UranOS: data reduction program for time-resolved U/Pb analyses
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Introduction

Improving analytical performance and growing instrumental capacities result in a growing number of high quality U/Pb and Th/Pb data. They were produced on a number of different systems, employing various calibration strategies. The inherent need for a time-effective data handling calls for user-oriented and transparent solutions, which provide quick, flexible and well-documented software with reproducible outputs and regular updates to include actual consensus in the strategy of data handling and processing.

The ***purpose*** of this program is to perform the data reduction including (i) proper visualization of the spread of raw data, (ii) optimizing the selection of time slices (iii) filtering the outliers, (iv) correcting the mass fractionation and (v) the drift through measurement session. The outputs are data tables for age calculation and plotting with Isoplot (Ludwig, 2003) and/or other programs.

UranOS needs own installation and for the proper function some service and example files must be placed in different directories of a PC running under Windows or MAC OSX (+Parallels Desktop) operating system.

Here we give only a very short explanation for the functions and some aid for the quick start and evaluation of the program. It is under continuous development and we would like to propose an inter-laboratory discussion for its improvement and updates. We imagine a system that calculates data with statistical parameters, which match with the consensus and expectations of the community dealing with U/Pb geochronology.

1. Basic concept

The default values (e.g. isotope ratios, preferred graphical options, compositions of standards, expected output) are stored in so called **default files**. One is always loaded automatically at the start of the program (`UranOS-defaults.def`), but the user can open, modify and save different default files.

The program has two running modes: individual and sequential data processing; the user has to select one at start. Changing mode needs restarting the program. Using **individual data processing mode** the raw data files can be opened, the fractionation can be visualized, the data reduction can be performed and the results can be exported. However, using this mode the data files are processed without their context and the exported data are not suitable for age calculation. For example no drift and fractionation correction can be performed if the user studies only individual files. The individual processing can be useful at the learning phase, at the beginning of the usage of UranOS and also later for a quick check of some files, e.g. at tuning the mass spectrometer.

Using the program in **sequential processing mode** the user can process standard-sample-standard sequences. One directory should contain one complete measurement session. Here the data reduction is strictly governed and can be

performed in four steps. (1): creating a master file, (2): processing standard measurement files, (3): calculation of the drift and the fractionation factors for the sample files by interpolation and (4): processing of sample files considering drift corrections.

2. Installation, Quick start

UranOS needs to perform a setup procedure. The setup kit contains all necessary files, but it can be performed only with administrator rights. After setup the user must place the default and example files into the directory: "C:\ UranOS-Defaults". In the very unusual case, that there is no C: drive in the PC the user can place the default directory somewhere else, but in this case the exact path must be typed into the "`start_path_UranOS.txt`" file. Consider, please that this file is an unformatted text file and it contains exclusively the path in plain text format. There are also example files in the default directory; they derived from several ICP-MS laboratories performing routinely U/Pb geochronology using more than five different ICP-MS instruments.

The current version can open files up to 6000 time slices and max. 100 analytes. At the sequential processing data from 2000 files can be stored in the master file.

The "individual data processing" mode is recommended at the beginning of learning/using UranOS to study the basic functions. Try the sequential processing only when the basic functions of individual processing are obvious.

2.1. Individual processing of data files

The program opens always automatically an example file by pressing [Individual processing]. This quick way should help at learning & testing UranOS, because the user does not need to browse and open files - simply press [Next Step]. Beyond the promptly opened example file user can load another example file or an own data file by pressing [Browse and next step].

2.1.1. Open data - specifying import filter

After installation UranOS opens promptly data files of **`.csv`**, **.xl** and **`.txt`** extensions. The default file contains parameters for the opening of the supplied example files. If the user has data files with different format then the parameters of their format can be saved into a personalized user's default file. This function is available by the menu "Specify import filter for the data files" (see Fig. 1). In this way the user can practically open any kind of table-formatted ASCII data files without time consuming and very boring individual conversions.

Parameters describing the format of the data table are the following:

a): which line contains the name of isotopes?
b): which line contains the first time slice (cps data)?
c): which column contains the first isotope?
d): which column contains the time of acquisition?

The import filter has to be specified only once, at the beginning of the regular usage of the program with the own data of the user. It is practical to store files with different structure in different directories together with their default files.

UranOS identifies the following analytes 238U, 235U, 232Th, 208Pb, 207Pb, 206Pb, Pb 204, Hg198, Hg199, Hg200, Hg201 and Hg202. The following analytes are obligatory: 238U, 206Pb, 207Pb and 208Pb, the others are optional. The above listed analytes will be identified irrelevantly of their position in the data file. UranOS will

