# Zirconium in rutile speedometry: constraining lower crustal cooling rates and residence temperatures

*Terrence Blackburn* [a]*, *Nobumichi Shimizu* [b], *Samuel Bowring* [a], *Blair Schoene* [c], *Kevin Mahan* [d]

[a] *Earth Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Ave, Cambridge, MA 02139.*
[b] *Woods Hole Oceanographic Institute, 266 Woods Hole Rd, MS# 23 Woods Hole, Ma. 02543*
[c] *Department of Geosciences, Princeton University, Guyot Hall, Princeton NJ 08544*
[d] *University of Colorado-Boulder, Dept of Geo Sci, Campus Box 399, 2200 Colorado Ave. Boulder, CO 80309*
* corresponding author contact: email: Terrence@mit.edu

## Abstract

The incorporation of zirconium into the mineral rutile ($TiO_2$) has been both empirically and experimentally calibrated to measure of rutile crystallization temperatures (Watson et al., 2006). This temperature sensitive system has been employed as a geothermometer with applications to a number of different geologic settings and rock types. Experimentally measured kinetics for Zr diffusion in rutile (Cherniak et al., 2007) indicate that Zr can be lost to temperature dependent diffusion, warranting further investigation of the geologic significance of calculated temperatures. Coupling diffusion kinetics with both analytical and numerical solutions to the diffusion equation provide a means to forward model the time and temperature dependency of the system. Modeled results indicate a strong dependency of Zr concentration in rutile on both: 1) initial cooling rate from high-temperatures following metamorphism/crystallization and 2) temperature and duration of long-term geologic residence. Zr concentrations measured in-situ in rutile from lower crustal (25-45 km depth) xenoliths reveal Zr concentrations in the approximate grain center that are consistent with temperatures measured by independent thermometers. Forward models for Zr diffusion show that preserving these temperature estimates in a 50 μm grain requires rapid cooling (>300 °C/Ma) from magmatic/metamorphic temperatures followed by long-term residence at temperatures <550°C. This provides a new way to determine cooling rates between 900-500 °C and for constraining the geothermal gradient at lower crustal depths. Modeled temperature-time paths for samples with both rutile Zr and U-Pb geochronological data permit evaluation/refinement of published diffusion kinetics. We propose the use of new diffusion kinetic values that permit the modeled temperature-time paths for these samples to remain self-consistent for both systems. Properly quantified, this system can be utilized as a high temperature geo-speedometer: a powerful tool for evaluating heat transfer rates at these very high and often unconstrained temperatures.

Keywords: Zirconium; Zr; rutile; diffusion; high; temperature; thermochronology; xenoliths; lower crust

## 1. Introduction:

Creating a comprehensive model for any solid system, whether a study in rock rheology to mantle dynamics or planetary cooling, requires a measure of a system's initial temperature. Geothermometry, as broadly defined, permits estimation of equilibrium temperatures for systems using empirical or experimental calibrations of a measured state of mineral phase equilibrium. Utilizing a temperature sensitive equilibrium of silica, zirconium and titanium in the minerals quartz, zircon and rutile, the Zr-in-rutile thermometer (ZRT) has recently been developed to constrain the crystallization temperatures of a variety of rocks. The original calibration of the system utilized temperature constraints from independent thermometers correlated with Zr concentration in rutile (Zack et al., 2004). The ZRT was verified and refined by several experimental studies (Ferry and Watson, 2007; Tomkins et al., 2007; Watson et al., 2006) resulting in a well-defined relationship between rutile Zr concentration and equilibrium temperature and pressure. This novel accessory mineral thermometer has been applied to a wide variety of rock types and extreme geologic environments, from ultra-high-temperature (UHT) granulites (Baldwin and Brown,

2008) to ultra-high pressure eclogites and blueschists (Spear et al., 2006; Zack and Luvizottow, 2006). The mobility of Zr in rutile by solid state diffusion was investigated by Cherniak et al. (2007) in order to evaluate the potential for diffusive loss of Zr from rutile. That experimental study indicates that Zr in rutile obeys thermally activated volume diffusion with an activation energy ($E_a$) and prefactor ($D_0$) of 170±30 kJ/mol and 9.8e-15 $m^2/s$, respectively (Cherniak et al., 2007). An important implication is that high temperature rocks (800-1000 ºC), including the previously studied granulites and high temperature eclogites, will only retain Zr associated with crystallization if initial cooling rates are extremely rapid ($>10^4$ ºC/Ma)(Cherniak et al., 2007). Therefore, the preservation of high-temperature systems recorded by the ZRT implies that the extremely rapid cooling required to preserve these concentrations is perhaps inherently linked with UHT/HT conditions.

The purpose of this paper is to systematically explore the temperature and time dependence of Zr concentrations in rutile by applying the experimentally determined diffusion kinetics (Cherniak et al., 2007) and numerical solutions to the diffusion equation to understanding *in situ* Zr concentration measurements in rutile. We show that the Zr-in-rutile system for lower crustal rocks may or may not yield a temperature of crystallization, but can record: 1) the cooling rate through a thermal window of approximately 1000-500 ºC and 2) a maximum temperature of long-term residence experienced by the sample. Quantifying the degree of Zr diffusion in rutile from lower crustal samples can constrain thermal histories not recorded by other thermochronometric techniques. Previously employed temperature sensitive systems such as the U-Pb and $^{40}Ar/^{39}Ar$ thermochronometers have an initial state with a concentration gradient of zero that increases only with the *in-situ* production of daughter isotope(s) and decreasing temperatures. The Zr in rutile system, however, begins with an extremely steep gradient making it highly susceptible to diffusive loss during initial cooling from magmatic/metamorphic temperatures, and thereby providing higher temperature cooling histories than the thermochronometers. Determining the amount of Zr lost by diffusion can provide new insight into the Earth's thermal history and allow users to quantify the rates of heat transfer in underexplored regions of the lower crust and upper mantle.

### 1.1 Geologic applications: High temperature cooling rates and long-term residence temperatures

There has been a great deal of interest in understanding the geologic setting of rocks recording high-temperature (HT) and ultra-high temperature (UHT) metamorphism. Despite the focus on these unusual rocks, the processes leading to their subsequent exhumation to the Earth's surface are contentious. This may be due to an incomplete determination of their P-t-T history, in particular at a gap between the UHT and HT conditions (>800 °C) recorded by geothermometers and the low to moderate temperatures (400-600 °C) recorded by thermochronologic systems (U-Pb, $^{40}Ar/^{39}Ar$). The Zr in rutile system has potential as a geospeedometer capable of describing the cooling rates of rocks through this unconstrained thermal window (700-1000 °C), thus providing insight into physical models for heat transfer in the Earth.

Similarly enigmatic are the long-term residence temperatures that lower to middle crustal rocks experience after the initial cooling from magmatic/metamorphic conditions. Geothermal gradients produced by mantle xenolith P-T arrays when extrapolated upwards yield lower crustal temperatures of 600 °C or more (McKenzie et al., 2005). Even higher lower crustal temperatures (>700 °C) are predicted from thermobarometric studies of lower crustal rocks. Meanwhile, thermal models utilizing surface heat flux measurements, often yield lower crustal temperatures of 500 °C or less (Jaupart and Mareschal, 1999; Pollack and Chapman, 1977). Similar temperatures are implied by U-Pb thermochronologic data from lower crustal xenoliths that record slow cooling over a billion years or more at lower crustal temperatures between 400-600 °C (Blackburn et al., 2011; Schmitz and Bowring, 2003). The Zr in rutile system is susceptible to diffusive loss at moderate temperatures over long periods of geologic time. This information will help to inform a new and independent measure of lithosphere geothermal gradients as recorded at lower to mid-crustal depths.

