Supplementary information S2 (user manual)

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

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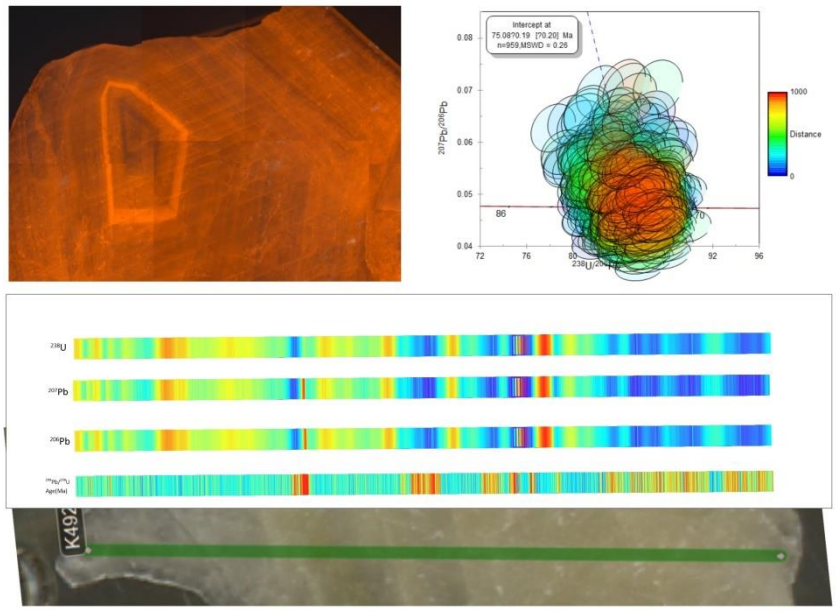
Bayesian Regression and Age Mapping Application for LA-ICPMS U-Pb Dating Data

User Manual of Brama v2.0



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I. Software operation procedures

1.1 Installation

Windows users can also download and run the packaged exe file directly.

Download **Brama2.0.exe:**

http://pan.ecut.edu.cn:80/link/F2F1BCCC219B83D15AB0756CA9B3234D

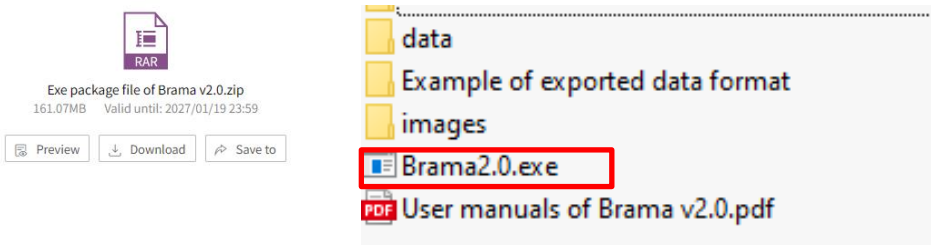


Fig. 1-1 Exe package files available for windows users.

The following steps 1.1.1-1.1.5 is run before the Brama source code runs for the first time.

1.1.1 Install Python 3.9

Python 3.9 is necessary to run the code. Download from https://www.python.org/downloads/ and follow the installation guide (Fig.1-2).

Fig. 1-2 Install Python 3.9.

1.1.2 Download Brama.

Download or clone this repository: https://github.com/sndjgm/Brama.

1.1.3 Open terminal/cmd and navigate to the Brama folder.

Open terminal/cmd and navigate to the Brama folder (Fig. 1-3).

- cd path/to/folder/ Brama

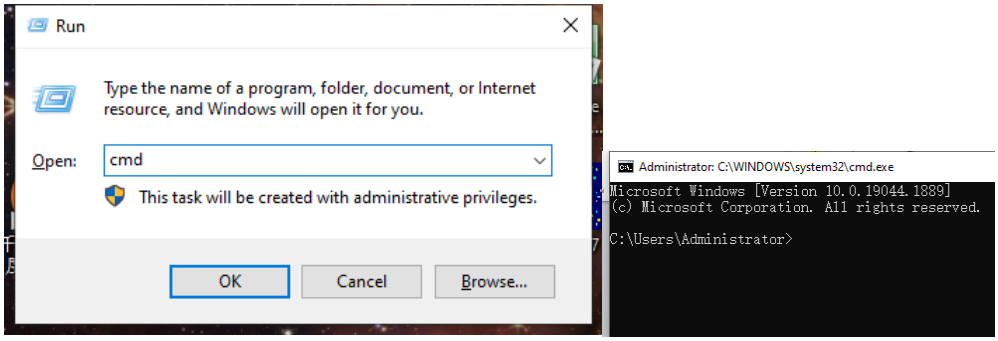


Fig. 1-3 Open terminal/cmd and navigate to the Brama folder.

1.1.4 Install python libraries required for Brama.

- pip install -r requirements.txt

  Required modules: PyQt5, numpy, pandas, xlwt, xlrd, matplotlib, scipy, xlutils, statistics, logging.

1.1.5 Run Brama from python.

- python Brama.py

If everything is already installed, follow only step 1.1.5.

1.2 Interface & Functionality

The main interface and functional partitions of the program are shown in Fig.1-4 after starting.

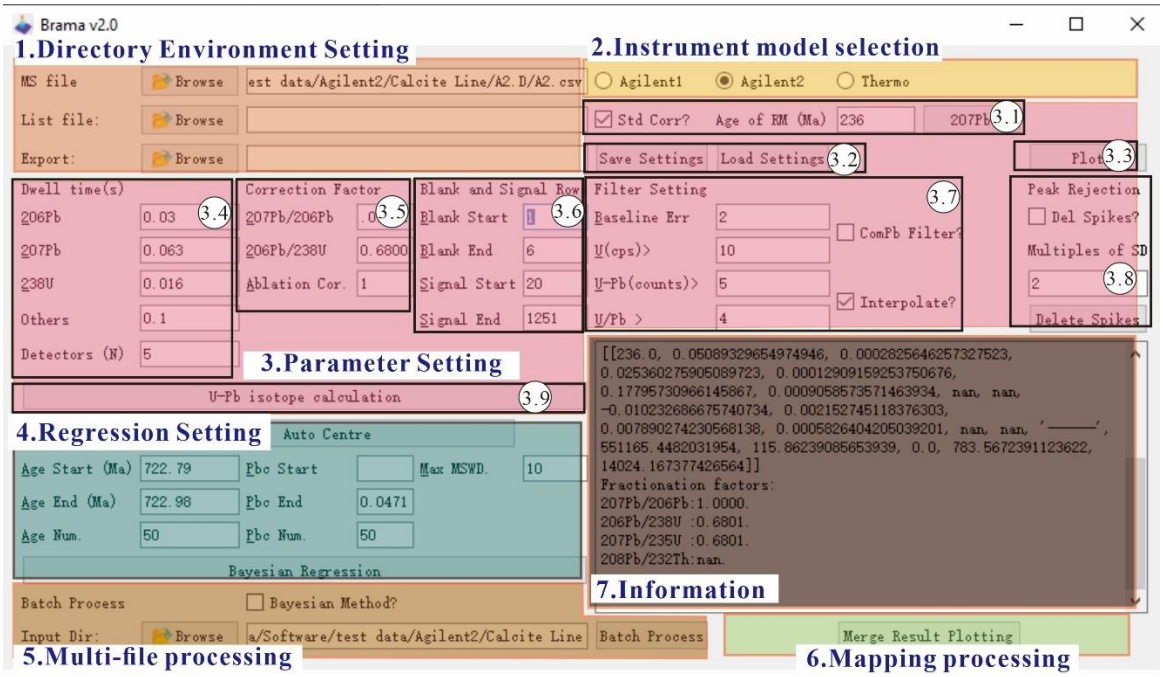


Fig. 1-4 The main interface of Brama and the division of functional areas

The software is divided into 7 functional areas. The main functional areas are

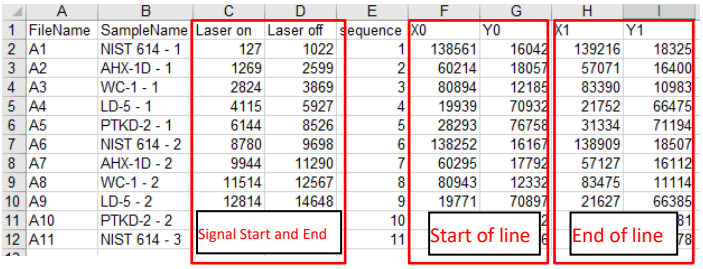
outlined as follows.

