Applications and Limitations of U-Pb Thermochronology to Middle and Lower Crustal Thermal Histories


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Abstract

Volume diffusion of Pb occurs over micron length scales in apatite and rutile at temperatures relevant to the evolution of the middle and lower crust. Continuous thermal history information can be resolved from inversion of intracrystalline U-Pb date profiles preserved within individual grains. Recent developments in microbeam analysis permit rapid measurement of these age profiles at sub-micron spatial resolution, thus heralding a new era for U-Pb thermochronology. Here, we review the theoretical, experimental and empirical basis for U-Pb thermochronology and show that rutile, in particular, presents an exceptional opportunity to obtain high-resolution thermal history information from the deep crust. We present a Bayesian procedure that is well suited to the inversion of U-Pb date profile datasets and balances computational efficiency with a full search of thermal history coordinate space. Complications relevant to accurate application of U-Pb thermochronology are discussed \textbf{i}) theoretically and \textbf{ii}) empirically, using a rutile U-Pb dataset from the lower crust of the Grenville orogeny. Purely diffusive date profiles are shown to be the exception to uniform, or step-like, young profiles, suggesting that processes other than thermally-activated volume diffusion may control U-Pb systematics in rutile residing in the lower crust. However, the data obtained from apparent diffusive profiles systematically match cooling histories inferred from other thermochronometers. This result emphasises the importance of integrating microtextural observations, and trace-element concentrations, with U-Pb age data in order to discriminate between diffusive and non-diffusive Pb transport mechanisms in accessory phases and thus minimize the risk of generating spurious thermal histories.
1. Introduction

Geodynamic processes impart characteristic thermal signatures to the lithosphere that are recorded by the distribution of daughter nuclides in minerals with radiogenic parent elements. The noble gas decay systems $^{40}\text{Ar}/^{39}\text{Ar}$ and $(\text{U-Th})/\text{He}$ harness thermal history information from temperatures $\leq 500$ °C and have been routinely applied to tectonic and geomorphological investigations of the middle and upper crust (Farley, 2002; McDougall and Harrison, 1999). Conversely, volume diffusion of Pb in apatite, rutile and, potentially, titanite is effective at temperatures characteristic of the deep crust (>400 °C).

U-Pb thermochronology can thus be used to constrain cooling from high temperature, and, by inference, exhumation rates of deep seated metamorphic and plutonic rocks in active and ancient orogenic belts (e.g. Cochrane et al., 2014; Flowers et al., 2006; Kooijman et al., 2010; Kylander-Clark et al., 2008; Mezger et al., 1989; Mezger et al., 1991; Möller et al., 2000) as well as long-duration cooling of cratonic lower crust to investigate continent stabilization (e.g. Blackburn et al., 2011; Blackburn et al., 2012; Davis, 1997; Davis et al., 2003; Schmitz and Bowring, 2003; Schoene and Bowring, 2007). Traditionally, U-Pb thermochronology has been applied using whole-grain isotope dilution analysis in which the measured U-Pb date is assigned to a nominal, volume-averaged closure temperature (Dodson, 1973). Whilst this approach has been successfully applied to constrain thermal histories of crustal rocks, interpolation between discrete temperature-time ($T$-$t$) data points derived from whole grain analyses i) yields low-resolution thermal history information and ii) assumes that the effective diffusion radius is the entire grain. In contrast, near-continuous thermal history information can be obtained through numerical inversion of within-grain U-Pb date profiles (Harrison et al.,
Until recently, measurement of U-Pb date profiles was only possible by secondary ion mass spectrometry (Grove and Harrison, 1999; Harrison et al., 2005); however, technological developments have enabled routine measurement of radiogenic Pb and trace-element concentrations at sub-micron spatial resolution by laser ablation inductively-coupled plasma mass spectrometry (e.g. Cottle et al., 2009; Smye and Stockli, 2014; Stearns et al., 2016; Steely et al., 2014). The ease, rapidity, precision, and spatial resolution of LA-ICP-MS herald a new era for deep lithosphere thermochronometry. 

Proliferation of high spatial resolution U-Pb measurements raises the challenge of accurately interpreting intracrystalline U-Pb date distributions as forming in response to a host of diffusive or non-diffusive processes. Various intragrain transport processes, including recrystallization, short-circuit diffusion, secondary growth and volume diffusion, can each affect the topology of a U-Pb date profile. Furthermore, the effect of neighboring mineral phases and the presence/absence of grain-boundary fluids may have significant effects on the boundary conditions for volume diffusion of Pb through accessory phases. In contrast, such effects have been shown to influence the incorporation of extraneous $^{40}$Ar (e.g. Kelley, 2002; Smye et al., 2013) and the efficacy of recrystallization (e.g. Villa and Hanchar, 2017) in K-bearing minerals. Developing an understanding of the kinetic controls on Pb transport over sub-micron length scales in accessory minerals is critical to accurately identifying U-Pb datasets that are suitable for U-Pb thermochronology, and avoiding generation of spurious or non-unique thermal histories. Complementary analysis of trace-element abundances collected from the same
analytical volume as U-Pb dates has the potential to shed light on these processes (e.g. Kylander-Clark, 2017; Kylander-Clark et al., 2013). Motivated by recent methodological advances, this paper reviews and demonstrates the basis for U-Pb thermochronology by evaluating the kinetic processes that control the topology of U-Pb date distributions.

2. (U-Th)/Pb thermochronometry

2.1 Theory

The physics describing volume diffusion-controlled thermochronology are well established (Dodson, 1986; Dodson, 1973; Fechtig and Kalbitzer, 1966); here, we provide an overview of fundamental concepts applied to the U-Pb system in apatite, rutile and titanite. Length scales ($L$) of Pb diffusion through monazite and zircon are predicted to be limited at temperatures $< 900$ °C ($L \approx 1$ µm for monazite and 3 µm for zircon at 900 °C, over 10 Myr); such short length scales of diffusive transport limits their use as thermochronometers to regions of the lithosphere cooling from (ultra-)high temperature conditions (Cherniak and Watson, 2001b; Cherniak et al., 2004). Therefore, we do not consider zircon and monazite further, but the concepts discussed below are relevant to monazite and zircon U-Pb thermochronology.

The concentration of radiogenic Pb, $C_r^i$, at radial position, $r$, within mineral $i$ residing at temperature $T$, for duration $t$, is given by:

$$\frac{\delta C_r^i}{\delta t} = D^i \nabla^2 + S_r$$  \hspace{1cm} (1)

where, $D^i$ is the diffusivity of Pb described by an Arrhenius law ($D^i = D_0^i e^{(-E_a^i/RT)}$), $D_0^i$ is the diffusivity at infinite $T$, $E_a^i$ is the activation energy and $R$ is the universal
gas constant), \( \nabla \) is the Laplacian operator and \( S_r \) represents radiogenic production of Pb, controlled by the spatially-dependent concentration of \( ^{238}\text{U}, ^{235}\text{U} \) and \( ^{232}\text{Th} \). From inspection of Equation 1, the concentration of radiogenic Pb at any point in time and space within a mineral grain reflects a competition between diffusive loss and radiogenic production. The rate of diffusive loss exceeds the rate of production at high temperatures, and vice-versa at low temperatures. Between these two end-member behaviours, there exists a region of \( T(t) \) space in which the rate of diffusive loss is comparable to the rate of radiogenic production; the absolute magnitude of this “partial retention zone” (PRZ) depends on \( D^i \), \( dT/dt \), and \( L \).

Figure 1 shows the relationship between PRZ and U-Pb date profile for single grains of apatite and rutile undergoing cooling during exhumation from the deep crust. Titanite is not considered here due to uncertainties over Pb diffusion parameters that are discussed in section 2.3. We assume here that Pb diffusive loss only occurs at the outermost grain boundary, and that each mineral crystallizes immediately prior to the onset of exhumation at 50 Ma. In this example, progressive exhumation advects heat to shallow crustal levels where conductive heat loss to the surface occurs. These competing effects increase \( dT/dz \) (gray geotherms, Fig. 1a) and dictate that exhuming rocks will experience a monotonically increasing \( dT/dt \) as long as exhumation continues. Figure 1a shows the thermal and vertical motion histories for three rocks initially located at 22.5, 30 and 37.5 km, respectively, that are exhumed along a continental geotherm (initially 680 °C at 40 km) at 1 km/Myr. The shallow sample (yellow markers, Fig. 1a) exhumes through temperatures <400 °C that are cold enough to inhibit significant diffusive loss of Pb from
both apatite and rutile (Fig. 1b); in this case, single grains of both minerals would preserve crystallisation ages at all but their outermost portions. The two more deeply seated samples are exhumed from depths at which initial temperatures are >500 °C; in both cases $L > 5 \mu m$ in apatite and rutile. However, significantly younger U-Pb dates are recorded by apatite grain interiors, whereas U-Pb dates in rutile grain interiors preserve the timing of crystallisation due to slow Pb diffusion. Diffusive rounding and degree of interior younging of the U-Pb date profile is controlled by the duration the rock resides within each mineral’s PRZ. We define PRZs for apatite and rutile as the values of $T(z,t)$ between which 10 and 90 % of radiogenic Pb is retained (gray bands, Fig. 1a). Using experimental diffusivity data, we calculate that the rutile PRZ spans ~13 km and temperatures between ~560 and 650 °C, whereas the apatite PRZ spans ~12 km and temperatures between 430 and 520 °C. Using this formulation, the depth and temperature interval of the PRZ vary with exhumation rate; slower exhumation decreases the depth range but increases the absolute depth of each PRZ. These calculations demonstrate the sensitivity of age profile topologies to different forms of $T(t)$ and also show that combined apatite and rutile thermochronology may independently constrain thermal history information over a temperature interval of ~250 °C. In constrast to traditional bulk-grain thermochronology, inversion of U-Pb date profiles for $T(t)$ can be done without any external constraints, avoiding potential biasing of thermal history.

Traditionally, U-Pb thermochronology has been applied to deep crustal rocks using the bulk closure temperature approach, in which a volume-average mineral age is correlated with a nominal closure temperature ($T_c$) that represents the temperature at which the grain
effectively closes to Pb loss during cooling. Based on Dodson’s $T_c$ concept (Dodson, 1973), this approach carries with it several stringent requirements, including knowledge of mineral-specific diffusion parameters, a zero-Pb concentration boundary condition, and constant, monotonic cooling. Whilst informative, the closure temperature approach yields thermal histories of limited resolution. This is apparent from inspection of the closure temperature ($T_c$) equation

$$T_c = \frac{E_a}{R \ln[AR T_c^2 D_0 / L^2 / E_a dT/dt]}$$

where $A$ is a geometry factor and the other variables are as introduced previously. The equation shows that $T_c$ is proportional to the inverse of the natural logarithm of a large product term, effectively dampening the sensitivity of $T_c$ to variations in $dT/dt$. Solving instead for time-dependent variations in $dT/dt$–as opposed to bulk $T_c$–provides a more sensitive means to calculate lithospheric thermal histories.

