Improved confidence in (U-Th)/He thermochronology using the laser microprobe: An example from a Pleistocene leucogranite, Nanga Parbat, Pakistan

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[1] The newly developed laser microprobe (U-Th)/He thermochronometer permits, for the first time, the ability to generate precise (U-Th)/He cooling ages for even very young (<1 Ma) samples with a spatial resolution on the order of tens of micrometers. This makes it possible to test the reproducibility of independent (U-Th)/He age determinations within individual crystals, further increasing the reliability of the method. As an example, we apply it here to a Pleistocene granite from Nanga Parbat, Pakistan, where previous constraints on the thermal history are consistent with rapid exhumation and cooling. Twenty-one (U-Th)/He dates determined on two monazite crystals from a single granite sample yield a mean of
748,000 years with a ~95% confidence level of ±19,000 years. There is no discernible variation in the distribution of (U-Th)/He ages in the cores of these crystals and therefore no evidence for the development of substantial diffusive-loss ⁴He zoning over 80% of the interior of the monazite crystals during postcrystallization cooling of the granite. Modeling of these data suggests that cooling at a mean rate of ~300 K/Ma would be necessary to produce the observed ages and the lack of a ⁴He gradient, which is consistent with preexisting constraints for Nanga Parbat. Increased precision in thermochronology permits more tightly constrained exhumation models, which should aid geologic interpretation.

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1. Introduction

[2] The (U-Th)/He geochronometer relies on the production of ⁴He from naturally occurring ²³⁵U, ²³⁸U, ²³²Th, and ¹⁴⁷Sm through alpha decay [e.g., Farley, 2002; Reiners, 2002]. Radiogenic ⁴He diffuses rapidly in minerals at relatively low temperatures (<300°C) compared to the daughter products of chronometers such as U-Pb, Lu-Hf, and Sm-Nd, which typically record the time elapsed since crystallization. Thus, (U-Th)/He dates are usually interpreted as cooling ages, with each mineral assigned a closure temperature (T_C) corresponding to that age based on the cooling rate, the size of the grain (or its effective diffusion dimension), and the temperature-dependent diffusivity of ⁴He in the mineral [Dodson, 1973]. The utility of the (U-Th)/He technique has been demonstrated for a wide range of applications, including meteorite chronometry, development of topography, tephrochronology, and most commonly determining the exhumation-induced cooling of samples in tectonically active regions [Farley et al., 2000; House et al., 1998; Min, 2005]. These studies have relied on whole-crystal or “conventional” (U-Th)/He age determinations, which often result in larger than expected systematic and random errors due to zoning and other unidentified complications [Boyce and Hodges, 2005; Tagami, 2003]. Generating large, statistically significant data sets requires the development of new methods to produce precise ages quickly. Furthermore, in many geologic settings, slow postcrystallization cooling will produce a ⁴He concentration gradient in the grain, with a predicted topology that is related to the specific thermal history of the sample [Dodson, 1986]. Exploiting internal gradients for tectonic studies also requires new techniques that can quantify intracrystalline ⁴He variations. The laser microprobe (U-Th)/He thermochronometer, implemented here on samples of an unknown (but under 1.5 Ma) age for the first time, can potentially address both of these issues.

[3] The fidelity of the laser microprobe (U-Th)/He technique [Boyce et al., 2006] has been previously demonstrated on the MOM monazite standard (Ataleia, Minas Gerais, Brazil). Monazite is a rare earth element phosphate mineral, nominally CePO₄, but commonly enriched in U, Th, and Sm. These centimeter-sized, gem-quality monazite crystals have different, but internally invariant U, Th, and Sm concentrations, making them ideal for any number of in situ techniques (including (U-Th)/He), and to date have been employed as standards in a half-dozen electron probe and ion microprobe laboratories around the world. Conventional (U-Th)/He ages (449.6 ± 9.8 Ma, 2SE) and laser microprobe (U-Th)/He ages (455.3 ± 3.7 Ma, 2SE)
agree within 1.3% for more than 30 total analyses on two different crystals. Given the general inability of (U-Th)/He laboratories around the world to reproduce any natural crystal standard to better than ~5% [Boyce and Hodges, 2005; McDowell et al., 2005; M. van Soest, personal communication, 2008], this agreement confirms that the laser microprobe can be used to generate cooling ages that are as accurate as conventional (U-Th)/He ages. However, dating unzoned centimeter-scale gem-quality crystals that are several hundred million years old is a far cry from dating typical crystals which are small, zoned, broken, included and otherwise more difficult to work with, in addition to typically being younger and therefore having much lower radiogenic He concentrations.

