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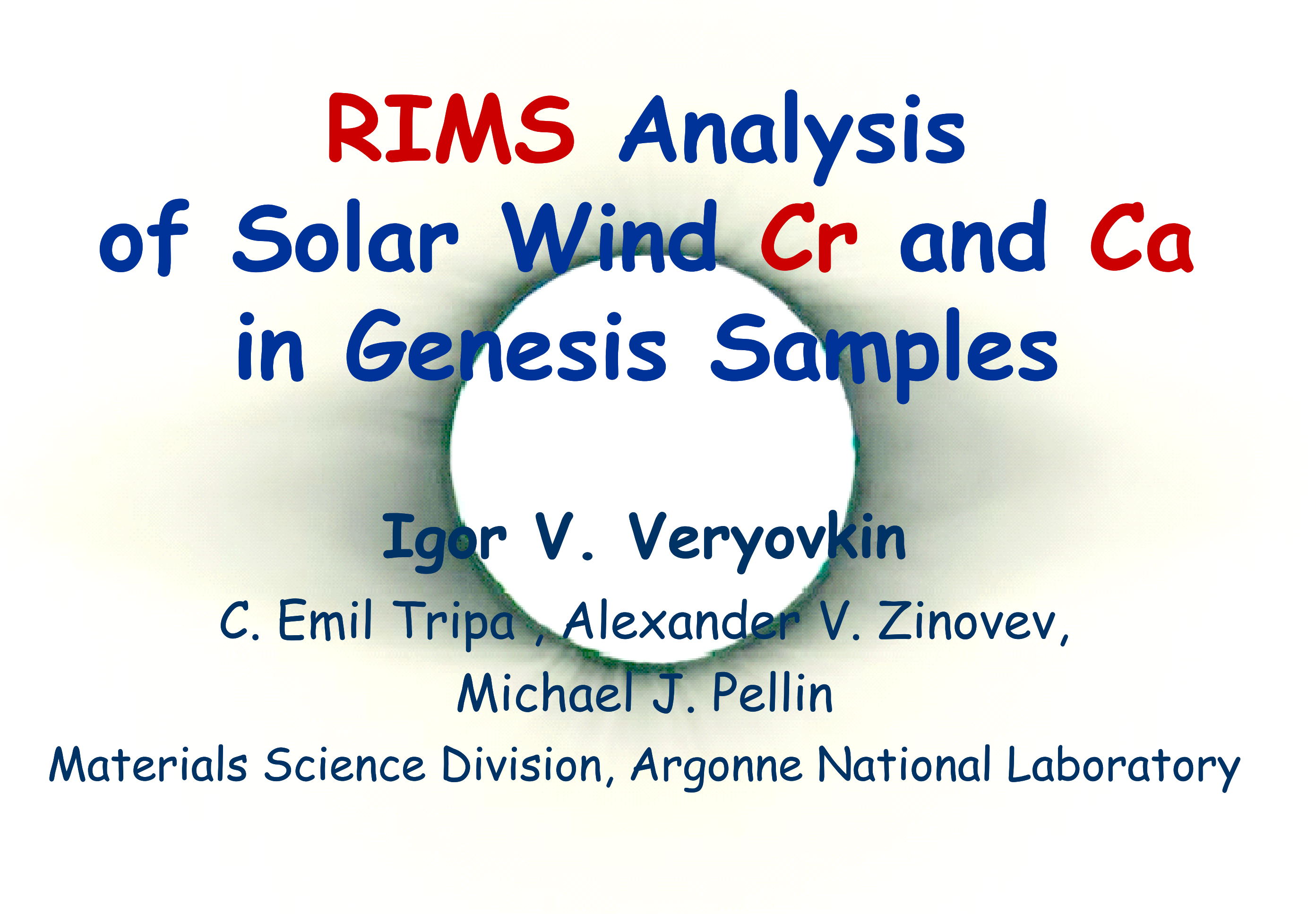

RIMS Analysis of Solar Wind Cr and Ca in Genesis Samples

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U.S. Department of Energy

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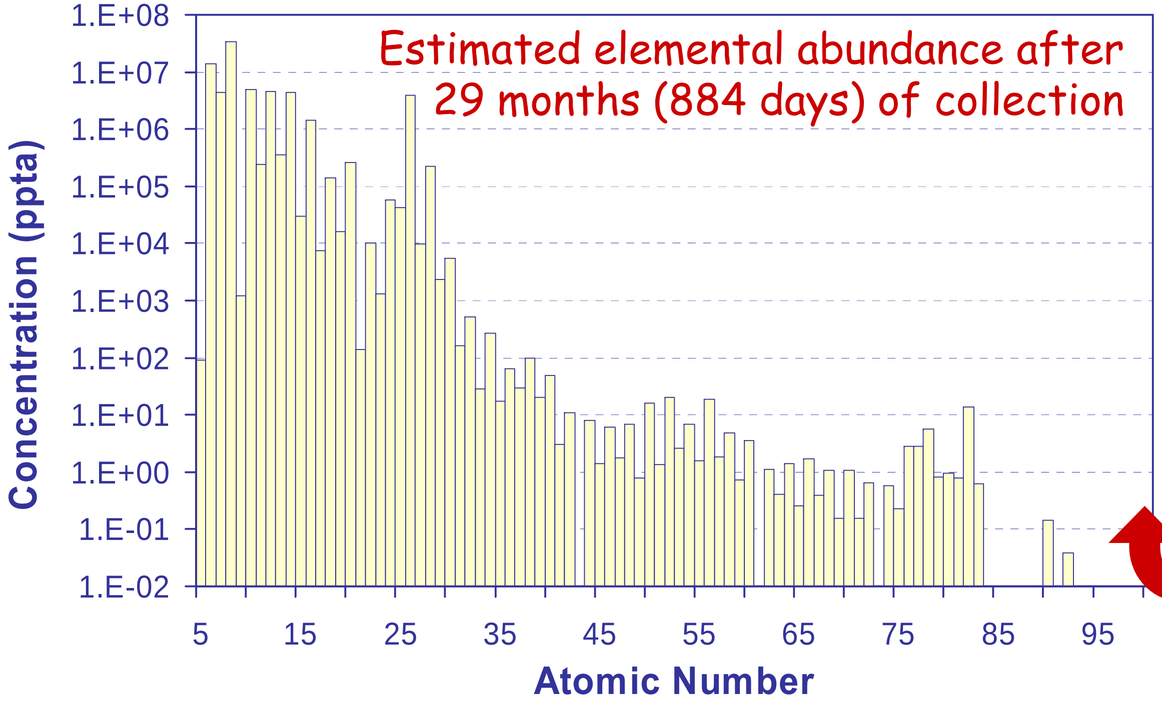
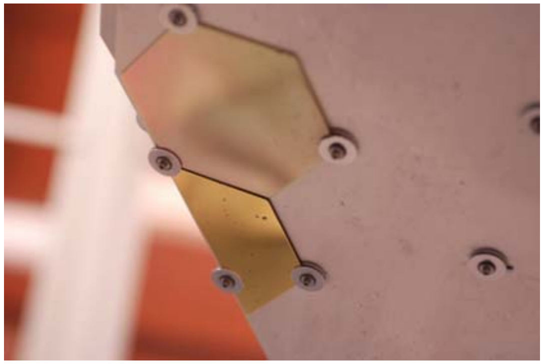
Genesis mission: a REAL analytical adventure


Estimated elemental abundance after 29 months (884 days) of collection

Expected and foreseen:
concentrations of many elements of interest are in the range of **atomic parts-per-trillion**.

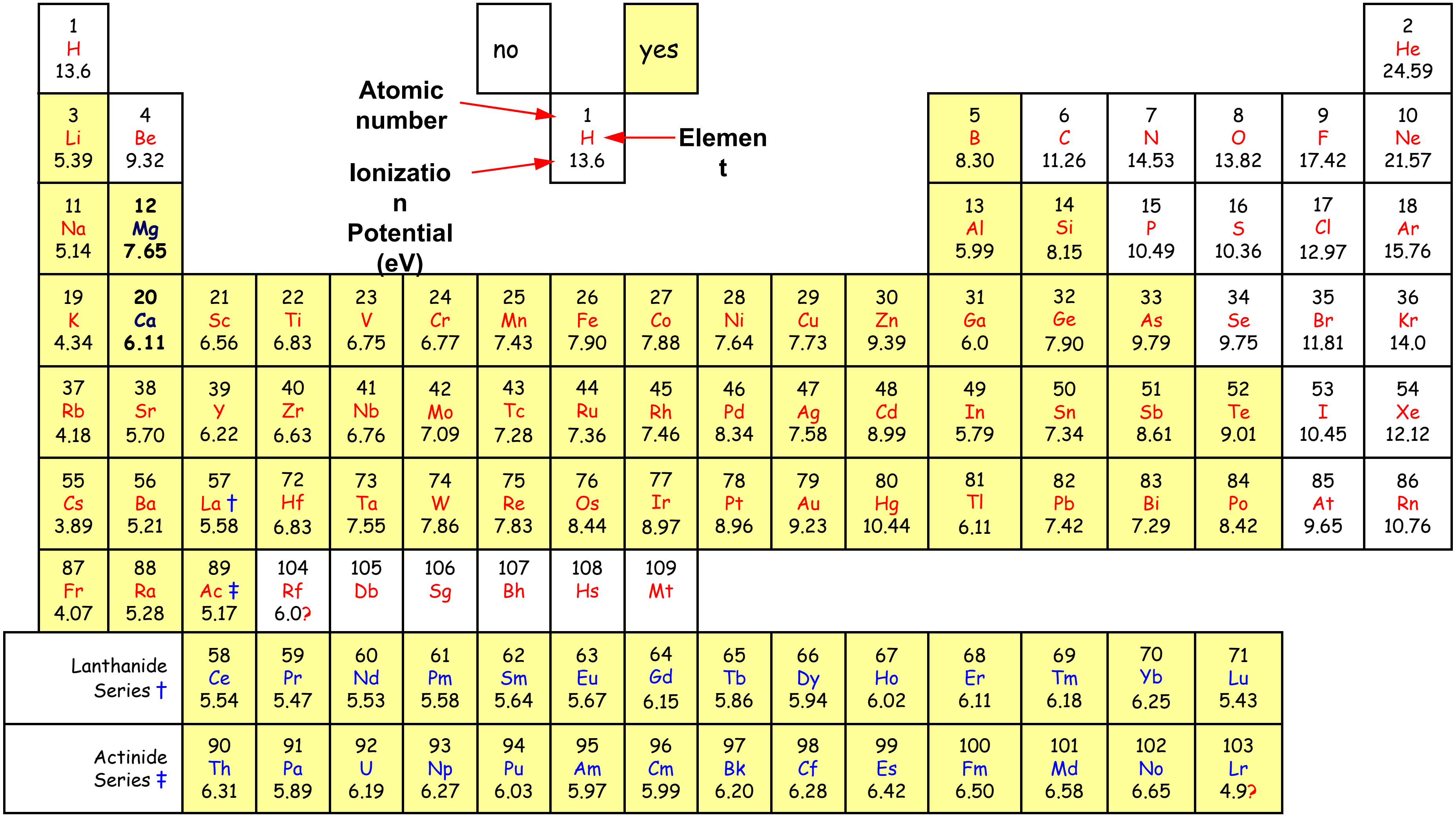
RIMS is the only analytical technique, which can measure such low elemental concentrations in such small samples

Unexpected but foreseen:
collectors are broken and contaminated due to crash landing of the sample return capsule



Periodic Table of RIMS

- Photons from conventional tunable lasers: ≥200 nm ~ ≤6.2 eV



1 H 13.6																	2 He 24.59
3 Li 5.39	4 Be 9.32											5 B 8.30	6 C 11.26	7 N 14.53	8 O 13.82	9 F 17.42	10 Ne 21.57
11 Na 5.14	**12** **Mg** **7.65**											13 Al 5.99	14 Si 8.15	15 P 10.49	16 S 10.36	17 Cl 12.97	18 Ar 15.76
19 K 4.34	**20** **Ca** **6.11**	21 Sc 6.56	22 Ti 6.83	23 V 6.75	24 Cr 6.77	25 Mn 7.43	26 Fe 7.90	27 Co 7.88	28 Ni 7.64	29 Cu 7.73	30 Zn 9.39	31 Ga 6.0	32 Ge 7.90	33 As 9.79	34 Se 9.75	35 Br 11.81	36 Kr 14.0
37 Rb 4.18	38 Sr 5.70	39 Y 6.22	40 Zr 6.63	41 Nb 6.76	42 Mo 7.09	43 Tc 7.28	44 Ru 7.36	45 Rh 7.46	46 Pd 8.34	47 Ag 7.58	48 Cd 8.99	49 In 5.79	50 Sn 7.34	51 Sb 8.61	52 Te 9.01	53 I 10.45	54 Xe 12.12
55 Cs 3.89	56 Ba 5.21	57 La † 5.58	72 Hf 6.83	73 Ta 7.55	74 W 7.86	75 Re 7.83	76 Os 8.44	77 Ir 8.97	78 Pt 8.96	79 Au 9.23	80 Hg 10.44	81 Tl 6.11	82 Pb 7.42	83 Bi 7.29	84 Po 8.42	85 At 9.65	86 Rn 10.76
87 Fr 4.07	88 Ra 5.28	89 Ac ‡ 5.17	104 Rf 6.0?	105 Db	106 Sg	107 Bh	108 Hs	109 Mt									
Lanthanide Series †		58 Ce 5.54	59 Pr 5.47	60 Nd 5.53	61 Pm 5.58	62 Sm 5.64	63 Eu 5.67	64 Gd 6.15	65 Tb 5.86	66 Dy 5.94	67 Ho 6.02	68 Er 6.11	69 Tm 6.18	70 Yb 6.25	71 Lu 5.43		
Actinide Series ‡		90 Th 6.31	91 Pa 5.89	92 U 6.19	93 Np 6.27	94 Pu 6.03	95 Am 5.97	96 Cm 5.99	97 Bk 6.20	98 Cf 6.28	99 Es 6.42	100 Fm 6.50	101 Md 6.58	102 No 6.65	103 Lr 4.9?		

no

yes

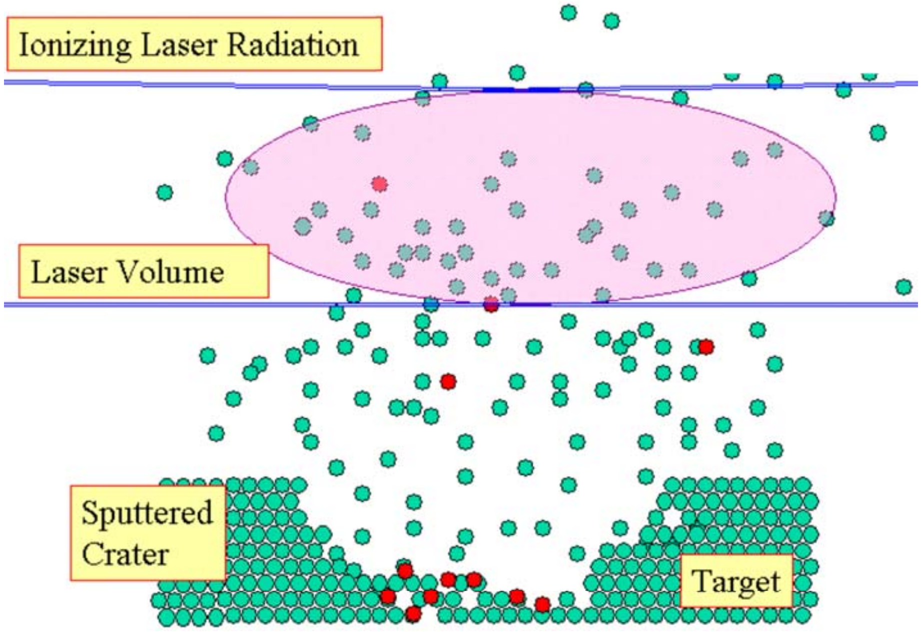
Atomic number

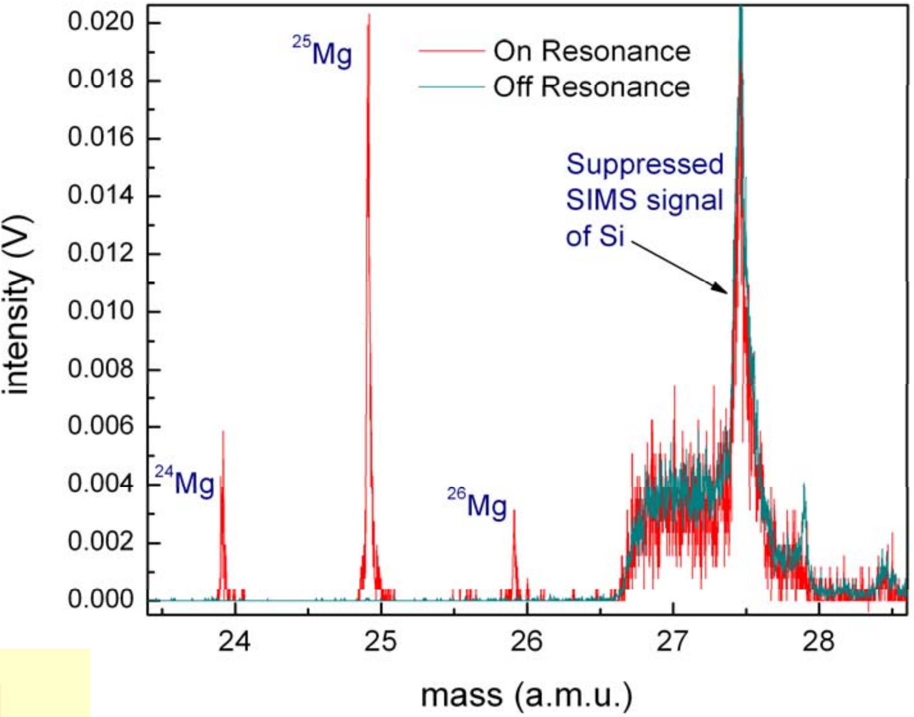
1
H
13.6

Element

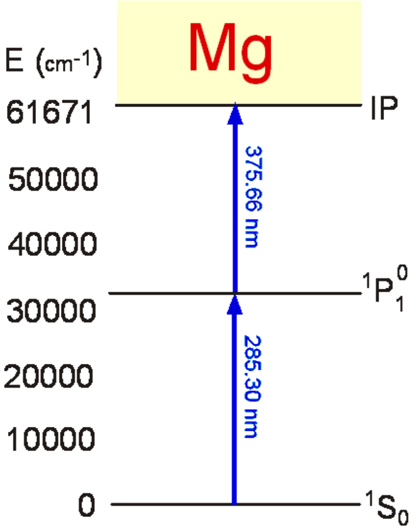
Ionization Potential (eV)

Laser Post-Ionization Secondary Neutral Mass Spectrometry (LPI SNMS): a variant of RIMS





- ✦ Energetic ion bombardment sputters sample material
- ✦ Vast majority of the sputtered flux are neutral atoms
- ✦ These neutrals are efficiently converted into ions by laser post-ionization



RIMS is very selective

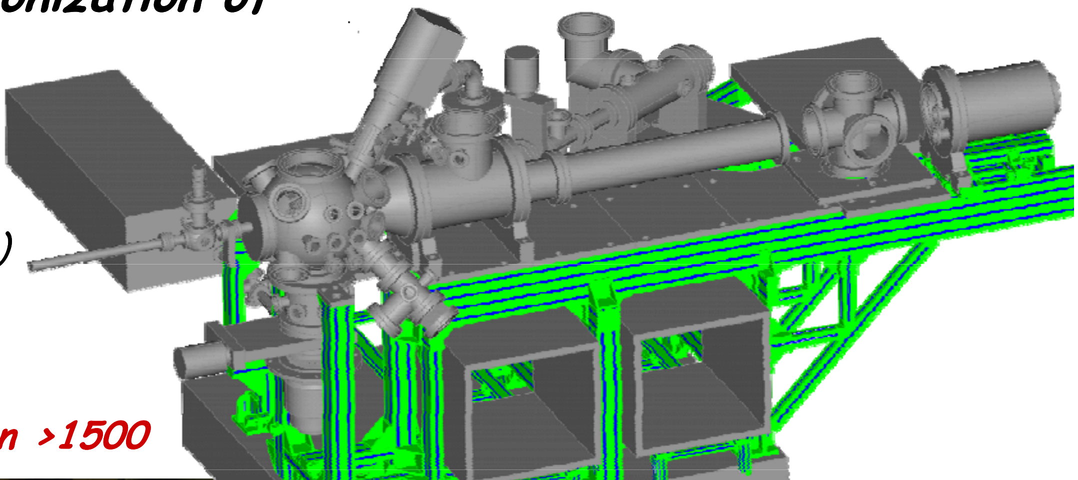
Resonantly-Enhanced Multi-Photon Ionization (REMPI) of Mg:
two colors - two photons