Figure 2 shows calculated U-Pb date profiles for a rutile grain (150 µm spherical radius) that has undergone a variety of different thermal histories, including slow cooling (black lines), reheating (purple), residence at elevated temperatures (orange), and two-stage growth at low temperature (red). The spatial integral of each $^{206}$Pb concentration profile ($\int_a C(r) dr$, where $a$ is the grain radius and $C$ is $^{206}$Pb concentration) is identical in each case, yielding whole-grain ages of 40 Ma with a homogenous distribution of $^{238}$U. These calculations illustrate the inability of bulk grain analysis to differentiate between various radiogenic Pb distributions that record thermal information of geodynamic interest.

2.2 Previous applications of U-Pb thermochronology to continental lithosphere
There is a large body of literature connecting U-Pb dates and distributions to the thermal structure of continental lithosphere. Motivated by the ubiquity of discordant zircon U-Pb dates, Wetherill (1956) devised a graphical method based on U-Pb concordia to assess the extent of diffusive loss of Pb following crystallization. Zircon grains that have undergone varying degrees of Pb loss during a post-crystallization thermal event should define a linear array in concordia space (i.e., discordia) with the upper and lower intercepts recording the timing of crystallization and the timing of reheating, respectively. In this model of episodic Pb loss, the position of an analysis along discordia is controlled by the length scale of Pb diffusion; smaller diffusive domains retain ages closer to the timing of reheating than larger domains. We note that Wetherill’s secondary Pb loss model is predicated on the assumption that a discordant array of U-Pb dates formed during reheating. Tilton (1960) followed by developing an analytical model for the continuous loss of radiogenic Pb, analogous to slow cooling. In contrast to Wetherill’s model, the continuous loss of Pb during cooling results in a curvilinear discordia. Tilton’s model is predicated on the assumption that the rate of Pb diffusion is not temperature-dependent.

Whilst both of these works were motivated by discordant zircon U-Pb datasets—a mineral now known to only lose Pb by diffusion under extreme temperatures (e.g. Cherniak and Watson, 2001a) or when metamict (e.g. Geisler et al., 2007)—their graphical and numerical approaches are relevant to minerals in which Pb is diffusively mobilized, including apatite, rutile and (potentially) titanite.

Mezger et al. (1989) observed that rutile U-Pb dates from the Archean Pikwitonei granulite terrane and the Proterozoic Adirondack terrane correlated with grain
dimensions. In conjunction with existing thermochronometric data, they used observed age versus grain-size correlations to estimate that the rutile U-Pb system closed to diffusive Pb loss at ~420 °C. Schmitz and Bowring (2003) collected whole-grain U-Pb dates from lower crustal xenoliths to constrain the thermal evolution of cratonic lithosphere beneath South Africa. Specifically, they demonstrated that rutile is a particularly effective thermochronometer at lower and middle crustal temperatures.

Schoene and Bowring (2007) used the topology of U-Pb date versus grain-size curves in conjunction with a numerical model of Pb diffusion to show that the Barberton Greenstone Belt underwent slow, non-linear cooling during the Archean and not later reheating. More recently, Blackburn et al. (2011) used a numerical solution to Eq. 1 to demonstrate that the combined effects of variable production rate and diffusion result in data topologies on a concordia diagram that permit distinction between slow cooling and reheating thermal histories. This method was subsequently applied to rutile and titanite grains from lower crustal xenoliths to estimate long-term cooling rates of the North American craton (Blackburn et al., 2012).

Each of the above studies focused on the use of whole-grain U-Pb thermochronology, but other studies have focused on in-situ measurement of intracrystalline U-Pb date profiles. Grove and Harrison (1999) measured Th-Pb date gradients in the outermost 1 µm of Himalayan monazite crystals using ion probe depth profiling. Sampled at 500 Å, the age profiles were interpreted as representing diffusive closure profiles that formed during rapid Pliocene cooling in the hanging wall of the Main Central Thrust. This study was the first to demonstrate the utility of directly inverting (U/Th)-Pb closure profiles for near-
continuous thermal history information. A number of subsequent studies have showed
that U-Pb closure profiles can be coarsely sampled using in-situ laser ablation traverses
across individual mineral grains (e.g. Vry and Baker, 2006; Warren et al., 2012; Zack et
al., 2011b). Kooijman et al. (2010) used such an approach to measure U-Pb closure
profiles in slowly cooled rutile from the Pikwitonei granulite terrane. Inversion of the
profiles using an updated closure temperature model showed that cooling of the terrane
slowed over time, from initial rates of ~2 °C/Myr to 0.4 °C/Myr. Using a combination of
whole-grain and laser ablation spot traverses, Cochrane et al. (2014) showed that apatite
U-Pb systematics are a sensitive recorder of transient variations in cooling rate between
~370 and 570 °C. Smye and Stockli (2014) applied laser ablation depth-profiling to
measure diffusive U-Pb date profiles in the outermost 30 µm of lower crustal rutile from
the Ivrea Zone. Numerical inversion of the profiles resulted in identification of a
reheating event, previously unrecognised by 40Ar/39Ar and K-Ar whole-grain
thermochronology (Siegesmund et al., 2008, and refs therein). Finally, Kohn and Corrie
(2011) and Stearns et al. (2016) applied laser-ablation depth profiling to collect U-Pb
dates and trace-element concentrations in the rims of individual titanite grains from the
Greater Himalayan Sequence and Pamir gneisses, respectively. In both studies, the
titanite grains experienced temperatures above 700 °C, theoretically sufficient to drive Pb
diffusion over micron length scales; however, Zr and Pb concentration profiles do not
conform to the topology predicted by diffusive loss from grain boundaries, even though
some of them mimic typical diffusion profiles. These observations suggest that growth
and/or recrystallization controlled the distribution of Zr and radiogenic Pb.
2.3 Pb diffusion kinetics

Application of U-Pb thermochronology requires \textit{a priori} knowledge of the diffusivity of Pb through the target mineral lattice. Here, we review experimental and empirical constraints on Pb diffusion rates through apatite, rutile and titanite, noting that an extensive body of literature exists concerning the energetics of Pb diffusion through accessory phases (e.g. Cherniak, 2010; Van Orman and Crispin, 2010 and refs therein). Specifically, we focus on the comparison between laboratory- and field-based estimates of Pb diffusivity.

2.3.1 Experimental Pb diffusivities

Diffusion of Pb through apatite was first experimentally measured by Watson et al. (1985) at temperatures between 900 and 1250 °C and, subsequently, at lower temperatures, between 600 and 900 °C, by Cherniak et al. (1991). Arrhenian parameters from both studies are in broad agreement and predict closure of apatite grains to Pb loss between ~450 and ~550 °C for 100-1000 µm diffusion radii cooling at 1 °C/Myr. Lead diffusion through natural and synthetic rutile was experimentally measured by Cherniak (2000) at temperatures between 700 and 1100 °C using Rutherford Backscattering Spectrometry (RBS). Despite different trace-element compositions, results for diffusion through natural and synthetic rutile are similar. The resultant diffusion law yields closure temperatures between ~590 and ~720 °C for the same cooling parameters considered above for apatite. Pb diffusion in natural titanite was measured by Cherniak (1993) also using RBS; these parameters result in orientation-independent closure temperatures between ~570 and ~660 °C for the thermal history and diffusion domain sizes used for
apatite above. Therefore, experimentally derived Pb diffusivities define an order of relative closure to Pb loss, $T_{\text{rutile}} > T_{\text{titanite}} > T_{\text{apatite}}$.

2.3.1 Empirical constraints on Pb diffusivities

Despite the influence that experimentally-derived Pb diffusion rates have had on the interpretation of thermochronometric datasets from middle and lower-crustal terranes, a significant number of empirical U-Pb studies show that rutile U-Pb dates are younger than co-genetic titanite dates, contradicting the experimentally-based closure order (e.g. Bibikova et al., 2001; Christoffel et al., 1999; Connelly et al., 2000; Corfu and Easton, 2001; Cox et al., 1998; Flowers et al., 2005; Flowers et al., 2006; Kylander-Clark et al., 2008; Mezger et al., 1989; Möller et al., 2000; Norcross et al., 2000; Schärer et al., 1986; Schmitz and Bowring, 2003; Wit et al., 2001). Various explanations for this disagreement between experimental and empirical estimates of Pb diffusivities have been presented, including: i) fast diffusion of Pb through rutile facilitated by a reduced diffusion domain size by ilmenite and zircon exsolution (Lee, 1995; Zack and Kooijman, 2017), or by the presence of hydrogen within defective natural rutile crystals (Schmitz and Bowring, 2003); ii) slower diffusion of Pb through titanite than predicted by experiments (Gao et al., 2012; Kohn, 2017; Marsh and Smye, 2017; Schärer et al., 1994; Spencer et al., 2013; Zhang and Schärer, 1996); and iii) mechanisms other than volume diffusion as the dominant process controlling Pb mobility through titanite. Regarding the latter point, a growing body of evidence suggests that recrystallization or coupled substitutions are the dominant mechanisms controlling U-Pb and trace element systematics in titanite (Garber et al., 2017; Marsh and Smye, 2017; Stearns et al., 2016; Stearns et al., 2015).
To further assess compatibility between experimental and empirical estimates of Pb diffusivities in U-Pb thermochronometers, Figure 3 shows a comparison between empirical and laboratory-based Pb diffusivities for apatite (Fig. 3a), rutile (Fig. 3b), and titanite (Fig. 3c). Estimates of $D_{\text{Pb}}$ are calculated from the empirical data using a forward modelling procedure in which best fit values of $E_a$ and $D_0$ are determined by minimizing the misfit between computed and published U-Pb date profiles or age-grain size curves for a specified thermal history. We defined the misfit as $\chi^2 = \sum_{i=1}^{n} \left( \frac{(t_d^i - t_m^i)}{\sigma} \right)^2$, where $n$ is the total number of data points, $t_d^i$ is the measured age, $t_m^i$ is the computed age and $\sigma$ is the data point uncertainty. This analysis is appropriate for estimating permissible values of $D_{\text{Pb}}$ through apatite and rutile due to the significant number of U-Pb datasets in which the U-Pb systematics have been shown to be dependent on grain dimension and in which the thermal history is independently constrained by other thermochronometers. However, due to its elevated $T_c$, there is a scarcity of studies that directly constrain the intracrystalline U-Pb date distribution profile for titanite; accordingly, estimates of $D_{\text{Pb}}$ in titanite were calculated with a different approach. Using estimates of the duration spent ($t$) at peak conditions, grain size ($a$) and fraction of radiogenic Pb retained, we used values of the combined parameter $Dt/a^2$, which is relevant for different degrees of Pb loss from a purely spherical mineral grain (Crank, 1979, his eq. 6.19), to solve for $D_{\text{Pb}}$. For reference, values of $Dt/a^2 < 0.03$ are required for the central region of a crystal to preserve its original U-Pb date; values of $Dt/a^2 > 0.40$ are required for >95% Pb loss from the mineral core.
Several thermochronometric studies place relatively precise limits on $D_{Pb}$ in apatite for crustal temperatures. DeWitt et al. (1984) measured whole-grain U-Pb apatite dates from Proterozoic crystalline basement of the Halloran Hills, southeastern California. Rocks that yielded 1710 Ma zircon dates also produced concordant, ~140 Ma apatite dates, interpreted to suggest that the apatite U-Pb dates record resetting during Jurassic metamorphic reheating. As cogenetic hornblende K-Ar ages are also reset, peak temperatures during the Jurassic event must have exceeded ~500 °C (Harrison, 1982).

