Appendix B

Python programs for data reduction

B.1 Advantages of *Python* for MC-ICP-MS data reduction

Isotopic data collection using MC-ICP-MS entails significant data reduction. The Neptune Plus and Neptune MC-ICP-MS used in the University of Minnesota (UMN) Isotope Lab export run data as DAT, EXP, and TDT files. The data files contain beam counts per cycle of major isotopes and isotopic ratio, collected on either SEM or cups depending on method used. Current protocol involves reducing EXP run data via a series of Excel spreadsheets, most of which contain Excel Macros programs for data filtration. Excel spreadsheets must be customized for your sample information, machine parameters, and spike used. Data import consists of copy-pasting EXP run data into the Excel spreadsheet body, increasing data reduction time. Additionally, Macros programs need to be in an Excel Macro-Enabled Workbook (.xlsm) file, or linked to a working .xlsm file.

The complexities of working with data reduction spreadsheets in the UMN Isotope Lab has led to error introduction and a lack of process monitoring. The UMN Isotope Lab receives over 20 scientific visitors each year, who complete sample preparation, chemistry procedures, and machine analysis on their own after limited staff instruction. Often Excel spreadsheets are used by visitors with little knowledge regarding the process of data reduction, which can lead to errors importing data and changing spreadsheet parameters. Additionally, visitors often run a large amount of samples in a limited amount of time. The use of Excel spreadsheets not only increases reduction time but requires personal data management tactics to keep track of spreadsheets during and after data reduction.

Furthermore, a new method of using Faraday cups to measure high intensity beams at low counting errors has been developed for the UMN Isotope Lab (Pythoud et al. *in prep*).

This method greatly reduces machine run time, but involves a new set of Excel spreadsheets for data reduction. Teaching visitors not only this new machine method, but this new data reduction procedure, impinges upon limited Isotope Lab staff time.

The lab's current system for data reduction via Excel spreadsheets has not been monitored. Visitors often receive access to spreadsheets through a staff member, who may or may not have the most current or applicable version. This may lead to continuation or propagation of errors, and could result in the publication of inaccurate data processed at the UMN Isotope Lab.

In order to consolidate and validate data reduction methods for the UMN Isotope Lab, we transformed all ^{230}Th dating functions into user-friendly *Python* programs. *Python* is an object-oriented, high-level programming language developed in the early 1990s. This interpreted language was created with an emphasis on readability, and thus is ideal for a lab environment where source code data processing functions may need to be periodically edited. Stand alone data reduction programs have been developed for analyzing data on either the SEM or Faraday cups. SEM measurements include reagent blanks, chemistry blanks, SEM spiked standards and samples. Cups measurements include cups unspiked and spiked standards and samples. All programs use a *Tkinter* graphical user interface (GUI) for data upload, completely separating the user from the program scripts. Programs can be run either as *Python* files or system-specific executable files, and are available via GitHub repositories at https://github.com/junissen.

This chapter will discuss the processes involved in data reduction and how each Python program functions. We believe these programs significantly improve work flow for users and quality control of lab results. Further work involves converting ^{230}Th- ^{231}Pa data reduction methods into Python programs, thus retiring all Excel spreadsheets used by the UMN Isotope Lab.

B.2 Reagent Blank Calculation

Blanks are periodically run by lab individuals to ensure minimal contamination is coming from chemistry reagents. These are most important when reagents are refilled or lab equipment is cleaned. Reagents blanks can either be separated to test each individual reagent, or combined to test reagents as a whole. All reagent blanks consist of combining a typical amount of each reagent used in a chemistry batch, drying down with nitric acid, and diluting with water, 1% nitric acid, and a minimal amount of hydrofluoric acid. This sample is then run on the MC-ICP-MS using the SEM configuration on the background method.

Calculating reagent blanks is the simplest data reduction done in the UMN Isotope Lab. The signal measured while the sampler is in wash solution is subtracted from the total signal measured while the sample is in the reagent blank. This provides the reagent blank signal in counts per second (cps). The signal in cps is then converted into a reagent blank weight using the total solution weight, ionization efficiency, and uptake rate. Blanks are measured on the ag (10^{-18}g) and fg (10^{-15}g) level.

Current methods for reducing reagent blanks involve a single Excel spreadsheet with tabs for the wash signal, total signal, and data reduction. Wash measurements and signal measurements for both U and Th must be copied and pasted from EXP data files. To streamline this process, the *Python* program uploads each file needed and reduces the data internally, exporting an Excel table with reagent blank weights after calculation is complete.

To begin, a GUI is generated and prompts the user for data input. The user must input the blank name, solution weight, uptake rate (mg/sec), ionization efficiency (%) and include an export file name for the resulting Excel table. The file type (.xlsx) must be included as a part of the file name. The user then has the option of altering their Th method. During a method run on the MC-ICP-MS, it is possible to continue running after the solution is spent, resulting in a sharp spike followed by a decay of the ion beam. An example of this is shown in Figure B.1. Additionally, peak spikes can occur on occasion during the sample run. For this reason, it is possible for the user to edit the data file to delete anomalies, save as a .xlsx file, and upload into the program.

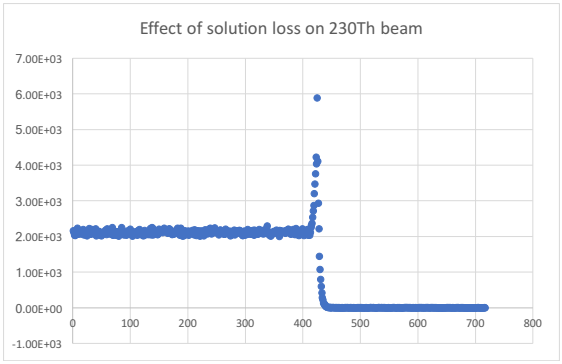


Figure B.1: Example of the effect of solution loss on ^{230}Th ion beam. The solution is completely used up by ≈400 cycles, resulting in a sharp spike and decay of ion beam intensity.

To correct for this with minimal effort, the program allows you to specify the last cycle number you would like analyzed. The program will then only reduce the specified cycles. The user is also given this option for the U method. An example of the GUI windows which result from choosing to alter or not to alter methods are show in Figure B.2.

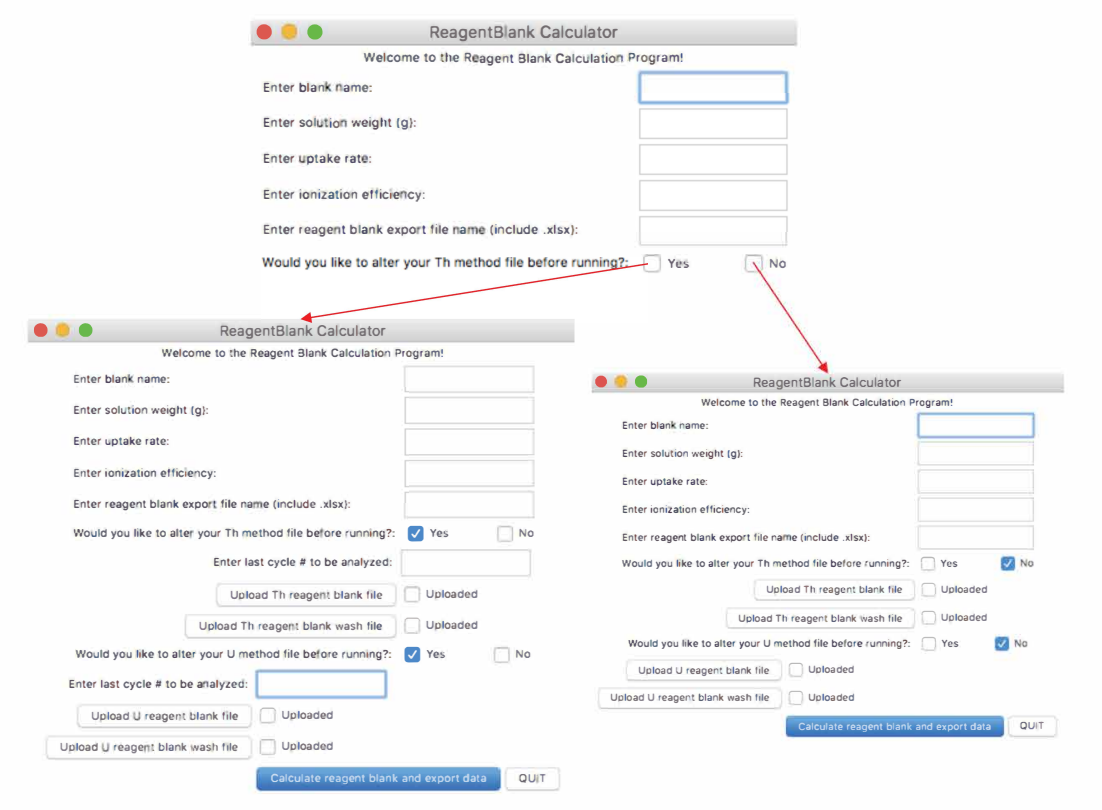


Figure B.2: Example of GUI windows for altering or not altering reagent blanks

The user can upload the wash and method files by clicking on the "Upload" button and choosing the file via a drop-down directory. Once the file has been chosen, the uploaded button will show a check mark. Once all the files have been uploaded, the user clicks on "Calculate reagent blank and export data" to begin the program. An example of the complete program with data input is shown in Figure B.3.

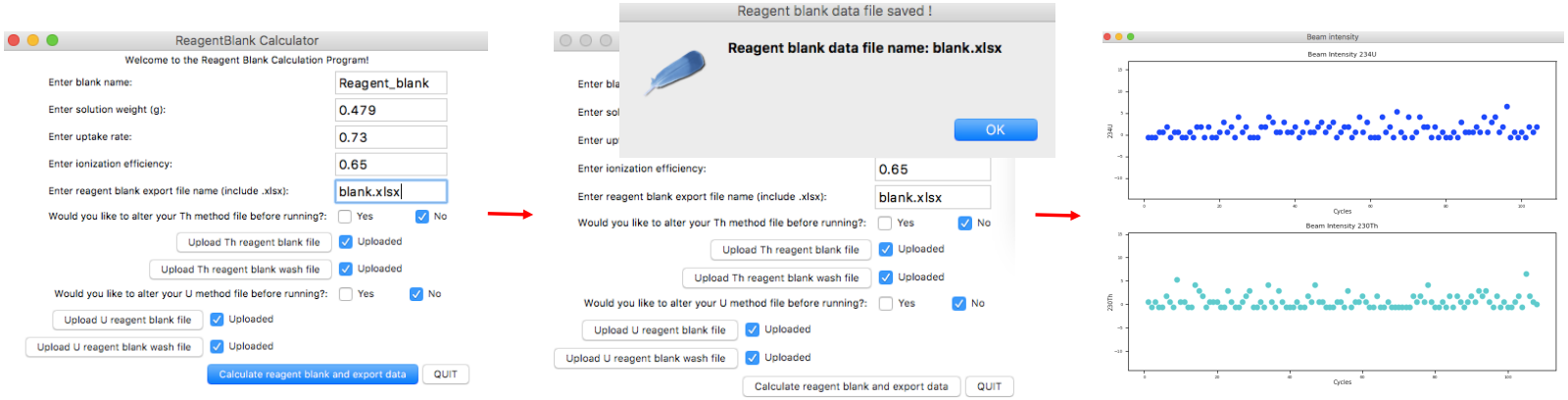


Figure B.3: Example of steps for reagent blank calculation using program

The program results in an Excel spreadsheet export under the filename chosen, and plots the ^{234}U and ^{230}Th beam to ensure beam stability. The Excel export is located in the same directory as the *Python* programs. Figures B.4 and B.5 show the results of the *Python* reagent blank program and the traditional Excel data reduction method. Figure B.4 shows the formatting of the program's Excel export.

