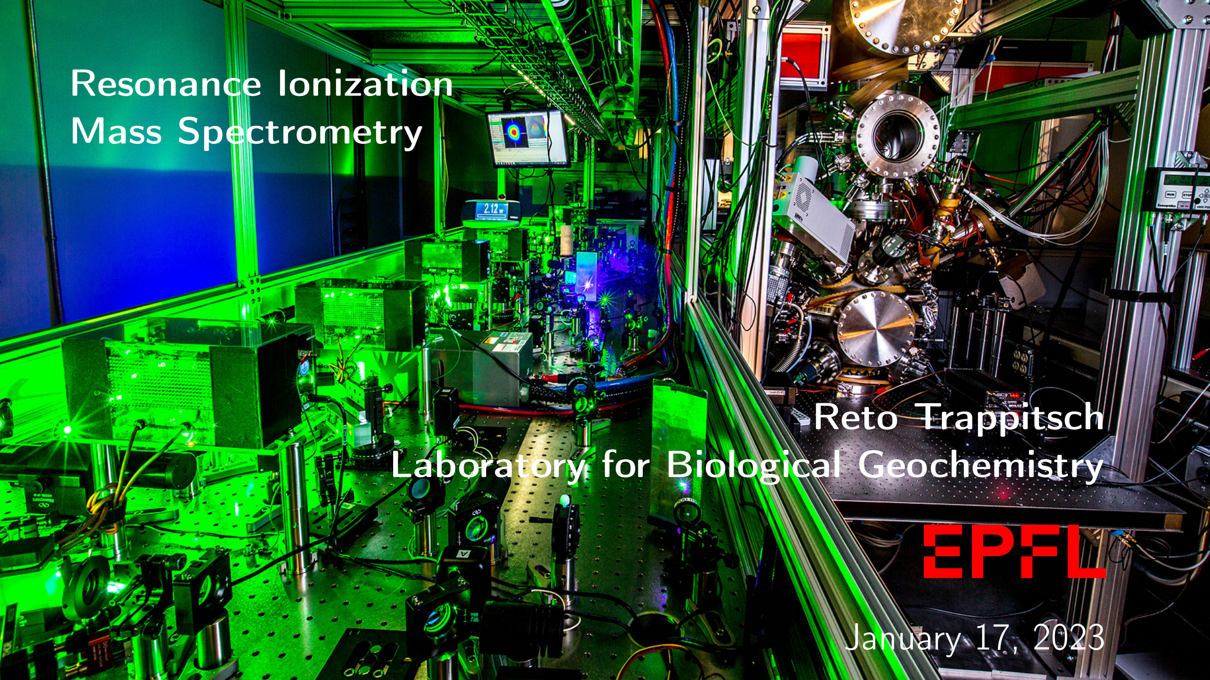
Resonance Ionization Mass Spectrometry



Reto Trappitsch

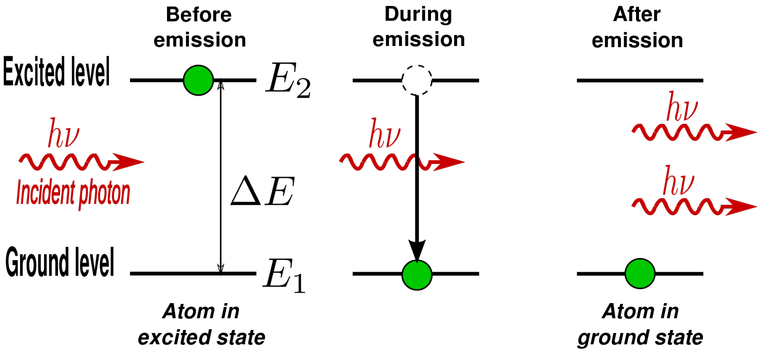
Laboratory for Biological Geochemistry

EPFL

January 17, 2023

An Idea as Old as the Laser

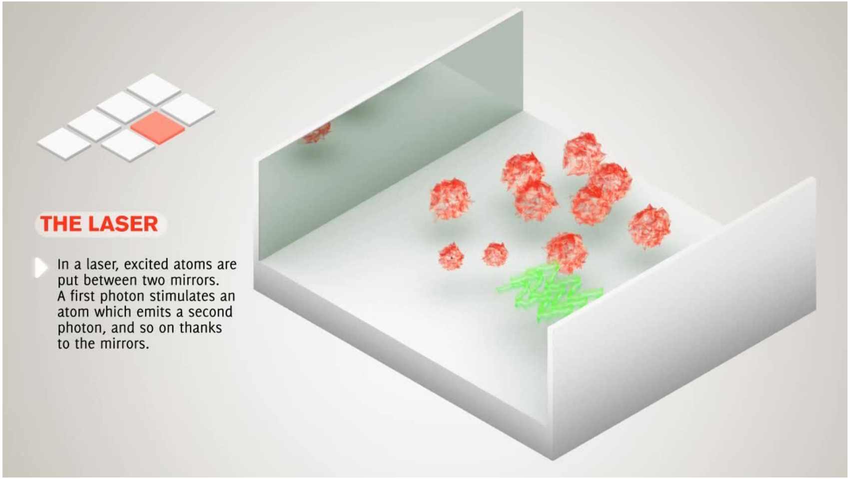
Laser: Light Amplification by Stimulated Emission of Radiation



$$E_2 - E_1 = \Delta E = h\nu$$

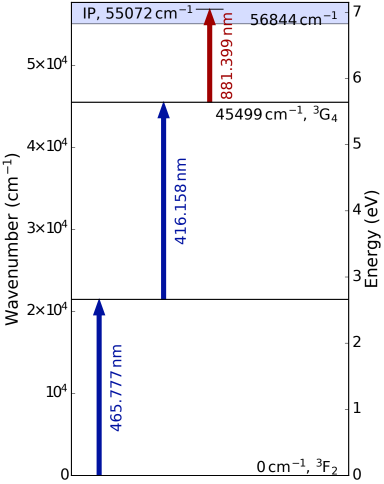
Credit: Wikipedia, V1adis1av

Laser Principle



Credit: Wikipedia, Juboroff

The Process of Stimulated Emission is Reversible



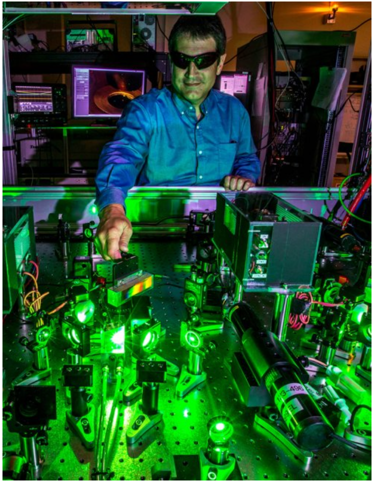
- Ionization of titanium (Trappitsch+, 2018)
- Absorption cross section σ is approximately equal to the square of wavelength λ

$$\sigma \approx \lambda^2$$

- Visible wavelength (400-800 nm): $\sigma \approx 10^{-9}\,\mathrm{cm}^2$
- Lifetime τ of a state is in the order of 10 ns
- Required photon flux to saturate transition:

$$\phi = \frac{1}{\tau} \times \frac{1}{\sigma} \approx 10^{17}\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$$

Pulsed Lasers can Achieve the Saturation Requirements



- For a pulsed laser at 1 kHz repetition rate, $\sim$ 10 ns pulse width, this photon flux corresponds to
  $\rightarrow$ **A few mW average power**
- Requirement increased due to Doppler and power broadening and laser spectral bandwidth
- Pulsed lasers at 1 kHz, $\sim 10\,\mathrm{ns}$ pulse width can achieve up to about $2\,\mathrm{W\,mm^{-2}}$

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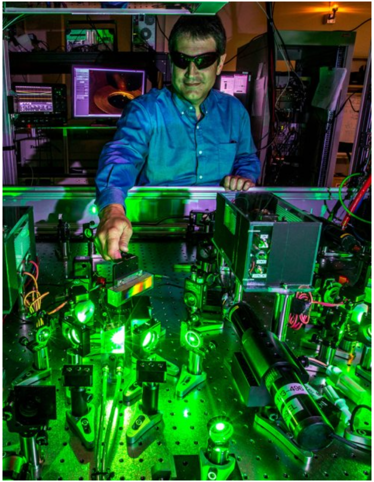