Assuming >90 % loss of radiogenic Pb ($Dt/a^2 > 0.40$), the reported grain diameter of 200 µm and durations of reheating from 10 to 50 Myr results in minimum values for $D_{Pb}$ in the range 1-5 × 10^{23} m^2/s (DeW84 box, Fig. 3a). Cliff and Cohen (1980) showed that apatite from a metatonalite of the Hercynian basement complex in the Eastern Alps was reset during Alpine Barrovian metamorphism at 20-30 Ma. Recent geochronological work shows that peak metamorphic temperatures between 550 and 650 °C persisted for <10 Myr following the Alpine collision at ~35 Ma (Schneider et al., 2015; Smye et al., 2011). For grain radii between 200 and 500 µm, values of $D_{Pb}$ greater than 3 × 10^{22} and 5 × 10^{23} m^2/s, respectively, are required to promote >90 % Pb loss (C&C80 box, Fig. 3a).

Permissible combinations of $E_a$ and $D_0$ were also derived from three U-Pb apatite whole-grain TIMS datasets from localities with well-constrained cooling histories. Gulson (1984) constructed a $^{207}$Pb-$^{206}$Pb apatite isochron from whole-grain mineral separates collected from the slowly-cooled Broken Hill orebody, New South Wales, Australia. Diffusivities were calculated using the $^{40}$Ar/$^{39}$Ar-based thermal history for the Broken Hill block proposed by Harrison and McDougall (1981). Best-fit diffusivities form a poorly defined (~4 log units range in $D_{Pb}$) envelope that overlaps with the experimental
regression ($G84$ envelope, Fig. 3a). The large uncertainty associated with this estimate reflects uncertainty in the cooling rate (2-4 °C/Myr) and range of grain diameters considered (100 µm to 1 mm). Estimates of $D_{Pb}$ were also derived from the apatite dataset of von Blackenburg (1992), who measured whole-grain U-Pb ages from apatite in a granodiorite and tonalite sample pertaining to the Bergell pluton, Central Alps. This dataset is of particular value as it permits assessment of $D_{Pb}$ in apatite ($vB92$ envelope, Fig. 3a) from a thermal history characterised by fast cooling, > 80 °C/Myr (Samperton et al., 2015; Villa and von Blankenburg, 1991), in contrast to the Broken Hill calculation. Finally, Krogstad and Walker (1994) showed that the cores of large (1-2 cm diameter) apatite crystals yield concordant U-Pb ages that are 15-40 Ma younger than the age of crystallization of the Tin Mountain pegmatite body in the Black Hills, South Dakota. Precise U-Pb monazite, Rb-Sr muscovite, and K-Ar mica analyses independently constrain cooling rates to 2-3 °C/Myr (Redden et al., 1990; Riley, 1970), enabling determination of a tightly constrained (< 2 log units) envelope of permissible values of apatite $D_{Pb}$ ($K&W94$ envelope, Fig. 3a).

Each of these calculations resulted in estimates of $D_{Pb}$ in apatite that overlap the experimentally-derived values of Cherniak et al. (1991). With the caveat that we considered only five whole-grain U-Pb apatite datasets, this analysis implies that i) the experimental diffusion parameters accurately estimate $D_{Pb}$ in natural apatite regardless of cooling rate and ii) the effective diffusion domain for Pb in apatite is comparable to, or defined by, grain dimensions.
For analysis of $D_{\text{Pb}}$ in rutile, we considered three U-Pb datasets that clearly demonstrate a length scale dependence of U-Pb date on either grain size or distance from the crystal rim. Mezger et al. (1989) showed that U-Pb rutile dates from the Proterozoic Adirondack terrane correlate with grain size. Combining pre-existing zircon, garnet and monazite U-Pb dates with amphibole and biotite $^{40}\text{Ar}/^{39}\text{Ar}$ dates, the authors estimated a time-integrated cooling rate for the Adirondack Highlands of 1.5 °C/Myr between 1030 and 800 Ma; using this cooling rate they assigned values of $T_c$ of 420 °C for grain radii between 90 and 210 µm and 380 °C for grain radii between 70 and 90 µm. However, subsequent reinterpretation of these data in light of upward-revision of values of $T_c$ for monazite and titanite results in values of $T_c$ between 500 °C and 540 °C (Vry and Baker, 2006). We solved for permissible combinations of $E_a$ and $D_0$ that best fit Mezger’s whole-grain rutile U-Pb ages from the Adirondack Highlands; the resultant $D_{\text{Pb}}$ envelope ($M89$, Fig. 3b) overlaps experimental estimates of $D_{\text{Pb}}$ between ~700 and 800 °C. Vry and Baker (2006) used LA-MC-ICP-MS to collect in-situ Pb-Pb ages over the outer 300 µm of mounted rutile crystals from granulite facies rocks of the Reynolds Range, Australia. Using the established cooling rate of 2-3.5 °C/Myr, we estimated $D_{\text{Pb}}$ by minimizing the misfit between Vry’s Pb-Pb dates and those calculated over a 300 µm depth increment for rutile grains with diameters between 500 µm and 2 cm. The resultant best-fit envelope ($V06$, Fig. 3b) is relatively imprecise, spanning ~3 log units in $D_{\text{Pb}}$, which reflects the range of cooling rates considered. Finally, Kooijman et al. (2010) also used in-situ LA-ICP-MS to collect $^{207}\text{Pb}/^{206}\text{Pb}$ age profiles across individual grains of metamorphic rutile from granulite facies metapelites of the Archean Pikwitonei terrane, Manitoba, Canada. Traverses of 35 µm spots across 15 grains with diameters between
120 and 280 µm yielded concordant ages decreasing by ~200 Ma from core to rim. This work built upon the previous work of Mezger et al. (1989) who established that rutile U-Pb systematics in the Pikwitonei granulites exhibited a strong grain-size dependence. Following Mezger et al. (1989) and Kooijman et al. (2010), we calculated $D_{Pb}$ using time-integrated cooling rates between 0.5 and 1.5 °C/Myr by assessing the misfit between modelled and observed $^{207}$Pb/$^{206}$Pb age profiles. Due to the well-defined nature of the closure profiles, our analysis resulted in a precise best-fit $D_{Pb}$ envelope ($K10$, Fig. 3b) that spans 1-2 log units.

Each of the field-based rutile U-Pb datasets yield estimates of $D_{Pb}$ that are both internally consistent and in excellent agreement with the experimental results of Cherniak (2000) between 650 and 750 °C. Our analysis of these three rutile U-Pb datasets demonstrates that laboratory rates of Pb diffusion can be extrapolated down-temperature to accurately interpret rutile U-Pb ages under conditions relevant for the middle and lower crust. This further highlights the potential for rutile to be used as a high-temperature U-Pb thermochronometer.

Empirical estimates of $D_{Pb}$ in titanite are complicated by the fact that titanite can react and grow over an expansive $P$-$T$ range, encompassing conditions well beneath its $T_c$ (e.g. Frost et al., 2001; Kohn, 2017). Furthermore, there is a scarcity of studies that document a length-scale dependency of U-Pb dates in titanite crystals. Here, we expand the compilation of estimates of $D_{Pb}$ in titanite from Kohn (2017) using the combined parameter $Dt/a^2$, as introduced above. Verts et al. (1996) dated whole titanite grains
along a traverse through a contact aureole surrounding the Red Mountain pluton, Laramie
Anorthosite Complex, Wyoming. Titanite grains in samples that experienced $T > 700 \, ^\circ C$
were shown to be completely reset to the age of pluton emplacement, whereas samples
that experience peak $T < 700 \, ^\circ C$ define an array of ages spread between emplacement and
a pre-emplacement regional metamorphic event. Samples within ~0.6 km of the pluton
are estimated to have experienced peak temperatures between 700 and 1030 °C for $10^4$-
$10^5$ years; combined with observed grain diameters of 100-400 µm, we estimate that $D_{Pb}$
exceeded $2 \times 10^{-20} \, m^2/s$ ($V96$, Fig. 3c). This estimate is valid for $T$ between 700 and 1030
°C, but the authors acknowledged that “...young U-Pb sphene ages in samples at greater
distances must be produced by metamorphic growth of sphene.” Scott and St-Onge
(1995) obtained whole-grain U-Pb ages from metamorphic titanite in a mafic tonalite
gneiss from the Ungava/Trans-Hudson Orogen, Canada. They showed that in one sample,
titanite grains ranging from 100 to 1000 µm in diameter yielded identical dates. Peak
conditions for the metamorphic event were precisely constrained by multimineral
thermobarometry to between 660 and 700 °C for <70 Myr. Under these conditions,
diffusion rates $<3 \times 10^{25} \, m^2/s$ (S&SO95, Fig. 3c) are required for a 50 µm radius titanite
grain to retain radiogenic Pb (i.e. $Dt/a^2 < 0.03$). Garber et al. (2017) showed that the cores
of Precambrian titanite crystals from the Western Gneiss Region, Norway, escaped
resetting despite being subjected to peak temperatures of 750-800 °C for 20-40 Myr
during Caledonian metamorphism. For a titanite crystal of 200 µm diameter to preserve
Precambrian core ages requires that $D_{Pb} < 4 \times 10^{25} \, m^2/s$ (G17, Fig. 3c). Marsh and Smye
(2017) used LA-ICP-MS to collect U-Pb spot age profiles across large (~0.5 mm radius)
titanite grains from the Grenville orogen. Despite peak metamorphic temperatures of 750-
800 °C that persisted for <50 Myr, the authors did not observe any systematic core-to-rim age variability. Retention of Pb under these conditions requires that $D_{Pb} < 2 \times 10^{25} \text{ m}^2/\text{s}$ (M&S17, Fig. 3c). Finally, Holder et al. *in review*, used LA-ICP-MS to directly measure Pb and trace element concentration profiles in large (0.5-1 cm diameter), ultrahigh temperature titanite from southern Madagascar that conform to diffusion theory. They showed that the observed length scales of Pb diffusion through titanite from two samples that experienced peak temperatures of 750-800 °C and 900-1000 °C are consistent with values of $D_{Pb}$ from $-3 \times 10^{21}$ to $-1 \times 10^{22} \text{ m}^2/\text{s}$ and from $-2 \times 10^{25}$ to $-6 \times 10^{27} \text{ m}^2/\text{s}$, respectively ($H1$ and $H2$, Fig. 3c).

