Mineral Chemistry: Modern Techniques and Applications to Exploration

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Background, Outline

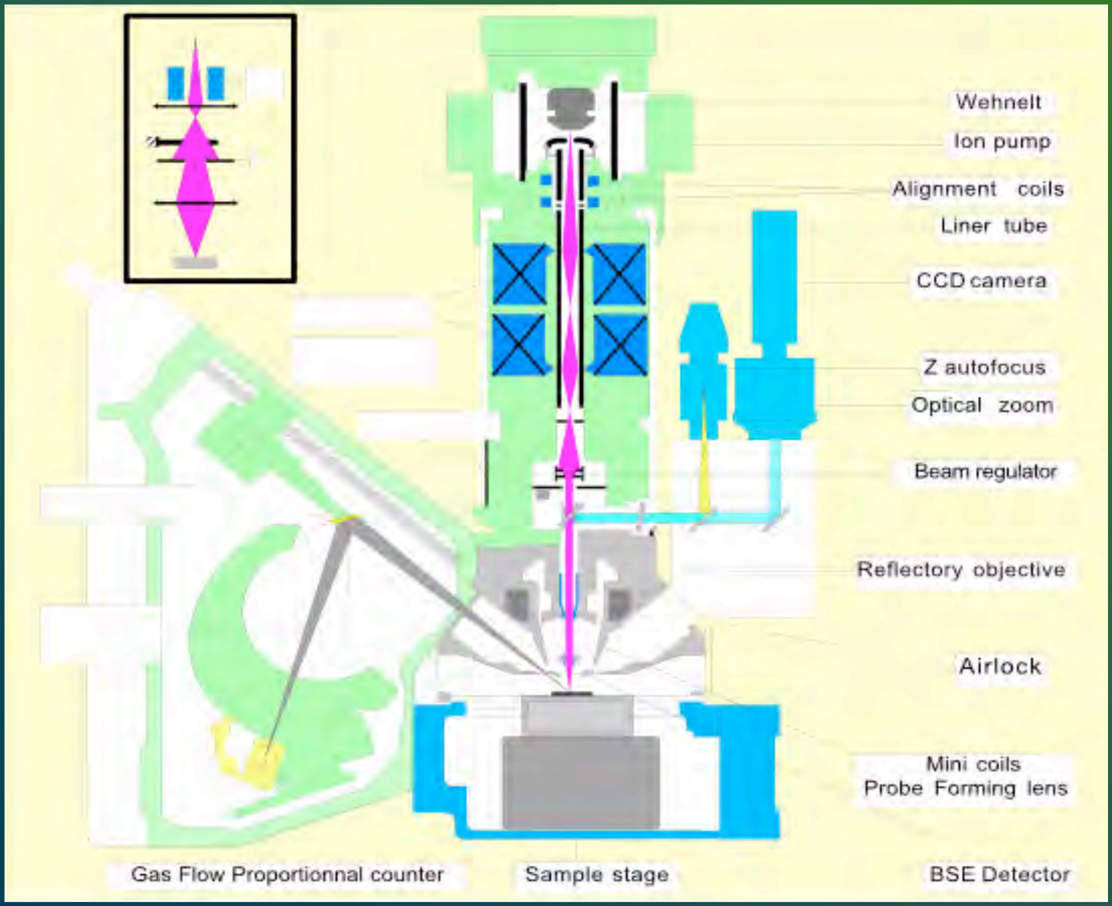
Mineral Chemistry and Mineral Exploration

- **Must use *in situ* analytical techniques**
- **Wide range of techniques: widely variable cost, value/$$**
- **Focus on most widely used, cost-efficient technologies**
- **Examples of applications -- rest is up to your imagination**

This talk:

- **Major elements: EMP**
- **Trace elements: LAM-ICPMS, Proton microprobe**
- **Isotopic analysis (low precision): LAM-ICPMS vs ion probe (U-Pb)**
- **Isotopic analysis (high precision): LAM-MC-ICPMS**

In situ Major Element Analysis: Electron Microprobe



- Mature techology (from 1960s)
- Electron beam; X-ray generation
- Spot sizes 1µm
- EDS vs WDS spectrometers
- Major elements (%); minor elements (200-500 ppm)
- Imaging - BSE, CL
- Mapping (major elements)

In situ Major Element Analysis: Electron Probe

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WDS: ***wave-length dispersive*** **analysis (crystal spectrometers)**

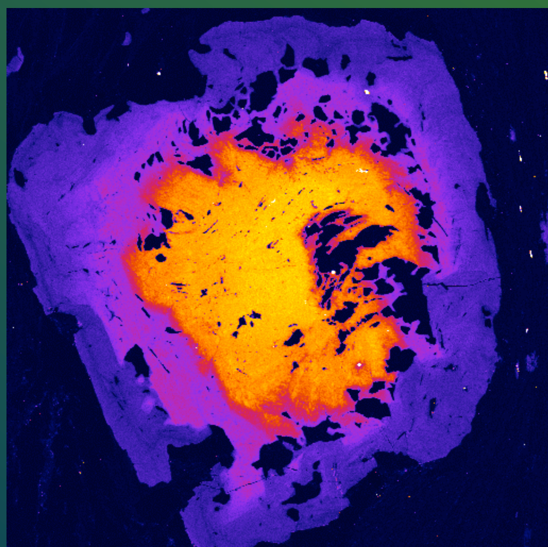
- **precise analysis -- detection limits 200-500 ppm**
- **one element at a time, on each spectrometer**
- **higher resolution, higher intensity with larger crystals ($$)**
- **Data quality depends on counts (time)**
- **element mapping of areas to 50 x 80 mm (≤5 elements)**

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

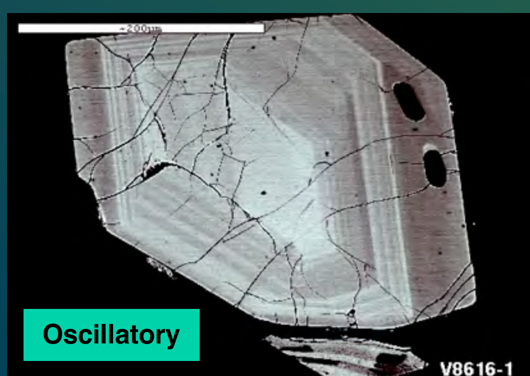
- **energy spectrum: *rapid* phase identification (saves time)**
- **analysis of *major* elements (use as extra spectrometer)**
- **rapid mapping of 9-32 elements, areas 1.5 x 1.5 mm**

