshold at higher damage levels than titanite, as shown by the offset damage percolation thresholds in figure 5.

In the one case (eastern craton off-plateau) where zircon has eU nearly as low as titanite (~70 ppm and ~32 ppm, respectively), the ZHe and THe dates overlap (~950 and ~1000 Ma, respectively, Fig. 4d). This is consistent with the two minerals having comparable He retentivity at low damage levels, as previously documented (Fig. 5; Reiners
Figure 5. Figure modified from Baughman et al. (2017). Closure temperature versus alpha dose plot for zircon (grey) and titanite (black, yellow) samples previously published by Guenthner et al. (2013) and Baughman et al. (2017). Black dashed line represents titanite damage percolation threshold and grey dashed line represents zircon damage percolation threshold at which point He retentivity decreases. Yellow titanite samples are additionally interpreted in this contribution.
and Farley, 1999; Guenthner et al., 2013; Baughman et al., 2017). Kaapvaal zircon and
titanite samples with low eU (<50 ppm) are likely to record cooling through pre- damage
percolation threshold temperatures of ~220-150°C based on previously published titanite
diffusion experiment and modern T_c data for eastern off-plateau samples FW82-037 and
FW82-038 represented with yellow squares in figure 5, for which THe data are interpreted
for this study. Titanite sample FW82-037-05, yields a present day T_c of 150°C, falls at a
lower damage level than the titanite percolation threshold at which point He retentivity
decreases (Fig. 5 vertical dashed black line), and records several Proterozoic dates (>1000
Ma). The modern day T_c of 150°C provides a minimum thermal resetting temperature for
titanite and zircon with similarly low eU (<50 ppm) that yield similarly old He dates (>900
Ma) from the larger dataset.

At moderate eU values where ZHe and THe data are both available for comparison
(there are no titanite with eU > 210 ppm), the THe dates are younger than the zircon with
the same eU (Figure 4a). For example, in the central craton, titanite and zircon with similar
eU (~150-185 ppm) yield dates of 250 Ma and 800 Ma, respectively (Fig. 4a). This is
compatible with the titanite damage percolation threshold (Fig. 5 – vertical dashed black
line) at which He retentivity decreases being located at lower damage levels than the zircon
threshold (Fig. 5 – vertical dashed grey line; Baughman et al., 2017). However, because the
dated titanites typically have far lower eU (11-201 ppm, Table 1) than most of the zircons
(67-1780 ppm, Table 1), in general titanite from this dataset accumulate significantly less
damage and are thus more retentive and record older dates than the zircon. THe dates are
older than ZHe dates in each of the regions (Fig. 3, 4) consistent with titanite accesses a
higher temperature portion of the Kaapvaal’s thermal history. THe and ZHe datasets
therefore provide complementary thermal history information despite their similar
potential closure temperature windows of 200-<50°C (Guenthner et al., 2013, Baughman et
al., 2017, Powell et al., 2016). Several recent studies show a similar pattern of THe date >
ZHe date in individual samples, particularly in settings with protracted thermal histories
such as the Colorado Rocky Mountains (Johnson et al., 2017; Anderson et al., 2017). Our
coupled THe and ZHe data in the Kaapvaal craton allows us to take advantage of radiation
damage effects on titanite and zircon to decipher the craton’s deep-time thermal history.

THe and ZHe data are additionally affected by grain size. THe dates are positively
correlated with grain size at low eU, suggesting increased He retentivity with larger grain
sizes (Fig. S2). This is compatible with a grain size controlled diffusion domain (Dodson,
1973; Farley, 2000), and is only pronounced at low eU, where radiation damage has less
control of He diffusivity. Variable titanite grain size (50-140 μm equivalent spherical
radius) may contribute to additional data scatter not correlated with eU (Fig. S1a). ZHe
data do not show a grain size correlation within individual samples (Fig. S3), but the two
southeastern off-plateau samples do show a positive correlation with grain size between
samples (Fig. S3c). Sample SA16-24 has a 3x greater grain size and older dates (~230 Ma)
compared to AGC01-4 (~120 Ma). This discrepancy in ZHe date may result from increased
He retentivity and a higher Tc for sample SA16-24. For simplicity we choose to focus
subsequent thermal history discussion on sample AGC01-4.

5.2. Thermal history implications from data patterns

The THe and ZHe dates from across the Kaapvaal craton span 1.2 Gyr and provide
the opportunity to decipher cryptic portions of the craton’s thermal history and assess
spatial variability in the craton's thermal evolution. Here we first describe new insights gained by qualitatively considering 1) the oldest (U-Th)/He dates and related geologic constraints, 2) the negative date-eU correlations, and 3) the youngest dates. In the next section we use inverse and simple forward thermal history modeling to quantitatively evaluate if the spatially variable ZHe results can be explained by differences in post-300 Ma burial magnitudes.

The oldest dates from each of the 4 regions are from titanite, are associated with low eU, and range from ~900-1200 Ma. Geologic constraints from the central craton appear to require significant reheating at 1.2-1.1 Ga, consistent with other published thermochronologic data in the southeast craton. Emplacement of 1.4-1.35 Ga alkaline and carbonatite complexes, some as close as 30 km to our central craton samples WKC-00-37 and RK3, preserve original volcanic structures, and indicate that the central cratonic basement was at the surface by ~1.35 Ga (Fig. 2a,b; Hanson et al., 2006). Plagioclase 40Ar/39Ar data for a Bushveld complex sample in the central craton suggest cooling through temperatures of 150-200°C by 1.4 Ga (Fig 2a,b; Cassata et al., 2009). Together these additional constraints require a post 1.35 Ga reheating event (>150°C) to reset central craton low eU and low damage THe dates to ~1.1 Ga. Titanite fission-track analysis (Tc = ~280°C) from the southeastern most Kaapvaal craton and northern most Namaqua-Natal province yield dates of 1100 ± 200 Ma (Fig. 2a,c, Jacobs and Thomas, 2001) and suggest the southern craton was fully reset to temperatures above the THe and ZHe closure temperature at that time. We therefore, interpret a related ~1.1 Ga reheating event to have reset the eastern and southeastern samples in addition to the central craton samples to Proterozoic dates. This 1.1 Ga timing is coincident with the large-scale high-temperature
Namaqua-Natal orogenesis that affected the eastern and southern craton (Fig. 1b; e.g., Jacobs et al., 2008; Eglington, 2006) and with Umkondo LIP emplacement (Fig. 1b; e.g., Hanson et al., 2004). The oldest Th empirical data thus may record thermal resetting due to crustal heating and/or burial associated with these events.

The negative Th empirical pattern (1200-135 Ma, 10-200 ppm eU), and negative ZHe empirical pattern (1000-30 Ma, 60-1800 ppm eU) require slow cooling and/or partial resetting during one or more post-1100 Ma reheating event(s). The entire craton was affected by some level of reheating during deposition of the 300-183 Ma Karoo basin, which still covers much of the craton today (Fig. 1a). Reheating associated with Karoo burial likely partially or fully reset the higher damage and thus lower $T_c$ titanite and zircon, and might also account for some or all of the observed negative date-eU correlations. Protracted cooling from ~1100-300 Ma, and/or additional reheating events within that time frame may also contribute to observed negative date-eU patterns. As there is no evidence for additional reheating events, we favor a combination of slow cooling and Karoo burial reheating and partial resetting to explain Th empirical and ZHe empirical negative date-eU patterns.

The youngest ZHe empirical dates from on-plateau are 200 Ma, compared to the young ZHe empirical dates of 120-100 Ma from the off-plateau eastern and southeastern regions at equivalent mid-high eU. These dates of ~120-100 Ma are consistent with ~100 Ma AHe empirical dates ($T_c = ~70^\circ C$) for southeastern on- and off-plateau samples EKC02-40 and AGC01-4, that have been previously published by Flowers and Schoene (2010), and are interpreted to record several km of rapid exhumation following Karoo burial. The youngest ZHe empirical data are from the eastern off-plateau region, have the highest eU and thus greatest damage, and yield Cenozoic dates. These ZHe empirical dates are younger than nearby AHe empirical results and suggest the most
damaged samples are recording cooling through temperatures less than AHe as previously documented by other workers (Johnson et al., 2017).

To explore spatial and elevation pattern variability in our data, we compare our central on-plateau data to southeastern off-plateau data from sample AGC01-4 (Fig. 6a). The data from these regions overlaps across the limited eU range (10-200 ppm), however, the ZHe date-eU patterns are distinct (Fig. 3). Central craton ZHe dates span ~850-200 Ma and are negatively correlated across their entire eU span of 200-700 ppm, compared to the reproducible southeastern ZHe date of ~118 ± 15 Ma for 5 analyses with an eU span of 300-600 ppm (Fig. 6a). This ZHe younging trend may be explained by increased Karoo burial temperatures to the east. Increased burial to the east is consistent with older >350 Ma central AFT dates (Tc ~ 110°C) that were not fully reset by Karoo burial (Gallagher et al., 1998) and Cretaceous <150 Ma AFT dates in the southeast that were fully reset by Karoo burial. The lack of a ZHe date-eU correlation in the southeastern off-plateau sample suggests burial temperatures of at least 150°C and fast exhumation through the zircon Tc window (Gallagher et al., 1998; Flowers and Schoene, 2010; Baughman et al., 2018). We test whether increased burial temperatures towards the east can reproduce our spatially variable ZHe data patterns using inverse and simple forward modeling in the next section.

5.3. Thermal history modeling: Can variable Karoo burial explain spatial differences in date-eU patterns

The most significant result of this study, for which the geologic implications are highlighted in the next section, is that the maximum THe and ZHe dates of ~1.1 Ga require heating of the cratonic basement to temperatures sufficient to cause complete He loss from
Figure 6. HeFTy inverse thermal history modeling. A) ZHe-date-eU plot of central on-plateau zircon (blue triangles) and southeastern off-plateau (red triangles). Dashed black lines mark bins in which samples were averaged for inverse model inputs (Fig. S4). Solid blue line marks the modeled date-eU path of the best fit time temperature history of central craton inverse model results (B) and solid red line marks modeled date-eU path of best fit time temperature history of southeastern off-plateau inverse model results (C). HeFTy inverse model results shown in B) and C). Grey boxes show applied thermal history constraints. Green and pink lines denote “acceptable” and “good” fit tT paths, respectively, while the solid black line is the “best”-fit result. Refer to the text and Table S2 for additional details about model inputs.
the zircon and titanite crystals. Geologic relationships and the \((U-\text{Th})/\text{He}\) dates themselves can be used to draw this key conclusion without thermal history modeling. The primary aim of our modeling here is to quantitatively assess if the first-order data patterns defined by the grains that yield \(<1.1\) Ga dates can be explained using geologically reasonable thermal histories. To accomplish this we simulate ZHe data for both on-plateau central craton (\(>1650\) m) and off-plateau southeastern craton (\(<650\) m) samples. We first use inverse modeling to determine if the ZRDAAM model can satisfy the data and geologic constraints, followed by forward modeling to specifically evaluate if spatial variability in Karoo basin burial magnitudes alone can account for the differences in the on- vs. off-plateau data patterns. We don’t attempt to interpret the post-1.1 Ga portion of the history in detail, in part owing to uncertainties in some aspects of the radiation damage model for zircon He diffusion kinetics. Rather, we emphasize that the data patterns are entirely sensible when considering the geologic context and the first-order understanding of He diffusion in zircon.

### 5.3.1. Inverse modeling

Inverse thermal history modeling was performed using HeFTy modeling software to constrain possible tT histories that satisfy the ZHe results and honor geologic information while using the ZRDAAM (Guenthner et al., 2013). The THe data were not simulated because titanite He retentivity is clearly affected by radiation damage (Baughman et al., 2017), but no radiation damage model is yet available for titanite. For each model, 10,000 random tT paths were forced through user defined tT constraint boxes based on geologic and other thermochronologic data. HeFTy identifies “acceptable-” and “good-fit” thermal
histories that satisfy the He date, eU and grain size of modeled U-Th/He data based on goodness-of-fit statistics, (Ketcham, 2005; Ketcham et al., 2009). Measured ZHe data are binned based on eU and the mean eU, grain size, date, and standard deviation of the date or 15%, whichever is greater for error calculation of each bin is input as a separate parameter (Fig. 6a, Fig. S4, Table S1). Central craton ZHe data record additional scatter beyond the first order influence of radiation damage, which may be the result of eU zonation (Fig. 6a). As we did not collect in-situ U and Th concentration profiles for our samples, we do not attempt to model this complexity and favor averaging.

