

Supplementary information (S1) Equation for data treatment

Brama: a new freeware python software for reduction and imaging of LA-ICP-MS data from U-Pb scans

Guoqi Liu^{*a}, Thomas Ulrich^b, Fei Xia^a, Yang Xiao^c

I . Method for simulating data

The isotopic compositions of radioactive and common Pb can be obtained according to the Stacey-Kramers model of crustal Pb evolution.¹ Using the subscripts “m”, “r” and “c” for measured, radioactive and common Pb, respectively, we can write:

$$\left(\frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}}\right)_r = (e^{\lambda_{238}t} - 1) * 9.735 \quad (1)$$

$$\left(\frac{{}^{207}\text{Pb}}{{}^{204}\text{Pb}}\right)_r = (e^{\lambda_{235}t} - 1) * 9.735 * \frac{1}{137.88} \quad (2)$$

$$\left(\frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}}\right)_c = 18.700 - (e^{\lambda_{238}t} - 1) * 9.735 \quad (3)$$

$$\left(\frac{{}^{207}\text{Pb}}{{}^{204}\text{Pb}}\right)_c = 15.628 - \left(\frac{{}^{207}\text{Pb}}{{}^{204}\text{Pb}}\right)_r \quad (4)$$

$$\left(\frac{{}^{207}\text{Pb}}{{}^{206}\text{Pb}}\right)_r = \frac{1}{137.88} * \left(\frac{e^{\lambda_{235}t} - 1}{e^{\lambda_{238}t} - 1}\right) \quad (5)$$

Where λ_{235} and λ_{238} are the decay constants of ${}^{235}\text{U}$, ${}^{238}\text{U}$, respectively, and t is the time elapsed for the mineral since U-Pb isotope closure. When using f_{206} to denote the proportion of common ${}^{206}\text{Pb}$ of total measured ${}^{206}\text{Pb}$, the measured U-Pb isotopes can be expressed as functions as follows:

$$\left(\frac{{}^{207}\text{Pb}}{{}^{206}\text{Pb}}\right)_m = \left(\frac{{}^{207}\text{Pb}}{{}^{206}\text{Pb}}\right)_r + \left(\left(\frac{{}^{207}\text{Pb}}{{}^{204}\text{Pb}}\right)_c - \left(\frac{{}^{207}\text{Pb}}{{}^{204}\text{Pb}}\right)_r \right) * f_{206} \quad (6)$$

$$\left(\frac{{}^{238}\text{U}}{{}^{206}\text{Pb}}\right)_m = \left(\frac{1}{e^{\lambda_{238}t} - 1}\right) * (1 - f_{206}) \quad (7)$$

Denoting the measured average count intensity of ${}^{206}\text{Pb}$ by ${}^{206}\text{Pb}_m$, the average count intensity of ${}^{207}\text{Pb}$ and ${}^{238}\text{U}$ can be expressed as follows:

$$^{207}\text{Pb}_{\text{cps}} = ^{206}\text{Pb}_{\text{cps}} * \left(\frac{^{207}\text{Pb}}{^{206}\text{Pb}} \right)_m \quad (8)$$

$$^{238}\text{U}_{\text{cps}} = ^{206}\text{Pb}_{\text{cps}} * \left(\frac{^{238}\text{U}}{^{206}\text{Pb}} \right)_m \quad (9)$$

Equations (6) ~ (9) are functions of t , f_{206} and $^{206}\text{Pb}_m$, thus we can use them for U-Pb isotope simulations.

According to the long-term laboratory signal error monitoring of reference materials, different counts correspond to errors between 2% and 23% (Table S1).

Table S1 Daily signal monitoring of NIST glass and calcite standards under line scan and point analysis

Data/Materials	Error				
	NIST 614	AHX	WC	LD	K492
8/1/2022 Line scan	2%	13%	23%	21%	
8/13/2022 Line scan	2%	12%	13%	21%	
9/15/2022 Points	7%	17%	10%		10%

II. Isotope calculation

Quadrupole ICP-MS instruments measure mass numbers sequentially (Fig. S1), therefore outlier processing, baseline correction, and interpolation calculations are required before isotope calculations can be performed.