Recommendation: **Need both EDS and WDS, integrated**

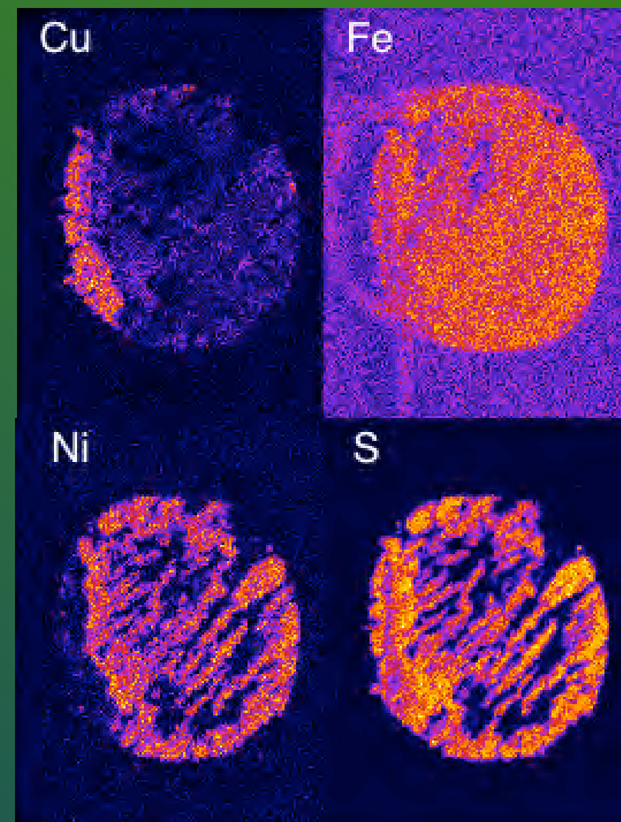
Major Element Imaging: Electron Probe



Ca map of garnet: WDS scan 5 x 5 mm

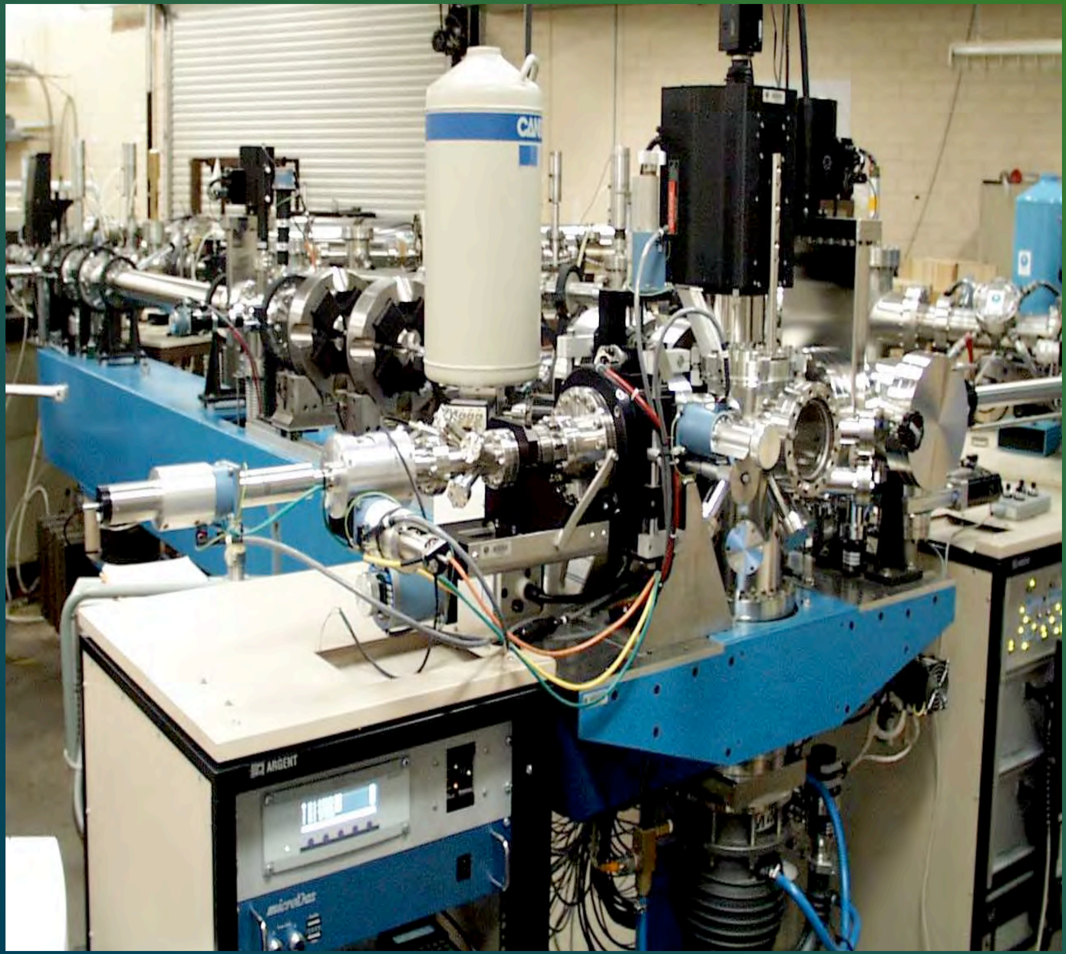


BSE image of zoned zircon



EDS maps of mantle sulfide, 100μm

In situ Trace-Element Analysis: Proton Microprobe (PMP)

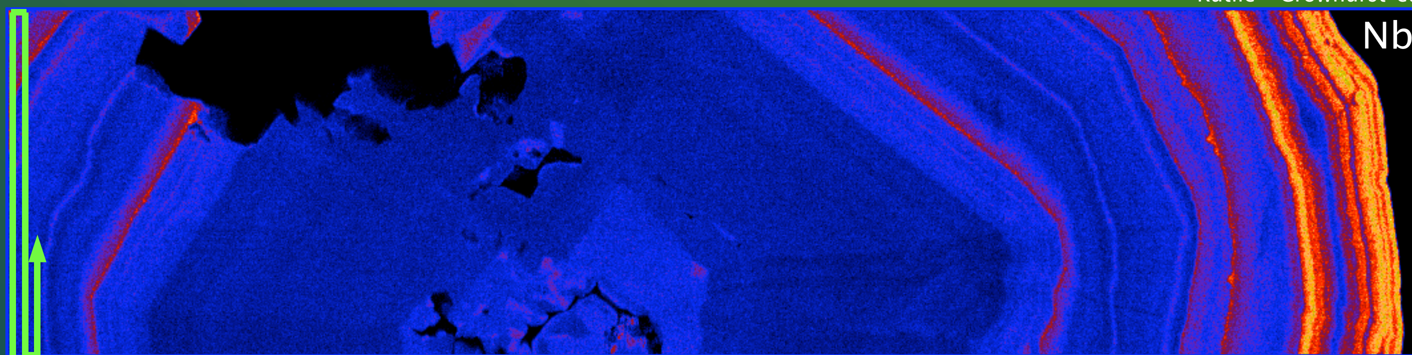


- Beam line on 3MeV accelerator; electromagnetic focussing
- PIXE (X-rays) + PIGE (gamma rays, light elements)
- Non-destructive, standardless EDS analysis (ppm) of minerals, fluid inclusions
- Imaging (element maps); analysis in each pixel

Proton Microprobe: Imaging

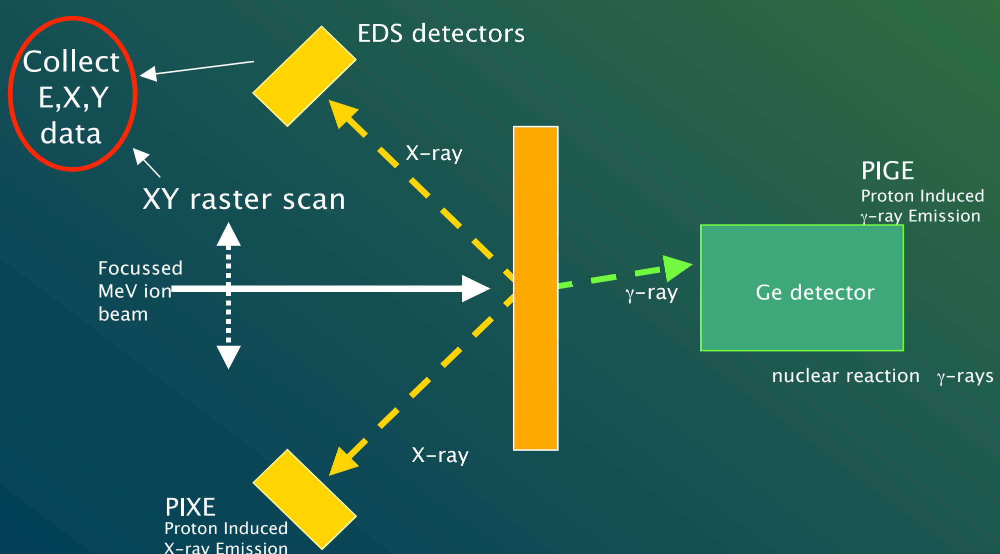
PIXE and PIGE Elemental Imaging

Rutile - Crowhurst et al.

