

Data reduction software for
LA-ICP-MS/LA-MC-ICP-MS

Guide Book *for* **ICPMSDataCal**

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2016-8-23

Please join QQ group (40230239) for update, discussion and suggestion.
(Download QQ from <http://im.qq.com/download/>)

Whatever you are familiar with this software, it is suggested to firstly read the following sentences if you are planning to calculate your LA-ICP-MS data using this software. This may make your data more reasonable and explicable!

Isotopic fractionation in LA-ICP-MS analysis is mainly related to laser ablation depth, ablation spot size and laser energy density. For a given analysis sequence, spot size and laser energy are generally fixed. Different ablation depths are thus the major factor limiting effectively calibration against external standards. For zircon U-Pb isotopic dating, nonlinear variation of isotopic fractionation with time will restrict the accurate calibration of isotopic age, which would be highlighted for analysis at a small spot size (e.g., <20 μ m). In order to reasonably and effectively calibrate the samples, the following rules are suggested for selecting the TRA signals:

Basic rules for selecting the signals:

- The signal intervals (including start position and length) of the samples and calibration standards should be the same as most as possible.
- Mark and describe the abnormal signal/data during setting the signal intervals, which is helpful for you to reasonably choose or eliminate the final data!

Steps for selecting the signals:

1. In order to using a uniform integrating interval length for most analyses, firstly look at the signals of all analyses to select a “best” length of integrating intervals;
2. Set the signal integrating intervals of external standards (e.g., 91500) for correcting isotopic fractionation in the mode of “Fixed integrating time”;
3. Set the start positions of signal integrating intervals of samples one by one in the mode of “Fixed integrating time”. Mark the samples with shorter signal length than the “best” values in the “Comments” box;
4. Set the signal integrating intervals of marked samples with shorter signal length than the “best” values in the mode of “Unfixed integrating time”.








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1. Introduction and Installation

1.1. Introduction of ICPMSDataCal

ICPMSDataCal is written in the Visual Basic programming language and works on Microsoft Excel (**Excel2016 for ICPMSDataCal 11**). It gives users of the laser ablation ICP-MS a unique analytical environment, based on the interactive selection of background and sample intervals from the time-resolved signals provided by the (MC)-ICP-MS. It provides real-time and on-line data reduction for the LA-(MC)-ICP-MS analyses, and features linked graphics and analysis tables, greatly improving both productivity and the flexibility of analysis. At present, data analyzed by (MC)-ICP-MS of Agilent, Thermo X and Neptune, Elan, Varian, and Nu Plasma and Attom can be directly used without additional adjustment. In order to guide the users through the data reduction software, this manual includes the specific operations of different applications (e.g., U-Pb dating of zircon, trace element analyses of mineral and melt/fluid inclusion, and isotope analyses of Li, Sr, Nd, Hf, Os, Pb). In addition, the software is upgrading and modifying based on the different requirements. The functions and features of ICPMSDataCal mainly include:

-  It integrates the calibration and correction methods for trace element analysis by LA-ICP-MS (Lin et al., 2016; Liu et al., 2008; Liu et al., 2010b). Besides trace elements of the silicate mineral (Liu et al., 2008), the carbonate (Chen et al., 2011), metal oxide (Gao et al., 2010) and sulfide minerals and single melt/fluid inclusion (Zhang et al., 2011) can also be calculated. In addition to the traditional calibration method of single external standard combined with internal standard normalization, multiple-reference material calibration combined with ablation yield correction (MRMC-AYC) and multiple-reference material calibration combined with internal standard normalization (MRMC-ISN) can be used.
-  The time-dependent sensitivity drift in the analyses can be corrected by the measurements of quality control reference materials, which can be easily chosen by the user;
-  The isotopic ratios of Li (Xu et al., 2013), Sr (Tong et al., 2016), Nd (Xu et al., 2015), Hf (Hu et al., 2012; Liu et al., 2010a) and Os (Zhu et al., 2016) measured by LA-MC-ICP-MS can be calibrated and corrected;
-  Data reduction of zircon U-Pb isotopic dating and trace element analyses can be quickly done at one time (Liu et al., 2010b);
-  The used external standards can be automatically identified and easily changed (replace, add and delete) by the user;
-  The unfinished data reduction can be processed continually as long as the relevant “data summery file” was saved;
-  Data reduction for solution-ICP-MS analysis can also be done by ICPMSDataCal.

TRA: Time Resolved Analysis

MRMC-ISN: multiple-reference material calibration combined with internal standard normalization.

MRMC-AYC: multiple-reference material calibration combined with ablation yield correction

SimpMRMC: simple multiple-reference material calibration

1.2. Installing ICPMSDataCal

ICPMSDataCal works on Microsoft Excel. Therefore, Microsoft Excel has to be installed on the computer for ICPMSDataCal to run.

Step 1: Installing ICPMSDataCal

Download “ICPMSDataCal” directory from the QQ group (40230239) to the hard drive.

Step 2: Create an ICPMSDataCal shortcut on the desktop

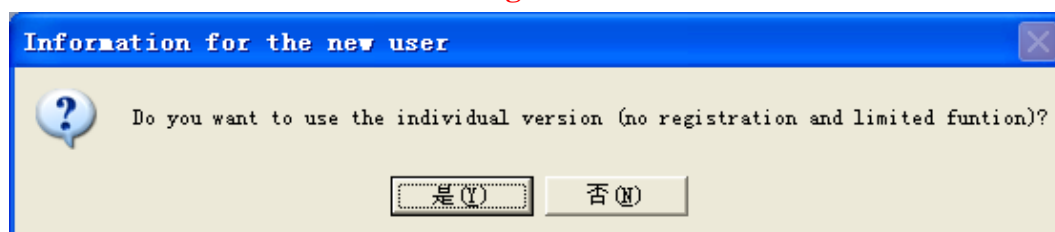
Within Windows Explorer, select the “ICPMSDataCal.exe” file in the ICPMSDataCal directory by clicking on it once. From the FILE menu select “Create Shortcut”. Move the file called “Shortcut to ICPMSDataCal.exe” onto the desktop and rename the file ICPMSDataCal, if required.

*Step 3: Registration for license or **Use without registration***

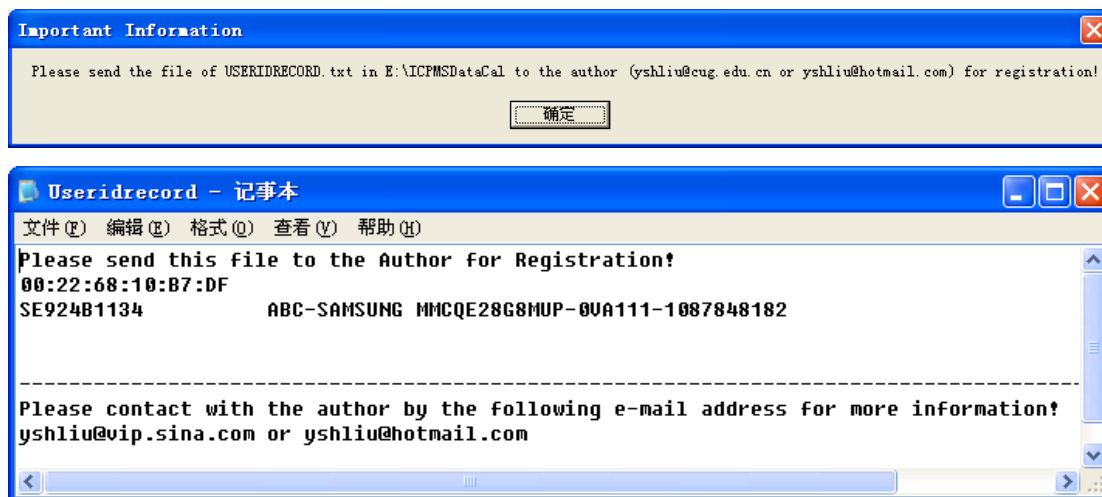
Although ICPMSDataCal is a free software for personal user, the user is required to register for license. The following information for registration will appear in running of “ICPMSDataCal.exe” if you are a new user.



If “No” is selected, the following dialog box will appear. Here, you can select “Yes” to use this software without registration.



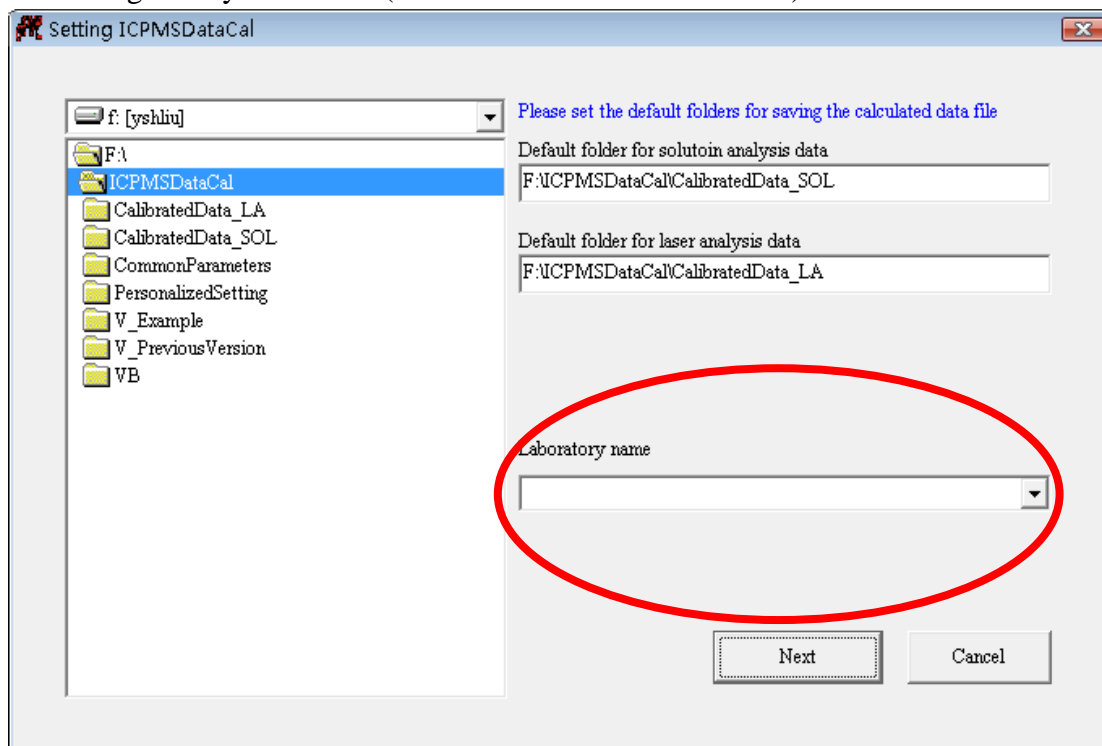
Otherwise, if “No” is selected, please send the file “Useridrecord.text” (located in the same directory as the main program “ICPMSDataCal.exe”) to the author (yshliu@hotmail.com) according to the following information to ask for the registration file.



When get the registered file of “AutUseChec.exe” from the Author, copy it to the “ICPMSDataCal” directory to replace the existed one.

Step 4: Setting for the new user

Dialog box of “Setting ICPMSDataCal” will appear in the first running of ICPMSDataCal if you are registered. Here, you can set the default directory to save the calculated/calibrated files, and MUST select or input the **Correct Laboratory Name** as given by the author (select “CUG user” if not stated).



