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The Continuing Evolution of Laser Ablation (U-Th)/He Methods: From Dates to Intracrystalline Isotopic Distributions

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Abstract

Since initially developing laser ablation (U-Th)/He procedures for high-spatial-resolution dating of monazite more than a decade ago, our research group has refined the technique to the point that laser ablation dating of apatite, titanite, and zircon is now routine in the Arizona State University (Group 18) laboratories. We are actively exploring applications to additional minerals. Compared to conventional single-crystal (U-Th)/He dating, the laser ablation alternative offers some important advantages. Following appropriate analytical protocols, laser ablation dates require no alpha ejection corrections. In principle, most factors commonly believed to cause high apparent age dispersion in conventional datasets – parent element zoning, alpha particle implantation, and the presence of high-(U+Th) inclusions – can be mitigated using the laser ablation method. Analytical throughput is greatly enhanced compared to the conventional method because sample dissolution is not required for U+Th+Sm analysis. This is especially beneficial for detrital studies; in this presentation, we review examples of Group 18 research involving (U-Th)/He and U/Pb laser ablation double dating of detrital apatite and zircon. The principal limitations to the method are that: 1) relatively large grain sizes ([?] 100 μm) are sometimes required for especially young or low-(U-Th) materials; and 2) analytical uncertainties for these materials can be as much as a factor of two larger for laser ablation dates than for conventional dates due to a combination of the much smaller masses analyzed and uncertainties in the U, Th, and Sm concentrations of available appropriate standards. Frontier applications of this technology advance our understanding of the intracrystalline distribution of radiogenic 4He in accessory minerals. Here we show examples of both two-dimensional mapping of 4He in polished crystal interiors and one-dimensional depth profiling as practiced in the Group 18 laboratories. Zoning in 4He is very common in older crystals, and 4He distribution patterns can be much more complex than what might be expected simply from alpha ejection or grain-scale diffusive loss during cooling. Much of this complexity reflects non-concentric zoning in parent elements and, for older crystals, spatially variable radiation damage that results in spatially variable 4He diffusivity. The potential impacts of such phenomena on thermal and exhumation history modeling argue for a greater reliance on microanalytical procedures in (U-Th)/He thermochronology moving forward.

The Continuing Evolution of Laser Ablation (U-Th)/He Methods

From Dates to Intracrystalline Isotopic Distributions

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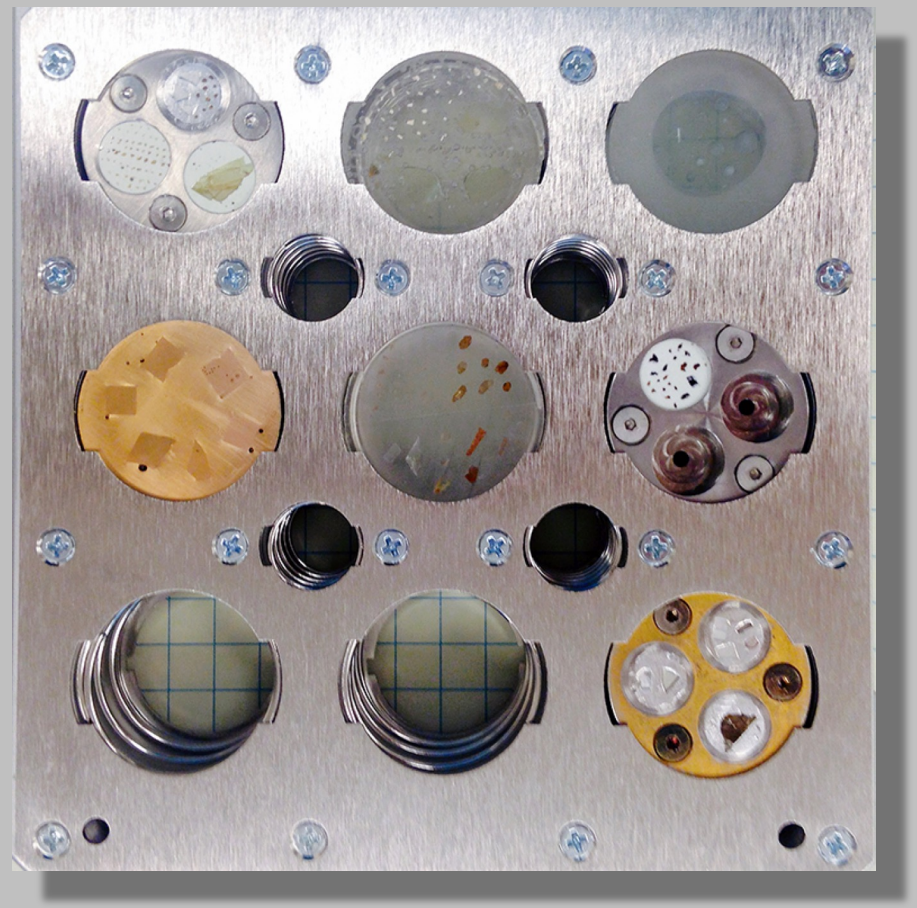


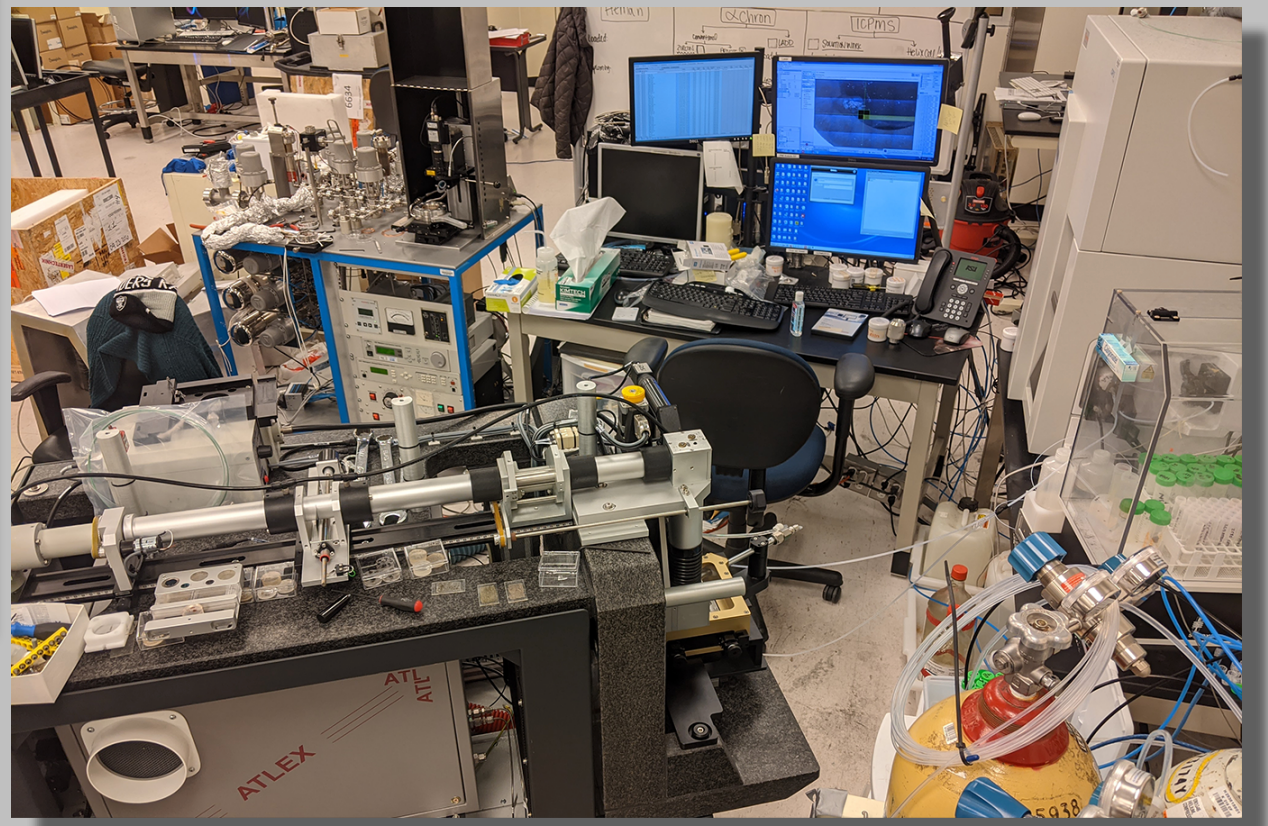
ArF Excimers (λ = 193 nm) Are the Best, Widely Available Lasers for Microprobe Dating