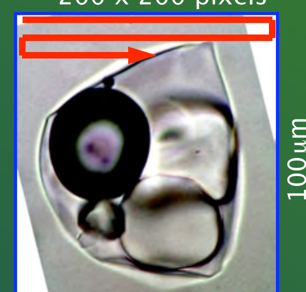


4000 x 1000 pixels

Mode 1: Beam scanning in Y, stage stepping in X

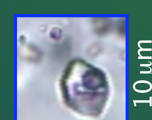


200 x 200 pixels



2: Beam raster in X and Y

(~2 interlaced frames per second)



Proton Microprobe: Basics

MeV Ion Beam Interactions

- Predictable, smooth slowing down behaviour
  - small energy uncertainty.
- Negligible beam deflection and scattering
  - travel in straight lines.
- Non-destructive.
- Insensitive to chemical state.

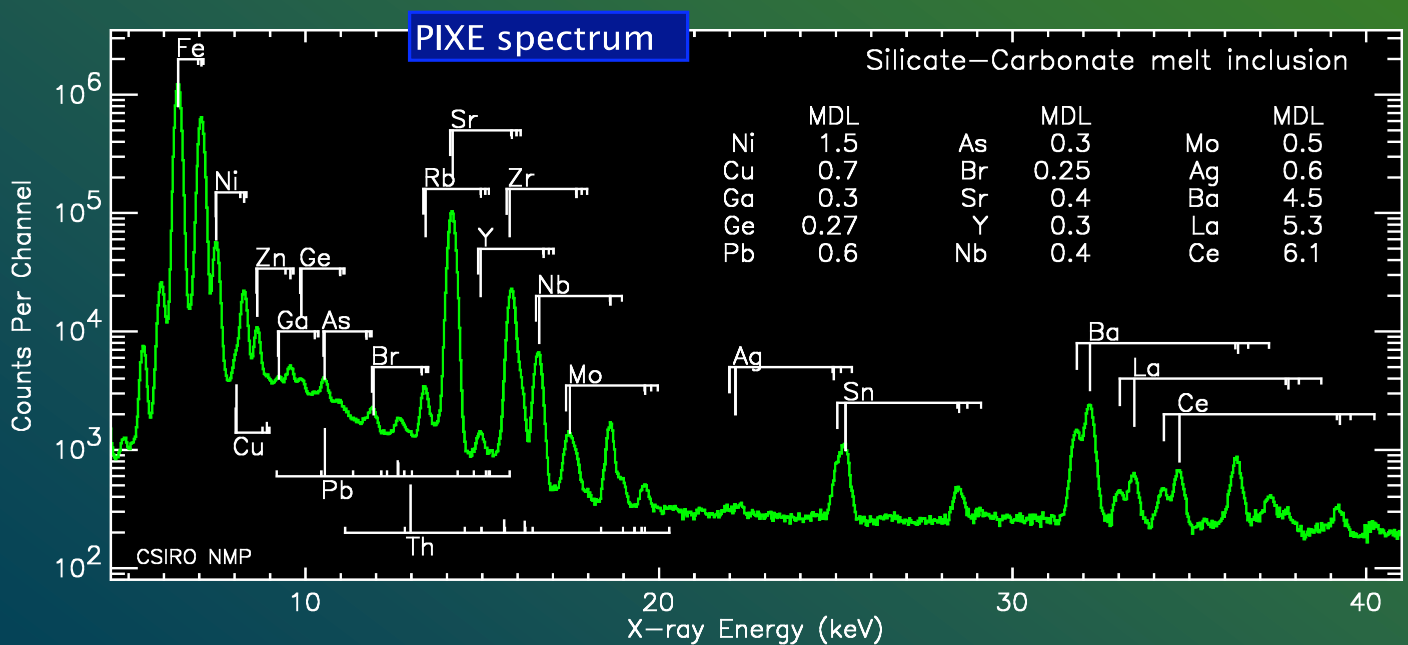
Methods:

PIXE – Proton Induced X-ray Emission ::

- Ionization of inner shell atomic electrons.
- Low continuum background.

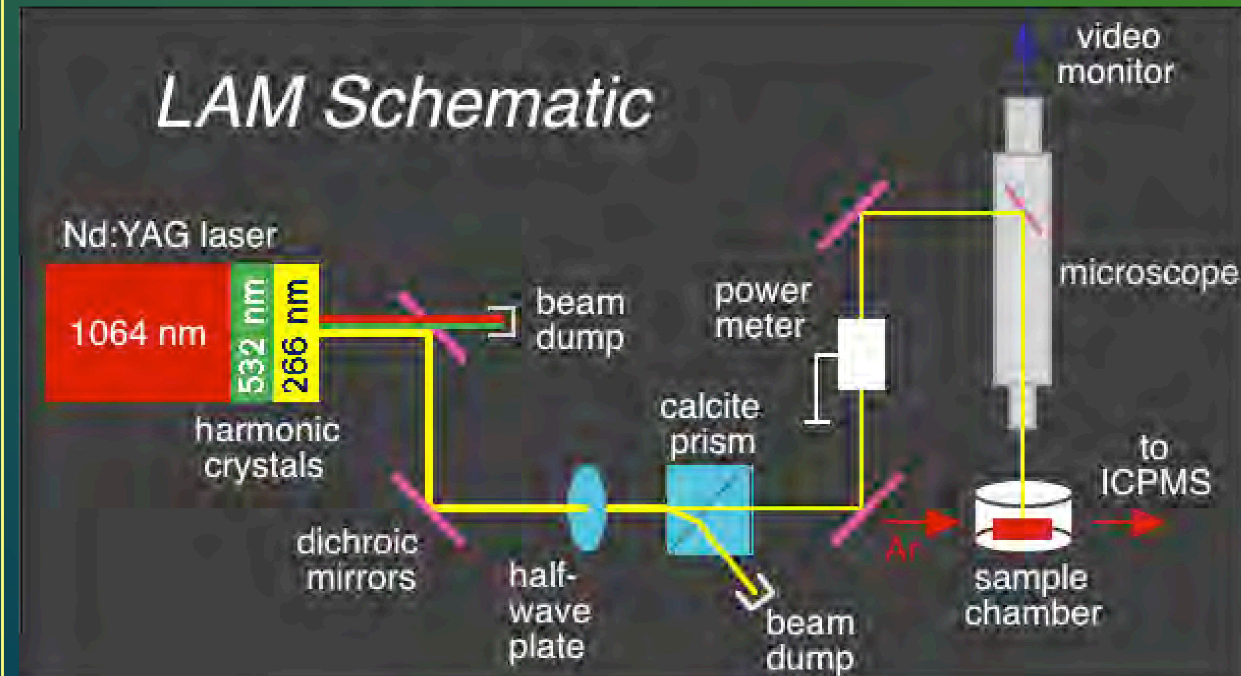
PIGE – Proton Induced γ-ray Emission :

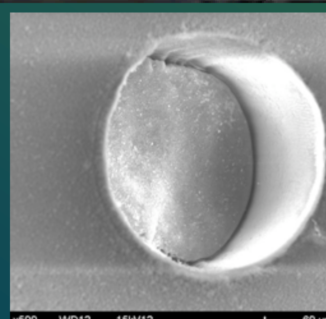
- Nuclear reactions on light nuclei, (e.g. Li, Be, B, F, Na, …).

