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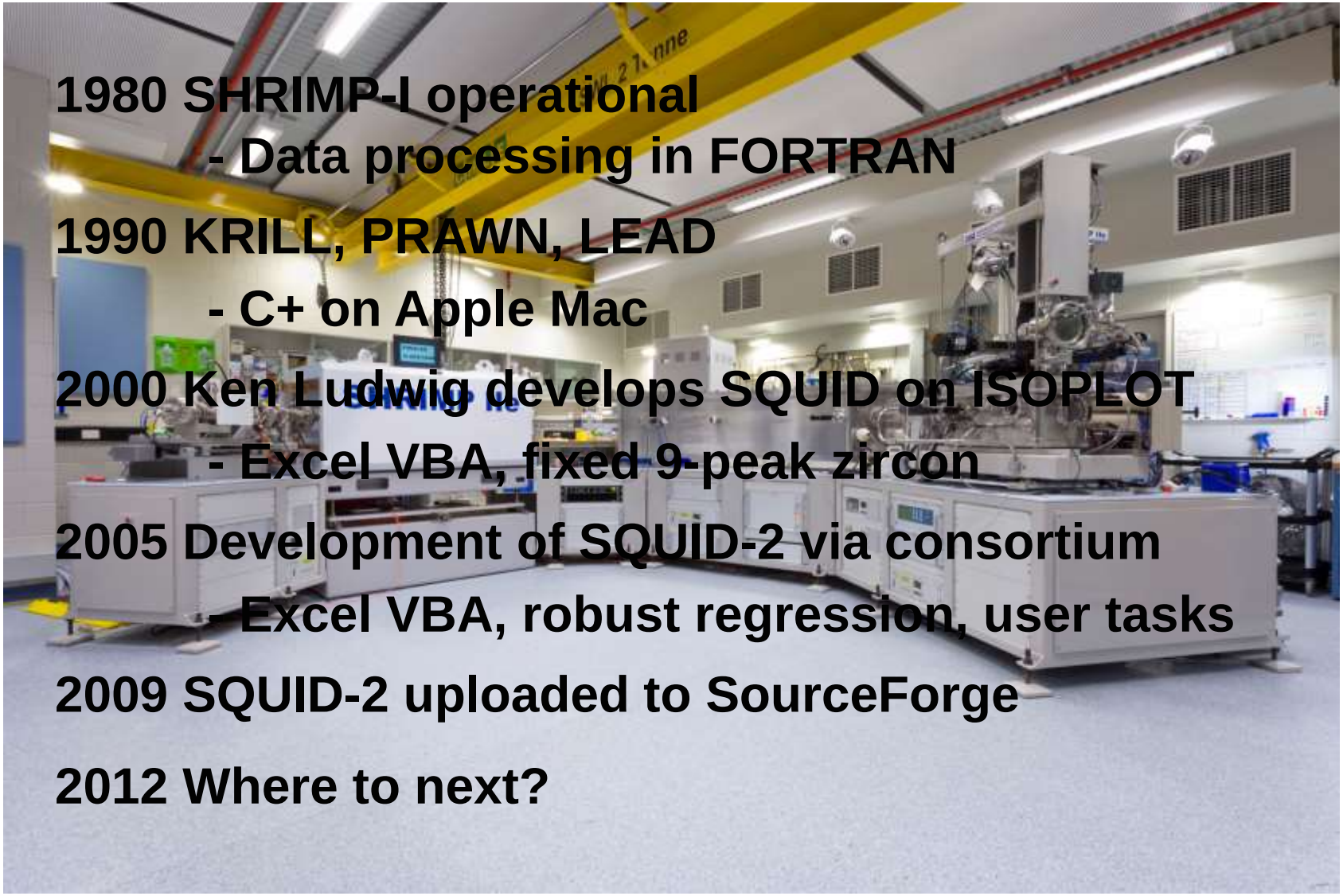
Geoscience Australia

SQUID from the Sea to the Cloud – the past, present and future of SIMS data processing

Statistical Interpretation of Age Information, LA-ICP-MS and Beyond

Keith Sircombe, Simon Bodorkos, Andrew Cross, Les Sullivan

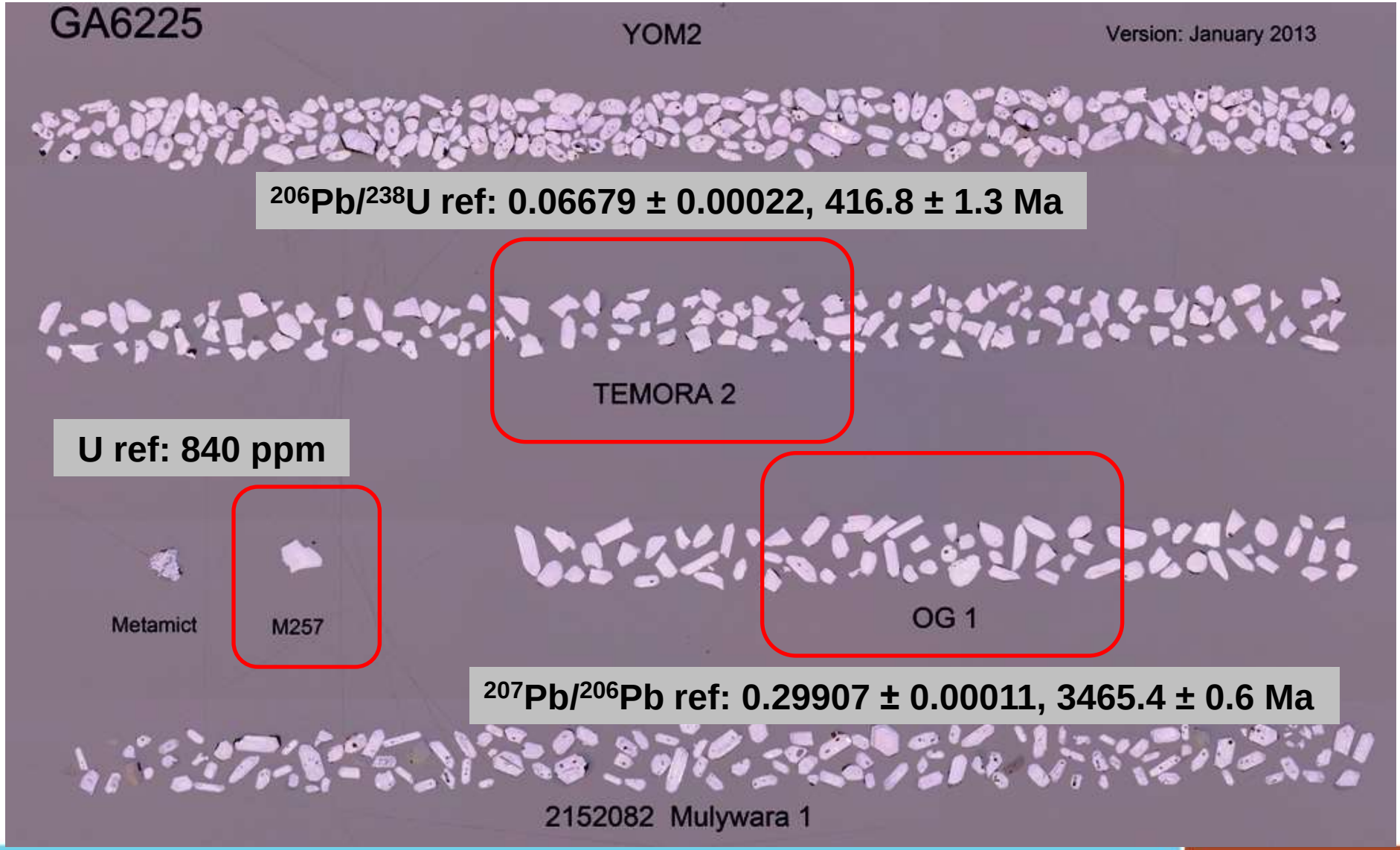
A brief history of crustacean data processing



