Zirconium in rutile speedometry: New constraints on lower crustal cooling rates and residence temperatures

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ABSTRACT

The incorporation of zirconium into the mineral rutile (TiO_2) has been both empirically and experimentally calibrated as a 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 numerical solutions to the diffusion equation provides 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 following high-temperature metamorphism/crystallization and 2) temperature and duration of long-term geologic residence. Zr concentrations measured in rutile from lower crustal xenoliths that resided at 25–45 km depths for 2000 My, 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 a Zr record of these initial temperatures in the center of a rutile crystal with a 50 μm radius requires rapid cooling ($>300\,°C/Ma$) from magmatic/metamorphic temperatures followed by a long-term residence (2000 My) at temperatures $<550\,°C$. This provides a new way to determine cooling rates between 900 and 500 °C and for constraining the temperature of the deep crust. Modeled temperature–time paths using combined rutile Zr and U–Pb geochronological data permit evaluation/refinement of published diffusion kinetics. 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.

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1. Introduction

Creating a comprehensive model for any solid Earth system, whether a study in rock rheology, mantle dynamics or planetary formation, often 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. This previous 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 9.8 e–15 m^2/s, respectively (Cherniak et al., 2007). An important implication derived from this study is that high temperature rocks (800–1000 °C), including the previously studied granulites and high temperature eclogites, will only retain the Zr concentration associated with UHT/HT conditions if cooling rates following these high temperatures are extremely rapid ($>10^4\,°C/M$; (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 intracrystal 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 °C (Fig. 1a) and 2) a maximum estimate for the long-term residence temperature 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

Fig. 1. 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. Note that the boundary at the grain edge changes from high concentrations equivalent to equilibrium temperatures, to concentrations <200 ppm that correlate to lower crustal temperatures <600 °C. This change in boundary condition during cooling permits the diffusive loss of Zr. The Pb system, however, begins with zero retained radiogenic Pb, and does not build a diffusion profile until sufficient time and decreased diffusivity permit 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.

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 (Fig. 1b). 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 provides a measure of cooling rates between 700 and 1000 °C; a temperature range that other thermochronometers remain insensitive to. Determining the amount of Zr lost from rutile 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.
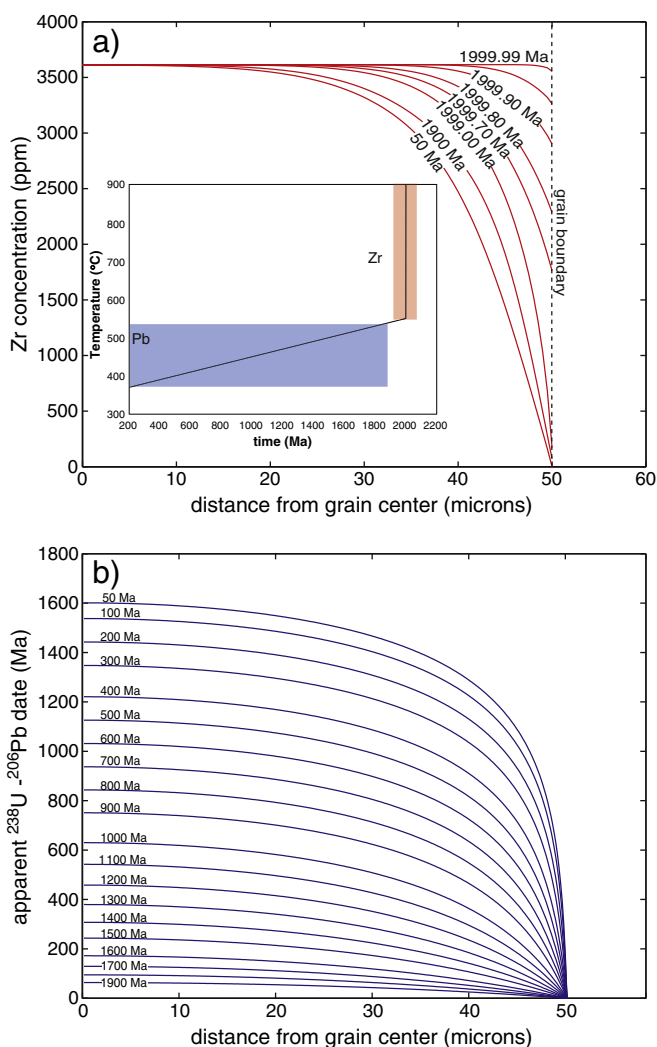
1.1. Geologic applications: high temperature cooling rates and long-term residence temperatures