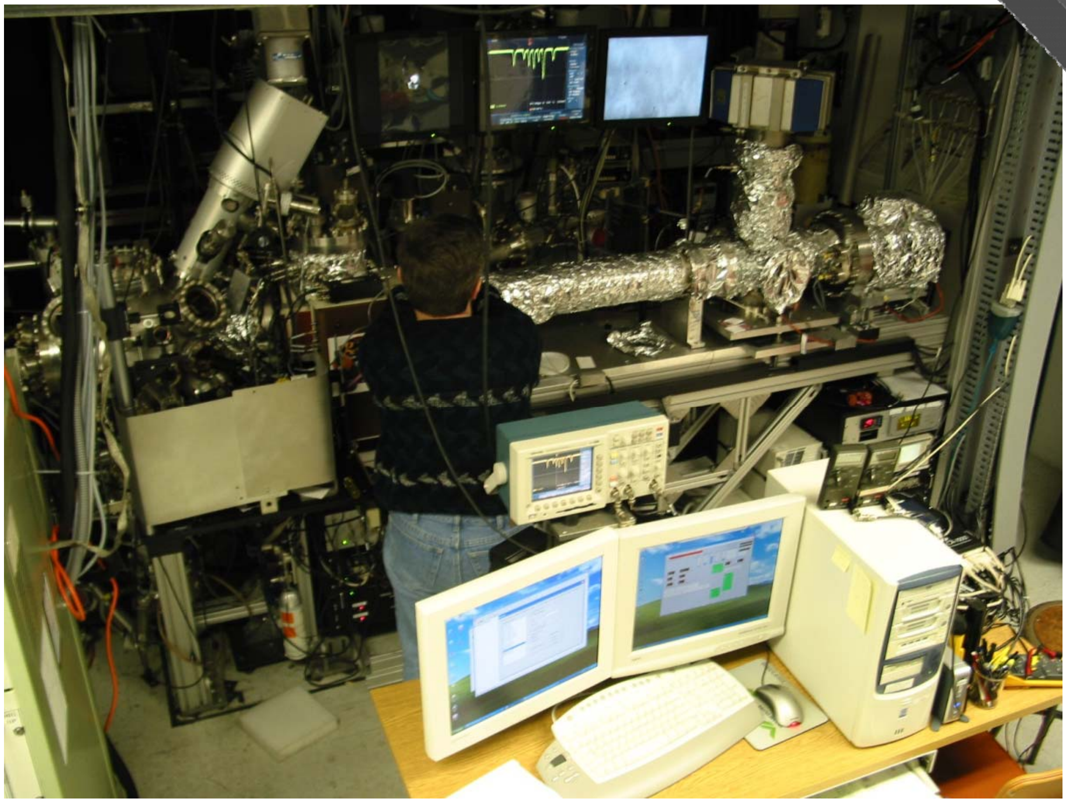
- ✧285.30 nm (resonance step)
- ✧375.66 nm (ionization step)

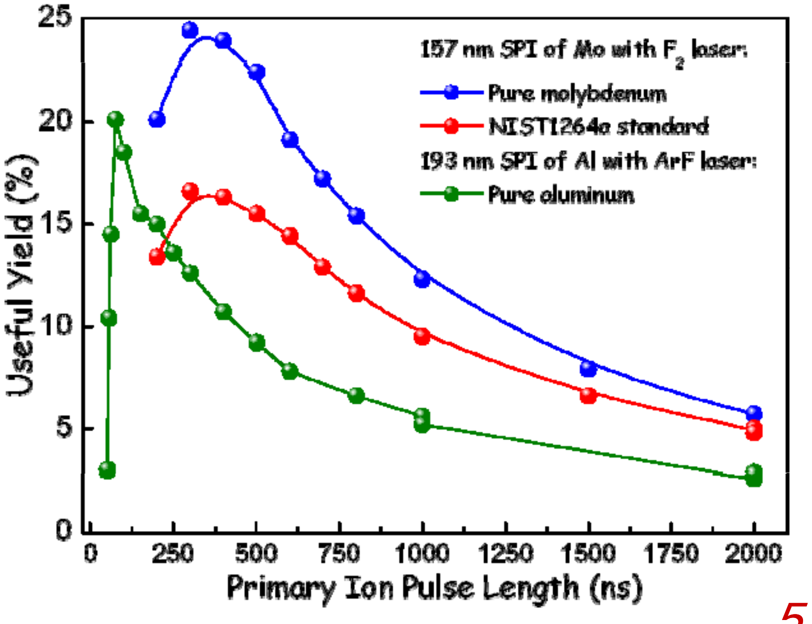
New SARISA: ultrahigh efficiency MS instrument

Surface Analysis by Resonance Ionization of Sputtered Atoms:

- Designed during 1999-2001 to perform RIMS analyses of Genesis samples
- Thoroughly optimized for LPI SNMS
- Constructed in 2004 (prototype – in 2002)
- Fully operational since 2005
- **The most sensitive in the world ion sputtering based MS instrument**
  - **Useful Yield >20% @ Mass Resolution >1500**

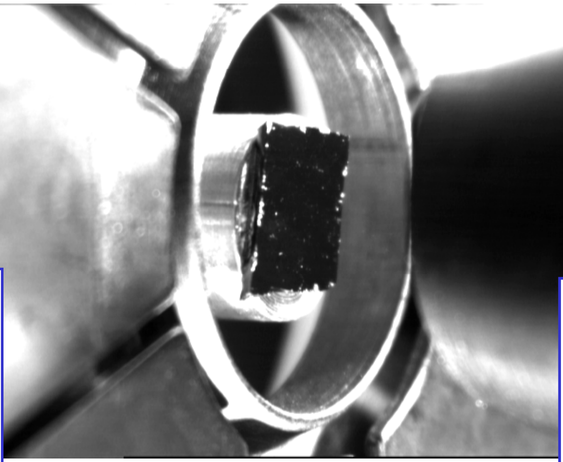






Genesis sample in SARISA

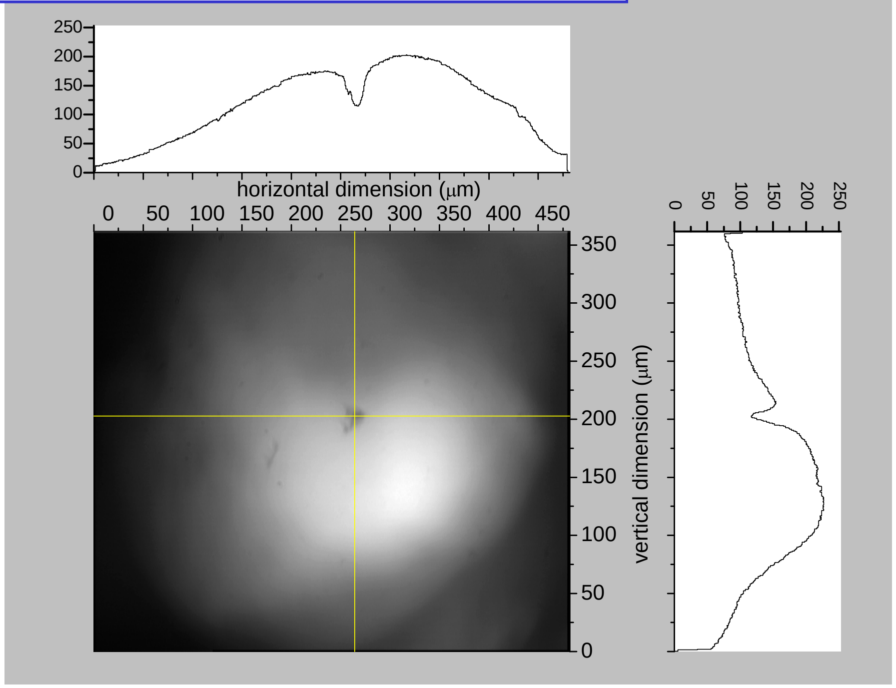
Sample #60178

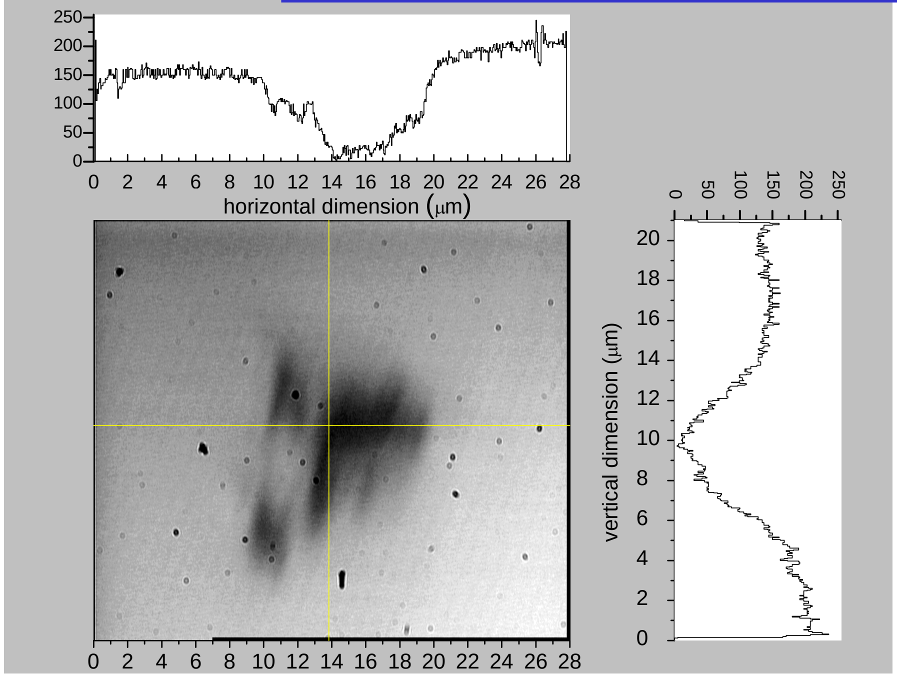


- Si wafer from array B or C
- Sample size ~ 6 mm x 6 mm

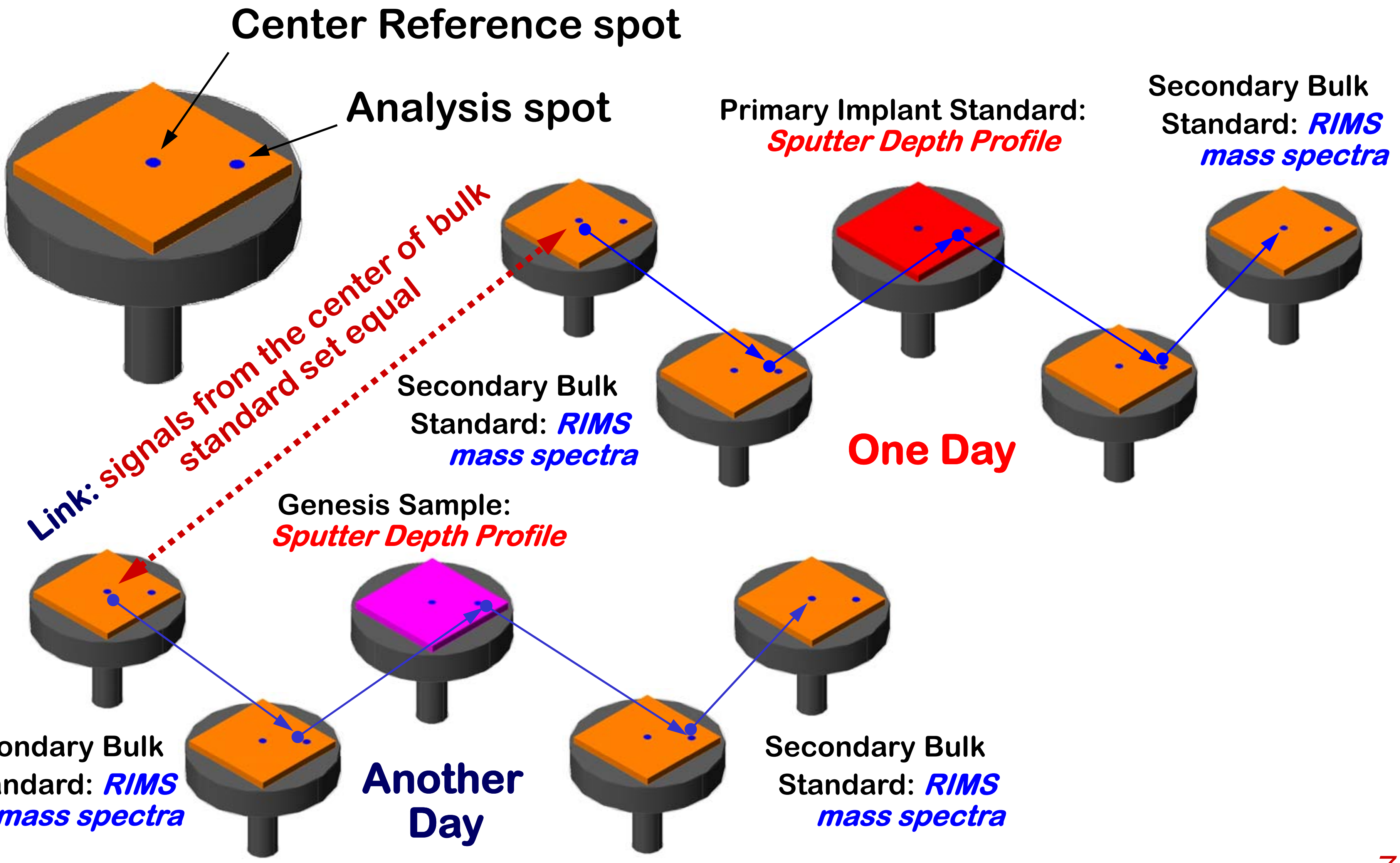
10 μm particulate seen in the low magnification camera

10 μm particulate seen in the high magnification camera





Experimental protocol:
the OLD one (2006-2007)



Center Reference spot

Analysis spot

Link: signals from the center of bulk standard set equal

Primary Implant Standard: *Sputter Depth Profile*

Secondary Bulk Standard: *RIMS mass spectra*

Secondary Bulk Standard: *RIMS mass spectra*

One Day

Genesis Sample: *Sputter Depth Profile*

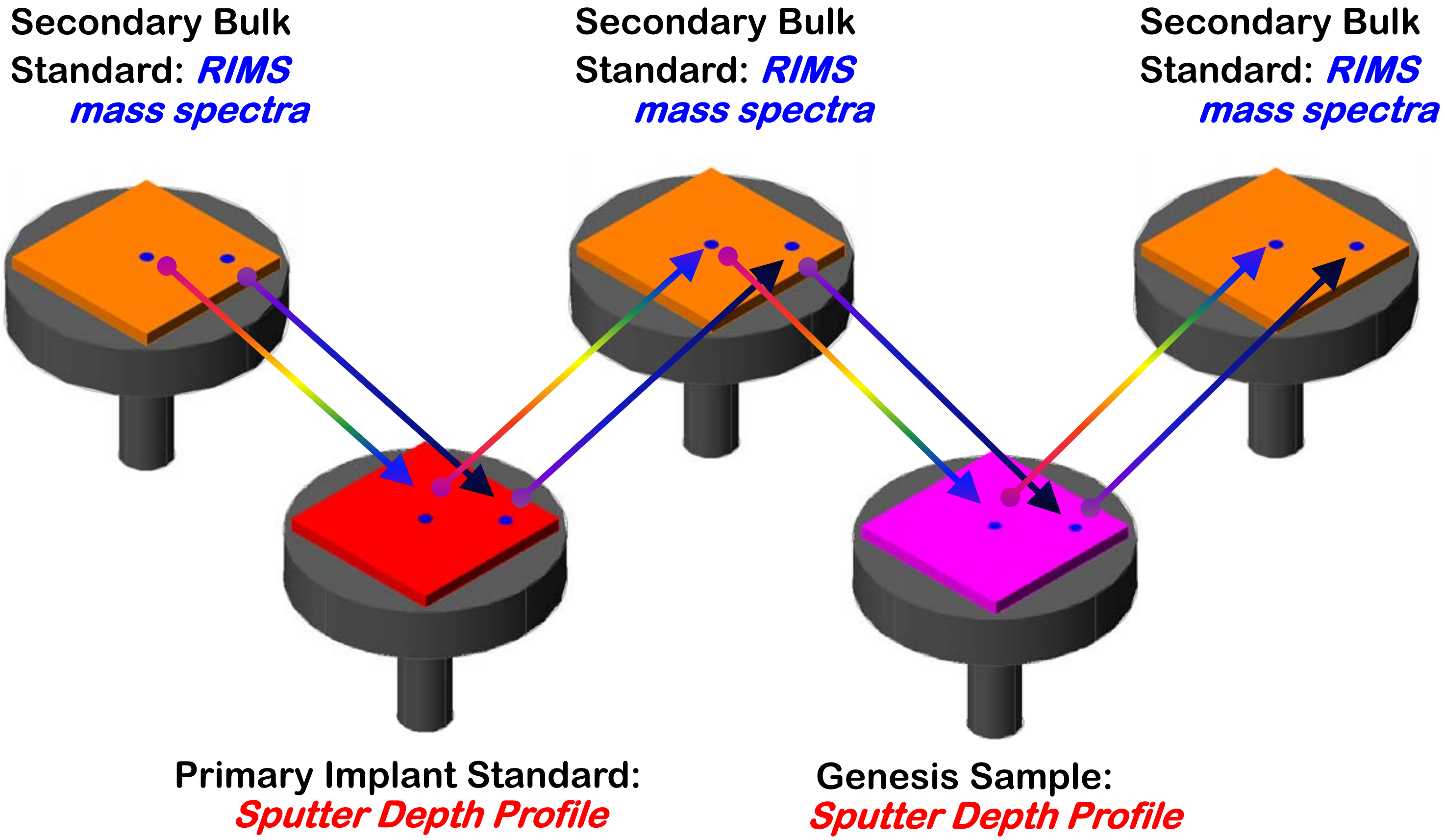
Secondary Bulk Standard: *RIMS mass spectra*

Another Day

Secondary Bulk Standard: *RIMS mass spectra*

Experimental protocol: the NEW one (from 2008)

All measurements in One Day



Secondary Bulk Standard: ***RIMS mass spectra***

Secondary Bulk Standard: ***RIMS mass spectra***

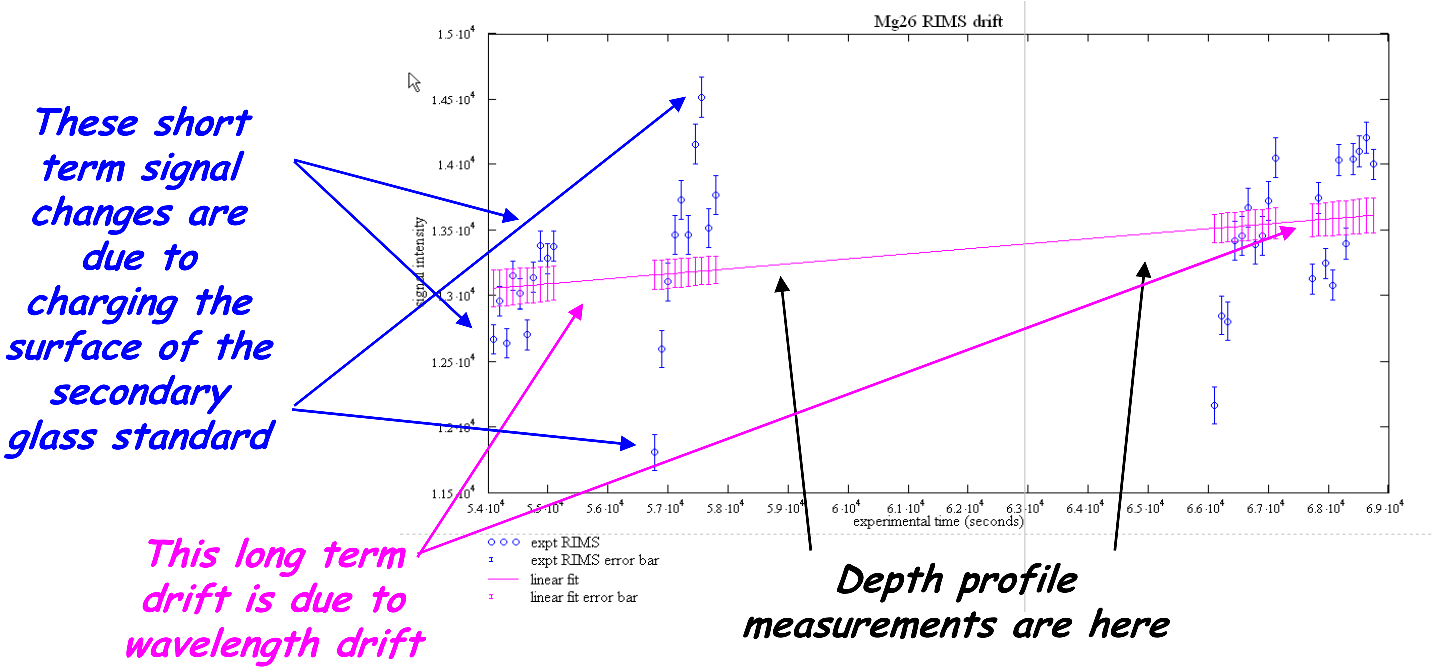
Secondary Bulk Standard: ***RIMS mass spectra***