1.2.1 Directory environment setting:

set the path of mass spectrometry file, List file and output result directory.

Ms file: Select the raw MS data as CPS from the mass spectrometer output (CSV) file. The data columns for “Time(s)”, “207Pb”, “206 Pb” and “238U” must be included.

List file: A "*.xls" laser log file containing “File Name”, “Sample Name”, “Laser on”, “Laser off”, “sequence”, location coordinates “X0”, “Y0”, “X1” and “Y1” (Fig.1-5).



	A	B	C	D	E	F	G	H	I
1	FileName	SampleName	Laser on	Laser off	sequence	X0	Y0	X1	Y1
2	A1	NIST 614 - 1	127	1022	1	138561	16042	139216	18325
3	A2	AHX-1D - 1	1269	2599	2	60214	18057	57071	16400
4	A3	WC-1 - 1	2824	3869	3	80894	12185	83390	10983
5	A4	LD-5 - 1	4115	5927	4	19939	70932	21752	66475
6	A5	PTKD-2 - 1	6144	8526	5	28293	76758	31334	71194
7	A6	NIST 614 - 2	8780	9698	6	138252	16167	138909	18507
8	A7	AHX-1D - 2	9944	11290	7	60295	17792	57127	16112
9	A8	WC-1 - 2	11514	12567	8	80943	12332	83475	11114
10	A9	LD-5 - 2	12814	14648	9	19771	70897	21627	66385
11	A10	PTKD-2 - 2			10				
12	A11	NIST 614 - 3			11				

Fig. 1-5 Example of List file format

Export: The directory where the data is exported to and saved. The default setting is the current working directory of the software.

1.2.2 Instrument model selection:

Agilent1: Reads data from line 4 (Fig. 1-6).

Agilent2: Reads data from line 3 (Fig. 1-6).

Thermo: Reads data from line 14 (Fig. 1-6).

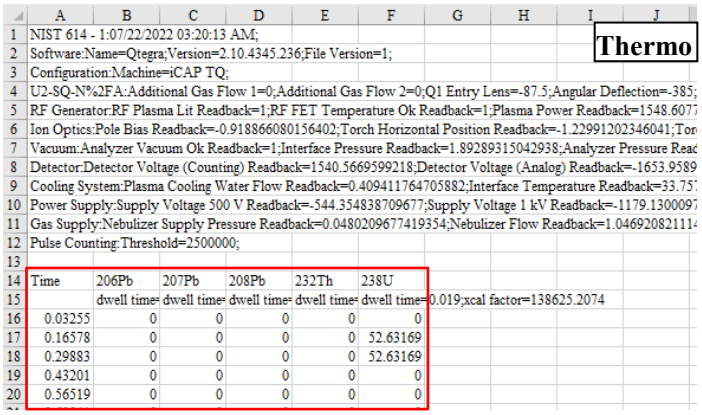
Agilent1

	A	B	C	D
1	C:\Agilent\2021\Paul Slezak\Aug21-PS_Limerick_			
2	Intensity V CPS			
3	Acquired : 07/22/2022 03:20:13 AM using Batch Aug21-PS_Limeri			
4	Time	206Pb	207Pb	208Pb
5	0.03255	0	0	0
6	0.16578	0	0	0
7	0.29883	0	0	0
8	0.43201	0	0	0
9	0.56519	0	0	0
10	0.69841	0	0	0
11	0.83158	0	0	0

	E	F
1	232Th	238U
2		
3		
4	0	0
5	0	0
6	0	52.63169
7	0	52.63169
8	0	0
9	0	0
10	0	0
11	0	0

Agilent2

	A	B	C	D	E	F
1	NIST 614 - 1					
2	start:0					
3	Time	206Pb	207Pb	208Pb	232Th	238U
4	15.61013	0	15.87303	0	0	0
5	15.74328	0	15.87303	0	0	0
6	15.87632	0	15.87303	0	0	0
7	16.00943	0	15.87303	0	0	0
8	16.14252	0	0	0	0	0
9	16.27566	0	15.87303	0	0	0
10	16.40867	0	0	0	0	0
11	16.54169	0	15.87303	0	0	0



	A	B	C	D	E	F	G	H	I	J
1	NIST 614 - 1:07/22/2022 03:20:13 AM;									
2	Software:Name=Qtegra;Version=2.10.4345.236;File Version=1;									
3	Configuration:Machine=iCAP TQ;									
4	U2-SQ-N%2FA:Additional Gas Flow 1=0;Additional Gas Flow 2=0;Q1 Entry Lens=-87.5;Angular Deflection=-385;									
5	RF Generator:RF Plasma Lit Readback=1;RF FET Temperature Ok Readback=1;Plasma Power Readback=1548.607									
6	Ion Optics:Pole Bias Readback=-0.918866080156402;Torch Horizontal Position Readback=-1.22991202346041;Tor									
7	Vacuum:Analyzer Vacuum Ok Readback=1;Interface Pressure Readback=1.89289315042938;Analyzer Pressure Read									
8	Detector:Detector Voltage (Counting) Readback=1540.5669599218;Detector Voltage (Analog) Readback=-1653.9589									
9	Cooling System:Plasma Cooling Water Flow Readback=0.409411764705882;Interface Temperature Readback=33.757									
10	Power Supply:Supply Voltage 500 V Readback=-544.354838709677;Supply Voltage 1 kV Readback=-1179.1300097									
11	Gas Supply:Nebulizer Supply Pressure Readback=0.0480209677419354;Nebulizer Flow Readback=1.046920821114									
12	Pulse Counting:Threshold=2500000;									
13										
14	Time	206Pb	207Pb	208Pb	232Th	238U				
15		dwell time=	dwell time=	dwell time=	dwell time=	dwell time=	0.019;xcal factor=138625.2074			
16	0.03255	0	0	0	0	0				
17	0.16578	0	0	0	0	52.63169				
18	0.29883	0	0	0	0	52.63169				
19	0.43201	0	0	0	0	0				
20	0.56519	0	0	0	0	0				

Thermo

Fig. 1-6 Example of raw data format from two quadrupole mass spectrometers.

1.2.3 Parameter settings:

❖ (3.1) Standard bias fractionation factor calculation.

Age of RM (Ma): Age of the reference material.

207Pb: Calculate the standard bias fractionation factor. The results of the calculation are displayed in the information display window (Fig. 1-7). A file named "result_all.csv" will be generated in the current working directory of the software.

