Supplementary Information for "Isotope ratio analysis of individual sub-micron particles via spICP-TOFMS"

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Table S1. Instrument operating conditions.

Sample Introduction	Apparatus	Baffled cyclonic quartz spray chamber with PFA PrepFAST nebulizer
	Sample uptake	45 µL min-1
	Nebulizer gas flow (Ar)	0.8 L min-1
	Additional gas flow (Ar/He)	0.05 / 0.46 L min-1
ICP	Torch/Injector	iCAP Q Quartz torch with 2 mm quartz injector
	Sampler/Skimmer cones	iCAP Q Nickel Samples (X Series) with Skimmer (with insert)
	Sampling depth	5 mm
	Plasma power	1550 W
	Gas flow (auxillary/cooling)	0.8 / 14 L min-1
	Transport efficiency	~10-14%
CCT	CCT mass	286 V
	CCT bias	-2.68 V
	CCT gas flow (He)	6.1 mL min-1
TOF	TOF repetition rate (spectral acquisition)	83 kHz
	TOF spectral time resolution	1.2 ms
	Notch filter mass/voltage	35.6 / 2 V, 40 / 2.5 V, 16.3 / 3 V

Table S2. Isotopic abundances and sensitivities in microdroplet calibration solution. The concentrations and sensitivities in in the first and second columns of each category were from the droplet solution used for monazite samples and the galena particle sample, respectively.

Isotope	**Isotopic Abundance (%)**	**Isotopic Mass**	**Isotope Concentration (ppb)**		**Average Sensitivity (cts/g)**	
^{147}Sm	15.00	146.91	22.07	N/A	2.12E+17	N/A
^{149}Sm	13.82	148.92	20.62	N/A	2.30E+17	N/A
^{204}Pb	1.40	203.97	2.03	2.83	1.44E+17	1.56E+17
^{206}Pb	24.10	205.97	36.35	49.23	1.72E+17	2.18E+17
^{207}Pb	22.10	206.98	33.49	45.36	1.68E+17	2.18E+17
^{208}Pb	52.40	207.98	79.80	108.08	1.75E+17	2.05E+17
^{232}Th	99.98	232.04	75.48	N/A	2.42E+17	N/A
^{238}U	99.27	238.05	75.69	N/A	2.39E+17	N/A