The two regions are modeled separately (Fig. 6b,c) but share several thermal constraints including 1) cooling to <300°C by 3.0 Ga based on biotite Ar-Ar dates for the southeastern craton (Tc ~300°C) of that age (Fig. 2a, Layer et al., 1992), 2) near surface temperatures of 40-20°C at 1.4-1.2 Ga based on preserved volcanics of that age in the central craton (Fig. 2a), 3) reheating from 180-250°C between 1.2-1.0 Ga required to fully reset THe dates from this study to that age and coincides with major Namaqua-Natal orogenesis, and 4) cooling <40°C at ~300 Ma based on the regional unconformity between the oldest Karoo sedimentary rocks and Archean basement. Post-300 Ma constraints vary for the two regions and are based on regional low temperature AFT and AHe data that record variable Karoo basin heating/burial magnitudes. The central craton constraints include 1) maximum temperatures of 110°C during 300-180 Ma Karoo basin burial based on AFT dates >350 Ma that preclude greater heating (Gallagher et al., 1998, Fig. 2a), and 2) cooling between 90-60°C from 150-100 Ma based on central craton AHe data (Beucher et al., 2013, Fig. 2a). Southeastern craton constraints include allowing 1) reheating up to 180°C during Karoo basin burial based on THe dates up to 1.1 Ga that were not fully reset
during Karoo time, 2) cooling beneath 110°C between 150-100 Ma based on regional AFT data (Gallagher et al., 1998, Fig 2a) and 3) cooling beneath 90°C at 100 Ma based on AHe dates of that age from the same sample (Flowers and Schoene, 2010). Finally both models end with present-day surface temperature conditions. Table S1 is a model input table following the approach of Flowers et al. (2015) that reports additional details of how the data were treated in the tT simulation.

Figure 6 shows the inverse thermal history results for the central craton (Fig 6b,) and southeastern craton (Fig 6c). In all inverse models “acceptable” fits are highlighted in green and “good” fits in pink, the best-fit path of each model is bolded in black, and imposed tT constraints are marked by grey boxes. We encountered difficulty fitting an inverse model to the highest eU grain from the central craton. The initial model resulted in only a few acceptable fits and no good fits when the highest eU grain (724 ppm) was included as an input parameter. The current zircon radiation damage and annealing model, which uses fission track damage and annealing kinetics, has known calibration issues and has been shown to underestimate measured high damage data (Johnson et al., 2017, Anderson et al., 2017, Willet et al., 2017, Powell et al., 2016). We therefore focus our modeling efforts on grains with <700 ppm eU to avoid this known complication.

Two key results emerge from the inverse thermal modeling of the central and southeastern regions of the Kaapvaal craton shown in figure 6. First, a variety of tT paths honor the ZHe data, geologic information, and previous thermochronology from both the high elevation and low elevation regions of the craton, thus demonstrating the non-uniqueness of the thermal history as constrained by ZHe data. This is particularly true for the 3,000 – 400 Ma tT history (Fig. 6b,c). Second, the model can reproduce measured data
with newly identified reheating at 1.2-1.0 Ga as required by THe data of that age, and variable levels of Karoo burial. To further investigate the effect of variable Karoo burial on the resulting date-eU correlations from the two regions, we conduct a series of simple forward models.

5.3.2. Forward modeling

We next used forward modeling to assess if variable Karoo burial can explain the on- and off-plateau variability in the measured ZHe date-eU patterns, while honoring geologic constraints and holding the 3,000-300 Ma thermal history of the craton constant. The forward model approach requires the input of a particular tT path, grain size and eU concentration information to generate a date-eU curve for comparison against measured date-eU results. We use the mean grain size of each sample suite, and a range of eU from 0-1000 ppm. The models use a simplified input tT path based on the geologic and thermochronologic constraints imposed for inverse modeling in section 5.3.1. For each model we hold the 3000 – 300 Ma thermal history constant (Fig. 7a) based on like THe date-eU patterns (Fig. 3a), which suggest a similar early thermal history between the two regions. For model 1 we impose linear cooling between 3000 – 1350 Ma and 1000 – 300 Ma (Fig. 7a, solid black line), but impose maximum Karoo burial temperatures of 85°C and 160°C for on- vs. off-plateau models, respectively, (Fig 7a, blue and red lines respectively), consistent with AFT results (Gallagher et al., 1998).

Figure 7b plots forward model date-eU curves for input tT paths (Fig. 7a) with measured central on-plateau and southeastern off-plateau data for direct comparison. Model 1 (solid blue, and solid red line) can reproduce measured data to first order. We next
Figure 7. HeFTy forward thermal history modeling. A) Forward model input tT paths. B) ZHe date-eU plot for central on-plateau (blue triangles) and southeastern off-plateau (red triangles) samples. Blue lines mark forward model results for the central craton and red lines show forward model results for southeastern off-plateau. Average grain size of each sample is used as the model input.
vary the 3000-1400 Ma (Fig. 7a – Model 2 dotted line) and 1000-300 Ma (Fig. 7a – Model 3 dashed line) tT history to test if variable older thermal histories can also reproduce measured data patterns. Inverse modeling results from 4.3.1. and present geologic and thermochronologic constraints do not allow for a more detailed prediction of the pre-Karoo cooling paths. Forward models 2 and 3 are also able to satisfy the measured results to first order. (Fig. 7b, blue and red dotted and dashed lines).

Regardless of variable 3000-300 Ma tT paths that are only partially constrained by independent data, the variable ZHe date-eU patterns from on- and off- the southern African Plateau can be explained by differences in Karoo burial alone, which lends more confidence to our ability to robustly interpret the 1.2-1.0 Ga signal in the THe data. Increased burial and subsequent higher burial temperatures in the eastern craton (currently seaward of the southern African plateau) can account for young ZHe dates (<170 Ma) fully reset by Karoo burial. Less burial in the distinctly on-plateau central craton can account for older ZHe dates (>300 Ma) and a strong negative date-eU correlation, consistent with inverse modeling work from the eastern off-plateau Phalaborwa carbonatite (Baughman and Flowers, 2018).

5.4. Implications for substantial burial of the Kaapvaal craton during Namaqua-Natal orogenesis

A key result of our work is that the oldest THe and ZHe dates require full resetting at ~1.1 Ga, thus documenting a major, previously unidentified, reheating event across the craton. Mesoproterozoic, 1.4-1.3 Ga preserved volcanics indicate the craton basement was near the surface at that time, and must have been reheated above minimum 150°C between
1.3 and 1.1 Ga to reset the dates of that age constrained by a diffusion experiment and modern 150°C $T_c$ estimate of low eU and low damage Kaapvaal titanite (Fig. 5; Baughman et al., 2017).

The ~1.1 Ga timing coincides with activity in the major, 1.2-1.0 Ga, ~1,500 km-long, Namaqua-Natal orogenic belt to the south (present-day coordinates; Fig 1b, e.g., Jacobs et al., 2008). The eastern Natal section of the Mesoproterozoic volcanic arc is composed entirely of 1.25-1.03 Ga juvenile crust, the result of north-vergent subduction (Jacobs, 1993). The orogenic belt reached peak, high-temperature granulite facies metamorphism of ~800°C at 1.05 Ga (McCourt et al., 2006; Eglington, 2006) with subsequent cooling to <350°C by 0.95 Ga (Jacobs et al., 1997), signaling rapid exhumation (>10 km, inferred from >400°C cooling) of the region at that time. The craton was additionally affected by widespread Umkondo LIP emplacement at 1116-1106 Ma (Hanson et al., 2006), which may have elevated the geotherm. We therefore propose that craton-wide burial by sediments shed from the Namaqua-Natal orogenic belt caused reheating of the Kaapvaal craton basement to >150°C at this time. A 30°C/km geothermal gradient for the proposed Namaqua-Natal basin, consistent with estimates from the Paleoproterozoic Witwaterand basin overlying the Kaapvaal craton (Frimmel et al., 1997), along with 20°C surface temperatures, would require ~4.5 km of sediment burial to reset the dates at 1.1 Ga. That burial estimate is reduced to 3 km if the geothermal gradient was raised to 40°C/km during Umkondo LIP emplacement. The hypothesized Namaqua-Natal basin has been completely eroded from the rock record.

The inferred Proterozoic cratonic burial phase by detritus derived from the bounding Namaqua-Natal orogeny is similar to ~300-183 Ma Karoo Basin deposition
associated with the similarly located, north-vergent Paleozoic Cape orogen (Fig. 2b, e.g., Catuneanu, 2004). The Karoo Basin developed in a massive retroarc foreland system, has been partially eroded away, but is still partly preserved today (Fig. 1; e.g., Catuneanu et al., 2005). Our data points toward an analogous, but more substantial, depositional episode that buried the craton during and following Namaqua-Natal orogenesis.

Thermochronometric studies within the Canadian Shield and Australia reveal Phanerozoic burial episodes that have been fully removed from the rock record (e.g., Gleadow et al., 2002; Kohn et al., 2002, 2005; Flowers, 2009; Flowers et al., 2012; Ault et al., 2013), and we suggest that the same phenomena occurred during the Proterozoic in southern Africa.

6. CONCLUSIONS

The and ZHe dates help constrain burial and erosion patterns across the Kaapvaal craton over ~1100 Myr. Low eU titanite yield He dates of ~1000-1200 Ma. We estimate the closure temperatures of these titanite at that time to be ≥150°C based on diffusion experiment results for the same eastern craton samples (Baughman et al., 2017). The THe dates and their estimated closure temperatures, in conjunction with 1.4 Ga preserved volcanics in the central craton (e.g., Hanson et al., 2006) that require the basement be at the surface by that time, indicate reheating to ≥150°C at 1.1 Ga. Our preferred mechanism for reheating is widespread ~4 km sedimentary basin burial sourced from the rapidly exhumed (>10km) 1.2-1.0 Ga Namaqua-Natal orogenic belt on the craton margin (e.g., Eglington, 2006). Higher geotherms may have been enhanced by Umkondo LIP magmatism (e.g., Hanson et al., 2004), which would reduce the burial magnitudes required to explain the data. This inferred Namaqua-Natal burial has similarities with the 300-183 Ma Karoo
Supergroup deposited in the massive retroarc foreland system developed during the Cape orogeny (Catuneanu, 2004; Catuneanu et al., 2005). ZHe date-eU patterns differ spatially from on- and off- the southern African plateau. For the same eU, on-plateau zircon yield older dates than off-plateau zircon. This pattern that can be explained by greater Karoo burial off- than on-plateau. This interpretation is supported by old on-plateau AFT dates (>350 Ma; Gallagher et al., 1998) from the central craton that were not fully reset by Karoo burial, compared to younger off-plateau AFT results (~150-100 Ma; Gallagher et al., 1998; Brown et al., 2002). TH e and ZHe data from cratonic regions can thus provide thermal history information about both different and overlapping portions of the tT path. Together the thermochronometers have potential to access temperatures from ~220°C to the near-surface, and can help decipher significant gaps in thermal knowledge for these ancient settings.

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Kohn, B.P., Gleadow, A.J.W., Brown, R.W., Gallagher, K., O'Sullivan, P.B., Foster, D.A. (2010) Shaping the Australian crust over the last 300 million years: Insights from...