recognize isotopes written in any of the following ways: 238U, U-238, 238U, 238-U, 238U(LR) or 238U(HR). If the data file contains more Hg isotopes then the user is prompted to choose one of them to be plotted and used later for Hg-based correction procedures. The data file can be complex; UranOS calculates the average blank corrected cps and the blank also for the analytes, which are not used for age calculation (e.g. Zr, Ca or Si).
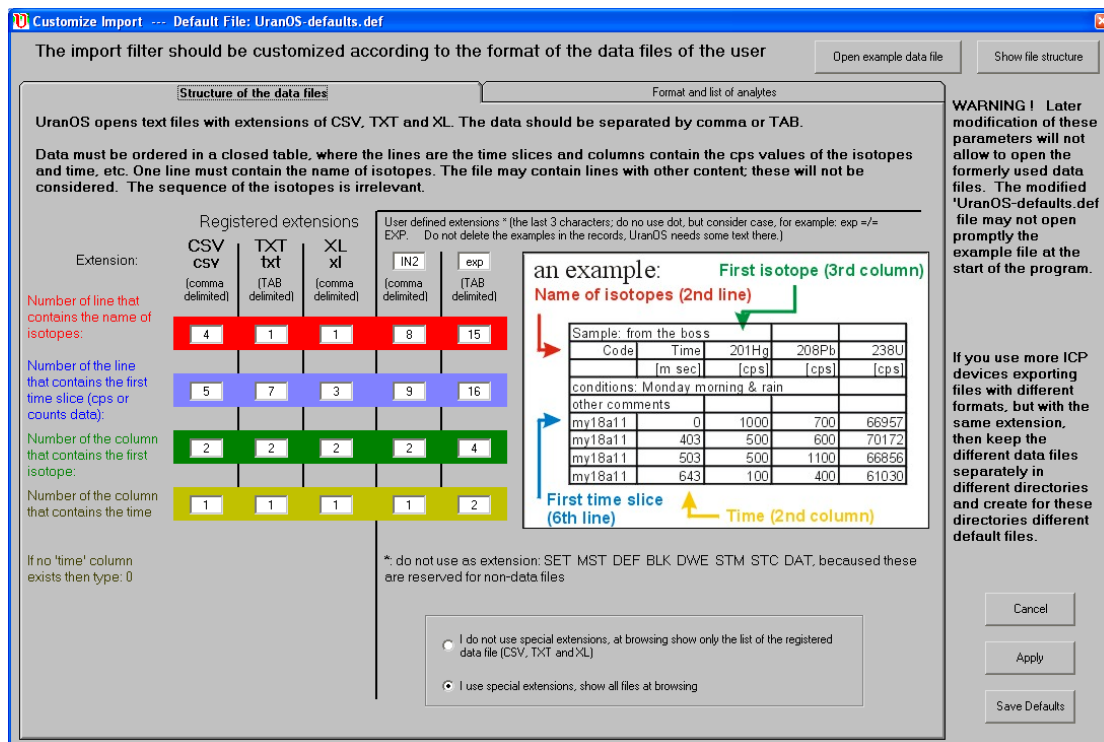

Fig. 1: Window of the universal import filter. Users can customize the import by these four parameters and can define the special extensions. This procedure has to make only once.

2.1.2. Time slice selection

The first step at the explanation of the functions of UranOS is the time slice selection simply by using the automatically opened example file. Start the program and press [Next Step]. Now you see the main window that contains two bigger plots. The upper one contains always the rough cps data. By left and right mouse clicks mark an interval within the ablation signal. Appearing white background shows the selected interval and below the plot two numbers indicate the first and last time slices considered. Right of the plot the two black numbers indicate the numbers of total and selected time slices. Now press SHIFT, and by left and right mouse clicks mark a section on the left part of the plot, to select an interval for background calculation. The blank interval is indicated right of the plot by numbers on cyan colored background. Now the fields of results and the other plots are already containing data, and thus we can explain the parts of the main window.

2.1.3. Structure of the main window

The organization of the main window follows a scheme: data processing by scanning the information from top left towards bottom right through the entire window (Fig. 2). Top left corner of the window shows the file name and the name of the default file used. The left-middle and right parts show sequentially the parameters

for the optimization of the time interval selection and at the end of data reduction the user can save or copy the results using the buttons placed into the bottom right corner.
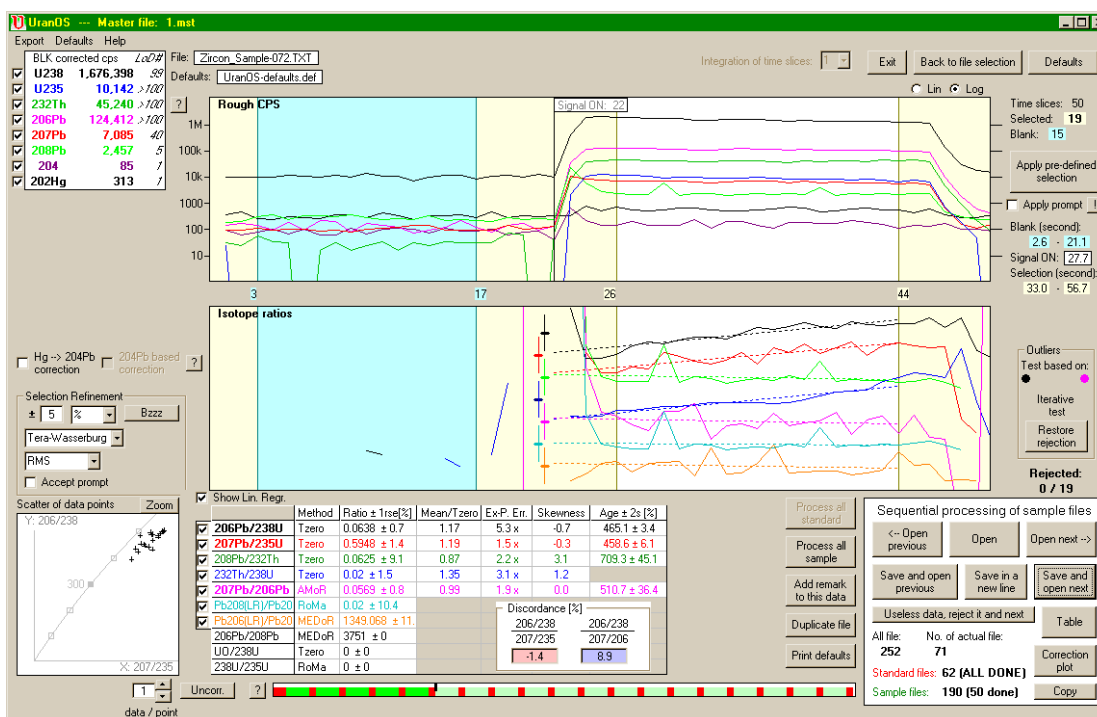

Fig. 2: Main window of UranOS. The selection of time slices (and the blank) can be performed quickly, by left and right mouse clicks (and SHIFT & mouse clicks).