When the "**Std Corr?**" checkbox is checked the age of the standard needs to be entered, the bias fractionation factor is calculated after deduction for common Pb in the standard (^{207}Pb method, Chew et al., 2014). In contrast, when the "**Std Corr?**" checkbox is unchecked, the common Pb in the standard is ignored. The bias fractionation factor can also be verified by the standard calculation results.

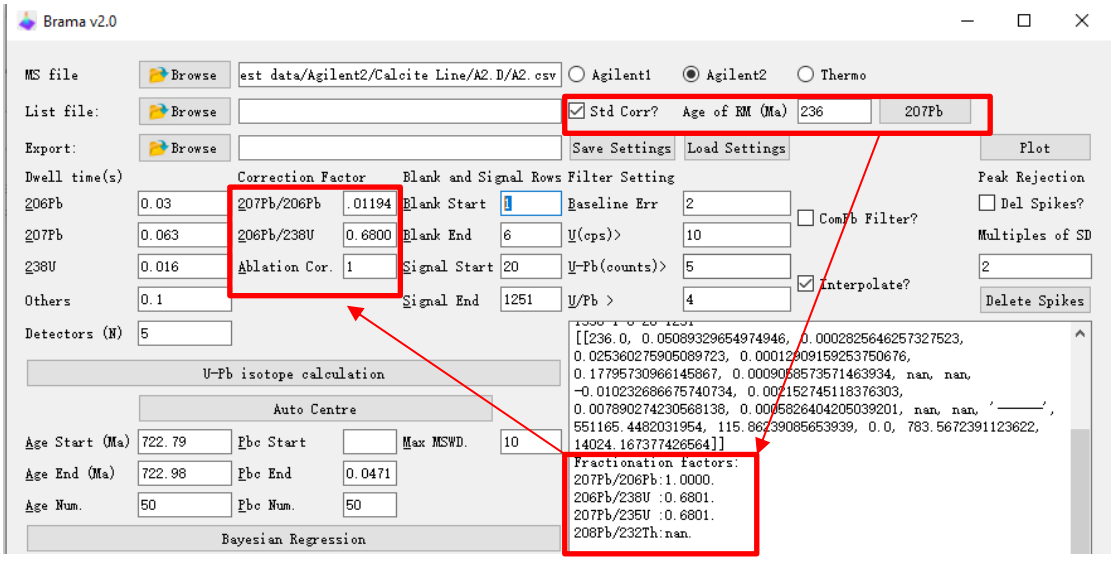


Fig. 1-7 Diagram of the calculation steps for standard bias fractionation factor.

❖ (3.2) Save or load config file.

<Save Settings> and <Load Settings> buttons to save or load config files("Config.ini"; Fig. 1-8).

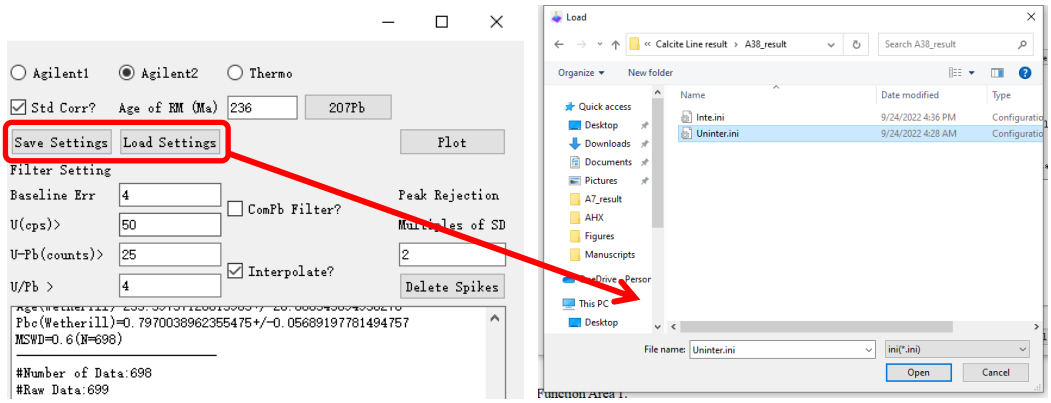


Fig. 1-8 Config file to save or load data processing parameters

❖ (3.3) Plot signal intensity vs. rows.

Click the button <Plot> to display the raw data signal graph (Fig. 1-9). The blanks and signal start/stop rows can be read from the graph and be filled in **(3.6).**

❖ (3.4) Dwell time.

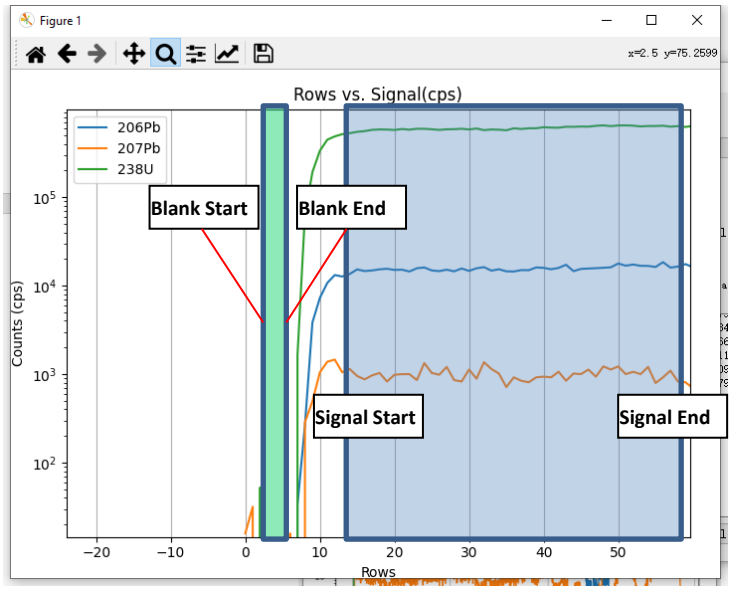


Fig. 1-9 Raw data signal display interface

The mass spectrometer detector isotope dwell time corresponding to ^{206}Pb, ^{207}Pb and ^{238}U can be entered in this field, respectively. The "**Others**" contains the sum of dwell time other than ^{206}Pb, ^{207}Pb, ^{238}U. The "**Detectors (N)**" can be entered as the number of masses being used.

206Pb：Dwell time of ^{206}Pb (seconds).

207Pb：Dwell time of ^{207}Pb (seconds).

238U：Dwell time of ^{238}U (seconds).

Others：Sum of dwell time of masses other than ^{206}Pb, ^{207}Pb, ^{238}U.

Detectors (N)：The number of masses.

❖ (3.5) Correction factor.

207Pb/206Pb: The standard bias fractionation factor for $^{207}Pb/^{206}Pb$, which equals the measured $^{207}Pb/^{206}Pb$ divided by the true value.

206Pb/238U: The standard bias fractionation factor for $^{206}Pb/^{238}U$, which equals the measured $^{206}Pb/^{238}U$ divided by the true value.

Ablation Cor.: Fractionation factor due to laser ablation. When set to 1, **206Pb/238U** refers to combined standard bias fractionation factor for $^{206}Pb/^{238}U$.

The "**207Pb/206Pb**" and "**206Pb/238U**" are the standard bias fractionation factors for $^{207}Pb/^{206}Pb$ (Corr76) and $^{206}Pb/^{238}U$ (Corr86), respectively. The "**Ablation Cor.**" (f) was used to correct for the $^{206}Pb/^{238}U$ fractionation factor ($Corr86' = Corr86/f$). The value of f is around 1, when f=1 means no ablation correction is performed.