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 (Baldwin and Brown, 2008; Harley, 1998). Understanding the time-scales and conditions for UHT petrogenesis and the subsequent exhumation of these samples holds important information on the conditions and composition of the deep crust and the plate tectonic processes operating to exhume them (Hacker et al., 2005). Despite the focus on these unusual rocks, the time-scales and processes leading to their subsequent exhumation to the Earth's surface remain unclear (Baldwin et al., 2004; O'Brien and Rötzler, 2003). 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 previously 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. There remains a 100–200 °C discrepancy in lower crustal temperature estimates inferred from different sources of data used for measuring the lithosphere's geothermal gradient. Geothermal gradients produced by mantle xenolith P–T arrays when extrapolated upwards yield lower crustal temperatures of ~500 °C or more (McKenzie et al., 2005). Meanwhile, thermal models utilizing surface heat flux measurements, often yield lower crustal temperatures of 400 °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 and 600 °C (Blackburn et al., 2011; Schmitz and Bowring, 2003). By measuring Zr concentrations in rutile from a suite of lower crustal xenoliths over a range of depths, one can place maximum estimates on the long-term residence temperatures for these samples. The Zr-in-rutile system's sensitivity to holding temperature over geologic time can be employed to place limits on the temperatures experienced at middle to lower crustal depths and resolve the discrepancy between mantle xenolith and surface heat flux/model geothermal gradients. This information will help to inform a new and independent measure of lithosphere temperature conditions as recorded at lower to mid-crustal depths.

2. Methods

To quantify a sample's thermal history over the 1000–500 °C temperature range in which the Zr-in-rutile system is sensitive, 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 intracrystal measurement techniques is often complicated by variations in grain orientation, and level of sectioning into the grain. Because of these variations, any intracrystal Zr measurement from a rutile crystal with a 3-D Zr diffusion profile will lack sufficient spatial control with which to infer any meaningful information about the diffusion profile and thus the time-temperature history of the sample. In short, a singular "spot" analysis represents a spatially uncontrolled sub-sampling of a diffusion profile and by itself has limited significance. Previous ZRT studies have commonly used an ion microprobe (SIMS) or electron microprobe (EMP) techniques for Zr analyses. Because the majority of published ZRT data were acquired using these techniques, the numerical modeling results presented here will focus on extracting information from these in-situ data.

A criterion for evaluating Zr diffusion from intracrystal measurements 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 a particular t–T history (Fig. 2a). Numerical modeling presented here will focus on extracting information pertaining to a sample's time–temperature history based on the retention or loss of equilibrium conditions within the grain center. Importantly, the center retention criterion can be evaluated using SIMS or EMP 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 rutile 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 $\pm 2.5\%$, and the session-to-session reproducibility of the slope is within $\pm 5\%$. 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 were collected from rutile samples mounted length-wise, ground down/sectioned so that the approximate grain center was exposed and polished. Spot analyses were made from both the grain centers and grain tips.

2.2. Modeling Zr diffusion in rutile

Modeled intracrystal Zr diffusion profiles for rutile are produced using numerical forward models and are used to evaluate the temperature and time dependence of Zr retention/diffusion within rutile. 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 (Blackburn et al., 2011; Schoene and Bowring, 2007). The finite difference model employed here utilizes a Crank–Nicholson solution to the spherical form of the diffusion equation and results in an intracrystal Zr concentration profile for any pre-assumed time–temperature path. The spherical form of the diffusion equation
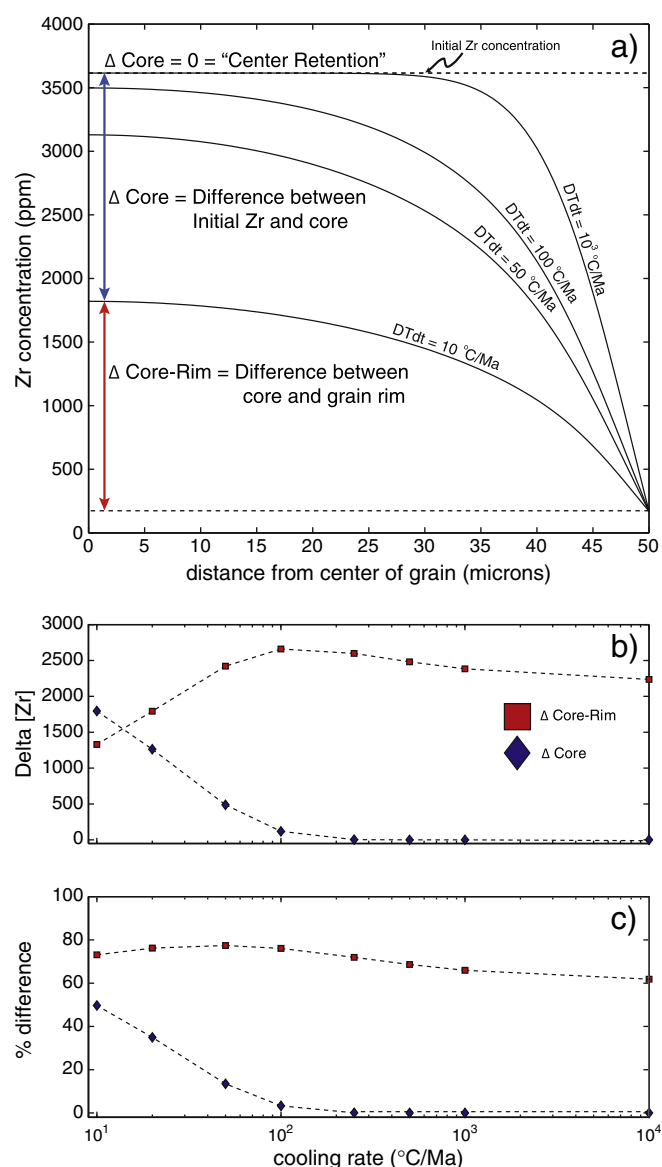
Fig. 2. Effect of initial cooling rate on internal Zr concentration diffusion profiles. Results of forward modeled calculations for internal diffusion profiles with variable cooling rate. (a) A minimum cooling rate of ~300 °C/Ma) is required to maintain center retention ($E_a = 200$ kJ/mol, 50 μm radius). Modeled boundary condition assumes minimum temperature of 600 °C, correlating to 170 ppm Zr. 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 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.