Below the name of used files the white field shows the blank corrected cps values of the considered isotopes. Cps values are calculated as average of individual cps data corrected by the average blank. xLoD indicates the ratio of signal intensity to the limit of detection. Any value exceeding 100 is represented by the ">100" symbol. Limit of detection is calculated as average blank + 3 times s.d. of the blank of the given analyte.

Now we consider the time series plot again. Press SHIFT and change slightly the selection of the background or without shift modify the selection of the data interval. You can observe the interlinking of all records and plots. In this way the sensitivity of the system to different selections can be studied and the reliability of results can be estimated. Sometimes, *especially in case of low counts the mean cps, xLoD values and isotope ratios are reacting highly sensitively even to minor change in selection of time slices*.

UranOS looks for the beginning of the laser signal using the following criterion: the sum of each time-resolved U, Th and Pb signals must strictly increase in 9 consecutive time slices. The data files from the different laboratories are very different; thus, it is difficult to find an overall and robust criterion to identify the start of signal. This marking can be moved any time simply by clicking on the label. (It is planned to allow the user to parameterize the "Signal ON" criterion in the Defaults window.)

The lower plot shows the time-resolved isotope ratios. The color coding of the two plots are different, but consequent. The colors of the results of five isotope ratios (from black to magenta) are applied for the lower time series plot. The vertical scaling of the isotope ratio plot is scaled in a way that the actual signal selection is best

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viewed in the window. Left of the "Signal ON" label there are horizontal and vertical bars indicating the mean and 2 s.d. range of the given ratio in the selected interval. That is why the vertical zooming of the curves changes along the whole plot when modifying the selection.

Left of the isotope ratio plot there are several options for refinement of selection and in the lower left corner the scatter of isotope ratios are plotted, scaled to window size. The numeric field below the isotope ratio plot indicates the raw isotope ratios along with the statistical parameters chosen in the Defaults window.

The buttons at the bottom right corner are used to save or copy the results and to load the next data file immediately. Outlier test and rejection of suspicious data, furthermore the modification of the defaults can be performed by the buttons positioned at the right margin and top right corner of the main window. The details of these functions will be discussed below.

2.1.4. Filtering of input data

The time resolved record frequently contains noisy signal. By increasing the number of time slices the biasing effect of the individual spikes can be reduced. However, the signal length has some physical limits. That is why it is crucial to reduce the impact of the few, but anomalous data points. Currently, UranOS implements this by two methods: refinement of selection and rejection of outliers.

2.1.4.1 Refinement of selection (should be switched on in the Default window)

The refinement works in the following way: select an arbitrary, "flat-looking" interval and press the button [Bzzz]. The refinement algorithm now slightly modifies the selection boundaries (e.g. max by ± 5%) and tests *all* possible selection combinations within this range. The program will offer the selection, which yields the highest reduction of the residual error (i.e. the deviation from an expected Gaussian distribution). If you press the [Accept] button, the program automatically recalculates all results and re-draws the plots (Fig. 3). If you are not satisfied with the result, simply click again the time series plots.
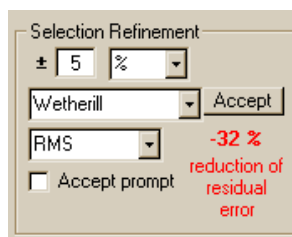

Fig. 3: Part of the main window after pressing [Bzzz] button. The "Selection Refinement" procedure identifies the best time slice selection within a small tolerance interval having less residual error than the original selection of user.

The following options are available at the refinement: (1) specifying the range of the tested intervals as expressed in % or in the number of time slices, (2) specifying which pair of isotope ratios should the test be based on, and (3) specifying the tested statistical parameter. The selection will be optimized using one of two isotope ratio pairs. Selecting "Wetherill" the $^{206}Pb/^{238}U$ and the $^{207}Pb/^{235}U$ ratios are used, while selecting "Tera-Wasserburg" considers the $^{207}Pb/^{206}Pb$ and the $^{238}U/^{206}Pb$ ratios for selection refinement. Either the *residual error* or the *skewness* can be used as the parameter for optimizations. Isotope ratios in each time slice should, in theory,

express repeated measurements (in case of "homogeneous" material and no or an already corrected time-dependent isotope ratio fractionation), they should follow Gaussian distribution. Both parameter describe the normality (skewness does this a bit more indirectly) and they offer an opportunity for a more reliable time interval selection. The optimization algorithm looks for the selection that will yield a minimum sum of the absolute values of the two residual errors. In our view the two isotope ratios should be tested and not in the context of the expected U/Pb age. We consciously did not choose the concordance as a goodness parameter for the optimization, because such a process would result in a forced and unreliable migration of any true discordant data point towards the isochron.