Figure S1. A) The date-eU plot and B) ZHe date-eU plot for all Kaapvaal craton samples, color-coded by region and distinguished by sample. Plots have different eU axis scales, to show relative data distribution. The 2 sigma analytical uncertainty of the dates are encompassed by the symbols. A conservative 20% eU uncertainty is plotted for titanite and 15% for zircon. Pp=previously published in Baughman et al. (2017). All samples are from Archean rocks unless noted in the legend.
Figure S2. The date versus grain size for each region A) central on-plateau, B) southeastern on-plateau, C) southeastern off-plateau, and D) eastern off-plateau. Individual samples identified by symbol shape and individual analyses color-coded by eU.
Figure S3. ZHe date versus grain size for each region A) central on-plateau, B) southeastern on-plateau, C) southeastern off-plateau, and D) eastern off-plateau. Individual samples identified by symbol shape and individual analyses color-coded by eU.
Figure S5. HeFTy forward model results for A) model 1, B) model 2, and C) model 3 plotted against measured ZHe dates. Solid lines yield model output for average grain size and envelopes encompass grain size standard deviation.
Figure S4. ZHe-date-eU plot for measured central on-plateau and southeastern off-plateau dates (blue and red triangles, respectively) and binned results (black triangles) used for inverse model data inputs.
1. Thermochronologic data

**Samples and data* used in simulations**

| Kaapvaal central craton on-plateau | ZHe data, 2 samples: WKC-00-37, RK3 |
| Kaapvaal southeastern craton off-plateau | ZHe data, 1 sample: AGC01-4 |

Data necessary for modeling the above samples are reported in Table 1.

**Data treatment, uncertainties, and other relevant constraints**

- **Treatment:** ZHe data for WKC-00-37 and RK3 binned based on eU values (<200 ppm, 200-250 ppm, 251-300 ppm, 301-375 pm, 376-500 ppm, 501-700), with the mean of each bin modeled as a separate constraint. Central ZHe grain with 724 ppm eU was modeled for Fig S4 and not included as an input for Fig 6b.
- **He dates (Ma):** Mean uncorrected He date of each eU bin. Uncorrected date corrected for a-ejection in HeFTy using Ketcham et al. (2011).
- **Error (Ma) applied in modeling:** 1s standard deviation or 15% (whichever was larger) of mean raw date for each eU bin.
- **r (um):** Mean equivalent spherical radius of each eU bin.
- **eU (ppm):** Mean eU of each eU bin.

2. Additional geologic information

**Kaapvaal craton**

<table>
<thead>
<tr>
<th>Assumption</th>
<th>Explanation and data source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling &lt;300 °C at ~3000 Ma</td>
<td>Based on regional Kaapvaal craton Ar-Ar dates (Layer et al., 1992), and basement rock crystalization age of 3000-3600 Ma (e.g., Poujol et al., 2003).</td>
</tr>
<tr>
<td>40-20 °C between 1400-1200 Ma</td>
<td>Preserved volcanics of this age in central craton shows basement exposed at surface (Hanson et al., 2006).</td>
</tr>
<tr>
<td>250-180 °C between 1200-100 Ma</td>
<td>Age of oldest Th results in this study. Timing coincides with Namaqua-Natal orogenesis (e.g., Jacobs et al., 2008).</td>
</tr>
<tr>
<td>40-20 °C at ~300 Ma</td>
<td>Unconformity between oldest Karoo supergroup units and Archean basement, implies basement is within several km of surface at start of Karoo Basin burial (e.g., Catuneanu et al., 2005).</td>
</tr>
<tr>
<td>110-20 °C at 300-150 Ma</td>
<td>Timing of Karoo Basin burial 300-183 Ma (e.g., Catuneanu et al., 2005). Box allows for reheating, but only up to 110 C as AFT dates were not reset in the central craton by Karoo burial</td>
</tr>
<tr>
<td>110-60 °C at 150-100 Ma</td>
<td>AHe date in central craton of that age.</td>
</tr>
<tr>
<td>180-20 °C at 300-150 Ma</td>
<td>Timing of Karoo Basin burial 300-183 Ma (e.g., Catuneanu et al., 2005). Box allows for reheating, but only up to 180 C as all Th dates were not reset by Karoo burial.</td>
</tr>
<tr>
<td>120-20 °C at 180-120 Ma</td>
<td>Nearby AFT data indicate cooling to &lt;120 °C by ~150 Ma (Gallagher et al., 1998).</td>
</tr>
<tr>
<td>110-60 °C at ~100 Ma</td>
<td>AGC01-4 AHe date (Flowers and Schoene, 2010)</td>
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<tr>
<td>20-0 °C at present</td>
<td>Currently at surface.</td>
</tr>
</tbody>
</table>

3. System- and model-specific parameters

- **He kinetic model:** ZRDAAM (Guenthner et al., 2013) for ZHe data.
- **Statistical fitting criteria:** “Good” fits are defined as those for which the mean of the GOF statistics assessed is 0.5, and the minimum is 1/(N+1), where N is the number of statistics used (Ketcham et al., 2009). Those thermal histories that fit all data a
- **Modeling code:** HeFTy v1.9.1
- **Number of tt paths attempted:** 10,000
- **tt path characteristics:** Episodic, 18 linear segment

---

**Table S1.** Thermal history input table modeled after Flowers et al. [2015] used for Figure 6.
CUMULATIVE REFERENCES


Dodson, M. H. (1973) Closure temperatures in cooling geological and petrological systems. Contributions to Mineralogy and Petrology 40, 259-274.


Renne, P. R., Tobisch, O. T., and Saleeby, J. B. (1993) Thermochronologic record of pluton emplacement, deformation, and exhumation at Courtright shear zone, central Sierra Nevada, California. Geology 21, 331-334


APPENDIX 1

Coupled (U-Th)/He and Raman spectroscopy regional elevation study of the Ancient Gneiss Complex, Kaapvaal craton

A1.1. Introduction and Motivation

Radiation damage (often measured as alpha dose) has a strong influence on He retentivity and thus the temperature sensitivity or closure temperature of zircon and titanite (U-Th)/He thermochronology (Guenthner et al., 2013; Chapter 2). Alpha dose can be calculated based on the U and Th concentration of a sample and assuming a time since damage has accumulated (e.g., Nasdala, 2005). Alpha damage accumulation and annealing kinetics are not well understood by the community, therefore, even with a strong understanding of the thermal history of a region it is difficult to assess overall damage levels (Johnson et al., 2017; Anderson et al., 2017; Mackintosh et al., 2017; Powell et al., 2016). Luckily, Raman spectroscopy can be used to independently and quantitatively assess radiation damage accumulation. We put this tool to good use in Chapter 2, Influence of radiation damage on titanite He kinetics, to qualitatively characterize variable radiation damage accumulation for four Kaapvaal craton titanite samples.

The technique is more quantitative for zircon (because there are fewer Raman peaks to characterize!) and can be additionally used to assess whether or not damage annealing has occurred during the sample’s history (e.g., Nasdala et al., 2001; 2005; Palenik et al., 2003). By coupling (U-Th)/He thermochronology and Raman Spectroscopy we can
more robustly interpret thermal histories, assess the internal consistency between these complimentary datasets, and identify geologic implications.

We applied these tools to the Ancient Gneiss Complex (AGC) in the eastern Kaapvaal craton on two samples straddling the southern African Plateau at elevations of 650 m and 1493 m to develop this coupled technique and decipher the Paleozoic and Mesozoic burial and unroofing history on and off the plateau.

**A1.2. Using Raman Spectroscopy**

Raman spectroscopy, a non-invasive technique, has been used, especially in zircon (eg., Nasdala et al. 2001, Palenik et al., 2003, Guenthner et al., 2013), to characterize the amount of radiation damage experienced by the mineral. In Raman spectrometers a laser irradiates a small area on a sample to produce two types of scattering: elastic, and non-elastic scattering (Fig A1.1). The elastic scattering of the photons (Rayleigh scattering) causes the emission of photons at the same wavelength after they were excited to a virtual state. This scattering is filtered out and is much more intense than Raman scattering. Raman scattering, unlike Rayleigh scattering, experiences a shift in frequency since it is a type of inelastic scattering. There are two types of Raman scattering: Stokes and anti-Stokes. In Stokes scattering the frequency \( \nu_0 - \nu \) is shifted downwards as a result of the molecule moving from a lower vibrational level to a higher one. In anti-Stokes scattering produces mirror spectra of Stokes scattering but with a lower intensity because the shift is from higher vibrational levels to lower ones and thus is usually not shown (Fig A1.1). The resulting Raman spectra is controlled by the chemistry and bond strength of the material.
Figure A1.1. Figure taken from Ferraro and Nakamoto (1994) illustrating Stokes, Rayleigh, and anti-Stokes scattering. Rayleigh scattering at 0 cm$^{-1}$ is the most intense.
Raman spectroscopy can be specifically used to assess 1) alpha dose and 2) the extent of annealing in zircon based on the position and shape of the major $V_2SiO_3$ peak (Fig. A1.2a), zircon peak at $\sim 1000$ cm$^{-1}$ Raman shift). The full-width at half the maximum (FWHM) of the main, isolated peak has been directly correlated to alpha dose, with a tighter peak consistent with low damage and a broad peak consistent with high damage and possible metimictization (Fig. A1.2a,b). With increasing damage the major peak also shifts to a lower value due to changing bond strength (Fig. A1.2a, e.g., Nasdala et al., 2001, Palenik et al., 2003). If a grain has experienced no damage annealing then shift and FWHM should vary linearly as shown in figure A1.2c. However, if the sample is reheated at any stage in its thermal history once damage has begun accumulating the shift will recover and move to a higher value, but the FWHM will not. Therefore samples that plot above the linear shift-FWHM relationship indicate some level of annealing, the further off of the line the greater level of annealing the grain has experienced (Fig. A1.2c, Nasdala et al., 2002).

A1.3. Setting, samples, and methods

I acquired ZHe data and Raman spectroscopy for 2 samples from the Archean Ancient Gneiss Complex (AGC), part of the Kaapvaal craton in South Africa and Swaziland. AHe data was originally published for these samples by Flowers and Schoene (2010), and THe and ZHe results are presented in Chapter 2 and Chapter 4 of this dissertation respectively. The two samples, EKC02-40 and AGC01-4 are from on- and off- of the southern African Plateau (Fig. A1.3). A high elevation, low relief plateau residing at an average elevation $>1000$m surrounded by the high relief Great Escarpment. The samples span $\sim 850$ m of elevation, are both from $>3.0$ Ga gneiss, and were once buried under the
Figure A1.2. A) From Nasdala et al. (2005), showing qualitative change of Raman spectra based on damage accumulation. Top spectrum is least damaged, bottom spectrum is most damaged. There are obvious changes of the $\nu_3$(SiO$_4$) band with increasing damage including, x-axis – band shift, and y-axis – band broadening. B) Curve from Palenik et al. (2003), showing the relationship between measured $\nu_3$(SiO$_4$) peak FWHM and associated alpha dose. C) Relationship presented by Nasdala et al. (2002) showing linear relationship between the shift and width of the FWHM of the Raman $\nu_3$(SiO$_4$) peak for zircon. Non-linear behavior indicates annealing.
Phanerozoic Karoo basin, still locally preserved to the east and south of the AGC. Our goals are to assess thermal history differences spatially correlated with on- and off-plateau using coupled He dating and Raman spectroscopy.

Zircon grains were hand selected based on color, quality, and size for grain mount placement. Epoxy was poured over the grains in a ring-shaped mold and polished to expose a smooth surface of each grain. Zircon Raman spectra were acquired on a Horiba LabRAM HR Evolution Raman microscope-spectrometer using the 532 nm laser at room temperature from the 100 cm\(^{-1}\)-1700 cm\(^{-1}\) range of bandwidths for each of 10 grains per sample. Point spectra, with a minimum of 3 point analyses per grain in a lateral transect were acquired for each sample. Once all of the spectra were obtained several corrections were performed including: 1) a baseline correction to account for any photoluminescence that may have affected the spectra, 2) normalizing all of the spectra to the highest peak because Raman intensity depends on many factors including the intensity of the laser beam and the frequency of the light and finally 3) the location, width, and amplitude of the prominent V\(_3\)SiO\(_4\) peak was measured using Horiba’s LabSpec 6 peak fitting program.