Primary Implant Standard: ***Sputter Depth Profile***

Genesis Sample: ***Sputter Depth Profile***

Analysis spots on standards and Genesis always have the same coordinates (locations)

Sources of uncertainties identified by 2008



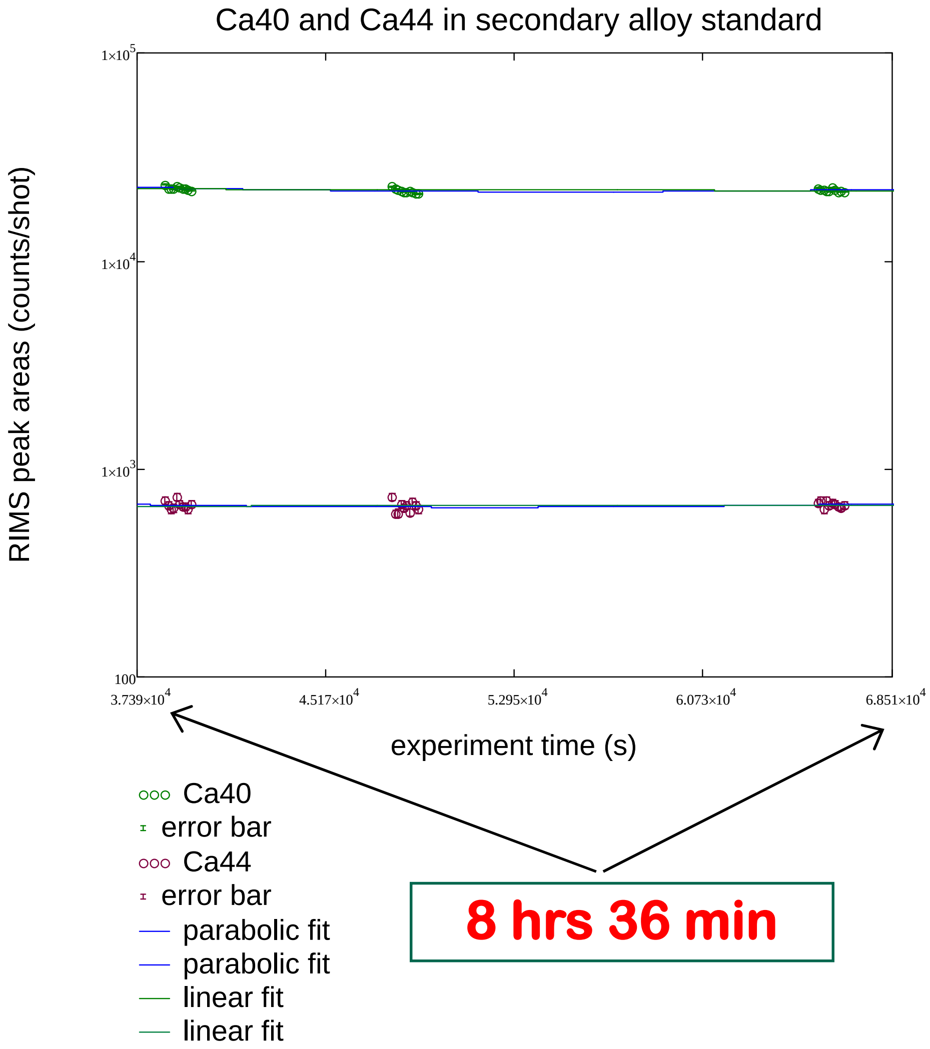
These short term signal changes are due to charging the surface of the secondary glass standard

This long term drift is due to wavelength drift

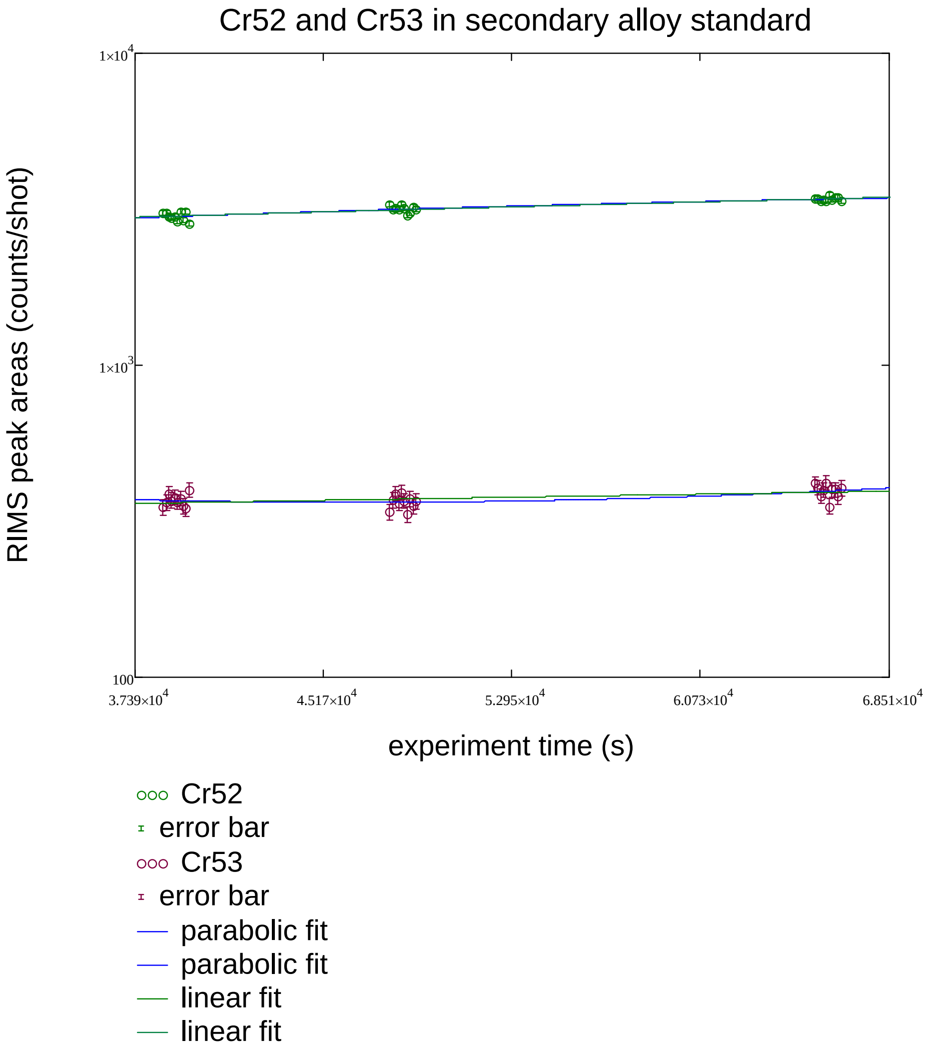
Depth profile measurements are here

- Surface charging observed for glass samples used as secondary standards.
- Drift in wavelengths of tunable lasers resulted in long term signal variations for both standards and Genesis samples
- Unstable primary ion current resulted in
  - ☐ increased uncertainties in the shape of the sputter depth profile (during the sputtering step)
  - ☐ extra fluctuation in RIMS signals
- Background levels (suppressed SIMS) not measured with sufficient precision, accuracy and number of data points

RIMS Signal drifts now

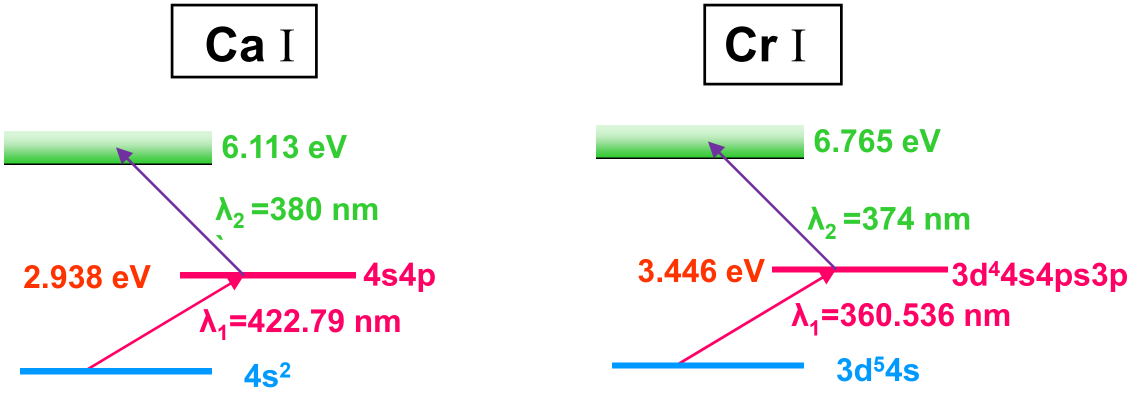


8 hrs 36 min

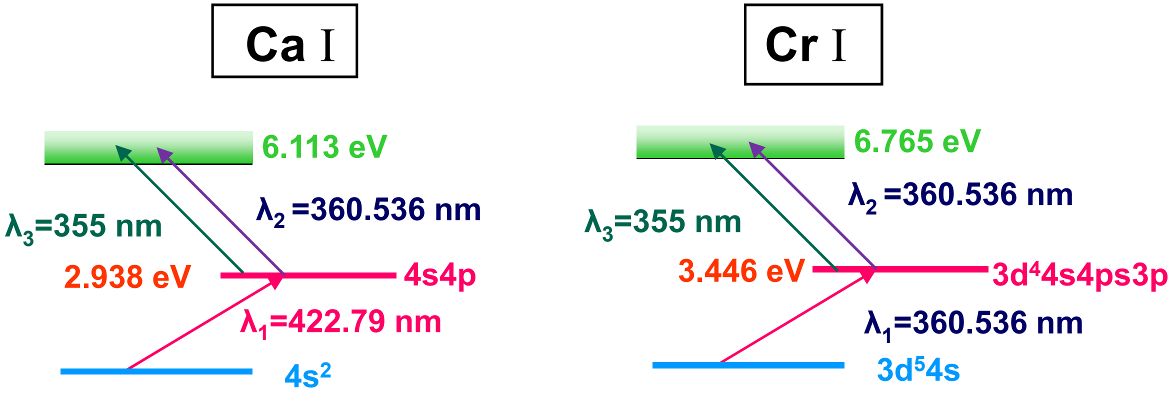


- **Secondary bulk standard is now Al alloy**
  - ☐ **Charging problems are eliminated**
  - ☐ **Grains are still an issue for some elements**

RIMS of two elements with two tunable lasers

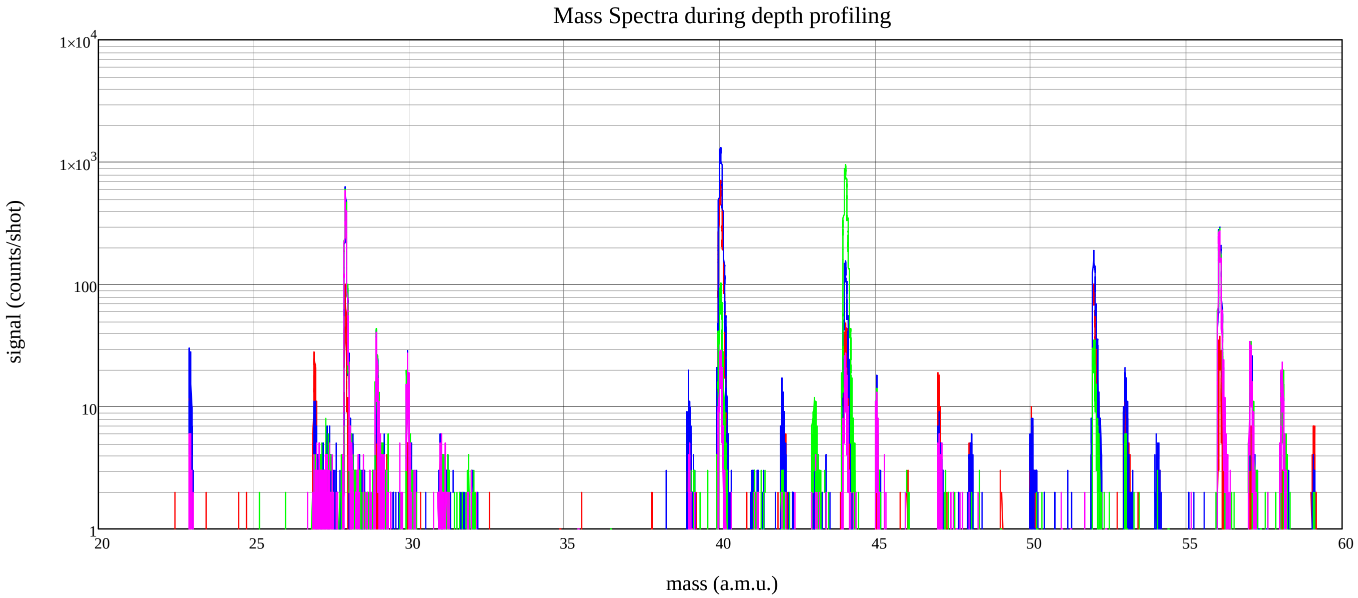


RIMS schemes for Ca and Cr

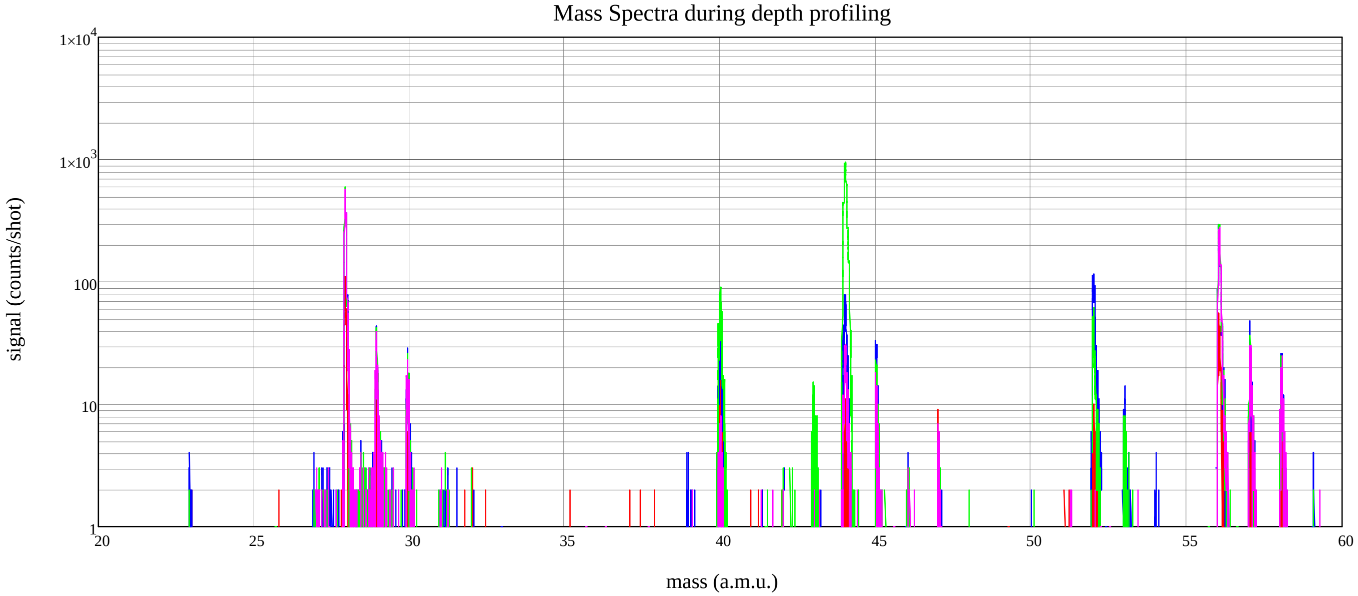


RIMS schemes for Ca and Cr used these experiments:
two tunable (422.79 nm and 360.536 nm) and
one fixed wavelength (355 nm) lasers

