



Mineral Chemistry: Modern Techniques and Applications to Exploration

Simon Jackson
Geological Survey of Canada
Ottawa, ON

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Introduction

Mineral Chemistry and Indicator Mineral Exploration

- Must use in situ analytical techniques – speed and cost effectiveness
- Wide range of techniques: widely variable cost, value/\$\$
- Focus on most widely used, cost-efficient in situ technologies

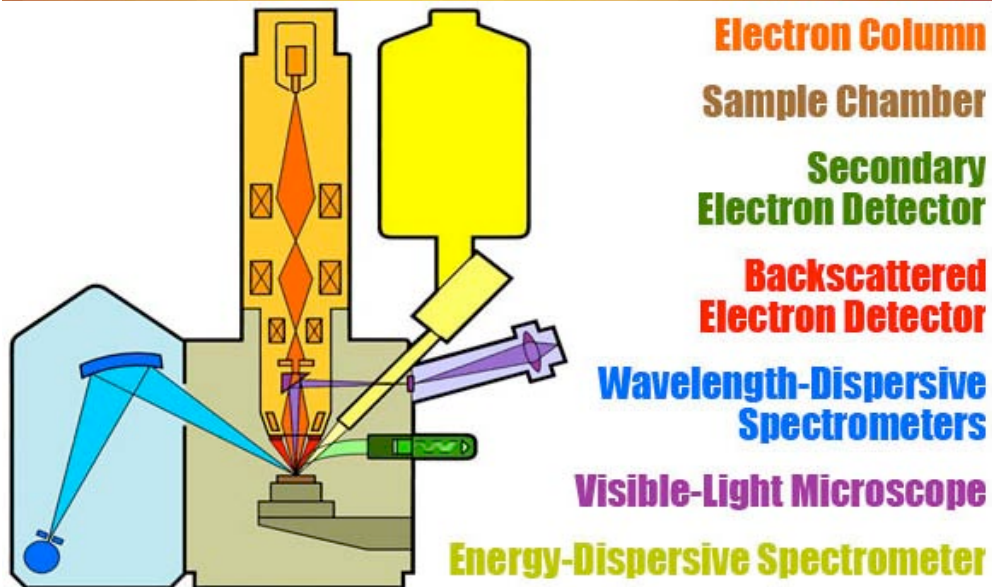
Instrumentation, figures of merit, major applications of:

- Major and minor elements by EPMA
- Trace elements by LA-ICP-MS
- Low precision isotopic analysis (U-Pb) by LA-ICP-MS, Ion Probe
- High precision isotopic analysis by LA-MC-ICP-MS
- Integration of multiple techniques





In Situ Major Element Analysis: Electron Probe Micro-Analyzer (EPMA)



probelab.geo.umn.edu/electron_microprobe.html



<http://cgc.rncan.gc.ca/labs/ebeam/images/sx50.jpg>

- Electron microprobe
- Mature technology (from 1960s)
- Collimated electron beam → X-ray generation
- Spot sizes 1-2 μm x few μm
- Sequential WDS crystal spectrometers
- Simultaneous EDS spectrometer
- High continuum background → major elements (%)
- Minor elements (200-500 ppm)
- Imaging - BSE, CL, SEM
- Mapping (major elements)

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EPMA - Calibration and Figures of Merit

Calibration

- Calibration against mineral standards
- ZAF matrix correction

WDS: wavelength dispersive analysis (crystal spectrometers)

- one element at a time, on each (~5 spectrometers)
- 10 min analysis → detection limits of 200-500 ppm
- lower detection limits require very long count times
- higher resolution, higher intensity with larger crystals (\$\$)
- precise - data quality depends on counts (time)
- element mapping (≤ 5 elements)

EDS: energy-dispersive analysis (Si(Li) detector)

- simultaneous energy spectrum → rapid phase identification
- analysis of major elements (use as extra spectrometer)
- rapid multi-element mapping

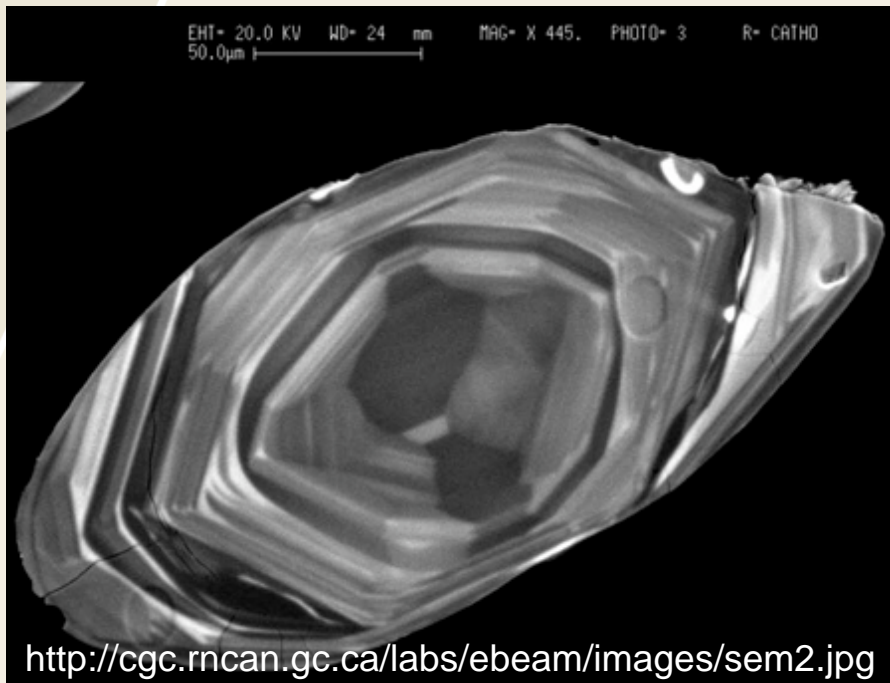
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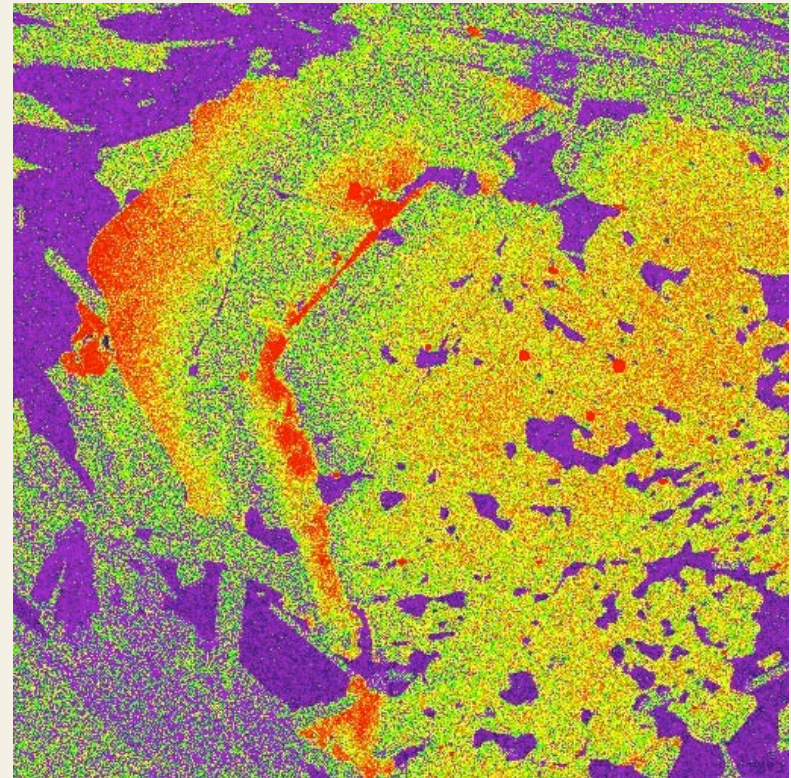
Electron MicroProbe: Imaging

BSE/CL Imaging of Zircons



Imaging to assess growth history of zircon for later trace element/U-Pb/Hf isotope analysis

X-ray mapping (Ca)



Gt growth in pressure shadows in Stewart River metapelite → 2 deformation events (courtesy: R. Berman)



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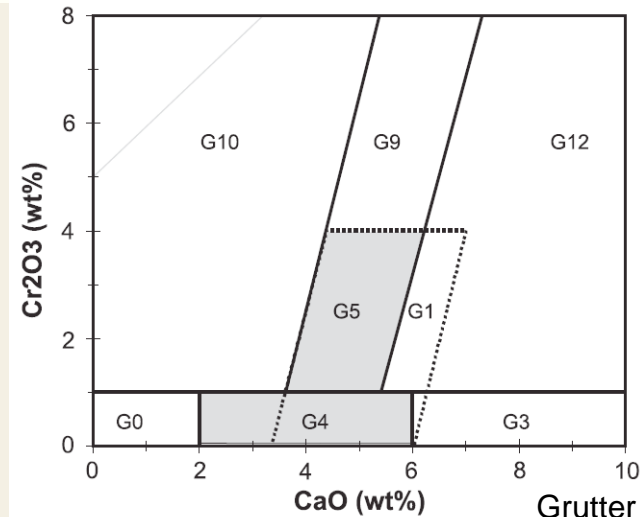
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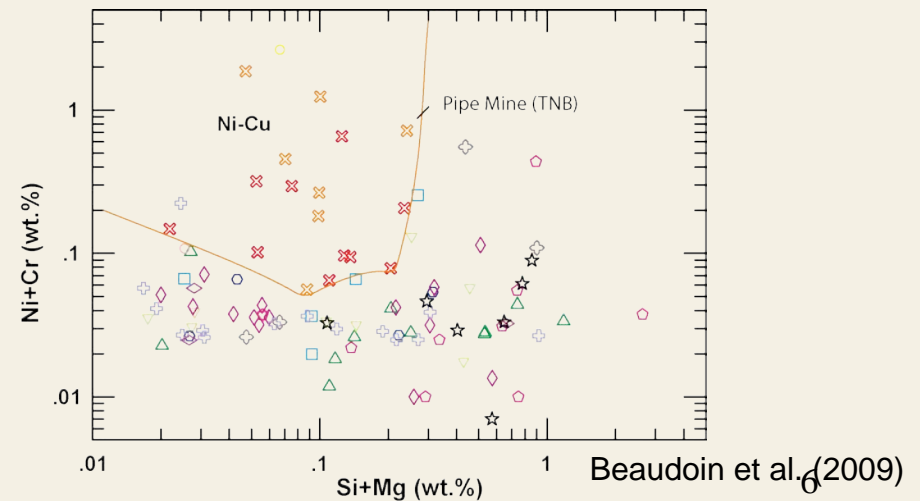


Applications of EPMA in Indicator Mineral Analysis

- Typing garnets and ilmenites in diamond exploration; e.g., 'G10' Garnet
- Discriminating sources of Fe-Ox minerals
- Discriminating sources of placer gold
- Providing major element data for calibrating LA-ICP-MS trace analysis



Grutter et al. (2004)

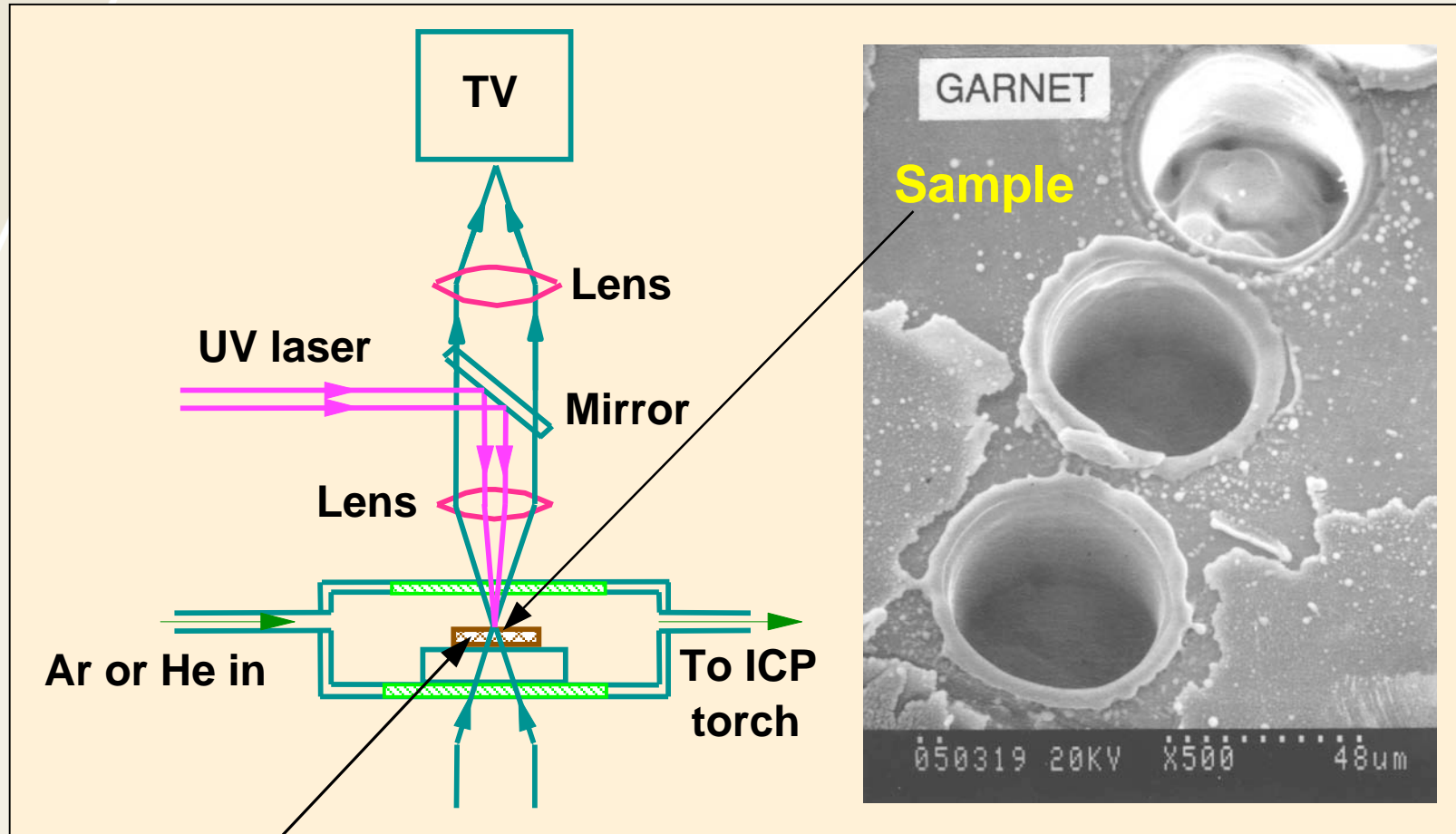


△ IOCG □ Kiruna ▽ IOCG-like ○ BIF ◇ Porphyry ◊ Skarn ● Cr
 ◆ VMS ☆ Opemiska ◊ Archean Porphyry ◆ Fe-Ti ● V × Ni-Cu





