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 ususal

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	*sample*			
file04asdfgh	*sample*			
file05_std_GJ1	standard			
file06_std_GJ1	standard			

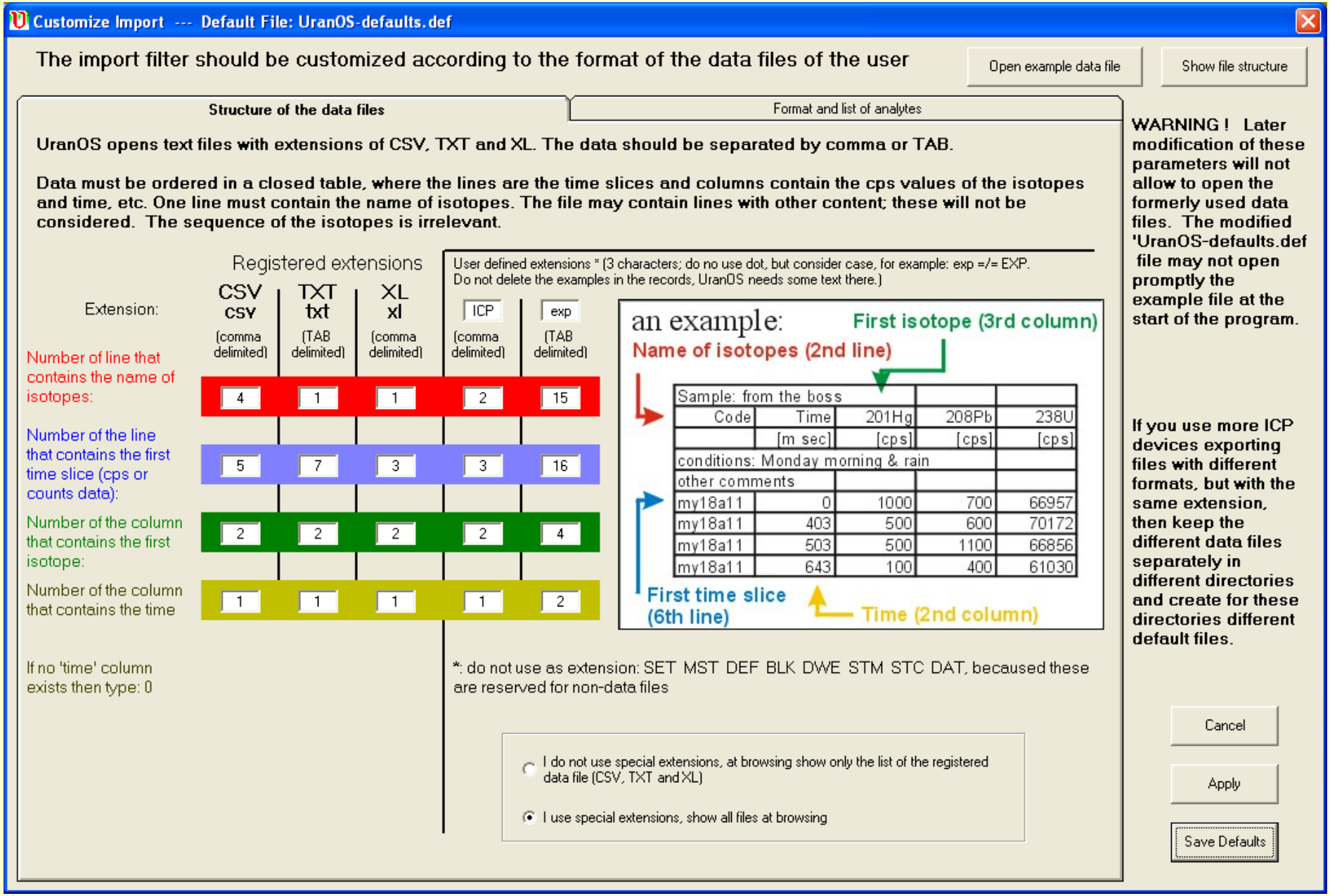
STEP 1	Creation of the empty master file with manual or automatic recognition of standards
STEP 2	Sequential processing of standards
STEP 3	Drift and fractionation correction (using the nomional values of standards)
STEP 4	Sequential procesing of samples
calculated	and calculation of corrected isotope ratios, ages and variable statistical parameters