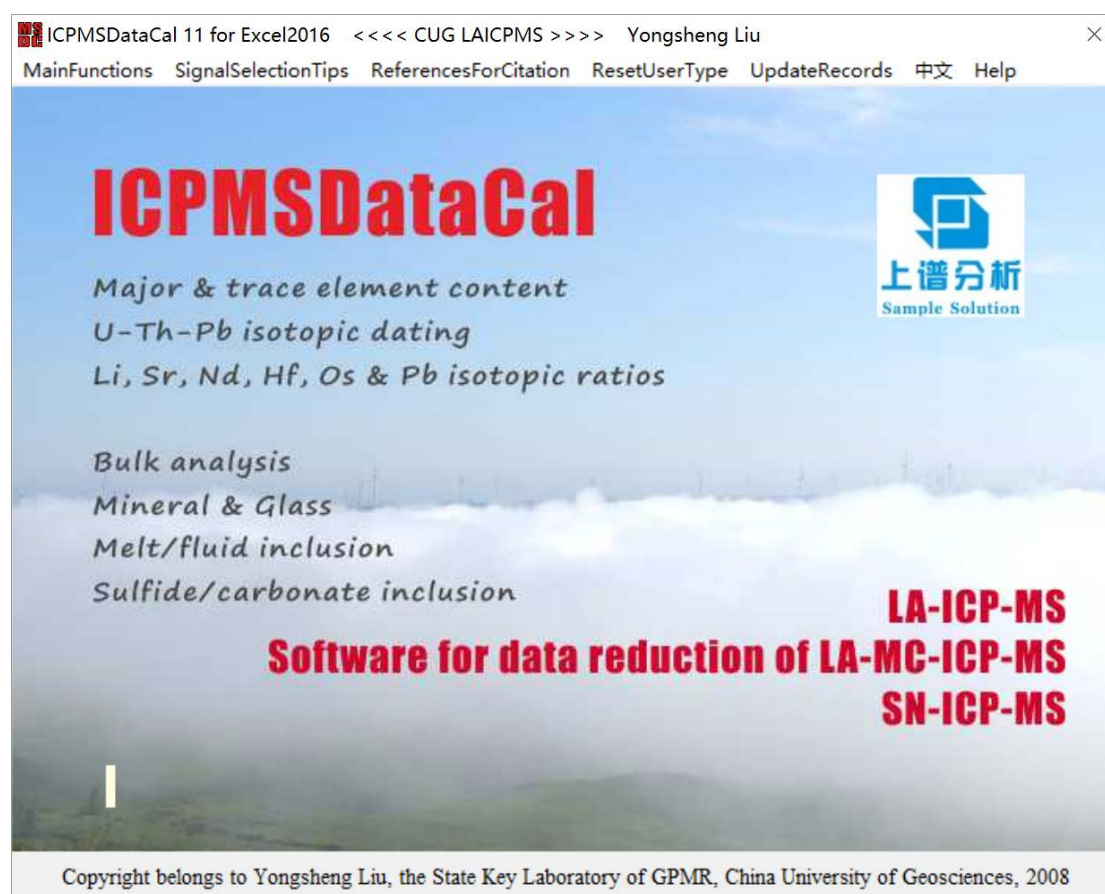
Step 5: Run ICPMSDataCal

Double-click the ICPMSDataCal icon on the desktop, or if no shortcut was created, open Windows Explorer. Navigate to the ICPMSDataCal directory, and double-click the “ICPMSDataCal.exe” file. The ICPMSDataCal screen will then appear, and the software is ready to be used.

2. Overview of Interactive User Interfaces

ICPMSDataCal consists of four major interactive user interfaces (“windows”):

2.1. The “ICPMSDataCal” window.



Main Functions includes:

- 1) Calculate raw data off-line
- 2) Change calculated data
- 3) Calculate raw data on-line
- 4) Element periodic table
- 5) Calculation coefficient of element and oxide

Tips for signal selection gives the user some suggestions for selecting TRA signals in reducing data of LA-(MC-)ICP-MS.

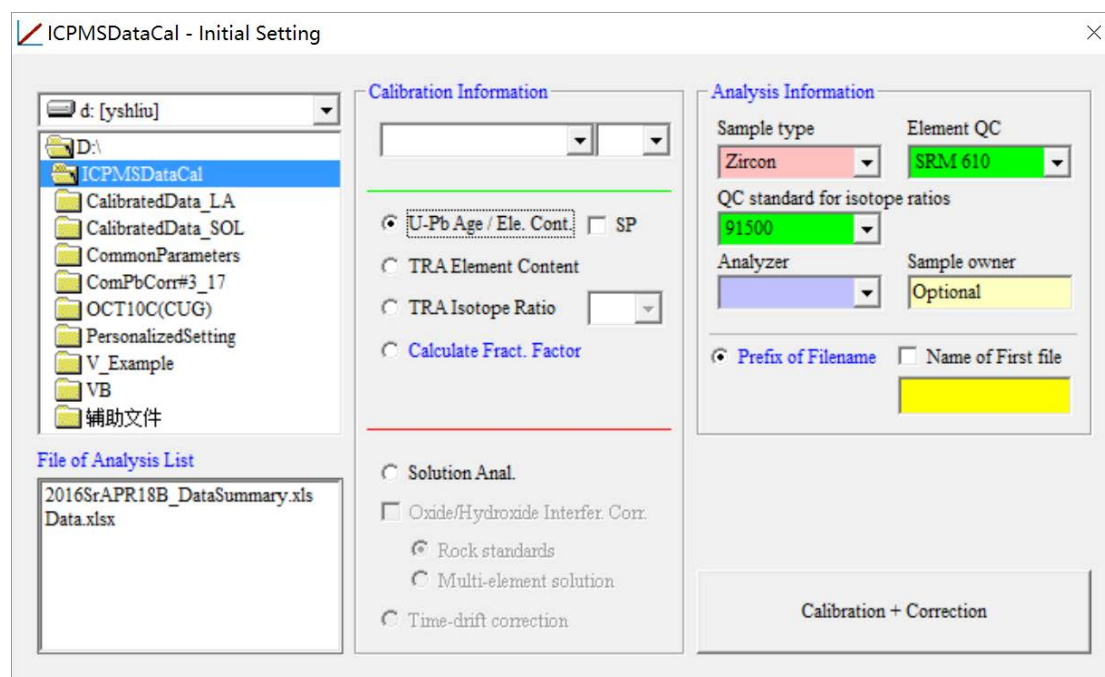
References for citing show the reference list for this software.

2.2. The “Initial setting” window

The “Initial setting” window calls for the user to input/select the information of calibration, analysis and raw data file. Element QC is required for calibration of element content analysis, and External standard for isotope ratios is required for isotopic analysis (e.g., zircon U-Pb dating). Prefix of data filename for LA-ICP-MS or Analysis No. for solution-ICP-MS analysis must be correctly inputted. Analyzer and sample owner are used for printing the final report.

For solution-ICP-MS analysis:

Rock standards: calibration against multiple external rock standards (e.g., BHVO-2, AGV-2 and RGM-2); **Multi-element solution:** calibration against in-house standard solutions.



At a click of the “Calculation/Calibration” button, correcting time-dependent sensitivity-drift, selecting integration intervals for the ‘background’ and ‘signal’ counts of TRA analysis, calculating/calibrating element contents and isotopic age, drawing REE and SPIDER diagrams will be conducted automatically. As a default option, the integration intervals for the ‘background’ and ‘signal’ counts were selected using a simple algorithm, and the element contents were calibrated against multiple-reference materials without applying an internal standard. These should be checked and re-set interactively by the user in the “Signal Selection” and “Multi-standard Calibration” windows.

Important information:

- Instrument, data type and analysis number (or prefix of datafile name) must be correctly selected or inputted. The name of quality control sample (QC) should be correctly inputted for element analysis (the default QCs are GSE-1G or SRM 610 for LA-ICP-MS analysis and QC for solution analysis), otherwise the time-dependant sensitivity drift will not be corrected. The reasonable zircon reference (e.g., 91500) must be selected as external standard for U-Pb isotopic dating.
- One EXCEL file containing analysis sequence should be saved as Prefix_List.xls (e.g., JUN12C_List.xls) or copy the pre-existed setting file (e.g., JUN12C_Setting.xls) in the directory where the datafiles are saved before Calculate/Calibrate TRA data using ICPMSDataCal.

JUN12C_List.xls

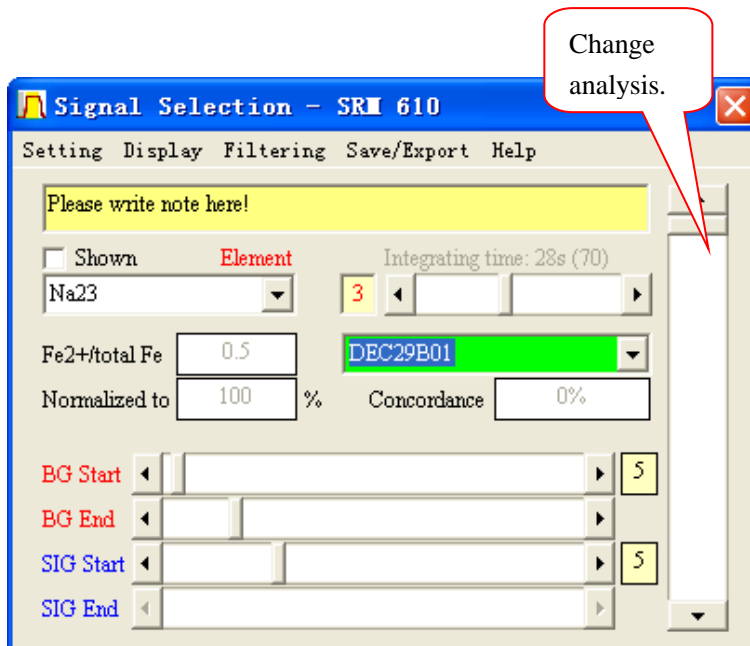
Spot No.	Sample	Spot size	HV	Energy	Rep. rate
JUN12C01	GSE-1G	16	26	60	5
JUN12C02	91500	16	26	60	5
JUN12C05	DMP552-01	16	26	60	5
.....	Spot No. and Sample must be inputted.				

2.3. The “Signal Selection” window

Time resolved laser signals are viewed and integration intervals are selected by the user in the “Signal Selection” window.

Comments for the current analysis can be inputted in the yellow box (e.g., Good data), which will be shown in the last report.

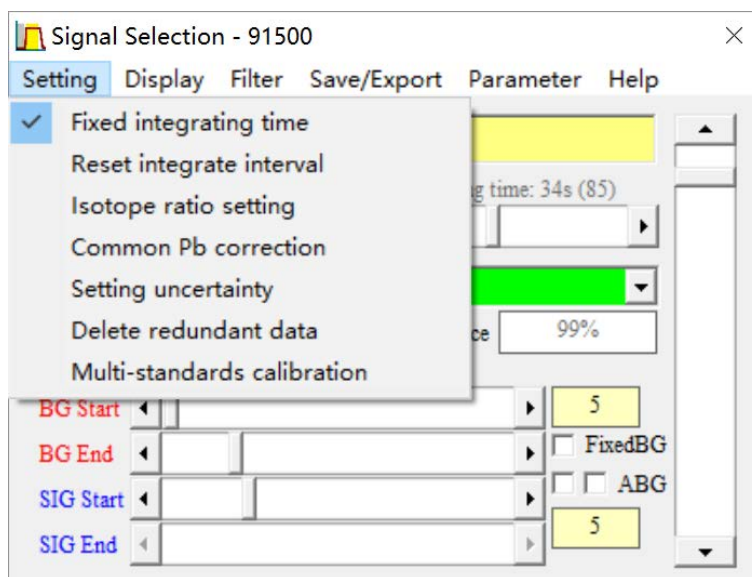
- The integration intervals of background and signal can be selected using four scroll bars. In the fixed-integrating-time mode, integration interval of signals can be universally changed using the scroll bar of “Integrating time”. The integration interval length of signal for current analysis is shown following the text of “Integrating time” (e.g. 26s).
- The $\text{Fe}^{2+}/\text{totalFe}$ ratio and total metal oxide (generally 100wt% for volatile-free mineral and glass) should be reasonably set for element analysis with method without using internal standard. The total carbonate or sulfide (generally 100wt%) should be inputted for carbonate or sulfide minerals.
- Signal variations of one element can be highlighted by selected the element in the element list box (e.g. Si29), and hidden/shown by clicking the Shown (Hidden) checkbox.
- Here, concordance of U-Pb dating (e.g., 99%) is calculated as $100 \times (1 - \text{abs}(68\text{Age} - 75\text{Age}) / \text{average}(68\text{Age}, 75\text{Age}))$.



