Laser microprobe (U–Th)/He geochronology

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Abstract

A new analytical method had been developed to enable high-spatial-resolution (U–Th)/He dating of accessory minerals. It involves the use of a focused ArF excimer to ablate pits in a polished grain surface, with the evolved gases spiked for isotope-dilution measurement of radiogenic 4He. These data are converted to concentrations by precise measurement of each pit using an optical interferometric microscope. U, Th, and Sm concentration measurements are made using one of several alternative microanalytical techniques (e.g., wavelength-dispersive electron microprobe analysis or laser-ablation, inductively coupled plasma mass spectrometry). By way of illustration, we present both conventional and laser microprobe (U–Th)/He dating results for a Brazilian monazite sample. Laser microprobe data (28 measurements on two crystal fragments) yield a weighted mean (U–Th)/He date of 455.3 ± 3.7 Ma (2SE). This result is statistically indistinguishable from the mean conventional (U–Th)/He date for three separate grain fragments: 449.6 ± 9.8 Ma (2SE). The agreement of conventional and laser ablation dates should encourage a wide variety of applications of the technique, including: (1) detrital mineral dating for provenance and unroofing studies; (2) the dating of broken, included, highly zoned, or irregular grains which are not easily corrected for α-ejection; and (3) measuring 4He loss profiles that can be inverted to determine cooling histories.

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1. Introduction

The oldest method of isotopic dating, (U–Th)/He geochronology has enjoyed a renaissance over the past few years and has become an important tool for a wide variety of earth science studies (e.g., House et al., 1998; Min et al., 2003; e.g., Tagami et al., 2003). Nevertheless, the technique is still in a developmental stage; as new accessory minerals are calibrated for (U–Th)/He chronometry, efforts continue to refine and improve analytical methodologies. Here, we introduce a new analytical approach that addresses two major problems encountered in conventional (U–Th)/He geochronology. The first is the need to correct single-crystal dates for the loss of radiogenic 4He by α-particle ejection (Farley et al., 1996). The second is the propensity of accessory minerals to display complex chemical zoning patterns that both complicate the α-ejection correction (Hourigan et al., 2005) and cloud the assignment of an unambiguous closure temperature to a particular (U–Th)/He date (e.g., Boyce et al., 2005).

Unlike the well-established use of defocused lasers to heat and consequently degas individual crystals for He analysis (House et al., 2000), the new method described here involves the use of an excimer laser to ablate small pits in the polished surface of a mineral in order to extract gas for He isotopic measurements. Concentrations of U, Th, and Sm are then measured on the same surface using one of several microanalytical instruments,
the choice of which depends largely on the abundance of the parent elements in the dated mineral. We demonstrate the viability of the method by comparing conventional and laser microprobe dates for gem-quality Brazilian monazite with the application of the two methods yielding statistically indistinguishable results. In addition, this exercise shows how replicate laser microprobe analyses can—in some cases—be combined to increase the precision of (U–Th)/He dates beyond the level normally obtained using the conventional approach.

2. Method description

Laser microprobe (U–Th)/He dating involves eight steps, diagrammed in Fig. 1: (1) mounting and polishing of a crystal fragment in preparation for electron microprobe analysis; (2) characterizing the crystal via backscat-
tered electron (BSE), cathodoluminescence (CL) or X-ray mapping; (3) remounting the crystal in indium for helium analysis; (4) ablating pits in the polished surface to extract gases; (5) isolating and analyzing the extracted He; (6) measuring the volume of the ablated pit; (7) measuring concentrations of U, Th, and Sm in or in close proximity to the pit ablated for He extraction; and finally (8) the calculation of apparent ages and uncertainties.

2.1. Sample selection and preparation

As is the case for other (U–Th)/He dating techniques, laser microprobe studies require careful hand-picking of crystals or crystal fragments that are free of optically visible inclusions or signs of alteration. The minimum grain size suitable for the technique depends on the concentration of radiogenic $^4$He in the sample. Unless they are very old or very large, most apatites and titanites—minerals frequently used for conventional (U–Th)/He thermochronology (Reiners and Farley, 1999; Farley, 2000)—are not sufficiently rich in radiogenic $^4$He, given current analytical limitations. Zircon, xenotime, and monazite (Farley and Stockli, 2002; Reiners, 2005) have higher concentrations of U and Th (and therefore $^4$He), and are more amenable to laser microprobe analysis. Practically speaking, samples of these minerals with grain sizes of 200 $\mu$m or larger are ideal, but we have worked successfully with samples as small as 60 $\mu$m.