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

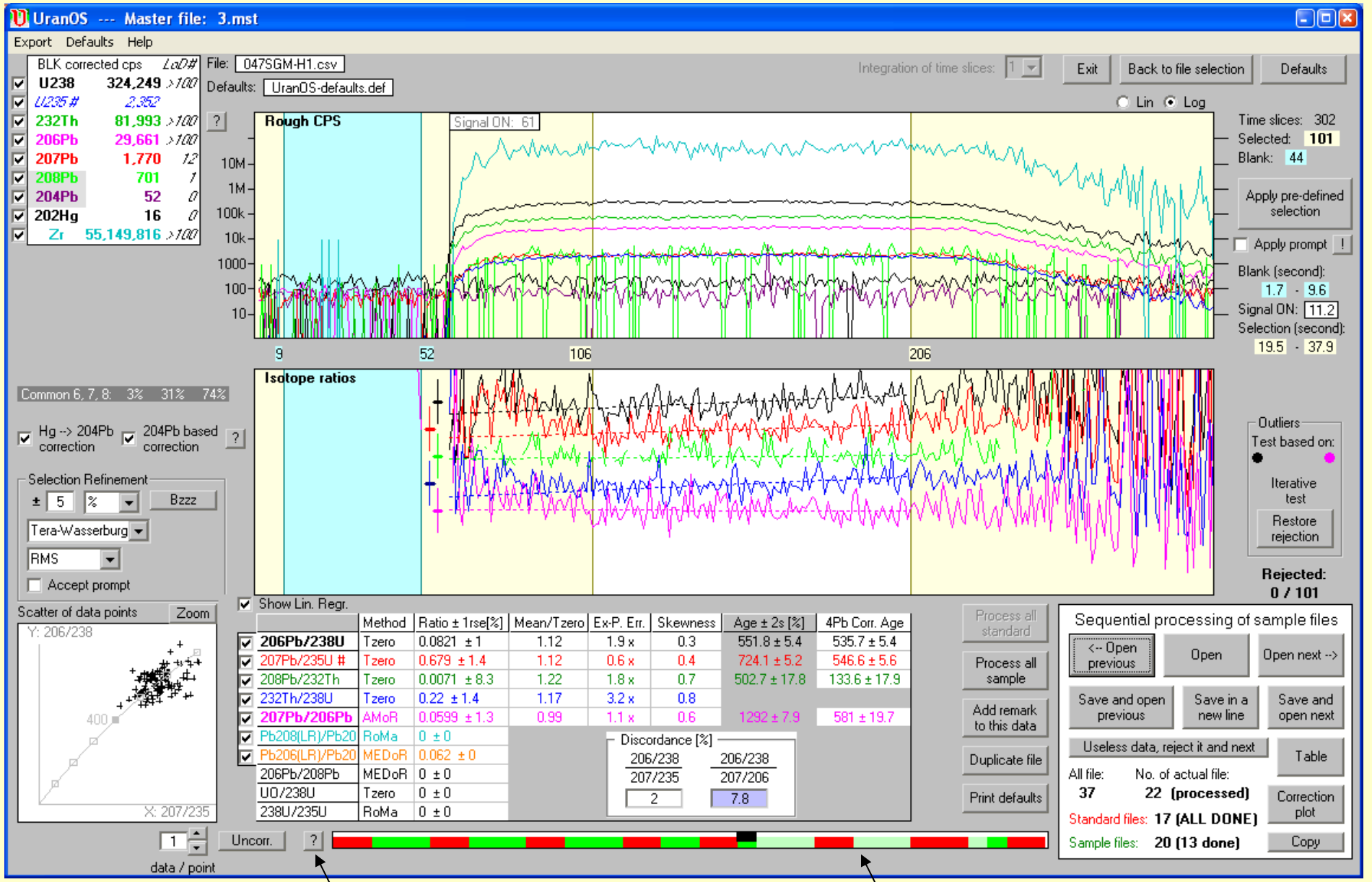
Major features

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



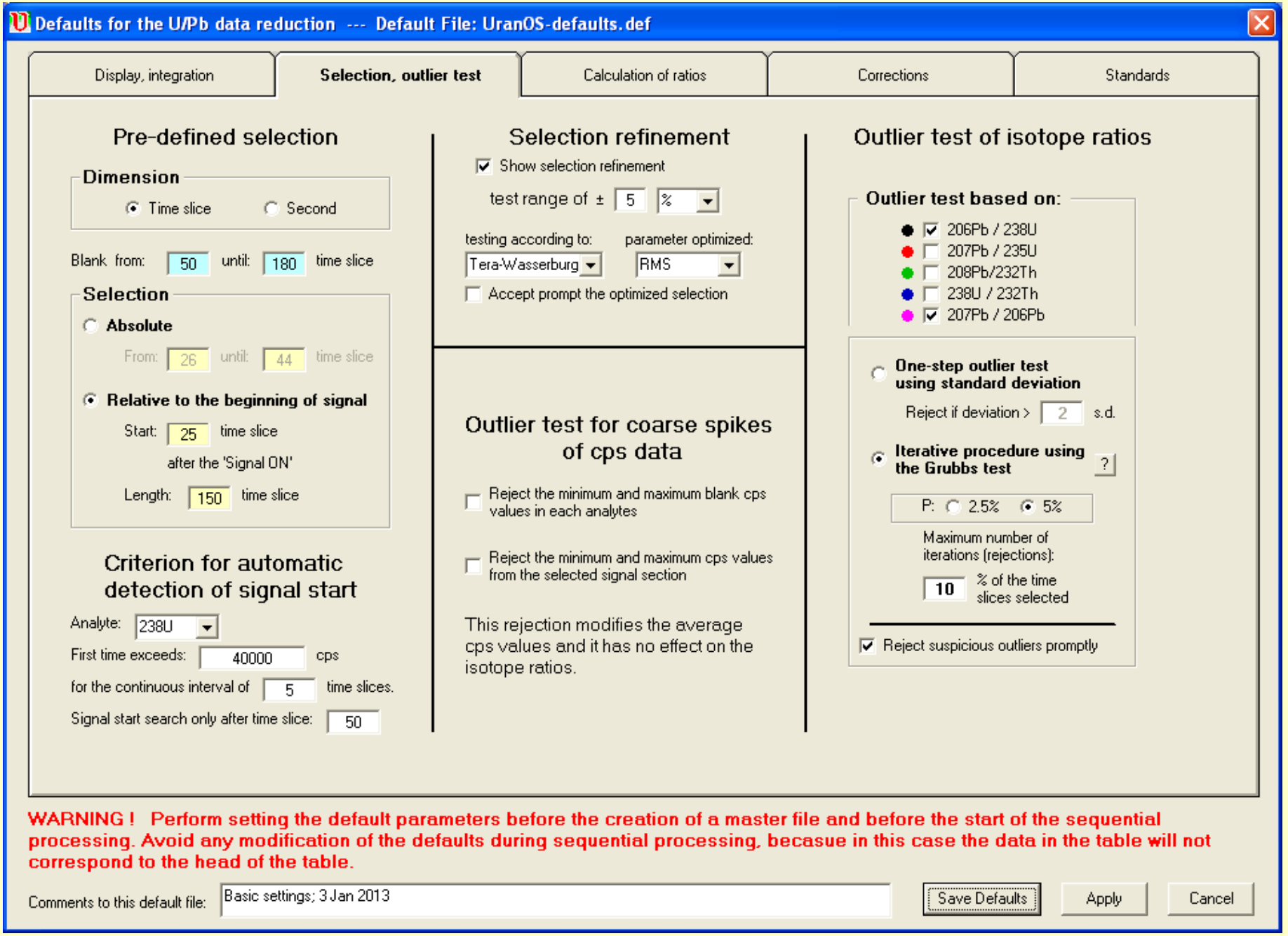
The major window shows the time resolved data and ratios & some of the the calculated values



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)



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
? ( ) 235U cps calculated from 238U
( ) 238U cps calculated from 235U

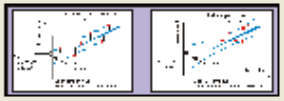
Isotope ratio for calculation of the missing or badly detected U isotope
238U / 235U: 137.88