Our analysis demonstrates that, between 700 and 1000 °C, Pb diffusion in natural titanite occurs at rates that are 2-4 log units slower than predicted by experiments Cherniak (1993), similar to experimental rates of Sr diffusion (Cherniak, 1995)(Fig. 3c), as previously suggested by Garber et al. (2017), Kohn, (2017), Kohn and Corrie (2011), Marsh and Smye (2017) and Stearns et al. (2016; 2015). This shows that titanite U-Pb dates derived from crustal rocks are more likely to record processes other than thermally-enhanced volume diffusion, such as deformation, fluid flow, and recrystallization. Empirical studies have shown that all, some, or none of these behaviours may be significant in titanite during thermal events; though in some cases metamorphism foments (albeit slow) Pb diffusion and fluid-driven recrystallization (e.g. Garber et al., 2017), other studies have shown that titanite may entirely escape recrystallization during >700 °C heating and fluid flow, such that trace-element growth zoning (including Pb) is preserved (e.g. Stearns et al., 2016). Likewise, though titanite recrystallization may be
associated with U-Pb age resetting, recent atomic-scale work even suggests that Pb is not necessarily mobilized from the titanite lattice during intracrystalline deformation (Kirkland et al., 2018). Further, there are a range of complex chemical substitutions in the titanite lattice (e.g. Prowatke and Klemme, 2006), such that Pb mobility may be partially coupled to the diffusive behaviour of other elements. Given the broad spectrum of titanite petrological behaviors, any attempt to tie titanite U-Pb data to a thermal history i) requires extensive geochemical characterization to exclude the influence of non-diffusive processes, ii) must account for growth or recrystallization zoning profiles that potentially mimic diffusion profiles (Stearns et al., 2016), and iii) must account for highly imprecise Pb diffusion parameters (this study). For these reasons, we suggest that titanite is better suited to “petrochronology”, i.e., records of interactions between minerals, fluids, and melts, rather than “thermochronology”, i.e., thermally activated intracrystalline diffusive records.

2.4 Measurement of U-Pb date profiles

Traditionally, U-Pb thermochronology has been performed using whole-grain age versus grain size correlations (e.g. Blackburn et al., 2011; Schoene and Bowring, 2007). The length-scale dependency of thermally activated volume diffusion means that a single thermal history is expected to generate a predictable age v. grain size trend which can then be inverted for cooling rate. The strength of such an approach is that the U-Pb isotopic composition of individual grains can be measured precisely with state-of-the-art ID-TIMS techniques. This means that both $^{206}\text{Pb} - ^{238}\text{U}$ and $^{207}\text{Pb} - ^{235}\text{U}$ dates can be used in the derivation of thermal histories, in contrast to the typical 1-5% $^{206}\text{Pb} - ^{238}\text{U}$ date
Figure 1 shows that the steepest age gradient within a U-Pb date profile occurs proximal to the grain rim (at least for the case of homogenous U growth zoning). Given that accessory mineral grain sizes are typically on the order of 100 µm, distinction between thermal histories and effective Pb diffusion radii requires direct sampling of the profile at spatial resolutions better than a few microns. Slowly cooled accessory minerals with U-Pb date profiles in excess of ~100 µm can be sampled in-situ with laser-ablation spot traverses (e.g. Cochrane et al., 2014; Kooijman et al., 2010). The benefit of this approach is that spot traverses can be collected in-situ, thus preserving the micro-textural context of each grain; furthermore, individual grains can be characterised for major- and minor-element zoning prior to laser ablation, which is important for distinguishing between competing formation mechanisms. However, spot measurements integrate Pb concentration profiles with a resolution determined by spot diameter; typical spot diameters are 20-100 µm, meaning that unless the Pb diffusion length scale is >> 100 µm, resultant thermal history information will be imprecise or even unresolvable. Furthermore, the error function form of a diffusion profile means that material analysed within a single laser spot will be spatially weighted to reflect the zone with the highest concentrations (i.e. grain cores); this restricts the precision of derivative thermal history information. Furthermore, non-central sectioning of individual grains can lead to aliasing of the diffusion profile and overestimating the time-integrated magnitude of diffusion.
In contrast, depth profiling affords sampling of a mineral age or concentration profile at sub-micron intervals. This approach is based on the ability to resolve discrete variations in mineral chemistry or age as a function of depth into the crystal’s interior. First proposed by Zeitler and Williams (1988) and Zeitler et al. (1989), depth profiling of U-Pb accessory phases has traditionally been undertaken using secondary-ion mass spectrometry (SIMS) (e.g. Abbott et al., 2012; Breeding et al., 2004; Kelly et al., 2014; Lee et al., 1997; McFarlane and Harrison, 2006; Trail et al., 2007). However, the moderate sputtering rate of SIMS depth profiling (~0.075 µm per mass scan) limits pit depths to less than a few microns. In contrast, the aggressive pit excavation associated with LA-ICP-MS analysis has resulted in the emergence of two distinct depth-profiling methodologies. Continuously pulsed ablation (e.g. Kohn and Corrie, 2011; Paton et al., 2010; Smye and Stockli, 2014; Tollstrup et al., 2012) has the benefit of rapid data acquisition and the ability to sample intracrystalline gradients over tens of microns—typical for U-Pb date zonation in slowly cooled rutile and apatite. Both aerosol mixing of the analyte and time-dependent elemental fractionation restrict the spatial resolution and analytical precision of the approach. Various smoothing devices and downhole fractionation correction schemes are regularly employed to minimize such effects. In contrast, single-pulse ablation and derivative methodologies (e.g. Cottle et al., 2009; Cottle et al., 2012; Stearns et al., 2016; Steely et al., 2014; Viete et al., 2015) avoid these complications by integrating total counts collected in discrete laser pulses. By reducing ablation volume, sample mixing is minimized. Cottle et al. (2009) demonstrated an ablation rate of 0.1 µm per pulse which approaches the typical analytical volumes.
associated with SIMS depth profiling. Finally, the recent advent of Laser Ablation Split Stream (LASS) analysis heralds a new era for depth profiling in which complementary U-Pb date and trace-element information are collected from the same sub-micron analytical volume. This approach has great potential to resolve distinct diffusive and non-diffusive mechanisms for elemental zonations by assessing how length scales of elemental zonation conform to the relative order predicted by experimental diffusivities (e.g. Stearns et al., 2016; Viète et al., 2015).

2.5 Inversion of U-Pb date profiles

Given the complex relationship between age data and thermal history, extracting thermal histories information from measured U-Pb profiles is suited to treatment as an inverse problem. Various algorithms have been previously applied, including different Bayesian approaches (e.g. Gallagher, 1995; Gallagher, 2012; Willett, 1997) and basic Monte Carlo methods (e.g. Grove and Harrison, 1999; Ketcham et al., 2000; Smye and Stockli, 2014). The latter techniques are straightforward to implement but are prohibitively inefficient in searching large ranges of thermal histories and may not yield any solutions in large and precise datasets (Vermeesch and Tian, 2014). Here, we describe a new Bayesian approach that is well suited to the inversion of U-Pb date profile datasets in balancing computational efficiency with searching thermal history coordinate space. It comprises of the following steps:

1. Generate a random $t-T$ history. Draw a small number (e.g. 5) of values for each of these two parameters from a preset range, and interpolate between these ‘anchor
points’ with a piecewise cubic hermite polynomial function. Monotonic thermal histories can be enforced by ensuring that the anchor points are arranged in increasing order before the interpolation.

2. Predict the expected U-Pb depth profile. Given one or more sets of kinetic parameters and a specified (spherical, elliptical, cylindrical, tetragonal or hexagonal) geometry, simulate the combined radiogenic ingrowth and volume diffusion of U and Pb for the specified $t-T$ history using a Crank-Nicolson finite difference approach.

3. Compare the expected U-Pb depth profile(s) with the measured one(s). Let $N$ be the number of depth profiles ($N \geq 1$) and let $n_i$ be the number of U-Pb date measurements in the $i^{th}$ profile (for $1 \leq i \leq N$). Further let $t_{ij}$ be the $j^{th}$ U-Pb date estimate of the $i^{th}$ profile (for $1 \leq j \leq n_i$) and $\sigma[t_{ij}]$ its standard error. Finally, let $d_{ij}$ be the depth at which $t_{ij}$ was measured. The goodness-of-fit of the predicted depth profile to the measured values can then be quantified by the following log-likelihood function:

$$LL = \sum_{i=1}^{N} \sum_{j=1}^{n_i} \left( \frac{t_{ij} - t[d_{ij}]}{\sigma(t_{ij})} \right)^2$$

where $t[d_{ij}]$ is the predicted age at depth $d_{ij}$, obtained from the piecewise polynomial interpolation that was discussed in step 1.

4. Modify the $t-T$ path obtained in step 1, rerun steps 2 and 3, and reject or accept the
new \( t-T \) path depending on the new log-likelihood value. Repeat until the algorithm has converged to a representative set of ‘likely’ \( t-T \) solutions. It is customary to ignore the first ~20% of the solutions to account for the ‘burn-in’ time required to locate the solution space.