2.3.1. Setting

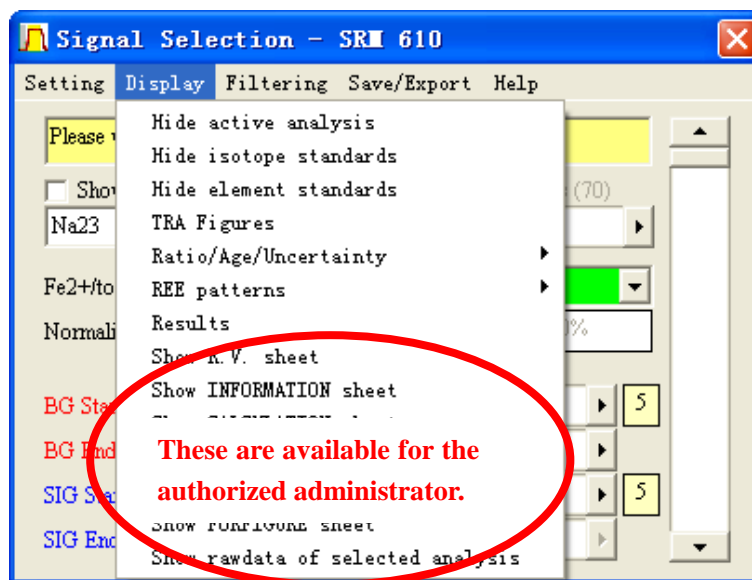
- Fixed integrating time**, applying fixed / unfixed integrating time. In the fixed-integrating-time mode, the end of integration interval of signal cannot be changed;
- Reset integrate interval**, resetting the integrate interval of selected sample to be the default;
- Isotopic ratio setting**, showing the window of setting parameter for correcting isotopic fractionation and interference;

- ✚ **Reset the ages of BCC and DM**, changing the ages of BCC and DM in plotting the diagram of $\epsilon\text{Hf}(t)$ -age.
- ✚ **Delete redundant data**, deleting the redundant data (useful for analyzing single inclusion data);
- ✚ **Calculate Inclusion/Host ratio**, showing the window specially for calculating element contents in single inclusion;
- ✚ **Multi-standards calibration**, changing between “Signal Selection” and “Multi-standard Calibration” windows.



2.3.2. Display

- ✚ **Hide/Show active analysis**: Hide/show the age (in the signal selection screen) and REE pattern (in the REE pattern screen) of specific analysis;
- ✚ **Hide/show isotope standards**: Hide/show all standards for U-Pb dating (e.g., 91500 and GJ-1);
- ✚ **Hide/show element standards**: Hide/show all standards for trace element analysis (e.g., SRM 610, GSE-1G and BCR-2G);
- ✚ **TRA Figure/REE Patterns**: Change between the TRA signal and REE pattern screens;
- ✚ **Ratio/Age/Uncertainty**: Change between isotopic ratio, uncertainty and age screens (only for data reduction of U-Pb isotopic dating);
- ✚ **Results**: Show the results that will be printed finally.



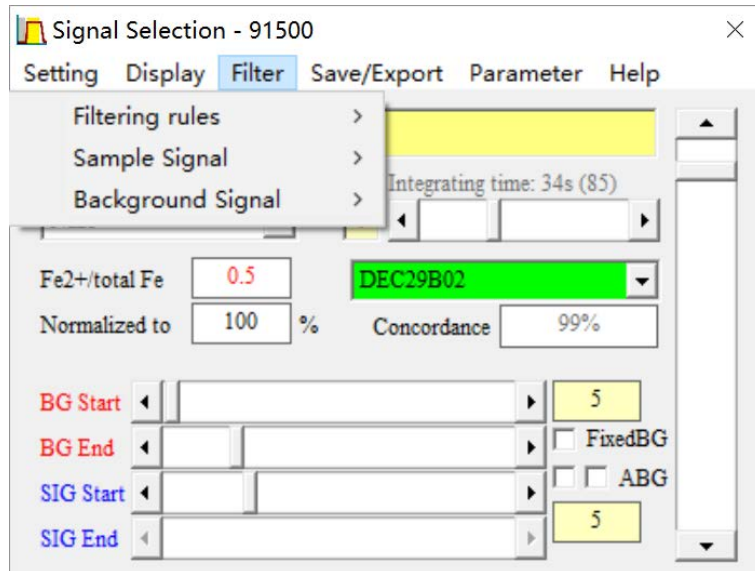
2.3.3. Filtering

Filtering rules: Select rule for filtering the signal peaks.
2 sigma rule, data xi will be deleted if $|xi-X|>2\sigma$ (X=average, probability of xi with $|xi-X|>2\sigma$ is 4.6%).

3 sigma rule, data xi will be deleted if $|xi-X|>3\sigma$ (X=average, probability of xi with $|xi-X|>3\sigma$ is 0.27%).

Filtering peak:
 Filtering signal peaks of specific element for the active analysis.

Recover filtering:
 Recovering the filtered signals to the original state for the specific element.



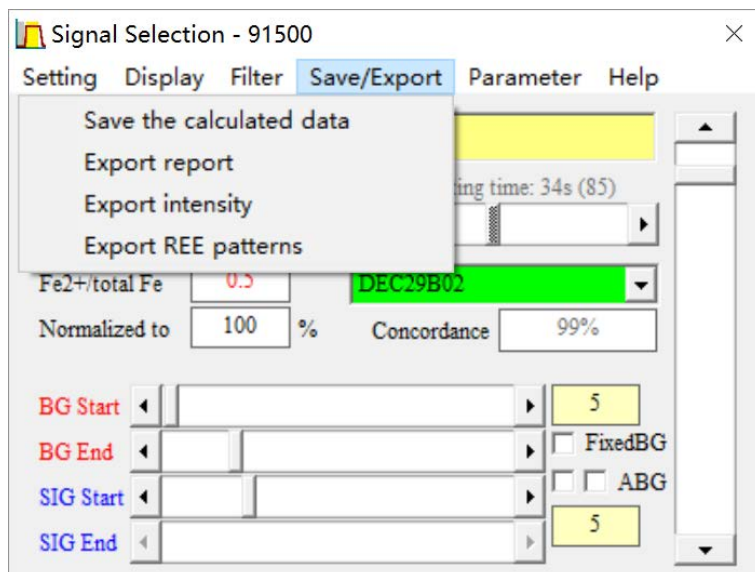
2.3.4. Save/Export

Save the calculated data: Saving the calculated data, which can be changed later;

Export report:
 Exporting data of ages and/or element contents;

Export intensity:
 Exporting the calculated signal intensity data;

Export REE patterns: Saving the REE patterns as an Excel file.



2.4. The “Multi-standard Calibration” window

External calibration curves can be checked and reset (if needed) in the “Multi-standard Calibration” window. Comments for the selected element could be inputted in the yellow box (e.g., Good data), which will be shown in the final report.

As a required option, one element (e.g., Si29) must be set as a normalizing element or internal standard by check box of Used as normalizing (internal standard) element.

For LA-ICP-MS data, unit of elements in the final report can be set as wt% (major element) or ppm (trace element) using the list box of “Major/Trace”. For Sol-ICP-MS data, data calibration style can be set using the list box of “Count/Concentration”.

External calibrations for element contents:

- ✧ *No Calibration*, no additional external calibration is applied;
- ✧ *Experiential Correct*, manually modifying the slope and intercept of external calibration curves;
- ✧ *Simple Linear Fit*, calculating the external calibration curves by simple linear fitting;
- ✧ *Content-weighted*, calculating the external calibration curves by concentration-weighted linear fitting.

✧ *Time-drift correction*, Correct time-dependent mass discrimination.

✧ “Standard list box” lists all the analyzed reference materials, used as the default external calibration standards. The following five operations can be done on these reference materials:

- ✧ *Delete one STD of one element*, Remove the selected element of the selected reference material;
- ✧ *Add one STD of one element*, Recover the selected element of the selected reference material;
- ✧ *Delete one STD completely*, Remove the selected reference material;
- ✧ *Add all STD of one element*, Recover all reference materials for the selected

element;

✧ *Recover to default*, Recover to the default setting.

2.4.1. TRAanalysis

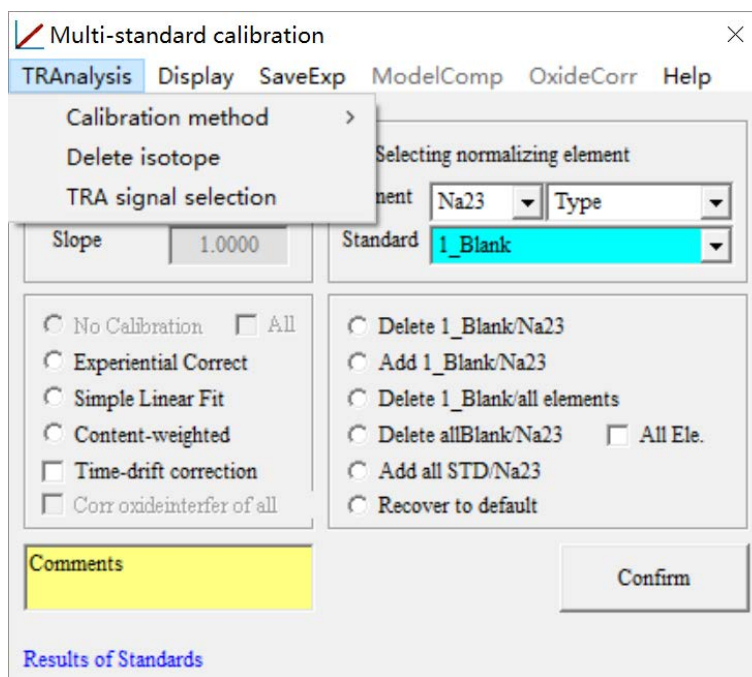
✚ *Calibration method*,

set the calibration strategy as you want (MRMC-AYC = Calibration against multiple reference materials without using an internal standard, MRMC-ISN = Calibration against multiple reference materials with internal standard normalization and

SimpMRMC = Simple calibration against multiple reference materials). The default option is ES-AYCF Calibration! SimpMRMC is designed for MC-ICP-MS.

✚ *Delete isotope/Add isotope*, deleting/adding the selected isotope, which is specifically designed for MRMC-AYC calibration. One isotope for one element must be used for MRMC-AYC calibration. The unwanted isotopes must be deleted by “Delete isotope”.

✚ *TRA signal selection*, go back to the “Signal Selection” window.



2.4.2. Display

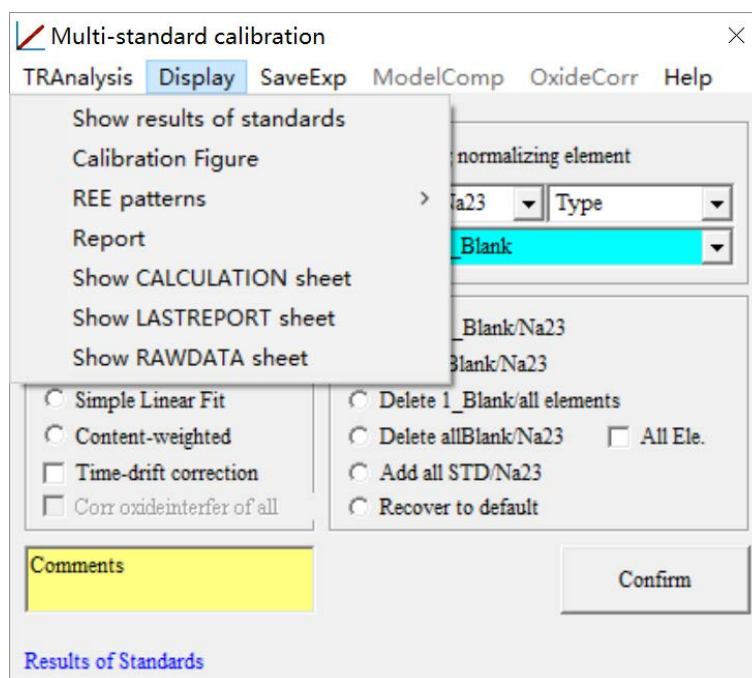
✚ *Show results of standards*, show the final results of the selected element for all analyzed standards, which is specifically designed for solution-ICP-MS analysis.

✚ *Calibration Figure*, showing the calibration figure

🌈 **REE Patterns**, showing the REE patterns of all analyses.

“Hide analysis/Show analysis” under the <**REE Patterns**>, showing/hiding the REE pattern of analysis selected in the blue list box (e.g., MAY07B16).

🌈 **Report**, showing the final data.



2.4.3. SaveExp

🌈 Same as 2.3.4.