## 2. Methods

To quantify a sample's thermal history through the temperature range in which the retention of Zr in rutile is sensitive to time and temperature, one must either: 1) characterize the diffusion profile of Zr within a single grain or 2) measure the Zr concentrations in grains of variable size. Accurate measurement of a diffusion profile using *in-situ* techniques is often difficult because of variability in the grain orientation, degree of abrasion/polishing into the grain, a 3-D diffusion profile, and variability in grain dimensions within a single sample. Previous ZRT studies have commonly used an ion microprobe (SIMS) or electron microprobe (EMP) for Zr analyses. Because the majority of published data was acquired by SIMS or EMP, the numerical modeling results presented here will focus primarily on extracting information from these *studies*. A criterion for evaluating Zr diffusion from *in-situ* data must be developed in order to place meaningful limits on a sample's thermal history. The essential constraint employed here is the presence or absence of 'center retention' – a term previously used by Cherniak et al., (2007) to describe whether equilibrium Zr concentrations within the core of the grain have been preserved after particular t-T history (Fig 1). Importantly, center retention can be quantified using *in-situ* techniques. An independent measure of the system's initial temperature is required for comparison, with the further assumption that both thermometers are recording the same maximum temperatures.

### *2.1 Zr laboratory methods*

In this study, Zr concentrations were determined using a Cameca IMS 1280 ion microprobe at the Northeast National Ion Microprobe Facility at Woods Hole Oceanographic Institution. A beam of negatively charged oxygen ions ($^{16}O^{-}$) with a current ranging from 750 pA to 1.1 nA was focused to a spot of approximately 10 – 15 μm. Secondary ion intensities of $^{46}Ti^{+}$ and $^{90}Zr^{+}$ were measured by jumping magnetic field from $^{46}Ti$ to $^{90}Zr$ cyclically 10 times for each analysis with a mass resolving power of 5500. Natural and synthetic rutiles standards with Zr concentrations ranging from 4.45 ppm to 769 ppm (Zack et al., 2004) were used to determine a relationship between Zr contents and $^{90}Zr/^{46}Ti$ intensity ratios (a calibration line). The calibration line is expressed as: Zr (ppm) = 7.22E5 * ($^{90}Zr/^{46}Ti$) with an error (2σ) for the slope of ±2.5%, and the session-to-session reproducibility of the slope is within ±5%. For the range of concentrations encountered here (>2500 ppm), the largest uncertainties are derived from the calibration line slope error described above, since errors for $^{90}Zr/^{46}Ti$ measurements are much less than 1% (2σ). Zr measurements was collected from rutile samples mounted length-wise, ground down to an approximate grain center and polished. Spot Analyses were made from both the grain centers and grain tips.

### *2.2 Modeling Zr diffusion in rutile*

Both numerical and analytical solutions to the diffusion equation are used to evaluate the temperature and time dependence of Zr retention within rutile. Analytical solutions from Crank (1956) are restricted to a constant diffusivity and thus isothermal conditions. Isothermal calculations are useful for setting limits on Zr diffusion during long-term residence within the crust as well as evaluating the accuracy of numerical results. Numerical solutions to the diffusion equation using experimentally determined kinetics have previously been employed to develop accurate and stable solutions to model diffusion in other temperature dependent systems (Ketcham, 2005). The finite difference model employed here utilizes a Crank-Nicholson solution to the spherical form of the diffusion equation and results in an intra-grain Zr concentration profile for any pre-assumed time temperature path. The initial Zr concentration is homogeneously distributed and set to a value that corresponds to the initial temperature for the model run using the algorithm from Ferry and Watson (2007).

### *2.2.1 Cooling rate sensitivity*

Forward modeled results indicate that quickly cooled grains retain the initial concentration, while slowly cooled grains allow diffusive loss of Zr, resulting in a rounded Zr profile within a single grain. The internal diffusion profile as well as the relationship between grain size and Zr concentration are highly sensitive to cooling rate, allowing the system to be used as a speedometer. Figure 1a shows the internal diffusion profiles for a range of cooling rates ($10^2 – 10^6$ °C/Ma, for an initial temperature of 900 °C). With decreasing cooling rate the difference between the initial core concentration and the measured core concentration (Δ core) will consistently increase. If the measured core concentration is equal to the initial core concentration, then ‘center retention’ conditions are meet. To utilize this data as a geospeedometer one must have an independent measure of the systems initial temperature. Though the difference between core and rim concentrations of a single grain is indicative of a diffusion profile, there is *not* a systematic relationship between cooling rate and this value and one cannot extract meaningful t-T information from this measure (Fig 1). For a 50 µm radius grain within an initial temperature of 900 °C, cooling rates as low as 300 °C/Ma can meet ‘center retention’, assuming the highest experimentally determined activation energy (200 kJ/mol) within the reported uncertainty (170±30 kJ/mol, Cherniak et al., 2007). Cooling rates of at least $10^4$ °C/Ma and $10^6$ °C/Ma are required to meet center retention of 170 kJ/mol and 140 kJ/mol Ea, respectively; rates that exceed expectations for cooling in the dry and conductive lower crust. Increased temperatures are accompanied by an increase in Zr diffusivity, requiring even faster cooling to preserve UHT conditions. For example, with an initial temperature of 1000 °C, cooling rates of over 2500 °C/Ma are required to maintain center retention. At lower temperatures of 800 °C, cooling rates of at least 100 °C/Ma will meet center retention (50 µm). Similarly, decreasing the grain size to 20 µm will require increased cooling rates (>1500 °C/Ma) to meet center retention for an initial temperature of 900 °C.

### *2.2.2 Isothermal holding and constraining maximum residence temperatures*

The retention of Zr within rutile grains over the geologic time-scales preserved in cratonic continental lithosphere (~300-3000 Ma) depends on holding temperature. Following initially rapid cooling, forward models assuming isothermal holding can be used to construct a center retention partial retention zone (CR-PRZ) as a function of increasing temperature or depth through the lithosphere (Fig. 2). The CR-PRZ extends to temperatures of ~500-550 °C (depending on grain size) and abruptly decreases to zero over a narrow ~100 °C range. Preservation of center retention within a sample can be used to infer long-term residence at temperatures less than ~550 °C; a seemingly critical temperature that is relatively insensitive to initial Zr concentration (i.e. equilibrium temperature) (Fig. 2). This 550 °C serves as a maximum value, as it uses the maximum activation energy permitted by the reported uncertainty (200 kJ/mol) (Cherniak et al., 2007). Lack of center retention may be the result of either slow cooling ($<10^3$ °C/Ma) through 700-1000 °C or holding at temperatures > 550 °C. The presence of center retention permits the conclusion that both a minimum initial cooling rate *and* long-term residence below ~550 °C were met. By further assuming a lithospheric geothermal gradient, one can correlate these Zr concentrations to a particular depth allowing us to map the Zr in rutile Partial Retention Zone for this assumed geothermal gradient. Varying the assumed geothermal gradient will cause this PRZ to move either closer (hotter geotherm) or further (colder geotherm) from the Earth's surface.