provides a suitable replacement for cylindrical grains with equivalent surface to volume ratios (Meesters and Dunai, 2002). Unlike analytical solutions to the diffusion equation, numerical models are not restricted to a constant diffusivity and allow testing of time–temperature paths in any form. The initial Zr concentration within a modeled rutile crystal 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) (Fig. 1a). Employing this model for measuring rock cooling rates and residence temperatures is based on two assumptions: 1) equilibrium is attained continuously at grain edges at all temperatures and (2) the system is continuously saturated with Zr at all times. These assumptions make it possible to convert all Zr concentrations to temperatures with the experimental calibrations for Zr and temperature. Further, the homogenous initial condition assumes that any variations in the initial Zr concentration as a result of changes in

temperature or Zr activity during rutile crystallization are negligible. Equilibrium conditions at the grain edge are modeled using a boundary condition that changes with temperature and time, reflecting the equilibrium Zr concentration within the surrounding host rock (Fig. 1a) (also using the algorithm from Ferry and Watson (2007)). Exponential cooling paths, typical for rocks in the lithosphere, result in a significant early decrease in temperature and are thus accompanied by an early decrease in Zr at the grain edge. The resulting large concentration gradient between the high Zr concentrations within rutile and low concentrations in the host rock leads to the possible diffusive loss of Zr (Fig. 1a). The purpose of this model is to constrain: 1) the minimum initial cooling rates required to preserve Zr concentrations consistent with metamorphic/igneous temperatures and 2) place a maximum estimate on the long-term residence temperatures required to preserve Zr over geologic time scales.

2.2.1. Cooling rate sensitivity

The retention of Zr concentrations consistent with equilibrium conditions within a rutile grain is highly sensitive to the sample's cooling rate, allowing the system to be employed as a geospeedometer. Forward modeled results indicate that quickly cooled grains retain Zr concentrations consistent with initial temperatures, while slow cooling allows for the diffusive loss of Zr from the rutile crystal, resulting in a rounded Zr profile and (potentially) sufficient loss of Zr so that center retention criteria are no longer met. Fig. 2a shows the internal diffusion profiles for a range of cooling rates (10^1–10^5 °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 (Fig. 2). If the measured core concentration is equal to the initial core concentration, then center retention criteria are met. To utilize the relationship between initial and measured core concentration 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 (Δ core-rim), the relationship between cooling rate and this value is also dependent upon core concentration value (Fig. 2). For a 50 µm radius grain within an initial temperature of 900 °C, cooling rates as low as 500 °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 more than 2500 °C/Ma are required to maintain center retention. At lower initial temperatures of 800 °C, cooling rates of at least 100 °C/Ma will meet center retention for a crystal with a 50 µm radius. Similarly, decreasing the grain radius 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. Constraining maximum residence temperatures

Following initially rapid cooling, the future preservation of Zr in the system is then dependent upon the long-term residence temperature of the system. Forward models assuming initially rapid cooling followed by isothermal holding can be used to explore the relationship between long-term residence temperature and the concentration of Zr within the center of a rutile crystal. The resulting center retention partial retention zone (CR-PRZ) shown in Fig. 3, describes the Zr concentration within the center of crystals with radii between 10 and 50 µm as a function of increasing temperature or depth through the lithosphere. Plotted along with the CR-PRZ are the experimental (Ferry and Watson, 2007; Tomkins et al., 2007; Watson et al., 2006) and empirical calibrations of Zr (Zack et al., 2004) for comparison.

Grains retaining Zr concentrations consistent with initial high temperature equilibrium extend to isothermal holding temperatures of 450–550 °C, where the range in temperature correlates to grain sizes of 10 and 50 µm. At these low holding temperatures, diffusion is slow enough to prevent the diffusive loss of Zr, yielding a reliable record of initial temperature conditions. At temperatures greater than 600 °C, diffusion is sufficient to permit the loss of Zr associated with initial temperatures and instead yield Zr concentrations consistent with the isothermal holding temperatures (Fig. 3). This indicates that rutile residing above 600 °C will yield Zr concentrations that correlate to the sample's temperature at the time of exhumation towards the surface. The ~450–600 °C temperature window between these two regimes marks the CR-PRZ for the system, a region where grains experience partial loss of Zr derived from initial high temperature equilibrium, yet still yield Zr concentrations hundred's to thousand's of ppm higher than the Zr concentrations predicted by the experimental and empirical calibrations for these temperatures (Fig. 3). The convergence between the CR-PRZ at temperatures >600 °C and the experimental calibrations is the direct result of our model's use of a changing boundary condition where the Zr concentration at the grain edge corresponds to the system temperature. If the model employed a zero concentration boundary condition for the grain edge, the CR-PRZ would be near identical at temperatures above 600 °C, yet would decrease to zero concentrations with increasing temperature.