The mechanics of this iterative Markov Chain Monte Carlo (MCMC) process are handled by Foreman-Mackey et al. (2013)‘s implementation of the Goodman and Weare (2010) ensemble sampler. This general-purpose algorithm (which is also known as the ‘MCMC Hammer’) has several benefits over traditional MCMC methods. Most importantly, it simplifies the modification step of the \( T-t \) paths and is able to search the possible solution space in parallel by evaluating an ensemble of ‘walkers’. This results in an increased convergence rate that enables rapid global exploration of thermal histories. The above algorithm is implemented in a MATLAB function named \textit{UPbeat}, which includes an intuitive graphical user interface. The software and its source code are available from \url{http://UPbeat.london-geochron.com}. In its present form, \textit{UPbeat} does not readily accommodate external \( T-t \) constraints such as temperatures at specific times, or specific rates of cooling/heating. In our view, it is better to use external constraints to validate the inverse model results, rather than bias them (Vermeesch and Tian, 2014). A final important quality of our software is its ability to handle large datasets comprised of multiple depth profiles from the same sample; the use of multiple profiles increases the algorithm’s power to resolve the thermal history, which allows the user to increase the number of anchor points or to consider non-monotonic cooling histories without sacrificing precision. However, we stress that this approach is predicated on identifying
U-Pb date profiles that are diffusive in nature, with an effective diffusive radius equivalent to the grain size (i.e. each profile conforms to an error function and has the same age at the outermost depth interval).

To demonstrate the MCMC inversion approach applied to U-Pb thermochronology, we present results of an example inversion of a rutile U-Pb date profile measured using the depth-profiling methodology outlined in Smye and Stockli (2014) (Fig. 4). The example shown is from an unpublished rutile U-Pb depth profile dataset collected from a suite of Permian lower crustal granulites from the Pyrenees that were exhumed during Cretaceous (~100 Ma) hyper-extension of the crust and mantle lithosphere in southwestern France and northern Spain (Hart et al., 2017, and references therein). An additional example is contained in Fig. 14, showing a joint inversion for two sets of three rutile U-Pb depth profiles from the Grenville orogeny. These figures clearly exhibit the power of our model to rapidly discard non-permissible thermal histories, and to converge on a best-fit thermal history through the rutile PRZ.

3. Additional controls on U-Pb date profiles

U-Pb thermochronology is dependent on diffusive transport of Pb, which should yield core-rim age profiles similar to that shown in Figure 5a. However, there are numerous alternative Pb transport mechanisms other than grain-scale volume diffusion that can influence the topology of U-Pb date profiles; these processes are equally relevant to within-grain differences in a range of trace elements, including either or both U and Pb.
The section is focused on how such processes can be distinguished using intracrystalline U-Pb or trace-element profiles.

3.1 Secondary growth

Overgrowths reflect a hiatus in crystal growth and are most often characterized by a sharp change in \(\frac{dC}{dr}\), where \(C\) is radiogenic Pb or trace-element concentration. Growth of rims at temperatures sufficient to drive diffusive Pb transport will result in a smoothed core-rim boundary; conversely, low-temperature rim growth will result in a step-like discontinuity. On a Tera-Wasserburg concordia plot, a simple core-rim overgrowth relationship (disregarding common Pb) will result in discordia with upper and lower intercepts at the U-Pb isotopic compositions of the core and rim, respectively (Fig. 5b). The extent to which analyses spread along the discordia is governed by the width of the core-rim interface relative to the spatial resolution of the analytical technique (Fig. 5b). Rim overgrowths may be a common feature of zircon grains (e.g. Cottle et al., 2009), suggesting that pre-existing crystal facets are kinetically favourable sites for new growth compared to newly nucleated crystals. However, rutile and apatite overgrowths are less commonly observed in U-Pb datasets, plausibly because their reactive nature means that they are unlikely to survive multiple metamorphic cycles.

3.2 Recrystallisation

Recrystallisation involves re-growth and re-ordering of disordered portions of the crystal lattice due to i) lattice strain from thermodynamic incompatibility of trace-element species incorporated at different \(P-T\) conditions (e.g. Stünitz et al., 2003), ii) differential
stresses exerted by the surrounding matrix (e.g. Twiss, 1977; Urai et al., 1986), or

periods of undersaturation/saturation with respect to grain boundary fluid phases (e.g.

Villa, 1998; Williams et al., 2011a). Unlike secondary growth, there may be negligible

addition of new material to the crystal grain. Instead, structural reordering of the mineral

lattice promotes loss of incompatible elements, including radiogenic Pb. The

susceptibility of the U-Pb thermochronometers to recrystallization is controlled by ionic

bond strength (Dahl, 1996; Dahl, 1997; Villa, 1998). Whilst there is little evidence for

apatite recrystallization at temperatures relevant to its PRZ (Chamberlain and Bowring,

2001), recrystallization of apatite has been documented under amphibolite- to granulite-

facies conditions during monazite-forming reactions (e.g. Bingen et al., 1996) and at low-

temperatures (<150 °C) in the presence of Cl- and F-bearing fluids (Boudreau et al.,

1986; Romer, 1996). Not withstanding the propensity for rutile to exsolve Fe-oxides and

zircon, there is some evidence to suggest that rutile is commonly affected by pervasive,

grain-scale recrystallization (e.g. Mücke and Chaudhuri, 1991; Rösel et al., 2014). A

coherent body of evidence shows that resetting of the U-Pb and trace-element systematics

of monazite (Crowley and Ghent, 1999; Poitrasson et al., 1996; Poitrasson et al., 2000;

Seydoux-Guillaume et al., 2002; Williams et al., 2011b) and titanite (Hawkins and

Bowring, 1999; Spencer et al., 2013; Stearns et al., 2016; Stearns et al., 2015; Zhang and

Schärer, 1996) is controlled by recrystallization. Such minerals often exhibit step-like

boundaries across which trace-element concentrations and U-Pb dates differ markedly

(e.g. Fig. 5c), consistent with recrystallization proceeding by a reaction front mechanism.

In contrast to diffusion, there is no elegant length-scale dependency that can predict

elemental (re)distributions associated with recrystallization; rather, partial
recrystallization typically results in patchy, fracture-controlled, or twin-plane controlled within-grain U-Pb date and trace-element differences (e.g. Garber et al., 2017; Putnis, 2009; Spencer et al., 2013). The degree of chemical change associated with recrystallization is controlled by changes in the solubility and transport of components in grain boundary media (e.g. Putnis, 2009); prolonged recrystallization thus has the potential to preserve a record of time-dependent variations in P-T conditions or fluid chemistry, (e.g. Stearns et al., 2016). These factors mean that recrystallization can result in a variety of topologies on U-Pb concordia plots.

3.3 Common Pb

Incorporation of common Pb—the portion of non-radiogenic Pb within a U-bearing mineral—results in discordant age data. U and Pb are fractionated during mineral growth because the two ions have different charges (U$^{4+}$ vs. Pb$^{2+}$) and ionic radii (U$^{4+}$=1.00 Å; Pb$^{2+}$=1.29 Å, in VIII-coordination) (Shannon, 1976). However, isovalence between Ca$^{2+}$ and Pb$^{2+}$ means that titanite and apatite commonly incorporate common Pb during (re)crystallization, whereas common Pb concentrations in rutile are typically subordinate to titanite and apatite (e.g. Chew et al., 2011; Frost et al., 2001; Zack et al., 2011b). Provided that the common Pb component has a single isotopic composition, the incorporation of variable quantities of common Pb defines discordia in Tera-Wasserburg coordinate space with upper and lower intercepts defined by the isotopic composition of the non-radiogenic and radiogenic components, respectively (Figs. 5a-d). If uncorrected, common Pb can yield apparent inversely zoned U-Pb date profiles in which rim ages exceed interior ages (e.g. if rim analyses contain more common Pb than core analyses).
Inherited Pb—a specific type of common Pb—is incorporated when crystal growth occurs at the site of a radiogenic precursor phase. It is an uncommon feature of rutile and apatite U-Pb systematics, but several studies have documented inherited Pb components in titanite (Romer and Rötzler, 2003; Zhang and Schärer, 1996). Inherited Pb will form discordia with upper and lower intercepts defined by the age of the inherited and radiogenic components, respectively—similar to secondary growth. An accurate common Pb correction is required in order to discriminate between the various Pb transport mechanisms discussed here. For example, comparison of uncorrected U-Pb analyses displayed on the Tera-Wasserburg diagrams in Figs. 5a and 5b shows that mixing with common Pb can obscure the characteristic data topologies associated with volume diffusion and secondary growth.

3.4 Inclusions and exsolution

Mineral inclusions sampled during analysis cause mixing between U-Pb compositions of the host and inclusion phases. Here, we restrict our treatment of inclusions to those mineral phases older than the host. Similar to secondary growth and inherited Pb, incorporation of included phases during an in situ measurement will result in discordia with end-member U-Pb isotopic compositions defined by the included and host phases. Optically visible inclusions should obviously be avoided during analysis, but optically minute micro-inclusions are commonplace in titanite, rutile and apatite, (e.g. Schmitz and Bowring, 2001). In theory, closed-system exsolution of zircon and ilmenite from rutile should not alter the bulk U and Pb budget of a crystal; the process is predicted, however, to redistribute both U and Pb between host rutile and lamellae phases, according to
relative solubilities. In the case of zircon lamellae, in which U$^{4+}$ readily substitutes for Zr$^{4+}$, the age of the zircon needles will reflect the timing of exsolution. Mixed analyses of host and lamellae will spread between the age of the host and exsolution. Partitioning experiments also suggest that U is weakly fractionated from Pb during ilmenite exsolution (Klemme et al., 2006; Klemme et al., 2005).

3.5 Short-circuit diffusion

Mineral lattices are imperfect and commonly contain extended defects, including dislocations, micropores, microfractures and subgrain boundaries. These defects have the potential to act as fast diffusion pathways, the effects of which have been studied in depth by the materials science community (Joesten, 1991; Le Claire and Rabinovitch, 1984; Ruoff and Balluffi, 1963). The large difference in ionic radii between Pb$^{2+}$ and parent U$^{4+}$ (0.29 Å) means that radiogenic Pb does not energetically favour the crystallographic site occupied by parent U. Consequently, daughter atoms of Pb are predicted to partition into structural defects and subsequently undergo rapid diffusive transport relative to the rate of lattice volume diffusion. An important prediction of short circuit diffusion theory is the presence of flat or, more generally, intracrystalline concentration profiles that are controlled by the density of structural defects and relative diffusivities between defect and host (Lee, 1995) rather than by the size of the grain. Investigations of short-circuit diffusion in thermochronometers have been focused on the $^{40}$Ar/$^{39}$Ar (e.g. Lo et al., 2000; Lovera et al., 2002) and (U-Th)/He systems (e.g. Shuster et al., 2004). Short-circuit behaviour of Pb has been observed in zircon following the formation of microfractures arising from lattice expansion during metamictization (Geisler et al., 2007). Networks of
ilmenite and zircon exsolution lamellae in rutile could plausibly form fast diffusion pathways for radiogenic Pb where the bulk grain $T_c$ is controlled by the density of exsolution plates.

