Undergraduate Researcher Guide

CU Thermochronology Research and Instrumentation Lab (CU TRaIL)
Department of Geological Sciences

June 2020, written and compiled by Becky Flowers, with input from Jim Metcalf and Lon Abbott

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CU TRaIL Website: https://cutrail.org

1. WELCOME!

Welcome to the CU TRaIL. We are a (U-Th)/He facility in the Department of Geological Sciences. (U-Th)/He dating is a tool used to constrain the timing, duration, and rates of various Earth processes, and is applicable to an array of tectonic, structural, petrological, stratigraphic, geomorphic, and planetary studies.

We are excited that you will be working in our lab. Undergraduates are an important part of our lab's research program. You may be assisting with various lab activities in a paid undergraduate position, or you may be working on your own research project. Regardless, we are happy to help support you. Before you get started, please read this entire document. It is important that you know some basics about our facility, training procedures, and the people working in it. For additional information beyond what is below, please visit our lab website: https://cutrail.org

2. TRaIL FOLKS

Undergraduate researchers in our lab work directly with a mentor, who may be a graduate student, postdoc, or other departmental researcher. Many of you work with Dr. Lon Abbott, who runs the GEOL undergraduate research seminar, and with whom we have a longstanding collaborative relationship. ***However, before you begin working on any TRaIL equipment, you must meet briefly with Becky Flowers and Jim Metcalf, who run the lab and are responsible for all activities occurring in TRaIL.***

Dr. James (Jim) Metcalf - james.metcalf@colorado.edu

Jim is the TRaIL lab manager and a research associate. Jim has extensive experience building and managing noble gas facilities. He oversees the day-to-day operations of the TRaIL, maintains and improves lab equipment and protocols, trains most users, ensures lab cleanliness, and performs most of the analytical work in the lab. These analyses include work for in-house projects, as well as contract analyses for numerous external clients. The income from these analyses supports the lab. Jim also conducts his own research, as well as research associated with projects in the group. You can read more about Jim on his website at: https://jamesrmetcalf.com/

In addition to your direct mentor, Jim is a key individual who you will interact with during your time in TRaIL. You should touch base with Jim before beginning work in the lab, which you can arrange by reaching out to him via email at james.metcalf@colorado.edu.

Prof. Rebecca (Becky) Flowers - rebecca.flowers@colorado.edu

Becky is the TRaIL lab director, lab PI, and faculty in GEOL. The lab is the centerpiece of her research program. You can read more about the Thermochronology and Geochronology group on her website at: https://rebecca-flowers.com/

You should touch base with Becky before starting work in TRaIL, which you can arrange by reaching out to her via email at rebecca.flowers@colorado.edu. This could be a brief meeting in the lab so she knows who you are, you know who she is, and she can obtain your contact information. Becky maintains a list of all TRaIL users with their contact information, so that it's possible to communicate quickly with all users if this becomes necessary (such as during the coronavirus disruption). Becky is made aware of all analyses moving through the lab. Her own undergraduate research experiences played an important role in shaping her career path, and one of TRaIL's goals is to provide such opportunities to GEOL undergraduates.

The TRaIL is proud of its undergraduate support, and in some cases may be willing to subsidize analyses for committed undergraduates working on projects that lead to honors theses. You and your mentor should talk with Becky directly about this if it is needed for your project.

Becky has weekly group meetings that involve informal presentations by group members and occasional paper discussion. This can be an excellent way to learn about the general process of scientific research. If you're interested in attending these meetings, please contact Becky directly via email.

Becky also teaches a graduate geochronology class every other fall, consisting of a mix of lecture and discussion. If the timing is right, if this class would benefit your research projects, and if you are willing to commit to trying your best in this graduate-level course, then please discuss this with Becky. She's willing to admit the occasional undergraduate to this class on a case-by-case basis.

TRaIL graduates students, postdocs, and lab visitors

Graduate students and postdocs are often in the lab. The lab also has visitors on a regular basis. If you encounter someone you don't know in the lab, please introduce yourself. If you ask about their research then you might learn something!

3. PHILOSOPHY OF UNDERGRADUATE RESEARCH PROJECTS

If you are working on a research project, it's important to realize that research is a discovery process. There is no guarantee that your samples will yield the minerals you are seeking or the outcome that you are hoping for. It is important to remain flexible and open-minded throughout your project. The primary purpose of undergraduate research is to gain experience, develop critical thinking skills, and perhaps complete a document (such as an honors thesis) that clearly outlines the rationale for your research endeavor, your methods, results, and conclusions. You might even attend a national meeting (such as GSA or AGU) and present your project.

Regardless of the specific outcomes of your project, the scientific experience of doing research is a critical learning experience and key resume-builder no matter what your path will be after CU. Evidence of research and experience writing an associated document are sought after by employers in diverse Earth science fields and by graduate programs regardless of research focus. Most of the undergraduates working in our lab don't go on to graduate school, although some do. Three recent TRaIL undergrads have been awarded prestigious NSF Graduate Research Fellowships to support their graduate school research endeavors (Ryan Stoner in 2018, Coleman Hiett in 2019, and Spencer Zeigler in 2020).

You should also consider applying for external research funding to support your work, as that is another great resume builder. For example, Noah McCorkel received a GSA undergraduate research grant to support his work in the TRaIL.

4. MINERAL SEPARATION, CRYSTAL SELECTION, AND ANALYTICAL ACTIVITIES

4.1. The Critical Importance of Cleanliness in all TRaIL activities

Our lab's reputation depends on its ability to maintain a clean, efficient, and fully functional facility. <u>Cleanliness in all facets of the mineral separation, mineral picking, and analytical process is absolutely crucial.</u> Users must sign-in on login sheets to document when each piece of equipment was used on what sample. Please keep the benches clear when not in use, label everything that is yours, and respect other samples that may be out. If samples are cross-contaminated, then this can compromise data interpretations that ultimately may be published in the peer-reviewed scientific literature. Moreover, because of the large number of lab users, it's critical that equipment be left clean and fully functional for others to use. If users do not respect these guidelines, then the privilege of using TRaIL equipment will be revoked.

User guides developed by TRaIL are available for all TRaIL equipment. However, if you have any questions whatsoever when carrying out any of these steps, PLEASE ASK! We are also always interested in hearing perspectives on how our protocols and procedures can be improved.

4.2. Online EH&S Lab Safety and Hazardous Waste Generation Training

You must take the online Lab Safety and Hazardous Waste Generation training through the CU Environmental Health & Safety office before using heavy liquids or beginning mineral picking.
https://ehs.colorado.edu/training/hazardous-waste-generator-instruction/
When you receive your online certificate, then you must send this to Jim for approval to begin heavy liquid and mineral picking activities.

4.3. TRaIL Equipment and Locations of Activities in Benson Earth Sciences

TRaIL uses and/or oversees several spaces in the Benson Earth Sciences Building. This section is intended to orient you on the locations of TRaIL equipment.

SamPLER Lab (BESC 1B35) - Formerly known as the Rock Shop. This is a Dept facility. A Dept lab RA oversees the SamPLER lab. The lab RA changes on an annual basis. Please be sure to learn who the lab RA is and reach out to meet that individual.

- ***1B35A*** - The rock crusher and disk mill, used in the first steps of the mineral separation process, are housed here. This equipment is overseen by the Dept. It is essential that you receive training and certification on its use from the SamPLER lab manager. This is not a dangerous piece of equipment when used properly, but use of it entails more

risk than any other step in the mineral separation process; it is imperative that you use it correctly.
- ***1B35B:*** The Wilfley table is housed here. This equipment belongs to and is overseen by TRaIL. The rest of the space and equipment in this room (such as the rock saws) belong to and are overseen by the Dept.

BESC 1B45: This space is overseen by TRaIL. It houses the frantz and heavy liquid operations, which belong to and are overseen by TRaIL. The equipment in this space will be moved to BESC 125 during the 2020-21 academic year.

BESC 125: A portion of this space belongs to TRaIL. It houses our microscopes and picking operations.

BESC 225: This space and all the equipment in it belongs to TRaIL. Instrumentation includes an ASI Alphachron He extraction and measurement line, and an Agilent 7900 quadrupole inductively coupled plasma-mass spectrometer (ICP-MS). We soon will install an ESI excimer laser and an optical profiler. Jim is designing and building a second, custom, He extraction and measurement line.

BESC 4th floor space: We also have a hood on the 4th floor in a clean lab overseen by Lang Farmer. This is where we conduct mineral dissolutions. Undergraduates working in TRaIL have no need to access this space.