**A1.4. (U-Th)/He results**

Figure A1.4 shows ZHe, AHe, and THe results for samples EKC02-40 and AGC01-4. ZHe dates for high elevation sample EKC02-40 are older (~350-200 Ma) than AGC01-4 (174-102 Ma) and are negatively correlated with eU (~300-500 ppm). AGC01-4 ZHe results show only a slight negative date-eU correlation defined by on low eU analysis (174 Ma, 107 ppm). The five remaining AGC01-4 analyses (eU of 289-573 ppm) yield a reproducible date of 117.5 ± 15.5. ZHe results are additionally published in Chapter 4 of this dissertation.
Figure A1.3. A) Simplified map of the Kaapvaal craton, southern Africa showing the location of Ancient Gneiss samples AGC01-4 and EKC02-40. B) Topographic transect showing the ~850 m elevation difference between samples across the Great Escarpment from Flowers and Schoene (2010).
AHe published by Flowers and Schoene (2010) for the two samples are indistinguishable at 100 ± 7 Ma for EKC02-1 and 101 ± 8 Ma for AGC01-4.

The dates of 889-135 Ma overlap between the two samples and are negatively correlated with their 32-200 ppm span of eU. The dates are additionally published in Chapter 2 of this dissertation.

A1.5. Raman spectroscopy results and inferences

A subset of Raman spectra from EKC02-40 and AGC01-4 are presented in Figure A1.5. Both samples contain grains which produce spectra with tight peaks centered on the V₃SiO₄ peak (Fig. A1.5a), which suggests low radiation damage accumulation, and grains which produce Raman spectra with highly shifted and diffuse peaks that are (or nearly are) unrecognizable (Fig. A1.5b), which suggests significant damage accumulation. Finally, transects were taken across individual grains to assess spatial variability in Raman spectra (Fig. A1.5c,d). AGC01-4 grain 9 shows slight differences in spectra between the core and rim. The rim produces a much more intense and tighter V₃SiO₄ peak compared to the core, suggesting lower radiation damage accumulation on the rim compared to core. EKC02-40 grain 2 reveals only small, broad V₃SiO₄ peaks across the grain and similar overall spectra results suggesting high damage and little damage variability across the grain.

Figure A1.6 shows the shift vs FWHM of the major V₃SiO₄ peak for several individual zircon from samples EKC02-40 and AGC01-4. The two samples occupy equivalent shift-FWHM space. Some samples plot on the line representing no annealing developed by Palenik et al. (2003), and several analyses plot above the line suggesting partial annealing.
Figure A1.4. Date-eU plot for Ancient Gneiss Complex samples EKC02-40 and AGC01-4. AHe results are published in Flowers and Schone (2010). THe results are published in Chapter 2 of this dissertation. ZHe dates are published in Chapter 4 of this dissertation.
Figure A1.5. Individual Raman point spectra are presented for AGC samples. A) Relative low damage results, B) relatively high damage results, C and D) transect results for AGC01-4 and EKC02-40 respectively.
I use the FWHM of the V$_3$SiO$_4$ peak for spectra that do not show evidence of annealing to estimate alpha dose. Spectra that shows signs of annealing is not robust because the FWHM is slow to recover and alpha dose may be overestimated. The FWHM of unannealed samples fall between 12-20 cm$^{-1}$, which corresponds to an alpha dose of 80-180 (alpha x 10$^{16}$)/g (Fig. A1.7). When plotted on the Tc vs alpha dose plot for zircon (Guenthner et al., 2013), discussed in length in Chapter 2, AGC zircons fall near the zircon radiation damage threshold at which point He retentivity decreases (Fig. A1.8). Alpha dose can also be calculated using parent U and Th concentrations and assigning a damage accumulation time. If min and max ZHe dates are used to bracket damage accumulation time for samples AGC01-4 and EKC02-40, then alpha dose estimates fall between 9-50 (alpha x 10$^{16}$)/g, before the damage percolation threshold (A1.8a). If recorded THe dates are used, then alpha dose estimates are higher and fall between 50-400 (alpha x 10$^{16}$)/g, at and past the damage percolation threshold at which point He retentivity decreases (Fig. A1.8b).

A1.6. Preliminary implications

1. THe dates record an older and hotter part of the AGC thermal history compared to zircon

2. Both on- and off-plateau samples record rapid exhumation through the AHe partial retention zone at ~100 Ma, consistent with uplift and unroofing associated with southern African Plateau uplift.

3. Different ZHe data patterns between samples indicate variable post 350 Ma burial and exhumation history. This pattern is consistent with increased exhumation off-
Figure A1.6. Shift versus FWHM of the $v_3\text{SiO}_4$ Raman peak for individual point spectra from Ancient Gneiss Complex samples, plotted on the linear relationship defined by Nasdala et al., 2002.
Figure A1.7. $v_3\text{SiO}_4$ FWHM versus alpha dose curve defined by Palenik et al. (2003). AGC unannealed sample results fall between the arrows.
Figure A1.8. Plots of $T_c$ versus alpha dose for zircon from Guenthner et al. (2013). Orange bands correspond to alpha dose estimates calculated using ZHe date accumulation time (A) and THe date accumulation time (B). Green band indicates Raman alpha dose estimate.
plateau and less burial on-plateau. A similar pattern was used to describe variable ZHe patterns in Chapter 4.

4. Both samples yield similar alpha dose estimates based on FWHM measurements and occupy similar shift-FWHM space. Both samples show evidence for partial annealing.

5. The Raman results suggest a similar long-term thermal history of damage accumulation and partial annealing via reheating between samples.

6. FWHM calculations can be used to assess modern accumulated radiation damage. Ancient Gneiss Complex zircon record alpha doses of 80-180, coinciding with the zircon damage percolation threshold.

7. Using ZHe dates as the damage accumulation time in alpha dose estimates underestimates accumulated damage. Several zircon grains from sample EKC02-40 have clearly surpassed the damage percolation threshold as ZHe dates are negatively correlated with eU. THe dates provide a more reasonable estimate of alpha dose as they predict more accumulated damage compared to zircon, past the damage percolation threshold at which point He diffusivity increases.

8. I interpret a similar Proterozoic history to explain the equivalent levels of damage accumulation, annealing, and similar THe date-eU patterns between samples.

9. I interpret different post Karoo thermal histories for the two regions including increased Mesozoic exhumation off-plateau associated with uplift of the southern African Plateau to explain variable in the ZHe date-eU patterns.
A1.7. References


APPENDIX 2

Titanite (U-Th)/He data from off the Kaapvaal craton, southern Africa

A2.1. Motivation

Titanite (U-Th)/He (THe) data were collected from Proterozoic and Phanerozoic mobile belts surrounding the Kaapvaal craton to understand the post-accretionary history of these regions and assess the relationships between on and off craton unroofing. The eventual goal is to link unroofing patterns with known tectonic, geodynamic, and magmatic events in these regions. THe is particularly useful because it accesses a deeper timeframe, due to its mid-temperature sensitivity, compared to apatite (U-Th)/He dating and other low temperature thermochronometers, which are readily reset by minimal burial. THe dating can be used to assess exhumation during a period for which there are major time and temperature gaps in current datasets. Zircon (U-Th)/He (ZHe) data may be collected in the future for the same and nearby samples, using the coupled THe-ZHe approach applied in Chapter 4.

A2.2. Samples

Titanite and zircon separates were provided by the South African Council for Geosciences. Figure A2.1 and table A2.1 provide sample location and information. THe data were collected specifically within the Orange River Basin, Cape Fold Belt, and in western Namibia (Fig. A2.1).
Figure A2.1. A) Simplified geologic map of southern Africa, showing sample locations. I have preliminary THe data for all samples denoted as circles (titanite only) and squares (titanite and zircon bearing). B) Simplified terrane map of southern Africa. C) Topographic map of southern Africa.
A2.3. Preliminary results and implications

Single-grain fragment THe data are reported in Table A2.1. Figure A2.2 is a plot of THe date versus eU for a) Orange river samples, b) Cape Fold Belt samples, and c) western Namibia samples. The uncertainty of each date is reported at 2$$\sigma$$, includes propagated U, Th, Sm and He analytical error, and is smaller than the symbols in Figure A2.2.

A2.3.1. Orange River

The oldest THe dates within the Orange River basin are from the near craton boundary sample, FS1890, and cluster between ~900-1000 Ma. The remaining samples yield dates between 700-100 Ma, and show a limited negative correlation with eU. Data patterns are variable between samples (Fig A2.2a).

The dates of 900-1000 Ma match the on-craton He data trend observed in Chapter 4 of this dissertation. The ~1.0 Ga dates from that study are interpreted to record reheating and THe date resetting across the craton at that time, possibly the result of >4km of burial associated with Namaqua-Natal orogenesis.

The negative THe date-eU patterns of off-craton, Orange River basin samples require slow cool and/or partial resetting during one or more post 700 Ma reheating event(s). Samples may have been affected by thermal resetting associated with nearby Pan-African orogenesis (Fig A2.1a; 700-500 Ma) and are known to be reheated during Paleozoic-Mesozoic Karoo burial following Cape orogenesis. The youngest THe dates of ~100 Ma at the highest eU (>200 ppm) were fully reset by Karoo burial and likely record known Mesozoic exhumation previously constrained by AFT and AHe dating and linked to southern African Plateau uplift (Brown et al., 2002; Tinker et al., 2008; Flowers and Schoene et al., 2010; Stanley et al., 2013).
A2.3.2. Cape Fold Belt

The date-eU patterns are variable between the 3 samples. Western most sample VG1 yields a negative date-eU correlation of 450-330 Ma over an eU span of 120-170 ppm. These dates are equal to and older than the timing of Cape supergroup deposition (Fig. A2.2b). Original source rock information of samples is unknown but may be sedimentary. Therefore, titanite may include inherited He that was not fully degassed by later Cape orogenesis. This is consistent with Ar-Ar muscovite dates (closure temperature ~350°C) of similar age interpreted as a detrital signal (Hansma et al., 2016).

Sample HPS3 records an average date of 208 ± 20 Ma and HPS4 records an average date of 152 ± 5 Ma over a wide eU span of 70-330. Both post-date Cape Orogenesis dated at ~ 300-230 Ma (Hansma et al., 2016; Hälbich et al., 1983; Gresse and Theron, 1992) and likely record subsequent exhumation and cooling. 150 Ma dates are slightly older than AFT dates from this region which record rapid exhumation between 140-120 Ma (Tinker et al., 2008).