### *2.2.3 Testing crystallographic control on diffusion*

Rutile belongs to the tetragonal crystal system, implying that element diffusion rates may vary between the *c* and *a*=*b* axes. Published Zr in rutile diffusion data (Cherniak et al., 2007) indicate that *c*-axis diffusion is the dominant direction for Zr loss. Assuming *c*-axis diffusion, grains mounted parallel to the *c*-axis (length-wise) would allow the *c*-axis diffusion profile to be mapped by several spot analyses from core to rim (Fig. 3a). Any measured variation with Zr concentration would reflect the actual diffusion profile (fig 3a). If diffusion along the *a*-*b* axis was operating and grains were oriented parallel to the *c*-axis (Fig 3b,c), the variation in Zr concentration revealed by *in-situ* analyses would depend on the degree of polishing into the grain (Fig. 3d). Furthermore, any observed variation in concentration from core to rim would yield an *apparent* profile (Fig. 3d). The actual diffusion profile for *a* or *b* axis diffusion, with information pertaining to the time-temperature history of the sample, can only be constructed through a series of measurements through the grain parallel to the *a* or *b* axis. If the centers of several grains of approximately the same grain size were analyzed, with each grain (unavoidably) polished to a different depth, we can anticipate a range of Zr concentrations that reflect the true variation of values along some portion of the true diffusion profile (Fig 3d). For example, in a quickly cooled sample, the Zr in rutile system would record a uniform concentration among grains, independent of the level of polishing. Slow cooling however, will yield significant variations in Zr concentration from grain to grain. These data would only be symptomatic of diffusion and because the data is not spatially controlled one cannot reconstruct a diffusion profile.

A test for the direction of diffusion can be constructed by measuring the core and tip Zr concentration for several grains oriented length-wise and polished perpendicular to the *c*-axis (as illustrated in fig 3). By plotting the difference in observed Zr concentration between the core and rim vs. the core concentration one can elucidate which of the three options presented in figure 3 is likely operating. This analysis presumes that a diffusion profile does exist within a grain. If the difference between core and rim is consistently large (>100's of ppm) and is insensitive to the core concentration, then c-axis diffusion is operating (fig 3a). If the difference between core and rim concentrations is zero, then *a* or *b* axis diffusion is dominating the system (fig. 3b). Lastly if diffusion is operating in all directions we can anticipate that the level of polishing will effect the concentration measured within the core resulting in both a positive correlation between core and rim differences and the core concentration.

## 3. Geologic Setting: Pressure-Temperature-time constraints

Zr concentration in rutile grains were measured from middle to lower crustal xenolith samples, derived from the Archean Medicine Hat Block (MHB) and adjoining Great Falls Tectonic Zone (GFTZ), both located within Montana, USA (Fig 4 inset). Previous published data for samples SG02 and SG05 from the MHB include, major element/phase thermobarometery and pseudosection analysis, U-Pb rutile thermochronology and U-Pb zircon geochronology (Blackburn et al., 2011). Previously unpublished U-Pb rutile and zircon data for sample ROB1 from the GFTZ are included in the appendix. Pressure estimates for each sample are 0.8 and 1.0 GPa for SG02 and SG05 and 1.3 GPa for sample ROB1. Temperature estimates from pseudosection construction lie between 800-950 °C for SG02 and 700-900 °C for SG05. Garnet-biotite thermometry for these sample yield temperatures on the lower end of this range at ~700 °C. Garnet-Biotite and Garnet-clinopyroxene-thermometry yield temperature estimates of 800 and 750 °C respectively for ROB1 (Mahan et al., in prep). Zircon U-Pb data record Archean protolith formation for the shallowest sample SG02, with zircon overgrowths at ~1800 Ma from what is interpreted to be the timing of the amalgamation of the MHB craton onto North America (Gorman et al., 2002). Zircon from SG05 and ROB1 record crystallization between ~1680 and 1800 Ma (ROB 1 see DR Table 3). Rutile U-Pb thermochronometry from each of these samples record a post-Archean cooling history (Blackburn et al., 2011). Paleoproterozoic zircon U-Pb dates and a post-Archean cooling history both suggest that measured Zr concentrations and ZRT temperatures from these samples were derived during this younger orogenic event.

Following the Proterozoic orogenic event rutile U-Pb thermochronometric data record extremely slow cooling through the ~400-600 °C rutile Pb PRZ. The shallowest sample SG02 yields U-Pb rutile dates over a range of ~1400 to 1000 Ma, where the largest rutile crystal yields the oldest date and the smallest crystal the youngest – consistent with volume diffusion. The next deepest sample SG05 yields dates between 1100 and 650 Ma, also correlating with grain size. The deepest, 45 km sample from the nearby GFTZ records cooling between ~550 and 50 Ma. The significant span of dates within each sample combined with a younging downward with sample depth are interpreted to indicate prolonged lower crustal residence and slow relaxation of a conductive geotherm (Blackburn et al., 2011).

## 4. Results

Zirconium concentration measurements for the xenolith samples ranged between ~2800-3500 for the shallowest sample SG02, ~3800-5000 ppm for the deeper xenolith SG05 and between ~165 and 1600 ppm for the deepest sample ROB1 (core Zr concentrations plotted Figure 2, and 4). Multiple spot analyses within single grains were measured yet systematic variations in Zr concentration were only detected within sample ROB1, where spot measurements close to the grain tip decrease by as much as 120 ppm (0-50%) when compared to the core measurement (figure 1e). Shallower xenolith samples SG02 and SG05 were homogenous on the ~100-200 ppm level, with these small-scale variations (2-3%) both increasing and decreasing towards the grain edge. A full report of measured data is included in data repository table 1. The measured concentrations yield temperatures of ~870-900 °C for SG02, ~900-940 °C for SG05 and ~600-800 °C for ROB1 using the Ferry and Watson (2007) thermometer. Center retention is met for all three samples with at least one analysis from each sample reaching concentrations consistent with or exceeding independent temperature estimates (fig 4a). For the ~50 µm grains in sample ROB1 this implies initial cooling rates of at least ~300 °C/Ma, followed by long-term residence at temperatures less than ~550 °C. The smaller range of grain sizes (~20-30 µm radius) from SG02 and SG05 require lower long term holding temperatures of ~ 500-520 °C and faster cooling rates on the order of 2000 °C/Ma.

Deviations from this center retention value were observed in each sample. In the shallow sample SG02, deviations of up to 20-26 % are observed for a range of ~10-25 μm (radius) grains, up to 30- 60% difference over a range of 10-50 μm grains in the 35km sample SG05 and up to 130-160 % for 30-45 μm grains from the 45km deep sample ROB1 (fig 4c). The trend of increasing percent variation with xenolith residence depth suggests an increase in the diffusive loss of Zr with sample depth (fig 4c).

Results for sample ROB1 for the previously devised test (section 2.2.3) for the direction of diffusion are shown in figure 3e. This test can only be conducted on samples with diffusion profiles. ROB1 was chosen for this analysis based on the observation that the deepest sample is likely to have diffusion profiles and the observed variation in core measurements (as great as 160%). The majority of core-rim pairs are consistently low (<100 ppm) with only a few analyses defining a rough positive correlation between core concentration and delta/core rim (fig. 3e). This is consistent with the expectation that the level of polishing affects the measured core and rim value, suggesting that diffusion is dominantly occurring out of the *a* and *b* crystallographic axis.

## 5. Discussion

### *5.1 Evaluating rapid cooling rates*

A limit on the body size of this intrusion can be placed by examining the rates of cooling predicted for 2 end-members of cooling within the lithosphere: 1) conduction only and 2) magmatic cooling. The well-insulated and dry lower crust should thus represent a near end-member of slower cooling that can be approximated by a purely conductive thermal model where the time-scale of cooling (*t)* is proportional size of the intrusive body and the temperature of the surrounding country rock ($t\sim pluton\ radius^2$)(Spera, 1980). We can refine this calculation using a model for the temperature dependent thermal diffusivity Whittington (2009) and a analytical half-space solution from Carslaw and Jager (1959). For a minimum country rock temperature of 400 °C the largest intrusive body sizes that yield cooling rates of at least $10^3$ °C/Ma is ~5 km.