The epoxy used to make grain mounts for many kinds of microanalytical projects in geochemistry are unsuitable for (U–Th)/He work because volatiles trapped in cured epoxy can stream off the grain mount in an ultrahigh vacuum extraction line, resulting in poor He isotopic analyses. Thus the technique requires a two-step, grain-mounting process. First, the fragment is mounted in epoxy and polished by hand to 0.05 $\mu$m, assuring a flat and smooth starting surface. Then, the grain is plucked from the epoxy and the fragment is placed on a glass slide—polished face down—and a nugget of indium is pressed on to the crystal to form an indium mount. The two-step approach is necessary because, although indium is sufficiently malleable for this method to produce a relatively sturdy mount for He analysis, the grain is not sufficiently well encased by the indium to permit grinding and polishing without it being plucked out in the process.

2.2. Characterization of samples

Because many accessory minerals exhibit complex chemical zoning that can result in apparent (U–Th)/He age variations, it is advantageous to develop a compositional map of the grain prior to He analysis. This can be done relatively easily by applying a conductive coating material to the surface of the initial epoxy mount and acquiring the desired backscattered electron and/or cathodoluminescence maps with an electron microprobe. One potential problem with adding this step to the sample preparation procedure is the possibility that the electron beam may cause He degassing near the sample surface, but our work thus far has not shown evidence of this phenomenon. The effect is likely minimized by the need to re-polish the sample after imaging to remove the conductive coating of carbon or gold, as the upper micron or two of sample itself is usually removed along with the coating.

2.3. Laser ablation

Helium extraction for (U–Th)/He microanalysis requires the use of an instrument capable of the controlled excavation of a sample pit. Although ion microprobes are suitable for this application, our efforts have focused on the use of laser technology. The way in which a laser beam interacts with a crystal depends on the material’s absorbed energy density for the wavelength of interest (Ready, 1971). We wish to achieve laser ablation, which can be defined for our purposes as the vaporization of a well-defined volume without significant heating of the surrounding material. Excimer lasers are excellent tools for ablation for a variety of reasons. First, the short-wavelength energy they produce is absorbed well by all minerals used for (U–Th)/He geochronology. Second, they produce extremely stable and well-defined beams that result in ablation pits that are geometrically simple and easily measured (Fig. 2). Finally, they are capable of producing focused beams with extremely high energy densities and thus ablate with no discernable effect on the material outside the ablation pit.

2.4. Gas purification and helium isotopic measurement

Prior to the experiment, the indium grain mount is placed on a copper or stainless steel planchette in a 6.875 cm diameter, ultrahigh-vacuum sample chamber fitted with a silica viewport that permits transmission of the laser beam. The chamber is mounted on a computer-controlled stage and connected to a gas purification system such as those used for conventional (U–Th)/He geochronology. In general, the low sample gas volumes produced during laser ablation mean that less gettering capacity is required than for conventional analyses, and that the gas cleanup may be done more rapidly. As is the case with con-
ventional (U-Th)/He analyses, helium isotopic data can be measured for laser ablation studies with sufficient precision using a small quadrupole mass spectrometer.

2.5. Ablation pit measurement

After analysis, the sample is removed from vacuum chamber and volumes of ablation pits are measured. A variety of alternative devices can be used for these measurements, including mechanical profilometers, confocal laser microscopes, and optical interferometric microscopes. In the course of our proof-of-concept study, described here, we found that the precision and accuracy of these measurements contributes greatly to the overall success of the technique. For this reason, we have chosen the optical interferometric microscope for our volume measurements.

2.6. U, Th, and Sm measurements

Once the pits have been measured, the grain mount is ready for U, Th, and Sm measurements. For zircons, one of the most widely available instruments for such measurements is a laser-ablation cell attached to an inductively coupled plasma mass spectrometer (LA-ICPMS). Our preferred protocol for laser microprobe (U-Th)/He dating of zircon involves re-occupying the pre-existing ablation pit with the laser used for LA-ICPMS analysis; by drilling the pre-existing hole slightly wider and deeper to extract material for trace element analysis, this approach minimizes the effects of sample heterogeneity on calculated dates. For monazite and xenotime, measurements of sufficient quality can be done with an electron microprobe. In practice, U, Th, and Sm can be measured prior to He analysis (concurrent with electron microprobe mapping), or a number of spots surrounding the ablation pits can be measured after ablation.

