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# Constraints on the U–Pb systematics of metamorphic rutile from in situ LA-ICP-MS analysis

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ABSTRACT

In situ laser ablation ICP-MS U–Pb dating of metamorphic rutile from granulite facies metapelitic rocks of the Archaean Pikwitonei granulite domain (Manitoba, Canada) provides constraints on Pb diffusion and characterizes the closure behavior of rutile. The analysis of transects of 35-μm spots across 15 rutile grains having a size of 120 to 280 μm yielded concordant ages with core ages of ca. 2450 Ma and core-to-rim younging towards 2280 Ma. Age profiles indicate that volume diffusion of Pb occurs in rutile implying that the ages represent cooling ages. To investigate the closure behavior of Pb in rutile closure temperature profiles ($T_c(x)$) were constructed based on different models combined with experimentally-determined diffusion parameters. The classical $T_c(x)$ model of Dodson (1986; Mat. Sci. Forum 7, 145–154) indicates a rapid decrease of $T_c$ in the rims of grains, providing unrealistic estimates for the cooling rate when combined with U–Pb ages. A new $T_c(x)$ model was constructed based on the analyzed age profiles that are described by an error function. This model shows a more steady decrease in $T_c$ throughout the grain from ca. 640 °C in the core (depending on grain size) to a rim intercept ($T_{c,rim}$) of 490 °C ($\pm 7$, $2\sigma$), which is interpreted to be the extrapolated theoretical absolute temperature of insignificant Pb diffusion in rutile. The new model provides a better description of the relation between age and $T_c$ for the analyzed grains. However, both $T_c(x)$ models demonstrate that even in small grains the variations of $T_c$ can be significant making it impossible to derive one representative $T_c$ for Pb in rutile. The error function-based $T_c(x)$ model allows the determination of cooling rates, which show a decrease over time from ca. 2.2 to 0.4 °C/Ma agreeing well with previous estimates for the Pikwitonei granulite domain. This consistency supports the validity of our model and indicates that cooling rates can be estimated from single grains by LA-ICP-MS U–Pb dating of rutile providing constraints on the cooling history of a metamorphic terrane. The slow cooling rates imply that exhumation was slow (<0.1 mm/yr) and was controlled by surface erosion.



## 1. Introduction

Rutile ($TiO_2$) is a common accessory mineral in many metamorphic rocks. The phase is stable over a wide range of *P–T* conditions and provides a single-phase thermometer when crystallized in a Zr-saturated environment (Ferry and Watson, 2007; Tomkins et al., 2007; Watson et al., 2006; Zack et al., 2004a). It is very robust in sedimentary environments and therefore also used for provenance studies (e.g. Meinhold et al., 2008; Triebold et al., 2007; Zack et al., 2002, 2004b). Rutile may incorporate up to 200 ppm U allowing U–Pb dating with an excellent analytical precision and has been used as a geochronometer that provides important constraints on the cooling history of metamorphic terranes (e.g. Davis, 1997; Heaman and Parrish, 1991; Kylander-Clark et al., 2008; Mezger et al., 1989; Miller et al., 1996; Treloar et al., 2003). For a reliable interpretation of the U–Pb ages knowledge of the closure temperature ($T_c$) for Pb diffusion is essential. In this context various studies have been done, but there is a discrepancy of closure temperature estimates. The pioneering study was done by Mezger et al. (1989), who applied ID-TIMS to rutile grains having a grain size of 90–210 μm from the Proterozoic Adirondack terrane, New York, USA. Their approach was to compare their age results to ages and known closure temperatures of other dated minerals in the same terrane. This resulted in a $T_c$ estimate for Pb in rutile of ca. 400 °C. Using new $T_c$ estimates for other minerals, Vry and Baker (2006) revised this value upwards to 540 °C. In addition, they performed a similar comparative study based on their results from laser ablation MC-ICP-MS Pb–Pb dating of the outer 100–200 μm of rutile grains from the Reynolds Range, Australia, which suggests a grain size-independent apparent $T_c$ of 630 °C. Cherniak (2000) studied Pb diffusion in rutile by performing heating experiments on natural and synthetic grains at 700 to 1100 °C. This calibration resulted in a $T_c$ estimate of ca. 600 °C for 100 to 200 μm large grains.

To provide further constraints on Pb diffusion and its $T_c$ in rutile we analyzed U and Pb isotopes in rutile grains from granulite facies

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metapelitic rocks of the Archaean Pikwitonei granulite domain (Manitoba, Canada). These rocks are very suitable for this study, because peak-metamorphic age and conditions and the following cooling history are well constrained (Mezger et al., 1989). Furthermore, a setting of slow cooling at high temperatures is ideal for estimating closure temperatures, because age uncertainties are small compared to the duration of cooling.

The concept of closure temperature was first defined by Dodson (1973). He postulated that the $T_c$ of a geochronological system may be defined as its temperature at the time corresponding to its apparent age and derived an analytical solution for $T_c$. The concept was expanded for the case of slowly diffusing species, such as Pb in rutile, which may develop a closure temperature profile ($T_c(x)$; Dodson, 1986). This model was further expanded to include the case of arbitrarily limited diffusion, which applies to a wide range of geochronological systems (Ganguly and Tirone, 1999). Because experiments predict a low diffusivity of Pb in rutile (Cherniak, 2000), we expect that Pb diffusion profiles may be preserved in the selected rutile grains enabling the construction of $T_c(x)$ profiles.

This study aims to present a routine for the precise and accurate Pb–Pb– and U–Pb dating of rutile using laser ablation single collector ICP-MS. An advantage of this technique is that it allows in situ analysis in thin section preserving textural information. It has been shown that the presence or absence of a sink in a rock may greatly affect the effective $T_c$, for example for the Rb–Sr system in biotite (Jenkin, 1997; Jenkin et al., 2001). In situ analysis enables evaluation of the minerals surrounding rutile grains that may act as a sink for the diffusing Pb. Another important advantage of the technique is the high spatial resolution, which allows the analysis of small-spot transects across individual rutile grains and hence the construction of age profiles. If these age profiles represent diffusion profiles that originated from volume diffusion during slow cooling, we aim to constrain $T_c(x)$ for Pb diffusion. The resulting $T_c(x)$ profiles are based on natural samples, but the fundamentally different approach compared to earlier field-based studies provides independent constraints. In addition, we will determine cooling rate estimates based on single grains, which provide constraints on the cooling history of the metamorphic terrane.

## 2. Geologic setting

For this study Archaean samples from the Pikwitonei granulite domain in the northwestern Superior Province, Manitoba, Canada (Fig. 1) were investigated. Together with the amphibolite-facies Cross Lake subprovince in the east, this granulite domain comprises a large tonalite gneiss–greenstone belt in the northwest of the Superior Province. The transition between the two units is prograde and continuous and does not appear to have structural or lithological discontinuities. The study area is dominated by felsic gneisses, foliated to massive granitoids and amphibolites. Subordinate amounts of arenaceous and argillaceous metasedimentary rocks occur, intercalated with banded iron formation, metagabbros, calc-silicate rocks and marbles (Weber and Scoates, 1978). During the Hudsonian orogeny (ca. 1900–1700 Ma), the Churchill- and Superior Provinces collided, resulting in local retrogression of the Archaean granulite facies rocks in and near the Thompson mobile belt (Baragar and Scoates, 1981).