A2.3.3. Western Namibia

Sample RM150 records scattered dates of 415-95 Ma that are potentially correlated with their eU span of 50-350 ppm (Fig. A2.2c). A negative date-eU pattern is indicative of radiation damage decreasing the He retentivity of titanite (Chapter 2). More data is required to flesh out the observed He data pattern and meaningfully interpret results.
Table A2.1. (U-Th)/He data

<table>
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<th>Cape Fold Belt</th>
<th>Western Namibia</th>
</tr>
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</tr>
<tr>
<td>Sm</td>
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<tr>
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<td>2.109</td>
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</tr>
</tbody>
</table>

Sample notes:
- U-Th: uranium-thorium age
- He: helium age
- Th/U: thorium-to-uranium ratio
- 2o: error on age

Notes:
- Morphology used for volume and concentration estimates: rec-rectangular prism
- Mean length measurement
- Mean width measurement
- Equivalent spherical radius
- ND-No data
- eU: effective thorium concentration, weights U and Th for their alpha productivity, computed as [U] * 1.096 * [Th]
Figure A2.2. $THe$ versus date-eU plot for A) Orange River basin separates, B) Cape Fold Belt separates, and C) western Namibia separates. eU uncertainties are 20%. Date uncertainties are plotted at 2$\sigma$, and include uncertainties on $U$, Th, Sm, and He measurements. Sample color and shape correspond to Figure A2.1a.
A2.4. References


APPENDIX 3

Additional samples collected

A3.1. Introduction

I collected 50 rock samples during 2 field seasons (2014 and 2016) within South Africa and Swaziland. Sample location are presented in figure A3.1. The majority of samples were collected from outcrop, some were taken from the Cape Town University “Mantle Room”, and several titanite and zircon separates were acquired from the South African Council for Geosciences (those are not included in this section, but were used in Chapter 2, Chapter 4, and Appendix B). Figure A3.1a highlights 4 different major sampling locations including a) samples from the Phalaborwa carbonatite complex with data published in Chapter 3 of this dissertation, b) samples from the Ancient Gneiss Complex, several of which were used in chapter 4 and Appendix A of this dissertation, c) younger 2.0, 1.4, and 1.0 Ga aged samples from the Bushveld complex or that intrude the Bushveld complex, most of which have not been analyzed, and d) Limpopo region samples, most of which have not been analyzed. The following section outlines several additional project ideas that correspond to these sample locations and are not addressed earlier in this dissertation.
Figure A3.1. A) Simplified geologic map of southern Africa, showing locations of all samples collected during the 2014 and 2016 field seasons. Boxes group samples based on location and purpose, a – Phalaborwa carbonatite complex, b – Ancient Gneiss complex, c – Proterozoic Bushveld complex and other alkaline complex and kimberlite samples, and d – Limpopo region. B) Topographic map of southern Africa, showing same distribution of samples. Box covers area shown in Fig. A3.1c. C) Zoomed in topographic map of Limpopo region of southern Africa, which denotes the Kaapvaal craton and Limpopo Belt. Samples locations differ from Fig. A3.1a,b. Samples for which I acquired Th and Jess Stanley previously acquired AHe data are shown, in addition to locations for which we have apatite separates, rock samples and Melinda Fault samples.
A3.2. Purpose of sample collection

A.3.2.1. Mid-temperature THe and ZHe thermochronometric dating on younger, 2.0, 1.4, and 1.0 Ga samples

Samples that postdate Archean basement rock of the Kaapvaal craton (Fig. A3.1a – box c) were collected with the intended purpose of isolating the Proterozoic thermal history evolution of the Kaapvaal craton by removing any older integrated Archean time-temperature signal. The younger igneous complexes provide additional geologic surface constraints compared to the Archean (>3.0 Ga) basement rock. Several collected samples are kimberlite pipes and contain xenoliths that can be used to a) assess the lithospheric column and sedimentary cover at the time of emplacement, and b) estimate amount of exhumation since eruption. Other samples have preserved volcanics indicating surface exposure at the time of emplacement. These samples may be useful in further assessing ~1.1 Ga Namaqua-Natal orogenic reheating across the craton, identified in chapters 3 and 4 of this dissertation, and later reburial or cooling events.

A.3.2.2. Erosion history of the Limpopo River drainage basin, South Africa, from apatite (U-Th)/He thermochronology

Most of the Kaapvaal craton drains into the dominant Orange River system to the west, where several low T thermochronometric constraints exist, however the Limpopo region is part of the eastward draining Limpopo River catchment. Recent studies within the Mozambique basin, fed by the Limpopo river, reveal significant Miocene sedimentation and the authors suggest Limpopo area erosion as the sediment source (Said et al., 2015). A Miocene thermochronologic exhumation signature has not been documented anywhere on the craton or within the ~2.6 Ga Limpopo mobile belt. Low-temperature apatite-He data
from transects along and across the Limpopo river will allow us to assess the timing and extent of recent Limpopo unroofing and compare to Orange River basin AHe and AFT datasets (Kounov et al., 2013; Kounov et al., 2009; Tinker et al., 2008, Stanley et al., 2013).

Apatite separates, AHe data collected by Jess Stanley, and rock sample locations are shown on Figure A3.1c. Additionally, preliminary THe data has been collected for 3 samples from the northern Kaapvaal craton (Fig. A3.2, Table A3.1). THe dates at low eU and low damage are 400 Ma and may signal Pan-African thermal resetting. This pattern is substantially different from the eastern, southeastern, and central craton THe date-eU patterns depicted in Chapter 4. The youngest THe dates from the Limpopo region are Cenozoic and additional AHe data may help constrain the thermal history responsible for younger dates.

A.3.2.3. Cretaceous Limpopo fault reactivation

The Kaapvaal and Zimbabwe cratons were sutured across the high-grade metamorphic Limpopo belt by 2.6 Ga (Kreissig et al., 2001) and were reactivated in the Paleoproterozoic as the region extended (e.g., Kamber et al., 1995). There is structural evidence (Dhansay et al., 2016) and AFT thermochronometric evidence (Belton and Raab, 2010) for Cretaceous reactivation of this much older Late Archean fault system within the northern Kaapvaal craton and Limpopo Belt. Collaborator Taufeeq Dhansay of the South African Council for Geosciences is interested in a combined thermochronology and structural geology project to assess general slip timing and magnitude. Preliminary AHe analyses were collected from two samples within the Melinda fault footwall (Fig. A3.1c; Fig. A3.3; Table A3.1). The near fault trace sample and sample from 30 km down the footwall block yield dispersed Cretaceous dates, with no discernable data pattern difference
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<th>Th (ppm)</th>
<th>Sm (ppm)</th>
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b) Morphology used for volume and concentration estimates. Where two morphologies noted, the average volume and concentration results were used. rec-rectangular prism, cap-capsule, hex-hexagonal prism with 2

c) mean length measurement

d) mean width measurement

e) equivalent spherical radius

f) ND-No data

g) εU - effective uranium concentration, weights U and Th for their alpha productivity, computed as [U] ** 0.235 * [Th]

h) All uncertainties conservatively assumed to be 20% for titanite and 15% for apatite.

i) Analytical uncertainty based on uncertainties in U, Th, and He measurements

j) δ18O is alpha-ecrion correction of Ketchum et al (2011) assuming a hexagonal prism geometry. NA- not applicable because analyzed grain is a fragment.

k) Only whole crystals are corrected for alpha ejection.

l) 2o Uncertainty based on U, Th and He measurements
Northern craton: off-plateau

Figure A3.2. The date vs. eU for northern craton (Limpopo region) samples labeled in Fig. A3.1c in green. The and ZHe date-eU information for other craton regions used in chapter 4 including central, eastern, and southeastern craton shown in grey. This additional data provided for pattern comparison between northern craton results and the rest of the Kaapvaal craton. eU uncertainties are 20%. Date uncertainties are plotted at 2σ, and include uncertainties on U, Th, Sm, and He measurements. Grey bands in (a) represent timing of geologic events in and surrounding the Kaapvaal craton.
Figure A3.3. Apatite (U-Th)/He date vs. eU plot for two samples from the Melinda fault footwall in the northern Kaapvaal craton.
between samples (Fig. A3.3). Additional samples were collected across known faults with the assistance of Taufeeq Dhansay (Fig. A3.1a,b).

**A3.3. References**


APPENDIX 4

Apatite (U-Th)/He thermochronology from the Cape Fold Belt, South Africa

A4.1. Introduction

The southern African Plateau is a major topographic feature with elevations of 1.0-1.5 km. It is surrounded by passive, extensional margins on three sides suggesting that collisional tectonic forces did not contribute to surface uplift (de Wit, 2007). Seismic tomography reveals chemically and thermally distinct material in the lower mantle below South Africa, leading some to suggest that this “African superplume” provides dynamic support of the region’s elevations (e.g., Nyblade and Robinson, 1994). The uplift history of the plateau continues to be debated, but robustly deciphering the timing of uplift is critical to assess processes responsible for observed elevation gain. Apatite fission track (AFT) and (U-Th)/He (AHe) thermochronometry indicate Cretaceous unroofing, suggesting a phase of Mesozoic elevation gain, that is temporally coincident with the emplacement of large igneous provinces and kimberlite pipes (e.g., Tinker et al., 2008; Flowers and Schoene, 2010; Stanley et al., 2015). AFT is sensitive to temperatures of 110-60°C (Fitzgerald and Gleadow, 1990), equating to exhumation through depths of 2-4 km, while AHe reveals cooling from 70-30°C or depths of 1-3 km (Farley, 2000; Flowers et al., 2009). I collected AHe data from the Cape Fold Belt for samples for which AFT data already exists (Tinker et al., 2008) with the goals of a) evaluating the consistency of AFT and AHe thermochronometry results using the most recent He diffusion kinetic model (Flowers et al., 2009), and b) deciphering the timing of near surface exhumation across the Great
Escarpe separating the high elevation, low relief southern African Plateau, and the low elevation coast.

In the past, some AFT and AHe datasets have been discrepant, especially in cratonic setting studies like that in the interior of southern Africa because small differences in the two systems are magnified due to the prolonged thermal histories of the samples (Flowers and Kelley, 2011). The most recent He diffusion kinetic model that takes into account the effect of radiation damage on He retentivity may help explain these previous inconsistencies, but this has not yet been comprehensively evaluated in a range of cratonic settings (Flowers and Kelley, 2011). Because vertical profile sampling via a borehole requires all samples to have undergone an internally consistent thermal history, acquiring and simulating AHe data and comparison with AFT results will allow me to assess the compatibility of the methods. Discrepancies would suggest that a variable other than those accounted for in the new He diffusion kinetic model (which includes temperature, radiation damage, grain size and U-Th zonation) must exist (Flowers et al., 2009). Fully understanding He diffusion kinetics is critical to our ability to interpret low temperature thermochronometry. AHe results can also be used to assess spatial variability and unroofing and uplift patterns across the escarpment.

**A4.2. Sample characterization**

Apatite separates were provided by Justine Tinker and others and have been previously analyzed for AFT thermochronology (Tinker et al., 2008). Twenty-five outcrop samples, mainly from the 300-183 Ma Karoo supergroup, were provided from a transect across the Great Escarpment within the Cape Fold Belt (Fig. A4.1) and AHe data were
Figure A4.1. Simplified geologic map of southwestern South Africa showing sample and borehole locations.
collected for 6 samples highlighted in figure A4.1. Samples were also provided for 3 bore holes, but no AHe data were collected.

**A4.3. Preliminary results and implications**

Preliminary results are provided in Table A4.1 and Figure A4.2 plots AHe date against eU (A) and grainsize (B). Samples are color coded and the average AFT date of each sample is shown as a solid line across eU values. AHe dates range from 130-60 Ma, covering the Cretaceous to Early Paleogene. These dates are overall consistent with Cretaceous exhumation identified by AFT results from the area (Tinker et al., 2008) and AHe and AFT studies across southern Africa (Brown et al., 2002; Tinker et al., 2008; Flowers and Schoene et al., 2010; Stanley et al., 2013). The data are dispersed within and between samples and do not yield any correlation with eU or grainsize (Fig. A4.2), suggesting something other than radiation damage and grainsize is responsible for the dispersion. More work is needed to characterize the apatite from this study and explain results.

AHe dates are younger than the AFT date for 3 of 4 samples (only including samples with multiple AHe analyses), consistent with AFT accessing a higher temperature and older portion of the thermal history compared to AHe dating.

There is no data pattern or obvious spatial variability between on- and off-platueau samples. More data is required to assess the pattern and timing of exhumation across the escarpment.