Heating and Melting

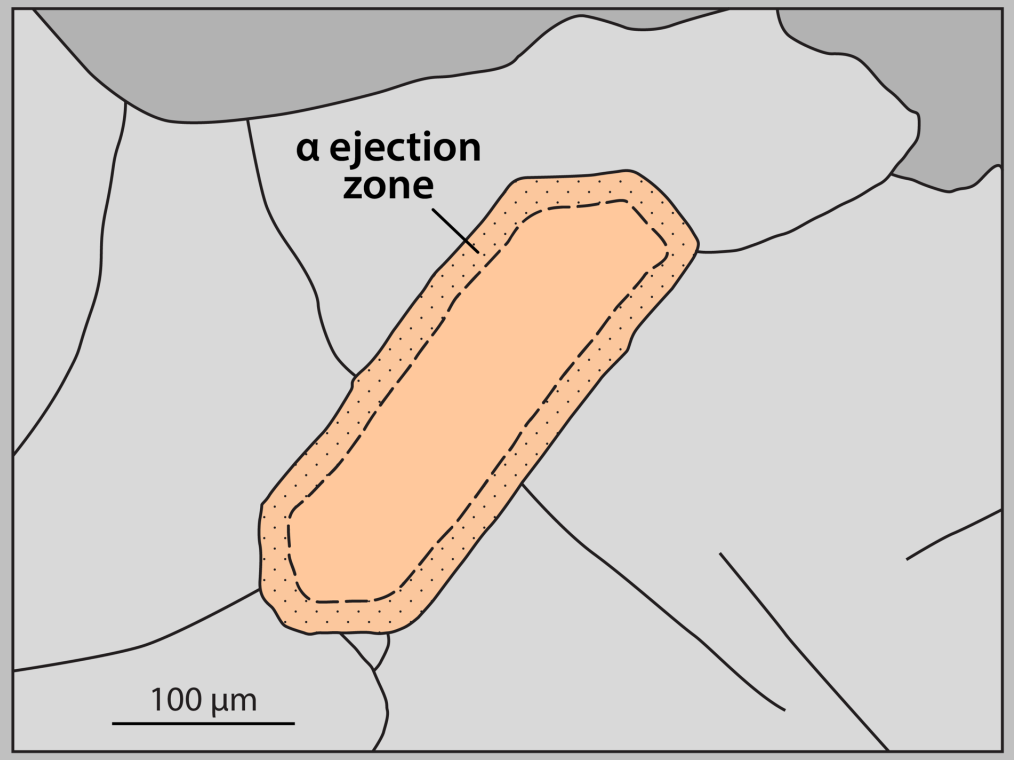
Ablation

Decreasing Collateral Heating
Increasing Spatial Resolution

Ultraviolet Laser Ablation Microprobe (UVLAMP) Methods Offer Some Important Advantages Over More Conventional Methods



Alpha Ejection Corrections Amplify the Uncertainty Inherent to Conventional (U-Th)/He Dating



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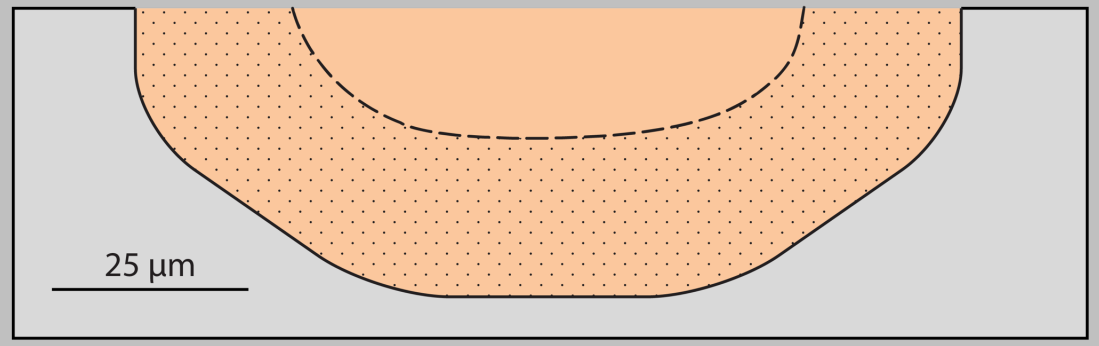
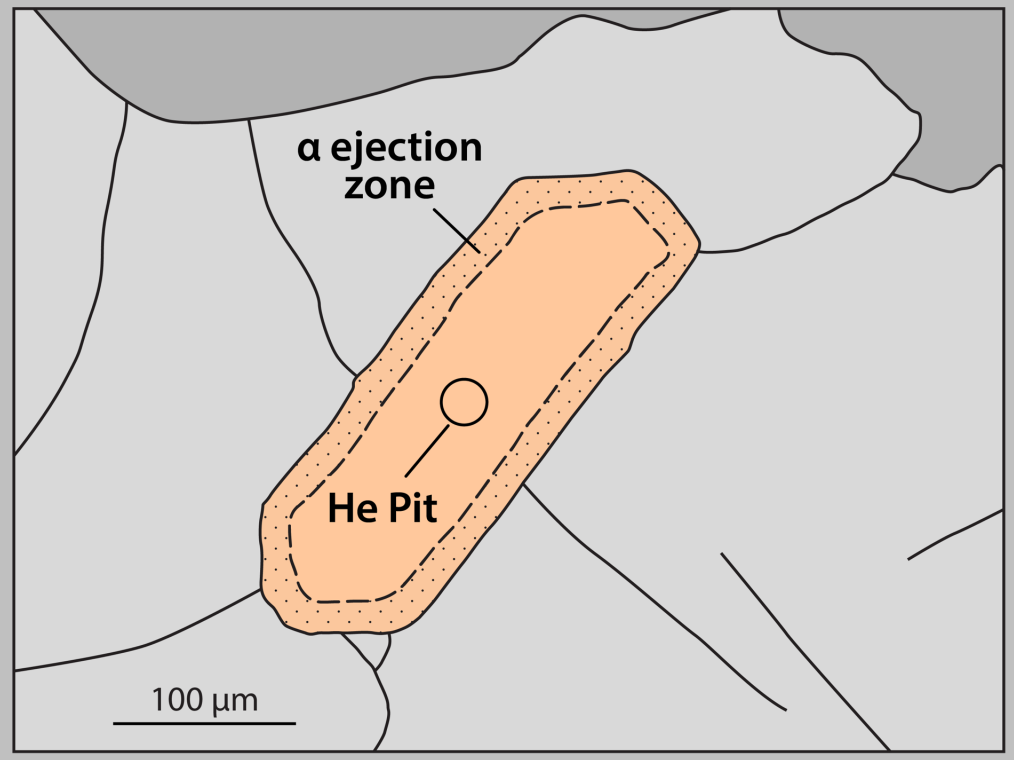