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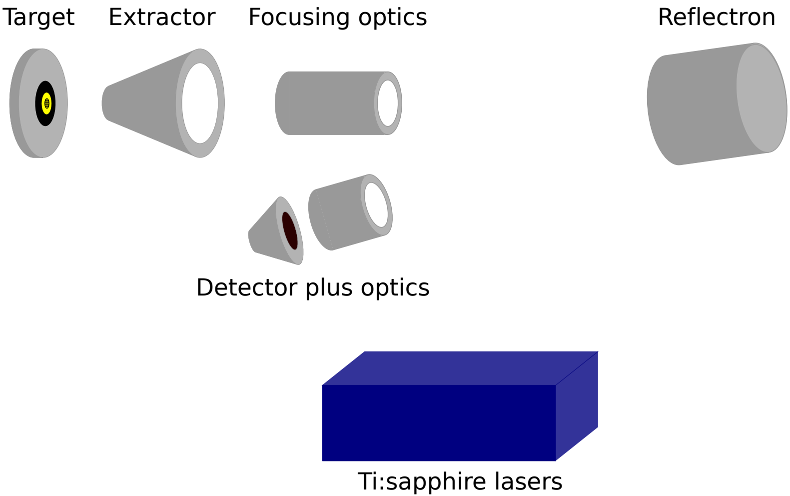
- For a DC instrument (e.g., SIMS):
  - Pulsed laser-on time: $10^{-8}\,\mathrm{s} \times 1000\,\mathrm{Hz} = 10^{-5}$
  - Average power requirement would **hundreds of Watts** for a continuous-wave laser

We Need a Pulsed Mass Spectrometer: Time of Flight



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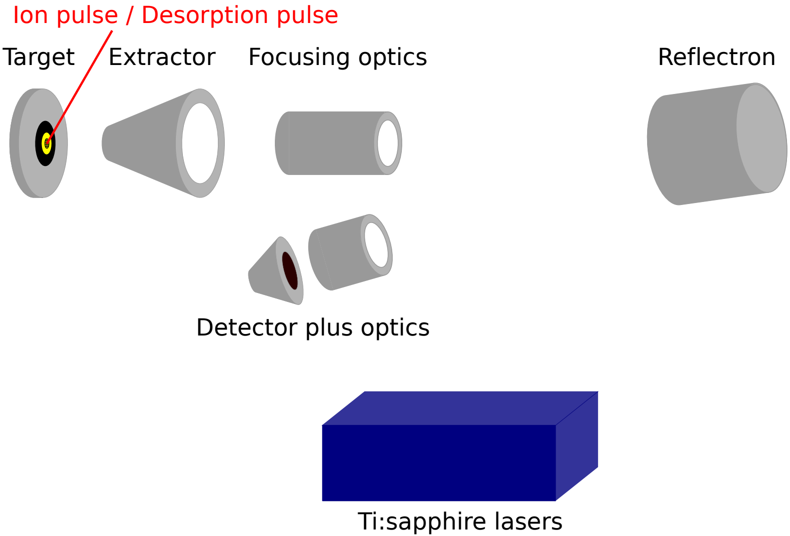

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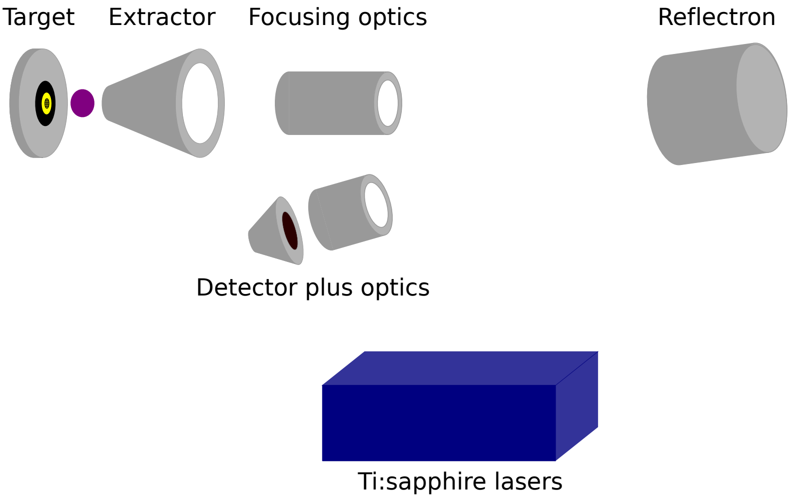

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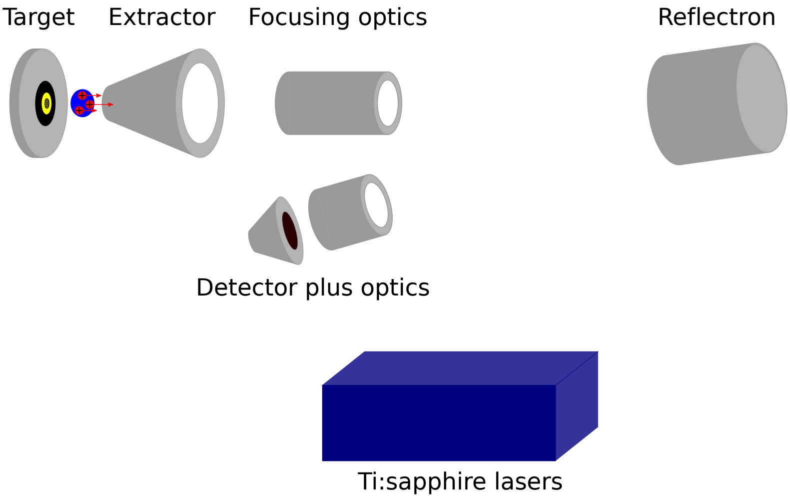

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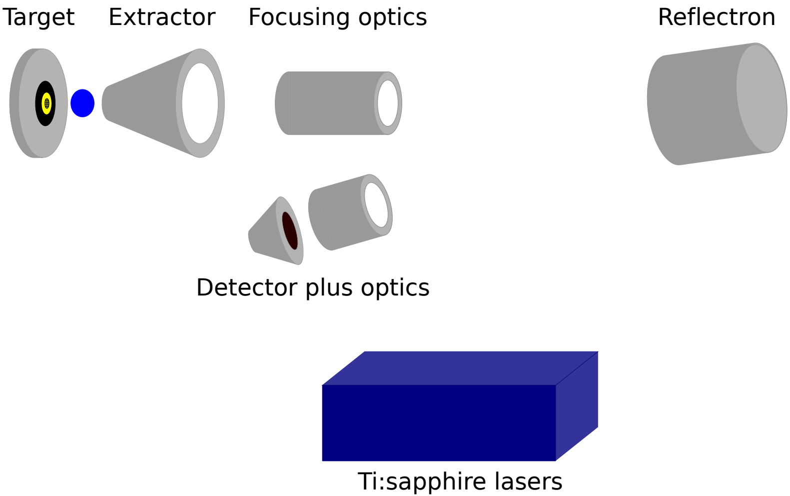

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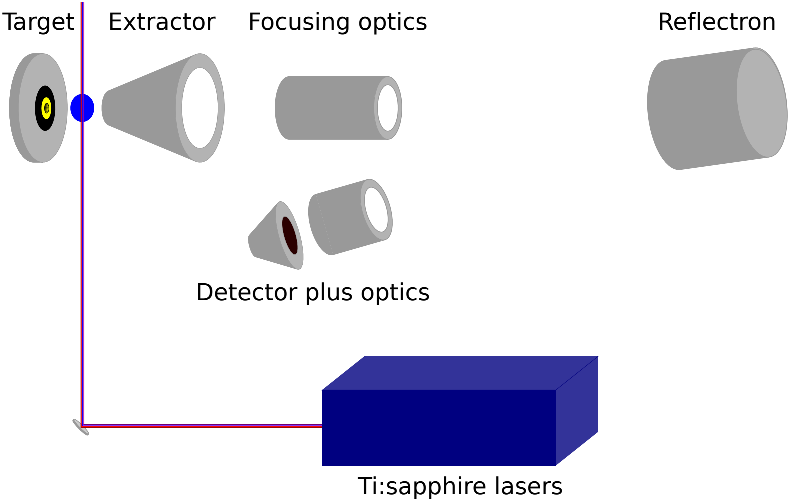