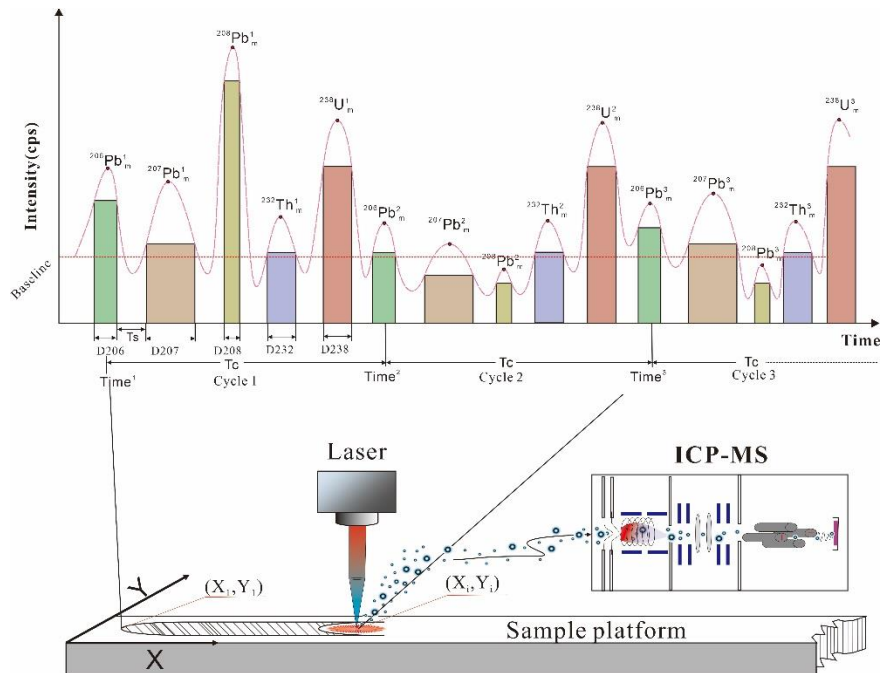


Fig. S1 Schematic diagram of the detector time versus signal intensity for a quadrupole mass spectrometer. The height of the color bar above indicates the signal intensity (cps) of different mass (^{206}Pb , ^{207}Pb , ^{208}Pb , ^{232}Th and ^{238}U) repetition scans, and the width indicates the dwell time of different masses.

Denoting $^{206}\text{Pb}_m^i$, $^{207}\text{Pb}_m^i$ and $^{238}\text{U}_m^i$ are average count intensity (cps) corresponding to the cycle i measurement of ^{206}Pb , ^{207}Pb and ^{238}U measured by the ICP-MS instrument. Time^{b0} and Time^{b1} denote the start (row $b0$) and end (row $b1$) of the background measurement, respectively. $D206$, $D207$ and $D238$ are the detector dwell times of ^{206}Pb , ^{207}Pb and ^{238}U (Fig. S1). $^{206}\text{Pb}_{int}^i$, $^{207}\text{Pb}_{int}^i$ and $^{238}\text{U}_{int}^i$ are counts of cycle i sampling measurement of ^{206}Pb , ^{207}Pb and ^{238}U . Baseline correction can be calculated using the following three steps.

First, as shown in Fig. S1, assuming that N mass numbers are chosen, the detector scan time gap T_s and the cycle time interval T_C are calculated based on the detector time and the background analysis time using the following equations:

$$T_C = \frac{(\text{Time}^{b1} - \text{Time}^{b0})}{(b1 - b0)} \quad (10)$$

$$T_s = \frac{T_C - (D206 + D207 + D238 + \dots)}{N} \quad (11)$$

Next, we define $B206$, $B207$ and $B238$ as the background counts of ^{206}Pb , ^{207}Pb and ^{238}U , respectively. They can be calculated based on the average counts intensity (cps) of the ^{206}Pb , ^{207}Pb and ^{238}U background measurements:

$$B206 = D206 * T_C * \sum_{b0}^{b1} ^{206}\text{Pb}_{int} \quad (12)$$

$$B207 = D207 * T_C * \sum_{b0}^{b1} ^{207}\text{Pb}_{int} \quad (13)$$

$$B238 = D238 * T_C * \sum_{b0}^{b1} ^{238}\text{Pb}_{int} \quad (14)$$

Finally, the background is subtracted for each sampling datum as:

$$^{206}\text{Pb}_{int}^i = \text{D206} * ^{206}\text{Pb}_m^i - \text{B206} \quad (15)$$

$$^{207}\text{Pb}_{int}^i = \text{D207} * ^{207}\text{Pb}_m^i - \text{B207} \quad (16)$$

$$^{238}\text{U}_{int}^i = \text{D238} * ^{238}\text{U}_m^i - \text{B238} \quad (17)$$

Outlier processing can be performed by rejecting data with abnormally high or low counts or replacing the outliers with interpolated data. The first method can be used to filter the data by setting the lowest U, Pb counts or/and U/Pb ratio. As shown in Fig. S1, when the measured U counts are below the instrument's detection limit, the interpolation calculation for the outlier data in each signal datum in the original data file can be written as:

$$^{238}\text{U}_{intr} = ^{238}\text{U}_{int}^{i-1} + \left(^{238}\text{U}_{int}^i - ^{238}\text{U}_{int}^{i-1} \right) * \left\{ \frac{\text{Time}^i - \text{Time}^{i-1} - (T_C - 0.5 * \text{D238} - 0.5 * \text{D206} - T_S)}{\text{Time}^i - \text{Time}^{i-1}} \right\} \quad (18)$$

$$^{207}\text{Pb}_{intr} = ^{207}\text{Pb}_{int}^{i-1} + \left(^{207}\text{Pb}_{int}^i - ^{207}\text{Pb}_{int}^{i-1} \right) * \left\{ \frac{\text{Time}^i - \text{Time}^{i-1} - (0.5 * \text{D207} + 0.5 * \text{D206} + T_S)}{\text{Time}^i - \text{Time}^{i-1}} \right\} \quad (19)$$

$$^{206}\text{Pb}_{intr} = ^{206}\text{Pb}_{int}^{i-1} \quad (20)$$

Where as $^{206}\text{Pb}_{intr}$, $^{207}\text{Pb}_{intr}$ and $^{238}\text{U}_{intr}$ are the interpolated value for ^{206}Pb , ^{207}Pb and ^{238}U .

