



University of Göttingen  
GÖochronology

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

(and 7 other questions)

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**Many thanks to the 31 different labs that supplied example files until now**

<http://www.sediment.uni-goettingen.de/staff/dunkl>

## Quick and brief answers to Matt's questions

Uncertainty propagation protocol/workflow

Gaussian error propagation - as usual

Common Pb correction methods

204-based with Hg-correction

Method of inter-element and inter-isotope fractionation correction

fractionation and drift correction by lin., log, polynom regressions

Weighted mean/linear regression support

ROM, MOR, Median and T-zero intercept

Rejection criteria

2 s.d. and iterative Grubbs test (preferred) and 2sd

Handling/storage of reference values for normalization

User-edited table is loaded promptly with the preferred values & methods

Key differences from other available packages

?

## Workflow

- 1) Universal input (opens any kind of tables)
- 2) Sequential processing of standards and samples:

file name	type	measured isotope ratios	fractionation factors for the different isotope ratios	fractionation corrected isotope ratios, ages, etc.
file01_std_GJ1	standard			
file02_std_GJ1	standard			
file03_qwerty	<i>sample</i>			
file04asdfgh	<i>sample</i>			
file05_std_GJ1	standard			
file06_std_GJ1	standard			

STEP 1

Creation of the empty master file with manual or automatic recognition of standards

STEP 2

Sequential processing of standards

STEP 3

Drift and fractionation correction (using the nominal values of standards)

STEP 4

Sequential processing of samples

calculated

and calculation of corrected isotope ratios, ages and variable statistical parameters

- 3) Export for Isoplot or for database (user defined table format)

## Major features

standalone, no plug-ins required

Windows based, but works on MAC and Linux

real time: NO, the program assumes equal time between laser shots

universal input, any kind of table can be opened

pre-defined 'laser on' detection and signal selection criteria,

batch processing, re-processing of sequences by one click

instrumental Hg-emission correction,

common Pb correction (204), (206, 208 in preparation)

iterative outlier test, insensitive to spikes

individual scan rejection by user: NO, subjective data handling excluded

stores of standard values,

4 averaging methods, incl. T-zero intercept, (expon. corr. in preparation)

drift correction by linear, log, polynom. regressions,

plotting of residuals of standard measurements,

all details of processing are archived,

user-designed export table format,

logging: generates automatically for each sequence a 'Data Reduction Synopsis'

all equations are explained in the Help

# The universal import filter allows to open any kind of ordered, tabular data file

U Customize Import --- Default File: UranOS-defaults.def ✕

The import filter should be customized according to the format of the data files of the user

Structure of the data files

Format and list of analytes

UranOS opens text files with extensions of CSV, TXT and XL. The data should be separated by comma or TAB.

Data must be ordered in a closed table, where the lines are the time slices and columns contain the cps values of the isotopes and time, etc. One line must contain the name of isotopes. The file may contain lines with other content; these will not be considered. The sequence of the isotopes is irrelevant.

Registered extensions

Extension:	CSV CSV <small>(comma delimited)</small>	TXT txt <small>(TAB delimited)</small>	XL xl <small>(comma delimited)</small>	ICP <small>(comma delimited)</small>	exp <small>(TAB delimited)</small>
Number of line that contains the name of isotopes:	4	1	1	2	15
Number of the line that contains the first time slice (cps or counts data):	5	7	3	3	16
Number of the column that contains the first isotope:	2	2	2	2	4
Number of the column that contains the time	1	1	1	1	2

If no 'time' column exists then type: 0

User defined extensions \* (3 characters; do not use dot, but consider case, for example: exp != EXP. Do not delete the examples in the records, UranOS needs some text there.)

an example:

Sample: from the boss					
Code	Time	201Hg	208Pb	238U	
	[m sec]	[cps]	[cps]	[cps]	
conditions: Monday morning & rain					
other comments					
my18a11	0	1000	700	66957	
my18a11	403	500	600	70172	
my18a11	503	500	1100	66856	
my18a11	643	100	400	61030	

\* do not use as extension: SET MST DEF BLK DWE STM STC DAT, because these are reserved for non-data files

I do not use special extensions, at browsing show only the list of the registered data file (CSV, TXT and XL)

I use special extensions, show all files at browsing

**WARNING !** Later modification of these parameters will not allow to open the formerly used data files. The modified 'UranOS-defaults.def' file may not open promptly the example file at the start of the program.

If you use more ICP devices exporting files with different formats, but with the same extension, then keep the different data files separately in different directories and create for these directories different default files.