Extending laser microprobe (U-Th)/He of monazite to such samples was the motivation of this study.

2. Nanga Parbat as a Test of (U-Th)/He Thermochronometry

The Nanga Parbat-Haramosh region of Pakistan includes dramatic exposures of granitic and high-grade metamorphic rocks that record the development of very high geothermal gradients during the most recent stages of Himalayan orogenesis [Craw et al., 1997; Winslow et al., 1994]. Structural, geomorphic, and geochemical data suggest that surface uplift and rock exhumation rates of the Nanga Parbat massif over the past few million years may have been among the highest on Earth, resulting in local relief in excess of 7000 m and young cooling ages that are often within error of zero [George et al., 1995; Koons et al., 2002; Treloar and Rex, 1990; Winslow et al., 1996; Zeitler et al., 1982, 1989, 2001]. Nanga Parbat provides an ambitious test of the ability of the laser microprobe (U-Th)/He method to generate meaningful ages on very young samples.

3. Nanga Parbat Monazites

In this study, we apply the laser microprobe (U-Th)/He method to monazite crystals from a biotite + cordierite + tourmaline leucogranite that crosscuts foliation in the host gneisses above Fairy Meadows camp, north of the summit of Nanga Parbat at an elevation of approximately 3500 m. Isotope-dilution, thermal ionization mass spectrometry U-Pb data for accessory minerals from this sample suggest crystallization ages of 1.2–1.4 Ma [Crowley et al., 2005]. We would expect the (U-Th)/He cooling ages of these samples to be significantly younger than the U-Pb crystallization ages, even in the case of rapid exhumation.

Two 250–300 μm diameter monazite crystals were prepared as described in detail below. Backscattered electron images of both crystals (Figure 1) display evidence for chemical zoning that corresponds to variations in U and Th concentration determined by electron microprobe analysis. Both crystals are fractured and included making them less than ideal candidates for conventional (U-Th)/He. Both crystals also have unusual shapes, and at least one of the two crystals (Figure 1, top) is incomplete, and would be difficult to correct for lost He due to alpha recoil [Farley et al., 1996].
U, Th, and Sm concentrations were measured by electron microprobe at The University of Massachusetts, following procedures outlined by Jercinovic and Williams [2005]. Care was taken to correct U concentrations for overlap of the Th family of X-ray lines (Th M-g, Th M3-N4, the associated high-energy M3-N4 satellite, and Th M5-P3) on U M-b (our analytical line for uranium). In each case, core and rim zones relatively depleted in U and Th (Th = 39,200 – 49,400 ppm; U = 5,700 – 8,000 ppm) are separated by an intervening zone of high U and Th (Th = 55,000 – 58,000 ppm; U = 8,100 – 8,200 ppm).

4. (U-Th)/He Methodologies

[7] Both conventional and laser microprobe (U-Th)/He methodologies require separate measurements for parent (U, Th, Sm) and daughter (He) elements, because there exists no single analytical instrument that can measure all of these elements with the abundance sensitivity and precision required for geochronology. Thus, all (U-Th)/He ages are the products of multiple analytical procedures for conventional (U-Th)/He. The resulting (U-Th)/He age must then be corrected for the alpha particles that are ejected from the crystal during nuclear decay. This correction is sensitive to the energy of the alpha particle, the physical model employed to calculate stopping distances, the composition and density of the mineral host, the size and shape of the crystal, as well as zoning and the presence of parent-rich inclusions. Such corrections can be in excess of 50% of the uncorrected age for small crystals, and any uncertainties in the correction should be (but often are not) propagated into the total uncertainty in the age.