In Situ Trace Element Analysis - Laser Ablation (LA)-ICP-MS



Sample = thin section, polished block, grain mount, rock sample



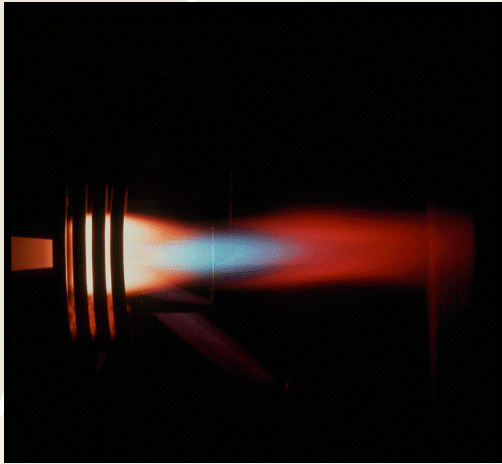
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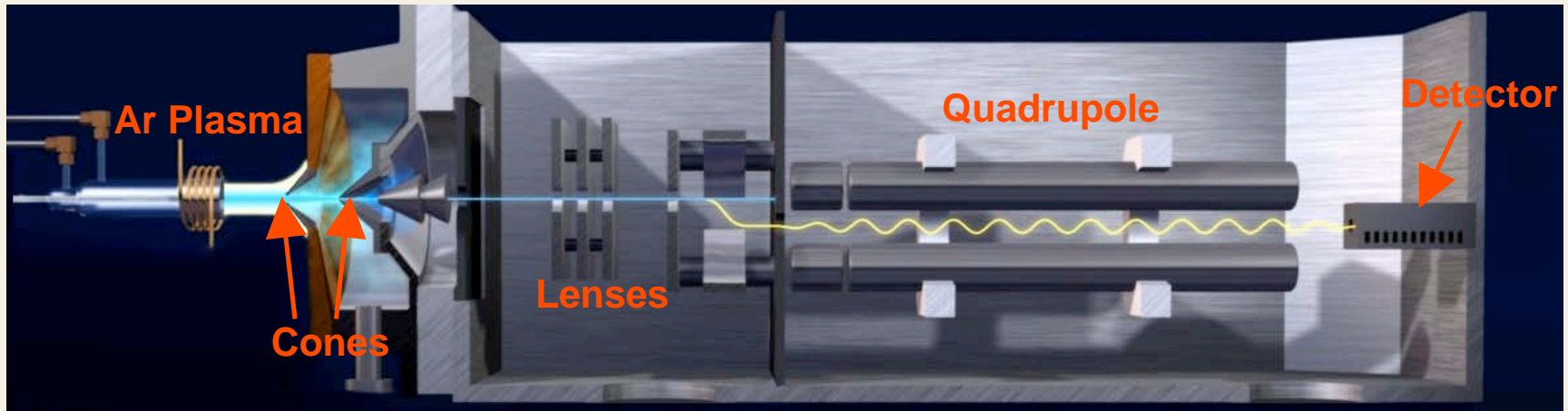


Fundamentals of (Quadrupole) ICP-MS



The Plasma-based instrument family

- ICP-AES/OES (atomic/optical emission spectroscopy)
 - ICP-MS – ion detection method:
 - Quadrupole
 - Magnetic sector single collector
 - Magnetic sector multi-collector
 - (Time of flight)
- Sequential
- Simultaneous





Which ICP-MS?

Quadrupole ICPMS:

- Rapid scanning of whole mass spectrum
- High sensitivity
- Reaction/collision cell reduces some overlaps
- Relatively low cost (<\$US 200,000)

Magnetic Sector (High-Resolution) ICPMS:

- Higher sensitivity than most quadrupole systems
- High resolution resolves overlaps for special applications (e.g., ArO on Fe), but at reduced sensitivity – fewer applications in dry plasma work (LA)
- Scans limited portions of spectrum rapidly, whole spectrum more slowly
- High cost (>\$US 300,000)



http://www.thermo.com/eThermo/CMA/PDFs/Product/productPDF_50760.pdf

Quadrupole ICP-MS: faster, more versatile and economic – preferred for LA work

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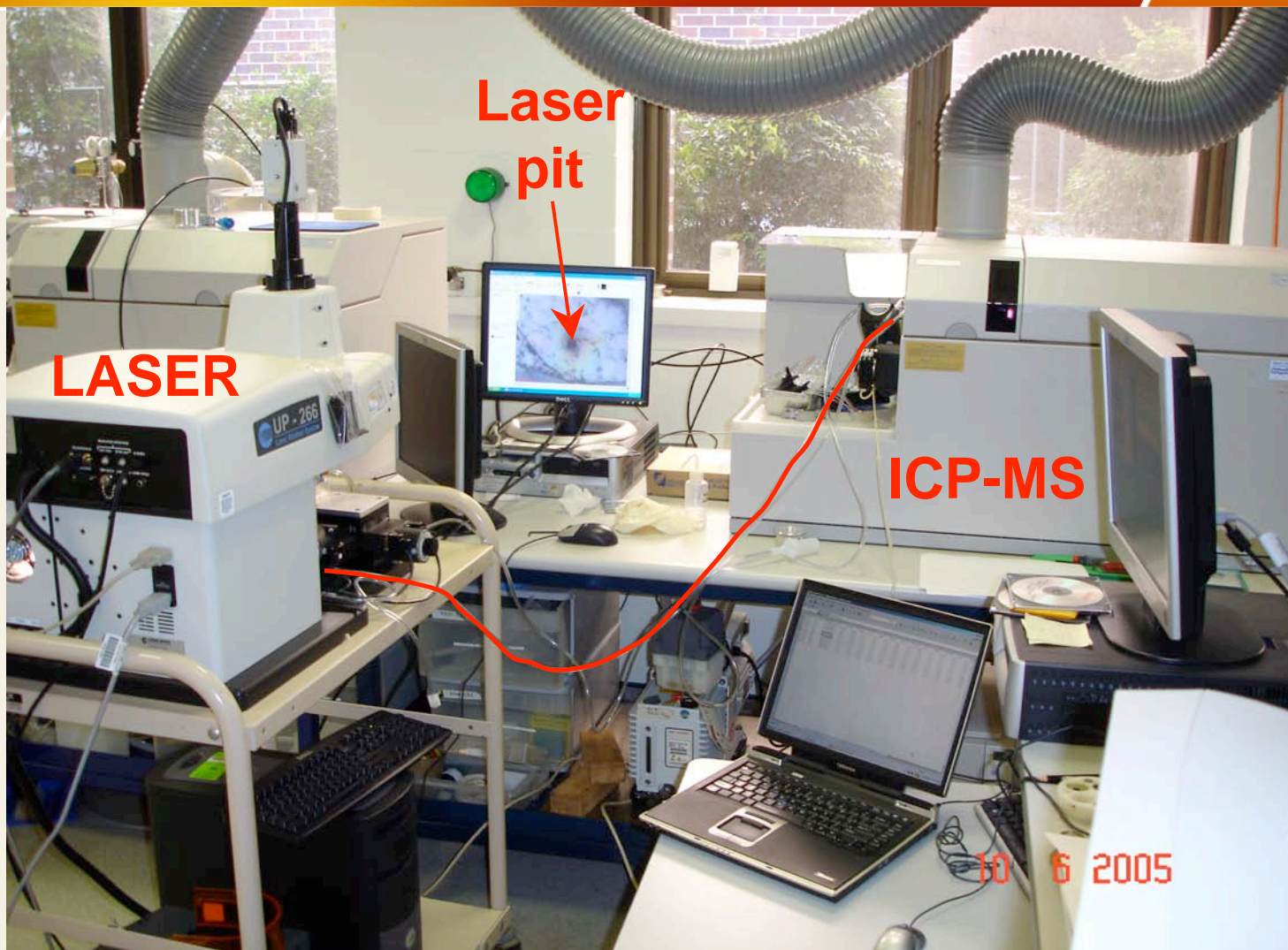
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LA-ICP-MS Set Up



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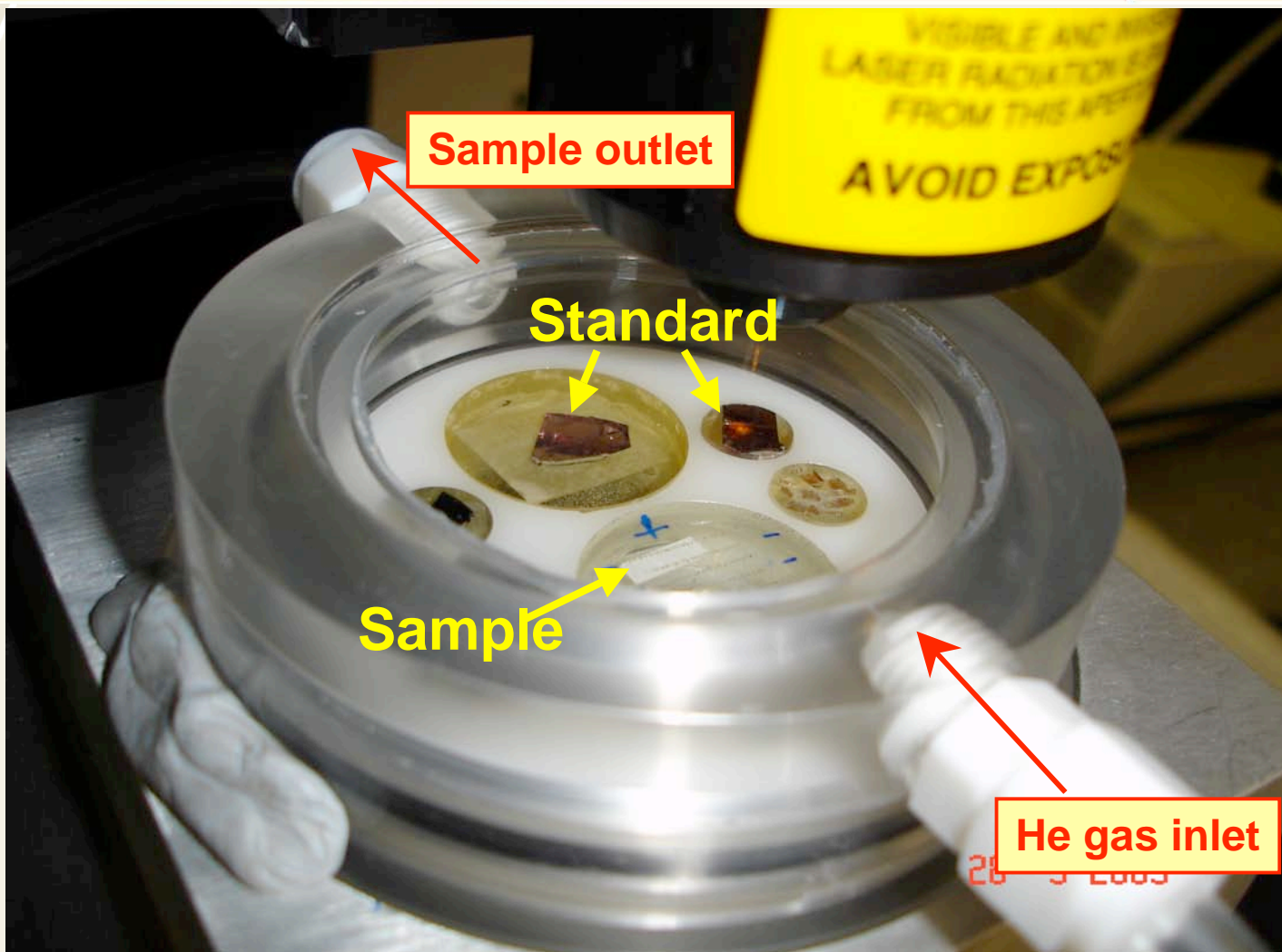
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Sample Cell