# The major window shows the time resolved data and ratios & some of the the calculated values

UranOS --- Master file: 3.mst

Export Defaults Help

File: 047SGM-H1.csv Integration of time slices: 1 Exit Back to file selection Defaults

BLK corrected cps *LoD#*

U238	324,249	>100
U235 #	2,352	
232Th	81,993	>100
206Pb	29,661	>100
207Pb	1,770	12
208Pb	701	1
204Pb	52	0
202Hg	16	0
Zr	55,149,816	>100

Defaults: UranOS-defaults.def

Time slices: 302 Selected: 101 Blank: 44

Apply pre-defined selection

Apply prompt

Blank (second): 1.7 - 9.6 Signal ON: 11.2 Selection (second): 19.5 - 37.9

Outliers Test based on: Iterative test Restore rejection

Rejected: 0 / 101

Rough CPS

Signal ON: 61

Isotope ratios

Common 6, 7, 8: 3% 31% 74%

Hg -> 204Pb correction 204Pb based correction

Selection Refinement ± 5 % Bzzz Tera-Wasserburg RMS Accept prompt

Scatter of data points Zoom Y: 206/238 X: 207/235

	Method	Ratio ± 1rsef[%]	Mean/Tzero	Ex-P. Err.	Skewness	Age ± 2s [%]	4Pb Corr. Age
206Pb/238U	Tzero	0.0821 ± 1	1.12	1.9 x	0.3	551.8 ± 5.4	535.7 ± 5.4
207Pb/235U #	Tzero	0.679 ± 1.4	1.12	0.6 x	0.4	724.1 ± 5.2	546.6 ± 5.6
208Pb/232Th	Tzero	0.0071 ± 8.3	1.22	1.8 x	0.7	502.7 ± 17.8	133.6 ± 17.9
232Th/238U	Tzero	0.22 ± 1.4	1.17	3.2 x	0.8		
207Pb/206Pb	AMoR	0.0599 ± 1.3	0.99	1.1 x	0.6	1292 ± 7.9	581 ± 19.7
Pb208(LR)/Pb20	RoMa	0 ± 0					
Pb206(LR)/Pb20	MEDoR	0.062 ± 0					
206Pb/208Pb	MEDoR	0 ± 0					
UO/238U	Tzero	0 ± 0					
238U/235U	RoMa	0 ± 0					

Discordance [%]	
206/238	206/238
207/235	207/206
2	7.8

Process all standard Process all sample Add remark to this data Duplicate file Print defaults

Sequential processing of sample files

<< Open previous Open Open next >>

Save and open previous Save in a new line Save and open next

Useless data, reject it and next Table

All file: 37 No. of actual file: 22 (processed) Correction plot

Standard files: 17 (ALL DONE) Sample files: 20 (13 done) Copy

data / point

Uncorr. ?

comments, warnings and explanations

status indicator (red: standard, green: sample)

**A part of the defaults** (in this page the user can set the pre-defined signal selection criteria and the mode of outlier test)

Defaults for the U/Pb data reduction --- Default File: UranOS-defaults.def

Display, integration    **Selection, outlier test**    Calculation of ratios    Corrections    Standards

### Pre-defined selection

**Dimension**

Time slice     Second

Blank from:  until:  time slice

**Selection**

Absolute

From:  until:  time slice

Relative to the beginning of signal

Start:  time slice  
after the 'Signal ON'

Length:  time slice

### Criterion for automatic detection of signal start

Analyte:

First time exceeds:  cps  
for the continuous interval of  time slices.

Signal start search only after time slice:

### Selection refinement

Show selection refinement

test range of  $\pm$   %

testing according to:  parameter optimized:

Accept prompt the optimized selection

### Outlier test for coarse spikes of cps data

Reject the minimum and maximum blank cps values in each analytes

Reject the minimum and maximum cps values from the selected signal section

This rejection modifies the average cps values and it has no effect on the isotope ratios.

### Outlier test of isotope ratios

**Outlier test based on:**

- 206Pb / 238U
- 207Pb / 235U
- 208Pb/232Th
- 238U / 232Th
- 207Pb / 206Pb

One-step outlier test using standard deviation

Reject if deviation >  s.d.

Iterative procedure using the Grubbs test ?

