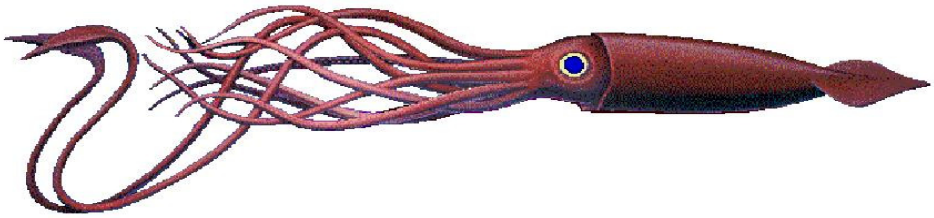
SQUID 2

Rev. 2.50

A User's Manual



Ken Ludwig
Berkeley Geochronology Center
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INDEX **100**

Introduction

Purpose of SQUID-2

SQUID-2.5 processes PD and XML files produced by a SHRIMP (Sensitive High Resolution Ion Microprobe) into a variety of parameters, including raw isotope ratios, radiogenic Pb isotope ratios, ages for the U-Th-Pb system. The processed data can be applied to a broad range of run tables and applications, ranging from U-Th-Pb geochronology, ^{230}Th/U geochronology, light stable-isotope geochemistry, and cosmochemistry. Processed data is placed in an *Excel* workbook that, for most output parameters, makes the formulae used in each data processing step explicitly available to the user.

Requirements

Software

SQUID-2 was developed using *Excel 2003* (service pack 3) and *Windows XP* (service pack 2). Earlier versions of *Excel* and other versions of *Windows* are probably compatible, but have not been tested. *SQUID-2* requires the *Isoplot* add-in (ver. 3.7 or later). *Only English versions of Windows and Excel are compatible with SQUID-2 and Isoplot.*

> ISOPLOT is BGC's Visual Basic Add-in for Microsoft's Excel® for data analysis and graphical presentation of geochronology, earth science and other radiogenic isotope data only.
>
> BGC's ISOPLOT is not the Isoplot® for analysis of any measuring system as described at (http://www.shainin.com/). BGC is not affiliated with Red X Holdings, LC. Isoplot® is a registered trademark of Red X Holdings, and is licensed to Shainin LLC.

At present, SQUID is not compatible with *Excel 2007*.

Hardware

WINDOWS

A mid- or high-range CPU (>1 Ghz non-Celeron, dual-core preferred) and 2 Gb or more RAM is recommended. The screen resolution should be at least 1280x800.

EMULATED WINDOWS UNDER MACINTOSH OS-X

At least two of the several programs enabling running of Windows on an Intel Mac, at least two – *Parallels* and *Fusion* – seem to work very well, with virtually no speed penalty compared to Windows. *Crossover* cannot run *Isoplot* or *SQUID*.

Before installing *SQUID* on your Mac, please ensure that your screen resolution is adequate. For wide-screen desktops, set your screen resolution from Windows (right-click anywhere on the desktop, select Properties/Settings) to about 1920x1200. For laptops or smaller desktop screens, use 1440x830 if possible.

Printer Setup

Upon first installation of *Excel*, *a printer must be selected* (via Page/Setup) before running *SQUID-2* or *Isoplot*, and the page size must be set to Letter or A4.

Input Data Files

SQUID-2.5 only processes PD or XML files for a single ion-counting collector.

Installation

1. If you're running Windows from an Intel Mac under *Fusion* (*Parallels* is incompatible), you must set Windows screen resolution to somewhat higher than the default setting. Right-click anywhere on the Windows desktop (*not* the Parallels or Fusion desktop) and select Properties, then Settings . If possible, set the resolution to either 1440 x 830 or 1920 x 1200 pixels

2. Remove or rename ***all*** existing *SQUID* and *Isoplot* add-in file on your computer. *Excel* tends to copy add-in files to its own folders, so you must to a *complete* search of your hard disks (including Hidden and System files) to make sure that *Excel* will not screw everything up by having multiple, incompatible copies of *Isoplot* and *SQUID* loaded at the same time.

3. Start *Excel* 2003. If you find that *Excel* has automatically loaded either *Isoplot* or *SQUID*, close *Excel* and go back to step 2.

4. Select Tools/Add-ins from the *Excel* toolbar at the top of *Excel*'s window (Figs. 1, 2). Check any boxes labeled *Isoplot* or *SQUID* in the Add-ins list. *Excel* should display a message each time saying that the add-in can't be found, and asking if the *Isoplot* or SQUID add-in should be deleted from its list. Click Yes. If such a message does *not* appear. close *Excel* and go back to step 2.

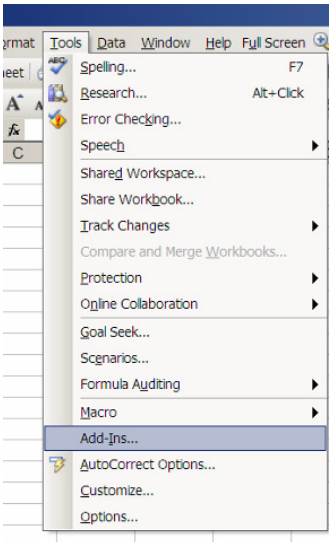


Figure 1

5. Transfer the *SQUID-2.5* folder containing the matched pair of *SQUID-2.5* and *Isoplot 3.7* add-ins the *SquidUser* folder, and the *SQUID-2.5* manual to your computer. Make sure that the folder in which the *SQUID-2.5* folder resides is one for which you have full read/write permission. This folder should probably not be on a network drive.

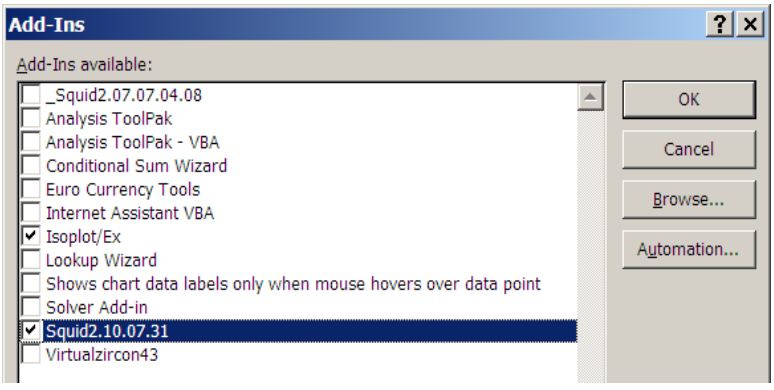


Figure 2

6. With the Tools/Add-ins box open, click Browse and navigate to the folder containing *SQUID-2.5* and its compatible *Isoplot*. Select the *Isoplot* add-in, click OK, then OK again from the Add-ins box.

7. Repeat Step 6, but this time select the *SQUID-2.5* add-in. *SQUID-2.5*'s splash screen should appear if installation was successful.

8. Before trying out *SQUID-2*, close, then re-open *Excel*. The compatible pair of *SQUID-2.5* and *Isoplot* should now load automatically whenever *Excel* is opened.

Data Reduction for U-Pb Geochronology

Click in the *SQUID* toolbar (p. 36) or select Process a Pb-U-Th Run from the *SQUID* drop-down list, then navigate to and select the PD or XML file of interest. The data-reduction setup panel for U-Pb geochronology will appear (Fig. 3).

Two Run Tables will appear in the pink box at the left of the panel, the first being the Run Table for the data-reduction *Task* already in memory, the second the Run Table for the actual PD or XML file. If the two run tables don't match, *SQUID* will refuse to process the file.

Note that when you select a PD or XML raw-datafile, *SQUID* will attempt to find a data-processing *Task* whose Run Table matches that of the PD file. This *Task* may or may not be the one desired. If not, select the proper *Task* – say, *Zircon, canonical ANU +UO2* – from the *Task* dropdown.

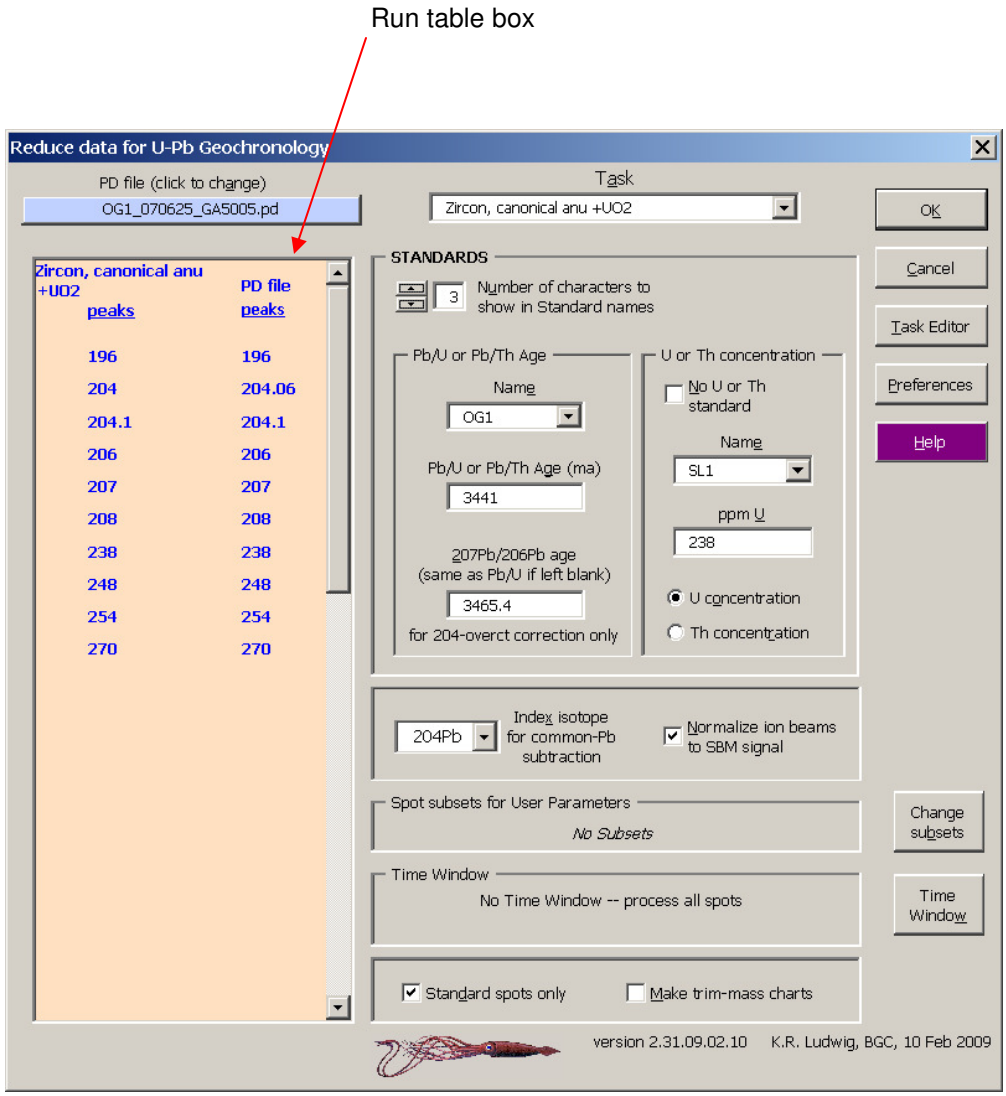


Figure 3: Setup panel for U-Pb Geochronology data reduction.

U-Pb/Th-Pb Standards

Specifying standards when starting data reduction

SQUID requires a $^{206}Pb/^{238}U$ or $^{208}Pb/^{232}Th$ standard to be among the analyzed spots in the PD file. A standard for U or Th concentration is optional, and can be either the same or different from the age standard. To specify a standard from the U-Pb data-reduction panel,

1. Select the number of initial characters to characterize the age–standard spots (e.g. 4 for Standard spots with names such as SL13-1.1, SL13-2.1, SL13-3.1…), then select the name of the age standard from the spot-name fragment dropdown.

2. Enter the $^{206}Pb/^{238}U$ (or $^{208}Pb/^{232}Th$) age of the Age Standard. *Enter the Age Standard's (apparent) $^{207}Pb/^{206}Pb$ age only if different from its Pb/U or Th/U age.*

3. Select the U or Th concentration standard (if any) and enter its U or Th concentration.

The Common U-Pb Standards List

You can specify up to 50 common U-Pb age and/or concentration standards from the Preferences panel (p. 57). When the U-Pb data-reduction panel is being filled out, SQUID will look for spot names whose first few characters match those of an age standard. If a match is found, that standard's name, Pb/U age (if defined), Pb/Pb age (if defined), and U or Th concentration (if defined) will entered into the appropriate boxes.

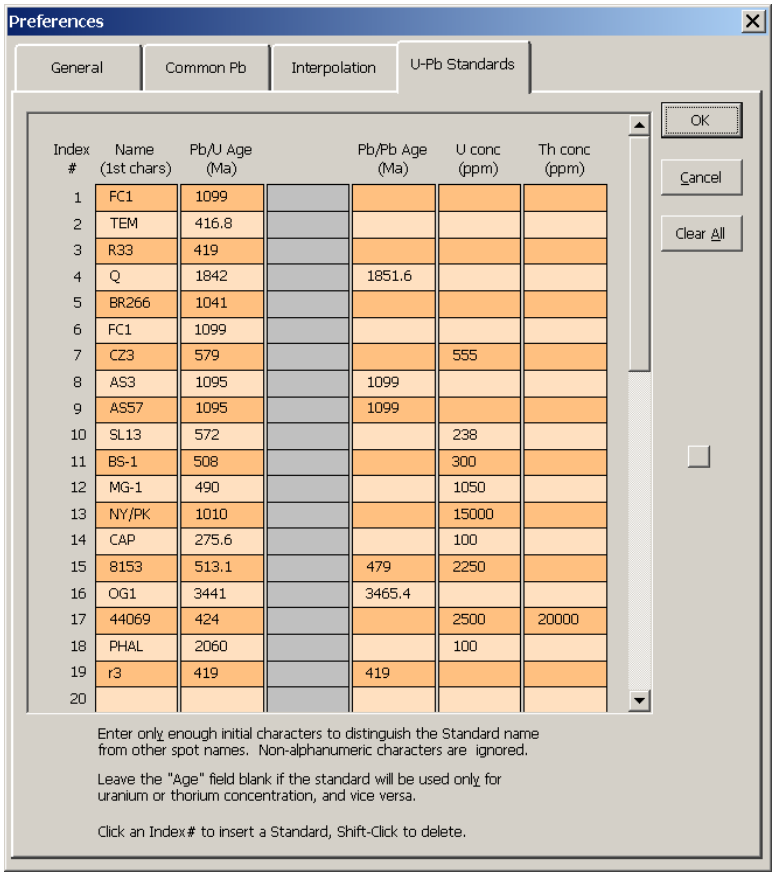


Figure 4: The *U-Pb Standards* page of the *Preferences* panel.

Specifying the common-Pb index isotope (U-Pb geochron panel)

Select ^{204}Pb, ^{207}Pb, or ^{208}Pb from the Index isotope… dropdown (common-Pb isotope ratios are specified in the Preferences panel; p. 52). The use of common Pb index isotopes is discussed in pages 46, 63, 44, and 95)

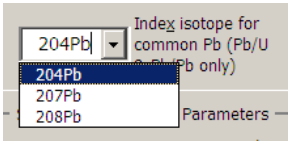


Figure 5: Selecting the index isotope for correction of common Pb.

SBM Normalization

Indicate whether or not the secondary ion beam (pp. 34 , 59, 61, 96, 97) is to be normalized to the SBM (secondary beam-monitor).

Trim Mass Charts

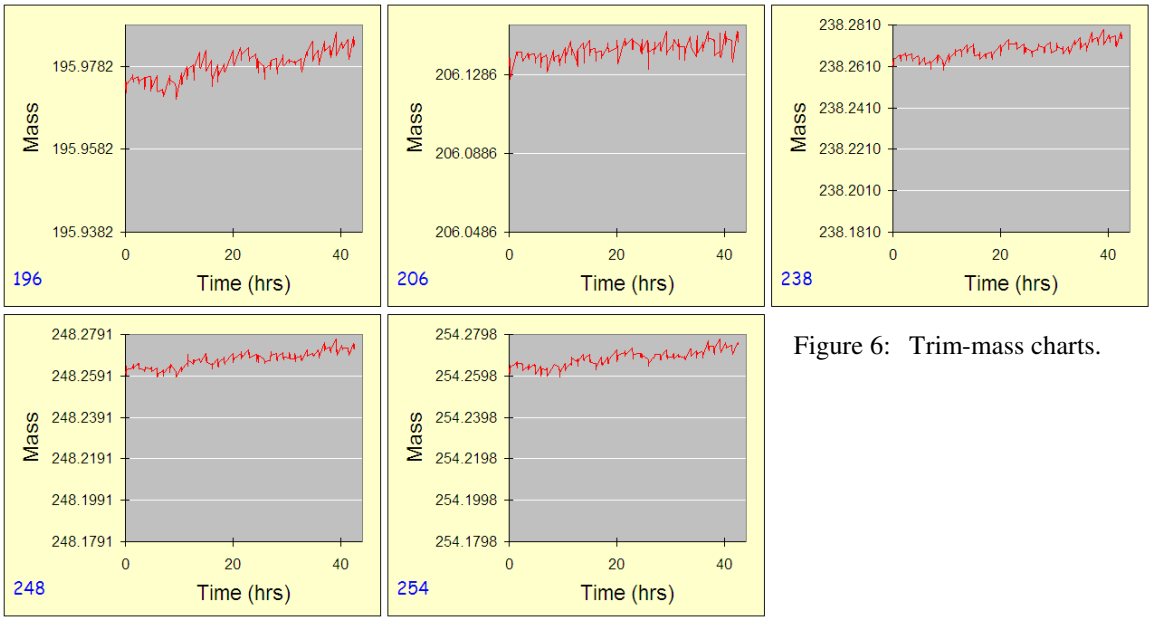


Figure 6: Trim-mass charts.

If the Make trim-mass graphics box is checked when starting data reduction, *SQUID* will construct scan-by-scan charts of the trim masses for each of the centered mass stations (for Standard spots only).

Click OK.

Data reduction will typically take a few tens of seconds, and yield an *Excel* workbook containing not only the usual StandardData and SampleData sheets, but also the original PD data, condensed and reformatted for ease of examination (Fig. 8, p. 7). An optional Within-Spot Ratios sheet (Fig. 7), containing the calculated scan-by-scan isotope ratios for each spot-burn can also be requested (from Preferences; p. 52).

178m0.1. 1	Time	204 /206	err	Time	207 /206	err	Time	208 /206	err	Time	206 /238	err	Time	208 /248	err
6-10-16, 16:33	112.5	1.8E-06	1.8E-06	139.75	0.29983	0.00159	147.5	0.26374	0.00243	154.25	1.45176	0.00959	176	0.06533	0.00059
Spot# 4	242	-1.5E-05	1.6E-05	269.25	0.29984	0.0016	276.75	0.26424	0.00245	283.75	1.41334	0.00931	305.25	0.06609	0.0006
	371.5	-2.3E-05	1.5E-05	398.75	0.29957	0.00161	406.25	0.26904	0.00249	413.25	1.37414	0.00903	434.75	0.06565	0.0006
	501	-2E-05	1.9E-05	528.25	0.29968	0.00161	536	0.26401	0.00246	542.75	1.36088	0.00891	564.5	0.06456	0.00059
	630.5	-2.3E-05	1.5E-05	657.75	0.29945	0.00161	665.5	0.26276	0.00245	672.25	1.35988	0.00888	694	0.06425	0.00059

Within-Spot Ratios / SampleData / StandardData / ____GA_GA5003_06101615.11 w dis /

Figure 7: Fragment of an optional *within-spot isotope ratios*/sheet.

Condensed raw-data sheets produced by SQUID

When accessing a SHRIMP raw-data file *SQUID* first parses the PD or XML file, then converts it into a formatted, space-efficient and user-friendly format.

XML files:

- Can take as much as a minute to load and parse,
- Can only yield a "Short" condensed raw-data sheet (see below) If the XML file contains more than about 65,000 lines,
- Contain extra information such as primary beam current, stage position, and Qt1y-Qt1z settings, all of which can be plotted versus time as *Autocharts* (p. 30).
- Can easily accommodate future additions to existing data parameters.

PD files:

- Load and parse rapidly,
- Can always produce "Long" (see below) condensed raw-data sheets if desired.

From the Preferences panel (p. 52), you can specify whether or not the condensed sheet should retain the unformatted raw data in the first column of the condensed sheet (hidden by default), thus automatically archiving the original PD or XML file. Such auto-archiving slows down data-processing slightly, so if these files are normally archived elsewhere, is not recommended. Auto-archived condensed sheets are identified as PD file, Long rather than PD file, Short (for a PD file) in the top row of the condensed sheet (Fig. 8).

	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AE
1	STERN_GA5005_07062511.58.pd, 25/06/2007, 11:58 AM																PD file, short									
2	SHRIMP RG v2.46 ACQUISITION PRAWN DATA FILE																									
3	analyst STERN, mount GA5005,																									
4	**117 Spots**																									
5																										
6							*T.1.1, 2007-06-25 12:16*				*10 peaks, 6 scans*															
7		tot cts				tot cts					tot cts					tot cts					tot cts				
8	2	mass		tot cts	trim	20	mass		tot cts	trim	20	mass		tot cts	trim	10	mass		tot cts	trim	30	mass		tot cts	trim	5
9	Secs	195.913	±1sig	SBM	mass	Secs	204.057	±1sig	SBM	mass	Secs	204.097	±1sig	SBM	mass	Secs	206.049	±1sig	SBM	mass	Secs	207.047	±1sig	SBM	mass	Sec
10	16	31343.8	177	366825	195.912	29	2.0000	1.41	3663750	204.057	51	0.0000	0.00	3659015	204.097	75	5433.3	73.7	1828407	206.049	96	967.144	37.2	5486041	207.047	11
11	171	33188.7	182	364846	195.915	183	2.0000	1.41	3649334	204.059	205	0.0000	0.00	3649302	204.099	229	5258.3	73.4	1821901	206.049	251	898.001	30.0	5457595	207.047	27
12	319	34146.1	185	361688	195.914	332	1.0000	1.00	3618083	204.059	354	0.0000	0.00	3613908	204.099	378	5084.8	71.4	1809463	206.050	399	900.001	31.8	5515429	207.048	41
13	469	34799.0	187	364457	195.915	481	1.0000	1.00	3638475	204.060	503	1.0000	1.00	3629826	204.100	527	5186.5	117	1812860	206.050	549	875.556	31.2	5434350	207.048	58
14	618	35465.2	217	361853	195.914	630	1.0000	1.00	3616917	204.059	652	0.0000	0.00	3617268	204.099	676	5012.7	70.8	1808556	206.050	698	881.001	29.7	5423708	207.049	71
15	767	35971.1	204	360583	195.913	779	0.0000	0.00	3601385	204.057	801	0.0000	0.00	3603056	204.097	825	5128.4	71.6	1799586	206.049	847	840.001	30.6	5408522	207.047	86
22																										
23							*OG1A.1.1, 2007-06-25 12:38*				*10 peaks, 6 scans*															
24		tot cts				tot cts					tot cts					tot cts					tot cts				
25	2	mass		tot cts	trim	20	mass		tot cts	trim	20	mass		tot cts	trim	10	mass		tot cts	trim	30	mass		tot cts	trim	5
26	Secs	195.915	±1sig	SBM	mass	Secs	204.059	±1sig	SBM	mass	Secs	204.099	±1sig	SBM	mass	Secs	206.050	±1sig	SBM	mass	Secs	207.048	±1sig	SBM	mass	Sec
27	16	31839.2	178	372678	195.909	29	3.0000	1.73	3722318	204.054	51	1.0000	1.00	3716532	204.094	74	42669.9	207	1855114	206.046	96	38043.4	273	5559677	207.045	11
28	172	33657.6	210	369814	195.912	184	3.0000	1.73	3694847	204.057	206	0.0000	0.00	3690998	204.097	230	42196.2	225	1843363	206.047	252	37756.5	194	5528330	207.045	27

Figure 8: PD file after condensation and reformatting by *SQUID*.

Reduced-data sheets produced by SQUID

The *StandardData* Sheet

The Standard sheet contains processed data for only the Age Standard spots. Among the changes from *SQUID-1* are:

- Additional data-columns containing the results for any *Task* equations (e.g. the *Log UO/U* and *Log Pb/U* columns in the example at right; p. 20).
- Up to eight user-specified, *Task*-linked plot insets, (e.g. *Log UO/U* versus *Log Pb/U*) each linked to one or two of the data columns (p. 30).
- A minimum Pb/U external error can be assigned to the Age Standard in the *Preferences* panel (p. 52).[1]
- Automatically-generated Concordia plots for the Age-Standard data can be requested (p. 53).

238 /196	% err	Log UO/U	% err	Log Pb/U	% err	4-corr 206Pb /238U calibr. const	% err	Age (Ma)	±1σ
0.103	0.55	0.809	0.22	-0.791	0.42	~~0.00385~~	~~0.57~~	408	2
0.087	0.52	0.817	0.23	-0.772	0.46	0.00389	0.55	413	2
0.170	0.41	0.818	0.17	-0.767	0.33	0.00393	0.39	417	2
0.279	0.35	0.818	0.13	-0.765	0.22	0.00395	0.30	419	1
0.313	0.35	0.818	0.11	-0.766	0.20	0.00394	0.25	418	1.0
0.160	0.38	0.824	0.16	-0.755	0.28	0.00391	0.36	415	1
0.331	0.31	0.820	0.11	-0.762	0.20	0.00396	0.30	420	1
0.151	0.39	0.820	0.16	-0.766	0.29	0.00389	0.41	413	2
0.110	0.43	0.821	0.19	-0.752	0.35	0.00401	0.42	425	2
0.343	0.38	0.820	0.11	-0.759	0.20	0.00398	0.24	422	1.0
0.165	0.38	0.821	0.16	-0.762	0.28	0.00392	0.35	416	1
0.148	0.39	0.814	0.17	-0.760	0.30	~~0.00406~~	~~0.37~~	430	2
0.287	0.36	0.812	0.12	-0.767	0.21	0.00404	0.26	428	1
0.232	0.43	0.825	0.17	-0.745	0.25	0.00399	0.39	423	2
0.371	0.38	0.825	0.11	-0.747	0.19	0.00399	0.34	423	1
0.259	0.42	0.825	0.13	-0.753	0.23	0.00394	0.29	418	1

Wtd Mean of Std Pb/U calibr. 0.00395
1σ error of mean 0.21%
1σ external spot-to-spot error 0.90%
MSWD 8.85
Prob. of fit 0.00
rejected spot(s) 1, 20
For visualization & preliminary evaluation only

Redo

Figure 9: Portion of StandardData worksheet showing the U/Pb calibration columns.

- A correction can be applied for obvious secular drift of the Standard calibration-constant (p.10).

CORRECTION FOR OVERCOUNTS ON ^{204}PB

SQUID will attempt to quantitatively assess the presence of non-^{204}Pb counts at the ^{204}Pb mass position by 1) assuming precise concordance of the ^{206}Pb/^{238}U-^{207}Pb/^{235}U ages, and also 2) assuming precise concordance of the ^{206}Pb/^{238}U-^{208}Pb/^{232}Th ages. The (resistant) mean value of the calculated 204-overcounts on the age-

204Pb /206Pb (fr. 207)	204Pb /206Pb (fr. 208)	7-corr 206Pb /238U const. delta‰	8-corr 206Pb /238U const. delta‰
		204 overcts /sec. (fr. 207)	204 overcts /sec. (fr. 208)

Figure 10: Column headers for 204 overcounts on the U-Pb age standard.

[1] Assigning a reasonable external error, based on an experienced operator's judgment from past data-sets, is important if the age standard has low enough count-rates that the counting statistics errors mask a (smaller) external variance. In such a case, if the sample spots have a significantly higher count rate, so that the external error is comparable to or greater than their counting-statistics errors, the errors assigned by *SQUID* to the sample spots will be underestimated, so that even well-behaved, age-equivalent spots will not yield a statistically coherent Group.

standard spots can then, if desired, be used to correct ^{204}Pb measurements for all of the Sample spots when the samples are Grouped (p.9). The output-columns related to calculation or 204 overcounts are shown in Fig. 10.

The *SampleData* Sheet

As in *SQUID-1*, the Sample sheet contains the basic raw and processed data for all spots but those of the Age Standard. For U-Pb geochronology, *the Sample Sheet is to be used only as an intermediate step in producing the final, Grouped Sample worksheets*.

Sample Grouping and Age Extraction

`Data reduction for U-Pb geochronology is not complete until the sample–spot data has been grouped by spot name. Group names are selected from one or more of six drop-down lists containing all Spot names, trimmed to the number of initial characters shown in # of characters spinner-box (red arrow, fig. 11). The dropdown lists will not show spot-name fragments unless at least 2 spots are thus defined.

To Group samples,

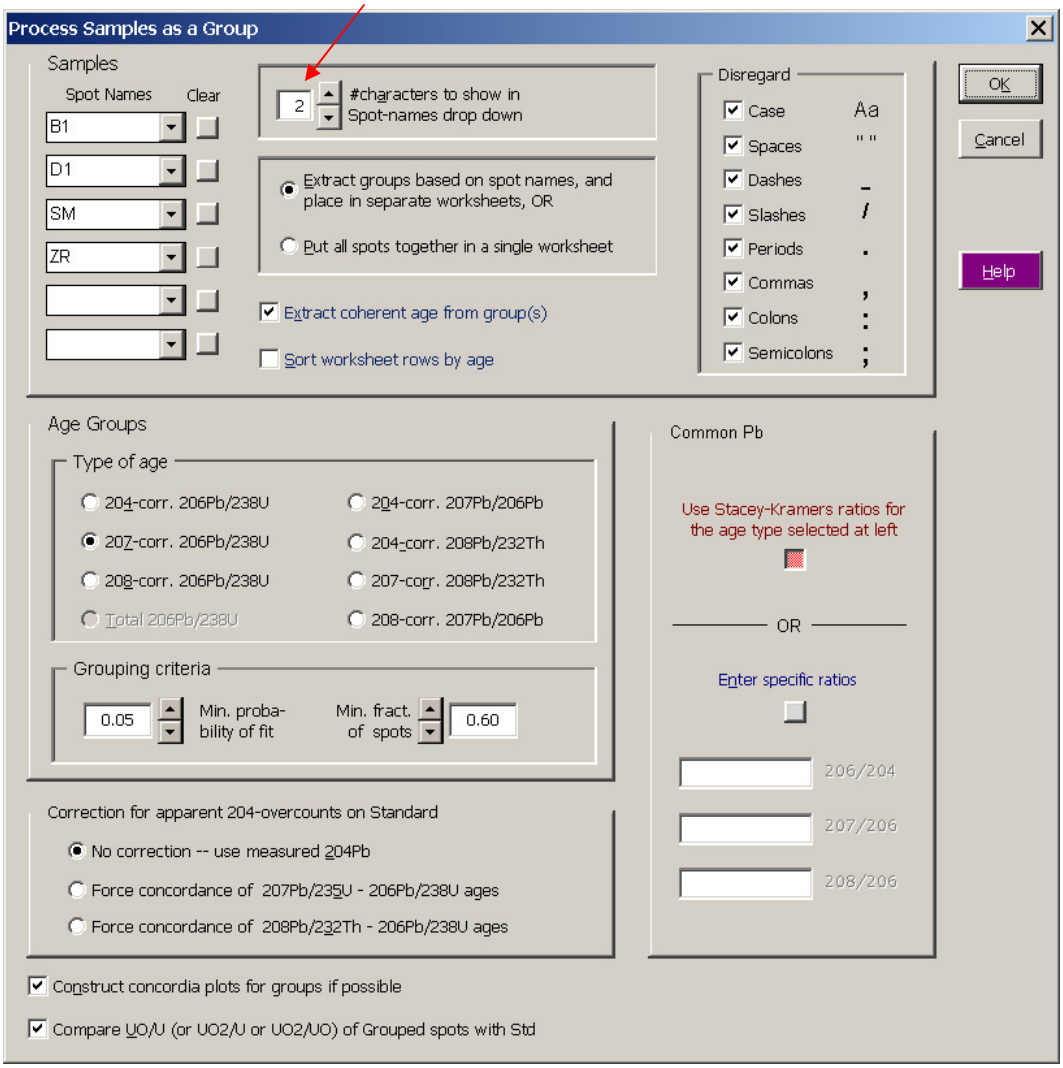


Figure 11: The Sample Grouping panel.