The *P–T–t* paths established for the high-grade metamorphism in the Pikwitonei granulite domain indicate that the area underwent a complex metamorphic history during the Archaean. Several thermal maxima were reached at different times across the study area over a period of 150 Ma, the last of which occurred throughout the area around 2640 Ma. During this last high-grade metamorphism, peak *P–T* conditions were about 7.0 kbar and 750 °C at Cauchon Lake and about 7.5–8.0 kbar and 820 °C at Natawahunan Lake (Mezger et al., 1990). Estimated time-integrated cooling rates for both areas are 0.5–1.5 °C/Ma based on geothermometry and zircon, amphibole, biotite and rutile ages (Mezger et al., 1989).

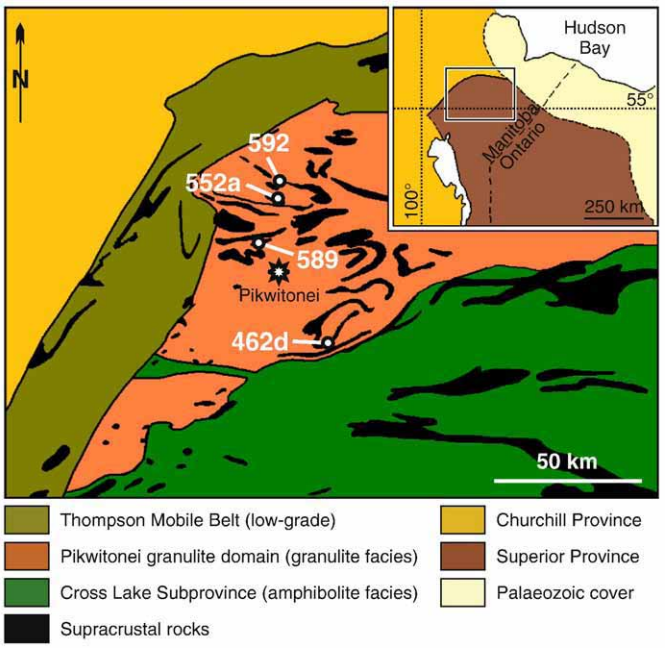


**Fig. 1.** Geological map of the northwestern Superior Province after Manitoba Mineral Resources (1980) showing the sample locations. The inset shows the location of the Pikwitonei granulite domain at the NW margin of the Superior Province.

## 3. Sample descriptions

Four metapelitic gneiss samples that contain abundant rutile were analyzed, comprising one sample from the amphibolite granulite facies transition zone in the Cauchon Lake area (sample 462d), and three samples from the granulite terrane in the Natawahunan Lake area (samples 552a, 589 and 592; Fig. 1). Sample 462d is a metapelite containing garnet, plagioclase, quartz, biotite, K-feldspar, cordierite, sillimanite, spinel, rutile, and ilmenite. Sample 589 has a similar mineralogy but contains more K-feldspar and biotite. Sample 592 is a metapelite containing quartz, garnet, cordierite, biotite, sillimanite, and rutile. Sample 552a is a paragneiss having leucocratic layers of K-feldspar, quartz and plagioclase, as well as peraluminous layers containing garnet, sillimanite, corundum, rutile, ilmenite, and traces of biotite. These samples were selected, because the rutile has already been subjected to high-precision U–Pb dating by ID-TIMS (Mezger et al., 1989; results summarized in Table 1) and do not show low-grade alteration (e.g., sagenite in biotite, or pinitization of cordierite) as a result of Hudsonian overprinting.

To evaluate the $T_c$ of Pb diffusion in rutile it is essential to select rutile grains that formed during prograde- or peak metamorphism. In the selected samples some rutile is included in garnet and sillimanite,

**Table 1**
Compiled ID-TIMS U–Pb age data for the studied samples from Mezger et al. (1989).

| Sample | Grain radius (μm) | Ages (Ma)[a] | | |
|---|---|---|---|---|
| | | $^{206}Pb/^{238}U$ | $^{207}Pb/^{235}U$ | $^{207}Pb/^{206}Pb$ |
| 462d | 90–210 | 2330 | 2387 | 2436 ± 10 |
| 462d | 90–210 | 2390 | 2411 | 2429 ± 1 |
| 462d | 90–210 | 2424 | 2426 | 2427 ± 1 |
| 552a | 70–80 | 2328 | 2329 | 2330 ± 1 |
| 589 | 90–210 | 2358 | 2361 | 2363 ± 2 |
| 589 | 90–210 | 2343 | 2353 | 2362 ± 1 |
| 592 | 150–210 | 2327 | 2324 | 2322 ± 1 |
| 592 | 120–150 | 2314 | 2314 | 2315 ± 1 |
| 592 | 60–80 | 2295 | 2294 | 2294 ± 1 |

[a] Uncertainties on isotope ratios and ages are 2σ in the least significant digits.

which indicates that the phase developed during prograde metamorphism. The selected rutile grains are either reddish-brown and transparent or dark-brown and almost opaque. Most grains are round to slightly elongate and are nearly euhedral (Fig. 2). No correlation can be observed between the color and shape of grains. The two color types were analyzed separately by Mezger et al. (1989), but no systematic differences in the concentrations of U and Pb or in the Pb isotope ratios were observed. The grain size ranges from 100 to 300 μm for samples 462d, 589 and 592. Grains in sample 552a are smaller ranging from 50 to 150 μm. For each sample the biggest grains were selected for the measurement of age profiles. Optical studies on the thin sections revealed only few visible inclusions in the rutile grains and care was taken to avoid cracks when positioning the laser spots (Fig. 2).

## 4. Analytical techniques

The laser ablation ICP-MS analyses were done at the Institut für Mineralogie, Universität Münster, using polished thin sections of the samples (30 μm thickness). For each sample two thin sections were studied and rutile grains were selected using a light microscope. Samples were analyzed using a Thermo-Finnigan Element II sector field ICP-MS coupled to a New Wave UP193HE ArF Excimer laser system. The standard ablation cell having a volume of 25 $cm^3$ provided by New Wave was used, combined with an in-house built sample holder that fits thin sections and additional standards. The instrument parameters for both the laser and the ICP-MS are listed in Table 2. During an analysis, the masses 206, 207, 208, 232 and 238 were measured in e-scan mode. Rutile contains almost no Th and therefore insignificant thorogenic $^{208}Pb$ allowing the approximation of common Pb contents based on $^{208}Pb$, which is more precise than those based on the less abundant $^{204}Pb$ isotope (e.g. Zack et al., 2008). A laser spot size of 35 μm was used and the total ablation time was 45 s, including 15 s during which the shutter remained closed to measure the gas blank (i.e., background). All spots were pre-ablated by firing three laser shots using a 45-μm spot size to remove common Pb from the surface, which may have been introduced during sample preparation. Corrections for laser-induced elemental fractionation and instrumental mass bias were done by bracketing groups of 5 unknowns by 2 measurements of the R10 standard rutile (Luvizotto et al., 2009).