2.7. Age calculation

After calculation of 4He concentrations from 4He molar and pit volume data, parent and daughter concentrations can be combined in the (U-Th)/He decay equation (Farley et al., 2002), in order to solve iteratively for age. Uncertainties are calculated via a Monte Carlo method (e.g., Press et al., 1992), assuming normally distributed uncertainties for U, Th, Sm, He, and volume measurements. For most analyses, at least ~75% of the total age uncertainty stems from the uncertainty in the volume measurement. In contrast, all three parent elements (U, Th, and Sm) contribute no more than a total of ~15%, and helium measurements are responsible for only ~10% of the total uncertainty. In a case where individual pits are expected to yield equivalent ages, such as the proof-of-concept case described here, the weighted mean and standard error of the mean of all of the independent age determinations produces a reliable estimate of the cooling age of the sample.

3. Comparative conventional and laser microprobe dating of brazillian monazite

In order to demonstrate the laser microprobe method, we present here the results of a study of a gem-quality, orange-brown monazite from Ataleia in the Minas Gerais state of Brazil. We worked on two large (~1 cm³) fragments that exhibited sharp crystal faces, MOM1 and MOM3. Backscattered electron and X-ray mapping using the Cameca SX-Ultrachron at the University of Massachusetts at Amherst showed no discernable indication of chemical zoning in Y, Sm, U, or Th within these crystals. X-ray diffraction analysis of a fragment of MOM1 by M. Donohue in the Department of Physics at Harvard University resulted in values of $a = 6.77355$ Å, $b = 6.9963$ Å, $c = 6.4850$ Å, and $\beta = 103.627^\circ$. The excellent agreement of these results with established values (e.g., Ni et al., 1993, 1995) suggests a well-defined crystal structure that has not been compromised by radiation damage that might affect He retentivity (Garver et al., 2005).

3.1. Conventional (U-Th)/He analyses

The MOM3 crystal was crushed and three fragments were dated at Yale University. Analytical procedures for the conventional laser-heating monazite (U-Th-Sm)/He ages followed routine procedures used for zircon (Reiners, 2005), except small crystal fragments were analyzed and no $\alpha$-ejection corrections were made (these fragments were carefully selected to be from the interior of the crystal and more than 20 μm away from the nearest crystal face so as to eliminate the need to correct the He results for $\alpha$-particle ejection (Farley et al., 1996)). Roughly equidimensional, 30–60 μm diameter crystal fragments of MOM3 were wrapped in ~1 mm Nb foil packets. The foils then were placed in a Cu planchette, the planchette was overlain with a KBr coverslip, and the entire assembly was sealed within an ultrahigh-vacuum (~10⁻⁹ Torr) sample chamber connected to the He purification/measurement line. For He extraction, each foil was heated to ~1000–2000 °C for fifteen minutes using a 1064 nm Nd:YAG laser focused through a sapphire viewport. Re-heating and re-extracts of each sample yielded negligible 4He (~<0.05% of initial extraction). Extracted gas was spiked with ~8 × 10⁻¹³ mol of 3He, cryogenically concentrated, purified additionally by gettering, and expanded into a gas-source quadrupole mass spectrometer. 4He/3He was measured for about 10 s following gas release and nominal equilibration time. The results were corrected for background and interferences on mass 3 (HD⁺ and H₂⁺), and compared with the 4He/3He measured on pipetted aliquots of a manometrically calibrated 4He standard processed by the same methods. 4He in the unknown sample is assumed to be the product of the 4He content of the standard with the ratio of the 4He/3He measurements on the unknown and the standard. Linearity of this calibration approach has been confirmed in the Yale helium lines over
about four orders of magnitude of $^4$He signal. Samples were processed with several “hot blanks” and “line blanks” to check the measured $^4$He/$^3$He of laser extraction procedures on empty Nb foil envelopes, and $^4$He/$^3$He of $^3$He-only shots. Nominal $^4$He blanks from these procedures range from 0.05 to 0.1 fmol; the measured $^4$He of these monazite aliquots was 6–7 pfmol.