Marking the "Accept prompt" option the user can achieve a semi-automatic selection refinement; if the [Bzzz] command found improvement in the tested parameters then the selection is modified promptly.

2.1.4.2. X-Y (concordia) plot: normalized scatter of data points

At the bottom left corner of the main window the X-Y plot shows the scatter of the individual isotope ratios of the selected interval according to the "Wetherill" or "Tera-Wasserburg" systems. Note that data spread is always scaled to window size. The pattern of the data points gives an idea on the type of the isotope ratio distribution and may also be indicative of time-dependent fractionation. Fig. 4 shows different examples. Data set A was generated by a hole-drilling laser, thus the temporal fractionation is significant and the distribution is strongly elongated. Data set B was generated by rastering mode and the symmetric distribution refers negligible fractionation. This observation, especially if we parameterize the fractionation can be used at the selection of the averaging method (see below).

The X-Y plot visualizes also the complexity of the achieved data. Different signals derived from e.g. zones, cores or lead-loss areas of the crystal appear more characteristically than on the time series plots (see Fig. 4c).

Anomalous single data (~spikes, ~outliers) are also well detectable in this kind of plot. For the evaluation of the spikes UranOS offers off-line integration of neighboring data points (this is a visual tool only, and will not affect the calculations). To the right of the X-Y plot a text box indicates how many data points are amalgamated and it can be modified by the scroll buttons. At the amalgamation of data points the integration most spikes will disappear, but if the studied material is zoned, then the amalgamated data points remain clustered around the characteristic values of the individual zones/domains.
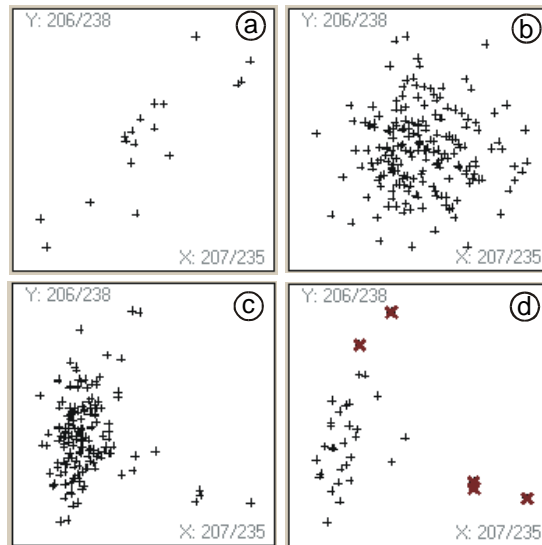
Fig. 4: The X-Y plot shows the normalized scatter of pairs of isotope ratios to be used for age determination. a: A strongly elongated distribution refers to fractionation during ablation. b: The distribution is very symmetric indicating only negligible fractionation. In this case the arithmetic mean or the median should represent the average of the selected interval. c: Complex distribution warns the material is heterogeneous. Spikes can be excluded from the calculation, because the anomalous data points form a cluster and they are arranged in a trend. Age bias, inclusions or ablation-related processes are responsible for the unusual distribution. d: Using 2 s.d. criterion for rejection these remote data point can be marked for omission.

2.1.4.3. Test / rejection of outliers

UranOS offers a simple and robust outlier test according to standard deviation (Fig. 5). The number of outliers is indicated at the right side of the window. The outliers are also indicated by tiny tick-marks at the top of the time series plot of isotope ratios. The colors mark, according to which criterion is a given data point considered as outlier. By pressing [Reject outliers] they can be rejected and the results & plots re-calculated. The rejected time slices are marked by vertical gray lines in the time resolved plots and by a bold brown X on the X-Y plot (Fig. 4d). If now the selection is modified again (manually or by Bzzz) the rejected data points are restored. The test does not consider all five isotope ratios; the ones the test is based on are marked by their color codes; they can be set in the default window (see below). However, UranOS currently rejects the entire time slice in which one or more outlying isotope ratios were marked for deletion.
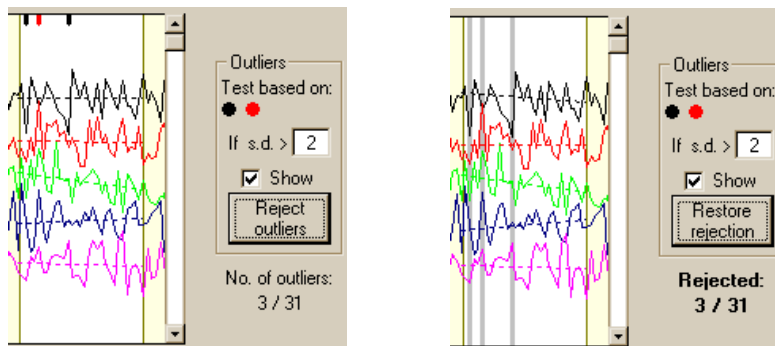
Fig. 5: Part of the main window indicating outliers determined by 206Pb/238U and 207Pb/235U (Wetherhill) isotope ratios using 2 s.d. criterion. After pressing [Reject outliers] button the rejected time slices are indicated by gray bars and all values are re-calculated.

2.1.5. The Default file

The default files (extension: **.def**) contain essential data for the quick performance of the program and numerous personal preferences. These files can be opened by the menu of the start window "Open default file". The content can be modified by the default window loading it from the start window and from the main window.