**Table 2**
LA-ICP-MS details and operating parameters.

| Laser ablation system | | ICP-MS | |
|---|---|---|---|
| Model | New Wave Research UP193HE | Model | Element2, Thermo-Finnigan |
| Type | Excimer | Type | Magnetic sector field |
| Wavelength | 193 nm | Forward power | 1330 W |
| Spot size | 35–45 μm | Scan mode | E-scan |
| Repetition rate | 10 Hz | Scanned masses | 206, 207, 208, 232, 238 |
| Laser fluency | ~5 $J/cm^2$ | Cooling gas (Ar) | 16 l/min |
| Laser warm up | 15 s | Auxiliary gas (Ar) | 1.0 l/min |
| Ablation time | 30 s | Sample gas (Ar) | 1.1 l/min |
| Washout time | 120 s | Carrier gas (He) | 0.8 l/min |

Data were processed offline using an in-house Excel spreadsheet. The measured isotope signals were corrected for gas blank and the plotted $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{238}U$ ratios were carefully monitored to exclude anomalous parts of the signal related to inclusions or common Pb enrichment. A common Pb correction was applied to analyses if the contribution of the estimated common $^{206}Pb$ to the total measured $^{206}Pb$ exceeded 1%. The isotope ratios for the common Pb were calculated using the evolution model for terrestrial Pb by Stacey and Kramers (1975). The time-dependent elemental fractionation of $^{206}Pb/^{238}U$ was corrected by applying a linear regression through the ratios excluding outliers (>2$\sigma$ from reference line) and extrapolating to the $y$-axis to get $^{206}Pb/^{238}U$ at time zero, i.e., the moment the laser shutter was opened. This value is assumed to be affected only by instrumental mass bias, and not by dynamic fractionation that occurs during laser ablation (Sylvester and Ghaderi, 1997). Subsequently, instrumental drift and -mass bias were corrected by normalization to the reference rutile R10 (Luvizotto et al., 2009), which was measured using the same laser settings as the unknowns. The uncertainties were propagated by quadratic addition of the precision of each individual analysis and the external reproducibility obtained from the standard rutile during the analytical session. The reported $^{207}Pb/^{235}U$ values were calculated from $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ assuming a natural abundance of 137.88 for $^{238}U/^{235}U$. The uncertainties were estimated by propagating uncertainties of both ratios.

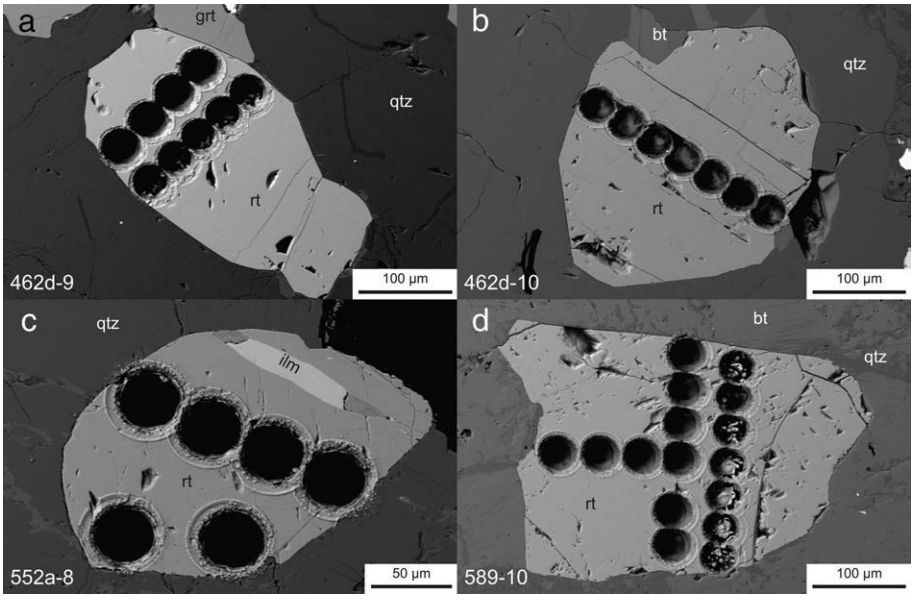


**Fig. 2.** Backscatter electron (BSE) images of a selection of rutile grains after LA-ICP-MS U–Pb analysis. The 35 μm spots are clearly visible.

As a quality-check we measured rutile grains from sample SP-1 (Adirondack terrane, New York), dated at 911 ± 2 Ma by ID-TIMS (Mezger et al., 1989), as unknowns. The acquired data for these grains (Fig. 3) indicate a reproducibility of ± 3% for $^{206}Pb/^{238}U$ and ± 4% for $^{207}Pb/^{206}Pb$. All errors are reported at the 2$\sigma$-level. The construction of concordia diagrams and linear regressions were performed using Isoplot 3.00 (Ludwig, 2003).

## 5. Results

The U–Pb isotope data and calculated ages for a total of 15 studied rutile grains are presented in Appendix **A**. The results for a selection of grains are presented in concordia diagrams in Fig. 4a. All samples define arrays of points that are concordant within the analytical uncertainty, covering a range of 150 to 190 Ma. Sample 462d from the amphibolite-to-granulite transition displays the oldest ages ranging from 2490 to 2360 Ma. The samples from the higher grade area yielded younger ranges. Samples 552a and 589 both show ages from 2450 to 2260 Ma. Ages in sample 592 range from 2480 to 2300 Ma.

The age profiles (Fig. 4b) indicate that ages systematically decrease from core to rim throughout grains, independent of grain size. In general, the age differences also increase towards the rims. Age differences between core and rim within single rutile grains range from 50 Ma (462d-10) to 190 Ma (592-3).

## 6. Modeling Pb diffusion

The U–Pb data indicate large age heterogeneity within grains. In general, age variations in minerals can result from recrystallization, growth zoning or volume diffusion. However, the processes of recrystallization or growth are unlikely to account for the continuous age variations throughout the rutile grains over the wide range of up to 190 Ma. Measured concordant ages are significantly younger than the crystallization age of the prograde- to peak-metamorphic assemblage to which rutile belongs (ca. 2640 Ma; Mezger et al., 1990), which indicates that age variation is due to volume diffusion of Pb during cooling. This is supported by the absence of resolvable age plateaus and the systematical core-to-rim decrease in age and increase in age gradient. This implies that all ages are cooling ages that record points in time when the system effectively closed for Pb. Because radiogenic Pb in the 'closed' part of grains should be effectively immobile, the $^{207}Pb/^{206}Pb$ age profiles are not biased by variations in U concentration. This is supported by the lack of systematic relation between U concentration and $^{207}Pb/^{206}Pb$ age (Appendix **A**). The age profiles are therefore equivalent to Pb concentration profiles formed by Pb diffusion from a homogeneous concentration that equals the amount of Pb produced by U present in the core of grains. The $^{207}Pb/^{206}Pb$ ages plotted as a function of the distance from the grain rim should follow Fick's Law for diffusion and would be described by an error function (e.g. McFarlane and Harrison, 2006). To test this, we fitted error functions to the profiles by taking the inverted error function ($erf^{-1}$) of the concentration term and modeling core and rim ages to get an optimal linear fit through the data (Fig. 5). A modeling constraint was that the regression lines go through the origin by definition. Outliers beyond 3$\sigma$ were rejected before performing linear regression. Converting the regression results back through the error function provides the modeled diffusion profiles (Fig. 4b). The modeled core ages show a large variation with differences up to 125 Ma within samples. However, with the exception of 462d-1 and 589-12, the differences between rim ages are significantly smaller ranging from 25 to 65 Ma (Table 3). As a measure of data quality, the $R^2$ values of model fits are given in addition to the modeled core and rim ages. The similar rim ages in single samples and the good fit of the error functions further support the notion that age heterogeneity in grains resulted from Pb volume diffusion.