Parent nuclide contents of degassed monazites were measured by isotope dilution and solution ICPMS. Monazite-bearing Nb-foils were spiked with 0.4 ng of $^{233}$U, 0.6 ng of $^{229}$Th, and 0.6 ng of $^{147}$Sm. Foil, crystal, and spike were bombarded in Teflon vials at 225 °C for 72 h. Samples were then heated to dryness, after which they were re-bombed and dissolved in HCl at 200 °C for 24 h to re-dissolve refractory fluoride salts. After a final dry down, the sample was re-dissolved in 6% HNO3 and 0.8% HF, and this solution (≈2–4 ml total) was introduced to the ICPMS via an all-PFA sample introduction system with a sapphire injector. Ratios of $^{238}$U/$^{233}$U, $^{232}$Th/$^{229}$Th, and $^{152}$Sm/$^{147}$Sm were quantified by 2000 measurements of the average intensities in the middle 10% of peak widths in low-resolution mode on an Element2 high-resolution ICP-MS. $^{238}$U/$^{233}$U is also measured to check reagents for Pt contamination and mass fractionation. U and Th contents were calculated from multiple determinations of isotope ratios on pure spike and spiked normals containing 1–4 ng of isotopically normal U and Th. Procedural blanks for U and Th are determined by processing empty Nb foil envelopes, and average about 2 and 5 pg for U and Th, respectively.

The results of the conventional analyses (Table 1) are statistically indistinguishable and the three derived dates (450 ± 17 Ma (2σ), 449 ± 17, 450 ± 18) can be combined to report a weighted mean (U–Th)/He age of 449.6 Ma for MOM3 with an uncertainty—quoted at two standard errors of the weighted mean (2SE)—of 9.8 Ma.

### 3.2. Laser microprobe (U–Th)/He analyses

Sections through MOM1 and MOM3 were polished and mounted in indium for laser ablation. For the proof-of-concept study reported here, we used a Lambda Physik Compex 102 ArF excimer laser fitted to a New Wave Research DUV-193 beam preparation and targeting system at MIT. Lasing in the deep ultraviolet part of the spectrum at 193 nm, this system is capable of producing flux densities of greater than 100 TW/m$^2$. By applying 10–20 pulses of 100 mJ energy at a lasing duration of 2–4 s and pulse frequency of 4–10 Hz, we were able to ablate pits into the prepared sample surfaces that are approximately 25 μm in diameter and ~3–6 μm in depth. In all cases, these pits were more than 20 μm inside the crystal margins and thus the laser microprobe He measurements (like the conventional measurements) need not be corrected for α-particle ejection. As described earlier, the liberated gasses were spiked and purified and their isotopic composition measured by isotope dilution analysis. The mixture of $^3$He and $^4$He is passed over Saes C-400 and ST-172 cold getters to extract reactive gasses, and the remainder is expanded into a Balzers Prisma 200 quadrupole mass spectrometer with a channeler multiplier for measurement of $^3$He and $^4$He with a sensitivity of ~3500 A/mol. Total system blanks for $^4$He are typically in the range of $1.5 \times 10^{-16}$ mol, while $^4$He blanks are $\sim 3 \times 10^{-14}$ mol. All measurements are made in a fixed-range mode, with unusually large gas loads accommodated by computerized shifts (for measurement of both isotopes) to higher fixed ranges. Analysis times, including ablation, range from 5 to 10 min per sample.

The resulting data were converted to $^4$He concentrations using volume measurements of each pit. For this study, we used an ADE Phase Shift MicroXAM instrument. Vertical-scanning interferometers such as the MicroXAM rely on interference of a primary beam of light (~550 nm) with the light reflected from the surface. The interference pattern (a function of the height of the surface) is captured digitally as the stage is moved vertically, resulting in a 3D map of the surface (Fig. 3). Measurement of an ablation pit can be made in less than one minute, with a nominal lateral resolution of 0.5 μm and a vertical resolution of ~1 nm. After initial processing with MapVue AE™ software to level the surface and interpolate missing pixels, custom software developed at MIT is used to calculate pit volumes. Replicate analyses indicate a reproducibility of ~1.5% (2σ) for volume measurements made with the MicroXAM, and we propagate a more conservative 2% uncertainty into all ages.