- Click  in the *SQUID* toolbar, or press the Group Me button at the top of the SampleData sheet.
- Select the number of initial spot-name characters to define a Group (red arrow, below),
- Indicate whether case is significant in the name fragments, and whether or not to ignore spaces, dashes, slashes … when identifying name-fragment matches,
- Specify from 1 to 6 spot-name groups,
- Indicate if a statistically-coherent age group is to be extracted from each spot-name group.
- If age grouping is requested, then
- Indicate whether the data-rows in each grouped-sample worksheet should be sorted by spot age,
- Specify the type of age to use for age grouping, the criteria that define an age group, and whether to construct a concordia-plot inset for the spot group,
- Specify the method of correction, if any, for ^{204}Pb overcounts (*No correction* is recommended unless you have a good understanding of the concept),
- Define the common-Pb ratios for the groups.

Correcting U-Pb Geochronology data for Secular Drift of Age-Standard Spots

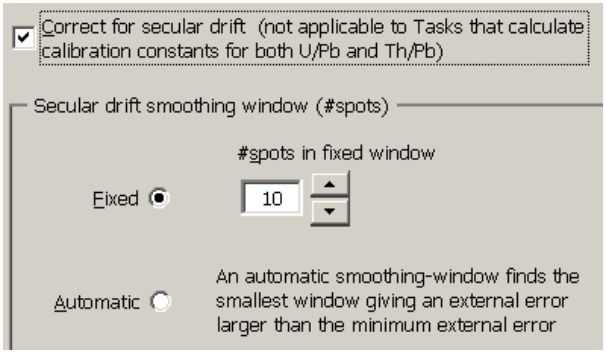


Figure 12: Setting parameters for correction of secular drift of the U/Pb calibration constant. (*Preferences* panel).

Normally, the calibration constant (e.g. $Pb^+/U^+ \div UO^+/O^+$) measured for the different Pb/U or Pb/Th age-standard is expected to remain, within some statistical scatter, constant during the length of the analytical session, so that extracting the true Pb/U or Pb/Th ratios of samples is a simple matter of normalizing the sample calibration constant to the average value of the Standard spots. If, however, the analyst can plainly see a trend in the Standard calibration constants (whether monotonic or cyclic), it is possible that the Sample spots will have been similarly affected. *SQUID-2* provides a very flexible, tuneable, assumption-independent method for dealing with such cases, enabled by checking the secular drift box (right) in the Preferences/Interpolation panel (p. 52).

If the user has selected Specified, the secular drift correction algorithm starts by fitting an outlier-resistant smoothed-spline curve (a LOWESS fit; Cleveland, 1979) to the Standard calibration constants, using a moving window for smoothing comprising the specified number of spots. Instead of the usual weighted-average chart, *SQUID-2* will then construct a chart showing the rela-

tive change of the calibration constant versus spot-time, and the corresponding smoothed-spline curve.

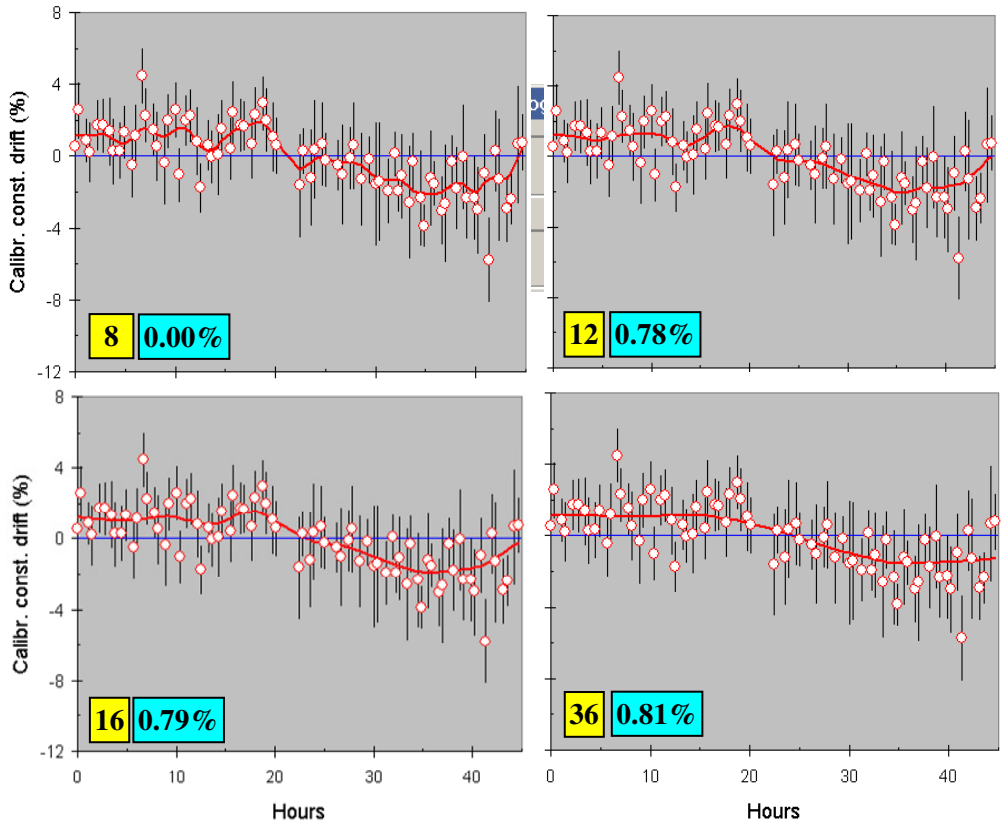


Figure 13: Showing the effect of different smoothing-window widths (yellow boxes, in number of spots) on the secular drift curve of the Age Standard calibration constant relative to its median value (red line). Estimated external (non-counting statistics) error is shown in the blue boxes. Small red circles indicate the Age standard calibration constant, black vertical lines their 2σ internal errors.

If, however, the user has selected Automatic for the smoothing window, *SQUID-2* will automatically find the largest smoothing-window that yields an external scatter no greater than the assigned Minimum acceptable external error for the age Standard.(p. 57). The Min. spots parameter (p. 12) sets the lower bound on the automatic smoothing-window.

The secular drift of Age Standard's calibration constant (relative to the median value) is then used to correct the calibration constants of the Standard spots (i.e. to remove the presumed effects of the Standard's drift).

Note that secular-drift correction will only be applied for Tasks with a single parent-daughter system (Pb/U or Pb/Th) specifically calculated (that is, where calculation of the non-Primary parent-daughter ratio is specified as Indirectly *in the* U-Pb Special Equations panel (p. 27).

Caveats in using secular drift correction

It can be argued that calibration-constant secular drift should not occur in a properly constructed mount analyzed with a properly functioning SHRIMP, and that when such behavior is observed the best remedy is to solve the instrumental problem rather than trying to cleverly manipulate the data. To the extent that this is the case, it is quite possible that attempting to correct for such drift will degrade rather than improve the accuracy and precision of the resulting U/Pb ages. Of particular concern is the possibility that, though the apparent external scatter of the Standard spots mad be reduced, drift-corrected Sample spots of the same true age will have increased scatter (thus making it impossible to find a coherent statistical group without excessive rejection), as well as displaying an more-or-less inverse secular drift from the Standard.

Note also that the algorithm used to infer external scatter from the secular-drift curve may yield under- or over-estimated values, as it has not seen extensive testing with real data.

Reducing General Isotope Data

For *SQUID-2*, all analyses that will not be used for U-Pb geochronology are considered *General Isotope* analyses. For *General Isotope* analyses, no separate StandardData worksheet is produced (though normalization to a standard is straightforward), and the only data columns that are automatically produced are those for burn time, cps of the Trim-Mass Reference peak, and the isotope ratios specified for the *Task*. Basic processing such as correction for mass fractionation, correction for isobaric interferences, secular changes in ratios, and normalization to a standard are readily handled by *Task* equations.

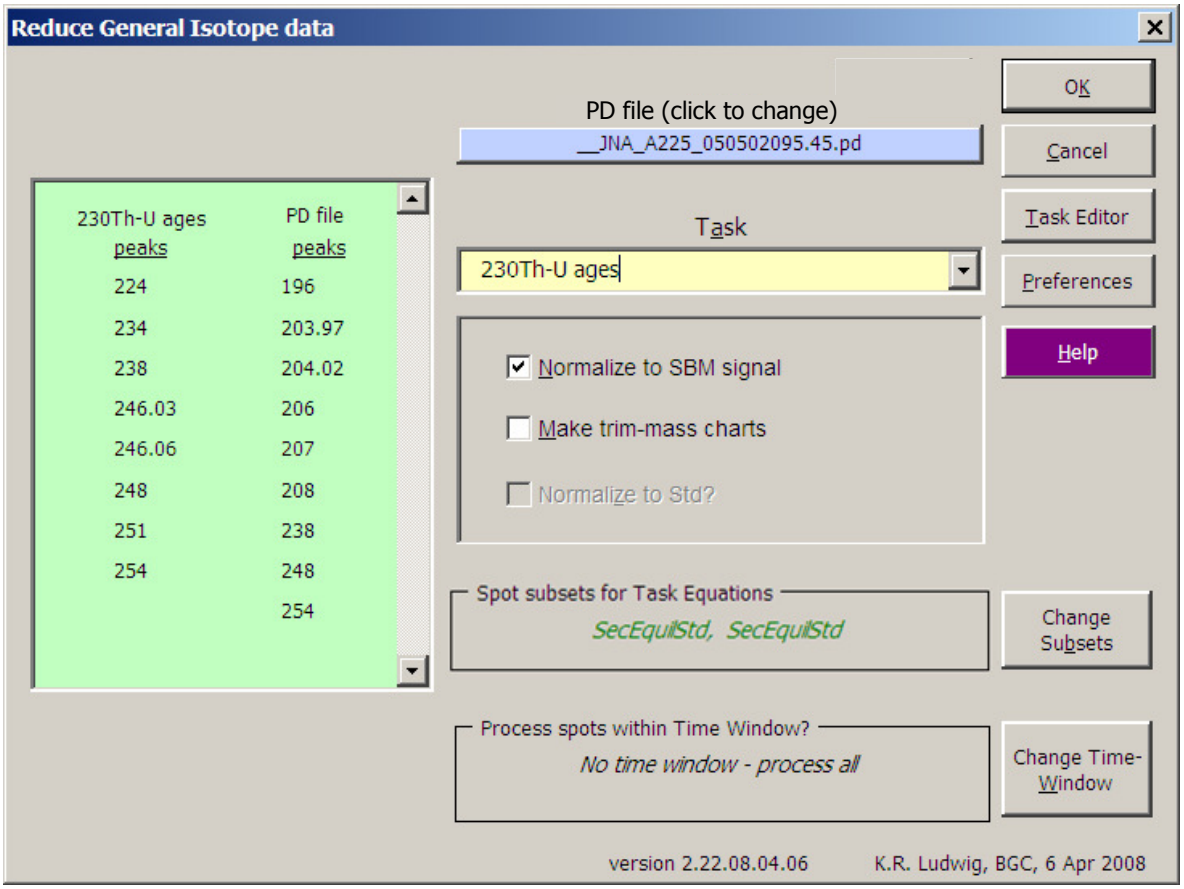


Figure 14: Setup panel for General Isotope Ratio data reduction.

The Reduce General Isotope data panel for General Isotope data (Fig. 14) is similar to, though much simpler than that of U/Pb geochronology.

Tasks

Introduction

Tasks are the templates used by *SQUID-2* to process the raw PD files. Each *Task* contains the algorithms by which the data is processed into final isotope ratios, ages, element concentrations, and any other parameter of interest to the user.

The gateway into defining, viewing, and editing *Tasks* is the *Task Editor* panel (Fig. 13 – press  on the *SQUID-2* toolbar). There are two classes of *Tasks*: U-Pb Geochronology and Isotope Ratio. The former is specifically constructed for processing analyses on minerals such as zircon into a complete set of relevant total and radiogenic isotope ratios, together with their associated ages. The latter is for any other type of analysis.

Each *SQUID-2 Task* is defined by an *Excel* workbook (*.xls) file contained by the *SquidUser* folder, located in the same folder as the *SQUID-2* add-in file. Names of *Task* files always begin with *SquidTask_ ,* followed by the name of the *Task* and name or initials of the *Task*'s creator.

Existing *Tasks* defined in the default *SquidTasks* file are shown in the scrollbox at the lower left of the panel. After you create any additional *Tasks* of your own, all of your interactions with the *Task* editor will be to modify existing *Tasks* via one or more of the *Edit/view* buttons.

Task definition is a four or five step process (General Isotope and U-Pb geochron data, respectively), in which you will:

1. Define mass stations for the PD file's Run Table,
2. Specify isotope ratios to be calculated from the Run Table,
3. Define equations for calculation of U/Pb (or Th/Pb) and $^{232}Th/^{238}U$ ratios and for U (or Th) concentration (U-Pb geochron only),
4. Define equations for any additional data-processing, and
5. Specify chart insets for *x-y* plots, means, or secular trends of any of the final data columns.

The best way of to get an idea of what a *Task* consists of is to go through the process of creating one from scratch, using, for example, the canonical (ANU-RSES) run table and equations.

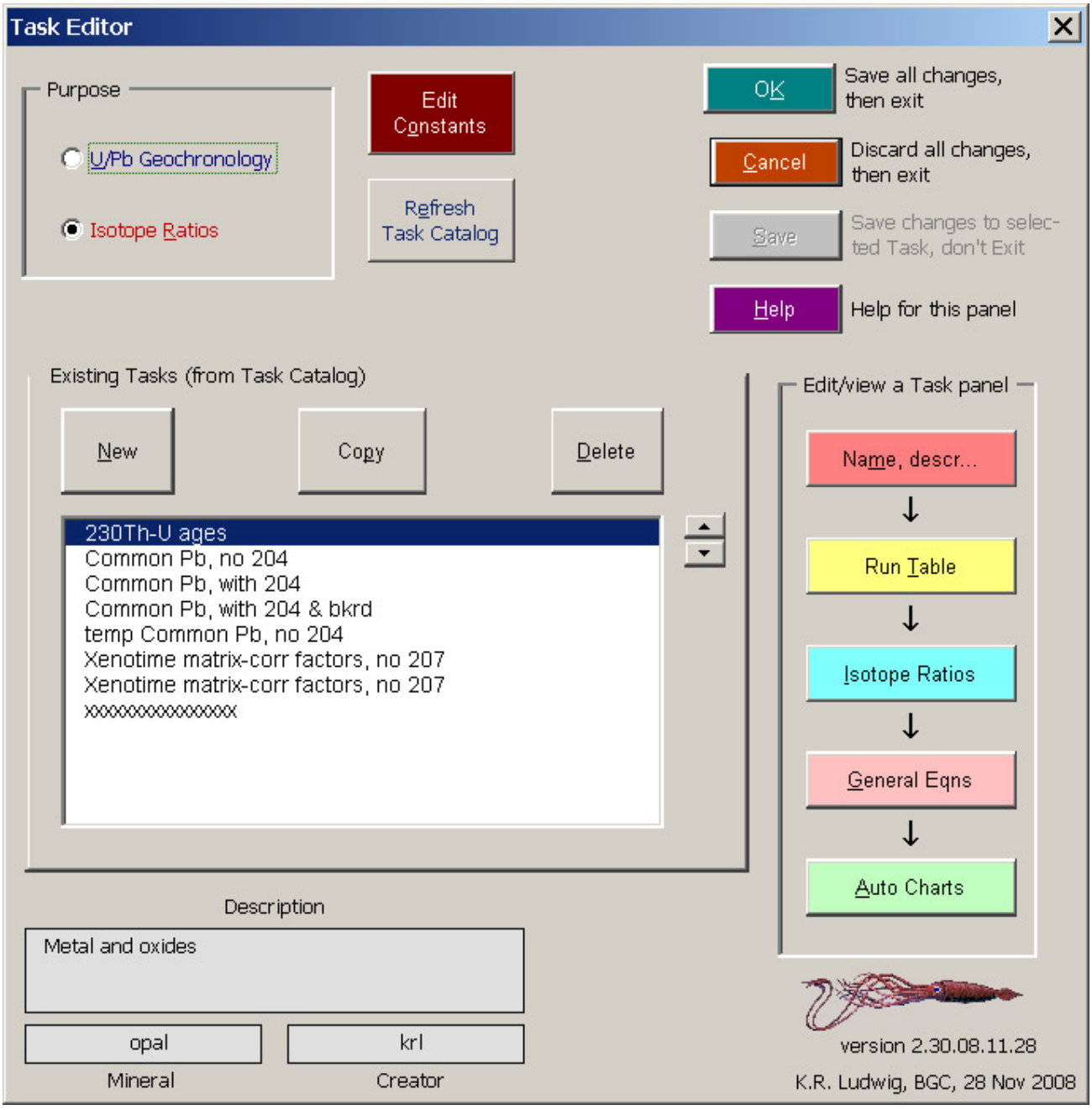


Figure 15: First panel of the Task Editor.

The Task Name Panel

Each *Task* is assigned a unique name (Figure 16) – preferably a reasonably pithy one that fits within the *Task* list-box of the *Task* Editor. The *Task* Description should contain additional information about the purpose of the *Task* and type of data required. The *Primary Mineral* and C*reator name of initials* fields are self explanatory.

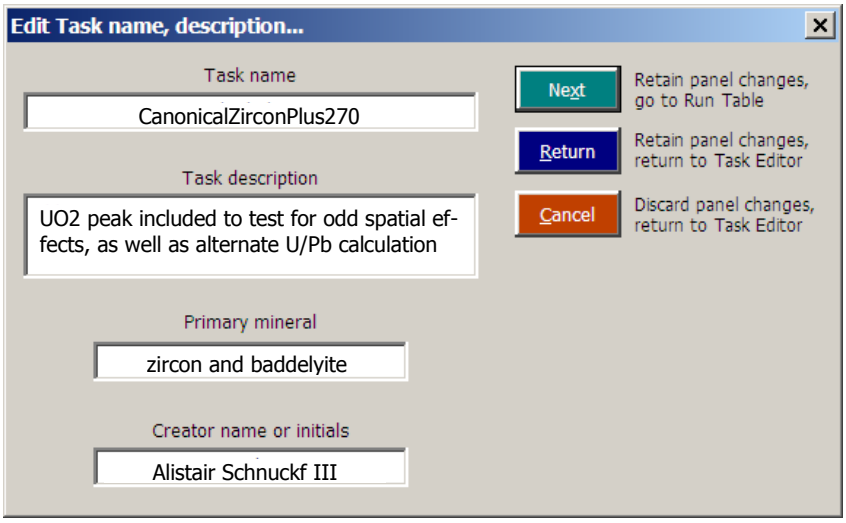


Figure 16: The Task name, description, mineral, and creator panel.

The Run Table Panel

Defining the Run Table

From the Existing *Tasks* list of the *Task* Editor (Fig. 15), click the New button, thus invoking a blank Run Table panel. For illustration, figure 17 shows a completed Run Table panel (for U-Pb/zircon) , but of course when defining a new *Task*, all of the entries in the right-hand scrollbox will be empty. The steps for definition of the canonical zircon Run Table are:

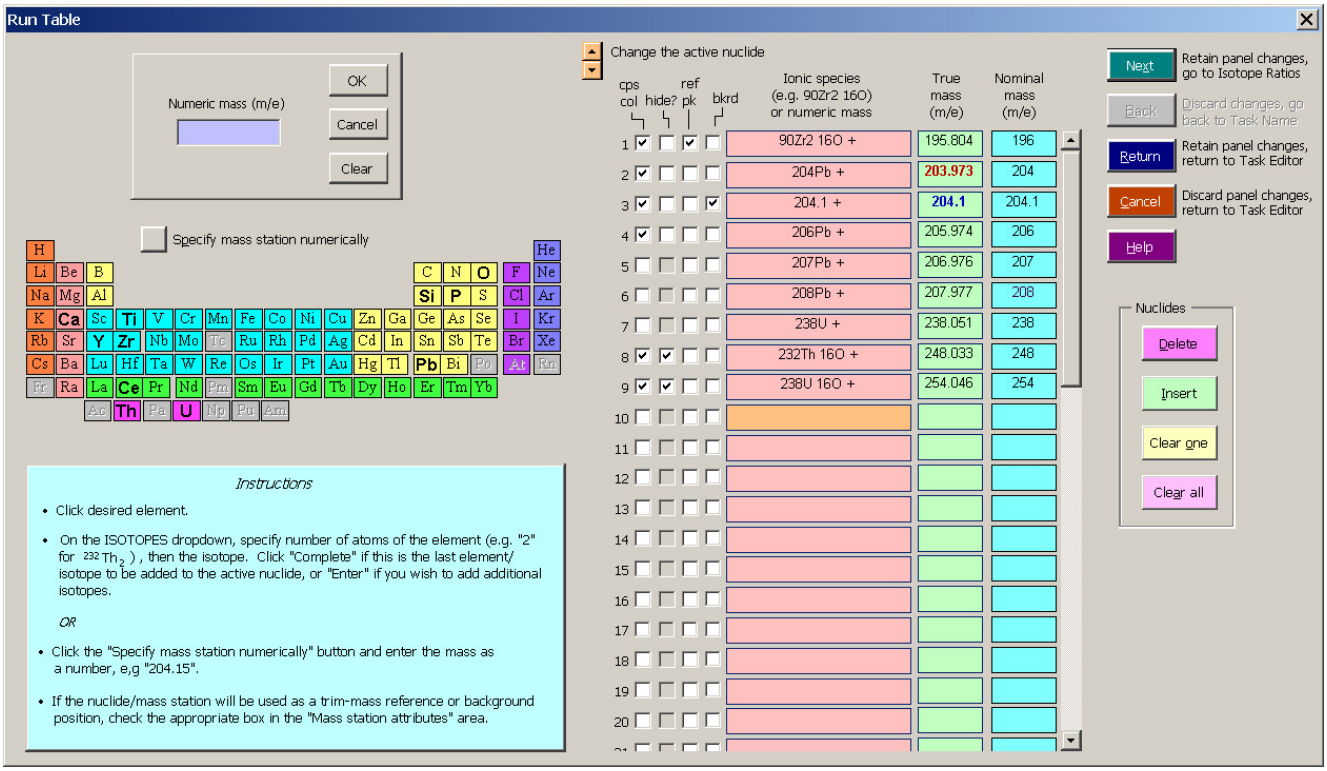


Figure 17: The Run Table panel.

1. Set the active Ionic Species or numeric mass box (the one in the right half of the panel) to Scan Order 1, using either the mouse or the control. The active Ionic Species… box is tan rather than pink, as for the Ionic species box for scan order 10 in the example panel (figure 17). We now wish to enter $^{90}Zr_2{}^{16}O^+$ for the first mass position in the run table.

2. Click on the zirconium (Zr) box in the periodic table.

   The resulting isotope selection dropdown (figure 18) will show all of the stable and long-lived isotopes of the element, with the most abundant selected by default (relative abundances are shown to the left of the isotopes). In this case, the default of ^{90}Zr is fine (to select any other Zr isotope click on one of the black isotope boxes).

3. Select the number of atoms of this isotope in the ionic species (using the How Many spin-box), then click OK. $^{90}Zr_2$ + will appear in the active Ionic Species box in the right half of the panel.

4. We know that the final nuclide will have a charge of +1, so we can leave the Charge box as it is.

5. Click the *Enter* button, which will dismiss the *Select Isotope* panel, then click on the yellow ***O****(xygen)* box in the periodic table. Select ^{16}O, quantity 1, charge

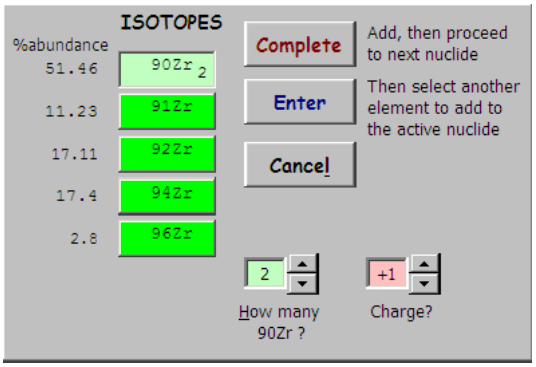


Figure 18: The *Select isotope* box.

1. Click the *Complete* button. The nuclide (ionic species) box should now contain $^{90}Zr_2$ ^{16}O + ref in the Ionic species box, with 195.804 as its mass to charge ratio, and the active ionic species box should move down one in the list.

6. Check the small *ref pk* box to the left of the Ionic species box (figure 20) so that this nuclide will be used as the reference mass for any Trim Mass graphics

7. Enter the singly-charged ^{204}Pb ion as the next (scan order 2) ionic species/mass station by selecting Pb as the element, and ^{204}Pb as the isotope. Click *Complete* again to move to scan order 3.

In PD files that this *Task* will process, scan number 3 is the background mass of, say, 204.09. Because the background "mass" doesn't correspond to that of any actual nuclide, you must click the Specify mass station numerically button (just above the periodic table; figure 17), type in 204.09, then click OK. Now check the *Bkrd* box to the left of the Ionic species box to indicate that this mass station is to be used for background. Move on to the next mass station as before.

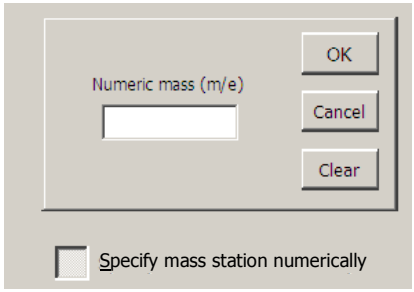


Figure 19: The *Specify mass numerically* box.

And so on.

Note that if the ionic species you are defining is, say, doubly or triply charged, you can specify the charge with the spin-button to the right of the box you used to enter the numeric mass. The mass/charge ratio of the ionic species will automatically adjust.

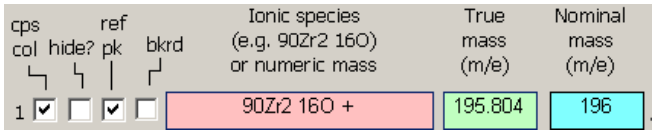


Figure 20: Completed entry for scan order #1.

If you want to have a column containing the (total) counts/second of a mass station placed on the output worksheets, check the corresponding *cps col* box to the left of the *ref pk* box (figure 20). *Cps col* boxes are automatically checked for reference and background mass-stations, and also for the ^{204}Pb and ^{206}Pb mass stations.

When you're done, look at the Nominal mass column to the right of the True mass column. The Nominal masses are usually (but not always) an integer, but *SQUID-2*, if necessary, will have added just enough additional decimal places to distinguish the masses of each mass station from the other. Thus true mass of 204.09 that you entered for the background mass-position will be shown as 204.1 to distinguish it from the nominal 204 assigned to the $^{204}Pb^{+}$ mass station. When referring to the isotope ratios or mass positions of the Run Table in the Equations panels, always use these nominal masses.

Specifying Isotope Ratios

The next step is to specify which isotope ratios should be calculated. The order of the ratios will be preserved in the output worksheets, but otherwise is unimportant. To enter a ratio,

- Click on a blue ratio-box (figure 21) to activate it (its color will change from blue to orange when activated),
- Click on one of the nominal masses in the green boxes to the left (say 204) to use as the numerator of the ratio,
- Click on another of the green boxes to select the denominator isotope (say 206), giving 204/206 in the ratio box, whose color will have changed back to blue.
- To clear the ratio box and start over, click it a third time.
- The ratio boxes don't have to be all filled in sequence – empty boxes are ignored.

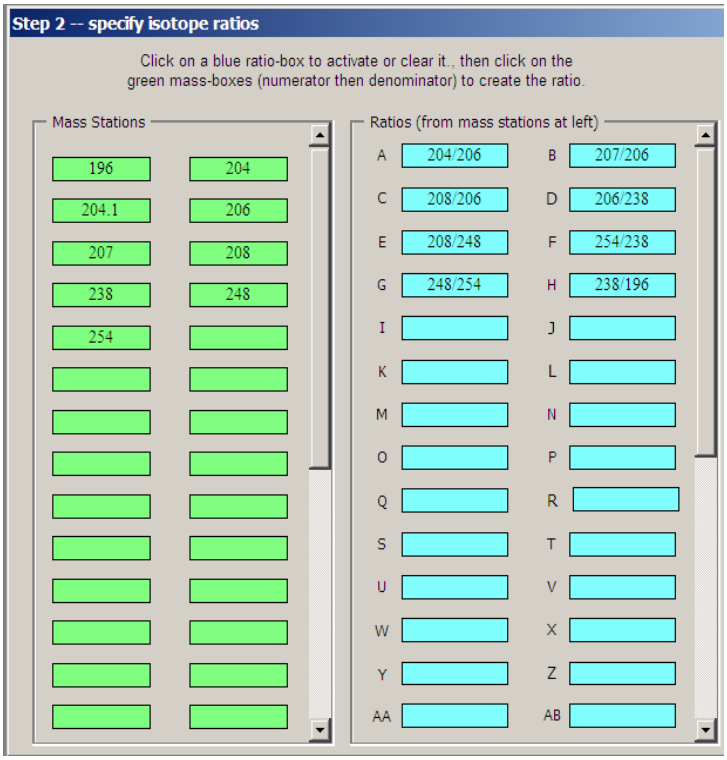


Figure 21: The Isotope Ratios panel.