Comparison of two pieces of the same stuff



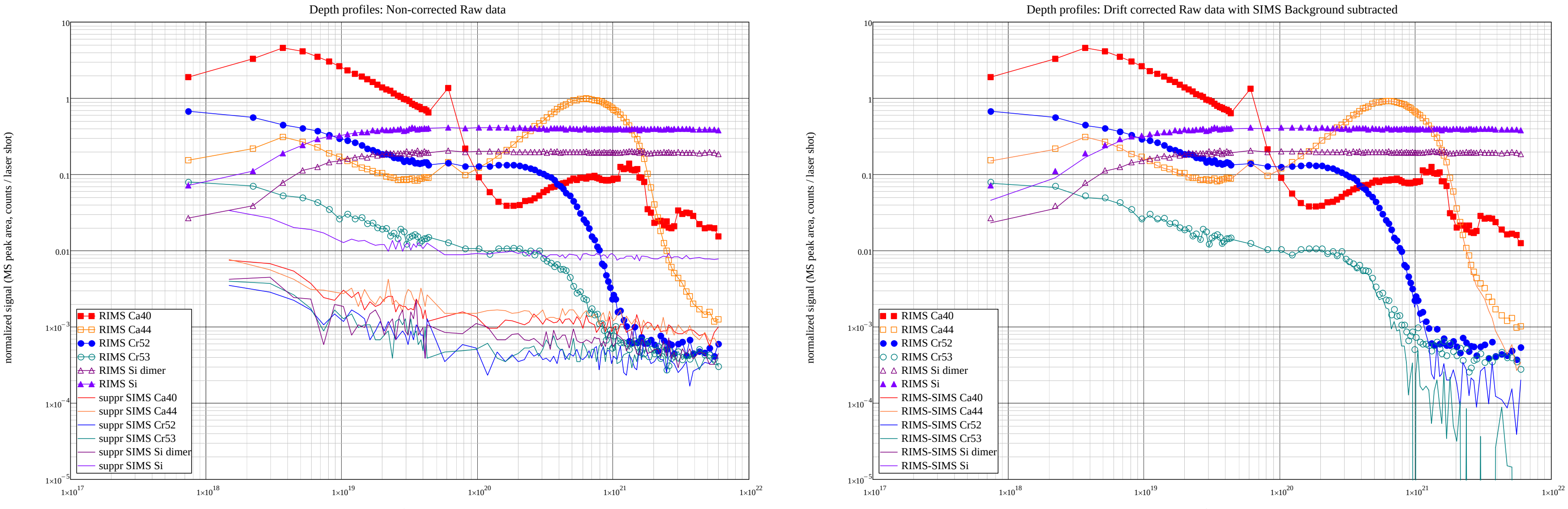
Old L52
Implant Standard



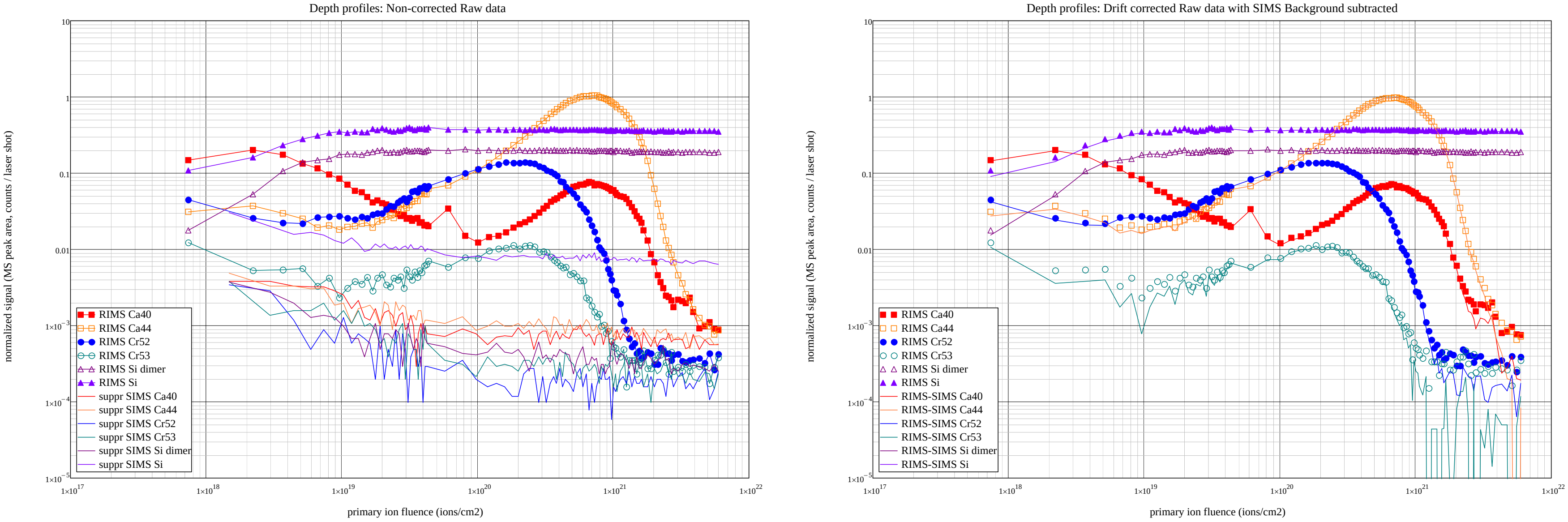
New L52
Implant Standard

Comparison of two pieces of the same stuff

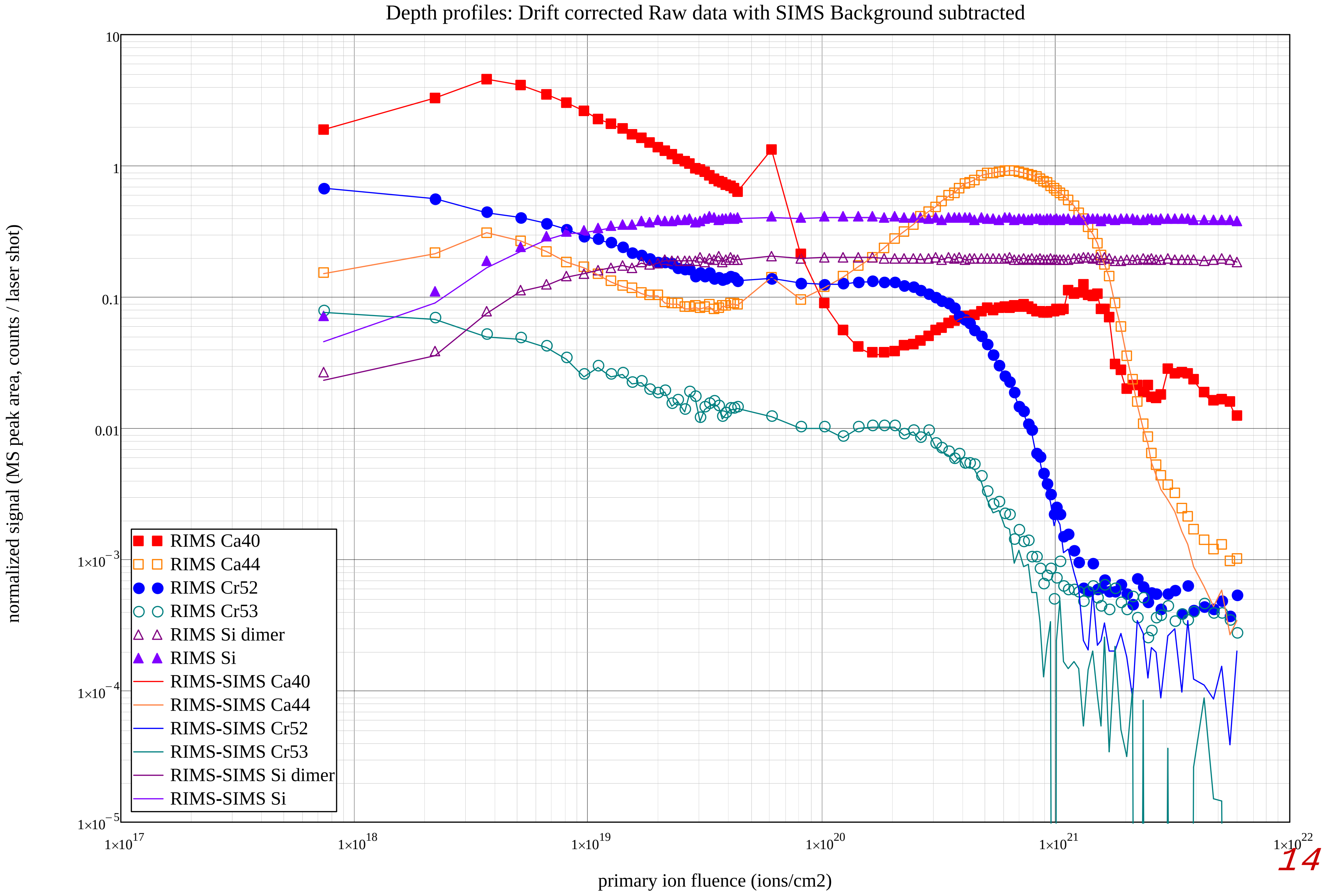
“Old” L52 Implant Standard



“New” L52 Implant Standard

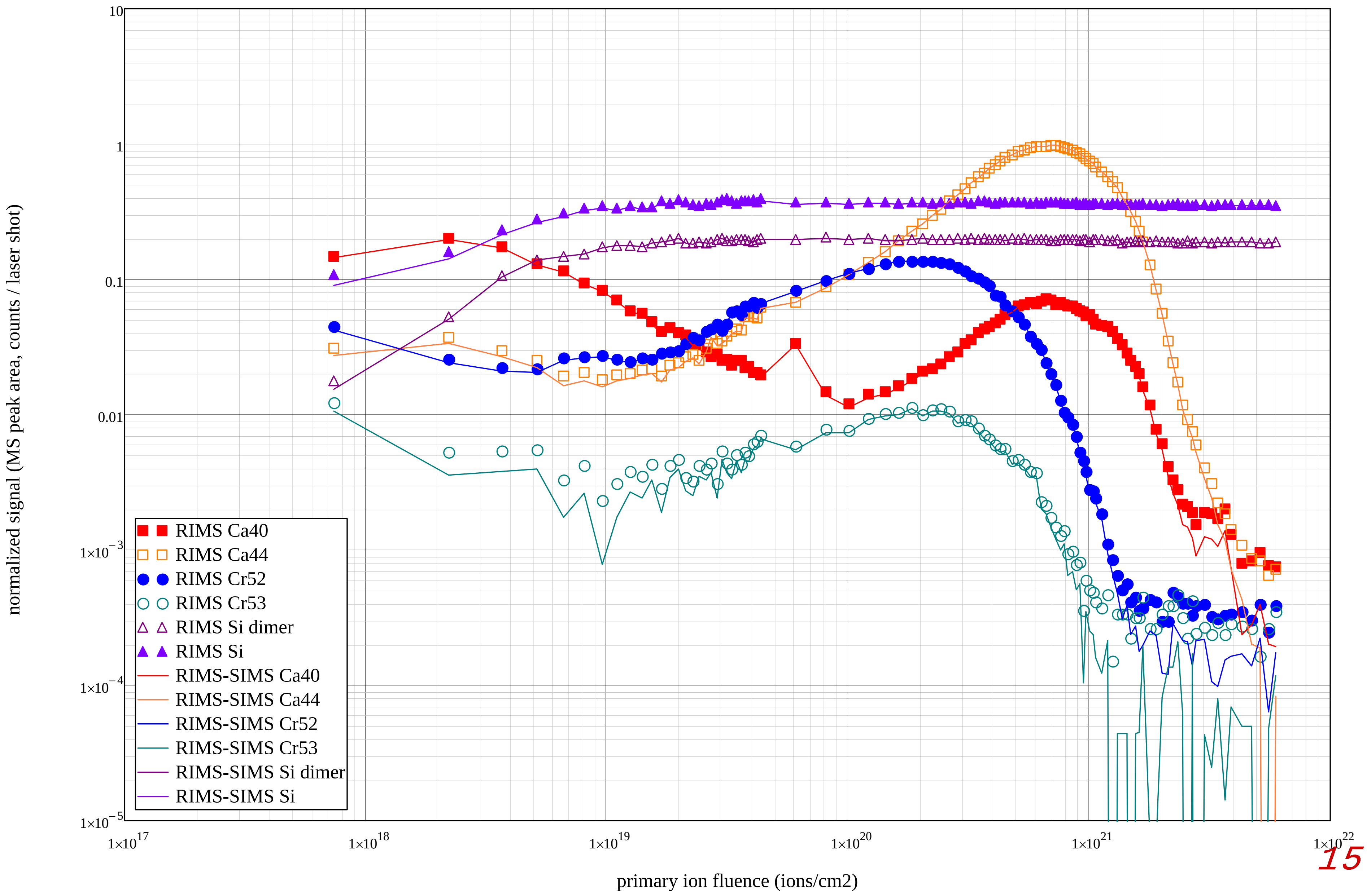


"Old" L52 implant

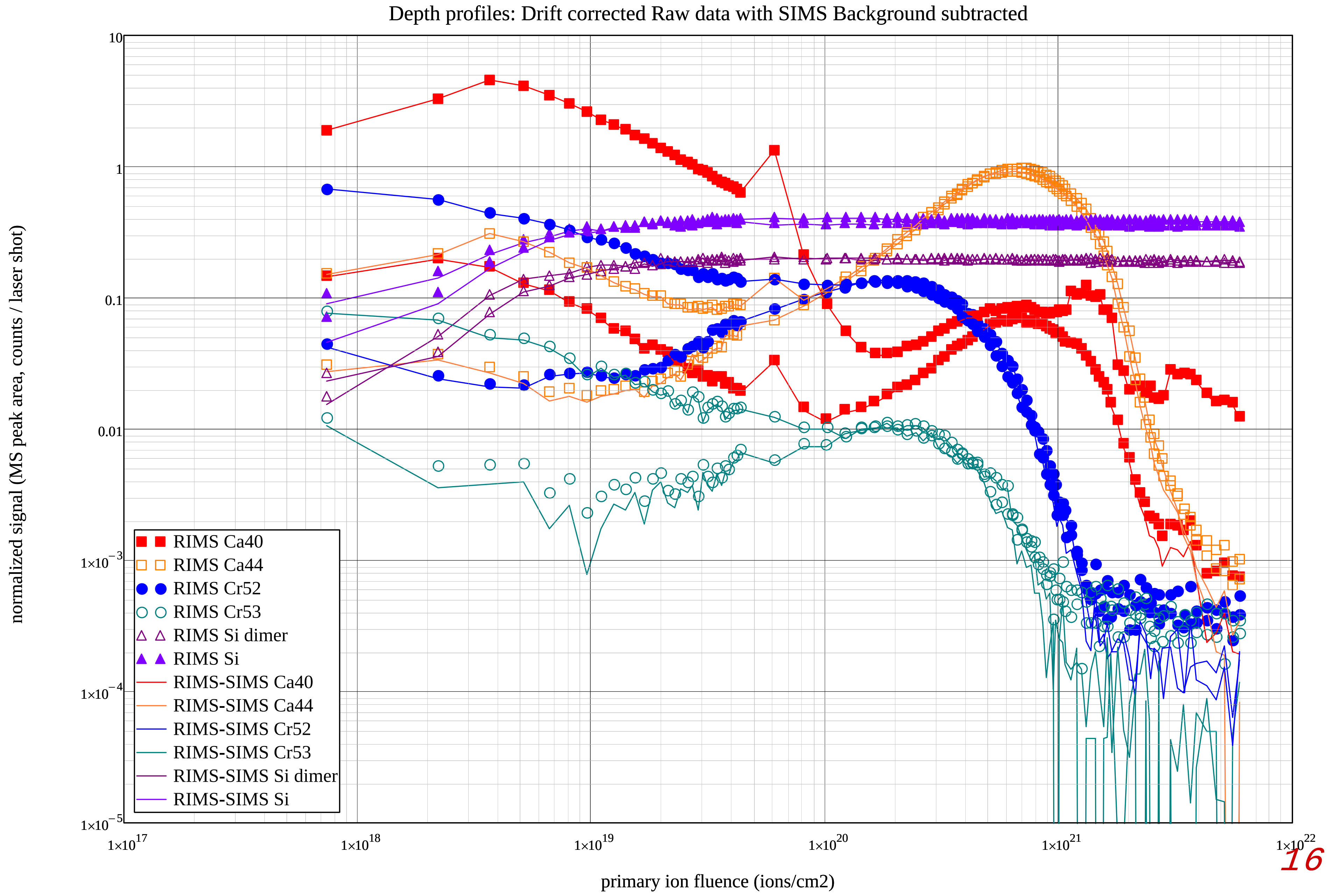


“New” L52 implant

Depth profiles: Drift corrected Raw data with SIMS Background subtracted



"New" over "old" L52 implant



Ca and Cr Fluencies:
"old" L52 pretending to be Genesis

- as presented at Science Team Meeting

^{40}Ca	^{44}Ca	^{52}Cr	^{53}Cr
(6.39±0.08) x10^{12}	(2.73±0.01) x10^{13}	(2.69±0.05) x10^{13}	(2.10±0.24) x10^{12}
Based on→	3x10^{13}	3x10^{13}	←Based on

Ca and Cr Fluencies:

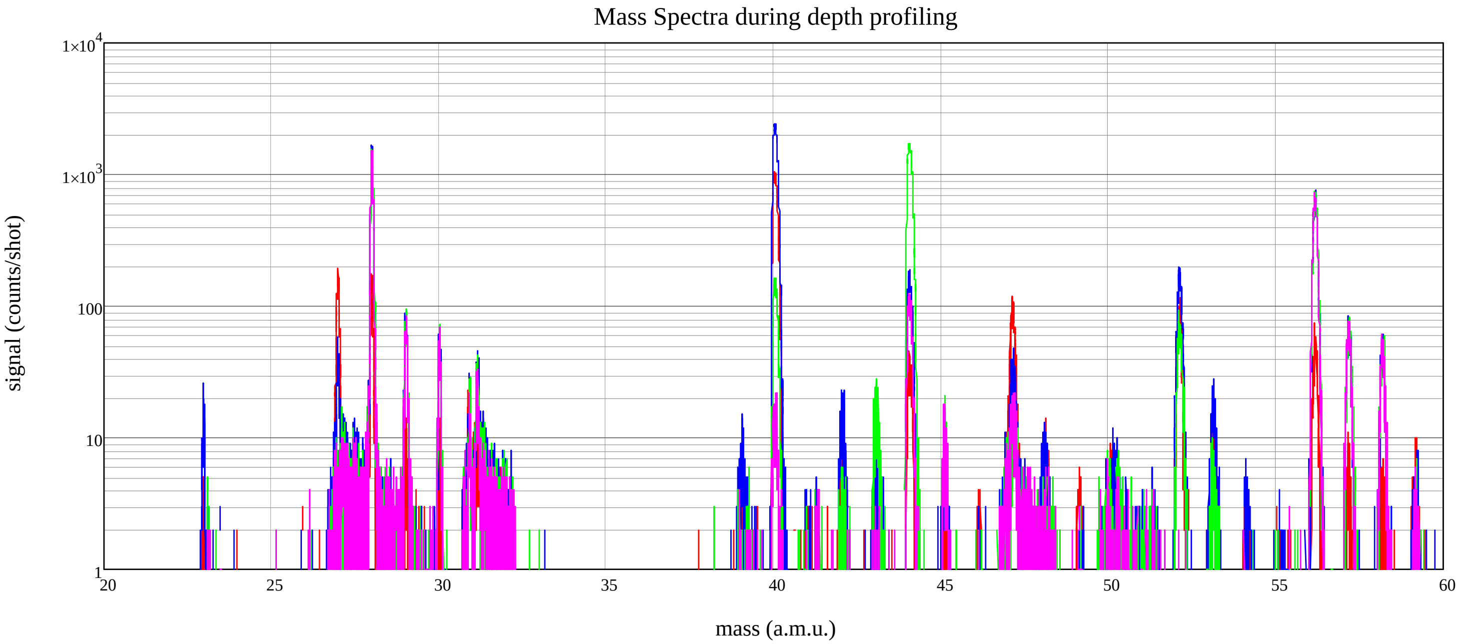
"old" L52 pretending to be Genesis

- *recalculated using corrected integration algorithm*

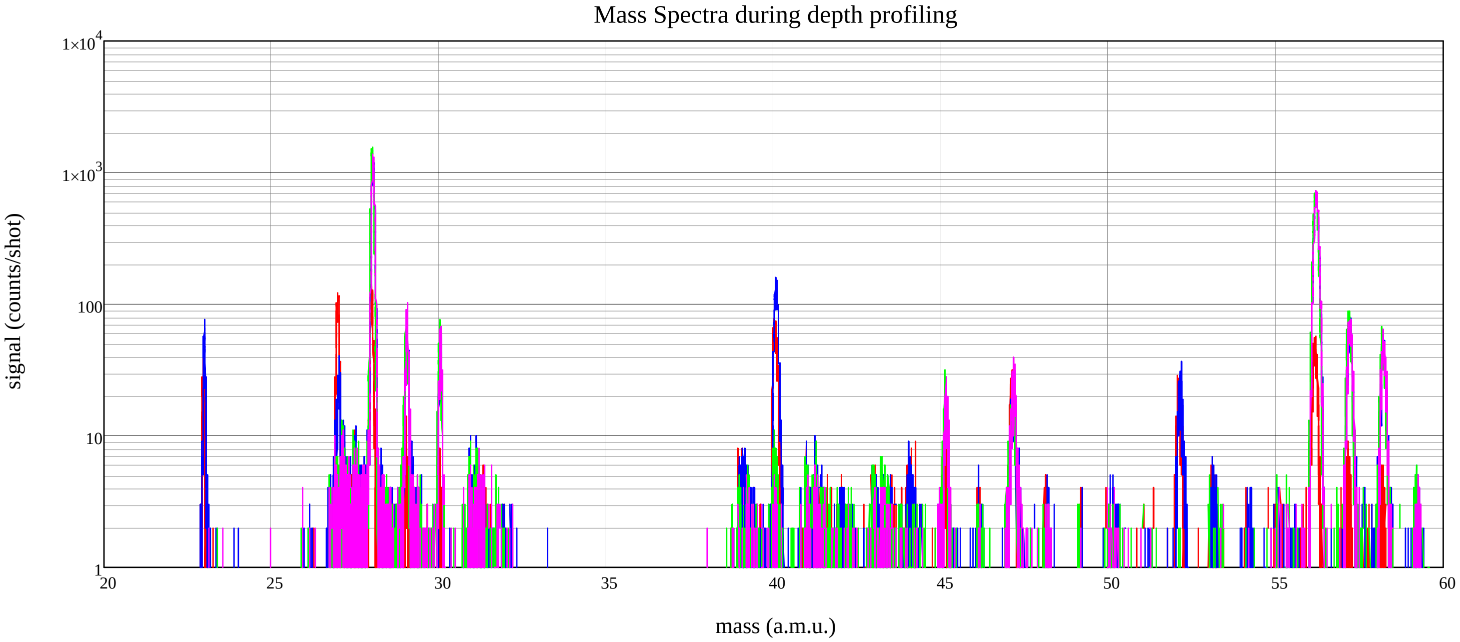
(as presented at LPSC-XXXX)