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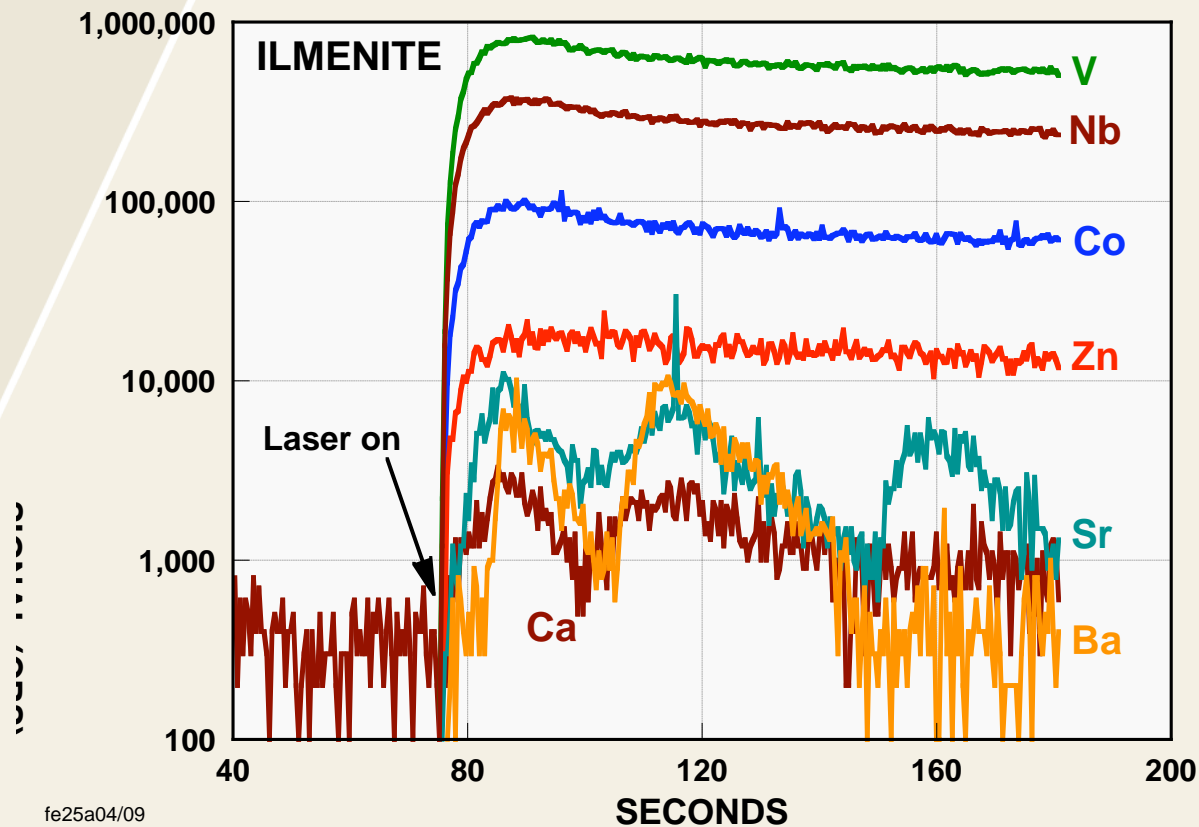
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Time Resolved Analysis and Data Processing



- Often complex signals – zoning etc., esp. hydrothermal minerals)
- Provides valuable information on distribution of trace elements in ablation volume
- Signals must be selectively integrated
 - specialized software
 - difficult to automate

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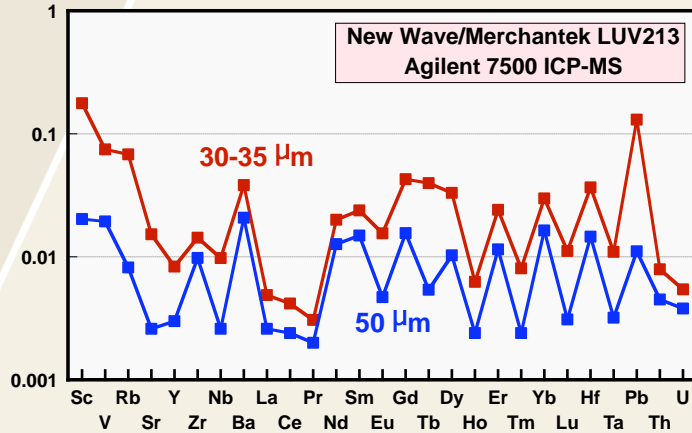
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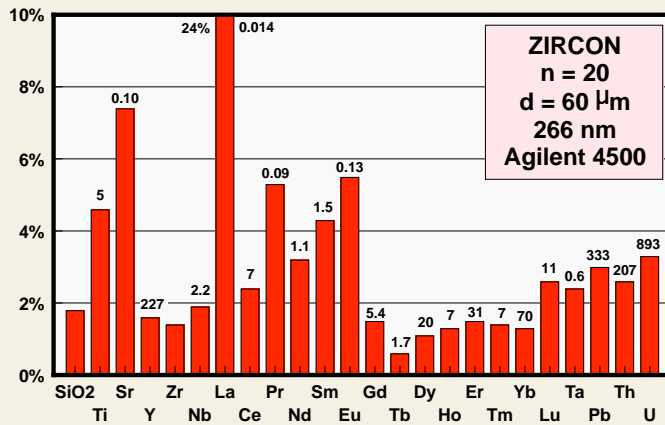


LA-ICP-MS - Calibration and Figures of Merit

LAM-ICP-MS DETECTION LIMITS



LAM-ICP-MS PRECISION



Calibration

- Robust relatively matrix-intolerant calibration with synthetic glasses
- Requires concn. of 1 (major) element in sample

Figures of merit

- rapid - 3-5 min per analysis (manual); 2-3 minutes (automated) – 500 analyses/day
- spatially resolved (<10 - >100 μm resolution)
- depth profiling (1 μm resolution)
- multi-element (40-50 elements)
- precise (ca. 2%)
- detection limit to low ppb at 30-40 μm resolution (spot size dependent)
- 'accurate' (see fine print for conditions)
- individual fluid and melt inclusions
- isotope ratios, esp. U/Pb (down to 0.1-1% RSD)

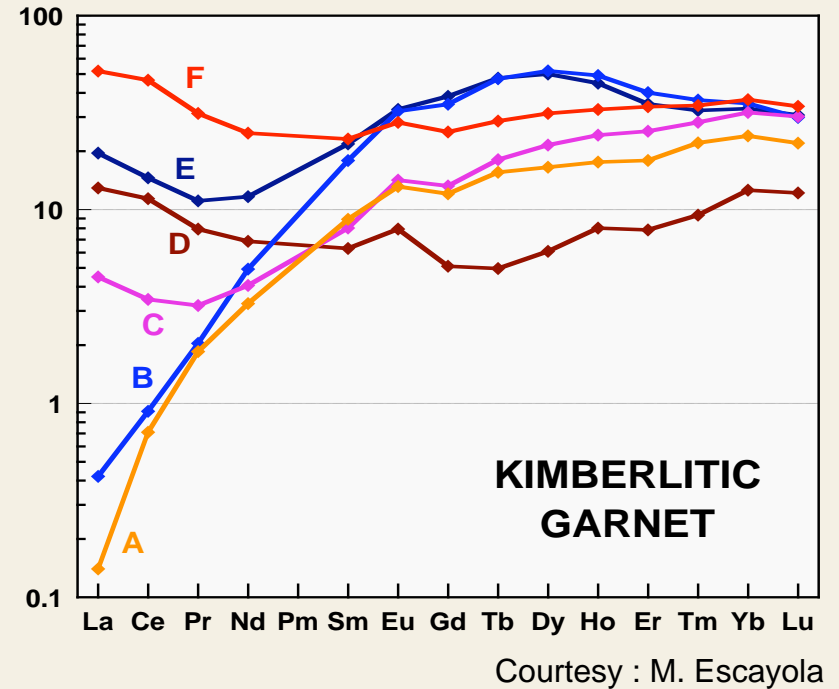
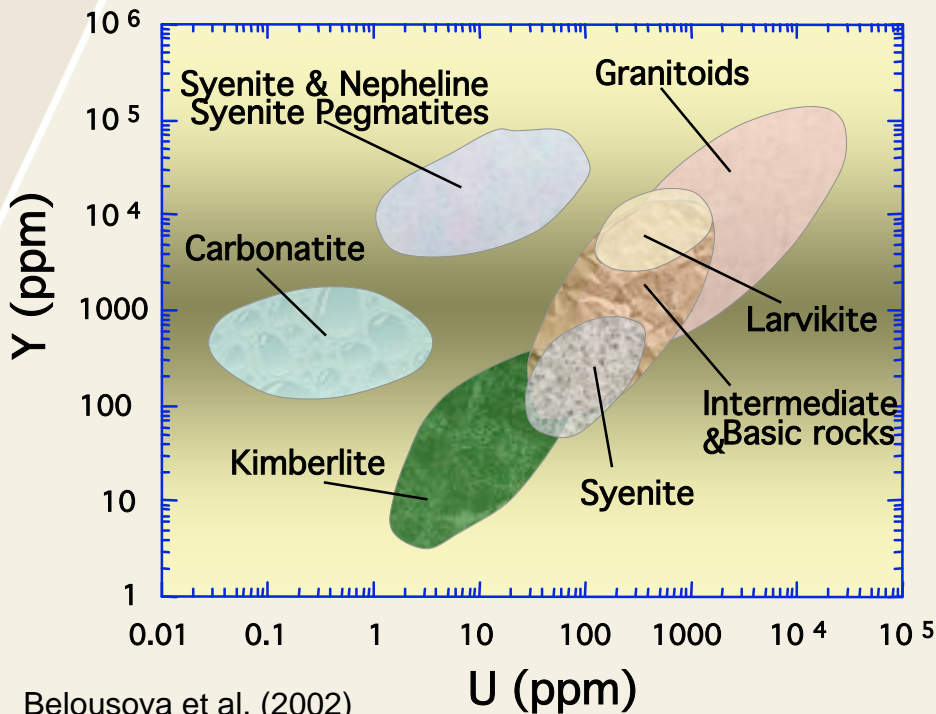