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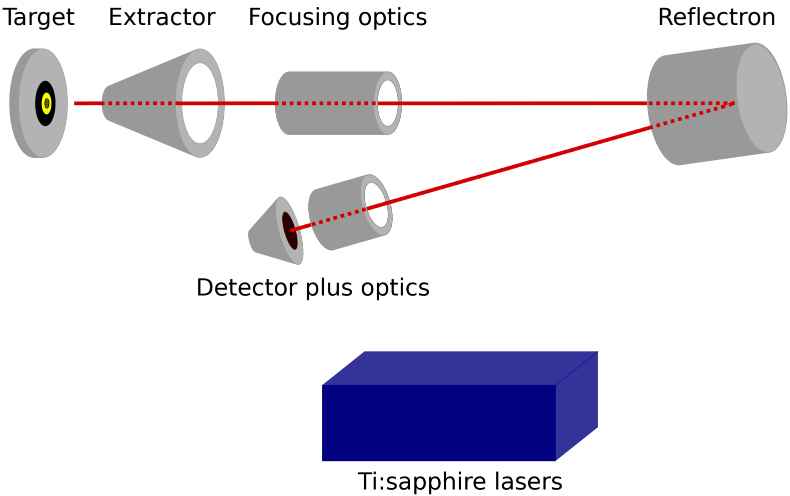
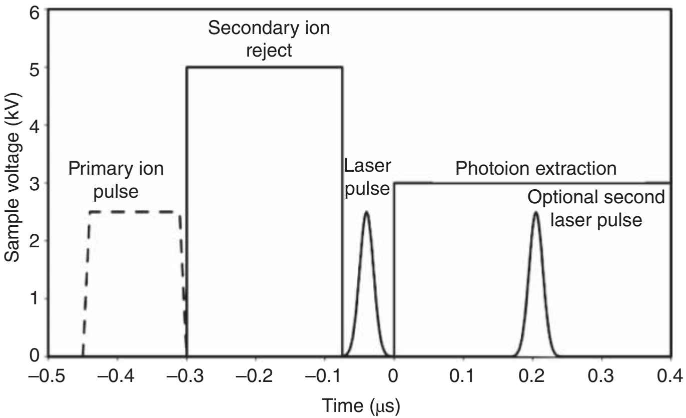


Measurement Cycles repeat at 1 kHz

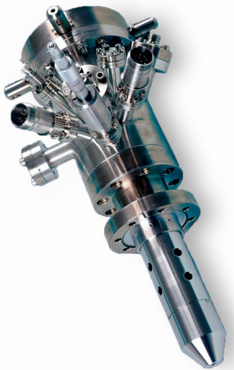
1. Desorption / Sputtering of sample
2. Ejection of secondary ions
3. Resonance ionization of photoions
4. Extraction
5. Mass / Charge separation and detection

Optional second ionization laser pulse allows for separation of isobars



Savina and Trappitsch (2021)

Sample Removal: Sputtering vs. Laser Desorption

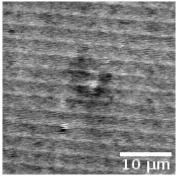


Ionoptica IOG-25Ga

- Sputtering with Ga ion beam
  - $< 100\,\text{nm}$ spatial resolution
  - Motionless blanking required
  - Trade off beteween high current or high spatial resolution
  - Duty cycle compared to SIMS: $\sim 10^{-4}$
- Desorption laser
  - Various wavelength possible to couple with different materials
  - Spot-size down to around $1\,\mu\text{m}$
  - Very low secondary ion backgrounds can be achieved

Sample Removal: Sputtering vs. Laser Desorption

EKSPLA 1064 nm Desorption Laser



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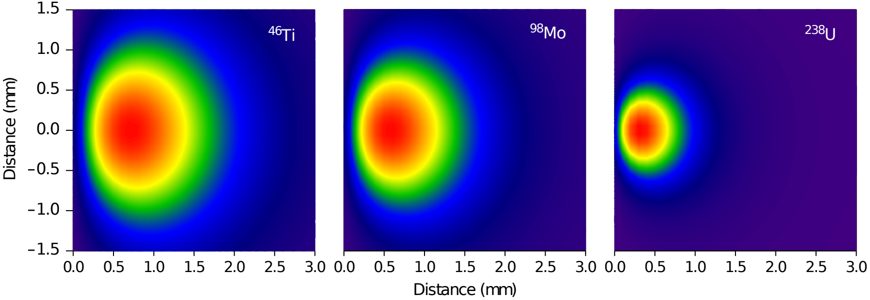
Ionizing of Neutral Atoms: You only get One Chance!

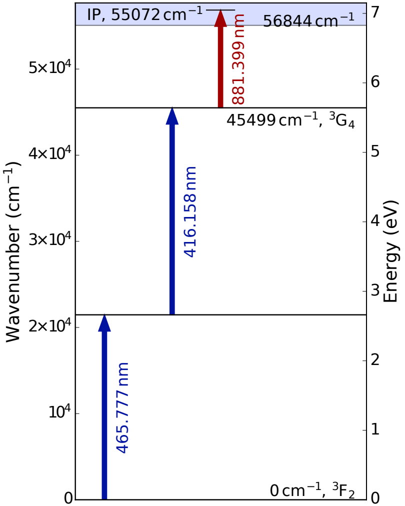


Savina and Trappitsch (2021)

- Ionization laser beam size: $\sim$1.5 mm diameter cylinder
- Laser intercepts cloud of neutrals above sample surface
- Neutrals that do not get ionized in first shot will be lost due to cloud expansion

Multi-step Laser Ionization of, e.g., Titanium (Trappitsch et. al, 2018)

- Resonance Ionization of Titanium requires three lasers
- Each ionization step is highly selective
- Ionization schemes need to be tested:
  - Spectroscopy of states above ionization potential
  - Saturation: Irradiance counts!
- Ti has low lying states
  - Understand population of these states
  - Scheme specific
  - Here: majority after sputtering in ground state



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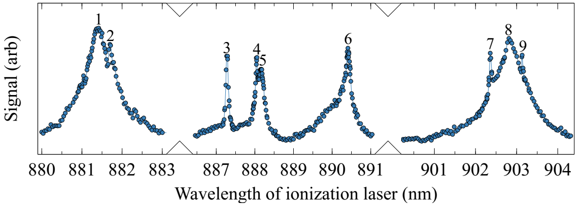

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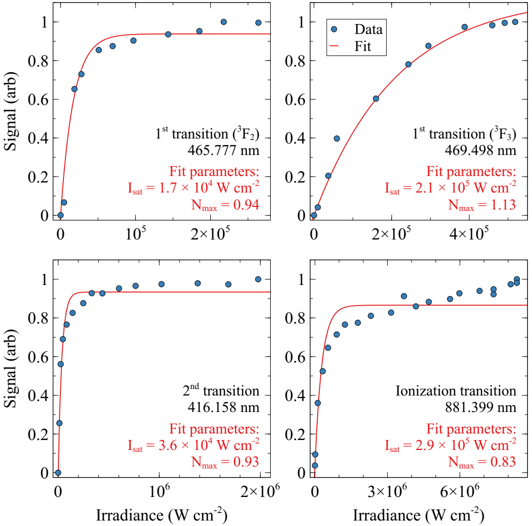