^{40}Ca	^{44}Ca	^{52}Cr	^{53}Cr
(6.84±0.08) x10^{12}	(2.71±0.01) x10^{13}	(2.73±0.03) x10^{13}	(2.06±0.11) x10^{12}
Based on→	3x10^{13}	3x10^{13}	←Based on

RIMS Mass spectra (December 19, 2008)



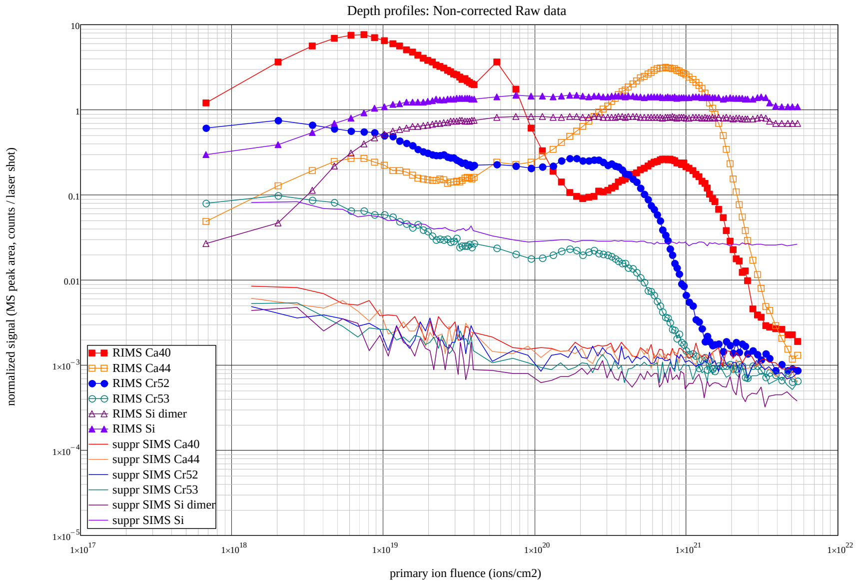
Implant Standard

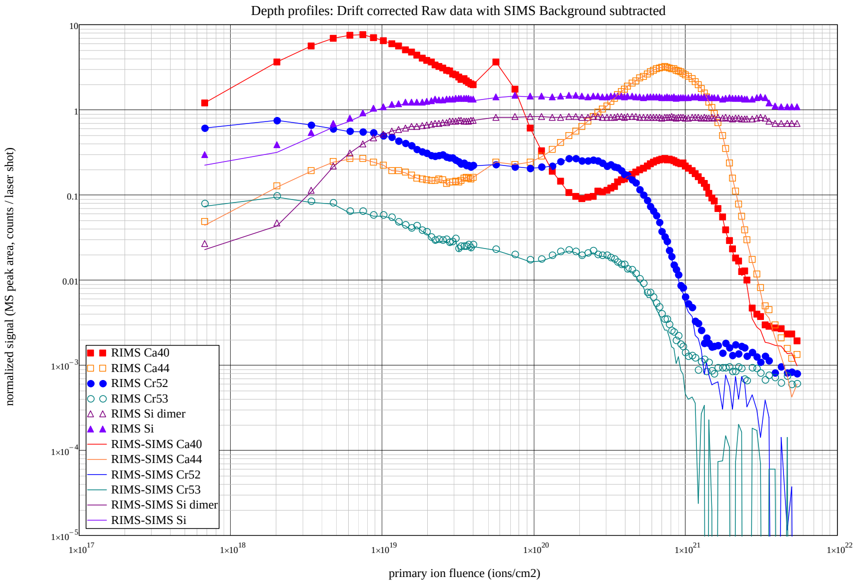


Genesis #60179

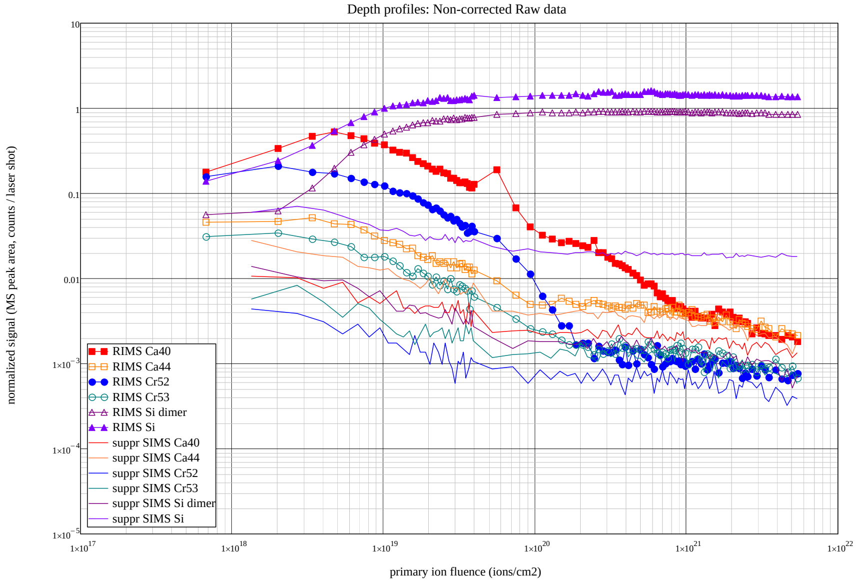
Depth profiles (December 19, 2008)

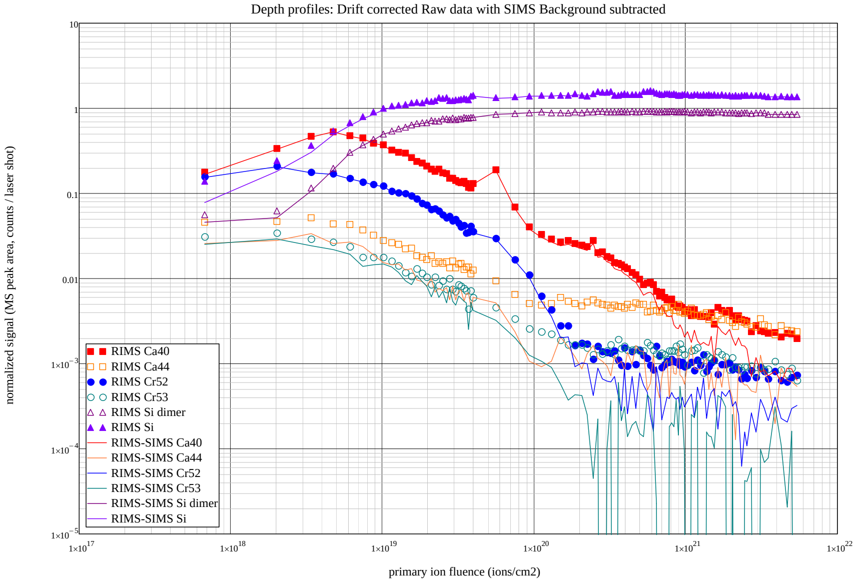
Implant Standard


Depth profiles: Non-corrected Raw data


Depth profiles: Drift corrected Raw data with SIMS Background subtracted

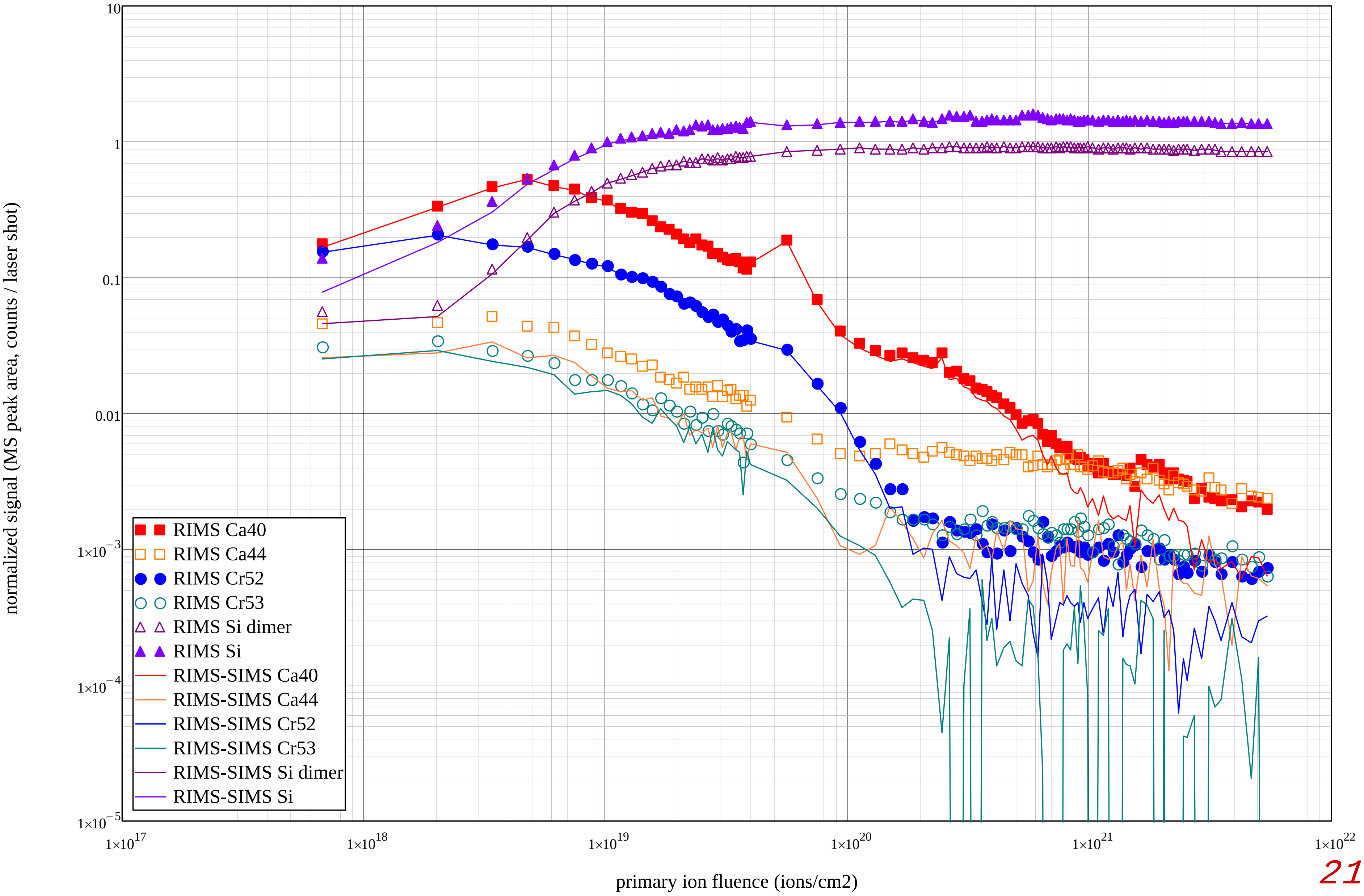
Genesis #60179


Depth profiles: Non-corrected Raw data

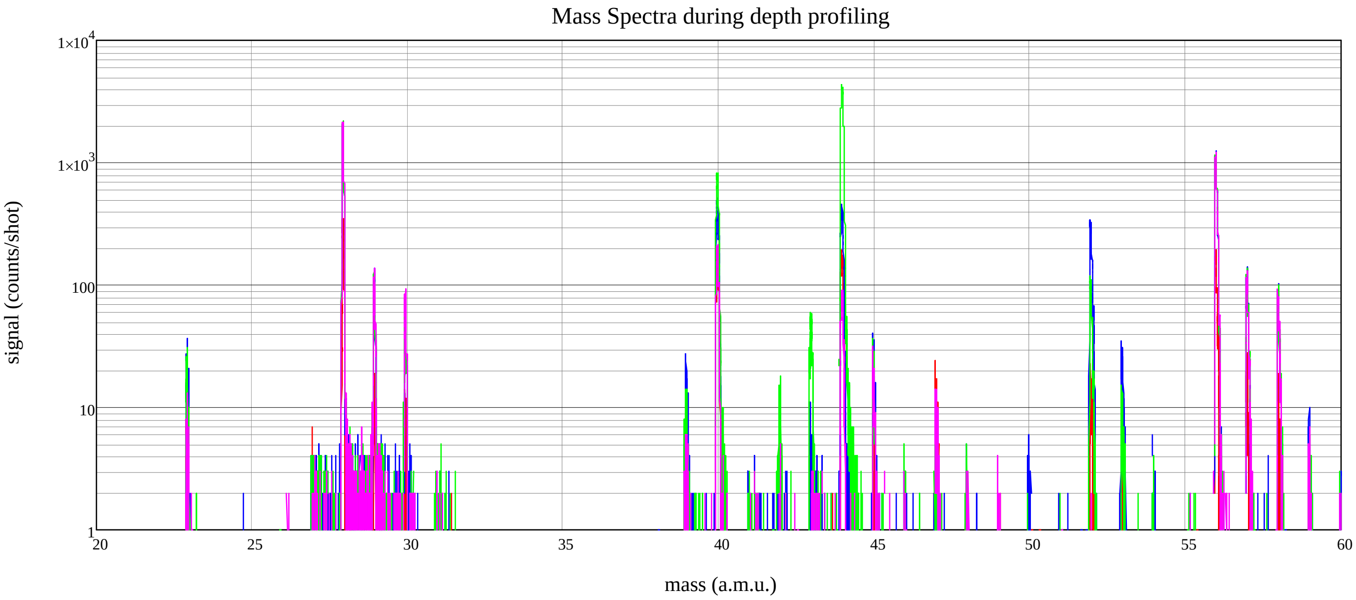

Depth profiles: Drift corrected Raw data with SIMS Background subtracted

Genesis #60179 measured December 19, 2008

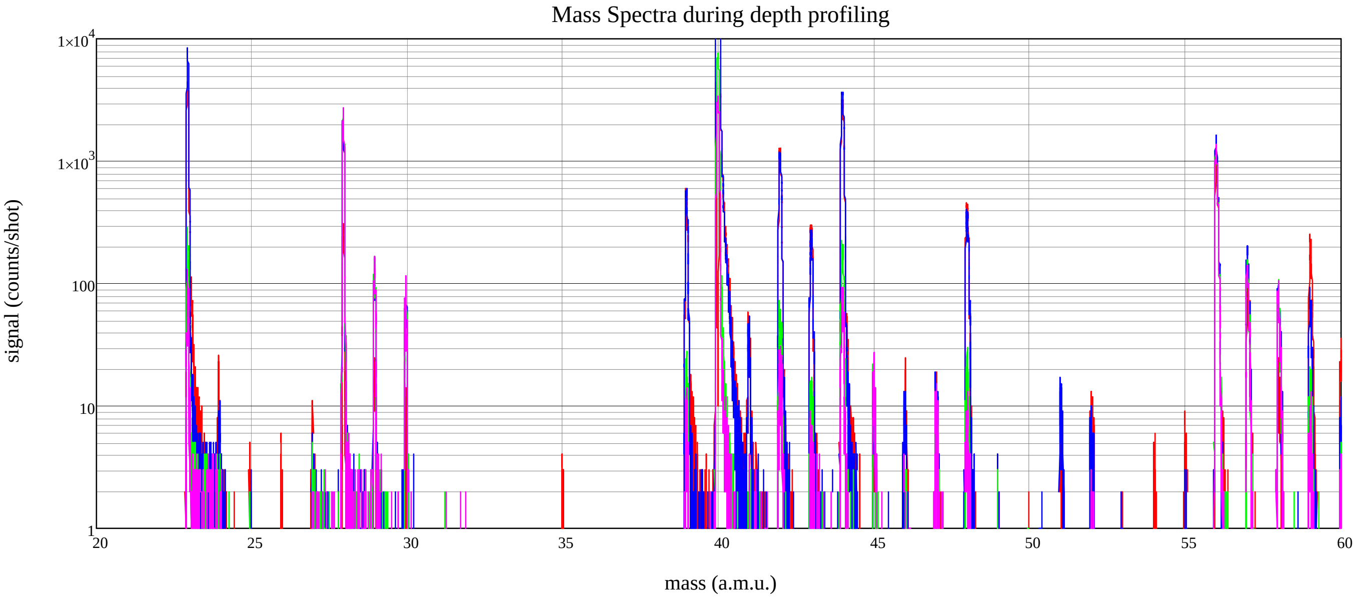
Depth profiles: Drift corrected Raw data with SIMS Background subtracted



RIMS Mass spectra (February 19, 2009)



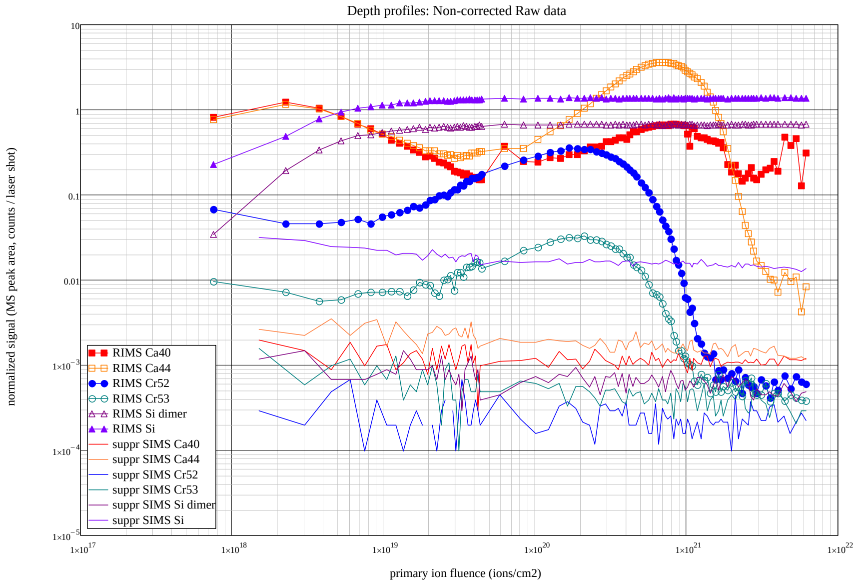
Implant Standard

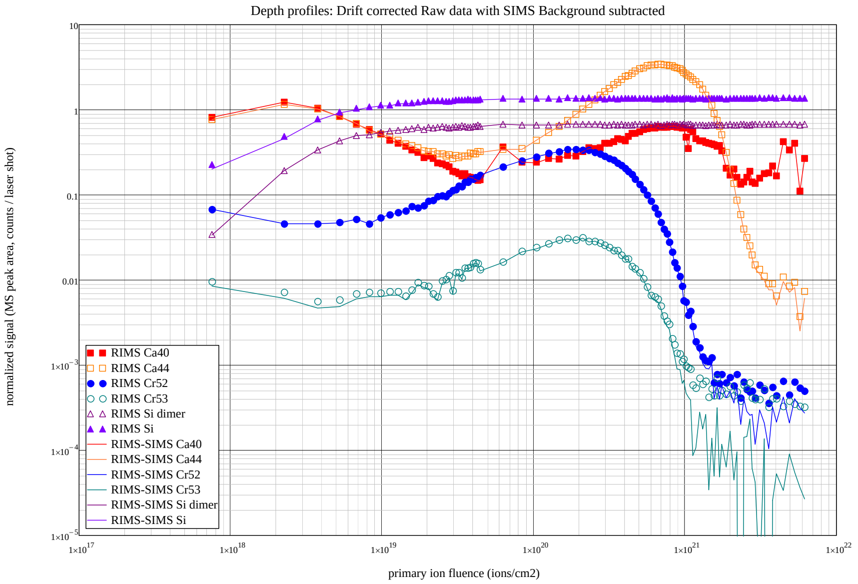


Genesis #60476

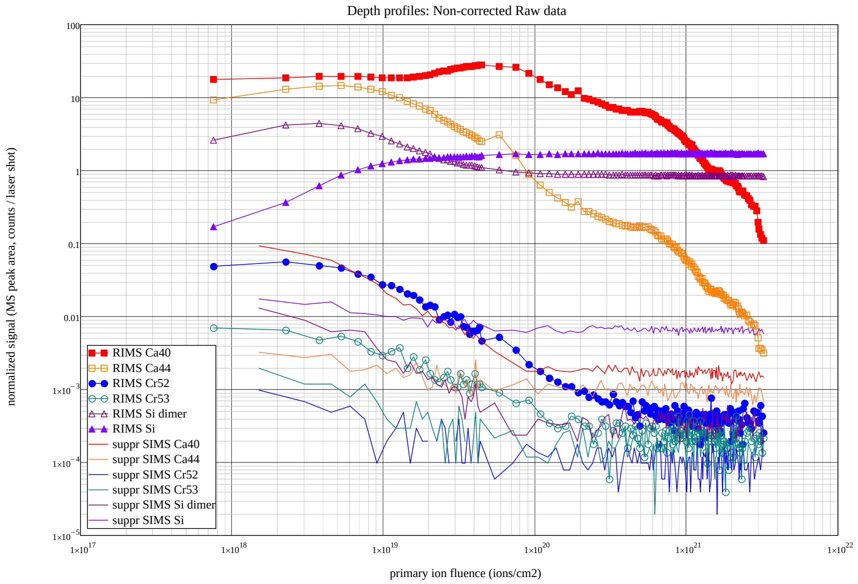
Depth profiles (February 19, 2009)