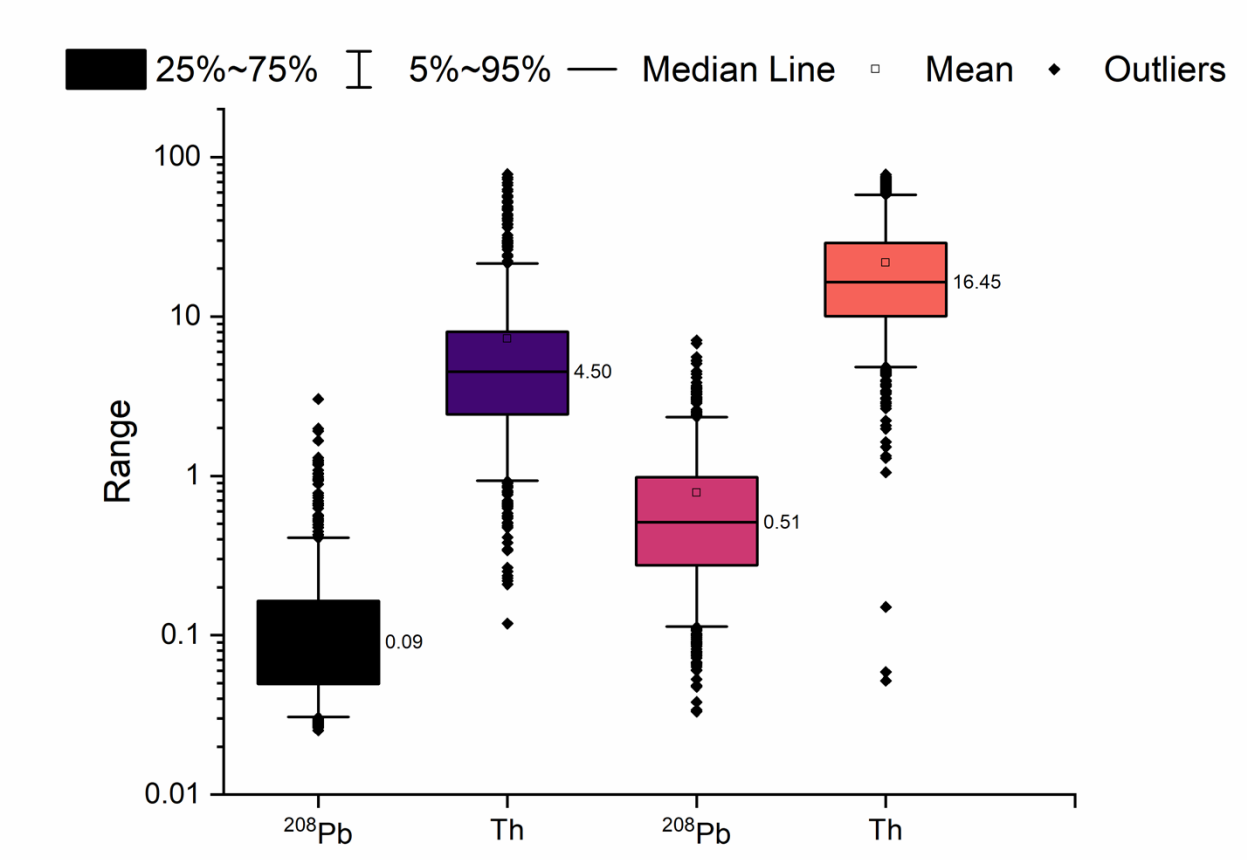
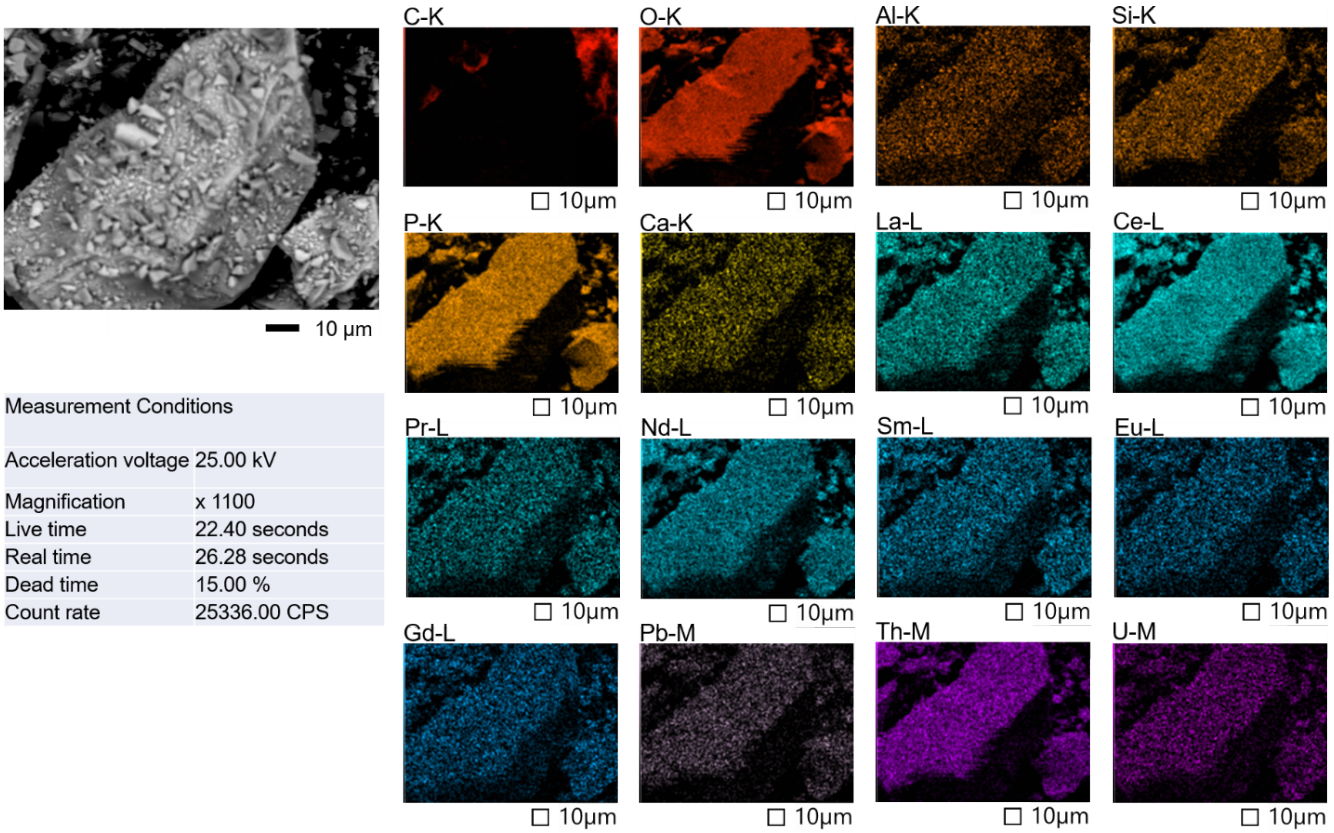
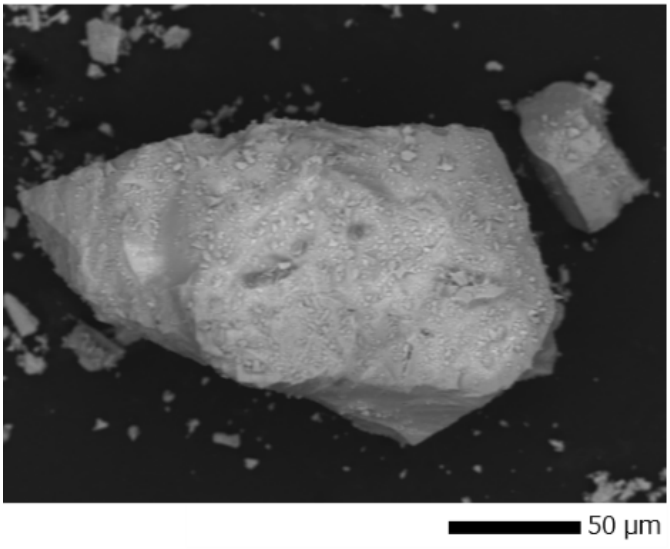