Details: the seven questions

1. Uncertainty propagation protocol/workflow
2. Common Pb correction methods
3. Method of inter-element and inter-isotope fractionation correction
4. Weighted mean/linear regression support
5. Rejection criteria
6. Handling/storage of reference values for normalization
7. Key differences from other available packages ✓

Workflow: sample



Workflow: data acquisition*

SET 1	TITLE: 433.002.1.1		DEAD TIME / ns: 12		Normalise to SBM OFF.	
name	1	2	3	4	5	
196Zr2O	31894	33987	34971	36422	36960	
204Pb	2	2	2	2	4	
Bkgnd	0	1	3	4	1	
206Pb	5980	6021	5762	5764	6005	R
207Pb	1044	1099	1089	990	1092	
208Pb	585	604	564	572	636	
238U	15651	16112	16269	16903	17073	R
248ThO	22677	22819	22825	22969	23202	
254UO	37947	37813	38126	38394	38550	
270UO2	14543	14200	14037	14325	14162	

FLAGS: **I** Insufficient counts to center; **C** Fail to center; **R** Fail F test - passes by rejection; **F** Fail F test - acc

* assuming single-collector and focussed on $^{206}Pb/^{238}U$

Workflow: ‘raw’ data formats

```
- <set>
    <par name="date" value="2011-05-12" />
    <par name="time" value="13:17:52" />
    <par name="qt1y" value="-193" />
    <par name="qt1y_volts" value="-4870.4" />
    <par name="qt1z" value="263" />
    <par name="egy" value="0.00" />
    <par name="egz" value="0.00" />
    <par name="prealphay" value="553" />
    <par name="pbm" value="-2.5nA" />
    <par name="eisie_cps" value="5.000000,10.000000,15.000000,20.000000,25.000000" />
    <!--  eisie cps have zeros subtracted  -->
    <par name="eisie_date_time" value="1904-1-1T10-0-0" />
  - <scan number="1">
    - <measurement>
        <par name="detectors" value="12" />
        <par name="trim_mass" value="195.787512" />
        <par name="time_stamp_sec" value="17.000000" />
        <par name="autocentering_result" value="ok" />
        <!--  can be "ok" "failed" "insufficient counts"  -->
        <par name="autocentering_detector" value="1" />
        <data name="196Zr2O">3928,3908,3909,3869,3921,3949,3889,3935,3921,3910</data>
        <data name="SBM">55911,55929,55945,55996,56022,55978,55971,55926,55948,55942</data>
      </measurement>
    - <measurement>
        <par name="detectors" value="12" />
        <par name="trim_mass" value="203.952521" />
        <par name="time_stamp_sec" value="33.000000" />
        <par name="autocentering_result" value="ok" />
        <!--  can be "ok" "failed" "insufficient counts"  -->
        <par name="autocentering_detector" value="1" />
        <data name="204Pb">0,0,1,1,0,0,2,1,2,0</data>
        <data name="SBM">559348,559293,559382,559156,559134,559189,558956,558949,559049,559017</data>
      </measurement>
    - <measurement>
        <par name="detectors" value="12" />
        <par name="trim_mass" value="204.002521" />
```

Details: uncertainty propagation

ELSEVIER

Chemical Geology 197 (2003) 111–142

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Assessment of errors in SIMS zircon U–Pb geochronology using a natural zircon standard and NIST SRM 610 glass

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Received 21 March 2002; accepted 26 September 2002

Abstract

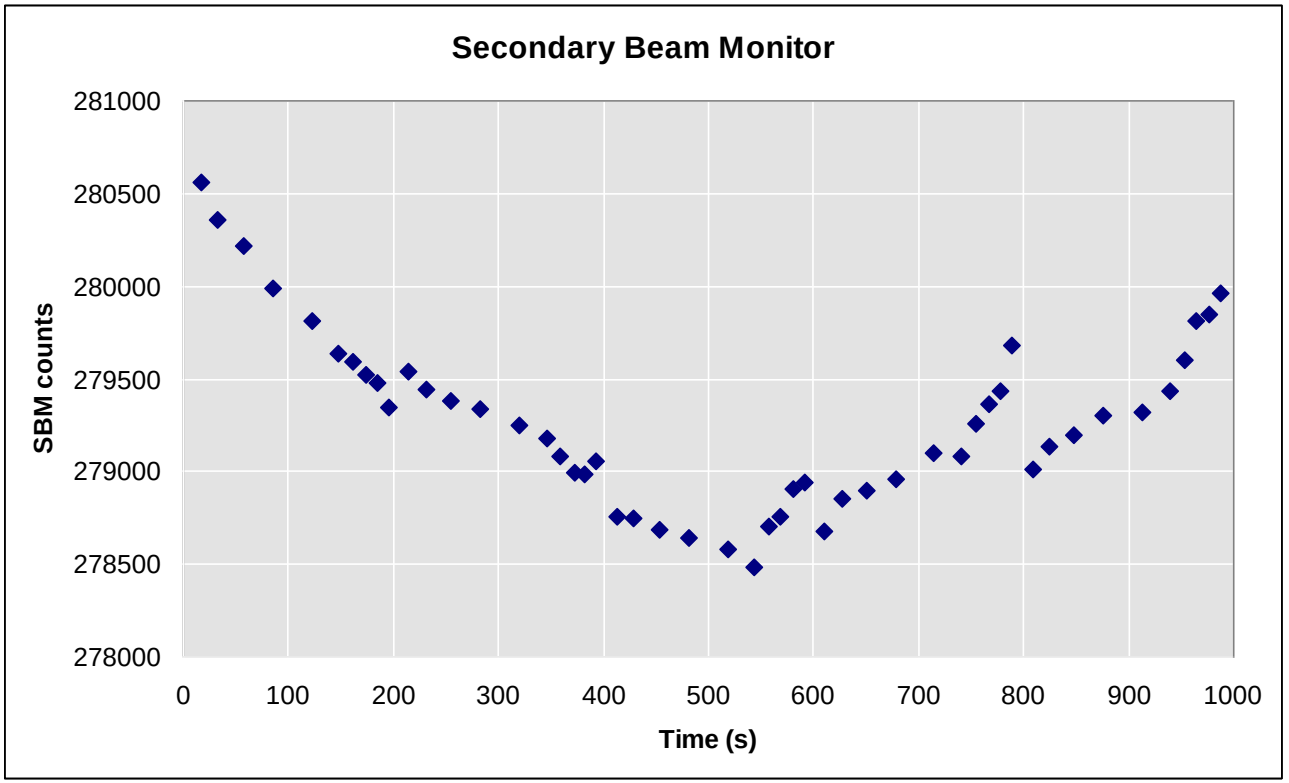
Analytical errors calculated for individual spot $^{206}Pb/^{238}U$ measurements of zircon analyzed using high mass resolution secondary ion mass spectrometry (HR-SIMS, e.g., SHRIMP II) were assessed using natural zircon (z6266) and synthetic glass standards (NIST SRM 610). Evidence for U/Pb homogeneity of these materials includes new thermal ionization mass spectrometry (TIMS) U–Pb analyses of 22 fragments of z6266 zircon from two laboratories, which are identical within error and yield a weighted mean $^{206}Pb/^{238}U$ age of 559.0 ± 0.2 Ma. TIMS U–Pb analyses of the SRM 610 yielded homogeneous $^{206}Pb/^{238}U = 0.2566$.