Major and trace element concentrations were measured for MOM1 and MOM3 using the Cameca SX-Ultrachron (Table 2). The most important measurements for our purposes were those of U, Th, and Sm, and we closely followed the analytical protocols for these elements outlined in Jeremic and Williams (2005). In particular, care was taken to correct all U concentrations for overlap of the Th M-γ, Th M3-N4, the associated high energy M3-N4 satellite, and the Th M5-P3 lines with the U M-β peak. These analyses indicate that neither MOM1 and MOM3 are zoned in these three elements, but the two crystals are compositionally dis-

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**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>MOM3C</th>
<th>MOM3A</th>
<th>MOM3B</th>
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<td>$^4$He (2σ)</td>
<td>2.8</td>
<td>3.2</td>
<td>3.4</td>
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<tr>
<td>U (ng)</td>
<td>0.1443</td>
<td>0.1564</td>
<td>0.1709</td>
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<td>U (2σ)</td>
<td>0.0054</td>
<td>0.0060</td>
<td>0.0065</td>
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<tr>
<td>Th (ng)</td>
<td>9.33</td>
<td>10.34</td>
<td>11.13</td>
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<tr>
<td>Th (2σ)</td>
<td>0.30</td>
<td>0.33</td>
<td>0.39</td>
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<tr>
<td>Th/U</td>
<td>66.3</td>
<td>67.8</td>
<td>66.8</td>
</tr>
<tr>
<td>Sm (ng)</td>
<td>4.33</td>
<td>4.92</td>
<td>5.42</td>
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<tr>
<td>Sm (2σ)</td>
<td>0.13</td>
<td>0.15</td>
<td>0.16</td>
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<tr>
<td>Age (Ma)</td>
<td>449.7</td>
<td>449.2</td>
<td>449.8</td>
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<tr>
<td>Age (2σ)</td>
<td>16.9</td>
<td>16.9</td>
<td>18.1</td>
</tr>
<tr>
<td>Percent (2σ)</td>
<td>3.8%</td>
<td>3.8%</td>
<td>4.0%</td>
</tr>
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</table>

Conventional (U–Th)/He data.
tinctive. For MOM1, we determined $U = 1516 \pm 11$ ppm, $Th = 83240 \pm 130$ ppm, and $Sm = 30250 \pm 370$ ppm; for MOM3, the values were $U = 1344 \pm 14$ ppm, $Th = 63866 \pm 77$ ppm, and $Sm = 27800 \pm 1800$ ppm. (For each, the errors are reported at 2SE.) The reason for this grain-to-grain inconsistency in composition is unknown, but we note that the lower average concentration of $^4$He in pits from MOM3 (which has lower parent element abundances) is consistent with the discrepancy being real and not simply an analytical artifact.

In all, we determined 18 laser microprobe (U–Th)/He ages for MOM1 (Fig. 4 and Table 2) with an error-weighted mean for all analyses of 453 ± 14 Ma (2$\sigma$). Ten ablation pits on the MOM3 section yield a similar weighted mean, albeit with more scatter, of 459 ± 25 Ma. Despite the compositional differences in MOM1 and MOM3, the two populations of ages are indistinguishable within error, and thus we can combine them all to determine a weighted mean age

Laser microprobe (U–Th)/He data.

### Table 2

U, Th, Sm, He, volume, and ages, with 2$\sigma$ uncertainties for laser microprobe (U–Th)/He

<table>
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<tr>
<th>Spot #</th>
<th>$^4$He (mol)</th>
<th>$^4$He (2$\sigma$)</th>
<th>Volume (µm$^3$)</th>
<th>Volume (2$\sigma$)</th>
<th>U (ppm)</th>
<th>U (2$\sigma$)</th>
<th>Th (ppm)</th>
<th>Th (2$\sigma$)</th>
<th>Sm (ppm)</th>
<th>Sm (2$\sigma$)</th>
<th>Age (Ma)</th>
<th>Age (2$\sigma$)</th>
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<td>24</td>
<td>1516</td>
<td>11</td>
<td>83243</td>
<td>130</td>
<td>30253</td>
<td>370</td>
<td>466.1</td>
<td>9.5</td>
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MOM1 weighted mean 453.3 $\pm$ 13.7 3.0% 2SE 3.4 0.8%

MOM3 weighted mean 459.3 $\pm$ 25.3 5.5% 2SE 9.1 2.0%

MOM1 and MOM3 weighted mean 455.3 $\pm$ 19.2 4.2% 2SE 3.7 0.8%
of 455 Ma for the MOM monazites. While both standard deviations of this mean is ~19 Ma, a more useful statistic to describe our confidence in the calculated value is the standard error of the weighted mean. Thus, at the ~95% confidence level, we infer the (U–Th)/He age of the sample to be 455.3 ± 3.7 Ma. This result is well within uncertainty of the conventional (U–Th)/He date for MOM3 of 449.6 ± 9.8 Ma.