2.4.4. ModelComponent

This is specially designed for LA-ICP-MS analysis and calibration with method of MRMC-AYC to set the model component type of the analyzed minerals (e.g., silicate, carbonate, sulfide).

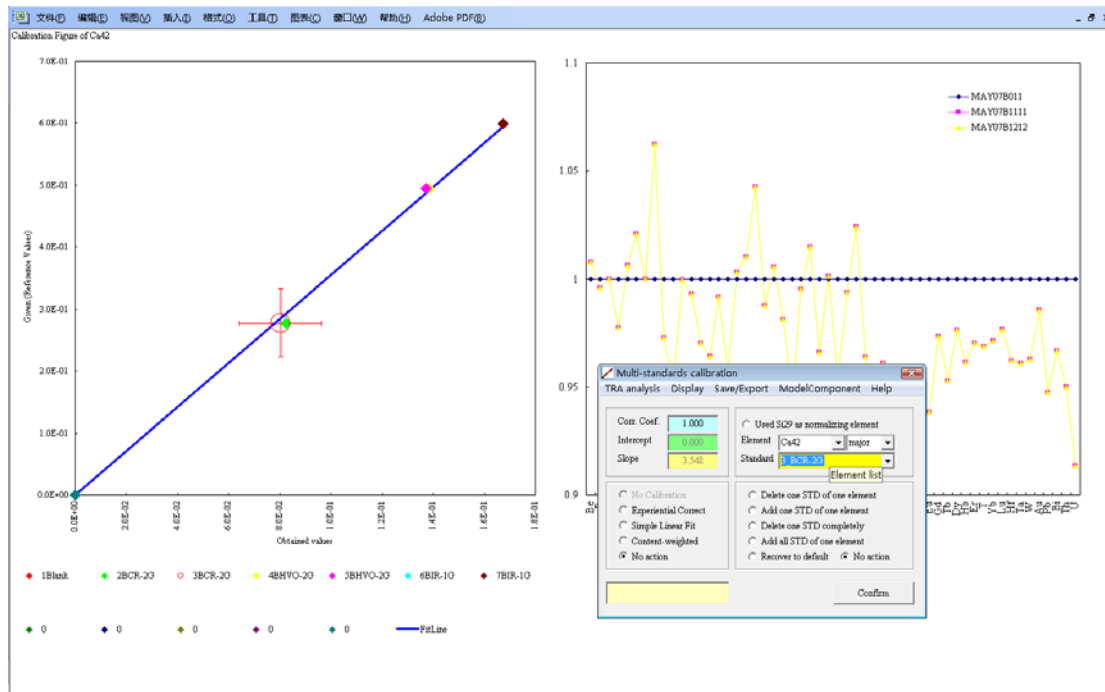
3. Getting started

3.1. Element content calibration of TRA

ICPMSDataCal provides two calibration methods for element contents: (1) multiple-reference material calibration combined with internal standardization (MRMC-IS), and (2) multiple-reference material calibration combined with ablation yield correction (MRMC-AYC). Sample type or model component must be correctly set for MRMC-AYC. Detection limits of element analysis (LOD) by LA-ICP-MS are calculated using the following equation:

$$LOD = 3 \cdot \sigma_{background}^i \times \frac{C_{RM}^i}{cps_{RM}^i}$$

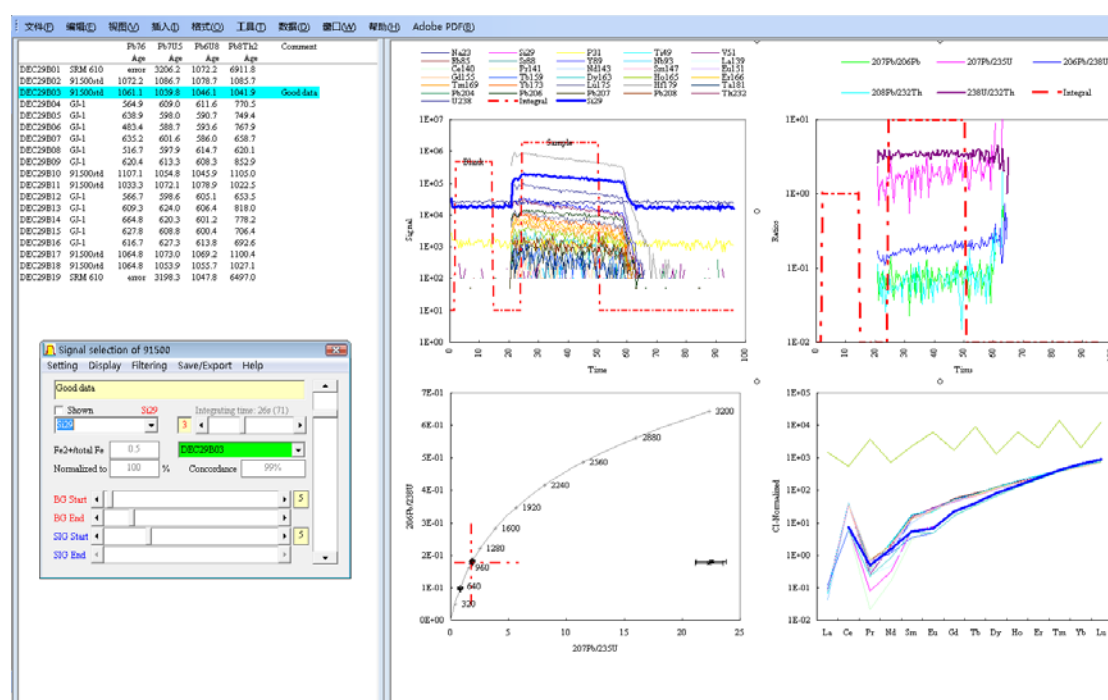
Element contents can then be calculated and checked in the window of “Multi-standards calibration” (section 2.4.) after finishing the selection of signal integration interval.



3.2. Zircon U-Th-Pb dating & element content analysis

The significant U-Pb fractionation necessitates selecting the same part of the signal (relative to the rise-time of the signal) for standard analyses and unknowns, which is set as a default option by ICPMSDataCal. The detailed description of calibration strategy of isotopic fractionation and uncertainty propagation were reported by Liu et al. (2010a).

3.2.1. Setting of U-Th-Pb isotopic dating



Time-resolved signal and ratio variations, calculated isotope ratios, age estimates and age uncertainty estimates are displayed in this window. The position of the analyses on the Concordia diagram and REE pattern plot is also shown.

The position and integrating length of the background and sample signals can be easily changed. If the integrating length was set to be fixed, the start position of sample signals can only be changed, and the total integrating length can be set by “Integrating time” slider bar. If signals of one analysis of reference zircon for correcting isotopic fractionation are probably wrong, it can be easily deleted in the dialog box of “*Isotopic ratio setting*”. Common Pb can also be corrected using the counts of ^{204}Pb by this software, which is generally useful for the high ^{204}Pb sample (e.g., titanite). Common Pb correction using ^{204}Pb could cause large uncertainty for the low ^{204}Pb sample, and thus is not recommended. Common Pb of low ^{204}Pb sample can be corrected using ComPbCorr (Andersen, 2002, Chem Geol).

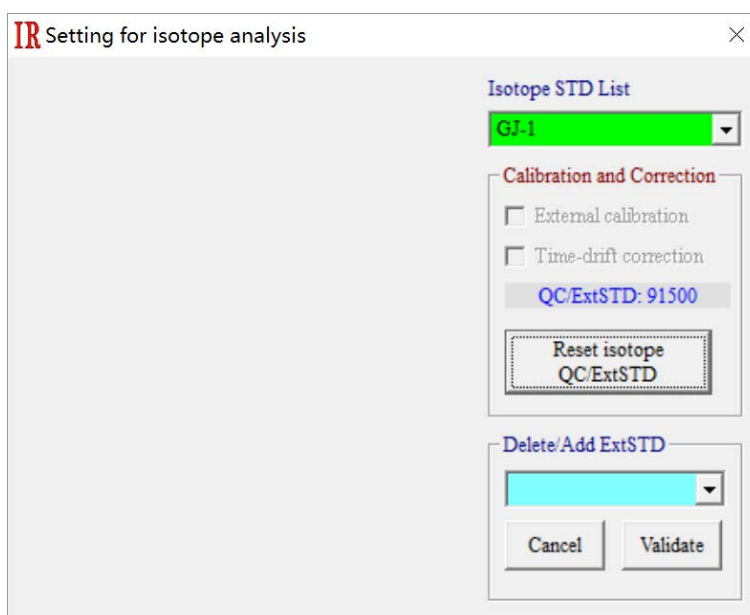
3.2.2. Correcting U-Th-Pb isotopic fractionations

Calibration and Correction:

- ✚ **External Calibration:** External calibration against the selected standard if it is checked.
- ✚ **Time-drift correction:** Time-dependent drift of mass discrimination is correct if it is checked;
- ✚ **Rest isotope QC/ExtSTD:** Reset the standard used for external calibration and time-drift correction;
- ✚ **Cancel/Validate:** Delete or add the selected QC standard in the blue box.

Delete/Add ExtSTD:

Reference zircon (e.g., 95100 or GJ-1) used for correcting isotopic fractionation can be freely changed using the list box of Zircon Standards. As the default, all analyses of the selected reference zircon are used in correcting isotopic fractionation. Anyone analysis of the reference zircon can be deleted (added) using the button of Cancel (Validate).

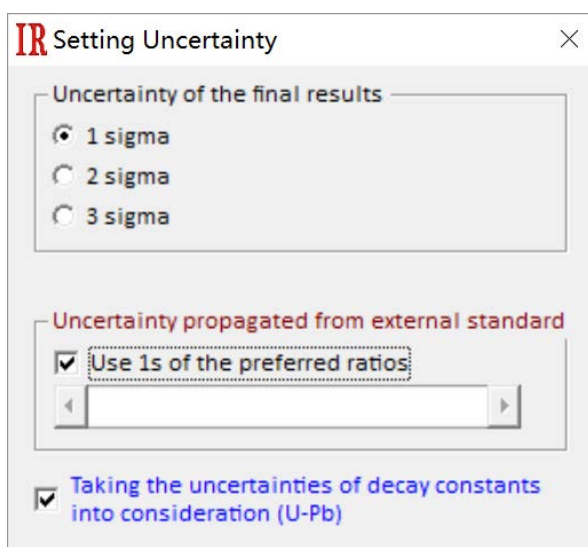


Common Pb Correction:

Correcting the common Pb using the measured Pb^{204} , Hg^{201} or Hg^{202} . The common Pb compositions can be manually changed or theoretically calculated (default setting).

Setting Uncertainty:

Uncertainty of preferred values for the external standard propagated to the ultimate results of the samples can be changed using the slide bar of Uncertainty of external standard. 1σ values of the preferred ratios are used as default.