The bias correction factors of $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ compared to the reference values of the standards are denoted by Corr8/6 and Corr7/6. The subscripts “Std-tr” and “Std-m” are used for true and measured values of the standard, respectively. If the standard does not contain common Pb, the standard bias correction can be written as:

$$\text{Corr7/6} = \frac{\left(\frac{^{207}\text{Pb}}{^{206}\text{Pb}} \right)_{\text{Std-m}}}{\left(\frac{^{207}\text{Pb}}{^{206}\text{Pb}} \right)_{\text{Std-tr}}} \quad (21)$$

$$\text{Corr8/6} = \frac{\left(\frac{^{206}\text{Pb}}{^{238}\text{U}} \right)_{\text{Std-m}}}{\left(\frac{^{206}\text{Pb}}{^{238}\text{U}} \right)_{\text{Std-tr}}} \quad (22)$$

If the standard contains common lead, correcting for it is done with the ^{207}Pb method.² Afterwards the standard bias fractionation factor is calculated using equation (21) ~ (22). To facilitate the calculation, the true values of the standards were calculated using the S&K method.¹

$\frac{^{238}\text{U}}{^{206}\text{Pb}}$ and $\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$ are the radioactive U-Pb isotopic composition of the minerals, and they can be calculated using the following equations:

$$\frac{^{238}\text{U}}{^{206}\text{Pb}} = \text{Corr8}/6 * \frac{D206}{D238} * \frac{^{238}\text{U}_{intr}}{^{206}\text{Pb}_{intr}} \quad (23)$$

$$\frac{^{207}\text{Pb}}{^{206}\text{Pb}} = \text{Corr7}/6 * \frac{D207}{D206} * \frac{^{207}\text{Pb}_{intr}}{^{206}\text{Pb}_{intr}} \quad (24)$$

Denoting the absolute errors of $^{206}\text{Pb}_{int}$, $^{207}\text{Pb}_{int}$ and $^{238}\text{U}_{int}$ by $\Delta 206$, $\Delta 207$ and $\Delta 238$, they are given by:

$$\Delta 206 = \sqrt{(^{206}\text{Pb}_{int} + 2 * B206)} \quad (25)$$

$$\Delta 207 = \sqrt{(^{207}\text{Pb}_{int} + 2 * B207)} \quad (26)$$

$$\Delta 238 = \sqrt{(^{238}\text{U}_{int} + 2 * B238)} \quad (27)$$

Denoting the relative percentage errors of $\frac{^{238}\text{U}}{^{206}\text{Pb}}$ and $\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$ by δ_{86} and δ_{76} , they can be calculated by the following equation:

$$\delta_{86} = 100 * \sqrt{\left(\frac{\Delta 206}{^{206}\text{Pb}_{int}}\right)^2 + \left(\frac{\Delta 238}{^{238}\text{U}_{int}}\right)^2} \quad (28)$$

$$\delta_{76} = 100 * \sqrt{\left(\frac{\Delta 207}{^{207}\text{Pb}_{int}}\right)^2 + \left(\frac{\Delta 206}{^{206}\text{Pb}_{int}}\right)^2} \quad (29)$$