4. Discussion

The agreement of the weighted mean laser microprobe and conventional laser heating (U–Th)/He ages on this sample to within 1.3% indicates that laser microprobe (U–Th)/He geochronology can be used to produce robust cooling ages. The amount of scatter observed for individual spot ages is always less than 6% of the weighted mean age, comparable to the reproducibility in previous conventional (U–Th)/He studies (e.g., House et al., 2000; e.g., Reiners, 2005). However, it must be pointed out that the materials used in the conventional studies (unlike the monazite described here) contain parent element zonation likely responsible for some of their previously observed scatter (Boyce and Hodges, 2005; Hourigan et al., 2005). Regardless, these results are encouraging, with the average deviation of the laser microprobe (U–Th)/He age from the weighted mean of the conventional monazite ages being less than 2%, which is approximately equal to the typical uncertainty on an individual spot age.

The variation that is observed (especially in MOM3) is likely caused by errors in the volume measurement. As mentioned in the description of the methodology, the uncertainty in the volume measurement is difficult to quantify. This is primarily because we must rely on the reproducibility of individual hole measurements to constrain the uncertainty. However, this does not account for any accuracy problems that may exist, nor any sensitivity of the volume measurement to the individual hole characteristics such as aspect ratio, wall steepness, pre-ablation topography of the surface, or material reflectivity, any or all of which may change volume estimates.

One possible concern regarding the method is the extent to which ⁴He is extracted unintentionally from the region around the ablation pit during the experiment. Ablation without extensive “collateral heating” is absolutely essential to the method because we must quantitatively extract all of the ⁴He from a measurable volume in order to calculate the ⁴He concentration, which is in turn used to calculate a date. If heating causes some ⁴He to diffuse out of the surrounding material during the experiment, then we overestimate both the concentration of ⁴He in the volume and the (U–Th)/He age of the sample. Compared to other lasers commonly used in geochemical applications, the nanosecond-scale pulse rate of the ArF excimer implies very limited collateral heating—though more than would be expected from picosecond or femtosecond lasers. The most direct way we have to assess the impact of collateral heating on laser-ablation (U–Th)/He geochronology is through the comparison of laser microprobe (U–Th)/He and conventional (U–Th)/He ages. For the Brazilian monazite, the two techniques yield statistically indistinguishable ages. In addition, if collateral heating were a problem with the technique, we would anticipate different ages for different size ablation pits: larger pits with lower surface-area/volume ratios should yield younger ages than smaller pits. In our study, we ablated pits that varied in surface/volume ratio by roughly 20%, yet we found that the ages for the largest and smallest pits differed by less than 2%, and the pit with the larger surface/volume ratio was slightly younger, not older. Thus, we see no empirical evidence for ⁴He released from the pit walls, and we conclude that collateral heating does not affect the accuracy of ArF excimer laser microprobe (U–Th)/He geochronology of monazite. However, such collateral heating may be an issue for (U–Th)/He microprobe dating using other types of lasers, or ArF excimers operated at conditions different from those we employed in this study.

5. The added value of laser microprobe (U–Th)/He geochronology

The laser microprobe (U–Th)/He method yields more ages in a given amount of time than conventional methods despite the polishing and remounting required. This is primarily due to the substantial investment of time required to select crystals that are unbroken, inclusion-free, and have a regular geometry—all of which are necessary for robust α-ejection corrections. Since the laser microprobe can be used to specifically target portions of a grain that are farther that the nominal α-ejection distance from the grain rim, the α-ejection correction is rendered unnecessary. Typical α-ejection corrections for conventional (U–Th)/He ages range...
from 10% to more than 60% of the age. Ejection correction uncertainties are rarely propagated into the final age, and in most cases do not take into account possible uncertainties in the measurement of grains or heterogeneous parent element distributions. Such uncertainties—while typically ignored—should contribute substantially to the practical age uncertainty, and eliminating the need for such corrections should lead to improvements in the overall accuracy of (U–Th)/He dating. Because the new technique is insensitive to the external geometry of the crystal, grains that are otherwise difficult to date (or at least to date well) are now tractable. If no inclusion- and fracture-free, euhedral crystals are present in a particular mineral separate, laser-microprobe (U–Th)/He may provide the only means of extracting cooling age information from the sample.