Cross Section

The Basic UVLAMP Technique Involves Two Ablation Extractions of Material, One for Helium and One for Other Elements



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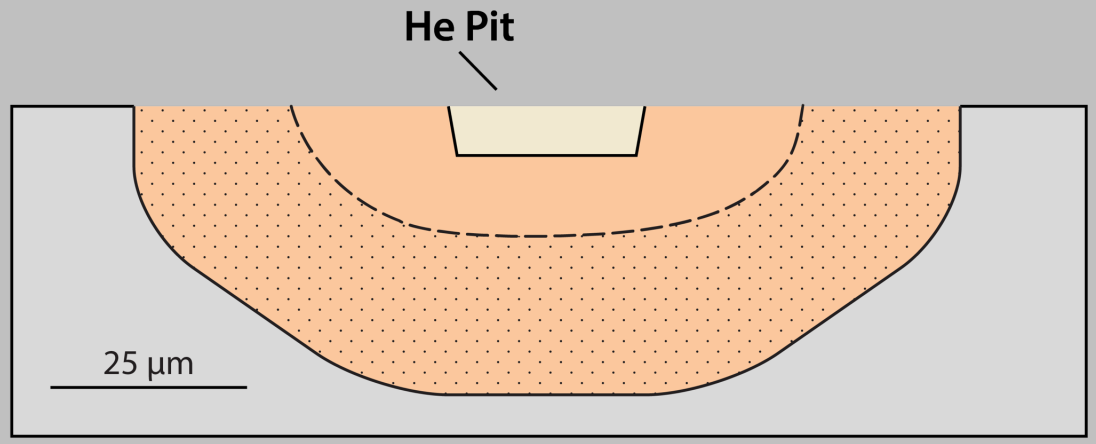

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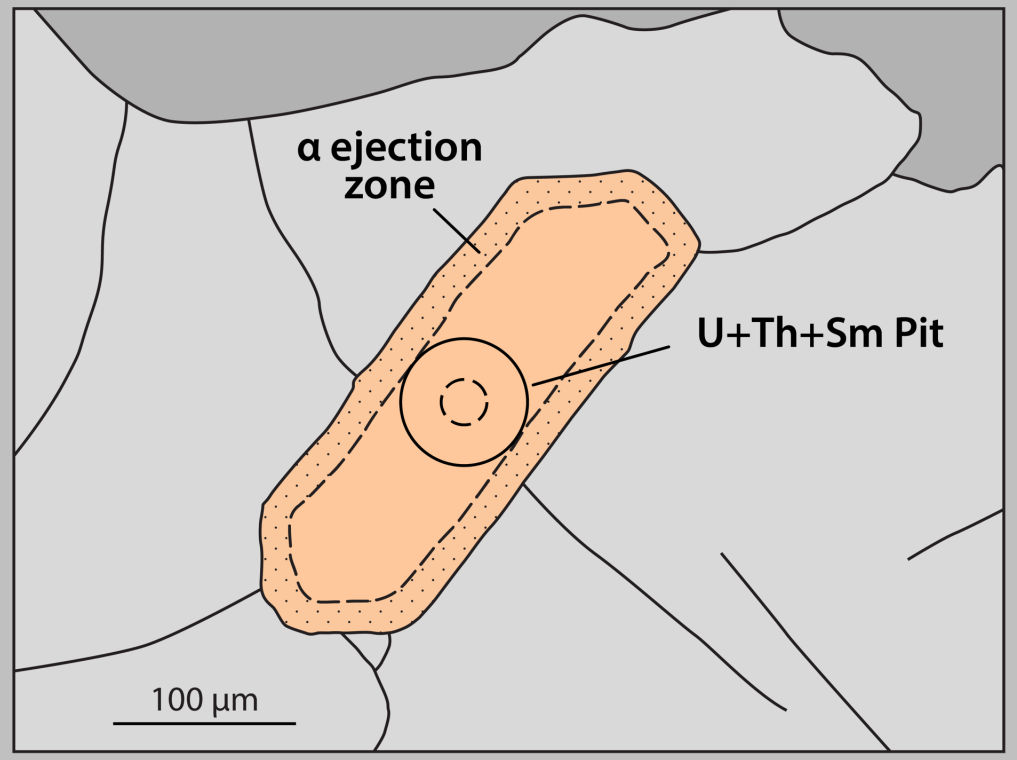

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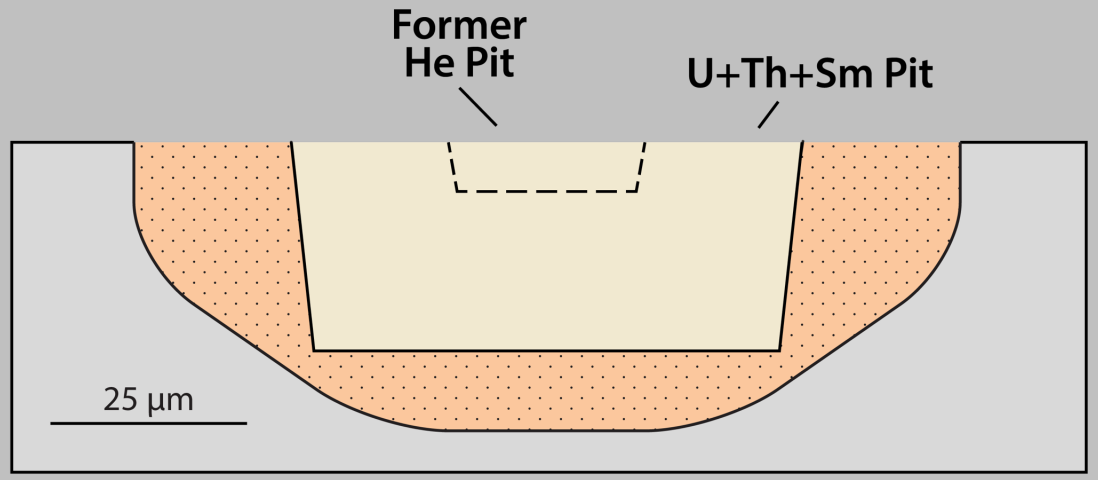
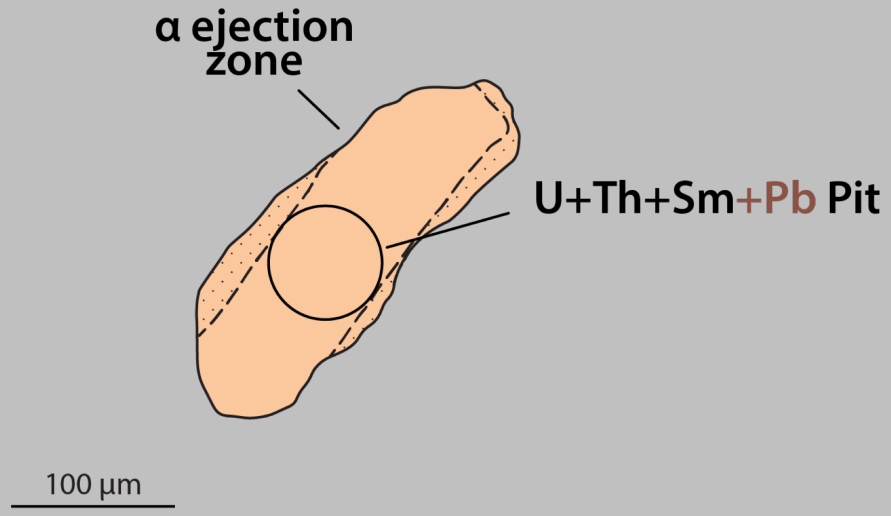