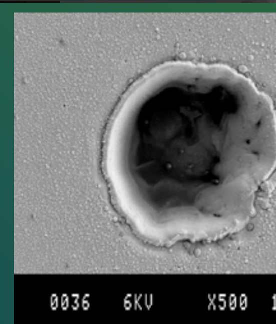


	MDL		MDL		MDL
Ni	1.5	As	0.3	Mo	0.5
Cu	0.7	Br	0.25	Ag	0.6
Ga	0.3	Sr	0.4	Ba	4.5
Ge	0.27	Y	0.3	La	5.3
Pb	0.6	Nb	0.4	Ce	6.1

In situ Trace-Element Analysis: LAM-ICPMS

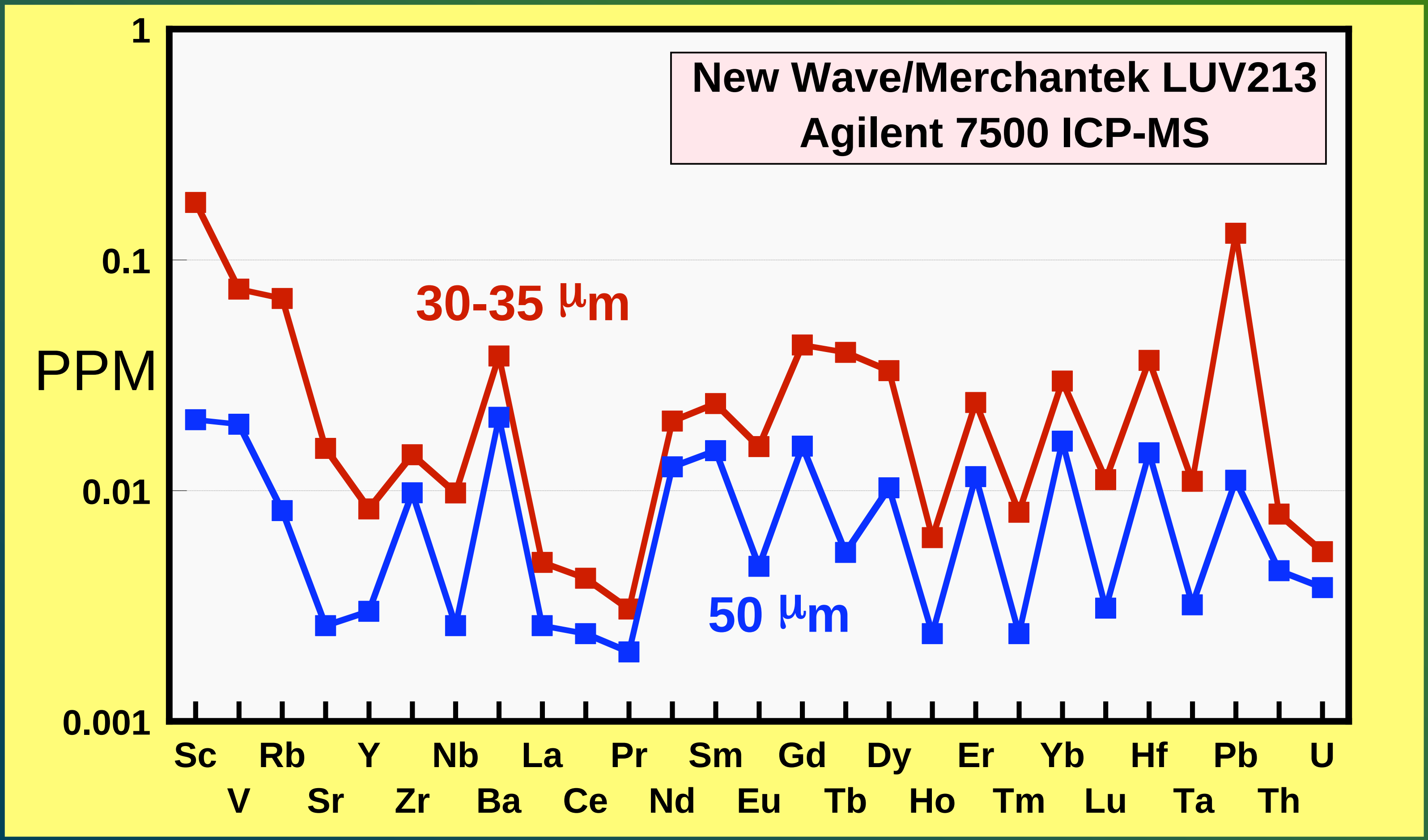






- Laser Microprobe + ICPMS
- Spatial resolution 20-80 μm
- Typically 30-40 elements/spot
- ppb detection limits
- Minerals, fluids, fluid inclusions

LAM-ICPMS: Detection Limits



Which ICPMS ?

Quadrupole ICPMS :

- Rapid scanning of whole mass spectrum
- High sensitivity
- Relatively low cost ($US 150,000)
- Reaction/collision-cell ICPMS ($US 180,000)
    - elimination of some overlaps

High-Resolution (double focussing) ICPMS:

- Higher sensitivity (2x) (in principle, rarely in practice)
- Resolves overlaps (eg ArO on Fe) for special applications
- Scans *portions* of spectrum rapidly, whole spectrum slowly
- High cost ($US 320,000)

Quadrupole ICPMS more versatile, economic

LAM-ICPMS: Laser Hardware

Options: Laser microprobe (commercially available)

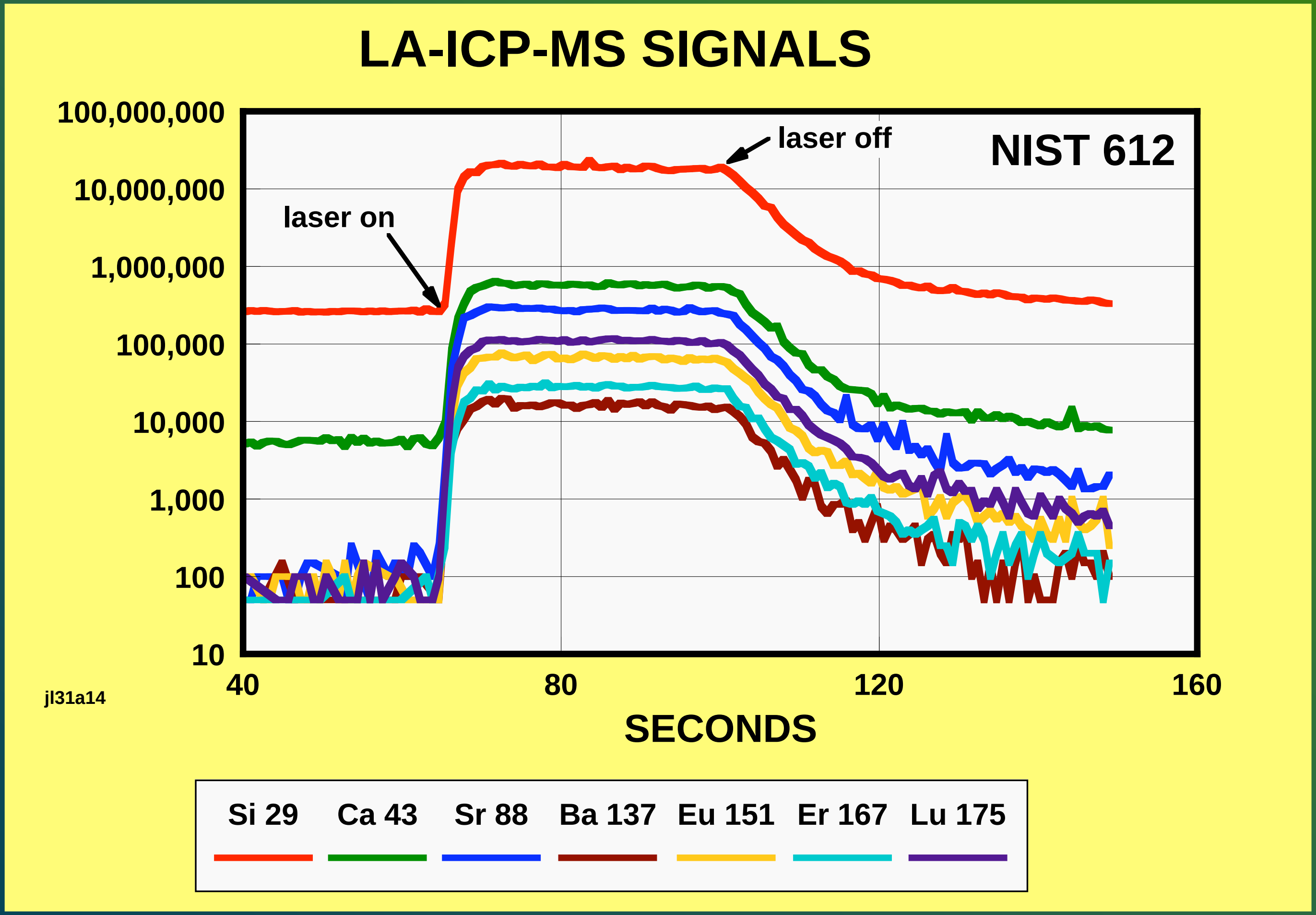
Nd:YAG (solid state) -- most widespread.

