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CONCH: A Visual Basic program for interactive processing of ion-microprobe analytical data ☆

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Abstract

A Visual Basic program for flexible, interactive processing of ion-microprobe data acquired for quantitative trace element, ^{26}Al–^{26}Mg, ^{53}Mn–^{53}Cr, ^{60}Fe–^{60}Ni and U–Th–Pb geochronology applications is described. Default but editable run-tables enable software identification of secondary ion species analyzed and for characterization of the standard used. Counts obtained for each species may be displayed in plots against analysis time and edited interactively. Count outliers can be automatically identified via a set of editable count-rejection criteria and displayed for assessment. Standard analyses are distinguished from Unknowns by matching of the analysis label with a string specified in the Set-up dialog, and processed separately. A generalized routine writes background-corrected count rates, ratios and uncertainties, plus weighted means and uncertainties for Standards and Unknowns, to a spreadsheet that may be saved as a text-delimited file. Specialized routines process trace-element concentration, ^{26}Al–^{26}Mg, ^{53}Mn–^{53}Cr, ^{60}Fe–^{60}Ni, and Th–U disequilibrium analysis types, and U–Th–Pb isotopic data obtained for zircon, titanite, perovskite, monazite, xenotime and baddeleyite. Correction to measured Pb-isotopic, Pb/U and Pb/Th ratios for the presence of common Pb may be made using measured ^{204}Pb counts, or the ^{207}Pb or ^{208}Pb counts following subtraction from these of the radiogenic component. Common-Pb corrections may be made automatically, using a (user-specified) common-Pb isotopic composition appropriate for that on the sample surface, or for that incorporated within the mineral at the time of its crystallization, depending on whether the ^{204}Pb count rate determined for the Unknown is substantially higher than the average ^{204}Pb count rate for all session standards. Pb/U inter-element fractionation corrections are determined using an interactive $\log_e$–$\log_e$ plot of common-Pb corrected $^{206}Pb/^{238}U$ ratios against any nominated fractionation-sensitive species pair (commonly $^{238}U^{16}O^+/^{238}U^+$) for session standards. Also displayed with this plot are calculated Pb/U and Pb/Th calibration line regression slopes, y-intercepts, calibration uncertainties, standard ^{204}Pb- and ^{208}Pb-corrected $^{207}Pb/^{206}Pb$ dates and other parameters useful for assessment of the calibration-line data. Calibrated data for Unknowns may be automatically grouped according to calculated date and displayed in color on interactive Wetherill Concordia, Tera–Wasserburg Concordia, Linearized Gaussian ("Probability Paper") and Gaussian-summation probability density diagrams.

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Keywords: Secondary ion mass spectrometry; SIMS; SHRIMP; Isotope analysis; Radiometric age; Geochronology; Data reduction; Visual Basic

☆ Code available from server at http://conch.perthshrimp.com

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1. Introduction

Ion microprobes are now widely applied to the determination of trace-element concentrations, isotopic analyses and U–Pb and Th–Pb formation ages of a wide range of minerals (e.g. zircon, monazite, xenotime, titanite, perovskite, baddeleyite and galena). In practice, this technique can generate vast quantities of numerical data that require complex processing in order to extract useful information. The secondary ion spectrum formed during ion-microprobe analysis of even chemically simple minerals is commonly highly complex, and will usually include monomers, molecular and multiply charged species. Furthermore, the relative efficiency of emission of secondary ions from the sample during ion-microprobe analysis commonly varies unpredictably during the analysis session, requiring the periodic analysis of standards of known composition in order to correct for this instrumentally induced drift. Data processing therefore usually involves complex calibration and isobaric corrections before the measurements can be converted into a meaningful result. The monitoring and sound interpretation of ion-microprobe data commonly requires a high degree of understanding of a large number of complex parameters, yet a trend is emerging in which non-specialist users are required to acquire and process ion-microprobe data under relatively little supervision.

CONCH is a computer program coded in Microsoft Excel Visual Basic for Applications that allows flexible, interactive processing of ion-microprobe geochronology, isotopic and trace element data. The software runs on both Macintosh and IBM-compatible platforms and will operate most effectively using Excel '97 (Macintosh) or Excel 2000 (Windows). A freeware (Linux OpenOffice) version is also in preparation. The algorithms developed are applicable to the processing of ion-microprobe data obtained for a wide range of applications.

The aims of this contribution are to:

1. outline some features of the CONCH application and aspects of the data reduction approach, and
2. briefly describe its application to the processing of ion-microprobe zircon, titanite, perovskite, monazite, xenotime and baddeleyite U–Th–Pb, and Th–U disequilibrium analyses.

CONCH can generate processed data reports (as spreadsheets) and output files (as tab-delimited text files) containing automatically or manually edited background-corrected count rates, ratios and uncertainties and may therefore be applied to the processing of secondary ion mass spectrometry (SIMS) data obtained for a wide variety of applications. However, for the sake of brevity, this contribution outlines geochronological applications of CONCH; only limited discussion of other applications has been included herein.

Copies of the latest version of the program, a "User's Guide" that provides a comprehensive description of the software (including installation instructions and Tables describing the function of every control) and example input files may be downloaded from: http://conch.perthshrimp.com or obtained on request from d.nelson@curtin.edu.au

2. Input and output file formats

CONCH is currently adapted to read tab-delimited text data files such as those output by the Sensitive High-Resolution Ion MicroProbe (SHRIMP), but the code could be adapted to process single-collector ion-microprobe data files in other input formats. SHRIMP output (raw data) files, as well as CONCH-processed data files in several different formats, may be read directly by CONCH. All processing control parameters are assigned sensible default values but these are editable, via a Set-up dialog (see Fig. 1), prior to reading the input data file.

2.1. Input (ion-microprobe output) files

An ion-microprobe analysis commonly consists of a matrix of integers, each corresponding to the number of secondary ion counts measured over a specified integration time, acquired during one or more passes through the mass spectrum of interest. For example, SIMS U–Pb analysis of a zircon typically involves a series (commonly 4–10 sets) of measurements of the abundance of the species $^{90}Zr_2^{16}O^+$, $^{204}Pb^+$, background (for example, at mass station 204.1), $^{206}Pb^+$, $^{207}Pb^+$, $^{208}Pb^+$, $^{238}U^+$, $^{232}Th^{16}O^+$, $^{238}U^{16}O^+$ and possibly also $^{238}U^{16}O_2^+$. The count rate measured at each mass station (after subtraction of the background count rate) is proportional to the secondary ion intensity of each species, determined using an ion counter or faraday cup.

CONCH distinguishes between standard analyses and analyses of unknowns from different samples in the input file by the matching of part of the analysis

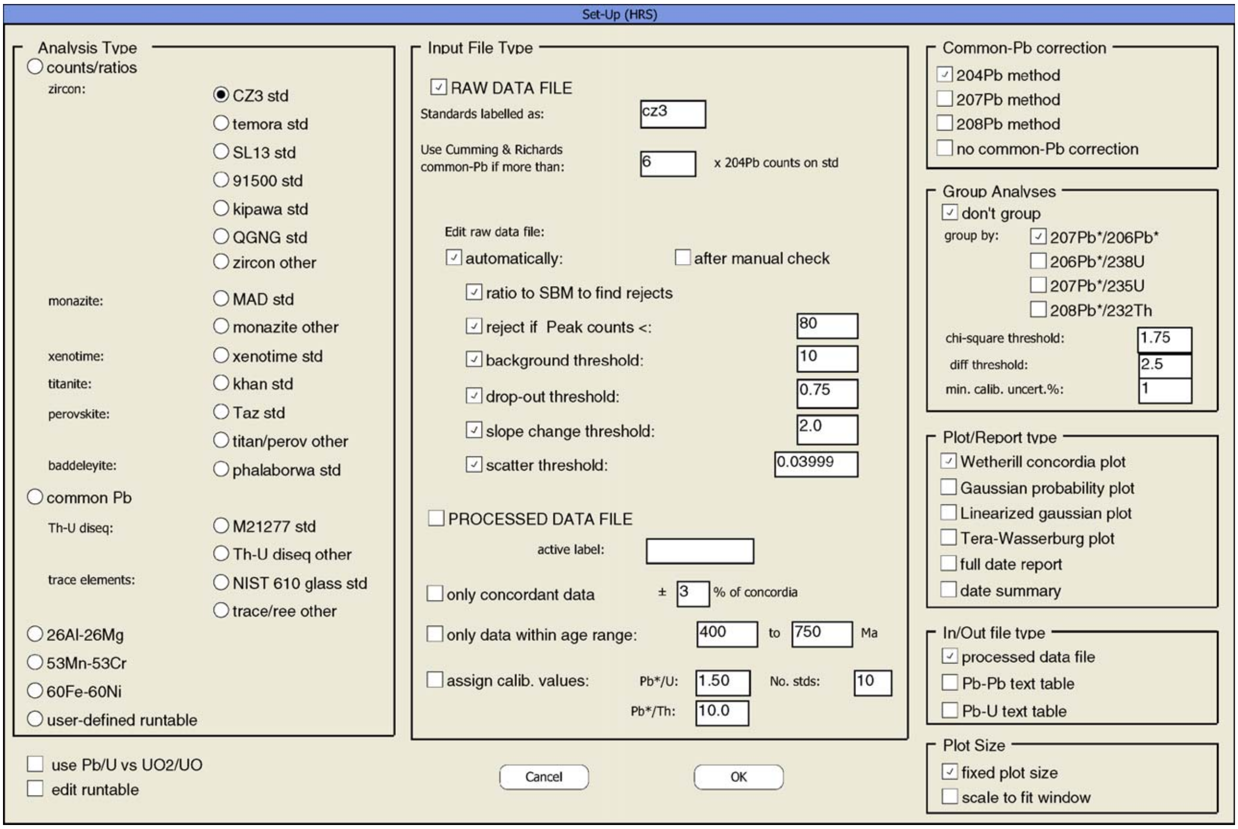

Fig. 1. Set-up dialog. Default checkboxes are checked.

label string with user-specified standard and sample label strings specified in the Set-up and Standards dialogs. The user may specify a label string to identify standard analyses in the Set-up dialog; separate labels for concentration and Pb/U standards may be defined using the Run-table dialog.

2.2. CONCH processed data output files

Following editing of the counts, CONCH directs processed data to its Report Sheet. However, to allow ion-microprobe data obtained on the same sample during different analysis sessions to be combined, grouped and plotted, processed data output by CONCH may also be written to files in a form that can also be read, combined with new data and further reprocessed by CONCH. Exceptions to this are the processed data output files generated by the Counts/Ratios, Al–Mg, Mn–Cr, Fe–Ni and REE/trace element analysis types, which cannot be input into CONCH for reprocessing. CONCH-processed data files in four different output formats may be input directly into CONCH. "Processed Data" output files are tab-delimited text files containing the processed data for each unknown in each 94-entry line (or, in the case of "Standards Calibration" output files, 102-entry line), terminated by a carriage return, in the order that they were read from the ion-microprobe (raw data) input file. The "Standards Calibration" output file format enables a comprehensive long-term record of calibration parameters obtained during the analysis of mineral standards during different sessions to be accumulated within a single "Calibration" file that may be directly read by CONCH for grouping, plotting and reporting. CONCH can also generate, and read, files containing ^{204}Pb-, ^{207}Pb- and ^{208}Pb-corrected data in a "table" text format ready for publication. Counts/Ratios, Al–Mg, Mn–Cr, Fe–Ni and REE/trace element analysis types generate output files with a much-simplified format. An example of a processed data output file generated by the Al–Mg analysis type is shown in Fig. 2.