III. Figures of point mode and line scan mode simulation sampling

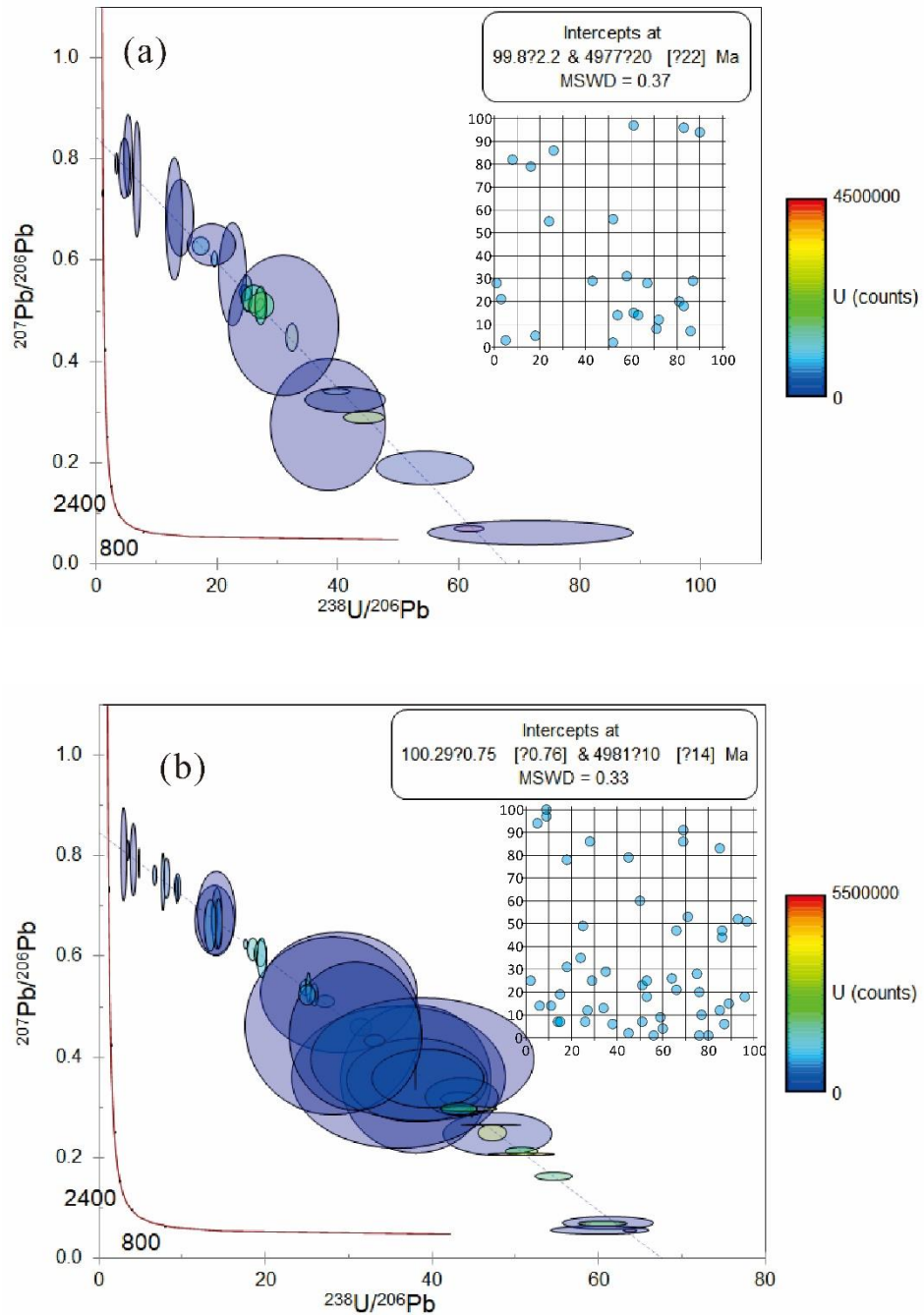