Preservation of high Zr concentrations associated with metamorphism/igneous events can be used to infer a residence at temperatures less than ~550 °C (for durations of 2000 My); a value that is insensitive to initial Zr concentration (i.e. equilibrium temperature) (Fig. 3). This 550 °C estimate 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 cooling at rates <10^3 °C/Ma through 700–1000 °C or holding at temperatures >550 °C. The presence of center retention permits the conclusion that both requirements of a minimum initial cooling rate of 10^3 °C/Ma and long-term residence below ~550 °C were met. Variations from these simple cooling paths, such as short reheating events, can potentially go unrecorded. For example, samples experiencing long-term residence at 450 °C, could still retain center retention while being reheated to 600 °C for 100 My or to 800 °C for <2 My. Higher temperatures or longer durations of reheating will result in the loss of center retention. Predictably, the system becomes more sensitive to reheating events at higher residence temperatures, i.e. durations of reheating are even shorter if long-term residence is 550 °C. The system's sensitivity to reheating events allows users to conclude that if center retention is observed, the majority of the sample's time–temperature history is consistent with rapid initial cooling (>10^3 °C/Ma) followed by residence below 550 °C. By assuming a geothermal gradient for the region, a temperature can be assigned to each xenolith depth, permitting measured Zr data to be compared to the modeled CR-PRZ (Fig. 3). Varying the assumed geothermal gradient will cause the CR-PRZ to move either closer (hotter geotherm) or further (colder geotherm) from the Earth's surface.

2.2.3. Detecting volume diffusion with intracrystal analyses

This study's use of center retention criterion to place constraints on the time–temperature history of the sample provides a means to evaluate histories without the requirement of producing a direct measure of a crystal's internal diffusion profile. Despite this, it is worthwhile exploring how volume diffusion may manifest itself within a dataset produced by intracrystal measurement techniques. Fig. 4 presents a schematic illustration of the data that could result from an internal transect of Zr "spot" analyses oriented parallel to the c-axis of a grain. We consider cases of both isotropic (Fig. 4a) or anisotropic (Fig. 4b and c) diffusion operating. Experimental diffusion data for Zr in rutile were measured for diffusion parallel to the c-axis (Cherniak et al., 2007).
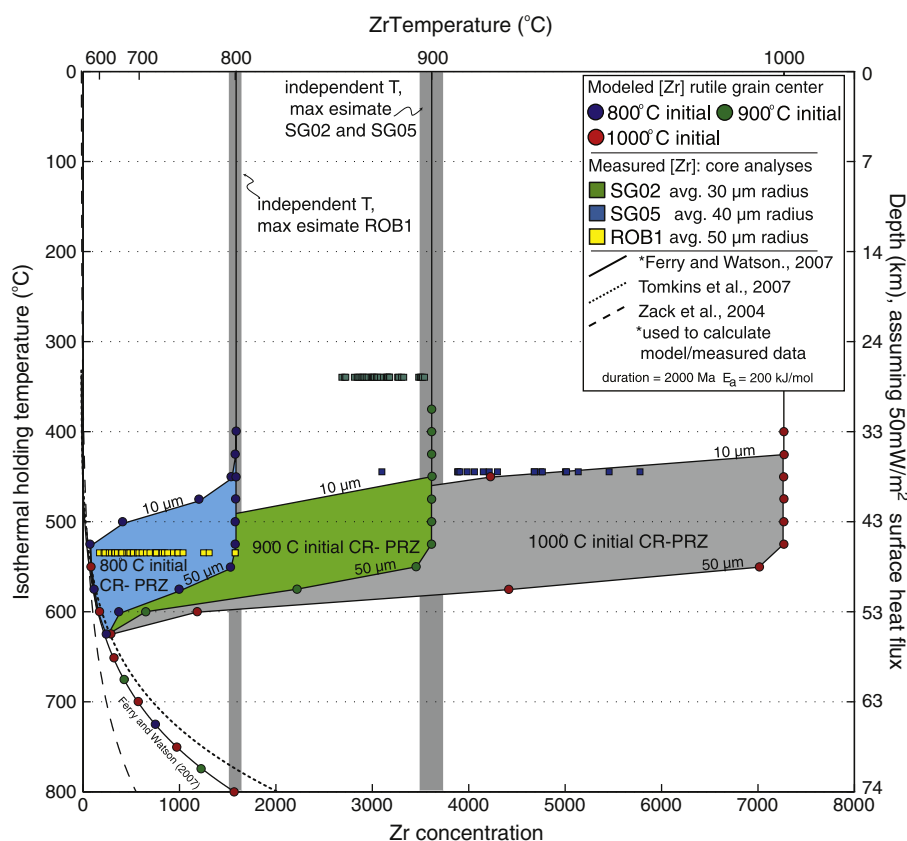
Fig. 3. Center retention partial retention zone (CR-PRZ). Modeled Zr concentrations for the center of a rutile grain plotted as a function of isothermal holding temperature. Model runs assume an initially rapid cooling rate ($>10^3$ °C/Ma) followed by isothermal holding at variable temperatures for a duration of 2000 My. All runs use a maximum E_a of 200 kJ/mol. Center retention is maintained at isothermal holding temperatures less than 450–550 °C (depending on grain size). At temperatures >600 °C diffusion is sufficient to permit loss of Zr associated with initial high temperatures, yielding Zr concentrations that record long-term residence temperatures. The CR-PRZ lies between these two regimes (450–600 °C), where rutile grains retain a portion of Zr derived from initial high temperature equilibrium, yet still yield concentrations far higher than what is predicted by experimental Zr calibrations for these temperatures (<170 ppm). Zr measurements from grain centers for Montana xenoliths are plotted as a function of depth (assuming a geothermal gradient of 50 mW/m2). 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 their history.