Workflow

Processing stage	Source of uncertainty	Description
U-Pb isotopic analysis of unknown zircon	Counting statistics - Propagated to ratios via double interpolation	Within-spot uncertainty
Background and common Pb corrections	Common Pb	Within-spot uncertainty
Assessing reference ('repeatability')	U-Pb discrimination	Within-session uncertainty S&A: "internal" L: "external spot-to-spot"
Calibration to reference ('reproducibility')	Age calibration	Between-session uncertainty S&A: "external" L: "error of mean"

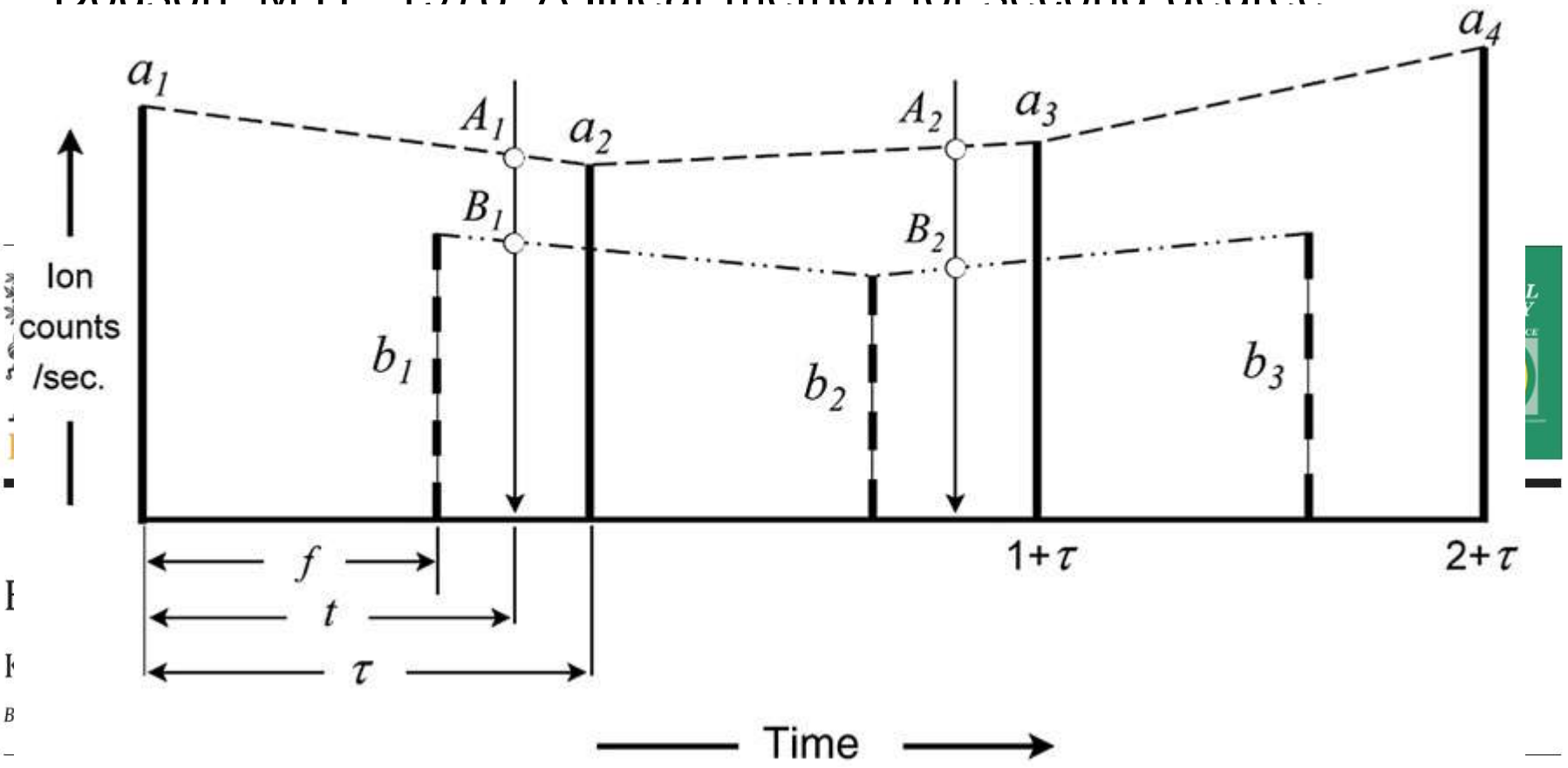
Workflow: Initial processing

- Normalise counts to Secondary Beam Monitor as portion of total secondary signal (typically <1% variation)
- Subtract background measurement taken near ^{204}Pb mass



Workflow: ratio calculation – double interpolation

Dodson, M.H., 1978. A linear method for second-degree



ARTICLE INFO

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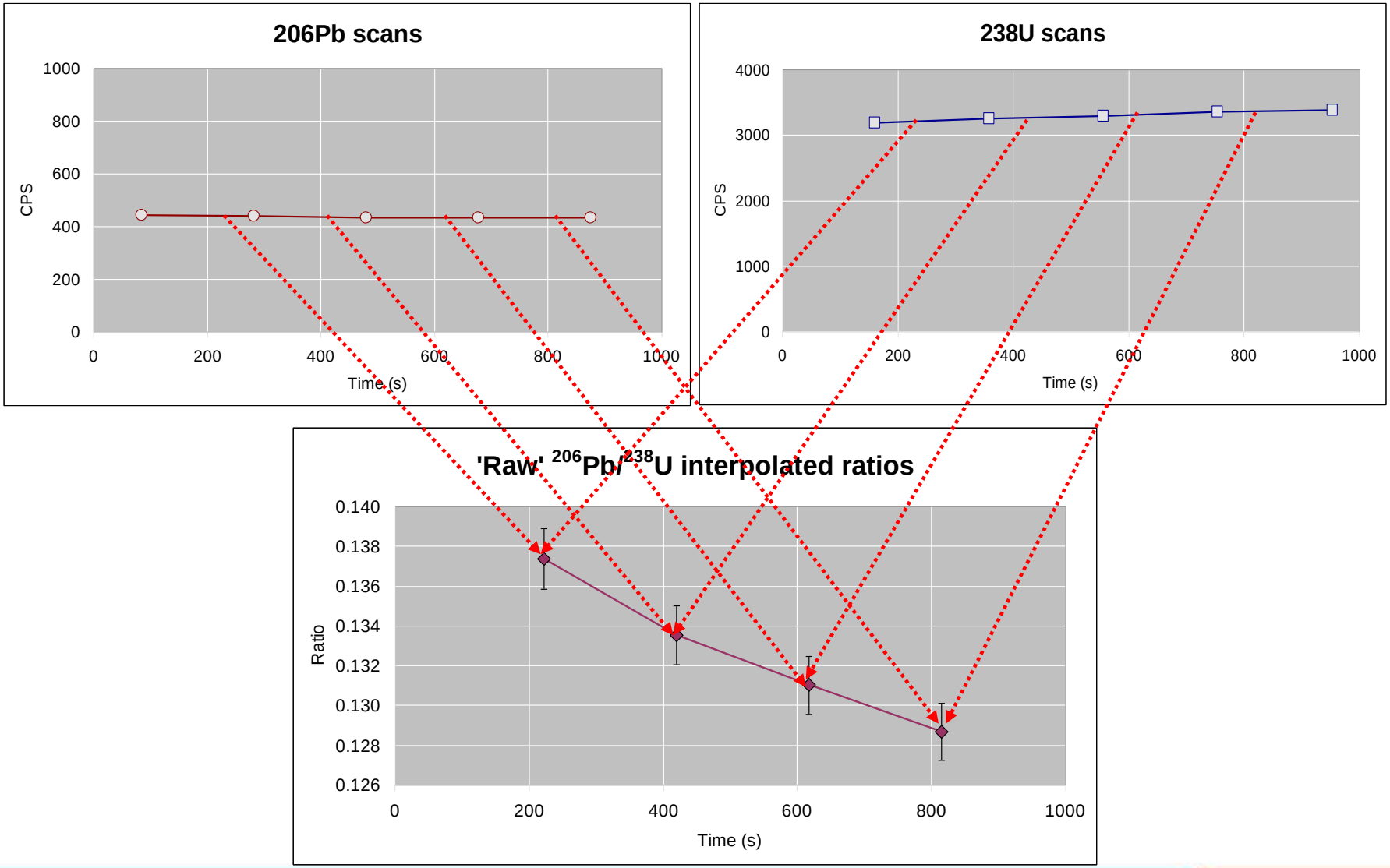
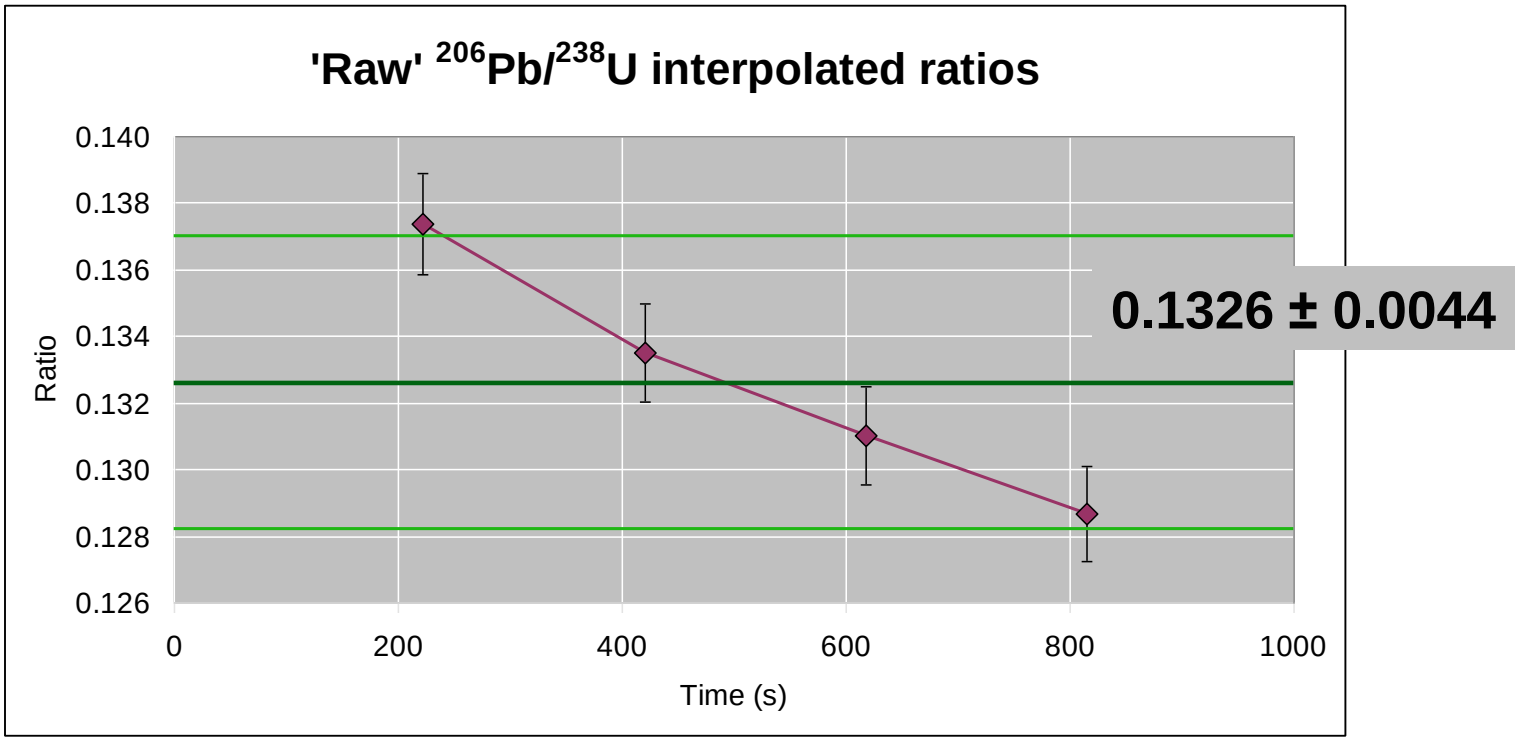
ABSTRACT