	1_Reagent_blank	229Th	230Th	232Th	233U	234U	235U	236U	238U
1_fileinfo	Reagent_blank								
2_regblank		11.95735	3.55648	17.66556	150.8113	17.46626	2.464434	139.965	360.7554
3_2s err		74.6386	17.89997	10.64751	99.52776	21.03001	0.94897	73.97839	59.98159
4_units		ag	ag	fg	ag	ag	fg	ag	fg
5_param	Run info	Sln wt	U.R.	I.E					
6_param		0.479	0.73	0.65					
7_param		g	mg/sec	%					

Figure B.4: Results of *Python* reagent blank data reduction

Reagent blank for all reagents calculated by Excel

	229Th	230Th	232Th	233U	234U	235U	236U	238U
Reagent blank weight	11.96	3.56	17.67	150.81	17.47	2.46	139.96	360.76
2σ Abs. error	± 74.64	± 17.90	± 10.65	± 99.53	± 21.03	± 0.95	± 73.98	± 59.98
	ag	ag	fg	ag	ag	fg	ag	fg

Figure B.5: Results of Excel reagent blank data reduction

Reagent blank data reduction provides the same results for the *Python* program as the traditional Excel spreadsheet, with minimal effort. The Excel spreadsheet created by the program can then be stored for later reference if needed. The *Python* Reagent Blank Calculation is the simplest of the *Python* programs created for the UMN Isotope lab, and contains 745 lines of code and documentation. At 25 lines of code per page, this is approximately 30 pages.

B.3 Chemistry Blank Calculation

Chemistry blanks are run with each sample batch to determine the amount of contamination that may have occurred during chemistry procedures. These blanks are minimally spiked (< 2μg) and run identically to samples with the same amount of reagents. U and Th fractions are run as blank methods on the SEM, after ensuring backgrounds are low enough to run. Signal isotopic ratios of the measured isotope versus spike isotope are calculated by subtracting the machine wash values from the total signal. The ratios must then be corrected for isotopic fractionation that occurs in the sample during ionization by the plasma source. The ion beam is originally disproportionately enriched in light isotopes, and only with time does the ratio of light to heavy isotopes decrease. The amount of mass fractionation occurring can be determined by comparing the known spike $\frac{236}{233}$ ratio and the measured $\frac{236}{233}$ ratio. These should be equal, and any deviation is a result of mass fractionation.

As the amount of fractionation occurring is dependent upon isotope mass, we can correct for fractionation at other masses. The exponential law provides the most accurate correction, and is show in Equation B.1 below, using the $\frac{230}{229}$ ratio as an example. The variables in the exponent are atomic masses of isotopes.

$$\frac{230}{229}_{(corrected)} = \frac{230}{229}_{(measured)} * \left(\frac{spike\frac{236}{233}}{signal\frac{236}{233}}\right)^{\frac{ln\frac{230}{229}}{ln\frac{236}{233}}} \tag{B.1}$$

The blank isotopic ratios are finalized by subtracting the spike isotopic ratios from the resulting fractionation corrected ratios, and converted into chemistry blank weights using the atomic weight and amount of spike isotope in the blank. Chemistry blanks for the UMN Isotope Lab are ideally under 20 ag ^{230}Th, 500 fg ^{232}Th, 60 ag ^{234}U, 5 fg ^{235}U and 500 fg ^{238}U, but are typically significantly higher due to reagent contamination or contamination during chemistry.

Current data reduction for chemistry blanks involves an Excel spreadsheet that must be customized for spike used and raw data must be copied and pasted into the spreadsheet. The *Python* data reduction program for chemistry blank uses a GUI and begins with a prompt for changing spike concentration. Over time, evaporation can occur as spike bottles are opened and spike dispensed, resulting in a change in absolute spike concentrations. Lab users must monitor spike evaporation with time, and recalculate absolute spike concentrations in pmol/g. Evaporation results in little to no change in spike isotopic ratios. The program allows you to manually change the ^{233}U spike concentration, and calculates the resulting change in ^{229}Th based off of isotopic ratios of spike used. This option is shown in Figure B.6, where clicking "yes" to changing preset spike values results in a second GUI window

where you are prompted to manually change the concentration. Once changed, pressing the "submit" button will save the new ^{233}U spike concentration, update the ^{229}Th spike concentration, and return the user to the main GUI window to continue.

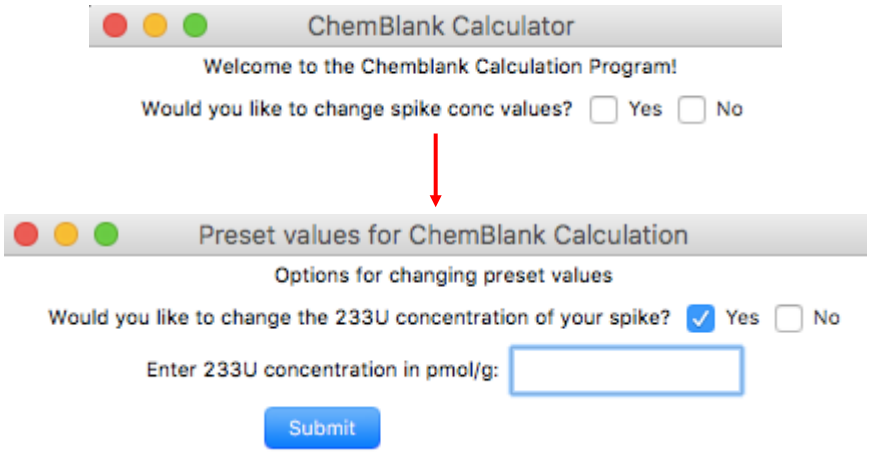


Figure B.6: Option to change spike concentration for chemistry blank program

The chemistry blank program allows you to alter Th and U methods to correct for beam spiking if the solution runs out. Additionally, it allows for an edited .xlsx file to be uploaded. The chemistry blank program requires the user to input the blank name, spike used, spike weight (g), weight of U solution (g), weight of Th solution (g), uptake rate (mg/sec), ionization efficiency (%) and filename for the resulting Excel export with .xlsx extension. An example of the program is show in Figure B.7 for chemistry blank B28.

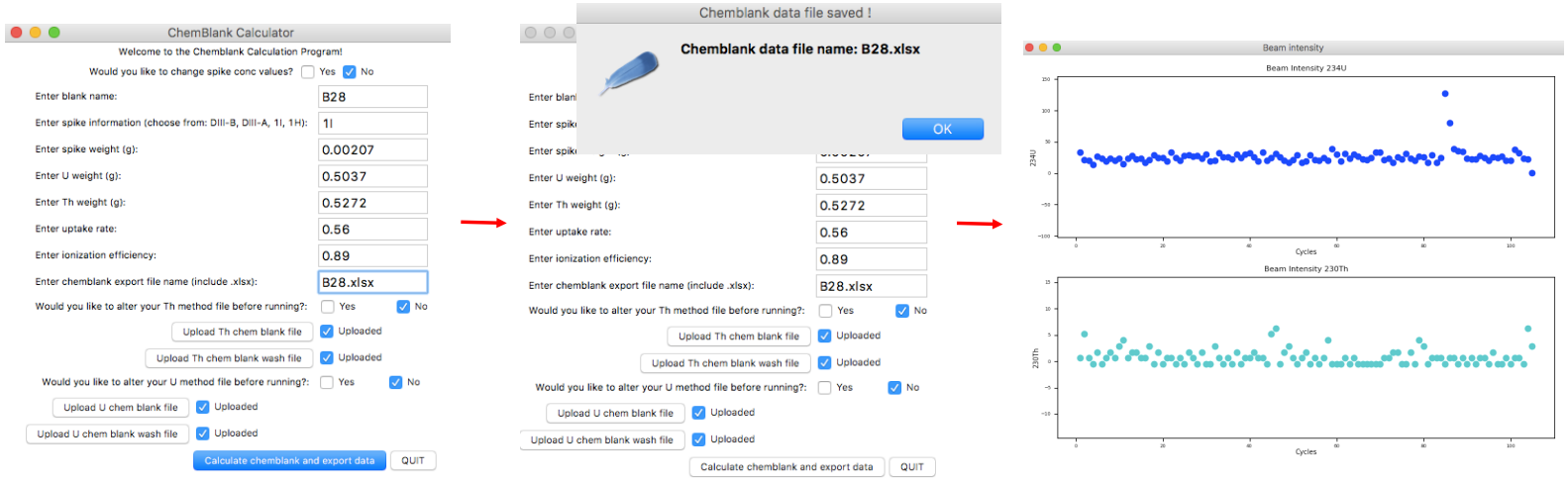


Figure B.7: Example of steps for chemistry blank calculation using program

The program exports an Excel spreadsheet of results under the filename provided in the same directory as the *Python* chemistry blank program. The results of data reduction for chemistry blank B28 using both the *Python* program and traditional Excel spreadsheets are show in Figures B.8 and B.9. Figure B.8 shows the formatting of the program's Excel export. The chemistry blank data will be required for the *Python* age calculation program, which will pull chemistry blank weights from specified cells. Thus, the formatting of this spreadsheet must be maintained if the user wishes to use it while reducing age data.

	1_Chemblank	229Th	230Th	232Th	233U	234U	235U	238U
1_fileinfo	B28							
2_yields		66.21122			79.9601			
3_chemblank			22.92755	186.1442		316.2409	41.36938	2692.519
4_2s err			26.57541	15.25279		124.0121	12.87434	219.3719
5_units		%	ag	fg	%	ag	fg	fg
6_param	Run info							
7_param		Spike used	Spike wt	Th wt	U.R.	U wt	I.E.	
8_param		1l	0.00207	0.5272	0.56	0.5037	0.89	
9_param			g	g	mg/sec	g	%	

Figure B.8: Results of *Python* chemistry blank data reduction

Chemistry blank values for B28 calculated by Excel

	230Th	232Th	234U	235U	238U
Chemistry blank weight	22.93	186.14	316.24	41.37	2692.52
2σ Abs. error	± 26.58	± 15.25	± 124.01	± 12.87	± 219.37
	ag	fg	ag	fg	fg

	Th	U
Chemistry yield	66.21%	79.96%

Figure B.9: Results of Excel chemistry blank data reduction

Chemistry blank data reduction provides the same results for the *Python* program as the traditional Excel spreadsheet, with minimal effort. The Excel spreadsheet created by the program can be stored by the user, and can be used in reducing age data later on. The *Python* Chemistry Blank Calculation contains 1123 lines of code and documentation. At 25 lines of code per page, this is approximately 45 pages.