[8] In conventional (U-Th)/He chronometry, single crystals are evaluated under high magnification transmitted-light microscopy for inclusions, fractures, breakage or other imperfections. Acceptable crystals are measured (in 3-D) and loaded into microcrucibles of Pt or Nb. This measurement, and the ejection correction derived from it are generally not considered to be significant in calculating (U-Th)/He ages, but the recent work of Evans et al. [2008] has demonstrated that measurements made by experienced analysts can vary by 4–9%, and in one case differed from a value calculated by computed microtomography by 24%. This suggests that grain measurement is a nonnegligible additional source of uncertainty that should be incorporated into final age error estimates for conventional (U-Th)/He.

[9] The measured crystals are then loaded into an ultrahigh vacuum laser chamber or resistance furnace and gently heated to release He. Care must be taken not melt the crystal, as vapor-phase loss of Th (and or U) may occur [House et al., 2000]. Crystals are then retrieved and dissolved in concentrated acids for analysis of U, Th, and Sm, which is usually accomplished by isotope-dilution, inductively coupled plasma mass spectrometry. The resulting (U-Th)/He age must then be corrected for the alpha particles that are ejected from the crystal during nuclear decay. This correction is sensitive to the energy of the alpha particle, the physical model employed to calculate stopping distances, the composition and density of the mineral host, the size and shape of the crystal, as well as zoning and the presence of parent-rich inclusions. Such corrections can be in excess of 50% of the uncorrected age for small crystals, and any uncertainties in the correction should be (but often are not) propagated into the total uncertainty in the age.

4.2. Laser Microprobe (U-Th)/He

[10] The end result of this effort is that each crystal can only yield one (U-Th)/He age, and the pain-taking work required to find “perfect” crystals must be multiplied if replicate analyses are to be performed. It should be noted that the reasons for this degree of selectivity are multifold. Inclusions rich in parent elements (such as zircon or monazite) may contribute a significant fraction of radiogenic He to a relatively parent-element-poor host crystal, but the parent elements in the inclusion may not be accounted for if the inclusion is not dissolved along with the host. Inclusions can also represent a form of extreme zoning, which could result in erroneous alpha-ejection corrections: An inclusion that dominates the parent-element budget of the crystal (such as a zircon or monazite inclusion in apatite) would necessitate a ~50% alpha-ejection loss correction if located at the surface of the host, and a 0% correction if the inclusion was sufficiently far from the surfaces of the host crystal to prevent any alpha escape by recoil. Broken crystals (anhedral or subhedral fragments) are also likely to result in erroneous ejection corrections, as the original shape and size of the crystal is not easily estimated. At best the analysis of such grains results in larger, poorly constrained uncertainties, and at worst it results in calculated dates that contain no real age information. In the case of detrital samples, being selective about grain quality could skew the resulting age populations because different populations of crystals may have experienced varying transport conditions and distances that result in systematic textural differences.
by hand (to 0.05 μm grit) in order to produce a smooth, flat surface. This serves several purposes: First, the polishing exposes the interior of the crystal that is less likely to be affected by alpha-ejection-induced helium loss, obviating the ejection correction (and the associated error, which is difficult to quantify) which typically must be made to whole-grain (U-Th)/He ages [Farley et al., 1996; Hourigan et al., 2005]. Second, this polishing allows the internal parent element variations to be evaluated directly and with high fidelity. In most cases, qualitative mapping such as that provided by X-ray or backscattered-electron analysis is performed, followed by quantitative analysis by electron microprobe, secondary ion mass spectrometer, or other in situ technique. Recent developments in 3-D tomographic imaging of U and Th at the subgrain scale [Evans et al., 2008] may lead eventually to high-resolution 3-D maps of parent elements within crystals, but even the knowledge of 2-D zoning provided by mapping polished grain interiors promotes judicious placement of laser microprobe analyses in order to avoid regions of particularly strong zoning, inclusions or other complications. Finally, careful polishing generates a flat and smooth surface to serve as a reference for measuring ablation pit volumes.