Within a magma chamber there are several additional processes operating to both cool and heat the system. Cooling processes include conduction, both at the intrusion wall as well as within the magma, convection both within the magma and externally by hydrothermal circulation. The efficiency of this cooling is highly variable and dependent upon such variables as magma composition and viscosity, magma water content, and the depth of intrusion (Spera, 1980). These processes potentially culminate in cooling timescales (*t*) far shorter than from just heat conduction alone ($t \sim pluton\ radius^{1.3}$), permitting the intrusion body sizes larger than 5 km (Spera, 1980).

The fact that center retention is met by samples from the lower crust at all depths between ~25-45 km indicate that only small and localized regions of the lower crust are heated during magmatism and/or metamorphism and then cool rapidly due to low temperatures in the surrounding country rock. In the case of xenoliths from Montana, the presence of 1800 Ma zircon growth and the lack of any Archean cooling signature recorded by the rutile U-Pb system suggest the partial remelting and massive reheating of an Archean protolith occurred during amalgamation of the MHB terrane onto the North American craton. Heat from this event could be lost at rates up to $10^3$ °C/Ma if rocks were juxtaposed onto colder material.

### *5.2 Differences in t-T path sensitivity between the Zr and Pb systems in rutile*

The experimentally measured diffusion kinetics for Pb and Zr in rutile are similar enough that calculated Dodson closure temperatures (Dodson, 1973) for the two systems ($T_C$=450-1100 °C) are within uncertainty over nearly all cooling rates and grain sizes of geologic interest ($DTdt$ = 0.1-1000 °C/Ma, $a$ = 10-200 µ*m*). Similarly, each system behaves near identically for isothermal holding calculations (Crank, 1956). Yet the U-Pb rutile system provides time-temperature constraints on the low-temperature (400-600 °C) cooling history of rocks. Though the Zr in rutile system is also sensitive to long-term thermal relaxation, this system also responds to the initial cooling rate from magmatic or metamorphic temperatures. The cause for thethis difference in each systems cooling rate sensitivity lies in the relative difference between internal concentration gradients of each diffusant at the time of system formation. The Zr in rutile system begins within a high initial concentration that correlates to equilibrium temperatures, and is therefore highly sensitive to diffusive loss at grain boundaries (Fig 5A).. The rutile Pb system however, has zero radiogenic lead at the time of system formation. Only with decreased temperatures/diffusion can in-situ production of Pb begin to build a profile of Pb. Figure 5 plots the internal concentration profiles of Pb and Zr within a rutile grain for the same time-temperature path (fig 5 inset). Zr concentration decreases dramatically along the rutile edge in a time frame where still no Pb retention has occurred. The two systems complement one another to provide complete (>900-400 °C) constraints on a sample's time-temperature history.

### *5.3 Combining U-Pb and Zr rutile systems and refining Pb/Zr diffusion kinetics*

A time-temperature path for the lower crustal xenoliths from Montana can be determined by finding the thermal histories that fit observed data from both the Zr and U-Pb systems. The Zr system sets a limit to the *maximum* temperature limit for the lower crust; samples residing at temperatures higher than this maximum will result in a loss of Zr center retention. The U-Pb system, however, provides a *minimum* temperature limit to this long-term residence: measured U-Pb data require slow cooling through the rutile Pb PRZ, faster cooling rates will result in model dates that are too old and lack the observed discordance and ~500 Ma spread dates in grain size vs. age (Fig 6). By testing a series of t-T paths with initially rapid cooling followed by slow cooling through a range of residence temperatures, we can find which paths yield forward modeled data that agrees with both U-Pb and Zr rutile data. Finding a time-temperature path that fits each system provides an independent test for the diffusion kinetics for Pb in rutile, the accuracy of which has been debated due to the differences between apparent field closure (400-500 °C) (Mezger et al., 1989) and Dodson closure temperatures calculated using the measured Pb in rutile kinetics ($T_C$=485-630 °C, DTdt = 0.1-100 °C/Ma) (Cherniak, 2000; Dodson, 1973).

The temperature range at which Pb retention in rutile occurs is highly sensitive to the diffusion kinetics of the system. The diffusion kinetics, however, have little effect on the interpreted cooling rate, as this value is interpreted from the topology of U-Pb data utilizing the U-Pb system's dual decay scheme (Blackburn et al., 2011). A lower $E_a$ for Pb would permit cooling at a lower temperature and not effect the conclusion of ~0.05-0.1 °C/M cooling rates. Zr diffusion kinetics are at their maximum for this analysis, suggesting a lower activation energy for Pb diffusion is the only variable remaining to be explored. The nominal published Pb kinetics for Pb diffusion in rutile are: $E_a$ 250±12 kJ/mol and ($D_0$) of and 3.9e-10 $m^2/s$ (Cherniak, 2000). Additional experiments for Pb diffusion in rutile by Cherniak (2000) used natural rutile samples with data reported for both *c*-axis diffusion (260 ± 30 kJ/mol, 6.9e-10$m^2/s$), normal to *c*-axis diffusion (220 ± 22 kJ/mol, 2.08e-11$m^2/s$) (Fig. 6b inset). This large range of kinetic values may reflect true variation in Pb diffusion due to rutile crystal orientation and/or composition.

Measured rutile U-Pb data from each xenolith and the forward modeled U-Pb data following Blackburn et al. (2011) are plotted on a concordia diagram in figure 6a. The measured U-Pb data are bracketed by modeled data with cooling paths that are initially rapid (2000 °C/Ma) until a specified inflection temperature ($T_{infl}$), followed by slow cooling at a rate between 0.05-0.1 °C/Ma (Fig 6). Using the nominal diffusion kinetics for Pb, the inflection temperatures that yields a good fit with the data are is consistently too to high to permit the retention of Zr (Fig 6d).

To satisfy both systems, the kinetics for Pb diffusion in natural rutile (220 ± 22 kJ/mol, 2.08e-11 $m^2/s$) with an activation energy of at most ofleast 220 kJ/mol (Fig 6b inset) are required.

The use of the diffusion kinetics for Pb diffusion perpendicular to the *c*-axis is supported by previously published grain size vs. age relationships in rutile, which show a stronger correlation to grain width than to grain length (Blackburn et al., 2011). It is important to note that this analysis assumes a maximum Zr $E_a$ of 200 kJ/mol and values for Pb would change if a lower Zr value were used. Lower $E_a$ values for Zr diffusion, however, were shown previously to require cooling rates to meet center retention far above those anticipated in the conductively cooling lithosphere. Because of this we conclude that a value of 200 kJ/mol/ 9.8e-15 $m^2/s$ for Zr and 220 kJ/mol/2.08e-11$m^2/s$ for Pb diffusion in rutile provide the most internally self-consistent $E_a$ values. This corresponds to a Dodson $T_C$ for Pb in rutile of 420-570 °C (*DTdt* = 0.1-1 °C/Ma, *a* = 10-100 μm); values that are consistent with field studies (Anderson et al., 2001; Corfu and Easton, 2001; Corfu and Stone, 1998; Flowers et al., 2006; Mezger et al., 1989; Miller et al., 1996; Moller et al., 2000; Schmitz and Bowring, 2003). These kinetics are used to conclude a lower crustal history where maximum residence temperatures of 500 °C at depths up to 35 km and 550 °C at a depth of 45 km are met within <0.5 Ma following orogenesis at ~1800 Ma. This initial rapid cooling is followed by prolonged slow-cooling at rates between 0.05-0.1 °C/Ma, where the shallowest xenoliths cool first and the deepest last.