No bore hole data exists, but could be useful for reconstructing the thermal history of isolated regions and reconstructing the He partial retention zone during the Cretaceous.
Table A4.1. (U-Th)/He data

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<th>T (µm)</th>
<th>W (µm)</th>
<th>Rs (µm)</th>
<th>Mass (µm)</th>
<th>U (ppm)</th>
<th>Th (ppm)</th>
<th>Sm (ppm)</th>
<th>Ce (ppm)</th>
<th>He (nmol/g)</th>
<th>Th/U</th>
<th>Uncorrected date (Ma)</th>
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<th>AFT date (Ma)</th>
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1. A-particle
2. Mean length measurement
3. Mean width measurement
4. Equivalent spherical radius
5. U - effective uranium concentration, weights U and Th for their alpha productivity, computed as [U] * 0.235 / [Th]
6. U uncertainty conservatively assumed to be 15%
7. Double analytical uncertainty based on uncertainties in U, Th, and He measurements
8. Pt is alpha-ejection correction of Ketcham et al. (2011) assuming a hexagonal prism geometry.
9. Average AFT date from Tinker et al. (2008)
Figure A4.2. AHe date versus A) eU and B) grainsize given as the equivalent spherical radius (r). Samples are color coded and the average AFT date for each sample is denoted by the solid line or corresponding color. eU uncertainties are 215%. Date uncertainties are plotted at 2σ, and include uncertainties on U, Th, Sm, and He measurements.
A4.4 References


A5.1. Teaching philosophy

In my experience, and according to most geoscience education literature, successful teaching demands an active learning environment, flexibility, powerful student communication, and the fostering of critical thinking skills. I have had the benefit of teaching and mentoring in several capacities including, classroom lectures, labs, field courses, undergraduate theses, tutoring, and working directly with two NSF funded Research Experiences for Undergraduates (REUs) that support underrepresented groups in the geosciences. As a teacher, I feel it is my responsibility to instill a sense of understanding, curiosity, and social responsibility as students learn critical earth science concepts that they will take with them if not as geologists, then as engaged citizens, and science supporters and ambassadors. I’m an energetic and expressive teacher and am thankful that my geologic focus of tectonics, earth materials, and structural geology easily lends itself to hands-on activities, group learning, and relatable content to invoke a student’s sense of place.

A5.2 Mentoring and support of underrepresented groups

Teaching does not only happen in the classroom, nor as a professor is teaching geologic content the only job requirement. I have invested significant time during my graduate career working with underrepresented students and promoting visible diversity
in geoscience. My work with the NSF funded RESESS (for underrepresented students) and GeoLaunchpad (for community college students) programs permitted me the opportunity to teach not only geoscience skills and curricula but professional development material including professional, informal and academic science communication. I organized a weekend fieldtrip focused on Colorado geology and a daylong science communication symposium to expose undergraduate and graduate students to a diverse range of geoscience research and workforce employment opportunities, and science communication skill building.

**A5.3. Classroom and field teaching experience**

While at Univ. Colorado Boulder I acted as the Teaching Assistant to the Intro to Fieldwork class three times, the TA for Structural Geology once, the Head Tutor of the Geological Sciences Dept. Tutoring Room, and instructor of record for Introduction to Geology (~135 students). Following my undergraduate education at Colgate University, I was the sole TA of the university’s 18 person, 6-week long field camp. These experiences allowed me to hone my teaching skills and implement active learning strategies.

Through these teaching and outreach experiences I have created a significant amount of original education content, which I will present in the following subsections: Worksheets, assignments/activities, professional and student development, and day-long + activities.

**A5.4. Original material**

**A5.4.1. Worksheets:**
The worksheets were created for an Introduction to Geology course to highlight major themes and connections. While the information is not original, students appreciated the tailored note taking sheets and I observed a noticeable increase in understanding and retention of the topics covered.
Worksheet A5.1. The Rock Cycle

The Rock Cycle

Sedimentary Rock

- Weathering and Erosion
- Sedimentation, compaction and lithification

Metamorphic Rock

- Heat and Pressure

Igneous Rock

- Weathering and Erosion

Magma

- Melting
- Solidification

Sediment

- Weathering and Erosion

Basalt

Granite

Fossiliferous Sandstone

Gneiss

Marble

Granite

Sedimentary Rock

Metamorphic Rock

Igneous Rock

Magma

Sediment
## Igneous Rocks

### Crystalline Igneous Rocks

<table>
<thead>
<tr>
<th>Rock Texture</th>
<th>Felsic</th>
<th>Intermediate</th>
<th>Mafic</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Intrusive</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystal size?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cooling rate?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Where does it form?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Extrusive</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Chemical composition

- Silica content?
- Color?
- Melting/Crystallization Temp?
- Viscosity?
- Where does it form?

### Other Extrusive Igneous Rocks

- **Glassy:**
- **Pyroclastic:**
Which minerals crystallize out of a magma melt first?

Which minerals melt first when heat is added?

Which minerals lead to violent/explosive volcanic eruptions?

Which minerals will weather to clays?
## Worksheet A5.4. Sedimentary Rock Classification

<table>
<thead>
<tr>
<th>Grain size</th>
<th>Rock Type</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse</td>
<td>Clastic</td>
<td>Quartz</td>
</tr>
<tr>
<td>Medium</td>
<td>Derived from?</td>
<td>Texture?</td>
</tr>
<tr>
<td>Fine</td>
<td>Processes required?</td>
<td>Depositional environment?</td>
</tr>
<tr>
<td>Very fine</td>
<td>Derived from?</td>
<td>Texture?</td>
</tr>
<tr>
<td>plant grains</td>
<td>Derived from?</td>
<td>Texture?</td>
</tr>
</tbody>
</table>

- **Clastic** rock type contains:
  - Quartz
  - Calcite
  - Salts (gypsum/halite)

- **Chemical** rock type contains:
  - Plant fragments

**Processes required?** for each type depend on the specific depositional environment.

**Depositional environment?** for each type influences the texture and derivation of the rock.
# Metamorphic Rocks

## Metamorphic grade

<table>
<thead>
<tr>
<th></th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
<th>Very high</th>
</tr>
</thead>
<tbody>
<tr>
<td>Foliated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Texture</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Observation?**

**Processes required?**

## Composition

<table>
<thead>
<tr>
<th></th>
<th>Variable</th>
<th>Quartz</th>
<th>Calcite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Texture</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Observation?**

**Processes required?**

**Protolith?**

**Possible environment/type of metamorphism?**

**Heat?**

**Pressure?**

**Composition**

- **Quartz**
- **Calcite**
- **Variable**

**Protolith?**

**Possible environment/type of metamorphism?**

# Worksheet A5.5: Metamorphic Rock Classification
A5.4.2. Activities/assignments

The following assignments were created with the purpose of ensuring students made connections between geologic processes and their impact on everyday life and human society.

Activity 5.1. Stress, Strain, and Deformation Structures

Learning goals:

1. Identify the cause and effect relationship between stress and strain, and the cause and effect relationship between strain and structures.
2. Recognize properties that effect strain and resulting deformation structures?
   i. What is the effect of temperature?
   ii. What is the effect of strain rate (strain/time)?
3. Identify the different types of geologic structures to be expected given variable stress and strain.
4. Assess the relationship between our analog models and reality.
   i. Give an example from anywhere around the world where Earth stresses have led to permanent strain.
      i. What stresses (pressure) are affecting the system?
      ii. What is the resulting strain?
      iii. What are the resulting structures?
      iv. What is the timescale that the system operates on?

Rocks can bend and break when stresses (force/area) are applied to them. This is common in tectonically active areas like western California and the Himalaya, both on active tectonic plate boundaries.

Part I: Exploring how temperature and strain rate affect deformation

Directions:

1. Form groups of 3–4 students.
2. Collect a container of room temperature “slime” (basically Silly Putty).
3. Begin filling out the attached chart. Record your observations: What happens when you slowly pull the slime apart (tension) – aka apply a low strain rate? What happens when you pull quickly (high strain rate)?
4. When ready collect a container of cold slime and repeat step 3. Make sure to record noticeable differences between cold and room temperature slime!
5. When ready collect a container of warm slime and repeat step 3. Make sure to record noticeable differences between warm, cold, and room temperature slime!
Questions:
1. Which strain rate and temperature combination is mostly likely to undergo brittle deformation (break)?

2. Which strain rate and temperature combination is most likely to undergo ductile deformation (stretch)?

3. What is the general effect of strain rate and temperature? How might they work together or compete to lead to brittle or ductile failure?
Part II: **Stress**, **Strain**, and **Structures**

Directions:
1. Using the 6 deformation structures below – assign each one to the corresponding stress regime and type of strain in the chart below (1 per box).
2. Label what the deformation structure is in the chart below.
3. Record observations of each deformation structure in the chart below including sense of movement if it can be identified.

<table>
<thead>
<tr>
<th>Compression</th>
<th>Tension</th>
<th>Shear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brittle</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ductile</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **A.** [Link](http://earth.leeds.ac.uk/learnstructure/index.htm)
- **B.** [Link](From: www.uoregon.edu/millem/LVSS.html)
- **C.** [Link](From: http://www.nygeo.org/foldedrock.jpg)
- **D.** [Link](From: www.fault-analysis-group.ucd.ie)
- **E.** [Link](From: structuralgeo.files.wordpress.com)
- **F.** [Link](From: http://www.alexstrekeisen.it/english/meta/boudinage.php)

---

**Stress Regime Chart**

<table>
<thead>
<tr>
<th>Stress Regime</th>
<th>Compression</th>
<th>Tension</th>
<th>Shear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brittle</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ductile</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Questions:
1. Use arrows to show the maximum shortening direction of structures C. and E.
2. Use arrows to show the maximum extension direction of structures D. and F.
3. Give an example of a location currently under stress and undergoing strain.

a. What stresses are present?

b. What type of strain is present?

c. What structures are present?

d. What is the likely strain rate of this area? How long has it been being strained?

e. What is the temperature of the material being strained?

f. Describe how stress, strain, and structure are related at your chosen location.
Answers to matching activity:

<table>
<thead>
<tr>
<th>Compression</th>
<th>Tension</th>
<th>Shear</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Brittle</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reverse Fault</td>
<td>Normal Fault</td>
<td>Strike-Slip Fault</td>
</tr>
<tr>
<td><a href="http://www.nygeo.org/foldedrock.jpg">Image</a></td>
<td><a href="http://www.fault-analysis-group.ucd.ie">Image</a></td>
<td><a href="http://www.uoregon.edu/millerm/LVSS.html">Image</a></td>
</tr>
<tr>
<td><strong>Ductile</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Folds</td>
<td>Boudins</td>
<td>Ductile Shear</td>
</tr>
<tr>
<td><a href="http://www.nygeo.org/foldedrock.jpg">Image</a></td>
<td><a href="http://www.alexstrekeisen.it/english/meta/boudinage.php">Image</a></td>
<td><a href="http://earth.leeds.ac.uk/learnstructure/index.htm">Image</a></td>
</tr>
</tbody>
</table>
Activity 5.2. Worksheet associated with NOVA Documentary

NAME: __________________________________________

GEOL 1010-02: Introduction to Geology
In-Class Activity #4: NOVA – In the Path of a Killer Volcano: The Eruption of Mount Pinatubo

Question 1: List several volcanic deposits. What types of hazards are associated with these volcanic materials?

Question 2: What are some of the warning signs of an imminent volcanic eruption? What tools do scientists use to measure eruption precursors?

Question 3: Why is volcanic prediction scientifically, socially, and politically a tricky business?

Reflect: What are some of the major consequences of volcanic eruptions? How do you feel about the response of the American scientists in light of these consequences?
Activity 5.3. Opinion Editorial Assignment

Op-Ed (Opinion Editorial)

An op-ed is a type of newspaper article in which the author shares their opinion and picks and defends one side of an argument. The best op-eds present a clear debate and then back up their preferred side with an evidence-based argument. Remember you are trying to convince the reader to come to your side of the argument!

Assignment Guidelines:
1. Write an op-ed on any topic of your choice that includes human and Earth interaction.
   a. Climate change (this is a big one, you could write about increased severe weather, melting of ice sheets, rising sea level, desertification)
   b. Land use
   c. Hydraulic Fracturing
   d. Natural resource extraction
   e. Agricultural irrigation
   f. Artificial dams
   g. Water or air pollution
   h. ANYTHING ELSE THAT INVOLVES PEOPLE AND THE EARTH!
2. Your article should be between 450-550 words (1 page single spaced)
3. Set up the debate in order to best argue your side
4. Please provide researched evidence on your topic of choice and cite your references!

You can receive up to 3 percentage points towards your overall grade! If your article is well-written and your opinion is well argued and supported by evidence then you will receive all 3 points!