After characterization, the crystals are repolished to remove the carbon coating required for electron microprobe analysis. The crystals are then remounted in indium, a necessary step because epoxy, dental acrylic, and other organic-rich potting materials are not compatible with the ultrahigh vacuum environment required for He analyses. Samples are then placed into the ultrahigh vacuum laser chamber with a sapphire or UV glass window (UV glass was used for the analyses in this paper) and ablated with a deep UV laser (such as the Lambda Physik excimer laser, operating at a nominal wavelength of 193 nm) to release He. Typical ablation pits are ~20–100 μm in diameter, and 1–50 μm deep, depending on the He concentration and purpose of the measurement (sequential depth profiles versus single-age pits). Radiogenic helium released by ablation is spiked with a known amount of ³He, purified by active metal getters, and measured by isotope dilution on a quadrupole mass spectrometer following the procedures outlined by Boyce et al. [2006]. Ablated volumes are then measured by optical interferometry or laser confocal microscopy, allowing He concentrations to be determined.

In contrast to conventional (U-Th)/He, the effective spatial resolution of a few tens of microns or less of the laser microprobe allows multiple measurements to be performed on individual crystals. In addition, the laser microprobe allows broken, irregular or included grains to be analyzed, further reducing the time required to find suitable crystals by relaxing quality constraints. The ability to date crystals of varying quality also reduces the risk of skewing ages in mixed populations of crystals such as detrital samples.

5. Results and Discussion

Calculation of (U-Th)/He ages and uncertainties is accomplished by iterative application of a forward modeling Monte Carlo method and the ⁴He production equation (commonly referred to as the “(U-Th)/He age equation”) extended to include secular disequilibrium in the intermediate daughter products of ²³⁸U, following a conceptualization similar to that of Farley et al. [2002]. This is discussed in detail below.

Targeting regions of the core and intermediate zones away from the ejection depleted crystal surfaces, we were able to determine (U-Th)/He dates for 14 ablation pits in Crystal 1 and 7 pits in Crystal 2. Each pit had a diameter of ~20 μm and a depth of ~12–14 μm (inset of Figure 1), measured using a Carl Zeiss Instruments LSM 5 Pascal confocal laser microscope. Reflected laser source light is detected by confocal microscopy, providing depth resolution in addition to lateral resolution. Combined with a moving stage, this allows a surface to be mapped in high resolution, creating a nanoscale digital elevation model, from which volumes can be calculated. Nominal resolution of this instrument is ~25 nm in the vertical direction, with a horizontal resolution of <0.25 μm. The uncertainty is this volume measurement as calculated from the voxel uncertainties would be negligible. However, the absolute accuracy of these measurements is unknown, because no “volume standards” exist for concavities such as ablation pits (and “bump-height standards” are not relevant for ablation pits given the reduced amount of laser light returning from pit bottoms). In addition, there is uncertainty derived from the assumptions regarding the flatness of the original surface from which the pit volume is subtracted. Because of this, we estimate the uncertainty of the pit volume at 5% (2σ), but we acknowledge that this is only an estimate and that future efforts to calibrate the precision and accuracy of pit volume measurements need to be made, preferably with multiple techniques and independent assessments of volume.
In all cases, the pits were far enough from the crystal surfaces to avoid regions of extracrystalline alpha ejection, but some pits required minor corrections for zone-to-zone alpha exchange as described below, following the methodology of Boyce and Hodges [2005]. Although this correction results in a negligible change in the calculated mean age, it was performed for each spot, and an estimate of the increased uncertainty (geometric mean of concentrations on either side of a relevant zone boundary) from the correction was incorporated into the age calculation.