P:  2.5%     5%

Maximum number of iterations (rejections):  
 % of the time slices selected

Reject suspicious outliers promptly

**WARNING ! Perform setting the default parameters before the creation of a master file and before the start of the sequential processing. Avoid any modification of the defaults during sequential processing, because in this case the data in the table will not correspond to the head of the table.**

Comments to this default file:

# A part of the defaults (in this page the user can set e.g. the averaging methods for the different isotope ratios)

Defaults for the U/Pb data reduction --- Default File: UranOS-defaults.def
✕

Display, integration

Selection, outlier test

**Calculation of ratios**

Corrections

Standards

**Limit of detection calculated**

with the average BLK (LoD = BLK + 3x s.d.)     without BLK (LoD = 3x s.d.)

**U cps re-calculation**

No recalculation of U cps values    Isotope ratio for calculation of the missing or badly detected U isotope

?  235U cps calculated from 238U    238U / 235U

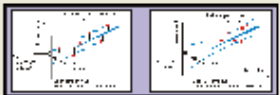
238U cps calculated from 235U

**207/235 calculation in sequential processing mode**

from the ratio of 207Pb and the measured (or calculated) 235U cps values     from corrected 206Pb/238U and 207Pb/206Pb ratios

**Error of Tzero given as**

Parallel intercept     Confidence interval



**Calculation methods of the analyte ratios:**

	RoMa	AMoR	MEDoR	Tzero	Decimal places:
206Pb / 238U	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input type="text" value="4"/>
207Pb / 235U	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input type="text" value="4"/>
208Pb / 232Th	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input type="text" value="4"/>
232Th / 238U	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input type="text" value="2"/>
207Pb / 206Pb	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="text" value="4"/>

**User selected analyte ratios**

! <input type="text" value="Pb208(L)"/> / <input type="text" value="Pb206(L)"/>	<input checked="" type="radio"/> RoMa	<input type="radio"/> AMoR	<input type="radio"/> MEDoR	<input type="radio"/> Tzero	<input type="text" value="3"/>
<input type="text" value="Pb206(L)"/> / <input type="text" value="Pb204(L)"/>	<input type="radio"/> RoMa	<input type="radio"/> AMoR	<input checked="" type="radio"/> MEDoR	<input type="radio"/> Tzero	<input type="text" value="3"/>
<input type="text" value="206Pb"/> / <input type="text" value="208Pb"/>	<input type="radio"/> RoMa	<input type="radio"/> AMoR	<input checked="" type="radio"/> MEDoR	<input type="radio"/> Tzero	<input type="text" value="0"/>
<input type="text" value="U0"/> / <input type="text" value="238U"/>	<input type="radio"/> RoMa	<input type="radio"/> AMoR	<input type="radio"/> MEDoR	<input checked="" type="radio"/> Tzero	<input type="text" value="3"/>
<input type="text" value="238U"/> / <input type="text" value="235U"/>	<input checked="" type="radio"/> RoMa	<input type="radio"/> AMoR	<input type="radio"/> MEDoR	<input type="radio"/> Tzero	<input type="text" value="1"/>

**Intercept calculated at**

Tzero = start laser

Tzero =  time slices after start laser

Tzero = start selection

1: RoMa: Ratio of Mean cps (all data) ?

2: AMoR: Arithmetic Mean of Ratios (with rejection)

3: MEDoR: Median of Ratios (all data)

4: Tzero intercept by lin. regr. (with rejection)

Selection guide for averaging methods

**WARNING ! Perform setting the default parameters before the creation of a master file and before the start of the sequential processing. Avoid any modification of the defaults during sequential processing, because in this case the data in the table will not correspond to the head of the table.**

Comments to this default file: Basic settings; 3 Jan 2013

Save Defaults

Apply

Cancel



# Correction of drift and fractionation of standard measurements

standards are normed to the nominal values (squares),  
 circles represent the interpolated fractionation factor for the samples  
 interpretation can be done by linear, log and poly regressions  
*(in this example 2nd order polynomial)*

the spread of the standard ages  
 is plotted on residual (target) plots  
 (AA: average absolute difference)

the white field represent 2% deviation from the nominal age

U Correction of drift and fractionation of standard measurements (the interpolated correction factors will be used for the samples)

All data: **252**  
 Number of STDs: **62**  
 Rejected: **1**

Status of master file: interpolation unsaved

**Fractionation factor (FF)** [measured ratio / nominal ratio of standard]

**206Pb/238U**

■ standard  
 □ rejected standard  
 × negative  
 ○ interpol. values for samples

	206/238	207/235	207/206
A.A. difference [%]	1.1	2	3.5
A.A. discordance [%]		2.4	4
MSWD	0.7	0.7	0.6

Deviation from the nominal ages of the standards [%]

207/235

207/206

Restore rejected data

Show error bars (1s)

Horiz. scale zoomed

Vert. scale zoomed

Scale only to unrejected data

Linear regr. a: 0.8442 b: 0.00012 r<sup>2</sup>: 0.31 s. d. 0.01348 Resid. [%] 1.25 Show

Log. regr.