CONCH will, as a (user-editable) default action, concatenate ".data" to the input (ion-microprobe raw data) file name to name the processed data output file. In addition to its use in determining calibration curves and sensitivity factors, each standard analysis is also processed as an unknown, using calibration values and uncertainties determined from the pooling of all session standards following editing by the user.

3. Analysis run-tables

A generalized report giving ratios and their uncertainties can be generated using CONCH's Counts/Ratios analysis type, but for a more sophisticated treatment (correction of each species for background counts, for example), CONCH requires knowledge of the identity of the mass species in the analysis. A shortcoming of acquisition data files generated by the SHRIMP acquisition software is that they do not specify which species have been measured. The CONCH user must therefore provide the species measured and measurement order in a "run-table" (see Fig. 3). CONCH includes a number of commonly used default run-tables for each mineral (and will make a context-informed guess, informing the user of this when, for example, the number of mass stations specified in the CONCH run-table selected by the user does not match that in the input file), but it may occasionally be necessary to modify a default run-table or prepare a new one. For most applications, CONCH presently allows up to 16 mass stations to be specified; for the Trace/Rare-earth analysis type, up to 32 mass stations are allowable. The mass-station order may be edited using the Run-table dialog (see Fig. 3), accessed via the Set-up dialog. In order for CONCH to use each species measured appropriately (i.e. as a calibration numerator, or to subtract the background counts from the counts obtained for all other species), CONCH identifies a set of strings (e.g. "Zr2O 196", "Pb206", "Backgrnd", "UO2 270", "Cup-in", etc.) as corresponding to mass species having a particular function. Unrecognized strings entered into the "mass station labels" editboxes and strings used inappropriately (use of the wrong species as a calibration numerator or denominator, or an attempt to generate a diagram requiring a species not included in the run-table, for example) are trapped and brought to the attention of the user.

All other analysis details (analysis label, number of sets, scans, stations, counts, integration times, analysis times and secondary beam monitor counts) are assigned for each analysis via the input (SHRIMP raw data output) file, with error-checking to notify the user of any values outside the expected range.

4. Editing of raw counts data

During measurement using an ion-microprobe, the secondary ion intensity may fluctuate with transient fluctuations in the primary ion intensity and there may be errors in peak centering of the secondary ion species of interest on the detector. The first step in the processing of ion-microprobe data is detection of peak-centering problems and aberrant counts on each species.

CONCH enables input data for all species of each analysis to be displayed for manual editing on a set of plots of counts (as checkboxes) for each mass station versus analysis time, on the Counts Sheet (see Fig. 4). Counts determined using the Secondary Beam Monitor, measured simultaneously with those of each species, are also plotted. Counting statistics-based "error bars" ($\pm\sqrt{n}$, where n is the number of counts for each measurement) may be added by selecting this option in the Plot Options dialog. A regression line is fitted through the counts obtained for each species. The user may delete any "aberrant" counts by simply clicking on (or "un-checking") their checkboxes. A dropdown control or the "Next Analysis" or "Previous Analysis" menu items in the "CONCH" worksheet menu bar enables the user to display count plots for any analysis.

In addition to the manual editing of counts for each analysis, CONCH allows automatic identification and display only of scans that include aberrant counts. For automatic identification of outliers, mass-station counts may be ratioed to counts taken on the Secondary Beam Monitor via a checkbox in the Set-up dialog. Count rates for each mass species during an analysis will not necessarily be randomly distributed about a mean value but may change variably as the secondary ion intensity changes. As a consequence, standard statistical techniques based on an assumed distribution function cannot reliably identify count outliers. Software identification of anomalous count values is therefore undertaken using a "neural network" approach, with threshold values for parameters optimized for the detection of the analytical problems commonly encountered and intended to be identified (e.g. peak-centering errors, baseline and peak spikes, etc.). Peak-centering errors occur more often during the first

CONCH Al26-Mg26 Report

26Mg/24Mgcorr ratio corrected for mass fractionation using 25Mg/24Mg = 0.12663

Delta-26Mg normalized to 26Mg/24Mg = 0.139432

uncertainties +/- sigma

Standards only

Analysis	Mg24 cts/s	Mg25 cts/s	Mg26 cts/s	Al27 cts/s	Al27/Mg24 meas	+/-	diff	Mg25/Mg24 meas	+/-	diff	Mg26/Mg24 meas	+/-	diff	Mg26/Mg24 corr	diff	f(permil/AMU)	delta 26Mg	Analysis time
std-1	203111	25716	28257	386831	1.90453	0.00522	4.22	0.12661	0.00084	-0.08	0.13912	0.00088	0	0.13916	-2.2	-0.14	-2.2	12.53
std-2	161904	20632	22695	319956	1.97621	0.00603	15.31	0.12743	0.00094	0.78	0.14018	0.00099	1.04	0.13841	5.3	6.37	5.3	13.05
std-3	165538	20967	23349	327581	1.97889	0.00597	15.9	0.12666	0.00093	-0.02	0.14105	0.00099	1.91	0.14099	11.6	0.23	11.6	13.33
std-4	174123	22745	25547	386729	2.22101	0.00641	51.88	0.13063	0.00092	4.18	0.14672	0.00098	7.55	0.13787	52.3	31.57	52.3	16.4
std-5	172021	22306	25328	387106	2.25035	0.00652	55.45	0.12967	0.00092	3.16	0.14724	0.00099	8	0.14041	56	24.03	56	16.72
std-6	174248	22769	25387	392750	2.25397	0.00649	56.27	0.13067	0.00092	4.23	0.14569	0.00098	6.56	0.13683	44.9	31.89	44.9	17.02
std-7	209701	26453	29077	390292	1.86118	0.00504	-3.98	0.12615	0.00082	-0.63	0.13866	0.00087	-0.51	0.13972	-5.5	-3.82	-5.5	18.77
std-8	203482	25692	28151	382995	1.88221	0.00516	0.06	0.12626	0.00084	-0.48	0.13835	0.00088	-0.85	0.13915	-7.8	-2.89	-7.8	19.05
std-9	202798	25657	28193	383967	1.89334	0.0052	2.14	0.12651	0.00084	-0.19	0.13902	0.00088	-0.11	0.13928	-3	-0.92	-3	19.33
std-10	203808	25756	28244	385567	1.89182	0.00518	1.86	0.12637	0.00084	-0.35	0.13858	0.00088	-0.59	0.13914	-6.1	-2	-6.1	19.6
std-11	202482	25671	28024	385966	1.90617	0.00523	4.51	0.12678	0.00084	0.12	0.1384	0.00088	-0.79	0.13807	-7.4	1.19	-7.4	19.88
std-12	208361	26577	29167	393627	1.88915	0.00512	1.38	0.12755	0.00083	1.02	0.13998	0.00088	0.96	0.13797	3.9	7.27	3.9	21.63
std-14	208687	26548	29146	399619	1.91492	0.00517	6.2	0.12721	0.00083	0.63	0.13966	0.00087	0.61	0.13838	1.7	4.62	1.7	22.02
std-15	205870	26015	28373	392532	1.9067	0.00519	4.65	0.12637	0.00083	-0.36	0.13782	0.00087	-1.44	0.1384	-11.6	-2.08	-11.6	22.28
std-16	151884	18854	20270	251205	1.65393	0.00538	-41.25	0.12413	0.00096	-2.59	0.13346	0.001	-5.54	0.13888	-42.9	-19.73	-42.9	23.9
std-17	239507	29275	31851	392198	1.63752	0.00425	-55.09	0.12223	0.00076	-5.67	0.13299	0.00079	-7.45	0.14273	-46.2	-34.76	-46.2	0.42
std-18	235289	29419	31598	383620	1.63042	0.00427	-56.41	0.12503	0.00077	-2.06	0.13429	0.0008	-5.78	0.13774	-36.8	-12.59	-36.8	0.68
averages					1.92072			0.12684			0.13948			0.13901				
weighted means					1.88187			0.12668			0.13912			0.13905		0.39	-2.7	
estimated uncertainties (+/-1 std dev)					0.00128			0.00021			0.00022			0.00022			4.3	
observed uncertainties (+/-1 std dev)					0.04362			0.00051			0.00096			0.00035		3.64	9.6	