4.4. Typical Steps for Individual Whole Crystal (U-Th)/He Data Acquisition

The purpose of this section is to provide a brief overview of the various steps you may be engaged in during your time in TRaIL. You will be provided more detail on all of the steps below during your training. You must be trained and approved on all equipment before using it independently. Please refer to the appropriate TRaIL user guides for different pieces of equipment during your training.

Figure 1 (from Flowers et al., in prep) depicts the workflow associated with (U-Th)/He data acquisition. The approximate time associated with the mineral separation steps is noted below.

Note that because of the many samples moving through the lab, both Jim and Becky must be made aware in advance when your grains will be ready for analysis so that we can schedule them for the analytical steps. Becky and Jim discuss and prioritize samples in the analytical queue on a weekly basis. The turnaround time between crystal preparation and data acquisition may be several weeks for apatite (more for zircon) depending on the number of grains and the priority of other materials moving through the lab at the same time.

Mineral Separation - You will likely complete these yourself after you've been trained
- Sample sledged into fist-sized chunks. Set aside a fist-sized piece (do not crush all of it) in case thin sections or other data are desired in the future.
- Use of jaw crusher, disk mill, and sieve in 1B35A (plan on this work taking half a day).
- Use of Wilfley table in 1B35B (you can Wilfley one sample in a couple of hours).
- Initial frantz steps in BESC 1B45 (soon to be transferred to BESC 125) (you can set

this up and then feed it between classes, but it will take several hours to get through a sample).

- Heavy liquids in BESC 1B45 (soon to be transferred to BESC 125) (half a day).
- Final frantz steps in BESC 1B45 (soon to be transferred to BESC 125) (likely several hours, this may require more monitoring than the initial frantz steps).

Crystal Selection - You will likely complete these steps yourself after you've been trained.

- Microscope work to select individual crystals for analysis in BESC 125.
- Take photographs and then measure the selected crystals using the 2D grain images.
- Record measurements and other grain details using the excel file template and associated documentation for this purpose.
- Pack selected crystals into Nb metal packets for analysis.

Analytical Process - You will be shown these steps, but won't complete them yourself.

Jim will offer a short "TRaIL curriculum" once each semester to undergraduates working in TRaIL so that you can become familiar with the steps associated with the analytical process. Although you will not perform these steps independently, if you acquire and interpret data as part of a research project, it's important that you know the first-order aspects of the analytical process. Please be proactive about inquiring when the you can get this overview of the analytical steps from Jim.

- He degassing and measurement of samples under ultrahigh vacuum in a noble-gas extraction and measurement line (the ASI Alphachron in BESC 225). Line blanks, metal packet blanks, reference standards, and mineral age standards are also analyzed.
- Removal from the ASI Alphachron, followed by crystal spiking and dissolution (in BESC 425).
- U, Th, and sometimes Sm analysis by ICP-MS (on the Agilent 8900 in BESC 225). Line blanks, metal packet blanks, reference standards, and mineral age standards are also analyzed.
- Data reduction.

See supplementary material at the end of the PDF for a more a detailed description of the analytical methods associated with data acquisition.

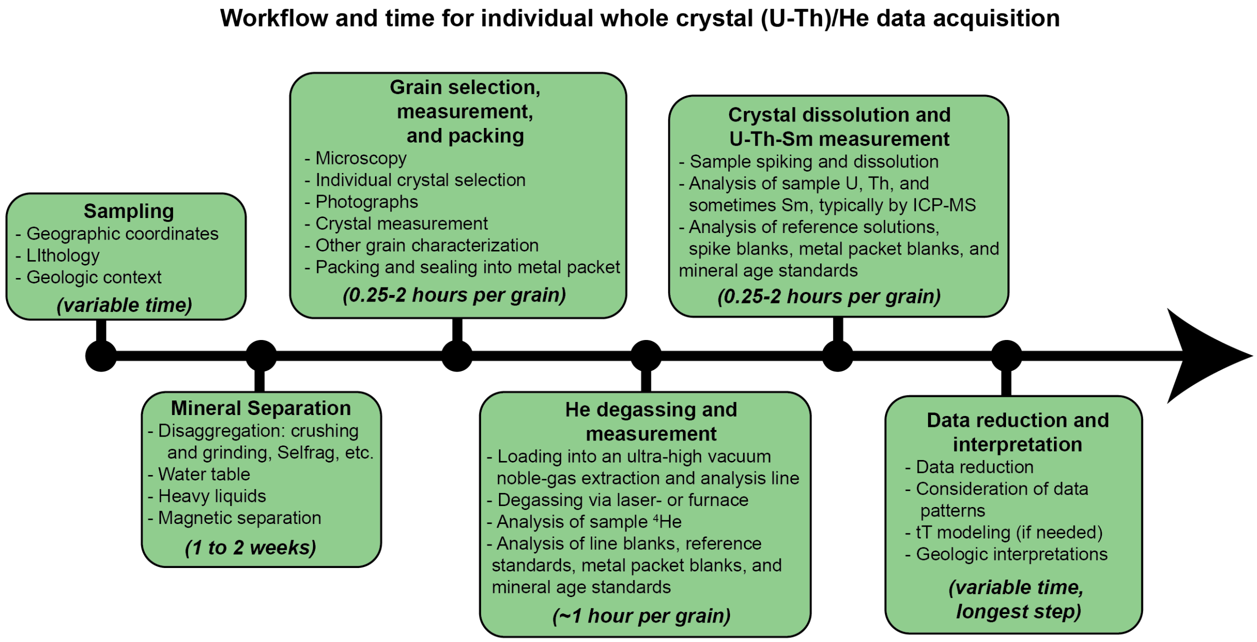

Figure 1. Summary of workflow and approximate time for individual whole-crystal (U-Th)/He analyses.

5. BACKGROUND READING

Prior to obtaining your data, you should read some background on the technique and how to think about your data. A good starting place is our summary on "(U-Th)/He chronology" for the Encyclopedia of Geology, which is included at the end of this pdf:

Metcalf, J.R. and Flowers, R.M., 2020, (U-Th)/He Chronology, Encyclopedia of Geology, 2nd Edition, in press.

If interested, we are happy to provide a pdf of the following chapter that provides a deeper dive into the technique

The (U-Th)/He system, Chapter 11, In, Geochronology and Thermochronology, 1st Edition. Peter W. Reiners, Richard W. Carlson, Paul R. Renne, Kari M. Cooper, Darryl E. Granger, Noah M. McLean, and Blair Schoene.

If you're interested in still further reading, we can also make a folder available to you containing a suite of papers from our recent reading seminar entitled "Fundamentals of (U-Th)/He Chronology". You can dive as deeply into this scientific field as you have the time and interest.

6. DATA EXPLANATION, COMPILATION, QUALITY, AND INITIAL PLOTS

Step 1: Understand the Data Columns on Your Data Spreadsheet

When you receive your data, the first thing you should do is make sure that you understand the significance of all the data columns.

***Full Sample Name* –** Sample Name, the subscripts such as _a01 or _z01 refer to separate analyses from the same sample

***length and width* –** measurements of the grain dimensions in micrometers. Each grain is measured from two different angles to ensure that the grain geometry is fully captured. These values are used to calculate alpha ejection corrections and crystal volumes and masses using the techniques described by Ketcham et al., (2011).

***2X Term* –** Notes whether or not the grain is doubly terminated.

***Np* –** The number of pyramidal terminations of the grain, used in the alpha ejection correction.

***Dim Mass* –** The dimensional mass (in micrograms) is calculated based solely on the volume of the crystal (determined from the measurements) and average grain density.

***rs* –** The radius of a sphere with an equivalent surface area to volume ratio as your crystal. This value is required if you wish to do any thermal modeling of your grains using HeFTy.

***4He (nmol/g)* –** the amount of 4He measured in the crystal via isotope dilution. This includes all of the He if multiple degassing steps were required. The **±** column is 1-sigma analytical uncertainty.

***U (ppm)* –** the amount of total U in the sample, measured via isotope dilution on an ICP-MS. The **±** column is 1-sigma analytical uncertainty. A value of 0.00 indicates measurements that are not larger than analytical uncertainty.

***Th (ppm)* –** the amount of total Th in the sample, measured via isotope dilution on an ICP-MS. The **±** column is 1-sigma analytical uncertainty. A value of 0.00 indicates measurements that are not larger than analytical uncertainty.

***Sm (ppm)* –** the amount of total Sm in the sample, measured via isotope dilution on an ICP-MS. The **±** column is 1-sigma analytical uncertainty. A value of 0.00 indicates measurements that are not larger than analytical uncertainty.