Applications of LA-ICP-MS In Indicatory Mineral Analysis

Diamond Exploration

- Garnets: Ni geothermometry
- Garnet/ilmenite geochemistry



Regional exploration

- Zircon, apatite geochemistry

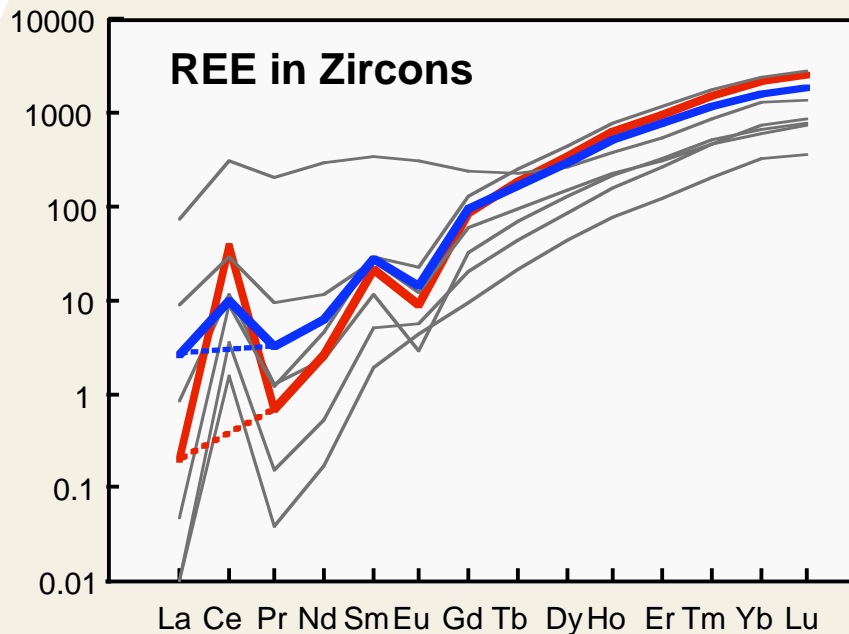




Applications of LA-ICP-MS In Indicator Mineral Analysis

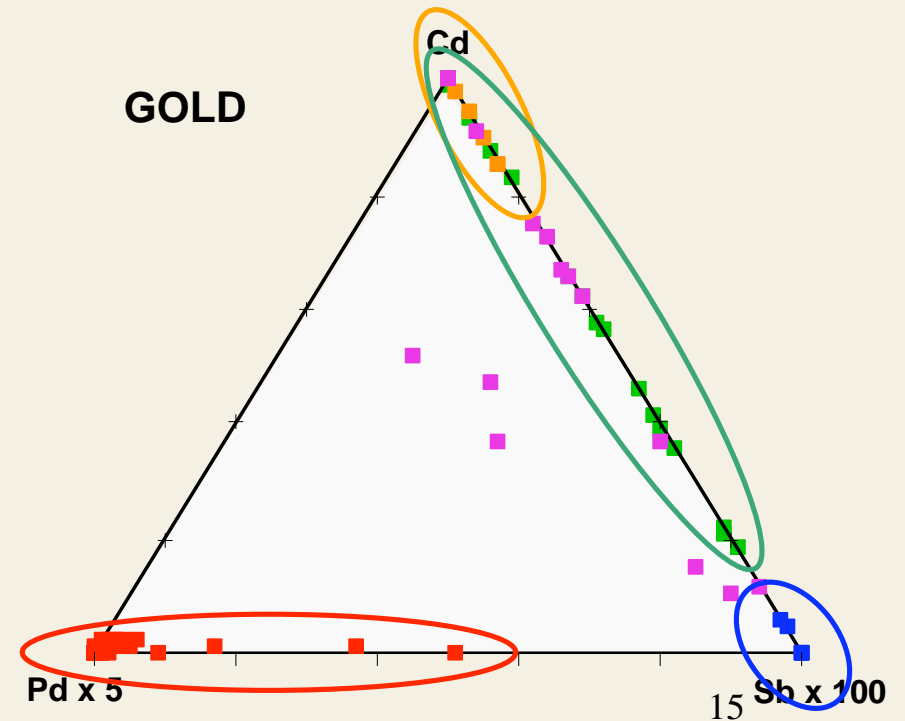
Porphyry Cu-Au

- Zircon REE geochemistry



Gold

- Detrital gold discrimination





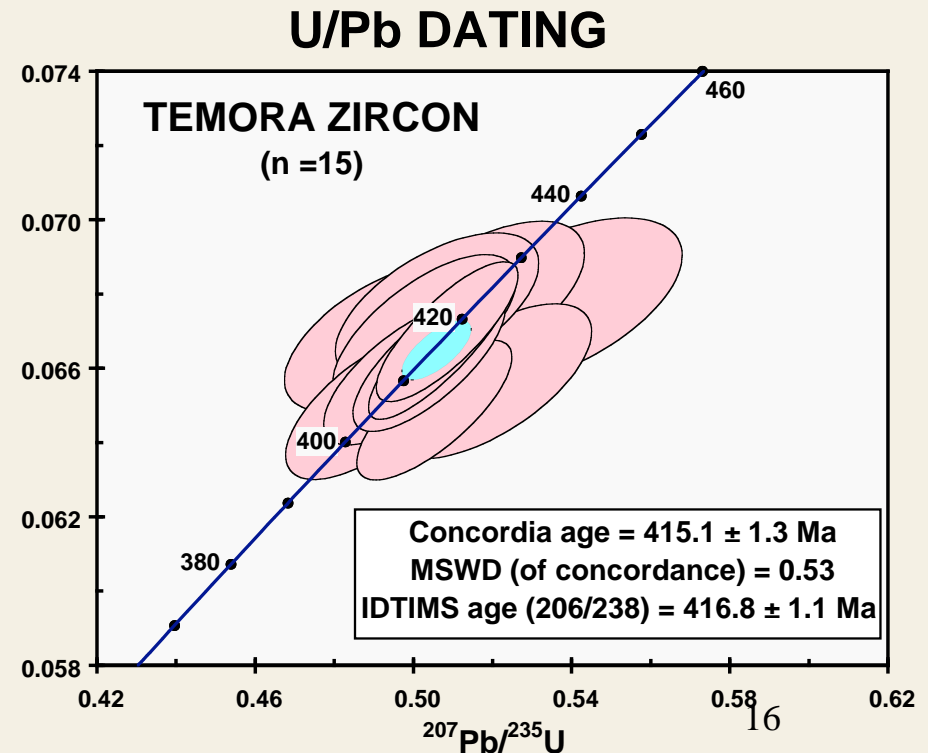
In-situ Dating: U-Pb in Zircon, Monazite

TIMS single-grain analysis:

- benchmark technique
- ultimate precision (~0.1%)
- but slow, complex chemistry
- zircons may be multistage
 - requires in situ techniques
 - 20-50 μm resolution

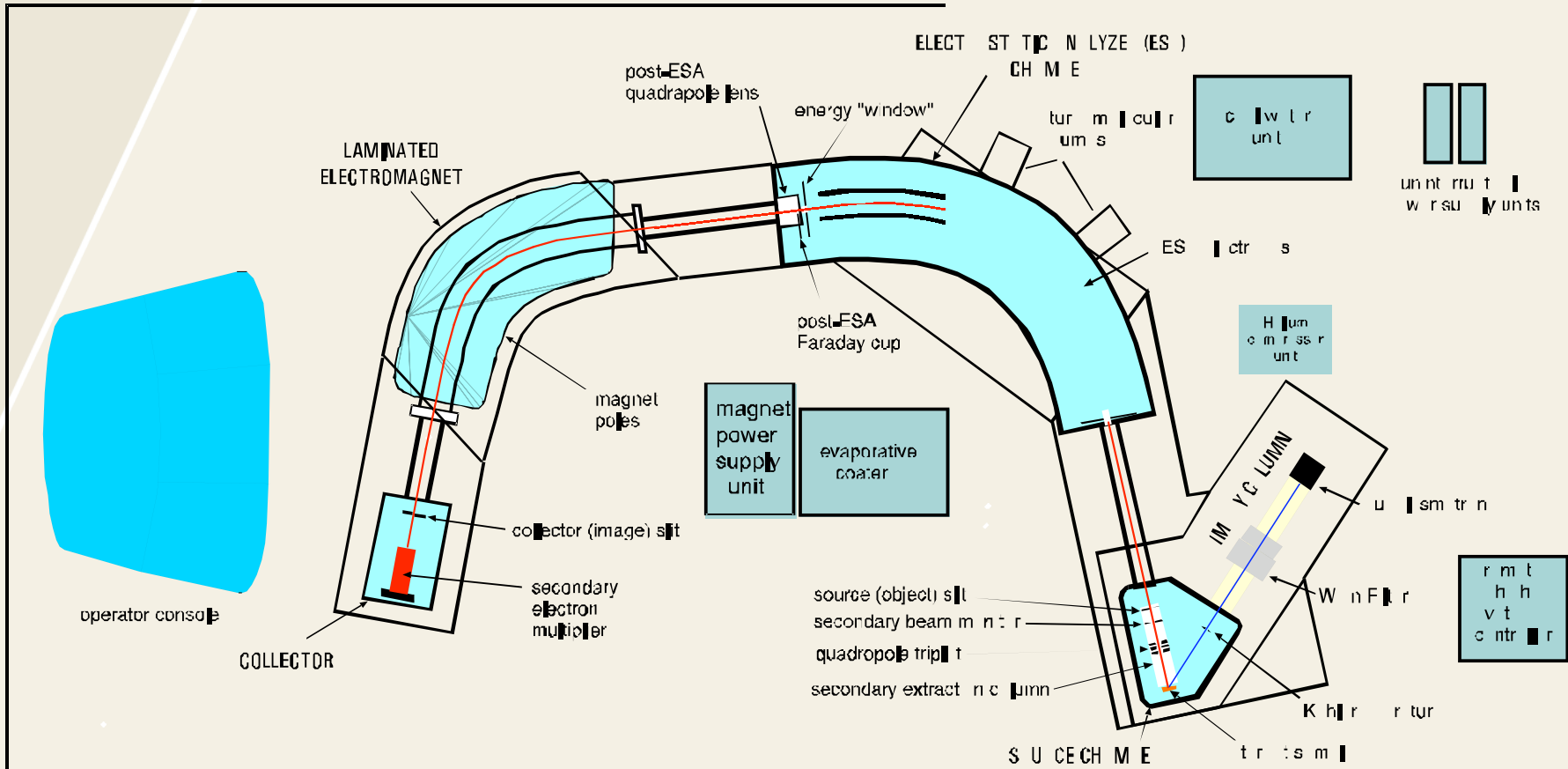
1-2% precision very useful:

- Ion microprobe
 - SHRIMP
 - CAMECA
- LA-ICPMS





Ion Microprobe (SHRIMP)



J.C. Roddick Ion Microprobe Laboratory





Ion Microprobe (SHRIMP)



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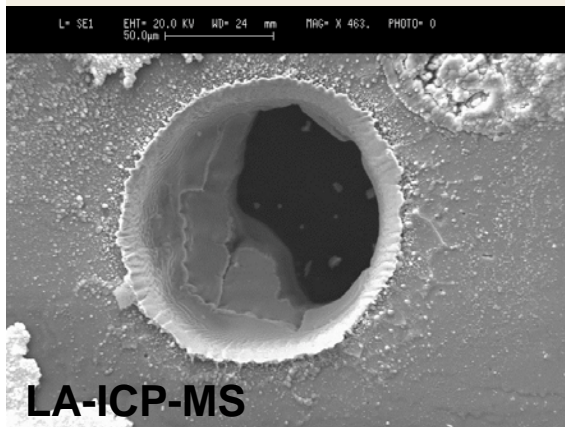
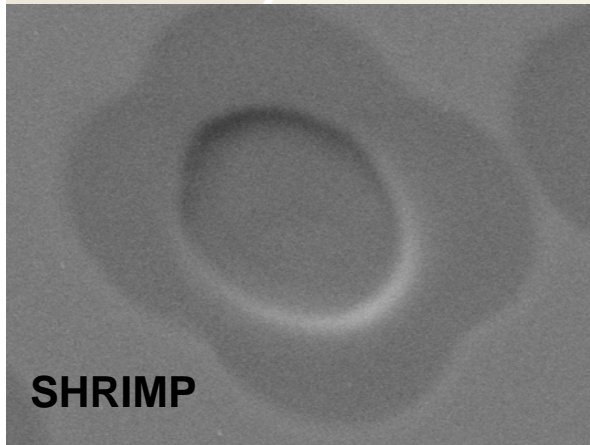
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Comparison of Ion Probe and LA-Q-ICP-MS



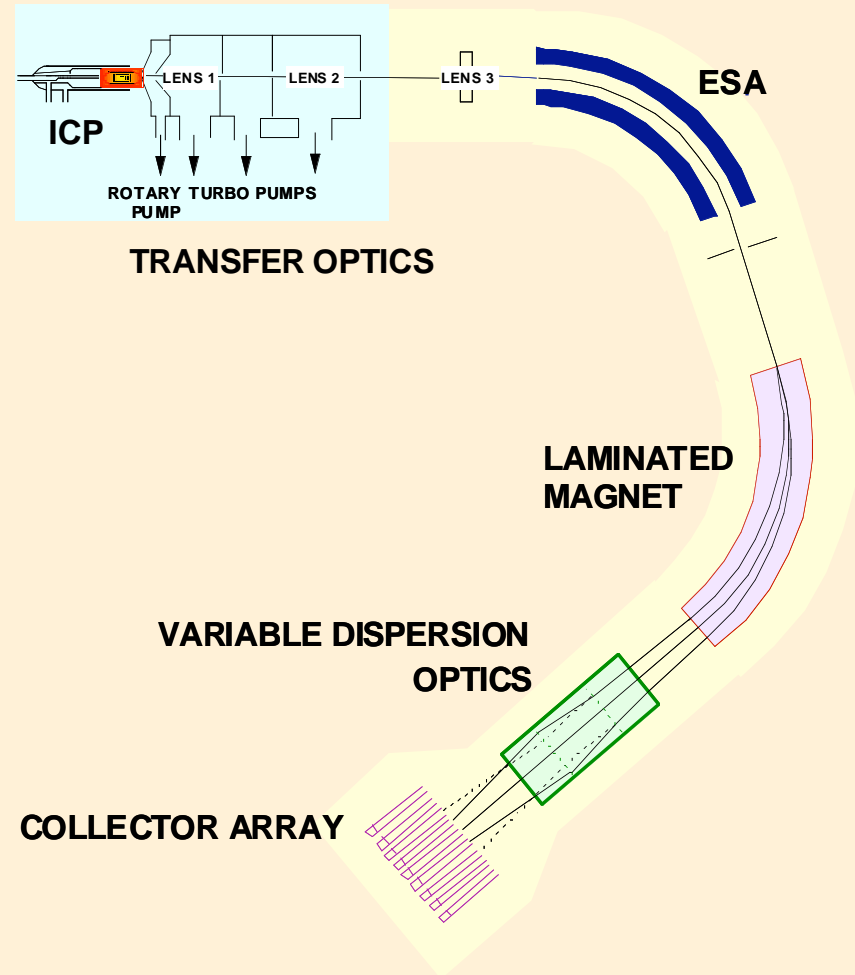
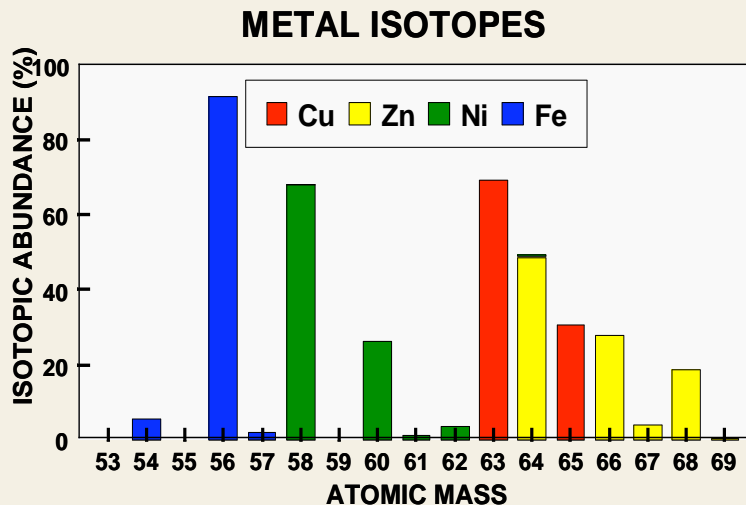
	SHRIMP	LA-Q-ICP-MS
Precision (2 σ)	ca 1-2 %	ca. 1-2%
Spatial resolution	5-35 μm diameter 1-2 μm deep (slow drilling rate, minimal sample consumption)	15-60 μm diameter >15 μm deep (1 $\mu\text{m/s}$ drilling rate, moderate sample consumption)
Relative throughput - analyses	10-30 min/analysis	3-5 min (manual) = 60-80 per day 1-2 min (automated) = 500-1000 per day!
Common Pb correction	^{204}Pb correction	^{204}Pb correction compromised by Hg
Other capabilities	O, S, C isotopes; traces elements (matrix sensitive \rightarrow mineral standards)	Trace elements (relatively matrix insensitive \rightarrow glass standards)
Capital Costs	High (>\$1M)	Moderate (<\$500,000)