❖ (3.6) Blank and signal rows.

This region is used to set the background and signal starting and ending row number in the time-dependent spectrum.

Blank Start: Background start rows.

Blank End: Background end rows.

Signal Start: Signal start rows.

Signal End: Signal end rows.

❖ (3.7) Filter setting.

This region is used to sets the parameters related to data filtering.

Baseline Err (%): A minimum % error given by the number in "**Baseline Err**" is quadratically added to these errors to account for the reproducibility of measurements

on signals that are oscillating because of the pulsed laser output. This is estimated to be about 4% for 5 Hz and 1% for 10 Hz based on the scatter of non-varying ratios measured on large peaks such as $^{207}Pb/^{206}Pb$ ratios from zircon.

U (cps) >: The minimum U cps set by the filtered data. Rejects very low U and Pb signals, if U & Pb < "**U (cps)**".

U-Pb (counts) >: The minimum U and Pb counts set by the filtered data. Makes sure every datum has this minimum number of counts.

ComPb Filter?: Whether to perform filtration of common Pb.

U/Pb >: If "**ComPb Filter?**" is checked, signals with low $^{238}U/^{206}Pb$ will be omitted. The minimum $^{238}U/^{206}Pb$ value is set by the number in "**U/Pb (counts) >**". Ignore data with too low U/Pb (<0 if filter is off).

Interpolate?: If "**Interpolate?**" is checked, raw data are interpolated. Quadrupole measurements of different masses occur at different times so interpolation should reduce scatter. Data are compressed so that the smallest Pb mass count numbers are not allowed to be lower than defined in "**U-Pb (counts)**".

- (3.8) Peak Rejection.

  Del Spikes?: When this checkbox is checked, spike filtering is performed before the data processing.

  Multiples of SD : The threshold number used to perform filtering of signal spikes.

  Delete Spikes: Displays the signal plot of the data after filtering the spikes.

The "**Delete Spikes**" button will give a prompt and then scans through the 206, 207 and 238 signals and compares them to the signal immediately before and after. If the ratios of the signal over both the before and after signals exceed the threshold number specified in "**Multiples of SD**", the data will be deleted.

- (3.9) **U-Pb isotope calculation**: Performs isotope calculations and saves the results in the export directory of the settings (Fig. 1-10).

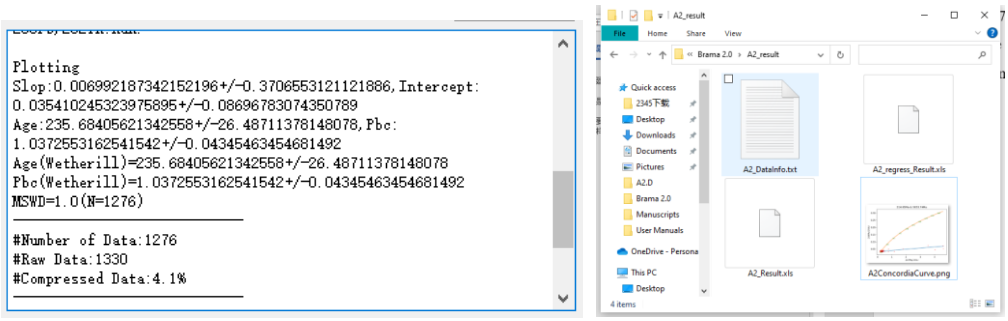


Fig. 1-10 The results are displayed in the information window and the result file is saved after executing the U-Pb isotope calculation command.

1.2.4 Regression settings:

Auto Center: When **Auto Center** is clicked, the program automatically performs Bayesian regression based on the age calculated from the Wetherill coordinates. Users can also set the Bayesian regression age and common Pb starting and ending values and set the maximum MSWD value of the exported result data (Fig. 1-11).

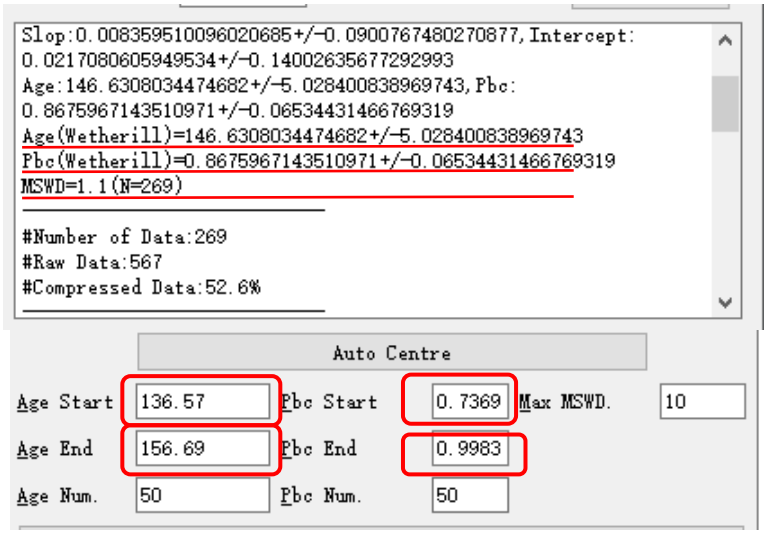


Fig. 1-11 Automatic setting of Bayesian regression age and common Pb range

Age Start and **Age End**: Age range for Bayesian regression.

Age Num.: The number of steps for Age.

Pbc Start and **Pbc End**: Common Pb (Pbc) range for Bayesian regression.

Pbc Num.: The number of steps for Pbc.

Max MSWD.: If the datum exceeds this deviation from the best fit plane it is rejected (strikethrough).

Bayesian Regression: Determines the sum of probabilities with respect to the

measured datum of discrete points within a linear band represented by the age and common Pb interval.

1.2.5 Multi-file processing:

Input Dir and **Bayesian Method?**: Set the MS file storage directory and choose whether to perform Bayesian regression calculation.

Batch Process: Multi-files isotope calculation or Bayesian regression calculation. The List file (1.2.1) **List file**) needs to be set up before the **batch process**.

1.2.6 Merge Result Plotting

Merge Result Plotting: Merges and plots the spatial distribution of isotope counts.

1.2.7 Information

Displays operational status and information.

1.3 Single file data processing procedure-Calcite dating

1.3.1 Data Preparation

Prepare a line scan data folder containing raw mass spectrometry data for NIST glass, matrix-matched standards, and samples (Fig. 1-12). Example files are stored in：\data\Calcite Line\， where 'A1.csv' and 'A2.csv' refer to the Ms file of NIST 614 and matrix-matched standard AHX (age=236Ma), respectively (Fig. 1-12).

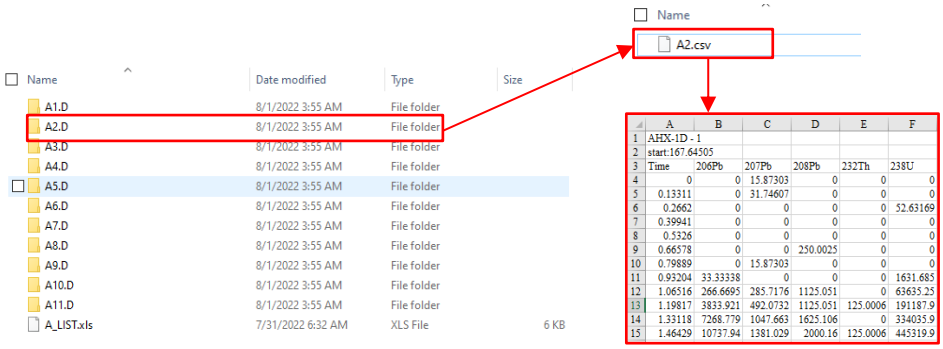


Fig. 1-12 Raw mass spectrometry data folders and file formats.