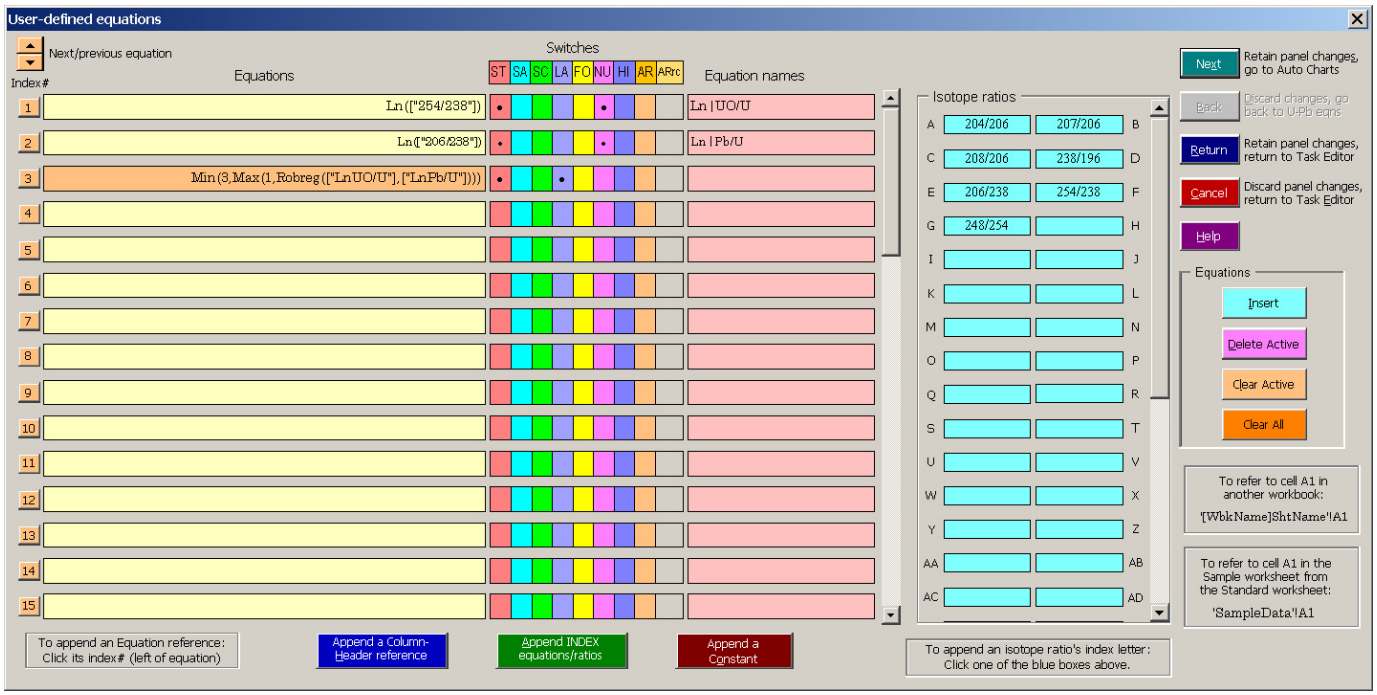


Figure 22: The General Equations Task panel.

The Equation Panels

Basics

Task equations are the backbone of the built-in flexibility of *SQUID-2*. The variables in a *Task Equation* can be any of the worksheet cells in the processed-data sheet(s), including isotope ratios, and the results of other *Task* equations. There are two Equation panels for U-Pb geochronology, and one for General Isotope data. I will discuss the General Equations panel first, as it exists in *Tasks* for both U-Pb/geochronology and General Isotope Ratios.

The simplest type of equation have no "switches" (p. 23) set, and use only the *Tas*'s isotope ratios and numeric constants as arguments for the algebraic functions. Equation results are placed in the SampleData or StandardData output sheets, in data columns to the right of all of the isotope-ratio output columns. If no switches are set, uncertainties for each of the equation results are calculated numerically by *SQUID-2*, with all of the relevant isotope-ratio errors and error correlations correctly propagated.

For example, consider a U-Pb/zircon *Task* that has two User Equations defined (in addition to the four "special" U-Pb equations), as shown above.

	Equation	Equation Name
(1)	Ln(["254/238"])	Log UO/U
(2)	Ln(["^{206}Pb/^{238}U"])	Log Pb/U

The first part of the output worksheet will look something like the example in Figure 23, with the results of the two equations (red arrows) placed in columns to the right of the *Task*'s specified isotope ratios.

REFERENCING AN ISOTOPE RATIO IN THE EQUATIONS PANEL:

To add an isotope-ratio reference as an argument in a *Task* equation, you can:

- Type in the literal ratio, enclosed in square brackets plus a quotation mark, e.g. [“207/206”], or
- Type in the ratio's *index letter* (adjacent to the blue isotope-ratio boxes, as in figure 22, enclosed in square brackets without quotation marks, e.g. [b], or
- Just click on the blue isotope-ratio box for the ratio you want.

Spot Name	Date/Time	Hours	Bkrd cts /sec	Tot 204 cts /sec	Tot 206 cts /sec	204 /206	% err	207 /206	% err	208 /206	% err	206 /238	% err	208 /248	% err	254 /238	% err	248 /254	% err	238 /196	% err	Log UO/U	% err	Log Pb/U	% err
r33-1.1	2005-05-02, 10:28	0.0	0.05	0.08	395	8.8E-5	69	0.0575	1.6	0.208	2.1	0.162	0.76	0.00868	1.9	6.45	0.41	0.598	0.32	0.103	0.55	0.809	0.22	-0.791	0.42
r33-2.1	2005-05-02, 10:44	0.3	0.00	0.11	352	3.2E-4	22	0.0567	1.7	0.192	2.3	0.169	0.81	0.00893	2.1	6.55	0.44	0.553	0.35	0.087	0.52	0.817	0.23	-0.772	0.46
r33-3.1	2005-05-02, 11:48	1.3	0.10	0.08	670	-2.2E-5	93	0.0551	1.2	0.200	1.6	0.171	0.59	0.00890	1.5	6.58	0.32	0.583	0.25	0.170	0.41	0.818	0.17	-0.767	0.33
r33-4.1	2005-05-02, 12:53	2.4	0.00	0.00	1108	---	100	0.0553	1.0	0.152	1.4	0.172	0.39	0.00883	1.3	6.58	0.26	0.445	0.26	0.279	0.35	0.818	0.13	-0.765	0.22
r33-5.1	2005-05-02, 13:59	3.5	0.00	0.05	1256	3.7E-5	85	0.0552	1.0	0.188	1.2	0.172	0.35	0.00864	1.1	6.58	0.22	0.561	0.19	0.313	0.35	0.818	0.11	-0.766	0.20
r33-6.1	2005-05-02, 15:04	4.6	0.00	0.09	561	1.7E-4	22	0.0558	1.4	0.231	1.6	0.175	0.53	0.00908	1.5	6.63	0.32	0.668	0.27	0.138	0.39	0.822	0.17	-0.757	0.30
r33-7.1	2005-05-02, 16:12	5.7	0.20	0.13	593	-1.2E-4	12	0.0538	1.4	0.239	1.6	0.173	0.51	0.00864	1.5	6.64	0.31	0.716	0.25	0.148	0.38	0.822	0.16	-0.762	0.29
r33-8.1	2005-05-02, 17:19	6.9	0.06	0.04	614	-3.8E-5	85	0.0564	1.4	0.211	1.6	0.174	0.50	0.00887	1.5	6.58	0.30	0.629	0.26	0.150	0.47	0.818	0.16	-0.759	0.29

Figure 23 A reduced zircon SampleData worksheet for a Task having two user-defined equations (red arrows).

If you append a ratio by just clicking its ratio box, the ratio will be appended to the end of the existing expression (if any) in the active equation-box. You can choose which style will be used by toggling between Index (appends the letter-index of the ratio, e.g. [h]) and Literal (appends the ratio itself, e.g. [“238/196”]) with the 

button.

ADDING A REFERENCE TO A NAMED NUMERIC CONSTANT:

You can define, view, and insert up to 250 constants constants (such as the decay constant of ^{238}U, natural $^{238}U/^{235}U$ ratio, age of a secondary standard…) by clicking 

at the bottom the Equation panel. Select a constant from the dropdown (figure 24), then click Append to append the constant to the end of any existing text in the active Equation box. The constant will appear either as its name enclosed in angled brackets, e.g. <Lambda238>.

Constants can also be edited from the main *Task* Editor panel, via the 

button..

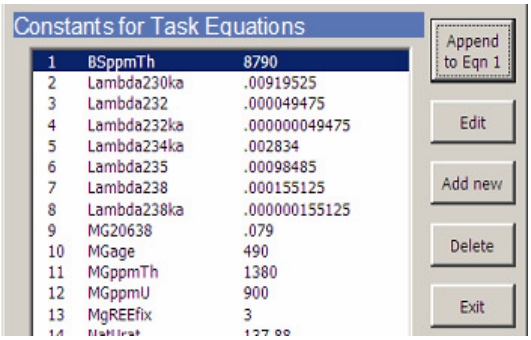


Figure 24: The Constants dropdown.

Named numeric constants are stored both in the User Preferences workbook and with the *Task* itself. If a conflict in the values stored for a named *Task* is detected when the *Task* is loaded, you will be prompted to resolve the conflict, and the selected value will be made consistent in both of the stored locations.

ADDING A REFERENCE TO OTHER TASK EQUATIONS:

Any equation can use the results of any other equation as an argument. To do this, you can

1. Type in the name of the equation (see below), enclosed in square brackets plus a quotation mark, e.g. **`["Log UO/U"].`** Case, spaces, and slashes (/) are ignored by *SQUID*, so you don't have to type them in when defining an equation.

2. Type in the equation's index number (in the orange equation# box to the left of the equation box itself), enclosed in square brackets without quotation marks, e.g. **`[13]`**, or

3. Just click the equation-number box to the left of the equation box.

Unless you use the FO switch (see below), you should make only *forward* references to other equations – that is, to higher-numbered equations – so that the results of the equation referred to will have been calculated when needed.

EQUATION NAMES:

Each *Task* equation must be assigned a name in the corresponding Equation Name box (figure 20). The equation name will be used as the column header for the equation's output column the SampleData or StandardData worksheet and, if the equation's SC switch is set, as an *Excel* range name[2]. To avoid overly-wide columns for the equation results, you can use the | character to indicate a linefeed. Thus an equation name entered as

Mean rad.|ppm Pb|(uncorr.)

would appear in the equation's column header as:

For Array Equations (see p. 25) whose output occupies more than a single column, you can specify names for each of the output columns using a double vertical-line (||) as the column-delimiter. Thus the output for a name such as

[2] *SQUID* will ignore non-alphanumeric characters (underscore excepted) in SC equation names, as only alphanumeric characters are permitted in *Excel* range names. Initial number-characters are also forbidden.

Th230 | raw age | (ka) | | err | | Init | 234/238 | | err

assigned to the array equation

Th230AgeAndInitial([3],[±e],[1],[±f], ,true)

with the ARrc switch marked as 14 (output occupies 1 row, 4 columns) would be something like:

Th230 raw age (ka)	*err*	*Init 234/238*	*err*
104.22	1.44	1.1472	0.0001

EQUATION Switches

To provide more control over how and when the *Task* Equations are evaluated, *SQUID-2* provides up to 7 "switches" that can be turned on or off for each equation. The Switches and their abbreviations are (shown in blue font if restricted to U-Pb/geochron):

Switch	Function
Standard	The equation is placed only in the *Standard* output sheet (default is both).
SAmple	The equation is placed only in the *Sample* output sheet (default is both).
Single **C**ell	The equation results occupy a Single Cell rather than a column, and operates on whole columns of data rather than the data in just one row.
LAst	The equation is to be calculated last, after all of the other equations without the LA switch, and after all of the columns produced automatically (e.g. radiogenic isotope ratios, U concentration, apparent ages…) by SQUID-2. The column-order of calculation for U-Pb geochronology is: • Isotope ratios as specified in the *Task*. • *Task* equations for which neither the SC nor LA switches are set. • Automatically calculated columns (radiogenic isotope ratios, U concentration, apparent ages…). • *Task* equations whose SC, but not LA switch is set. • *Task* equations with the LA switch set. The order of calculation within each category follows the equation index-number.

FOrmula	The *Formula* for the *Excel* equation is to be placed in the output cell(s), rather than its numeric result.
NUmeric	The *Numeric value* of the *Excel* formula for the equation is to be placed in the output cell(s), rather than its *Excel* formula.
HIdden	The worksheet column containing the Equation results will be hidden.
ARray formula	The equation is an Excel Array Formula whose output can occupy more than one row and/or column.
ARrc	The number of rows and columns occupied by the output of the array formula (two numbers separated by a space).

The ST *and* SA *switches (U-Pb/geochron):* When examining and calculating data that is relevant to, say, just the age-standard spots, the output of user equations that have been created for this purpose (say to examine the Log(Pb/U) vs. Log(UO/U) slope) would only clutter up the Sample output sheet. With the ST switch *on*, the column headers and output for such equations will be calculated and placed only on the Standard sheet. Conversely, the SA switch restricts the equation to the Sample worksheet. If neither of these switches is *on*, the equation is placed on both sheets.

The SC *switch (U-Pb/geochron):* This switch specifies an equation that operates on whole columns of data, using *Excel* functions such as *Average, Median, STDEV…*, and *Isoplot* or *SQUID* functions such as *BiWt, RobReg, AgePb76*, *Th230age, InitU234238…..* An SC-switched equation is placed in only one cell (rather than each cell in a data column). Thus if interested in, say, the median of the measured 204/206 ratios, one would create an equation with the formula

Median(["204/206"]

The LA *switch (U-Pb/geochron):* If a cell reference in a (numerically evaluated) User Equation hasn't been calculated and placed on the output sheet, the output cell of the equation will either incorrect or an *Excel* error. Unless the Equation's SC switch is *on*, data for isotope ratios and lower-numbered equations will always exist. However, the radiogenic-isotope and age-columns created by *SQUID-2* are placed on the output sheet *after* all equations, *except* for those equations whose LA switch is *on.*

The FO *and* NU *switches: SQUID* puts the results of its calculations in the output-sheets cells as either the numeric value of the calculation (e.g. 1.234) or as an *Excel* formula (e.g. =$C13/$F13-SQRT($AE13-$AF13)*["ppmu"]). Advantages of a NUmeric result are:

- Quickest start-to-finish data- processing,
- Least "fragile" output sheets, in that the equation-result cells are invulnerable to changes or errors in the source cells arising from later changes to the worksheet,
- Automatically-calculated errors are (if the equation references only isotope-ratio columns) rigorously accurate, and placed in the column to the right of the equation column.

Advantages of a FOrmulaic result are:

- The equation's output cells are updated automatically when changes are made to cells referenced by the equation,
- Other equations on whose results are referenced by an FO equation need not have been calculated before the FO equation.
- The user can check the contents of the equation cells to make sure that the equation actually implements the user's intent.

The H switch: If set, this switch causes the column containing the Equation's results to be hidden (useful if the output worksheet is too cluttered with non-essential information). To unhide a hidden column, select the two columns flanking the hidden column, then unhide with Format/Column/Unhide. To unhide *all* hidden columns in a worksheet, select all cells by clicking on the blank rectangle at the interestion of the Row and Column indices.

The AR switch: This switch, which requires some knowledge of *Excel*'s Array functions, adds another level of flexibility in data processing. You will have to use the *Excel* documentation to learn the general ins and outs of Array Functions, but an important feature is that the output of these functions can occupy not just one cell, but any group of contiguous cells with an arbitrary number of rows and columns. For example, the complete output of the *Isoplot* array function,

230ThAgeAndError()

occupies (up to) 5 contiguous cells in the same row, comprising

Age, age±, initial $^{234}U/^{238}U_{AR}$, initial±, age-initial error correlation

Other array functions may occupy, say, a 2-column by 5-row range. You must therefore specify the number of rows and columns in the output sheets that *SQUID-2* will need to reserve. To do this, enter first the number of rows (1 to 9), then the number of columns(1 to 9) in one of the Equation panel's AR #rows #cols boxes, without spaces or commas – for example, as 24 to indicate a 2 row by 4 column output range.

If the array function's output range occupies both multiple rows and multiple columns, the output cells can be referred to by other equations by their assigned name plus the characters for the #rows and #columns. For example, the second row, first column of a 3-row by 2-column array-function output named "ThAge" would be named "ThAge21". See p. 22 regarding other naming conventions for Array equations.

If, for an Array equation, you specify fewer rows or columns than the maximum possible for the equation (e.g. 2 rows, 1 column instead of the 3 rows by 2 columns that the Array function in the equation's *can* populate), only the that number of rows/columns will be occupied in *SQUID-2*'s reduced-data worksheet.

The above description of how to use Array Functions is admittedly inadequate, but should be enough to allow you to experiment until better documentation is written.

Restricting equations to subsets of spots

The operation of a *Task* equation can be restricted to a specific suite of spots that, like the Age Standard spots, can be grouped by the first few characters of their spot names. Subset-restricted equations can be defined either at the time of data reduction (p. 29) or as part of the *Task* equations. When a *Task* equation is restricted to a subset of spots, cells in the equation's output column will be empty for all spots but those in the subset.

Subset-restricted equations are normally defined along with the data-reduction *Task* (p. 26). You can, however, also restrict any equation to a spot subset at the time of data reduction, which is convenient if the names of the subset spots tends to vary from one PD file to another. Instructions are within the panel itself.

Spot subsets are defined for a *Task* equation by appending the appropriate spot-name fragment to the Equation Name, enclosed in curly braces, e.g. Mean 207Pb/206Pb rad. {qgng}.

Spot subsets are useful when you want to use certain spots as a normalizing standard for some parameter. For example, suppose that, for U-Pb geochronology data, you wish to correct Pb isotope ratios for mass fractionation, and that you have included in the grain mount a secondary standard, say RRhy, with a known $^{207}Pb^{*}/^{206}Pb^{*}$ (the Age Standard $^{207}Pb/^{206}Pb$ being insufficiently precise). To do this, one could:

1. Add an equation consisting simply of the SampleData sheet's radiogenic $^{207}Pb/^{206}Pb$ column, e.g. ["4corr207*/206*"] with the SA, FO, and LA switches,

2. Name the equation, e.g. RRrhy rad 7/6 {rrhy} ,

3. Add an equation for the resistant mean of the RRhy $^{207}Pb/^{206}Pb$, e.g. BiWt(["rrhyrad7/6"] , named, say, Mean RRrhy rad7/6 , with the SA, SC, FO, and LA switches. Note that neither this equation nor the two that follow are marked as Subset equations, since they operate on all of the spot-data within each column.

4. Add an equation for the mass-fractionation factor for Pb, e.g. ["Mean RRrhy rad7/6"]/0.10736 with the SA, FO, and LA switches, where the number in the denominator is the known $^{207}Pb/^{206}Pb$ for the RRrhy standard. Name the equation, say, MassFract ,

5. Add an equation (approximate, since the 204/206 is to be left uncorrected) for the fractionation-corrected $^{207}Pb/^{206}Pb$ of all of the non-RRrhy spots, e.g. ["4corr207*/206*"]*["MassFract"], named, say, Fract. corr. 207*/206* .

You can also restrict *Task* equations to spot subsets via the data-reduction startup panels (p. 26), to avoid defining separate *Tasks* if only the names of, say, a normalizing standard change from one PD file to another.

REFERENCING ERROR COLUMNS

To reference an error column of an isotope ratio or *Task* equation, include **+–** just after the left-hand square bracket, e.g. [+-3], [+-LogUO/U], [+-b], or [+-207/206]. The reference will then refer to the column immediately *after* that of the reference immediately following.

Example (complex):

Sum([1]/([+-1]/100*[1])^2)/Sum(1/([+-1]/100*[1])^2)

with switches

SC = TRUE, AR = TRUE, ARrc = 1 1

will yield the error-weighted mean of the column-values for *Task* equation 1.

"Special U-Pb" Equations

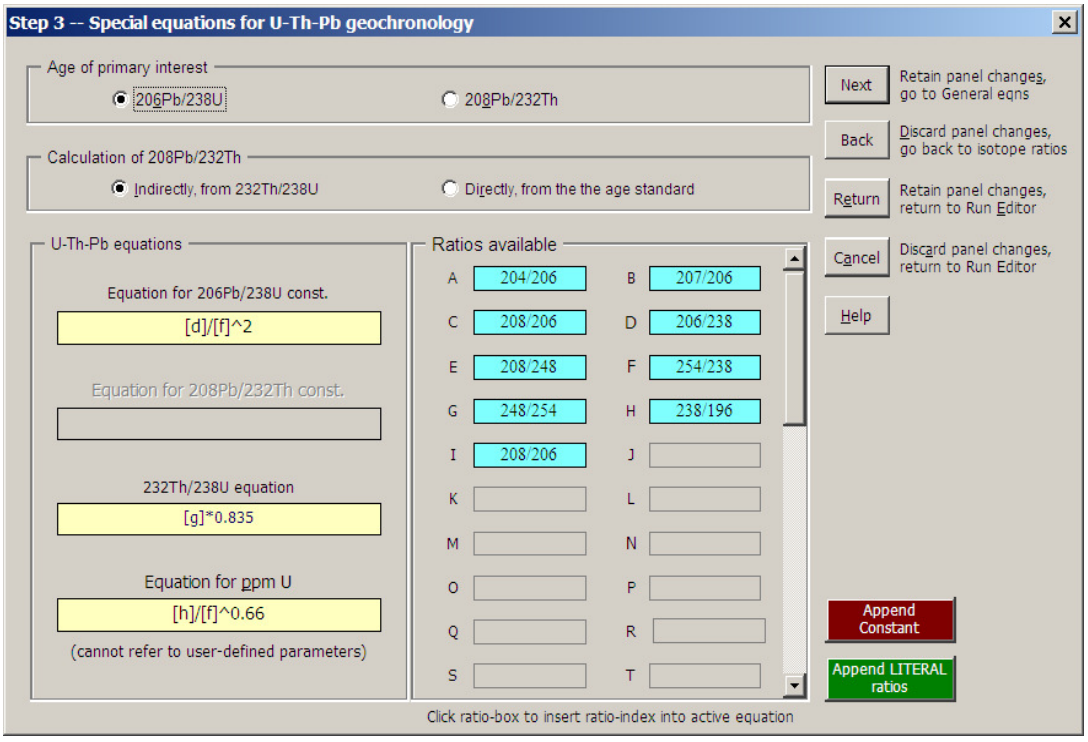


Figure 25: The U-Pb Special Equations panel.

Tasks for U-Pb geochronology have this extra panel, which pertains only to the particular needs of this type of analysis. In this panel, you will specify:

- Which parent-daughter pair is the one of primary interest (^{206}Pb-^{238}U or ^{208}Pb-^{232}Th),

- Whether you want the $^{232}Th/^{238}U$ calculated directly, by an equation that you specify, or indirectly, from calculated $^{206}Pb/^{238}U$ and $^{208}Pb/^{232}Th$ ratios,

As well as:

- The normalizing equation to use for Pb/U (or Pb/Th),
- Either the normalizing equation to use for Pb/Th (direct calculation of Pb/Th) or an equation to calculate Th/U from the isotope ratios defined in the isotope ratio panel, and
- The normalizing equation for [U] (or [Th]) from a concentration standard.

By "normalizing equation" I mean an expression whose numeric value remains constant for the parameter of interest. Thus in the present example,

$$\frac{\text{Pb/U}}{(\text{UO/U})^2}$$

is expected to be constant (during the analytical session) for any given value of Pb/U, and

$$\frac{\text{U/Zr}}{(\text{UO/U})^{0.66}}$$

should be constant for any given U/Zr (the proxy for [U]).

Swapping data columns with U-Pb Geochronology *Tasks*

For U-Pb geochronology data, *SQUID* produces several data-columns having to do with calibration constants, radiogenic-isotope ratios and U-Pb ages that are produced in addition to and independent of any *Task* equations. Most of these data columns reference one or more of the isotope-ratio columns, which cannot normally be directly modified by *Task* equations, thus limiting the ability of the user to compensate for factors such as isobaric interferences and mass fractionation.

However, *Task* equations can be modified using a "column swapping" feature, which permits modification of any of the isotope ratio columns[3], and thus most of the otherwise-unmodifiable *SQUID* columns. The general idea is to create a *Task* equation that modifies (corrects) an isotope ratio in some way (say by correcting the ratio for an isobaric interference), then to add

[3] The four "Special U-Pb" equations are exceptions, as they are calculated directly from the within-scan peak-height measurements.

"<=>" to the equation directing *SQUID* to exchange the modified value with the original result.

For example, suppose there is an interference on ^{204}Pb that is roughly proportional (say about double) to the counts on mass 203. The correction can be made as follows:

1. Add the *Task* equation ["204/206"] – 2*["203/206"] <=> ["204/206"],

2. Name the equation.

When done, the 204/206 column of output-data sheet will contain the raw (measured) 204/206 minus double the measured 203/206, and retain the original 204/206 column header, and the *Task* equation's column will contain the original (measured) 204/206, with the header RAW 204/206.

Referencing data in other workbooks or worksheets

For U-Pb *Tasks*, the same column header can exist in both the SampleData and StandardData worksheets. *SQUID* will first look for the referenced column-header in the worksheet doing the referencing, then (if not found) in the other (StandardData or \SampleData) worksheet.

To reference data in either another workbook or to override the above procedure, you must include the workbook and worksheet name using *Excel*'s syntax (required characters in red), e.g.

To refer to cell A1 in another workbook:

'[WorkbookName]SheetName'!RowColAddress

or

'[WorkbookName]SheetName'! RangeName

for example:

'[MonaziteStdData]CorrectionFactors'!B23

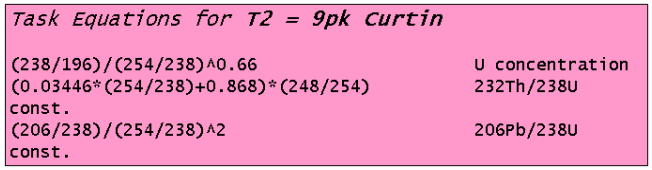
to reference cell B23 in the worksheet "CorrectionFactors", contained in the workbook "MonaziteStdData".

To refer to cell A1 in another worksheet in the same workbook as the PD file being processed:

'SampleData'!A1

Viewing Task Equations in the reduced-data workbook

Equations associated with the data-reduction Task used for data reduction are always shown in either the *StandardSpots* or *SampleSpots* (U-Pb geochronology or General Isotope Ratio Tasks, respectively) worksheets via the *Equations Box* (see example at right). If the Attach Task sheet to reduced-data workbook box in *Preferences* is checked, the equations will also be shown in the attached Task sheet.



Equation Tips

- Use the sqBiWeight (p. 88) or Median functions instead of *Excel*'s Average to avoid worrying about outliers.

If you need to use an error-weighted mean, use the sqWtdAv function (p. 91).

- Use the RobReg function (p. 91) instead of Slope, Linest, Yorkfit, or Yorkslope functions, again to eliminate sensitivity to outliers.

- Use the Min and Max functions to restrict the range of an output, e.g. Min(3, Max(1, Median(["CalibrSlope"])) to force CalibrSlope within the range of 1 and 3.

- To deal with initial disequilibrium in the ^{238}U or ^{235}U decay chains, use one of the relevant *Isoplot* functions (p. 89),

DisEq68Age	DisEq68Ratio
DisEq75Age	DisEq75Ratio
DisEqPbPbAge	DisEq76Ratio

The Autocharts Panel

The final panel in the definition of a *Task* is for Auto Charts (figure 26). Auto Charts are simple *x-y* or weighted average plots of any of *SQUID-2* 's output sheets that are placed as insets in the these sheets. Up to 8 *Autocharts* (p. 30) can be requested. You can choose the *x* and (if not a weighted average plot) *y* axes from any of the output sheet's column-headers using the *x-y* drop-down. You may also request that an (outlier resistant) linear regression be calculated and plotted for *x*-y data, or an (outlier resistant) mean for just the *y* data. If Y mean is selected, the *x* axis is always Hours.

For U-Pb geochronology Tasks, Autocharts will be created only for the age-standard spots.

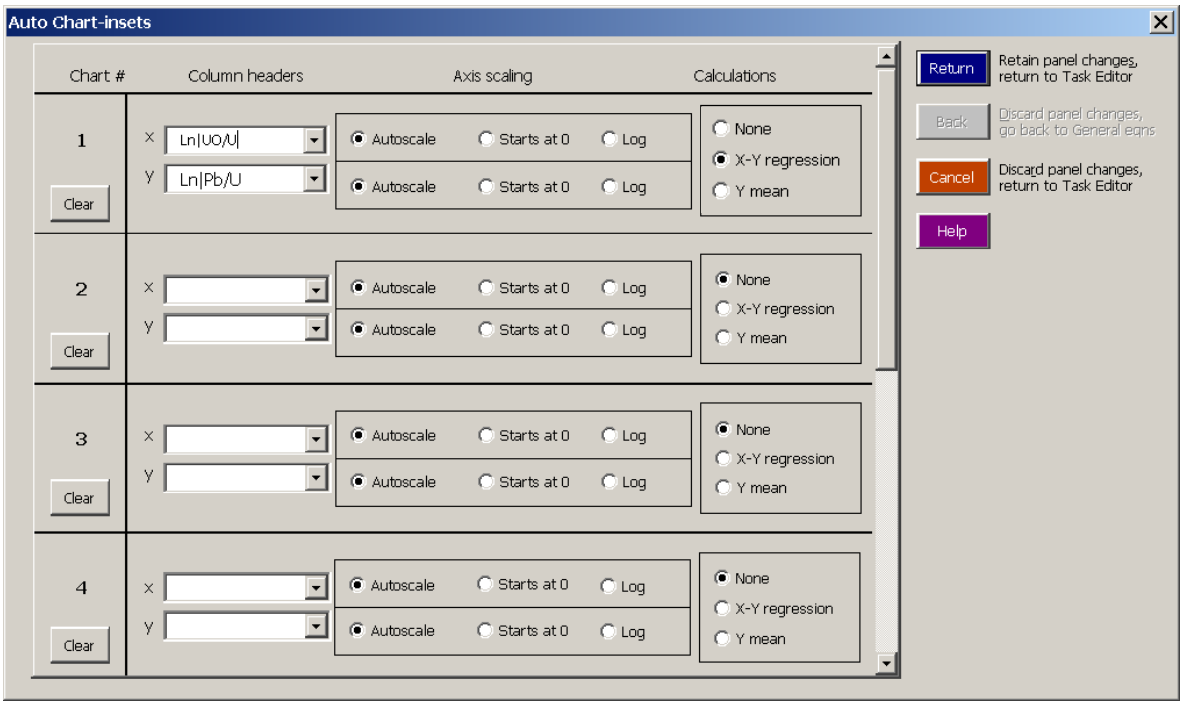


Figure 26: The Auto Charts panel.

In figure 26 (above), for example, the results of the two (user-defined) equations corresponding to Ln(^{206}Pb/^{238}U) versus Ln(254/238) are plotted, as well as the line and numeric results of the *x-y* regression.

Normally, *Autocharts* will be placed on the reduced-data worksheet of the spots themselves. will be placed on the *Standards* reduced-data sheet

Setting a "Time Window" for spots

Data reduction can be restricted to any sequentially-measured series of spots. For U-Pb geochronology, the series of spots is defined by the bracketing Age-Standards. For General Isotope data, the time window is defined by any pair of bracketing spots.