3.2.3. Element content analysis in U-Th-Pb isotopic dating

[Please see section 3.1.](#)

3.2.4. Export data of U-Th-Pb isotopic dating

[Please see section 2.3.4.](#)

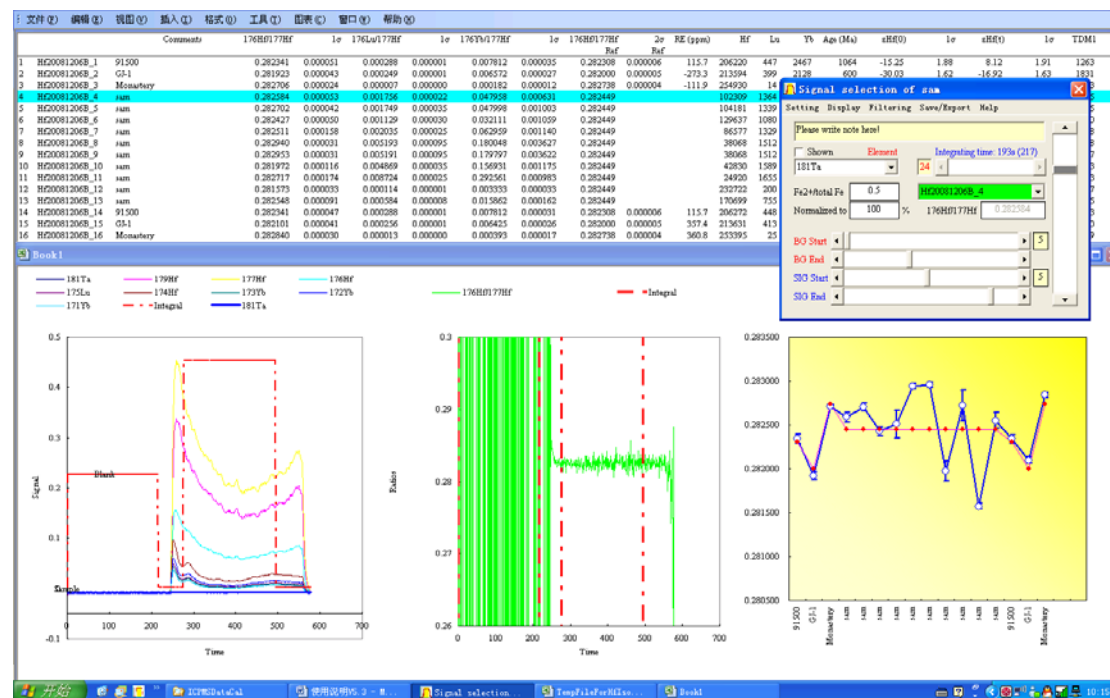
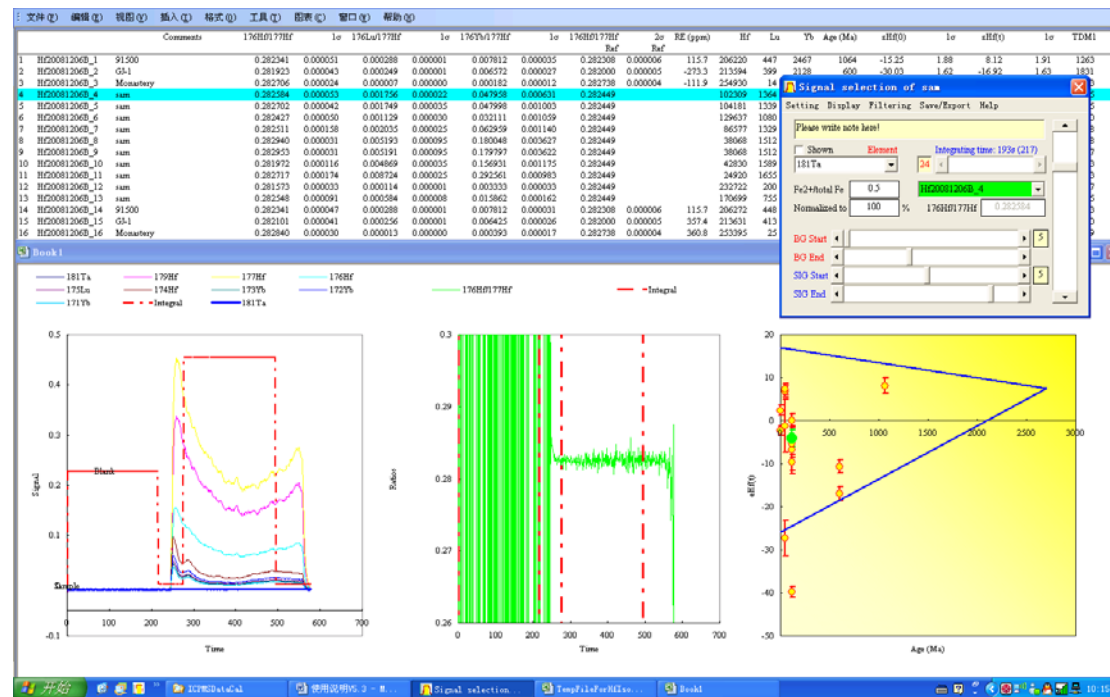
Standard bracketing and linear fitting of adjacent standards are applied to correct the isotopic fractionation by this software. If the external standard was analyzed once (≥ 2 analyses were suggested) before and after the samples, the age results of the external standards will be always the preferred values. Thus, it is suggested to set the signal integrating intervals of external standards (e.g., 91500) according to the signal variations rather than the calculated ages.

In addition to the U-Th-Pb isotopic ratios, ages and element contents, error correlation coefficients used for plotting Concordia diagram were also given in the final report.

3.3. Hf isotopic analysis of zircon

3.3.1. Signal selection for zircon Hf isotopic analysis

Signal selection for zircon Hf isotopic analysis is the same as U-Th-Pb isotopic dating and element analysis (Section 3.2.). The following two windows can be easily changed using the display menu of “Signal selection”. Ages of bulk continental BCC and DM in the figure of Age- $\epsilon_{\text{Hf}}(t)$ can be reset by “Reset the ages of BCC and DM”.



3.3.2. Correction of Hf isotopic fractionation

✚ **Method for obtaining FF (Hf):** three methods can be used to calculate the fractionation factor of Hf isotopes. *Using synchronous FF:* FF of each sample is calculated according to the measured isotopes of Yb, Lu and Hf of the sample itself. *Measured by STD:* FF calculated according to one zircon standard (e.g., 91500) are used to correct isotopic fractionation of Hf. Effective signal length and ablation rate, and thus mass discrimination caused by laser ablation may vary from one sample to another. Therefore, it is not suggested to

Setting for isotope analysis

Fractionation factor of measured element (FF)		
	91500 Ave	NOV23B03
179Hf/177Hf	-0.4417	-0.3308
173Yb/171Yb	-0.9070	-0.5763

Method for obtaining FF (Hf)

☒ Using synchronous FF
☐ Using average FF
☐ Measured by STD

Method for obtaining FF (YbLu)

☒ Using synchronous FF
☐ Measured by pure STD

☐ ignore 176Yb/176Lu interferences on 176Hf

Isotope STD List

91500

Calibration and Correction

☐ External calibration
☐ Time-drift correction

QC/ExtSTD: 91500

Reset isotope QC/ExtSTD

Delete/Add ExtSTD

Cancel Validate

use the FF calculated according to zircon standard unless Yb and Lu contents of the sample are too low to correctly calculate FF.

✚ **Method for obtaining FF (YbLu):** two methods can be used to calculate the fractionation factors of Yb and Lu isotopes. *Measured by pure STD:* FF of Yb and Lu can be obtained by measuring Lu-Hf-free and Yb-Hf-free samples.

✚ **Calibration and Correction** and **Delete/Add ExtSTD** are the same as section 3.2.2.

The detector settings of different MC-ICP-MS instruments are different. Isotope sequence analyzed by the specific instrument should be correctly set in the following file for Hf isotopic analysis with Nu instrument,

“...\ICPMSDataCal\PersonalizedSetting\AnalyzedElementHf.txt”

Exponential rule is used for correcting Lu-Hf isotopic fractionations. Interferences of ^{176}Lu and ^{176}Yb on ^{176}Hf are corrected according to the recommended $^{176}\text{Lu}/^{175}\text{Lu}$ (0.02656, Blichert-Toft et al., 1997, CMP) and $^{176}\text{Yb}/^{173}\text{Yb}$ ratios (0.7876, McCulloch et al. 1977, GCA) and measured signals of ^{175}Lu and ^{173}Yb . The detailed description of calibration strategy of isotopic fractionation and uncertainty propagation were reported by Liu et al. (2010, J. Petrol.).

$$R_{\text{true}} = R_{\text{measured}} * \left(\frac{M2}{M1} \right)^f \Rightarrow \log \left(\frac{R_{\text{true}}}{R_{\text{measured}}} \right) = f * \log \left(\frac{M2}{M1} \right) \Rightarrow f = \frac{\log \left(\frac{R_{\text{true}}}{R_{\text{measured}}} \right)}{\log \left(\frac{M2}{M1} \right)}$$

$$R_{\text{true}}^{^{179}\text{Hf}/^{177}\text{Hf}} = 0.7325 (\text{Blichert - Toft et al., 1997}), \quad \frac{M179}{M177} = 1.011318$$

$$R_{\text{true}}^{^{173}\text{Yb}/^{171}\text{Yb}} = 1.1248 (\text{Blichert - Toft et al., 1997}), \quad \frac{M173}{M171} = 1.011711$$

$$R_{\text{true}}^{^{172}\text{Yb}/^{171}\text{Yb}} = 1.5264 (\text{Blichert - Toft et al., 1997}), \quad \frac{M172}{M171} = 1.005851$$

$$R_{\text{true}}^{^{176}\text{Yb}/^{173}\text{Yb}} = 0.7876 (\text{McCulloch et al., 1977, GCA})$$

$$R_{\text{true}}^{^{176}\text{Lu}/^{175}\text{Lu}} = 0.02656 (\text{Blichert - Toft et al., 1997, CMP})$$

Table 6 Hf isotopic composition values for JMC 475 from the literature and this study

	Patchett ³¹ (ID-TIMS) ^a		Blichert-Toft <i>et al.</i> ^{6b}	Kleinmanns <i>et al.</i> ³³	This study (± 2 sd)		This study (± 2 sd)	
	IUPAC (1998)	n	TIMS/P54	(Nu Plasma)	(IsoProbe)	n	(Nu Plasma)	n
$^{174}\text{Hf}/^{177}\text{Hf}$	0.008710 ± 50	25	N/A		0.008674 ± 32	41	N/A	
$^{176}\text{Hf}/^{177}\text{Hf}$	0.282195 ± 15	25	0.28216	0.282169 ± 16	0.282163 ± 26	79	0.282159 ± 38	20
$^{178}\text{Hf}/^{177}\text{Hf}$	1.467100 ± 100	25	1.467168	1.467290 ± 80	1.467417 ± 232	79	1.467304 ± 147	20
$^{179}\text{Hf}/^{177}\text{Hf}$	0.732500		0.732500		0.732500		0.732500	
$^{180}\text{Hf}/^{177}\text{Hf}$	1.886510 ± 120	25	1.886666	1.88680 ± 30	1.886765 ± 290	75	1.886683 ± 625	20

^aThe author has suggested a baseline interference by Re and some values may not be final. ^bN

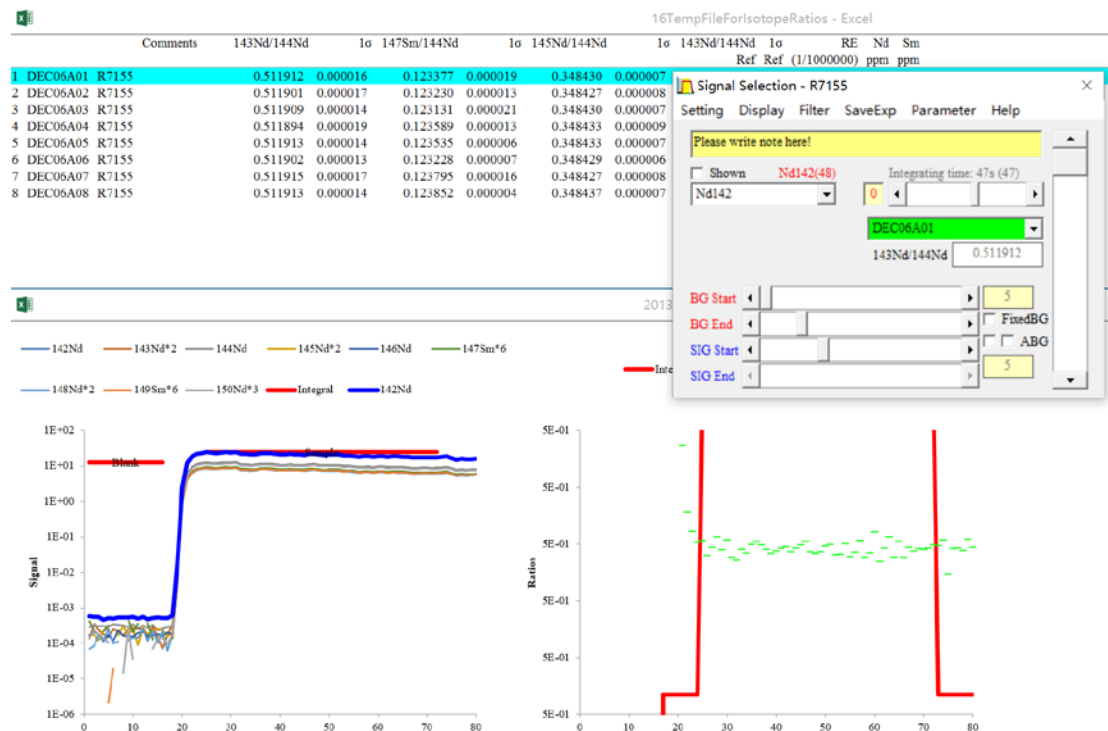
Hf isotope ratio analysis using multi-collector inductively coupled plasma mass spectrometry: an evaluation of isobaric interference corrections

Table 7 Yb isotopic composition values

	TIMS/P54 ^{6,9}	IUPAC (1998) ²⁴	This study ± 2 sd (TIMS)	n	This study (IsoProbe)	n
$^{168}\text{Yb}/^{171}\text{Yb}$	0.00951	0.00889	0.008865 ± 22	2	0.008845 ± 63	19
$^{170}\text{Yb}/^{171}\text{Yb}$	0.2137	0.21289	0.212645 ± 6	2	0.212531 ± 49	19
$^{172}\text{Yb}/^{171}\text{Yb}$	1.5264	1.52871	1.532075 ± 272	6	1.532227 ± 75	19
$^{173}\text{Yb}/^{171}\text{Yb}$	1.1248	1.12955	1.132685		1.132685	
$^{174}\text{Yb}/^{171}\text{Yb}$	2.2163	2.22899	2.242466 ± 160	6	2.242716 ± 266	19
$^{176}\text{Yb}/^{171}\text{Yb}$	0.8859	0.89356	0.901821 ± 189	4	0.901864 ± 508	19
$^{176}\text{Lu}/^{175}\text{Lu}$	0.02656	0.026512	0.026549		N/A	

3.4. Nd isotopic analysis

Signal selection for Nd isotopic analysis is the same as U-Th-Pb isotopic dating and element analysis (Section 3.2.), as shown following.