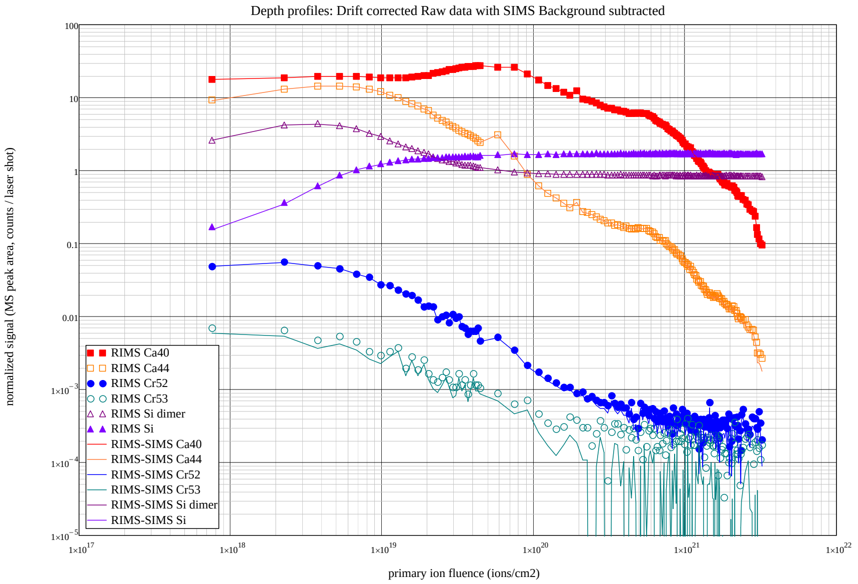
Implant Standard


Depth profiles: Non-corrected Raw data


Depth profiles: Drift corrected Raw data with SIMS Background subtracted

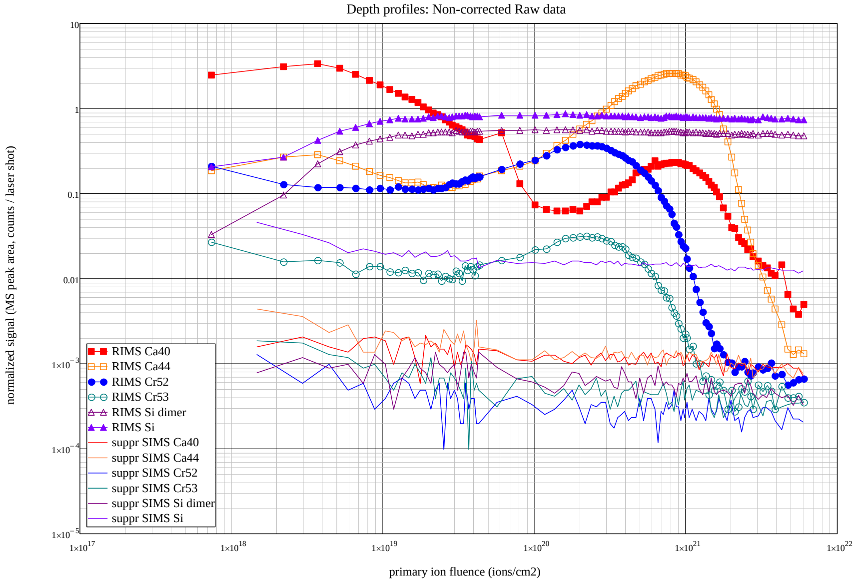
Genesis #60476

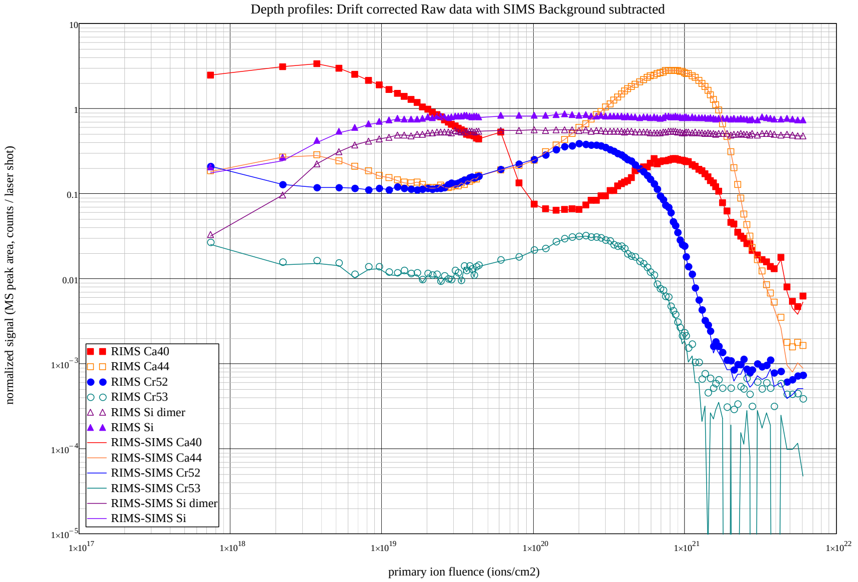

Depth profiles: Non-corrected Raw data


Depth profiles: Drift corrected Raw data with SIMS Background subtracted

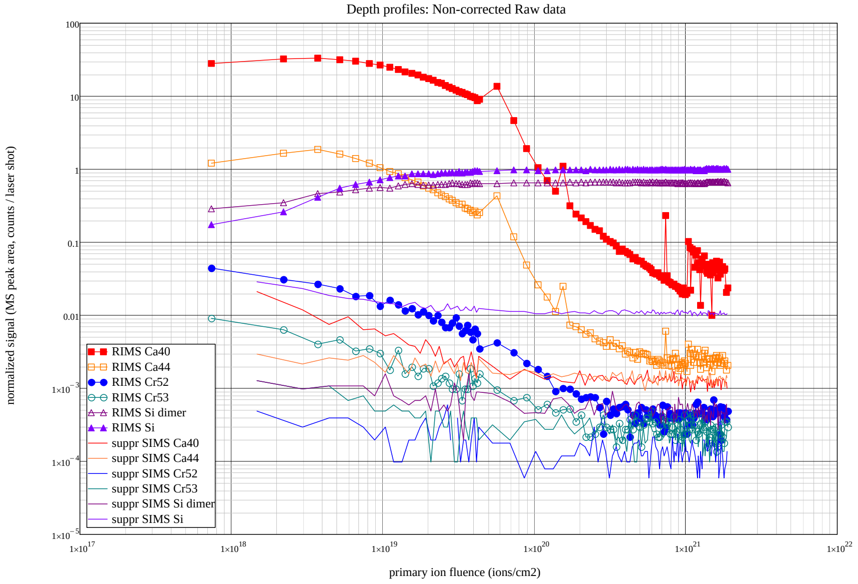
Depth profiles (March 4, 2009)

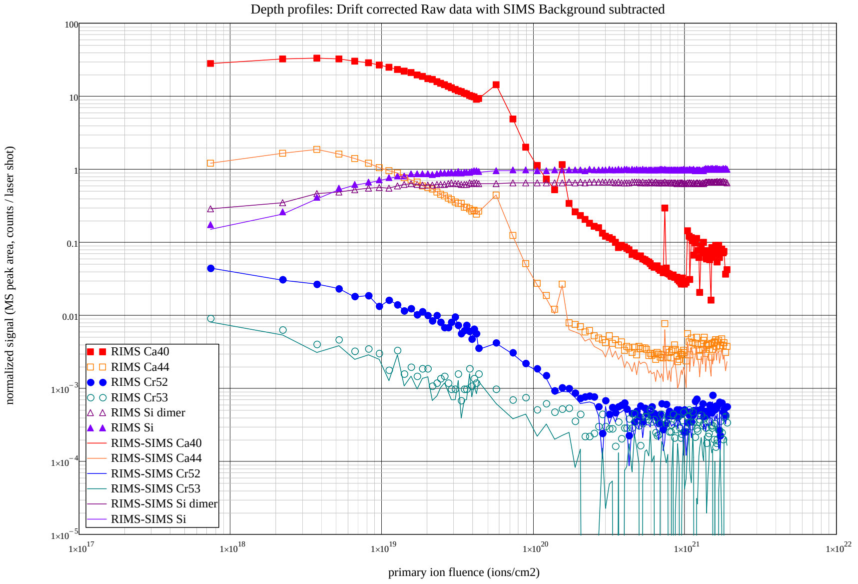
Implant Standard


Depth profiles: Non-corrected Raw data

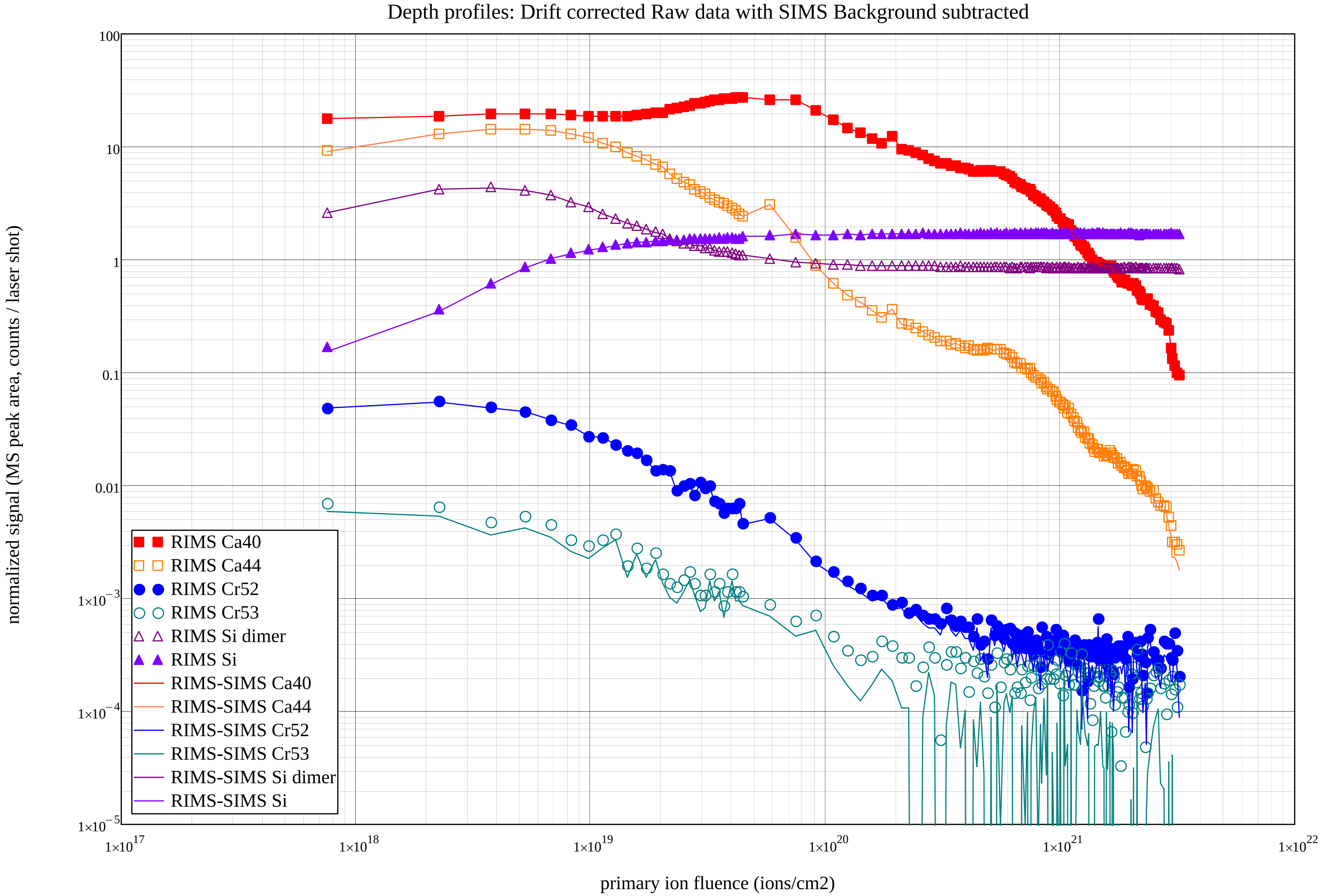

Depth profiles: Drift corrected Raw data with SIMS Background subtracted

Genesis #60476

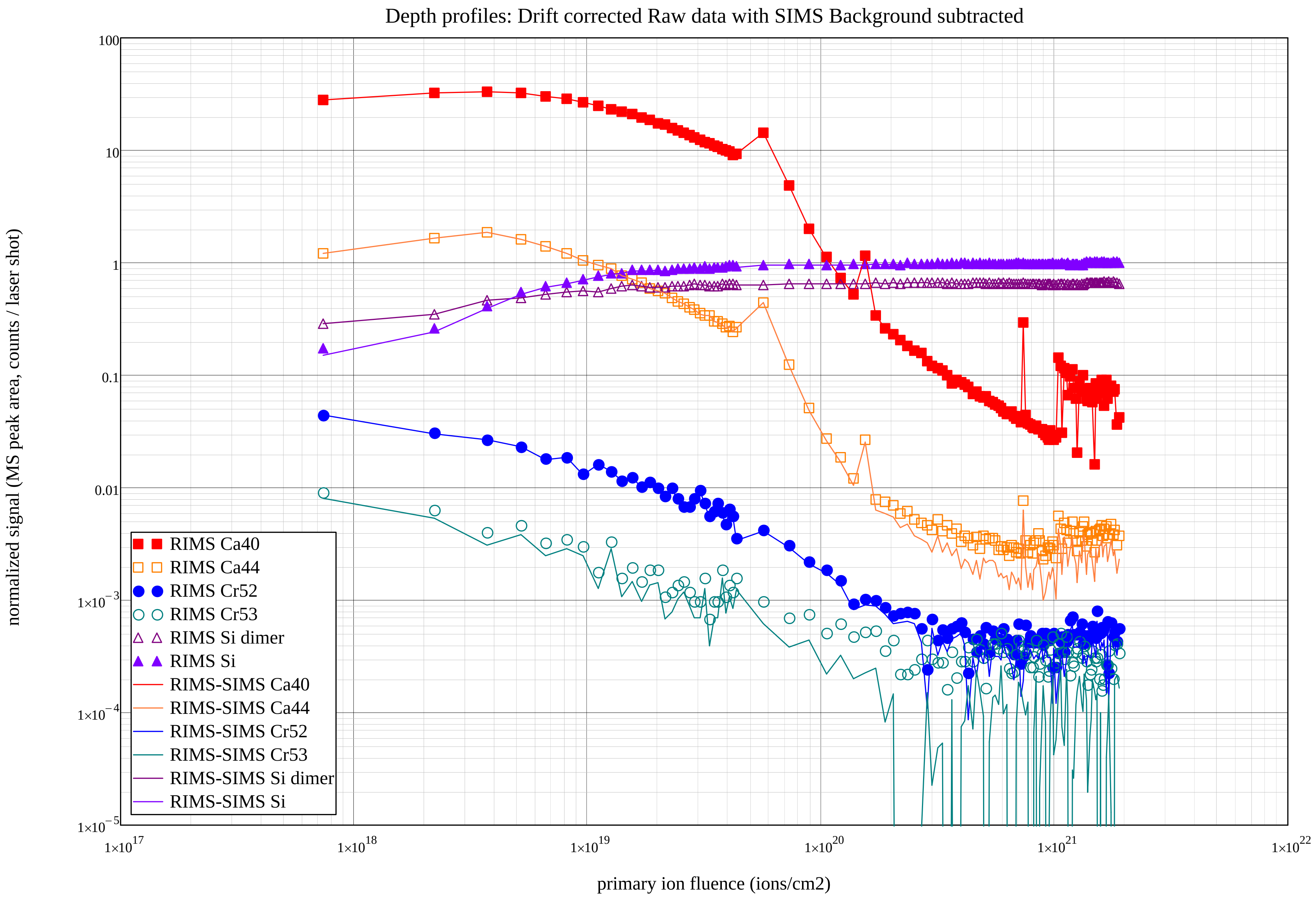

Depth profiles: Non-corrected Raw data


Depth profiles: Drift corrected Raw data with SIMS Background subtracted

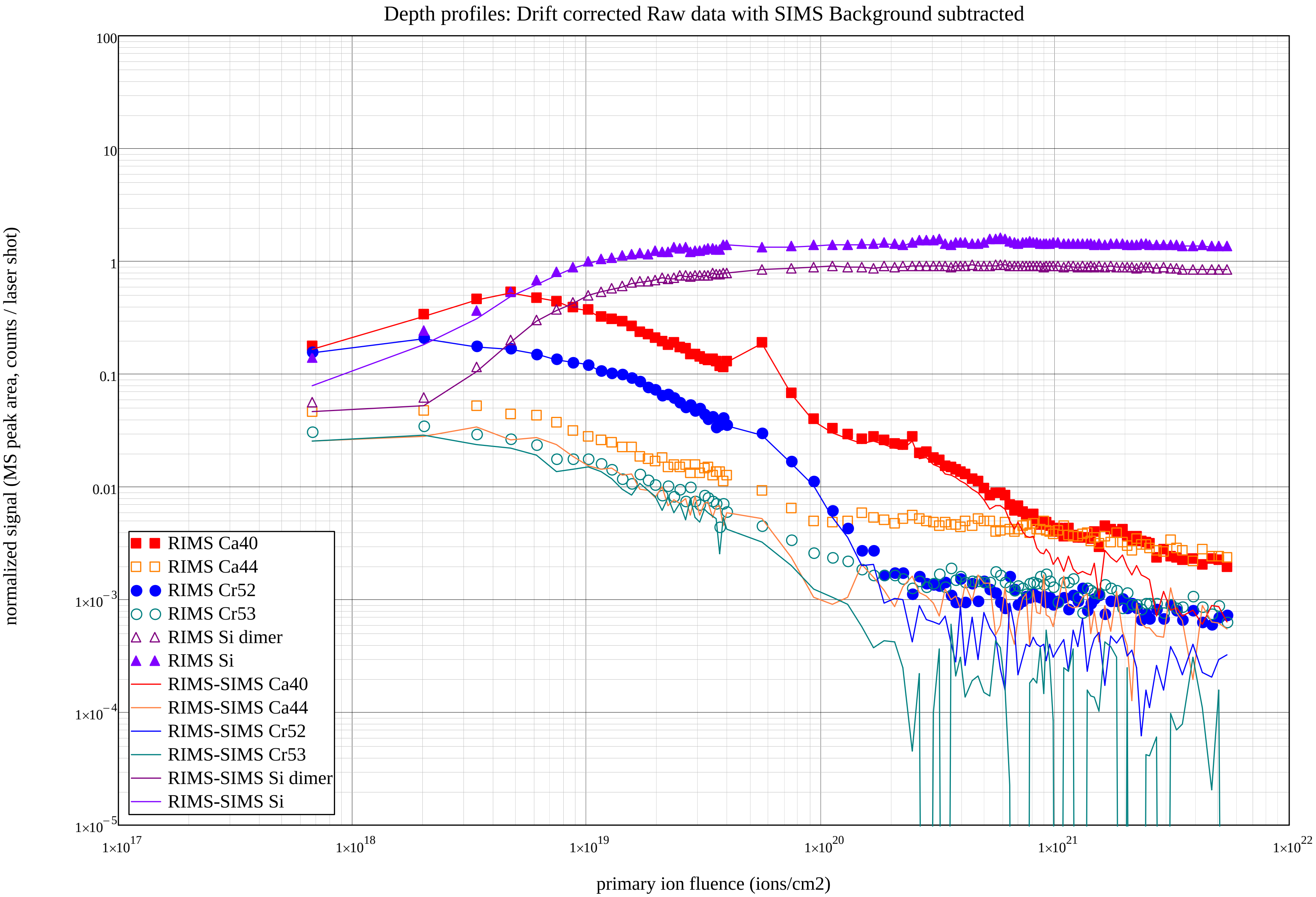
Genesis #60476 measured February 19, 2008