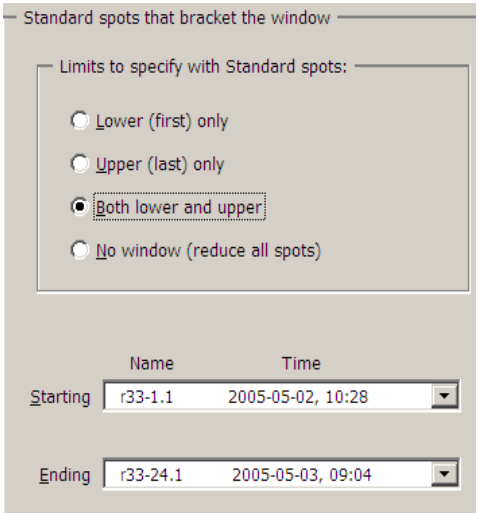


Figure 27: The Time Window panel.

Specifying Subset-restricted equations at the time of Data Reduction

A "subset-restricted equation" is a user-defined *Task* equation that will operate only on a subset of the spots in the PD file, where the subset is defined by the initial characters of the spot names. This can be very useful, for example if one wishes to know the mean U concentration of just those spots whose names start with "MG".

Subsets can be assigned either by the data-reduction *Task* (p. 37) or at the time of data reduction by clicking the Subsets button on the data-reduction panel.

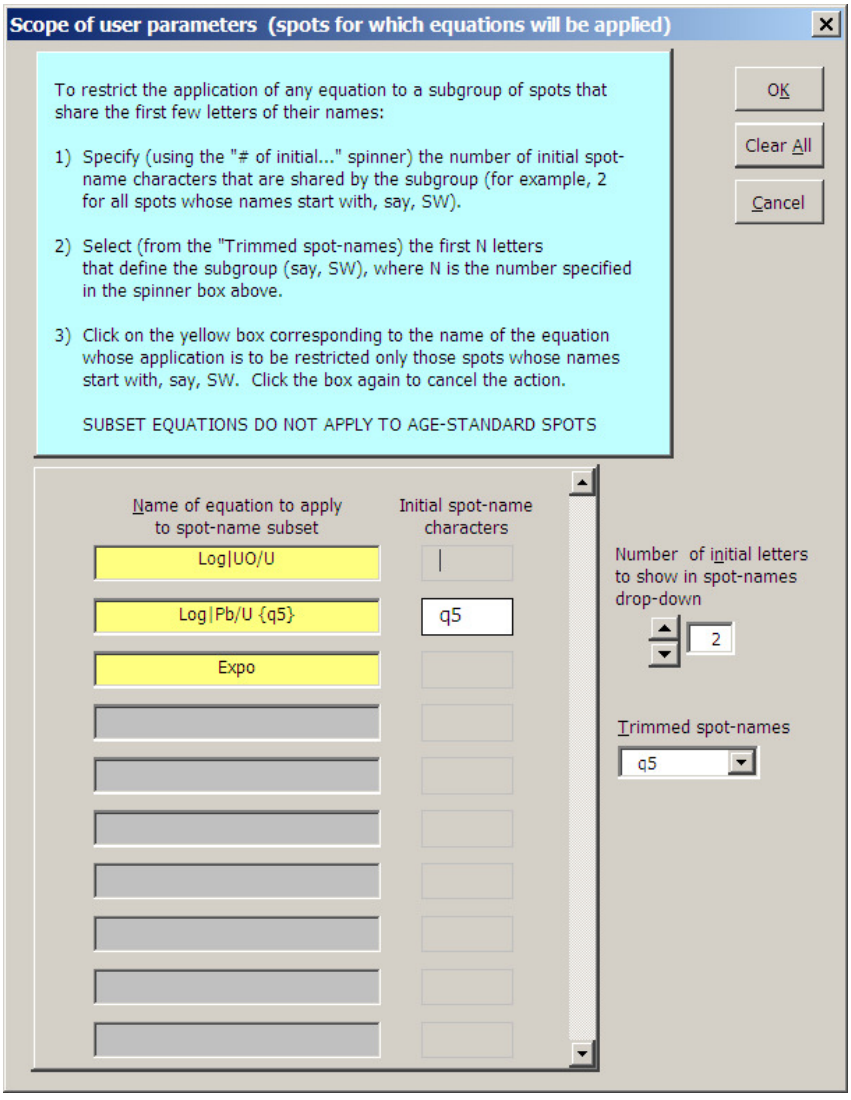


Figure 28: The Subset panel for specifying subset equations at the time of data reduction.

Invoking Excel's *Solver* as part of a Task

Excel includes a powerful *Solver* add-in that numerically finds the solution to a wide variety of nonlinear equations having more than one unknown. In particular, *Solver* will calculate and place in specified worksheet cells the values for one or more parameters that minimize the value in another cell. Thus one could determine the values of, say, *a*, *b*, *c*, and *d* that minimize the sums of squared weighted residuals (or, equivalently, the sigma-mean of a column of data), thus providing a least-squares solution to an column of scattered data that you wish to fit to, say, $y=ax^3+bx^2+cx+d$.

To have a *Task* invoke *Solver*, add a *Task* equation into the list of *Task* Equations and enter first the location of the (single) cell whose contents are to be minimized, followed by semicolon, then the location of the parameters whose values you wish to optimize. Assign a name (which will be ignored) to the equation, followed by <<solve>>. Enter two worksheet range-names(or cell addresses) separated by a semicolon. The first of these names specifies the single cell whose contents are to be minimized, the second the range containing the parameters to adjust, for example

SumWtdResids;CubicEquationCoefficients

where SumWtdResids is the range-name of the parameter to be minimized, and CubicEquation-Coefficients is the name of the range containing, the trial values for *a*, *b*, *c*, and *d*. If the parameters to adjust are in separate cells, separate the range names or cell addressed by a comma. For example

SumWtdResids; Coef1, Coef2, Coef3, Coef3, Coef4

If the cell whose value is to be minimized is part of an Array equation, you can use the row-column values to specify which parts of the Array-function output to use. Thus if a *Task* equation named biwtthpbage is defined as sqBiWeight(WeightedResids) with the .FO, .AR switches set and with ARrc = 3 2 *i.e.* (3 rows, 2 columns), the output cells created by *SQUID-2* might look like:

xeno1 mean 8*/2 age	
994.25	*Biweight Mean*
21.77	*Biweight Sigma*
14.19	*95%-conf. error*

If the cell *BiWeight Sigma* contains the parameter to be minimized, the Task equation would look like

biwtthpbage(2,1); Coef1, Coef2, Coef3, Coef3, Coef4

indicating the value in the second row, first column of the Array equation's output.

Solver will be invoked after all of the data columns in the output worksheet have been calculated and filled with values.

Isotope-Ratio Chart-Insets

After PD-file data reduction is complete, and if the Construct within-scan… box in the *Preferences* panel (p. 52) is checked, SQUID will construct a *Within-scan isotope ratios/eqns* sheet (figures 7, 29) as part of the data reduction process, so that chart insets of any of the isotope ratios or Equation results can be constructed on demand.

To invoke one or more within-scan isotope-ratio (or within-scan equation) chart, select the cell(s) whose row (s)and column(s) correspond to the spot(s) and isotope ratio/equation(s) of interest, then click the  button in the *SQUID* toolbar.

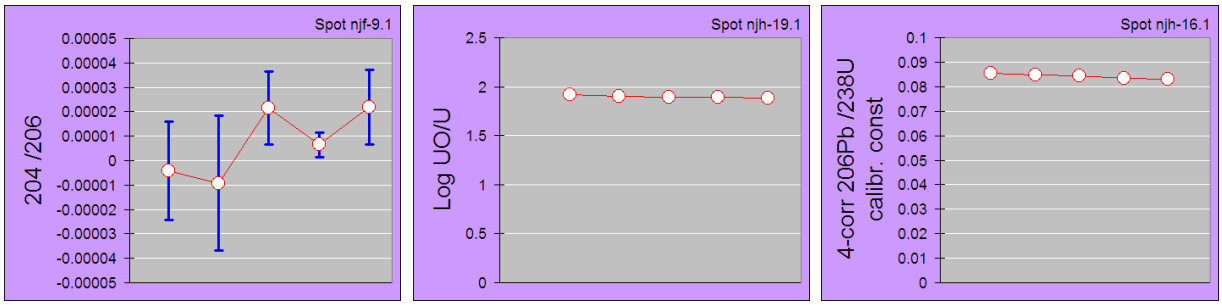


Figure 29: Some isotope ratio and Equation result charts

The Y-axis of the chart-insets will be auto-scaled to the data plotted, unless the "Set Y-axis minimum on isotope-ratio charts to zero" box in *Preferences* is checked.

Spot Scan-Graphics

You can request spot-scan graphics – by which I mean charts of the total counts at each mass station for each peak jump – for any spot, by selecting one or more cells whose rows correspond to the desired spots (in either the StandardData or SampleData worksheets), then clicking the  button in the *SQUID toolbar*. The resulting charts (figure 30a) – one for each mass station plus one for the SBM – will all be placed on a single new worksheet having the same name as the spot.

Clicking the  button produces spot-scan graphics for *all* of the spots in the raw-data file. This can take several minutes. For extremely large files or run-tables, it is possible for *Excel* to run out of memory, resulting in some obscure and misleading error message such as "too many fonts".

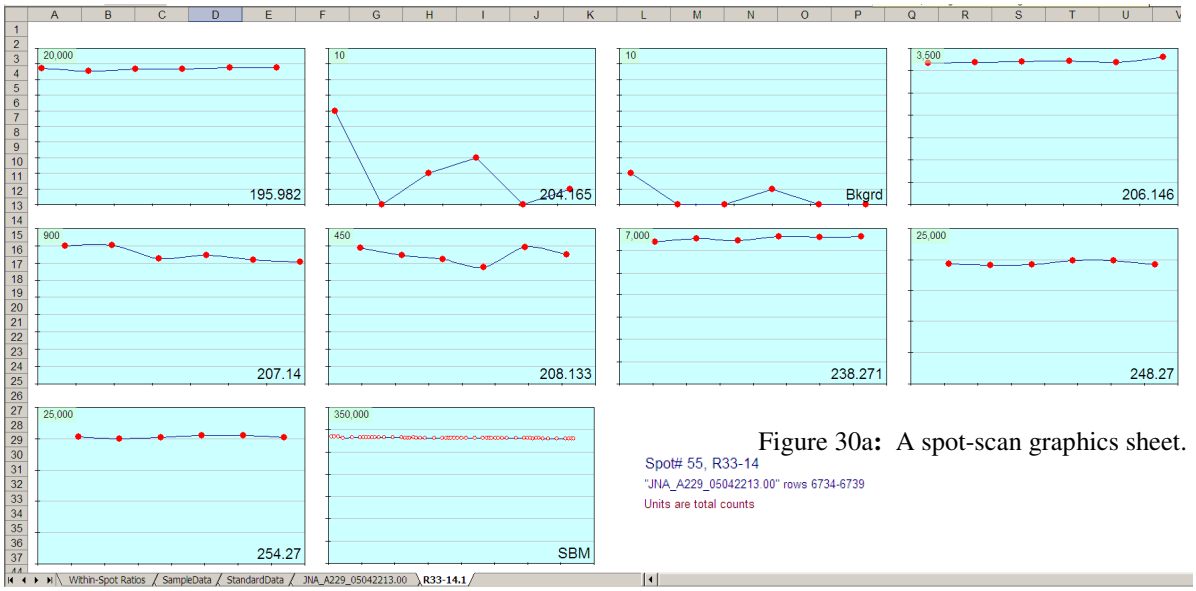


Figure 30a: A spot-scan graphics sheet.

Manual Rejection of Scan Outliers Via Spot Scan-Graphics

SQUID's algorithm for within-scan isotope-ratio and equation means is extremely resistant to outliers, so that manual rejection by the user of individual scans (peak-top measurements) should not be needed. If, however, you do wish to reject scans for whatever reason, you can do so from any spot-scan graphics sheet in the following way:

1. Request construction of spot-scan graphics for the desired spot.
2. Click on the chart for the mass station of interest. A bar containing numbered light-blue boxes will appear at the top of the chart (figure 30*b*).
3. Click on the box corresponding to the scan number to be rejected (figure 28*c*). The box will turn light red, the rejected data-point will disappear from the chart, the curved line through the data points will be redrawn, and the values in the condensed PD file worksheet will change as shown in figure(to un-reject a scan, click again on the numbered, light-red box).

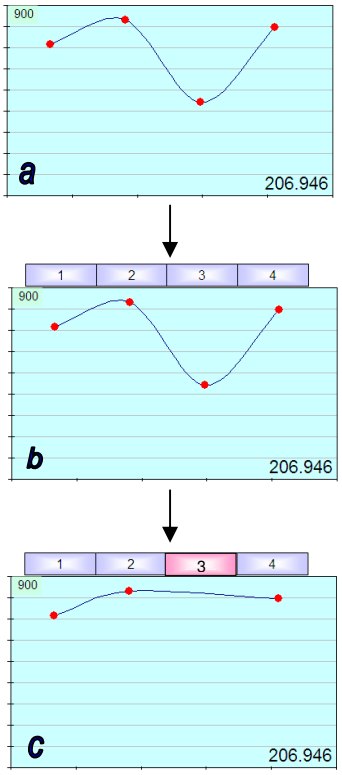


Figure 30b: Manual rejection of scan 3 of mass 207.

Now, when you re-process the PD file, *SQUID* will ignore the rejected scan (figure 31).

	tot cts	
30	mass	
Secs	206.946	±1sig
67	716.599	33.1
182	830.449	28.1
297	444.143	19.7
411	794.447	35.7

→

	tot cts	
30	mass	
Secs	206.946	±1sig
67	716.599	33.1
182	830.449	28.1
297	REJ	19.7
411	794.447	35.7
67	716.599	33.1
182	830.449	28.1
411	794.447	35.7

← Source data for plot after rejection.

Figure 31: Change in the condensed PD file for the chart in 28b after scan rejection.

Remember that deleted scans will only affect subsequent processing of the PD file, and will have no effect on existing SampleData or StandardData worksheets.

Appendix I -- The *SQUID-2* Toolbar

(to make the toolbar visible, select View/Toolbars/Squid2 from the *Excel* dropdown menus)


Load and process data from a U-Pb geochronology PD file.


Load and process data from a General Isotope PD file.


Group samples from a processed U-Pb geochronology workbook.


Condense and reformat one or more PD files.


Task Editor


Preferences


Construct one or more chart insets of the within-spot isotope ratios for the spot and ratio defined by the selected row and column of the SQUID StandardData or SampleData worksheet. To obtain more than one plot at a time, select more cells, each indicating an isotope ratio.


Construct charts of cps versus time for one or more spots defined by the selected row(s) of the SQUID StandardData or SampleData worksheet, for all of the mass stations.


Construct charts of cps versus time for *all* spots in both the StandardData and SampleData worksheets, for all of the mass stations.


"Freeze" the active worksheet by replacing all cell-formulae with their numeric results.


"Freeze" all of the worksheets in the workbook.


Make a publication-type table from the processed U-Pb geochronology data.


Widen all columns of the worksheet by 1 point.


Narrow all columns of the worksheet by 1 point.


Update all SQUID and Isoplot references to the currently-installed versions.


Quit SQUID 2 (uninstall the SQUID add-in). You can re-install SQUID 2 at any time


Unhide/Rehide toggle for hidden columns in SQUID 2's SampleData and StandardData sheets.


Show this description of the toolbar buttons.

Appendix II: Algorithms Used by *SQUID-2*

Weighted averages, "means", Internal and External errors

The term "weighted average" is generally used to imply a mean weighted by the inverse variance (variance = σ^2) of the assigned errors to each data point, so for *N* data points,

$$\bar{x} = \frac{\sum_{}^{N} \frac{x_i}{\sigma_{x_i}^2}}{\sum_{}^{N} \frac{1}{\sigma_{x_i}^2}}$$

with the "internal" error on $\bar{x}$ (that is, the error propagated from just the *N* σ_{x_i}) calculated as

$$\sigma_{\bar{x}}^2 = \frac{1}{\sum \frac{1}{\sigma_{x_i}^2}}$$

The *MSWD* parameter

Two extremely useful parameters associated with the error-weighted average are the *MSWD* and *probability of fit*. *MSWD* (mean square of weighted deviates)[5] is defined as the mean of the *N* inverse-variance weighted residuals, (residual = measured *x* minus weighted-mean *x*), squared. So

$$\frac{\sum \left(\frac{x_i - \bar{x}}{\sigma_{x_i}} \right)^2}{N-1}$$

(note that degrees of freedom is used as the divisor rather than *N*).

Intuitively, one can see that, if each σ_i is truly the cause of scatter from $\bar{x}$, on average the residuals for the x_i should be σ_i, so that the expected mean of the both the weighted residuals, and their square should be about 1. An *MSWD* much greater than one, therefore, implies that the assigned data-point errors are unlikely to be responsible for the observed residuals (or amount of scatter), and an *MSWD* much less than one implies that the assigned data-point errors are probably too high.

Probability of fit

It turns out that $MSWD \times \upsilon$, where υ (=N-1 for a simple weighted average) follows a chi-squared distribution about υ, so that the probability that one will obtain a given *MSWD* or greater – in other words, the *probability of fit*, can be calculated from the *Excel* function as

= CHIDIST(*MSWD* * υ, υ).

External errors and Weighted Averages assuming the presence of external errors

If the probability of fit is low – say less than 0.05 – it is likely that some other source of error in addition to the assigned data-point errors is present. If one assumes that this *external error* is the same from data point to data point, so that for each data point the true variance is

$$^{total}\sigma_{x_i}^2 = {}^{internal}\sigma_{x_i}^2 + {}^{external}\sigma^2$$

where $\sigma_{internal}$ is the data point's assigned error and that this external error has a Gaussian distribution (both of which seem to be the case for SHRIMP analyses), its (likely) magnitude can be calculated. For U-Pb geochronology SHRIMP analyses, if the age standard analyses indicate that an external error for the U/Pb calibration constant (likely) exists, as indicated by a low probability of fit, the additional variance should be added to the internal variance of the sample (non-standard) spots before taking a weighted average.

To solve for the external error, we first set up the Maximum Likelihood Error (MLE) equation,

$$\mathsf{L}\left(\bar{x},\sigma_E^2\right) = \text{constant} - \frac{1}{2}\sum\log\left(\sigma_{x_i}^2+\sigma_E^2\right) - \frac{1}{2}\sum\frac{\left(x_i-\bar{x}\right)^2}{\sigma_{x_i}^2+\sigma_E^2}$$

where $\bar{x}$ is the MLE estimate of the true (mean) *x* and σ_E^2 is the constant, external variance. We then set up the first-derivative constraints which, when solved (numerically) yield the desired MLE $\bar{x}$ and σ_E^2.

$$\frac{\partial\mathsf{L}}{\partial\left(\sigma_E^2\right)} = -\frac{1}{2}\sum\frac{1}{\sigma_{x_i}^2+\sigma_E^2} + \frac{1}{2}\sum\frac{\left(x_i-\bar{x}\right)^2}{\left(\sigma_{x_i}^2+\sigma_E^2\right)^2} = 0$$

$$\frac{\partial L}{\partial\bar{x}} = +\sum\frac{x_i-\bar{x}}{\sigma_{x_i}^2+\sigma_E^2} = 0$$

So

$$\bar{x} = \frac{\sum\frac{x_i}{\sigma_{x_i}^2+\sigma_E^2}}{\sum\frac{1}{\sigma_{x_i}^2+\sigma_E^2}} \quad \text{and} \quad \sum\frac{\left(x_i-\bar{x}\right)^2}{\left(\sigma_{x_i}^2+\sigma_E^2\right)^2} = \sum\frac{1}{\sigma_{x_i}^2+\sigma_E^2}$$

Uncertainties of the two parameters are given by inversion of the negative values of the second derivatives of L, which are

$$\frac{\partial^2\mathsf{L}}{\partial\left(\sigma_E^2\right)^2} = +\frac{1}{2}\sum W_i^2 - \sum W_i^3 r_i^2 \qquad \frac{\partial^2 L}{\partial\bar{x}^2} = -\sum W_i \qquad \frac{\partial^2\mathsf{L}}{\partial\bar{x}\partial\left(\sigma_E^2\right)} = -\sum W_i^3 r_i$$

where $W_i = \frac{1}{\sigma_{x_i}^2 + \sigma_E^2}$ and $r_i = x_i - \bar{x}$, and then substituting zero for the r_i (their expected value) to obtain the expected value of the second derivatives,

$$-E\frac{\partial^2 L}{\partial(\sigma_E^2)^2} = -\frac{1}{2}\sum W_i^2 \qquad -E\frac{\partial^2 L}{\partial\bar{x}\partial(\sigma_E^2)} = 0 \qquad -E\frac{\partial^2 L}{\partial\bar{x}^2} = +\sum W_i$$

The variance-covariance matrix of $\bar{x}$ and σ_E^2 is then obtained by inverting the Fisher Information Matrix,

$$\mathbf{F} = \begin{pmatrix} -\frac{1}{2}\sum W_i^2 & 0 \\ 0 & +\sum W_i \end{pmatrix} = \begin{pmatrix} \sigma_{\bar{x}}^2 & cov(\bar{x},\sigma_E^2) \\ cov(\bar{x},\sigma_E^2) & \sigma_{\sigma_E^2}^2 \end{pmatrix}$$

Outlier rejection for the integrations comprising a single scan of a peak

SHRIMP's raw-data PD file reports the secondary ion-beam counts as ten integrations for each mass station, regardless of the time of the integration. If the median of these ten integrations is <100, *SQUID-2* identifies 95%-confidence outliers as being any integration whose value is outside the Poisson distribution for the 10-integration median, and uses the mean of remaining integrations. If the median is ≥100 counts, *SQUID-2* uses the Tukey's Biweight algorithm to obtain an outlier-resistant mean.

Within-spot isotope ratios

If either the numerator or denominator peak of a ratio comprises fewer than 32 counts during a burn (that is, the sum of the peak-top integrations for the *n* scans), isotope ratios are calculated as the ratio of the sum of the peak-top counts for the two isotopes rather than by interpolation.

Otherwise, *SQUID-2* calculates ratios and NU-switched *Task* equations either regressing the double-interpolated ratios (, 1978) versus time and takes the value of the regression at mid-burn time to cancel out any secular trends during the burn. The errors of individual interpolations are calculated by

$$T = \frac{1+f}{2} \qquad f_1 = \frac{1-f}{2} \qquad f_2 = \frac{1+f}{2}$$

$$A_i = f_1 a_i + f_2 a_{i+1} \qquad B_i = f_2 b_i + f_1 b_{i+1}$$

$$\sigma_{r_i}^2 = \frac{1}{B_i^2}\left[f_1^2 a_i^2 \frac{\sigma_{a_i}^2}{a_i^2} + f_2^2 a_{i+1}^2 \frac{\sigma_{a_{i+1}}^2}{a_{i+1}^2} \right] + \frac{A_i^2}{B_i^4}\left[f_2^2 b_i^2 \frac{\sigma_{b_i}^2}{b_i^2} + f_1^2 b_{i+1}^2 \frac{\sigma_{b_{i+1}}^2}{b_{i+1}^2} \right]$$

where

a and b are the two peaks comprising the ratio $r = a/b$,

T is the time of interpolation,

f is the fraction of the time interval between successive integrations of peaks a or b,

i is the scan-number index,

σ_a and σ_b are the counting-statistic errors of peaks a and b, and

A and B are the interpolated values of a and b.

Because each pair of time-adjacent interpolated ratios shares two of the four peaks used to calculate each ratio, the errors of such ratio pairs of necessarily correlated, which must be taken into account when calculating the error and *MSWD* of the mean ratios for a spot, using

$$\rho_{r_i, r_{i+1}} = \frac{1}{4} \frac{1 - f^2}{B_i B_{i+1} S_{r_i} S_{r_{i+1}}} \left(\frac{\sigma^2_{a_{i+1}}}{r_i \, r_{i+1}} + \sigma^2_{b_{i+1}} \right)$$

Good approximations, which assume the absence of major changes in the size of the peaks during the spot burn, are

$$\frac{S^2_{r_i}}{r_i^2} \approx \frac{1 + f^2}{2} \left(S_a^2 + S_b^2 \right)$$

and

$$\rho_{r_i, r_{i+1}} \approx \frac{1}{2} \frac{\left(1 - f^2\right)}{\left(1 + f^2\right)}$$

For non-negligible error correlations, the general formula for the weighted mean and error must be used,

and

$$\sigma^2_{\bar{r}} = \frac{1}{\sum_{i,j} \Omega^{ij}}$$

where Ω^{-1} is the variance-covariance matrix for the interpolated ratios r_i , and Ω^{ij} indicates the element in the ith row, jth column of Ω. If the r_i are uncorrelated, Ω^{-1} is simply the diagonal matrix for the inverse variances of the r_i. For doubly-interpolated ratios, however, the near-diagonal terms are nonzero, so the variance-covariance matrix is:

$$\bar{r} = \frac{\sum_{i,j} r_i \, \Omega^{ij}}{\sum_{i,j} \Omega^{ij}}$$

$$\Omega^{-1} = \begin{pmatrix} \sigma^2_{r_1} & \operatorname{cov}(r_1, r_2) & \cdots & 0 \\ \operatorname{cov}(r_1, r_2) & \sigma^2_{r_2} & \operatorname{cov}(r_3, r_2) & \cdots \\ 0 & \operatorname{cov}(r_2, r_3) & \cdots & \cdots \\ \cdots & \cdots & \cdots & \operatorname{cov}(r_{N-1}, r_N) \\ 0 & \cdots & \operatorname{cov}(r_N, r_{N-1}) & \sigma^2_{r_N} \end{pmatrix}$$

If user Preferences specify that isotope ratios be calculated as the estimated value at mid-burn time via a linear regression versus time, the error-weighted linear regression must again take into account the error correlations between time-adjacent ratios, so that, for

$$r_i = mt_i + b$$

where r_i are the doubly-interpolated isotope ratios and t_i are the corresponding times of interpolation, and m, t is the time-slope and intercept of the linear regression. The best-fit slope and intercept are given by

$$m = \frac{2WP_{tr} - P_t P_r}{4WM_t - P_t^2} \qquad b = \frac{P_r - mP_t}{2W}$$

where

$$P_{tr} = \sum\sum\left(t_i r_j + t_j r_i\right)\boldsymbol{\Omega}^{ij} \qquad M_t = \sum\sum t_i t_j \boldsymbol{\Omega}^{ij}$$
$$P_t = \sum\sum\left(t_i + t_j\right)\boldsymbol{\Omega}^{ij} \qquad P_r = \sum\sum\left(r_i + r_j\right)\boldsymbol{\Omega}^{ij}$$
$$W = \sum\sum\boldsymbol{\Omega}^{ij}$$

and Ω is defined in p. 40.

Error for the slope and intercept are obtained from inversion of

$$\mathbf{F} = \begin{pmatrix} M_t & P_t \\ P_t & W \end{pmatrix}$$

which gives

$$\mathbf{F}^{-1} = \begin{pmatrix} \sigma_m^2 & cov(m,b) \\ cov(m,b) & \sigma_b^2 \end{pmatrix}$$

The error in r at any time t is then obtained from

$$\sigma_r^2 = t^2\sigma_m^2 + \sigma_b^2 + 2\,cov(m,b)$$

Outliers of within-spot interpolated ratios

For calculation of isotope-ratio means by either a simple weighted average or error-weighted linear regression at mid-burn time, the following algorithm is used:

1. the effect on the *MSWD* (of the error-weighted average) of removing each of the *n*-1 ratios is calculated (*n* = # scans), and the ratio whose rejection results in the greatest reduction in *MSWD* is determined.

2. If this lowest *MSWD* is lower than the no-rejection *MSWD* by a selected factor[6], the point is rejected. A second rejection pass is permitted if there are more than 8 or 9 (weighted average and linear regression, respectively) ratios.

3. If the probability-of-fit of the weighted average or linear regression is ≤0.05, the internal sigma-mean of the weighted average is accepted as the 1-sigma error. If not, a $\sqrt{}$ *MSWD* multiplier is applied.

The regression is error-weighted (by counting statistics), and removes outliers by sequentially deleting each data point (the isotope ratio or equation result). If any single deletion drops the *MSWD* of the regression by a factor of 3 or more, the point is rejected and the process repeated. The maximum permitted number of rejections is 1 for fewer than 9 ratios or equations, 2 if more. Or,

- Calculates the error-weighted mean of the interpolated ratios. If the probability of fit (calculated from the *MSWD* of the weighted mean) is greater than 0.05, this mean and standard error (propagated from the counting statistics errors of the individual scans) is accepted.

- Otherwise, the mean and standard error of the outlier-resistant Tukey's Biweight algorithm (Hoaglin *et al*, 1983) is used.

The Tukey's Biweight algorithm

The initial estimate of mean ($\bar{x}$) is the median; and of σ is MAD (the median absolute deviation from the median). Schematically, the algorithm is:

T= tuning const. × σ . The tuning constant is either 6 or 9; *SQUID-2* uses 6.

$\Delta = x_i - \bar{x}_j$ where x_i is the *i*th point of the data-set, and $\bar{x}_j$ is the *j*th iteration for $\bar{x}$.

Do:

For each data-point (*i*=1 to *n*),

If $|\Delta| < T$ then:

[6] 0.15, 0.2, 0.2, 0.25 for 3, 4, 5, 6, and 7 d.f. (=degrees of freedom; *n*-1 for weighted average, *n*-2 for linear regression), respectively, 0.3 for 8 or more d.f. Outlier rejection is forbidden for <3 d.f.

$$\Delta_i = x_i - \bar{x}_j$$

$$u_i = \Delta_i / T$$

End If

$$SA = \sum_i \left[\Delta_i \left(1 - u_i^2\right) \right]^2$$

$$SB = \sum_i \left(1 - u_i^2\right)\left(1 - 5u_i^2\right)$$

$$SC = \sum_i u_i \left(1 - u_i^2\right)^2$$

$$\sigma = \sqrt{n \times SA} \,/\, |SB|$$

$$\bar{x}_{j+1} = \bar{x}_j + T \times SC \,/\, SB$$

Loop until $\sigma_j = \sigma_{j-1}$ and $\bar{x}_j = \bar{x}_{j-1}$

Within-spot, numerically-evaluated Task equations

Same as for isotope ratios, but instead the equation itself is calculated *N* times (*N* = #scans -1) at the mean time of all of the mass-stations involved in the equation. Errors of each scan's equation are calculated numerically by perturbing all of the peaks involved in the equation.

Overcounts on ^{204}Pb

Apparent overcounts on ^{204}Pb are calculated in two ways: 1) assuming that the true $^{206}Pb^*/^{238}U$ and $^{207}Pb^*/^{235}U$ ages are concordant, and 2) assuming that the true $^{206}Pb^*/^{238}U$ and $^{208}Pb^*/^{232}Th$ ages are concordant. The $^{204}Pb/^{206}Pb$ ratio required to achieve concordance is calculated, and thus the number of non-^{204}Pb counts that must be present to explain the apparent discordance.

Outlier-Resistant Linear Regression

This outlier-resistant linear regression algorithm is used by *SQUID-2* for *Task Autocharts*, and when invoked by the user in a *Task* equation. The regression-line slope/intercept is the median of all pairwise slopes/intercepts, with errors based on code in Rock & Duffy (1986), derived from Vugrinovich (1981).

Concordia Ages

See Ludwig (1998) for a detailed explanation of the definition and algorithm for the Concordia Age.