Cross Section

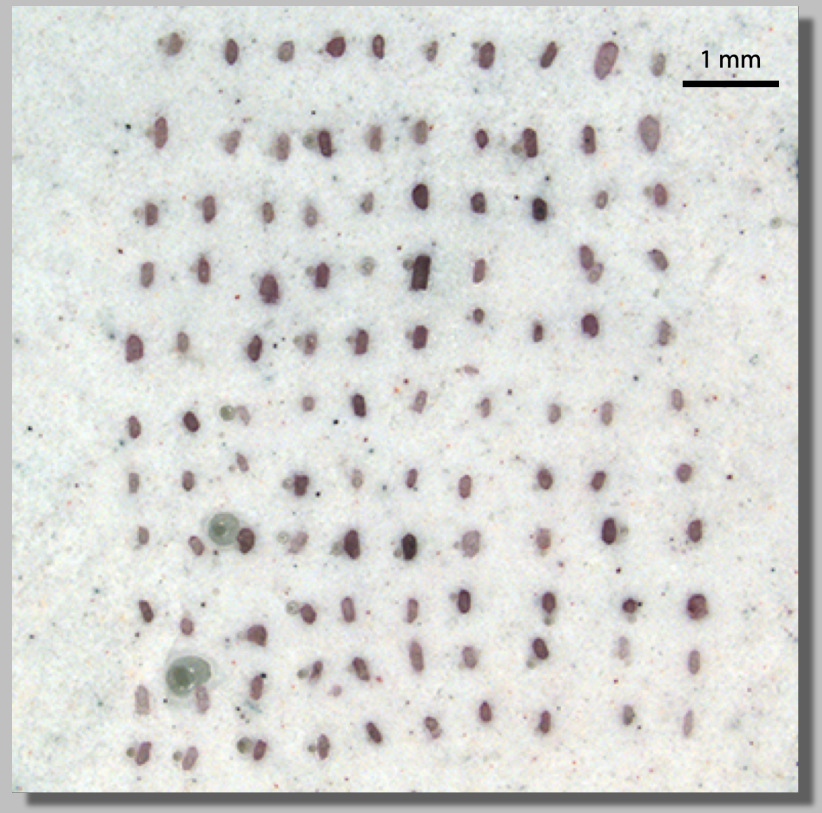
The UVLAMP Approach Can Be Used for All Minerals That Can Be Dated by Conventional (U-Th)/He

- ✓ Routine in the Group 18 Laboratories: Zircon, Apatite, Titanite
- ✓ Proven: Monazite, Xenotime
- ✓ Principal limitations are grain size, parent element abundances, and age
- ✓ Analytical uncertainties are appropriately larger than those for conventional work given the differences in analyte masses

The UVLAMP Approach Is Especially Useful for Detrital Sample Studies

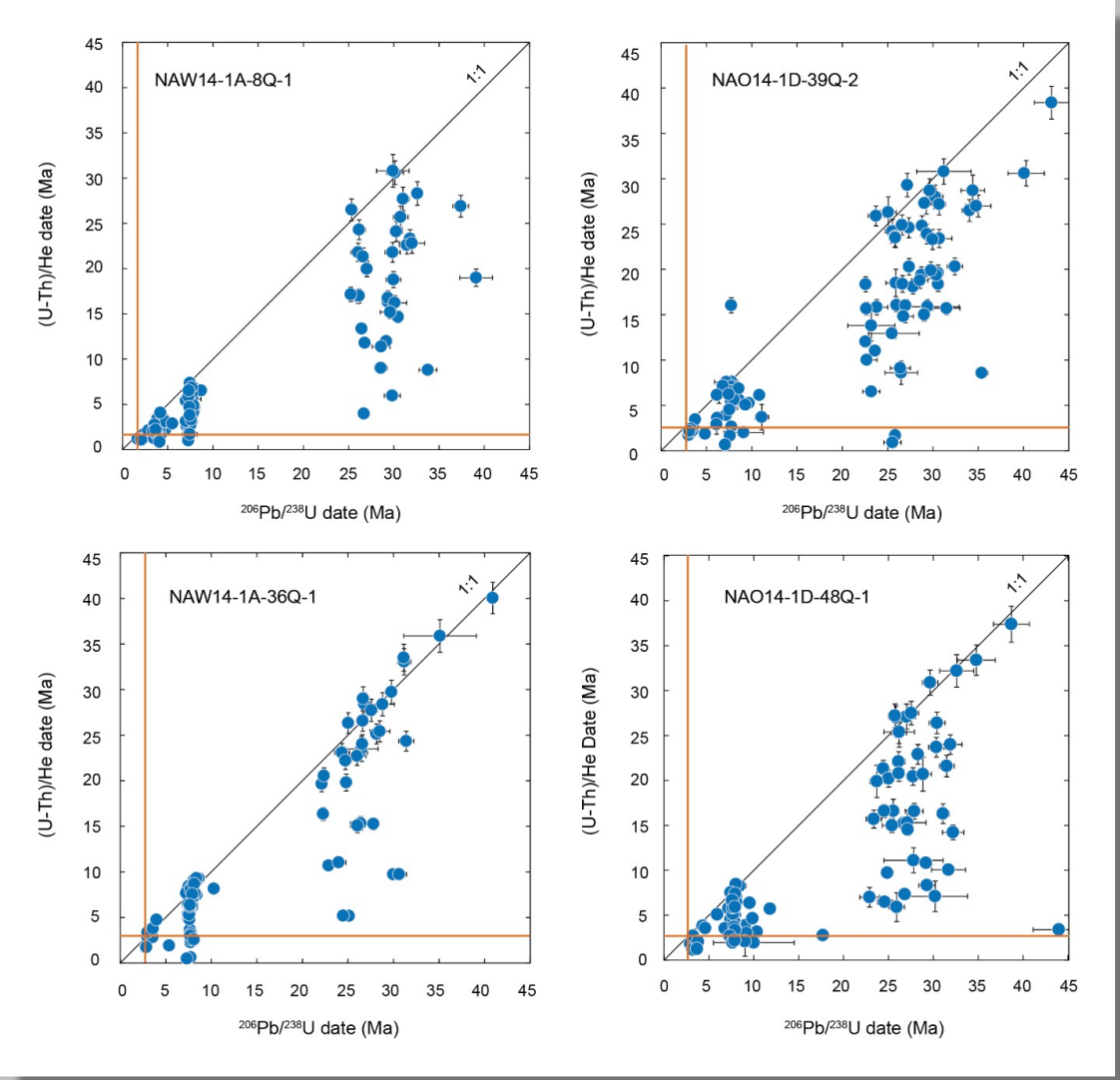


Polished Grain Mount



Laser Ablation "Double Dating" (LADD)

LADD Zircon Data From Ethiopian East African Rift Drill Cores Illustrate the Need for Adaptable Instrumentation



- ✓ Data include a combination of quadrupole and magnetic sector helium isotopic measurements

– Zawacki et al. (in review)

Laser Ablation Mapping Is the Next Frontier

SCIENCE ADVANCES | RESEARCH ARTICLE

GEOCHRONOLOGY

Seeing is believing: Visualization of He distribution in zircon and implications for thermal history reconstruction on single crystals

Martin Danišík,[1]* Brent I. A. McInnes,[1] Christopher L. Kirkland,[1,2,3] Brad J. McDonald,[1] Noreen J. Evans,[1] Thomas Becker[4]

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Zircon (U-Th)/He thermochronometry is an established radiometric dating technique used to place temporal constraints on a range of thermally sensitive geological events, such as crustal exhumation, volcanism, meteorite impact, and ore genesis. Isotopic, crystallographic, and/or mineralogical heterogeneities within analyzed grains can result in dispersed or anomalous (U-Th)/He ages. Understanding the effect of these grain-scale phenomena on the distribution of He in analyzed minerals should lead to improvements in data interpretation. We combine laser ablation microsampling and noble gas and trace element mass spectrometry to provide the first two-dimensional, grain-scale zircon He "maps" and quantify intragrain He distribution. These maps illustrate the complexity of intracrystalline He distribution in natural zircon and, combined with a correlated quantification of parent nuclide (U and Th) distribution, provide an opportunity to assess a number of crystal chemistry processes that can generate anomalous zircon (U-Th)/He ages. The technique provides new insights into fluid inclusions as potential traps of radiogenic He and confirms the effect of heterogeneity in parent-daughter isotope abundances and metamictization on (U-Th)/He systematics. Finally, we present a new inversion method where the He, U, and Th mapping data can be used to constrain the high- and low-temperature history of a single zircon crystal.