In cases of isotropic (Fig. 4a) or anisotropic diffusion where diffusion is faster in the *a/b* direction than *c* (Fig. 4b), the variation in Zr concentration revealed by intracrystal analyses would depend on the depth of sectioning into the grain (Fig. 4d). Any observed variation in concentration from core to rim would yield an *apparent* profile dependent on the level of sectioning into the grain (Fig. 4a). Information pertaining to the time–temperature history of the sample, may be constructed through a series of measurements through the grain parallel to the *a* or *b* axis. If, however, Zr diffusion was anisotropic with the dominant direction of diffusion parallel with the *c*-axis, grains mounted parallel to the *c*-axis (length-wise) would allow the diffusion profile to be mapped by several spot analyses from core to rim (Fig. 4c). Any measured variation with Zr concentration would reflect the actual diffusion profile.

In the case of isotropic or *a/b* dominant diffusion, if the centers of several grains of approximately the same grain size were analyzed, with each grain (unavoidably) sectioned 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. 4d). 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 or high temperatures over long time-scales however, will yield significant variations in Zr concentration from grain to grain. This model predicts an increase in the variability in Zr from the centers of grains with increasing depth into the crust (xenolith depth). These data would only be symptomatic of diffusion and because the data is not spatially controlled one cannot reconstruct a diffusion profile. An enhanced measure of Zr diffusion could be provided by whole grain Zr concentration measurements over a range of rutile

grain sizes, where internal diffusion profiles are inferred based on variations in Zr with grain size.

3. Geologic setting: pressure–temperature–time constraints

Zr concentration in rutile grains was 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. 5c inset). Previous published data for samples SG02 and SG05 from the MHB include, major element/phase thermobarometry and pseudosection analysis, U–Pb rutile thermochronology and UPb zircon geochronology (Blackburn et al., 2011). Rutile and zircon data for sample ROB1 from the GFTZ are included in the appendix. Pressure estimates are 0.8 for SG02, 1.0 GPa for SG05 and 1.3 GPa for ROB1. Temperature estimates from pseudosection construction lie between 800–950 °C for SG02 and 700–900 °C for SG05. Garnet–biotite thermometry for these samples 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 (Barnhart, 2011). 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 (Mueller et al., 2002). Zircon from SG05 and ROB1 record crystallization between ~1680 and 1800 Ma (Blackburn et al., 2011). 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
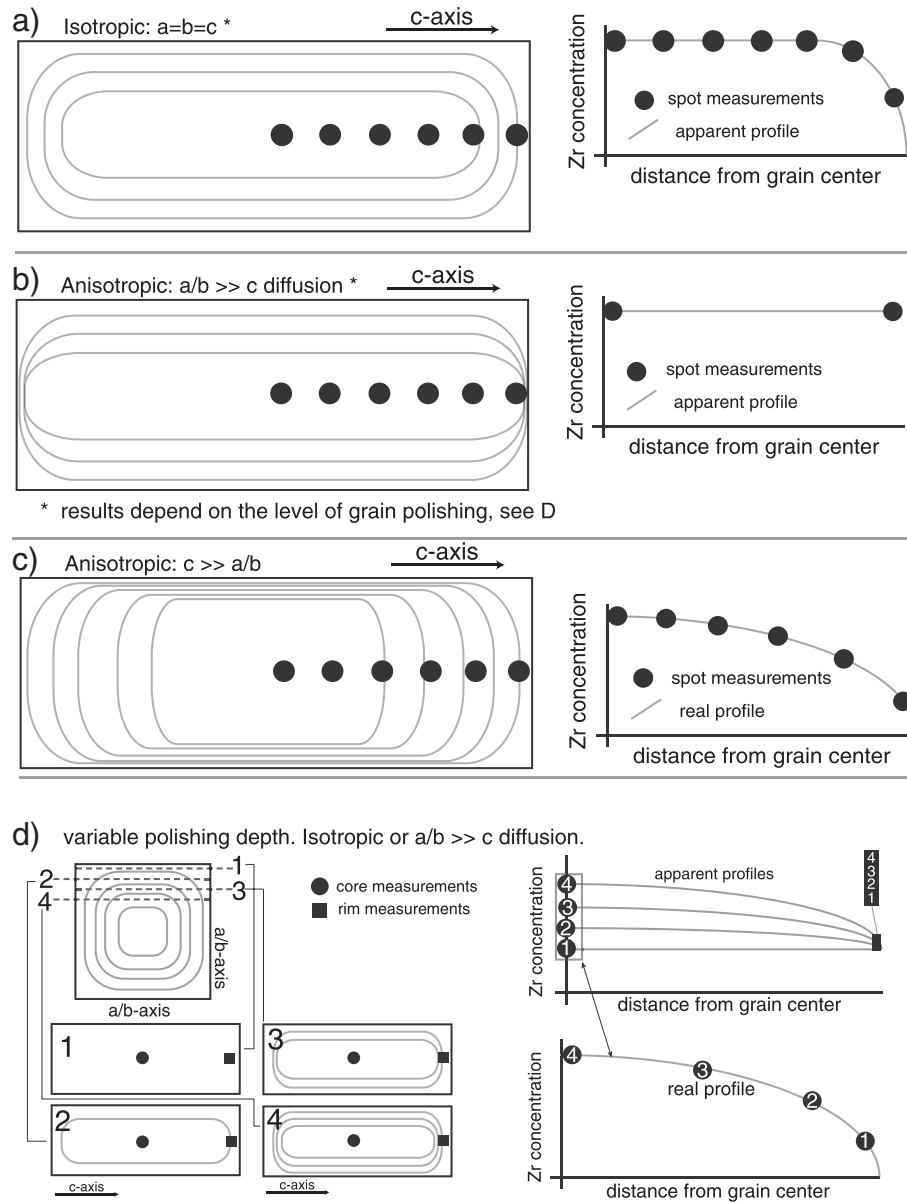
Fig. 4. Cartoon illustrating how volume diffusion manifests itself in intracrystal analyses. The lack of spatial control within a 3-D diffusion profile ensures that intracrystal analyses cannot directly constrain a Zr diffusion profile. Potential data that would result from (a) isotropic diffusion (b) *a–b* axis dominated diffusion and (c) *c*-axis dominated diffusion. If diffusion is isotropic or is faster along the *a/b* axis, the depth of sectioning into grains will affect the data produced from intracrystal analyses.