1.3.2 Import Data

As shown in Fig. 1-13, Click ①<import data>→②<select data format> import the Ms file.

Click③<show signal plot>→④<preview spike filtering result> to determine the

blank and signal rows and spike filtering settings. Fill in the blanks in ⑤<set blank and signal rows>.

Fill in the blanks in ⑥<set dwell time> according to the time selected in the software of the mass spectrometer and detector.

Fill in the blanks in ⑦<Filter setting> > according to mass spectrometry settings.

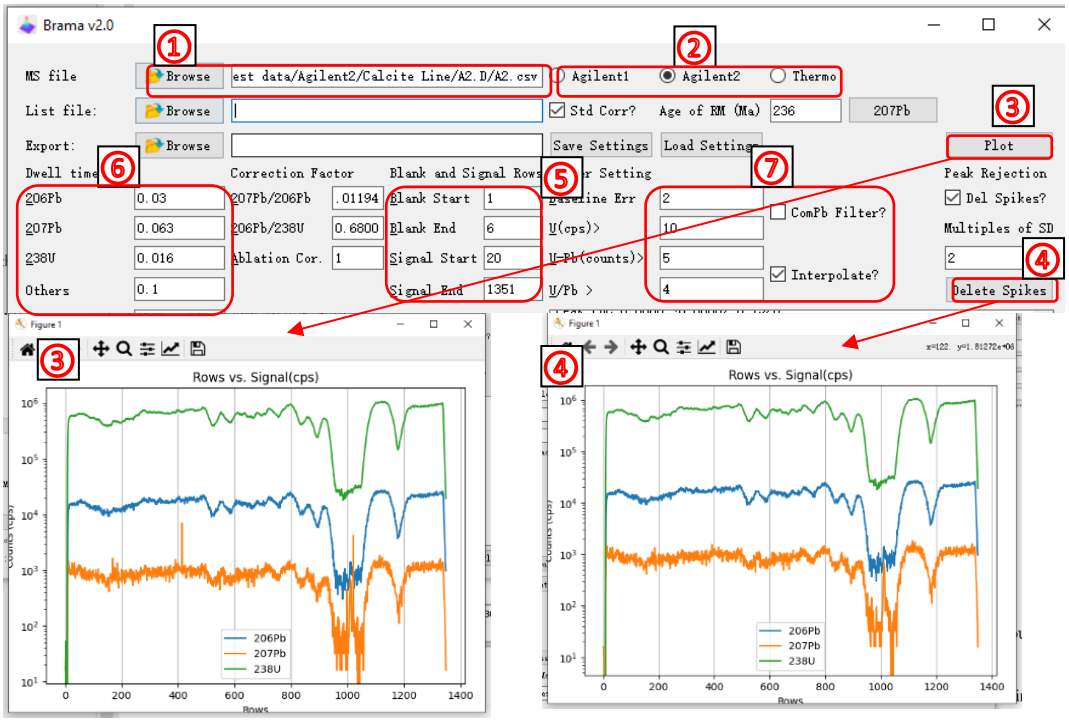
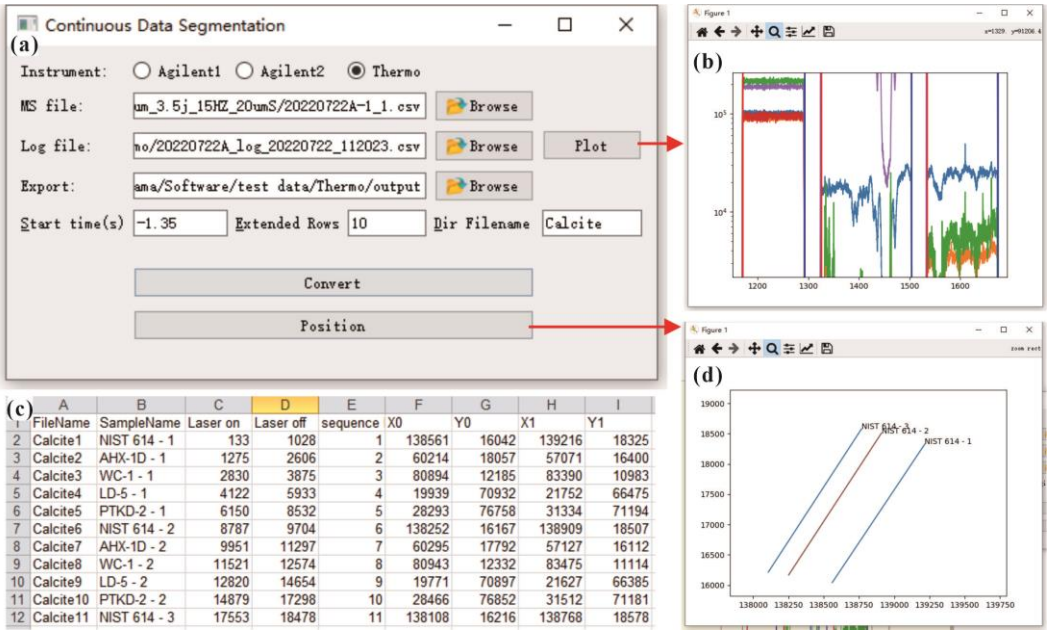


Fig. 1-13 Data import and signal display

Users can also load or save parameters via the <**Load Settings**> and <**Save Settings**> button config file.

For multiple sample processing or age distribution mapping, continuous signal data need to be segmented and matched with the position and timestamp information in the laser log file. The data conversion software “Continuous Data Segmentation” (Fig. 1-14a) extracts the background and signal time of the samples (Fig. 1-14b) and the sample position information (Fig. 1-14 d), according to the laser status, and generates a list file (Fig. 1-14 c) to store the above information.



	A	B	C	D	E	F	G	H	I
1	FileName	SampleName	Laser on	Laser off	sequence	X0	Y0	X1	Y1
2	Calcite1	NIST 614 - 1	133	1028	1	138561	16042	139216	18325
3	Calcite2	AHX-1D - 1	1275	2606	2	60214	18057	57071	16400
4	Calcite3	WC-1 - 1	2830	3875	3	80894	12185	83390	10983
5	Calcite4	LD-5 - 1	4122	5933	4	19939	70932	21752	66475
6	Calcite5	PTKD-2 - 1	6150	8532	5	28293	76758	31334	71194
7	Calcite6	NIST 614 - 2	8787	9704	6	138252	16167	138909	18507
8	Calcite7	AHX-1D - 2	9951	11297	7	60295	17792	57127	16112
9	Calcite8	WC-1 - 2	11521	12574	8	80943	12332	83475	11114
10	Calcite9	LD-5 - 2	12820	14654	9	19771	70897	21627	66385
11	Calcite10	PTKD-2 - 2	14879	17298	10	28466	76852	31512	71181
12	Calcite11	NIST 614 - 3	17553	18478	11	138108	16216	138768	18578

Fig. 1-14 Mass spectrometry file and laser log file matching interface (a), signal plot (b), List file format (c) and sampling point location map (d).