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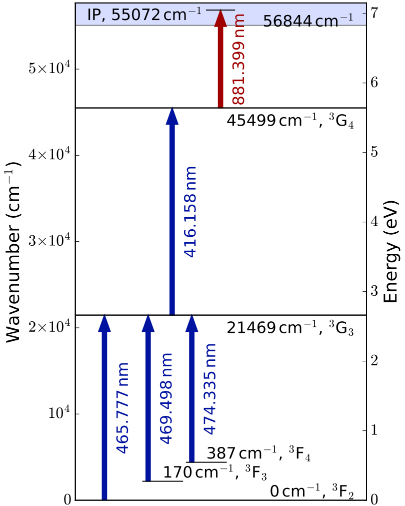
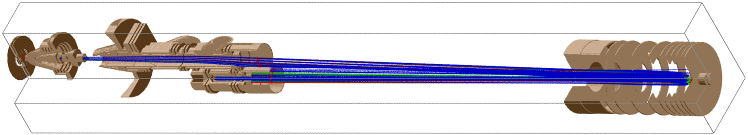
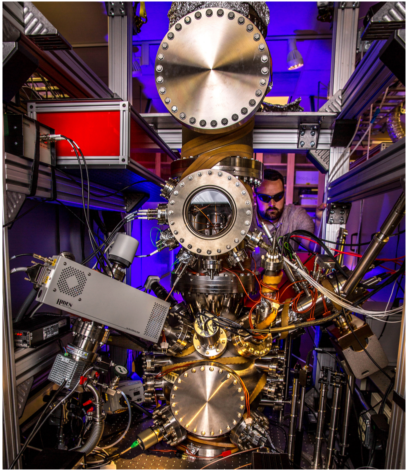


Separation of m/q in Time-of-Flight (TOF) Mass Analyzer

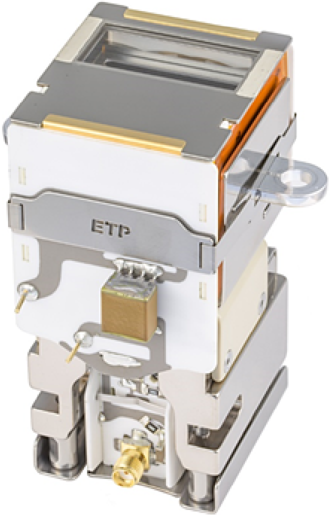
- Time of Flight Mass Analyzer
  - $\sim 3.5\,\mathrm{m}$ flight path
  - Grid-less reflectron to optimize transmission
  - Mass resolution $\frac{m}{\Delta m} > 1000$
- Difficulty: Map a photoion volume in time onto detector
- Lasers however take care of isobars





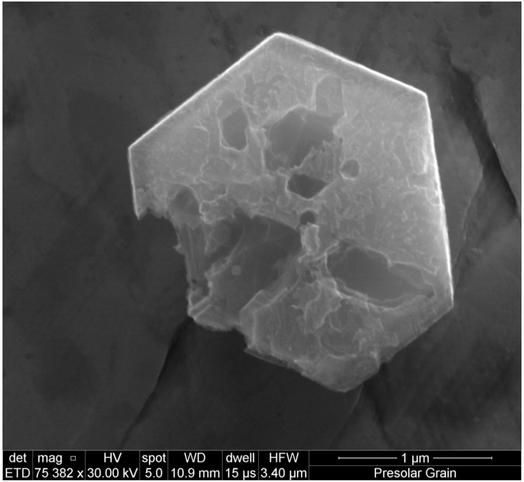
Ion Counting — Record every Arrival Time

- Ion counting detectors
  - Microchannel plate detectors (MCPs)
  - TOF Electron Multipliers
- Time-to-Digital Conversion: 80 ps time resolution
- Overall system dead-time: $\sim 700\,\mathrm{ps}$
- Reasonable count rates: $\sim 2,000\,\mathrm{cps}$

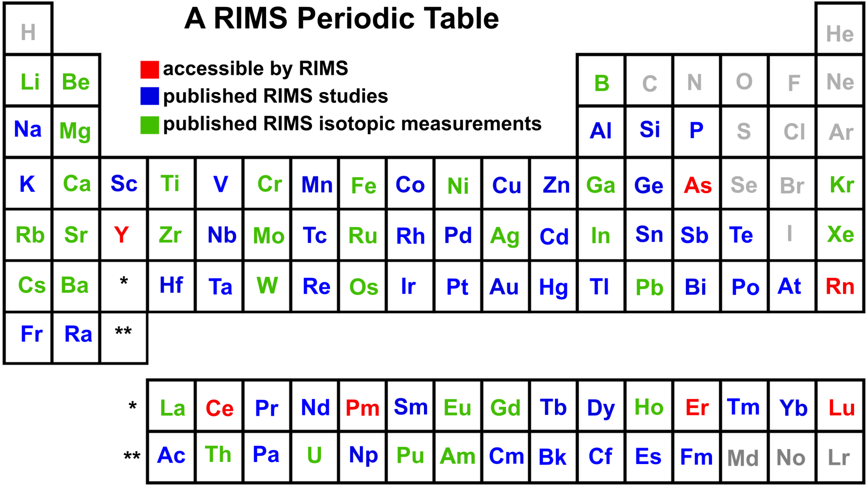


RIMS — A Versatile Technique for Trace Element Analyses

- High sensitivity for small, atom-limited samples
- Minimal sample preparation
- Resonance ionization with tunable Ti:Sapphire lasers
- High spatial resolution
  - $\sim 1\,\mu\text{m}$ for laser desorption
  - $< 100\,\text{nm}$ for ion sputtering
- High useful yield
  - 38% for U analysis (Savina+ 2018)
  - $\sim$ 18% for Ti analysis (Trappitsch+ 2018)
- Low backgrounds and high isobar suppression



A RIMS Table of Elements



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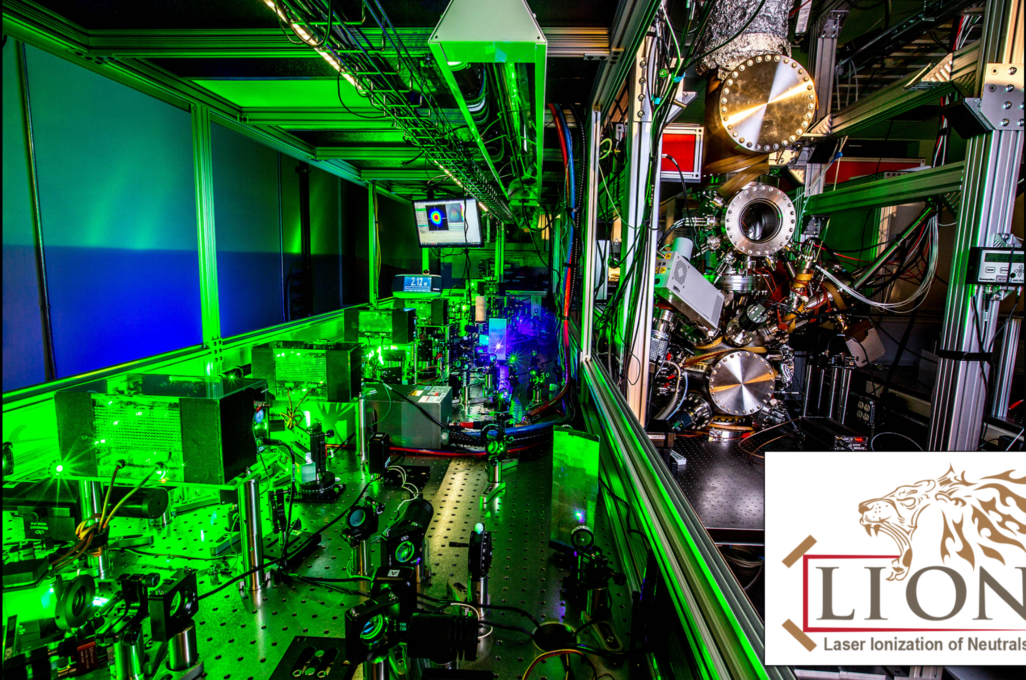
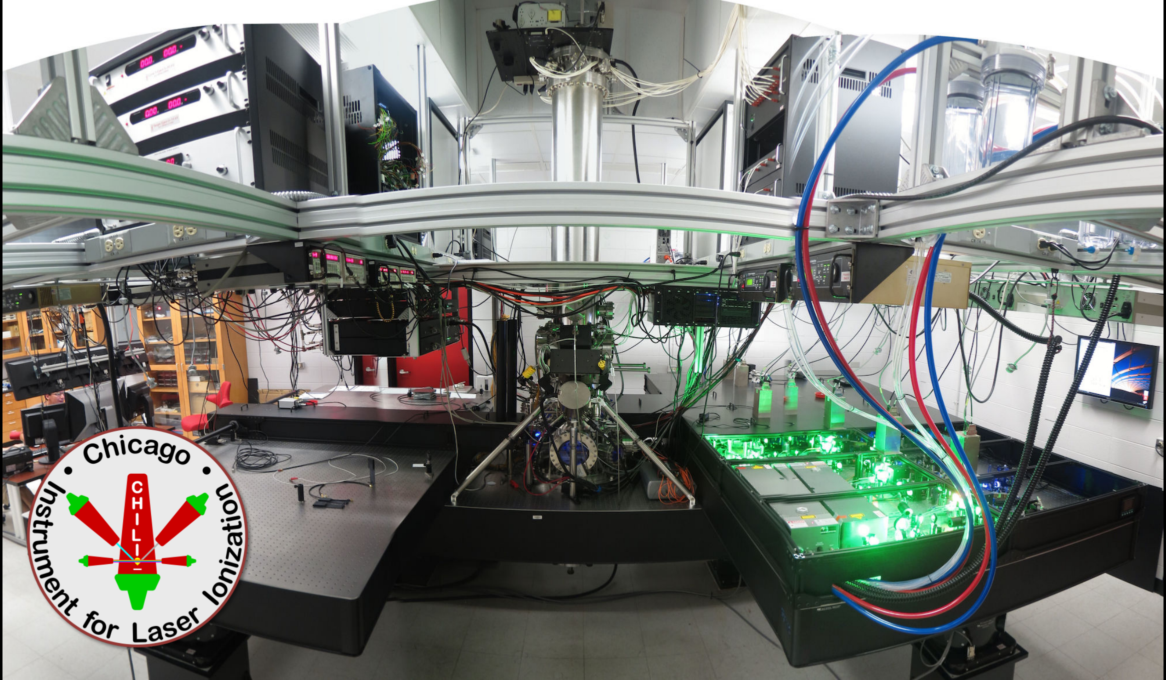
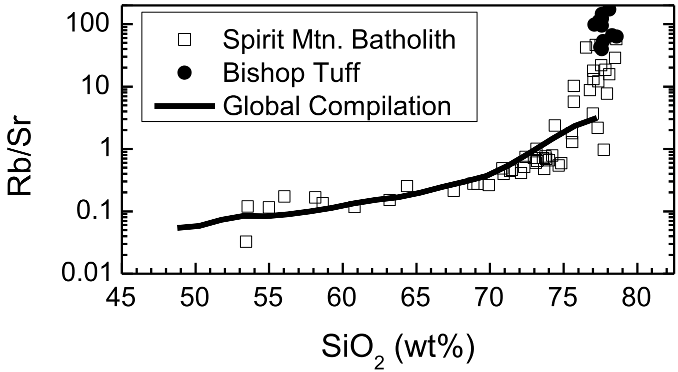