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 trend of younging downward with sample depth is 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 Figs. 3 and 5). 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. 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 toward the grain edge. A full report of measured Zr data is included in Table A.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. 5a). For the ~40–50 μm grains (radius) 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)
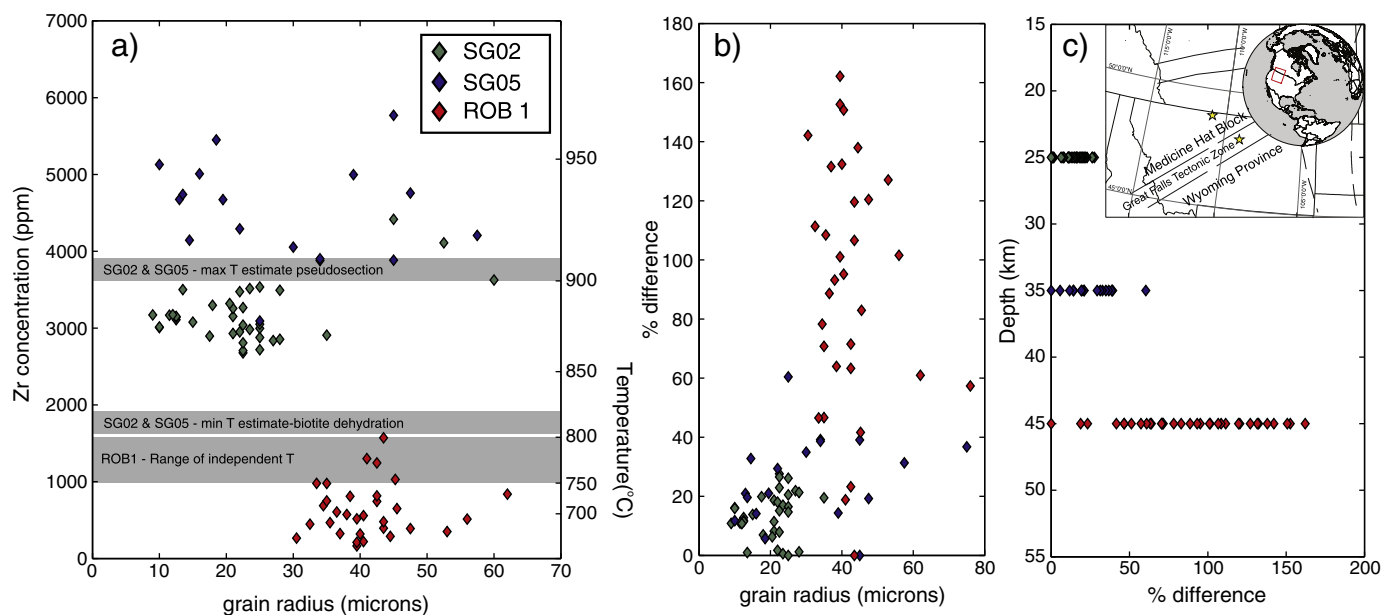
Fig. 5. Zirconium in rutile data for grain centers from Montana xenoliths. Each sample meets center retention, i.e. one or more core analyses match the independent constraints on sample temperature. (a) Over a narrow range of grain sizes, that differs for each sample, the concentration from a grain center 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 to reflect an increase in diffusive loss of Zr with depth.

from SG02 and SG05 requires 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 35 km sample SG05 and up to 130–160% for 30–45 μm grains from the 45 km deep sample ROB1 (Fig. 5c). The trend of increasing percent variation with xenolith residence depth suggests an increase in the diffusive loss of Zr with sample depth (Fig. 5c).