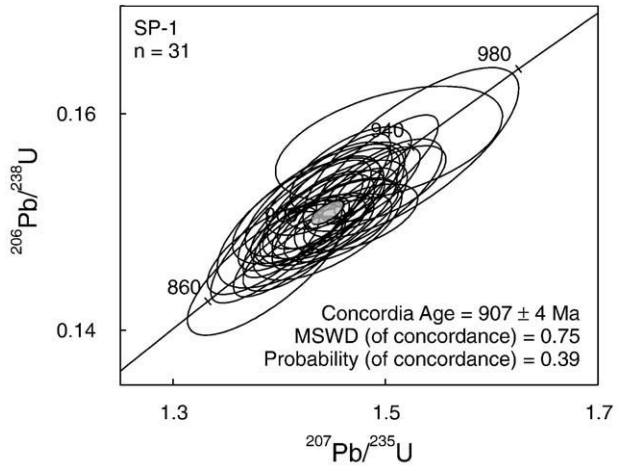


**Fig. 3.** Concordia diagram showing the results of 31 analyses of the SP-1 rutiles. The resulting concordia age is within error of the ID-TIMS age determined by Mezger et al. (1989).

## 7. Closure temperature ($T_c$) profiles

The age profiles reflect different temperatures at which the system closed for Pb throughout the grain. To constrain the cooling history from individual age profiles, constraints on $T_c(x)$ are required.

### 7.1. Classical approach to constrain $T_c(x)$

The first mathematical description of $T_c(x)$ was provided by Dodson (1986) and is defined by Eq. (1), in which $E_a$ is the activation energy for Pb diffusion in rutile (242 kJ/mol; Cherniak, 2000), $R$ is the gas constant, $D_0$ is the frequency factor, i.e. the diffusion coefficient at infinite temperature ($1.55 \cdot 10^{-10}$ $m^2$ $s^{-1}$ for natural rutile; Cherniak, 2000), $a$ is the active diffusion radius, $dT/dt$ is the cooling rate and $G(x)$ is the closure function, which is an array of values describing the curvature of the profile depending on the geometry of the studied crystal.

$$\frac{E_a}{RT_c(x)} = \ln\left(\frac{RT_c(x)^2 D_0 / a^2}{E_a dT/dt}\right) + G(x) \quad (1)$$

This equation is based on the following assumptions: 1) the matrix around the studied crystal behaves as a homogeneous infinite reservoir for the diffusing species, 2) the concentration of the species at the onset of cooling was homogeneous and 3) $T_c(x)$ is sufficiently removed throughout the crystal from the homogeneous state at $T_0$, the temperature at the onset of cooling. In the case of the studied grains, rim ages overlap independent of grain size or neighboring minerals, indicating that Pb was effectively removed from the grain boundaries by grain boundary diffusion, i.e., the first condition is satisfied. The second assumption is a priori fulfilled, because ages are considered rather than concentrations, whereas the absence of evident age plateaus in grain cores indicates that the third criterion is met. To investigate $T_c(x)$ in rutile, we have solved Dodson's (1986) equation for the studied grains using the model for spherical geometry (Table 3). The cooling rate at the spatially weighted mean age of each profile was estimated from a reconstruction of the cooling history, based on pre-existing thermo-chronometric data from the studied terrane (Mezger et al., 1989) and the assumption that $t \sim 1/T$ (Table 3). The latter condition often applies in the case of terranes undergoing slow cooling from (U)HT conditions (Dodson 1973) and is also satisfied by the studied terrane (Mezger et al., 1989).

The closure temperature profiles based on Dodson (1986) for the 15 studied rutile grains are presented in Fig. 6a. The profiles are very consistent and show a significant difference in $T_c$ between cores and rims, for example from 640 °C in the core to 510 °C at 4 μm from the