3.6 Parent zonation

Within-grain differences in U and Th concentrations lead to spatially dependent Pb production rates and gradients in radiogenic Pb concentrations that drive intracrystalline diffusion. Therefore, parent zonation influences the shape of U-Pb date profiles; because U and Th diffusion rates in minerals are nearly always more sluggish than Pb, diffusion of radiogenic Pb from regions of high U and Th will lead to artificially old ages in neighboring domains. An example suite of U concentration profiles from lower crustal rutile and apatite is presented in Fig. 6; specifically, these profiles are from rutile from the Ivrea Zone, and apatite and rutile from Corsica (Seymour et al., 2016). There is no systematic U zonation between these profiles: grains from the same sample exhibit a variety of topologies from inwardly to outwardly decreasing U concentrations and from smoothly varying profiles to those with sharp discontinuities. Profiles with sharp discontinuities in U concentration are consistent with secondary growth (e.g. yellow curve, Fig. 6b), whereas smoothly varying profiles are consistent with U incorporation during protracted growth (e.g. purple curve, Fig. 6a). To demonstrate the effect of U zonation on the shape of U-Pb date profiles, Fig. 7 presents calculated core-to-rim profiles for four U zonation types: uniform, secondary growth of a high-U rim, growth zoning controlled by Rayleigh fractionation, and oscillatory zoning. The profiles are calculated using experimental Pb diffusion parameters for rutile (Cherniak, 2000) and
cooling from 700 °C for 1 Ga at 0.3°C/Myr. The overgrowth scenario (Fig. 7c-d) shows that U-rich rims drive diffusion of radiogenic Pb toward the grain center, and restrict the loss of Pb across the grain boundary ($r/r_0 = 1$ in Fig.7) at elevated temperatures; this case assumes that the high-U rim formed soon (< 1 Ma) after the core. Growth zoning of U in which the core region is enriched (Fig. 7e-f) drives rimward diffusion of radiogenic Pb from adjacent high U domains through low U portions of the crystal, resulting in a concave U-Pb date profile with the oldest preserved date positioned away from the grain core. Oscillatory zoning in which U concentrations vary over micron length scales (Fig. 7g-h) produces an age profile characterised by discontinuities that are progressively dampened toward the grain rim. These calculations show that near-rim effects of U zonation are likely to be removed as a result of the large chemical potential gradient across the grain boundary (assuming a zero Pb matrix). Furthermore, it is important to note that unless intragrain U concentration differences are >10 ppm, the effect of U zonation on age topology will only be resolvable in old samples (>$\sim 10^7$ years) with significant ingrown radiogenic Pb. With the exception of the yellow curve, the magnitude of U zonation in the rutile profiles shown in Fig. 6a is typically <1 ppm over the 30 µm profile depth, whereas U zonation magnitudes in apatite (Fig. 6b) are between 4 and 20 ppm. Regardless, these considerations establish that the accuracy of a U-Pb date profile inversion will be enhanced by incorporating the specific within-grain U zonation.

3.7 Flux-limited boundary conditions

Chemical equilibrium between the surface of a mineral grain and the rock matrix can be impeded by a number of kinetic factors, including slow, or inefficient, grain-boundary
mass transport, slow intracrystalline diffusion and slow rates of dissolution of a source mineral phase and/or precipitation onto the surface of the target mineral. Each of these processes serve to limit the rate at which thermodynamic equilibrium is established between rock matrix and crystal surface (Dohmen and Chakraborty, 2004). Of particular relevance here are the cases when either the capacity of the grain boundary reservoir is limited by slow transport rates (i.e. absence of a fluid phase) or, when the rate of interface reaction is slow relative to the rate of intracrystalline diffusion. Both cases are expected to result in mineral concentration profiles with elevated rim concentrations and less curvature compared to the classic case in which intracrystalline diffusion is the rate-limiting transport process. Whilst the specific chemical parameters that control the behaviour of Pb in grain boundary fluids and across mineral-fluid interfaces under deep crustal conditions remain incompletely understood, the observation that accessory minerals, such as rutile, can exhibit disparate trace element concentration profiles with different rim concentrations in crystals from the same hand sample is strong evidence that flux-limited boundary conditions are potentially of great importance to the formation of trace element and U-Pb date profiles in accessory minerals (e.g. Kohn et al., 2016). It should also be noted that for the case in which a mineral grain has experienced temperatures above its PRZ, but with a flux-limited boundary condition, a flat internal U-Pb date concentration profile will likely be present (e.g. Fig. 5d).

4. Case study: lower crustal rutile from the Grenville Province
To demonstrate some applications and limitations of U-Pb thermochronology, we present a new rutile U-Pb and trace-element dataset from the exhumed lower crust of the Grenville orogen, eastern Canada.

4.1 Geological Background

The Grenville orogen is a major Mesoproterozoic orogenic belt spanning from southern Ontario to Labrador and exposes deep structural levels of a large, hot collisional orogen, similar in size and structure to the modern Himalayan-Tibetan system (Beaumont et al., 2006). The samples investigated in this case study (GB119C and GB132A) are both rutile-bearing mafic granulites that were collected from meter-scale mafic pods from the lower allochthonous domains of the Central Gneiss Belt (CGB; Fig. 8). Details of the samples, regional geology and geochronology are provided in the Supplementary Material; here, we summarize key information relevant to the interpretation of the rutile U-Pb dataset.

Phase equilibrium modelling, supported by multi-equilibria thermobartometry and single-phase solution thermometry in rutile and titanite, define a clockwise $P$-$T$ path for the samples, evolving from rutile growth at temperatures above 700 °C at $\sim$1.5 GPa to peak granulite facies conditions of $>800$ °C at $\sim$1-1.5 GPa (Grant, 1989; Marsh and Kelly, 2017). Zircon U-Pb geochronology constrains the timing of the early high-pressure metamorphism to 1090-1110 Ma (Ketchum and Krogh, 1998; Marsh and Culshaw, 2014) and the subsequent granulite-facies overprint to 1040-1080 Ma (Tuccillo et al., 1992; Slagstad et al., 2004). Hornblende $^{40}$Ar-$^{39}$Ar ages throughout the lower
allochthonous domains of the Grenville typically fall between 930 and 1000 Ma, clustering around 970 Ma, whereas mica and K-feldspar \(^{40}\)Ar-\(^{39}\)Ar ages cluster around ca. 900 Ma (Cosca et al., 1992; Cosca et al., 1991). Compilation of these data indicate an extended period of high temperature (~750–850 °C) metamorphism from ~1110–1040 Ma, followed by relatively slow cooling (<3 °C/Myr) to ~500 °C by ca. 970 Ma and ~300 °C by 900 Ma (Cosca et al., 1991). Thus, rutile from samples GB119C and GB132A formed at temperatures in excess of 700 °C, were subsequently exposed to temperatures in excess of 800 °C, and apparently remained above 700 °C for up to 80 Myr during the Ottowan phase of the Grenville orogeny that marked the transition from warm subduction to burial in lower orogenic crust.

4.2 Methods

4.2.1 LA-ICP-MS spot analyses

We collected U-Pb spot dates and depth profiles from samples GB119C and GB132A using LA-ICP-MS and LASS analysis, respectively. Spot dates were collected from polished thin sections at Laurentian University using an iCap-TQ ICP-MS coupled to a Photon Machines Analyte G2 laser ablation system. Optimal signal strengths were attained using a 65 µm spot diameter, a fluence of 2 J/cm\(^2\) and a repetition rate of 10 Hz. Oxide interferences were minimized by tuning gas flows such that UO/U < 0.5%. For U–Pb isotopic abundance measurements, correction for instrumental drift and laser-induced elemental fractionation was addressed via analysis of rutile standard R10 (Luvizotto et al., 2009), using a standard-sample-bracketing routine. Rutile R19 was used to assess age
accuracy; \(^{206}\text{Pb}/^{238}\text{U}\) ratios for R19 were consistently within \(2\sigma\) uncertainty of the ID-TIMS values reported by Zack et al. (2011a).

4.2.2 LA-ICP-MS depth-profile analysis

Trace-element concentrations and U-Pb date depth-profiles were collected from separated whole grains of rutile mounted (unpolished) on tape at the University of Texas following the methodology of Smye and Stockli (2014). Rutile R19 was used to assess age accuracy; \(^{206}\text{Pb}/^{238}\text{U}\) ratios for R19 were consistently within \(2\sigma\) uncertainty of the ID-TIMS values reported by Zack et al. (2011a).

4.3 Results

U-Pb isotope data for all LA-ICP-MS analyses are presented in the supplementary material.

4.3.1. LA-ICP-MS spot analyses

Matrix (n=8) and inclusion (n=3) rutile grains from sample GB119C yielded U-Pb spot analyses that define an array in Tera-Wasserburg concordia space; because some spots plot off concordia and others define U-Pb dates equivalent to or significantly younger than zircon U-Pb dates, the analyses are interpreted to indicate both Pb loss and mixing with common Pb (Fig. 9). Common-Pb corrected analyses are concordant within analytical uncertainty and yield a spectrum of dates between ~1050 and 800 Ma (Fig. S1). Figure 10a shows \(^{207}\text{Pb}\)-corrected \(^{238}\text{U}\)-\(^{206}\text{Pb}\) ages plotted as a function of distance from the grain rim for samples GB119C. From visual inspection of the figure, it is clear
that there is no systematic correlation between age and within-grain position, as would be
the case for volume diffusion in which the effective diffusion radius was equivalent to the
grain size. The relationship between U-Pb age and textural setting is demonstrated in Fig.
10c; note that the matrix grains yield a significant date spread (846-959 Ma) and that the
rutile grain included within garnet yields a significantly older age (972 Ma). The
remaining rutile inclusions in garnet yield ages of 904 and 1400 Ma, respectively; the
oldest age is consistent with incorporation of inherited radiogenic Pb from a precursor
phase.