The first issues in the default data are the abbreviations of mineral names and standard files (Fig. 6). For the quick and easy usage of sequential processing the coherent naming is crucial. It is strongly recommended to always use exactly the same text (even same case) to denote which file contains standard measurement.

The ratios of Hg isotopes are also stored and the work can be customized by the saving of defaults of the plotting options. Dwell times are used only at the calculation of extra-Poisson error. The parameters of selection refinements and the outlier test can be also saved. *The common lead corrections are in the current version still under test.* The nominal isotope ratios and concentrations of the most commonly used standard can be modified and saved and the used can add more standards. UranOS calculates and displays averages using different methods, but into the result file (or on the clipboard) only one result can be written. The user can specify here which method preferred and also the multiplicator of the error.
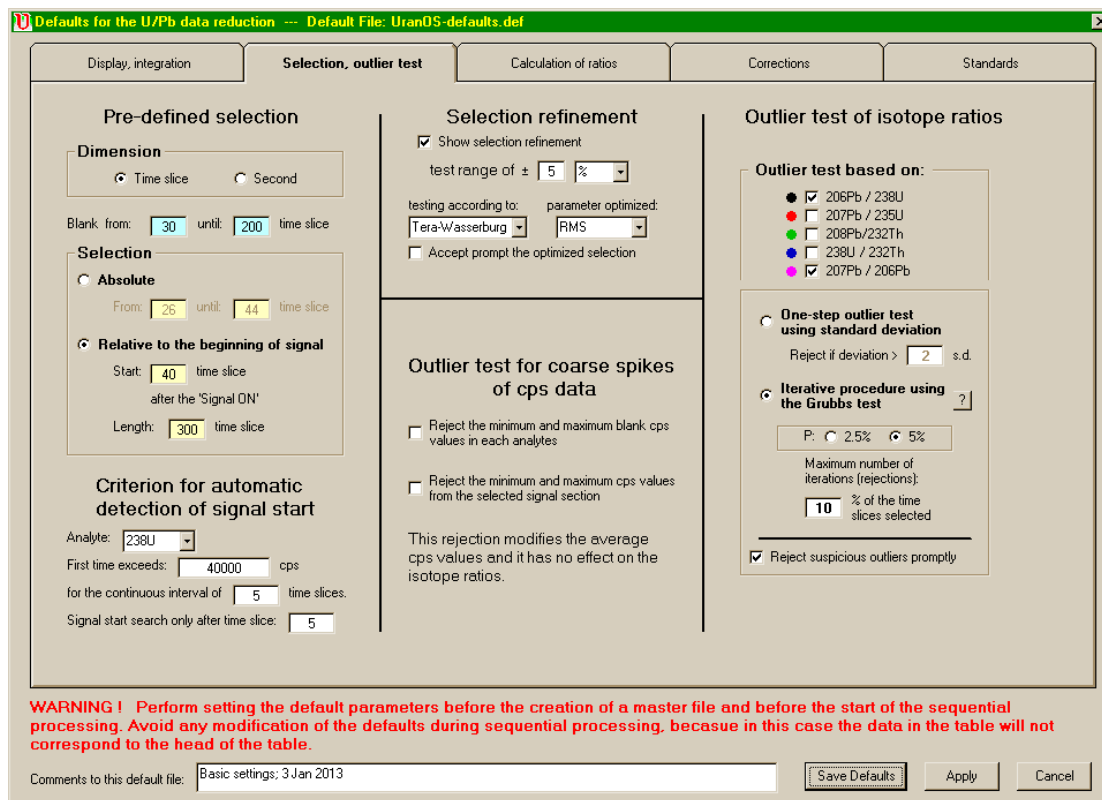

Fig. 6: One page of the 'Defaults Window' indicating a part of the preferences available to the users.

2.1.6. Results

Averages of the five processed isotope ratios are reported in three ways: arithmetic mean, median and the Tzero intercept of the selected range. The preferred values are marked by bold, and only these ones will be stored in the result file. In the first two cases, UranOS uses the individual isotope ratios in the selected time slices to calculate the arithmetic mean or the median. At the calculation of the median the rejections are not considered, as they have a negligible effect on the median. Note that using mean or median is reliable only for unfractionated isotope ratios (see e.g. Fig. 4).

Isotope ratio calculation using the Tzero intercept of the time-resolved trend is inevitable if fractionated isotope ratio curves are worked with. However, at the calculation of Tzero intercept a question arises: where is actually the Tzero? As this will largely depend on the LA setup used and ablation patterns obtained, UranOS offers three options: (a) at the lower limit of the current time interval selection (b) at the beginning of signal (laser ON) or (c) X time slices afterwards (see Fig. 6). Additionally, there is an option to use the arithmetic mean or the median of the 207Pb/206Pb ratio in the selected time range together with the Tzero intercept of all other isotope ratios. "M/Tz" parameter expresses the ratio of mean and Tzero intercept and it can be used as a robust measure of fractionation during ablation. If the deviation from 1 is significant the usage of Tzero intercept is suggested. The example data files in the default directory give examples for both fractionated and stable trends in the isotope ratios.

Errors of isotope ratios are calculated according to the empirical scatter of the individual data points, assuming normal (Gaussian) distribution. The errors are expressed as standard deviation or as standard error, at the 1 or 2 sigma level (Default window). In case a Tzero intercept is used, calculation is done *along* the linear regression line.