Measurement of isotope ratios via double interpolation of cyclic peak jumping produces error correlations between time-adjacent ratios which, if ignored, result in underestimated errors of their means. Equations that incorporate the error correlations are derived, and an example given for a typical U–Pb/zircon analysis via ion microprobe showing that isotope-ratio uncertainties for a single spot are usually underestimated by factors of 1.2–1.3.

Workflow: ratio calculation - double interpolation



Workflow: ratio calculation - double interpolation

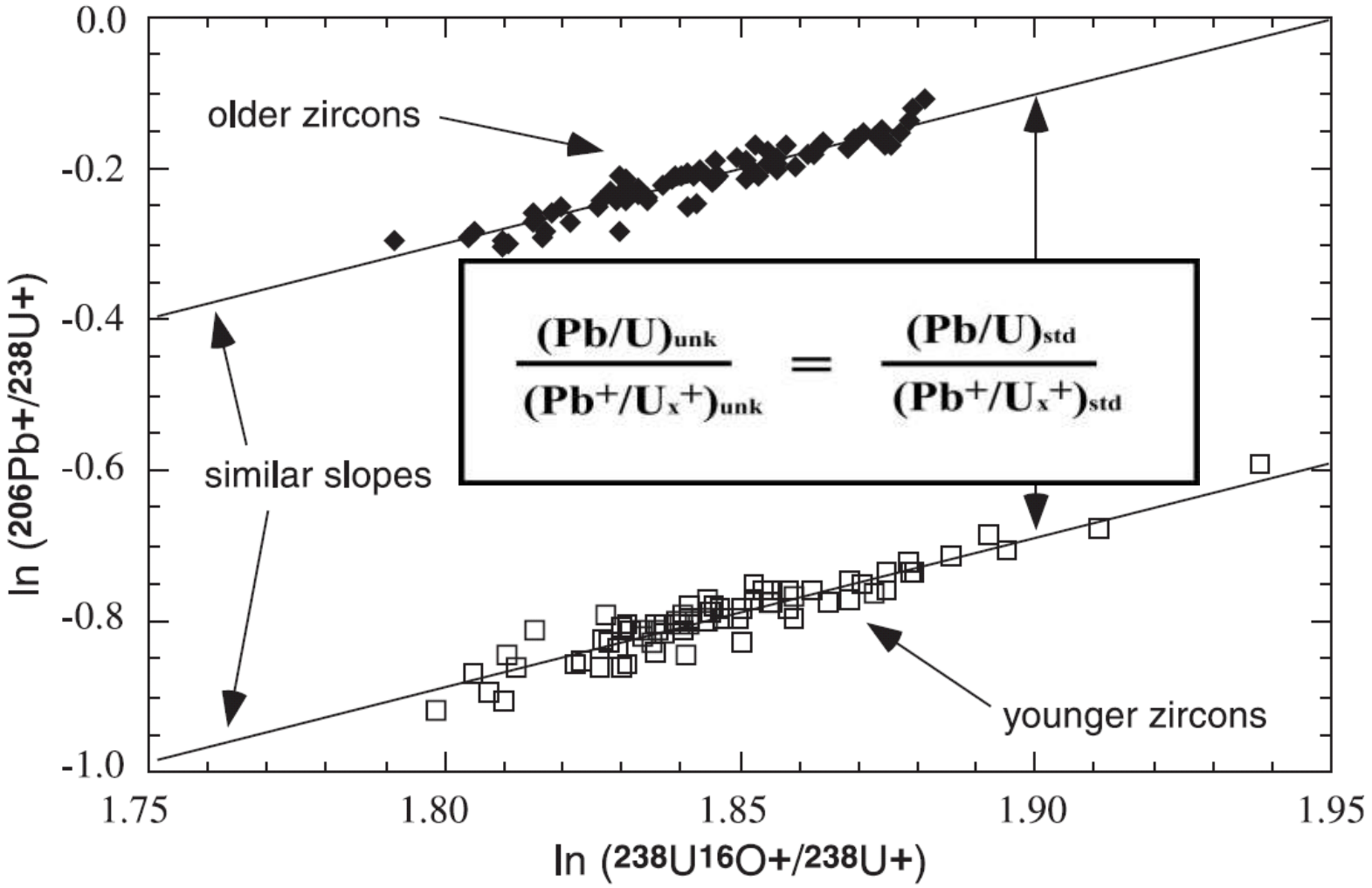


- *Outlier rejection by sequential removal of ratios and recalculation of MSWD. If MSWD reduction > set factor (3) then reject.*
- *If Prob. Fit > 0.05: weighted mean*
- *If Prob. Fit < 0.05: Tukey's Biweight*