Twenty-one of the twenty-two pits analyzed in the two monazite crystals yielded similar ages (Figure 2 and Table 1). Fourteen independent age determinations within Crystal 1 yield an error-weighted mean age of 746 ka and a mean uncertainty (2σ) of 51 ka (6.5%). The mean squared weighted deviation (MSWD) for the Crystal 1 mean age is 3.4, a value larger than that which might be explained simply by random experimental error if our estimates for the various error input parameters are correct [Wendt and Carl, 1991]. As a consequence, we multiplied the nominal uncertainty in the mean (two standard errors of the mean, here designated 2SE) by the square root of the MSWD [Ludwig, 2003] to arrive at a conservative estimate of 26,000 years (2SE) for the uncertainty in the error-weighted mean age of Crystal 1. Seven analyses of Crystal 2 yield a second mean age of 753 ± 33 ka (MSWD = 2.5), with one outlier analysis at 1.2 Ma which was rejected on both statistical grounds, and by an evaluation of the helium analysis, which exhibited an unusual gas evolution curve. It is the ability of the laser microprobe to generate multiple ages on individual crystals that enables us to robustly evaluate this single date as an outlier, a determination that would be difficult with the small replicate populations that typify conventional (U-Th)/He studies. Since the means for these two monazite crystals are statistically indistinguishable, we combined the 21 analyses to arrive at a mean age for both crystals of 748 ± 19 ka (2SE).

We can make several first-order conclusions from the 21 laser microprobe analyses on these two crystals. First, we note that the both the internal and external reproducibilities are quite good for both crystals, with 95% confidence intervals of 3.5% and 4.4% within the crystals, and means that agree within 7,000 years. The lack of variation observed in cooling ages from these crystals is indicative of the rapid cooling that this sample must have experienced, which we discuss further below. However, the MSWD for all 21 analyses (2.9) is in excess of what would be expected if there was not scatter beyond our estimates of the uncertainties. Thus our ability to discern variations between individual spots is at best at the level of variations greater than ~7%, and it is likely that the true uncertainties are slightly larger than our estimates.

Table 1. U and Th Measurements for Each Crystal

| Domain | U     | U 2σ | Th     | Th 2σ | Sm    | Sm 2σ |
|--------|-------|------|--------|-------|-------|-------|
| Crystal 1 |       |      |        |       |       |       |
| Core  | 7011  | 492  | 45719  | 1108  | 13584 | 1290  |
| Middle | 8209  | 540  | 57943  | 1294  | 14830 | 1282  |
| Rim   | 6024  | 218  | 49376  | 576   | 16071 | 677   |
| Crystal 2 |       |      |        |       |       |       |
| Core  | 7980  | 276  | 39176  | 504   | 15960 | 710   |
| Middle | 8101  | 257  | 55204  | 591   | 15968 | 607   |
| Rim   | 5689  | 404  | 46835  | 1076  | 15169 | 1272  |

*Uncertainties reported as two standard deviations from the mean.*
5.1. Calculating Effective Parent Element Concentrations due to Ejection Redistribution

[19] The relevant parent element concentrations for a given spot on the map are not the U, Th, and Sm concentrations at/within that volume, but are rather a function of the parent element distribution in the region surrounding (and in some cases, including) the volume being analyzed for He. This is counterintuitive for scientists accustomed to other in situ geochronologic techniques where the parent and daughter elements are located in approximately the same location. This is not true of (U-Th)/He because the alpha particles in a given region were actually (in the case where diffusion is negligible) generated roughly one ejection distance away and ejected (randomly) to that spot. In the case of a laser pit width that is less than the ejection distance, very little (theoretically none) of the He in the pit was generated by parent elements in the same volume because those U, Th, and Sm were ejecting all of their He outside of the pit. Therefore, we are justified, in many cases, in making measurements of the parent elements outside of the ablation pit. This implies that zoning in the region surrounding the ablation pit may affect the He content within the pit. Therefore, the importance of the alpha redistribution within zoned crystals is important to evaluate. In order to properly account for alpha recoil from a three-dimensional distribution of parent elements, we must create a model to calculate the “effective” parent element concentrations for each spot on the map of the crystal.