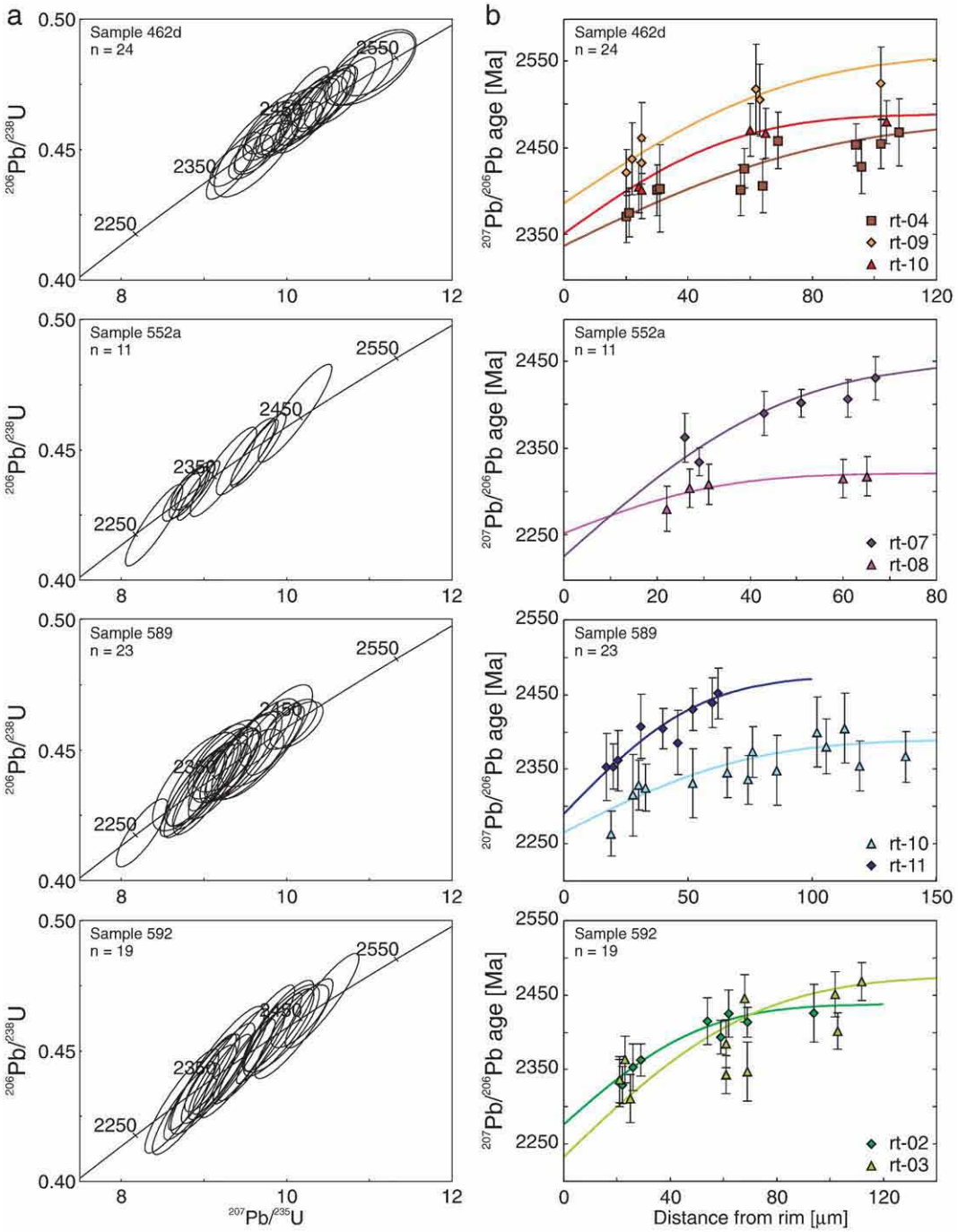


**Fig. 4.** (a) Concordia diagrams of the four samples showing results of 2–3 rutile grains per sample. (b) $^{207}Pb/^{206}Pb$ dates vs. distance from rim for the same rutile grains. The fit of the error function-based diffusion model for each age profile (solid lines) is provided in Table 3.

rim (462d-13). The estimated values for $T_{c,core}$ mainly depend on grain size and range from 594 to 639 °C (Table 3). The weighted mean closure temperatures ($T_{c,wm}$) that correspond to the weighted mean ages range from 546 to 587 °C (Table 3).

Combining spot age data with $T_c(x)$ after Dodson (1986) should provide cooling rates during the closure along the temperature conditions defined by $T_c(x)$. For this purpose, $T_c(x)$ may be calculated by iteration, using the mean cooling rate of the estimated cooling curves as input cooling rate for this model. However, a direct comparison of the shape of the age profiles with the shape of the $T_c$ profiles indicates that cooling rates calculated by this approach would dramatically increase with time due to the sharp decrease in $T_c$ compared to the steady age decrease. This conflicts with the observation that $t \sim 1/T$ for the slowly cooled study area, implying that the function proposed by Dodson (1986) may not describe $T_c(x)$ optimally, at least not in the outer margins of the grains. Assuming that the diffusing species obey Fick's Law for diffusion we have attempted to describe $T_c(x)$ for Pb in rutile through error function-based diffusion modeling using the age data as input parameters.

### 7.2. Error function (EF)-based approach to constrain $T_c(x)$

The age profiles record Pb diffusion over a specific distance from the rim of each grain ($x$) during a given time span ($\Delta t$) after the point in time ($t=0$) when temperature conditions have cooled to the closure temperature of the core of a grain ($T_{c,core}$). The EF-based model allows the reconstruction of $T_c(x)$ and the calculation of $T_{c,rim}$, the closure

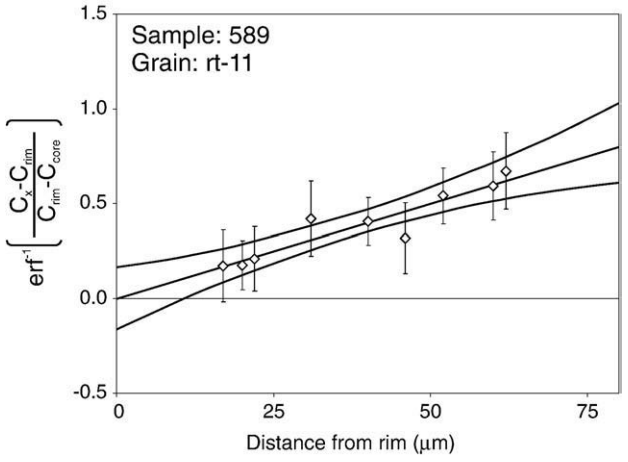


**Fig. 5.** Normalized concentration gradient for the $^{207}Pb/^{206}Pb$ profile of grain 589–11 ($2\sigma$ error bars) inverted through the error function ($\mathrm{erf}^{-1}$). The concentration terms ("C") were substituted with $^{207}Pb/^{206}Pb$ dates. The regression line with slope $(4Dt)^{-1/2}$ represents the best linear fit through the data and the origin.

temperature of the rim, which is the extrapolated theoretical temperature of insignificant Pb diffusivity in rutile. This is a theoretical $T_c$, because in an infinitesimal surface layer diffusion will continue until the system cools to absolute zero (Dodson, 1986).

A constraint on the diffusion history of individual grains is obtained by applying the operator $\mathrm{erf}^{-1}$ to the age data (Fig. 5), which transforms the data to a linear array. The slope of the linear regression through this array equals $(4Dt)^{-1/2}$. A value for $D$ can be calculated by approximating $t$ as the time interval in which differential volume diffusion occurred within the grains, i.e., as the difference between the modeled core and rim ages ($\Delta t$). In this case, $D$ is the time-integrated diffusion coefficient for Pb in rutile ($D_\Delta$; Table 3). Eq. (2) provides the relation between $D_\Delta$ and $D(t)$, which is the diffusion coefficient at a given time $t$ after Pb diffusion became insignificant in the grain cores.

$$D_\Delta = \frac{\int_0^{t_\Delta} D(t)dt}{\Delta t} \quad (2)$$

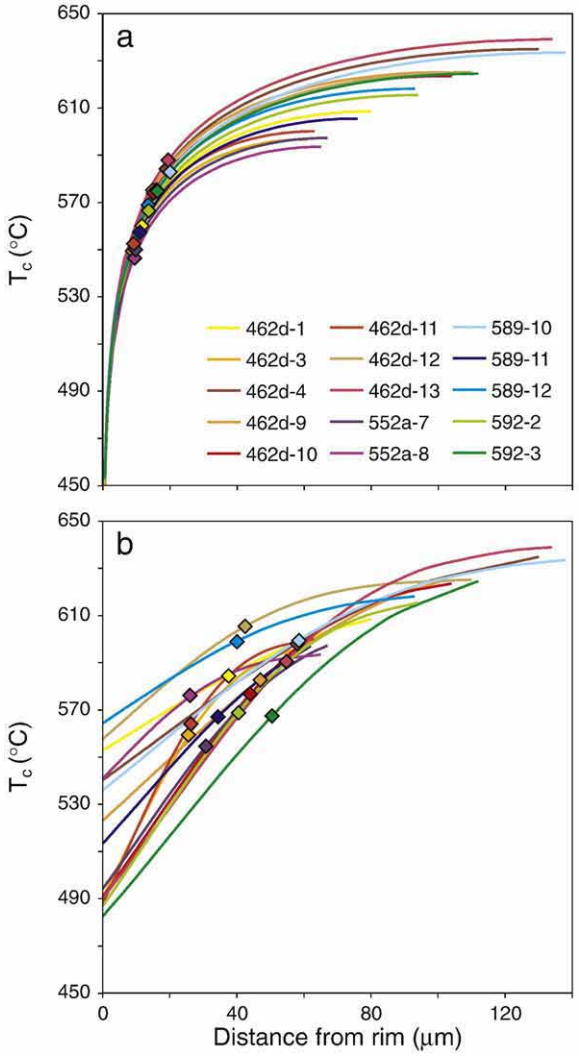


**Fig. 6.** $T_c(x)$ profiles for the analyzed rutile grains calculated using (a) the model of Dodson (1986) and (b) the error function-based model. Values of $T_c$ are plotted vs. distance from rim for all 15 studied rutile grains. Diamonds indicate the weighted mean closure temperatures ($T_{c,wm}$), which correspond to the weighted mean ages of the grains. The legend applies to both diagrams.