***eU (ppm)* –** the effective Uranium, a measurement of the total amount of radiation experienced by the crystal, equivalent to U + .235Th.

***He (ncc)* –** the total amount of He, blank corrected, in nano-cc's, measured from the sample. This is not referenced to the grain mass.

Re (%) - the percent of the total He that was degassed during the first laser extraction. For apatites, this number should be 99.9% or higher. Lower values are thought to indicate the presence of inclusions or other low-diffusivity zones. For zircons this value is not as instructive.

***U (ng)* –** the total amount of Uranium measured in the sample in nanograms. This is not referenced to grain mass.

***Th (ng)* –** the total amount of Thorium measured in the sample in nanograms. This is not referenced to grain mass.

Sm (ng) **–** the total amount of Samarium measured in the sample in nanograms. This is not referenced to grain mass.

Th/U **–** The Thorium/Uranium ratio for the sample.

Raw Date It (Ma) **–** the age calculated directly from He, U, Th, and Sm measurements. The **±** column is 1-sigma analytical uncertainty. This date, as well as the corrected date, are calculated iteratively using equation #34 from Ketcham et al., (2011).

Ft **–** The alpha-ejection correction calculated using the method of Ketcham et al., (2011). Ft is a measure of the fraction of He retained in the crystal after accounting for that lost due to ejection. An Ft of 1.00 would indicate that no He had been lost. An Ft of 0.75 would indicate that 25% of He had been lost due to ejection. This is a purely geometric correction

Corrected Date It (Ma) **–** The alpha-ejection corrected age, essentially equal to the Raw Age divided by the alpha-ejection correction, calculated iteratively using equation #34 from Ketcham et al., (2011).

Analytic. Unc (Ma) 2σ **–** 2-sigma uncertainty in millions of years, only including propagated direct analytical uncertainties for He, U, Th, and Sm. Analytical uncertainties can be considered the minimum uncertainty on a single measured date. Some uncertainties, like that associated with the alpha-ejection correction, are poorly quantified at present, making it challenging to properly include them in uncertainty estimates for single-grain (U-Th)/He dates. Ongoing work is aimed at improving our understanding of uncertainties associated with the alpha-ejection correction, to enable their appropriate incorporation into single-grain uncertainty estimates.

Values in Red – These indicate measurements that are close to background values or small. If the He, U, or Th values are red, then the blank corrected measured values for that sample are less than 5 times larger than the background values. Typical backgrounds are on the order of 0.002 ncc ^{4}He, 0.002 ng ^{238}U, and 0.004 ng ^{232}Th, although they will vary from run to run. Alpha-ejection corrections marked in red are just values smaller than 0.65. This is the standard cut-off CU TRaIL uses, preferring to analyze grains with Ft's at 0.65 or above. We will analyze smaller samples with the client's permission. Re (%) values in red indicate samples where less than 99.9% of the total He was degassed in the first heating step.

Notes – These are notes taken during the picking process. They generally relate to the size, shape, and quality of the grains. Again, these can be helpful when identifying unusual results.

The sheet will also include results for the Durango Fluorapatites, Fish Canyon Tuff zircons, or Fish Canyon Tuff titanites run in conjunction with your samples. These grains are interspersed throughout the runs for quality control purposes. Durango Fluorapatites have an accepted age of 31.4 Ma (McDowell et al., 2005), whereas Fish Canyon Tuff zircons and titanites have accepted ages of 28.2 Ma (Rivera et al., 2011; Gleadow et al., 2015).

Step 2: Compile Your Data into a Single Sensible Data Table

After you receive your data, you should compile it into a sensible form. If you receive your data in multiple batches, compile them into a single spreadsheet.

- For each sample, note the sample name, lithology, rock age, geographic coordinates (latitude and longitude or UTM), and elevation. The lithology and age may matter for understanding the causes of any data dispersion, so this information should be included.

- Analyses should be labelled a01, a02, a03, etc for apatite and z01, z02, z03, etc. for zircon.
- Although TRaIL will provide you with an Excel spreadsheet that contains all of the data described above, not all of this information must be included in your honors thesis summary tables. We recommend Ault et al., (2012) and Stanley et al., (2015) as examples of (U-Th)/He data tables that provide all of the necessary information but are not too large or unwieldy. Example data table templates can be downloaded from our website: https://cutrail.org/resources/

Step 3: Screen Your Data for Quality Using the Data Quality Checklist

Your next step should be to screen your data for quality. There are a variety of reasons why a specific analysis might be unreliable, as described in Table 1 at the end of this document. Use this checklist table to inspect your data. If you find a reason why an analysis might be suspect, don't remove it from your data table. Merely flag it with a star and a footnote for additional discussion and consideration with your mentor. It's essential that the TRaIL is applying the same first-order data quality criteria for all datasets being interpreted in-house.

Step 4: Data Plots

Next, you should make plots of (U-Th)/He date vs. eU and (U-Th)/He date vs. rs

Both eU and grain size can influence the temperature sensitivity of mineral crystals. For certain (but not all) types of thermal histories these effects may yield positive correlations between date and eU, and/or positive correlations between date and Rs. The presence or absence of such correlations can influence how you interpret your dataset.

Such plots also allow one to visually identify grains that appear to be outliers from the larger dataset. Any such outliers merit additional detailed inspection (re-visit the data quality checklist in Table 1). In some cases, factors that cannot be observed, such as U-Th zonation or He injection, may cause an analysis to be an outlier even if the grain does not clearly violate any of the criteria outlined in the data quality checklist.

In some circumstances it is also possible to encounter a sample with analyses that are "highly dispersed" for reasons that are not obvious. This problem tends to be exacerbated in samples that have protracted thermal histories. Again, U-Th zonation, He injection, or other factors that typically are unquantified or unmeasured may contribute to this dispersion. Your mentor will be able to help you decide whether a sample might be considered "highly dispersed" or not. For such dispersed samples that lack correlations with eU or grain size, it may be best to not attempt to interpret the significance of the data.

Step 5: Discuss Your Data with Your Mentor

After you've taken these initial steps, it's time to send your compiled dataset and plots to your mentor and schedule a time to discuss your data. It's critical that you ***first*** ensure that you have a reliable dataset and have screened your data for quality before getting too deep into its interpretation. Your ***second*** step is to interpret the significance of your results for your geologic problem. You should not interpret spurious outliers or inexplicably dispersed samples. After you're decided which data are reliable (quite possibly all of them are), you should use only these high quality for your interpretations.

7. INTERPRETING YOUR DATA

7.1. General Approach

Now comes the fun part. What do your data mean for the geologic problem that you're tackling?

You will work both independently and with your mentor to address this question. You may make additional plots in an effort to better understand the significance of your results. These might be plots of sample date versus elevation, or sample date versus distance along a transect. Typically you will be able to draw some first order geologic conclusions from your data based on the temperature sensitivity(s) of the mineral(s) you dated and the geologic context of your samples.

7.2. Thermal History Modeling

It is typical for more advanced members of the research group to carry out thermal history modeling of their datasets. It's generally not necessary for undergraduates to perform such modeling as part of their projects or honors theses.

Thermal history modeling involves using a He diffusion kinetic model for your mineral of interest in a tT (time-temperature) modeling program such as HeFTy to quantitatively determine the range of thermal histories that can explain your data while honoring other geologic and geochronologic constraints on the tT path. For this exercise to be worthwhile and done properly, it is important for you to: develop specific hypotheses that you want to test with the models, understand the fundamentals of the He diffusion kinetic model(s) used, understand the basics of the modeling program, and have an understanding of the independent geologic and geochronologic constraints on the thermal history and how to reasonably and defensibly incorporate these into your models. A good starting place for thinking about this modeling is the following paper, which we can provide as a pdf:

Flowers, R.M., Farley, K.A., and Ketcham, R.A., 2015, A reporting protocol for thermochronologic modeling illustrated with data from the Grand Canyon: Earth and Planetary Science Letters, v. 432, p. 425-435.

If you're an ambitious undergraduate who has acquired a dataset and made some preliminary interpretations of it, and if you have sufficient time and commitment to pursue thermal history modeling, then you should discuss this possibility with your mentor. TRaIL has additional background reading and guidelines for how to tackle such modeling. Again, it is important that TRaIL is applying the same first-order thermal history modeling philosophy for all datasets being interpreted in-house. Although we are always looking for ways to improve our modeling strategies, we do not want to be publishing or presenting interpretations of datasets based on wildly different criteria and rationale that might lead to contrasting interpretations. If you carry out thermal history modeling, it is important that you invest enough time in it to know what you're doing. This requires a significant additional time commitment.