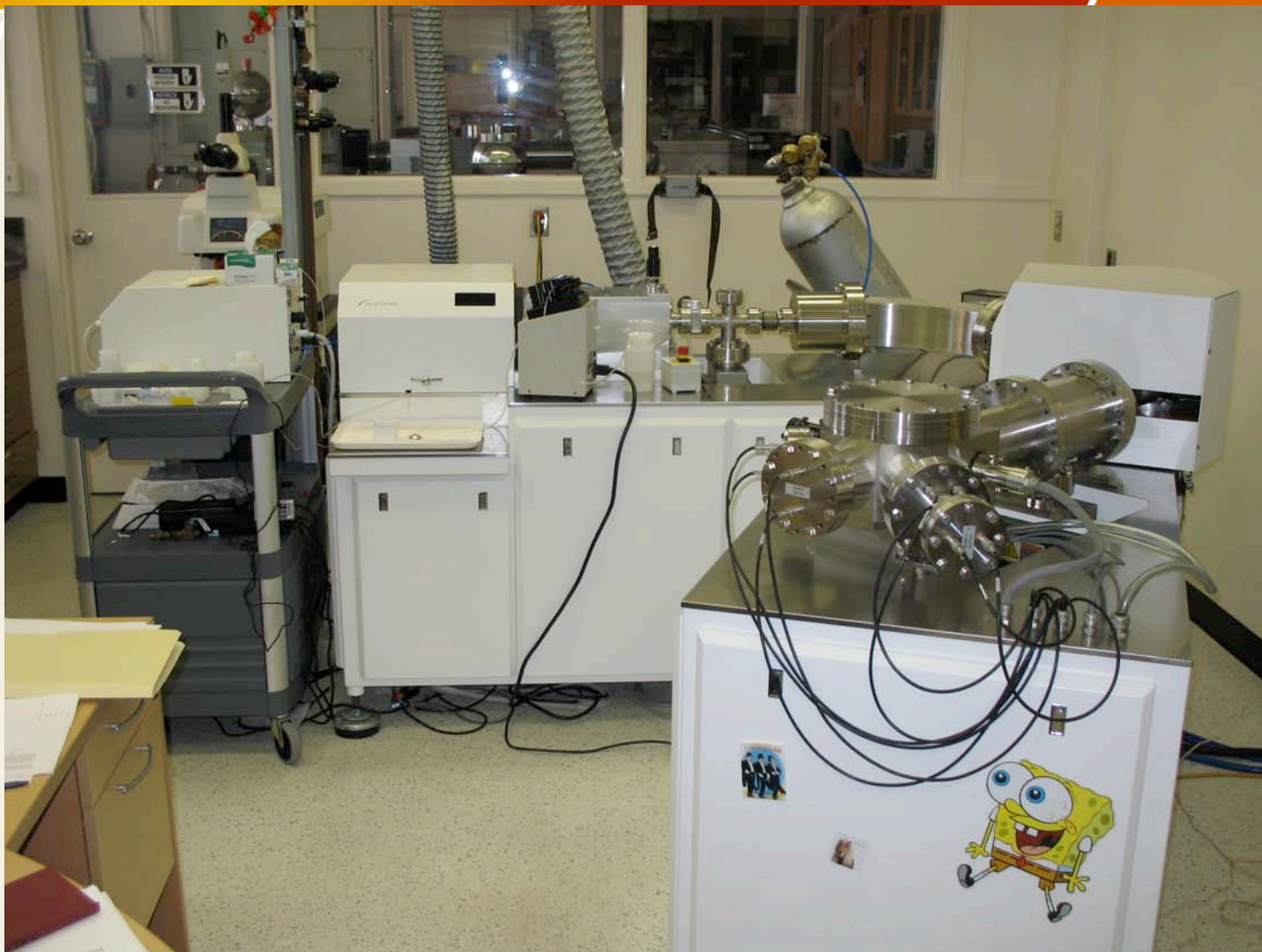
High Precision Isotopic Analysis by MC-ICP-MS

- MC → *high precision* isotopic analysis
- Radiogenic isotope analyses (e.g., Sr, Nd, Hf, Os, Pb) with ppm precision
- ICP → “**Non-traditional**” stable isotope analysis (e.g., Mg, Fe, Cu, Zn, Ni, Sb)
- ICP → **LA in situ** isotopic analysis; e.g., Hf in zircon, Pb in feldspar, Cu in cpy, Fe in magnetite – 0.1 ‰ in 3-5 minutes





LA-MC-ICP-MS



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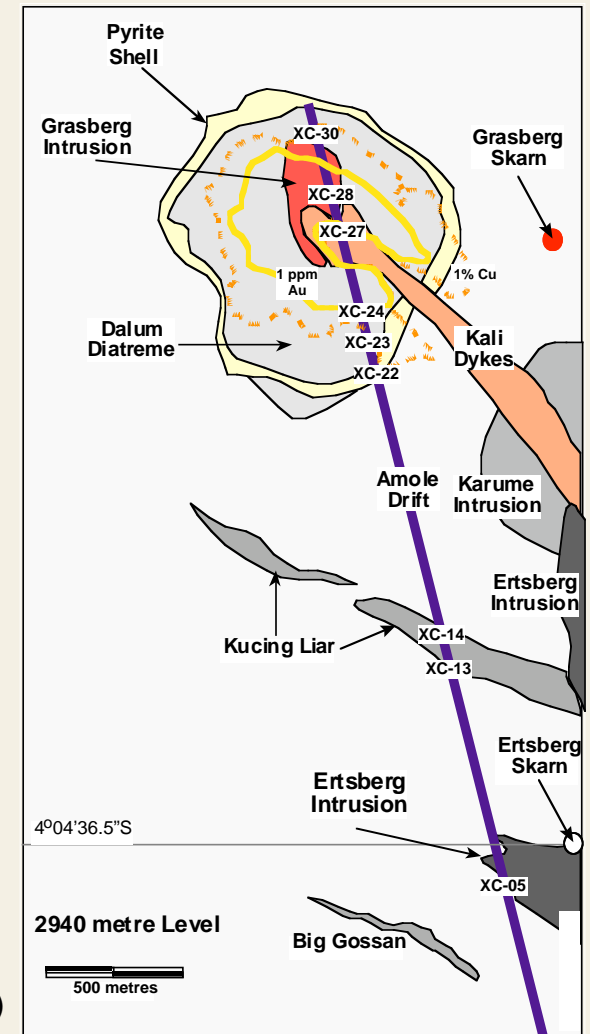
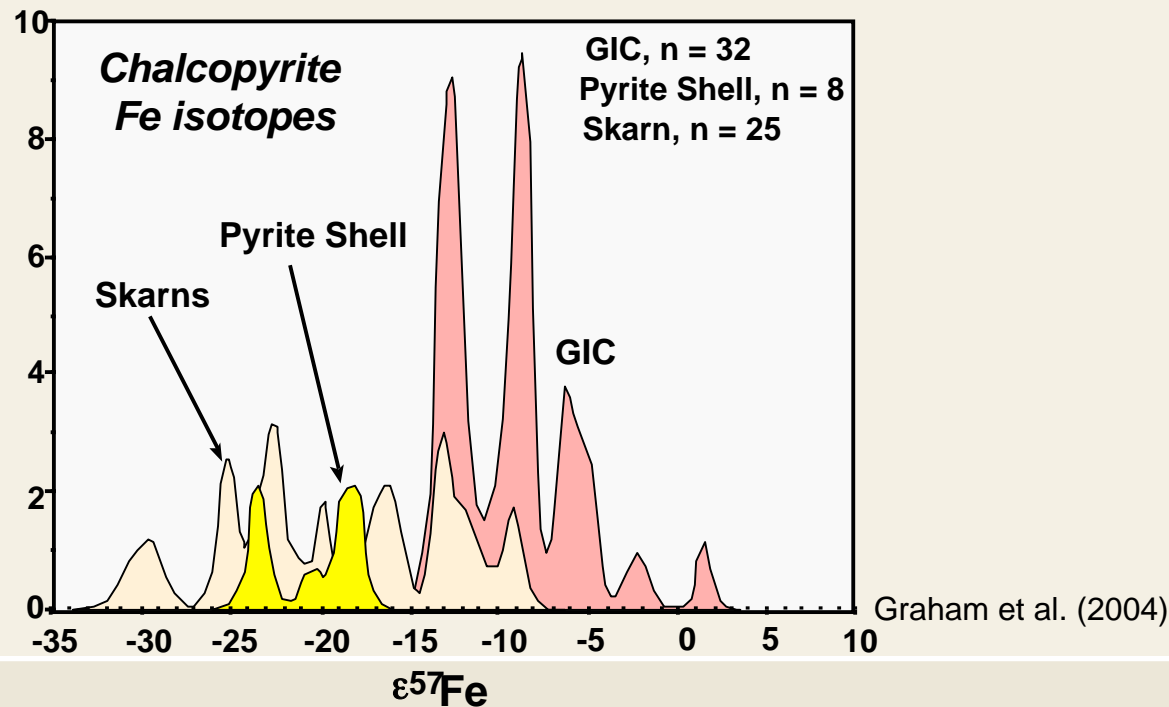
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Applications of LA-MC-ICP-MS in Indicator Mineral Analysis

- Fe isotopes in Fe-Ox minerals
 - Combined with elemental analyses
- Si isotopes in resitstate silicates
- Hf isotopes in zircon
 - Combined with trace element and U-Pb data

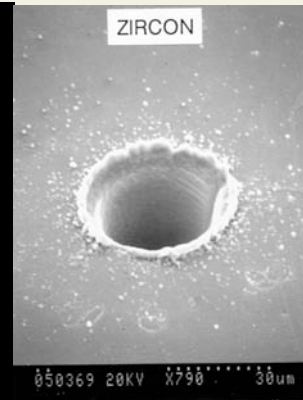
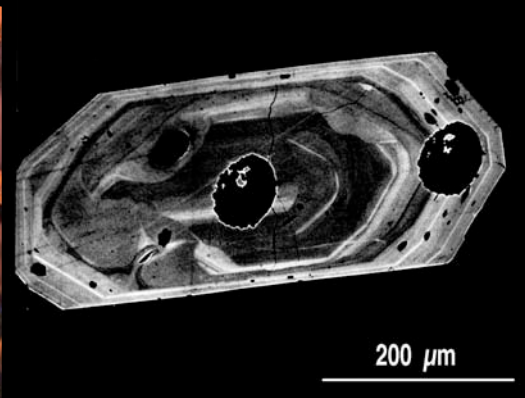




Integrated Trace, U-Pb & Hf Isotope Analysis of Zircon

The 'TerraneChron' Approach (<http://www.es.mq.edu.au/gemoc/>)

- Traditional heavy mineral separation
- Zircon grain picking (Leica UV binocular)
- Mounting of grains in polished blocks
- EPMA: BSE/CL imaging, Hf+Y+U+Th
- LA-ICPMS: U-Pb dating
- LA-MC-ICPMS: Hf isotope analysis
- (LA-ICP-MS REE provides more information; e.g, oxidation state)