**Table 3**
Results of Pb diffusion modeling.

| Sample[a] | Modeled age (Ma) | | Model fit | $n$[b] | $a$ | $D_\Delta$ | $T_{c,core}$ | $T_{c,wm}$ | $T_{c,wm}$ | $T_{c,rim}$ | $C_r$ (°C/Ma) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Core | Rim | $R^2$ | | (μm) | ($\times 10^{-25}$ m$^2$/s) | (°C) | Dodson | EF model[c] | EF model[c] | Dodson | EF model[c] |
| 462d-1 | 2457 | 2316 | 0.81 | 6 (7) | 80 | 2.8 | 609 | 560 | 584 | 553 | 0.7 | 0.4–0.3 |
| 462d-3 | 2465 | 2357 | 0.95 | 7 (9) | 61 | 1.0 | 597 | 549 | 559 | 491 | 0.7 | 2.2–1.2 |
| 462d-4 | 2476 | 2339 | 0.79 | 13 (13) | 130 | 4.9 | 635 | 583 | 598 | 540 | 0.7 | 0.8–0.6 |
| 462d-9 | 2547 | 2388 | 0.88 | 7 (7) | 102 | 3.1 | 625 | 575 | 583 | 523 | 0.8 | 0.8–0.5 |
| 462d-10 | 2489 | 2353 | 0.96 | 5 (5) | 104 | 2.2 | 624 | 573 | 577 | 491 | 0.7 | 1.2–0.8 |
| 462d-11 | 2495 | 2405 | 0.95 | 3 (3) | 63 | 1.0 | 600 | 552 | 563 | 488 | 0.8 | 1.5–1.0 |
| 462d-12 | 2422 | 2371 | 0.39 | 12 (12) | 110 | 4.6 | 625 | 575 | 605 | 558 | 0.7 | 1.5–1.2 |
| 462d-13 | 2505 | 2389 | 0.70 | 6 (7) | 134 | 3.4 | 639 | 587 | 590 | 490 | 0.8 | 1.7–1.0 |
| 552a-7 | 2434 | 2228 | 0.84 | 6 (6) | 67 | 1.0 | 597 | 550 | 554 | 494 | 0.6 | 0.6–0.4 |
| 552a-8 | 2322 | 2254 | 0.90 | 5 (6) | 65 | 1.6 | 594 | 546 | 576 | 541 | 0.6 | 0.9–0.7 |
| 589-10 | 2388 | 2265 | 0.48 | 14 (16) | 138 | 4.5 | 634 | 582 | 599 | 536 | 0.6 | 0.9–0.7 |
| 589-11 | 2460 | 2290 | 0.84 | 9 (12) | 76 | 1.6 | 606 | 557 | 567 | 513 | 0.7 | 0.6–0.5 |
| 589-12 | 2452 | 2385 | 0.64 | 11 (11) | 93 | 4.2 | 618 | 568 | 599 | 564 | 0.7 | 0.9–0.7 |
| 592-2 | 2434 | 2277 | 0.84 | 9 (9) | 94 | 1.7 | 616 | 566 | 569 | 487 | 0.6 | 1.0–0.7 |
| 592-3 | 2464 | 2233 | 0.55 | 10 (10) | 112 | 2.1 | 625 | 574 | 567 | 483 | 0.6 | 0.8–0.5 |

[a] Grain name comprises sample name and grain number.
[b] Number of analyses used with the total number of analyses in parentheses.
[c] EF model = error function-model, presented in this study.

For thermally-activated solid-state diffusion processes the diffusion coefficient $D(t)$ is related to absolute temperature $T(t)$ through the Arrhenius equation Eq. (3).

$$D(t) = D_0 \exp\left(\frac{-E_a}{RT(t)}\right) \quad (3)$$

Using the constraint that $T$ is approximately inversely proportional to $t$ during the slow cooling of the terrane, this provides the definition for $T(t)$ as given in Eq. (4).

$$T(t) = \left(\left(\frac{T_{c,rim}^{-1} - T_{c,core}^{-1}}{\Delta t}\right)t + T_{c,core}^{-1}\right)^{-1} \quad (4)$$

Eqs. (2–4) are combined to get:

$$D_\Delta = \frac{\int_0^{\Delta t} D_0 \exp\left[-E_a\left(\left(\frac{T_{c,rim}^{-1} - T_{c,core}^{-1}}{\Delta t}\right)t + T_{c,core}^{-1}\right)/R\right]dt}{\Delta t} \quad (5)$$

$T_{c,core}$ represents the temperature at $t=0$, the time when the system started to close for Pb. Because in most cases the peak-metamorphic temperature for the studied rocks will probably be significantly higher than $T_{c,core}$ (e.g. 750–820 °C for the samples from the present study; Mezger et al., 1989), this parameter is approximated by the core $T_c$ estimates based on Dodson's model for $T_c(x)$ (Table 3). These estimates are strongly dependent on grain size and agree with the expectation that diffusion of Pb in the cores of smaller grains occurred until a later stage and therefore at lower temperatures. Using Eq. (5), the $T_{c,rim}$ estimates for all studied rutile grains were calculated (Table 3). These establish $T(t)$ for each sample, which is combined with the age profiles to provide the EF-based $T_c(x)$ profiles (Fig. 6b). From these profiles cooling rates can be calculated for individual rutile grains, which decrease over time according to the predicted $t \sim 1/T$ relationship. Estimated cooling rates are on the order of 0.4 to 2.2 °C/Ma and typical differences within single grains range from 0.2 to 1.0 °C/Ma representing the decrease in cooling rate over the corresponding time period (Table 3).

The $T_c$ profiles are fairly consistent and show a gradual decrease in $T_c$ from core to rim and a slight steepening towards the rim. The $T_c$ difference between cores and rims is significant for all grains, the largest for grain 462d-13 with a $T_c$ of 640 °C in the core to 490 °C at the rim. The outer rim $T_c$ estimates range from 483 to 558 °C (Table 3), but 7 grains converge to a temperature around 490 °C ($\pm 7, 2\sigma$) (Fig. 6b). The 8 other grains provide higher $T_{c,rim}$ values of up to 564 °C. For further comparison with Dodson's model we used the EF-based model to estimate the weighted mean $T_c$ ($T_{c,wm}$) values corresponding to the weighted mean ages. These calculations provided $T_{c,wm}$ values of 554 to 605 °C (Table 3).