7.3. Completing an Honors Thesis

If you begin the research process early enough, there is the possibility that you can complete an Honors thesis on your project. If you write and orally defend an Honors thesis, you may be able to graduate with Latin Honors (cum laude, magna cum laude, or summa cum laude). The Honors thesis process is a rigorous one. ***To complete an honors thesis, you must register your thesis project with the Honors Program office the semester before you defend.***

See here for additional information from the College of Arts and Sciences about the honors thesis process: https://www.colorado.edu/honors/graduation.

If you might be interested in completing an honors thesis, then you should discuss this with your mentor, because it involves a significant time investment by both of you. If you decide to pursue this, then you can be provided with examples of honors theses recently completed in TRaIL. You will likely find it useful to read one or more of these to get a better sense for the structure and character of an honors thesis document. Four GEOL undergraduates completed honors theses in TRaIL in spring 2020, and we hope to continue a track record of theses into the future.

If you do complete an honors thesis, Jim and Becky would appreciate an invitation to your defense. Becky would also appreciate it if you would email her a copy of your final, post-defense honors thesis document submitted to CU, so that she has a record of such theses completed in TRaIL.

SUPPLEMENTARY INFORMATION

Analytical Methods

Individual whole crystal (U-Th)/He analyses carried out at the University of Colorado Boulder TRaIL (Thermochronology Research and Instrumentation Lab) use the following methods. Individual mineral grains are handpicked using a Leica M165 binocular microscope equipped with a calibrated digital camera and capable of both reflected and transmitted, polarized light. The grains are screened for quality, including crystal size, shape, and the presence of inclusions. After characterization, grains are placed into small Nb tubes that are then crimped on both ends. This Nb packet is then loaded into an ASI Alphachron He extraction and measurement line. The packet is placed in the UHV extraction line (~3 X 10^{-8} torr) and heated with a 25W diode laser to ~800-1100°C for 5 to 10 minutes to extract the radiogenic ^{4}He. The degassed ^{4}He is then spiked with approximately 13 ncc of pure ^{3}He, cleaned via interaction with two SAES getters, and analyzed on a Balzers PrismaPlus QME 220 quadrupole mass spectrometer. This procedure is repeated at least once to ensure complete mineral degassing. Degassed grains are then removed from the line, and taken to a Class 10 clean lab for dissolution.

Apatite grains, still enclosed in the Nb tubes, are placed in 1.5 mL Cetac vials, spiked with a ^{235}U - ^{230}Th – ^{145}Nd tracer in HNO_3, capped, and baked in a lab oven at 80°C for 2 hours. Zircon, titanite, and other more refractory phases are dissolved using Parr large-capacity dissolution vessels in a multi-step acid-vapor dissolution process. Grains (including the Nb tube) are placed in Ludwig-style Savillex vials, spiked with a ^{235}U - ^{230Th} - ^{145}Nd tracer, and mixed with 200 µl of Optima grade HF. The vials are then capped, stacked in a 125 mL Teflon liner, placed in a Parr dissolution vessel, and baked at 220°C for 72 hours. After cooling, the vials are uncapped and dried down on a 90°C hot plate until dry. The vials then undergo a second round of acid-vapor dissolution, this time with 200 µl of 6N Optima grade HCl in each vial that is baked at 200°C for 24 hours. Vials are then dried down a second time on a hot plate. Once dry, 200 µl of a 7:1 HNO_3:HF mixture is added to each vial, the vial is capped, and cooked on the hot plate at 90°C for 4 hours. Once the minerals are dissolved, regardless of the dissolution process, they are diluted with 1 to 3 mL of doubly-deionized water, and taken to the ICP-MS lab for analysis. Sample solutions, along with normal solutions and blanks, are analyzed for U, Th, and Sm content using an Agilent 7900 quadrupole ICP-MS. After the U, Th, and Sm contents are measured, He dates and all associated data are calculated on a custom spreadsheet using the methods described in Ketcham et al., (2011). The natural occurring 238U/235U ratio used in data reduction is 137.818 after Hiess et al. (2012). Every batch of samples includes standards run sporadically throughout the process to monitor procedures and maintain consistency from run to run. Long term averages of Fish Canyon Tuff zircons and Durango fluorapatites run in the CU TRaIL are 28.7 ± 1.8 Ma (n=150) and 31.1 ± 2.1 (n=85), respectively.

Table 1. TRaIL data quality checklist for individual (U-Th)/He analyses

Note: If you find a reason why a particular analysis might be suspect, don't remove it from your data table. Merely flag it with a star or use a different color for that analysis row for additional consideration and discussion with your mentor.

- [ ] Do any of your grains have FT values of <0.55? These should be flagged.
  If any of your grains have values less than this, flag it. An FT value of 1.00 would indicate that no He was ejected from the crystal. A value of 0.50 would indicate that half of the He has been lost. This is a geometric correction, and the magnitude of uncertainty increases for smaller grains. Below a threshold FT value of ~0.55, the uncertainty is so great that we no longer consider the data reliable. Note that the data spreadsheet that you receive uses a red color to mark grains with FT values of 0.65 or less to draw your attention to grains of smaller size.

- [ ] Do any of your grains have eU <5 ppm? These should be flagged.
  If any analyses have eU < 5 ppm, then the ICP data should be inspected more closely to confirm that the sample U is at least 3x above blank value. Analyses that are in the weeds for the U measurement are unreliable.

  Dates for low eU grains are also more vulnerable to bias from He implanation from adjacent crystals. If an analysis with <5 ppm eU yield dates that are anomalously old relative to others from the same sample, this may indicate it is biased by He implantation and should be excluded from interpretation.

- [ ] Are any of your grains have the He ncc value in red, indicating a He value less than 5x the background? If so, flag it.
  It's rare for TRaIL to analyze grains with He values only 5x above the background. These low values may indicate that the grain was lost from the packet.

- [ ] For apatite data, do all of your grains have Re (%) values > 99.9%? Grains with lower values should be flagged. Re values are not as instructive in zircon.
  Re (%) is the % of total He degassed during the first laser extraction. In apatites, low Re (%) values are conventionally thought to indicate the presence of inclusions that could bias the data. Although we now have reasons to think that low Re (%) values do not always indicate such a problem, it's good practice to flag any apatite analyses with anomalous values to consider them further.

- [ ] Do any of your analyses have strangely high uncertainties relative to the other grains? If yes, flag it.
  If so, this may indicate a problem with the He, U, or Th measurements.

- [ ] During picking, did you note any grains that had possible inclusions or other flaws? Do these correspond with outlier analyses? If yes, flag it.
  Although we strive to pick perfect crystals for analysis, for subpar samples we occasionally analyze crystals that might be imperfect. For example, you might be 95% sure that imperfection isn't a tiny inclusion, but not 100% certain. Or perhaps the crystal has minor surficial staining or a possible small fracture. All of these characteristics should be noted during grain selection. If any of these possibly flawed grains correlate with outlier analyses, then it may indicate a problem with the analysis and a reason to discard it from interpretation.

a0010 (U-Th)/He Chronology

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Glossary

dt0015 **α-Particle** ^{4}He nucleus composed of two protons and two neutrons.
dt0020 **α-Ejection** The expulsion of ^{4}He nuclei from a crystal due to their kinetic energy.
dt0025 **s^{-1}** A scientific unit denoting a rate of *per second*.
dt0030 **eU** Effective Uranium, a way to represent the Uranium and Thorium content of a mineral weighted by their α-particle production rates.
dt0035 **In situ** Measurements done in place on a small portion of a crystal, as opposed to whole grain measurements.
dt0040 **Partial retention zone** The temperature range, or corresponding depths in the crust, over which ^{4}He is partially lost from and partially retained in a crystal.
dt0045 **Thermochronology** Radiometric dating techniques where the retention of the daughter atom is temperature dependent.