5. Discussion

5.1. Evaluating rapid cooling rates

A limit on the body size of intrusive bodies for the lower crustal samples studied here 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 to the size of the intrusive body and the temperature of the surrounding country rock (t~pluton radius^2)(Spera, 1980). We can refine this calculation using a model for the temperature dependent thermal diffusivity from Whittington et al. (2009) and a analytical half-space solution from Carslaw and Jaeger (1959). For a minimum country rock temperature of 400 °C, the largest intrusive body radius that yields cooling rates consistent with the requirement of the Zr data presented here (>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~pluton radius$^{1.3}$), permitting the intrusion body sizes slightly larger than 5 km (Spera, 1980).

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. Cooling following this event could only occur at rates up to 10^3 °C/Ma if rocks were juxtaposed onto colder material. The fact that center retention is met by samples from the lower crust at all depths between ~25 and 45 km indicates that only small and localized regions of the lower crust, likely smaller than 5 km in radius, are heated during magmatism and/or metamorphism and then cooled rapidly due to low temperatures in the surrounding country rock.

5.2. Differences in t–T path sensitivity between the Zr and Pb systems in rutile

The U–Pb and Zr rutile systems deliver information used to constrain a different portion of sample's cooling history. The rutile U–Pb system is highly sensitive to a sample's low to moderate temperature cooling history (400–600 °C). Though long-term temperatures also control the Zr-in-rutile system, this system is highly sensitive to the initial cooling rate from magmatic or metamorphic temperatures; a temperature range the U–Pb system cannot constrain. The cause for difference in the temperature range at which each system is sensitive to lies in the relative difference between internal concentration gradients of each diffusant at the time of system formation. The Zr-in-rutile system begins with a high initial concentration that correlates to initial temperature conditions. As a rock cools and the concentration at the grain boundary decreases, a large concentration gradient develops between the high Zr concentrations within the grain and the lower concentrations in the surrounding matrix or host rock (Fig. 1a). The system's sensitivity to cooling rate from high temperatures is the direct result of this large concentration gradient; without rapid initial cooling, Zr concentrations that correlate to maximum temperatures would be lost by diffusion. The rutile Pb system however, has zero radiogenic lead at the time of system formation. Only with decreased temperature/diffusion can Pb produced by decay of U begin to accumulate and build a Pb diffusion profile. Fig. 1 plots the internal concentration profiles of Pb and Zr within a rutile grain for the same time–temperature path (Fig. 1 inset). Zr concentration decreases dramatically along the rutile grain rim in a time