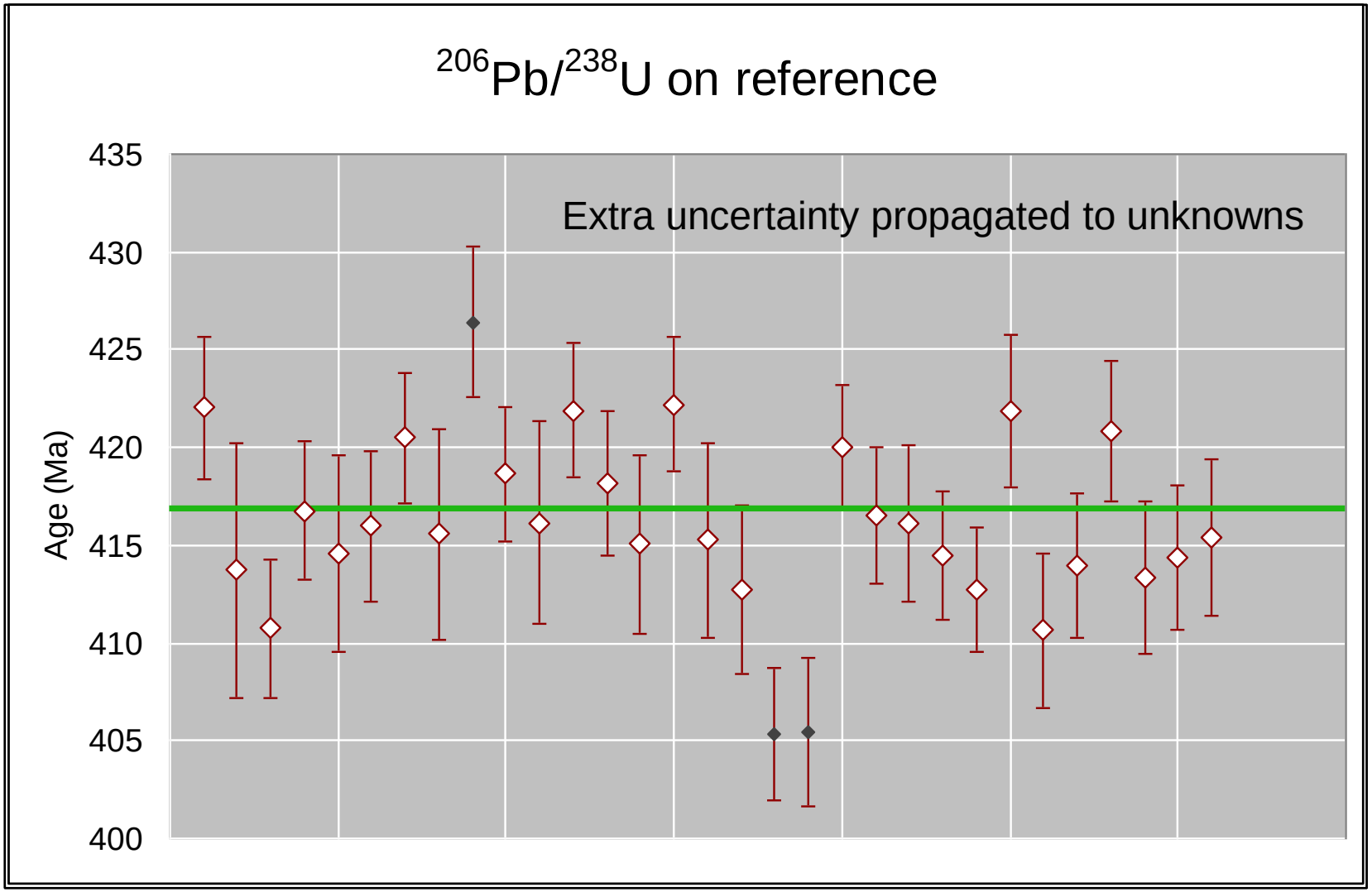
Workflow: normalise signal, common Pb, etc.

- Direct measurement of ^{204}Pb (^{207}Pb corr. in Phanerozoic)
- Calculation of assumed $^{204}Pb/^{206}Pb$ $^{204}Pb/^{207}Pb$ based on Stacey and Kramers (1975) two-stage model.
- Correction usually minor and generally reject analyses > 2% common Pb as unreliable measurements
- Correct ^{206}Pb and ^{207}Pb based ratios as required…
- Also monitor potential overcounts on ^{204}Pb by assuming concordance in reference $^{206}Pb^*/^{238}U$ and $^{207}Pb^*/^{235}U$ and calculating non-^{204}Pb counts to explain any discordance

Workflow: calculate calibration constant



Workflow: spot-to-spot uncertainty



Workflow: homework

SQUID 2

Rev. 2.50

A User's Manual

Ken Ludwig
Berkeley Geochronology Center
April 12, 2009

Details: the seven questions

1. Uncertainty propagation protocol/workflow
2. Common Pb correction methods ✓
3. Method of inter-element and inter-isotope fractionation correction ✓
4. Weighted mean/linear regression support ✓
5. Rejection criteria ✓
6. Handling/storage of reference values for normalization
7. Key differences from other available packages ✓

User-editable preferences worksheet

Microsoft Excel - Prelim reduction 24-01-2010.xls

File Edit View Insert Format Tools Data Window Isoplot Help Squid2 Adobe PDF

Type a question for help

Arial 11 75%

Reply with Changes... End Review... Security...

A57 T.50.1.1...dup1

Isotope Ratio

(errors are 1σ mid spot-time, for isotope ratios of the same element at mid spot-time, for isotope ratios of different elements at mid spot-time

SHRIMP SW v2.7

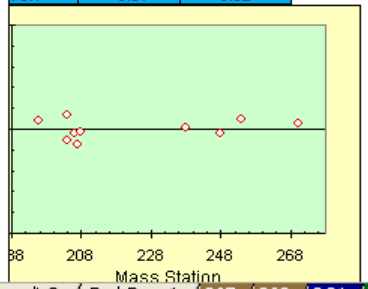
from file:

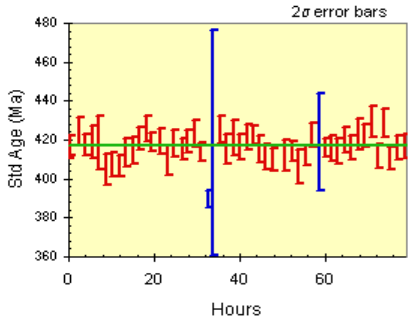
Spot Name	206/270	% err	270/254	% err	206/254	% err	Ln UO/U	% err	Ln Pb/U	% err	Expo	Expo_Used	Med 4/6	StDev 4/6	4-corr 206Pb/238U calibr. const	% err	Age (Ma)	±1σ	4-corr ppm 206*	4-corr 208Pb*/206Pb*	% err	ppm U	ppm Th	232Th/238U	% err	204 overcts /sec (fr. 207)	204 overcts /sec (fr. 208)	204/206 (fr. 207)	% err	(fr
T.34.1.1	0.06025	0.62	0.3947	0.41	0.02379	0.56	1.8427	0.24	-1.896	0.36					0.006960	0.61	414	2	0.062	0.148	3.08	246	119	0.499	0.40	0.0224	0.118	-4.1E-6	1E+3	
T.35.1.1	0.05976	1.12	0.3892	0.74	0.02327	1.00	1.8218	0.43	-1.938	0.63					0.006823	1.12	406	4	1.107	0.103	8.57	74	25	0.345	0.82	0.0274	0.022	0.000461	22	
T.36.1.1	0.06050	0.66	0.3876	0.44	0.02346	0.59	1.8265	0.25	-1.927	0.37					0.006928	0.64	412	3	0.209	0.167	3.17	221	110	0.513	0.42	0.0574	-0.099	0.000005	1E+3	
T.37.1.1	0.06040	0.77	0.3898	0.73	0.02384	0.69	1.8211	0.30	-1.915	0.44					0.007106	0.76	422	3	-0.425	0.088	4.83	159	39	0.254	0.64	-0.0225	-0.093	-1.8E-4	36	
T.50.1.1	0.06054	0.68	0.3911	0.45	0.02367	3.28	1.8190	0.27	-1.925	0.39					~~0.007043~~	~~3.06~~	~~419~~	~~42~~	-0.112	0.144	2.68	202	93	0.475	0.44	-0.0582	0.060	0.000058	100	
T.39.1.1	0.06062	0.61	0.3889	0.41	0.02359	0.55	1.8224	0.24	-1.925	0.35					0.006995	0.59	416	2	0.060	0.148	2.32	252	120	0.490	0.39	0.0300	0.083	-1.6E-5	309	
T.40.1.1	0.06011	0.84	0.3883	0.55	0.02335	0.75	1.8146	0.32	-1.943	0.47					0.006984	0.81	415	3	-0.225	0.155	18	133	67	0.520	0.52	-0.0483	0.065	0.000026	274	
T.41.1.1	0.06074	0.84	0.3869	0.55	0.02350	0.75	1.8218	0.32	-1.928	0.48					0.006966	0.81	414	3	0.114	0.144	17	126	59	0.482	0.54	0.0309	0.058	-3.4E-5	258	
T.42.1.1	0.06081	0.84	0.3894	0.55	0.02371	0.75	1.8117	0.32	-1.930	0.47					0.007060	0.81	420	3	0.336	0.086	5.31	131	38	0.301	0.65	0.0352	0.072	0.000077	92	
T.43.1.1	0.06079	0.79	0.3931	0.53	0.02391	0.71	1.8461	0.31	-1.888	0.46					0.006995	0.77	416	3	-0.101	0.092	4.01	136	37	0.278	0.64	-0.0719	-0.049	0.000146	47	
T.44.1.1	0.06210	0.96	0.3866	0.64	0.02399	0.86	1.8169	0.37	-1.914	0.55					0.007115	0.94	423	4	0.445	0.090	6.34	96	32	0.347	0.71	0.0371	0.126	0.000094	87	
T.45.1.1	0.06166	0.73	0.3893	0.49	0.02400	0.65	1.8216	0.28	-1.908	0.42					0.007101	0.72	422	3	0.342	0.146	3.23	165	78	0.490	0.47	0.1085	0.085	-6.8E-5	91	
T.46.1.1	0.06188	0.94	0.3881	0.62	0.02405	0.84	1.8192	0.37	-1.910	0.54					0.007225	0.95	429	4	-0.987	0.119	5.60	100	31	0.324	0.71	-0.1440	-0.127	0.000016	508	
T.47.1.1	0.06054	0.80	0.3866	0.53	0.02343	0.71	1.8279	0.31	-1.926	0.46					0.006924	0.77	412	3	0.051	0.155	3.00	140	64	0.469	0.52	-0.0253	-0.089	0.000100	68	
T.48.1.1	0.06140	0.91	0.3940	0.61	0.02422	0.81	1.8128	0.36	-1.907	0.52					0.007217	0.89	429	4	0.199	0.086	20	104	30	0.300	0.71	0.0196	0.055	0.000038	204	
T.38.1.1	0.05988	0.81	0.3877	0.53	0.02321	0.72	1.8192	0.31	-1.944	0.45					0.006899	0.77	411	3	0.053	0.112	3.62	139	46	0.344	0.59	0.0229	-0.040	-3.8E-5	180	
T.49.1.1	0.06014	0.79	0.3923	0.52	0.02360	0.71	1.8305	0.30	-1.916	0.45					0.006992	0.77	416	3	-0.400	0.168	3.14	140	67	0.496	0.50	-0.0939	-0.138	0.000039	175	
T.50.1.1...dup1	0.06099	5.01	0.3893	0.54	0.02385	0.76	1.8244	0.31	-1.916	0.47					0.007009	0.79	417	3	0.264	0.152	3.43	131	64	0.501	0.52	0.0375	0.046	0.000037	188	
																										-0.0035	-0.005			
																										±0.02	±0.02			

lass	SBM %offs	2σ err
95.8	+0.02	0.03
03.9	+0.03	0.03
204	-0.03	0.02
05.9	-0.01	0.03
06.9	-0.04	0.03
07.9	-0.01	0.04
238	+0.00	0.02
248	-0.01	0.02
254	+0.02	0.03
70.1	+0.01	0.02

Wtd Mean of Std Pb/U calibr. 0.007008
1σ error of mean 0.19%
1σ external spot-to-spot error 1.06%
MSWD 2.85
Prob. of fit 0.00
rejected spot #s 22,23,38
For visualization & preliminary evaluation only

Redo





Concordia9 ProbDens1 967 968 OG1 SampleData StandardData sq_100013_GA6

Draw AutoShapes

NUM

File Edit View Insert Format Tools Data Window Help

AE3 =100*$AT3*$I3

Errors are

Spot Name	204corr 206Pb /238U Age	1σ err	207corr 206Pb /238U Age	1σ err	208corr 206Pb /238U Age	1σ err	204corr 207Pb /206Pb Age	1σ err	204corr 208Pb /232Th Age	1σ err	208corr 207Pb /206Pb Age	1σ err	% Dis-cor-dant	7corr 206* /238	% err	4corr 208* /232	% err	8corr 206* /238	% err	Total 238 /206	% err	Total 207 /206	% err	4corr 238 /206*	% err	4corr 207* /206*	% err	4corr 207* /235	% err	4corr 206* /238	% err	err corr	8corr 238 /206*	% err	8corr 207* /206*
	204 corrected																																
OG1-7.1.1	3445	22	3409	51	3448	24	3470	4	3412	32	3475	6	+1	0.697	0.61	0.184	1.0	.7064	0.8	1.4	0.83	0.300	0.24	1.4	0.83	0.300	0.24	29.2	0.9	0.706	0.83	1.0	1.4	0.91	0.301
OG1-9.1	3455	25	3434	59	3457	26	3470	5	3429	43	3472	6	+1	0.703	0.71	0.185	1.4	.7092	0.9	1.4	0.92	0.300	0.30	1.4	0.92	0.300	0.30	29.3	1.0	0.709	0.92	1.0	1.4	0.97	0.300
OG1-15.1	3407	22	3338	47	3407	25	3462	7	3414	71	3461	12	+2	0.678	0.58	0.184	2.3	.6965	0.8	1.4	0.85	0.299	0.45	1.4	0.85	0.298	0.45	28.7	1.0	0.696	0.85	0.9	1.4	0.95	0.298
OG1-14.1	3411	25	3341	52	3412	26	3465	5	3381	44	3467	6	+2	0.679	0.64	0.182	1.4	.6974	0.9	1.4	0.94	0.299	0.31	1.4	0.94	0.299	0.32	28.7	1.0	0.697	0.94	0.9	1.4	0.99	0.299
OG1-10.1	3462	22	3467	57	3458	24	3459	4	3513	33	3451	5	-0	0.712	0.67	0.190	1.0	.7109	0.8	1.4	0.82	0.298	0.24	1.4	0.82	0.298	0.24	29.2	0.9	0.711	0.82	1.0	1.4	0.90	0.296
OG1-11.1	3440	22	3405	51	3442	25	3464	4	3417	33	3468	6	+1	0.696	0.62	0.184	1.0	.7050	0.8	1.4	0.83	0.299	0.24	1.4	0.83	0.299	0.24	29.1	0.9	0.705	0.83	1.0	1.4	0.92	0.300
OG1-12.1	3435	23	3389	53	3436	26	3469	4	3427	36	3470	6	+1	0.692	0.64	0.185	1.1	.7039	0.9	1.4	0.88	0.300	0.28	1.4	0.88	0.300	0.28	29.1	0.9	0.704	0.88	1.0	1.4	0.97	0.300
OG1-13.1	3422	25	3357	53	3427	27	3472	5	3368	39	3480	7	+2	0.683	0.64	0.181	1.3	.7005	0.9	1.4	0.93	0.301	0.31	1.4	0.93	0.300	0.32	29.0	1.0	0.700	0.93	0.9	1.4	1.02	0.302

Redo

Concordia Age

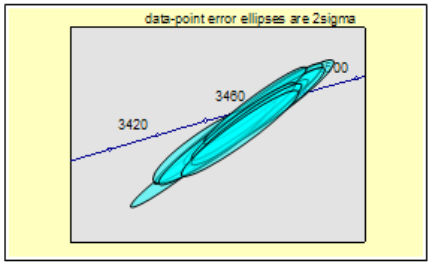
Mean age of coherent group (N=15) 3465.6
age error (95% conf.) 2.1
MSWD 0.89
Probability 0.57

To recalculate Concordia Age using different spots, select desired rows from the red columns then press button at right.