Nomenclature

dt0010 **λ** The decay rate of a radioactive isotope in s^{-1}.

s0010 Introduction

p0015 (U-Th)/He chronometry is based upon the accumulation of radiogenic ^{4}He produced during the decay of naturally occurring ^{238}U, ^{235}U, ^{232}Th, and ^{147}Sm in geologic materials. U, Th, and Sm all undergo one or multiple steps of alpha-decay, during which

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^{4}He is generated. (U-Th)/He dating is typically referred to as thermochronology because the retention or loss of the radiogenic daughter product, ^{4}He, is largely controlled by thermally activated volume diffusion. (U-Th)/He dates, therefore, are typically a function of the thermal history of a sample, and provide information about the rock's time-temperature path. U, Th, and Sm are not abundant in most common rock-forming minerals but are often concentrated in accessory phases like apatite, zircon, and titanite. (U-Th)/He dating of these minerals is a useful technique for understanding the timing and rate of a wide range of geologic processes including the onset and rate of erosional exhumation, the formation of large topographic features such as canyons and mountain peaks, deformation associated with fault activity, and the emplacement of kimberlites and other volcanic features.

s0015 Historical Development of the Technique

s0020 Early Attempts

p0020 (U-Th)/He dating was the first method used to radiometrically determine the age of geologic materials. In 1904, Ramsay and Soddy (1904) reported that He was produced during radioactive decay. Ernest Rutherford (1905) built upon this in 1905 when he argued that "alpha radiation" was actually composed of He atoms, that He was produced by a variety of radioactive elements and, that if the amount of radioactive material, amount of He, and rate of He production were known, it would be possible to calculate the age of material. Indeed, he determined a He date on fergusonite, a rare-earth element oxide, of about 40 Ma. Despite the analytical challenges of measuring He at that time in the early 20th century, scientists such as R.J. Strutt were able to determine He dates on a range of geologic materials. Strutt emphasized that He dates were likely *minimum values* because: …. "helium leaks out from the mineral, to what extent it is impossible to say." As early as 1910, Strutt (1910) produced minimum ages for a number of geologic horizons that even by today's standards are geologically reasonable, including a minimum estimate of 31 Ma for the Eocene and 710 Ma for the Archean. However promising, the "helium leakage" described by Strutt was largely seen as unpredictable and considered problematic enough that the technique was largely abandoned after the U-Pb geochronometer was introduced a few years later.

s0025 Revival and Milestones

p0025 Throughout much of the 20th century, He dating was used only occasionally in specialized applications, including dating very young basalts, corals, and meteorites. However, in 1987, Peter Zeitler and colleagues revisited the technique from the standpoint of thermochronology, a perspective developed in the 1960s and 70s by scientists working on K-Ar and Rb-Sr geochronology (Zeitler et al., 1987). Specifically, they used diffusion experiments to determine if in fact the "He leakage" problem that plagued earlier workers was instead a predictable process caused by volume diffusion through the crystal lattice. Indeed, their diffusion experiments suggested that He retention in apatite was predictable and primarily governed by thermally activated volume diffusion and, on geologic timescales, He could be retained within the crystal lattice. In 1994, Hans Lippolt and colleagues reported similar results from a wider range of apatites (Lippolt et al., 1994). A few years later, many of the fundamentals of the technique were published in a series of papers by Ken Farley and R.A. Wolf (Farley et al., 1996; Wolf et al., 1998). (U-Th)/He thermochronology advanced quickly in the following decades. Notable milestones include the development of laser-heating techniques capable of dating single crystals (House et al., 2000), expansion of (U-Th)/He dating to other common accessory minerals such as zircon and titanite (e.g., Reiners and Farley 1999; Reiners et al. 2002), quantification of the effects of radiation damage on ^{4}He diffusivity (Shuster et al., 2006; Flowers et al., 2009; Guenthner et al., 2013), inclusion of He diffusion kinetics into thermal modeling software packages (e.g., Ketcham, 2005), and development of in situ (U-Th)/He dating (e.g., Boyce et al., 2006).

s0030 Explosion in Popularity and Applicability

p0030 (U-Th)/He dating has become increasingly popular and is now used regularly to investigate a range of geoscience questions, including the formation of topography, the onset or rate of erosion and exhumation, the timing of fault activity, sediment routing, the thermal history of sedimentary basins, and the timing of bolide impacts (e.g., Reiners and Ehlers, 2005). Additionally, research is expanding to better understand the nature and effects of radiation damage in minerals, to develop new minerals as (U-Th)/He thermochronometers, and to constrain and exploit the causes of dispersion in (U-Th)/He datasets.

s0035 Fundamentals

s0040 He Production

p0035 ^{4}He nuclei are produced during radioactive decay of ^{238}U, ^{235}U, ^{232}Th, and ^{147}Sm when alpha particles (composed of two protons and two neutrons) are expelled from the nucleus and acquire two electrons. These ^{4}He atoms can be trapped in the crystal lattice and accumulate over geologic time. Each parent isotope produces 8, 7, 6, and 1 ^{4}He atoms, respectively, over the course of its decay chain, leading to the following age equation:

$$ {}^{4}\mathrm{He} = 8\times{}^{238}\mathrm{U}\left(e^{\lambda_{238}t}-1\right) + 7\times{}^{235}\mathrm{U}\left(e^{\lambda_{235}t}-1\right) + 6\times{}^{232}\mathrm{Th}\left(e^{\lambda_{232}t}-1\right) + {}^{147}\mathrm{Sm}\left(e^{\lambda_{147}t}-1\right) \quad (1) $$

where ^{4}He, ^{238}U, ^{235}U, ^{232}Th, and ^{147}Sm are the current number of atoms present in the mineral, λ_{238}, λ_{235}, λ_{232}, λ_{147} are the respective decay constants of the parent nuclides, and t is the accumulation time. The (U-Th)/He technique differs from most other radiometric chronometers in that one daughter nuclide can be produced by multiple distinct parent nuclides. This precludes the formulation of a simple age equation where the date is a function of a daughter to parent ratio. More importantly, this requires that the total amount (number of atoms) of both the daughters and parents must be measured in order to calculate a (U-Th)/He date.

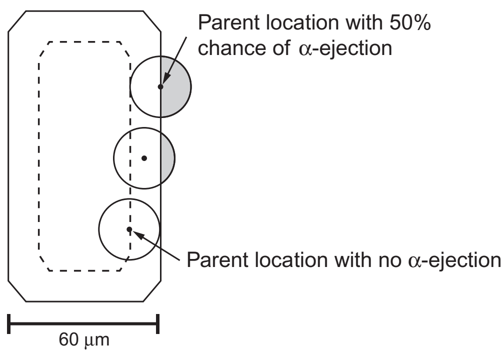
s0045 Alpha Ejection

p0040 The alpha particles (or ^{4}He atoms) produced during radioactive decay have significant kinetic energy and will travel, on average, ~15–20 μm through a crystal lattice before coming to rest (Farley et al., 1996). Each alpha particle can be emitted in any direction, which means that U, Th, or Sm atoms located within 20 μm of the edge of a crystal have a non-zero chance of expelling some of the ^{4}He they produce out of the crystal (Fig. 1). This phenomenon is called "alpha-ejection." Unlike ^{4}He lost due to diffusion, these ejected atoms are not a function of the thermal history of the sample and a correction must be made to account for this effect. The magnitude of this correction increases with decreasing crystal size owing to the larger surface to volume ratios of smaller crystals. Consequently, crystals with a minimum diameter of <50 μm (in the case of apatite) are generally not analyzed because the size of the correction becomes unreasonably large (>50%). The alpha-ejection correction is typically based on the size and shape of the crystal and a description (either assumed or measured) of the three-dimensional parent nuclide distribution in the grain. Broken or rounded crystals, or grains that are strongly zoned with respect to parent nuclides, can be more complex to accurately correct without additional data. Typically, two dates are reported for a single (U-Th)/He analysis: the "raw" or "uncorrected" date, calculated using the age equation, and the "corrected" date, which includes the estimated ^{4}He lost due to alpha-ejection.

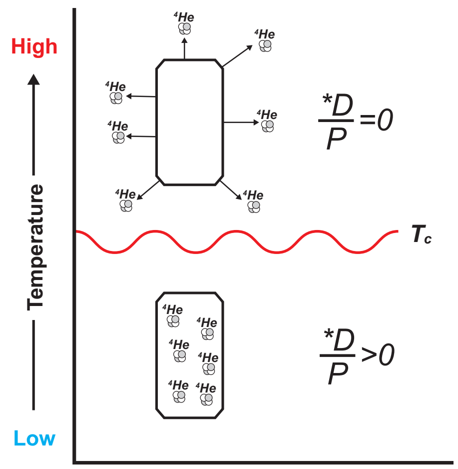
s0050 He Retention, Closure Temperatures, and the Partial He Retention Zone

p0045 ^{4}He that comes to rest in the crystal lattice can be trapped and accumulate over geologic timescales. "Closed system" behavior, where all of the ^{4}He that is produced and not ejected from the crystal is retained, is characteristic of relatively low temperatures (e.g., ≤60 °C for apatite crystals with little radiation damage). When the system is at higher temperatures, the grain acts as an "open system" in which the ^{4}He will diffuse out of the lattice instantaneously. The temperature of the transition from open to closed behavior for a cooling mineral system is referred to broadly as the "closure temperature," which provides a first-order measure of the temperature sensitivity of the thermochronometer (Fig. 2). The strict definition of closure temperature is the temperature of a cooling mineral system at the time of a thermochronometer's measured date (Dodson, 1973). The closure temperatures of the three minerals most commonly used in (U-Th)/He chronometry are ~60 °C for apatite (Farley, 2000) and ~180 °C for zircon and titanite (Reiners and Farley, 1999; Reiners et al., 2002), for crystals with relatively low levels of radiation damage. For monotonic cooling histories, (U-Th)/He dates from these minerals can be viewed as the time elapsed since each mineral last cooled through its respective closure temperature.