Downloaded from http://www.science.org at Arizona State University on September 01, 2021

INTRODUCTION

Zircon (U-Th)/He (ZHe) dating is a radiometric dating method based on the ingrowth of ^{4}He from the α decay of U, Th, and Sm. The method has some unique features, which allow it to address a wide range of geological questions on orogenesis, volcanism, landscape evolution, meteorite impact events, ore genesis, basin formation, and sediment provenance (*1*–*8*). Given the rapid diffusion of radiogenic He in zircon at high temperatures, the ZHe method is suited to low-temperature thermochronometry (*9*), recording the time-temperature evolution of zircon-bearing rocks at upper crustal levels [150° to 220°C (*10*); termed the zircon He partial retention zone (ZHePRZ)]. ZHe ages can be determined by measuring bulk He, U, and Th abundances in single zircon crystals (*9*, *11*–*13*) or by in situ laser ablation approaches in which subcrystal domains are targeted (*14*–*18*). When measured ZHe ages are coupled with a quantitative understanding of He retentivity, not only the timing of cooling but also the rate and style of this cooling through the ZHePRZ can be determined (*10*, *19*–*21*).

Although in many cases the ZHe method has provided ages and thermal histories that are reproducible, geologically reasonable, accurate, and compatible with other chronometers, a number of studies have reported overdispersed or anomalous ages (*22*–*27*) or diffusion behavior that did not follow normal Arrhenius models during step-heating experiments (*9*, *11*, *12*, *28*). Plausible explanations for this included heterogeneous distribution of parent nuclides and fragmentation of crystals (both complicating routine α-ejection correction) (*11*, *21*, *29*–*33*), radiation damage affecting He retentivity and closure temperature (*10*, *34*), and inclusions containing "excess" He (*11*, *35*, *36*). However, to date, our inability to spatially determine the He distribution in dated grains has made interpretation of complex ZHe data equivocal. Understanding the grain-scale He distribution and its relationship to the distribution of parent isotopes could provide a significantly improved understanding of these phenomena and their impact on the (U-Th)/He method.

Here, we describe a new methodology for in situ, high–spatial resolution (micrometer-scale) He analysis based on the combined application of laser ablation microsampling and noble gas mass spectrometry. For the first time, we can visualize the distribution of radiogenic He in minerals and compare it to the distribution of the key parent isotopes (U and Th). Using this approach, we construct high-resolution two-dimensional (2D) images of He abundance variations in a set of zircon crystals, which illustrate the impact of parent isotope zonation, radiation damage, and inclusions on (U-Th)/He systematics. By combining He mapping with other characterization techniques [for example, cathodoluminescence (CL) and Raman microscopy], potential issues associated with undetected fluid inclusions and heterogeneity in both the crystal lattice and the parent nuclide distribution can be better understood. Finally, we present a new procedure for thermal history reconstruction of single zircon crystals, allowing us to constrain the high-temperature history at magmatic temperatures via U-Pb geochronology and the low-temperature history within ZHePRZ via inversion of a directly measured He production-diffusion profile.

RESULTS

We have selected four zircon crystals that illustrate the salient issues arising from heterogeneous distribution of parent nuclides (I2-1, M14-4, and I2-9), intracrystalline variation in radiation damage (I2-9), and the presence of fluid inclusions (R-3) (Table 1). The crystals were extracted from Carboniferous granites from Sardinia (M14-4) and Bohemian Massif (R-3), and from a Proterozoic metagranite from India (I2-1 and I2-9) (Table 1). Representative CL and microscopic images, isotopic

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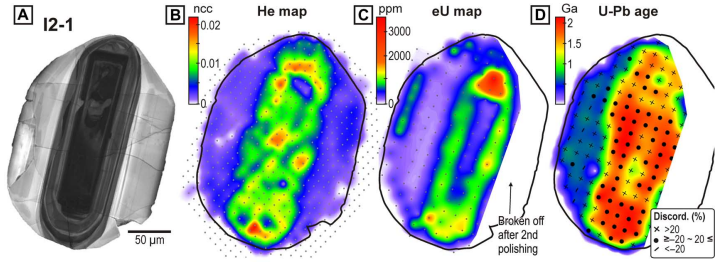
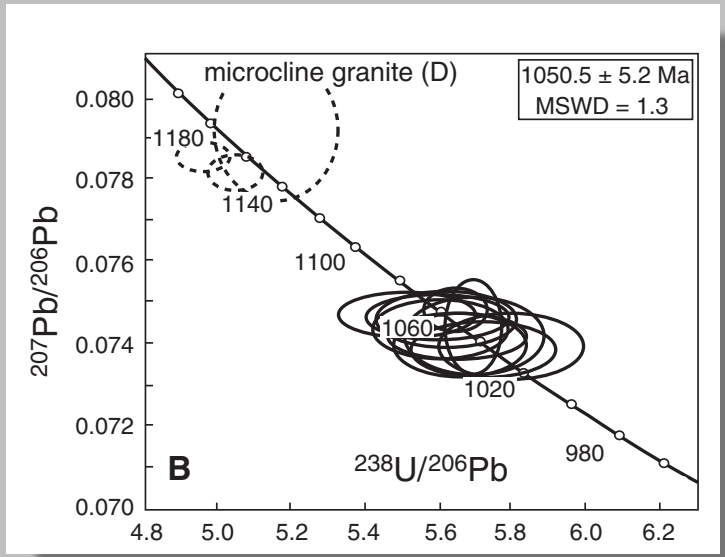


The Integration of Laser Ablation Mapping With Raman Mapping of Radiation Damage Can Be Even More Enlightening

Lyon Mountain Granite Zircons, Adirondack Mtns., NY



– Valley et al. (2011, Geosphere)