[20] The first step is to create a simplified map of the parent element concentrations in each crystal using the discrete spot analyses of U, Th, and Sm concentrations and the backscattered electron maps from the electron microprobe (Figure 3). Each crystal is defined to have three homogeneous zones, with concentrations defined by electron microprobe analysis (Table 1). The map of the crystal is surrounded by a zero boundary condition, as the concentrations of U, Th, and Sm outside the crystal were considerably (~1000x) less than the concentrations in the crystal. This assumption is likely true for the major mineral phases (feldspars, quartz, etc.) found in the leucogranite from which these monazites were derived, and is the same assumption made for conventional alpha-ejection corrections [Farley et al., 1996].

[21] Following the model of Boyce and Hodges [2005], we calculate the “effective” concentration of each parent element at each node in the elemental map by averaging all the parent element concentrations located one ejection distance away from the node of interest. We do this because these are the effective (or apparent) amounts of the parent elements that result in the amount of He observed at that node. Because this is a three-dimensional problem, we assume that there is no variation out of the plane of the map, a simplification necessary because the true compositions are not available as a function of depth. This assumption is less likely to effect the calculations for shallow pits in crystals with relatively long-wavelength zoning, where changes in composition over the depth of a pit are likely to be minimal. In order to account for out-of-plane effects, we calculate the position in the plane corresponding to the vertical projection of the points on the surface of an imaginary sphere centered on the node of interest. By sampling the sphere at ~10° increments in azimuth and inclination, and finding the nearest Cartesian grid points, we can map 3600 points lying near the surface of the sphere on to the map plane. The elemental concentrations for those points are then averaged, the value stored, and the process repeated for all points in the map.
The results of the model are shown in Figure 4 for each of the parent elements. As one would expect, regions near the edge of a crystal have a low effective parent composition, reflecting the fact that there is no contribution to nodes near the edge from any neighboring nodes outside the crystal. Regions of the crystal near zone boundaries also show effects of alpha ejection on effective parent element concentrations. Any node near a boundary will receive $^4$He from both sides of the zone, resulting in an effective parent element concentration that reflects the partial contribution from each zone.

Effective concentrations of U, Th, and Sm for a given analysis are calculated by averaging all the nodes within each ablation pit (Table 2). Uncertainties are propagated as averages, using the geometric mean of the uncertainties of the individual zones, except in cases where spots were completely contained within one zone, in which case the uncertainty on the concentrations from only that zone was propagated into the age calculation.

5.2. Secular Equilibrium and (U-Th)/He Ages

For very young samples such as these from Nanga Parbat, one must assess the possible importance of secular equilibrium on the production of uranium daughter products such as He and Pb [Farley et al., 2002; Schärer, 1984]. Secular disequilibrium is typically defined by estimated isotope ratios at the time of crystallization, or by measured isotope ratios at present. For the monazites dated in this study, any excess $^{230}$Th initially
present has decayed over the ~16–20 half-lives since crystallization at 1.2–1.4 Ma, and cannot be measured. Therefore we use estimated initial $^{230}$Th excesses based on Th/U ratios determined for melts in equilibrium with monazites from the host rock, which for these rocks are 0.41–1.11 [Crowley et al., 2005]. However, unlike for U-Pb geochronology, the amount of secular equilibrium present at the time of crystallization does not immediately impact the accumulation of He (assuming that crystallization occurs well above the He closure temperature of the crystal). The amount of time in between crystallization and the start of the (U-Th)/He clock (the “cooling interval”) decreases the effect of disequilibrium, as the system returns to secular equilibrium during that interval. The correction for $^4$He production by “excess” $^{230}$Th incorporated into the monazite structure during crystallization is in all cases here less than 5,000 years. Although this value is much smaller than the uncertainty in the ages, this correction has been applied, and the additional uncertainty stemming from this correction has been incorporated into the total uncertainty in age.