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	( )	( )	( )	(•)	4
207Pb / 235U	( )	( )	( )	(•)	4
208Pb / 232Th	( )	( )	( )	(•)	4
232Th / 238U	( )	( )	( )	(•)	2
207Pb / 206Pb	( )	(•)	( )	( )	4

User selected analyte ratios

		RoMa	AMoR	MEDoR	Tzero	Decimal places:
!	Pb208(L / Pb206(L	(•)	( )	( )	( )	3
	Pb206(L / Pb204(L	( )	( )	(•)	( )	3
	206Pb / 208Pb	( )	( )	(•)	( )	0
	U0 / 238U	( )	( )	( )	(•)	3
	238U / 235U	(•)	( )	( )	( )	1

Intercept calculated at

(•) Tzero = start laser
( ) Tzero = 3 time slices after start laser
( ) Tzero = start selection

Selection giude for averaging methods

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)

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, becasue 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

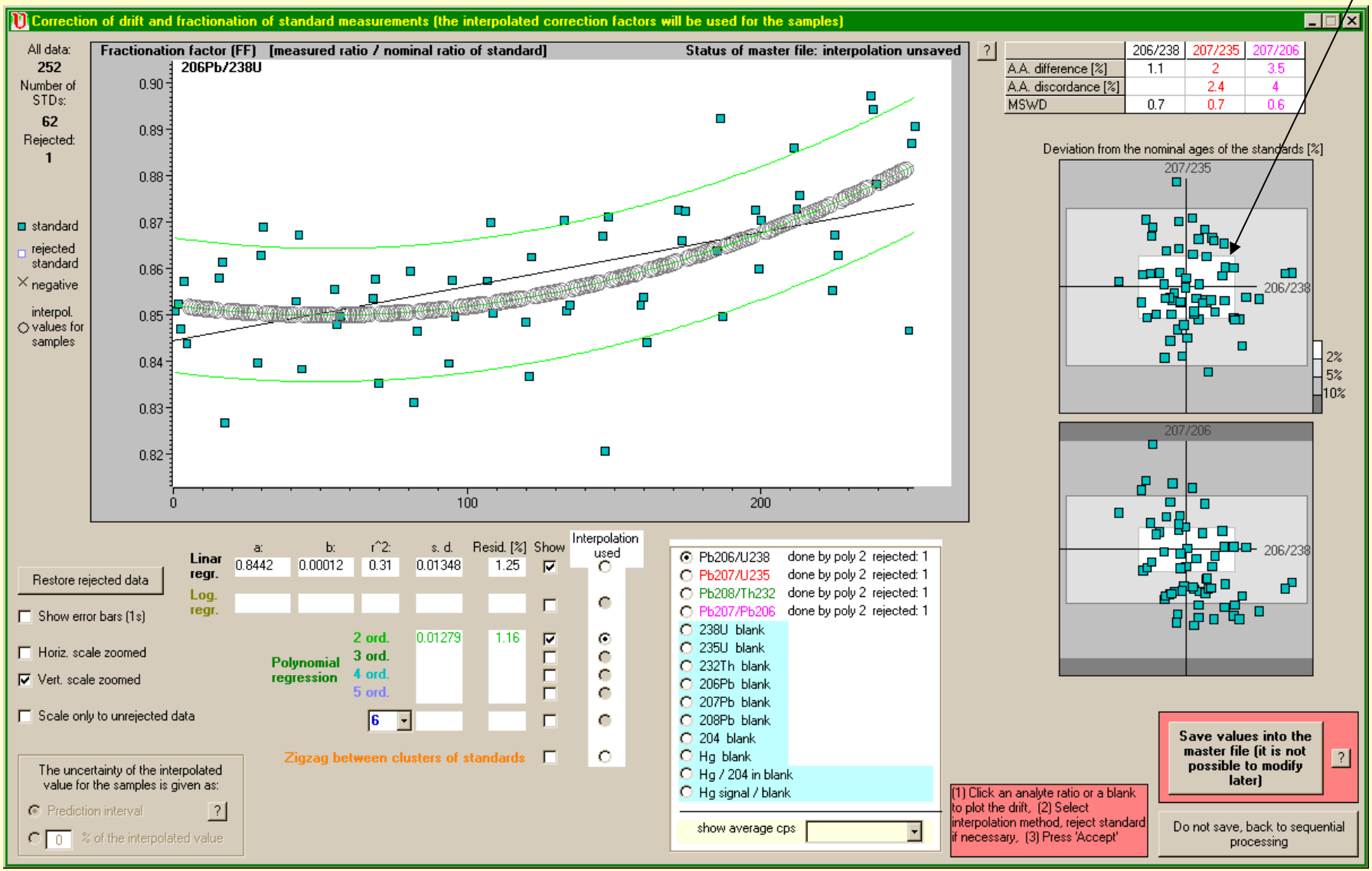
Save Defaults | Apply | Cancel

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



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 appaer in the signal.