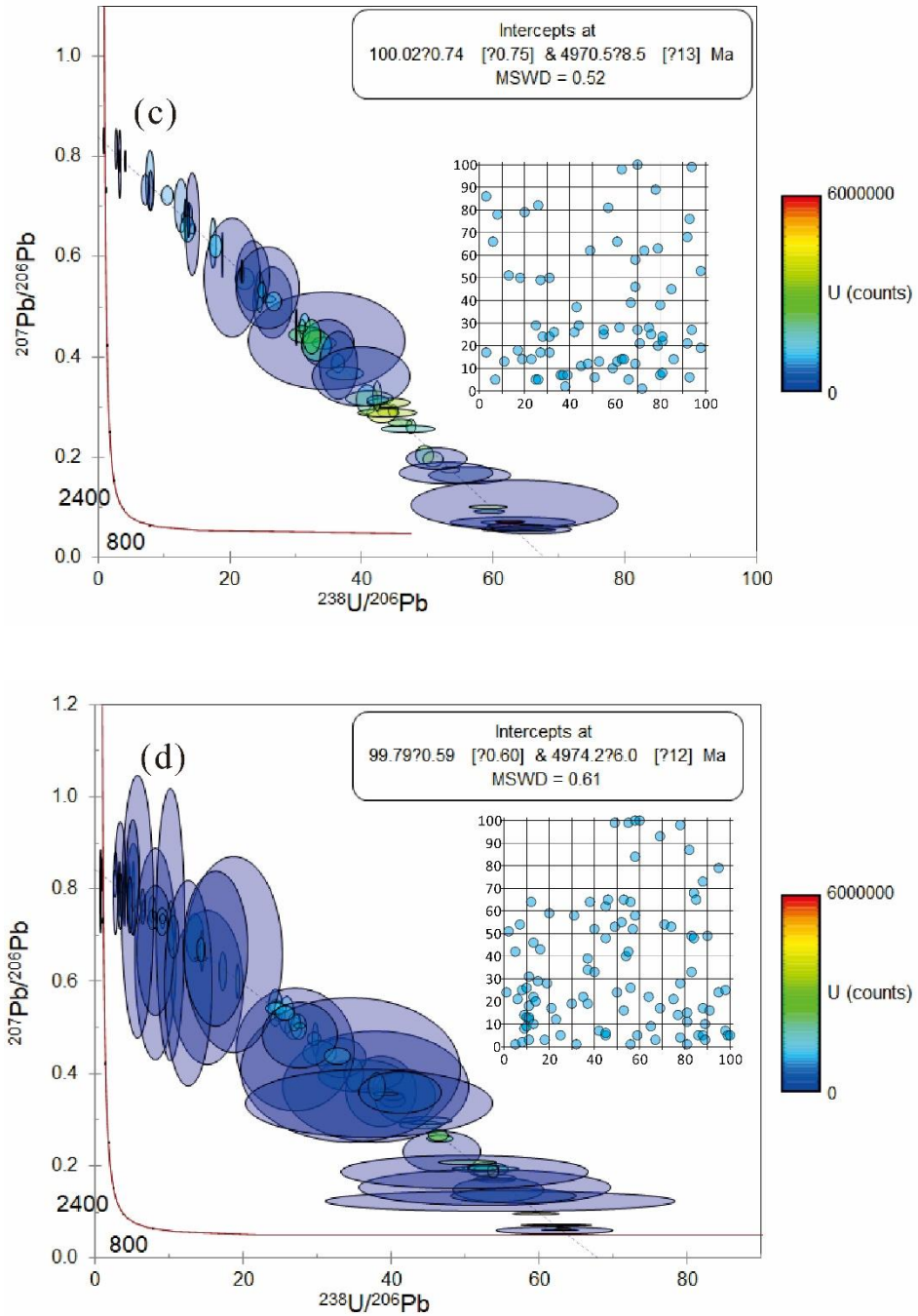
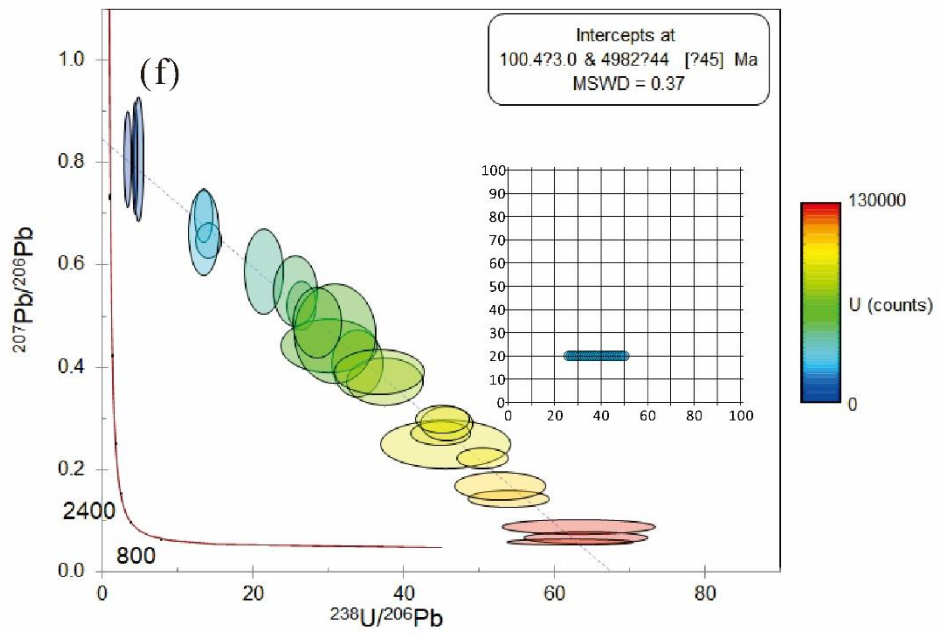
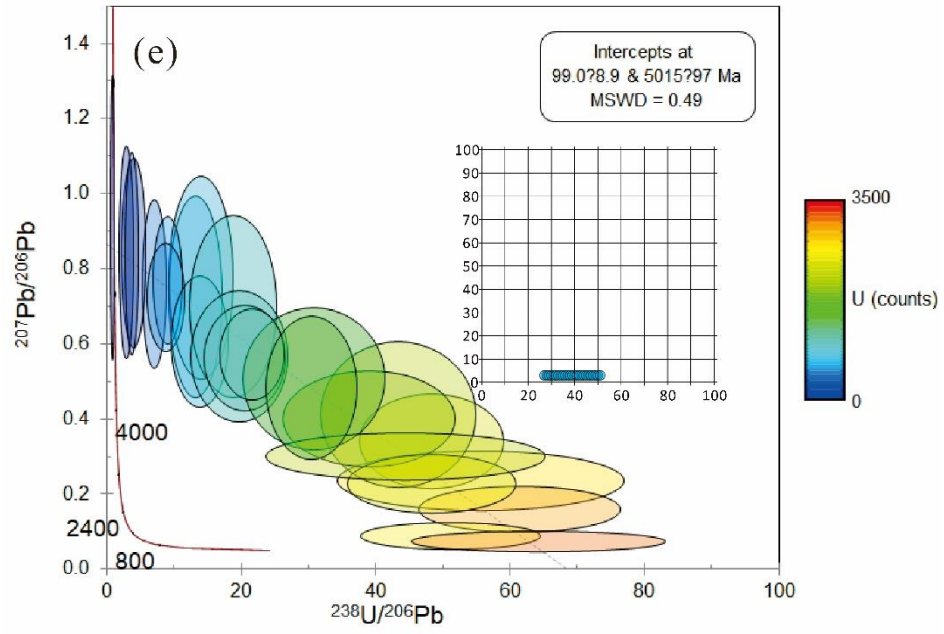