## 6. Conclusions

The use of temperature sensitive chemical reactions provides the fundamental basis for which geothermometry can yield reliable temperature estimates for a particular system within the Earth. The preservation of this state of chemical equilibrium, and thus the temperatures derived from any measurement, are susceptible to alteration through many processes, including diffusion. Experimental measurements of Zr in rutile indicate that Zr obeys temperature dependent volume diffusion (Cherniak et al., 2007). Forward modeled calculations presented here indicate a strong dependency of an internal diffusion profile with cooling rate and initial temperature. Characterizing the internal diffusion profile or the correlation between grain size and Zr concentration allows the system to be exploited as a geo-speedometer, used to estimate the sample cooling rate through a temperature range of ~500- 1000 °C. Analytical measurements of Zirconium in rutile have nearly always been conducted using *in-situ* techniques. The preservation of Zr concentrations that correlate to the equilibrium temperatures within the center of a rutile grain or ‘center retention’ provides a means to at least constrain aspects of a samples time-temperature history. This method requires independent measure of the systems initial temperature for comparison. Preservation of center retention within a grain is sensitive to both initial cooling rate of a system and long term holding temperature. This allows users to fill the once unconstrained gap between high magmatic and metamorphic temperatures and the temperatures recorded by moderate temperature thermochronometers. The Zr in rutile systems sensitivity to long-term residence temperature allows an independent maximum constraint to be placed on temperatures found deep within the lithosphere and a means to independently evaluate the accuracy of diffusion kinetics for Pb. We conclude here that the maximum activation energy for Zr diffusion within the reported uncertainty of 200 kJ/mol and that the experimentally determined values for Pb diffusion in natural rutile (220 kJ/mol, $D_0$ of 2.08e-11 $m^2/s$) yield are the most self-consistent. In the case of xenoliths from Montana, integrating ZRT data with independent temperature and pressure constraints allows a maximum estimate of 500-550 °C to be placed on temperatures within the lower crust providing a new data point for accurately constructing geothermal gradients for the lithosphere.

**Acknowledgments:** Primary funding for this project was provided through EarthScope grant EAR-0746205 to Bowring and EarthScope grant EAR-0746246 to Mahan.

## Figure Captions

Fig 1. Variable Effect of initial cooling rate vs.on internal Zr grain profiles. Results of forward modeled calculations for internal diffusion profiles with variable cooling rate. (A) A minimum cooling rate of ~$10^3$ °C/Ma) is required to maintain center retention ($E_a$ = 200 kJ/mol, 50 µm radius). The difference between initial core concentration and measured core concentration (Δ core) will consistently increase with decreasing cooling rate (B,C). The difference between the core and (near) rim concentration (Δ core-rim), though symptomatic of diffusion, does not yield a consistent relationship with cooling rate and is a less useful parameter for quantifying a thermal history. The presence or absence of ‘center retention’ is the key parameter employed in this study to quantify a samples thermal history. This requires an independent measure of a samples initial temperature.

Figure 2. ‘Center Retention’ Partial retention zone (CR-PRZ). Zr concentration for the center of a rutile grain plotted as a function of isothermal holding temperature and depth (assuming geothermal gradient). Center Retention is only preserved if initial cooling rates are at least $10^3$ °C/Ma, assuming an maximum $E_a$ of 200 kJ/mol. Center retention is maintained at shallow levels of the crust. At isothermal holding temperatures of 400-575 °C (depending on grain size) the center concentration will decrease gradually to zero. Zr measurements from grain centers for Montana xenoliths are plotted as a function of depth (assuming a geothermal gradient of 45mW/$m^2$). Center retention in each sample suggests each sample cooled quickly from initial temperatures (>$10^3$ °C/Ma) and resided at temperatures less than ~550 °C for the duration of the sample history.

Figure 3. Testing diffusion direction. Cartoon illustrating the potential data that would result from **(A)** *c*-axis diffusion, **(B)** *a*-*b* axis diffusion and **(C)** diffusion equal in all directions. **(A)** If *c*-axis diffusion were operating, the true diffusion profile could be mapped within-situ analyses parallel to *c*. **(D)** If diffusion occurs along the *a* or *b* axis, the depth of polishing into grains will effect the data produced from *in-situ* analyses. In this case the real diffusion profile of grains is constructed through analyses at variable depths of polishing. (**E**) Measured data from sample ROB1 where grains were oriented along the c-axis and core-rim pairs were acquired. A largeLarge range in measured Zr concentrations and geobarometric depth of 45km suggesting long term holding at temperatures ~500

°C further suggesting the likelihood for an internal diffusion profile. Low to positivePositive correlation between core concentration and delta core rim suggests the level of polishing effects the apparent profile measured, further suggesting that *a-b* axis diffusion does play a role in Zr diffusion..

Figure 4. Zirconium in rutile data for grain centers‘cores’ from Montana xenoliths. Each sample meets ‘center retention’, i.e. one or more ‘core’ analyses match the independent constraints on sample temperature. **(A)** Over a narrow range of grain sizes, that differs for each sample, the concentration from a grain center can vary from the maximum values that correlate to (or exceed) the independent T estimate by 100-1000’s ppm or **(B)** 1-160% . **(C)** The correlation with this % difference and depth is interpreted an increase in diffusive loss of Zr with depth.

Figure 5. Zr and Pb evolution in a single rutile grain. (**A**) Internal concentration profiles of Zr and **(B)** Pb for a 50 µm radius rutile grain that experienced the time-temperature path shown in figure inset. The initially high concentration profile for Zr causes the system to be highly susceptible to diffusive loss during the initial cooling following high temperatures associated with metamorphism/magmatism. The Pb system, however, begins with zero retained radiogenic Pb, and does not build a diffusion profile until sufficient time and decreased diffusivity permits the retention of radiogenic Pb. The Pb system is thus more sensitive to low-temperature (400-600 °C) diffusive loss. Together the Zr and Pb systems can constrain the time-temperature path of a single sample from over 1000 °C to less than 400 °C.

Figure 6. Refining Zr and Pb rutile diffusion kinetics. The coupled Zr and Pb in rutiles systems requires that an acceptable time-temperature path to remain consistent with both systems. (A-C) Measured U-Pb data from Montana xenoliths can be bracketed by forward modeled U-Pb produced following (2011) by a t-T path with initially rapid cooling from high temperatures followed by slow cooling at rates of  ~0.05-0.1 °C/Ma after a inflection temperature is meet. Note that forward modeled U-Pb data for a common cooling rate overlap despite different diffusion kinetics. Cooling rate dominates the position on concordia of modeled data, only the temperatures at which Pb retention occurs change with each set of kinetics. To maintain Zr concentrations in the center of a 20-50 µm grain for each sample, requires long-term residence temperatures < 500-550 °C depending on the grain size (D). Using the nominal Pb-diffusion kinetics for synthetic rutile experiments from Cherniak (2000) yields thermal histories with significant periods of time at temperatures above 500-550 ºC that permit diffusive loss of Zr at the grain center (D). Time-temperature paths using kinetics for Pb published for natural rutile perpendicular to the *c*-axis yields forward modeled data that match the U-Pb data and whose t-T paths permit center retention of Zr.

## References

Baldwin, J.A., Brown, M., 2008. Age and duration of ultrahigh-temperature metamorphism in the Anápolis–Itauçu Complex, Southern Brasília Belt, central Brazil – constraints from U–Pb geochronology, mineral rare earth element chemistry and trace-element thermometry. Journal of Metamorphic Geology 26, 213-233.

Blackburn, T., Bowring, S., Schoene, B., Mahan, K., Dudas, F., 2011. U-Pb thermochronology: creating a temporal record of lithosphere thermal evolution. Contributions to Mineralogy and Petrology, 1-22.