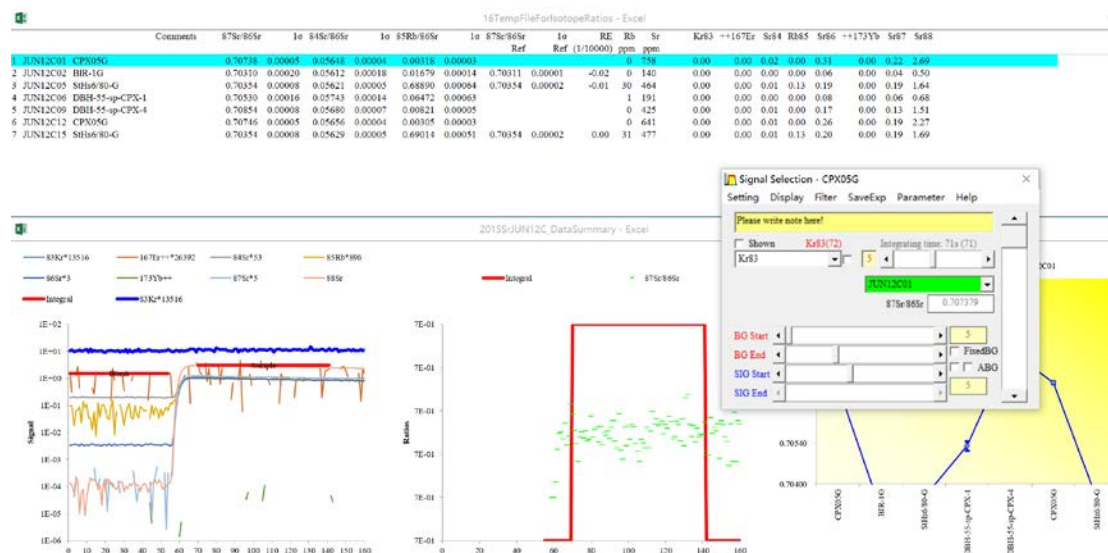


Method for correcting Nd isotopic fractionation was reported by Xu et al. (2015). The dialog box of correcting isotopic fractionation is the same as section 3.3.2, as shown following.

The figure shows the 'IR Setting for isotope analysis' dialog box. It includes sections for 'Fractionation factor of measured element (FF)', 'Method for obtaining FF (Nd)', 'Method for obtaining FF (Sm)', and 'Isotope STD List'. The 'Fractionation factor of measured element (FF)' section shows the 'Ave' method selected for '146Nd/144Nd' and '147Sm/149Sm' ratios. The 'Method for obtaining FF (Nd)' section shows 'Using synchronous FF' selected. The 'Method for obtaining FF (Sm)' section shows 'Using synchronous FF' selected. The 'Isotope STD List' section shows the 'DEC06A01' signal selected. The 'Calibration and Correction' section has checkboxes for 'External calibration' and 'Time-drift correction'. The 'Delete/Add ExtSTD' section has a dropdown menu and 'Cancel' and 'Validate' buttons.

3.5. Sr isotopic analysis

Signal selection for Sr isotopic analysis is the same as U-Th-Pb isotopic dating and element analysis (Section 3.2.), as shown following.



The detailed methods for correcting Sr isotopic fractionation and interference of Rb on Sr were reported by Tong et al. (2016). The dialog box of correcting isotopic fractionation is similar to section 3.3.2, as shown following. Fractionation factor of Rb for interference correction can be obtained by two methods: (1) obtained by separately measuring pure Rb sample (e.g., Rb solution), or (2) calculated or measured using an external standard.

IR Setting for isotope analysis

Fractionation factor of measured element (FF)

	StHs6/80-G	JUN12C01
88Sr/86Sr	-1.3205	-1.3262
87Rb/85Rb	-1.4678	-1.4750

Method for obtaining FF (Sr)

☒ Using synchronous FF
☐ Using average FF
☐ Measured by STD

☐ LinearFit
☐ Average

Method for obtaining FF (Rb | StHs6/80-G)

☐ Measured by pure STD
☒ Calculated using RM

☐ FF
☒ Ratio

☐ LinearFit
☐ Average

☐ Ignore 87Rb interferences on 87Sr

Isotope STD List

StHs6/80-G

Calibration and Correction

☐ External calibration
☐ Time-drift correction

QC/ExtSTD: StHs6/80-G

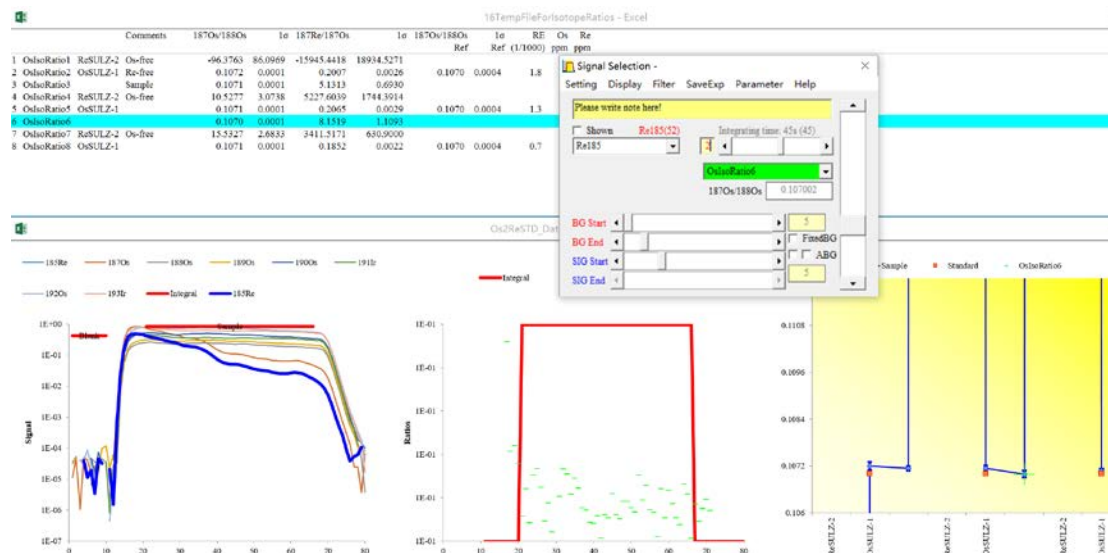
Reset isotope QC/ExtSTD

Delete/Add ExtSTD

Cancel Validate

3.6. Os isotopic analysis

Signal selection for Sr isotopic analysis is the same as U-Th-Pb isotopic dating and element analysis (Section 3.2.), as shown following.

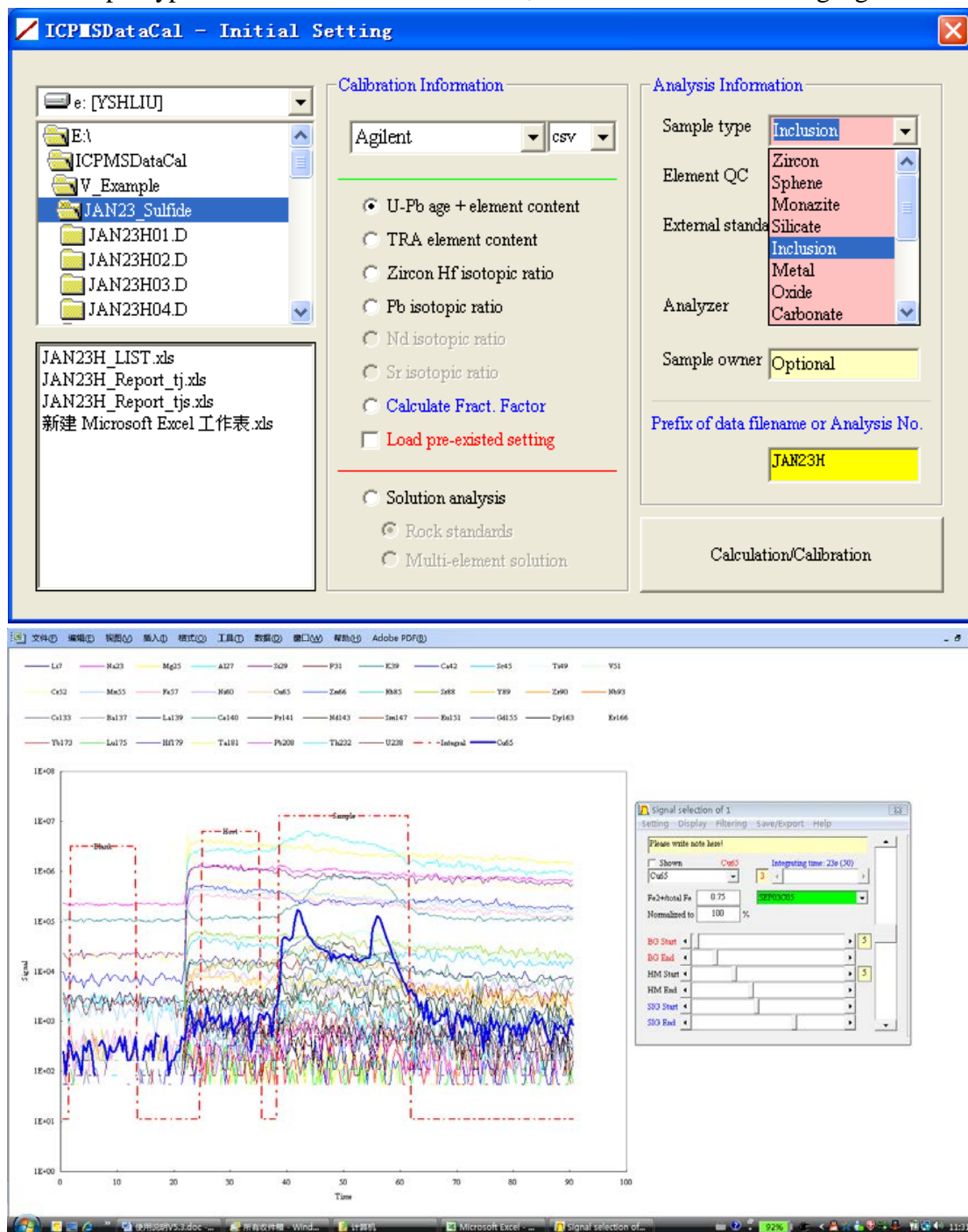


The detailed methods for correcting Sr isotopic fractionation and interference of Rb on Sr were reported by Zhu et al. (2016). The dialog box of correcting isotopic fractionation is similar to section 3.3.2, as shown following. Fractionation factor of Re for interference correction can be obtained by two methods: (1) obtained by separately measuring pure Re sample (e.g., Re solution), or (2) calculated or measured using an external standard.