Standards and Unknowns

Analysis	Mg24 cts/s	Mg25 cts/s	Mg26 cts/s	Al27 cts/s	Al27/Mg24 meas	+/-	diff	Mg25/Mg24 meas	+/-	diff	Mg26/Mg24 meas	+/-	diff	Mg26/Mg24 corr	diff	f(permil /AMU)	delta 26Mg	Mg24 Integ time (s)	Mg25 Integ time (s)	Backgnd Integ time (s)	Mg26 Integ time (s)	Al27 Integ time (s)	Analysis time
std-1	203111	25716	28257	386831	1.90453	0.00522	6.4	0.12661	0.00084	0.92	0.13912	0.00088	1.87	0.13916	-2.2	-0.14	-2.2	5	30	10	30	5	12.53
std-2	161904	20632	22695	319956	1.97621	0.00603	17.29	0.12743	0.00094	1.68	0.14018	0.00099	2.72	0.13841	5.3	6.37	5.3	5	30	10	30	5	13.05
std-3	165538	20967	23349	327581	1.97889	0.00597	17.9	0.12666	0.00093	0.88	0.14105	0.00099	3.61	0.14099	11.6	0.23	11.6	5	40	10	40	5	13.33
unk-1	16181	2023	2293	439237	27.14542	0.2173	116.31	0.12502	0.00295	-0.27	0.14171	0.00316	1.35	0.14536	16.3	-12.63	16.3	5	40	10	40	5	14.63
unk-2	13191	1725	1916	455098	34.49944	0.3047	107.09	0.13077	0.00335	1.47	0.14525	0.00355	2.2	0.1362	41.7	32.66	41.7	5	40	10	40	5	15.02
unk-2.1	13502	1708	1896	438574	32.48135	0.2838	107.86	0.1265	0.00325	0.21	0.14042	0.00344	0.87	0.14074	7.1	-1.13	7.1	5	40	10	40	5	15.83
std-4	174123	22745	25547	386729	2.22101	0.00641	53.99	0.13063	0.00092	5.13	0.14672	0.00098	9.3	0.13787	52.3	31.57	52.3	5	40	10	40	5	16.4
std-5	172021	22306	25328	387106	2.25035	0.00652	57.54	0.12967	0.00092	4.1	0.14724	0.00099	9.75	0.14041	56	24.03	56	5	40	10	40	5	16.72
std-6	174248	22769	25387	392750	2.25397	0.00649	58.38	0.13067	0.00092	5.18	0.14569	0.00098	8.31	0.13683	44.9	31.89	44.9	5	40	10	40	5	17.02
unk-3.1	27105	3438	3778	473539	17.47075	0.10911	142.97	0.12684	0.0023	0.44	0.13939	0.00242	0.8	0.13893	-0.3	1.62	-0.3	5	40	10	40	5	17.62
unk-3.2	22117	2775	2998	417814	18.89089	0.13034	130.58	0.12547	0.00253	-0.14	0.13555	0.00264	-0.71	0.13809	-27.8	-9.24	-27.8	5	40	10	40	5	17.93
unk-3.3	23243	2882	3134	434075	18.67589	0.12574	133.65	0.124	0.00245	-0.75	0.13484	0.00257	-1.01	0.14061	-32.9	-20.75	-32.9	5	40	10	40	5	18.25
std-7	209701	26453	29077	390292	1.86118	0.00504	-1.81	0.12615	0.00082	0.38	0.13866	0.00087	1.39	0.13972	-5.5	-3.82	-5.5	5	40	10	40	5	18.77
std-8	203482	25692	28151	382995	1.88221	0.00516	2.23	0.12626	0.00084	0.51	0.13835	0.00088	1.02	0.13915	-7.8	-2.89	-7.8	5	40	10	40	5	19.05
std-9	202798	25657	28193	383967	1.89334	0.0052	4.31	0.12651	0.00084	0.81	0.13902	0.00088	1.76	0.13928	-3	-0.92	-3	5	40	10	40	5	19.33
std-10	203808	25756	28244	385567	1.89182	0.00518	4.04	0.12637	0.00084	0.64	0.13858	0.00088	1.28	0.13914	-6.1	-2	-6.1	5	40	10	40	5	19.6
std-11	202482	25671	28024	385966	1.90617	0.00523	6.69	0.12678	0.00084	1.12	0.1384	0.00088	1.08	0.13807	-7.4	1.19	-7.4	5	40	10	40	5	19.88
unk-1.1	259427	31839	34989	481487	1.85597	0.00452	-3.13	0.12273	0.00073	-4.14	0.13487	0.00077	-3.25	0.14358	-32.7	-30.8	-32.7	5	40	10	40	5	20.68
unk-1.2	274037	34567	37030	515102	1.87968	0.00444	2.02	0.12614	0.00072	0.43	0.13513	0.00075	-3	0.13618	-30.9	-3.87	-30.9	5	40	10	40	5	20.95
unk-1.3	287614	36038	38543	523809	1.82122	0.00423	-11.32	0.1253	0.0007	-0.73	0.13401	0.00073	-4.58	0.13687	-38.9	-10.52	-38.9	5	40	10	40	5	21.22
std-12	208361	26577	29167	393627	1.88915	0.00512	3.58	0.12755	0.00083	2.04	0.13998	0.00088	2.86	0.13797	3.9	7.27	3.9	5	40	10	40	5	21.63
std-14	208687	26548	29146	399619	1.91492	0.00517	8.43	0.12721	0.00083	1.64	0.13966	0.00087	2.5	0.13838	1.7	4.62	1.7	5	40	10	40	5	22.02
std-15	205870	26015	28373	392532	1.9067	0.00519	6.85	0.12637	0.00083	0.64	0.13782	0.00087	0.43	0.1384	-11.6	-2.08	-11.6	5	40	10	40	5	22.28
unk-1.4	264646	32715	35391	509256	1.92429	0.00461	11.39	0.12362	0.00072	-2.97	0.13373	0.00076	-4.77	0.14032	-40.9	-23.78	-40.9	5	40	10	40	5	22.63
unk-1.5	208679	25984	27765	374774	1.79594	0.00491	-14.87	0.12452	0.00082	-1.57	0.13305	0.00085	-5.05	0.13761	-45.8	-16.7	-45.8	5	40	10	40	5	22.92
unk-1.6	211949	26030	28428	377868	1.78282	0.00484	-17.72	0.12281	0.00081	-3.66	0.13413	0.00085	-3.82	0.14259	-38.1	-30.14	-38.1	5	40	10	40	5	23.18
unk-1.7	213600	26456	28718	378573	1.77235	0.0048	-20	0.12386	0.00081	-2.39	0.13445	0.00085	-3.46	0.14053	-35.7	-21.88	-35.7	5	40	10	40	5	23.47
std-16	151884	18854	20270	251205	1.65393	0.00538	-39.56	0.12413	0.00096	-1.74	0.13346	0.001	-3.93	0.13888	-42.9	-19.73	-42.9	5	40	10	40	5	23.9
std-17	239507	29275	31851	392198	1.63752	0.00425	-53.31	0.12223	0.00076	-4.64	0.13299	0.00079	-5.48	0.14273	-46.2	-34.76	-46.2	5	40	10	40	5	0.42
std-18	235289	29419	31598	383620	1.63042	0.00427	-54.66	0.12503	0.00077	-1	0.13429	0.0008	-3.81	0.13774	-36.8	-12.59	-36.8	5	40	10	40	5	0.68
averages					6.48828			0.12613			0.13826			0.13936									
weighted means					1.87048			0.12583			0.13743			0.13924		-6.35	-1.4						
estimated uncertainties (+/-1 std dev)					0.00103			0.00017			0.00017			0.00017			2.6						
observed uncertainties (+/-1 std dev)					0.06523			0.0004			0.00072			0.00037		9.5	6.6						

Fig. 2. Processed data output file. Example shown is of ^{26}Al–^{26}Mg data.

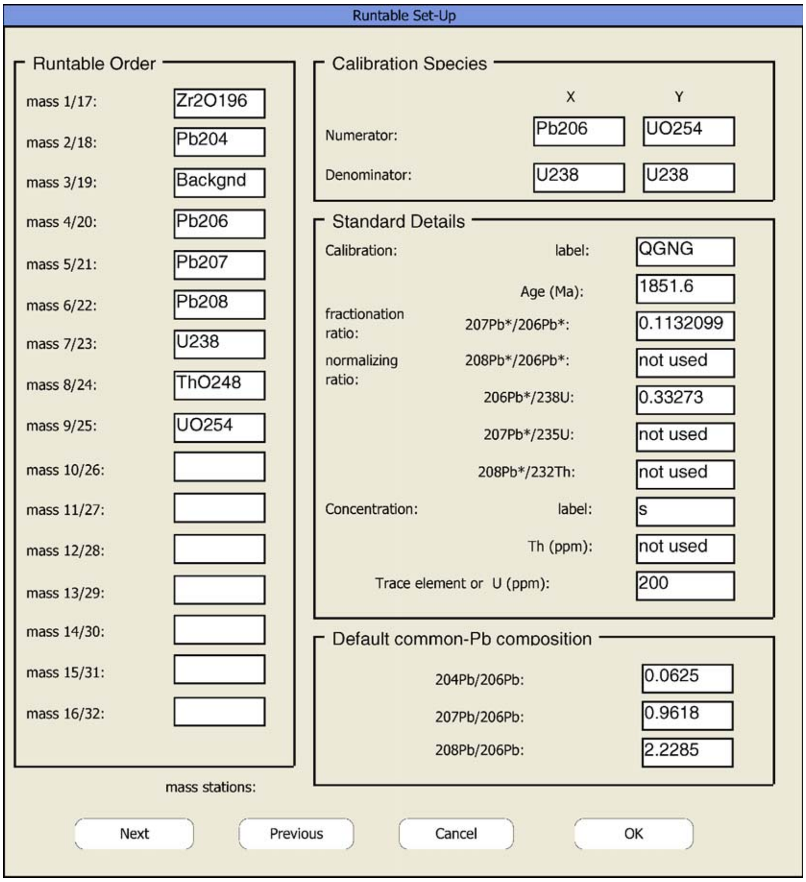

Fig. 3. Run-table dialog.

measurement of a secondary ion species. One parameter is optimized to identify this sort of outlier by comparing the difference in the slope and scatter of all counts from each mass station, with the slope and scatter for all counts less each one of the count measurements. A second parameter (the "drop-out" parameter in Fig. 1) may be optimized to identify other peak-centering errors (anomalously low counts) occurring after the first measurement. A Background counts upper threshold value may also be specified in Set-up to identify spikes at the background (e.g. 204.1) mass stations. Data from stations for which anomalous counts are automatically detected will be displayed in diagrams of counts (plotted as checkboxes) versus analysis time, for assessment by the user. Extensive testing has confirmed that, when the correct threshold settings are used, this automated data editing can reliably identify all known instrument-related measurement aberrations, including secondary beam spikes and centering failures (drop-outs). Automated editing thus enables convenient, consistent and efficient identification of aberrant counts. The threshold values of these parameters may be edited in the Set-up dialog.

Following editing, CONCH determines a count rate for each peak at the mid-time of the analysis by linear regression of the (edited) peak counts. Provided a background mass station has been identified in the run-table, the background count rate (calculated as the arithmetic average rate if more than one Background mass station has been specified) will then be subtracted from each of the mid-time count rates. Ratios of interest and their uncertainties are then calculated using mid-time count rates. Uncertainties based on counting statistics cannot take into account non-linear change (for example, exponential growth or decay) in the secondary ion intensity during the analysis. However, this systematic "within-analysis" effect should not be confused with uncertainties applicable to an entire analysis; augmentation or

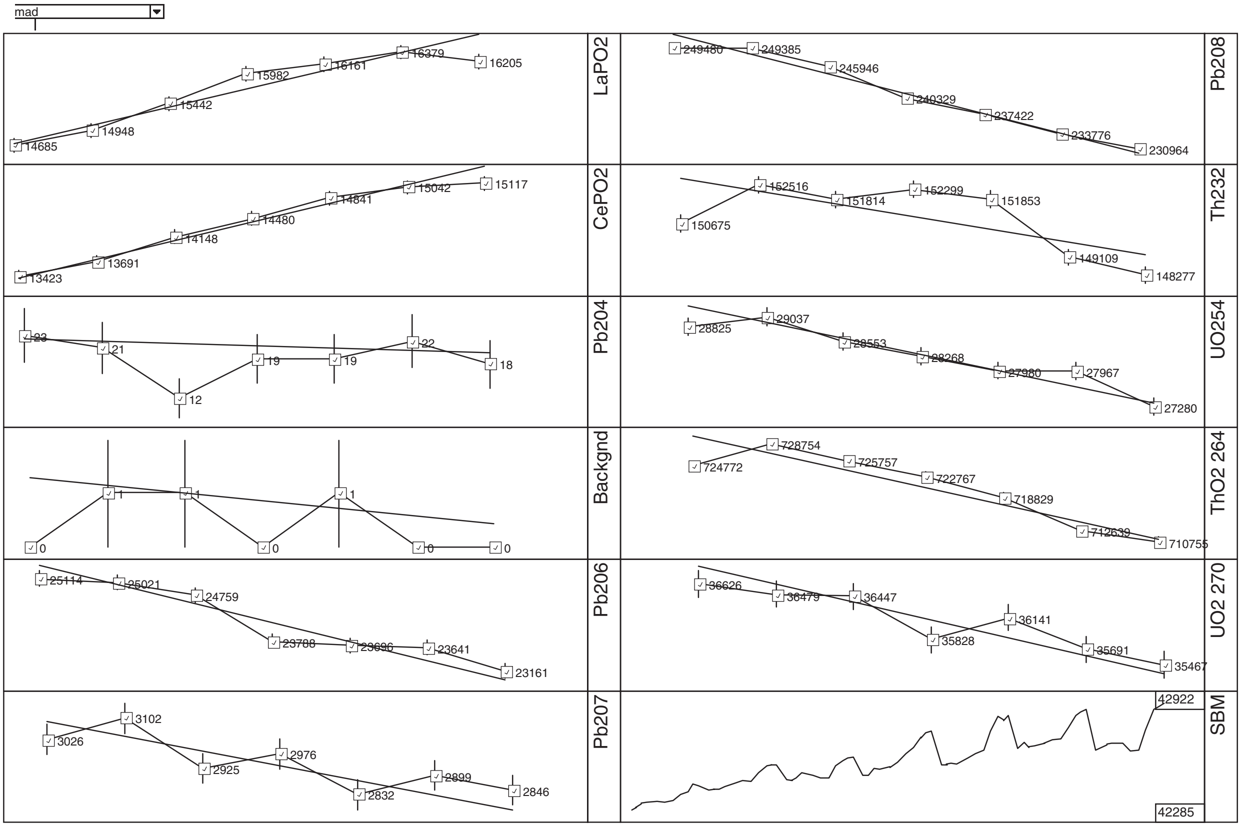

Fig. 4. Counts Sheet.

reduction of uncertainties, due (for example) to the success of exponential or spline curve fitting of the change in secondary ion intensity during the course of the analysis, may introduce systematic (i.e. non-random) biases into the distribution of ratios obtained for pooled analyses about their weighted mean values. Secondary ion intensity ''noise'' (arising from instability in the primary ion intensity for example) may increase the scatter of analyses around the weighted mean value beyond that based on counting statistics but because this additional uncertainty is random, it will not significantly bias the mean value of pooled analyses. Additional uncertainty that may be attributable to a high level of random ''noise'' in the secondary ion intensity is occasionally evident in the slightly elevated χ^2 parameter obtained for pooled analyses (see below).