An additional complication in conventional (U–Th)/He dating is chemical zonation. As recently demonstrated by Hourigan et al. (2005), intragrain variations in U and Th can result in errors in the ejection correction of 30% or more, even for “medium-sized” zircon crystals (200 × 100μm). Although it is possible to evaluate the likelihood of such errors in some cases through replicate analyses, intragrain variations in U and Th are sometimes systematic within a suite of crystals extracted from a single rock, resulting in a systematic but incorrect ejection correction (Tagami et al., 2003). With the laser microprobe technique, zoning patterns may be carefully characterized by cathodoluminescence or backscattered electron mapping and specific compositional domains can be dated. Such a capacity would be particularly valuable for monazite studies since composition may play a role in that mineral’s ability to retain helium (Boycie et al., 2005; Stockli et al., 2005). While the monazites used for this study are homogeneous, they are unusual in that regard, with most monazites containing complicated distributions of U, Th, and other trace elements (e.g., Boyce et al., 2005). If different zones in a slowly cooled monazite retain radiogenic helium to different degrees, they would have different closure temperatures and therefore different cooling ages. Laser microprobe (U–Th)/He may be able to determine different ages for different zones of a heterogeneous crystal.

It also should be possible to measure ⁴He depth profiles in minerals directly using the ~0.1 μm depth resolution of the excimer. Such profiles can be inverted to constrain cooling histories from single crystals, or simply used to expand the range of a thermochronometer by taking advantage of the core to rim variation in closure temperature (Dodson, 1986). Depth profiles also could be used to directly measure α-ejection profiles, in order to confirm the theoretical ejection distances commonly used in thermochronology. This could be done by sequentially ablating holes, measuring helium, then measuring the pit depth by optical interferometric microscopy as described in this study.

In principle, the technique described here also could be used to date minerals in polished rock sections. Preliminary experiments involving sequential polishing and back-scattered electron mapping of rock sections suggest that this could be an efficient method for locating large numbers of small U- and Th-rich minerals such as monazite or zircon. Moreover, target minerals can be identified without loss of petrologic context, which may prove to be important in low-temperature thermochronometry when the crystals of interest are found as inclusions in large, highly retentive phases (such as garnet) that may retard ⁴He diffusive loss from the inclusions.

Ultimately, the ability of this technique to produce large number of ages in a short time may prove to be most useful for the thermochronology of detrital samples. As demonstrated by Vermeesch (2004) and Andersen (2005), the utility of a detrital chronometry study is largely a function of being able to date a sufficient number of grains. In many instances, more than 100 dates are required for an adequate characterization of a polymodal detrital population. Picking more than 100 “perfect” crystals for a conventional (U–Th)/He study is likely to take many weeks of painstaking microscopy—if such crystals can be identified at all, since detrital grains are frequently abraded and or broken by fluvial transport. In the case of zircon, while the requirements for crystal perfection are somewhat more relaxed than for other minerals, the degassing and dissolutions are considerably more time consuming than the equivalent measurements of He, U, and Th using laser microprobes. With laser microprobe (U–Th)/He, detrital studies will be relatively straightforward and should quickly provide useful chronologic constraint for geologic studies of both modern and ancient sediments.

6. Conclusion

In this paper, we have demonstrated that laser microprobe (U–Th)/He chronometry can be used to determine robust and reliable ages that are equivalent to conventional (U–Th)/He measurements within uncertainties. For the MOM monazites described here, the conventional laser-heating (U–Th)/He age of 449.6 ± 9.8 Ma and the laser microprobe (U–Th)/He age of 455.3 ± 3.7 Ma agree within 1.3%, with the greatest outlier of the 28 individual laser microprobe spot ages corresponding to a deviation of only 7%. This compares favorably to estimates of reproducibility from previous conventional (U–Th)/He studies. The variation in individual ages observed is likely caused in large part by errors in volume measurements, and improvement of volume determinations should be the highest priority in efforts to improve the method. However, laser microprobe (U–Th)/He in its current state can provide large quantities of reliable ages in a short amount of time compared to conventional (U–Th)/He. In addition, use of the laser microprobe permits cooling age determinations from mineral separates lacking the euhedral, inclusion- and fracture-free crystals required for conventional (U–Th)/He. Finally, laser microprobe (U–Th)/He should allow direct measurement of ⁴He depth profiles, allowing cooling histories and ejection distances to be determined on single crystals.
Acknowledgments

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