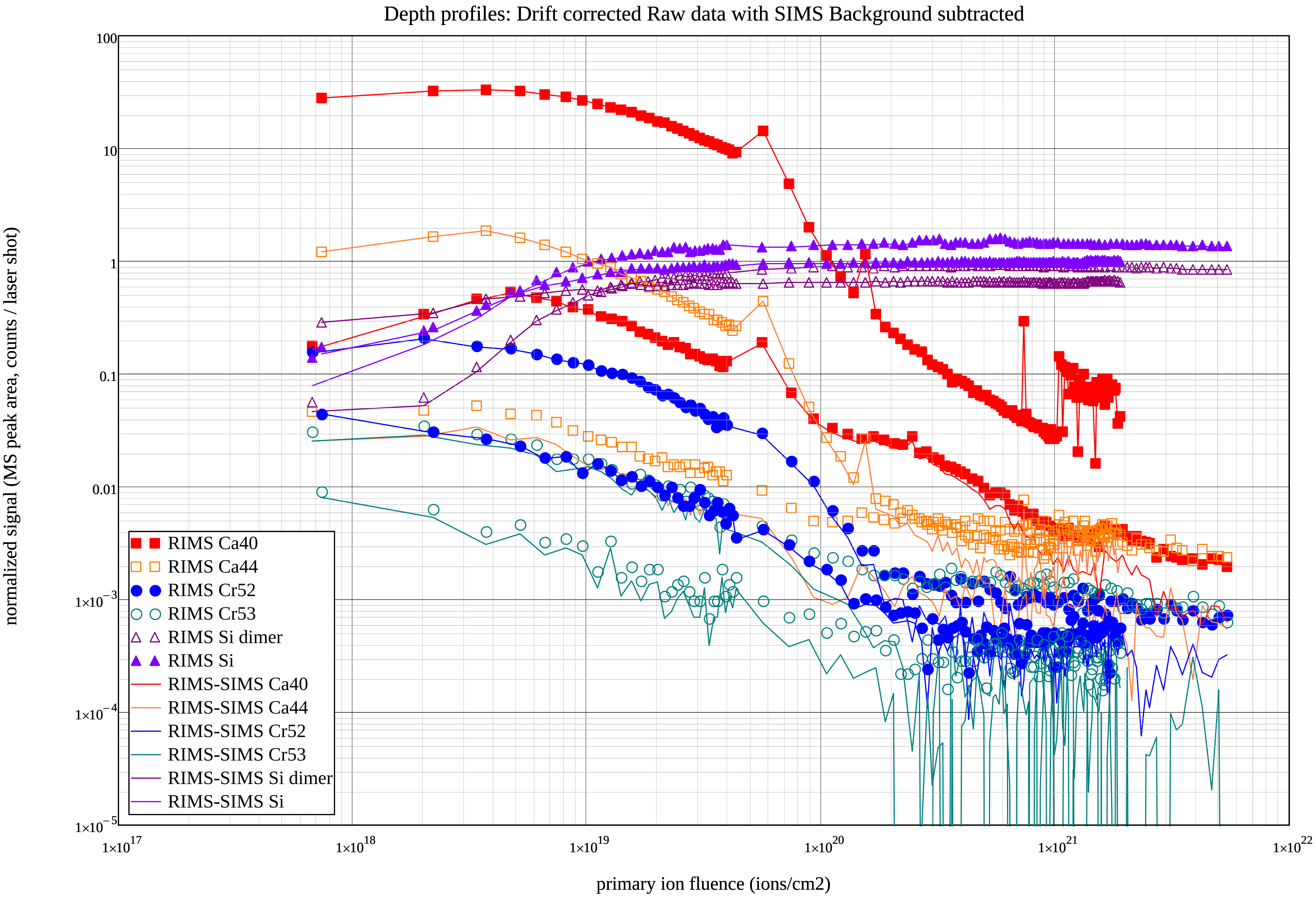
Genesis #60476 measured March 4, 2009



Genesis #60179 measured December 19, 2009



#60179 (12/19/08) vs #60476 (03/04/09)

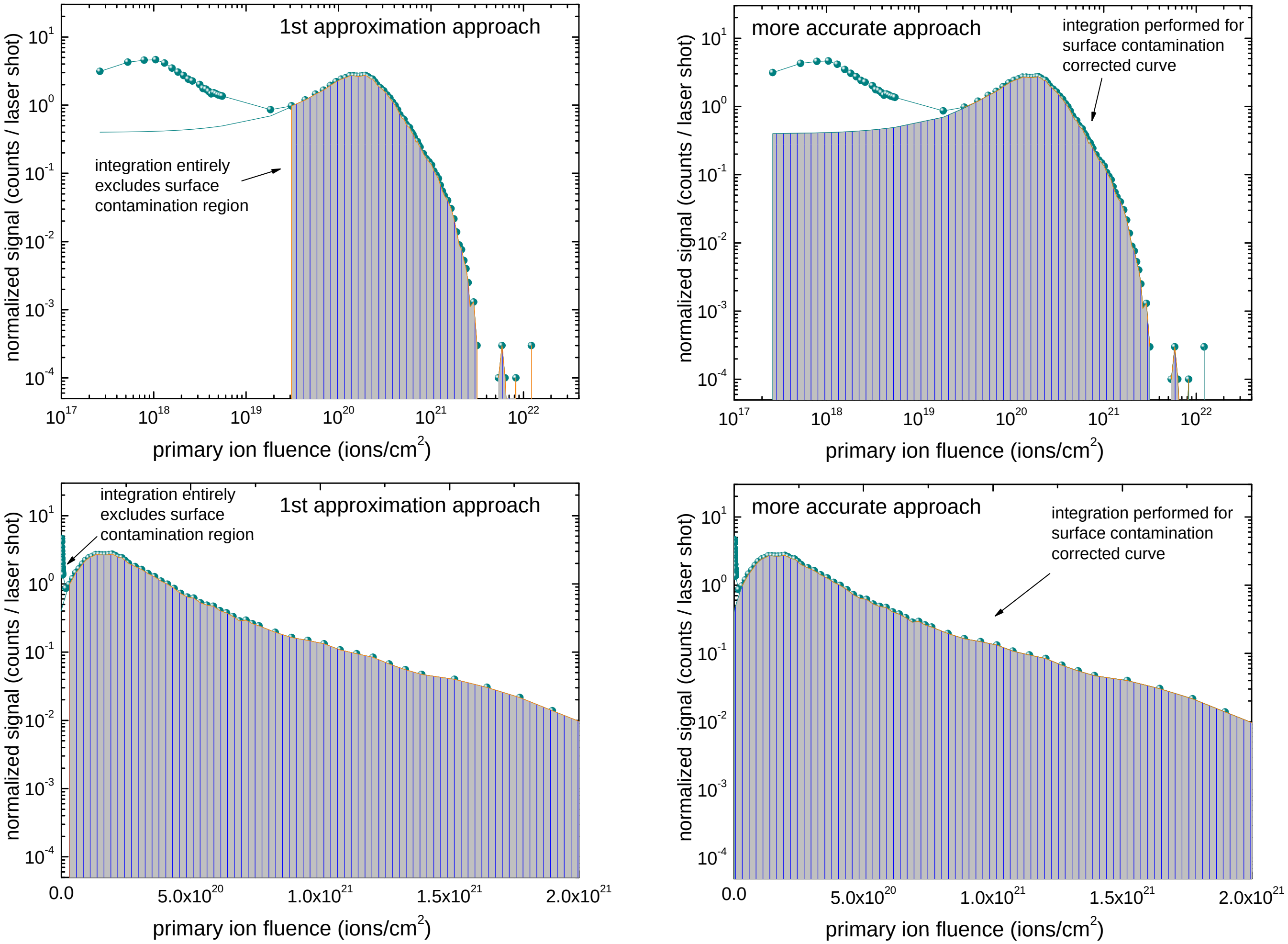


Simplified Data processing to determine SW fluence

- Correcting raw depth profiles for RIMS signal drift
  - Based on three groups of MS measurements on secondary standard
- Subtracting (suppressed) SIMS background
  - Based on quasi-simultaneous measurements during depth profiling
- Integrating depth profiles of Genesis and Implant Standard
  - Choosing integration limits such that surface contamination is not counted
  - Determining SW elemental fluencies from comparison between Genesis and Implant Standard

Depth Profile Integration

$$\frac{\text{Genesis Fluence}}{\text{Implant Fluence}} = \frac{\text{Integral(Genesis depth profile)}}{\text{Integral(Implant depth profile)}} \Rightarrow \text{Genesis Fluence} = \text{Implant Fluence} \times \frac{\text{Integral(Genesis depth profile)}}{\text{Integral(Implant depth profile)}}$$



Discrepancies between elemental abundances in solar wind determined by the simple integration (on the left) and by more accurate integration (on the right) ***are minor - <5%***

Summary of results

Genesis sample	Experiment Date	Ca^{40}	Ca^{44}	Cr^{52}	Cr^{53}
#60179	12/19/08	$(1.26\pm0.09)\times10^{11}$	$(3.42\pm0.98)\times10^{10}$	$(5.20\pm1.50)\times10^{11}$	$(2.08\pm1.58)\times10^{11}$
	12/22/08	$(8.68\pm1.21)\times 10^{10}$	$(1.85\pm0.97)\times10^{10}$	$(5.24\pm1.60)\times10^{11}$	$(2.88\pm1.57)\times10^{11}$
	02/25/09	$(1.34\pm0.06)\times10^{11}$	$(4.76\pm2.96)\times10^{9}$	$(1.66\pm0.33)\times10^{11}$	$(2.98\pm2.06)\times10^{10}$
#60476	02/18/09	3.7×10^{13}	$(9.78\pm0.16)\times10^{11}$	$(2.03\pm0.34)\times10^{11}$	$(3.54\pm2.41)\times10^{10}$
	02/19/09	4.71×10^{13}	$(1.17\pm0.01)\times10^{12}$	$(1.95\pm0.45)\times10^{11}$	$(3.05\pm3.00)\times10^{10}$
	03/04/09	$(2.41\pm0.02)\times10^{12}$	$(6.8\pm0.44)\times\times10^{10}$	$(1.27\pm0.25)\times10^{11}$	$(3.07\pm1.99)\times10^{10}$
	03/05/09	2.65×10^{13}	$(7.73\pm0.07)\times10^{11}$	$(1.03\pm0.20)\times10^{11}$	$(2.52\pm1.69)\times10^{10}$

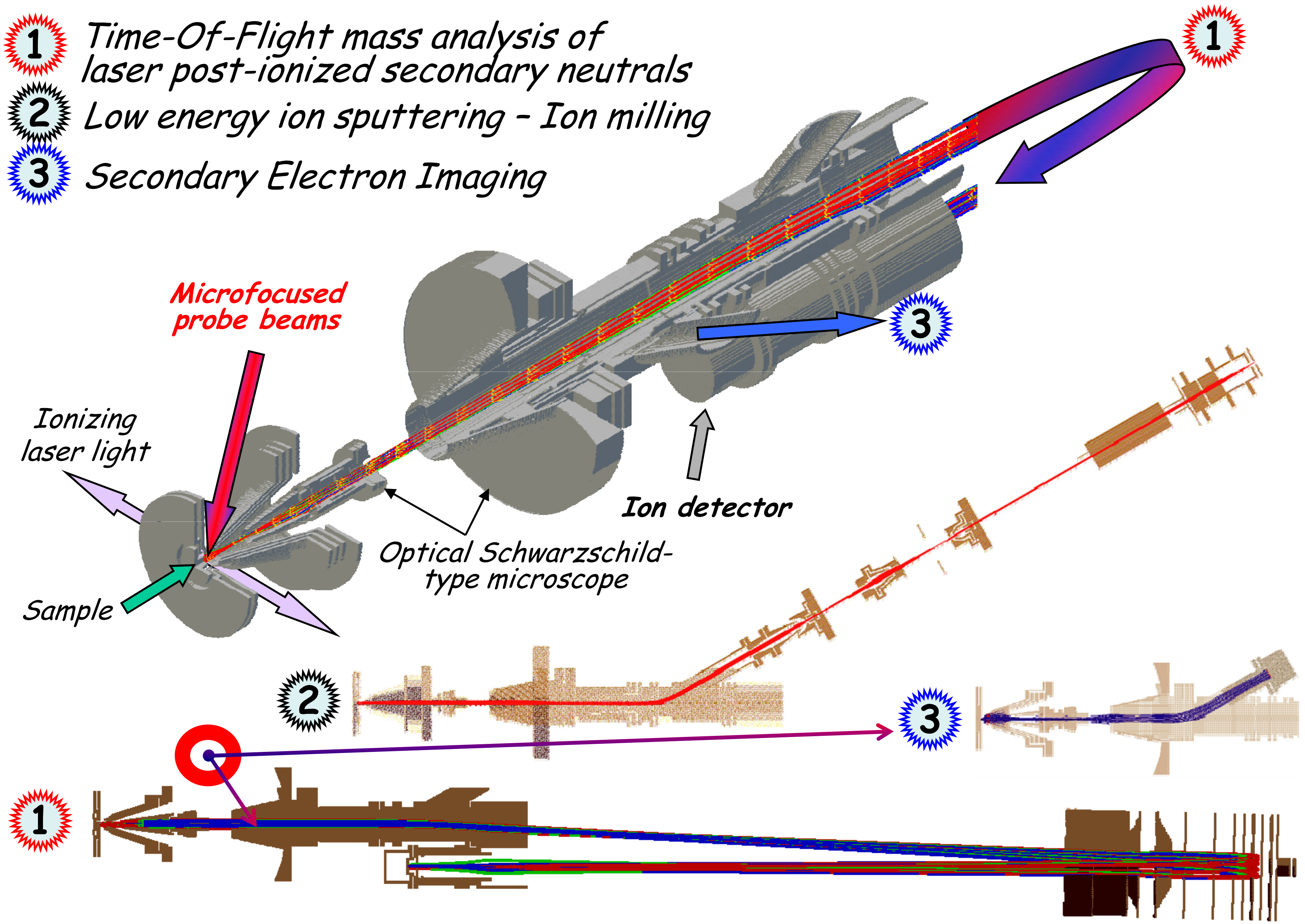
Summary of results –

recalculated using corrected integration algorithm (as presented at LPSC-XXXX)

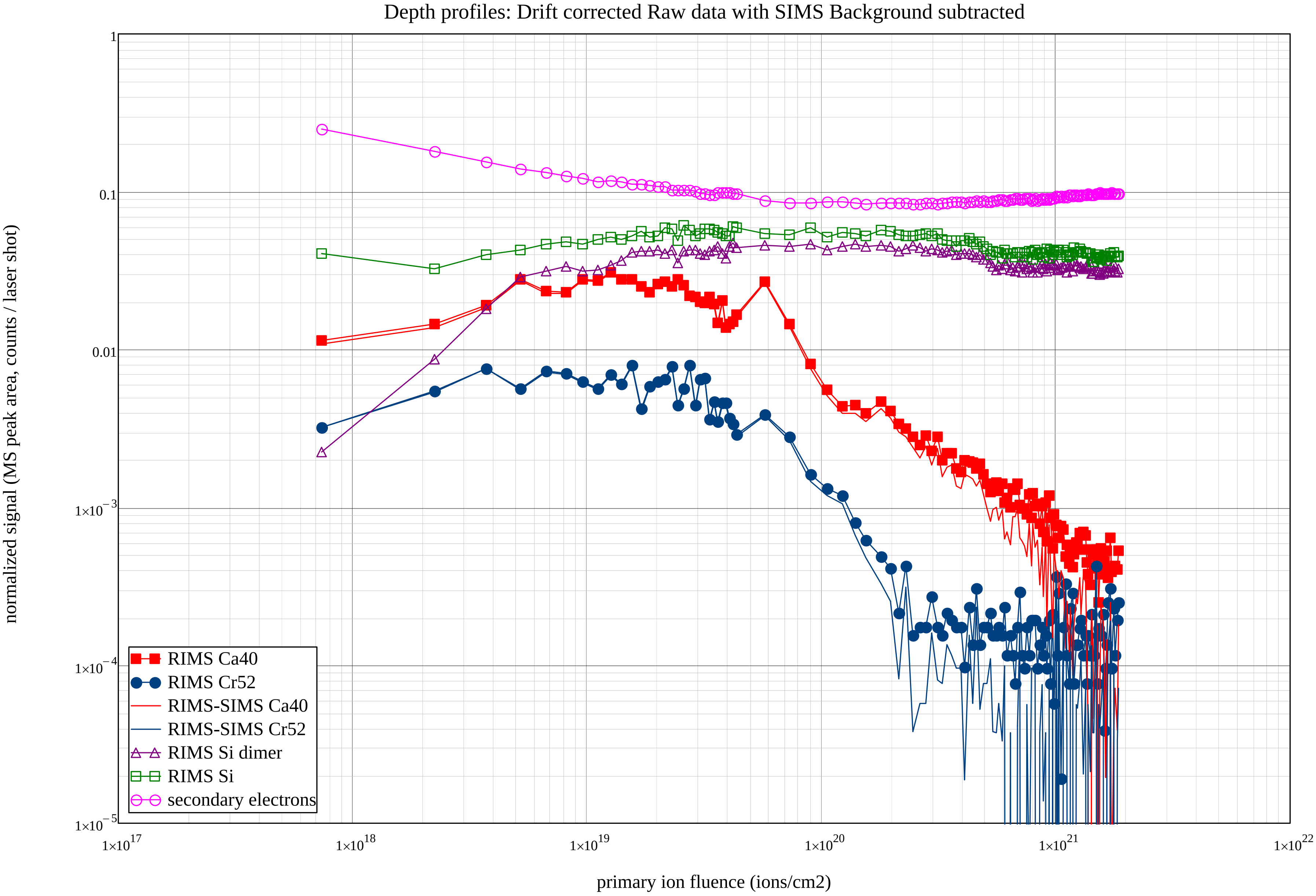
Genesis sample	Experiment Date	Ca^{40}	Ca^{44}	Cr^{52}	Cr^{53}
		Expected: **$1.33\text{x}10^{11}$ at/cm^2**		Expected: **$2.95\text{x}10^{10}$ at/cm^2**	
#60179	12/19/08	$(1.30\pm0.04)\times10^{11}$	$(6.26\pm1.41)\times10^{9}$	$(3.56\pm0.25)\times10^{11}$	$(5.06\pm1.29)\times10^{10}$
	12/22/08	$(7.30\pm0.67)\times10^{10}$	$(1.36\pm0.53)\times10^{10}$	$(2.30\pm0.45)\times10^{11}$	$(6.57\pm2.58)\times10^{10}$
	02/25/09	$(2.13\pm0.07)\times10^{11}$	$(5.15\pm1.66)\times10^{9}$	$(3.21\pm0.15)\times10^{11}$	$(3.71\pm0.49)\times10^{10}$
#60476	02/18/09	4.1×10^{13}	$(1.15\pm0.01)\times10^{12}$	$(3.57\pm0.49)\times10^{10}$	$(8.62\pm8.18)\times10^{8}$
	02/19/09	6.89×10^{13}	$(2.15\pm0.02)\times10^{12}$	$(1.09\pm0.14)\times10^{11}$	$(1.42\pm0.58)\times10^{10}$
	03/04/09	1.36×10^{12}	$(3.01\pm0.16)\times10^{10}$	$(4.54\pm0.70)\times10^{10}$	$(5.67\pm3.32)\times10^{9}$
	03/05/09	1.95×10^{13}	$(4.98\pm0.05)\times10^{11}$	$(1.37\pm0.21)\times10^{10}$	$(5.15\pm5.0)\times10^{8}$