The screenshot shows the 'IR Setting for isotope analysis' dialog box. It contains several sections for configuring the analysis. The 'Fractionation factor of measured element (FF)' section shows values for '189Os/188Os' (8.8588) and '187Re/185Re' (Error). The 'Method for obtaining FF (Os | OsSULZ-1)' section has three options: 'Using synchronous FF', 'Using average FF', and 'Measured by STD' (selected). The 'Method for obtaining FF (Re | ReSULZ-2)' section has two options: 'Measured by pure STD' and 'Calculated using RM' (selected). The 'Isotope STD List' section shows 'ReSULZ-2' selected. The 'Calibration and Correction' section has two checkboxes: 'External calibration' and 'Time-drift correction'. The 'Delete/Add ExtSTD' section has a dropdown menu and 'Cancel' and 'Validate' buttons. The 'Reset isotope QC/ExtSTD' button is also present.

3.7. Data reduction of melt, fluid and mineral inclusion

Sample type must be set to be “Inclusion”, as shown in the following figure.



3.7.1. Signal selection of melt inclusion analysis

In addition to setting integration intervals of BG and inclusion, integration

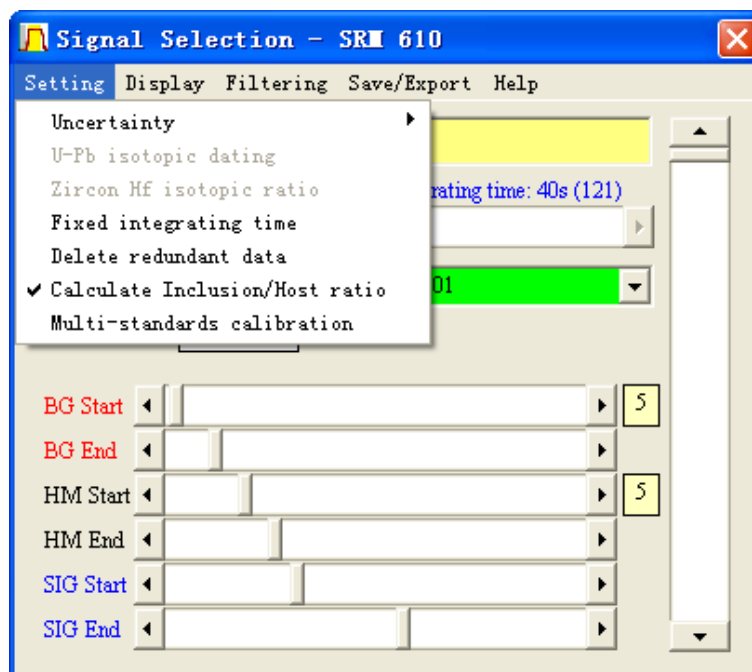
interval of the host mineral is required to be selected in the dialog box of signal selection for melt inclusion analysis (Section 3.4.2).

3.7.2. Calibration of element contents in inclusions

Setting for quantitative calculation of element contents in the inclusion could be done in the interface of “Calculate Inclusion/Host ratio”. (“Delete redundant data” could be used to delete the redundant data of host mineral.)

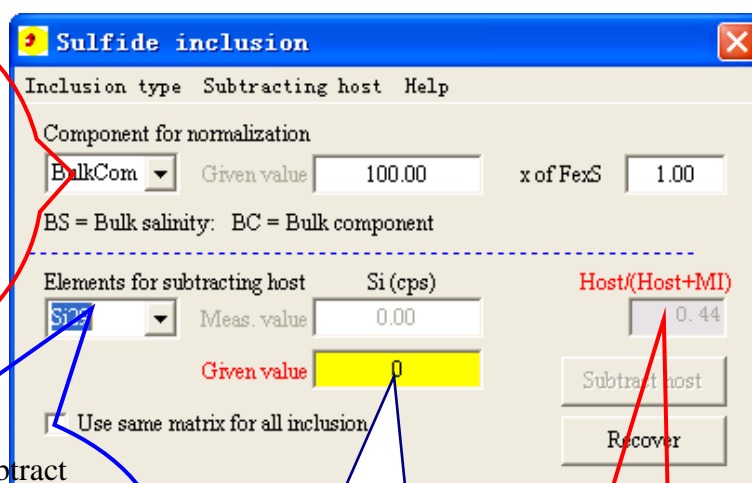
The inclusion type and subtracting host method must be firstly selected in the interface of “Calculate Inclusion/Host ratio”.

The contribution of host mineral could be subtracted using one of the following parameters: count of selected isotope, content or partition coefficient of one element, element ratio, $K_{dFe/Mg}$. If “Use same matrix for all inclusion” is checked, contribution of host mineral is subtracted applying a specific analysis of the host mineral for all inclusions.



Select internal standard (BulkSal = bulk salinity); MRM-AYC is used if BulkCom is selected.

If count is used to subtract the matrix, element with extremely low content in the inclusion should be selected.



Theoretical or measured value.

Proportion of the host mineral in the mixture.

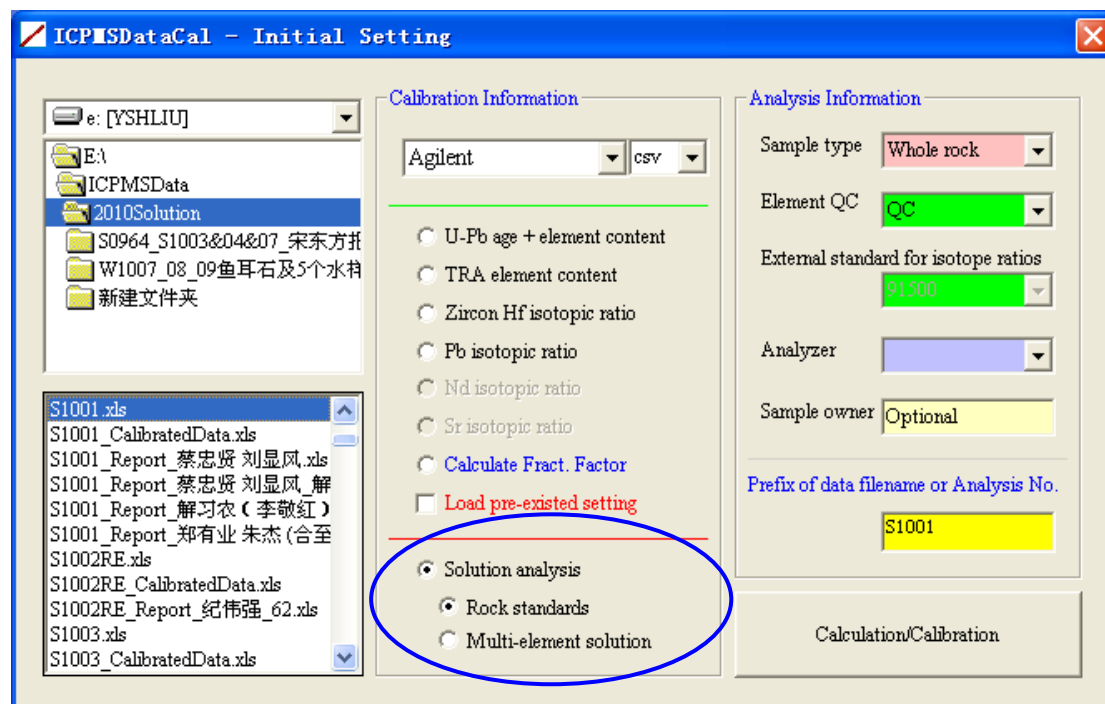
- If content of one element is used to subtract the contribution of host mineral, normalization method must be firstly set to be **BulkCom** (i.e., “MRMC-AYC”), which is mainly suitable for mineral and melt inclusions;
- If the content of one element in the inclusion is very low but high in the host mineral, contribution of the host mineral could be subtracted assuming the content of this element (or count of one isotope of the element) in the inclusion is zero, which is suitable for all kinds of inclusions;
- Partition coefficient of one element and element ratio is suitable for subtracting contribution of host mineral for all kinds of inclusions;
- $K_{d_{Fe/Mg}}$ is suitable for subtracting contribution of host mineral for the basaltic melt inclusions, and $K_{d_{Fe/Mg}}$ values are generally set to be 0.3 ± 0.03 .

Metal element contents in the melt or mineral inclusions can be quantitatively determined by internal standard normalization (MRMC-ISON) or ablation yield correction (MRMC-AYC)(BulkCom) methods. If MRMC-AYC method is used, Fe^{2+}/TFe ratio (x value of Fe_xS for sulfide) must be given. Metal element contents in the fluid inclusion can only be determined by internal standard (IS) method. IS could be one element or the bulk salinity (BulkSal).

Please see [section 2.4](#) for multiple-reference material calibration, data checking and final data exporting/saving.

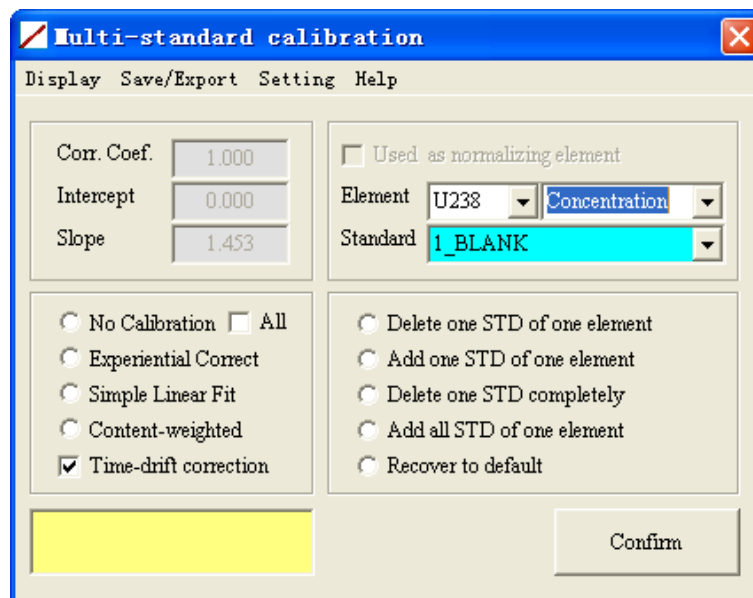
The element compositions of single fluid inclusion were determined according to the bulk salinity using the method of Heinrich *et al.*(2003). The bulk salinity is assumed to be the sum of all metal chlorides. The equivalent bulk salinity is calculated according to the following equation: $NaCl$ equivalent wt.% = $C_{NaCl} + 0.5 * [C_{KCl} + C_{FeCl_2} + C_{CaCl_2} + \dots]$ (Heinrich *et al.*, 1992).

3.8. Calibration of solution-ICP-MS analysis data



Rock standards: calibration against multiple external rock standards (e.g., BHVO-2, AGV-2 and RGM-2); **Multi-element solution:** calibration against in-house standard solutions. Please input the right name of Element QC if “QC” is not used.