Figure S1. Mass of Th and ^{208}Pb within all particles detected without (black and purple) and with (pink and orange) ^{238}U and ^{206}Pb. The masses of particles available to radiometrically date increase if we include the U-^{206}Pb system compared to particles with just Th-^{208}Pb. Almost all the particles detected with U were also detected with Th as U is ~20 times less abundant than Th in particles. Bigger particles are needed in order to use both system for age dating.



Measurement Conditions	
Acceleration voltage	25.00 kV
Magnification	x 1100
Live time	22.40 seconds
Real time	26.28 seconds
Dead time	15.00 %
Count rate	25336.00 CPS

Figure S2. SEM-EDS analysis of monazite particles was carried out to confirm the presence of radiogenic elements (both parent and daughter isotopes), specifically Th, U, and Pb. Backscatter electron (BSE) images and energy dispersive X-Ray spectroscopy were performed on a JEOL JSM-IT200 Scanning Electron Microscopy (JEOL, Peabody, MA). Monazite powder was pressed into the double-sided adhesive carbon stub (PELCO, TedPella, CA) already mounted on an aluminum pin (Zeiss 12.7 mm mount). Images and spectra were obtained with an acceleration voltage of either 15kV or 25 kV, at a working distance of ~10 mm and magnification between 500 to 5500 x. For EDS analysis, dead times were limited to 20%. From the images, monazite particles display heterogeneity both in size and shape, and therefore there is no single particle morphology representative of the entire population. However, from the EDS, we can see that elements such as U and Pb are less likely to be detected. We chose to analyze 25 random particles at least 2 µm in diameter. At this size, we would expect to be able to detect U, Th, and Pb if present, however, U was rarely detected, even in large particles. Below is an elemental map of a single monazite grain, and shows low amounts of U and Pb detected. In the smaller particles analyzed, only 6 of the 25 particles had values of U detectable from the background.



Element	Mass%
C	42.15±0.05
O	31.24±0.08
Al	0.13±0.01
Si	0.39±0.01
P	3.49±0.02
Ca	0.08±0.01
La	2.00±0.03
Ce	7.53±0.04
Pr	1.10±0.03
Nd	4.84±0.04
Sm	1.51±0.03
Eu	0.09±0.02
Gd	0.75±0.02
Th	4.34±0.04
U	0.36±0.03
Total	100.00