Carslaw, H.S., Jaeger, J.C., 1959. Conduction of heat in solids. Clarendon Press, Oxford.

Cherniak, D.J., 2000. Pb diffusion in rutile. Contributions to Mineralogy and Petrology 139, 198-207.

Cherniak, D.J., Manchester, J.E., Watson, E., 2007. Zr and Hf diffusion in rutile. Earth and Planetary Science Letters 261, 267-279.

Crank, J., 1956. Mathematics of diffusion. Clarendon Press, Oxford.

Dodson, M.H., 1973. Closure temperature in cooling geochronological and petrological systems. Contributions to Mineralogy and Petrology 40, 259-274.

Ferry, J., Watson, E., 2007. New thermodynamic models and revised calibrations for the Ti-in-zircon and Zr-in-rutile thermometers. Contributions to Mineralogy and Petrology 154, 429-437.

Gorman, A., R., Clowes, R., M., Ellis, R., , M., Henstock, T., J., Spence, G., D., Keller, R., G, Levander, A., Snelson, C., M., Burianyk, M., Kanasewich, E., R., Asudeh, I., Hajnal, Z., Miller, K., C., 2002. Deep Probe: imaging the roots of western North America. Canadian Journal of Earth Sciences 39, 375.

Jaupart, C., Mareschal, J.C., 1999. The thermal structure and thickness of continental roots. Lithos 48, 93-114.

Ketcham, K., 2005. Forward and Inverse modeling of low-temperature thermochronometry data. Mineralogical Society of America, Chantilly, Virginia.

McKenzie, D., Jackson, J., Priestley, K., 2005. Thermal structure of oceanic and continental lithosphere. Earth and Planetary Science Letters 233, 337-349.

Mezger, K., Hanson, G.N., Bohlen, S.R., 1989. High-precision U-Pb ages of metamorphic rutile: application to the cooling history of high-grade terranes. Earth and Planetary Science Letters 96, 106-118.

Pollack, H.N., Chapman, D.S., 1977. On the regional variation of heat flow, geotherms, and lithospheric thickness. Tectonophysics 38, 279-296.

Schmitz, M.D., Bowring, S.A., 2003. Constraints on the thermal evolution of continental lithosphere from U-Pb accessory mineral thermochronometry of lower crustal xenoliths, southern Africa. Contributions to Mineralogy and Petrology 144, 592-618.

Spear, F., Wark, D., Cheney, J., Schumacher, J., Watson, E., 2006. Zr-in-rutile thermometry in blueschists from Sifnos, Greece. Contributions to Mineralogy and Petrology 152, 375-385.

Spera, F., 1980. Thermal Evolution of Plutons: A Parameterized Approach. Science 207, 299-301.

Tomkins, H.S., Powell, R., Ellis, D.J., 2007. The pressure dependence of the zirconium-in-rutile thermometer. Journal of Metamorphic Geology 25, 703-713.

Watson, E., Wark, D., Thomas, J., 2006. Crystallization thermometers for zircon and rutile. Contributions to Mineralogy and Petrology 151, 413-433.

Whittington, A.G., Hofmeister, A.M., Nabelek, P.I., 2009. Temperature-dependent thermal diffusivity of the Earth/'s crust and implications for magmatism. Nature 458, 319-321.

Zack, T., Luvizottow, G.L., 2006. Application of rutile thermometry to eclogites. Mineralogy and Petrology 88, 69-85.

Zack, T., Moraes, R., Kronz, A., 2004. Temperature dependence of Zr in rutile: empirical calibration of a rutile thermometer. Contributions to Mineralogy and Petrology 148, 471-488.

***Highlights**

Highlights:

- Temperature dependent diffusion of Zr in rutile provides new t-T constraints on lower crust.
- The retention of Zr in rutile is dependent on both initial cooling rate and long-term temperature.
- Data from lower crustal xenoliths yield Zr temperatures consistent with other thermometers.
- This requires initial cooling rates from magmatic/metamorphic conditions > 1000 ºC/Ma.
- Preservation of Zr in rutile for 2.0 Ga requires lower crustal residence temperatures <550 ºC.

# Figure1

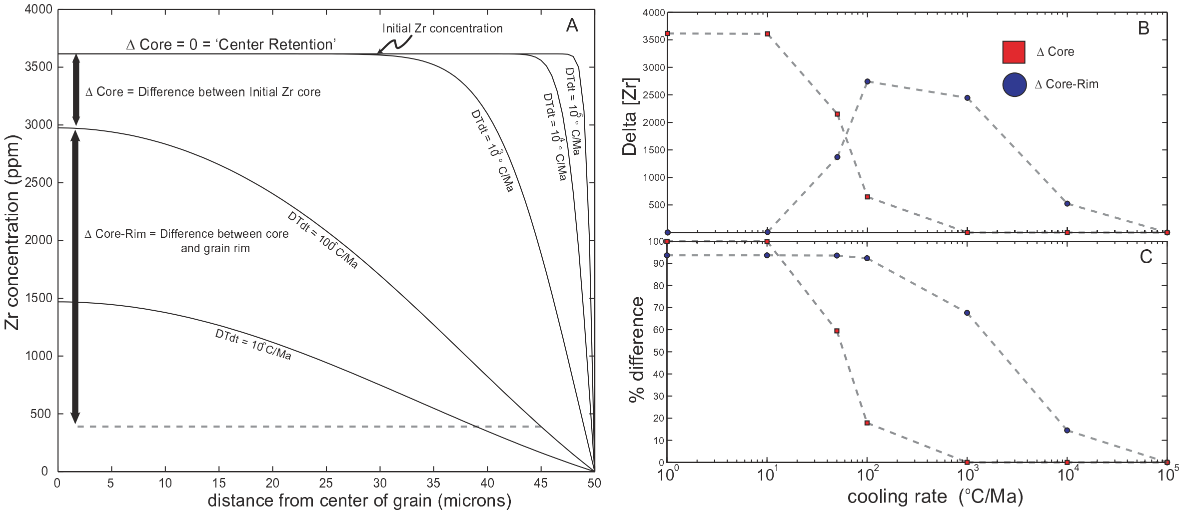

A
Initial Zr concentration
Δ Core = 0 = 'Center Retention'
Δ Core = Difference between Initial Zr core
Δ Core-Rim = Difference between core and grain rim
DTdt = 10°C/Ma
DTdt = 100°C/Ma
DTdt = 10³ °C/Ma
DTdt = 10⁴ °C/Ma
DTdt = 10⁵ °C/Ma
Zr concentration (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0
0
5
10
15
20
25
30
35
40
45
50
distance from center of grain (microns)
B
Δ Core
Δ Core-Rim
Delta [Zr]
4000
3500
3000
2500
2000
1500
1000
500
C
% difference
100
90
80
70
60
50
40
30
20
10
0
10⁰
10¹
10²
10³
10⁴
10⁵
cooling rate (°C/Ma)