Converting Tera-Wasserburg to Conventional-Concordia Slope-Intercept

With $x = {}^{238}U/{}^{206}Pb_{rad.}$ and $y = ({}^{207}Pb/{}^{206}Pb)_{rad.}$, $m = u/b'$ and $b = -m'/b'$, where *m, b, u* are as before and m', b' are the Tera-Wasserburg slope and intercept, the transformed errors are given by

$$S_m^2 = S_{b'}^2 \qquad S_b^2 = S_{m'}^2 + S_{b'}^2 - 2S_{m'}S_{b'}\rho_{m'b'}$$

$$\rho_{m,b} = \frac{S_{m'}\rho_{m',b'} - S_{b'}}{S_b}$$

where

$$S_m = \frac{\sigma_m}{m} \qquad \rho_{m,b} = \frac{\mathrm{cov}(m,b)}{\sigma_m \sigma_b}$$

$^{207}Pb/^{206}Pb$ age-error including errors in decay constants:

The simple (first-derivative expansion) expression for $^{207}Pb/^{206}Pb$ age-errors is:

$$\sigma_t^2 = \frac{\left(e^{\lambda_{238}t} - 1\right)^2 \sigma_r^2 + \left(u t e^{\lambda_{235}t}\right)^2 \sigma_{\lambda_{235}}^2 + \left(r t e^{\lambda_{238}t}\right)^2 \sigma_{\lambda_{238}}^2}{\left(u\lambda_{235}e^{\lambda_{235}t} - r\lambda_{238}e^{\lambda_{238}t}\right)^2}$$

where $r = {}^{207}Pb/{}^{206}Pb$ and $u = {}^{235}U/{}^{238}U$

208-Corrected Ages and Ratios

Constrain the $^{206}Pb^{*}/^{238}U$ age to equal the $^{208}Pb^{*}/^{232}Th$ age, so that

$$\frac{1}{\lambda_{238}}\mathrm{Ln}\left(1+\frac{\alpha_T-\alpha_0}{\alpha_T}\mathrm{r}\right)=\frac{1}{\lambda_{235}}\mathrm{Ln}\left(1+\frac{\beta_T-\beta_0}{\beta_T}\mathrm{R}\right)$$

Then define

$$r=\frac{^{206}Pb_T}{^{238}U} \qquad s=\frac{^{207}Pb_T}{^{235}U} \qquad f=\frac{^{206}Pb_0}{^{206}Pb_T} \qquad F=\frac{^{207}Pb_0}{^{207}Pb_T}$$

$$\varphi_T=\left(\frac{^{207}Pb}{^{206}Pb}\right)_T \qquad \varphi_0=\left(\frac{^{207}Pb}{^{206}Pb}\right)_0 \qquad u=\frac{^{238}U}{^{235}U} \qquad p=1-f=\frac{r^*}{r}$$

$$r^*=(1-f)r=pr=\frac{^{206}Pb^*}{^{238}U}$$

$$\begin{aligned}s^*&=\left(1-\frac{\phi_0}{\phi_T}f\right)\phi_T ur\\&=\left(\phi_T-f\phi_0\right)ur\\&=\frac{^{207}Pb^*}{^{235}U}\end{aligned}$$

$$\begin{aligned}m_1&=\lambda_{238}\left[1+(1-f)r\right]\\&=\lambda_{238}\left(1+r^*\right)=\lambda_{238}e^{\lambda_{238}t}\end{aligned}$$

$$\begin{aligned}m_2&=\lambda_{235}\left[1+(1-F)s\right]=\lambda_{235}\left[1+(\phi_T-\phi_0 f)ur\right]\\&=\lambda_{235}\left(1+s^*\right)\\&=\lambda_{235}e^{\lambda_{235}t}\end{aligned}$$

$$(\phi_T-\phi_0 f)u=\frac{s^*}{r} \qquad j_1=\frac{p}{m_1}-\frac{s^*}{rm_2} \qquad j_2=\left(\frac{r}{m_1}-\frac{ur\varphi_0}{m_2}\right)^{-1}$$

where *T* indicates total, *0* indicates common, and *t* = age. Find the partial differentials

$$\langle dt\rangle=\frac{p\langle dr\rangle-r\langle df\rangle}{m_1} \qquad \langle dr^*\rangle=p\langle dr\rangle-r\langle df\rangle$$

So that

$$\sigma_f^2=j_2^2\left[j_1^2\sigma_r^2+\left(\frac{ur}{m_2}\right)^2\left(\sigma_{\phi_T}^2+f^2\sigma_{\phi_0}^2\right)\right] \qquad cov(r,f)=j_1j_2\sigma_r^2 \qquad \sigma_{r^*}^2=m_1^2\sigma_t^2$$

and

$$\begin{aligned}\sigma_t^2&=\frac{p^2\sigma_r^2+r^2\sigma_f^2-2pr\,cov(r,f)}{m_1^2}\\&=\frac{\left(p-2rj_1j_2\right)p\sigma_r^2+r^2\sigma_f^2}{m_1^2}\end{aligned}$$

ignoring any covariance among the measured or common Pb-isotope ratios.

207-Corrected Ages and Ratios

Constrain the $^{206}Pb^{*}/^{238}U$ age to equal the $^{207}Pb^{*}/^{235}U$ age, so that

$$\frac{1}{\lambda_{238}}\mathrm{Ln}\left(1+\frac{\alpha_T-\alpha_0}{\alpha_T}\mathrm{r}\right)=\frac{1}{\lambda_{235}}\mathrm{Ln}\left(1+\frac{\beta_T-\beta_0}{\beta_T}\mathrm{R}\right)$$

Then define

$$r=\frac{^{206}Pb_T}{^{238}U} \qquad s=\frac{^{207}Pb_T}{^{235}U} \qquad f=\frac{^{206}Pb_0}{^{206}Pb_T} \qquad F=\frac{^{207}Pb_0}{^{207}Pb_T}$$

$$\phi_T=\left(\frac{^{207}Pb}{^{206}Pb}\right)_T \qquad \phi_0=\left(\frac{^{207}Pb}{^{206}Pb}\right)_0 \qquad u=\frac{^{238}U}{^{235}U} \qquad p=1-f=\frac{r^*}{r}$$

$$r^*=(1-f)r=pr=\frac{^{206}Pb^*}{^{238}U} \qquad s^*=\left(1-\frac{\phi_0}{\phi_T}f\right)\phi_T ur=(\phi_T-f\phi_0)ur=\frac{^{207}Pb^*}{^{235}U}$$

$$\begin{aligned} m_1&=\lambda_{238}\left[1+(1-f)r\right]\\ &=\lambda_{238}\left(1+r^*\right)\\ &=\lambda_{238}e^{\lambda_{238}t} \end{aligned} \qquad \begin{aligned} m_2&=\lambda_{235}\left[1+(1-F)s\right]\\ &=\lambda_{235}\left[1+(\varphi_T-\varphi_0 f)ur\right]\\ &=\lambda_{235}\left(1+s^*\right)=\lambda_{235}e^{\lambda_{235}t} \end{aligned}$$

where *T* indicates total, *0* indicates common, and *t* = age, and find the partial differentials

$$\langle df\rangle=j_2\left(j_1\langle dr\rangle-\frac{ur}{m_2}\langle d\phi_T\rangle\right) \qquad \langle dr^*\rangle=p\langle dr\rangle-r\langle df\rangle \qquad \langle dt\rangle=\frac{p\langle dr\rangle-r\langle df\rangle}{m_1}$$

from which follows

$$j_1=\frac{p}{m_1}-\frac{s^*}{rm_2} \qquad j_2=\left(\frac{r}{m_1}-\frac{ur\phi_0}{m_2}\right)^{-1} \qquad (\phi_T-\phi_0 f)u=\frac{s^*}{r} \qquad \sigma^2_{r^*}=m_1^2\sigma_t^2$$

and

$$\sigma_t^2=\frac{\left(p-j_1j_2r\right)^2\sigma_r^2+\left(uj_2r^2/m_2\right)^2\sigma_f^2}{m_1^2}$$

ignoring any uncertainty in φ_0 and any
cov

Equations for Isotope Geochronology

Simple Daughter/Parent ages ($r = e^{\lambda t} - 1$): $$\sigma_t^2 = \frac{\sigma_r^2}{\lambda^2 (1+r)^2} + t^2 \frac{\sigma_\lambda^2}{\lambda^2} \quad .$$

$$\frac{\sigma_t^2}{t^2} = \left[\frac{r}{\lambda t (1+r)} \right] \frac{\sigma_r^2}{r^2} + \frac{\sigma_\lambda^2}{\lambda^2}$$

$^{207}Pb/^{206}Pb$ age-error as a function of $^{207}Pb/^{206}Pb$ ratio and of errors in decay constants:

$$\sigma_t^2 = \frac{\left(e^{\lambda_{238} t} - 1\right)^2 \sigma_r^2 + \left(u t e^{\lambda_{235} t}\right)^2 \sigma_{\lambda_{235}}^2 + \left(r t e^{\lambda_{238} t}\right)^2 \sigma_{\lambda_{238}}^2}{\left(u \lambda_{235} e^{\lambda_{235} t} - r \lambda_{238} e^{\lambda_{238} t}\right)^2}$$

where $r = {}^{207}Pb/{}^{206}Pb$ $u = {}^{235}U/{}^{238}U$

Y-error in conventional concordia curve at a specified *X*: $$\sigma_Y^2 = \left[\sigma_{\lambda_{238}}^2 + \left(\frac{\lambda_{238}}{\lambda_{235}} \right)^2 \sigma_{\lambda_{235}}^2 \right] \left(t e^{\lambda_{238} t} \right)^2$$

X-error in conventional concordia curve at a specified *Y*: $$\sigma_X^2 = \left[\sigma_{\lambda_{235}}^2 + \left(\frac{\lambda_{235}}{\lambda_{238}} \right)^2 \sigma_{\lambda_{238}}^2 \right] \left(t e^{\lambda_{235} t} \right)^2$$

X- and *Y*-error in conventional concordia curve at a specified *t*: $$\sigma_X = t e^{\lambda_{235} t} \sigma_{\lambda_{235}}$$ $$\sigma_Y = t e^{\lambda_{238} t} \sigma_{\lambda_{238}}$$

Y-error in Tera-Wasserburg concordia curve at a specified *X:*

$$\sigma_Y^2 = \left(u X t e^{\lambda_{235} t} \right)^2 \left[\sigma_{\lambda_{235}}^2 + \left(\frac{\lambda_{235}}{\lambda_{238}} \right)^2 \sigma_{\lambda_{238}}^2 \right]$$

Equations for errors of common-Pb isotope ratios in zircon, sphene…

a = common ^{206}Pb, b = common ^{207}Pb, w = ^{204}Pb, b = blank, t = total, i = initial

α = common ^{206}Pb/^{204}Pb, β = common ^{206}Pb/^{204}Pb.

$$a_t = \frac{\alpha_b w_b + \alpha_i w_i}{w_t} = \frac{\alpha_b w_b + \alpha_i (w_t - w_b)}{w_t} = \frac{w_b}{w_t}\alpha_b + \alpha_i - \frac{w_b}{w_t}\alpha_i$$

$$d\alpha_t = \frac{w_b}{w_t} d\alpha_b + \frac{\alpha_b}{w_t} dw_b - \frac{\alpha_b w_b}{w_t^2} dw_t + (1 - \frac{w_b}{w_t}) d\alpha_i - \frac{\alpha_i}{w_t} dw_b + \frac{\alpha_i w_b}{w_t^2} dw_t$$

$$\sigma^2_{\alpha_t} = \left(\frac{\alpha_b - \alpha_i}{w_t}\right)^2 \sigma^2_{w_b} + \left[(\alpha_i - \alpha_b)\frac{w_b}{w_t^2}\right]^2 \sigma^2_{w_t} + \left(\frac{w_b}{w_t}\right)^2 \sigma^2_{a_b} + \left(1 - \frac{w_b}{w_t}\right)^2 \sigma^2_{a_i}$$
$$+ \left(\frac{\alpha_b - \alpha_i}{w_t}\right)^2 \left[\sigma^2_{w_b} + \left(\frac{w_b}{w_t}\right)^2 \sigma^2_{w_t}\right]^2 + \left(\frac{w_b}{w_t}\right)^2 \left[\sigma^2_{a_b} + \left(1 - \frac{w_t}{w_b}\right)^2 \sigma^2_{a_i}\right]$$

$$\mathrm{cov}(\alpha_t, \beta_t) = \frac{(\alpha_b - \alpha_i)(\beta_b - \beta_i)}{w_t^2} \sigma^2_{w_b} + \frac{(\alpha_i - \alpha_b)(\beta_i - \beta_b)}{w_t^2} \left(\frac{w_b}{w_t}\right)^2 \sigma^2_{w_t}$$
$$+ 2\left(\frac{w_b}{w_t}\right)^2 \mathrm{cov}(\alpha_b, \beta_b) + \left(1 - \frac{w_b}{w_t}\right)^2 \mathrm{cov}(\alpha_i, \beta_i)$$

Equations for Isotope Geochronology

Simple Daughter/Parent ages ($r = e^{\lambda t} - 1$): $$\sigma_t^2 = \frac{\sigma_r^2}{\lambda^2 (1+r)^2} + t^2 \frac{\sigma_\lambda^2}{\lambda^2} \quad .$$

$$\frac{\sigma_t^2}{t^2} = \left[\frac{r}{\lambda t (1+r)}\right] \frac{\sigma_r^2}{r^2} + \frac{\sigma_\lambda^2}{\lambda^2}$$

$^{207}Pb/^{206}Pb$ age-error as a function of $^{207}Pb/^{206}Pb$ ratio and of errors in decay constants:

$$\sigma_t^2 = \frac{\left(e^{\lambda_{238} t} - 1\right)^2 \sigma_r^2 + \left(u t e^{\lambda_{235} t}\right)^2 \sigma_{\lambda_{235}}^2 + \left(r t e^{\lambda_{238} t}\right)^2 \sigma_{\lambda_{238}}^2}{\left(u \lambda_{235} e^{\lambda_{235} t} - r \lambda_{238} e^{\lambda_{238} t}\right)^2}$$

where $r = {}^{207}Pb/{}^{206}Pb$ $u = {}^{235}U/{}^{238}U$

Y-error in conventional concordia curve at a specified *X*: $$\sigma_Y^2 = \left[\sigma_{\lambda_{238}}^2 + \left(\frac{\lambda_{238}}{\lambda_{235}}\right)^2 \sigma_{\lambda_{235}}^2\right] \left(t e^{\lambda_{238} t}\right)^2$$

X-error in conventional concordia curve at a specified *Y*: $$\sigma_X^2 = \left[\sigma_{\lambda_{235}}^2 + \left(\frac{\lambda_{235}}{\lambda_{238}}\right)^2 \sigma_{\lambda_{238}}^2\right] \left(t e^{\lambda_{235} t}\right)^2$$

X- and *Y*-error in conventional concordia curve at a specified *t*: $$\sigma_X = t e^{\lambda_{235} t} \sigma_{\lambda_{235}}$$ $$\sigma_Y = t e^{\lambda_{238} t} \sigma_{\lambda_{238}}$$

Y-error in Tera-Wasserburg concordia curve at a specified *X:*

$$\sigma_Y^2 = \left(u X t e^{\lambda_{235} t}\right)^2 \left[\sigma_{\lambda_{235}}^2 + \left(\frac{\lambda_{235}}{\lambda_{238}}\right)^2 \sigma_{\lambda_{238}}^2\right]$$

Miscellaneous Equations for Isotope Geochronology

$^{207}Pb/^{206}Pb$ age-error as a function of $^{207}Pb/^{206}Pb$ ratio and of errors in decay constants:

$$\sigma_t^2 = \frac{\left(e^{\lambda_{238}t} - 1\right)^2 \sigma_r^2 + \left(ute^{\lambda_{235}t}\right)^2 \sigma_{\lambda_{235}}^2 + \left(rte^{\lambda_{238}t}\right)^2 \sigma_{\lambda_{238}}^2}{\left(u\lambda_{235}e^{\lambda_{235}t} - r\lambda_{238}e^{\lambda_{238}t}\right)^2}$$

where $r = {}^{207}Pb/{}^{206}Pb$ $u = {}^{235}U/{}^{238}U$

Y-error in conventional concordia curve at a specified *X*: $$\sigma_Y^2 = \left[\sigma_{\lambda_{238}}^2 + \left(\frac{\lambda_{238}}{\lambda_{235}}\right)^2 \sigma_{\lambda_{235}}^2\right]\left(te^{\lambda_{238}t}\right)^2$$

X-error in conventional concordia curve at a specified *Y*: $$\sigma_X^2 = \left[\sigma_{\lambda_{235}}^2 + \left(\frac{\lambda_{235}}{\lambda_{238}}\right)^2 \sigma_{\lambda_{238}}^2\right]\left(te^{\lambda_{235}t}\right)^2$$

X- and *Y*-error in conventional concordia curve at a specified *t*: $$\sigma_X = te^{\lambda_{235}t}\sigma_{\lambda_{235}}$$ $$\sigma_Y = te^{\lambda_{238}t}\sigma_{\lambda_{238}}$$

Y-error in Tera-Wasserburg concordia curve at a specified *X:*

$$\sigma_Y^2 = \left(uXte^{\lambda_{235}t}\right)^2\left[\sigma_{\lambda_{235}}^2 + \left(\frac{\lambda_{235}}{\lambda_{238}}\right)^2 \sigma_{\lambda_{238}}^2\right]$$

X-error in Tera-Wasserburg concordia curve at a specified *Y*:

$$\sigma_X^2 = \left[\left(uXte^{\lambda_{235}t}\right)^2 \sigma_{\lambda_{235}}^2 + \left(1 + XY\lambda_{238}e^{\lambda_{238}t}\right)^2 \sigma_{\lambda_{238}}^2\right]\left(X^2te^{\lambda_{238}t}\right)^2$$

7
Equations for Isotope Geochronology

Simple Daughter/Parent ages ($r = e^{\lambda t} - 1$): $$\sigma_t^2 = \frac{\sigma_r^2}{\lambda^2 (1+r)^2} + t^2 \frac{\sigma_\lambda^2}{\lambda^2} \quad .$$

$$\frac{\sigma_t^2}{t^2} = \left[\frac{r}{\lambda t (1+r)} \right] \frac{\sigma_r^2}{r^2} + \frac{\sigma_\lambda^2}{\lambda^2}$$

$^{207}Pb/^{206}Pb$ age-error as a function of $^{207}Pb/^{206}Pb$ ratio and of errors in decay constants:

$$\sigma_t^2 = \frac{\left(e^{\lambda_{238} t} - 1\right)^2 \sigma_r^2 + \left(u t e^{\lambda_{235} t}\right)^2 \sigma_{\lambda_{235}}^2 + \left(r t e^{\lambda_{238} t}\right)^2 \sigma_{\lambda_{238}}^2}{\left(u \lambda_{235} e^{\lambda_{235} t} - r \lambda_{238} e^{\lambda_{238} t}\right)^2}$$

where $r = {}^{207}Pb/{}^{206}Pb$ $u = {}^{235}U/{}^{238}U$

Y-error in conventional concordia curve at a specified *X*: $$\sigma_Y^2 = \left[\sigma_{\lambda_{238}}^2 + \left(\frac{\lambda_{238}}{\lambda_{235}} \right)^2 \sigma_{\lambda_{235}}^2 \right] \left(t e^{\lambda_{238} t} \right)^2$$

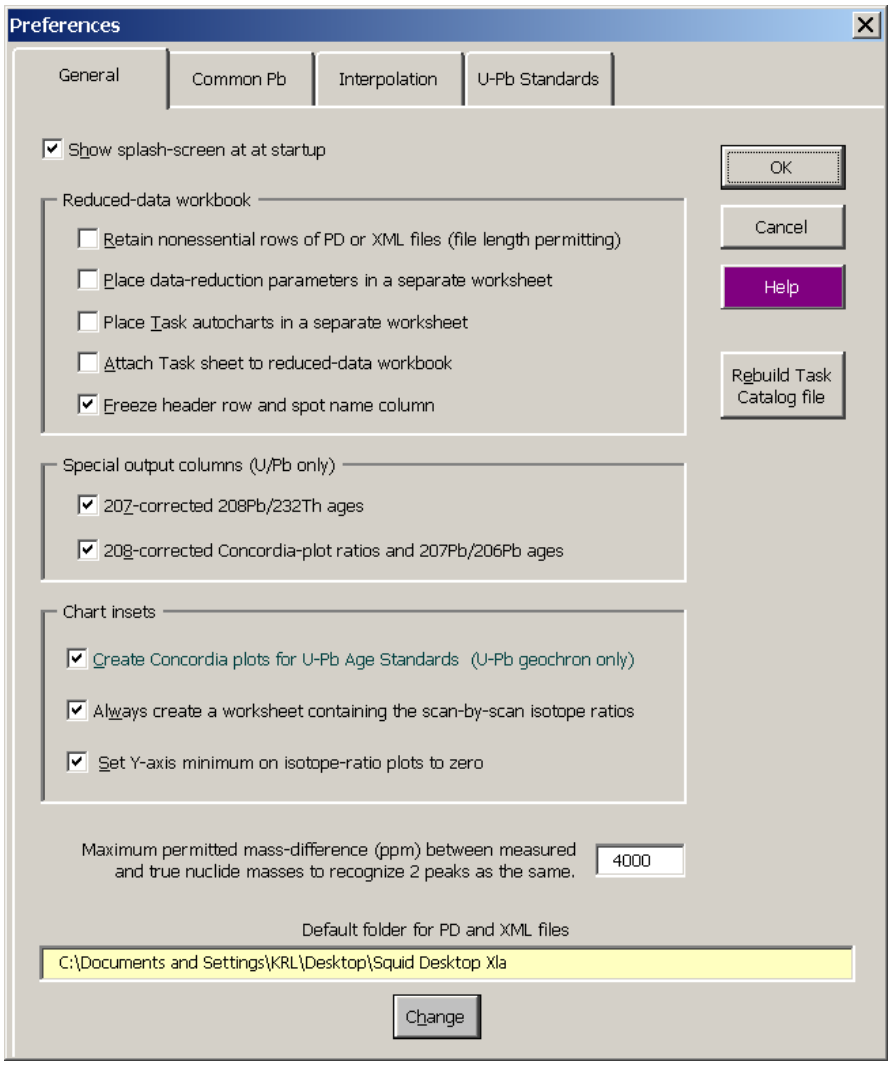
X-error in conventional concordia curve at a specified *Y*: $$\sigma_X^2 = \left[\sigma_{\lambda_{235}}^2 + \left(\frac{\lambda_{235}}{\lambda_{238}} \right)^2 \sigma_{\lambda_{238}}^2 \right] \left(t e^{\lambda_{235} t} \right)^2$$

X- and *Y*-error in conventional concordia curve at a specified *t*: $$\sigma_X = t e^{\lambda_{235} t} \sigma_{\lambda_{235}}$$
$$\sigma_Y = t e^{\lambda_{238} t} \sigma_{\lambda_{238}}$$

Y-error in Tera-Wasserburg concordia curve at a specified *X:*
ariance among the measured or common Pb-isotope ratios.

Appendix III: The *SQUID-2* Panels and Controls

Preferences (General *panel)*



Show splash-screen at startup

Display the *SQUID-2* splash screen when the *SQUID-2* add-in is installed.

Retain nonessential rows of PD or XML files (file length permitting)

If this box is checked, the entire original PD or XML file will be retained in the (hidden) columns **A** of the condensed raw-data worksheet. Because this will slow construction of the condensed sheet somewhat, and slightly increase the possibility of out-of-memory problems under some conditions, do this only if you do not intent to archive the original PD or XML files.

Even if the box checked, however, *SQUID-2* will be unable to retain the original lines of some large XML files, simply because the number of lines of these files exceeds the 65,336-row limit of *Excel* 2003.

Place data-reduction parameters in a separate worksheet

Put data-reduction parameters specified in the PD file and Preferences on a separate worksheet attached to the reduced-data workbook.

Place auto-charts in a separate worksheet

Put auto-charts in a separate worksheet rather than in the reduced-data worksheet.

Attach Task sheet to reduced-data workbook

Attach a copy of the *Task* sheet to the reduced-data workbook.

Freeze header rows and spot name column

Forces the first column (spot names) and the column-header row to always be visible when the output worksheets are scrolled.

207-corrected 208Pb/232Th ages

Check this box if you require an output-sheet column containing $^{208}Pb/^{232}Th$ ages corrected for common Pb with the assumption that the $^{206}Pb/^{235}U$ - $^{207}Pb/^{235}U$ ages are concordant.

208-corrected Concordia-plot ratios and 207Pb/206Pb ages

Check this box if you require output-sheet columns containing the $^{206}Pb/^{235}U$ - $^{207}Pb/^{235}U$ ages , errors, and error correlation where the common-Pb correction assumes concordance of the $^{206}Pb/^{235}U$ - $^{208}Pb/^{232}UTh$ ages. Checking this box also enables the calculation of 207-corrected $^{207}Pb/^{206}Pb$ ages.

Create concordia plots for U-Pb Age Standards (U-Pb only)

If checked, a small conventional concordia plot for the Standard spots will be placed within the Standard worksheet.

Always construct within-scan isotope ratio sheet

A within-scan isotope ratio sheet contains the within-spot (i.e. scan-by-scan) isotope ratio and *Task* equation results for each spot, formatted for clarity of viewing. This worksheet is required by *SQUID* for construction of chart insets of isotope ratios/*Task* equations**Error! Bookmark not defined.** versus time.

Set Y-axis minimum on isotope-ratio plots to zero

If unchecked, the Y-axis (the ratio values) for isotope-ratio chart-insets will be auto-scaled to the plotted data.

Maximum permitted mass-difference between measured and true nuclide masses…

If the apparent (PD file value) and true masses of a mass station are within this difference, *SQUID-2* will accept the measurement. Otherwise, *SQUID-2* will not recognize the mass station as simply a measurement error on the true mass, so that the Setup panel will refuse to reduced that PD file.

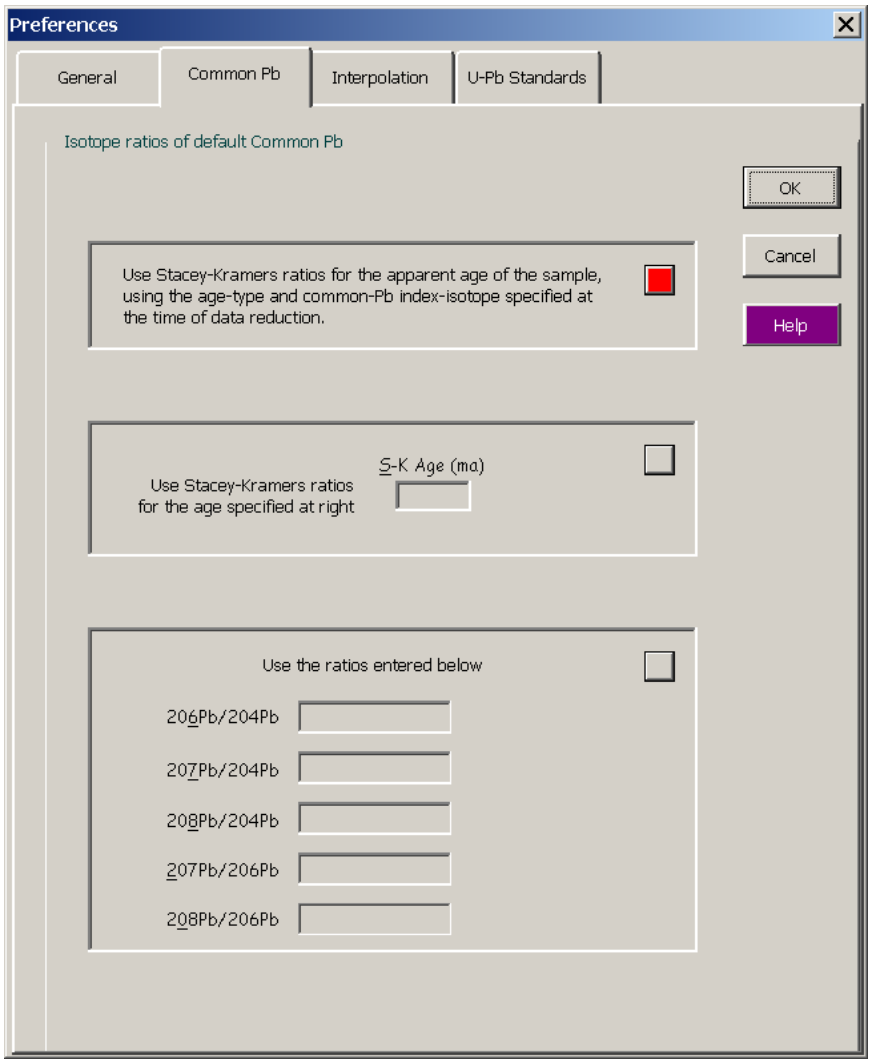
Default folder for PD and XML files

The folder *SQUID-2* opens when asking for a raw-data file to process.

Rebuild Task Catalog file

Reconstruct the TaskCatalog file (contains basic information about each valid Task file in the SquidUser folder, used to determine compatibiity for data reduction with a raw-data file.

*Preferences (*Common Pb *panel)*



Isotope Ratios of Common Pb (U/Pb geochron only)

Refers to the Pb subtracted from the total Pb to obtain the isotopic abundances of the spot's radiogenic Pb. These corrections will be applied in the StandardData and SampleData worksheets. The common Pb used for Grouped-sample worksheets is assigned separately.

Use Stacey-Kramers ratios for apparent age of sample

Use the single-stage evolution Stacey-Kramers ratios (Stacey and Kramers, 1975) for the sample's age using the age-type specified for data-reduction..

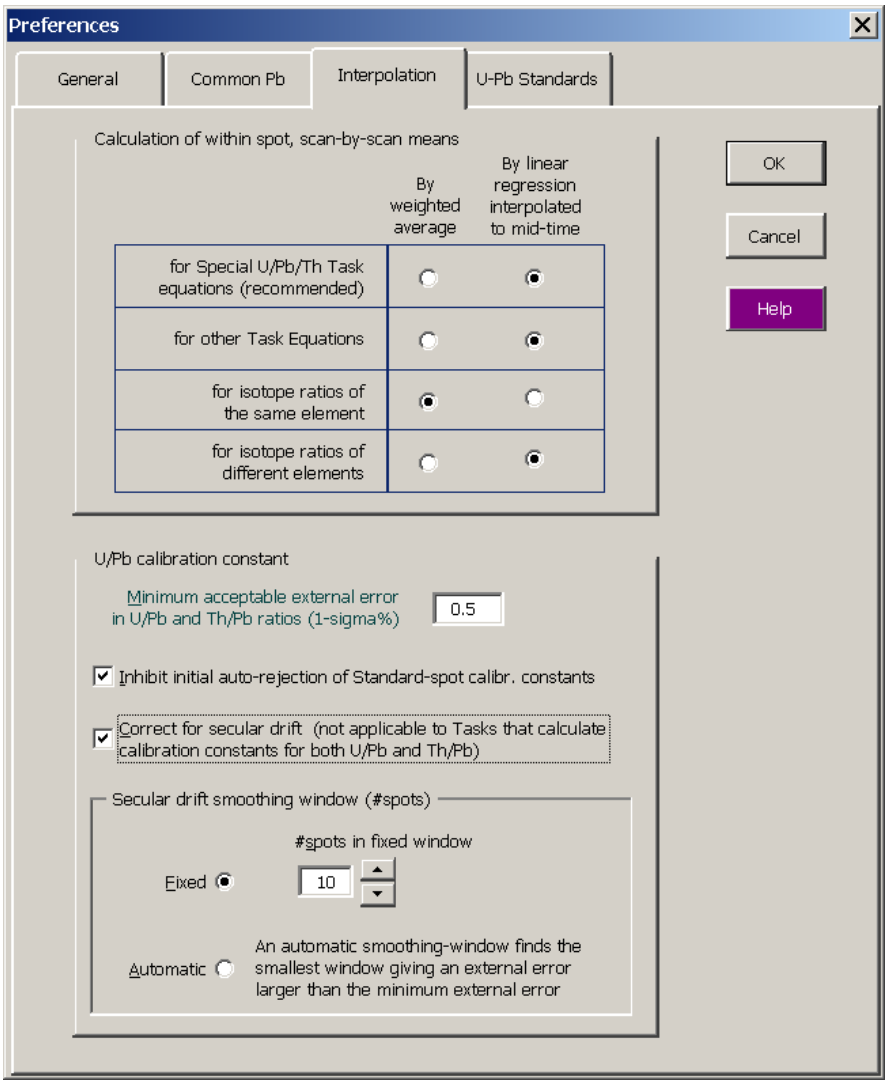
Use Stacey-Kramers ratios for the age specified at right

Use the Stacey-Kramers ratios corresponding to the specific age entered in the S-K Age= box.