B.4 Standard Calculation

Standards need to be run for both SEM and cups configuration before running samples to ensure the machine is correctly measuring isotopes. These standards are made to have set isotopic ratios and absolute concentrations, thus machine runs of the standards should always produce these values within error. If they do not, machine parameters may need to be adjusted. Sections B.4.1 and B.4.2 discuss the procedures for running standards on an MC-ICP-MS in SEM and cups configurations and the *Python* programs created for standard data reduction. The *Python* standard program can reduce both SEM and cups standard data, thus combining the functions of multiple Excel spreadsheets.

The *Python* standard program GUI menu allows you the option of choosing which method was used. The user merely needs to mark the checkbox of the method used, and the GUI will provide the necessary input and upload options, which will be discussed in Sections B.4.1 and B.4.2.

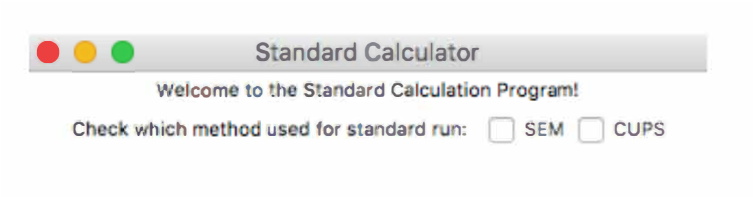


Figure B.10: Option to run SEM or cups standard

The *Python* standard data reduction program consists of 1926 lines of code. At 25 lines per page, this is approximately 77 pages.

B.4.1 Standard on SEM

Current procedure for SEM configuration involves running a dilute 112A standard. Concentrated 112A standard (at 1.6194 pmol/g ^{235}U) is diluted with ICP solution (water, 1% nitric acid, and trace hydrofluoric acid). Approximate ^{234}U background value of wash should be measured, as it used in calculating the δ^{234}U standard value. Abundance sensitivity ($\frac{^{237}U}{^{238}U}$) and ion counter yield ($\frac{^{235}U}{^{235}U}$) of the standard must be measured before standard method run, and should be < 0.7 ppm and 100% ± 0.2% , respectively.

The dilute standard is run under U method parameters, and should be run for 600-1000 cycles to reduce errors. The run data can be exported for data reduction as an EXP file. Current data reduction involves an Excel spreadsheet equipped with a Macros program which filters data and deletes anomalous values. Thus the spreadsheet must either be a .xlsm file or linked to a working .xlsm file, which can make spreadsheet sharing among lab users difficult.

Through SEM standard data reduction, the user should end up with the standard $\frac{^{236}U}{^{233}U}$ ratio, $\frac{^{235}U}{^{233}U}$ ratio, and δ^{234}U value. The $\frac{^{236}U}{^{233}U}$ ratio is the measured ratio value after filtering out anomalous values. To determine the $\frac{^{235}U}{^{233}U}$ ratio, the $\frac{^{236}U}{^{233}U}$ measured ratio must be corrected for ^{238}U tail. The $\frac{^{236}U}{^{238}U}$ ratio is assumed to be $\frac{1}{5}$ the value of the abundance sensitivity, and the $\frac{^{238}U}{^{235}U}$ is a constant (137.83). The correction for tailing at 236 is shown in Equation B.2.

$$\frac{^{236}U}{^{233}U}_{corr} = \frac{^{236}U}{^{233}U}_{meas} * (1 - \frac{(\frac{^{236}U}{^{238}U})_{AS}(\frac{^{235}U}{^{233}U})_{meas}(\frac{^{238}U}{^{235}U})}{(\frac{^{236}U}{^{233}U})_{spike})} \tag{B.2}$$

The measured $\frac{^{235}U}{^{233}U}$ can then be corrected for fractionation using the tail corrected $\frac{^{236}U}{^{233}U}$ value, as discussed in Appendix B.3.

The δ^{234}U value is in parts per mille (‰), and is $[\frac{^{234}U}{^{238}U}_{activity} - 1] * 1000$. The activity ratio of $\frac{^{234}U}{^{238}U}$ is the atomic ratio of $\frac{^{234}U}{^{238}U}$ multiplied by $\frac{\lambda_{234}}{\lambda_{238}}$. Determining the atomic ratio of $\frac{^{234}U}{^{238}U}$ in the standard involves correcting the measured $\frac{^{235}U}{^{233}U}$, $\frac{^{234}U}{^{233}U}$, and $\frac{^{234}U}{^{235}U}$ ratios for tailing and fractionation. First the measured $\frac{^{236}U}{^{233}U}$ ratio is corrected for tailing, as shown in Equation B.2, and the resulting $\frac{^{236}U}{^{233}U}$ is used to correct for isotopic fractionation for each ratio.

After correcting for tail and fractionation, the wash signal of ^{234}U is subtracted from the corrected $\frac{^{234}U}{^{235}U}$ ratio through the following conversion:

$$\frac{^{234}U}{^{235}U}_{corr,signal} = \frac{^{234}U}{^{235}U}_{corr,total} * (1 - \frac{^{234}U_{wash}}{(^{233}U_{meas}) * (\frac{^{235}U}{^{233}U}_{corr,total}) * (\frac{^{234}U}{^{235}U}_{corr,total})}) \tag{B.3}$$

This ratio must then be corrected for spike contribution to ^{234}U and ^{235}U.

$$\frac{^{234}U}{^{235}U}_{corr,final} = \frac{^{234}U}{^{235}U}_{corr,signal} * \frac{(1 - \frac{\frac{^{234}U}{^{235}U}_{spike}}{\frac{^{234}U}{^{235}U}_{corr,total}})}{(1 - \frac{\frac{^{235}U}{^{233}U}_{spike}}{\frac{^{235}U}{^{233}U}_{corr,total}})} \tag{B.4}$$

The resulting $\frac{^{234}U}{^{235}U}_{corr,final}$ ratio is converted into the atomic ratio of $\frac{^{234}U}{^{238}U}$ using the natural ratio of $\frac{^{235}U}{^{238}U}$, and reported as a δ^{234}U value, as discussed above.

Finalized results must be within error of the standard. The 112A standard used in the UMN Isotope Lab has a $\frac{^{235}U}{^{233}U}$ ratio of 14.63 and a δ^{234}U of -38.5 ‰. The $\frac{^{236}U}{^{233}U}$ ratio should be between 1.018 and 1.030.

The calculation of the SEM standard takes greater data reduction capabilities than reagent and chemistry blanks, as the method results must be filtered and significantly corrected. This can currently be done in Excel Macros-enabled spreadsheets, which can be cumbersome for users. Additionally, results of SEM standard data reduction do not need to be saved as a data file. The *Python* SEM standard program reduces user effort and does not produce an export file.

Figure B.11 shows the process for reducing 112A standard data on SEM configuration, with minimal user input. The program again allows the user to alter 112A method in case the solution runs out during the run. *Python* SEM standard data reduction program provides the same results as traditional Excel spreadsheets, as shown in Figure B.12.

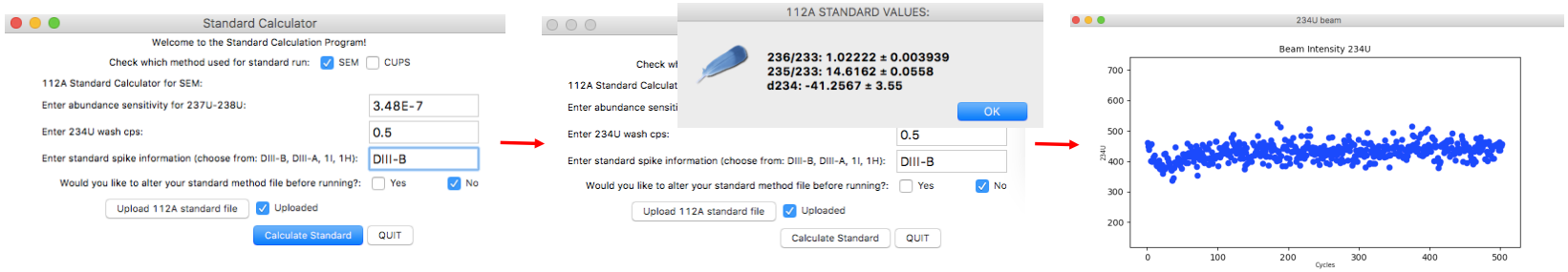


Figure B.11: Example of steps for SEM standard calculation using program

SEM standard results for Excel and Python

Excel 112A SEM standard results	
236/233	1.0222 ± 0.003939
235/233	14.6162 ± 0.0558
d234U	-41.2567 ± 3.55

Python 112A SEM standard results	
236/233	1.02222 ± 0.003939
235/233	14.6162 ± 0.0558
d234U	-41.2567 ± 3.55

Figure B.12: Results of *Python* and Excel SEM standard data reduction

B.4.2 Standard on cups

As cups methods are run at much higher beam intensities than are run on SEM, the effect of tails from higher beams becomes significant. The cups standard method not only verifies correct machine parameters, but also characterizes the ^{238}U tail correction factors. ^{237}U is measured to correct for ^{238}U tail, as any signal present at this mass is due to tailing.

To correct for tail, an unspiked 112A standard is run, and compared against a background wash method to determine the tail/237 correction factor at each isotope. Machine blank corrected tail/237 ratios are calculated for $\frac{233}{237}$, $\frac{233.5}{237}$, $\frac{234.5}{237}$, and $\frac{236}{237}$. Using the 2σ error for measured ratios, maximum and minimum tail ratios are calculated and a logarithmic line of best fit is calculated for each. A logarithmic equation best characterizes the decay of tail intensity per mass unit. Minimum and maximum tail ratios are calculated using both equations at masses ^{233}U, $^{233.5}$U, ^{234}U, $^{234.5}$U, ^{235}U and ^{236}U. The offset between the calculated ratio and measured ratio is determined for ratios $\frac{233}{237}$, $\frac{233.5}{237}$, $\frac{234.5}{237}$, and $\frac{236}{237}$. Based off these values, offset is determined for ratios $\frac{234}{237}$ and $\frac{235}{237}$ and tail/237 ratios are calculated for both. The user is left with finalized $\frac{233}{237}$, $\frac{234}{237}$, $\frac{235}{237}$ and $\frac{236}{237}$ ratios and 2σ errors. 2σ errors for tail are either the measured or calculated 2σ error based off run data, or 5% of tail ratio, depending on which is greater. Unspiked standard tail ratios are not only used in calculating the 112A spiked standard for cups, but are also used to correct for tails in sample method runs.