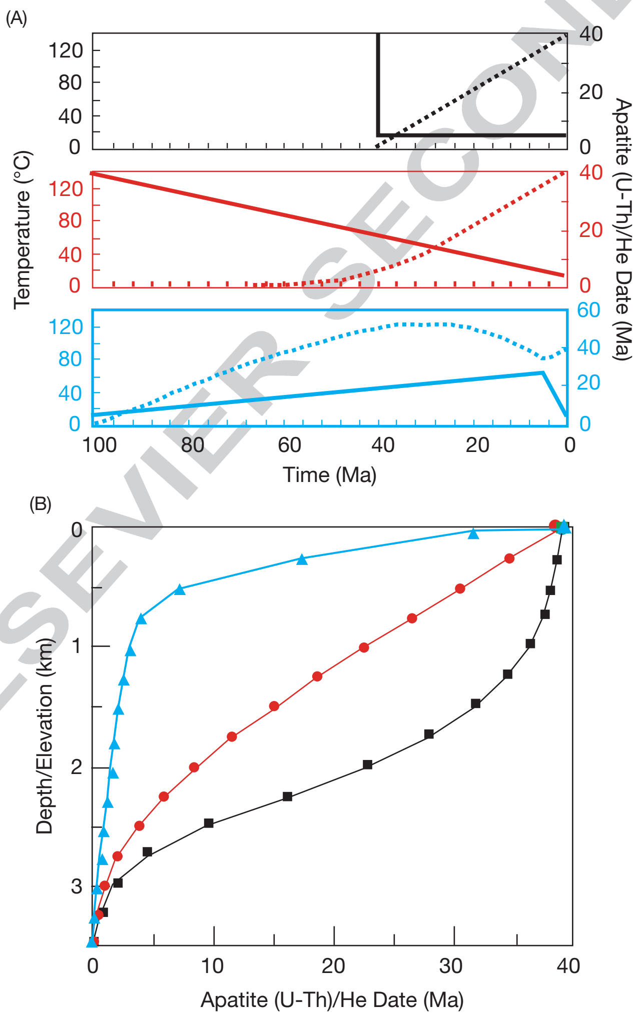
p0050 In reality, however, in most geologic settings the transition from open to closed behavior is not instantaneous, and there is a temperature range over which ^{4}He is only partially retained within the crystal (Wolf et al., 1998). The temperature span of this "He partial retention zone" is a function of several factors including the sample cooling rate, the crystal size, and the amount of accumulated radiation damage in the crystal. For common cooling histories and geothermal gradients, the apatite He partial retention zone corresponds to a 1–3 km depth range in the crust. Grains that reside in this zone for extended intervals develop (U-Th)/He dates that reflect the time-integrated history of He accumulation and loss rather than the timing of a specific rapid cooling event (Fig. 3).



f0010 **Fig. 1** Diagram illustrating alpha-ejection in apatite. Each circle represents the ~20 μm distance that ^{4}He atoms travel after being produced during radioactive decay. Shaded portions of the circles represent positions where ^{4}He can come to rest outside the crystal due to ejection, resulting in net ^{4}He loss from the grain. The dashed line shows the volume of the grain where ^{4}He will not be ejected. This volume is a larger proportion of the grain for larger crystal sizes.



f0015 **Fig. 2** Schematic diagram illustrating the closure temperature concept. ^4He is continuously produced by radioactive decay, but at high temperatures the crystal acts as an open system and ^4He will diffuse out of the crystal. Consequently, the radiogenic daughter (D*) to radioactive parent (P) ratio is always 0. In contrast, at low temperatures the ^4He is retained, and the daughter to parent ratio increases linearly with accumulation time. To first order, for a cooling mineral system, the temperature at which the system transitions from open to closed behavior is referred to as the closure temperature.



f0020 **Fig. 3** Figure illustrating the implications of the apatite He partial retention zone after Wolf et al. (1998). (A) The *bold lines* and the left y-axis show three distinct 100 My-long thermal histories, one with rapid cooling at 40 Ma (*top, black line*), one with slow monotonic cooling since 100 Ma (*middle, red line*), and one with slow heating for 95 My followed by rapid cooling (*bottom, blue line*). The dashed lines represent the evolution of the (U-Th)/He date for that sample (labeled on the right y-axis). Note that all three thermal histories will produce an apatite (U-Th)/He date of 40 Ma, even though only one of them actually involves a cooling event specifically at that time. (B) Date-elevation or date-depth relationship that each cooling history in (A) would produce, assuming a constant geothermal gradient. Note that although the topmost sample at the surface, as illustrated in (A), has the same date for each thermal history, the shape of each date-elevation, or date-depth relationship, is distinct.

s0055 ## Radiation Damage

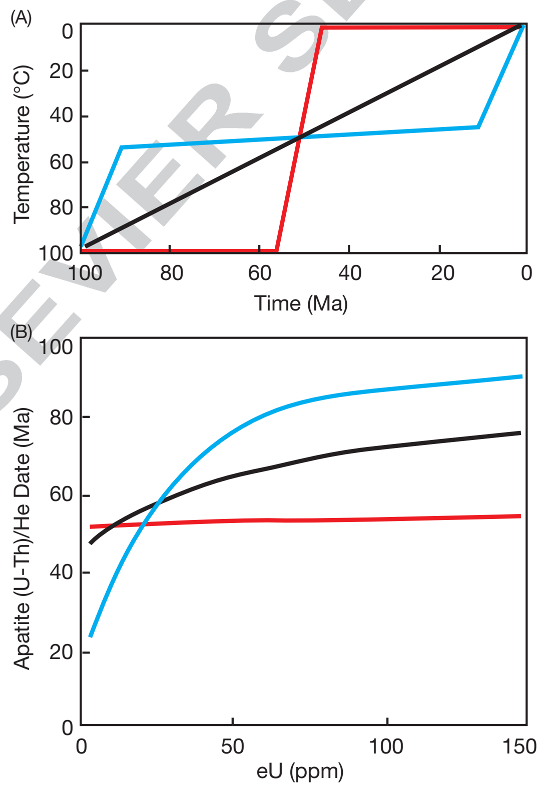
p0055 An important advance in understanding (U-Th)/He data has been the realization that the kinetics of He diffusion and, therefore, the closure temperature or temperature sensitivity of a particular mineral are a function of the amount of radiation damage that has accumulated in the crystalline lattice. This was first documented in apatite, where it was shown that radiation damage decreases the diffusivity of ^{4}He through the lattice, making it harder for ^{4}He to diffuse out of the crystal, effectively raising the apatite closure temperature (Shuster et al., 2006; Flowers et al., 2009). Thus, if apatite crystals from the same rock have different U and Th contents, they will accumulate radiation damage at different rates and will evolve to have different closure temperatures. This effect can be substantial, in extreme cases increasing the apatite closure temperature by 10s of °C. The diffusivity of ^{4}He in zircon and titanite are also a function of radiation damage (Guenthner et al., 2013). Moderate amounts of accumulated damage appear to decrease ^{4}He diffusivity, while higher damage amounts increase ^{4}He diffusivity and lower the zircon closure temperature. Because of these radiation damage phenomena, (U-Th)/He dates are commonly plotted against eU (effective Uranium, or U + 0.235*Th; Shuster et al., 2006), which weights U and Th by their relative He production rates. eU can be used as a proxy for radiation damage for grains that underwent the same thermal history. Trends in date-eU plots can be exploited to better decipher the sample's thermal history (Flowers et al., 2007, 2009; Fig. 4).