The U-Pb systematics of sample GB132A are similar to GB119C. U-Pb analyses of
matrix grains (n=12) define an array that is consistent with both Pb loss and mixing with
common Pb (Fig. 9b); common-Pb corrected analyses fall along concordia between ~800
and ~1040 Ma (Fig. S1b). Rutile grains large enough to permit measurement of multiple
spot ages do not yield rims with younger ages than grain cores (Fig. 10b)

4.3.2. LA-ICP-MS depth-profile analysis

We collected 45 and 53 depth profiles from individual rutile crystals from samples
GB119C and GB132A, respectively. The full U-Pb depth profile dataset is presented in
the supplementary material (Table S2), in addition to compilation plots of the different
profile topologies collected from GB119C (Fig. S2) and GB132A (Fig. S3). Both
samples exhibit U-Pb date profiles with three characteristic topologies: i) rounded
profiles with younger rim than core ages (GB119C n=13/45; GB132A n=4/53), including
some age profiles that increase over ~20 µm from ~900 Ma at grain rims to homogeneous
~1100 Ma cores (Fig. 11a; Figs. S2 and S3), ii) profiles with ages that vary linearly with depth (GB119C n=20/45; GB132A n=32/53; Fig. 11b; Figs. S2 and S3), and iii) profiles with sharp (typically <5 μm) spatial discontinuities in U-Pb dates (GB119C n=12/45; GB132A n=17/53; Fig. 11c; Figs. S2 and S3). HFSE concentrations are generally flat and do not correlate with U or Pb; Zr in particular has concentrations between 1100 and 1500 ppm and defines flat profiles even in grains in which the U-Pb profile decreases toward the grain rim.

4.4 Integrating spot and depth-profile U-Pb datasets

Having discussed the various kinetic processes that can affect intracrystalline U-Pb date distributions, here we integrate these two datasets with petrographic observations to identify conditions that are favourable for the formation of diffusive date profiles required for U-Pb thermochronology.

Zircon and rutile crystallized at ~1100 Ma as part of the dominant HP metamorphic assemblage; therefore, the occurrence of U-Pb ages between 800 and 1100 Ma shows that rutile grains in both samples must have undergone significant Pb loss since crystallisation. However, the absence of a systematic relationship between U-Pb spot date and position (Fig. 10) combined with the observation that the majority of U-Pb depth profiles (n=81/98) exhibit non-diffusive topologies is consistent with the following explanations: i) U-Pb systematics were affected by partial recrystallization of rutile grains following metamorphic growth (section 3.2), ii) Fickian-type volume diffusion of Pb through rutile did not operate over whole-grain length scales, or iii) diffusive loss of Pb
was flux-limited by grain boundary kinetic factors, but only in certain textural settings (section 3.7).

The presence of homogenous HFSE concentration profiles (Fig. 11) and the absence of significant chemical variations in matrix rutile (note homogeneous rutile BSE maps in Fig. 10) suggests that partial recrystallization – expected to yield patchy element distributions (Fig. 5c) – did not significantly affect the studied grains. Textural evidence for recrystallization of the Grenville rutile grains is limited to the presence of ilmenite exsolution lamellae that form micron-scale networks of variable density throughout both included and matrix grains. Although the role of exsolution on U-Pb systematics of rutile is unclear, experimental constraints on partitioning of Pb between rutile and ilmenite suggest that radiogenic Pb would not partition strongly into ilmenite on exsolution ($D_{Pb}^{rt-itm} = 3 - 30; (Foley et al., 2000; Klemme et al., 2006; Klemme et al., 2005)$).

Rather, as discussed in section 3.5, it is conceivable that the grain boundaries between exsolution plates and host rutile crystals operate as fast diffusion pathways that would result in Pb diffusive length scales smaller than the rutile grain, as observed in both GB119C and GB132A, and a lower value of Pb $T_c$. In this process, the loss of radiogenic Pb from a rutile grain would be controlled by the spacing between adjacent exsolution plates. Unfortunately, we were unable to establish a relationship between ilmenite lamellae density and U-Pb date due to the large laser spot sizes we used relative to the length scale of the lamellae networks. However, consistent experimental and empirical constraints on rutile $D_{Pb}$ (Fig. 3b) suggest a Pb diffusive length scale of $\sim 250-400 \, \mu m$ for the metamorphic conditions experienced by the studied rocks ($\sim 800 \, ^\circ C$ for $\sim 10-20 \, \text{Myr}$),
which should have been sufficient to homogenize nearly all grains in both samples. Therefore, though fast diffusion pathways may have locally modified individual date profiles, it is clear another process must be responsible for the retention of higher radiogenic Pb concentrations than predicted by volume diffusion.

Figure 12 is a rank-order plot of U-Pb dates collected from the outermost depth increment of the depth profiles. Rim ages spread from ~800 to 1100 Ma, the timing of zircon growth and, by inference, rutile growth, in each sample. Volume diffusion calculations predict that the U-Pb age of the outermost depth increment of a cooling crystal is independent of grain size and records the timing at which the grain passes through the base of the PRZ, closing to Pb diffusion (Dodson, 1986). The fact that both samples show a ~300 Myr spread in rim ages indicates that U-Pb systematics in the Grenville rutile dataset cannot be explained by intracrystalline volume diffusion. Such a spread in rim ages is, however, predicted by flux-limited Pb transport, where the local capacity of the grain boundary reservoir to accommodate Pb controls the extent to which Pb is lost from the host rutile grain (Dohmen and Chakraborty, 2004). Under these conditions, intracrystalline Pb diffusion can occur efficiently over the length scale of the rutile crystal, but the net loss of radiogenic Pb is independent of intracrystalline diffusion rate. One prediction of flux-limited Pb transport is that an inverse correlation will exist between rutile U-Pb age and proximity to a mineral phase that can structurally accommodate Pb. Figure 13 shows a box plot of common-Pb corrected U-Pb spot ages grouped according to the mineralogy of the nearest grain boundary phase. We identify no systematic correlation between any of the rock-forming mineral phases; in particular, the
lack of a correlation with proximity to plagioclase is surprising because plagioclase has been shown to be an important Pb sink (e.g. Chamberlain and Bowring, 2001). In the absence of texturally-controlled U-Pb rim ages, we suggest that dry grain boundaries could impede the rate of grain boundary transport of Pb and, ultimately, restrict the capacity of the grain boundary to host rutile-derived radiogenic Pb. An equally plausible explanation is that proximity to an Pb-bearing accessory phase could control the chemical potential gradient across rutile grain boundaries. Regardless, these observations highlight the importance of developing a more in-depth understanding of the physical and chemical controls on the behaviour of Pb along grain boundaries under deep crustal conditions.

The small number of depth profiles with monotonically increasing $^{238}\text{U}-^{206}\text{Pb}$ dates from rim to core share similar length scales of curvature and exhibit identical ages (within analytical uncertainty) over the outermost ~2 µm depth increment. This suggests that the boundary conditions for each of these grains during cooling were similar. Furthermore, each of the profiles conforms to the expectation of linearity when inverted through an inverse error function. These factors support the interpretation that profile formation was controlled by intracrystalline volume diffusion of Pb through rutile under conditions in which the effective diffusion domain was defined by grain dimensions. The occurrence of these profiles in the same samples as “non-diffusive” profiles may indicate heterogeneous or small-volume fluid flow along the grain boundary network that affected a limited number of grains.
Finally, it is important to note that the short length scales of diffusive Pb transport (~20 µm) were not resolvable by spot analysis of grain cross-sections. Whilst spot analysis enables ages and trace element concentrations to be directly related to textural features, the coarse sampling resolution of the technique limits the resolution of derivative thermal history information. Conversely, depth profiling enables high resolution thermal history information to be extracted from single crystals, but does not preserve microtextural relations. The Grenville case study presented here shows that both techniques are required in order to accurately identify diffusive date profiles that can be used to generate non-spurious thermal history information.

4.5 Tectonic implications

To ascertain the tectonic significance of the diffusive U-Pb date profiles, joint inversion of selected U-Pb date profiles from each sample was undertaken using the method outlined in section 2.5. The inversion computation was performed for monotonic cooling histories with a total of 10,000 iterations. Initial temperature was set at 825 °C, in agreement with thermobarometric constraints on peak temperatures. Grain-specific U profiles were used in conjunction with the diffusion parameters of Cherniak (2000). Resultant thermal histories for both samples are presented in Fig. 14; best-fit profiles are characterised by an early period of fast cooling from peak temperatures at rates of ~10 °C/Myr followed by slow cooling to <500 °C at <1 °C/Myr. These T-t trajectories are consistent with existing zircon U-Pb growth ages and hornblende $^{40}$Ar-$^{39}$Ar cooling ages for the allochthonous domain host gneisses (Fig. 15), passing through granitic melt crystallization conditions (~650 °C) between ~1080-1050 Ma and through 500 °C at
Recent studies have shown that the biotite Ar/Ar dates around 900 Ma require a further stage of cooling from the rutile PRZ that is not resolvable with the rutile dataset, or suggests that the biotite Ar/Ar dates are not cooling ages. Even recognizing the array of U-Pb date profiles, the rutile data therefore demonstrate how the methods described here are capable of providing accurate and near-continuous cooling history information from carefully selected individual crystals.

The non-linear cooling history presented here—as opposed to a slow, monotonic cooling over ~200 Myr previously assumed for the western CGB (Fig. 10)—has important implications for understanding tectonic processes in deep orogenic crust. An early phase of rapid cooling from HT eclogite/HP granulite conditions suggests that the metabasite pods were detached from lower crustal depths and exhumed to shallower crustal levels over <~100 Myr. Previous workers have suggested that exhumation of deep-seated mafic bodies within the Grenville orogeny is aided by a low-viscosity, low-density carapace of granitic and metasedimentary migmatites (Marsh and Culshaw, 2014). A similar process has been envisaged for other collisional orogens (e.g. Brown and Dallmeyer, 1996; Gordon et al., 2008; Little et al., 2011; Schulmann et al., 2008; Whitney et al., 2009) and is consistent with the results of geodynamic models (Beaumont et al., 2006; Jamieson et al., 2007), where post-subduction collision of rigid crustal blocks drives extrusion of the basal portions of lower allochthonous domains to shallow crustal levels. The well-documented extensional kinematics within the Shawanaga and overlying Parry Sound shear zones may have also contributed to rapid cooling from peak temperature.
conditions, prior to long-term residence at shallow levels of post-orogenic crust (Jamieson and Beaumont, 2011; Ketchum and Davidson, 2000; Wodicka et al., 1996).

5. Remaining Questions

This review and demonstration of U-Pb thermochronology serves to highlight several areas for future research.

1. What controls Pb mobility along grain boundaries in metamorphic rocks? A growing body of evidence shows the importance of flux-limited boundary conditions for the U-Pb systematics of accessory minerals in deep crustal metamorphic rocks. Experimental work constraining the solubility and diffusivity of Pb in grain boundary fluids of variable chemistry would be helpful. Furthermore, systematic characterisation of which phases act as sinks and sources for radiogenic Pb derived in apatite and rutile would enable targeted U-Pb thermochronology.