LION
Laser Ionization of Neutrals


Chicago
Instrument for Laser Ionization
CHILI

Potassic, High-Silica Hadean Crust (Boehnke+, 2018)

- Composition of the Hadean crust poorly understood
- Rb/Sr ratio correlates with SiO_2
- Analyzed 10 apatite inclusions in Archean zircons
- Sr isotope ratios indicate high Rb/Sr ratio
- Suggest a felsic crust formed by $\sim 4.4\,\mathrm{Ga}$



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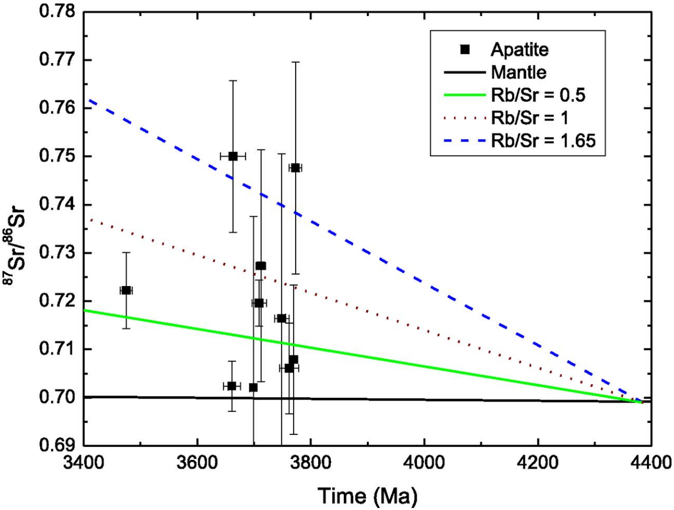
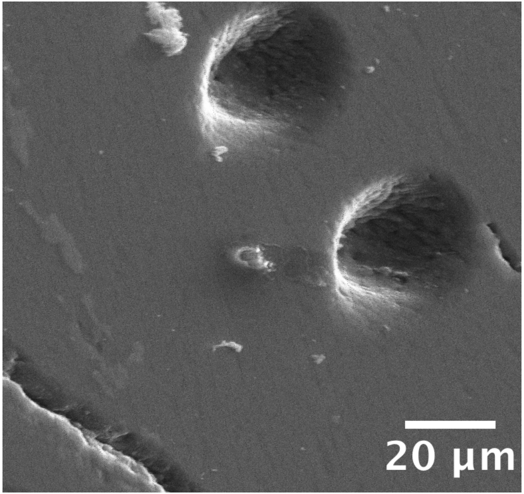


Did a Supernova Contribute ^{60}Fe to the Early Solar System?

- Long-standing controversy:
  - In-situ SIMS measurements: "High" ^{60}Fe
    $\rightarrow$ Implies supernova injection
  - Bulk ICPMS measurements: "Low" ^{60}Fe
    $\rightarrow$ Can be explained as "galactic background"
- Re-analysis by RIMS
- Correlated effects minimized thanks to normalization to $^{62,58}Ni$
- RIMS measurements do not detect the previously reported "high" ^{60}Fe content

Beware your measurement uncertainties!



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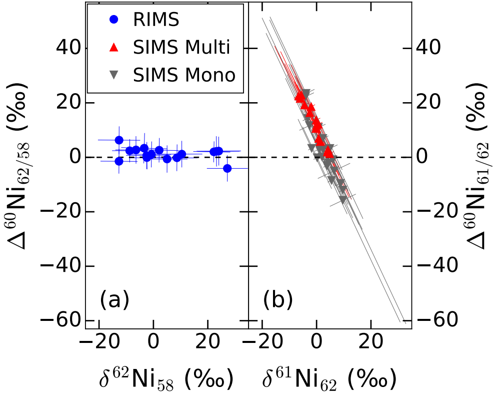
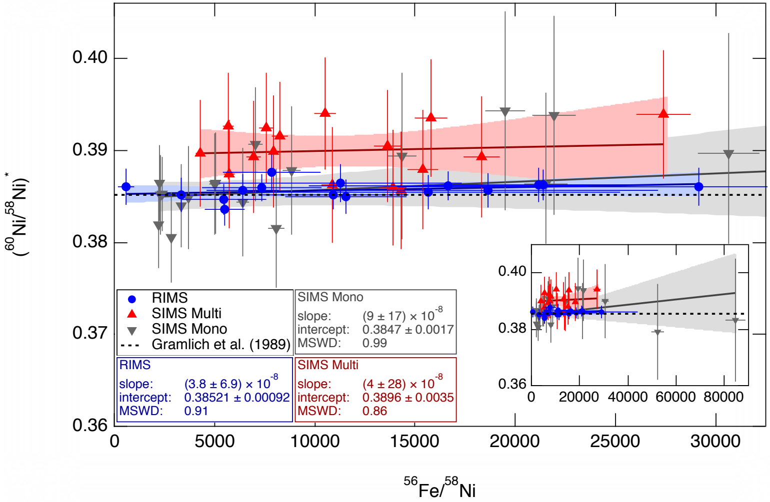