5. Correction for the presence of common Pb

In order to calculate $^{206}Pb^*/^{238}U$ (throughout this contribution, an asterisk indicates radiogenic-Pb isotopic abundance), $^{207}Pb^*/^{235}U$, $^{208}Pb^*/^{232}Th$ and/or $^{207}Pb^*/^{206}Pb^*$ dates for Zircon, Monazite, Xenotime, Titanite/Perovskite, Baddeleyite/Common-Pb and Th–U Disequilibrium analysis types, measured Pb/U, Pb/Th and Pb isotopic ratios must be corrected for the presence of non-radiogenic (or common) Pb. The contribution from the common-Pb correction to uncertainties in Pb*/U, Pb*/Th and $^{207}Pb^*/^{206}Pb^*$ dates varies as a function of age and can be substantial, particularly for dates younger than ca. 1 Ga (see Fig. 5). Abundance of the species ^{204}Pb is not affected by radiogenic decay, so the amount of common-Pb present is proportional to the ^{204}Pb abundance detected during the analysis. The default method for correcting for the presence of common Pb uses the ^{204}Pb abundance, but CONCH also offers the option of making no corrections, or corrections to Pb*/U and Pb*/Th ratios for the presence of common Pb using the ^{207}Pb- and ^{208}Pb-methods of Compston et al. (1984); these results are written to, and can be read directly and plotted by CONCH from the ''Processed Data'' output files. Assumptions required by these methods for the determination of meaningful Pb*/U and

Pb*/Th ratios are outlined in Compston et al. (1984).

Common Pb detected during ion-microprobe analysis of high-quality standards may have been added during conductive Au-coating of the surface of the epoxy mount. The proportion of ''inherent'' common Pb derived from within the mineral structure during analyses of unknowns may be estimated by subtraction of the session average ^{204}Pb counts (i.e. that derived from the mount surface) obtained for analyses on standards (which usually have insignificant inherent common-Pb) from the measured ^{204}Pb counts. This ''inherent'' common Pb may have been incorporated into the mineral during or possibly sometime after crystallization. Therefore, a common-Pb isotopic composition appropriate for the age of the mineral, such as that of the ore Pb growth curve of Cumming and Richards (1975), is appropriate. For analyses of unknowns with ^{204}Pb counts substantially higher than that measured on standards during the analysis session, CONCH incorporates an option for specifying common-Pb compositions calculated using the method of Cumming and Richards (1975). When ^{204}Pb counts (for monazite analyses, corrected for excess ^{204}Pb counts) on unknowns exceed a threshold value specified in the Set-up dialog multiplied by the average ^{204}Pb counts measured on the session standards (also corrected for excess ^{204}Pb counts where appropriate), common-Pb corrections are made using Cumming and Richards (1975) model compositions. The default but user-editable common Pb composition is specified in the Run-table dialog.

6. Editing of the session standards and determination of Pb/U calibration parameters

6.1. Calculation of Pb*/U dates

Due to ionization efficiency differences during sputtering, the representation of ion species in the secondary ion mass spectrum differs from their abundance in the target mineral. Provided that the analysis conditions are constant, the magnitude of this ''inter-element fractionation'' effect for any specific mineral analyzed during an analysis session is usually approximately constant. CONCH corrects for ''inter-element fractionation'' between Pb and U during any single analysis session, and determines

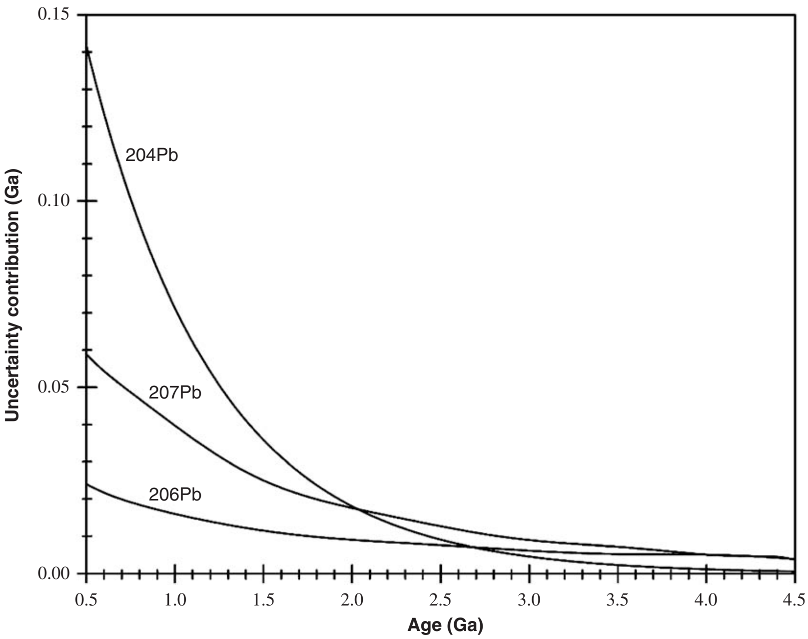

Fig. 5. Comparison of contribution to uncertainties in ^{207}Pb/^{206}Pb dates from counting statistics uncertainties associated with measurement of ^{204}Pb, ^{206}Pb and ^{207}Pb abundances. At younger dates, uncertainty in measurement of ^{204}Pb dominates age uncertainty, whereas for dates older than 2.5 Ga, uncertainty in ^{206}Pb and ^{207}Pb predominate. Curves assume 750 ppm U. For lower U concentrations, ^{204}Pb uncertainty dominates to older dates (i.e. assuming 100 ppm U, ^{204}Pb uncertainty > both ^{206}Pb and ^{207}Pb uncertainties for dates $\leqslant$3.0 Ga).

$^{206}Pb^*/^{238}U$ ratios (and Pb/U dates) for unknowns, using the simple relationship:

$$\frac{a_{unk}}{a_{std}} = \frac{A_{unk}}{A_{std}}, \tag{1}$$

where a_{unk} is the observed $^{206}Pb^*/^{238}U$ ratio for the unknown, a_{std} is the observed $^{206}Pb^*/^{238}U$ ratio for the standard, A_{unk} is the fractionation-corrected $^{206}Pb^*/^{238}U$ ratio calculated for the unknown and A_{std} is the "true" $^{206}Pb^*/^{238}U$ for the standard (for the CZ3 zircon standard, $A_{std} = 0.0914$, corresponding to a $^{206}Pb^*/^{238}U$ date of 564 Ma; Nelson, 1997). The $^{206}Pb^*$ abundance used is the radiogenic ^{206}Pb abundance; for standard analyses, this correction uses the ^{204}Pb counts determined during each standard analysis and a common-Pb $^{204}Pb/^{206}Pb$ ratio equivalent to that specified in the Run-table dialog (usually that of Broken Hill common Pb ore).

The observed $^{206}Pb^*/^{238}U$ ratio for a standard (a_{std}) is not constant within a session but varies unpredictability with instrument set-up, secondary ion tuning, and operator and sample parameters. Variation in Pb*/U ratios is correlated with variation in the ratio $^{238}U^{16}O/^{238}U$ (as well as with $^{238}U^{16}O_2/^{238}U$ and $^{238}U^{16}O_2/^{238}U^{16}O$ variation; see below). The relationship between $^{206}Pb^*/^{238}U$ and $^{238}U^{16}O/^{238}U$ variation determined for zircons analyzed using SHRIMP was earlier considered by Compston et al. (1984) to follow a quadratic law. However, Claoué-Long et al. (1995) suggested that the relationship between these parameters may be simplified to a power law of the form:

$$\frac{^{206}Pb^+}{^{238}U^+} = \alpha \times \left(\frac{^{238}U^{16}O^+}{^{238}U^+}\right)^k. \tag{2}$$

The value of α in Eq. (2) must be determined from sets of analyses obtained on the standard for each session, or for part of each session if the relationship between these parameters is unstable. On the basis of an investigation of standard analyses obtained during many sessions, Claoué-Long et al. (1995) determined empirically that, for the mineral zircon, $k \sim 2.0$ (see Eq. (2)) and may be assumed to be constant between analysis sessions (although it is commonly difficult to determine whether the value of k is constant within a single analysis session). As this "power law" relationship results in a linear correlation with slope $= k$ on a $\log_e - \log_e$ diagram, it is usually more convenient to plot $\log_e[Pb^*/^{238}U]$ against $\log_e[^{238}U^{16}O/^{238}U]$, rather than use the ratios $Pb^*/^{238}U$ and $^{238}U^{16}O/^{238}U$. CONCH calculates the slope and y-intercept of the $\log_e$–$\log_e$ calibration correlation, using the (user-specified) calibration species pairs in the Run-table dialog, and displays these in the Standards dialog (Fig. 6). For the processing of unknowns, the user may accept the default slope (i.e. $k = 2.0$ for zircon) in the "Slope Used" textbox of the Standards dialog, or may insert the calculated regression slope (given in the Regression Slope textbox) if this is preferred. For Zircon, Xenotime and Titanite/Perovskite analysis types, the default calibration ratios are $\log_e[Pb^*/^{238}U]$ and $\log_e[^{238}U^{16}O/^{238}U]$, whereas for the Monazite analysis type, the default ratios are $\log_e[Pb^*/^{238}U^{16}O]$ and $\log_e[^{238}U^{16}O_2/^{238}U^{16}O]$. CONCH fixes the position of the correlation line using weighted mean $\log_e$ values of the calibration ratios specified in the Run-table dialog obtained for the (user-edited) session standards. Using the observed $^{238}U^{16}O/^{238}U$ (or $^{238}U^{16}O_2/^{238}U^{16}O$ or $^{238}U^{16}O_2/^{238}U$, depending on that specified in the Run-table dialog) value for unknowns, the corresponding $^{206}Pb^*/^{238}U$ ratios along the correlation line are determined.