s0060 ## Measurement Protocols

p0060 As discussed above, the (U-Th)/He chronometer is unusual in that multiple parent nuclides (^{238}U, ^{235}U, ^{232}Th, and ^{147}Sm) can produce the radiogenic daughter atom (^{4}He). Unlike most other geochronologic techniques, the parent and daughter atoms cannot be measured on the same analytical instrument. However, all of these isotopes either must be measured on the same volume or the concentrations of the different analyzed volumes known to accurately determine a (U-Th)/He date. There are two broad approaches to (U-Th)/He dating: the conventional whole-crystal approach and the laser-ablation or in situ approach.

s0065 ### Conventional Whole-Crystal Methodology

p0065 The majority of published (U-Th)/He dates are conventional analyses on single whole crystals. Individual grains are first hand-picked from mineral separates based on size, morphology, and lack of inclusions. The larger the crystal, the more material there is to



f0025 **Fig. 4** Figure illustrating the effects of radiation damage on apatite (U-Th)/He dates after Flowers et al. (2009). (A) Temperature-time diagram showing three different thermal histories characterized by rapid (*red*), moderate (*black*), and slow (*blue*) cooling. (B) Apatite (U-Th)/He date versus eU plot showing the date versus eU (U + 0.235 X Th, a proxy for radiation damage) pattern produced by each thermal history. Note that although the date for an apatite with an ~20 ppm eU value would be similar for all three thermal histories, the broad date-eU patterns are clearly distinct.

measure, and the smaller the alpha-ejection correction. Geometric measurements of euhedral crystals are the simplest to convert into accurate volume and surface area values for calculation of isotopic concentrations and alpha-ejection corrections. Mineral inclusions can bias apatite (U-Th)/He dates to be incorrectly old, because U-Th rich mineral inclusions will generate ^{4}He during decay, but the inclusions are not dissolved during normal dissolution methods leading to "parentless" ^{4}He.

p0070 Once an appropriate crystal is selected, it is photographed and measured before being sealed into a small metal packet. These packets are then loaded into an ultra-high vacuum noble-gas extraction and analysis line where they are heated (usually with a laser) to degas all of the ^{4}He from the grain. The ^{4}He is typically spiked with a known amount of ^{3}He and then measured using a noble gas mass spectrometer. The metal packets that hold the grains are important for this heating step because they create an evenly heated microfurnace for the crystals. Early work indicated that heating a crystal directly with a laser beam could volatilize U and/or Th and lead to irreproducible ages. The introduction of the small metal sample packets appears to have largely eliminated this problem (House et al., 2000).

p0075 The degassed samples are then removed from the vacuum line, spiked with U, Th, and Sm tracers, and dissolved in acid. Typically, apatite samples are dissolved using dilute nitric acid, while more refractory phases such as zircon and titanite require more aggressive acid-vapor dissolution protocols using concentrated hydrofluoric and hydrochloric acid. Most facilities leave the degassed minerals in their metal packets for this process. These dissolved mineral solutions are then analyzed using inductively coupled plasma-mass spectrometry (ICP-MS). To measure multiple characteristics of a single grain, additional analyses must be conducted prior to conventional (U-Th)/He analysis that involves complete crystal dissolution. Examples include data from non- or minimally-destructive techniques such as laser-ablation-ICP-MS U-Pb geochronology, fission-track thermochronology, Raman spectroscopy, or electron microprobe analysis (e.g., Carrapa et al., 2009; Reiners et al. 2005).

s0070 Laser-Ablation In Situ Methodology

p0080 Laser-ablation in situ techniques have been less applied than whole-crystal analysis, but are receiving increasing attention (e.g., Boyce et al., 2006; Danišík et al., 2017). This higher-spatial resolution approach sub-samples a small portion of a grain for analysis using laser ablation instead of measuring the U, Th, Sm, and He concentrations of the entire crystal. Advantages over the whole-crystal method include avoiding the time-consuming dissolution steps required for refractory phases, the ability to interrogate complex sub-grain patterns of parent isotope zonation and directly measure ^{4}He diffusion profiles, consumption of less material from high-value samples, and better coupling of the high-spatial resolution results with other in situ information including measurements of radiation damage, REE patterns, and U-Pb dates.

p0085 The first step of in situ (U-Th)/He analysis is to mount the grains to present a flat crystal surface, and, if desired, polish to expose internal crystal portions. ^{4}He analysis, or U, Th, and Sm analysis, can then occur in either order. For the ^{4}He analysis, the sample is loaded into an ultra-high vacuum noble-gas extraction and analysis line, and an excimer laser is used to ablate a small pit. The energy of the excimer laser liberates the ^{4}He contained in the excavated material, which can then be spiked and measured in a manner similar to the conventional analysis. This analysis is followed by a procedure to accurately measure the size of the ablation pit in order to calculate the ^{4}He concentration of the sampled volume.

p0090 The sample is then placed in a sample chamber attached to an ICP-MS, and another pit is ablated. This ablated material is fed into the ICP-MS where U, Th, and Sm measurements are made. This pit must also be measured in order to calculate parent nuclide concentrations. The parent and daughter concentrations can then be used to compute the (U-Th)/He date. If the laser-ablation measurements are made in the crystal interior that is unaffected by He loss due to alpha-ejection, then an alpha-ejection correction is not applied.

s0075 Strategies for Interpreting Thermal Histories From (U-Th)/He Data

p0095 Like most radiometric dating schemes, calculating a date is straightforward in the (U-Th)/He system. However, assigning geologic meaning to the date can be complex. As discussed above, assigning a specific closure temperature to a thermochronometer and then interpreting the date as the time that has elapsed since the crystal cooled below that temperature may be reasonable for systems that undergo rapid cooling through the He partial retention zone. However, for more complex thermal histories this approach is not valid, because a wide range of thermal histories can generate a given (U-Th)/He date (Fig. 3). A variety of strategies can be employed to obtain additional information with which to decipher the thermal history significance of a (U-Th)/He dataset, and modeling tools can be applied to constrain the range of viable thermal histories that honor all of the available data.

s0080 Geologic Information

p0100 Geologic constraints are exceptionally important for the interpretation of (U-Th)/He data. These can include how the rock formed (e.g., intrusive or extrusive igneous rocks), stratigraphic estimates of when and how deeply a rock may have been intruded or buried, and unconformities that may require the sample to have been at the surface during its history. Independent geologic information should, when relevant, be incorporated into thermal models to better understand possible thermal histories.

s0085 ## Multiple Chronometers

p0105 Data from multiple geo- and thermochronometers provide critical information with which to more accurately interpret (U-Th)/He data and decipher continuous thermal histories over a broad temperature span. For example, dates from higher-temperature systems like zircon U-Pb or biotite $^{40}Ar/^{39}Ar$ limit the maximum sample temperatures and help constrain the amount of accumulated radiation damage in the crystal. Thermochronometers with overlapping temperature sensitivities, like apatite (U-Th)/He and apatite fission-track thermochronology, provide complementary information with which to more tightly resolve thermal histories within their overlapping temperature range (e.g., Stockli et al., 2000). An increasingly common approach is to obtain multiple types of geo- and thermochronologic dates on a single mineral crystal to maximize the thermal history information that can be extracted from the same material (i.e., U-Pb, fission-track, and (U-Th)/He dates on the same apatite crystal; Reiners et al., 2005; Carrapa et al., 2009).

s0090 ## Date-Elevation Relationships

p0110 A common approach to better understand (U-Th)/He data is to compare dates from multiple, related samples. Date-elevation or date-depth relationships have been used to better interpret low-temperature thermochronology data for decades (e.g., Fitzgerald et al., 1986). The basic idea is that samples that come from an intact mass of rock, but at different depths in the Earth, will experience the same thermal history offset by the geothermal gradient (the rate at which temperature increases with depth). For example, if a granite pluton is buried under 1 km of sediments, then the samples at the top and the bottom of the granite will undergo the same burial and heating history, but to different maximum temperatures. Thermochronologists will commonly sample from as large a range of paleo-depths as possible, using strategies that include sampling a large elevation range (e.g., House et al., 1997), sampling from the entirety of a tilted and exposed crustal section (e.g., Stockli et al., 2000), or sampling from a deep drillcore (e.g., House et al., 2002; Lorencak et al., 2004; Söderlund et al., 2005). (U-Th)/He data from large crustal sections can expose intact paleo-He partial retention zones, and date-elevation (or depth) patterns can directly record changes in cooling rates, paleo-geothermal gradients, or earlier histories of burial and/or erosion (Fig. 3).