## 8. Discussion

### 8.1. U–Pb spot analysis of rutile

The data show that precise and accurate Pb–Pb and U–Pb ages can be obtained from rutile using laser ablation ICP-MS. The ages presented in this study cover a range that includes the ages previously determined for the same samples by ID-TIMS (Mezger et al., 1989). However, the age heterogeneity that could be resolved from individual grains clearly demonstrates the potential of small-spot analysis. It indicates that the slight discordance of some whole-grain analyses reported by Mezger et al. (1989) represents age-mixing. Besides providing important additional geochronological information, the high spatial resolution of the technique opens the possibility for different applications. Age profiles determined by LA-ICP-MS may be combined with experimentally-determined Pb diffusion parameters for rutile to constrain $T_c(x)$. Because the spot analyses provide weighted mean ages of the material analyzed, spatial weighing will cause the age to be most representative for the core of the analyzed spot. Therefore, spatial resolution may restrict the precision of modeled age profiles, but should not introduce inaccuracy. Provided that a terrane underwent a single cooling history following the peak of metamorphism, combining $T_c(x)$ profiles with U–Pb age profiles allows estimates of cooling rates from single-grain analysis (Dodson, 1973; 1986; Ganguly and Tirone, 1999; 2001).

### 8.2. How accurate is the model?

The proposed model provides an estimate for $T_{c,rim}$ and allows the reconstruction of closure temperature profiles, which record the time-dependent cooling rate. To estimate the accuracy of the model, the validity of important assumptions and input parameters and the consequences of possible deviations have to be evaluated.

A major requirement for accurate diffusion modeling is that the zoning profiles of the rutile grains were analyzed through the grain center. Because the grains were analyzed in thin section there was no control on the third dimension of the grains. The consequence of not going exactly through the center of a grain would be that the measured core age is too low, resulting in flatter slopes of the fitted error functions. The difference in slopes of the error function within single samples indicates that not all analyzed profiles were exactly centered, but the limited range of $D_\Delta$ values based on the fitted error functions indicates that the effects are relatively small. The estimated rim ages are independent of the profile positioning and therefore similar within single samples. Exceptions that show older rim ages could reflect additional controls on diffusion. Because Pb diffusion in rutile should show little anisotropy (Cherniak, 2000), the positioning of analyzed profiles relative to crystallographic axes should not have influenced estimated rim ages. Although the influence of various impurities on Pb diffusion is unclear (Cherniak, 2000), we suggest that these may have played a role in restricting Pb diffusion in these specific grains.

An important parameter in our diffusion model is the temperature in the core at the time when the system started to close for Pb ($T_{c,core}$). There are different ways of estimating this temperature. Firstly, the peak-metamorphic conditions as determined by Mezger et al. (1989) could be used. However, it is expected that the rutile grains have grown under prograde metamorphic conditions. A second possibility is to analyze the Zr content of the grains and apply Zr-in-rutile thermometry (Tomkins et al. 2007; Zack et al. 2004a). It has been shown that these temperatures may reflect the peak conditions at which rutile grew, but to enable linking temperature with age the diffusivities of Pb and Zr in rutile have to be similar under the given conditions. The diffusion coefficient for Zr in rutile is potentially lower than that of Pb at temperatures exceeding ca. 600 °C (Cherniak, 2000; Cherniak et al., 2007). This implies that temperatures obtained by Zr-in-rutile thermometry may exceed the closure temperatures for Pb diffusion, resulting in large inaccuracy on $T_c(x)$ profiles and an underestimated $T_{c,rim}$. Therefore, we chose to base the core $T_c$ estimates on the model of Dodson (1986) combined with the experimentally-determined diffusion parameters of Cherniak (2000). As expected, these temperature estimates are strongly grain size dependent, with lower closure temperatures in cores of smaller grains. Furthermore, the curvatures of the $T_c$ profiles of Dodson and our model are very similar in the cores of grains making a comparison reasonable.

An input parameter in Dodson's model, which therefore also affects the $T_{c,core}$ estimate of our model, is the cooling rate. The cooling rates used were based on comparison with regional information on the $T_c$ and age of other minerals. These estimates are only approximations, because a very limited data set is available for the Pikwitonei area. However, the

effect on the temperatures resulting from Dodson's model is very small. An order of magnitude difference in input cooling rate only affects the $T_{c,core}$ with ca. 10 °C and is therefore insignificant. In addition, the cooling rate estimates that follow from our model, which are independent estimates, are in excellent agreement with the regional estimates indicating that the assumption is valid.

The determinations of $E_a$ and $D_0$, based on experiments (Cherniak, 2000) and on data from natural rock samples (Mezger et al., 1989) are subject to uncertainty. Nevertheless, both are consistent and seem to provide accurate estimates. In addition, a change of the parameters $E_a$ and $D_0$ would result in a direct translation of the $T_c$ profiles. Because changes in the calculated $D_\Delta$ are compensated by changes in $T_{c,core}$, only the absolute temperatures will change and the shape of the profiles will remain the same. This implies that the resulting cooling rate estimates will not be affected by inaccuracy of the diffusion parameters.

### 8.3. Comparing the $T_c(x)$ models

In this study, a fundamental difference between the error function-based model and the model proposed by Dodson concerns the input parameters. Dodson's model requires the input of an average cooling rate, whereas the presented model requires a core $T_c$ estimate. The cooling rate estimates are based on regional information and the core $T_c$ estimates are based on the results of Dodson's model. The cooling rates that follow from the presented model, although changing over time according to the relation $t \sim 1/T$, are in good agreement with the input cooling rates of Dodson's model confirming the validity of the input parameters. Depending on the available information on a terrane or isotope system, other model parameters may be estimated.

When comparing the $T_c$ profiles of both models, it is obvious that the most important difference is the trend of the profiles. The error function-based model displays a gradual change in $T_c$ with position in the grain, whereas Dodson's model shows a slow decrease throughout most of the grain and a very abrupt decrease close to the rim. This steep decrease is based on the assumption that Pb diffusion will continue in rutile grains undergoing steady cooling to surface temperatures (Dodson, 1986). Although in theory in the outermost part of the rutile Pb diffusion could continue (depending on diffusion parameters and availability of a Pb-sink), it is unlikely that this happens on the scale as is indicated by Dodson's model. Direct comparison between Dodson's model and measured ages would result in anomalously high cooling rates that increase with decreasing age. These aspects show that $T_c(x)$ described by the error function provides more realistic temperature distributions throughout the rutile grains, especially for outward grain segments. A study on Pb diffusion in monazite has shown that recent Pb-loss only occurred in the outer 50 nm of grains and, apart from the anomalous outer rim, the age data provided a well-constrained diffusion profile described by an error function (McFarlane and Harrison, 2006). We expect that age profiles as observed for monazite may also occur in rutile. However, considering that Pb diffusion in monazite is significantly slower than in rutile (e.g. Cherniak, 2000; McFarlane and Harrison, 2006), the scale at which recent Pb-loss affects rutile will be larger than 50 nm. At this point, we are not able to resolve this scale by LA-ICP-MS or to make valid predictions based on our model. It is, therefore, important to keep in mind that the extrapolated rim ages and $T_{c,rim}$ values are theoretical.

Despite the significant differences in slope- and trend of the $T_c(x)$ profiles of both models, the calculated weighted mean closure temperatures are very similar providing an average of 580 °C for the EF model and 567 °C for Dodson's model (Table 3). The EF-based $T_c(x)$ profiles largely plot below Dodson's $T_c(x)$ profiles (Fig. 6), but this is compensated by the steep $T_c$ decrease towards the rims of the latter profiles.