For the determination of Th/U ratios in zircon, CONCH uses the empirically determined relationship between $^{232}Th^+/^{238}U^+$ and $^{238}U^{16}O^+/^{238}U^+$ for zircon described by Williams et al. (1996)

$$\frac{^{232}Th}{^{238}U} = \frac{^{232}Th^{16}O}{^{238}U^{16}O} \times \left[0.03446 \times \left(\frac{^{238}U^{16}O}{^{238}U}\right) + 0.8680\right]. \tag{3}$$

$^{208}Pb^*/^{232}Th$ dates for zircon are calculated using:

$$\frac{^{208}Pb^*}{^{232}Th} = \frac{^{206}Pb^*}{^{238}U} \times \frac{^{208}Pb^*}{^{206}Pb^*} \bigg/ \frac{^{232}Th}{^{238}U}. \tag{4}$$

CONCH determines $^{208}Pb^*/^{232}Th$ dates for monazite applying the simple relationship given in Eq. (1), where a_{unk} is the observed $^{208}Pb^*/^{232}Th$ ratio for the unknown, a_{std} is the "corrected" $^{208}Pb^*/^{232}Th$ ratio for the monazite standard, A_{unk} is the fractionation-corrected $^{208}Pb^*/^{232}Th$ ratio calculated for the unknown and A_{std} is the "true" $^{208}Pb^*/^{232}Th$ ratio for the monazite standard. The "corrected" $^{208}Pb^*/^{232}Th$ ratio for each unknown is calculated using the observed $^{232}Th^{16}O_2/^{232}Th$ ratio and assuming a linear relationship between

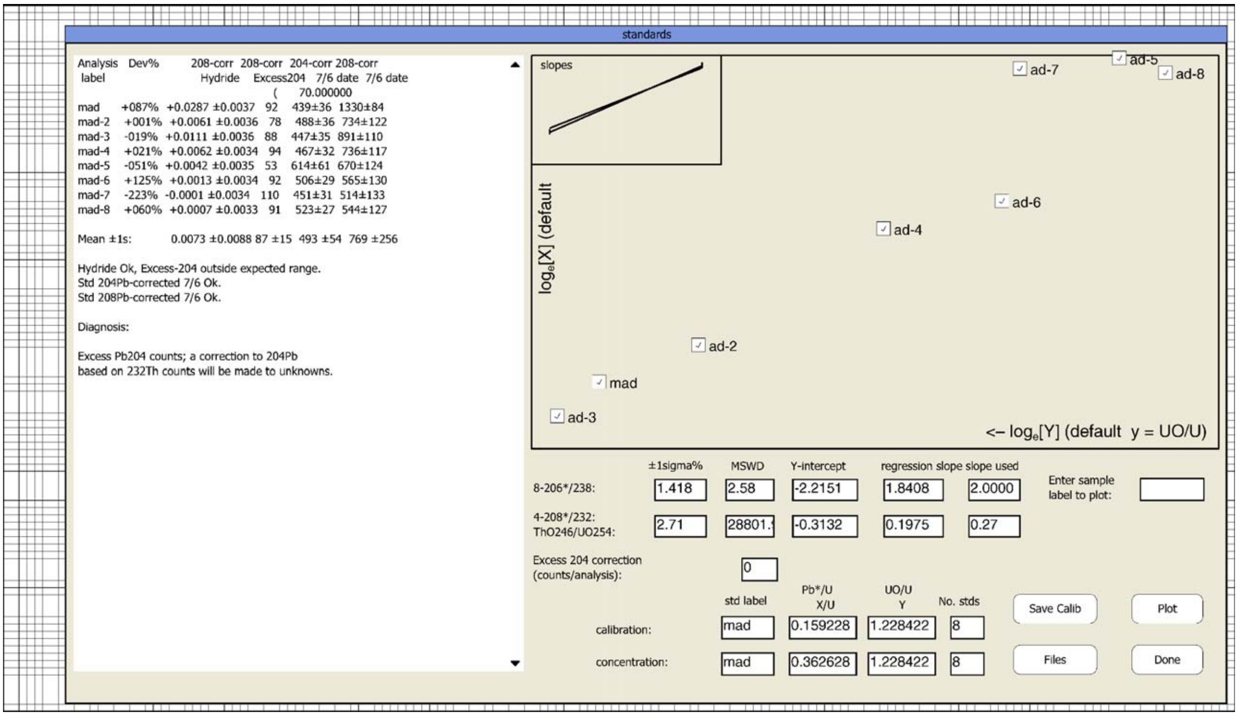

Fig. 6. Standards dialog. To alleviate congestion on calibration plot, checkbox labels have been shortened; only last 4 characters are shown.

^{208}Pb*/^{232}Th and ^{232}Th^{16}O$_2$/^{232}Th values:

$$\frac{^{208}\text{Pb}^*}{^{232}\text{Th}} = \left(\frac{^{208}\text{Pb}^*}{^{232}\text{Th}}\right)_{\text{meas}} \times \left(\frac{^{208}\text{Pb}^*}{^{232}\text{Th}}\right)_{\text{std}} \div \left\{\text{slope} \times \left(\frac{^{232}\text{Th}^{16}\text{O}_2}{^{232}\text{Th}}\right)_{\text{meas}} + y\text{ intercept}\right\}, \tag{5}$$

where slope and y-intercept is the slope and y-intercept of the ^{208}Pb*/^{232}Th and ^{232}Th^{16}O$_2$/^{232}Th calibration line determined from the (user-edited) session standard analyses. The calculated regression slope and y-intercept of the calibration line are displayed in textboxes in the Standards dialog. Uncertainties in ^{208}Pb*/^{232}Th ratios for individual monazite analyses do not include uncertainty associated with the determination of the Pb*/Th calibration line, but pooled ^{208}Pb*/^{232}Th dates include an uncertainty estimate based on the reproducibility of the standard ^{208}Pb*/^{232}Th measurements during the analysis session. Uncertainties cited for monazite ^{208}Pb*/^{232}Th dates may be based on the ''observed'' scatter about the weighted mean ^{208}Pb*/^{232}Th ratio of pooled analyses. A minimum uncertainty for Pb*/U may be specified in the Set-up dialog; a minimum uncertainty of 1% ($\pm 1\sigma$) is recommended.

6.2. Editing and assessment of data obtained for standards

For Zircon, Monazite, Xenotime, Titanite/Perovskite and Th–U Disequilibrium analysis types, log$_e$[^{206}Pb*/^{238}U] ratios obtained on the standard are plotted in the Standards dialog plot window (see Fig. 6) as checkboxes against log$_e$[^{238}U^{16}O$^+$/^{238}U$^+$] (or log$_e$[^{238}U^{16}O$_2^+$/^{238}U^{16}O$^+$]; the ratios plotted are the default ratios, or those specified in the Run-table dialog if this dialog's ''OK'' button was used). Standard analyses can be deleted from the calibration line by clicking on their checkboxes within the Standards dialog plot diagram. Also shown for comparison in the Standards dialog are an uncertainty-weighted regression line of these parameters for the standards and a line with the default slope (i.e. usually 2.0 for zircon using the calibration pair log$_e$[^{206}Pb$^+$/^{238}U$^+$]–log$_e$[^{238}U^{16}O$^+$]). The number of standards, calibration values and slopes, intercepts, uncertainties and MSWDs for uncertainty-weighted $\log_e[^{206}Pb/^{238}U]$–$\log_e[^{238}UO/^{238}U]$ (default ratios for zircon; $\log_e$ [calibration ratios] plotted are those specified in the Run-table dialog if the "OK" button on this dialog was used) and (for monazite) $^{232}Th/^{238}U$–$^{238}U^{16}O/^{238}U$ calibration regression values are also displayed in textboxes in the Standards dialog.

The presence of Pb-hydride (PbH^+) in the secondary ion mass spectrum will result in surplus counts at the ^{207}Pb and ^{208}Pb mass stations due to $^{206}Pb^1H^+$ and $^{207}Pb^1H^+$, respectively, and thus, measurement of elevated $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios. Pb isobars may be monitored by comparison of the ^{208}Pb-corrected $^{207}Pb^*/^{206}Pb^*$ ratios (corrected for common Pb using the composition specified in the Run-table dialog) obtained for analyses on the standard with the expected value. Isobaric interferences at $^{204}Pb^+$ may also be monitored by comparison of the ^{208}Pb-corrected $^{204}Pb/^{206}Pb^*$ ratios obtained for analyses on the standard with the expected value for this ratio. CONCH enables corrections to be made for excess ^{204}Pb counts (e.g. for isobaric interference at $^{204}Pb^+$ due, for example, to deposition on the mount surface of $^{186}W^{18}O^+$ derived from the tungsten heating filament commonly used in the conductive Au-coating process) detected during the analysis of standards; the average excess ^{204}Pb counts determined for standard analyses during the analysis session may be subtracted from the measured ^{204}Pb counts obtained for unknown analyses determined during that session, using the "Excess-204 correction" editbox in the Standards dialog (see Fig. 6).

Excess ^{204}Pb (calculated using the ^{208}Pb-corrected ^{206}Pb count rate and the common-Pb $^{204}Pb/^{206}Pb$ ratio from the Run-table dialog), "hydride" values (based on the ^{208}Pb-corrected $^{207}Pb^*/^{206}Pb^*$ ratio), and ^{204}Pb- and ^{208}Pb-corrected $^{207}Pb^*/^{206}Pb^*$ dates, with uncertainties for these parameters for each standard analysis, plus the calculated session means, are displayed in a scrollable list-box next to the calibration plot. Also provided within the scrollable list-box is a brief "diagnosis" statement indicating the significance of these and other relevant parameters (i.e. number of standard analyses for which the background count rates were higher than the ^{204}Pb count rates) obtained for the analysis session, as an aid to their correct interpretation.

6.3. Determination and treatment of Pb/U calibration uncertainties*

Uncertainties determined by CONCH for individual analyses include those arising from counting statistics and in the corrections for the presence of common Pb (see Section 5 above). For individual analyses, CONCH also provides uncertainties for Pb*/U ratios that includes those arising from counting statistics and in corrections for common Pb, but augmented by a contribution associated with the determination of the Pb/U–UO/U calibration curve (i.e. in the constant α in Eq. (2) given above) based on the reproducibility of the standard Pb/U measurements.

Uncertainties in Pb*/U for age groups derived from pooled analyses may also include uncertainty in the Pb*/U calibration, E, based on the reproducibility of the Pb*/U ratios of standard measurements,

$$E = \frac{C \times \mu_n}{\sqrt{n}}, \qquad (6)$$

where C is the calibration uncertainty (σ) based on reproducibility of standard determinations, μ_n is the weighted mean Pb*/U ratio determined for pooled analyses of unknowns and n is the number of standard determinations. This uncertainty may be summed in quadrature with the other sources of uncertainty.