112A standard is also run for cups configuration to verify machine parameters. However, a concentrated rather than dilute 112A spike solution is run to ensure high beam intensities. A background wash method is first collected, and current lab protocol is in transition from running backgrounds on SEM to running backgrounds on cups. The *Python* standard cups program allows for either. The concentrated 112A data undergoes a series of corrections, beginning with correction for isotope ratio drift that occurs due to a slow response time to changes in signal intensity from the amplifier system (Gourgiotis et al., 2014). Drift offset is calculated element-wise for the ^{234}U signal using the ^{234}U method integration time (1.049 seconds) and amplifier time constant (0.65 sec). The drift offset calculated in B.5 is then used to correct the measured $\frac{234}{233}$ ratio for drift in B.6.

$$^{234}U(i)_{drift} = ^{234}U(i)_{meas} + \left(\frac{^{234}U(i+1)_{meas} - ^{234}U(i-1)_{meas}}{2 * int\_time}\right) * amp\_time\_constant \tag{B.5}$$

$$\frac{234}{233}(i)_{drift\_corr} = ^{234}U(i)_{drift} * \frac{234}{233}(i)_{meas} \tag{B.6}$$

The drift corrected $\frac{234}{233}$ ratio and measured $\frac{235}{233}$, $\frac{236}{233}$, $\frac{238}{233}$ and $\frac{237}{238}$ ratios must then be corrected

for background machine values. This is done element-wise, using the machine blank values in counts per sec for both isotopes (mb), and the mean measured beam intensity in counts per second for the isotope on the bottom of the isotopic ratio (meas). For example, Equation B.7 illustrates what the correction would look like for the $\frac{234}{233}$ ratio.

$$\frac{234}{233}(i)_{mb\_corr} = \left(\frac{\frac{234}{233}(i)_{drift\_corr} - \frac{^{234}U_{mb}}{^{233}U_{meas}}}{1 - \frac{^{233}U_{mb}}{^{233}U_{meas}}}\right) \tag{B.7}$$

The machine blank corrected $\frac{237}{238}$ ratio is the abundance sensitivity and will be reported in data reduction for the standard cups measurement. Additionally, this value is used to convert tail/237 values into tail/238 values, which will be used in tail corrections.

Ratios are corrected for tailing using the tail/238 values calculated from the unspiked standard and spiked standard abundance sensitivity. This is done element-wise for machine blank corrected ratios $\frac{234}{233}$, $\frac{235}{233}$, $\frac{236}{233}$, and $\frac{238}{233}$. This is shown in Equations B.8 and B.9 using the $\frac{234}{233}$ ratio as an example, where first the isotope on the top of the ratio is corrected and then the isotope on the bottom of the ratio is corrected. The machine blank corrected mean $\frac{238}{233}$ ratio is used to convert the tail/238 ratio. As ^{238}U does not need to be corrected, the tail correction for $\frac{238}{233}$ only involves Equation B.9.

$$\frac{234}{233}(i)_{tail\_corr\_top} = \frac{234}{233}(i)_{mb\_corr} - \frac{234}{238}_{tail} * \frac{238}{233}_{mb\_corr\_mean} \tag{B.8}$$

$$\frac{234}{233}(i)_{tail\_corr\_final} = \frac{234}{233}(i)_{tail\_corr\_top} * \left(\frac{1}{1 - \frac{233}{238}_{tail} * \frac{238}{233}_{mb\_corr\_mean}}\right) \tag{B.9}$$

Additionally, tail corrected $\frac{238}{235}$ and $\frac{234}{238}$ ratios are calculated by dividing element-wise the tail corrected $\frac{238}{233}$ and $\frac{235}{233}$, and $\frac{238}{233}$ and $\frac{234}{233}$ ratios, respectively.

Tail corrected ratios $\frac{234}{233}$, $\frac{235}{233}$, $\frac{238}{233}$, $\frac{238}{235}$ and $\frac{234}{238}$ are corrected element-wise for isotopic fractionation using the correction discussed in Appendix B.3. These fractionation corrected ratios are then corrected for spike by subtracting isotope-specific spike ratios.

Desired values at the end of data reduction for cups spiked standard runs includes $\frac{234}{238}$ spike corrected ratio in ppm, the $\frac{237}{238}$ machine blank corrected ratio, the $\frac{236}{233}$ machine blank corrected ratio, the $\frac{238}{235}$ spike corrected ratio, and the $\delta^{234}U$ value. This is calculated using the $\frac{234}{238}$ spike corrected ratio as discussed in Appendix B.4.1. The reported $\frac{234}{238}$ ratio and 2σ absolute error will be used in standardization of U-measurements for samples run on cups, and the remaining values are to ensure proper machine calibration.

Calculation of standards using cups measurements entails extensive data reduction for both unspiked and spiked standards. The *Python* program for reducing cups standard data is packaged with the *Python* SEM standard program. *Python* is particularly useful for element-wise data reduction calculations, as data can be placed into a *Numpy* array, corrected element-wise using loops, and bundled into a new corrected array. The program first calculates the tail/237 values and errors of the unspiked standard, and then imports these values into the spiked standard data correction function.

The *Python* cups standard program results in a GUI window that provides data reduced values. The program provides the option of altering both the unspiked and spiked method runs, in case the solution is spent during run. Additionally, the data for the spiked standard wash can be run on either a cups or SEM configuration. As the program involves element-wise corrections, the data processing time is significantly greater than that for the *Python* SEM standard reduction. Figure B.13 provides an example of a cups standard run on the Neptune Plus MC-ICP-MS at the UMN Isotope Lab.

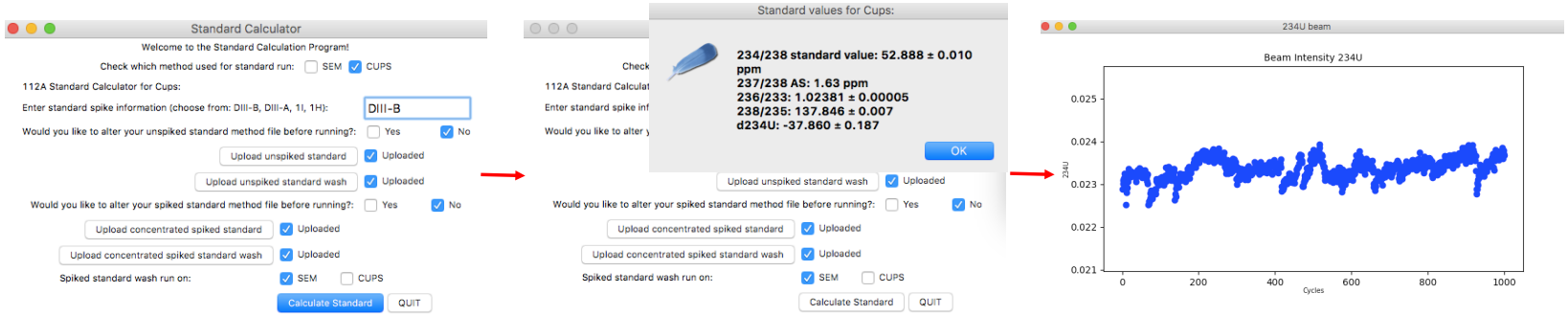


Figure B.13: Example of steps for Cups standard calculation using program

As is shown in Figure B.14, the *Python* program and Excel spreadsheet provide the same results for standards run on cups. Typically a user will run a spiked standard method a number of times throughout the day and recalculate the $\frac{234}{238}$ spike corrected ratio in ppm, to ensure the best normalization for their U samples. Thus the use of an automated data reduction program will greatly reduce user time and effort.

Cups standard results for Excel and Python

Excel Cups standard results	
234/238	52.888 ± 0.010 ppm
237/238	1.63 ppm
236/233	1.02381 ± 0.00005
238/235	137.846 ± 0.007
d234U	-37.860 ± 0.187

Python Cups standard results	
234/238	52.888 ± 0.010 ppm
237/238	1.63 ppm
236/233	1.02381 ± 0.00005
238/235	137.846 ± 0.007
d234U	-37.860 ± 0.187

Figure B.14: Results of *Python* and Excel Cups standard data reduction

B.5 Age Calculation

Determining the ages of carbonate formations through ^{230}Th dating requires users to collect powder along growth layers, run powder through chemical separation, and analyze U and Th isotopic ratios and concentrations on a mass spectrometer. These steps are described in full in Appendix A.2. The data reduction for converting U and Th isotopic ratios and concentrations into usable ages is extensive, and current methods require a series of Macros-enabled Excel spreadsheets. As measurements on Faraday cups become more common in the UMN Isotope Lab, the number of spreadsheets with which lab users will need to be literate will only grow. These spreadsheets require extensive user manipulation, which will be discussed in Appendix B.5.1, B.5.2, and B.5.3, and are prone to errors either by individual users or propagated between users. The conversion of age reduction functions into user-friendly *Python* is an important step in improving the quality and efficiency of the UMN Isotope Lab.

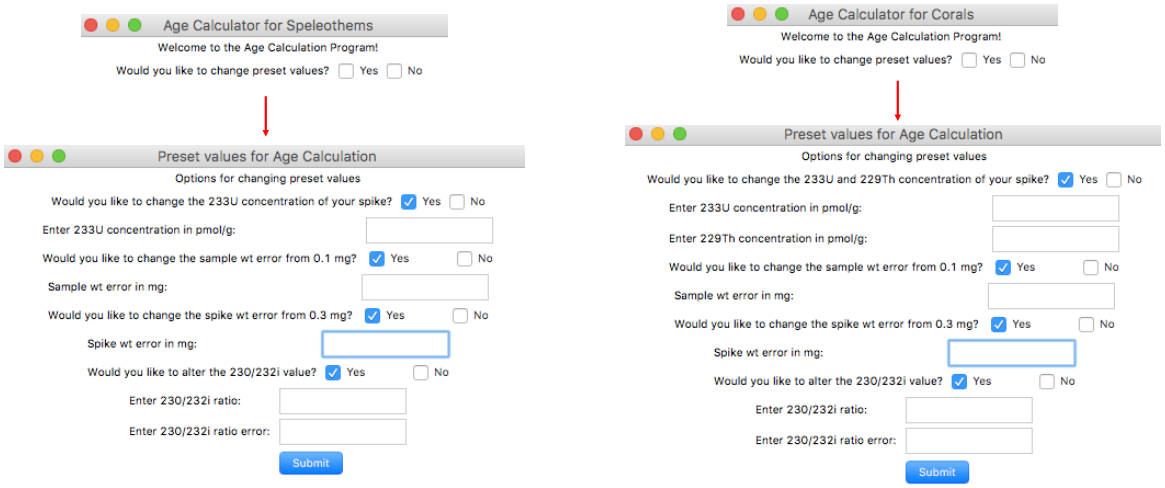
The *Python* Age Calculation program allows for data reduction using SEM or cups configurations. Additionally, the program allows you to manually change a number of preset values. These values include the ^{233}U and ^{229}Th concentrations of spike, the sample and spike weight errors, and the $\frac{230}{232}$ initial ratio and error. The program uses values that work for typical samples, thus reducing user input, but may not be appropriate for all scenarios.

^{233}U and ^{229}Th concentrations in $\frac{pmol}{g}$ have been set for each individual spike, but may change due to evaporative effects. Lab users must monitor their spike and change these values if needed. Sample weight error has been set to 0.1 mg and spike weight error to 0.3 mg, which is appropriate for weighted measurements using current balances. However, errors may be altered dependent on sample and spike weights used, and should be larger if spikes are measured volumetrically. Initial $\frac{230}{232}$ ratios are assumed to be bulk earth value (4.4E-6) with a 50% error, but can be adjusted if more accurate initial ratios are known.

Programs have been slightly altered for speleothems and corals. Speleothem spikes always have set isotopic ratios, thus any evaporative effects will result in constant changes in ^{233}U and ^{229}Th concentrations. To reduce user error, if the ^{233}U concentration preset value is manually changed, the ^{229}Th concentration is automatically calculated based off the spike used. However, for corals it may be necessary to use different spike concentrations. Thus ^{233}U and ^{229}Th concentrations can be entered separately. Speleothem and coral age reduction programs are otherwise identical.