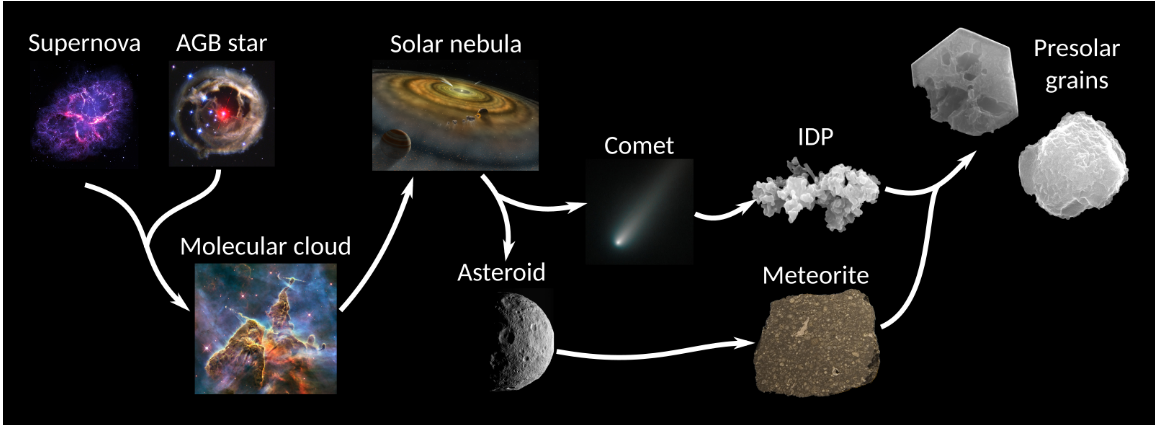
Trappitsch+ (2018)

^{60}Fe in Early Solar System can be Explained as Galactic Background

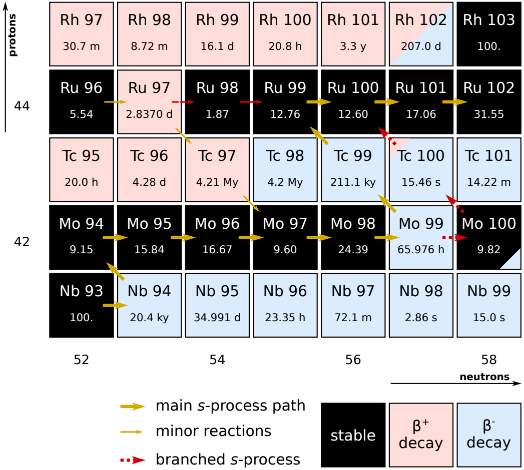


Trappitsch+ (2018)

Stardust grains: Tracing Stellar Nucleosynthesis



Observations of Live ^{99}Tc in AGB Stars



SPECTROSCOPIC OBSERVATIONS OF STARS OF CLASS S

PAUL W. MERRILL
MOUNT WILSON AND PALOMAR OBSERVATORIES
CARNEGIE INSTITUTION OF WASHINGTON
CALIFORNIA INSTITUTE OF TECHNOLOGY

Received February 27, 1952

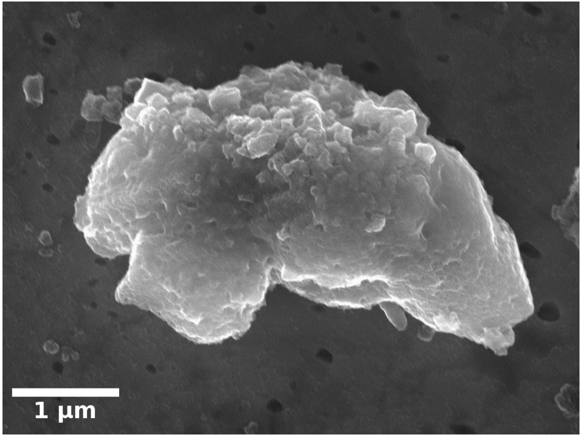
TABLE 2

INTENSITIES OF LINES AND BANDS

Star	Plate	Absorption					Emission					
		ZrO	*TiO*	*Ba* II	Low-Temp.	*Tc* I	*H*	*Fe* II	*Mg* I	*Si* I	*In* I	*Co* I
R And....	Ce 3522	8	3	5	8	4	10	3	2	3	3	2
U Cas.....	Pc 127	7	7	5	6	3	10	3	1	3	1	2
HD 22649.	Pc 192	2	2	5	6	1	0	0	0	0	0	0
R Gem....	Pc 68	5	0	10	7	5	10	3	2	2	3	3
S UMa....	Pc 110	1	0	7	4	1	10	3	1	2	1	1
T Sgr.....	Pc 124	7	0	7	5	3	10	3	2	3	4	3
R Cyg....	Pc 137	10	0	10	5	3	10	2	2	2	2	3
AA Cyg...	Pc 115	8	7	7	8	4	0	0	0	0	0	0
Z Del.....	Pc 112	2	7	3	3	1	10	3	1	2	0	2
χ Cyg.....	Ce 3762	5	20	3	10	3	10	3	2	5	4	2
o Cet......	Ce 4109	1	15	1	7	2	5	1	0	2	1	0
	Ce 5925	1	10	2	6	1	10	3	1	2	0	1
R Hya....	Ce 3390	1	15	3	7	1	7	3	1	3	0	1
R Leo....	Pc 40	0	20	1	10	0	10	4	4	6	3	0

Enhancements in ^{99}Ru in Presolar Stardust (Savina+, 2004)

- Ruthenium isotopic composition measured in µm-sized SiC grains by RIMS
- Comparison with slow neutron capture process models
  - ^{101}Ru/^{100}Ru agrees with models
  - ^{99}Ru/^{100}Ru elevated due to in-situ decay of ^{99}Tc
- Measurements require in-situ decay of ^{99}Tc
- Proof that these grains come from AGB stars (stars of class S)
- Many further measurements since
  - Stellar nucleosynthesis
  - Galactic chemical evolution



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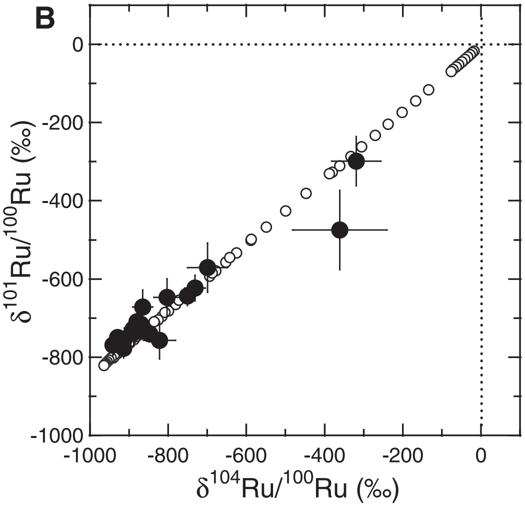

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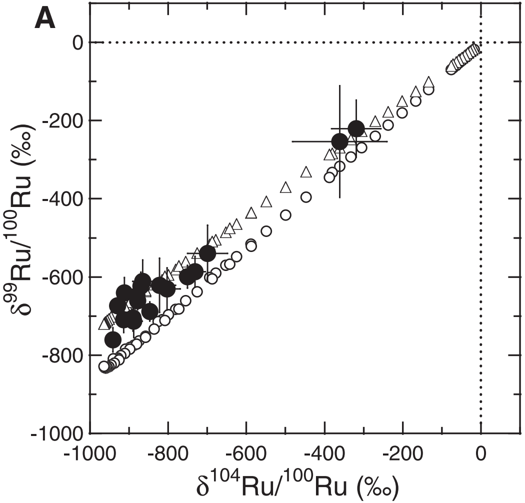
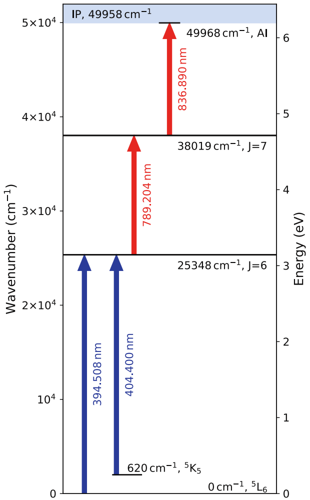


And there are Many More Uses for RIMS!

- Surface Chemistry
  - Oxidation state of U
  - Enabled by low-lying state
- Nuclear forensics
  - Verification
  - Attribution
- Radionuclides in the environment
  - Tracing nuclear accidents
  - Study remediation measures
- Medical applications
  - Ca metabolism
  - Drug uptake
- ...