Use the ratios entered below

Enter an arbitrary set of Pb-isotope ratios to use for common-Pb correction.

*Preferences (*Interpolation *panel)*



Calculation of within-spot, scan-by-scan means

The mean isotope ratios or Task Equation values assigned to each analyzed spot can be done either by

1. Calculating the outlier-resistant mean of the *N*-1 interpolations for the *N* peak-scans, or

2. Using an outlier-resistant linear regression of the interpolated values to determine the value of the interpolations atg mid-burn time,

Because in many (most?) analyses ratios or equations involving different elements seem to increase or decrease in a pseuo-linear manner during the spot burn, selecting the Linear Interpolation option generally results in better "internal" (within spot) precision. It can be argued that for consistency, other ratios or equations should be treated similarly.

U/Pb calibration constant

MINIMUM ACCEPTABLE EXTERNAL ERROR IN U/PB AND TH/PB RATIOS (1-SIGMA%)

SQUID-2 always calculates the most-probable external (that is, in addition to counting-statistics error) spot-to-spot error for the calibration constants of a U/Pb Task. If the Age Standard yields rather low count-rates for Pb, statistical resolution of any external error is poor, so that an apparent external error of zero is possible. If you believe that some external error is always present in SHRIMP U/Pb analyses, you may wish to specify a lower bound for the external error, regardless of the statistical calculation. The external error is included in the error assigned to sample-spot U/Pb ages, so is important to consider carefully.

INHIBIT INITIAL AUTO-REJECTION OF STANDARD-SPOT CALIBRATION CONSTANTS

If this box is unchecked, *SQUID-2* will attempt to reject obvious outliers (subject to later user revision) before calculating the weighted-mean calibration constant. Check the box to inhibit such rejection.

CORRECT FOR SECULAR DRIFT

If the calibration constant displays an *obvious* drift or variation with time (whether monotonic of cyclic), you can correct the sample spots for the observed drift by clicking this box.

SECULAR DRIFT SMOOTHING WINDOW (#SPOTS)

The secular-drift curve is calculated via the LOWESS algorithm (Cleveland, 1979), which fits an outlier-resistant smoothing-spline for a moving spot-window. The degree of smoothing is controlled by the size of the spot-window: the larger the window the greater the smoothing. Large windows are best for, say, a pseudolinear drift, smaller windows for drifts with abrupt changes or cyclic appearance. *SQUID-2* offers two choices for determining the width of the smoothing window: fixed (you specify the window) and automatic (*SQUID-2* determines the best window).

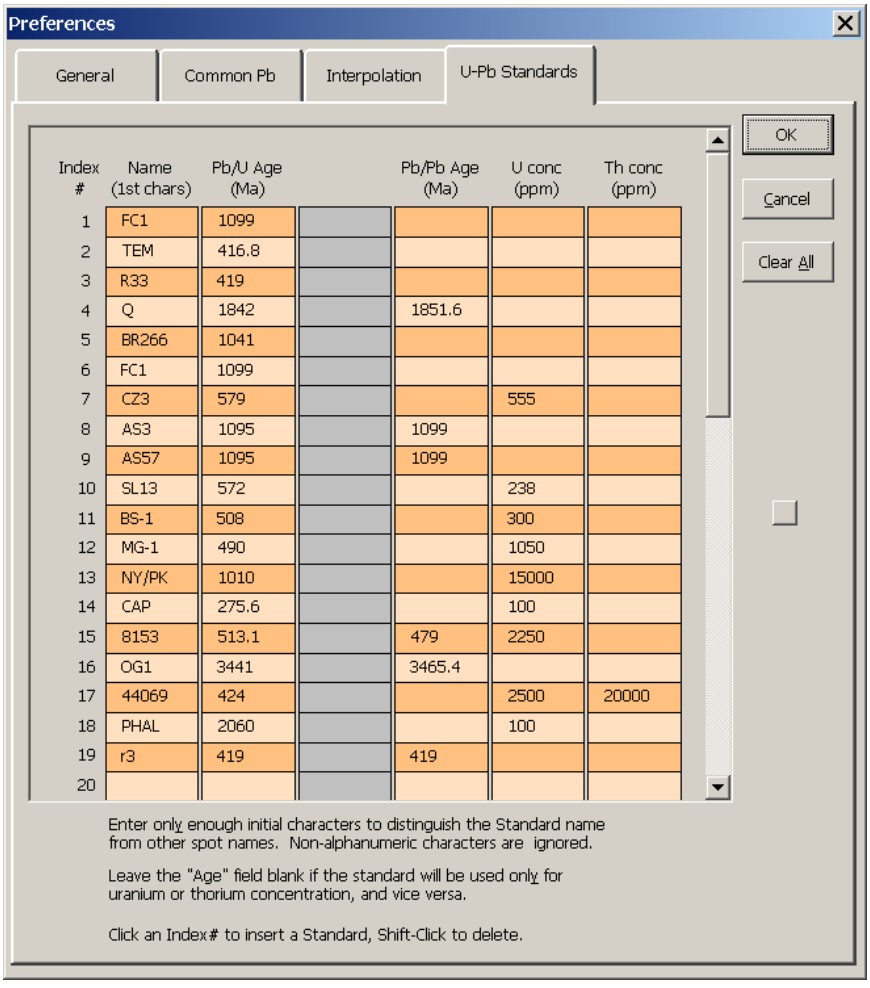
If you select Fixed, the initial smoothing window will be the one you specify here. *You can always change the smoothing window, however, after the data have been reduced.*

If you select Automatic, *SQUID-2* will find the largest smoothing window whose resulting external error is not less than the specified Minimum acceptable external error.

This Secular Drift Correction algorithm is experimental, should be used with care and trusted only after considerable comparison with conventional SQUID-2 data reduction.

*Preferences (*U-Pb Standards *panel)*

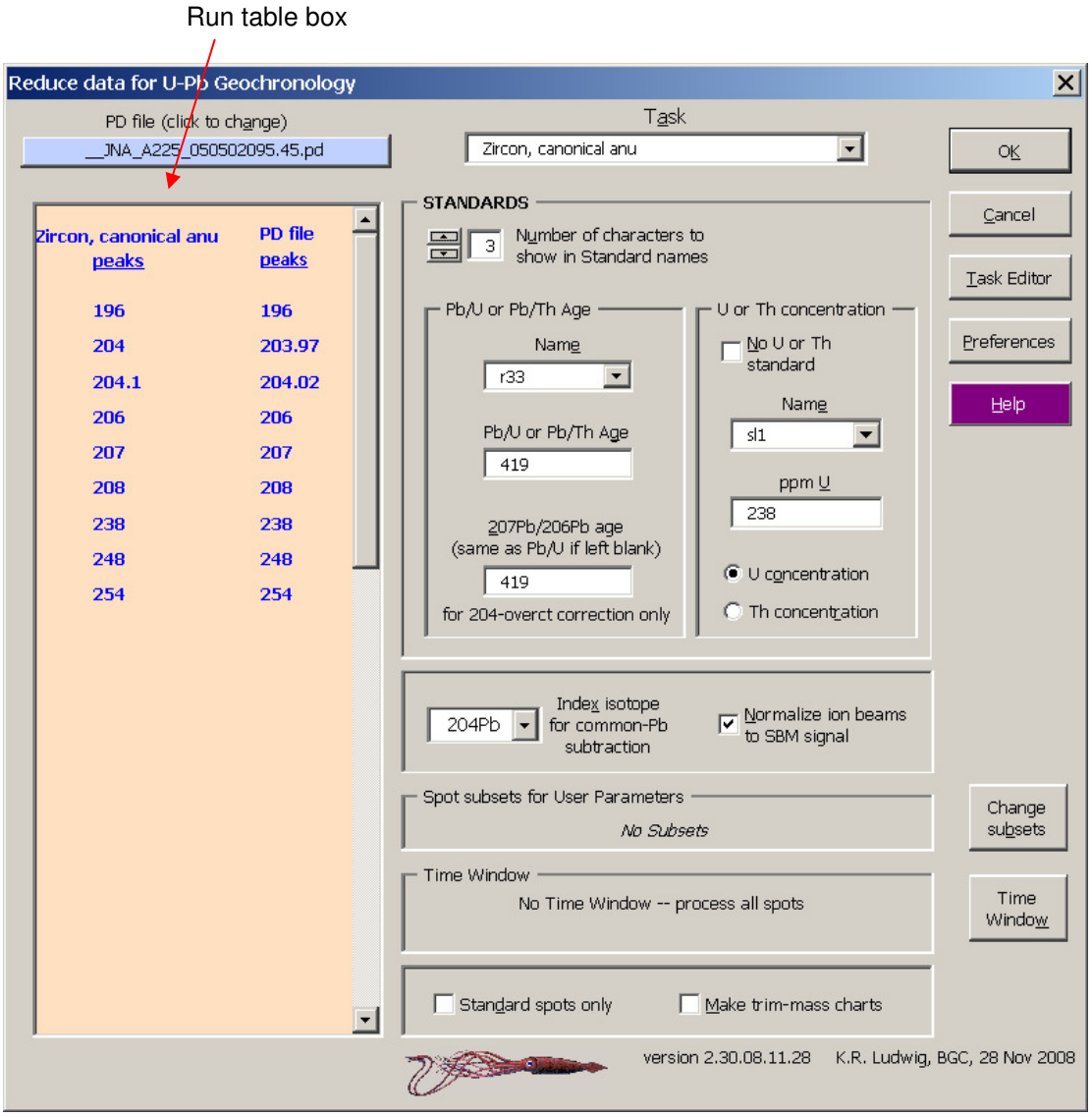
You can specify up to 50 common U-Pb age and/or concentration standards from this panel. When the U-Pb data-reduction panel is being filled out, SQUID will look for spot names whose first few characters match those of an age standard. If a match is found, that standard's name, Pb/U age (if defined), Pb/Pb age (if defined), and U or Th concentration (if defined) will entered into the appropriate boxes.



Index #	Name (1st chars)	Pb/U Age (Ma)		Pb/Pb Age (Ma)	U conc (ppm)	Th conc (ppm)
1	FC1	1099				
2	TEM	416.8				
3	R33	419				
4	Q	1842		1851.6		
5	BR266	1041				
6	FC1	1099				
7	CZ3	579			555	
8	AS3	1095		1099		
9	AS57	1095		1099		
10	SL13	572			238	
11	BS-1	508			300	
12	MG-1	490			1050	
13	NY/PK	1010			15000	
14	CAP	275.6			100	
15	8153	513.1		479	2250	
16	OG1	3441		3465.4		
17	44069	424			2500	20000
18	PHAL	2060			100	
19	r3	419		419		
20						

When adding Standards to the *U-Pb Standards* panel, keep in mind that *SQUID* will search the spot names for a Standard in the order that they appear in the \panel.

Reduce Data for U-Pb Geochronology



Task

Select any of the existing *Tasks* to use for data reduction.

New PD file

Load another PD file without leaving this panel.

Number of characters to show in Standard names

The number of initial spot-name characters that will be shown in the Name dropdowns, and that will be used to categorize a spot as a Standard.

Pb/U or Pb/Th Age

NAME

The initial spot-name characters that define a spot as a Standard.

PB/U OR PB/TH AGE

The *apparent* age of the Standard. Though this is generally the same as the true age, it can be different if the Standard is known, say, to have a consistent amount of Pb loses.

207PB/206PB AGE

By default (i.e. left blank), this is the same as the Pb/U or Pb/Th age. However, if, say, the Standard's Pb/U or Pb/Th age is discordant with its $^{207}Pb/^{206}Pb$ age, a different value can be entered here. *The Standard $^{207}Pb/^{206}Pb$ age is used only for 204-overcount calculation.*

U OR TH CONCENTRATION

The average concentration of either U or Th in the concentration standard

NAME

Select the initial characters of the U (or Th) concentration standard names. If no such standard was present in the mount, leave blank (the first item in the dropdown list).

PPM U (OR TH)

Enter the average concentration of U (or Th) for the concentration standard. Leave blank if there is no concentration standard

Index Isotope for common Pb

The common-Pb correction for radiogenic U-Pb isotope ratios can be corrected using any of ^{204}Pb (corrects assuming the default common Pb specified in *Preferences*), ^{207}Pb (corrects using the assumption of $^{206}Pb/^{238}U$-$^{207}Pb/^{206}Pb$ age-concordance) , or ^{208}Pb (corrects using the assumption of $^{206}Pb/^{238}U$-$^{208}Pb/^{232}Th$ age-concordance).

Normalize ion beams to SBM signal

Ion beams normalized to the signal of a perfectly reliable SBM (secondary beam monitor) should be unaffected by any instability in the secondary ion beam. If there are doubts as to the functioning of the SBM (i.e. the SBM is not constant over the mass range of the Run Table), leave unchecked.

Spot subsets for user parameters

Shows those spots for which one or more *Task* equations are specifically applied.

Time window

Shows the time window within which spot analyses are selected for data reduction. Other spots are ignored.

Trim mass charts

Construct trim-mass charts for each peak-centered mass station.

Task Editor

Invokes the *Task* Editor panels, returning to this Setup panel when done.

Preferences

Invokes the Preferences panel, returning to this Setup panel when done.

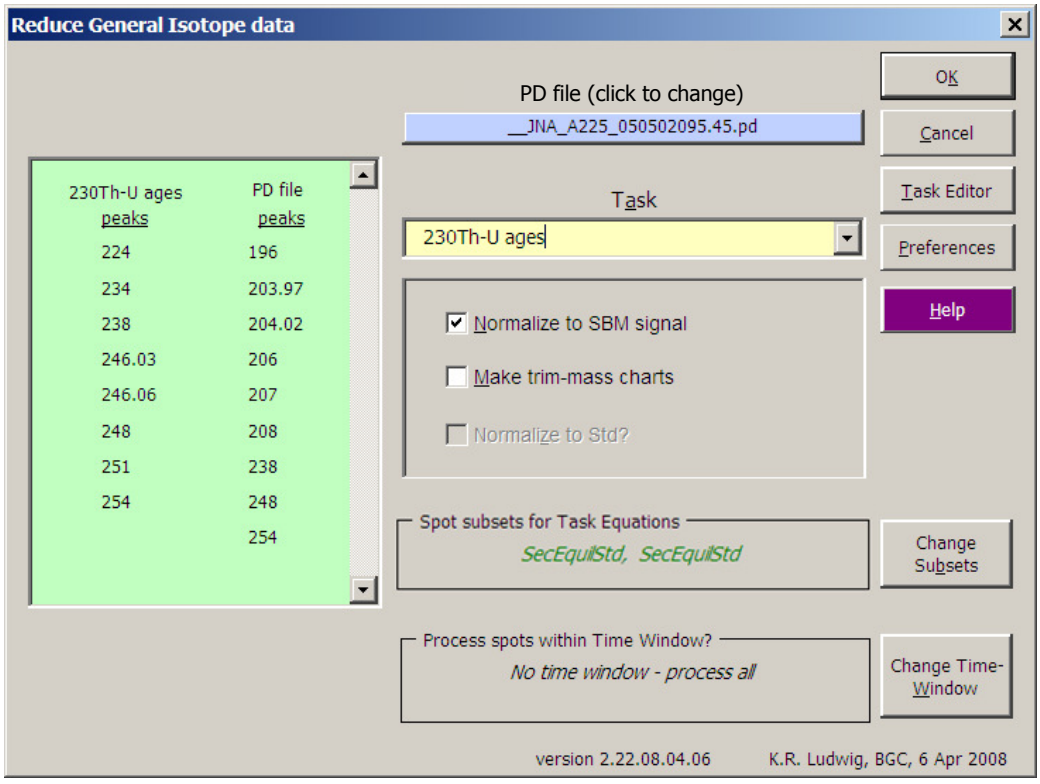
Change subsets

Specify *Task* equation that are to be applied only to a selected group of spots, based in the initial characters of the spot names.

Change Time-window

Define a time window within which spot analyses are selected for data reduction. Other spots are ignored.

Reduce General Isotope Data



New PD

Load another PD file, then return to this panel.

Task

Select the *Task* for data reduction from the dropdown list of all defined *Tasks*.

Normalize to SBM signal

Ion beams normalized to the SBM (secondary beam monitor may be unaffected by any instability in the secondary ion beam. If there are doubts as to the functioning of the SBM (i.e. the SBM is not constant over the mass range of the Run Table), leave unchecked.

Make trim-mass charts

Construct trim-mass charts for each peak-centered mass station.

Spot subsets for user parameters

Shows spots having *Task* equations that are specifically applied.

Process spots within Time Window?

The time window within which spot analyses are selected for data reduction. Other spots are ignored.

Change Subsets

Specify *Task* equation that are to be applied only to a selected group of spots, based in the initial characters of the spot names.

***Task* Editor**

Invokes the *Task* Editor panels, returning to this Setup panel when done.

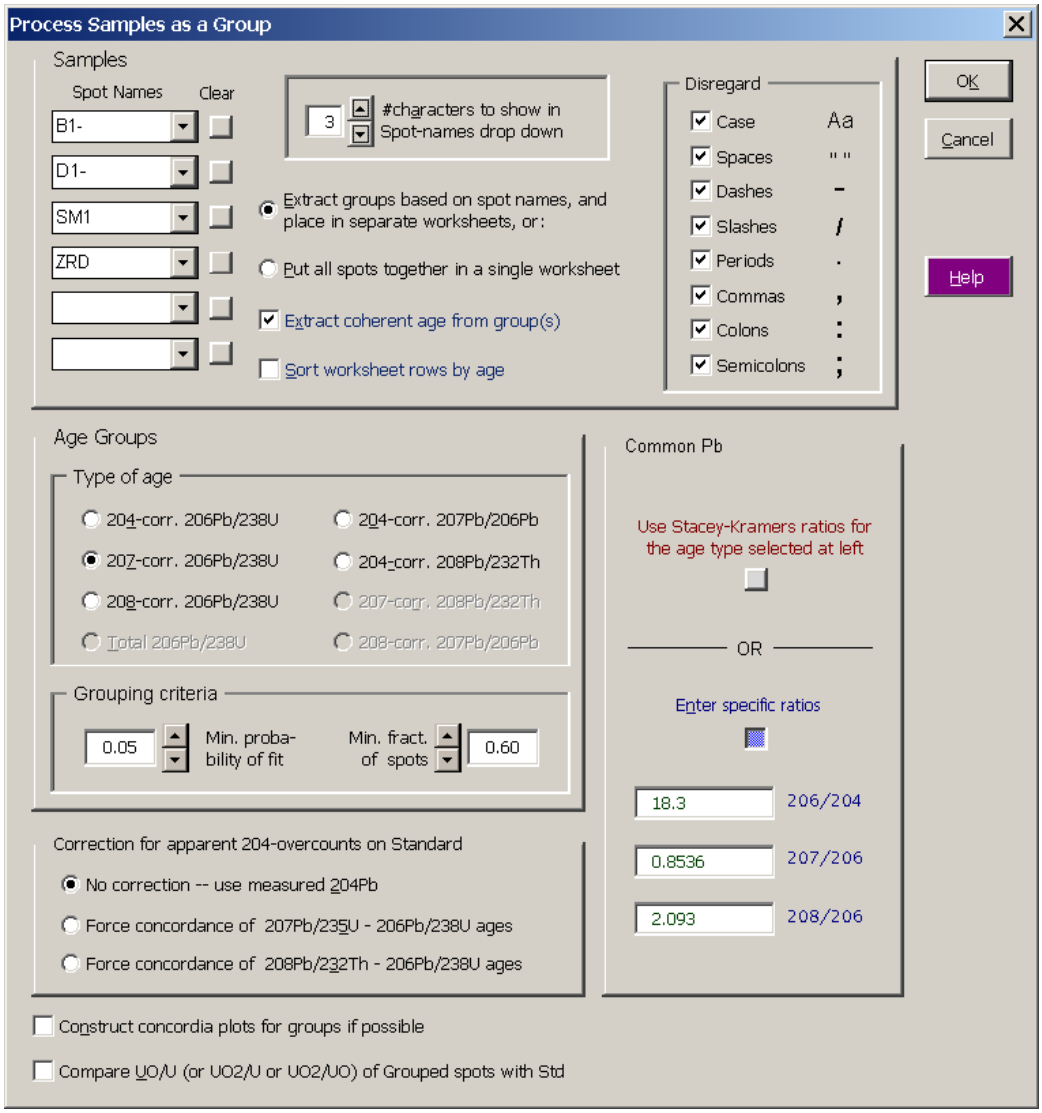
Preferences

Invokes the Preferences panel, returning to this Setup panel when done.

Change Time-window

Define a time window for spot data reduction.

Sample Grouping



Spot Names

From any of the 6 spot-name dropdowns, select from 1 to 6 spot name fragments to use as a selection criterion for each group. Only the initial number of characters shown in the dropdown will be used.

 # letters to show in Spot-names dropdown

Select how many of the initial spot-name characters will appear in the Spot Names dropdowns.

Disregard Case, Spaces, Dashes, Slashes…

Select characters that SQUID is to ignore when grouping the spot names.

Extract coherent age group

After grouping, extract a statistically coherent age grouping, if possible.

Sort samples by age

After grouping, sort the data alphabetically by spot name.

Group all spots together

Treat all spots in the Sample worksheet as a single group.

Age Groups: Type of U-Pb Age

The type of age to be used for spot age-grouping.

Total 206Pb/238U
The $^{206}Pb/^{238}U$ age, with no correction for common Pb.

204-corr. 206Pb/238U
Use the $^{206}Pb/^{238}U$ age, using ^{204}Pb as the index isotope for common-Pb correction.

207-corr. 206Pb/238U
Use the $^{206}Pb/^{238}U$ age, with ^{207}Pb as the index isotope for common-Pb correction, and assuming $^{206}Pb/^{238}U$-$^{207}Pb/^{206}Pb$ age-concordance.

208-corr. 206Pb/238U
Use the $^{206}Pb/^{238}U$ age, with ^{208}Pb as the index isotope for common-Pb correction, and assuming $^{206}Pb/^{238}U$-$^{208}Pb/^{232}Th$ age-concordance.

204-corr. 208Pb/232Th
Use the $^{208}Pb/^{232}UTh$ age, with ^{204}Pb as the index isotope for common-Pb correction.

204-corr. $^{207}Pb/^{206}Pb$
Use the $^{207}Pb/^{206}Pb$ age, with ^{204}Pb as the index isotope for common-Pb correction.

207-corr. 208Pb/232Th
Use the $^{208}Pb/^{232}UTh$ age, with ^{207}Pb as the index isotope for common-Pb correction.

208-corr. 207Pb/206Pb
Use the $^{207}Pb/^{206}Pb$ age age, with ^{207}Pb as the index isotope for common-Pb correction.

Age Groups: Grouping Criteria

Min. prob. of fit
The minimum acceptable probability-of-fit that defines an age group.

Min. fract. of spots

The minimum fraction of spots in the group that defines an age group.

Correction for 204 overcounts on Standard

How to correct for apparent overcounts at the ^{204}Pb mass position, using calculations from the Standard spots as a guide.

No correction – use measured 204Pb

Assume that there are no 204 overcounts

Force concordance of 207Pb/235U - 206Pb/238U ages

Subtract the mean 204 overcts/sec. (from 207) calculated in the Standard worksheet from each of the Sample spot ^{204}Pb measurements.

Force concordance of 208Pb/232Th - 206Pb/238U ages

Subtract the mean 204 overcts/sec. (from 208) calculated in the Standard worksheet from each of the Sample spot ^{204}Pb measurements.

Common Pb

Use Stacey-Kramers ratios for the age type specified at left

Correct each spot's U-Pb, Pb-Pb, and Th-Pb age assuming common-Pb isotope ratios calculated using the (single stage evolution) Stacey-Kramers method (Stacey and Kramers, 1975), for the age-type specified in the *Type of age"* box.

Enter specific ratios

Correct each spot's U-Pb, Pb-Pb, and Th-Pb age with the common-Pb isotope ratios specified in Preferences

Construct concordia plot for groups if possible

If an age group is requested and found, construct a concordia plot inset with the grouped worksheet.

Compare UO/U (or UO2/U or UO2/UO) of Grouped spots sith std

Construct a chart-inset in each Grouped Spots sheet showing the UO_n / UO_m ratio for the Standard and (in a different color) the Grouped spots. Values of *n* and *m* can range from 0 to 2, and depend on what was measured for the spots.

Time Window

Limits to specify with Standard spots

Lower (first) only
Ignore spot-analyses acquired before the Starting spot, process all spots after.

Upper (last) only
Ignore spot-analyses acquired after the Ending spot, process all spots before.

Both lower and upper
Ignore spot-analyses acquired before the Starting spot and after the ending spot.

No window (reduce all spots)
Cancel the Time Window.

Starting Name/Time

The first spot to process. For U-Pb geochronology, restricted to age standards.

Ending Name/Time

The last spot to process. For U-Pb geochronology, restricted to age standards.

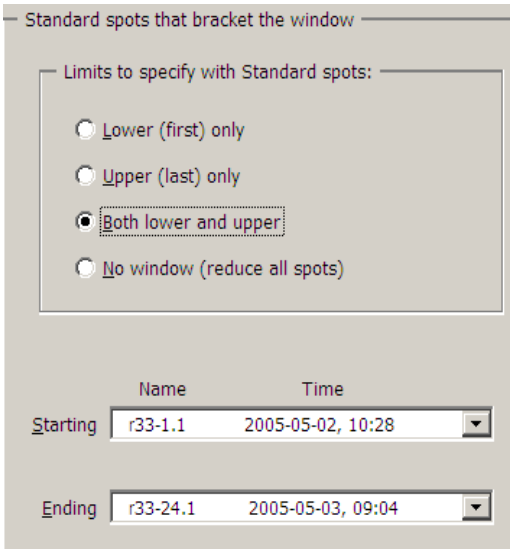
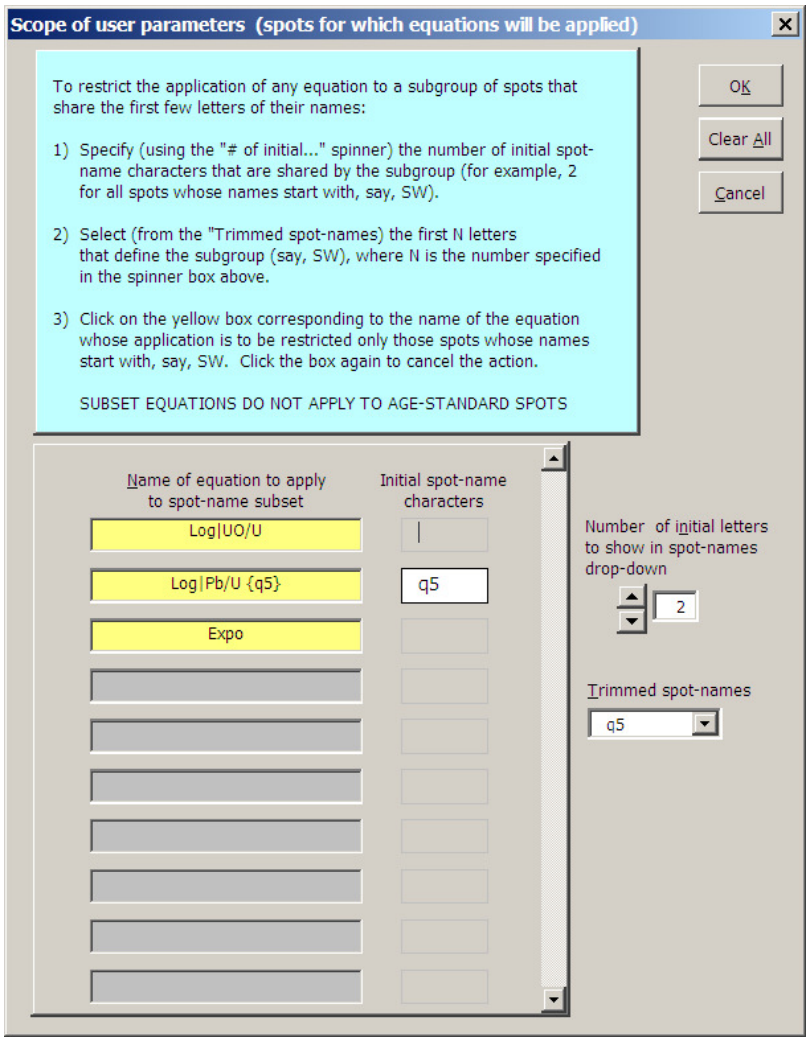


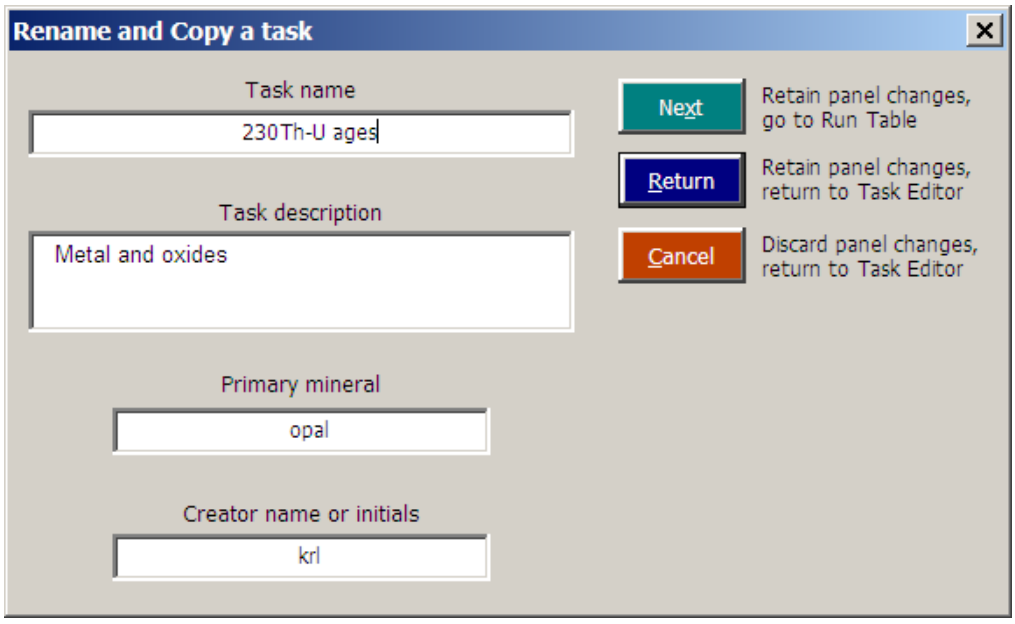
Figure 29: The Time Window panel.