2. What controls the mobility of Pb in titanite? Empirical and experimental studies are required to reconcile the disagreement between existing experimental diffusion parameters and empirically derived estimates of Pb diffusivity. A potentially fruitful topic of study is the comparison between length scales of Pb and trace-element zonation in high-grade titanite from metamorphic terranes.

3. How does exsolution affect Pb transport through rutile? Numerous workers have acknowledged the potential importance of exsolution lamellae in forming a short-
circuit diffusion network in rutile, potentially capable of reducing whole grain $T_c$ (Ewing et al., 2013; Lee, 1995; Zack and Kooijman, 2017). This mechanism would explain the absence of grain-scale diffusive profiles in rutile grains that can be shown to have lost radiogenic Pb. Confirmation of this hypothesis will require measurement of Pb concentration profiles normal to ilmenite/zircon lamellae-rutile interfaces.

4. Monazite and zircon U-Pb thermochronology. Microanalytical U-Pb analysis by SIMS or LA-ICP-MS can resolve U-Pb dates over sub-micron length scales. Such distances are comparable to those expected for diffusion of Pb in monazite and zircon in regions of the crust that have experienced temperatures above $>~900$ °C. Previous work has shown the utility of monazite Th-Pb (e.g. Grove and Harrison, 1999), and zircon U-Pb thermochronology (e.g. Wheeler et al., 2015), but the full potential of these minerals as high-temperature thermochronometers remains to be exploited. Furthermore, lattice distortion or metamictization in zircon allows Pb diffusion at lower temperatures than in undistorted crystals (Wheeler et al., 2013), extending the zircon PRZ and the temperature range over which thermal history information could plausibly be recovered.

5. Combined U-Pb thermochronology and trace-element speedometry. Diffusive trace-element zonation in accessory phases provides an additional record of thermal history. In contrast to U-Pb thermochronology, trace-element speedometry is unable to constrain the absolute timing of a thermal event; rather, the curvature of the concentration profile constrains the magnitude of time-integrated diffusion ($<D.t>$).
that has occurred since crystal formation. Provided that boundary conditions can be
constrained, and given that all diffusion profiles must be internally consistent, trace-
element speedometry could be combined with U-Pb thermochronology to yield high-
resolution thermal histories. The HFSEs in rutile (Cherniak et al., 2007; Kohn et al.,
2016; Marschall et al., 2013), Sr in apatite (Ague and Baxter, 2007) and Li in zircon
(Trail et al., 2016) hold particular promise in this regard.

6. Summary

Within-grain distributions of U-Pb dates and trace-element concentrations can now be
routinely and rapidly measured over sub-micron length scales, heralding a new era for U-
Pb thermochronology. Uranium-lead depth profiling of rutile and apatite provides an
extraordinary opportunity to obtain continuous thermal history information from rocks of
the middle to lower crust—a temperature range that is pertinent to a number of important
geodynamic processes. Routine application of U-Pb titanite thermochronology is
presently limited by uncertainty regarding the diffusion systematics of Pb in titanite.
Caution must be exercised to ensure that measured radiogenic Pb concentration profiles
are diffusive in nature; such profiles are rare in rocks of the deep crust due to the effects
of flux-limited boundary conditions and energetically favourable non-diffusive processes
such as recrystallization and short-circuit diffusion. Microtextural observations are
required to accurately discriminate between diffusive and non-diffusive U-Pb profiles.
Accordingly, U-Pb and trace element depth profiles should be integrated with spot
analyses to identify profiles suitable for inversion for thermal history information.
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Figure captions

Figure 1. U-Pb thermochronology. Panel A illustrates the effect of erosion on the temperature-depth evolution of three rock samples initially located at 22.5 (yellow particle), 30 (orange) and 37.5 km depth (red). Gray lines are geotherms, plotted at 2 Myr intervals. Shaded regions delineate the zones of partial retention for Pb in apatite and rutile. Calculations performed using an erosion/exhumation rate of 1 km/Myr. Panel B shows calculated $^{238}\text{U}-^{206}\text{Pb}$ date profiles for single grains of apatite and rutile in each of the three rocks shown in panel A after 50 Myr of erosion. Both apatite and rutile date profiles were calculated using experimentally determined Pb diffusion parameters (Cherniak, 2000; Cherniak et al., 1991) and a cylindrical geometry (200×250×100 µm).

Figure 2. Closure profiles and whole grain ages. Panel A shows four different thermal histories: progressive cooling (black line), lengthy residence at high temperatures (orange), reheating (purple) and low-grade metamorphism (red). Panel B shows
computed $^{238}\text{U}^{206}\text{Pb}$ date profiles for a rutile grain (100 µm equivalent spherical radius) after following each of the thermal histories displayed in A. The red line (low grade metamorphism) represents the profile shape typical of a secondary growth event occurring at low temperatures. Calculations were performed using a homogenous distribution of U, and the Pb diffusion parameters of Cherniak (2000). Note that the volume integral of each U-Pb date profile yields a whole-grain date of 40 Ma, independent of thermal history.

Figure 4. U-Pb date profile inversion. U-Pb data are shown for a lower crustal rutile from the Pyrenees. Panel A shows common-Pb corrected $^{238}\text{U} - ^{206}\text{Pb}$ date profile plotted against the best fit (maximum log likelihood) model $^{238}\text{U} - ^{206}\text{Pb}$ date profile (black line). Panel B shows the evolution of the log likelihood value as a function of iteration number; note the pre- and post-burn-in stages, where burn-in refers to a group of initial, explorative iterations. Panel C shows post-burn-in candidate thermal histories shaded according to log likelihood.

Figure 5. Controls on U-Pb date profile topology. Panel A shows a schematic sketch of a U-Pb date profile collected by LA-ICP-MS across a half-width of an accessory mineral grain, a common Pb-corrected plot of U-Pb spot date against position within the grain and an associated Tera-Wasserburg concordia diagram containing both corrected (bold ellipses) and uncorrected (faded ellipses) U-Pb analyses. For this case, the distribution of radiogenic Pb is controlled by volume diffusion from grain cores into the grain boundary medium. Panel B: as for A, but for a scenario in which a mineral grain undergoes a period of secondary growth. Panel C: as for A, but for partial recrystallization of an accessory mineral grain. Panel D: as for A, but for the case in which the grain boundary cannot host radiogenic Pb (flux-limited boundary condition). Note the importance of an accurate common Pb correction; uncorrected data topologies for each of these processes are non-unique. See text for discussion.

Figure 6. U zonation in rutile and apatite. Panel A shows a series of U concentration depth profiles from lower crustal rutile of the Ivrea Zone. Data are from Smye and
Panel B shows a series of U profiles from lower crustal apatite of Corsica; data are from Seymour et al. (2016). For both panels, colors correspond to different grains.

Figure 7. Effect of rutile U zonation on U-Pb date profile topology. Panels show U concentration and resultant U-Pb date profiles for commonly encountered types of U zoning in rutile: uniform U concentration (panels A, B), secondary growth (panels C, D), Rayleigh distillation (panels E, F) and oscillatory zonation (G, H). U-Pb age profiles were calculated using rutile Pb diffusion parameters (Cherniak, 2000) and a thermal history in which cooling occurred from 700 °C over 1 Ga at 0.3°C/Myr. See text for discussion.

Figure 8. Tectonic map of the Grenville orogeny. Note the locations of samples GB119C and GB132A. Map is modified after Marsh and Culshaw (2014); see Supplementary Material for detailed discussion of Grenville geology and explanation of the various structural units.

Figure 9. Tera-Wasserburg concordia plots for laser ablation U-Pb spot data. Panel A: analyses from sample GB119C; panel B: analyses for sample GB132A. Note the dispersion of analyses along concordia for both samples that is consistent with Pb loss during cooling from high temperatures. Analyses are uncorrected for common Pb.
Figure 10. Relationship between U-Pb spot date and within-grain position. Panels A and B show $^{207}$Pb-corrected spot dates plotted against distance from grain rims for samples GB119C and GB132A, respectively. Spot analyses from the same crystal have the same color; $m$ and $i$ refer to matrix and included rutile grains, respectively. Analytical errors are 2$\sigma$. Panel C shows the microtextural environment of a subset of the spot dates for sample GB119C; dates are common-Pb corrected.

Figure 11. Example U-Pb date and trace element concentration depth profiles.
Panel A: rounded U-Pb date profile and associate U, Zr and Nb concentration profiles; panel B: linear U-Pb date profile; panel C: step-like U-Pb date profile. Note the similarity between the shapes of the trace element profiles, independent of the type of U-Pb profile. Errors are 2$\sigma$.

Figure 12. Rutile rim U-Pb dates. Panel A: $^{238}\text{U} - ^{206}\text{Pb}$ dates from the outermost depth increment (~1 $\mu$m) of each depth profile collected from individual rutile crystals from sample GB119C; panel B: as for A, but for sample GB132A. Black horizontal line corresponds to the age of zircon crystallization; red circles correspond to the U-Pb date profiles used for joint inversion (Fig. 14). Errors are 2$\sigma$.

Figure 13. Relationship between adjacent mineral phase and U-Pb date. Panels A and B show box plots of $^{207}$Pb-corrected U-Pb spot dates grouped according to the mineralogy of the nearest grain boundary phase for samples GB119C and GB132A, respectively. Each box represents, from bottom to top, the second and third quartile (25
and 75% of the population), and the bar inside the box represents the median; whiskers represent the 10th and the 90th percentiles. Numbers beneath the boxes represent the number of analyses considered and outliers, when they occur, are represented by small black circles. Note the absence of a systematic relationship between date and mineralogy for both samples.

**Figure 14. Joint inversion of Grenville rutile U-Pb date profiles.** Panel A shows the fit between the U-Pb date profiles (sample GB119C) and forward modeled profile for the maximum log likelihood thermal history (black line in panel B). Panel B shows the candidate thermal histories color shaded for log likelihood; black line is the solution with the maximum log likelihood value. Panels C and D are as A and B, for sample GB132A.

**Figure 15. Grenville thermal history.** Black lines are thermal histories derived from inversion of rutile U-Pb data profiles (this study); grayscale arrow represents thermal history derived from interpolation between zircon U-Pb (Ketchum and Krogh, 1998; Marsh and Culshaw, 2014), hornblende $^{40}$Ar-$^{39}$Ar and biotite $^{40}$Ar-$^{39}$Ar whole grain dates (Cosca et al., 1992; Cosca et al., 1991).

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