The validity of the addition (in quadrature) of a calibration uncertainty based on reproducibility of Pb*/U ratio measurements of standards to Pb*/U ratios obtained for unknowns has recently been the subject of contention (Compston, 1999, 2001; Black and Jagodzinski, 2003). Compston (1999, 2001) attributed scatter in excess of that attributable to counting statistics and corrections for common Pb to heterogeneity in Pb/U within the standards that would not be expected to effect analyses of unknowns. In contrast, Black and Jagodzinski (2003) attributed the excess scatter to instrumental causes that will effect analyses of both standards and unknowns. Black and Jagodzinski (2003) and Stern and Amelin (2003) presented evidence confirming that the scatter in Pb*/U ratios determined using SHRIMP and the Pb/U–UO/U calibration approach is in excess of that attributable to sample Pb/U heterogeneity. If the excess scatter in Pb*/U (and also in Pb*/UO and Pb^*/UO_2) is due to an inherent inadequacy arising from use of the UO/U ratio (and also UO_2/U and UO_2/U) to correct for the large inter-element fractionation between Pb and U during SIMS analysis, as proposed by Stern and Amelin (2003), then such uncertainty should be propagated to corrected Pb*/U ratios determined by this method. However, reproducibility in Pb*/U is also a function of U and Pb count rates, which are dependent on U and Pb abundance in the target mineral, and on common-Pb corrections. As a consequence, reproducibility of the Pb*/U ratio for standards can only approximate that appropriate for unknowns.

For pooled analyses, CONCH calculates an "observed" uncertainty, based on the observed distribution of analyses about the weighted mean value, and an "expected" uncertainty determined by the addition in quadrature of uncertainties for individual analyses determined from counting statistics and the common-Pb correction. In addition, CONCH provides the user with a choice of two other uncertainty levels for fractionation-corrected Pb*/U ratios; those based on "observed" and "expected" uncertainties but with an additional uncertainty, based on reproducibility of the session standards, added to each analysis in quadrature, and those to which an uncertainty, based on reproducibility of the session standards, has been added in quadrature to the pooled "observed" and "expected" uncertainties. Provided that the reproducibility estimated from the Pb*/U ratio for standards is appropriate for unknowns, the pooled "observed" and "expected" uncertainties should be identical. The χ^2 parameter (see below) provides a convenient means of assessing whether this is the case.

Chi-square (χ^2) tests whether the observed frequencies in a distribution differ significantly from the frequencies that might be expected according to some assumed hypothesis (Moroney, 1984, p. 249). The χ^2 parameter compares the uncertainty determined from the observed distribution of individual analyses about the weighted mean value, with the uncertainty determined by addition in quadrature of the uncertainty for individual analyses based on counting statistics, the inter-element (Pb*/U and Pb*/Th) calibration (where appropriate) and the common-Pb correction;

$$\chi^2 = \frac{1}{(n-1)} \times \sum_{i=1}^{n} \frac{(x_i - \mu_n)^2}{\sigma_n^2 + \sigma_i^2}, \tag{7}$$

where n is the number of pooled x_i values (^{207}Pb/^{206}Pb, ^{207}Pb*/^{206}Pb*, ^{206}Pb*/^{238}U, ^{207}Pb*/^{235}U or ^{208}Pb*/^{232}Th ratios), μ_n is the weighted mean of all pooled x_i values, σ_n is the uncertainty in μ_n calculated by addition of all weighted individual uncertainties in quadrature, and σ_i is the uncertainty in the ratio x_i. χ^2 values for grouped analyses of less than or equal to unity indicate that scatter about the weighted mean value determined for the grouped analyses can be accounted for by analytical sources of uncertainty alone. A χ^2 value significantly greater than unity indicates that analyses are not normally distributed about the weighted mean value and that other (geological) sources of uncertainty are present within the grouped population. In these cases, the 95% confidence uncertainty cited for dates should be based on the observed, rather than the expected, scatter about the weighted mean ^{207}Pb/^{206}Pb (or Pb*/U) ratio of pooled analyses.

7. Assignment of analyses to age groups

Analyses may be automatically assigned to ^{207}Pb/^{206}Pb or common-Pb-corrected ^{207}Pb*/^{206}Pb*, ^{206}Pb*/^{238}U, ^{207}Pb*/^{235}U or ^{208}Pb*/^{232}Th age-groups (depending on that specified in Set-up) and displayed on Wetherill Concordia (Wetherill, 1956), Tera–Wasserburg Concordia (Tera and Wasserburg, 1974) or Linearized Gaussian diagrams in a group fill color, or on a Gaussian-summation probability density diagram. For the assignment of analyses to age groups, CONCH uses a statistically rigorous algorithm based on the following procedure. Common-Pb uncorrected or radiogenic (^{207}Pb*/^{206}Pb*, ^{206}Pb*/^{238}U, ^{207}Pb*/^{235}U or ^{208}Pb*/^{232}Th) ratios are weighted according to the inverse square of the individual analytical uncertainty to determine a weighted mean ratio for all pooled analyses obtained for the sample. Analyses are then rejected from the group using two criteria. A χ^2 value (see above) is calculated for the grouped analyses. If the χ^2 value is greater than a user-editable threshold value specified in Set-up (typically, a χ^2 threshold value of 1.75 is used), geological sources of uncertainty are assumed to be present within the group and the analysis whose ratio with assigned uncertainty is most different from the weighted mean value will be excluded from the group. In addition, a measure of the difference (D) between each analysis and the population weighted mean is calculated as follows:

$$D = \frac{x_i - \mu_n}{\sqrt{\sigma_{\text{pop}}^2 + \sigma_i^2}}, \tag{8}$$

where x_i is the analysis ratio, σ_i is the analysis standard deviation, μ_n the population weighted mean and σ_{pop} is the population standard deviation. Any ratio whose calculated D value is greater than a user-editable threshold value (typically, a threshold of ± 2.5 is used) from the group weighted mean will also be deleted from the group. The weighted mean value of the remaining analyses is then recalculated. This process is repeated until all remaining analyses are within both parameter thresholds. Analyses that belong with a valid group are then excluded from the pool and the process repeated until all remaining analyses have been grouped. This grouping method is statistically conservative, in that only the minimum number of clearly resolvable dates based on the uncertainty limits assigned to each individual analysis will be identified. Analyses with assigned uncertainties overlapping more than one age group will be assigned to the larger group (i.e. group containing more analyses), as larger groups are usually identified earlier during the grouping procedure. Extensive testing has confirmed that this automated grouping method is robust and generally superior to manual (and potentially subjective) analysis grouping methods. If required, analyses may be manually reassigned between groups on the Report Sheet (see below) and replotted. Aspects of the plots such as plot size, position and font sizes, may be edited via the Plot Options dialog (Fig. 7) which is summoned by the Plot Options button on the Counts Sheet, whereas the Preferences dialog (Fig. 8), summoned from the CONCH pull-down menu, sets default operation parameters and processing preferences.

8. Plotting of unknowns

U–Pb analyses may be plotted on either Wetherill Concordia (Wetherill, 1956; Fig. 9), Tera–Wasserburg Concordia (Tera and Wasserburg, 1974;

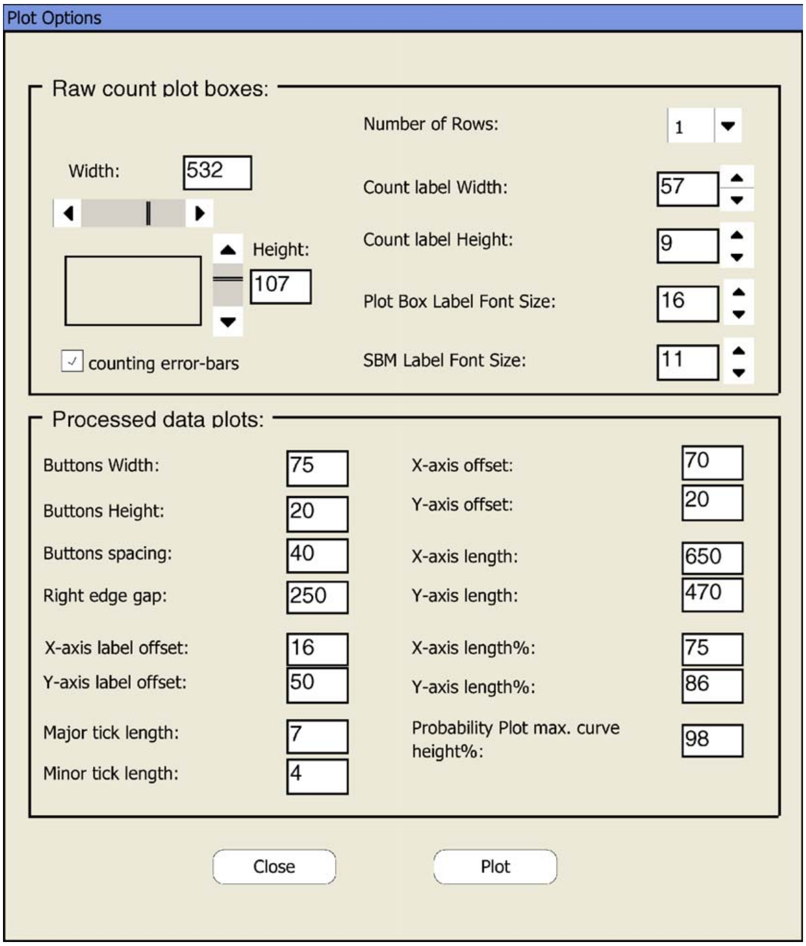

Fig. 7. Plot Options dialog.

Fig. 10), Linearized Gaussian (Fig. 11) or Gaussian-summation probability density (Fig. 12) diagrams. Where ^{206}Pb*/^{238}U and/or ^{207}Pb*/^{235}U ratios are unavailable (e.g. common Pb and baddeleyite analyses), ^{207}Pb/^{206}Pb or ^{204}Pb-corrected ^{207}Pb*/^{206}Pb* ratios may be plotted on Linearized Gaussian or Gaussian-summation probability density diagrams. CONCH initially calculates sensible x- and y-axis ranges and axis labels and tick intervals based on the ranges of the data to be plotted. The plot position, size and aspect, axis ranges, labeling, tick intervals and other aspects of the plots are user-editable and may be personalized via a "Plot Options" dialog (Fig. 7) and via the "Edit" dialogs (Figs. 13 and 14) summoned by the "Edit" button on each of the plot windows. On the Wetherill Concordia diagram, CONCH will (by default) plot the polygons in order of decreasing size, so that smaller polygons (i.e. more precise analyses) are plotted on top of, and are thus not obscured by, larger polygons.

The Gaussian-summation probability density diagram displays two probability density curves, the first of which includes all (including discordant) analyses, and the second of which includes only concordant analyses (i.e. ^{206}Pb*/^{238}U date within uncertainty of ^{207}Pb*/^{206}Pb* date at $\pm 2\sigma$ uncertainty level, or within a user-specified percentage of concordance). To generate these curves, CONCH uses the Gaussian distribution probability density function:

$$G(i) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x_i-\mu)^2/2\sigma^2}, \tag{9}$$

where x_i is the analysis ratio, μ is the mean and σ the analysis standard deviation. The probability density diagram is mainly used qualitatively with an arbitrary or no y-axis scale, to compare relative probabilities. In order to minimize rounding errors that result in steps in the curve, the curves have been scaled so that the maximum peak height of the second (concordant analyses only) curve is a fixed percentage (user-defined in the Plot Options dialog) of the y-axis length. The step size used to generate the curves can be reduced via the "Probability Plot Edit" dialog (Fig. 14) to generate smoother probability density curves once other aspects of the diagram have been ascertained.