**Figure2**

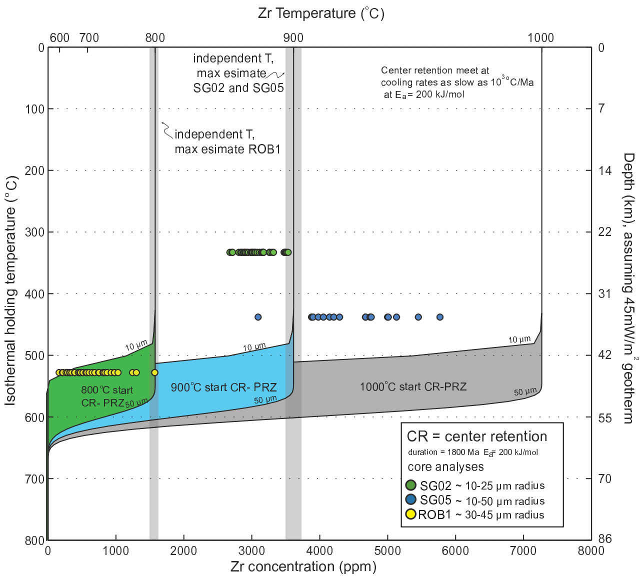

Zr Temperature (°C)
600
700
800
900
1000
independent T, max esimate SG02 and SG05
Center retention meet at cooling rates as slow as $10^{3}$ °C/Ma at $E_a$ = 200 kJ/mol
independent T, max esimate ROB1
10 μm
50 μm
800 °C start CR- PRZ
900°C start CR- PRZ
1000°C start CR-PRZ
CR = center retention
duration = 1800 Ma $E_a$ = 200 kJ/mol
core analyses
● SG02 ~ 10-25 μm radius
● SG05 ~ 10-50 μm radius
● ROB1 ~ 30-45 μm radius
Isothermal holding temperature (°C)
0
100
200
300
400
500
600
700
800
Depth (km), assuming 45mW/$m^2$ geotherm
0
7
14
22
31
42
55
70
86
Zr concentration (ppm)
0
1000
2000
3000
4000
5000
6000
7000
8000

**Figure3**

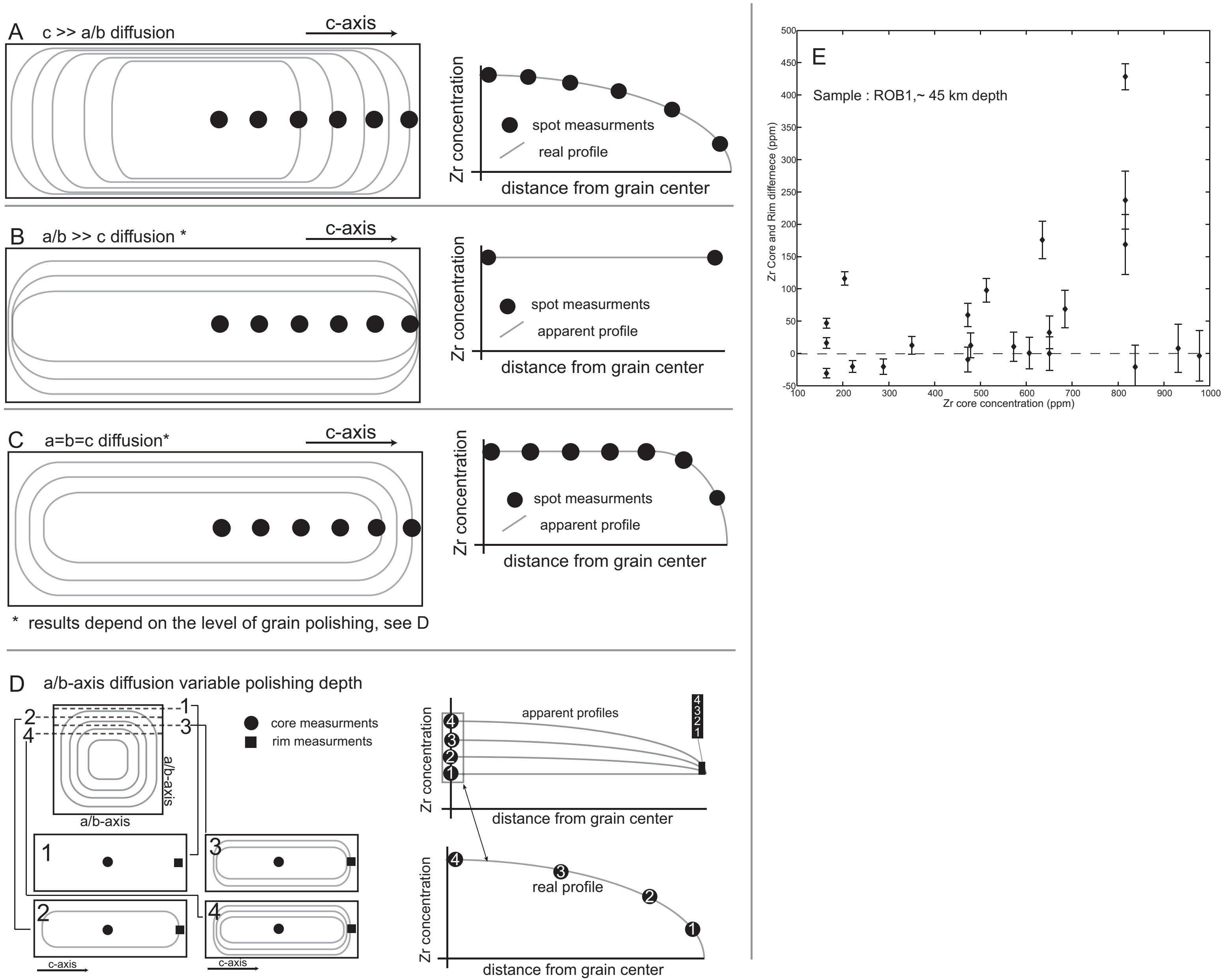
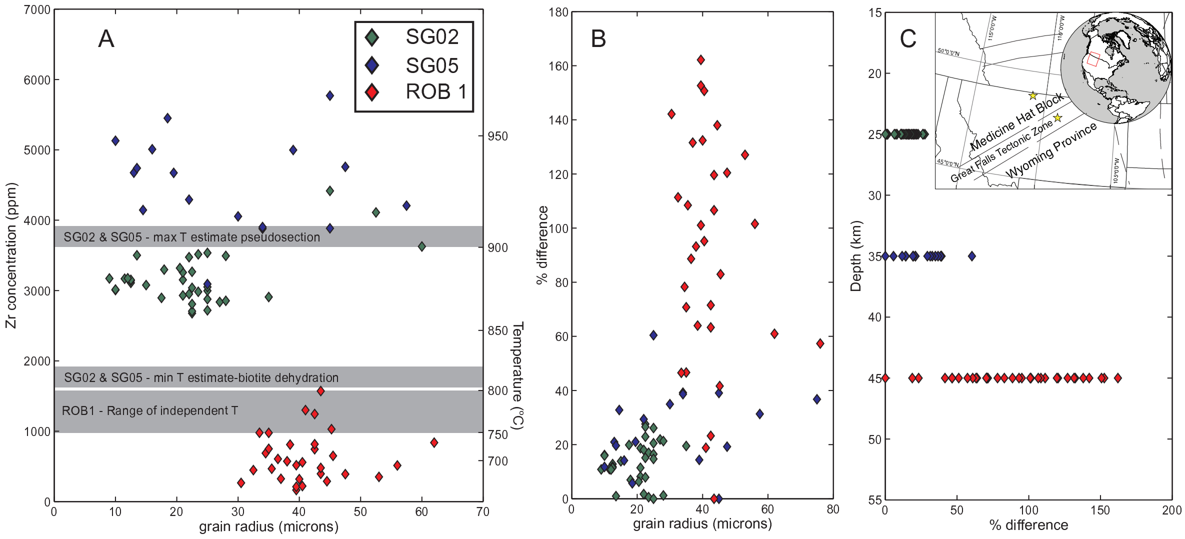