1.3.2 Standard bias fractionation factor setting

$^{206}Pb/^{238}U$ fractionation factor: As Fig.1-15 shows, ①Import the "A2.scv" (AHX) file according to step 1.3.2. ②Check the **Std Corr?** checkbox, ③enter the age in Age of **RM (Ma)**, and click the ④**207Pb** button. The result is displayed in ⑤Information window. Fill in the fractionation factor in ⑥ **Correction factor**.

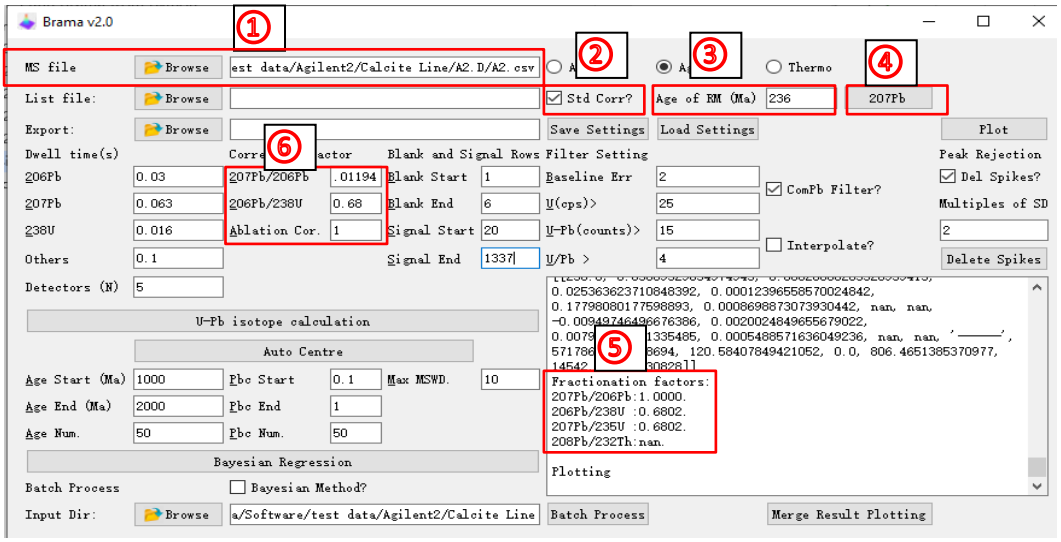


Fig. 1-15 Calculation steps of standard bias fractionation factor for $^{206}Pb/^{238}U$

$^{207}Pb/^{206}Pb$ fractionation factor: As Fig.1-16 shows, ①Import the "A1.scv" (NIST 614) file according to step 1.3.2. ②Uncheck the **Std Corr?** Checkbox and then click the ③**207Pb** button. ④Open the "result_all.csv" file in the current working directory of Brama, $^{207}Pb/^{206}Pb$ bias factors equals ⑤measured ratio (0.8813) divided by true ratio ($^{207}Pb/^{206}Pb$ NIST 614 = 0.8710).

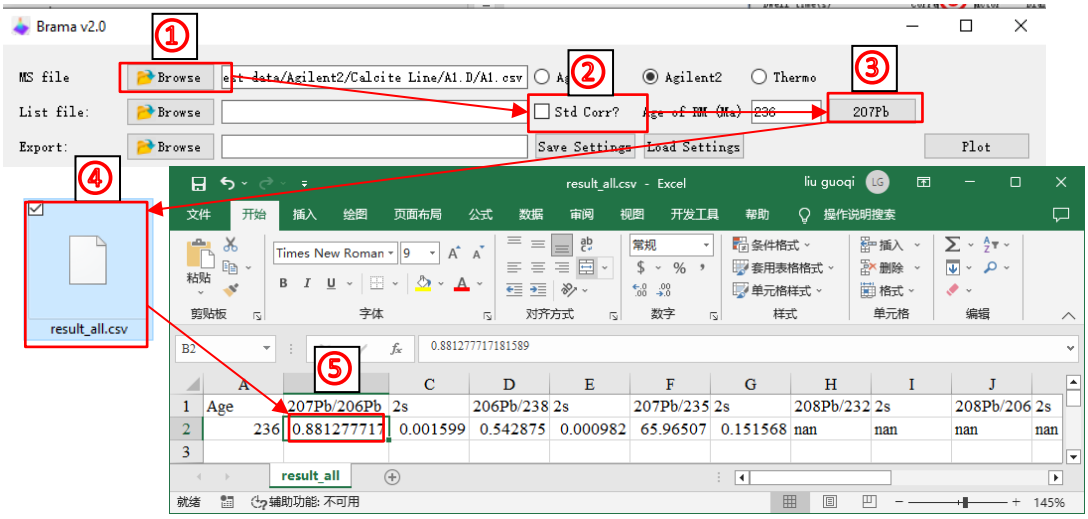


Fig. 1-16 Calculation steps of standard bias fractionation factor for $^{207}Pb/^{206}Pb$

1.3.3 U-Pb isotope calculation

After completing the above steps, click the button <**U-Pb isotope calculation**> to start the isotopic composition calculation. As shown in Fig. 1-17, the calculation results are presented in the Wetherill diagram, the information window and the exported "*_Result.xls".

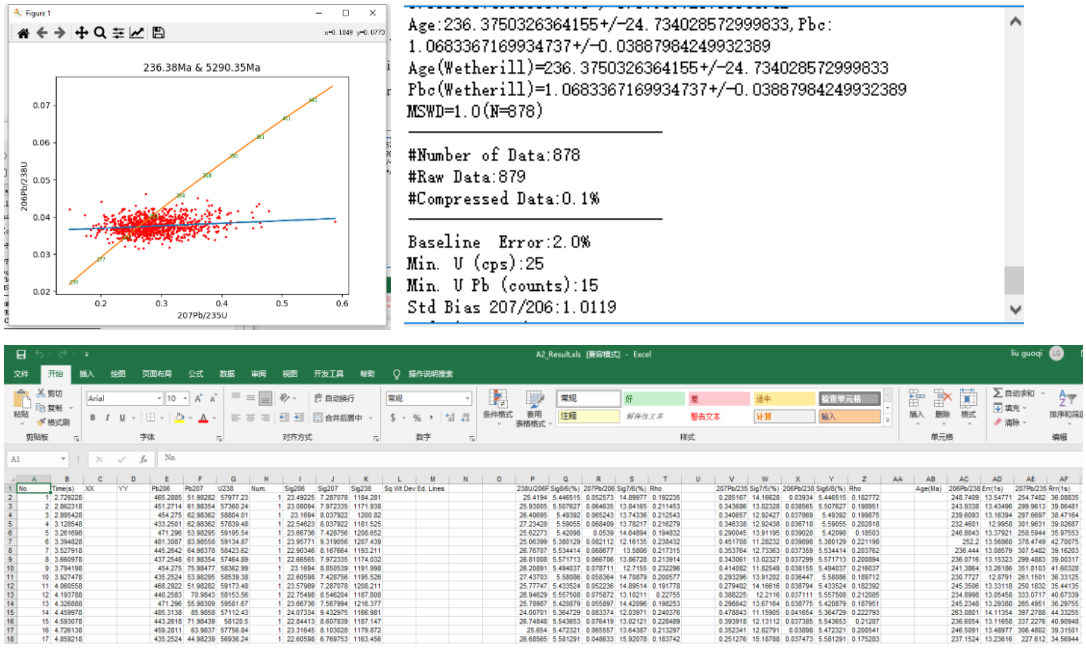


Fig. 1-17 Results of U-Pb isotope calculation

AHX yielded an age of 236.38 Ma, demonstrating that the calculated standard bias fractionation factor (step 1.3.2) is appropriate. The wc-1 yields an age of 255.3±5.3Ma and 252.6±5.4Ma using Wetherill and Tera-Wasserburg regressions (Fig. 1-18), which is consistent with the ID-IRMS method (254.4±