- **Intrinsic 1064 nm wavelength, reduced by harmonic-generator xls**
- **---> 266 or 213 nm; 213nm better absorbed, more controlled**
- **robust, low operating costs, “low” cost ($US 120K)**
- **193 nm solid-state now available -- no comparative data**

Excimer (ArF) - 193 nm; better ablation control, high power
high initial cost ($US 150-600K), higher operating costs

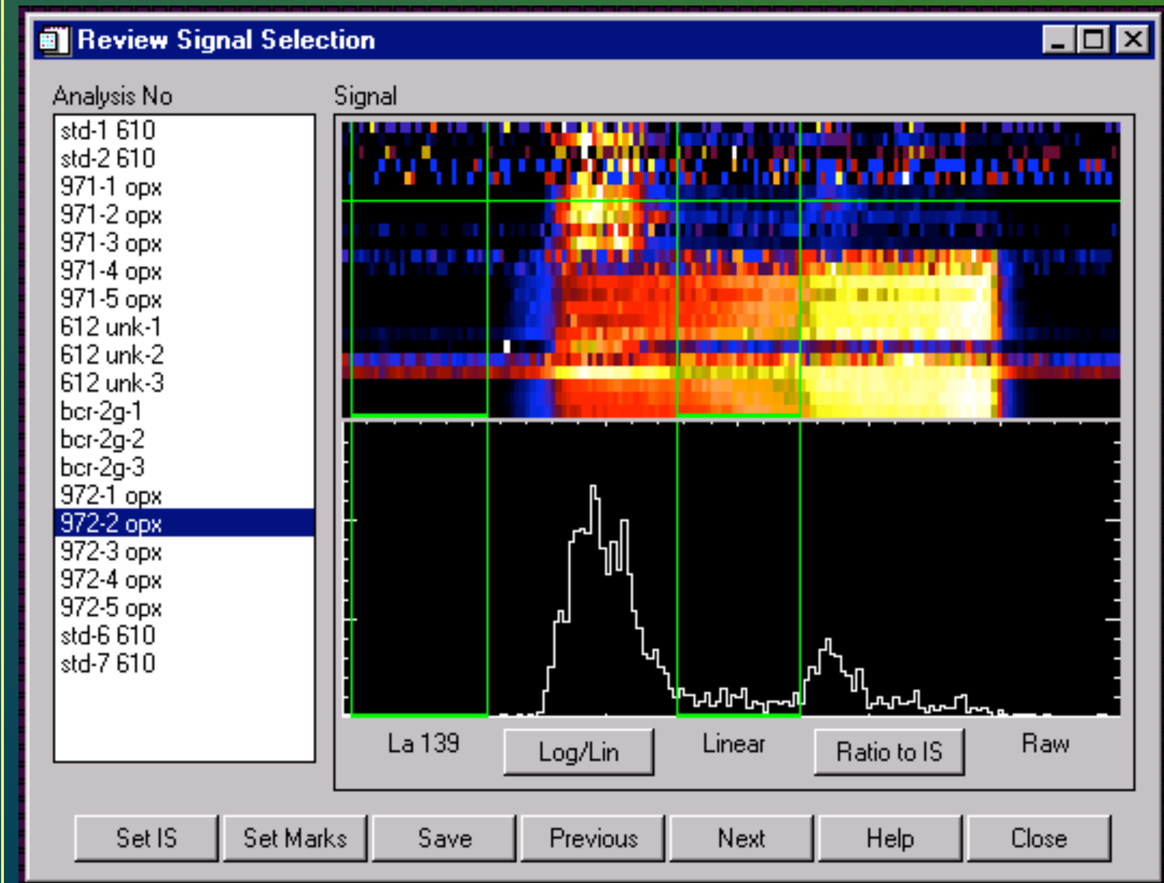
GEMOC: 213 nm as workhorse, 266 for sulfides, opaques, *diamond*

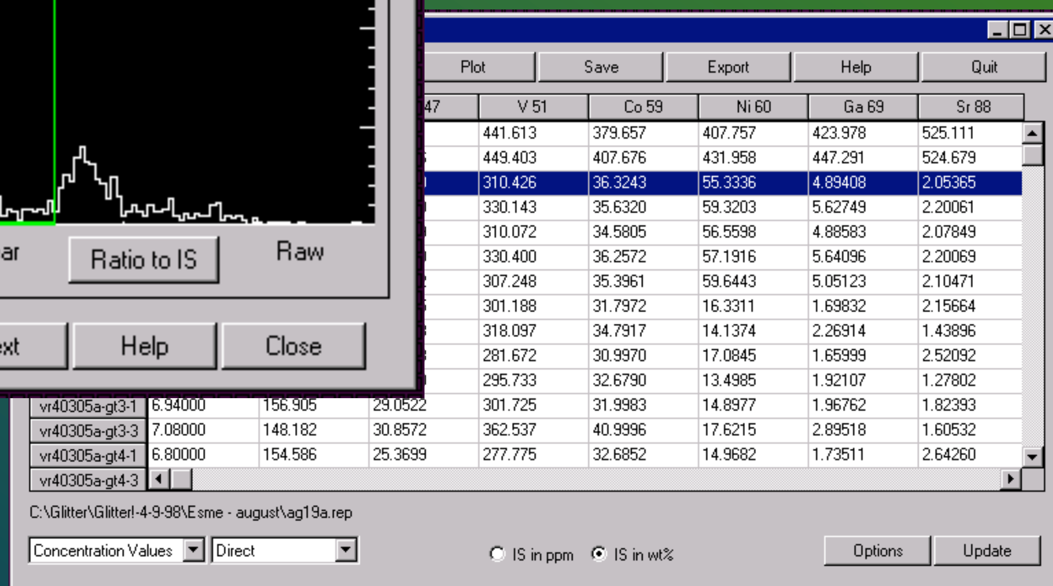
LAM-ICPMS Analysis: Time-resolved Signals