SARISA: just add a magnet and get what you want

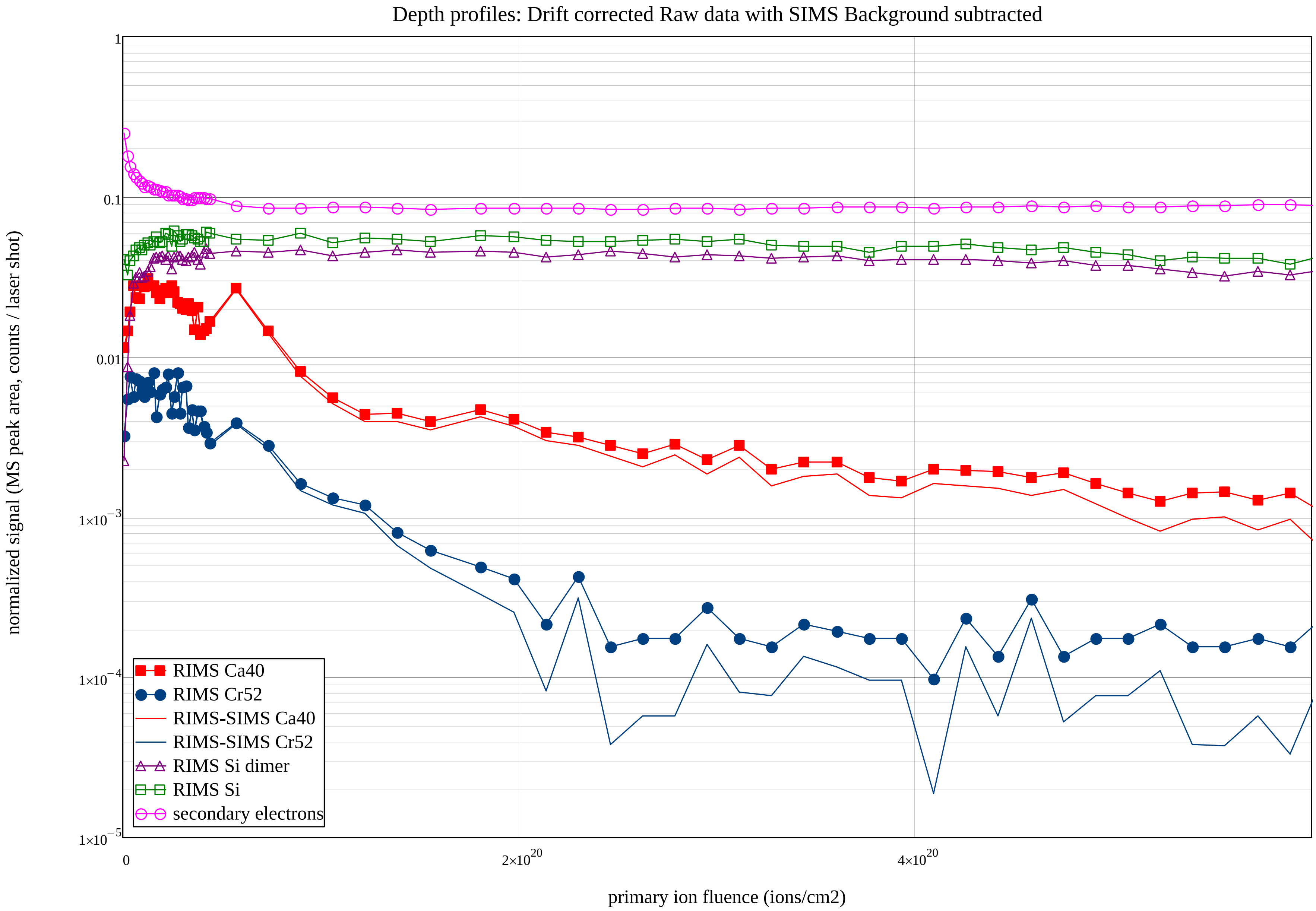
1. Time-Of-Flight mass analysis of laser post-ionized secondary neutrals
2. Low energy ion sputtering – Ion milling
3. Secondary Electron Imaging



How should we integrate depth profiles of SW implants: Genesis #60179 (March 17, 2009)



Genesis #60179 (March 17, 2009)
with secondary electron signal



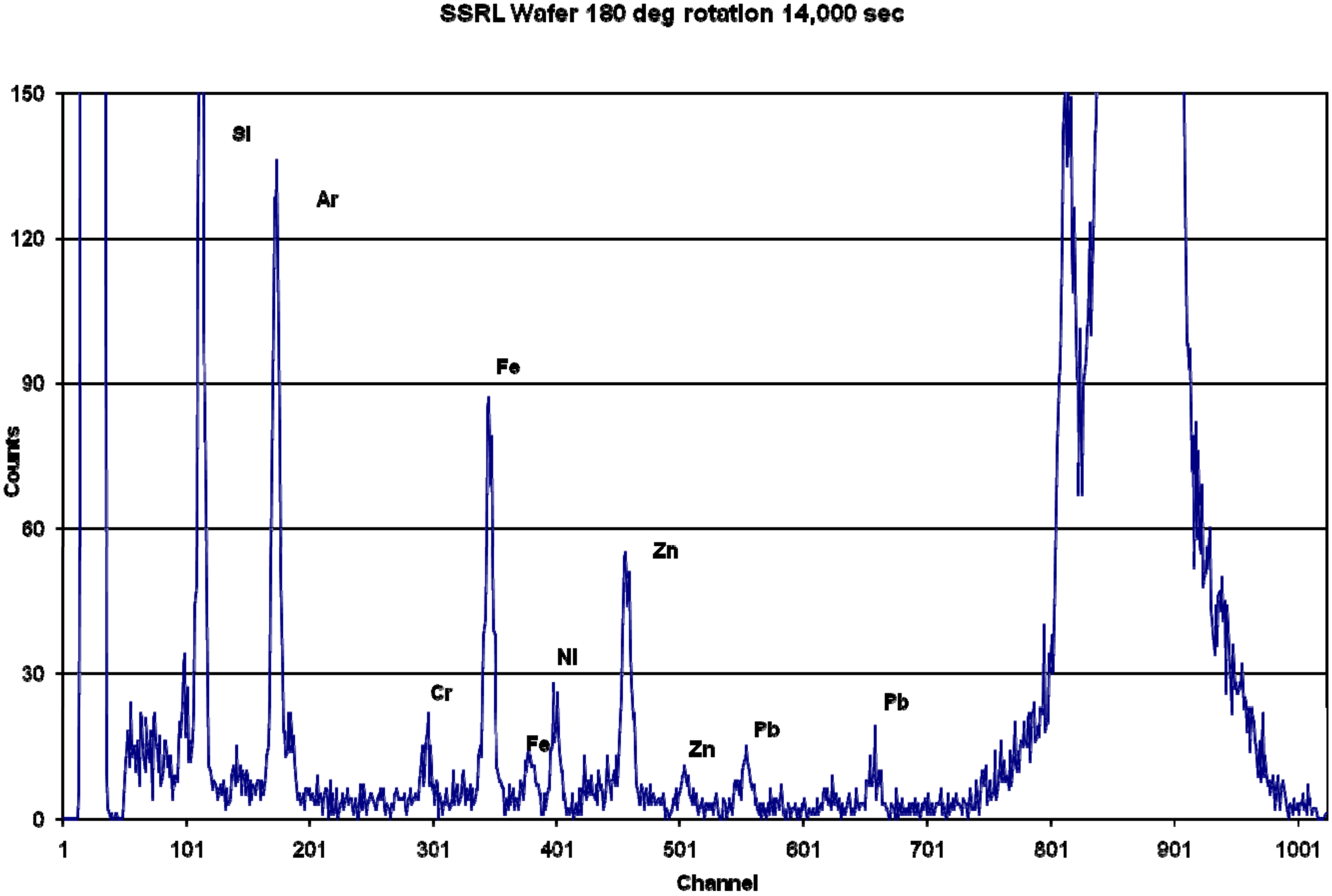
Conclusions

- Simultaneous RIMS of a few elements is the way to go
- **Chromium:**
  - Probably the last element to measure with ion sputtering
    - *Laser desorption will do the rest of periodic table*
  - Fluencies are consistently higher than expected
    - *Average 1.58x10^{11} at/cm^2 (2.95x10^{10} at/cm^2 expected for 852.83 days)*
    - *L52 Implant fluencies must be double checked*
      - Possibly with an added over the top implant
- **Calcium:**
  - No more measurements to do on #60476
  - Fluencies from #60179 are reasonable
    - *Average 1.16x10^{11} at/cm^2 (1.33x10^{11} at/cm^2 expected for 852.83 days)*
  - New measurements for Ca on a newly cleaned sample only
    - *Possibly characterized with TXRF prior to RIMS*
- **Magnesium:**
  - More measurements on #60476 simultaneously with Cr
  - For newly cleaned samples, three-element measurements are feasible in the nearest future (RIMS with sputtering)
- Enabling low energy sputtering column is high priority
- Back-side depth profiling with RIMS is still on our “to do” list

Conclusions - *(as presented at LPSC-XXXX)*

- Our RIMS results start to look good
  - Optimized experimental procedures and data processing protocols help to obtain reproducible and reasonable data
    - *Depth profile integration approach makes sense and does not contradict to Mother Nature*
      - Isotopic ratios calculated from Genesis depth profiles are reasonable
  - New measurements on cleaner samples are needed
- Simultaneous RIMS analysis for a few elements is the way to go
  - Cr , Ca and Mg can now be measured alltogether
      - Determination of isotopic ratios is feasible
  - Reliability of RIMS lasers is going to be now the major limiting factor

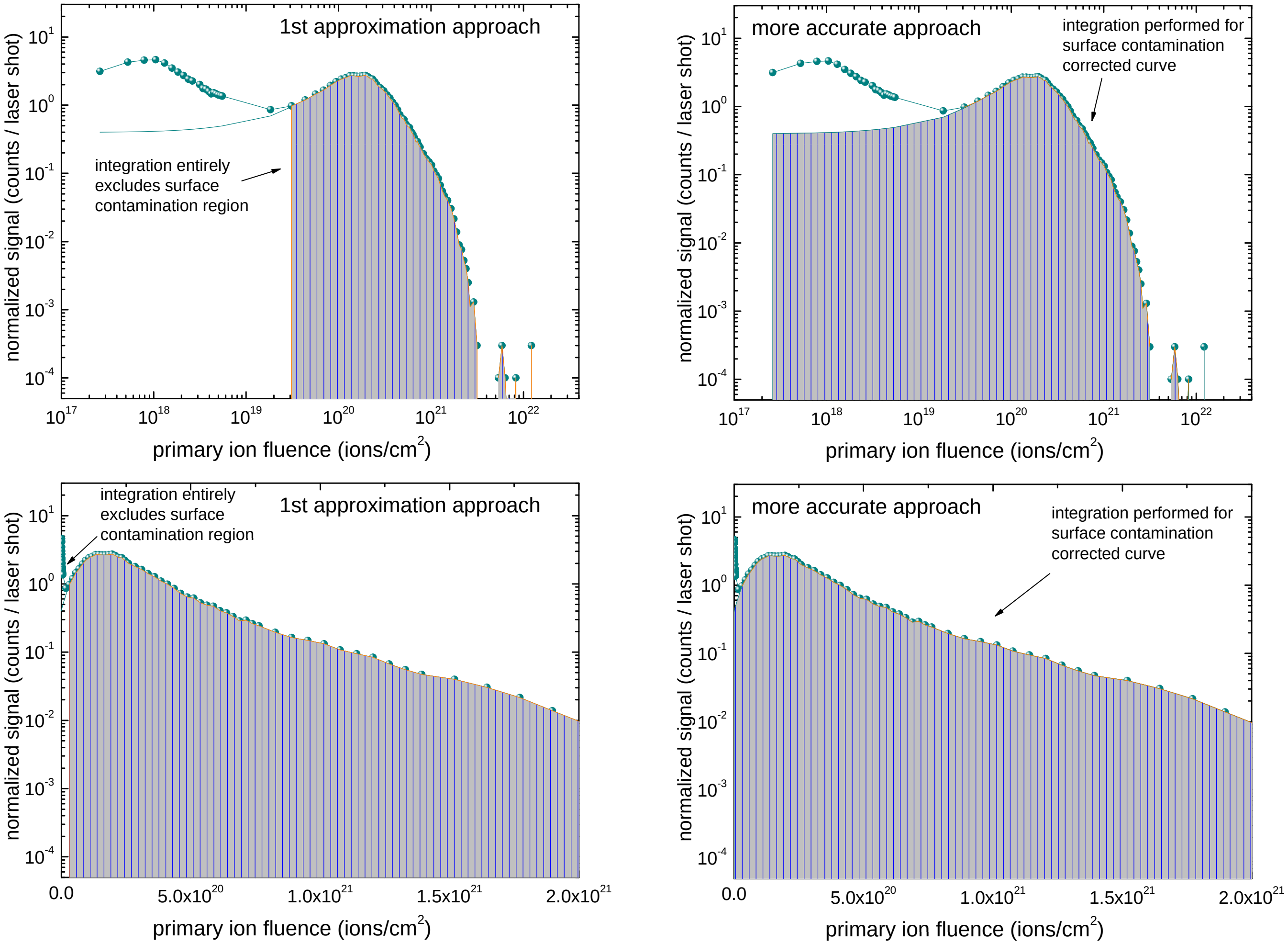
Near future: TXRF helping RIMS ?



Courtesy of Prof. M. Schmeling (Loyola University Chicago)

Depth Profile Integration

$$\frac{\text{Genesis Fluence}}{\text{Implant Fluence}} = \frac{\text{Integral(Genesis depth profile)}}{\text{Integral(Implant depth profile)}} \quad \Rightarrow \quad \text{Genesis Fluence} = \text{Implant Fluence} \times \frac{\text{Integral(Genesis depth profile)}}{\text{Integral(Implant depth profile)}}$$



Discrepancies between elemental abundances in solar wind determined by the simple integration (on the left) and by more accurate integration (on the right) ***are minor - <5%***

Acknowledgements

This work is supported

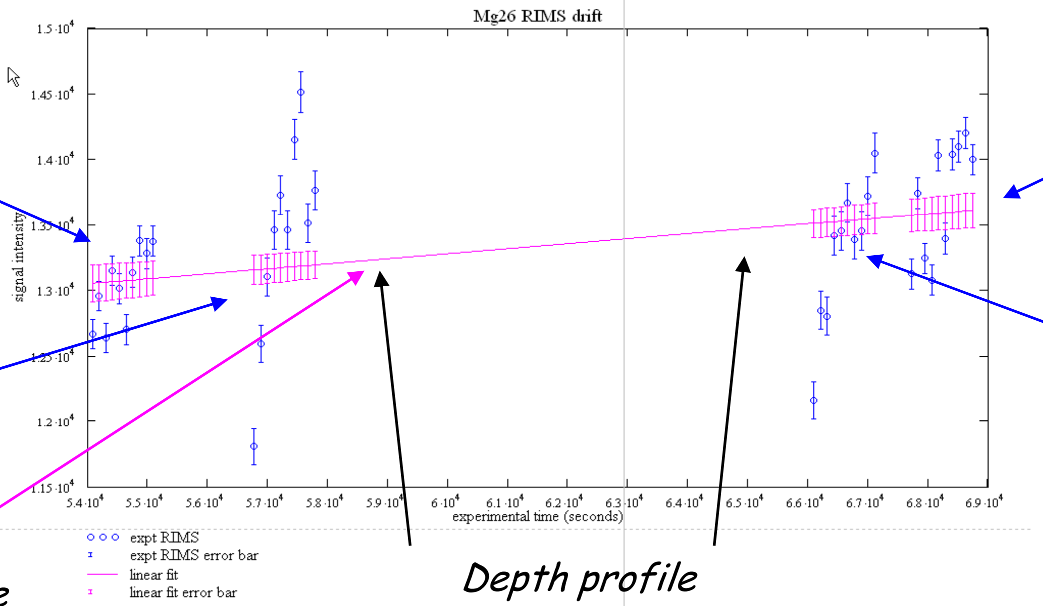
- *by NASA under Work Orders W-19,895 and W-10,091*
- *by the U. S. Department of Energy, BES-Materials Sciences, under Contract DE-AC02-06CH11357*

List of elements proposed for RIMS

Element	Atomic Number	Atomic Weight	First Ionization Potential (eV)	Solar System Abundance (relative to Si=10^6)	Estimated Solar Wind flux (cm^{-2}s^{-1})	Bulk Collector Fluence (cm^{-2}) 852.83 days	IS Collector Fluence (cm^{-2}) 333.67 days	CH Collector Fluence (cm^{-2}) 313.01 days	CME Collector Fluence (cm^{-2}) 193.25 days	Estimated Bulk Collector Concentration (ppm)	Estimated IS Collector Concentration (ppm)	Estimated CH Collector Concentration (ppm)	Estimated CME Collector Concentration (ppm)
Mg	12	24	7.646	1.10E+06	3.20E+04	2.36E+12	9.22E+11	8.65E+11	5.35E+11	4.716	1.84E+00	1.73E+00	1.07E+00
Al	13	27	5.695	8.50E+04	2.50E+03	1.84E+11	7.20E+10	6.76E+10	4.18E+10	0.368	1.44E-01	1.35E-01	8.35E-02
Ca	20	40	6.113	6.10E+04	1.80E+03	1.33E+11	5.18E+10	4.87E+10	3.01E+10	0.265	1.04E-01	9.73E-02	6.02E-02
Cr	24	52	6.765	1.40E+04	4.00E+02	2.95E+10	1.15E+10	1.08E+10	6.69E+09	0.059	2.31E-02	2.17E-02	1.34E-02
Ti	22	48	6.828	2.40E+03	7.20E+01	5.31E+09	2.07E+09	1.95E+09	1.20E+09	0.011	4.30E-03	4.04E-03	2.50E-03
Co	27	59	7.881	2.20E+03	6.70E+01	4.94E+09	1.93E+09	1.81E+09	1.12E+09	0.00987	3.86E-03	3.62E-03	2.24E-03
Se	34	79	9.752	6.20E+01	1.90E+00	1.40E+08	5.47E+07	5.14E+07	3.18E+07	2.80E-04	1.09E-04	1.03E-04	6.36E-05
Li	3	7	5.392	5.70E+01	1.70E+00	1.25E+08	4.90E+07	4.60E+07	2.84E+07	2.51E-04	9.79E-05	9.19E-05	5.69E-05
Sr	38	87.6	5.695	2.30E+01	7.00E-01	5.16E+07	2.02E+07	1.89E+07	1.17E+07	1.03E-04	4.04E-05	3.79E-05	2.34E-05
Be	4	9	9.32	7.30E-01	2.20E-02	4.72E+07	1.84E+07	1.73E+07	1.07E+07	9.43E-05	3.69E-05	3.46E-05	2.14E-05
Zr	40	91	6.033	1.10E+01	3.40E-01	2.51E+07	9.79E+06	9.19E+06	5.69E+06	5.01E-05	1.96E-05	1.84E-05	1.14E-05
Rb	37	85.5	4.177	7.10E+00	2.10E-01	1.55E+07	6.05E+06	5.68E+06	3.51E+06	3.10E-05	1.21E-05	1.14E-05	7.03E-06
Y	39	89	6.217	4.60E+00	1.40E-01	1.03E+07	4.04E+06	3.79E+06	2.34E+06	2.06E-05	8.07E-06	7.57E-06	4.68E-06
B	5	11	8.29	2.10E+01	6.40E-01	1.62E+06	6.34E+05	5.95E+05	3.68E+05	3.24E-06	1.27E-06	1.19E-06	7.36E-07

Old Data processing to determine SW fluence

- 1st step: Subtracting SIMS background.
  - Non-RIMS background signals are acquired by switching the post-ionization lasers off a few times during the acquisition of the depth profile. These numbers are directly subtracted from the total detected signals.
- 2nd step: Correcting for RIMS drifts.
  - Duration of sputter depth profile experiment is ~ 2.5 hrs. Therefore we had to account for possible drifts in the RIMS signal level. These drifts originate from minor changes in the RIMS lasers wavelengths and powers, and from thermal drifts in timing and voltages of the pulsing electronics of SARISA instrument.



Signal from center of secondary (glass) standard

Signal from analysis spot on secondary (glass) standard

Linear fit to account for the signal drift

Depth profile measurement happens here

Signal from center of secondary (glass) standard

Signal from analysis spot on secondary (glass) standard

- 3rd step: Correction for surface contamination using linear prediction algorithm.
  - Near-surface region of the depth profile is predicted based on the data points measured for deeper regions of the sample
- 4th step: Data normalization.
  - Standards and Genesis samples are compared using the signals from the center of the secondary standard as a reference
- 5th step: Depth Profile Integration.