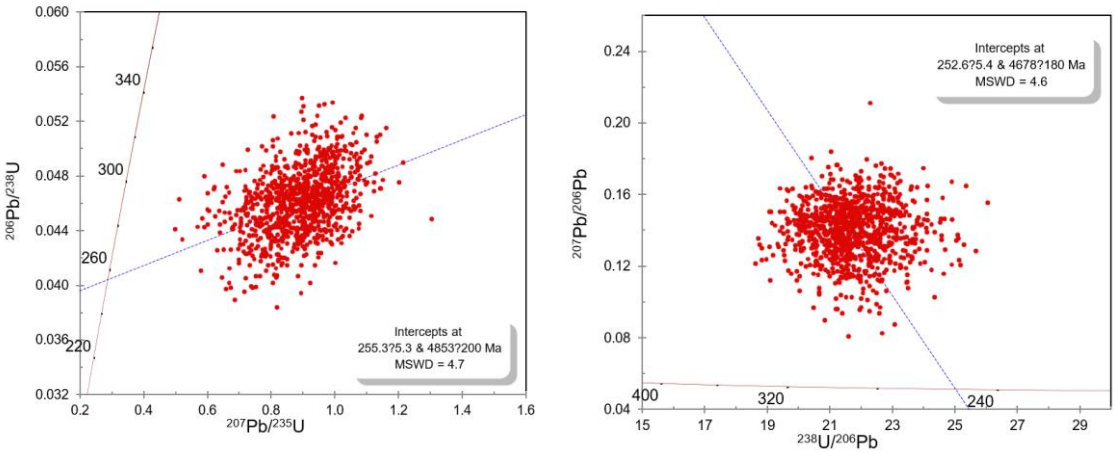


Fig. 1-18 Wetherill and Tera-Wasserburg diagram of wc-1 by Isoplot

6.4Ma, Roberts et al., 2017).

1.3.4 Bayesian Regression

According to the age and common lead composition from step 1.3.3, click the <**Bayesian Regression**> or <**Auto Centre**>, Bayesian regression results will be presented in three forms: probability density surface plots, probability density profiles, and information windows (Fig. 1-19, Fig. 1-20).

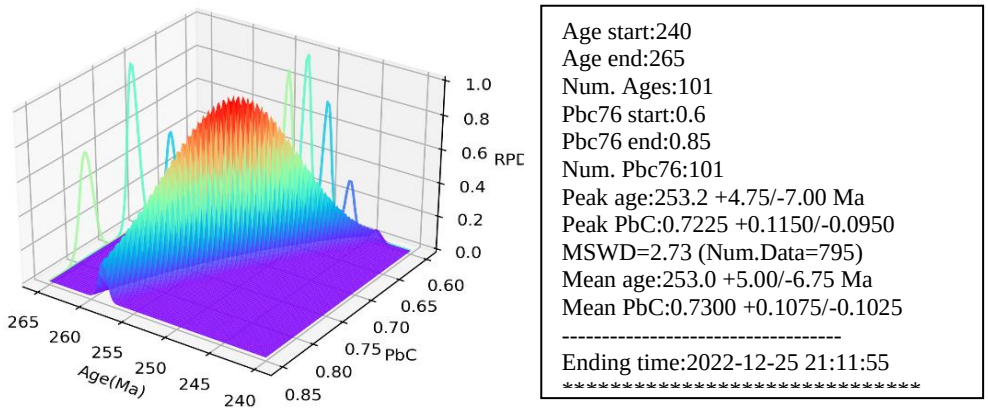


Fig. 1-19 Bayesian regression of all isotope data relative probability density surface plot

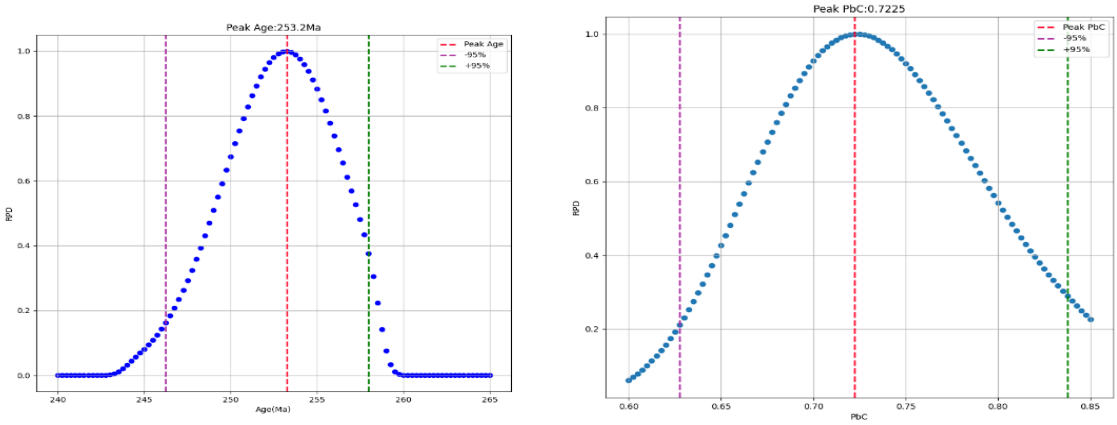


Fig. 1-20 Integrated relative probability density for the age and common Pb

1.4 Multi-file data processing procedure

1.4.1 Import Data

Import the list file as described in 1.2.1 and 1.2.2.

Import Ms files as described in 1.2.5.

1.4.2 Parameter Setting

Files used for batch processing should have the same settings, which are set in the same way as for single file processing. For details, see 1.3.2~1.3.2.

1.4.3 Batch Process

Click the button <**Batch Process**> for multi-files isotope calculation or Bayesian regression calculation.

1.4.4 Mapping

Click on the button <**Merge Result Plotting**> to map isotope ratios, mode ages and element counts (Fig. 1-21).