### 5.3. Cooling and Exhumation Rates From Thermochronometry

The simple fact that the weighted mean cooling age determined for these monazites is ~750 ka suggests that cooling must have been quite rapid, given the lack of evidence for late heating that could have caused He loss. We can model the cooling compatible with this rock, for a range of diffusion coefficients for helium in monazite consistent with published experimental data [Boyce et al., 2005; Farley, 2007], and the dimensions of our grains. The Ce-rich compositions of the Nanga Parbat monazites lead to an estimated $T_C$ of ~250°C for both crystals. In Figure 5 we have plotted the range of permissible $T_C$ values (including diffusion coefficient measurement uncertainties) against the observed distribution of ages, with superimposed contours of mean cooling rate in K/Ma. These cooling rates are not model dependent.
because they are mean values, representing an average over the (U-Th)/He cooling lifetime of the monazites, roughly comparable to the cooling age of 0.75 Ma. Considering the entire range of experimentally determined Tc values that would be calculated for monazites of this size using all the available He diffusion data in the literature, and the observed two standard deviation distribution of observed (U-Th)/He ages for both crystals. Large gray dashed rectangular box delineates the range of cooling rates compatible with the ages measured here and the entire range of experimentally determined Tc for natural and synthetic monazites of all studied compositions [Boyce et al., 2005; Farley, 2007]. Small gray scale rectangle covers range of cooling rates that are consistent with synthetic monazite of Farley [2007], with an activation energy of 196 kJ/mol and preexponential factor of 200 cm²/s) and the two standard errors of the mean age distribution determined in this study.

Figure 5. Contours of mean cooling rate (K/Ma) superimposed over the range of experimentally determined Tc versus the two standard deviation distribution of observed (U-Th)/He ages for both crystals. Large gray dashed rectangular box delineates the range of cooling rates compatible with the ages measured here and the entire range of experimentally determined Tc for natural and synthetic monazites of all studied compositions [Boyce et al., 2005; Farley, 2007]. Small gray scale rectangle covers range of cooling rates that are consistent with synthetic monazite of Farley [2007], with an activation energy of 196 kJ/mol and preexponential factor of 200 cm²/s) and the two standard errors of the mean age distribution determined in this study.

[26] Converting cooling rates to exhumation rates is often the ultimate goal of performing thermochronology, and this requires modeling that is

![Figure 6](image-url)
subject to many assumptions regarding the initial and boundary conditions as well as material properties of crust. The increased precision of laser microprobe (U-Th)/He ages can help constrain exhumation to a narrower range of possible models given all the other assumptions required. As an example, here we can use the simplified 1-D advection-diffusion model of *Braun et al.* [2006] to predict what exhumation rates are compatible with the range of possible \( T_C \) values and (U-Th)/He ages determined for Nanga Parbat monazites. Exhumation rates (Figure 7) compatible with the mean (U-Th)/He age of these monazites vary from \( \sim 2.7 \) km/Myr for “warmer” models (thermal boundary layer = 1500°C at 100 km) to \( \sim 3.4 \) km/Myr for “cooler” models (thermal boundary layer = 1000°C). Considering the full \( \pm 2\sigma \) uncertainty in the ages a range of possible \( T_C \) for these samples would result in a range of model exhumation rates from \( \sim 2.1 \) km/Myr to \( \sim 6 \) km/Myr. However, using the \( \pm 2\sigma \) uncertainty in the mean (U-Th)/He age (still including the range of \( T_C \) values) yields a narrower range of possible exhumation rates from \( \sim 2.5 \) km/Myr to \( \sim 3.9 \) km/Myr. Note that our ability to more tightly constrain the range of permissible exhumation rates derives directly from the low uncertainties of the (U-Th)/He data presented here. These low uncertainties were achieved because we were able to combine a large number of dates for a single rock sample. Compared to conventional (U-Th)/He dating of single crystals, laser microprobe (U-Th)/He dating provides a distinct advantage in studies that require the kind of high precision afforded by large numbers of replicate analyses.