Fig. S2 Tera-Wasserburg diagrams demonstrating the effect of "analysis" error and "sampling" method on the age results. The blue transparent circles in the 100×100 grid are the locations of the "analysis" points (error of 25% for 0~10 rows, 10% for 10~30 rows, and 3% for 30~100 rows). (a ~ d)

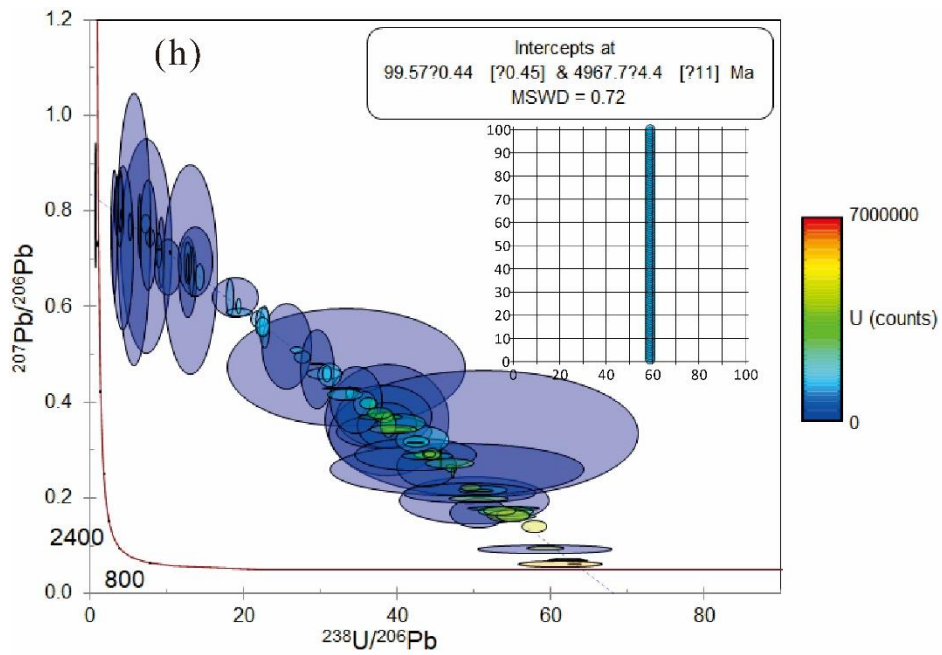
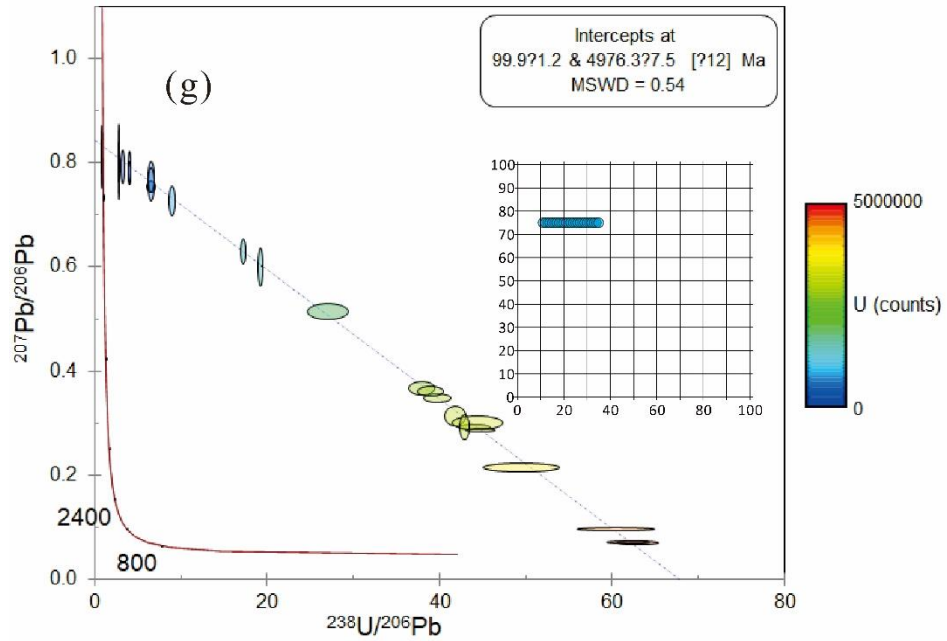
In point analysis, a different number of randomly sampled individual data are selected. (e ~ i) For the line scan sampling, different numbers and locations of data are selected.