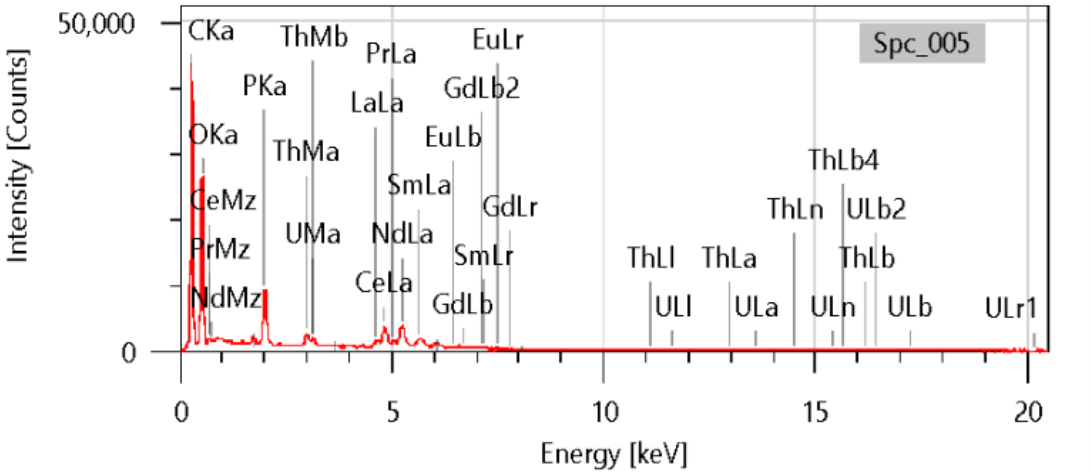


Figure S3. An SEM BSE image of a larger monazite particle where U was detectable. It is important to note differences in what is being analyzed; EDS analysis is more of a "bulk" technique as signal is not confined to just the area selected, and detection can depend on the material composition and morphology, especially for quantitative results. In spICP-TOFMS, signal is dependent on the particle and the background, and detection criteria of elements within a particle are determined via a signal-to-background ratio (count threshold) based on the intensity of the signal and the user-set likelihood of a false positive. EDS signal to noise ratio depends on the probe current (and diameter) and the length (time) of analysis, which affects the count rate and detector dead-time. Changing these parameters increases or decreases all signal which can allow for better resolution of peaks from background.

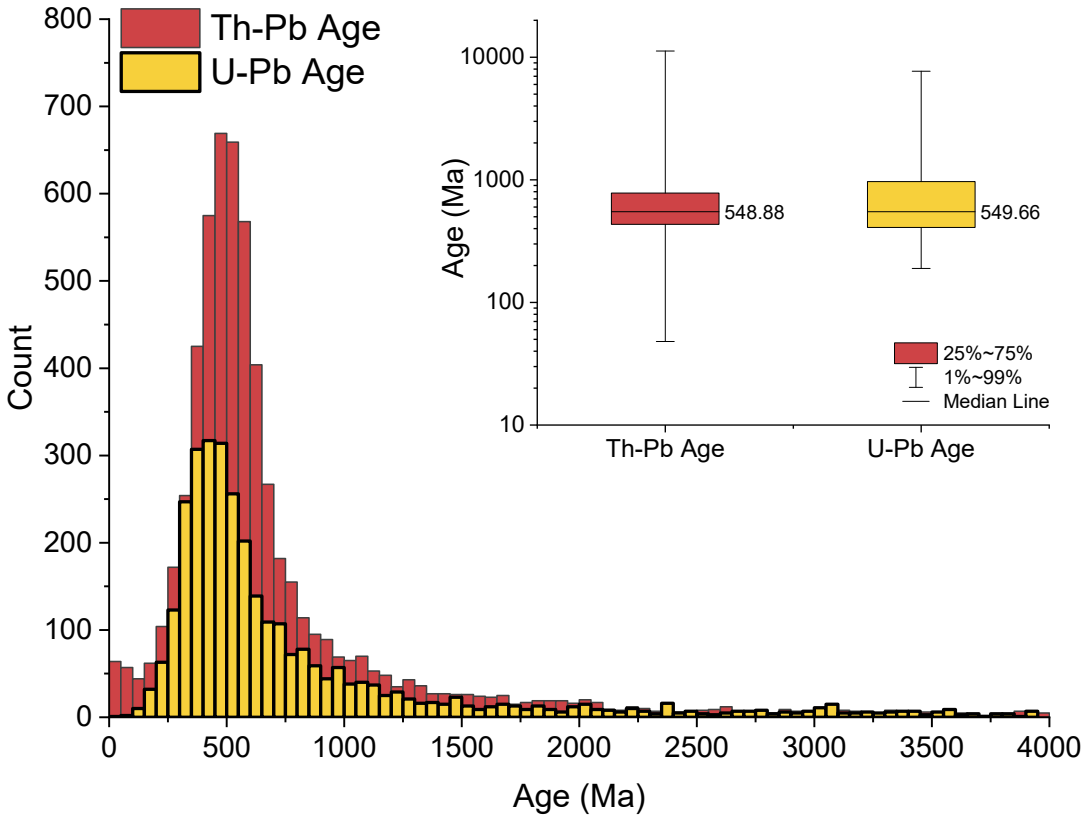


Figure S4. Histogram of the ages obtained. Inset graph shows box and whisker plots with the median labeled for both the Th-Pb determined ages (red) and the U-Pb determined ages (yellow).