Subsets

See instructions in the blue box at the top-left of the form (below).



Copy or Rename a Task



***Task* name**

Enter a name for the *Task* that distinguishes it from other *Tasks*.

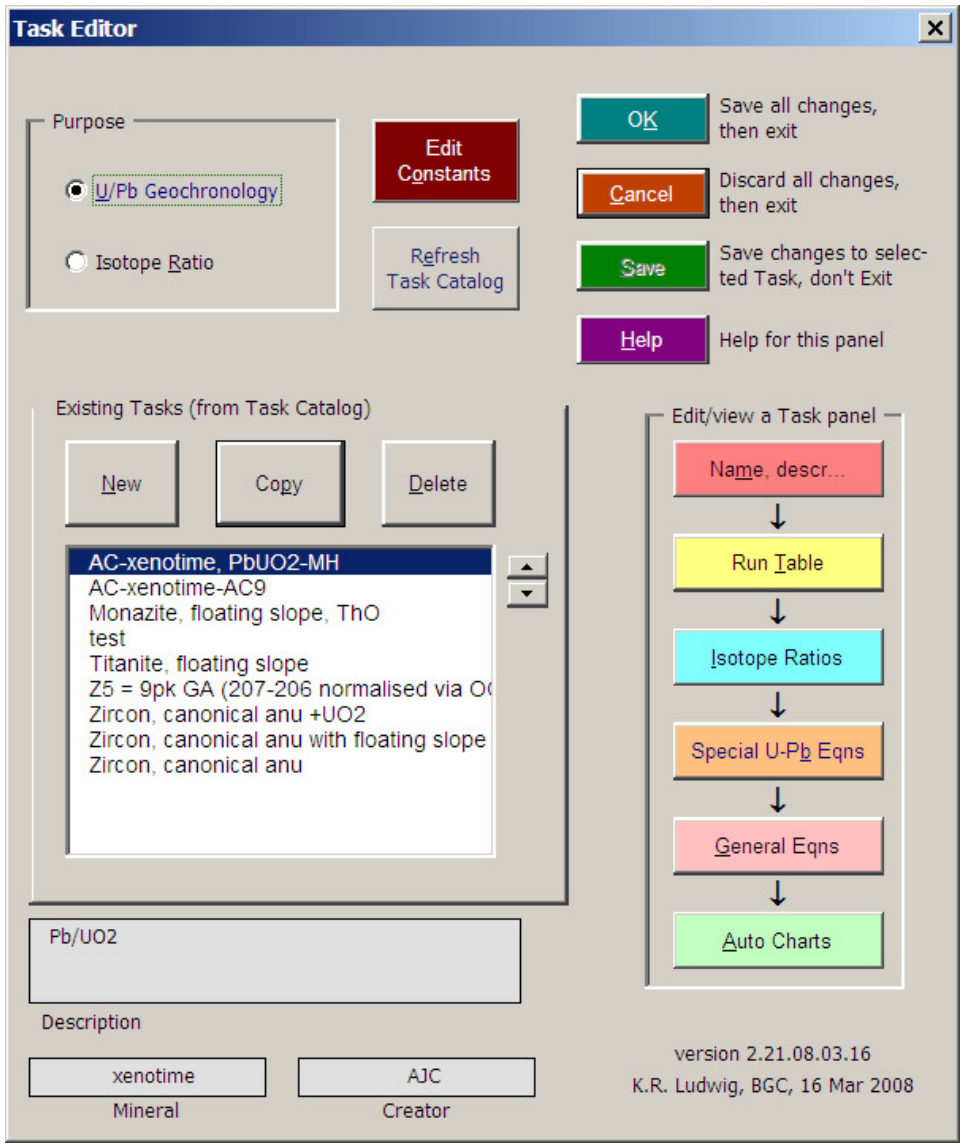
***Task* description**

Enter a brief description of the *Task*.

Primary mineral

The mineral that to which the *Task* will most-commonly be assigned.

Task Editor



U-Pb Geochronology

Edit/view the U/Pb geochronology *Tasks*.

Isotope Ratio

Edit/view the General isotope ratio *Tasks*.

Existing *Tasks*

NEW

Define a completely new Task.

RENAME OR COPY

Rename or copy the selected *Task*.

DELETE

Remove the selected *Task* (cannot be undone!).

SINGLE CLICK A TASK NAME

Selects the Task for editing by any of the colored buttons to the right.

DOUBLE CLICK A TASK NAME

Selects the Task and opens its General Equations panel.

Edit/view a panel for the selected *Task*

Click a colored button to edit or view the specified panel for the selected *Task*.

Refresh *Task* Catalog

Rebuild the *Task* Catalog by abstracting the name, description, mineral, and creator for each *Task* in the *SquidUser* folder.

OK

Save all changes and exit

Cancel

Discard all changes and exit.

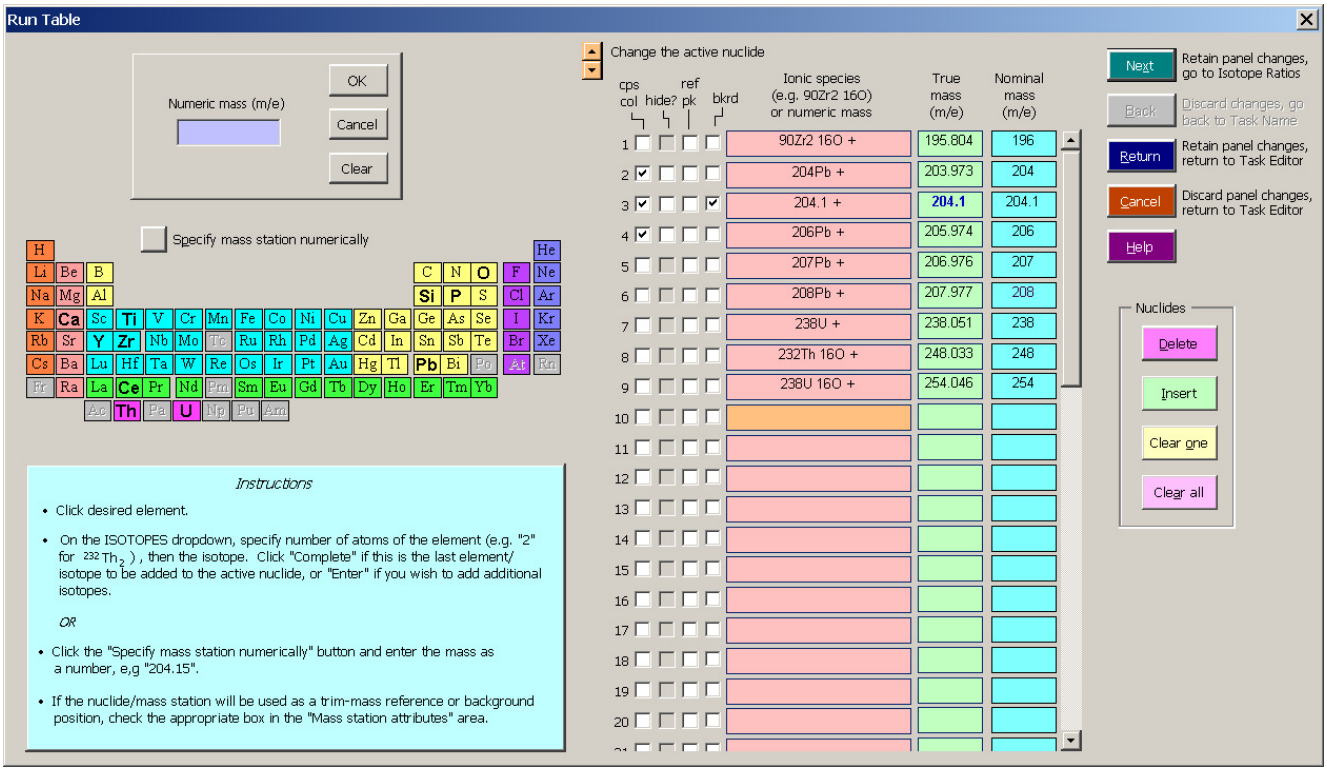
Constants

Edit/view the user-defined constants.

Save

Save all changes but remain in the *Task* Editor.

Run Table



Ionic species

Shows the ionic species (or numeric m/e) of the Active nuclide. The Active nuclide is shown in a tan box, the other nuclides in pink boxes.

Clear

Clear the Ionic Species box.

Specify mass station numerically

Type in the numeric value of the mass position for the active nuclide.

bkrd

Is the mass station to be used for background subtraction of the secondary ion beam?

ref pk

Is the mass station to be used as a trim mass reference (a trim mass reference is relevant only to the construction of optional charts of centered-peak trim masses versus time).

cps col

Construct a column in the processed-data worksheet for counts/second at this mass station?

Hide?

Hide the *CPS* column in the reduced-data workshet.

Periodic table of the elements

Commonly-used elements for geochronology are shown in bold font, short-lived elements (not selectable) in gray background, and rare earth elements in green boxes.

Next

Save any changes to the Run Table panel, then go to the next (isotope ratios) *Task* Editor panel.

Return

Save any changes to the Run Table panel, then return to the main *Task* Editor panel.

Cancel

Discard any changes to the Run Table panel, then return to the main *Task* Editor panel.

Insert

Insert a row of blank boxes (nuclide, true mass, nominal mass) before the Active Nuclide.

Delete

Delete the Active Nuclide and associated true- and nominal-mass boxes.

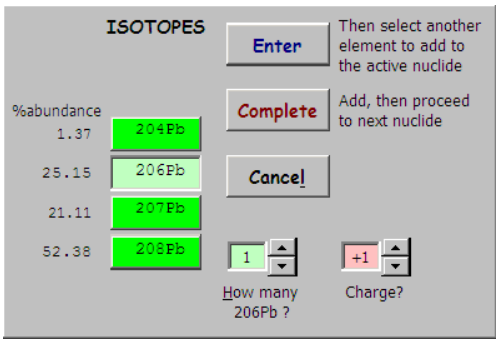
Clear one

Clear the Active Nuclide and associated true- and nominal-mass boxes.

Clear all

Clear all of the nuclide, true mass, and nominal mass boxes.

The Isotope Selection Sub-Panel



How many?

How many atoms of the selected isotope (blue) are in the Active Nuclide? Note that 1) all stable and long-lived isotopes of the selected element are shown, 2) the default isotope will be the most-abundant isotope, and 3) the relative isotopic abundances (summed to 100) of the natural element are shown at the left of the inset.

Charge

Specify the charge of the active nuclide.

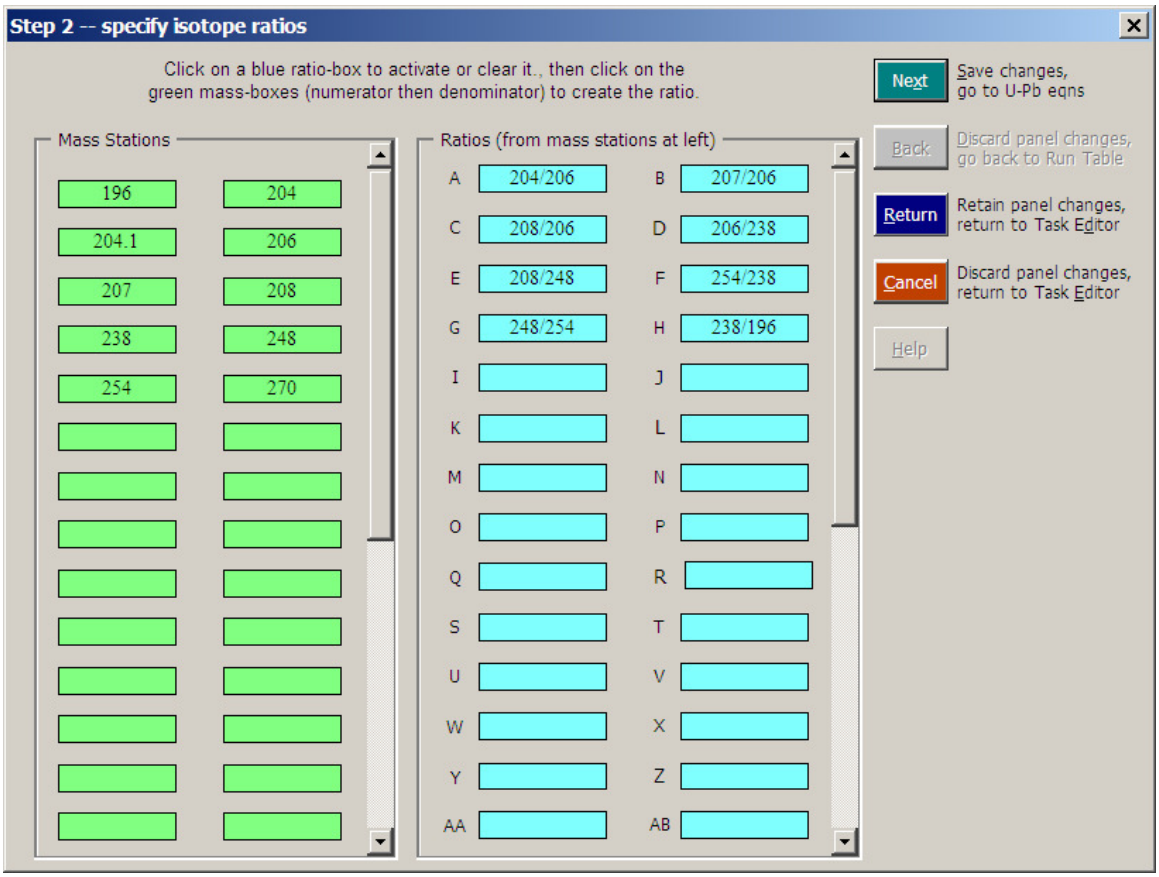
Enter

Enter this isotope in the active nuclide box then add another element or isotope.

Complete

Add this isotope to the active nuclide, then move down to the next mass station.

Isotope Ratios



Ratios (from mass stations at left)

To specify the calculation of an isotope ratio, 1) click on one of the blue isotope-ratio boxes to activate it (turns tan), 2) click on one of the green boxes (to left) to specify the numerator isotope of the ratio, 3) click on the denominator isotope. To clear ratio box, click it a second time.

Next

Save any changes to the Isotope Ratios panel, then go to the next panel (equations).

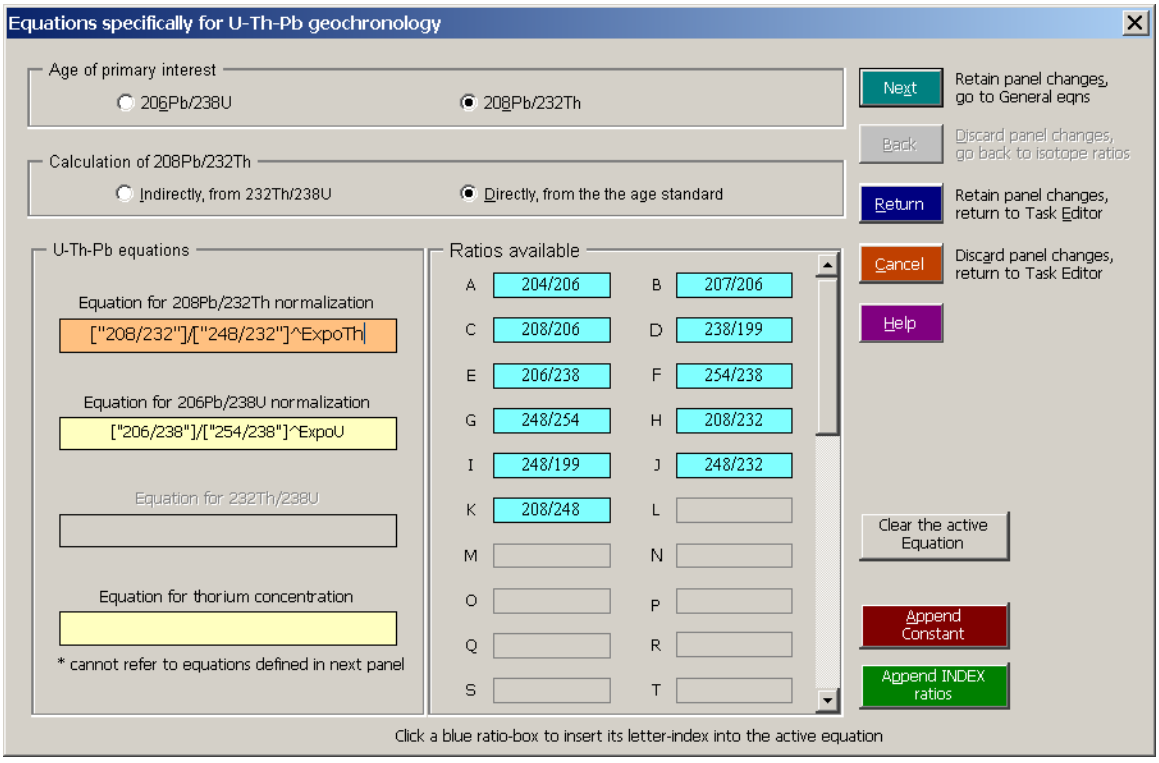
Back

Save any changes to the Isotope Ratios panel, then return to the main *Task* Editor panel.

Cancel

Discard any changes to the Isotope Ratios panel and return to the main *Task* Editor panel.

U-Pb Special Equations



AGE OF PRIMARY INTEREST

206Pb/238U

Use $^{206}Pb/^{238}U$ ages for normalization to the age standard.

208Pb/232Th

Use $^{208}Pb/^{232}Th$ ages for normalization to the age standard.

CALCULATION OF 208PB/232TH

Indirectly, from $^{232}Th/^{238}U$

Determine $^{208}Pb/^{232}Th$ ratios by multiplying the calculated (age-standard normalized) $^{206}Pb/^{238}U$ by the measured $^{208}Pb/^{206}Pb$ and the $^{232}Th/^{238}U$ calculated from the defined $^{232}Th/^{238}U$ equation.

Directly, from the age standard

Determine $^{208}Pb/^{232}Th$ ratios in the same way as the $^{206}Pb/^{238}U$ ratios (by normalizing the results of the $^{208}Pb/^{232}Th$ equation to that of the age standard).

Equation for 206Pb/238Uconst.

An expression derived from the measured isotope ratios that is (ideally) constant for a given $^{206}Pb/^{238}U$.

Equation for 208Pb/232Th const.

An expression derived from the measured isotope ratios that is (ideally) constant for a given $^{208}Pb/^{232}Th$.

232Th/238U equation

An expression derived from the measured isotope ratios that yields the true $^{232}Th/^{238}U$.

Equation for ppm U

An expression derived from the measured isotope ratios that is (ideally) constant for a given uranium concentration.

Next

Save any changes to the U-Pb equations panel, then go to the next panel (equations).

Back

Save any changes to the U-Pb equations panel, then go back to the previous (Isotope Ratios) panel.

Return

Save any changes to the U-Pb equations panel, then return to the main *Task* Editor panel.

Cancel

Discard any changes to the U-Pb equations panel and return to the main *Task* Editor panel.

Help

Display detailed information about *Task* Equations and Switches.

Append constant

Select (and/or edit) a constant from the dropdown list of defined User Constants and append to the active equation.

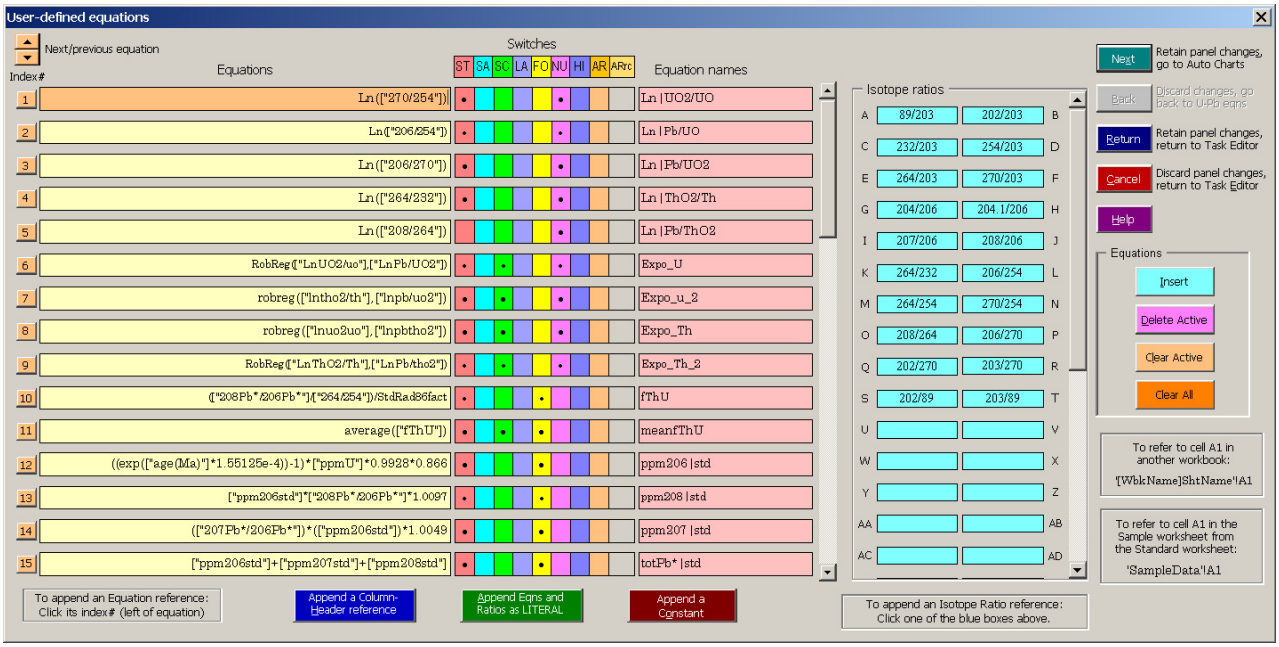
Append LITERAL ratios

When an isotope-ratio box is clicked, append the literal ratio to the active equation rather than its number.

Append INDEX of ratios

When an isotope-ratio box is clicked, append its index letter to the active equation rather than the literal ratio.

General Equations



Next/previous equation (spinner)

Click on one of the spinner arrows to move the active equation up or down.

ST, SA, SC, LA, FO, NU, HI, AR

Sets/clears the Standard, Sample, SingleCell, Last, Formula, Numeric, Hidden, or Array formula switches.

AR #rows #cols

If the AR switch is set, enter the number of rows and columns of the formula output, separated by a space.

Constants

Click to invoke the user-defined constants dropdown.

Append column-header reference

Click to invoke the column-headers dropdown.

Append LITERAL equations/ratios

Click to append the equation name (rather than its index#) and literal isotope-ratio (rather than its index letter) when an equation-number or isotope-ratio box is clicked.

Next

Save any changes to the Equations panel, then go to the next panel (Auto charts).

Back

Save any changes to the Equations panel, then go back to the previous (U-Pb equations or Isotope Ratios) panel.

Return

Save any changes to the Equations panel, then return to the main *Task* Editor panel.

Cancel

Discard any changes to the Equations panel and return to the main *Task* Editor panel.

Delete (active equation)

Delete the active equation and shift all higher-number equations down.

Insert (active equation)

Insert a blank equation box before the active equation.

Clear Active

Clear the active equation.

Clear All

Clear all equations.

Help

Display detailed information about *Task* Equations and Switches. Auto Charts

Column headers

Select the column headers of the *x* and *y* parameters to chart. The *x* parameter is not needed if a Y-mean calculation is specified.

Axis scaling

Autoscale

Let *SQUID* determine the bounds and tick intervals of the specified axis.

Starts at 0

Set the lower bounds of the specified axis at zero (*SQUID* determines the upper bound).

Log

Use logarithmic scaling for the specified axis.

Calculations

X-Y REGRESSION

Determine and plot an outlier-resistant best-fit line to the data.

None
Don't perform any calculations.

Y mean
Calculate and plot the outlier-resistant mean of the *y* values and make *hours* the *x* axis.

Back

Save any changes to the Auto Charts panel, then go back to the previous (Equations) panel.

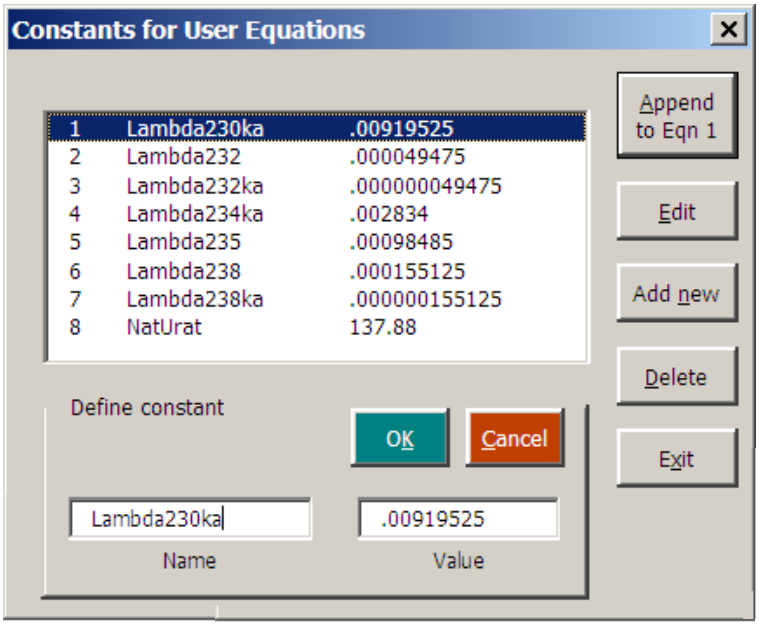
Return

Save any changes to the Auto Charts panel, then return to the main *Task* Editor panel.

Cancel

Discard any changes to the Auto Charts panel and return to the main *Task* Editor panel.

Constants



Edit

Change the name and/or value of the selected constant.

Add new

Add a new constant.

Delete

Delete the selected constant.

Exit

Close the Constants panel.

Append to Eqn 1

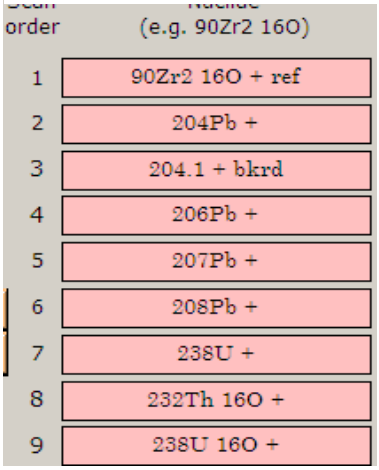
Place the constant at the end of the active equation .