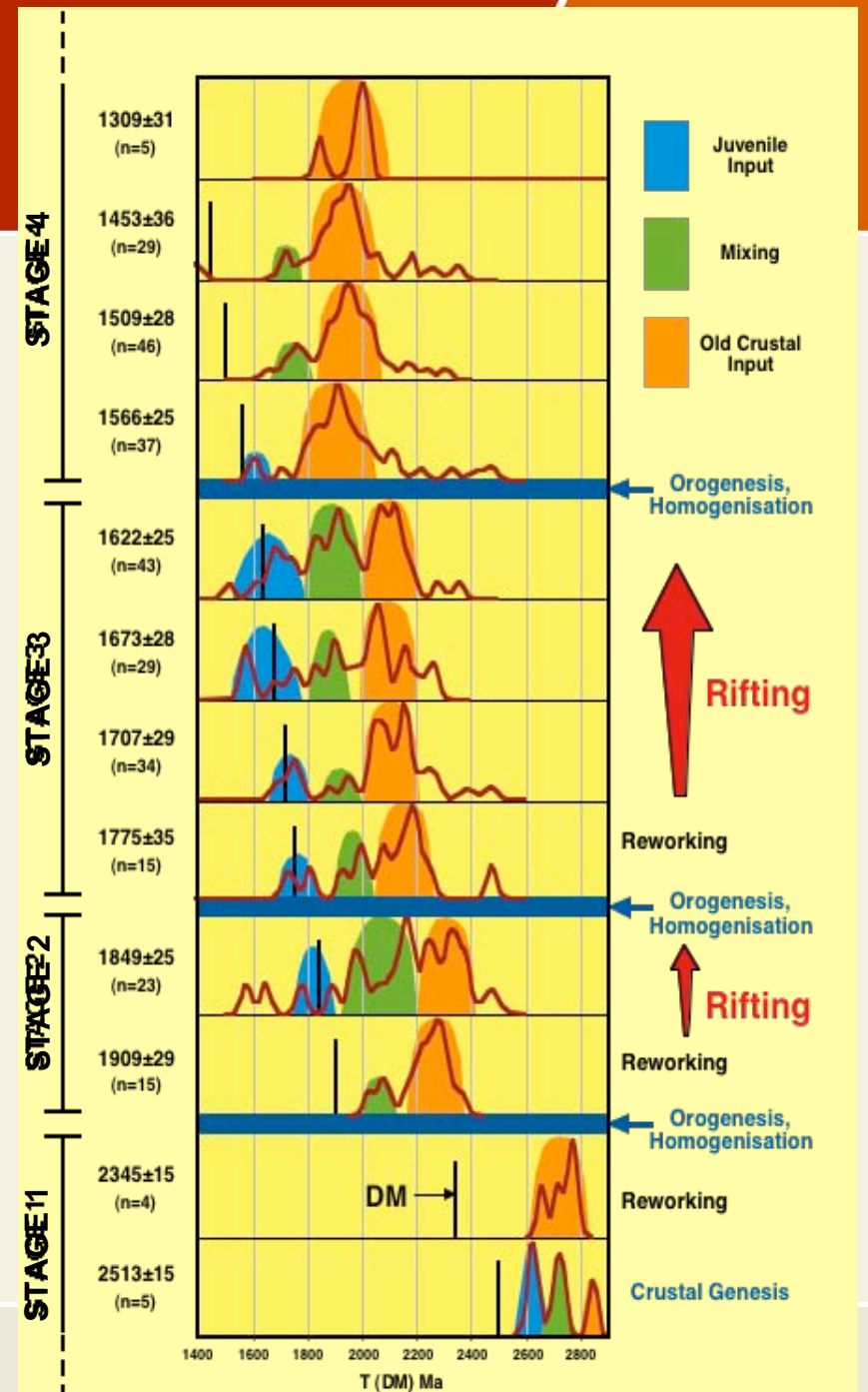
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Event Signatures of Mt. Isa E.S.

- Four major stages of crustal evolution
- Each stage has a distinct pattern of crustal recycling and juvenile mantle input
- Each stage (apart from the last) ends with a period of crustal homogenisation
- Some very depleted mantle sources
- Much of the Signature is actually derived from inherited zircons in metasediments - not outcropping geology!





Summary

- In-situ microanalysis: Essential for applications of RIM technology to mineral exploration
- Major (minor) elements: EPMA
 - offers best spatial resolution and accuracy
 - provides major element data required for LA-ICP-MS
- Trace (minor) elements: LA-ICP-MS
 - most rapid, cost-effective
- U-Pb dating
 - LA-ICP-MS quickest and cheapest
 - Ion microprobe provides best spatial resolution
- Isotopic analysis – LA-MC-ICP-MS
 - many new applications (Hf, Sr, Nd) for tracers
 - stable isotopes of metals - new and promising field
 - integration with chemical and dating adds an extra dimension

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Acknowledgements

- Geological Survey of Canada, particularly
 - Beth McClenaghan
 - Bill Davis
 - Monica Escayola
 - Rob Berman
- GEMOC, Macquarie University, especially:
 - Bill Griffin
 - Norman Pearson
 - Elena Belousova







Which Laser?

Shorter wavelength:

- ✓ *increased absorption*
- ✓ *reduced optical penetration*
- ✓ *more controlled ablation*
- ✓ *smaller particle size*
- ✓ *reduced matrix effects*
- ✓ *smaller spot size*
- x **greater cost and complexity**

213 nm is the current “industry standard”:

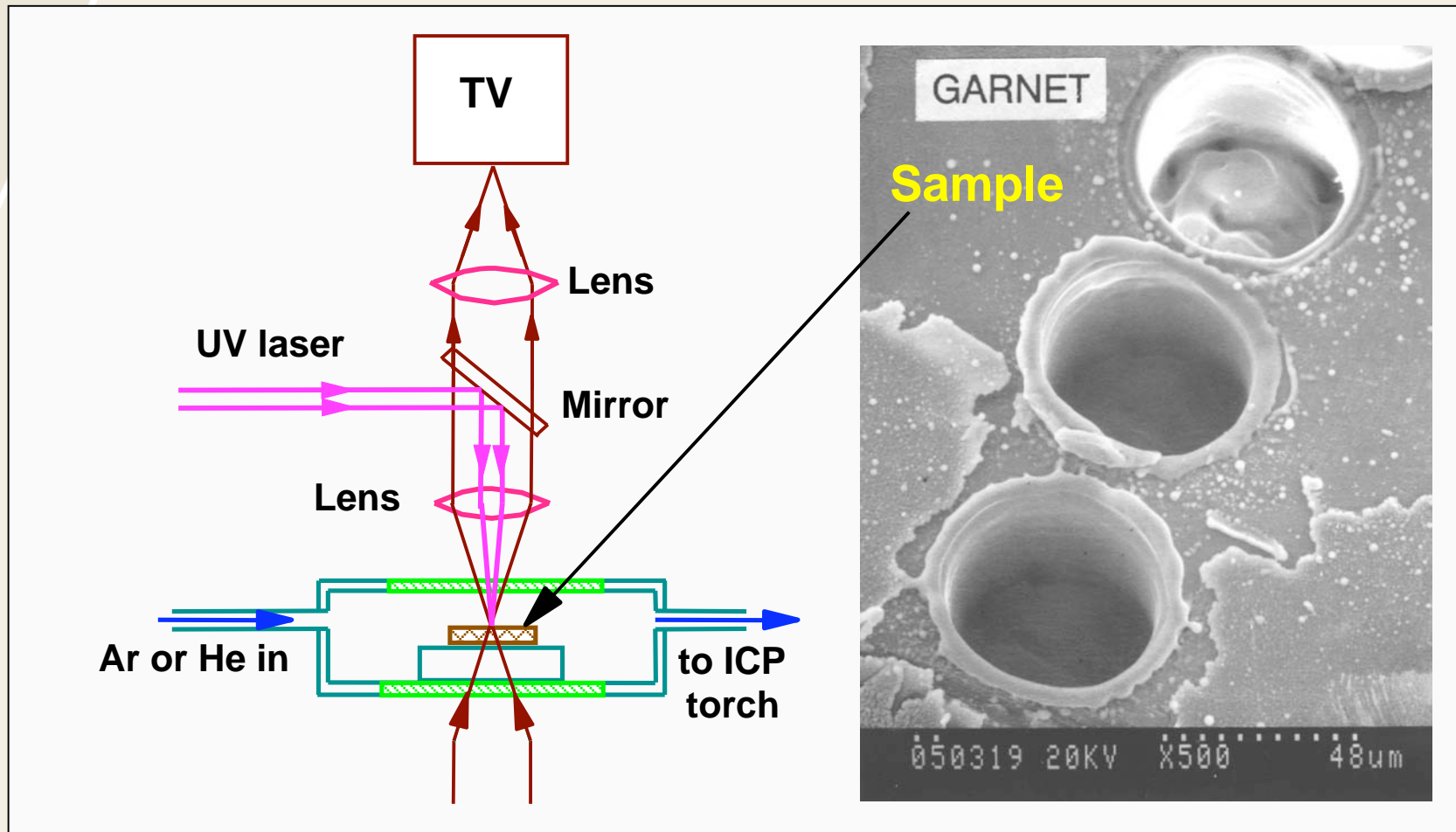
- solid state laser
- short wavelength
- short pulse width (metals)

193 nm required for the most demanding applications

- fluid inclusion analysis in quartz

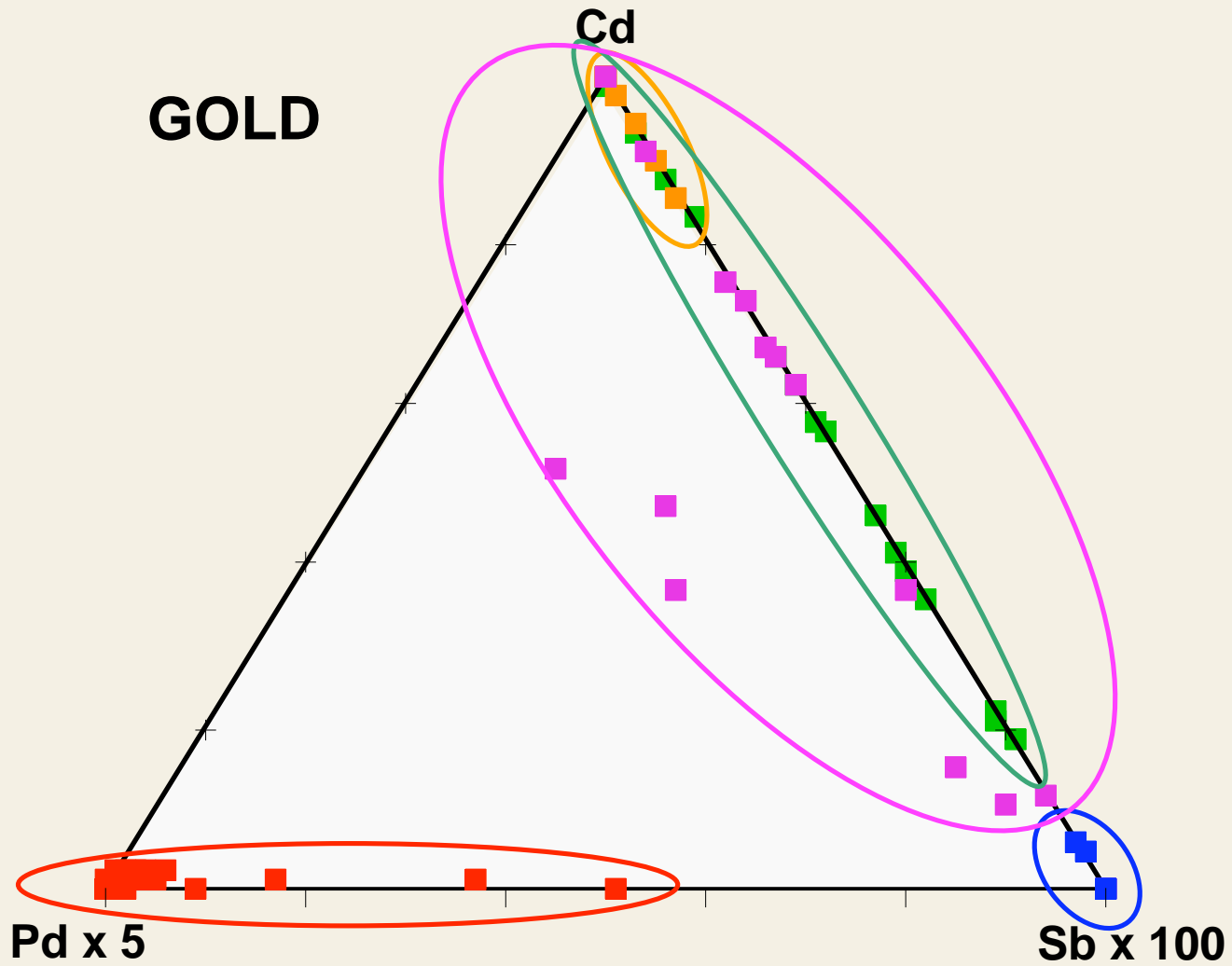
Source	Type	Wavelength
Nd:YAG	Fundamental	1064 nm (IR)
Nd:YAG	4th harmonic	266 nm (UV)
Nd:YAG	5th harmonic	213 nm (DUV)
Excimer	ArF	193 nm (DUV)
Nd:YAG	OPO	193 nm (DUV)