### 8.4. Constraints on $T_c$ and comparison with other studies

Although the estimated $T_c(x)$ profiles required the input parameters $D_\Delta$ and $T_{c,core}$, which seem to vary significantly among different grains, the results are consistent and the profiles of 7 different grains converge to a very well defined $T_{c,rim}$ of 490 °C ($\pm 7, 2\sigma$). The remaining 8 grains show more scattering- and higher rim temperatures. These grains were most likely not analyzed through the exact center of the grains. In this case, the time interval for the hypothetical diffusion experiment ($\Delta t$) would be underestimated resulting in an overestimated value for $D_\Delta$. The $T_c(x)$ profile modeled from these data would be higher than the $T_c(x)$ profile that was obtained from analyses through the exact core of the grain. The profiles that converge at 490 °C display steeper slopes of the error function than the profiles that provide a higher $T_{c,rim}$. The tight clustering around the lowest $T_{c,rim}$ values and the relatively steep slopes provide clear arguments that these $T_c(x)$ profiles are based on analyses that were done close to grain cores. These should therefore provide the most accurate representation of $T_c(x)$.

All constructed $T_c$ profiles clearly demonstrate that the closure temperature variations in single rutile grains can be significant, even in small grains. Therefore, it is impossible to define one single temperature for the closure of Pb in rutile. To enable comparison with results of previous studies we estimated weighted means of the closure temperatures ($T_{c,wm}$). The average $T_{c,wm}$ of the seven most reliable $T_c(x)$ profiles is $569 \pm 24$ °C, representing a range in grain size of 120 to 270 μm (Table 3). This temperature is in good agreement with the upwards-revised $T_{c,wm}$ of 540 °C for the slightly smaller rutile grains from the Adirondack Highlands of 90 to 210 μm (Mezger et al., 1989; revision by Vry and Baker, 2006). The suggested grain size-independent apparent $T_c$ of 630 °C that resulted from a LA-MC-ICP-MS study on rutile by Vry and Baker (2006) is significantly higher. Although in this study the grain size was significantly larger, ranging from 2 to 4 mm, only the outer rims were dated and the temperature difference is probably mainly the result of the different cooling rate of ca. 3 °C/Ma compared to ca. 1 °C/Ma for the Adirondack Highlands and the Pikwitonei Granulite Domain.

The method presented in this study has many advantages compared to previous studies on Pb diffusion and -closure temperatures. In the study of Vry and Baker (2006) laser ablation MC-ICP-MS was applied, but a 25 to 300 μm beam diameter was used and pit depths were 100 to 200 μm. As a result the dated volume was 10 to 100 times larger than in the present study and therefore similar to the whole-grain analyses applied by Mezger et al. (1989). In addition, the results of these studies are subject to additional uncertainties related to the age determinations and closure temperatures of other chronometric methods. The high spatial resolution of the technique applied here allowed the reconstruction of diffusion profiles that clearly demonstrate the strong grain size dependence of $T_c$. The diffusion profiles, in combination with the textural information, allow insight into any textural control on Pb diffusion in rutile. In the case of the studied grains, estimated rim ages and resulting closure temperatures are independent of neighboring phases. This indicates that Pb was effectively removed from the grain boundaries by grain boundary diffusion.

### 8.5. Regional implications

The age results from different sample locations are compared based on the rim age estimates, because these are independent of the position in the grain and reflect the time of absolute closure of the grains for Pb. The average rim age of sample 462d from the Cauchon Lake area is significantly higher (2372 Ma) than rim ages of the Natawahunan Lake samples (2241 Ma for location 552a, 2278 Ma for location 589, and 2255 Ma for location 592). The difference in rim age between the sample locations correlates to the difference in peak-metamorphic conditions, which were lower at the Cauchon Lake (750 °C, 7 kbar) compared to the Natawahunan Lake (820 °C, 7.5–8 kbar). Therefore, sample 462d from the Cauchon Lake cooled below the closure temperature for Pb at an earlier point in time.

As indicated by Mezger et al. (1989) the study area probably acted as a single rigid block after the peak-metamorphic conditions at ca. 2600 Ma. The fact that the average cooling rates are similar between the different sample localities (0.7–1 °C/Ma) is consistent with this statement and indicates that all studied rocks represent approximately the same level of crust at a given age. The cooling rate estimates based on the error function-model show a decrease over time from ca. 2.2 to 0.4 °C/Ma corresponding to the time interval from ca. 2500 to 2250 Ma. These estimates fit well with the results of Mezger et al. (1989), who estimated cooling rates of 1.8 °C/Ma directly after peak metamorphism (ca. 2600 Ma) to 0.5 °C/Ma at around 2300 Ma. This consistency contributes to the validity of our model and indicates that cooling rates can be estimated from single grains by U–Pb dating of rutile using LA-ICP-MS.

The estimated cooling rates may provide important constraints on the mechanisms that facilitate the exhumation of rocks. Considering that tectonically-driven exhumation, by normal faulting and ductile thinning, operates at rates of milli- to centimeters per year (e.g. Ring et al., 1999), associated cooling should be relatively rapid. In contrast, studies of cosmogenic nuclides such as $^{10}$Be have indicated that surface denudation is often a relatively slow process (e.g. Brown et al., 1995). The isostatic rebound from large-scale erosion is expected to result in slow exhumation (<0.1 mm/yr). Using an average thermal gradient of ca. 0.04 °C/m, this exhumation rate would imply slow cooling at rates less than 4 °C/Ma. This is consistent with the results of our study, indicating that exhumation of the Pikwitonei Granulite Domain was the result of surface erosion.

## 9. Conclusions

We have demonstrated that both precise and accurate U–Pb ages for rutile can be obtained by laser ablation ICP-MS. Age differences of up to 150 Ma were found in single rutile grains having a grain size of up to 280 µm. The age profiles across rutile grains indicate that volume diffusion of Pb occurred in rutile implying that the ages represent cooling ages. In situ dating by LA-ICP-MS has the advantage that textural information remains preserved. The nature of the minerals surrounding rutile has no significant effect on the rim age estimates indicating that Pb diffusion is probably assisted by grain boundary diffusion. The classical $T_c(x)$ model of Dodson (1986) indicates $T_c$ variations from 640 °C in the core to 510 °C at ca. 4 µm from the rim and a rapid $T_c$ decrease closer to the rim. A new error function-based $T_c(x)$ model was constructed, which provides a better description of the relation between age distribution and $T_c$ for the analyzed grains. This model combined with the diffusion data of Cherniak (2000) shows a steady decrease in $T_c$ throughout the grain from ca. 640 °C in the core (depending on grain size) to a rim intercept $T_{c,rim}$ of 490 °C ($\pm 7, 2\sigma$). This is interpreted to be the theoretical absolute temperature of insignificant Pb diffusion in rutile. Both $T_c(x)$ models demonstrate that even in small grains the variations of $T_c$ can be significant making it impossible to define one representative $T_c$ for Pb in rutile. The error function-based $T_c(x)$ model allows the determination of cooling rates, which show a decrease over time from ca. 2.2 to 0.4 °C/Ma agreeing well with previous estimates for the Pikwitonei granulite domain. This indicates that cooling rates can be estimated from single grains by LA-ICP-MS U–Pb dating of rutile providing constraints on the cooling history of a metamorphic terrane and, therefore, on the rate- and mechanisms of exhumation.

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## Appendix A. Supplementary Data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2010.02.047.

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