Conventional ZrnHe – 192-157 Ma

LADD

ZrnPb – 1128-495 Ma
ZrnHe – 309-101 Ma

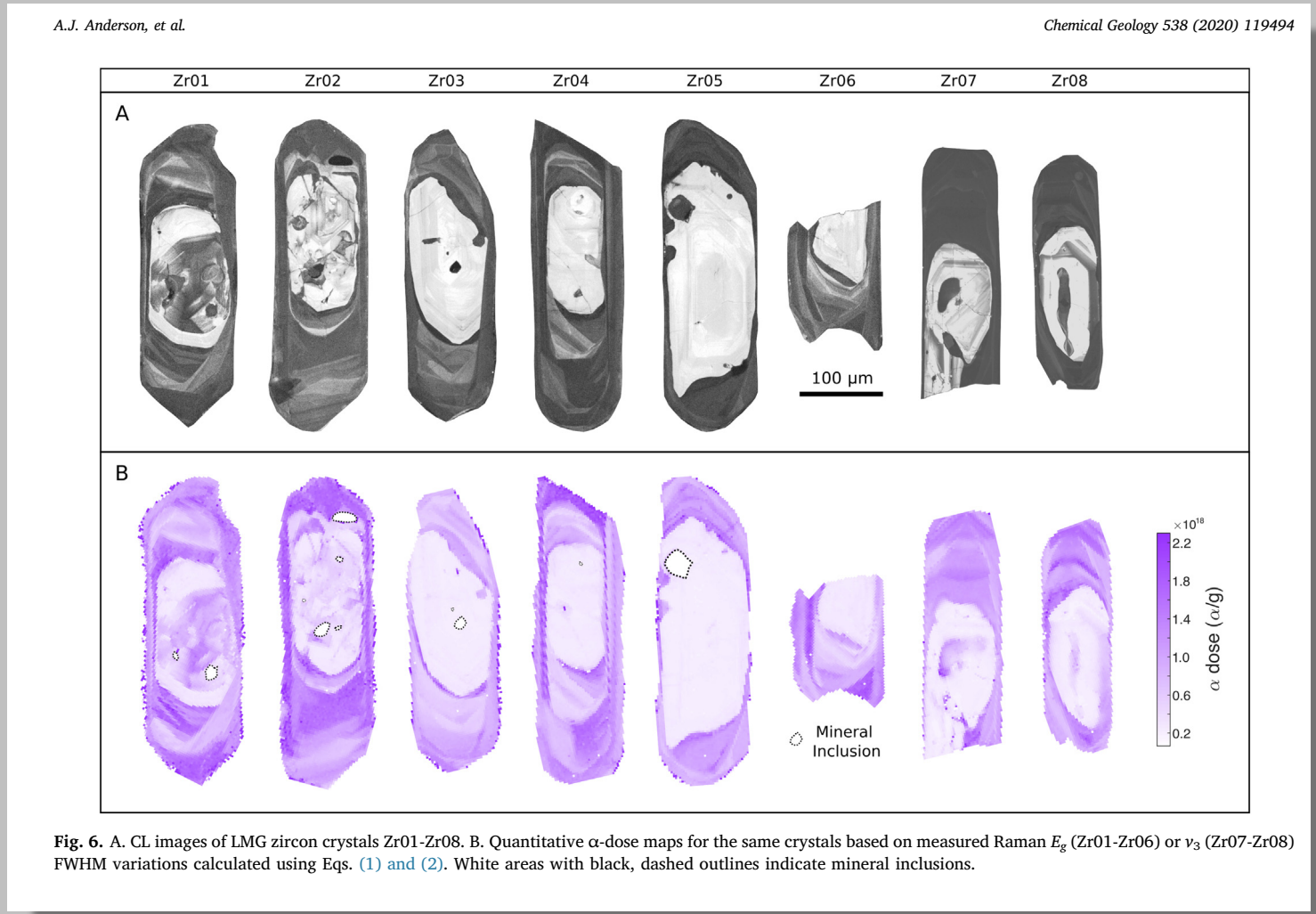
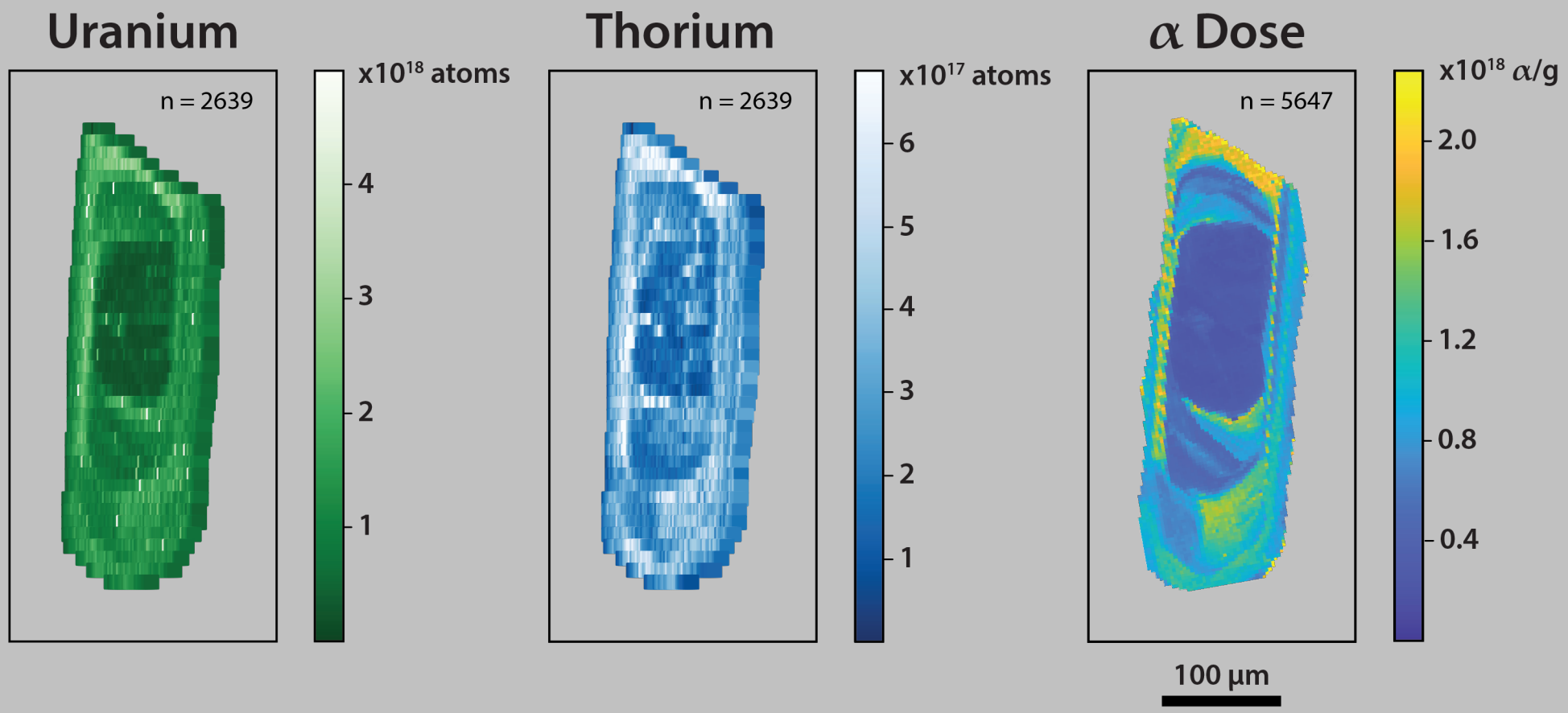
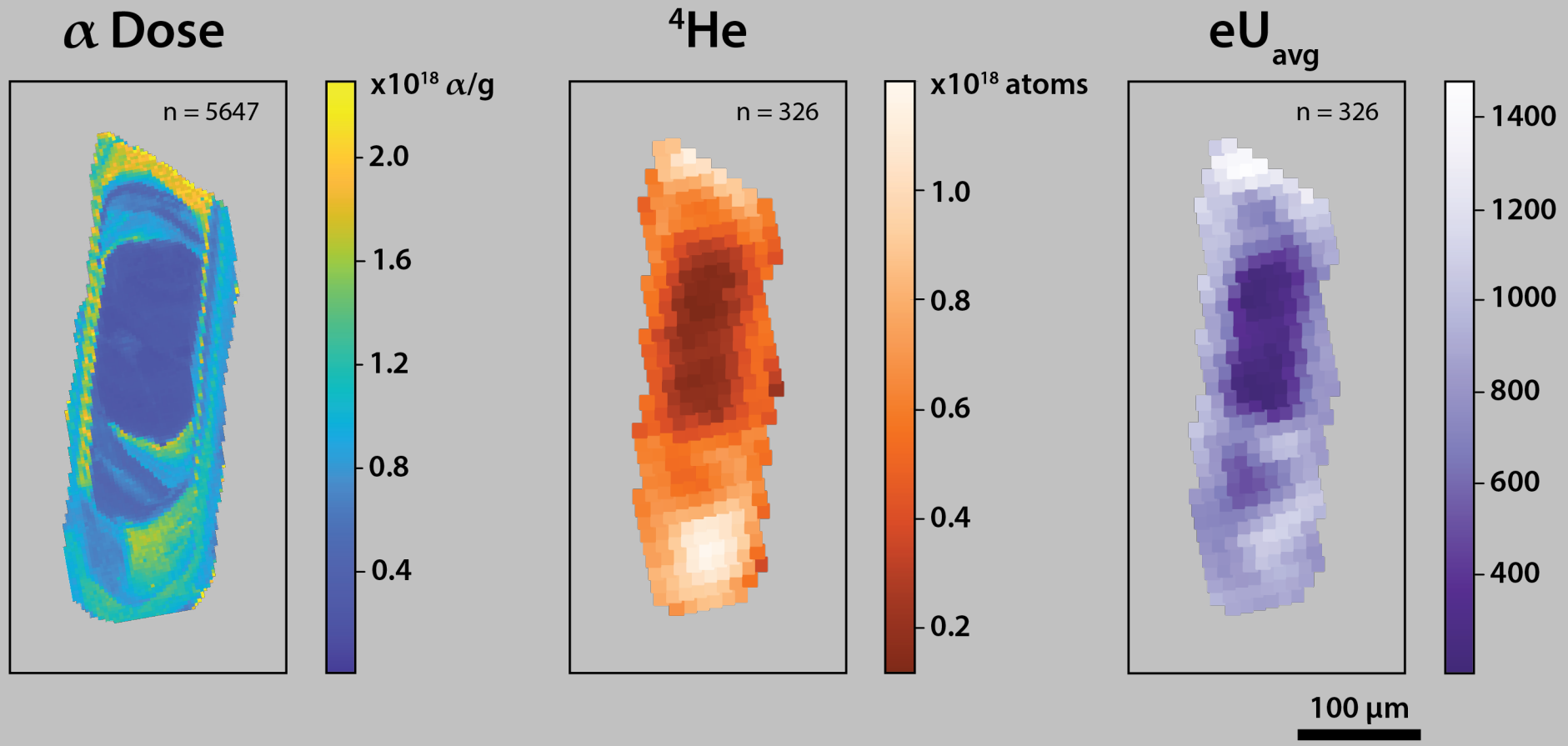