Polynomial regression 2 ord. 0.01279 1.16   
 3 ord.   
 4 ord.   
 5 ord.

Zigzag between clusters of standards

The uncertainty of the interpolated value for the samples is given as:

Prediction interval [?]

0 % of the interpolated value

Interpolation used:  Linear  Polynomial  Logarithmic

- Pb206/U238 done by poly 2 rejected: 1
- Pb207/U235 done by poly 2 rejected: 1
- Pb208/Th232 done by poly 2 rejected: 1
- Pb207/Pb206 done by poly 2 rejected: 1
- 238U blank
- 235U blank
- 232Th blank
- 206Pb blank
- 207Pb blank
- 208Pb blank
- 204 blank
- Hg blank
- Hg / 204 in blank
- Hg signal / blank

show average cps

Save values into the master file (it is not possible to modify later) [?]

Do not save, back to sequential processing

(1) Click an analyte ratio or a blank to plot the drift. (2) Select interpolation method, reject standard if necessary. (3) Press 'Accept'

## **Proposal for discussion I.**

### **1) Laser induced Hg emission**

UV light generates photo-ionisation of the deposited Hg from the chamber wall.

Ablation of Hg-free phases can monitor the instrumental Hg emission. It should be included routinely in the sequence if the instrument has remarkable Hg signal.

### **2) Reliability indicator for low counts**

Presenting millivolt or cps as an indication of the goodness of low signals (e.g. 207) are instrument and setting specific.

Some kind of universal signal height indicator is necessary. We suggest to use the LoD or the modified LoD (with or without consideration of the level of the blank).

### **3) Presence of zero counts in the data**

At the selection of the averaging method the user should consider that there are zeros in the time slices or not. If zeros are present in the selected time slices then the AMoR (arithmetic mean or ratios) can not be used. That is why UranOS warns automatically when zeros appear in the signal.

## Proposal for discussion II.

### 4) **Degree of the down-hole fractionation**

In order to express the down-hole fractionation we recommend to use the ratio of 'mean / T-zero' because this calculation considers all data, while the ratio of 'first half / second half' is based only on subsamples.

### 5) **Using more standards, especially for provenance studies**

This procedure would represent the mineralogical variation of dated grains better and would give a more reliable uncertainty estimation.

## Proposal for discussion III.

### 6) Grouping standards in the sequence

If the standards are not analysed individually in the sequence, but rather grouped then the 'short-wave' fluctuation (generated by counting statistics, heterogeneity, geometry problems, temperature oscillation of the instrument and several other factors) can be averaged and the real 'long-wave' trend can be monitored better.

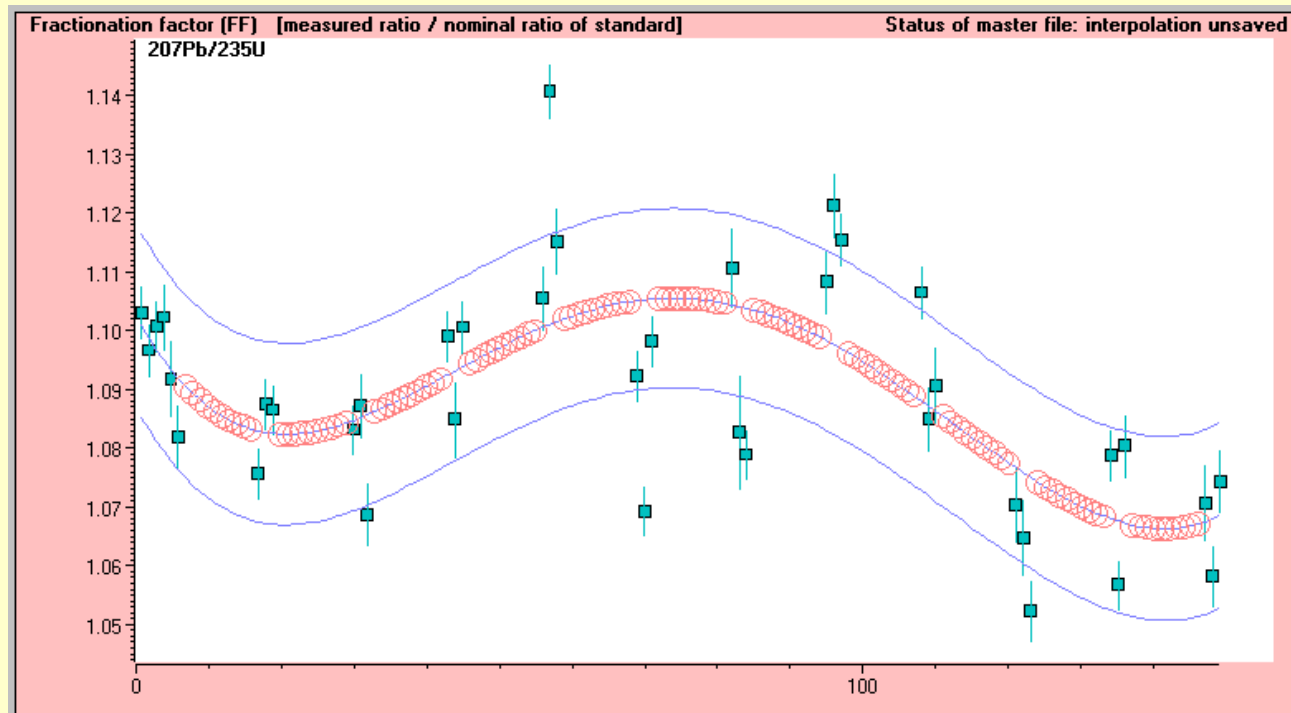
a) **S S S** u u u **S** u u u **S** u u u **S**