Figures B.15a and B.15b show the options for changing preset values for speleothems and corals, respectively. If the user chooses to change preset values, a secondary GUI window

will appear. The user can input whichever parameters they would like change. By clicking "Submit" those parameters will be updated and the user will be returned to the primary GUI window and be prompted for U-method.



(a) Preset options for speleothems

(b) Preset options for corals

Figure B.15: Options for changing preset values for speleothem and coral age data reduction

If the user does not wish to change preset values, clicking the "No" checkbox will take them directly to the U-method prompt. The user has a number of data reduction options. If U is run on SEM, it is assumed that Th is as well, as the ^{230}Th beam will not be high enough to run on cups. If U is run on cups, the ^{230}Th beam may or may not be high enough to run on cups as well. Thus, the Th may be run on SEM or on cups. The *Python* Age Calculation program provides all the above options, combining the functions of multiple Excel Macros-enabled spreadsheets. Examples of the GUI windows of these options are shown in Figure B.16, and the data reduction involved in all three are discussed in the following sections.

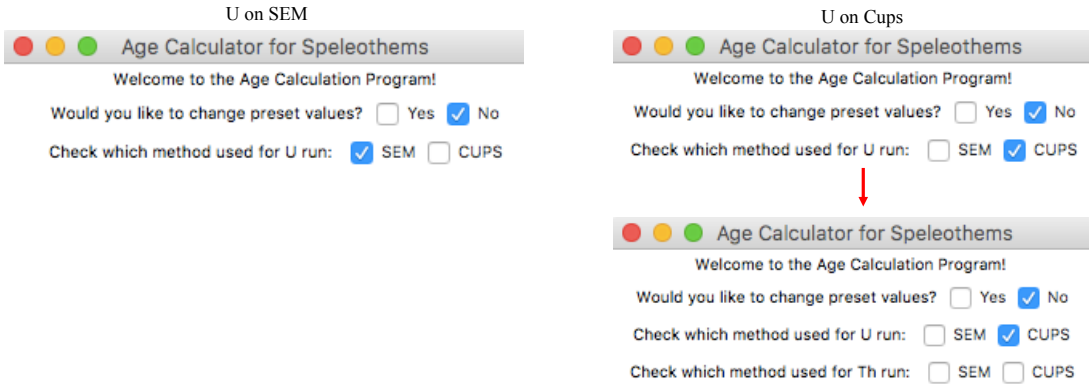
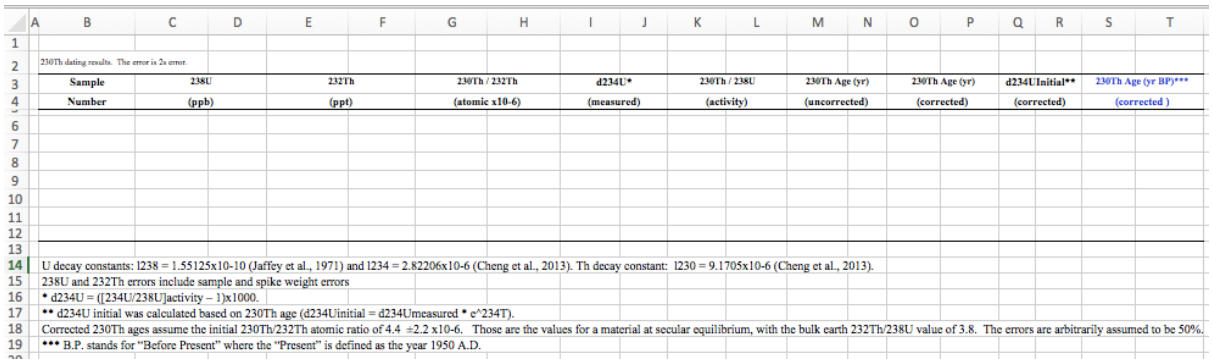


Figure B.16: Method options for U and Th for *Python* age data reduction

All method options require a number of input files. First, a chemistry blank Excel file must be uploaded in order to correct for chemistry blanks. The format of this file must match that of the Excel spreadsheet generated through the *Python* Chemistry Blank program. Additionally, an Excel spreadsheet must be uploaded into which the reduced data will be entered. The program will prompt the user for the row in which the data should be entered, thus the user can continue to compile data within the same spreadsheet, reducing files generated. An example of the Excel formats are shown in Figures B.17 and B.18 below, and a blank age file and default chemistry blank file are available for users on the GitHub repository.

	A	B	C	D	E	F	G	H	I
1		1_Chemblank	229Th	230Th	232Th	233U	234U	235U	238U
2	1_fileinfo	B28							
3	2_yields		66.21122			79.9601			
4	i_chemblank			22.92755	186.1442		316.2409	41.36938	2692.519
5	4_2s err			26.57541	15.25279		124.0121	12.87434	219.3719
6	5_units		%	ag	fg	%	ag	fg	fg
7	6_param	Run info							
8	7_param		Spike used	Spike wt	Th wt	U.R.	U wt	I.E.	
9	8_param		1l	0.00207	0.5272	0.56	0.5037	0.89	
10	9_param			g	g	mg/sec	g	%	

Figure B.17: Example of chemistry blank Excel format for upload



Sample Number	238U (ppb)	232Th (ppt)	230Th / 232Th (atomic x10-6)	d234U* (measured)	230Th / 238U (activity)	230Th Age (yr) (uncorrected)	230Th Age (yr) (corrected)	d234UInitial** (corrected)	230Th Age (yr BP)*** (corrected)

230Th dating results. The error is 2s error.

U decay constants: l238 = 1.55125x10-10 (Jaffey et al., 1971) and l234 = 2.82206x10-6 (Cheng et al., 2013). Th decay constant: l230 = 9.1705x10-6 (Cheng et al., 2013).
238U and 232Th errors include sample and spike weight errors
* d234U = ([234U/238U]activity – 1)x1000.
** d234U initial was calculated based on 230Th age (d234Uinitial = d234Umeasured * e^234T).
Corrected 230Th ages assume the initial 230Th/232Th atomic ratio of 4.4 ±2.2 x10-6. Those are the values for a material at secular equilibrium, with the bulk earth 232Th/238U value of 3.8. The errors are arbitrarily assumed to be 50%.
*** B.P. stands for "Before Present" where the "Present" is defined as the year 1950 A.D.

Figure B.18: Example of age spreadsheet Excel format for upload

For all collection methods, the data is inserted into the uploaded age file. All errors are 2σ. The data reduction for ^{230}Th age calculation results in the following values:

- ^{238}U in parts per billion (ppb) and error. Error includes the effect of spike and sample weight errors.
- ^{232}Th in parts per trillion (ppt) and error. Error includes the effect of spike and sample weight errors.
- $\frac{^{230}Th}{^{232}Th}$ atomic ratio in parts per million (ppm) and error.
- Measured δ^{234}U after corrections and error.
- $\frac{^{230}Th}{^{238}U}$ activity ratio and error.
- ^{230}Th age and error, before correction for initial ^{230}Th.
- ^{230}Th age and error, after correction for initial ^{230}Th.
- Initial δ^{234}U and error using corrected ^{230}Th age.
- Final ^{230}Th age and error in years before present (BP), where present is defined as 1950.

The *Python* Age Calculation program significantly reduces time needed for data reduction and improves user data management. Additionally, it consolidates age data reduction functions for all measurement methods at the UMN Isotope Lab. During the process of creating this program, data reduction calculations for all methods were reviewed and revised, providing the most accurate program for users and ensuring further improvements are centrally distributed. The *Python* Age Calculation program entails 5281 lines of code. At 25 lines per page, this approximately 211 pages.

B.5.1 Age Calculation for U and Th on SEM

Current data reduction for U and Th on SEM consists of a Macros-enabled Excel spreadsheet, modified for spike used, and requires data to be copied and pasted into separate sheets and reduced. First, the U method data is pasted into a U data reduction sheet. The method data is filtered by the Macros U-program to eliminate anomalous values. The U data is then reduced to provide the $\frac{^{235}U}{^{233}U}$ and $\frac{^{234}U}{^{235}U}$ ratios and 2σ errors corrected for tail and isotopic fractionation, as discussed in Appendix B.4.1. Additionally, the ^{233}U filtered counts, unfiltered counts, and mean intensity (in cps) are also generated. These 7 values are copied and pasted into the age data reduction sheet. The tail corrected $\frac{^{236}U}{^{233}U}$ and 2σ error are copied and pasted into the Th data reduction sheet, as they will be used to correct for isotopic fractionation in the Th isotopes. Additionally, the $\frac{^{237}U}{^{238}U}$ abundance sensitivity must be manually entered into both the U and Th data reduction sheets.

For Th data reduction, the Th method data is pasted into the sheet and filtered by the Macros Th-program to eliminate anomalous values. The mean intensity (in cps) of the $\frac{^{230}Th}{^{229}Th}$, $\frac{^{232}Th}{^{229}Th}$ and $\frac{^{230}Th}{^{232}Th}$ ratios are determined. The $\frac{^{230}Th}{^{229}Th}$ and $\frac{^{232}Th}{^{229}Th}$ ratios are then corrected for ^{232}Th and ^{229}Th tails. The $\frac{^{230}Th}{^{229}Th}$ ratio must be corrected for both tail effects, whereas the $\frac{^{232}Th}{^{229}Th}$ must only be corrected for the effect of ^{232}Th at ^{229}Th. The abundance sensitivity ratios for $\frac{^{230}Th}{^{232}Th}$ and $\frac{^{229}Th}{^{232}Th}$ are $\frac{1}{5}$ and $\frac{1}{15}$ of the $\frac{^{237}U}{^{238}U}$ ratio. The tail correction calculations are shown in Equations B.10 and B.11.

$$\frac{^{230}Th}{^{229}Th}_{tailcorr} = \frac{^{230}Th}{^{229}Th}_{meas} * \left(1 - \frac{\frac{^{230}Th}{^{232}Th}_{AS}}{\frac{^{230}Th}{^{232}Th}_{meas}}\right) * \left(1 - \frac{^{230}Th}{^{229}Th}_{AS}\right) \tag{B.10}$$

$$\frac{^{232}Th}{^{229}Th}_{tailcorr} = \frac{^{232}Th}{^{229}Th}_{meas} * \left(1 - \frac{1}{1 - \frac{\frac{^{229}Th}{^{232}Th}_{AS}}{\frac{^{229}Th}{^{232}Th}_{meas}}}\right) \tag{B.11}$$

The resulting tail corrected $\frac{^{230}Th}{^{229}Th}$ and $\frac{^{232}Th}{^{229}Th}$ is then corrected for isotopic fractionation using the tail corrected $\frac{^{236}U}{^{233}U}$ ratio imported from the U data reduction sheet. The Th data reduction sheet provides the $\frac{^{230}Th}{^{229}Th}$ and $\frac{^{232}Th}{^{229}Th}$ ratios and 2σ errors corrected for tail and isotopic fractionation, as well as the mean unfiltered ^{229}Th signal (in cps) and unfiltered counts. The 6 values are copied and pasted into the age data reduction sheet.