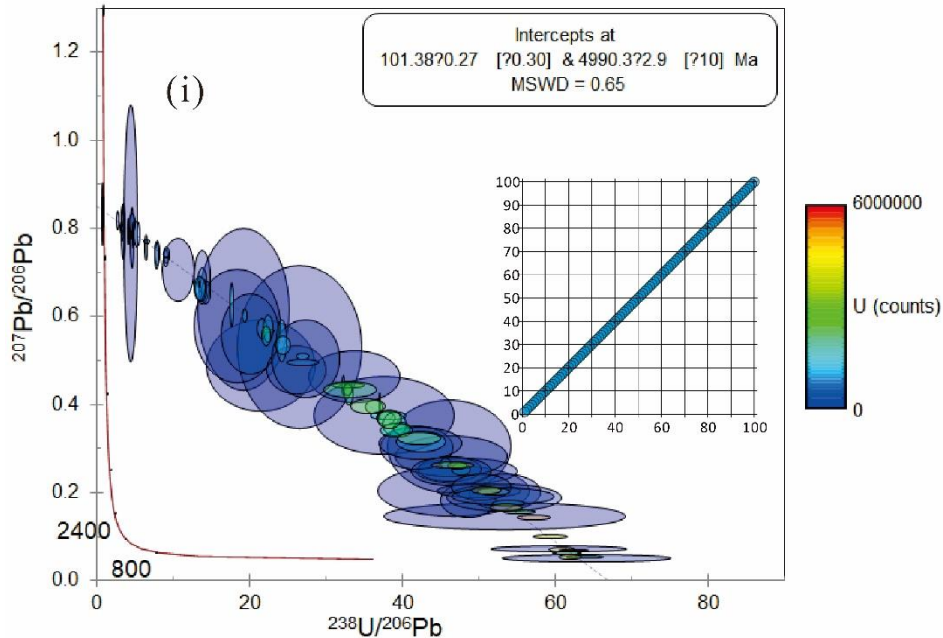
(Fig. S2 continued)



(Fig. S2 continued)



(Fig. S2 continued)



(Fig. S2 continued)

IV. Testing of simulated data

These data are derived from an age of 100 Ma, mixed with different proportions of common Pb and with analytical errors according to the U content. The data with $U < 5$ cps (counts per second) were filtered, and 9633 data were obtained for age regression calculation. Bayesian regression yielded an age of 100.3 ± 0.75 Ma ($N=9319$, $MSWD=0.01$) and a common $^{207}\text{Pb}/^{206}\text{Pb}$ ratios of 0.8388 ± 0.0072 (Fig. S3 a, b). The Tera-Wasserburg and Wetherill regression give similar results (Fig. S3 c, d).

To validate Brama in dealing with U-Pb elements and age-mapping applications, we simulated 100 rows \times 100 columns of common Pb-free U-Pb isotope data. The settings of ^{206}Pb , ^{207}Pb and ^{238}U initial values (cps) in the simulation program are shown in Fig. S4 a. The error weights were set according to the counts and the set values were randomly selected. The simulated scan lines as well as the age distribution model are shown in Fig. 1-23b. The simulation data were batch processed, and the results of ^{206}Pb , ^{207}Pb and ^{238}U elements and age distribution mapping are shown in Fig. S4 c, d, e, f. The results of the simulated data processed by Brama are consistent with the model of simulation.

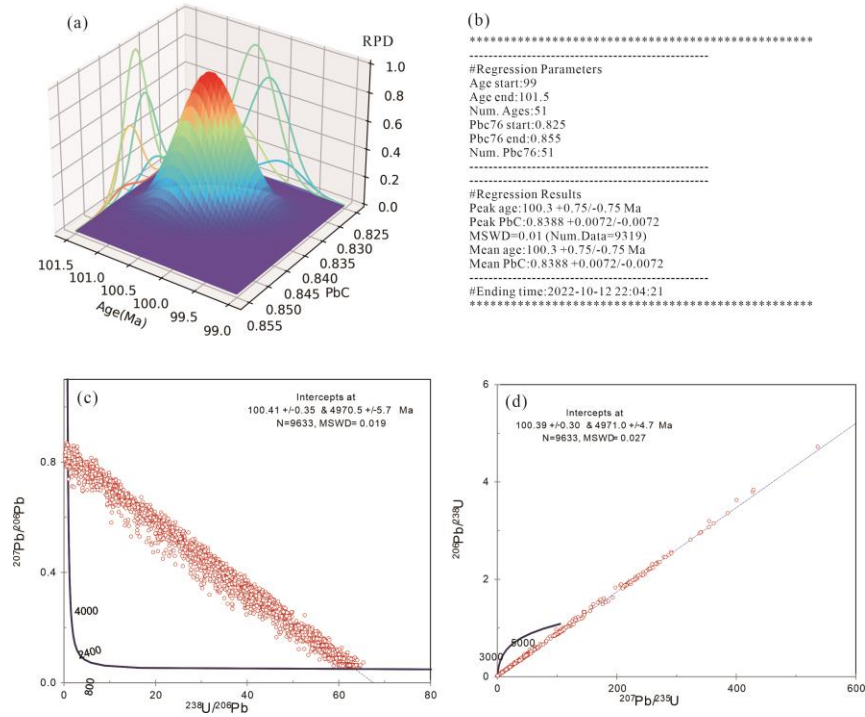


Fig. S3 U-Pb isotopic ages were calculated by simulating 100 Ma and mixed with different common Pb minerals. (a) Plot of the relative probability density of age and common Pb using Bayesian regression method.³ (b) Log file of Bayesian regression results. Results are shown for stimulation data using Tera-Wasserburg (c) and Wetherill (d) diagrams.