Fig. 6. A. CL images of LMG zircon crystals Zr01-Zr08. B. Quantitative α-dose maps for the same crystals based on measured Raman E_g (Zr01-Zr06) or ν_3 (Zr07-Zr08) FWHM variations calculated using Eqs. (1) and (2). White areas with black, dashed outlines indicate mineral inclusions.

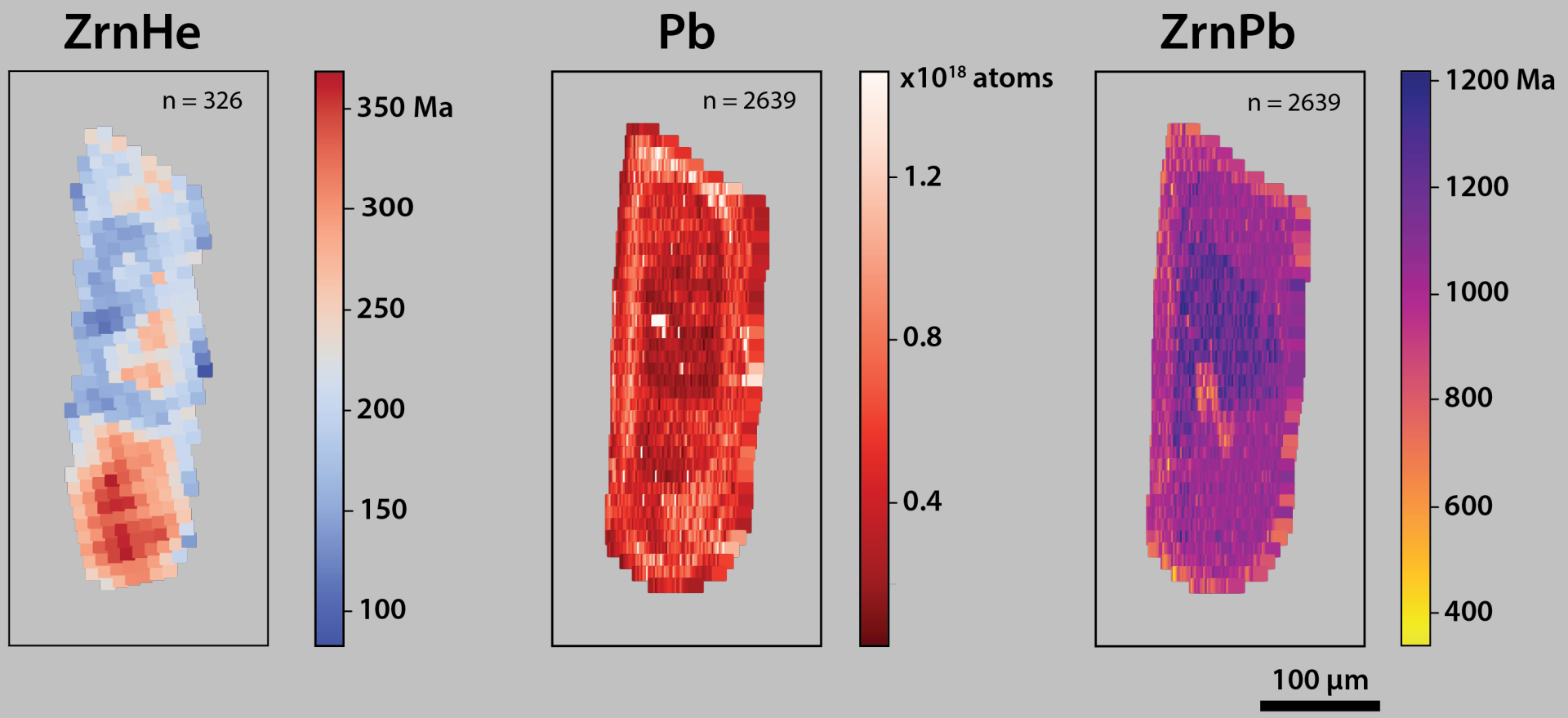
Raman and LA-ICPMS Methods Permit Rapid and Quantitative Mapping of Alpha Damage and Cation Abundances