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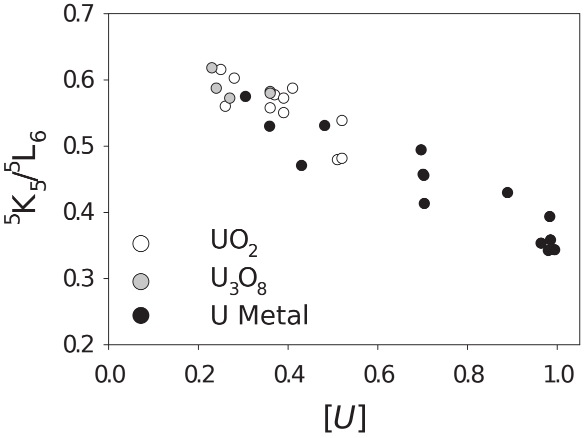

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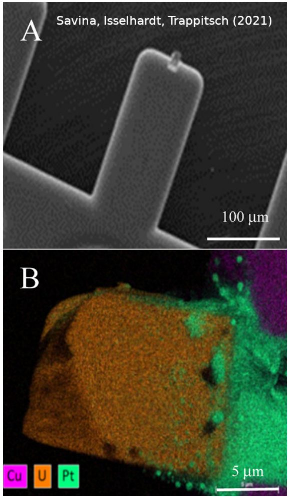

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  - Attribution
- Radionuclides in the environment
  - Tracing nuclear accidents
  - Study remediation measures
- Medical applications
  - Ca metabolism
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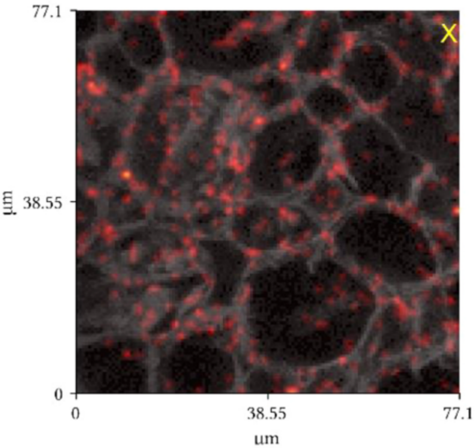

^{99}Tc in pisum sativum (Mandel+, 2022)

And there are Many More Uses for RIMS!

- Surface Chemistry
  - Oxidation state of U
  - Enabled by low-lying state
- Nuclear forensics
  - Verification
  - Attribution
- Radionuclides in the environment
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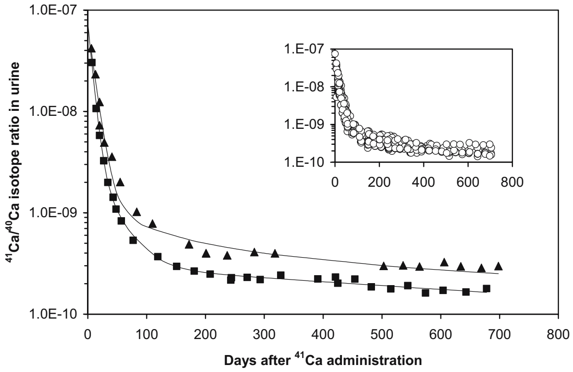
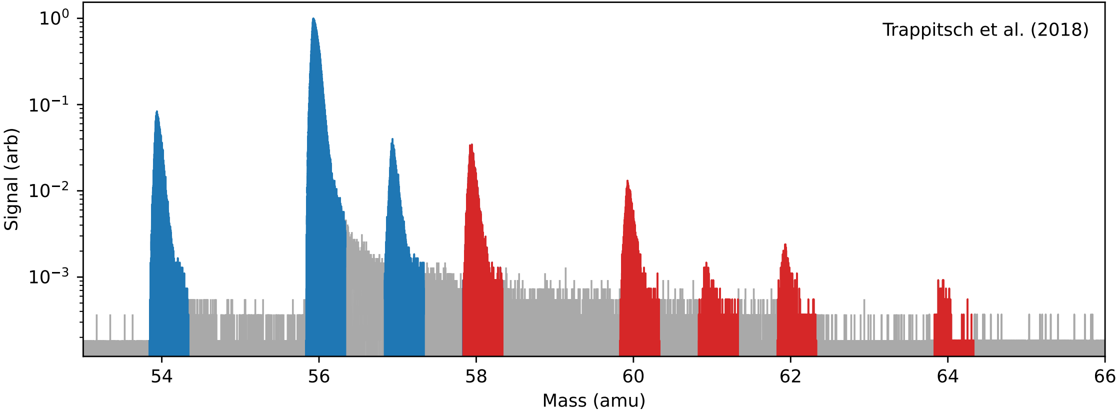


Denk+ (2006)

Simultaneous Measurements of Iron and Nickel



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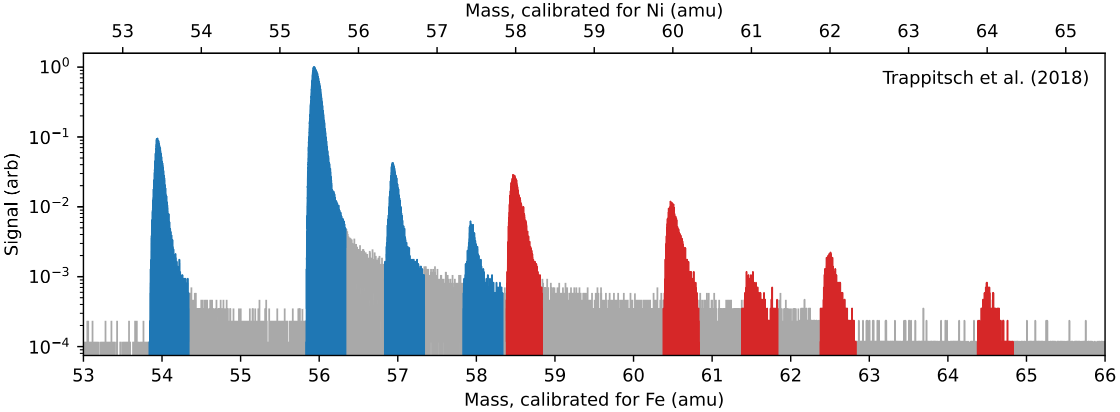
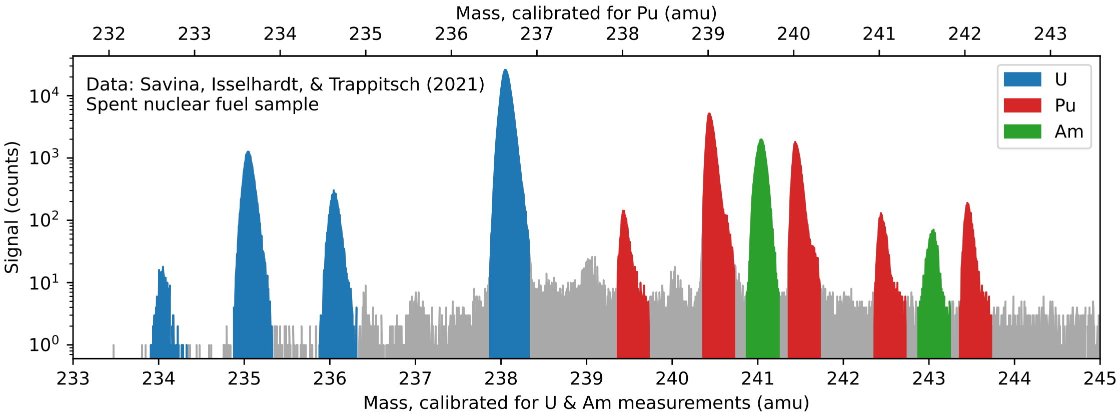
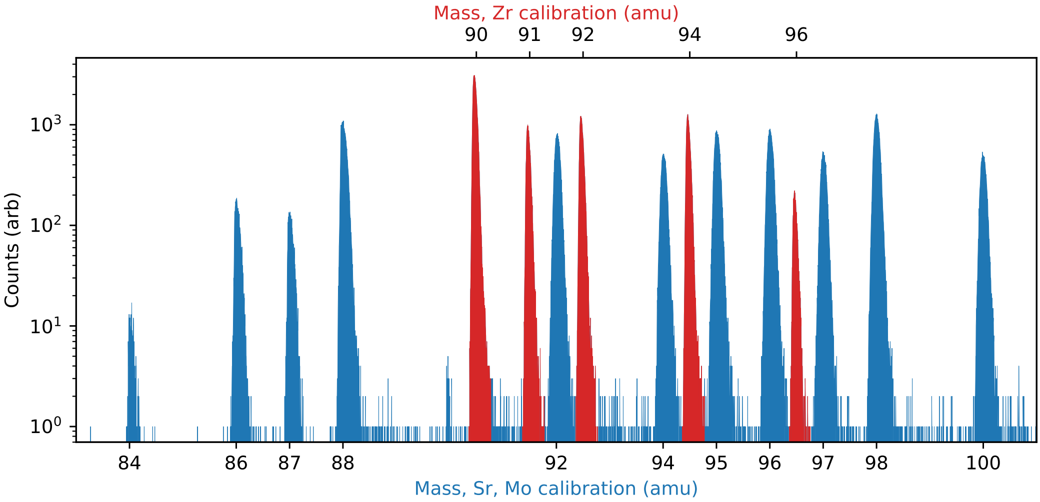