frame (<1 My) where 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 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 agree 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
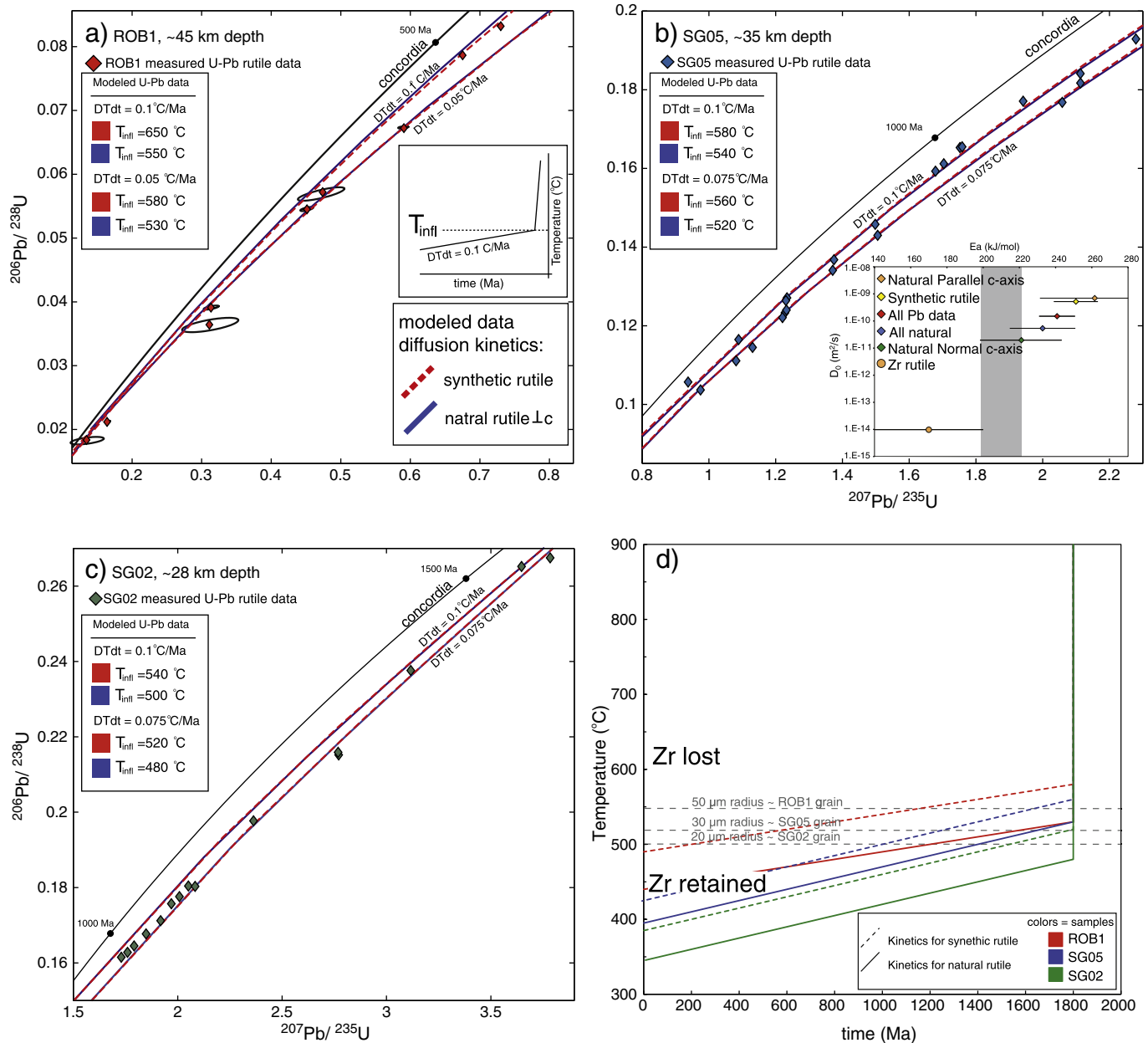
Fig. 6. Refining Zr and Pb rutile diffusion kinetics. The coupled Zr and Pb in rutile systems requires that an acceptable time–temperature path to remain consistent with both systems. (a–c) Measured U–Pb data (Blackburn et al., 2011; Blackburn et al., in press) from Montana xenoliths can be bracketed by forward modeled U–Pb produced following Blackburn et al. (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 an inflection temperature is met. 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 °C 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.

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 affect 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 affect the conclusion of ~0.05–0.1 °C/Ma cooling rates (Fig. 6). Zr activation energy is 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 kinetics for Pb diffusion in rutile measured in a synthetic sample are: $E_a\ 250 \pm 12\,kJ/mol$ and (D_0) of 3.9 e–10 m^2/s (Cherniak, 2000). Additional experiments for Pb diffusion in rutile by Cherniak (2000) used natural rutile samples with experimental data reported for both parallel to *c*-axis and normal to *c*-axis diffusion. Our regression of diffusion kinetics from this data yields an $E_a = 260 \pm 30\,kJ/mol$ and $D_0 = 6.9$ e–10 m^2/s for parallel to *c*-axis diffusion and $E_a = 220 \pm 22\,kJ/mol$ and $D_0 = 2.08$ e–11 m^2/s for normal to *c*-axis diffusion (Fig. 6b inset).

Measured rutile U–Pb data (Blackburn et al., 2011; Blackburn et al., in press) from each xenolith and the forward modeled U–Pb data following Blackburn et al. (2011) are plotted on a concordia diagram in Fig. 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 and 0.1 °C/Ma (Fig. 6). Using the nominal diffusion kinetics for Pb, the inflection temperatures that yield a good fit with the data are consistently too high to permit the retention of Zr (Fig. 6d). To satisfy both systems, the kinetics for Pb diffusion in natural rutile ($220 \pm 22\,kJ/mol$, 2.08 e–11 m^2/s) with a activation energy of at least 220 kJ/mol (Fig. 6b inset) are required. This value lies outside the uncertainty of activation energies reported for the synthetic rutile (Fig. 6a inset).

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 was 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 support a value of 200 kJ/mol, 9.8 e–15 m^2/s for Zr and 220 kJ/mol, 2.08 e–11 m^2/s for Pb diffusion in rutile as the most internally self-consistent values. This corresponds to a Dodson T_C for Pb in rutile of 420–570 °C ($DTdt = 0.1$–$1\,°C/Ma$, $a = 10$–$100\,\mu m$); 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. The initial rapid cooling is followed by prolonged slow cooling at rates between 0.05 and 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 the preserved Zr concentration on the rate at which the sample cools.

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. Measurements of Zr in rutile have nearly always been conducted using intracrystal measurement 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 constrain some aspects of a sample's time–temperature history. This method requires independent measure of the system's 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 system's sensitivity to long-term residence temperature allows an independent maximum constraint to be placed on temperatures within the lower crust 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 perpendicular to the *c*-axis (220 kJ/mol, D_0 of 2.08e-11 m^2/s) are the most self-consistent values. In the presented case study 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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.epsl.2011.11.012.

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