The "Extra-Poisson Error" expresses the ratio of the observed scatter in the individual data relatively to the Poisson uncertainty calculated from the cps and dwell time. Skewness is a measure of the deviation from the normality, and it is used as a goodness parameter at the refinement of selection (see above). The "rough concordance" is calculated using the raw isotope ratio pairs without any further correction, thus it is only informative. It assists the user in recognizing major age bias in the signal. Normal or reverse "rough" discordance is indicated by the colored background.

2.2. Sequential processing of standard-sample-standard file batches

2.2.1. Structure

At sequential processing of a measurement session (usually a couple of hours or one day) UranOS expects that:
(a): all data files are in the same directory,
(b): all data files have the same structure,
(c): the files contain serial numbers in a zero-filled format (001 ... 066 ... 255 and not 1 ... 66 ... 255) and that these numbers represent the measurement sequence,
(d): the names of the standard measurement files should contain an abbreviation that helps UranOS distinguishing them from the unknown measurements (e.g. "STD" or "Standard"; see default window),

(e): the names of the standard measurement files should contain the name of the standard exactly as it is registered in the default file (e.g. "Mud Tank" and not "Mud tank"; see Defaults window),

(f): the measurements took place approximately in the same time-span.

(g): the signal consists of a comparable number of time slices (note that for a convenient processing, also the lengths of the background collection need to be comparable).
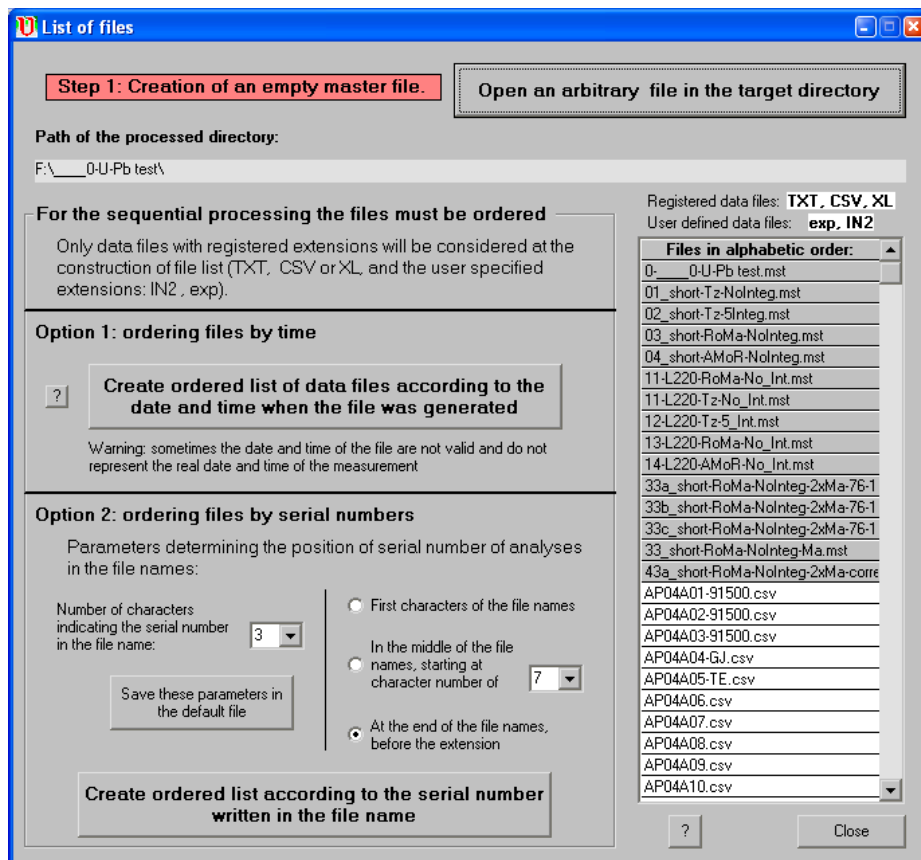

Fig. 7: User can specify the position of the sequential number of the measurements in the neration date/time of the files.

The serial number can be anywhere in the file name; just it must be always in the same position. The abbreviation of the standard and its name can be anywhere (see Fig 7).

The sequential processing takes place in four steps. First a master file is created and its content is filled step-by-step. The structure and build up of the master file is shown in Figure 8. Users can study this procedure on the example file series supplied in the 'sequential-example' sub-directory of the default directory.

file name	type	measured Pb206/U238	interpolated correction factor (CF) for Pb206/U238	corrected Pb206/U238
file01_std_GJ1	standard			
file02_std_GJ1	standard			
file03_qwerty	*sample*			
file04asdfgh	*sample*			
file05_std_GJ1	standard			
file06_std_GJ1	standard			

STEP 1 — Creation of the empty master file with distinguished STDs

STEP 2 — Sequential processing of STDs

STEP 3 — Interpolation and calculation of correction factors for the samples using the STDexpected / STDmeasured ratio

STEP 4 — Sequential procesing of samples
calculated — ... and calculation of corrected isotope ratios using CF

Fig. 8: Structure and temporal growth of the master file. This example demonstrates only one isotope ratio; the master file actually contains other isotope ratios, all cps values with errors and the conditions of time interval selection and data reduction.

2.2.2. 1st step: Creating a master file

Start the program and press [Create master file]. In the appearing window select drive and directory where the data files are. (The directory structure needs to be refreshed: apply double clicks up-down-levels in the directory tree until the file list of the aimed directory become visible in the list in the right). Define the position of the serial number in the file names by the available parameters (see Fig. 7) and press [Create ordered list ...].