Multi-Element Analysis Avoiding Isobaric Overlap

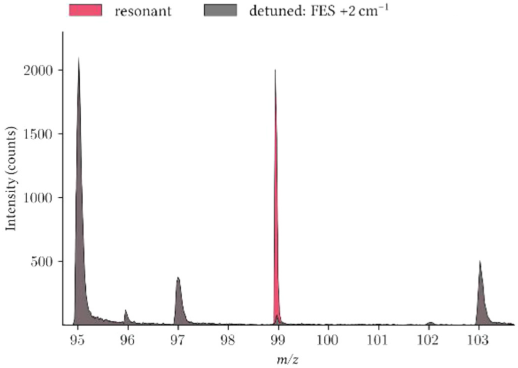


Simultaneous Sr, Zr, and Mo analysis (Shulaker+, 2022)



Signal and Noise: Quasi-Simultaneous Detection and Correction

- Quantitative analysis of noise possible by RIMS
- Signal: Lasers are on-resonance
- Noise: Detune laser to be off resonance
- Quasi-simultaneous
  - Tune additional laser and blink on-/off-resonance
  - Use single laser and electro-optic deflectors (in development)
- Optimal "blinking" rate depends on signal/noise



Mandel+ (2022)

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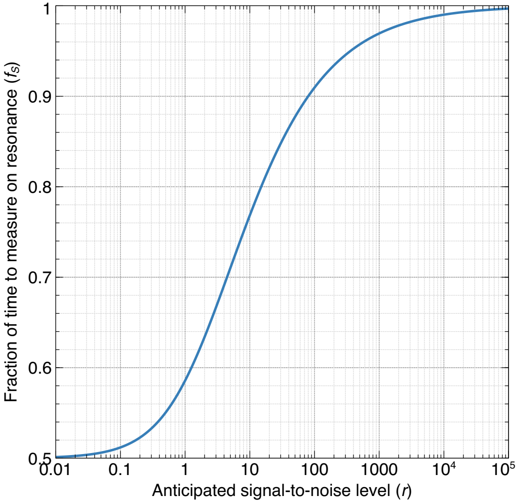
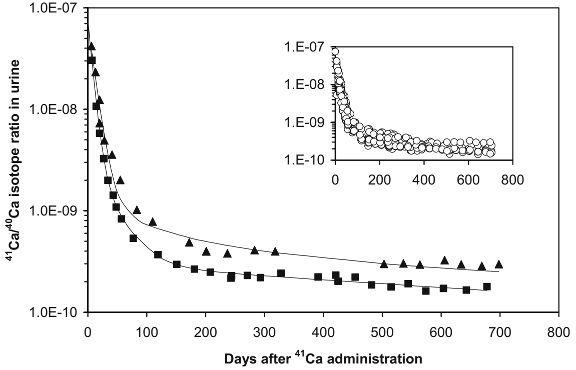


Full Disclosure — Limitations of RIMS

- Count rate limitations significantly limit the dynamic range
  - Narrowband cw lasers can be used in special cases to increase dynamic range
  - Example: ^{41}Ca/^{40}Ca analysis
- Duty cycle compared to SIMS: $\sim 10^{-4}$
- Desorption laser coupling depends on material and wavelength
  - Choose the right wavelength and pulse width
- Sample material might come off as molecules
  - In-vacuo surface chemistry



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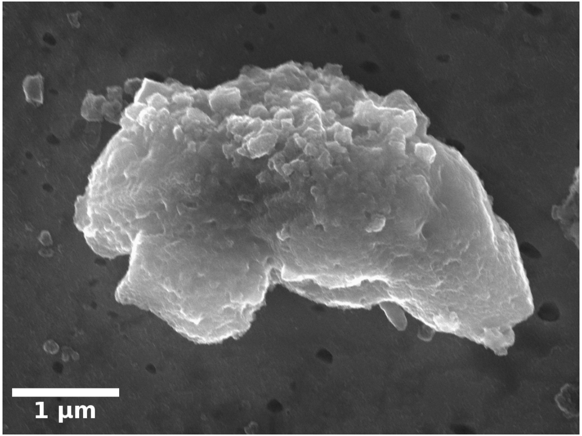
Hiden Analytical IG20

RIMS — A Tool for Your Analysis?

- Small, atom-limited samples
- Spot size:
  - $<100\,\text{nm}$ ion gun
  - $\sim 1\,\mu\text{m}$ desorption laser
- High useful yield: Up to $\sim 40\%$ (U)
- Isotope ratio uncertainties $\gtrsim 2‰$
- Isobar suppresion and separation
- Quantitavive background measurement

RIMS: An ultra-sensitive technique that is complementary to, e.g., NanoSIMS



Presolar SiC grain

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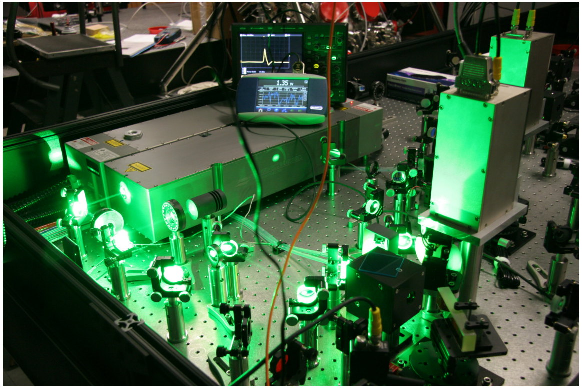

Laser cavity on CHILI

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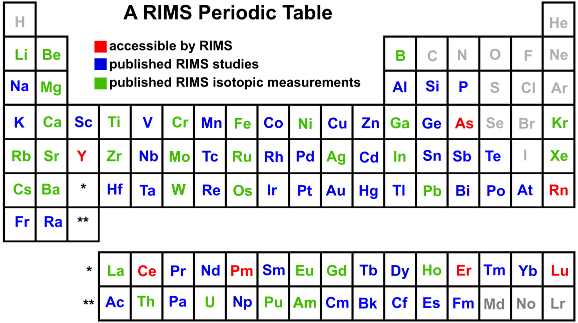

Savina and Trappitsch (2021)

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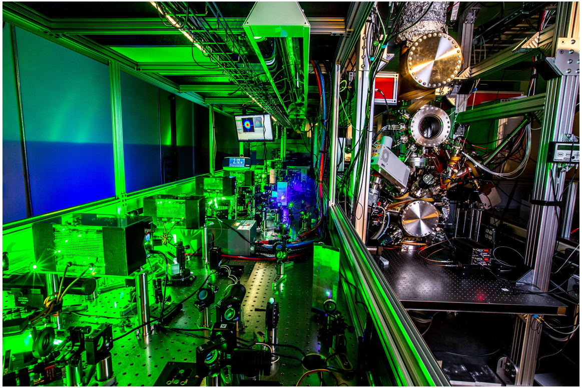

LION at LLNL

Collaborators

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- Ziva Shulaker
- David Willingham
- Mike Kristo

The University of Chicago

- Andy Davis
- Thomas Stephan
- Mike Pellin

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