GOLD



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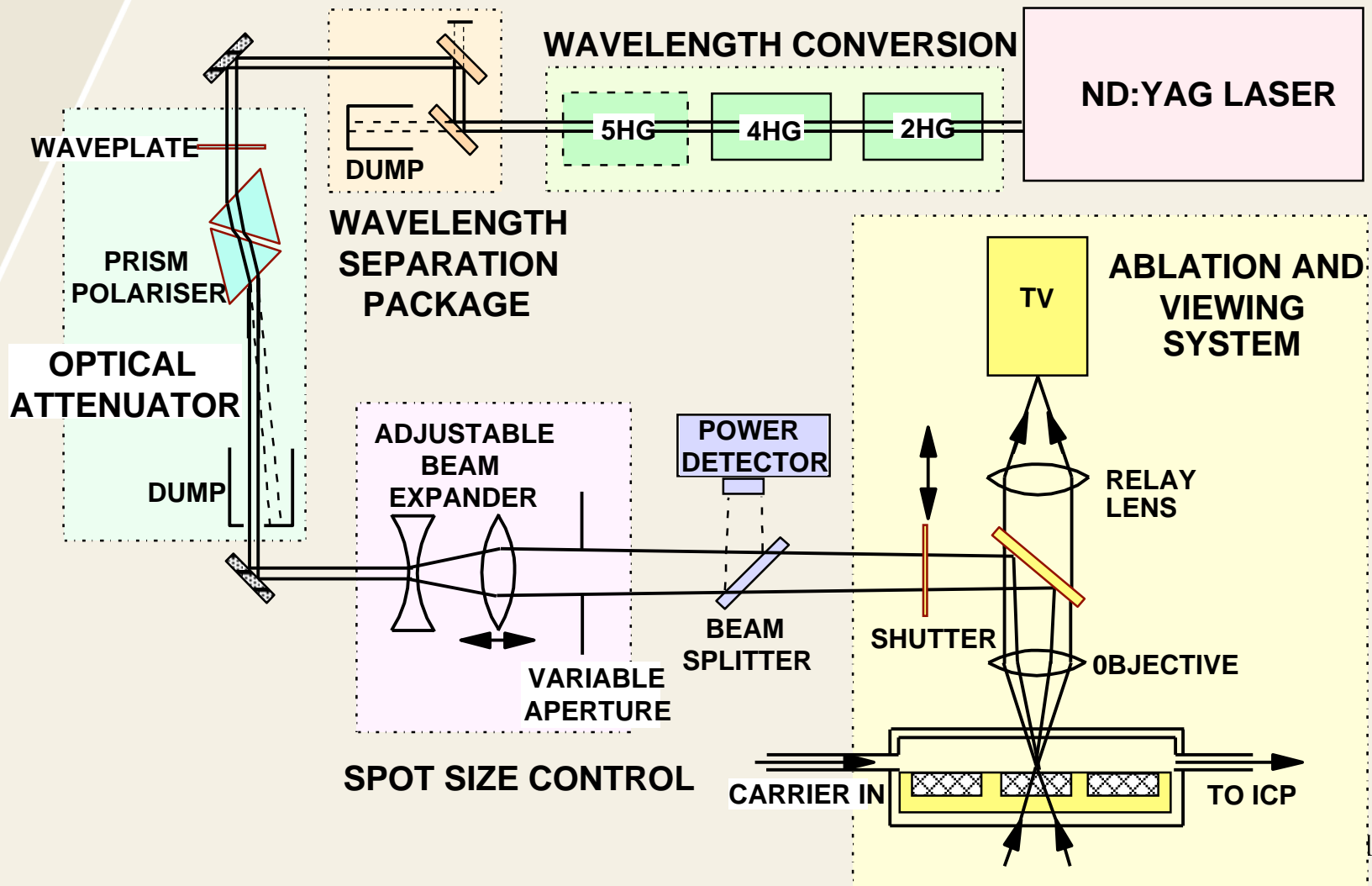
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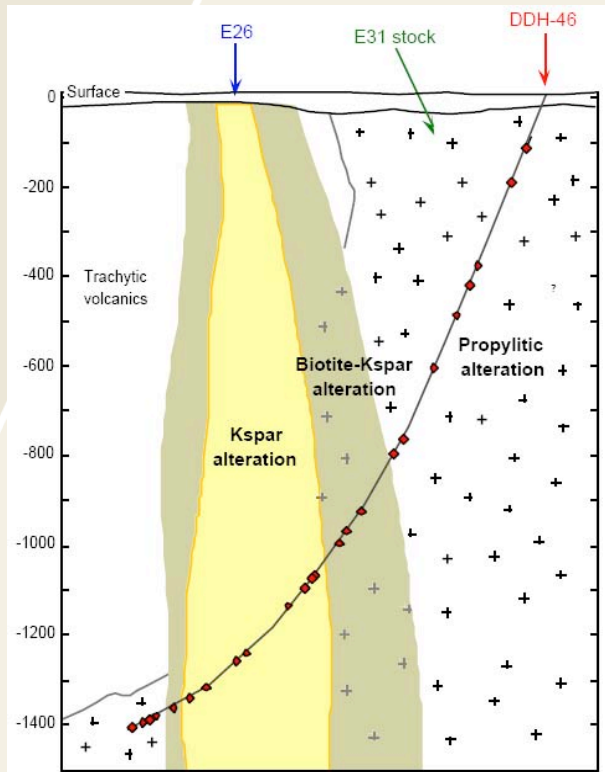
Schematic of a Nd:YAG LA System



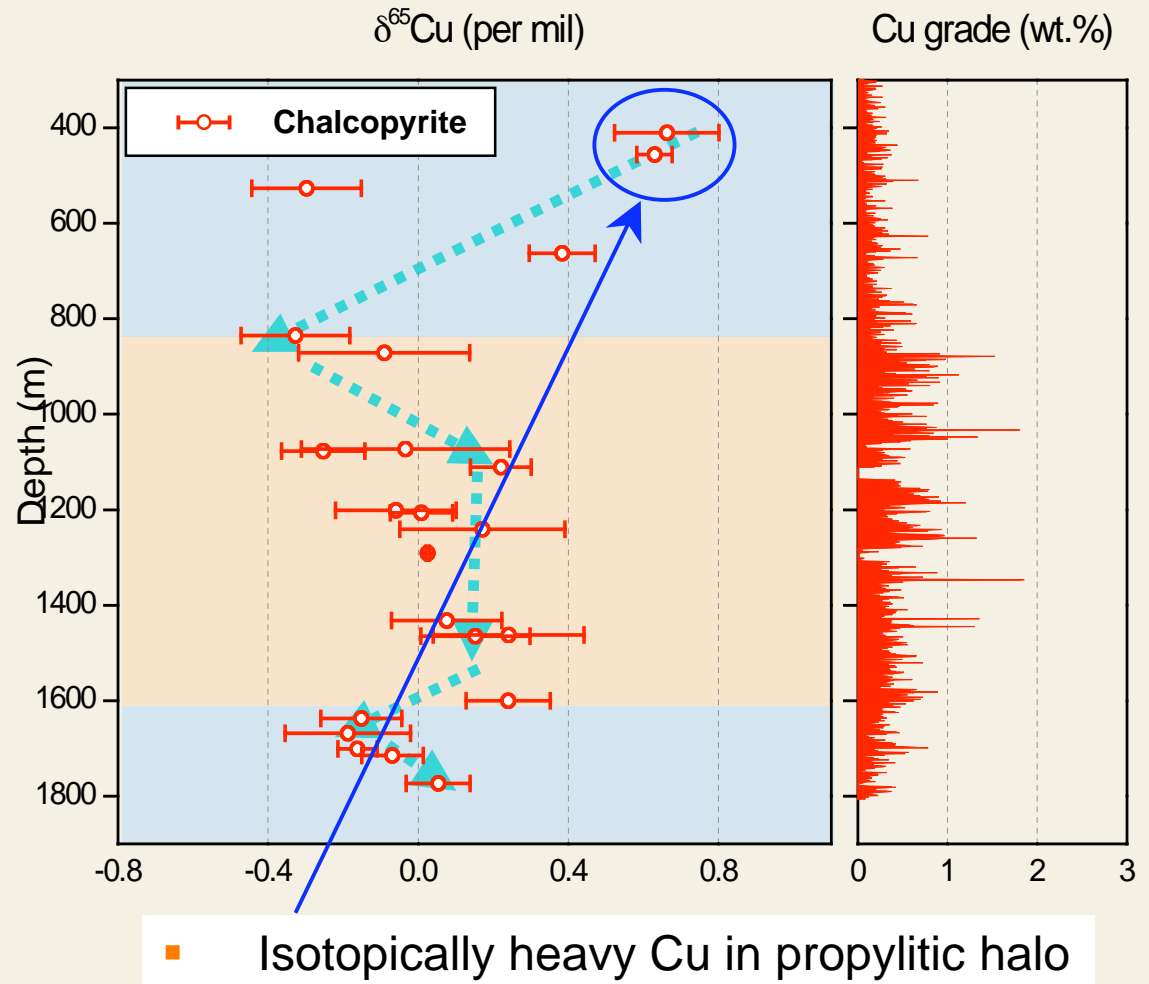


Northparkes Porphyry Cu-Au Deposit, N.S.W.

Cross section through E26 porphyry deposit



Cu grade (wt%)



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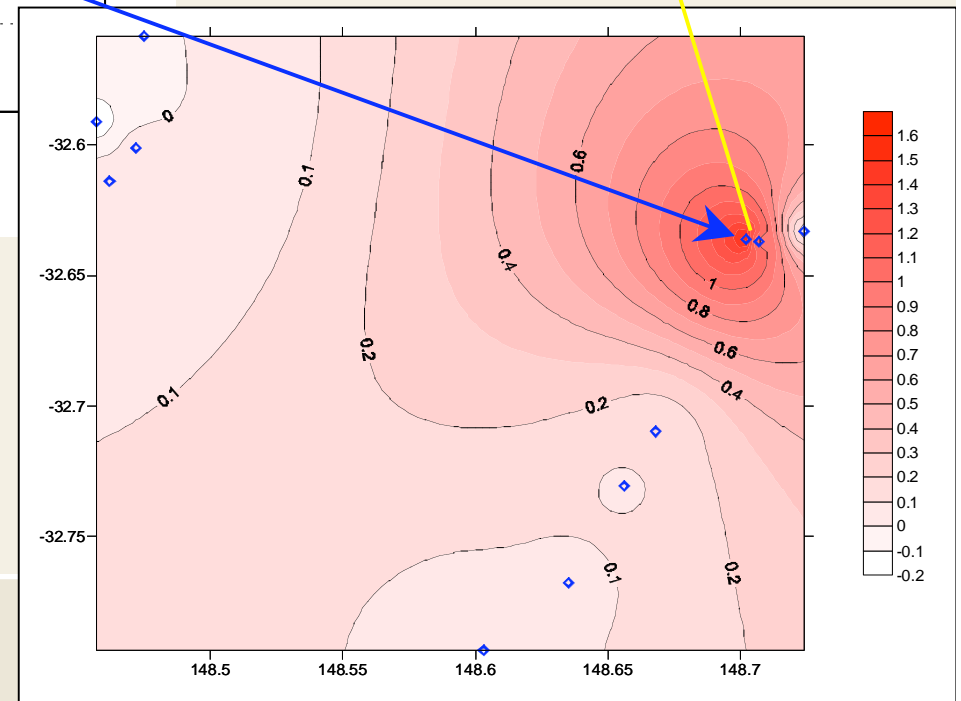
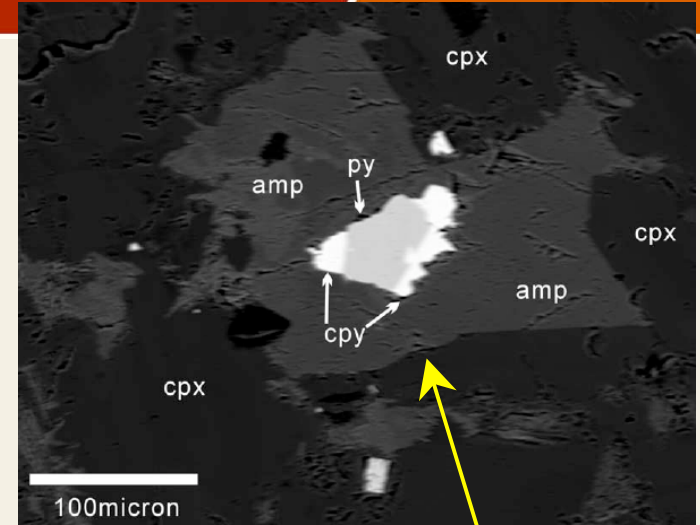
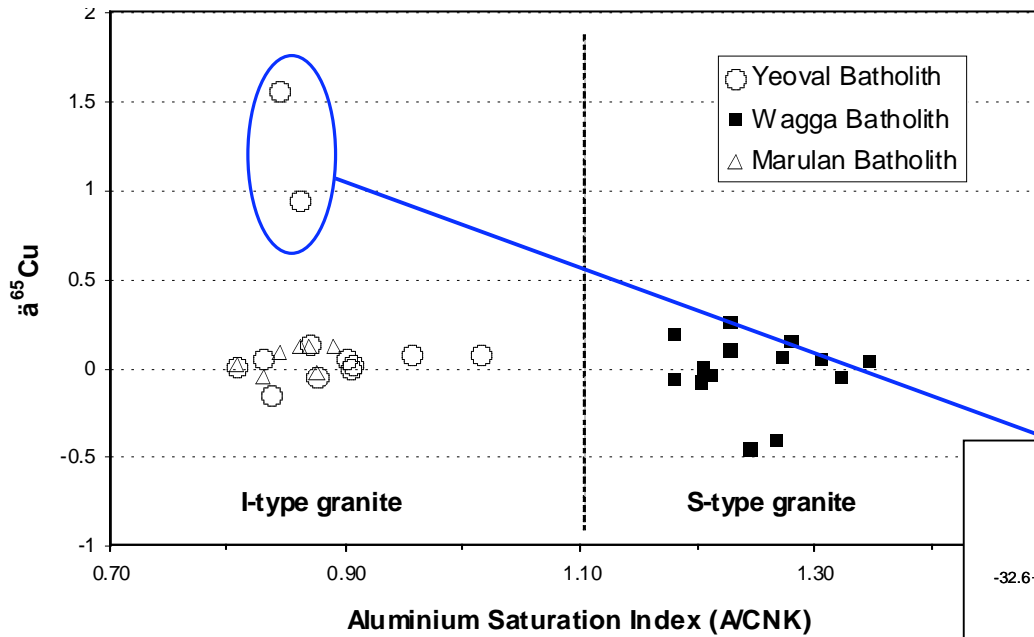
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Application Of Metal Isotopes In Mineral Exploration