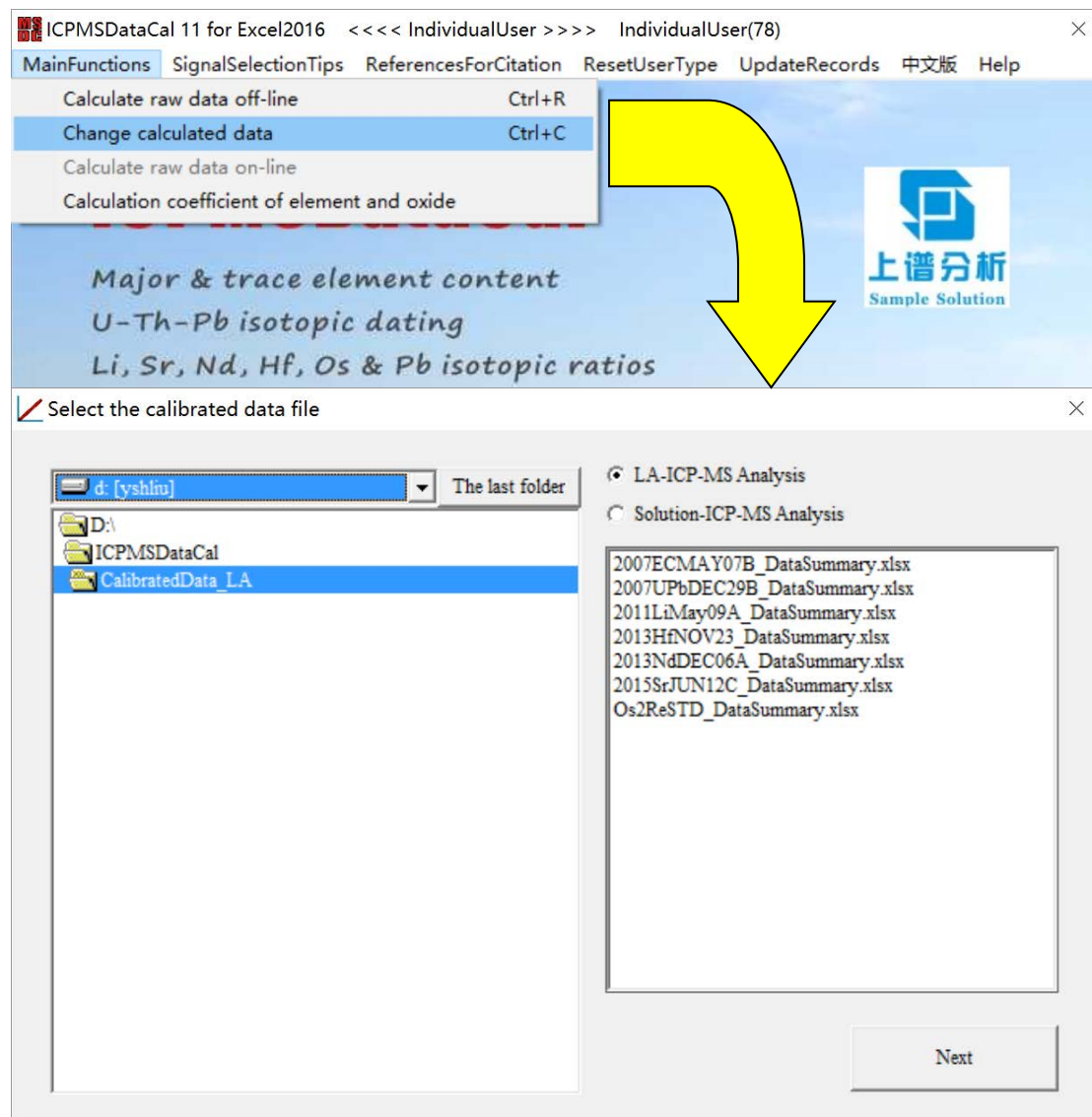
- At a click of the “Calculation/Calibration” button, correcting time-dependent sensitivity-drift, calculating/calibrating element contents and drawing REE and SPIDER diagrams will be conducted automatically.



- Check the calibration line of each element. (See [section 2.4.](#))
- Save or export the final report. (See [section 2.4.3.](#)).

3.9. Change the saved calculated data

The saved calculated data can be revised by the following methods: Select “Change calculated data” in the “Main Functions” menu of ICPMSDataCal window.



3.10. On-line calibration of LA-ICP-MS data



Select “Calculate raw data on-line” in the “Main Functions” menu of ICPMSDataCal window. The LA-ICP-MS raw data can then be checked and calibrated “on-line” if the software is installed in the computer controlling the ICP-MS.

In the mode of “Calculate raw data on-line”, the raw data of each analysis can be loaded by click the “Load Data” button in the window of “Signal Selection” (**The complete analysis sequence must be built before loading the raw data!**). The other initial setting and operation is the same as [section 3](#).

4. Maintenance and personalized setting

- Add more instrument:

“.....\ICPMSDataCal\CommonParameters\ICPMSInstrument.txt”

- Add sample type:

“.....\ICPMSDataCal\CommonParameters\SampleType.txt”

- Add laboratory assistant:

“.....\ICPMSDataCal\PersonalizedSetting\Analyzer.txt”

- Add isotope standard:

“.....\ICPMSDataCal\PersonalizedSetting\IsotopeStandard.txt”

- Revise the sequence of analyzed isotopes by Nu instrument for Hf isotopic analysis:

“.....\ICPMSDataCal\PersonalizedSetting\ AnalyzedElementHf.txt”

- Revise the length of datafile prefix (e.g., FEB26A) for LA-ICP-MS/Sol-ICP-MS analysis

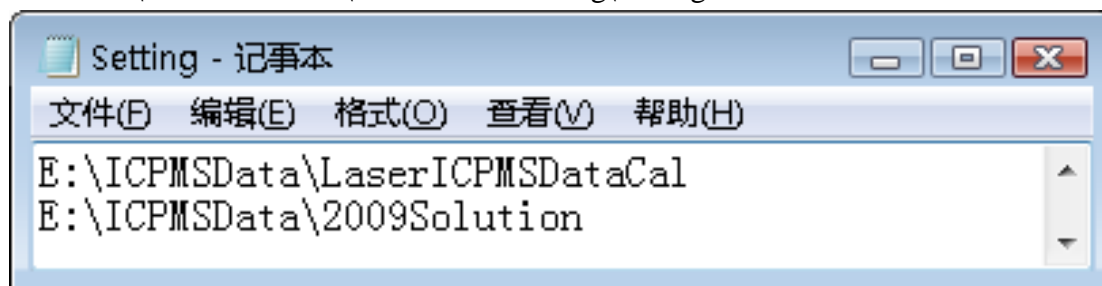
“.....\ICPMSDataCal\PersonalizedSetting\DataFileNameSetting.txt”

- Add standard for element content or element of standards:

“.....\ICPMSDataCal\CommonParameters\InternationalMaterials_RCV.txt”

	A	B	C	D	E	F	G	H	I
1	Note	Note	Type	Ref/Is	Name1	Name2	Si	Si(wt%)	SiO2(wt%)
2									
3	Blank	Solution	Element	Ref	BLANK	Blank	0	0	0
4	Andesite	Solution	Element	Ref	AGV-1	AGV1	275077	27.5077	58.84
5	Andesite	Solution	Element	Is	AGV-1	AGV1			0.58
6	Andesite	Solution	Element	Ref	AGV-2	AGV2	277000	27.7	59.3
7	Andesite	Solution	Element	Is	AGV-2	AGV2		0.35	0.7
8	Basalt, Hav	Solution	Element	Ref	BHVO-1	BHVO1	233469.5	23.34695	49.94
9	Basalt, Hav	Solution	Element	Is	BHVO-1	BHVO1			0.54
110	Blank	Laser	Element	Ref	Blank	BLANK	0	0	0
111	Glass	Laser	Element	Ref	BCR-2G	BCR2G	254320		54.4
112	Glass	Laser	Element	Is	BCR-2G	BCR2G	1870		0.4
113	Glass	Laser	Element	Note	BCR-2G	BCR2G			
114	Glass	Laser	Element	Ref	BHVO-2G	BHVO2G	230477.5		49.3
115	Glass	Laser	Element	Is	BHVO-2G	BHVO2G	467.5		0.1
116	Glass	Laser	Element	Note	BHVO-2G	BHVO2G			IV
117	Glass	Laser	Element	Ref	BIR-1G	BIR1G	222062.5		47.5

- Revise the default folder for saving the calculated file:
“.....\ICPMSDataCal\PersonalizedSetting\Setting.txt”



- Customize the content of final report:
“.....\ICPMSDataCal\PersonalizedSetting\LaboratoryInformation.txt”
If a specific report format is required, please contact with the author.

References

1. Andersen T., 2002. Correction of common lead in U-Pb analyses that do not report ²⁰⁴Pb. *Chemical Geology*, 192: 59-79.
2. Chen L., Liu Y.S., Hu Z.C., Gao S., Zong K.Q., Chen H.H., 2011. Accurate determinations of fifty-four major and trace elements in carbonate by LA-ICP-MS using normalization strategy of bulk components as 100%. *Chemical Geology*, 284(3-4): 283-295.
3. Gao C.G., Liu Y.S., Zong K.Q., Hu Z.C., Gao S., 2010. Microgeochemistry of rutile and zircon in eclogites from the CCSDB main hole: Implications for the fluid activity and thermo-history of the UHP metamorphism. *Lithos*, 115(1-4): 51-64.
4. Heinrich C.A., Pettke T., Halter W.E., Aigner-Torres M., Audétat A., Günther D., Hattendorf B., Bleiner D., Guillong M., Horn I., 2003. Quantitative multi-element analysis of minerals, fluid and melt inclusions by laser-ablation inductively-coupled-plasma mass-spectrometry. *Geochimica Et Cosmochimica Acta*, 67(18): 3473-3497.
5. Heinrich C.A., Ryan C.G., Mernagh T.P., Eadington P.J., 1992. Segregation of ore metals between magmatic brine and vapor-A fluid inclusion study using pixel microanalysis. *Econ. Geol.*, 87(6): 1566-1583.
6. Hu Z., Liu Y., Gao S., Liu W., Zhang W., Tong X., Lin L., Zong K., Li M., Chen H., Zhou L., Yang L., 2012. Improved in situ Hf isotope ratio analysis of zircon using newly designed X skimmer cone and jet sample cone in combination with the addition of nitrogen by laser ablation multiple collector ICP-MS. *Journal of Analytical Atomic Spectrometry*, 27(9): 1391-1399.
7. Lin J., Liu Y., Yang Y., Hu Z., 2016. Calibration and correction of LA-ICP-MS and LA-MC-ICP-MS analyses for element contents and isotopic ratios. *Solid Earth Sciences*, 1(1): 5-27.
8. Liu Y., Hu Z., Gao S., Günther D., Xu J., Gao C., Chen H., 2008. In situ analysis of major and trace elements of anhydrous minerals by LA-ICP-MS without applying an internal standard. *Chemical Geology*, 257(1-2): 34-43.
9. Liu Y.S., Gao S., Hu Z.C., Gao C.G., Zong K.Q., Wang D.B., 2010a. Continental and oceanic crust recycling-induced melt-peridotite interactions in the Trans-North China Orogen: U-Pb dating, Hf isotopes and trace elements in zircons of mantle xenoliths. *Journal of Petrology*, 51(1&2): 537-571.
10. Liu Y.S., Hu Z.C., Zong K.Q., Gao C.G., Gao S., Xu J., Chen H.H., 2010b. Reappraisal and refinement of zircon U-Pb isotope and trace element analyses by LA-ICP-MS. *Chinese Science Bulletin*, 55(15): 1535-1546.
11. Tong X., Liu Y., Hu Z., Chen H., Zhou L., Hu Q., Xu R., Deng L., Chen C., Yang L., Gao S., 2016. Accurate Determination of Sr Isotopic Compositions in Clinopyroxene and Silicate Glasses by LA-MC-ICP-MS. *Geostandards and Geoanalytical Research*, 40(1): 85-99.
12. Xu L., Hu Z., Zhang W., Yang L., Liu Y., Gao S., Luo T., Hu S., 2015. In situ Nd

- isotope analyses in geological materials with signal enhancement and non-linear mass dependent fractionation reduction using laser ablation MC-ICP-MS. *Journal of Analytical Atomic Spectrometry*, 30(1): 232-244.
13. Xu R., Liu Y.S., Tong X.R., Hu Z.C., Zong K.Q., Gao S., 2013. In-situ trace elements and Li and Sr isotopes in peridotite xenoliths from Kuandian, North China Craton: Insights into Pacific slab subduction-related mantle modification. *Chemical Geology*, 354(0): 107-123.
 14. Zhang C.L., Liu Y.S., Gao S., Zoltan Z., Hu Z.C., Gao C.G., 2011. Chemical compositions of phenocryst-hosted melt inclusions from the Sihetun basalt: Implications for the magma evolution (in Chinese with English Abs.). *Geochimica*, 40(2): 109-125.
 15. Zhu L., Liu Y., Ma T., Lin J., Hu Z., Wang C., 2016. In situ measurement of Os isotopic ratios in sulfides calibrated against ultra-fine particle standards using LA-MC-ICP-MS. *Journal of Analytical Atomic Spectrometry*, 31(7): 1414-1422.