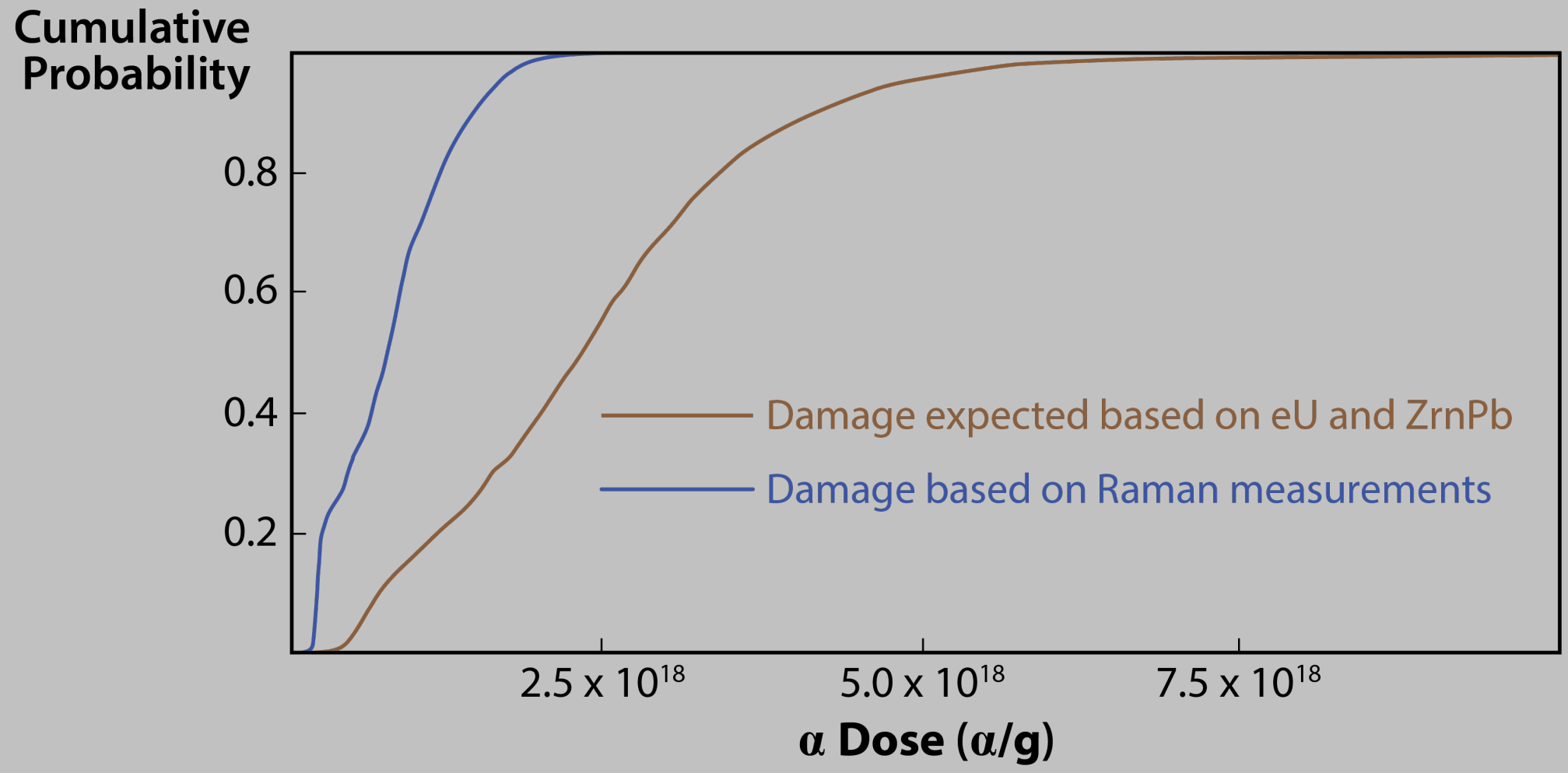
UVLAMP Mapping Reveals Helium Abundances and Intracrystalline Distributions at Somewhat Lower Spatial Resolutions



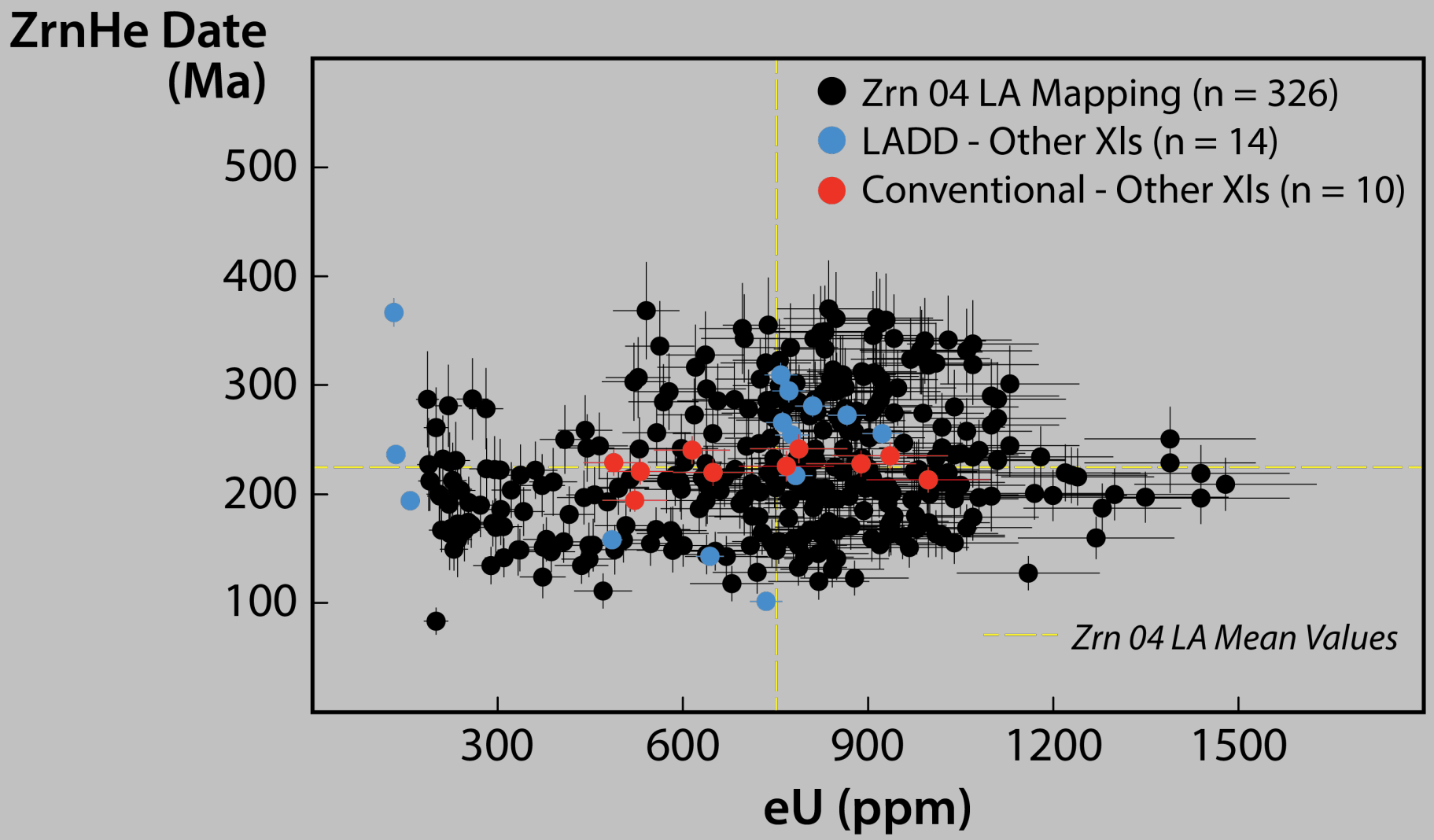
Intracrystalline U/Pb and (U-Th)/He Apparent Age Mapping is Made Possible by Combining UVLAMP and LA-ICPMS Data



Comparisons of Expected and Measured Alpha Damage Reveal the Degree of Damage Annealing



Intracrystalline (U-Th)/He Age-eU Relationships Are Enlightening



Major Points

- ✓ The UVLAMP method provides a valuable complement to conventional, single-crystal work
- ✓ UVLAMP (U-Th)/He and (U-Th)/Pb double dating is more efficient and less costly than the conventional approach
- ✓ Combined use of UVLAMP analysis and micro Raman spectroscopy allows relatively rapid, detailed mapping of He, Pb, U, Th, additional elements, and radiation damage in crystals of interest
- ✓ Integrated UVLAMP and micro Raman mapping could revolutionize our understanding of He kinetics in minerals.