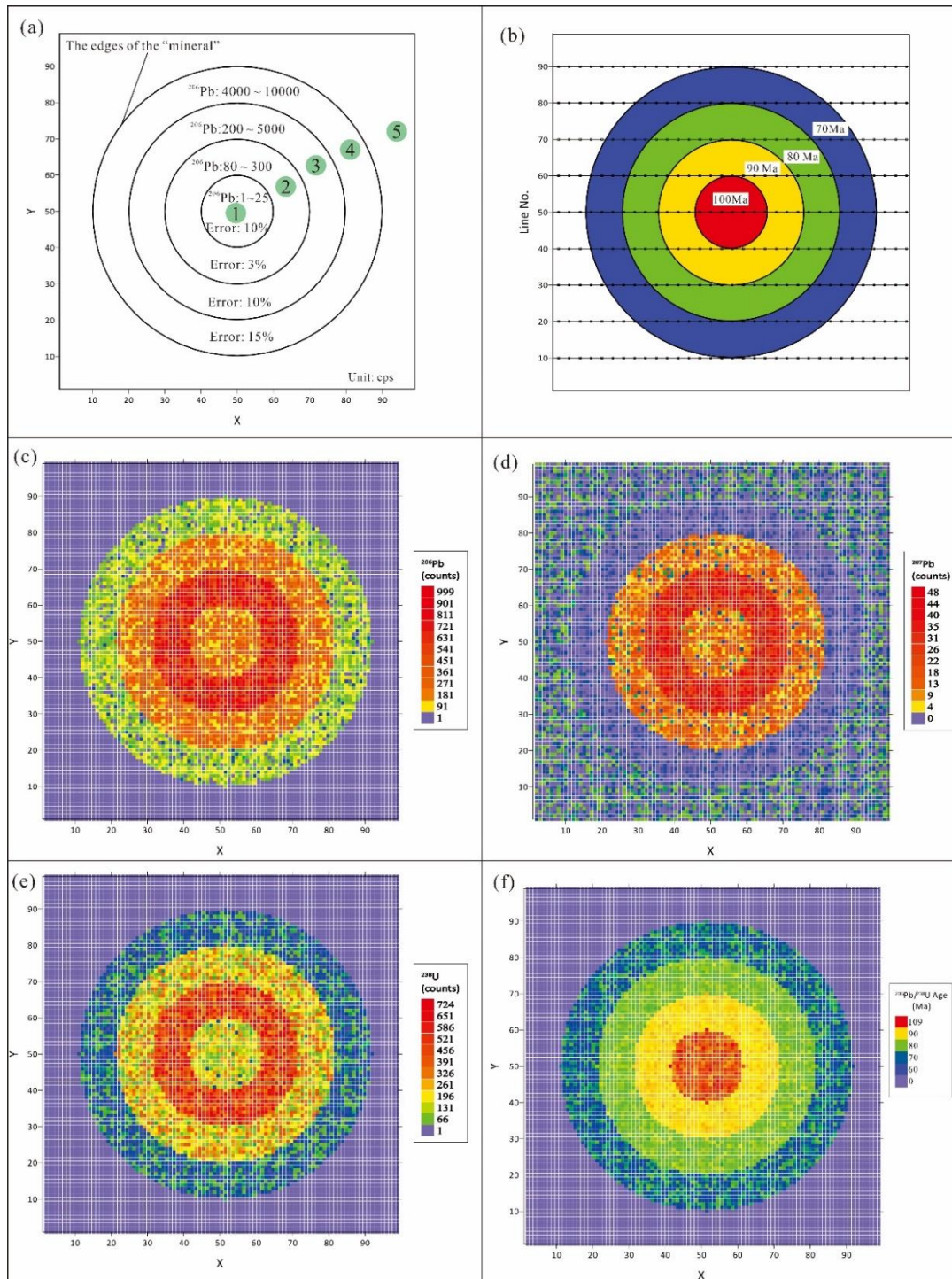


Fig. S4 Schematic of the simulated data structure and mapping of elements and ages derived from Brama. (a) Simulated Counting, error and zoning settings for 100×100 data. (b) Age distribution and line scan arrangements for simulated data. Mapping of ^{206}Pb (c), ^{207}Pb (d), ^{238}U (e) and $^{206}\text{Pb}/^{238}\text{U}$ ages for simulated data using Brama processing.

Reference

1. J. t. Stacey and J. Kramers, *Earth. Planet. Sc. Lett.*, 1975, **26**, 207-221.
2. D. M. Chew, J. A. Petrus and B. S. Kamber, *Chem. Geol.*, 2014, **363**, 185-199.
3. D. W. Davis and H. Rochín-Bañaga, *Chem. Geol.*, 2021, **582**, 120454.