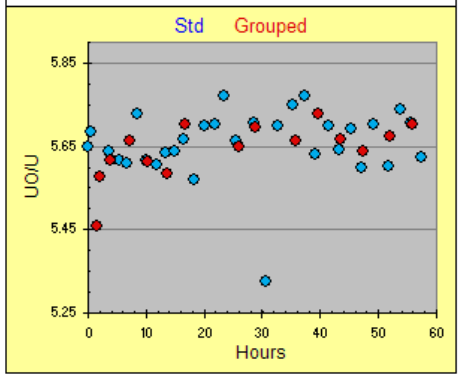
X-Y wtd mean (68%-conf. errs), incl. error from Standard:

1.421	0.3	0.299	0.07

on all 15 points.
Probability of equivalence = 0.23 (mswd = 1.2)
DISCORDANT (probability of concordance = .00045)



For visualization & preliminary evaluation only



Note: dependency on Isoplot!

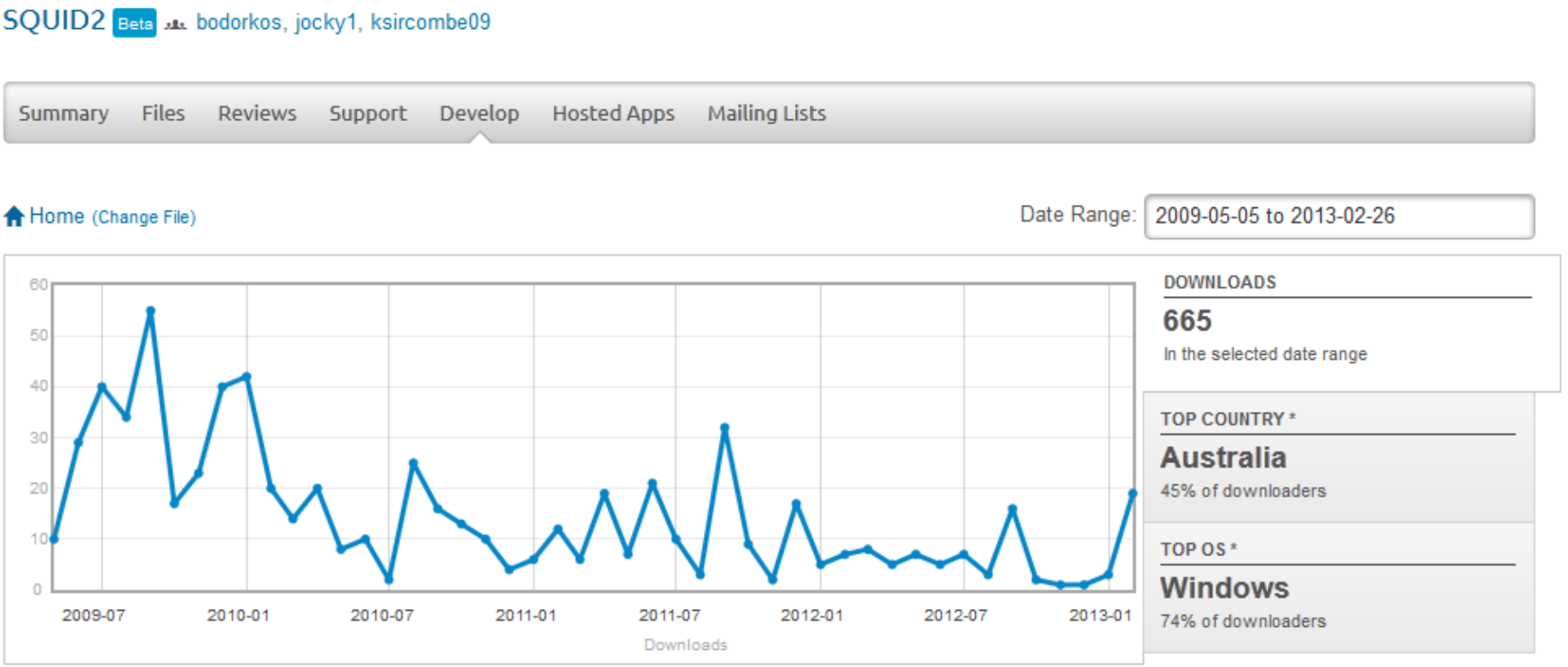
Data-reduction params | Within-Spot Ratios | 626 | OG1 | SampleData | StandardData

Ready

NUM

The bigger picture: SQUID in Open Source

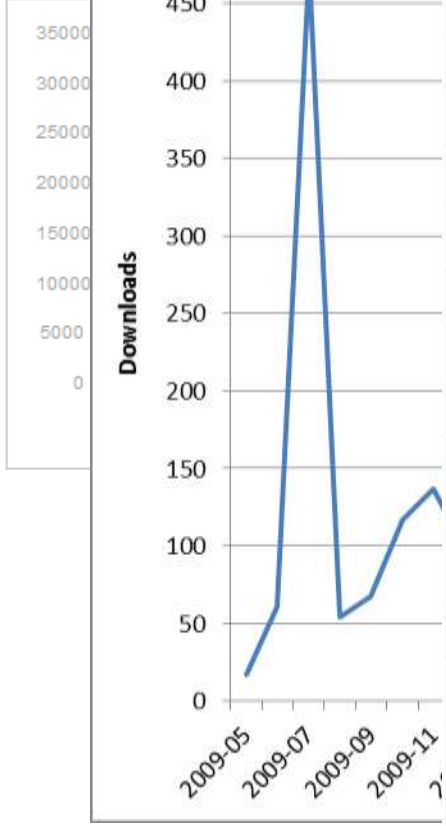
sourceforge.net/projects/squid2



ISOPLOT Beta bodorkos, jocky1,

Summary Files Reviews Suppo

Hom



1	United States	317	19%
2	China	172	10%
3	Australia	107	6%
4	Germany	101	6%
5	Canada	92	6%
6	United Kingdom	74	4%
7	Brazil	69	4%
8	India	65	4%
9	France	62	4%
10	Russia	48	3%
11	Japan	47	3%
12	Mexico	39	2%
13	Spain	36	2%
14	Taiwan	26	2%
15	Finland	25	2%
16	Colombia	23	1%
17	Turkey	21	1%
18	Switzerland	21	1%
19	Italy	19	1%
20	Chile	19	1%
	Other	271	16%
	Total last 12 months	**1654**	

SQUID-2: Issues

- Distribution and installation
- Version control
- Dependency on Excel (2003)
- Documentation of algorithms

Option #1: Update SQUID + ISOPLOT to Office 2010

- ☺ Bring applications up-to-date
- ☺ Encourage use
- ☹ Requires resources for developer/s