Due Date: Monday, April 30th, 2018
Activity 5.4. Place based project

Individual Place Based Project Information

1. Pick a place
2. Research that place and different geologic topics related to that place.
3. Create a Concept Sketch
   a. With images, drawings, and text share how each geologic topic relates to your place.
   b. Feel free to be creative.
   c. Must submit as PDF
   d. See Jacky’s example of Boulder, CO
4. Submit updated Concept Sketch PDF about every 2 weeks to D2L → Assessments → Dropbox → Individual Project check in
   a. Each check in requires 2 new geology topics!
   b. You will be graded on:
      i. 2 new topics
      ii. image, drawing, and text that relates different topic to your place
5. Final Project is due: Wednesday 5/2/18
   a. 10 topics total
   b. Will be graded on:
      i. completeness
      ii. accuracy
      iii. creativity

Check-in Due Dates in D2L:
Check-in #1: 3/7/18
Check-in #2: 3/19/18
Check-in #3: 4/6/18
Check-in #4: 4/18/18
Check-in #5: 4/30/18

Potential Geologic Topics (must do 10):
1. Rock Cycle 10. Geologic Time
2. Plate Tectonics 11. Hydrologic Cycle
4. Igneous Rocks 13. Rivers and Flooding
8. Geologic Structures 17. Climate
**Activity 5.4. Place-based project example**

**Geologic Time**

- **Paleozoic (250-540 Ma)**
  - maritime, cool alpine climate
  - shale, limestone, sandstone, conglomerate
  - coastal, plains, lowlands, mountains

**Resources: Mining, Geothermal**

- **Mineralogy**
  - Ore deposits: gold, silver, lead, copper and zinc veins
  - hydrothermally altered rock, metamorphosed limestone

**Volcanism**

- youngest, rocks found only on higher ridges and peaks (lateral continuity)

**Geologic Formations**

- **Sedimentary and Volcanic**

**Plate Tectonics**

- **Oceanic-continental subduction**

**Glaciers**

- **San Juan breccia**
  - deposited by running water (well sorted)

**Sedimentary Rock Cycle**

- erosion
- deposition
- burial
- compaction, cementation
- sedimentary rock

**Geologic Formations**

- **Mesas**

**Telluride**

- Picture: Mt. Sneffels

**Geologic Time**

- **San Juan breccia**
  - deposited by running water (well sorted)

**Mineralogy**

- Ore deposits: gold, silver, lead, copper and zinc veins
- hydrothermally altered rock, metamorphosed limestone
Activity 5.5. Energy Discussion – Hydraulic Fracturing

GEOL 1010-02: Introduction to Geology  Name: 

In-Class Activity #6 – Hydraulic Fracturing

Directions:
1. Form a group of 3-5 people
2. Read the 3 articles provided
3. Answer and discuss the below questions with your group. Turn in individually at the end of class.
4. Discuss where you fall on the hydraulic fracking debate and why, and/or what other information you would like to make a more informed decision or compelling argument.

Questions:
A. What is the role of the Environmental Protection Agency (EPA) and why did they compile this report?

B. Who is the targeted audience for each of the 3 articles?

C. What is the purpose of each of the 3 articles?

D. How do they differ in content and language?
Activity 5.6. Politicized Science

Name: ________________________________

GEOL1010 - In-Class Activity #13: Politicized Science

In small groups please fill out predictions for each graph. The x axis (1a and 1b = highest degree completed) represents the independent variable and the y axis (1a and 1b = probability believe climate is human caused) is the dependent variable. For part a predict how the independent variable affects the dependent variable for an individual. For part b predict how the independent variable affects the dependent variable based on political affiliation (independent, republican, democrat).

1a.

Highest degree completed

1b.

Highest degree completed

2a.

Science Knowledge level

2b.

Science Knowledge level
A5.4.3. Professional and student development

It has been my experience that students often learn geologic content, but their school careers and instructors do not often cultivate other critical skills required for academic and professional success. I developed the following content to both present to students and/or provide as reference material covering a range of topics.

Professional/Student development A5.1. “Being a good Mentee”

10 Tips for Being a Good Mentee

1. Take Responsibility for Your Own Learning

2. Develop Trust

3. Be Respectful of Your Mentor’s Time

4. Set Realistic Expectations with Your Mentor

5. Come to Each Meeting with A Prepared Agenda

6. Be Open About Your Needs, Accept Feedback from Your Mentor, and Provide Feedback to Them

7. Recognize Your Mentor’s Limitations and Appreciate Their Support

8. Take Appropriate Risks

9. Say Thank You and Keep in Touch

10. Be Flexible, Keep an Open Mind, and Have Fun!
Adobe Illustrator – 10 tips for early success!

Vectors graphic editor – i.e. Illustrator – PDF, EPS
- Series of vectors connected via nodes, everything has x-y coordinate position.
- Vector editors are often better for page layout, typography, logos, sharp-edged artistic illustrations (e.g. cartoons, clip art, complex geometric patterns), technical illustrations, diagramming and flowcharting.

Raster graphic editor (bitmap) – i.e. Photoshop – JPEG, PNG, GIFF, TIFF
- Bitmap, zero and ones, memory storage of bits, change resolution and color depth 1, 4, 8, 16, 24, 32, 48, or 64 bits per pixel – change # of colors possible.
- Bitmap editors are more suitable for retouching, photo processing, photorealistic illustrations, collage, and illustrations drawn by hand with a pen tablet.

10 Tips
1. Getting started:
   a. Open a new file – define: size, orientation, units
   b. Input necessary files – pictures, maps, graphs, etc. → drag in high quality images
2. Shape tool:
   a. Rectangle, star, polygon
   i. Define size
3. Line, pencil, paintbrush tool:
   a. Line → Line, arc, spiral
   i. Stroke size, dash, arrow
   b. Pencil → Can draw any shape
      i. Easily manipulate and correct
      ii. Great for tracing
   c. Paintbrush → Similar to pencil...but
4. Cut images:
   a. Oddly complicated...and called a clipping mask
   b. Define area you want to keep – shape tool, pencil
   c. Highlight both the graphic you want to clip and clipping mask, right click, select clipping mask.
5. Text:
   a. Written text
   b. Size, font, subscript
   c. Glyphs
6. Transform and arrange tool:
   a. Reflect, rotate, scale
      i. hold shift to scale uniformly
   b. Move forward, backward
7. Distribute and align
a. Great for graphs
b. Great for perfectionists!

8. Color:
   a. Eye dropper ➔ match color
   b. Color swatches
   c. RBG, CMYK ➔ define color

9. Organize
   a. Group objects
   b. Move forward, backward
   c. Layers

10. Save as
    a. .ai file
    b. PDF
    c. EPS
    d. Export as – JPEG, PNG, TIFF

Lots of great resources for quick help...but mostly I just google questions.
Preparing for your poster session
Use this worksheet to map out your poster spiel. Despite all the questions here, your spiel should only take 2-5 minutes. Think of a poster this way: It’s an opportunity for a conversation. Give your overview, and then leave it open for Q&A. This Q&A can very well be both ways, as the person at your poster may have some insight for you. Let them ask about the things they’re interested in after you give your overview.

Answer the questions below without worrying about the wording. Partial sentences are okay.

THE INTRO
Start with a what and why statement that leaves room for them to ask themselves the big question (And? What did you find?):

1) Answer what/why
What did you do? (No more than one sentence.)

Why did you do it? (No more than one sentence.)

2) Convey/expand on your goals
What were your goals? (No more than one sentence per goal. It’s okay to phrase them as questions, and/or use bullets.)

Now put it together. You may want to state your why before the what (we wanted to learn xx, so we yy). See what works.
THE BODY

This is where you give your tour, tell your story. Speak to your graphics. Find a path through your poster, focusing on your visuals, and spend only a couple sentences on each. Feel free to skip graphics. You can come back to them during the Q&A. The important thing is to hit your major points.

3) Major steps/points, listed as bullets:

- setting (what context does your visitor need? Geographical, historical, tectonic, technical?)

- what you did

- challenges and solutions (if any)

- results

THE CLOSING

3) Summarize your findings

What did you find? (No more than one sentence per finding/result.)

4) Big ideas

What do you want to leave your visitor with? Why does your work matter? What’s particularly awesome about it? (No more than three short sentences.) Who will this benefit? What knowledge does it add?
5) Future work (optional)

What would you like to do next? (No more than one sentence per point.)

Try it out.

If it’s too long, which it probably will be, figure out what to cut. Simplify, simplify, simplify. Remember they can ask you for more detail.

You may need to switch up the order of the points above. Maybe you need to start with some context, or ask a question. This is just meant to get you thinking about your major points and the big picture.

Practice again. Rinse, repeat.

Tips:
- Enthusiasm. (Genuine.) If you’re not interested, your visitor won’t be either.
- Speak to your graphics.
- Read your audience. If you know their background, choose your vocabulary accordingly. Feel free to check in to see if they’re familiar with the terminology you’re using, and be prepared to define or explain if they’re not, and/or stick with the big picture ideas.
- Speak simply.
- Stay out of the weeds unless asked to go there.
- Watch out for these words, and use them only in context: like, kind of, I guess, actually, just

Additional tips from SACNAS:
- Don’t apologize—it draws attention to the problems rather than emphasizing your results. Address issues if your visitor brings them up.
- Think of yourself as a tour guide.
- Remember you have business cards!
- Practice—your spiel will move along faster if you do.
Professional/Student development A5.4. Graduate school and student timeline

The Grad School Grind and Timeline!

WHEN, WHAT, WHO, HOW…successfully applying and choosing a graduate program!

NOW:
- Figure out what the heck you like you do!
  - Get as much research experience as you can
    - Talk with professors of classes you enjoy and see if they have work for you to do (preferably paid).
    - Look into research internships – they are becoming more and more expected for incoming grad students
  - Take classes that pique your interest
- Take lots of math, chemistry and physics!
  - If you go to a liberal arts college like me, these aren’t required…but they are often required for grad school.
- Make sure you can answer this question: “Why do you want to go to graduate school?”
  - Perhaps gaining work experience is the right choice?
  - Maybe a masters before a PhD…
  - What do you think you’d like to do with a graduate degree?
    - If your answer is “I don’t know…I just don’t have anything better to do” you probably shouldn’t go straight to grad school.

NOW-SUMMER before applying to grad school:
- Do lots of internet research on schools, grad programs, cities, and most importantly advisors and potential projects!
  - Use your connections! Do any of your professors, mentors, friends, former students have suggestions or know about advisors you are interested in?
  - Make spreadsheets
  - Further figure out what excites you!
  - Being interested in more than one potential advisor at a school is not a bad thing!
- Take advantage of every opportunity to ya know – network!
- Make sure you have good connections with potential recommendation letter writers (those letters are super important!)
- Study for the GRE

FALL that you are applying to grad school:
- Take the GRE
- Start sending out emails (like a lot of them!) to potential advisors, asking about projects, whether or not they are looking for students.
  - Get your name on their radar.
  - Send out a brief amount of info on yourself – focus on your research experience…potential advisors LOVE that!
  - Tailor the email and questions to their interests and programs
Decided whether or not you want to send your CV or resume. I didn’t, if they want it, they will ask for it. And they will certainly see it in your application.

In my personal experience about half the people I emailed responded at all, and of those half the replies gave me really useful info or were interested in chatting with me!

Be sure to answer emails quickly! These people are super busy (busier than you, I promise) and if they took the time to answer you, you better take the time to answer them!

Email examples:
Dear Professor Flowers,

My name is Jacky Baughman and I am a senior geology major at Colgate University in upstate New York. I hope to pursue a doctorate degree in tectonics and structural geology starting fall 2013. I am very interested in the University of Colorado, Boulder and specifically in the work you do regarding continental deformation utilizing thermo- and geochronology. My research background thus far has been primarily in the formation, structure, and contamination associated with the Marcellus gas shale, additionally, I worked with the USGS on uranium groundwater migration and contamination. However, my current research and thesis deal with the Harcuvar metamorphic core complex in Arizona. I am using petrographic analysis and electron backscatter diffraction in combination with thermochronology data from UC Santa Barbara to understand the thermal unroofing and potential two stage deformation of the complex as well as further investigate the possibility of low angle normal faulting.