On a Linearized Gaussian diagram (equivalent to plotting analyses on "Normal Probability Paper"), a cumulate probability density function will plot as a straight line, enabling the assumption of a Gaussian distribution of data about a mean value (i.e. individual analyses about a mean

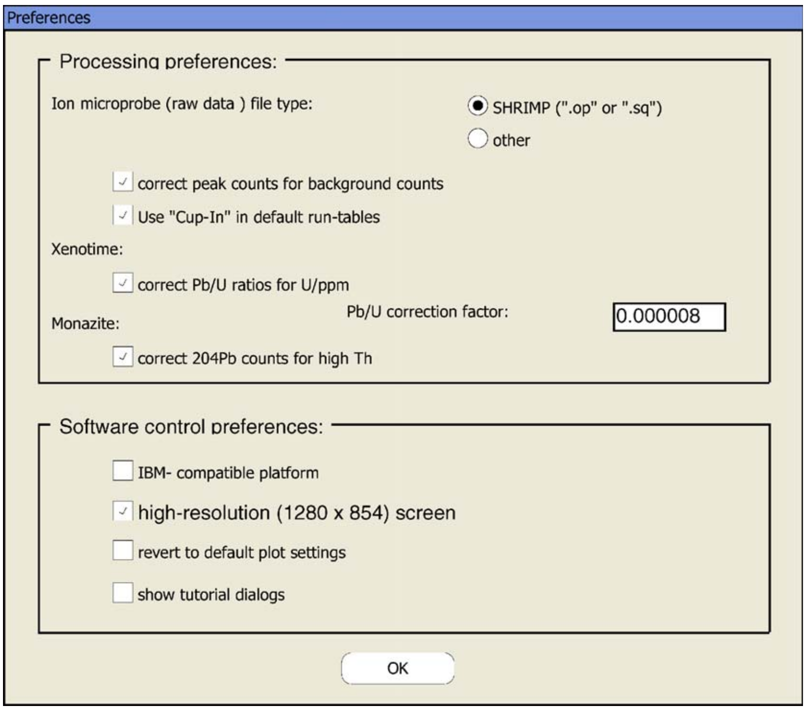

Fig. 8. Preferences dialog.

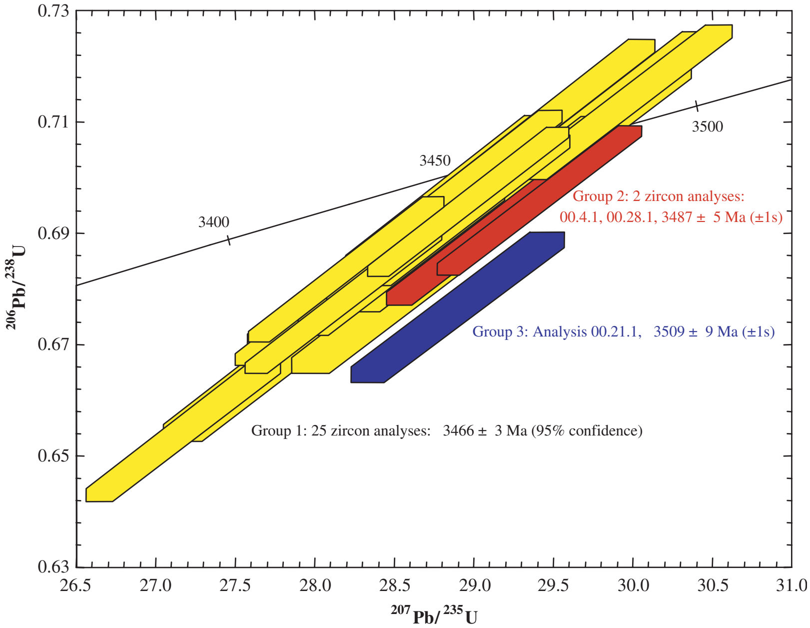

Fig. 9. Wetherill Sheet.

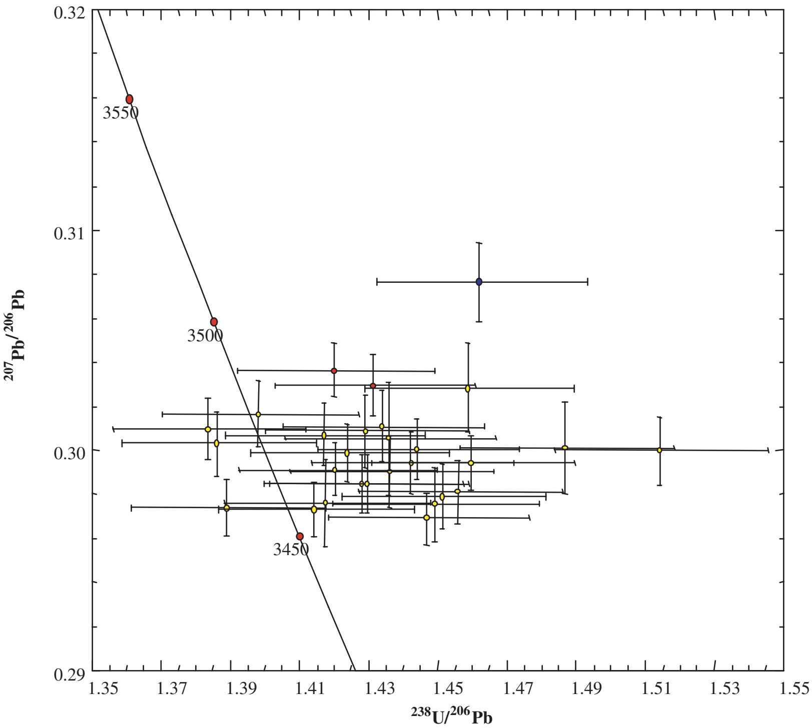

Fig. 10. Tera–Wasserburg Sheet.

$^{207}Pb^*/^{206}Pb^*$, $^{206}Pb^*/^{238}U$ or $^{207}Pb^*/^{235}U$ $^{208}Pb/^{232}Th$ date) to be assessed. In practice, this diagram has proven useful for investigation of causes behind rare examples in which a group of $^{207}Pb^*/^{206}Pb^*$, $^{206}Pb^*/^{238}U$, $^{207}Pb^*/^{235}U$ or $^{208}Pb^*/^{232}Th$ analyses do not show a Gaussian distribution about a mean

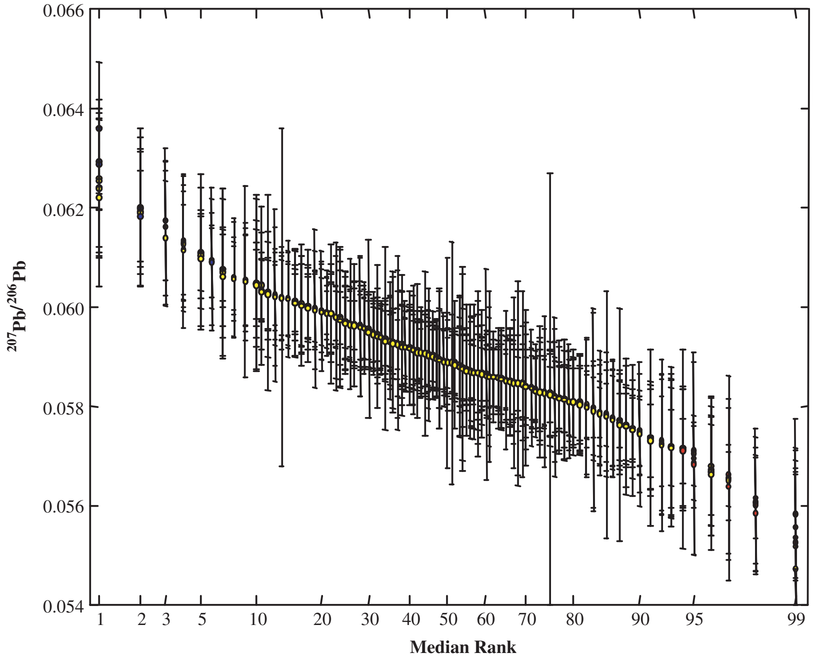

Fig. 11. An example of a Linearized Gaussian diagram generated by CONCH. Data shown are $^{207}Pb/^{206}Pb$ ratios obtained for analyses of CZ3 zircon standard on SHRIMP-2A during 2003.

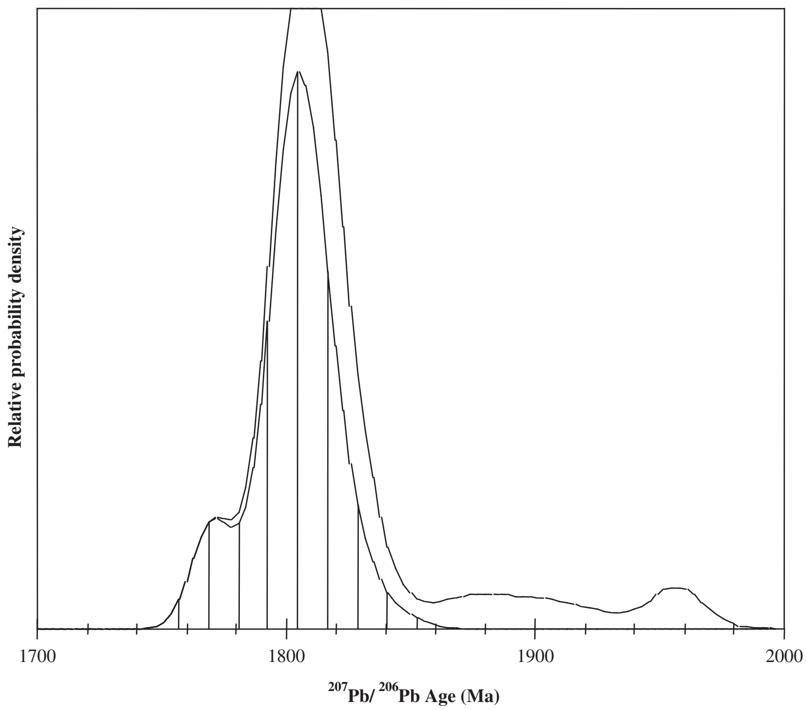

Fig. 12. Gaussian-summation probability density sheet.

value. A common cause of skewed distributions is the preferential loss of radiogenic-Pb from high-U analysis sites; on the Linearized Gaussian diagram, this manifests as a ‘‘tilted conical’’ arrangement of analyses, whereby analyses from higher-U sites and with smaller uncertainties, the uncertainty bars of

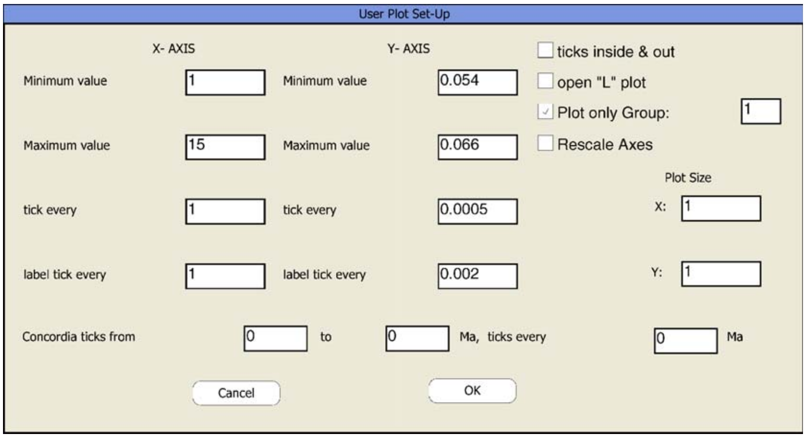

Fig. 13. Plot Edit dialog.