**5.4. Cooling Profiles by Laser Microprobe (U-Th)/He**

[27] During slow cooling, one would expect a internal age gradient from core to rim, reflecting the increased probability with which He near the edges of crystals will escape as a result of the random walks of diffusion. This commonly portrayed as a variation in closure temperature from core to rim [Dodson, 1986], and implies that a large portion of the temperature-time history of a rock can be obtained from a single crystal. In the case of a slowly cooled rock, one should be able to measure detectable differences in age between core and rims of single crystals, and thereby constrain multiple (T, t) points [Hodges et al., 1994; Hodges and Bowring, 1995]. With the submicron resolution of the Excimer laser in depth profiling mode, obtaining a near-continuous thermal history should be possible. However, in the case of a quickly cooled rock, one would expect a minimal gradient within the crystal, except that caused by alpha ejection or zoning in parent elements. We can model the age gradient we would expect to have formed in these crystals if they were crystallized at 1.5 Ma @ \( \sim 700°C \), and cooled to produce a closure age for He in monazite of \( \sim 750 \) ka. To do so we use HeFTy [Ketcham, 2005], a program for forward or inverse modeling of thermal histories constrained by thermochronometry. In doing so, we discover that the total range in age observed in the inner region of the crystal (away from the ejection-depleted rim) is never more than \( \sim 12\% \) relative to the maximum age in the core of the crystal. As all of our analyses are within this inner region, and the scatter of the data is on the order of the same size as the variations predicted (\( \pm 6\% \) at two standard deviations from the mean), our inability to resolve the gradient is consistent with this model.

[28] Although in this sample we are limited by scatter in the data (in large part) due to the young age of the sample, this study suggests that directly...
imaging intracrystalline $^4$He variations in accessory minerals using laser ablation should be feasible, especially given that conventional and laser microprobe (U-Th)/He ages have been demonstrated to agree within 1.3% for older standard materials. For very rapidly cooled samples with young ages and limited $^4$He diffusive-loss zoning (such as this example from Nanga Parbat, where the predicted spread in age in the core is only $\sim 100$ ka), the laser microprobe offers an opportunity to produce numerous replicate analyses in a short time, increasing the effective analytical precision to levels comparable to the most precise conventional (U-Th)/He results. For more slowly cooled samples, where the internal age gradient is larger and the mean age is greater (making it easier to generate analyses with reduced scatter, relative to the ages determined), it should be possible to directly image those age gradients and invert them for thermal histories. The high spatial resolution of this technique also permits effectively nondestructive thermochronology of rare samples (such as meteorites or lunar samples).

Of special importance to future applications is the capability of using the excimer laser for depth profiling with a nominal vertical resolution of $\sim 0.1$ $\mu$m (based on the theoretical limit of the depth of a single laser pulse). A more realistic and immediately obtainable resolution of $\sim 1$ $\mu$m could easily be achieved on monazite on the 5–10 Ma age range with no improvements in analytical abilities, as older samples have near-proportionally higher $^4$He contents, permitting smaller ablation volumes. Advances in ion-counting mass spectrometry are likely to increase our effective resolution with respect to measurement uncertainty, as they permit increased confidence in measurements of small amounts of He. For example, recent work at Arizona State University has demonstrated that measurement errors of better than 1.5% can be obtained on magnetic-sector mass spectrometers using a secondary electron multiplier for gas loads on the order of $10^{-11}$ cc $^4$He. This is approximately two orders of magnitude less $^4$He than is required for the same size error using a quadrupole mass spectrometer such as was used for this study (M. van Soest, personal communication, 2008). By combining high-resolution depth profiles of $^4$He concentration with appropriate production-ejection-diffusion models [Ketcham, 2005], it should be possible to develop extremely detailed reconstructions of the thermal evolution of appropriate samples for tectonic and landscape evolution studies. In addition, the rapid throughput permitted by laser microprobe (U-Th)/He can be used to generate the large two- and three-dimensional data coverage that would be well suited to interpreting three-dimensional thermokinetic models.

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