In situ Trace-Element Analysis: GLITTER software

G E M O C





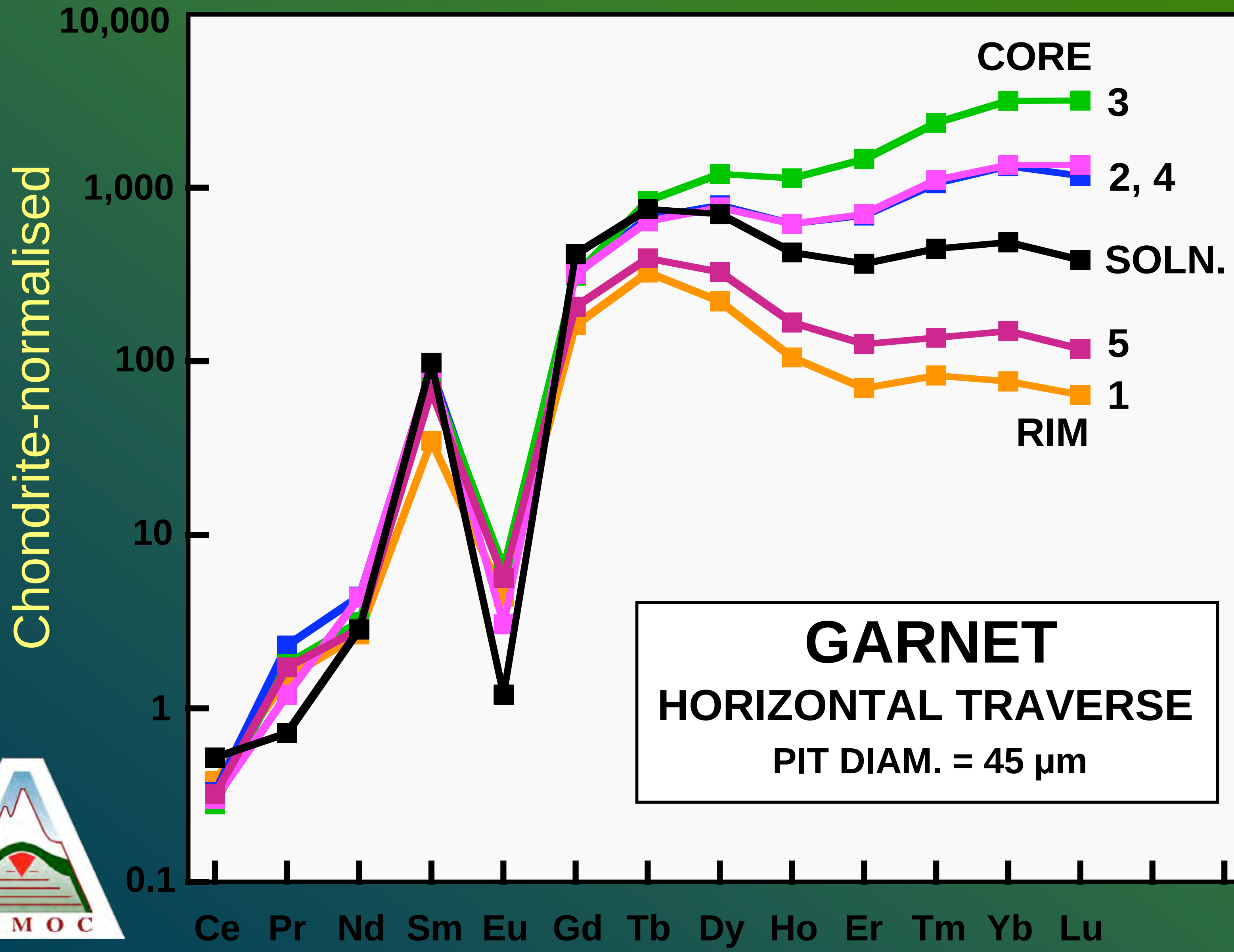
Time-resolved analysis essential; select integration intervals

On-line data reduction; linked review window, plots, results table

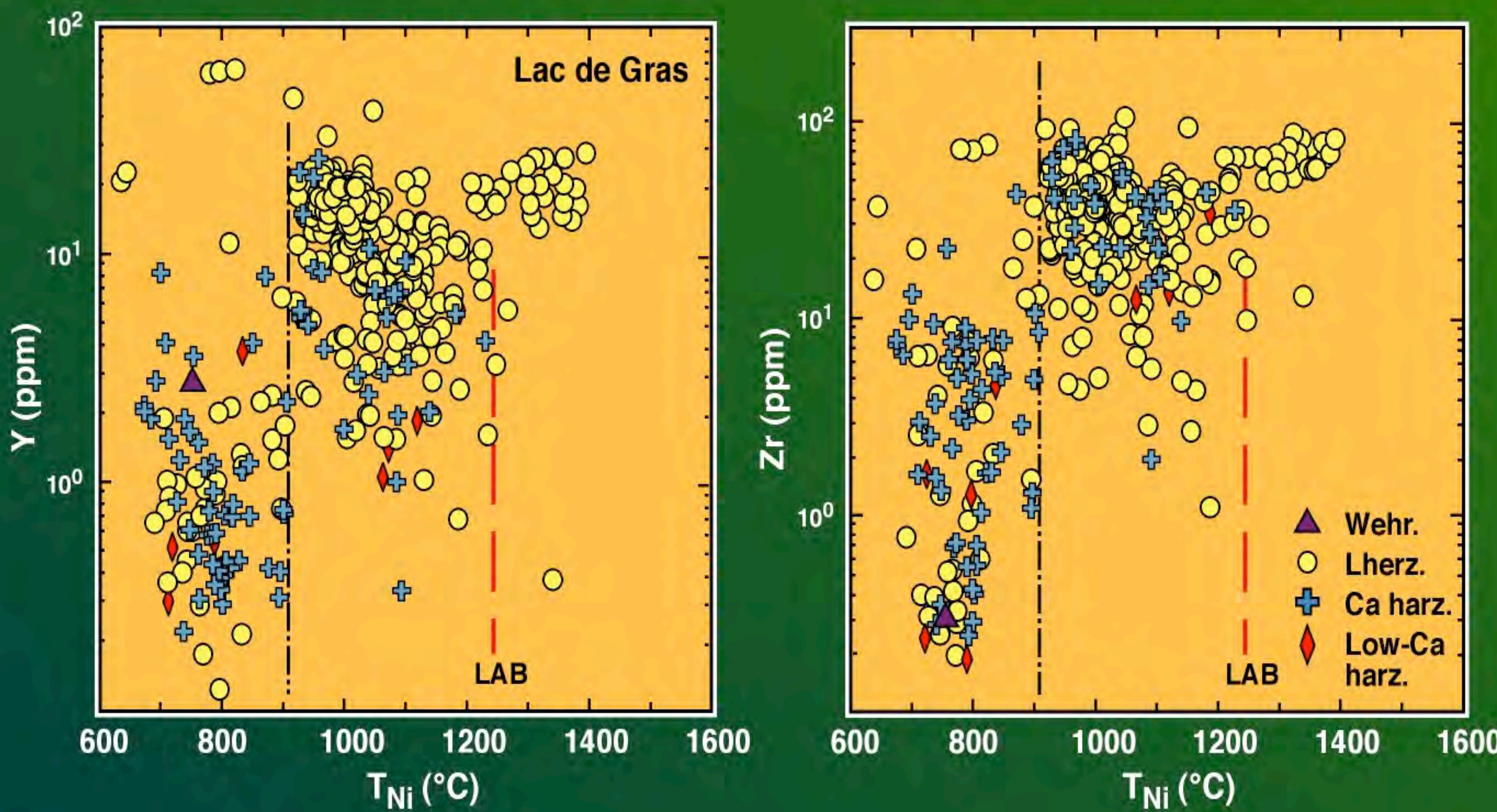
In situ Trace-Element Analysis: LAM-ICPMS