I am interested in working with your research group and saw that you were looking for a new PhD candidate starting next fall. I would love to learn more about research opportunities including the southern African Plateau project you may have available. Please feel free to contact me via email or phone.

Hope to hear from you soon and thank you for your consideration,

Jacky Baughman
Colgate University '13
jbaughman@colgate.edu
(585) 478-0943

**FALL that you are applying to grad school continued:**
- Identify the schools/people you are actually going to apply to! You probably shouldn’t be applying to 15 schools…It’s a lot of money, time, and probably a sign you don’t actually know what you want out of a grad school experience!
  - Stay organized!
    - Make spreadsheets about the application requirements of each school and deadlines

**FALL and WINTER:**
• Ask for recommendation letters (usually need 3) at minimum 1 month in advance of deadlines.
  o Give rec letter writers all of the info they may need to make their life as easy as possible.
    ▪ Stay organized!
    ▪ Give them your CV and anything else they ask for so they can best write a good rec letter.
    ▪ Tell them when the letter is due and if they need to email it somewhere, fill out a sheet provided by the university, or if you can/should mail it for them
    ▪ DON’T ask to see the rec letter…that’s rude!
  o Choosing letter writers
    ▪ Only ask people who will write good letters!
    ▪ Choose people in the field you are applying for. Best choices are people you have done research with (though likely not grad students, PhDs are important) or at least professors you have taken classes with. Don’t ask your favorite English professor…sorry.
• Write your applications!
  o Don’t wait till the last minute…revise and edit several times to write the best application you can!
  o Usually involves a personal statement and statement of purpose (research experience and interest statement, future plans statement). Sometimes it is one piece or writing or split into a couple different statements.
    ▪ Each school is different, however much of the writing can be adapted for each application.
    ▪ STAY ORGANIZED
    ▪ Get as many people as you can to read and edit your work. The application is important!
    ▪ You will also need to send GRE scores and official transcripts
  o On your application, make sure you flag the names of people you are interested in working with…that will help make sure they read your application!

WINTER:
• Apply
  o Most applications are due end of December or early January.
• Wait for responses

SPRING after applying:
• You may hear from potential advisors that want to email further, Skype or have a phone interview.
• You may start getting acceptance (and rejection) notifications!
• You may start setting up trips to go out and visit grad schools (usually paid for by the potential advisor or department)
• You should start thinking about lots of questions that are important to you!
This is often when the tides change and the ball is in your court...always act professional and respectful, but it might be you conducting the interview now on the school, the advisor, and grad students already in the department.

- Do what is best for you! But remember to not burn bridges!

- The campus visit:
  - Be flexible and go on a visit if that is an option!
    - Explore the town/city
    - Ask the grad students the hard questions:
      - Do you like your advisor?
      - Can I afford to live here on a grad student stipend?
      - What is the advising style?
      - What is the department culture?
      - Work/life balance?
      - Do people take vacations?
      - How are the courses?
      - What opportunities are available?
      - AND A MILLION MORE!
    - Ask the advisors the hard questions too:
      - What types of projects do you have going on?
      - Is there funding for me? (Don’t go to schools that can’t pay for you)
        - How much RA and how much TA?
      - What techniques to you employ
      - Will I have some say in the direction of the project?
      - What do most of the students you have graduated do?
      - How many grad students do you usually have (aka a way to learn if they have any time for you!)?
      - AND A MILLION MORE!
    - The school, the place, the people are all important...but the advisor, your relationship with the advisor and your interest in the project are most important!!

APRIL 15th: THE DEADLINE FOR ACCEPTING (or declining) OFFERS!

Decide as early as you can though! Your declining an offer may allow someone else to get made an offer!
A5.4.4. Daylong + activities

I had the opportunity to develop day long and multi day programming for several Boulder based intern groups including RESESS (Research experience in solid earth sciences for students), which pairs undergraduate students from underrepresented groups with intensive research projects over the summer, GeoLaunchpad, which exposes Colorado community college students to geoscience workforce options and provides an internship at the USGS or UNAVCO, and USIP (UNAVCO Student Intern Program) for graduate students seeking experience as scientific research support staff.
Group Activity A5.1. Geoscience career circle

I organized a weekly lunch series to provide the opportunity for interns to explore a variety of geoscience career paths from professionals in those fields.

Geoscience career sectors:

Industry
Consulting
Non-profit
Research
Academia
Government

Attendees

Industry: Matthew Findley, Sr. Environmental Specialist at DCP Midstream, MCFindley@dcpmidstream.com

Consulting: Sarah Tessendorf, Project Scientist II, UCAR, saraht@ucar.edu; Patrick Shabram, Viticultural Geographer, Patrick Shabram Geographic Consulting, Patrick.shabram@frontrange.edu

Non-profit: Tahlia Bear, Diversity and Career Officer, Geological Society of America (GSA), tbear@geosociety.org; Matthew Dawson, Program Officer, Education and Outreach, Geological Society of America (GSA), mdawson@geosociety.org

Research: Dan Broman, Civil Engineer, Bureau of Reclamation, daniel.p.broman@gmail.com

Academia: Dr. Kamini Singha, Professor, Hydrology, Department of Geology and Geological Engineering, Colorado School of Mines, ksingha@mines.edu

Government: Treasure Bailey, EPA, treasure.bailley@gmail.com

Potential Attendees

Kyle Coulon, Program and Development Officer, AISES, kcoulon@aises.org

Trevor Branch, Environmental Engineer, CTL Thompson, trevorbranch@gmail.com

Melissa Foster, USGS geologist, Melissa.a.foster@colorado.edu, Melissa.ann.foster@gmail.com
Group Activity A5.2. Weekend Front Range Field Trip

RESESS and GeoLaunchpad – CU Geological Sciences Field Trip
June 24-25, 2017

1) Basic agenda

- **Saturday 9:00:** Will pick up at Bear Creek apartments
- **Sat. night:** Dinner at the CU Mountain Research Station, sleep there.
- **Sunday:** 9:00 a.m. Depart for second day. Breakfast and lunch will be provided.

2) Transport: CU-Boulder will provide transportation. Please, no private vehicles!

3) Lodging & food: **Bring your own lunch for Saturday.** CU Mountain Research Station: dinner (Sat night) and breakfast (Sun morning) are provided, along with bag lunch for Sunday. Sleeping quarters are rooms with bunkbeds in a lodge (rustic). Bring a sleeping bag. The Mountain Research station is at 9500’ elevation and so can be cool at night.

4) What to bring:

- Lunch for Saturday
- Backpack
- Water bottle for Saturday
- Sunscreen
- Sunglasses
- Personal items (medications, camera, your favorite snacks etc.)
- An extra pair of socks
- Hats (one for sun protection, one for colder temps Sun morning)
- Wind jacket
- Fleece jacket (warm)
- Sturdy shoes or boots
- Sleeping bag – if you have one; if not, let us know and we can try to scrounge a borrowed one.
**Saturday, June 24th, 2017**

9:00 am – pick students up at Bear Creek apartments

Instructors include – Jacky Baughman, Megan Brown, Emily Fairfax, Rachel Glade and Simon Pendleton, all PhD candidates at CU Boulder in the Dept. of Geological Science

1\textsuperscript{st} stop – Eldorado Canyon state park

\textbf{A.} Hike from Visitor’s Center – observe Proterozoic basement (Boulder Creek granodiorite and Coal Creek quartzite) and nonconformity in the canyon. \textbf{Mini-presentation} - Proterozoic tectonics of Colorado region (Jacky)

Need these maps – quartzite ridge

\textbf{B.} Hike along Fowler Trail through stratigraphic section towards Dowdy Draw, bring lunch on the hike – \textbf{Mini-presentation} – Sedimentary rocks of the Front Range, records of Ancestral Rocky Mountains, Cretaceous Interior Seaway, Laramide Orogeny. (~2 miles flat hike) (Simon and others)

Fowler trail to Rattlesnake Gulch – pick students up at other end

2\textsuperscript{nd} stop – Boulder Creek Path – \textbf{Mini-presentation} – 2013 Front Range flooding (Gauge Station)

3\textsuperscript{rd} stop – Boulder Creek Path, below Barker Res - \textbf{Mini-presentation} – Beaver Dams (Emily Fairfax)

5:00 pm arrive at research station. Dinner from 6-7 pm

**Sunday, June 25th, 2016**

1\textsuperscript{st} stop – Panorama point (viewpoint) on Flagstaff road – \textbf{Mini-presentation} – Rocky hillslopes (Rachel Glade)

2\textsuperscript{nd} stop – Artists point (viewpoint) on Flagstaff road – \textbf{Mini-presentation} – Induced Seismicity (Megan Brown)

3\textsuperscript{rd} stop - Green Mountain (about 1.5-mile hike, lunch on hike) – \textbf{Mini-Presentation:} Green Mtn Kimberlite (Jacky Baughman)

Gregory canyon to ranger trail

Back in Boulder by 3 pm
Group Activity A5.3. Geoscience and Communication Symposium

Geoscience and Communication Symposium
CU Boulder, Benson Earth Sciences, Room 380
Monday, July 10th, 2017
9:45 am – 3:30 pm

SCHEDULE
9:45-10:00 Coffee
10:00-10:05 Welcome – Jacky Baughman
10:05-10:20 Where the sun don’t shine: Tales from an emerging lab – Garrett Boudinot
10:20-10:35 Carbon and Nitrogen Reduction in low Temperature – Dan Nothaft
10:35-10:50 Activity: “Convince me”
10:50-11:00 Break
11:00-11:15 Exploring electromagnetic seas – Neesha Regmi Schnepf
11:15-11:30 From Rock’n’Roll to Rolling Rocks – Mylène Jacquemart
11:30-11:50 Activity: “Communicating Challenging Problems”
12:00-1:30 Lunch (provided – Half-Fast subs – veggie and gluten free options available) Graduate student round table, facilitated by Megan Brown
1:30-1:45 From Diatoms to the Arctic: A Tour Through the Sciences – Graham Lau
1:45-2:00 Gas from the past: Linking surface and deep earth processes using He thermochronology – Colin Sturrock
2:00-2:20 Activity: “Explain your research using only 4-letter words or less”
2:20-2:30 Break
2:30-2:45 My Journey along I-70 – Megan Brown
2:45-3:00 A geophysicist’s guide to interpreting science and life – Kyren Bogolub
3:00-3:20 Activity: “Thinking on your toes”
3:20-3:30 Wrap up

The symposium will involve a series of presentations from CU Geological Sciences recent and current graduate students, and several activities focused on science communication. Presentations and activities aim to expose interns to active research in the geosciences, career paths, workforce experience and communication with a variety of audiences.

Coffee and morning treats will be provided starting at 9:45 am, and lunch will be provided from 12:00 – 1:30 pm. Over lunch interns and graduate students will participate in a round table discussion focused on preparing, applying and being a graduate student.

Interns, students, graduate students and anyone else associated with the geological sciences department is welcome to participate!
Thanks – and feel free to contact me at jaclyn.baughman@colorado.edu with any questions.
Jacky Baughman, PhD Candidate, CU Boulder

“Convince Me”
Break into small groups. Convince jury you’re not a witch. Convince jury the Earth is flat. Convince jury there’s a man in the moon. Convince jury spandex is the greatest material ever. Convince the jury animals understand people. Convince the jury that the decade of your choice is the GREATEST DECADE. Convince the jury that a period of geologic time of your choosing is the BEST.

“Communicating Challenging Problems”
Break into small groups, pick a problem, discuss how to best communicate it. Pitch it to the whole group in ~1-2 minutes.

“Explain your research using only 4-letter words or less”

“Thinking on your toes” – Give someone else’s presentation 15 or 20 seconds on each slide only.