The appearing table contains the list of files ordered according to their serial numbers. Review the table to see whether standard and sample files are distinguished and the type of the standard is correct. If necessary, changes in the cell contents of "Type" and "Std." can be made by double clicking on the cell. When the list corresponds to the actual measurement sequence, create the master file for this measurement session (i.e. for the actual directory) and press the [Save master file] button. Now, the master file is nearly empty, it actually only consists of a header and a list of the names of data files. The master file is a TAB-delimited text table, with the extension **.mst**. The program can open and show its content later on in any times and the master file can be duplicated in order to test alternative data reduction methods.

2.2.3. 2nd step: Processing the standards files

After saving the master file the program returns to the start window. User can continue the sequential processing by pressing [Open a master file] button. The file-open dialog window shows only the master file, but no other files of the directory. That is why moving files between different directories is not recommended when a master file is already generated.

After loading the master file the main window appears, but in the sequential processing mode it contains other information in text boxes and other possibilities for file operations than when UranOS is used in individual processing mode. The upper left corner of the window shows the name of the master file loaded. In the lower right corner appears a white field with buttons for quick file opening (Fig. 9). Using [Open previous] and [Open next] buttons the user can scan through the content of the directory without time consuming browsing. In the current step (processing standard files) only standard files can be opened. The [Open ...] buttons load no sample files,

they are jumped over. If the directory is very long (current version allows 1000 files to be processed) then click [Open] and from table of file list one data file can be opened by double clicking.
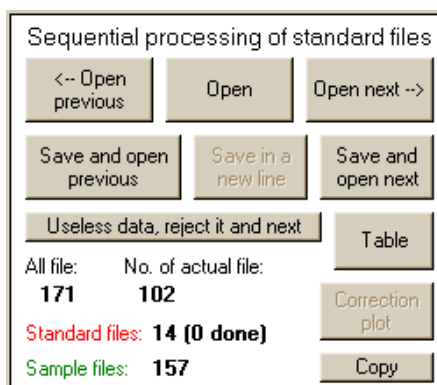

Fig. 9: Using UranOS in sequential mode the bottom left corner of the main window contains buttons for quick file operations. As long as the interpolation between the standard files is not yet done only standard files can be shown, while after the interpolation and drift correction only sample files can be shown.

As soon as the user select blank and sample intervals in the time resolved plots two other buttons for file manipulation become enabled. [Save results and open next] writes the result of the actual selection and data reduction promptly into the master file and opens the next (or previous) standard file. Sample files can not be processed in this step. The text boxes below the buttons show the position of the actually opened file and the state of the processing of standard files.

After processing at least one standard file the content of the master file can be seen by pressing the [Table] button. Now the content of the master file is available only in 'see only' mode, the user can not change the records or open files. If all standard files have been processed, then a big button appears in the middle of the upper time series plot that warns the user to perform the next step (Fig. 10).
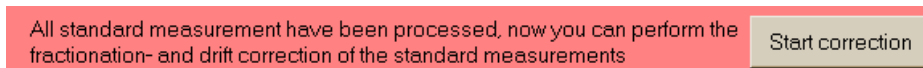

Fig. 10: When all standard measurements have been done a warning button appears and now the user has only one option: performing the drift correction.

2.2.4. 3rd step: Interpolation (drift correction)
By pressing the big warning button appears the Drift Correction window (Fig. 11). The X-axis indicates the position the standard files within the batch. The Y-axis is the normalized correction factor:

$$(FF = IsotRatioSTD_{measured} / IsotRatioSTD_{nominal}).$$

Only the standards are plotted. The plot can be zoomed and the individual data can be rejected by mouse clicks. UranOS offers several types of interpolation: linear, logarithmic, polynomial (up to 23 degrees) and zigzag method. The zigzag procedure performs linear interpolation between standards or between clusters of standards. For the effective decisions of the best interpolation method a robust measure of the fitting is presented: the average difference. The interpolated values for the samples are plotted by squares of pale colors along the line of the preferred interpolation method.

User can select the 206Pb/238U and 207Pb/206Pb isotope ratios, choose a preferred interpolation method, perform the rejection of outliers and press button [Select interpolation ...]. Beside the options of isotope ratios appear the sign "done" indicating that the interpolation is stored in the memory of the computer, but not yet saved. The interpolation of a given isotope ratio can be over-written by a new click on the button. The plot of measured 207Pb/235U ratios is only for demonstration, the fractionation factor of $FF_{206Pb/238U}$ will be used to correct this isotope ratio, because there are no certified values of the standards available for 207Pb/235U. That is why sign "calc." indicates that this value is calculated.