In the age data reduction sheet, the user must input the reduced values from the U and Th data reduction sheets, as well as the chemistry blank ^{238}U, ^{232}Th and ^{230}Th values and errors, the sample weight, the spike weight, the spike ^{233}U and ^{229}Th concentrations, and the machine background mean values for ^{233}U, ^{234}U, ^{235}U in cps and ^{230}Th in cpm.

Absolute concentrations of ^{238}U and ^{232}Th are determined using the $\frac{^{235}U}{^{233}U}$ and $\frac{^{232}Th}{^{229}Th}$ ratios corrected for tailing and fractionation, respectively. The $\frac{^{235}U}{^{233}U}$ ratio is corrected for wash using the ^{233}U unfiltered mean and the ^{235}U wash value, then converted into ^{238}U ppb after correcting for spike and chemistry blank values. The $\frac{^{232}Th}{^{229}Th}$ ratio is also corrected for spike and chemistry blank values, then converted into ^{232}Th ppt. Errors reported for ^{238}U and ^{232}Th concentrations include the effects of spike and sample weight errors. These weight errors are not included in further error propagation.

The absolute concentration of ^{230}Th in ppt is also calculated, though not reported. The tail and fractionation corrected $\frac{^{230}Th}{^{229}Th}$ ratio is further corrected for spike, ^{230}Th wash, and chemistry blank values. The calculated ^{230}Th concentration is divided by the calculated ^{232}Th concentration, to provide the $\frac{^{230}Th}{^{232}Th}$ atomic ratio, and reported in units of ppm. The calculated ^{230}Th concentration is also divided by the calculated ^{238}U concentration, to provide the $\frac{^{230}Th}{^{238}U}$ atomic ratio, which is converted into the activity ratio using the decay constants of ^{230}Th and ^{238}U.

The measured δ^{234}U value is also determined. The tail and fractionation corrected $\frac{^{235}U}{^{233}U}$ ratio is converted into a $\frac{^{234}U}{^{235}U}$ ratio and corrected for spike. The ratio is then converted into a $\frac{^{234}U}{^{238}U}$ ratio using the natural ratio $\frac{^{238}U}{^{235}U}$. The ratio is reported in δ notation using the calculation discussed in Appendix B.4.1.

The uncorrected age is first determined using the age equation discussed in Chapter 1.2.2, and does not take into account the effect of initial ^{230}Th. This equation is set to zero, as shown in Equation B.12, and iteratively solved for time (t). In the Excel data reduction, this entails the use of a Macros program, whereby the program runs through 150 iterations with a maximum change of 1E-11 to determine the most accurate value for variable t. This program attempts to find a variable t where the age equation most closely reaches zero, but due to the program format is capable of settling on values that are near to but not actually zero, thus increasing the age error. In the *Python* data reduction, the *Scipy* submodule function *fsolve* is used, which allows infinite iterations until a zero value is reached. This ensures lower age errors for the *Python* program, and improves data reduction capabilities.

$$0 = (\frac{^{230}Th}{^{238}U})_A - (1 - e^{-\lambda_{230}t} + (\frac{\delta^{234}U_m}{100})(\frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}})(1 - e^{(\lambda_{234} - \lambda_{230})t})) \qquad \text{(B.12)}$$

The corrected age is then determined by including the effects of initial ^{230}Th in the age equation. This correction is set to use the initial $\frac{^{230}Th}{^{232}Th}$ ratio of the bulk earth (4.4E-6), but can be changed by the user. This ratio is used to correct the $\frac{^{230}Th}{^{238}U}$ activity ratio as shown in

Equation B.13, and is again solved iteratively to find the corrected age (t) using Equation B.12.

$$(\frac{^{230}Th}{^{238}U})_A = \frac{^{230}Th\frac{pmol}{g} - (\frac{^{230}Th}{^{232}Th_i}e^{-\lambda_{230}t} *^{232} Th\frac{pmol}{g})}{^{238}U\frac{pmol}{g}} * \frac{\lambda_{230}}{\lambda_{238}} \tag{B.13}$$

Age errors are determined for both uncorrected and corrected ages by iteratively solving for age using the minimum and maximum values for $(\frac{^{230}Th}{^{238}U})_A$ and $\delta^{234}U_m$ in each equation and combining quadratically.

Finally, the initial $\delta^{234}U$ is calculated using the corrected age and decay constant for ^{234}U. Final age is reported in years BP.

The *Python* Age Calculation program includes the data reduction explained above, and significantly reduces user time, expertise, and data management efforts. All calculations are detailed in the source code, making it easier for the user to follow the data reduction process if desired. Figure B.19 illustrates the steps for the *Python* age calculation data reduction for SEM. The user must input the spike used, abundance sensitivity for U run, sample weight, spike weight, sample ID, and row number for age spreadsheet. The program also includes the option of using a different abundance sensitivity for the Th run, in case the U and Th solutions were run on different days. The user must upload their wash and method files for Th and U, with the option of altering method files for Th and U in case solution runs out. Additionally, the chemistry blank Excel file and age spreadsheet Excel file must be uploaded.

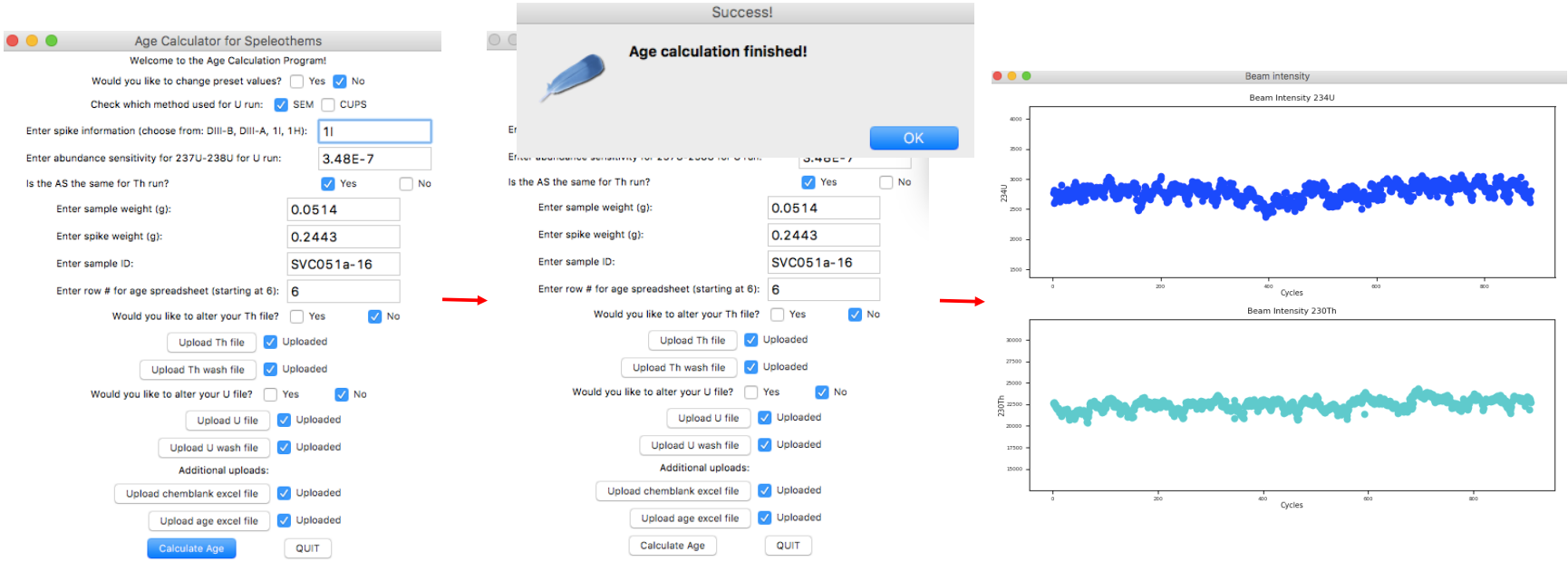


Figure B.19: Example of steps for SEM age calculation using program

As is shown in Figure B.20, the Excel spreadsheet and *Python* program provide the same output data for SEM measurements.

^{230}Th dating results. The error is 2s error.

Sample Number	^{238}U (ppb)	^{232}Th (ppt)	^{230}Th / ^{232}Th (atomic x10^{-6})	d^{234}U* (measured)	^{230}Th / ^{238}U (activity)	^{230}Th Age (yr) (uncorrected)	^{230}Th Age (yr) (corrected)	d^{234}U$_{Initial}$** (corrected)	^{230}Th Age (yr BP)*** (corrected)
SEM data reduction using *Python*									
SVC051a-16	1122.5 ±3.0	4905 ±28	3553 ±19	476.9 ±2.0	0.9415 ±0.0015	102949 ±353	**102871 ±357**	638 ±3	**102804 ±357**
SEM data reduction using Excel									
SVC051a-16	1122.5 ±3.0	4905 ±28	3553 ±19	476.9 ±2.0	0.9415 ±0.0015	102949 ±353	**102871 ±357**	638 ±3	**102804 ±357**

U decay constants: l238 = 1.55125x10-10 (Jaffey et al., 1971) and l234 = 2.82206x10-6 (Cheng et al., 2013). Th decay constant: l230 = 9.1705x10-6 (Cheng et al., 2013).
238U and 232Th errors include sample and spike weight errors
* d234U = ([234U/238U]activity – 1)x1000.
** d234U initial was calculated based on 230Th age (d234Uinitial = d234Umeasured * e^234T).
Corrected 230Th ages assume the initial 230Th/232Th atomic ratio of 4.4 ±2.2 x10-6. Those are the values for a material at secular equilibrium, with the bulk earth 232Th/238U value of 3.8. The errors are arbitrarily assumed to be 50%.
*** B.P. stands for "Before Present" where the "Present" is defined as the year 1950 A.D.

Figure B.20: Results of SEM data reduction using *Python* and Excel

B.5.2 Age Calculation for U on Cups and Th on SEM

Running high intensity beams on Faraday cups results in shorter run times and improved counting, and new methods with 10^{13} Ω resistors has allowed for samples with adequate U and Th concentrations to be run using this method. However, achieving high beam intensities for ^{234}U and ^{230}Th requires large sample sizes, which may not be feasible depending on the sample. As ^{234}U concentration is typically higher than ^{230}Th, there may be scenarios where it is possible to run U on cups but not Th, and Th must be run on a SEM configuration. Current data reduction for this method requires combining the functions of multiple Macros-enabled spreadsheets.

Before U and Th data reduction, the effect of the ^{238}U tail must be accounted for. This is done by analyzing an unspiked standard run, and determining the effect of the tail at each isotope. This is done for the age reduction the same way that it is done for the cups standard reduction, as described in Appendix B.4.2. The analysis results in the $\frac{233}{237}$, $\frac{234}{237}$, $\frac{235}{237}$ and $\frac{236}{237}$ ratios and 2σ errors.