Major applications -- GEMOC

- Silicates, oxides in mantle xenoliths (mantle petrology)
- Diamond indicator minerals (mantle petrology, exploration)
- Diamonds, other gemstones (genetic studies, forensics)
- Sulfides; PGEs, other traces (ore deposit studies, mantle)
- Zircons (dating, crustal evolution)
- Feldspars, apatite, titanite etc (granite petrology; indicators)
- Fluid inclusions (ore deposit studies)
- Fish bones, teeth, etc (environmental studies)
- Synthetic materials (physics applications)

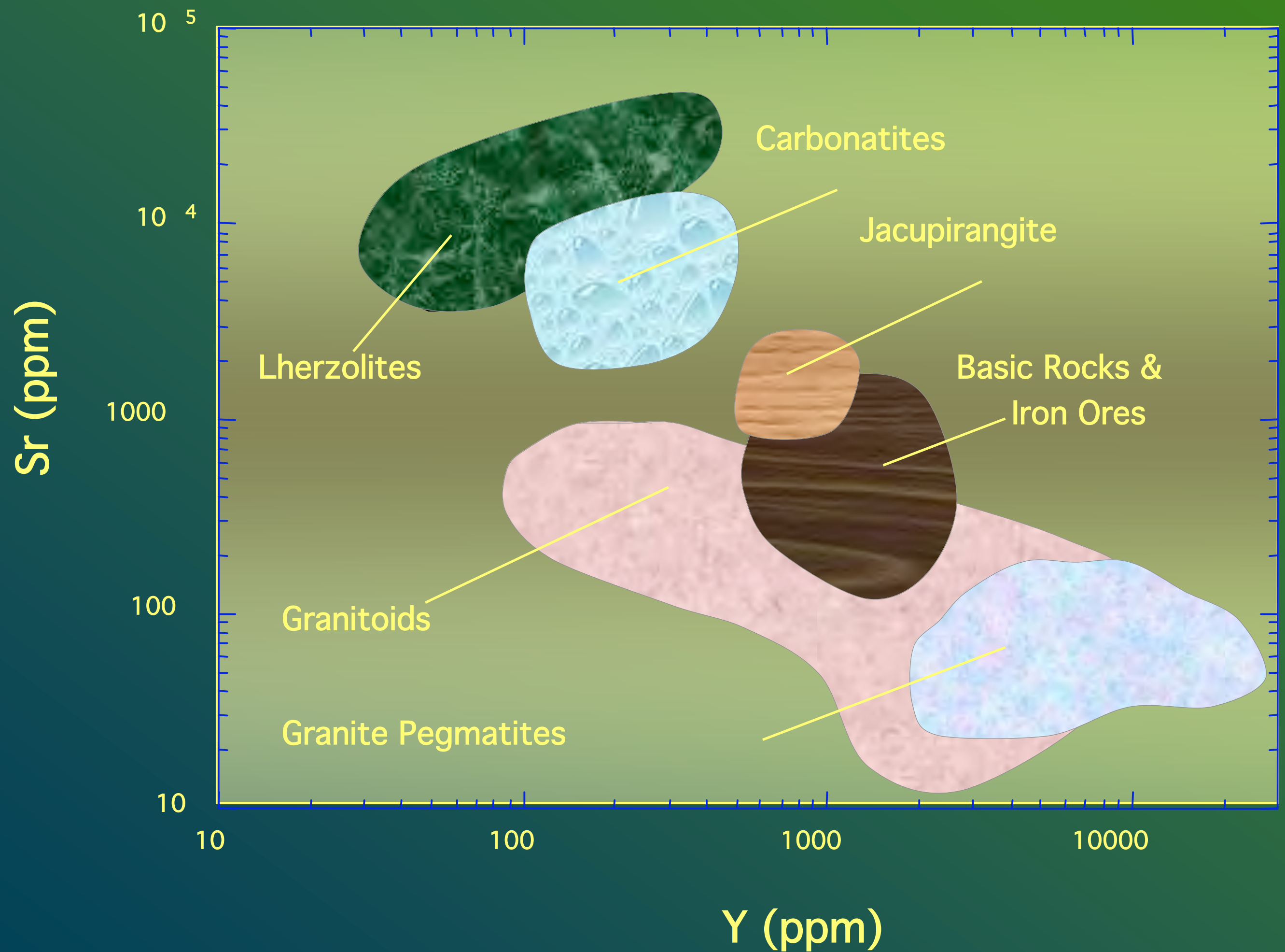

Chondrite-normalised
10,000
1,000
100
10
1
0.1
CORE
3
2, 4
SOLN.
5
1
RIM
GARNET
HORIZONTAL TRAVERSE
PIT DIAM. = 45 µm
Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Lac de Gras: Layered Lithospheric Mantle



Slave-Kaapv. Workshop 2001

Apatite Trace Elements: Recognition of Host Rock Type



In situ Trace Element Analysis: Comparisons

Proton Microprobe

- Rapid, non-destructive, good MDLs but limited # elements
- *Imaging capability*
- High capital cost, not widely available

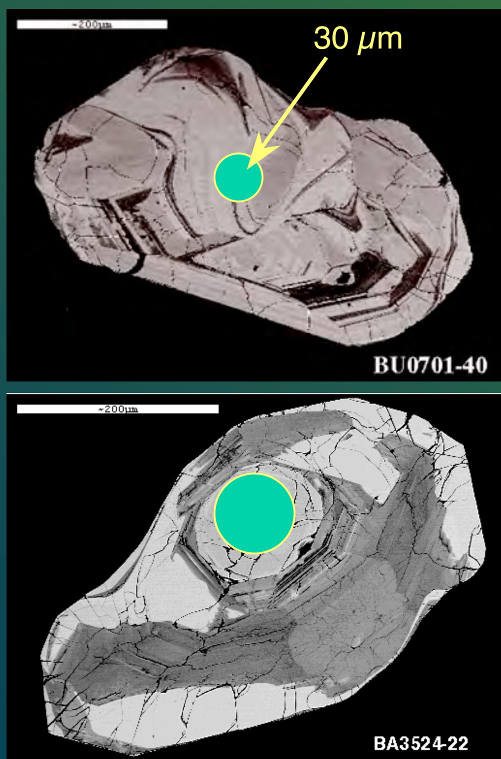
Ion Probe

- Lower MDLs; matrix-sensitive (standardisation); few elements
- Data quality depends on counts -- very slow (expensive)
- Better spatial (depth) resolution -- few microns

LAM-ICPMS

- Rapid, insensitive to matrix, very low MDLs, largest # elements
- Low capital costs, widely available, relatively low cost/analysis
- Depth resolution less than ion probe, ≈ PMP