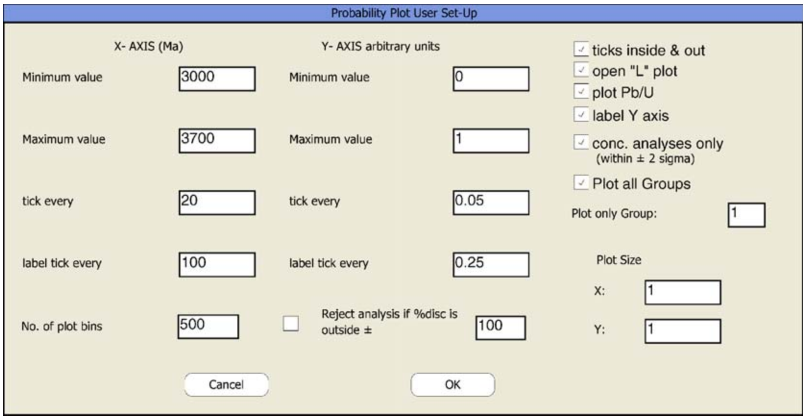

Fig. 14. Gaussian-summation probability density diagram Edit dialog.

which form a "cone", are concentrated at the lower ("tilted") right-hand side of the plot. To generate the Linearized Gaussian diagram, CONCH uses *Benard's Approximation* to calculate a median rank (MR), as a percentage, for each point:

$$MR = \frac{x_i - 0.3}{n + 0.4}, \tag{10}$$

where x_i is the analysis ratio and n is the total number of analyses.

Switching between any of the diagrams, assessment and editing of the group assignment and generation of the processed data file, is readily achieved using buttons located in the diagram windows and on the Report Sheet. Group labels that include a comma-delimited list of the analysis labels within the group, the group date and its uncertainty, may be added to analyses on the diagrams using the Summary button. The diagrams generated by CONCH may be imported into any graphics program to produce publication-quality figures.

9. Report types

The analysis type specified in the Set-up dialog determines the Report type generated by CONCH. All are initially written to the Report Sheet (see Fig. 2 for an example). Saving of a Report text file to disk may be initiated by the "Save As" dialog, summoned using the "Report File" button on the Report Sheet.

9.1. The Generalized Report type

The Generalized Report type, selected using the Counts/Ratios analysis type in the Set-up dialog, may be generated from any readable

DATEREPORT- 204Common-Pb Correction method Analyses grouped by 207Pb*/206Pb*

Group No. 1

Sample	206/238	+/-	diff	207/235	+/-	diff	208/232	+/-	diff	207/206	+/-	diff
64.02.1	0.528	0.008	-0.18	13.742	0.226	-0.2	0.0984	0.0016	0.29	0.18878	0.00055	0.06
64.03.1	0.534	0.008	0.57	13.974	0.231	0.78	0.1003	0.0016	1.41	0.18965	0.00076	1.17
64.04.1	0.537	0.008	0.88	13.995	0.225	0.89	0.0987	0.0016	0.47	0.18899	0.00054	0.43
64.05.1	0.551	0.009	2.38	14.283	0.232	2.07	0.0986	0.0016	0.42	0.18817	0.00056	-1
64.06.1	0.529	0.008	-0.09	13.794	0.224	0.02	0.0982	0.0016	0.16	0.18922	0.00057	0.8
64.07.1	0.532	0.008	0.34	13.88	0.226	0.39	0.1004	0.0016	1.49	0.18907	0.00057	0.54
64.08.1	0.522	0.008	-0.87	13.599	0.23	-0.8	0.0987	0.0016	0.48	0.18887	0.00087	0.14
64.10.1	0.534	0.008	0.52	13.91	0.226	0.52	0.0985	0.0016	0.37	0.18894	0.00062	0.3
64.12.1	0.537	0.008	0.83	14.051	0.228	1.11	0.1001	0.0015	1.35	0.18993	0.00078	1.5
64.14.1	0.525	0.01	-0.46	13.744	0.308	-0.14	0.0931	0.0019	-2.52	0.18994	0.00178	0.67
64.15.1	0.529	0.008	-0.08	13.786	0.223	-0.01	0.0959	0.0015	-1.32	0.18908	0.0006	0.54
64.16.1	0.528	0.008	-0.19	13.685	0.216	-0.46	0.0981	0.0015	0.1	0.18801	0.00045	-1.54
64.17.1	0.526	0.008	-0.46	13.728	0.224	-0.26	0.0969	0.0015	-0.63	0.1894	0.00065	0.98
64.18.1	0.523	0.008	-0.79	13.56	0.22	-1	0.0974	0.0015	-0.3	0.18808	0.00061	-1.05
64.19.1	0.523	0.008	-0.79	13.592	0.218	-0.87	0.0963	0.0015	-1.04	0.18852	0.00052	-0.41
64.20.1	0.518	0.008	-1.47	13.382	0.215	-1.83	0.0964	0.0015	-0.97	0.18751	0.00072	-1.67

n=16		Mean	Exp.s.e.	Obs.s.e.	Age(Ma)		Exp.s.e.		Obs.s.e.
206/238									
	unweighted	0.52965	0.00209	0.00196					
	weighted	0.52952	0.00207	0.00195	2739.4	8.7	-8.7	8.2	-8.2
	calibrated		0.00337	0.0033		14.2	-14.2	13.9	-13.9
	95%confidence		0.00718	0.007		30.2	-30.3	29.5	-29.7
chi-sq:	0.83								
207/235									
	unweighted	13.7941	0.05762	0.05489					
	weighted	13.7886	0.0569	0.05554	2735.3	3.9	-3.9	3.8	-3.8
	calibrated		0.0895	0.0887		6.1	-6.2	6.1	-6.1
	95%confidence		0.1908	0.189		13	-13.2	12.9	-13.1
chi-sq:	0.9								
208/232									
	unweighted	0.09788	0.00039	0.00047					
	weighted	0.09793	0.00039	0.00044	1888.4	7.2	-7.2	8	-8
	calibrated		0.001	0.001		18.7	-18.7	19	-19.1
	95%confidence		0.0022	0.0022		39.9	-39.9	40.6	-40.7
chi-sq:	1.17								
207/206									
	unweighted	0.18889	0.00019	0.00017					
	weighted	0.18875	0.00015	0.00015	2731.3	1.3	-1.4	1.3	-1.4
	95%confidence		0.0003	0.0003		2.9	-2.9	2.9	-2.9
chi-sq:	0.93								

Student's t for 16 analyses: 2.13

GroupNo. 2

Sample	206/238	+/-	diff	207/235	+/-	diff	208/232	+/-	diff	207/206	+/-	diff
64.09.1	0.524	0.008	0	13.508	0.221	0	0.0989	0.0016	0	0.18699	0.00061	0

n=1		Mean	Exp.s.e.	Obs.s.e.	Age(Ma)	Exp.s.e.			Obs.s.e.
206/238									
	unweighted	0.52965	0.00209	0.00817					
	weighted	0.52395	0.00817	0.00817	2715.9	34.5	-34.6	34.5	-34.6
	calibrated		0.00858	0.00858		36.2	-36.4	36.2	-36.4
207/235									
	unweighted	13.7941	0.05762	0.22055					
	weighted	13.5082	0.2205	0.22055	2715.9	15.3	-15.6	15.3	-15.6
	calibrated		0.2307	0.2307		16	-16.3	16	-16.3
208/232									
	unweighted	0.09788	0.00039	0.00158					
	weighted	0.09892	0.00158	0.00158	1906.7	29	-29	29	-29
	calibrated		0.0018	0.0018		33.8	-33.9	33.8	-33.9
207/206									
	unweighted	0.18889	0.00019	0.00061					
	weighted	0.18699	0.00061	0.00061	2715.8	5.4	-5.4	5.4	-5.4

File	8-206Pb/238U%	4-208Pb/232Th%	standards	unknowns	cal.slope
DesktopFolder: data file	1.418	2.71	8	18	2

Fig. 15. Report Sheet showing an example of a Date Report.

ion-microprobe output (raw data) file. It is not necessary to identify mass species in the raw data input file using a run-table for this report type. However, if mass species are not identified, either by use of a run-table or from a SHRIMP ".sq" file type in which the mass species are recorded, then background corrections cannot be made to count rates. The Generalized Report tabulates count rates (as counts/s) and ratios of the count rates, using a denominator mass that may be specified in the "Denominator-Y" textbox of the Run-table dialog, the ratio's uncertainty based on counting statistics, and its D value (see Eq. (8)). If no denominator has been specified, the default denominator is the first species of each analysis read from the input file. Standard analyses are tabulated (in the order that they were read from the input file) separately, and averages, weighted means and observed and expected uncertainties for ratios obtained for standards are also listed. Next, each standard and unknown analysis, with averages, weighted means and observed and expected uncertainties for ratios obtained for all analyses, are tabulated in analysis order.

Al–Mg, Mn–Cr and Fe–Ni report types will also tabulate mass fractionation-corrected and normalized $^{26}Mg/^{24}Mg$, $^{53}Cr/^{52}Cr$ and $^{60}Ni/^{62}Ni$ ratios, their averages, weighted means and observed and expected uncertainties, using normalization ratios specified in the Run-table dialog.

9.2. The Date Report type and User-editing of age groups

The Date Report is the report type written to the Report Sheet for Zircon, Monazite, Xenotime, Titanite/Perovskite, Baddeleyite/Common Pb and Th–U Disequilibrium analysis types. The layout of the Date Report type (see Fig. 15) facilitates user-editing of age groups and printing. Because analyses belonging to different groups are displayed in different fill colors on the diagrams, the Date Report on the Report Sheet and the Wetherill Concordia, Tera–Wasserburg Concordia, Linearized Gaussian and Gaussian-summation probability density diagrams should be used together, so that the consequences of reassigning analyses among age groups can be assessed using the diagrams. Depending on the "Group by" option selected in the Set-up dialog, analyses will be assigned to $^{207}Pb/^{206}Pb$, $^{207}Pb^*/^{206}Pb^*$, $^{206}Pb^*/^{238}U$, $^{207}Pb^*/^{235}U$ or $^{208}Pb^*/^{232}Th$ age groups, based on the χ^2 and D threshold parameters specified in the Set-up dialog that are used to define these groups. Analyses may be manually redistributed among age groups by inserting an integer corresponding to the new age group in the cell to the right of the analysis (column 14) to be moved on the Report Sheet and selecting the "Recalc" button on the Report Sheet. The validity of the move may be assessed by examination of the analysis's D value and the new group's χ-value on the revised Report Sheet and examined graphically on the diagrams. A "Processed Data" output file can be written to disk using the "Files" button on the Report Sheet.

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