Example Tasks

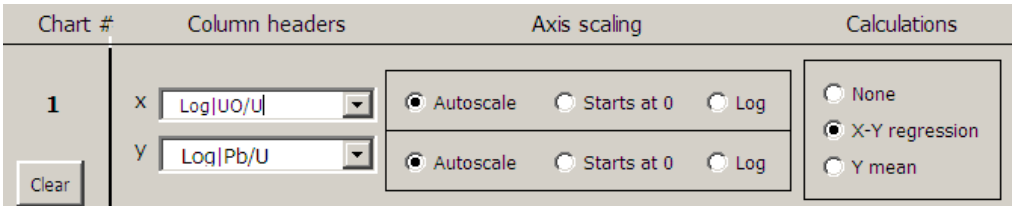
Zircon

CANONICAL ANU, 9 PEAKS

Run Table



Task Equations

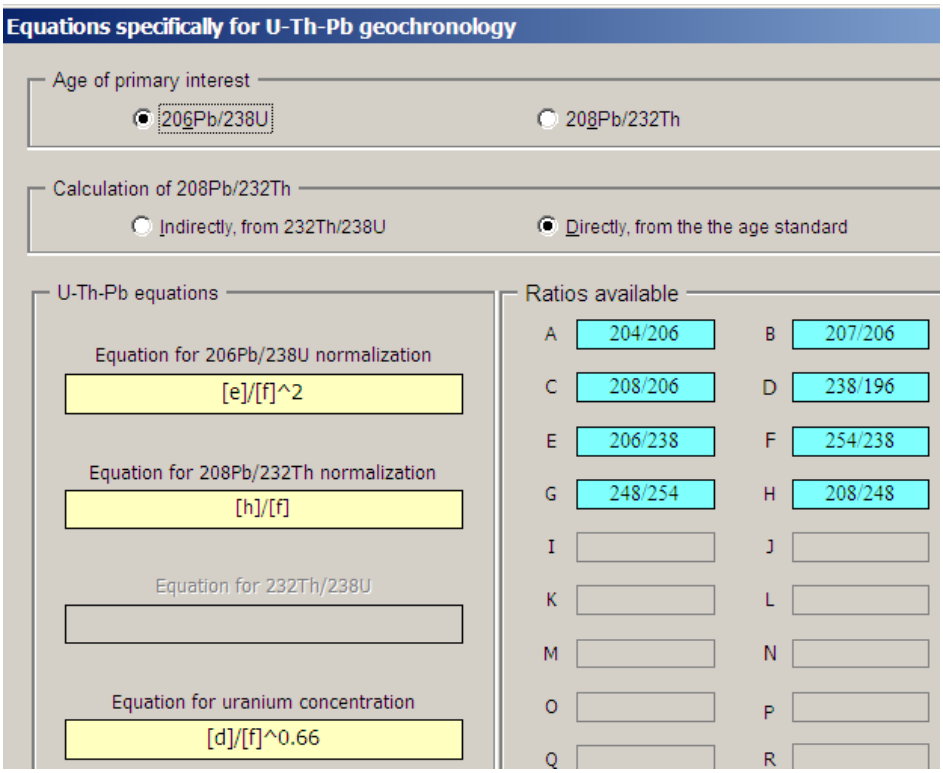


Auto Charts

`

ZIRCON U-PB WITH DIRECT PB/TH

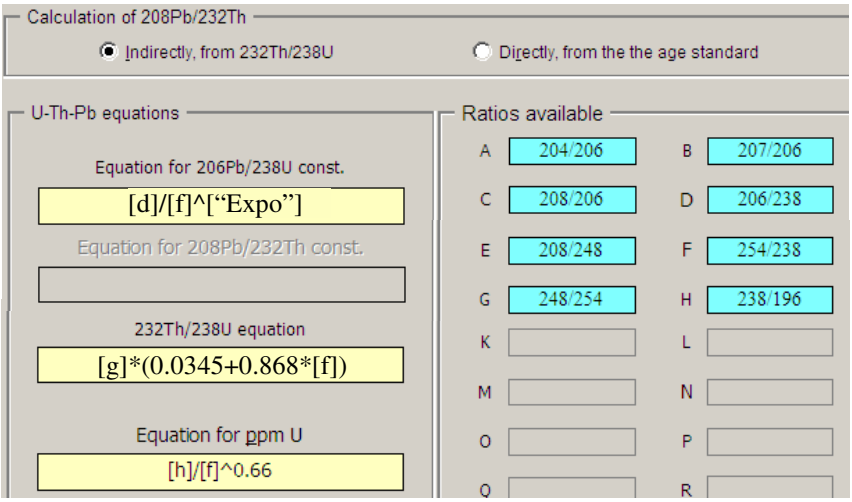
(other panels as Canonical Zircon U-Pb)

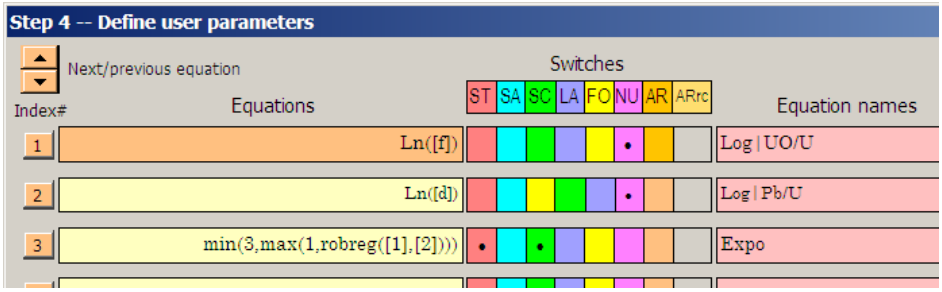


Isotope Ratios and Special U-Pb Equations

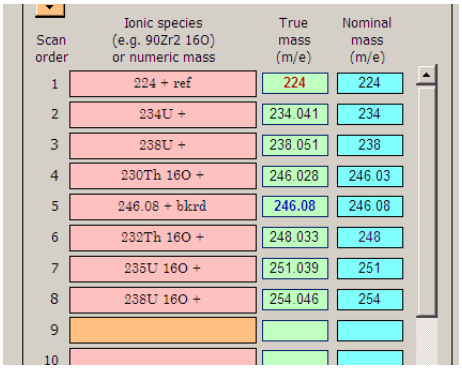
ZIRCON WITH "FLOATING SLOPE"

(other panels as Canonical Zircon U-Pb)

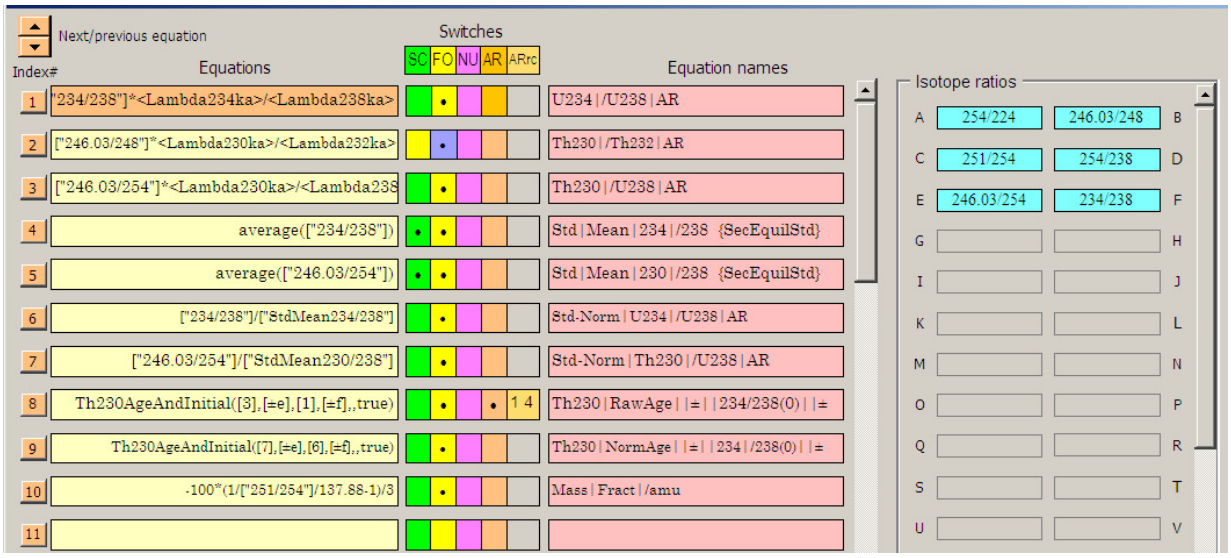




^{230}Th ages, insignificant ^{232}Th



Scan order	Ionic species (e.g. 90Zr2 16O) or numeric mass	True mass (m/e)	Nominal mass (m/e)
1	224 + ref	224	224
2	234U +	234.041	234
3	238U +	238.051	238
4	230Th 16O +	246.028	246.03
5	246.08 + bkrd	246.08	246.08
6	232Th 16O +	248.033	248
7	235U 16O +	251.039	251
8	238U 16O +	254.046	254
9			
10			



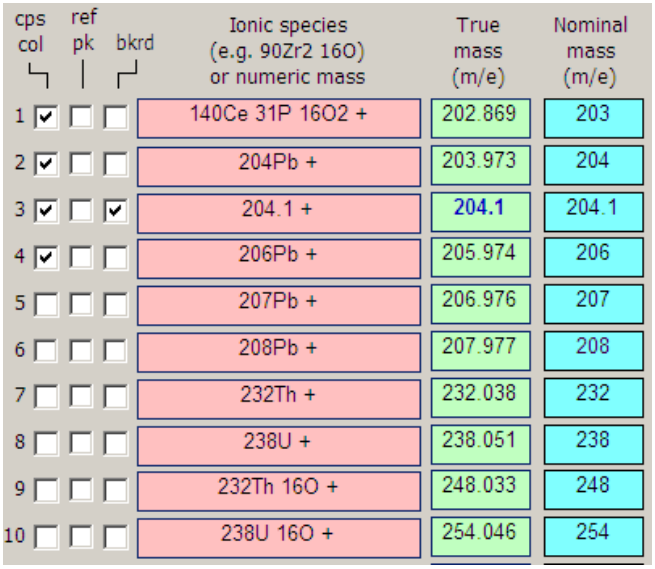
Next/previous equation

Index#	Equations	SC	FO	NU	AR	ARrc	Equation names
1	"234/238"]*<Lambda234ka>/<Lambda238ka>		•				U234 | /U238 | AR
2	["246.03/248"]*<Lambda230ka>/<Lambda232ka>		•				Th230 | /Th232 | AR
3	["246.03/254"]*<Lambda230ka>/<Lambda238		•				Th230 | /U238 | AR
4	average(["234/238"])	•	•				Std | Mean | 234 | /238 {SecEquilStd}
5	average(["246.03/254"])	•	•				Std | Mean | 230 | /238 {SecEquilStd}
6	["234/238"]/["StdMean234/238"]		•				Std-Norm | U234 | /U238 | AR
7	["246.03/254"]/["StdMean230/238"]		•				Std-Norm | Th230 | /U238 | AR
8	Th230AgeAndInitial([3],[=e],[1],[=f],,true)		•		•	1 4	Th230 | RawAge | |=| |234/238(0)| |=
9	Th230AgeAndInitial([7],[=e],[6],[=f],,true)		•				Th230 | NormAge | |=| |234| /238(0)| |=
10	-100*(1/["251/254"]/137.88-1)/3		•				Mass | Fract | /amu
11							

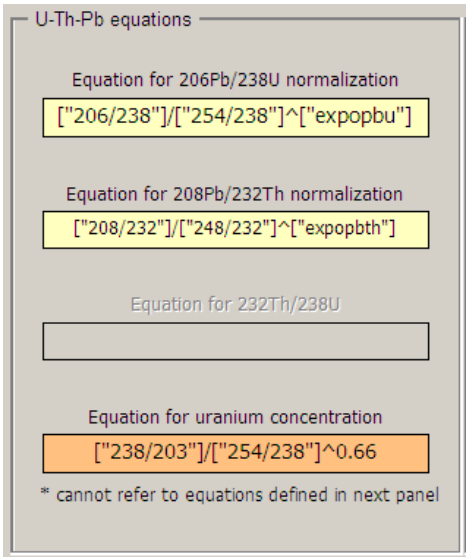
Isotope ratios

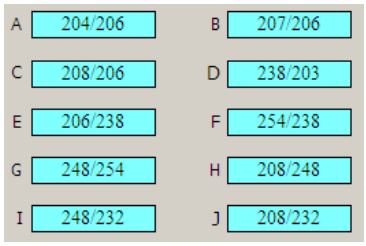
A	254/224	246.03/248	B
C	251/254	254/238	D
E	246.03/254	234/238	F
G			H
I			J
K			L
M			N
O			P
Q			R
S			T
U			V

Simple Monazite

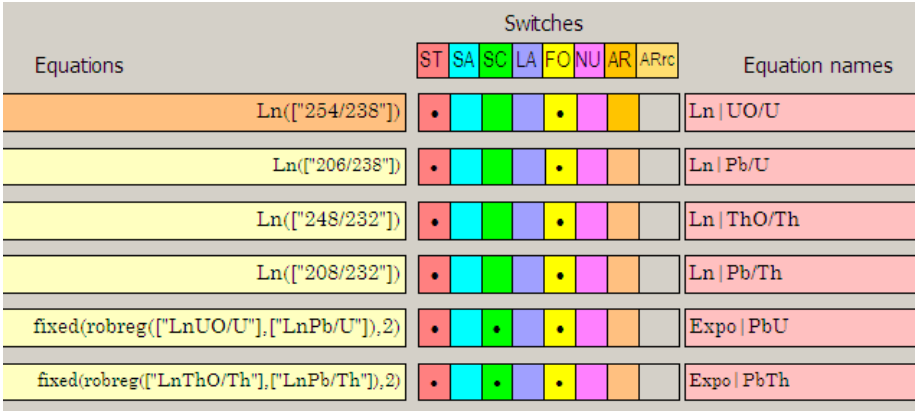


cps col	ref pk	bkrd	Ionic species (e.g. 90Zr2 16O) or numeric mass	True mass (m/e)	Nominal mass (m/e)
1	☑	☐	140Ce 31P 16O2 +	202.869	203
2	☑	☐	204Pb +	203.973	204
3	☑	☑	204.1 +	204.1	204.1
4	☑	☐	206Pb +	205.974	206
5	☐	☐	207Pb +	206.976	207
6	☐	☐	208Pb +	207.977	208
7	☐	☐	232Th +	232.038	232
8	☐	☐	238U +	238.051	238
9	☐	☐	232Th 16O +	248.033	248
10	☐	☐	238U 16O +	254.046	254





A	204/206	B	207/206
C	208/206	D	238/203
E	206/238	F	254/238
G	248/254	H	208/248
I	248/232	J	208/232



Equations	ST	SA	SC	LA	FO	NU	AR	ARrc	Equation names
Ln(["254/238"])	•				•				Ln | UO/U
Ln(["206/238"])	•				•				Ln | Pb/U
Ln(["248/232"])	•				•				Ln | ThO/Th
Ln(["208/232"])	•				•				Ln | Pb/Th
fixed(robreg(["LnUO/U"],["LnPb/U"]),2)	•		•		•				Expo | PbU
fixed(robreg(["LnThO/Th"],["LnPb/Th"]),2)	•		•		•				Expo | PbTh

Appendix IV: Weighted Average Algorithm for U/Pb Age Standards

- Reject points whose difference (R_i) between the internal error and median internal error is greater than $5 \times Nmad$, where

$$Nmad = 1.4826\left(1+\frac{5}{N-2}\right)\sqrt{\text{Median}(R)}$$

and N is the number of Age Standard spots.

- Calculate the weighted average of the remaining points in the usual way (weighted by internal errors only), e.g.

$$\bar{x} = \frac{\sum\left(x_i \Big/ {}^{int}\sigma_{x_i}\right)^2}{\sum 1 \Big/ {}^{int}\sigma_{x_i}^2} \;,\quad \sigma_{\bar{x}} = \sqrt{1 \Big/ \sum \frac{1}{{}^{int}\sigma_{x_i}^2}} \;,$$

where ${}^{int}\sigma_{x_i}$ is the "internal" error of the spot calibration constant.

-

- If the probability-of-fit of the above weighted average is less than 0.05 (as calculated from the χ^2 distribution of the *MSWD* about *N*-2), calculate another weighted average, but this time assuming that a constant (but unknown) "external" error also exists for each datapoint. The Maximum Likelihood Estimator of both the mean calibration constant and the "external" error, $\sigma_{ext.}$, are determined by simultaneously solving

- $$\bar{x} = \frac{\sum x_i \left(\sigma_{x_i}^2 + \sigma_{ext.}^2\right)^{-1}}{\sum\left(\sigma_{x_i}^2 + \sigma_{ext.}^2\right)^{-1}} \qquad \text{and} \qquad \sum \frac{\left(x_i - \bar{x}\right)^2}{\left(\sigma_{x_i}^2 + \sigma_{ext.}^2\right)^2} = \sum \frac{1}{\sigma_{x_i}^2 + \sigma_{ext.}^2}$$

Apparent outliers are then rejected if:

The wtd residual of the point is less than *Toler*, where *p* is the number of the rejection "pass", and $E_{\bar{x}}$ is the 95%-conf. error of $\bar{x}$ as determined via (3), above, and

$$Toler = \left(1+\frac{p-1}{4}\right)\sqrt{4\left(\sigma_{int}^2 + \sigma_{ext}^2\right) + E_{\bar{x}}^2} \;,$$

- The number of un-rejected points is no fewer than 85% of the original number, and
- The data point is nonzero.

Steps *3-4* are repeated until no rejections occur. Note that with each "pass" through steps *3-4* the bar for rejection (*Toler*) is raised.

Note that the rejection algorithm is *not at all rigorous*. Its intent is merely to offer the user an example of possible true outliers, and that the user should only accept the results of the above rejection algorithm if he or she would select the same rejections independently, preferably on the basis of objective criteria such as $^{204}Pb/^{206}Pb$, U or Th concentration, *et cetera*.

Appendix V: Some Useful *Excel* and *Isoplot* Functions

Native Excel Functions

AVERAGE

Argument: Values range

Output: The simple average of the numbers.

MEDIAN

Argument: Values range

Output: The median of the numbers.

STDEV

Argument: Values range

Output: The standard deviation of the population. Divide by $\sqrt{n}$ for the standard error of the mean.

LINEST

Arguments: Y-range, X-range [, include stats]

The x- and y-ranges are usually 2 columns of numbers; add the optional *IncludeStats* if slope- and intercept-errors are desired in the output.

Output: Parameters for a simple *y* on *x* linear regression. Typically, from a 1×1 up to 3×2 row/column output-range containing

Slope	Intercept
±slope	±inter
Rho	

where the errors (±) are 1 standard error, and rho is the *x*-*y* correlation coefficient.

INTERCEPT

Arguments: Y-range, X-range

Output: The intercept of a simple *y* on *x* linear regression.

SLOPE

Arguments: Y-range, X-range

Output: The slope of a simple *y* on *x* linear regression.

MAX, MIN

Arguments: Values range

Output: The maximum or minimum value of the range.

sqBiWeight

Arguments: RangeIn, [, Tuning], [, Mean only = False], [, All comers = False]

RangeIn contains the input values in a single column;
Tuning (optional) must be 6 or 9, controls the degree of outlier resistance, 6 being more outlier-resistant than 9;
Mean only (optional) If False (default) returns the mean and standard error in two (1 × 2 row/column) cells; If True, returns the mean only, in one cell.
All comers (optional) If False (default), accepts only non-blank cells with numeric contents without the strikethrough font attribute; if True, accepts all non-blank, numeric cells in the input range.

Output: The Tukey's biweight (Hoaglin *et al*, 1973) outlier-resistant mean. More efficient than the median for distributions that are fundamentally Gaussian. For SHRIMP data, BiWt is almost always preferable to the simple average.

ChiSquare

Arguments: MSWD, Degrees of freedom

MSWD is the mean square of weighted deviates of a weighted mean or regression (see p. 37);
Degrees of freedom the degrees of freedom for the calculation (= *N*-1 for a weighted average, *N*-2 for a linear regression).

Output: The probability of fit (probability that the specified *MSWD* or greater will occur for the specified degrees of freedom).

Concordia

Arguments: $^{207}Pb/^{235}U$, $^{207}Pb/^{235}U$ err, $^{206}Pb/^{238}U$, $^{206}Pb/^{238}U$ err [,$^{207}Pb/^{235}U$ - $^{206}Pb/^{238}U$ err. corr.] [, with decay-const errs = False] [, %errors = False] [, σ-level of errors]

Output: The *Concordia Age* (Ludwig, 1998) for the specified U/Pb ratios and errors.

ConcordiaTW

Arguments: $^{238}U/^{206}Pb$, $^{238}U/^{206}Pb$ err, $^{207}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ error [, $^{238}U/^{206}Pb$ - $^{207}Pb/^{206}Pb$ err. corr.]

Output: The *Concordia Age* (Ludwig, 1998) for the specified U/Pb ratios and errors.

DisEq68Age

Arguments: $^{206}Pb/^{238}U$, initial $^{234}U/^{238}U$ activity ratio, initial $^{230}Th/^{238}U$ activity ratio

Output: The corresponding $^{206}Pb/^{238}U$ age.

DisEq68Ratio

Arguments: Age (ma), initial $^{234}U/^{238}U$ activity ratio, initial $^{230}Th/^{238}U$ activity ratio

Output: The corresponding $^{206}Pb/^{238}U$ ratio.

DisEq75Age

Arguments: $^{207}Pb/^{235}U$, initial $^{231}Pa/^{235}U$ activity ratio

Output: The corresponding $^{207}Pb/^{235}U$ age.

DisEq75Ratio

Arguments: Age (ma), $^{207}Pb/^{235}U$, initial $^{231}Pa/^{235}U$ activity ratio

Output: The corresponding $^{207}Pb/^{235}U$ ratio.

DisEq76Ratio

Arguments: Age (ma), initial $^{234}U/^{238}U$ activity ratio, initial $^{230}Th/^{238}U$ activity ratio, initial $^{231}Pa/^{235}U$ activity ratio

Output: The corresponding $^{207}Pb/^{206}Pb$ ratio.

DisEqPbPbAge

Arguments: $^{207}Pb/^{206}Pb$ ratio , initial $^{234}U/^{238}U$ activity ratio, initial $^{230}Th/^{238}U$ activity ratio, initial $^{231}Pa/^{235}U$ activity ratio.

Output: The corresponding $^{207}Pb/^{235}U$ age.

Drnd

Arguments: Number The number to be rounded;
SigFigs The number of significant figures to return.

Output: The number rounded to the specified number of significant figures

ExternalSigma

Arguments: ValuesAndErrors (2-column range), [PercentErrs = False], [SigmaLevel = 1]

Output: The external 1-sigma error required to account for the presence of extra scatter (that is, not accounted for by the assigned errors) of the Values.

HalfLife

Arguments: IntegralNuclideMass [, InMyr]

Output: The half life of the nuclide in years (default) or millions of years.

InitU234U238

Arguments: Age (Ka), meas. $^{234}U/^{238}U$ activity ratio

Output: The corresponding initial $^{234}U/^{238}U$ activity ratio.

La230, La232, La234, La235, La238

Arguments: None

Output: The decay constant, in years^{-1}, of ^{230}Th, ^{232}Th, ^{234}U, ^{235}U, or ^{238}U, respectively

Lambda

Argument: Integral nuclide mass

Output: The decay constant, in years^{-1}, of the indicated nuclide.

Log10

Argument: Value

Output: The corresponding base-10 logarithm.

Mad

Argument: Numeric range

Output: The median absolute deviation from the median of the range.

MSWD

Arguments: ValuesAndErrors (2-column range), [PercentErrs = False], [SigmaLevel = 1]

Output: The *MSWD* (mean square of weighted deviates) parameter for the weighted average of ValuesAndErrors.

NukeMass

Arguments: Nuclide [, significant figures]

Output: Mass of the nuclide (^{12}C=12.000)

Pb76

Argument: Age (ma)

Output: The radiogenic $^{207}Pb/^{206}Pb$ for that age

ProbFit

Arguments: ValuesAndErrors (range), [PercentErrs = False], [SigmaLevel = 1]

Output: The probability that the assigned errors will yield at least the amount of observed scatter of the Values.

RobReg

Arguments: x-range, y-range [, with y-intercept = False] [, include errors = False]

Output: The results of a robust (resistant) linear regression of a suite of *x*-*y* points as a 1×2 to 1×4 cell range containing the line's Slope, (optional) Slope error (95%-conf.), (optional) Y-intercept, (optional) Y-intercept error. Output of the optional parameters depends on the values of *with y-intercept* and *include errors*.

SingleStagePbT

Arguments: $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$

Output: The Stacey-Kramers single-stage Pb-growth curve age corresponding to the input values

SingleStagePbR

Arguments: Age (Ma), Which ratio

Output: The Stacey-Kramers single-stage Pb-growth curve isotope ratio corresponding to the input values. The isotope ratio returned is $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, or $^{208}Pb/^{204}Pb$ for *Which ratio* = 0, 1, or 2, respectively.

sqWtdAv

Arguments: Values range, Errors range [, PercentErrsIn=False] [, PercentErrsOut=False] [, CanReject=False]

Output: Up to a 7×2 cell range where the first column contains the weighted mean, 1σ (prob. fit >0.05) or 68.3%-confidence (prob. fit <=0.05) error in the weighted mean, external error for the data points (if prob. fit <=0.05), probability of fit, number of data-points rejected, index-numbers of rejected data-points (if non-zero). The second column contains explanatory labels for the values in the first column.

StudentsT

Arguments: Degrees of freedom [, confidence limit = 95]

Output: The Students's-*t* value for the specified (or default) confidence limit.

Th230Age

Arguments: $^{230}Th^{238}U$ activity ratio, $^{234}U/^{238}U$ activity ratio

Output: The $^{230}Th/U$ age (Ka) for the specified activity ratios.

Th230AgeAndInitial

Arguments: $^{230}Th^{238}U$, $^{230}Th/^{238}U$ err, $^{234}U/^{238}U$, $^{234}U/^{238}U$ err [, $^{230}Th/^{238}U$ -$^{234}U/^{238}U$ err-correl] [, errors as %] [, σ-level] [, with decay-const errs,] [as atomic ratios])

Output: A 1×5 cell range containing the $^{230}Th/U$ age (Ka), age error, initial $^{234}U/^{238}U$ activity ratio, error in $(^{234}U/^{238}U)_0$, error correlation between age and initial ratio.

Th230U238AR

Arguments: Age (ka), initial $^{234}U/^{238}U$ activity ratio

Output: The $^{230}Th/^{238}U$ activity ratio for the specified age and initial ($^{234}U/^{238}U$).

ThUfromPb86

Arguments: Age (ma), meas. $^{208}Pb/^{206}Pb$, meas. $^{206}Pb/^{204}Pb$, initial $^{206}Pb/^{204}Pb$, initial $^{208}Pb/^{204}Pb$

Output: The $^{232}Th/^{238}U$ corresponding to the input ratios, calculated assuming that the system's $^{206}Pb/^{238}U$ and $^{208}Pb/^{232}Th$ ages are concordant.

U234age

Arguments: Present-day $^{234}U/^{238}U$ activity ratio , Initial $^{234}U/^{238}U$ activity ratio

Output: The $^{234}U/^{238}U$ age, in Ka, for the input ratios

U234ageAndErr

Arguments: $^{234}U/^{238}U$ activity ratio, $^{234}U/^{238}U$ err, Initial $^{234}U/^{238}U$ activity ratio, error [, as %errors]

Output: The $^{234}U/^{238}U$ age (Ka) and error, in a 1×2 cell-range.

U234U238AR

Arguments: Age (ka), initial $^{234}U/^{238}U$ activity ratio

Output: The present-day $^{234}U/^{238}U$ activity ratio

YorkInter

Arguments: xyValues&Errors range [, errors in as %] [, σ-level]

Output: The *Y*-intercept of a 2-error linear regression. The *xyValues&Errors range* must comprise a 4- or 5-column range, where the columns contain *x*, *x*-error, *y*, *y*-error, *x*-*y* error correlation (the last column is optional, and assumed to be zero if missing).

YorkInterErr95

Arguments: xyValues&Errors range [, errors in as %] [, σ-level]

Output: The 95%-conf. *Y*-intercept of a 2-error linear regression. The *xyValues&Errors range* must comprise a 4- or 5-column range, where the columns contain *x*, *x*-error, *y*, *y*-error, *x*-*y* error correlation (the last column is optional, and assumed to be zero if missing).

YorkMSWD

Arguments: xyValues&Errors range [, errors in as %] [, σ-level]

Output: The *MSWD* of a 2-error linear regression. The *xyValues&Errors range* must comprise a 4- or 5-column range, where the columns contain *x*, *x*-error, *y*, *y*-error, *x*-*y* error correlation (the last column is optional, and assumed to be zero if missing).

YorkProb

Arguments: xyValues&Errors range [, errors in as %] [, σ-level]

Output: The probability of fit of a 2-error linear regression. The *xyValues&Errors range* must comprise a 4- or 5-column range, where the columns contain *x*, *x*-error, *y*, *y*-error, *x*-*y* error correlation (the last column is optional, and assumed to be zero if missing).

YorkSlope

Arguments: xyValues&Errors range [, errors in as %] [, σ-level]

Output: The slope of a 2-error linear regression. The *xyValues&Errors range* must comprise a 4- or 5-column range, where the columns contain *x*, *x*-error, *y*, *y*-error, *x*-*y* error correlation (the last column is optional, and assumed to be zero if missing).

YorkSlopeErr95

Arguments: xyValues&Errors range [, errors in as %] [, σ-level]

Output: The 95%-conf. slope-error of a 2-error linear regression. The *xyValues&Errors range* must comprise a 4- or 5-column range, where the columns contain *x*, *x*-error, *y*, *y*-error, *x*-*y* error correlation (the last column is optional, and assumed to be zero if missing).

Appendix VI: Useful *Isoplot* Tools for *SQUID*

- Concordia plots
- *X*-*Y* plots
- Cumulative Gaussian plots
- Histograms
- Linearized Gaussian plots
- Multicomponent deconvolution (Sambridge & Compston's *MIX*)
- Weighted averages, Tukey's Biweight means, Medians
- (^{230}Th/^{238}U) – (^{234}U/^{238}U) plots, including evolution curves and isochrons.
- Ages of stacked beds (Bayesian constraints).
- Youngest detrital zircon

Appendix VII: Definitions of Terms

204 corrected

The amount of common Pb to subtract is calculated assuming the isotope ratios assigned in Preferences, using 204 as the index isotope.

207 corrected

The true $^{206}Pb/^{204}Pb$ is calculated by assuming that the true radiogenic-Pb isotope ratios yield concordant $^{206}Pb/^{238}U$ – $^{207}Pb/^{235}U$ ages, determining the $^{206}Pb/^{204}Pb$ that produces this result, then subtracting common-Pb using 204 as the index isotope and the isotope ratios assigned in Preferences.

208 corrected

The true $^{206}Pb/^{204}Pb$ is calculated by assuming that the true radiogenic-Pb isotope ratios yield concordant $^{206}Pb/^{238}U$ – $^{208}Pb/^{232}Th$ ages, determining the $^{206}Pb/^{204}Pb$ that produces this result, then subtracting common-Pb using 204 as the index isotope and the isotope ratios assigned in Preferences.

Array function or formula

See p. 25.

Common Pb

For the purposes of *SQUID*, the Pb present at the time the mineral to be dated formed. Also comprises environmental Pb has contaminated the grain.

Concordance

The state of having equivalent $^{206}Pb/^{238}U$ – $^{207}Pb/^{235}U$ – $^{207}Pb/^{206}Pb$ apparent ages.

Concordia

The locus of concordant ages on the $^{206}Pb_{rad}/^{238}U$ – $^{207}Pb_{rad}/^{235}U$ or $^{238}U/^{206}Pb$ – $^{207}Pb/^{206}Pb$ diagram.

Concordia age

The most probable age of a system having a arguably concordant U-Pb ages.

Constants

Constants defined and named by the *SQUID* user and available for use in *Task* equations.

Discordance

The absence of equivalent $^{206}Pb/^{238}U$ – $^{207}Pb/^{235}U$ – $^{207}Pb/^{206}Pb$ apparent ages for a U/Pb system.

Dropdown

An *Excel* or *SQUID* menu of items from which the user can choose.

Error correlation

A statistical measure of how much two parameters covary. An error correlation of 1 implies a precisely proportional straight-line relationship between two parameters, zero implies complete independence of one parameter with the other, -1 implies a precisely proportional negative variation of one parameter with respect to another.

The formula for the error correlation is: $$\frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum (x_i - \bar{x})^2 \sum (y_i - \bar{y})^2}}$$

When referring to errors, the error correlation reflects the likelihood that the error in one parameter's measurement is in the same direction (too high or too low) as that of the other parameter.

External error

A component of measurement error that is constant from sample to sample but not comprised by the assigned analytical error.

Grouping

to be added

Internal error

The analytical error assigned to a measurement.

Ionic species

A particular molecular combination of elements and isotopes with a particular charge.

Isoplot

to be added

m/e

Mass/charge of an ionic species, often loosely substituted by "mass".

MSWD

Mean Square of Weighted Deviates (see p. 37).

Normalizing equation

An equation that yields a constant value when a parameter of interest (Pb/U, [U], …) is constant, so that the ratio of normalizing equations for an unknown sample to a standard equals the ratio of the unknown's parameter value to the standard parameter value.

Panel

A *Excel* dialog box that allows the user to make one or more choices.

PD file

Probability of fit

The probability that the observed weighted-mean or weighted-regression *MSWD* will be exceeded if the assigned data-point errors are entirely responsible for the observed scatter. See p. 37.

Radiogenic Pb

Pb produced *in situ* by the decay of U and Th in a mineral or rock.

Range

A suite of worksheet cells (usually contiguous) in an *Excel* worksheet.

Resistant (mean, regression…)

A mean or regression calculated using an algorithm that is insensitive to outliers in the data.

Robust (mean, regression…)

See above.

Sample sheet

The worksheet containing the reduced SHRIMP data for all spots but the U-Pb age standard, and named "SampleData".

SBM

Stands for Secondary Beam Monitor, a collector that measures the secondary ion beam at a point in the flight tube and ion optics such that, in favorable cases, essentially the entire secondary ion beam is meas..

Scan order

The order of a mass station in the peak-jump (mass-jump) sequence of a SHRIMP analysis.

Single cell formula

A *Task* equation that operates on a columnar range of data, whose output occupies a single cell, rather than a data column.

Spot

A single spot on a mineral grain, used for one SHRIMP analysis and assigned a unique name as part of the analysis.

Stacey-Kramers

Refers to the single-stage Pb isotope growth curve presented by Stacey and Kramers (1975). Predicts the average crustal Pb-isotope ratios at a specified age.

Standard sheet

The worksheet containing the reduced SHRIMP data for the U-Pb age standard, and named "StandardData".

Trim mass reference

The mass station to be used as a reference when constructing charts for the trim masses used for each spot.

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Index

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