Proposal for discussion II.

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

In order to express the down-hole fractionation we recomment 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

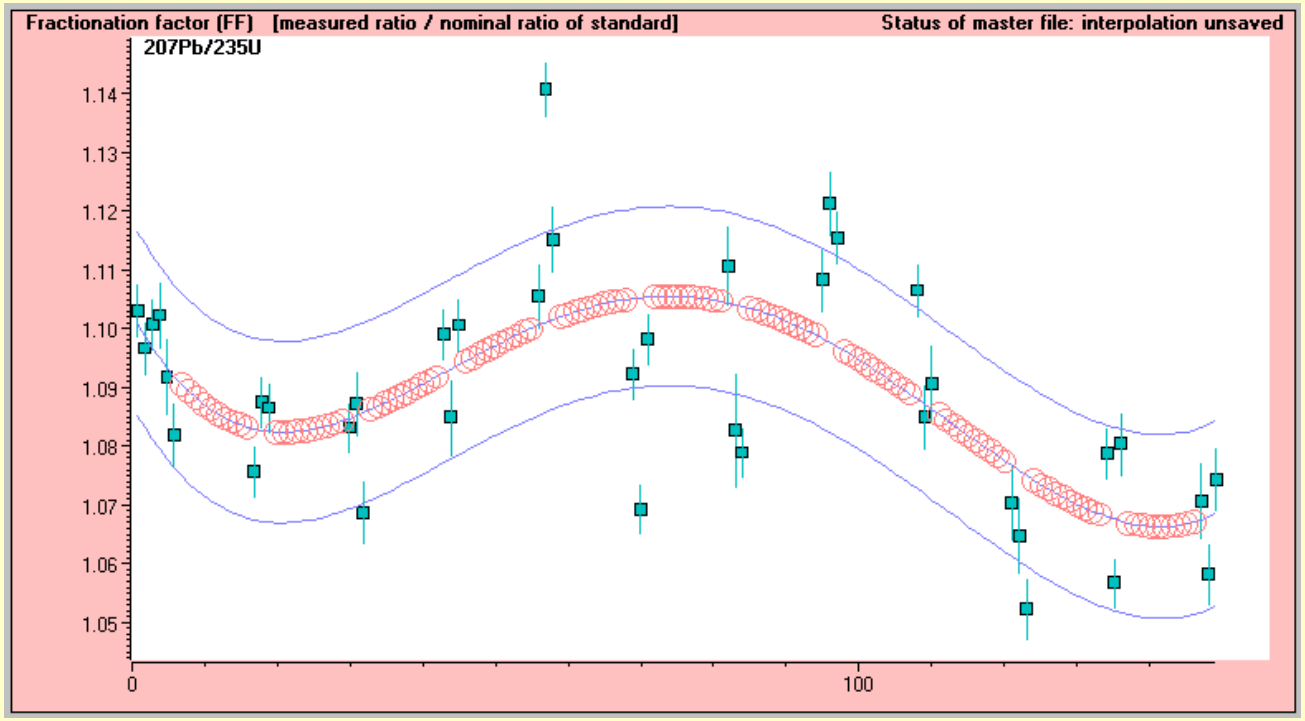
If the standards are not analysed individually in the sequence, but rather grouped then the 'short-wave' fluctuation (generated by counting statistics, heterogeneity, geometry problems, temperature oscillation of the instrument and several other factors) can be averaged and the real 'long-wave' trend 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 u **S S** u 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**tandard and **u**nknows 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 automaticaly and can be printed/archived

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*************** 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 [%].
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