b) **S S S** u u u u u u **S S** u u u u u u **S S**

c) **S S S** u u u u u u u u u u **S S S** u u u u u u u u u u **S S S**

In these schematic examples the ratio of **S** standard and **u** unknowns are the same, but the grouping would express the actual trend in a more robust way.

A real example for a 'long-wave' trend monitored by ternary standards groups.



## Proposal for discussion III.

7) Propagation of the uncertainty of drift & fractionation correction by the **prediction interval**.

Error propagation from drift + fractionation correction:

- two philosophies:

(a) considering the nearest sub population of the standards

(b) considering all standards and assuming a model for regression

We prefer option (b) and in this case the prediction interval is a reliable estimation for the propagated error; the standard error underestimates it.

$$erFF_{6/8} = t_{\alpha} * s * \sqrt{1 + \frac{1}{n} + \frac{(x - \bar{X})^2}{\sum (x - \bar{X})^2}}$$

The mode of data reduction used for a session is logged automatically and can be printed/archived

```
***** UranOS Data Reduction Synopsis *****
***** UranOS Version 2.00

Date of ICP measurements: 03/07/2007
Master file created: 1 Mar. 2013      Printed: 4 Mar. 2013
Master file: C:\UranOS-Defaults\sequential-example-253\2.mst
Default file: UranOS-defaults.def    last update: 03/03/2013
No. of files: 252      No. of std. files: 62
No. of time slices: 50      No. of analytes: 8
Hg202 Pb204 Pb206 Pb207 Pb208 Th232 U235 U238

----- CPS -----

Integration of scans: NO
Criterion for automatic signal start detection: 238U threshold: 40000 cps
Pre-defined selection: from 40 time slices after 'Signal ON', length: 300
Reject minimum and maximum blank cps values in each analytes: NO
Reject minimum and maximum cps values from the selected signal section: NO
Limit of detection calculated as: blank + 3 sd
U isotopes: both measured.

----- Analyte ratios -----

206Pb/238U ratio calculated by Tzero (Intercept of lin. regression)
207Pb/235U ratio calculated by Tzero (Intercept of lin. regression)
207Pb/206Pb ratio calculated by AMoR (= Arithmetic Mean of Ratios)
208Pb/232Th ratio calculated by RoMa (= Ratio of Mean)
Outlier test of analyte ratios based on: 206/238 207/206
Preferred outlier test: Iterative Grubbs test of the most extreme data

----- Common lead correction -----

When applied, then 204Pb-based correction is using the Stacey-Kramers Pb
isotope ratios according to the uncorrected 206/238 age.

----- Drift and fractionation correction -----

206/238 correction by linear -- rejected: 1 standard.
207/235 correction by poly 4 -- rejected: 1 standard.
208/232 correction by logar. -- rejected: 1 standard.
207/206 correction by linear -- rejected: 1 standard.
Propagated uncertainty of drift and fractionation correction: Prediction
interval (ca. 1 sd).

----- Uncertainties given as -----

Uncertainties of cps values, isotope ratios and fractionation factor are given
as 1x relative standard error [%].
Uncertainty of the blank cps is given as 1x standard deviation [cps].
Uncertainties of the calculated ages are given as 2 rse [%].
```