s0095 ## Date-eU Relationships

p0115 As noted above, it is now well documented that He diffusion kinetics are a function of the amount of radiation damage that has accumulated in the crystal lattice. This phenomenon has been well-documented in apatite, zircon, and titanite, which are the most common minerals used in (U-Th)/He dating (e.g., Shuster et al., 2006; Flowers et al., 2009; Guenthner et al., 2013; Baughman et al., 2017). Depending on the phase and the amount of accumulated damage, He diffusivity can either increase or decrease, thereby making individual grains from the same sample either more or less retentive. A simplistic way to think of this is that variations in radiation damage turn crystals into thermochronometers with slightly different closure temperatures. In apatite, for example, a low-damage grain may correspond to a closure temperature of ~60 °C, whereas a high-damage grain from the same sample may have a closure temperature ~100 °C. The differences or similarities in the (U-Th)/He dates for these grains thus are a function of the sample's thermal history in this temperature range. If the dates are similar it implies that the sample cooled quickly through the 100–60 °C temperature range, and if the dates are dissimilar it implies a more complex thermal history. Patterns of (U-Th)/He dates plotted versus eU, therefore, are a function of the type of thermal history that a sample experienced (Fig. 4; Flowers et al., 2007, 2009; Guenthner et al., 2013). It is common to date multiple single-grains from the same sample to best exploit an eU range. This approach is directly analogous to the use of multiple thermochronometers from the same sample to determine thermal histories, as described above.

s0100 ## $^{4}He/^{3}He$ Thermochronology

p0120 $^{4}He/^{3}He$ thermochronology is a variant of (U-Th)/He dating that can determine the spatial distribution of radiogenic ^{4}He in the crystal (Shuster and Farley, 2003). The ^{4}He distribution is a function of the parent isotope distribution, alpha-ejection, the crystal retentivity, and the thermal history. In this technique, grains are irradiated with an energetic proton beam that produces an even distribution of ^{3}He atoms via spallation reactions. A single crystal is then subjected to a stepwise degassing experiment and the $^{4}He/^{3}He$ release spectra used to solve for the distribution of radiogenic ^{4}He in the grain. With knowledge of the parent isotope distribution and alpha-ejection parameters, these data can be used to resolve the ^{4}He diffusion profile at the crystal margin, which is a function of the grain's ^{4}He retentivity and the thermal history. This diffusion profile, when coupled with (U-Th)/He data, provides additional information about the lower-temperature portions of the time-temperature path than accessible with only a bulk crystal (U-Th)/He date. Although the $^{4}He/^{3}He$ method is far more time-consuming than (U-Th)/He dating, the lower-temperature constraints it can provide may be key for addressing some geologic questions (e.g., Flowers and Farley, 2012).

s0105 ## Thermal History Modeling

p0125 As discussed above, an individual (U-Th)/He date represents the time-integrated history of He loss and retention. Thermal history modeling allows thermochronologists to explore the range of time-temperature paths that are compatible with both geologic constraints and the thermochronologic data. Modeling is often most useful as a way to test hypotheses regarding the consistency of the input data, boundary conditions, and geologic constraints with particular broad histories (e.g., cooling vs. reheating) or to impose time-temperature limits on specific portions of the history (e.g., Flowers et al., 2015). Modeling is less useful for determining which single time-temperature path is correct. The most widely-used modeling packages are freeware, with both forward (where a He date is calculated from an input thermal history) and inverse (where thermal histories are calculated from input He dates) modeling approaches available.

p0130 HeFTy and QTQt are two software packages that are commonly used for this purpose (Ketcham, 2005; Gallagher, 2012). Both rely on the same underlying He diffusion kinetic models and track ^{4}He production and diffusion, as well as radiation damage accumulation and annealing, during a specific time-temperature path. However, the philosophical approaches and statistical methodologies of these two programs differ. A full comparison between these two software packages is beyond the scope of this article, so the reader is referred to Gallagher and Ketcham (2018) for a more detailed discussion.

p0135 (U-Th)/He data record the thermal history of a sample but using that information to describe the motion of rocks in the upper crust requires additional assumptions or information regarding the shape and temporal evolution of the geotherm and crustal isotherms. Higher temperature thermochronometers generally relate to deeper crustal processes where over short distances the isotherms can be reasonably assumed to be relatively flat. Lower-temperature systems, like (U-Th)/He, reflect cooling in the upper crust where even moderate relief can impose significant topography upon near-surface isotherms. Modeling software such as Pecube can calculate the time-variant 3-D thermal fields below complex and evolving topography, and therefore determine which landscape evolution histories are consistent with (U-Th)/He (or other thermochronometer) data sets (Braun et al., 2012). Like HeFTy and QTQt, Pecube works by comparing data calculated from model thermal histories to measured data, but Pecube differs in its ability to calculate upper crustal thermal histories from realistic relief and erosion scenarios.

s0110 Applications of (U-Th)/He Thermochronology

s0115 Exhumation and Cooling

p0140 Perhaps the most straightforward geologic processes to constrain with (U-Th)/He thermochronology are those that cause the direct cooling of rocks, including exhumation caused by erosion (e.g., Kirby et al., 2002; Ehlers and Farley, 2003) or normal faulting (e.g., Stockli et al., 2000; Reiners et al., 2002). Date-elevation sampling strategies (Fig. 3) and/or the incorporation of multiple thermochronometers can provide high-quality constraints on the onset, magnitude, and duration of exhumation due to these processes.

s0120 Burial Heating

p0145 Burial by sedimentary or tectonic processes can fully or partially reset samples by heating enough to fully or partially degas trapped radiogenic He. (U-Th)/He data from regions that have undergone one, or multiple, episodes of burial and reheating will reflect these events. Interpreting the (U-Th)/He data in the context of local and regional geologic information (e.g., depositional histories, unconformities, and cross cutting relationships) can place important constraints on the timing and magnitude of burial (e.g., Flowers et al., 2007; Ault et al., 2009; Carrapa et al., 2009; Fosdick et al., 2015).

s0125 Detrital Thermochronology

p0150 Detrital thermochronology is a useful technique that measures thermochronologic dates on sediment (either modern or preserved in sedimentary rocks) to understand the processes that produced and transported the sediment. (U-Th)/He dating is commonly used in tandem with U-Pb dating of detrital zircon, apatite, or other minerals to constrain both mineral crystallization and cooling. Detrital thermochronology studies are typically aimed at deciphering the source region, its erosion rates and history, and sediment routing systems (e.g., Rahl et al., 2003; Stock et al., 2006; Carrapa et al., 2009).

s0130 Other Applications

p0155 (U-Th)/He dating is increasingly applied to a wide range of minerals (e.g., hematite, goethite, magnetite, rutile, perovskite) to address a diverse range of problems. Examples include studies to constrain the fingerprints of wildfire reheating (e.g., Reiners et al., 2007), bolide-related impact reheating (e.g., Van Soest et al., 2011; Kelly et al., 2018), the timing of hydrothermal mineralization (e.g., Wernicke and Lippolt, 1994; Chakurian et al., 2002), and the timing of slip along brittle fault surfaces (e.g., Ault et al., 2015).

s0135 Ongoing Work/Future Directions

p0160 (U-Th)/He dating is a commonly used and reliable thermochronologic technique, but the method is still growing. Frontiers in (U-Th)/He dating include developing additional minerals as (U-Th)/He thermochronometers, better understanding the nature of radiation damage accumulation and annealing and its effects on He diffusivity in different mineral phases, and refining the ability to model (U-Th)/He datasets. In addition, advances in analytical techniques like laser-ablation in situ dating, ramped-heating diffusion methods, and new approaches to measure or calculate alpha-ejection corrections are improving our understanding of the data. Together these advances are expanding the range of questions that can be effectively addressed with (U-Th)/He techniques.

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Abstract:

(U-Th)/He chronometry is a radiometric dating method based on the accumulation of radiogenic helium produced by the decay of naturally occurring uranium, thorium, and samarium in geologic materials. Helium retention in a mineral is largely dependent upon temperature. The technique is commonly referred to as (U-Th)/He thermochronology because (U-Th)/He dates usually reflect the sample's thermal history rather than the sample's formation age. U and Th bearing accessory minerals like apatite, zircon, and titanite are the most common targets for (U-Th)/He dating, but numerous other minerals are under investigation for use as He chronometers. The temperature sensitivities of the most common He dating targets are ~60–70 °C for apatite and ~150–180 °C for zircon and titanite. Consequently, (U-Th)/He dating is most typically used to constrain upper crustal and lower temperature processes.

Keywords: (U-Th)/He; Helium; Radiometric dating; Thorium; Uranium

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