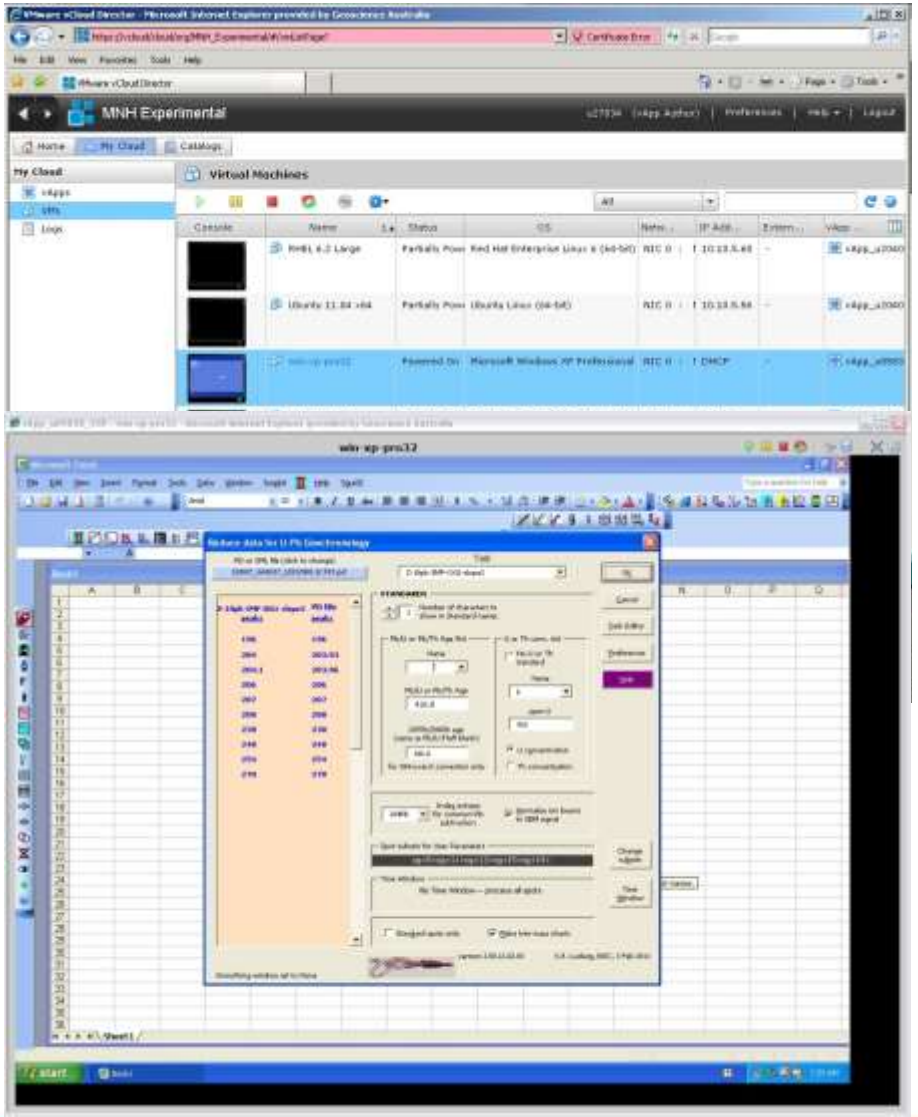
Option #2: Testing virtualisation at GA

- Enterprise-scale ‘vCloud’
- Server runs WinXP, Office 2003. Accessible by browser, behaves like desktop
- Successful tests of SQUID-2

☹ Installation issues

☹ Potential on-going cost for licences

☺ A way forward??



Option #3: New application?

☺ Reduce dependency on Windows/Excel environment

☺ Engage new users and developers

☹ Time consuming review of options and management of new development (i.e. no hero-coding)

☹ Create new dependencies?

☹ Resources for developers

☹ Debugging, maintenance, upgrades

Trends and drivers

BLE RESEARCH
FIC COMPUTING

NATA

WORLD RECOGNISED
ACCREDITATION

ISO

ed in creating reproducible computational research
o overcome them.

plied Mathematics at the University of Washington), Ian M. Mitchell (an associate professor of computer science at the University of British Columbia), and myself. One of our aims was to improve the visibility of the nascent group of tool

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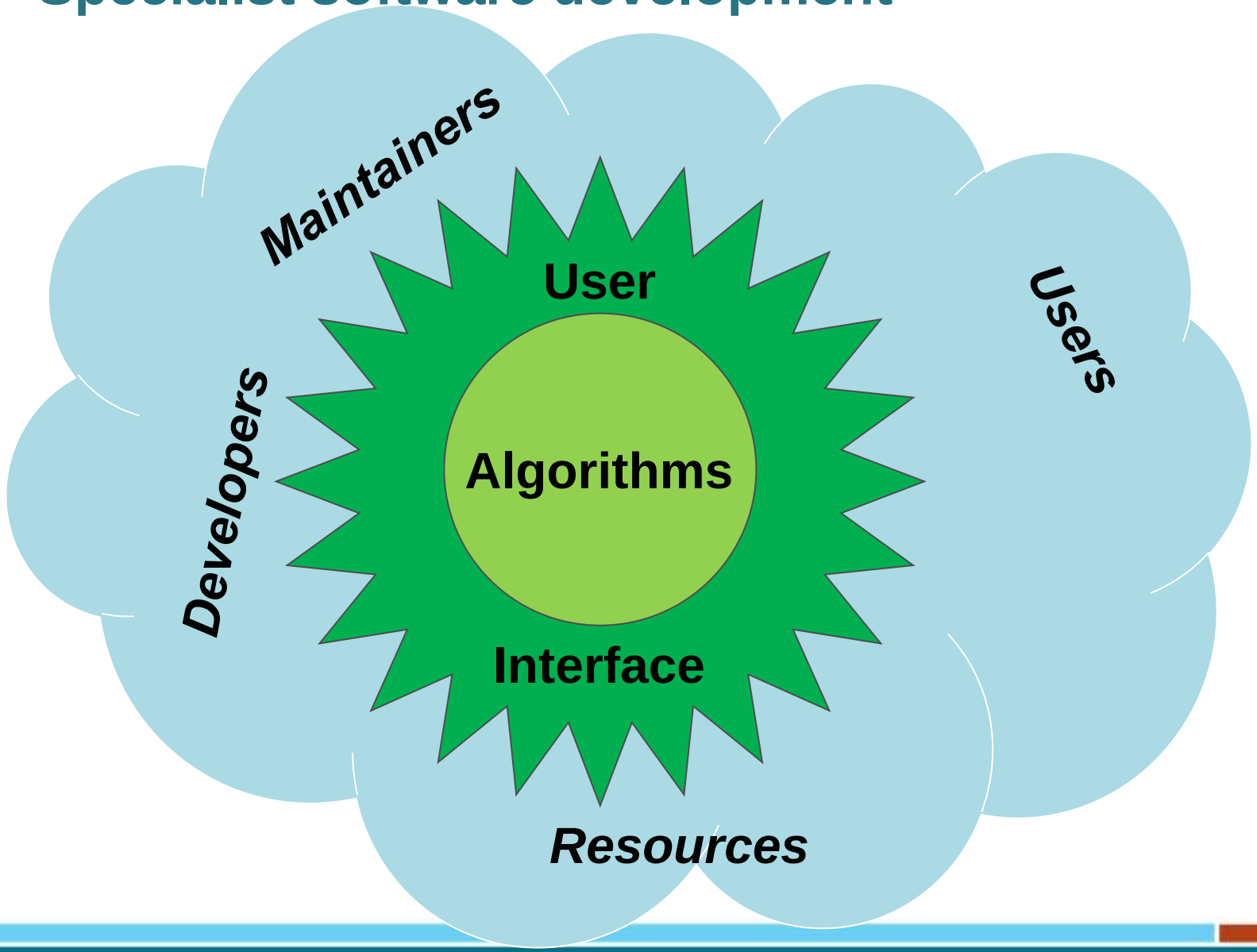
VICTORIA STODDEN
Columbia University

Specialist software development



Some hard-won advice

- **Algorithms ≠ user interface**
- **No silver bullet**
- **Maintenance, maintenance, maintenance: an application isn't just for Christmas**

SQUID 2020?

- Open source
  - algorithms and documentation
  - reproducible, standard test data sets
  - broad developer/maintenance community
- Platform-independent data processing
  - virtualisation in Cloud, web access
  - web service enabled with links to other labs, data

Your ideas, collaboration?

(anyone working on Isoplot?)

Questions? Discussions?

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