Cu isotopes in SE Australian granites



- Local anomalous Cu isotope values identified in Yeoval granite
- Macroscopically “fresh” outcrops possess microveinlets containing chalcopyrite



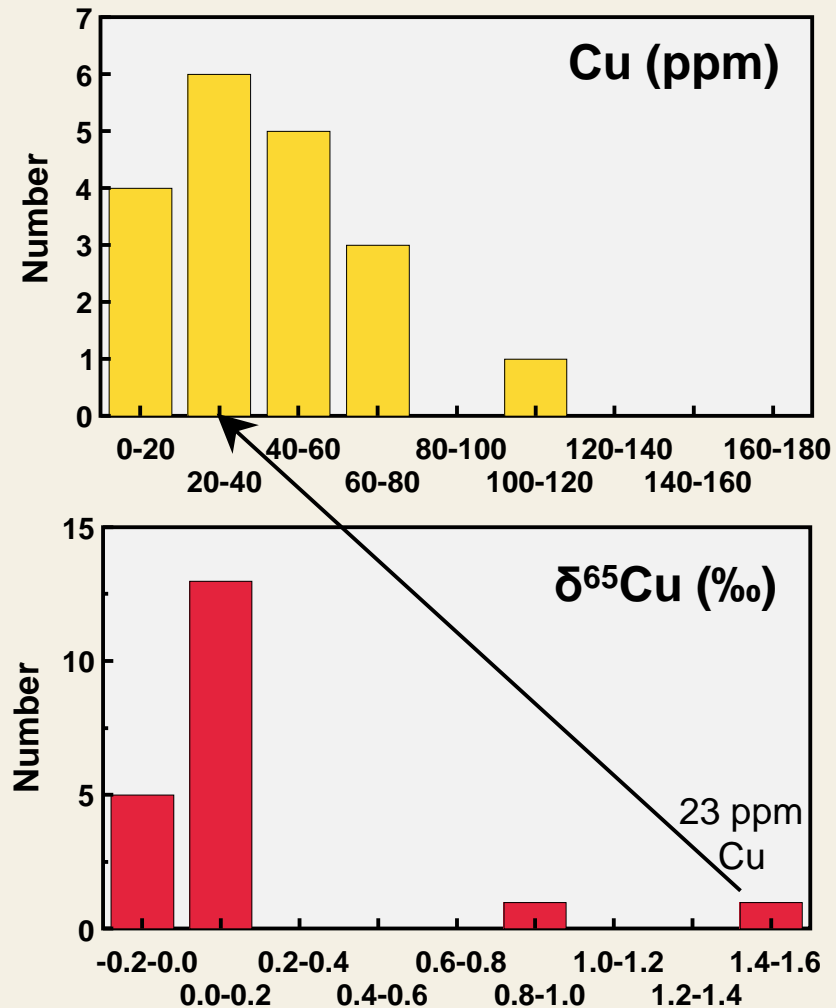
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Application Of Metal Isotopes In Mineral Exploration

- Cu isotopes are sensitive indicators of cryptic hydrothermal activity
- e.g., distal portions of hydrothermal Cu deposits, margins of porphyry systems
- can be more sensitive than element geochemistry

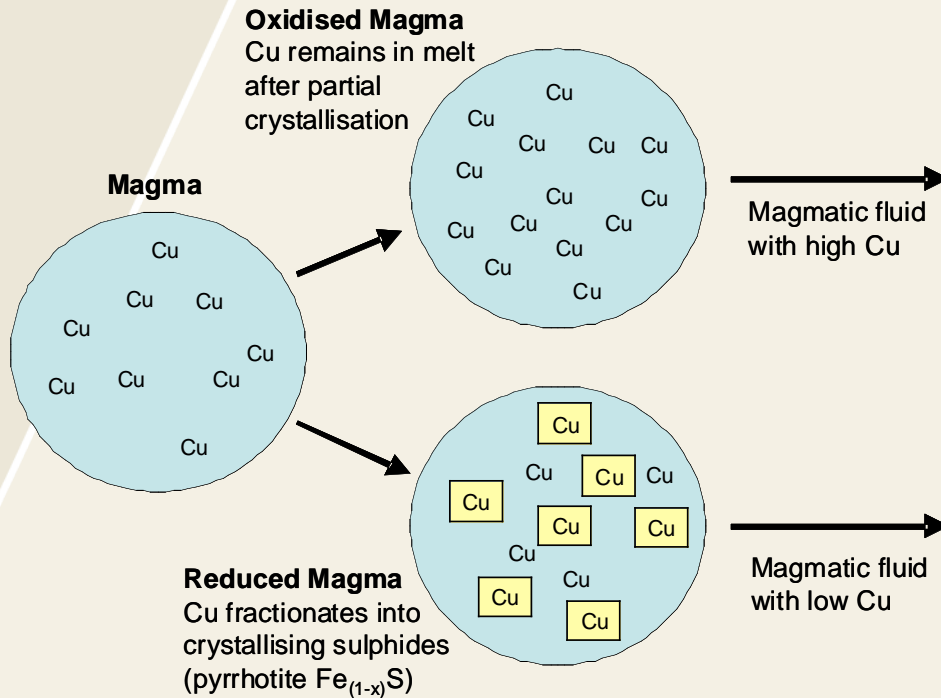
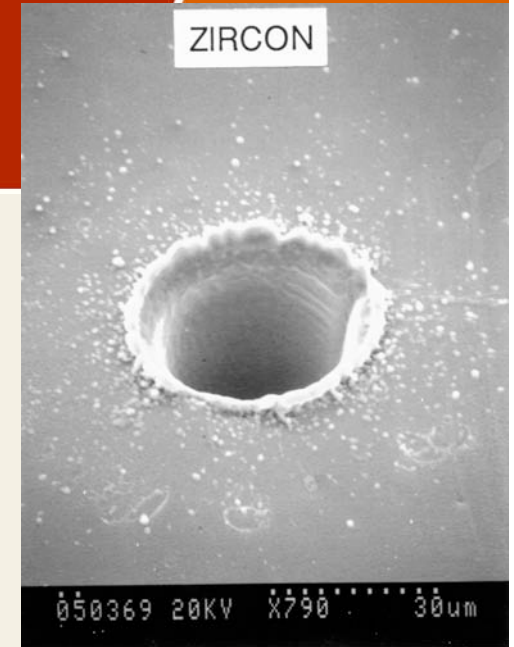


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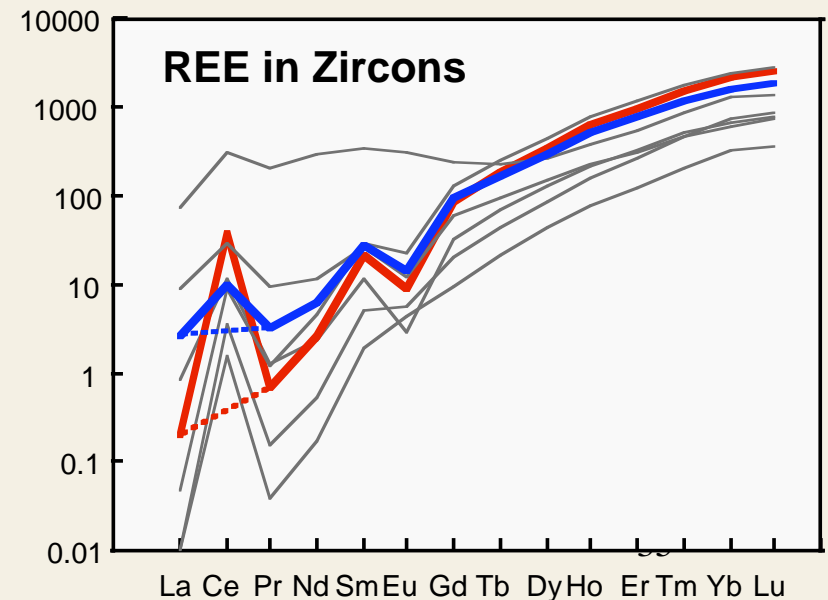


Zircon REE as a Proxy for Magma Oxidation State



Laser Ablation pit in Zircon

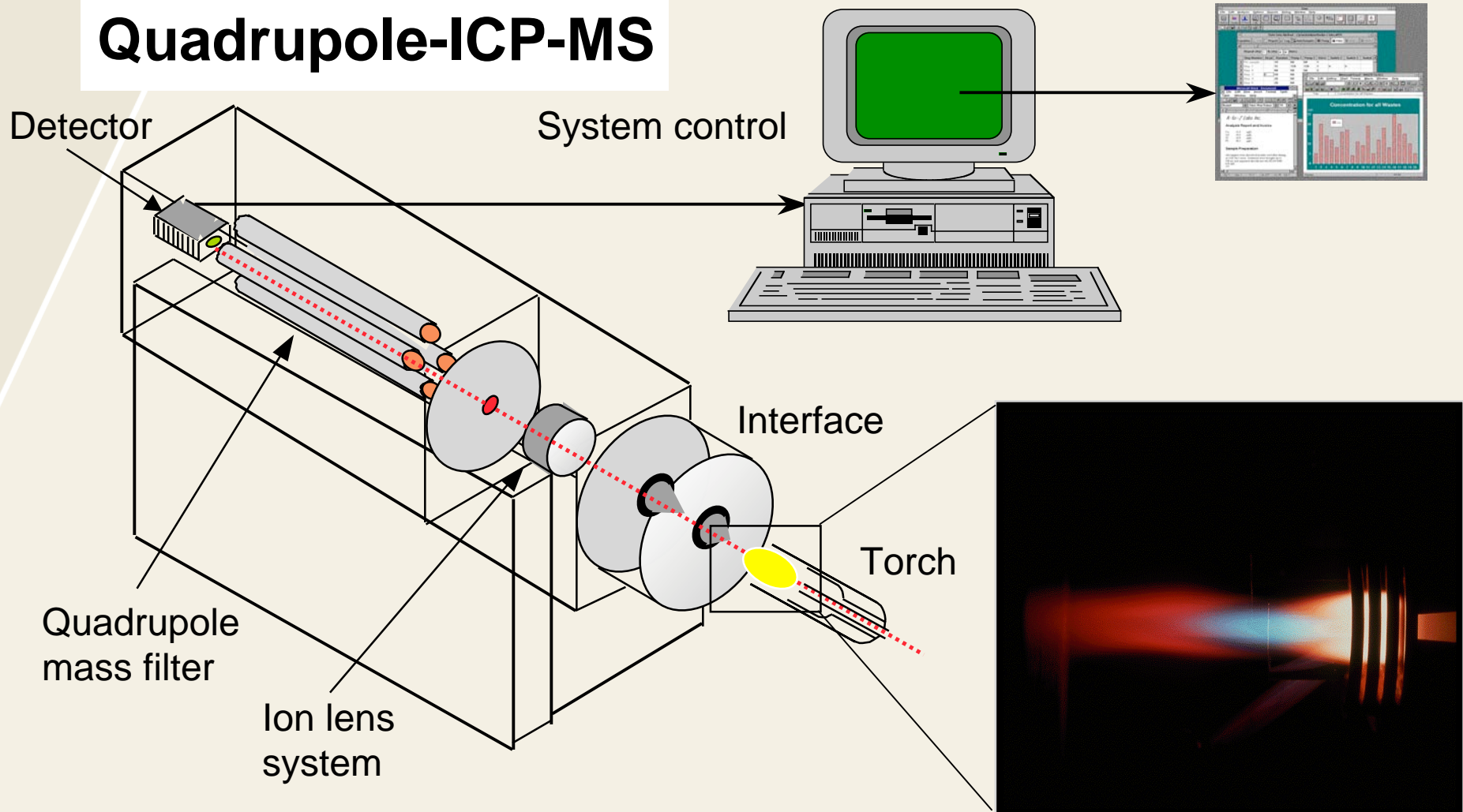
- zircon REE systematics (esp. Ce^*/Ce) are a sensitive proxy for magma oxidation state, and, therefore,
- prospectivity of intrusive rocks for associated mineralization





Fundamentals of Sequential ICP-MS

Quadrupole-ICP-MS



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