A
c >> a/b diffusion
c-axis
Zr concentration
spot measurments
real profile
distance from grain center
B
a/b >> c diffusion *
c-axis
Zr concentration
spot measurments
apparent profile
distance from grain center
C
a=b=c diffusion*
c-axis
Zr concentration
spot measurments
apparent profile
distance from grain center
* results depend on the level of grain polishing, see D
D
a/b-axis diffusion variable polishing depth
1
2
3
4
a/b-axis
a/b-axis
core measurments
rim measurments
c-axis
c-axis
Zr concentration
apparent profiles
4 3 2 1
distance from grain center
Zr concentration
real profile
distance from grain center
E
Sample : ROB1,~ 45 km depth
Zr Core and Rim differnece (ppm)
-50
0
50
100
150
200
250
300
350
400
450
500
100
200
300
400
500
600
700
800
900
1000
Zr core concentration (ppm)

**Figure4**


A
SG02
SG05
ROB 1
SG02 & SG05 - max T estimate pseudosection
SG02 & SG05 - min T estimate-biotite dehydration
ROB1 - Range of independent T
Zr concentration (ppm)
0
1000
2000
3000
4000
5000
6000
7000
Temperature (°C)
700
750
800
850
900
950
grain radius (microns)
0
10
20
30
40
50
60
70
B
% difference
0
20
40
60
80
100
120
140
160
180
grain radius (microns)
0
20
40
60
80
C
Depth (km)
15
20
25
30
35
40
45
50
55
% difference
0
50
100
150
200
50°0'0"N
45°0'0"N
115°0'0"W
110°0'0"W
105°0'0"W
Medicine Hat Block
Great Falls Tectonic Zone
Wyoming Province

# Figure5

**Click here to download Figure: Figure_5_Zr_Pb_profiles_v2.eps**

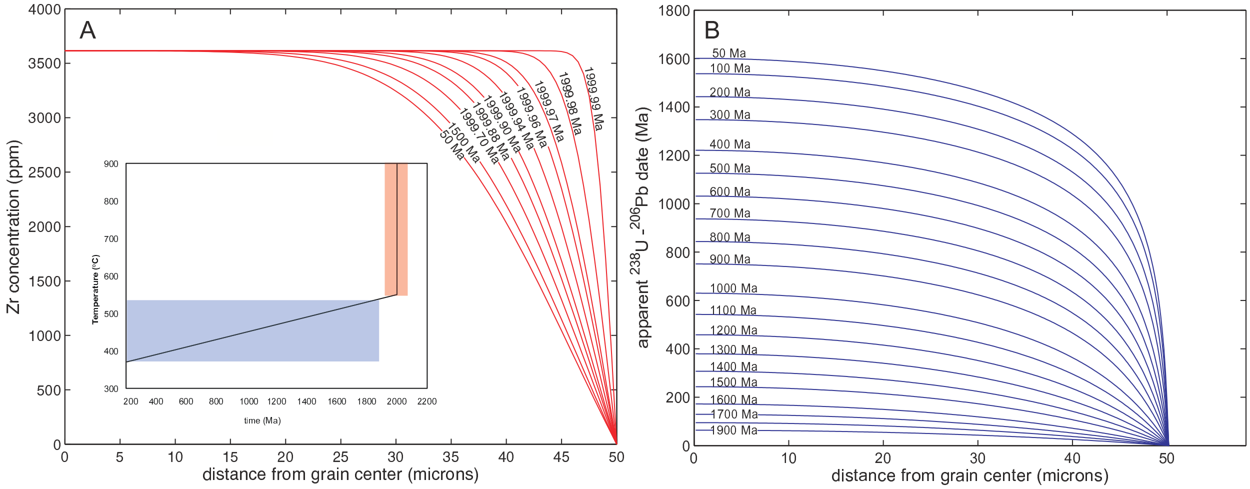
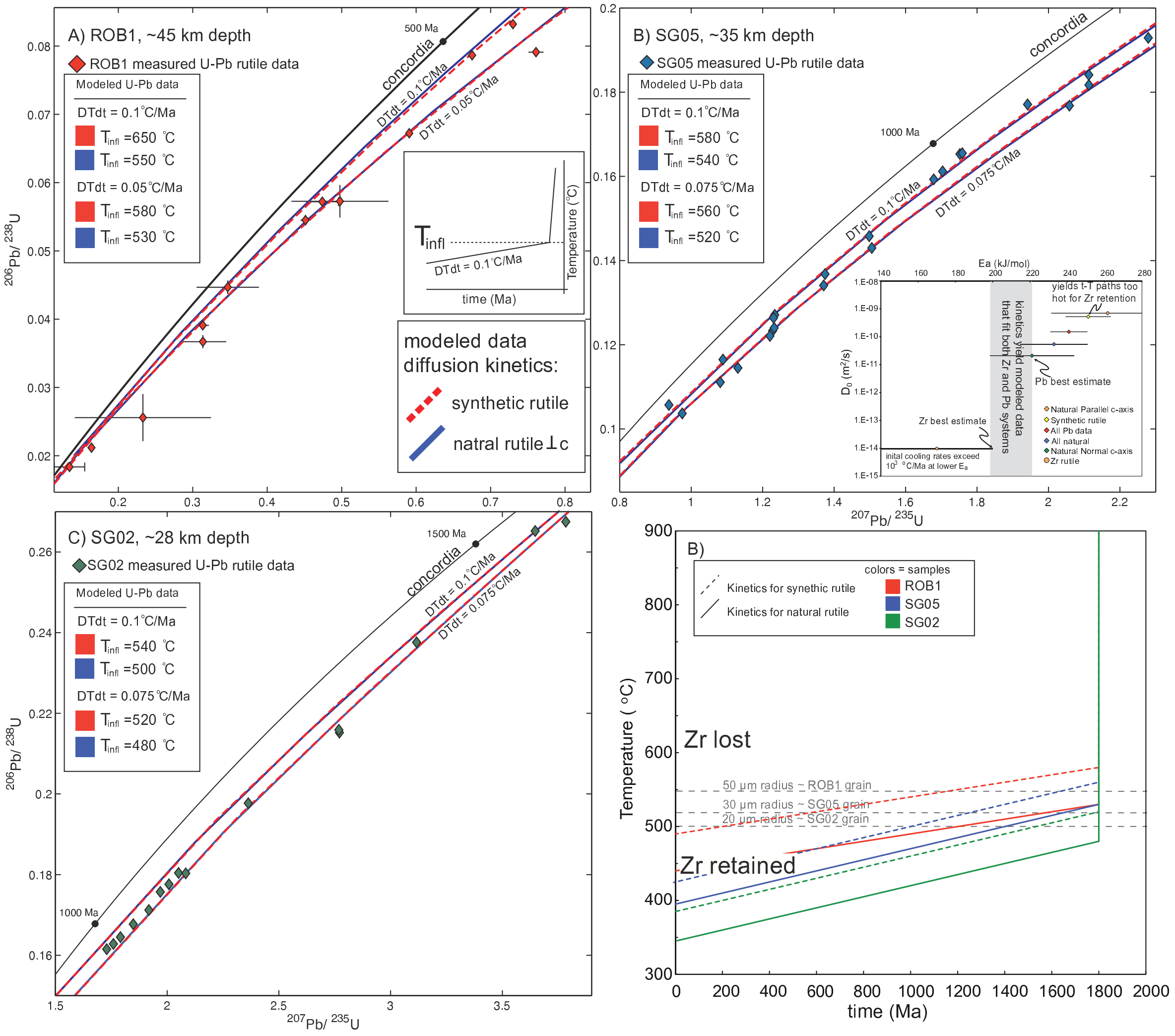


**Figure6**

Click here to download Figure: Figure_6_UPb_Ttpaths.eps



**DR table 1**

DR table 2