For U cups data reduction, the corrected ^{238}U concentration (in ppb) and δ^{234}U values must be calculated, along with their 2σ errors. U method data is corrected for drift, machine backgrounds, tail, and fractionation in the same way as the concentrated spiked standard, as described in Appendix B.4.2. The tail corrected $\frac{^{236}U}{^{233}U}$ and error will be used in the Th SEM data reduction. The drift, machine background, tail, and fractionation corrected $\frac{^{234}U}{^{233}U}$, $\frac{^{235}U}{^{233}U}$, $\frac{^{238}U}{^{233}U}$, $\frac{^{238}U}{^{235}U}$ and $\frac{^{234}U}{^{238}U}$ ratios are further corrected for spike and chemistry blanks. To correct for spike, the spike specific ratios are merely subtracted from the corrected ratio mean. The correction is no longer element-wise.

To correct for chemistry blanks, chemistry blank ratios must be calculated. The chemistry blank weights of ^{234}U, ^{235}U and ^{238}U are converted into ratios over ^{233}U using the isotopic mass, spike weight, and ^{233}U spike concentration. These are subtracted from the spike

corrected $\frac{^{234}U}{^{233}U}$, $\frac{^{235}U}{^{233}U}$, $\frac{^{238}U}{^{233}U}$ ratios. For the $\frac{^{238}U}{^{235}U}$ and $\frac{^{234}U}{^{238}U}$ ratios, the chemistry blank ratios are converted into the proper ratio using the spike corrected values.

The ^{238}U concentration in ppb is calculated using the $\frac{^{238}U}{^{233}U}$ chemistry blank corrected ratio, spike weight, sample weight, ^{233}U spike concentration and isotopic mass. The 2σ errors with and without sample and spike weight errors are calculated.

The chemistry blank corrected $\frac{^{234}U}{^{238}U}$ ratio is then normalized to the 112A standard. This standard has a $\frac{^{234}U}{^{238}U}$ ratio of 137.832 ± 0.015 (Cheng et al., 2013). The difference between the spiked standard $\frac{^{234}U}{^{238}U}$ ratio, which should be monitored throughout the run time, and the actual 112A $\frac{^{234}U}{^{238}U}$ ratio is subtracted from the chemistry blank corrected $\frac{^{234}U}{^{238}U}$ ratio. The resulting normalized $\frac{^{234}U}{^{238}U}$ ratio is converted to a δ^{234}U value as is the 2σ error after propagation.

The Th data reduction is the same as described in Appendix B.5.1, and results in tail and fractionation corrected $\frac{^{230}Th}{^{229}Th}$ and $\frac{^{232}Th}{^{229}Th}$ ratios and 2σ errors. Additionally, the ^{229}Th unfiltered mean in cps is produced. To first correct for machine background, blank/signal ratios are determined for $\frac{^{229}Th}{^{229}Th}$, $\frac{^{230}Th}{^{229}Th}$, and $\frac{^{232}Th}{^{229}Th}$ by dividing the machine blank ^{229}Th, ^{230}Th, and ^{232}Th beam intensities by the ^{229}Th unfiltered mean. To correct for the blank, Equation B.14 is used, with the $\frac{^{230}Th}{^{229}Th}$ ratio used as an example.

$$\frac{^{230}Th}{^{229}Th}_{mb,corr} = \frac{\frac{^{230}Th}{^{229}Th}_{tail/frac,corr} - \frac{^{230}Th}{^{229}Th}_{mb}}{1 - \frac{^{229}Th}{^{229}Th}_{mb}} \tag{B.14}$$

The machine blank corrected $\frac{^{230}Th}{^{229}Th}$ and $\frac{^{232}Th}{^{229}Th}$ ratios are then corrected for spike by subtracting spike specific isotopic ratios. Chemistry blank ratios of $\frac{^{230}Th}{^{229}Th}$ and $\frac{^{232}Th}{^{229}Th}$ are calculated using the isotopic blank weight, isotopic mass, spike weight, and ^{229}Th spike concentration. These ratios are then subtracted from the $\frac{^{230}Th}{^{229}Th}$ and $\frac{^{232}Th}{^{229}Th}$ spike corrected ratios. The two ratios are also combined to provide the fully corrected $\frac{^{230}Th}{^{232}Th}$ ratio. The corrected $\frac{^{230}Th}{^{229}Th}$ and $\frac{^{232}Th}{^{229}Th}$ ratios are used to calculate the absolute concentrations of ^{230}Th and ^{232}Th in ppt, using the sample weight, spike weight, ^{229}Th spike concentration, and isotopic mass. The relative 2σ errors are also calculated, with two errors for ^{232}Th, both using and not using the contribution of sample and spike weight errors.

Final values from U and Th data reduction are ^{238}U (in ppb and $\frac{pmol}{g}$), ^{232}Th (in ppt and $\frac{pmol}{g}$), ^{230}Th (in ppt and $\frac{pmol}{g}$), δ^{234}U (in δ units), and the $\frac{^{230}Th}{^{232}Th}$ atomic ratio. From the $\frac{pmol}{g}$ values for ^{238}U, ^{232}Th, ^{230}Th, the atomic ratios for $\frac{^{232}Th}{^{238}U}$, $\frac{^{230}Th}{^{238}U}$, and $\frac{^{230}Th}{^{234}U}$ are calculated, and further converted into activity ratios using the decay constants for ^{230}Th, ^{232}Th, and ^{238}U.

The age calculation is the same as described in the previous section (B.5.1). First the $\frac{^{232}Th}{^{238}U}$ activity ratio is used to iteratively solve for time using the age equation. Then the activity ratio is corrected for the effects of initial ^{230}Th and again time is solved iteratively, producing the corrected age.

Current Excel data reduction methods for U on cups and Th on SEM involve six active sheets in a Macros-enabled spreadsheet. This requires significant transfer of data between sheets and knowledge of the reduction methods. The *Python* program significantly reduces user input. The program requires the user to input spike used, abundance sensitivity for Th run, sample weight, spike weight, sample ID, and row number for age spreadsheet. In addition, the user must enter the $\frac{234}{238}$ ratio and error in ppm of the spiked standard run. This value is produced through the *Python* Standard Calculation program. If multiple spiked standards are run throughout the day, the user should use the average. The user must upload the wash and method file for unspiked standard, Th, and U. All three method files have the option to alter them in case solution runs out. This is particularly useful in cups measurements, as often minimal solution is used and sampling time should be as long as possible. As in the SEM data reduction, a chemistry blank Excel file and age spreadsheet Excel file must be uploaded. Figure B.21 illustrates the steps for the *Python* age calculation data reduction for U on cups and Th on SEM.

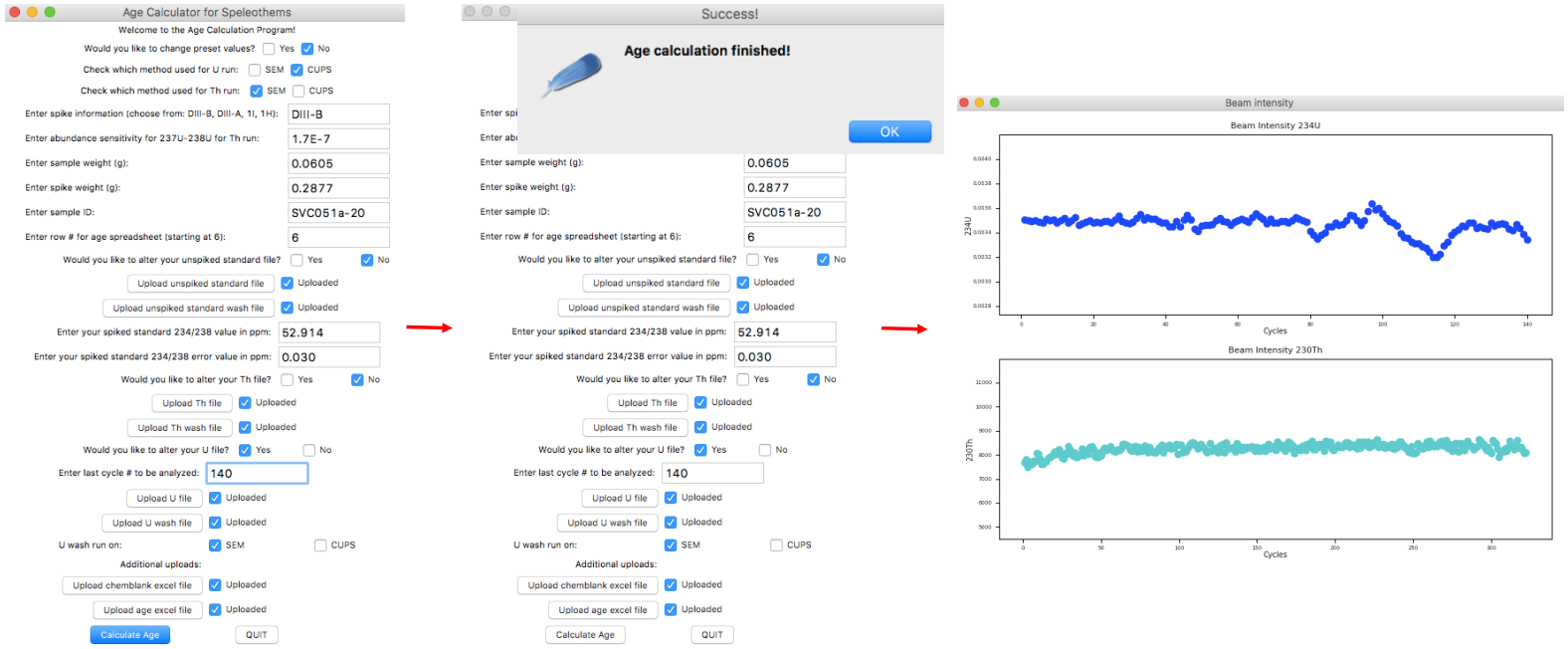


Figure B.21: Example of steps for U on cups and Th on SEM age calculation using program

As is shown in Figure B.22, the *Python* program to reduce data for U on cups and Th on SEM provides the same results as the traditional Excel spreadsheet.

^{230}Th dating results. The error is 2s error.

Sample Number	^{238}U (ppb)	^{232}Th (ppt)	^{230}Th / ^{232}Th (atomic x10^{-6})	d^{234}U* (measured)	^{230}Th / ^{238}U (activity)	^{230}Th Age (yr) (uncorrected)	^{230}Th Age (yr) (corrected)	d^{234}U$_{initial}$** (corrected)	^{230}Th Age (yr BP)*** (corrected)
U on cups and Th on SEM data reduction using *Python*									
SVC051a-20	1128.6 ±2.3	4930 ±27	3582 ±18	633.9 ±1.7	0.9490 ±0.0013	88444 ±227	**88374 ±232**	813 ±2	**88307 ±232**
U on cups and Th on SEM data reduction using Excel									
SVC051a-20	1128.6 ±2.3	4930 ±27	3582 ±18	633.9 ±1.7	0.9490 ±0.0013	88444 ±227	**88374 ±232**	813 ±2	**88307 ±232**

U decay constants: l238 = 1.55125x10-10 (Jaffey et al., 1971) and l234 = 2.82206x10-6 (Cheng et al., 2013). Th decay constant: l230 = 9.1705x10-6 (Cheng et al., 2013).

238U and 232Th errors include sample and spike weight errors

* d234U = ([234U/238U]activity – 1)x1000.