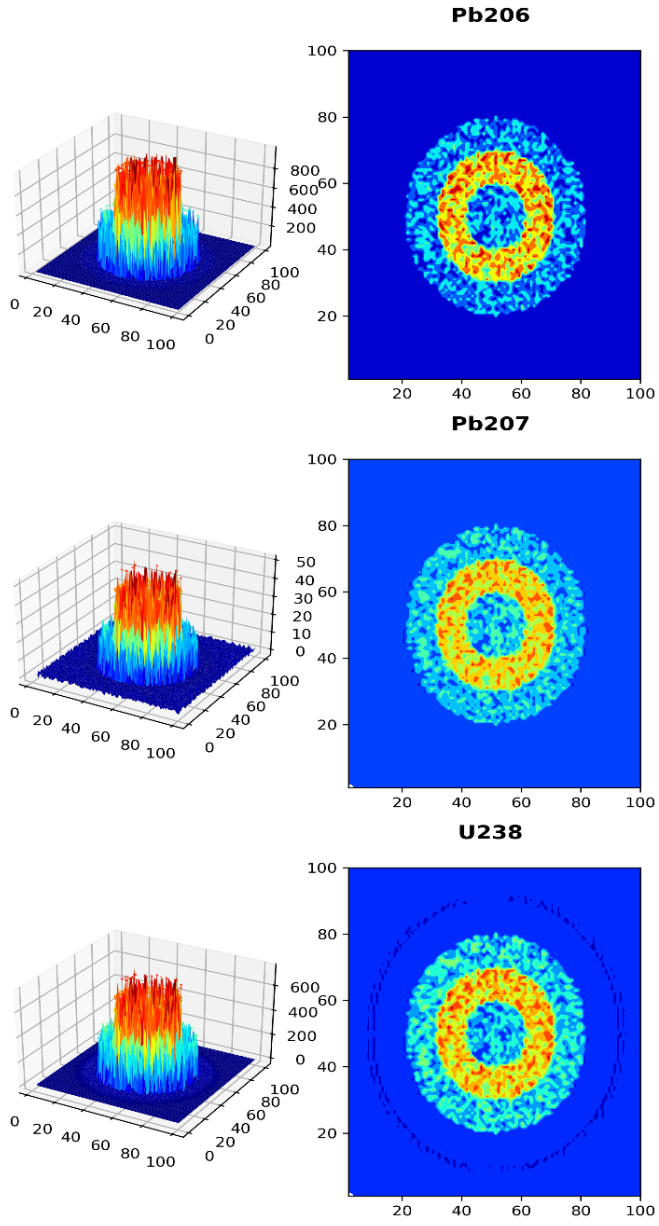


Fig. 1-21 Spatial distribution of U-Pb isotope ratios

II. Description of the results document

The result files are stored in the output folder, and the name of the folder is: mass spectrometry file name + "_result". Take the mass spectrometry file as "**A00.csv**" (the folder is "A00_result"), the output file name and content are as follows (Fig. 2-1) ：

A00_DataInfo.txt：Parameters of software settings and operation results (Fig. 2-2 c).

A00_Result.xls：U-Pb isotope calculation results.

A00_3D.png：Surface plot of relative probability density of all isotope data (Fig. 2-2 a).

A00_Scatter.png：Integrated relative probability density plots for the age and common Pb (Fig. 2-2 b, d).

A00ConcordiaCurve.png: Wetherill regression plot.

A00_regress_Result.xls：After Bayesian regression processing, the data were filtered according to Max MSWD.

A00AHX.ini: configuration file for data processing parameters.

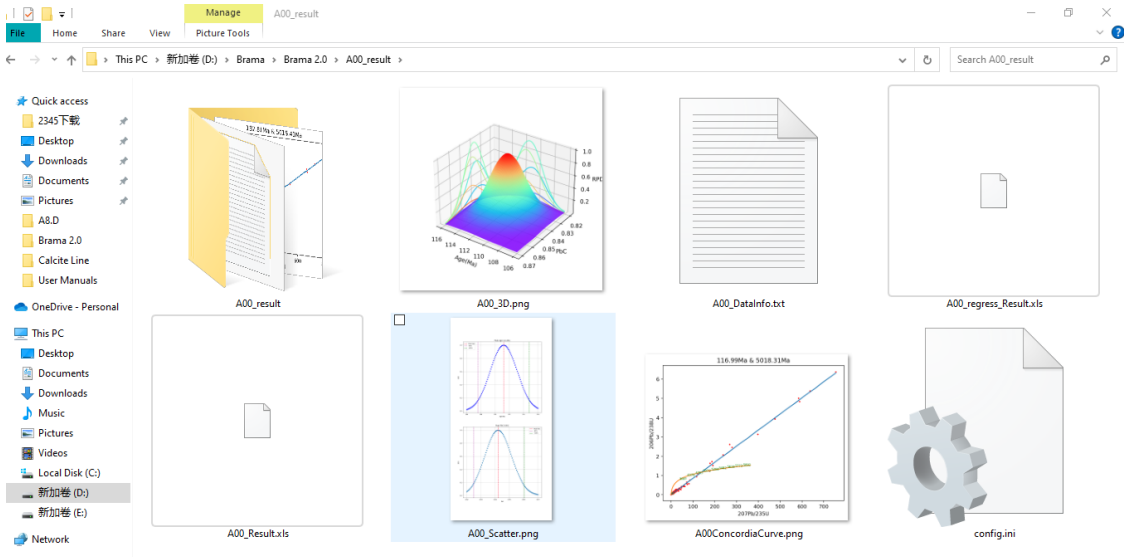


Fig. 2-1 Data format exported by Brama

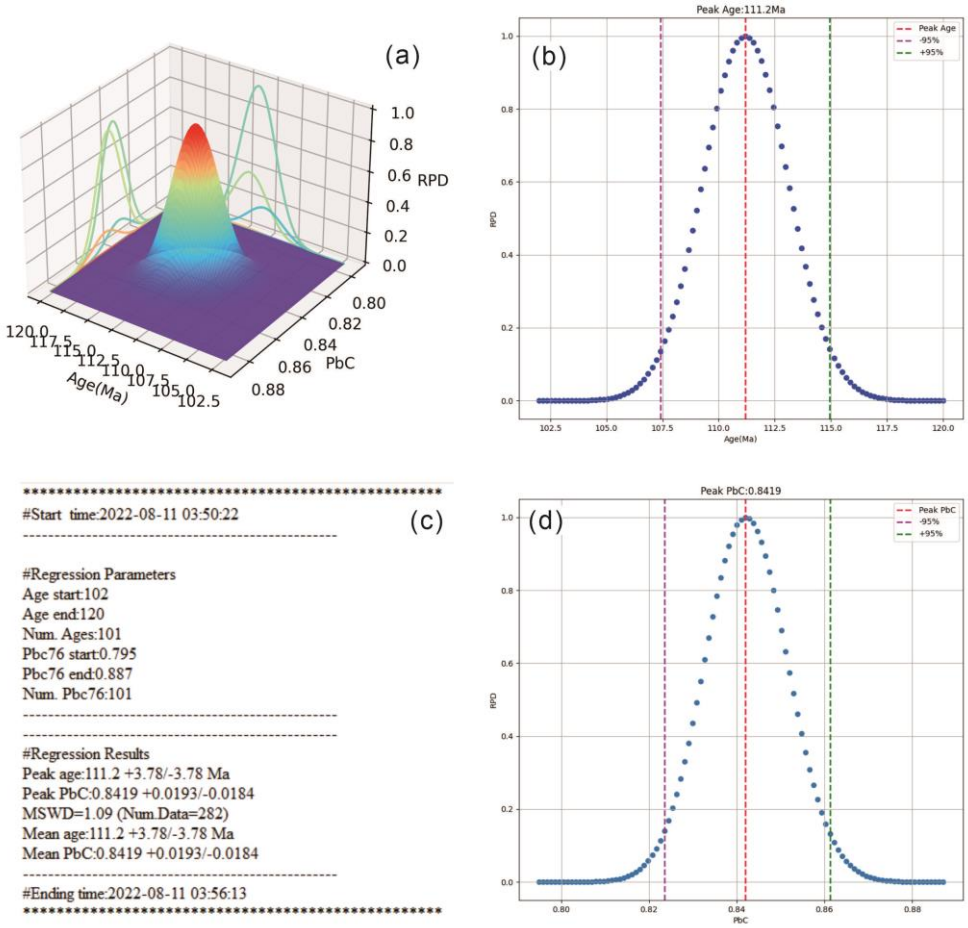


Fig. 2-2 Plots of the results acquired by Bayesian regression methods (data from Davis and Rochín-Bañaga, 2021).

(a) Relative probability density (RPD) surface.

(b) Relative probability density of age integrating along the axis of common lead.

(c) Log file of Bayesian regression results.

(d) Relative probability density of common lead integrated along the age axis.