If interpolations are performed for both the 206Pb/238U and 207Pb/206Pb isotope ratios the button [Save values into the master file] bacames enabled. Warning: for a given master file the user can press this button only once. The interpolation can not be changed later on! The interpolation can be viewed later, but the standard measurements and correction factors are unchangeable.
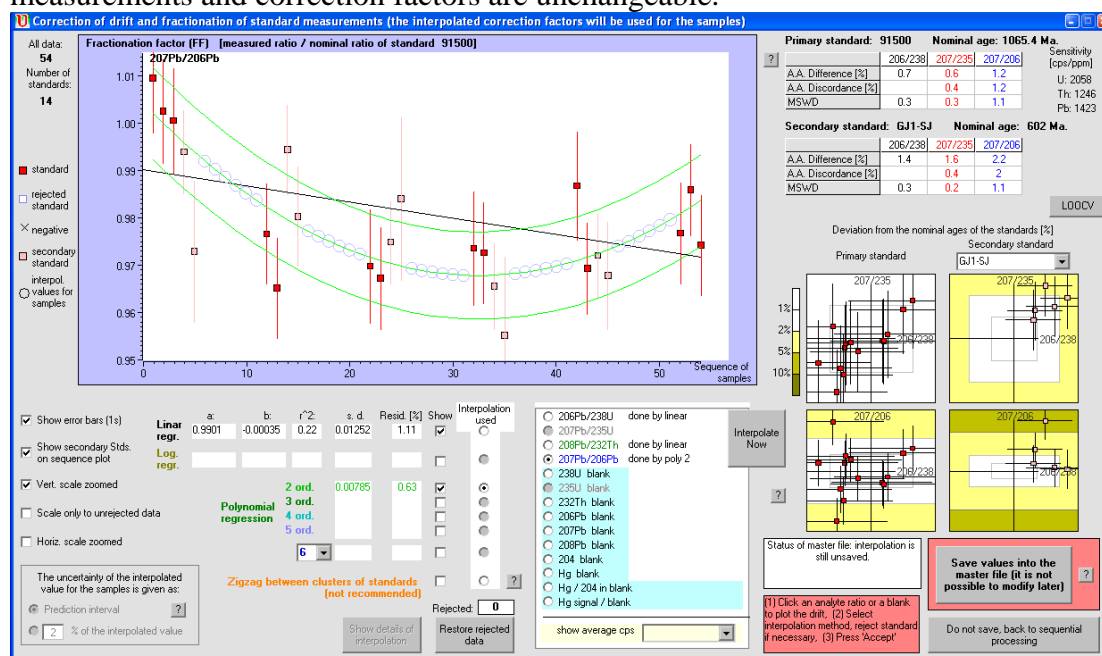
Fig. 11: Interpolation between the standards, rejection of suspicious values and calculation of correction factors for the samples.

2.2.5. 4th step: Processing sample files and export

After "burning" the FFs into the master file the user can open and process the sample files similarly to the sequential processing of standard files. The content of the master file can be seen by the [Table] button.

Fig. 12: The content of the master file can be checked by any time during the processing of data files. Color coding helps the navigation in the table; the measured, corrected, CPS and blank data are distinguished.

There are three options to export the data to the clipboard or saving them into an export file. [Full export] puts the master file as it is, [Selected export] creates export according to the pre-defined selection criterion of the user and [Quick export] puts on the clipboard a table that can be used as import table for ISOPLOT.

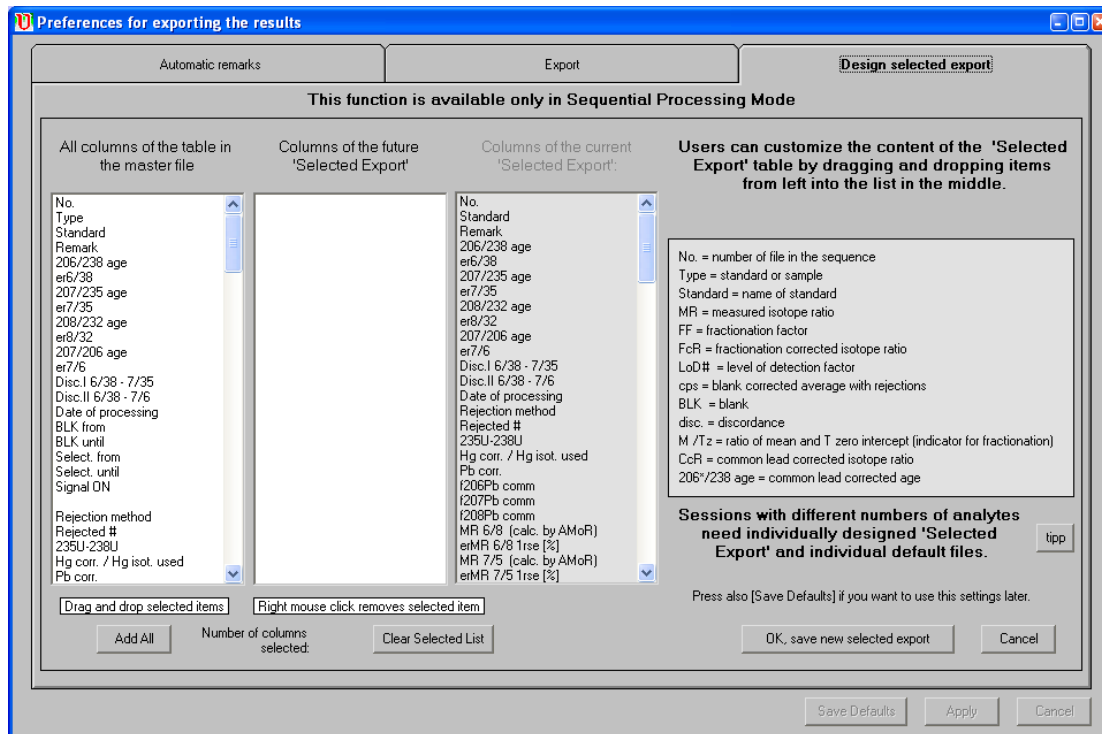The user-defined export table can be designed or modified in the menu: Defaults / Preferences for Export.

Fig. 13: User defined options for the export of the processed values.

Reference

Ludwig, K. R. 2003: Isoplot 3.00 – A geochronological toolkit for Microsoft Excel. Berkeley Geochronology Center Special Publication 4, 1–70.