** d234U initial was calculated based on 230Th age (d234Uinitial = d234Umeasured * e^234T).

Corrected 230Th ages assume the initial 230Th/232Th atomic ratio of 4.4 ±2.2 x10-6. Those are the values for a material at secular equilibrium, with the bulk earth 232Th/238U value of 3.8. The errors are arbitrarily assumed to be 50%.

*** B.P. stands for "Before Present" where the "Present" is defined as the year 1950 A.D.

Figure B.22: Results of data reduction for U on cups and Th on SEM using *Python* and Excel

B.5.3 Age Calculation for U and Th on Cups

If the ^{230}Th beam is high enough, it is also possible to run both U and Th on Faraday cups. This method can considerably reduce both user time and age errors. Current data reduction for both Th and U on cups requires a Macros-enabled spreadsheet.

To determine ^{230}Th ages for cups measurements, the unspiked standard, U wash and U method results are reduced using the same procedure as the one outlined in the previous section (Appendix B.5.2). This produces the corrected ^{238}U concentration and error (in ppb) and the corrected δ^{234}U value and error (in δ units). All errors are 2σ, and the ^{238}U errors with and without spike weight errors are calculated. Additionally, the tail corrected $\frac{^{236}U}{^{233}U}$ and the machine blank corrected $\frac{^{237}U}{^{238}U}$ ratios and their respective errors must be determined, as they will be used in the Th data reduction for cups.

Th reduction on cups involves the same corrections as the U method. Drift offset is calculated element-wise for ^{230}Th signal using the ^{230}Th method integration time (1.049 seconds) and amplifier time constant (0.65 sec). The correction is the same as that described in Appendix B.4.2, using the ^{230}Th measured beam rather than the ^{234}U measured beam. The measured $\frac{^{230}Th}{^{229}Th}$ and $\frac{^{230}Th}{^{232}Th}$ ratios are corrected element-wise for drift by dividing the drift offset by the measured ratio.

The drift corrected $\frac{^{230}Th}{^{229}Th}$ and $\frac{^{230}Th}{^{232}Th}$ ratios and the measured $\frac{^{232}Th}{^{229}Th}$ ratio are corrected for machine background values using the calculation described in Appendix B.4.2. However, ratios must be corrected for tailing effects of both ^{232}Th and ^{229}Th. To correct for tailing effects, the tail ratios for tail/229 ($\frac{^{230}Th}{^{229}Th}$ and $\frac{^{232}Th}{^{229}Th}$) and tail/232 ($\frac{^{230}Th}{^{232}Th}$ and $\frac{^{229}Th}{^{232}Th}$) are determined using the $\frac{^{237}U}{^{238}U}$ abundance sensitivity. These tail ratios correct for tailing effects of both ^{232}Th and ^{229}Th element-wise for all three isotope ratios, using slightly different

equations, as shown in B.15, B.16, and B.17. The mean machine blank corrected $\frac{^{232}Th}{^{229}Th}$ ratio is used in all three to correct for the effect of tailing of ^{232}Th and ^{229}Th on each other.

$$\frac{^{230}Th}{^{229}Th}(i)_{tail,corr} = \frac{\frac{^{230}Th}{^{229}Th}(i)_{mb,corr} - \frac{^{230}Th}{^{229}Th\,tail} - (\frac{^{230}Th}{^{232}Th\,tail} * \frac{^{232}Th}{^{229}Th\,mb,corr})}{1 - (\frac{^{229}Th}{^{232}Th\,tail} * \frac{^{232}Th}{^{229}Th\,mb,corr})} \tag{B.15}$$

$$\frac{^{232}Th}{^{229}Th}(i)_{tail,corr} = \frac{\frac{^{232}Th}{^{229}Th}(i)_{mb,corr} - \frac{^{232}Th}{^{229}Th\,tail}}{1 - (\frac{^{229}Th}{^{232}Th\,tail} * \frac{^{232}Th}{^{229}Th\,mb,corr})} \tag{B.16}$$

$$\frac{^{230}Th}{^{232}Th}(i)_{tail,corr} = \frac{\frac{^{230}Th}{^{232}Th}(i)_{mb,corr} - (\frac{^{230}Th}{^{229}Th\,tail} * \frac{^{232}Th}{^{229}Th\,mb,corr})}{1 - \frac{^{230}Th}{^{232}Th\,tail}} \tag{B.17}$$

All three ratios undergo element-wise fractionation correction, using the tail corrected $\frac{^{236}U}{^{233}U}$ ratio, and the mean fractionation corrected ratios are further corrected for spike and chemistry blanks using the method described in the previous section (Appendix B.5.2). The fully corrected $\frac{^{230}Th}{^{229}Th}$, $\frac{^{232}Th}{^{229}Th}$, and $\frac{^{230}Th}{^{232}Th}$ ratios are used to determine absolute isotopic concentrations and the $\frac{^{230}Th}{^{238}U}$ activity ratio. This ratio is then used to calculate the uncorrected and corrected ^{230}Th ages, as previously described. All reduced data is exported into the provided Excel age spreadsheet.

All data reduction methods for cups measurements have been included in the *Python* Age Calculation program. Current procedure involves five active sheets on a Macros-enabled spreadsheet, with considerable data transfer between sheets. The *Python* significantly simplifies cups data reduction, with minimal user input but still allowing for data improvement. The program requires the user to input spike used, sample weight, sample ID, and row number for age spreadsheet, as well as the spiked standard $\frac{^{234}U}{^{238}U}$ ratio and error in ppm. The program requires the wash and method files for the unspiked standard, Th, and U runs to be uploaded. Options to alter any or all of the three method files are offered. Additionally, both Th and U wash files can be run on either a cups or SEM configuration. The user must again upload an Excel chemistry blank file and age spreadsheet file. Figure B.23 shows the steps of the *Python* Age Calculation program for cups. For this sample, the U method file was manually altered to eliminate peak instability, and saved and imported as a .xlsx file.

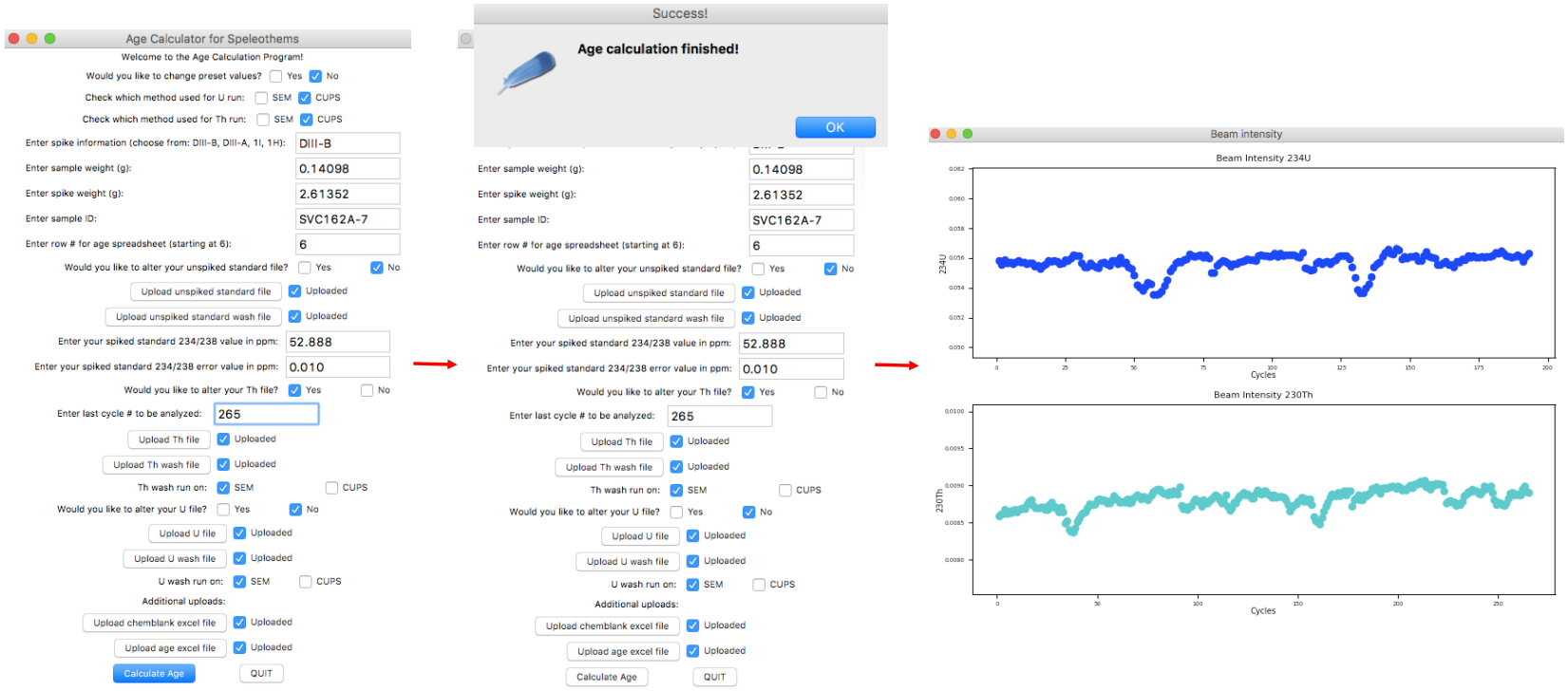


Figure B.23: Example of steps for Cups age calculation using program

As is shown in Figure B.24, the Excel spreadsheet and *Python* program provide the same output data for cups measurements.

^{230}Th dating results. The error is 2s error.

Sample Number	^{238}U (ppb)	^{232}Th (ppt)	^{230}Th / ^{232}Th (atomic x10^{-6})	d^{234}U* (measured)	^{230}Th / ^{238}U (activity)	^{230}Th Age (yr) (uncorrected)	^{230}Th Age (yr) (corrected)	d$^{234}U_{initial}$** (corrected)	^{230}Th Age (yr BP)*** (corrected)
Cups data reduction using *Python*									
SVC162A-7	4566.3 ±3.3	1315 ±1	49215 ±19	486.7 ±0.4	0.8593 ±0.0003	88695 ±58	**88691 ±58**	625 ±1	**88624 ±58**
Cups data reduction using Excel									
SVC162A-7	4566.3 ±3.3	1315 ±1	49215 ±19	486.7 ±0.4	0.8593 ±0.0003	88695 ±58	**88691 ±58**	625 ±1	**88624 ±58**

U decay constants: l238 = 1.55125x10-10 (Jaffey et al., 1971) and l234 = 2.82206x10-6 (Cheng et al., 2013). Th decay constant: l230 = 9.1705x10-6 (Cheng et al., 2013).

238U and 232Th errors include sample and spike weight errors

* d234U = ([234U/238U]activity – 1)x1000.

** d234U initial was calculated based on 230Th age (d234Uinitial = d234Umeasured * e^234T).

Corrected 230Th ages assume the initial 230Th/232Th atomic ratio of 4.4 ±2.2 x10-6. Those are the values for a material at secular equilibrium, with the bulk earth 232Th/238U value of 3.8. The errors are arbitrarily assumed to be 50%.

*** B.P. stands for "Before Present" where the "Present" is defined as the year 1950 A.D.

Figure B.24: Results of data reduction for Cups using *Python* and Excel