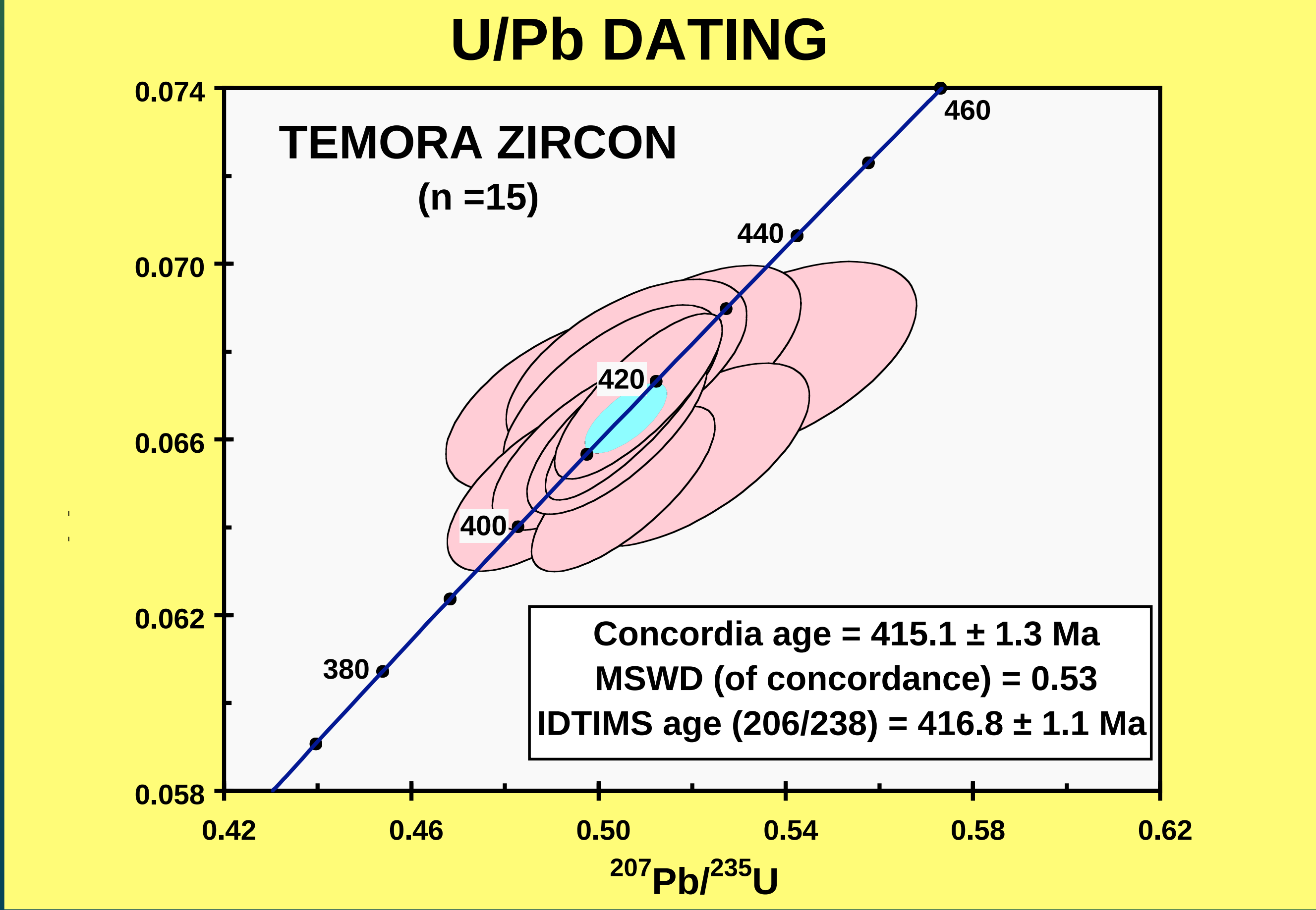
In-situ Dating: U-Pb in Zircon, Monazite



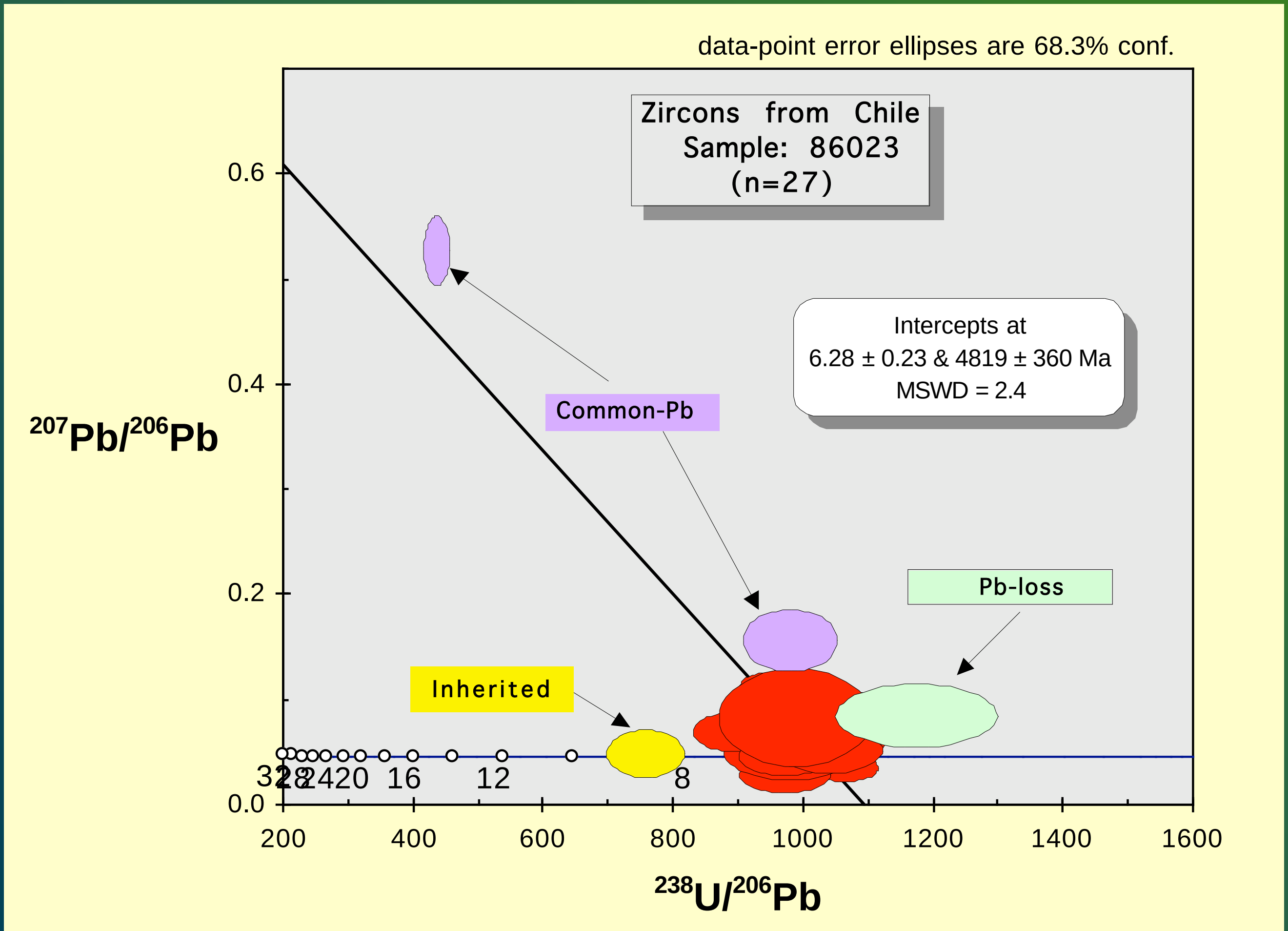
BSE/CL images of zircons

- TIMS single-grain analysis: most precise
  --but zircons heterogeneous, multistage
  --need 20-50 μm resolution
- Pb contents low, but ±1% precision very useful
- Ion microprobe (SHRIMP, CAMECA) good but slow & expensive (cost/analysis)
- LAM-ICPMS: similar precision, faster, cheaper
  - ablation volume larger (10-50 μm deep)
- GEMOC: Q- ICPMS + Nd:YAG laser (213 nm); GLITTER on-line data reduction
- 40-50 analyses/day, 5 - 6000 analyses/year

LAM-ICPMS U-Pb Dating:
Temora Zircon Standard



LAM-ICPMS Dating: U-Pb in Zircon



Chilean Porphyry

Inverse-concordia plot

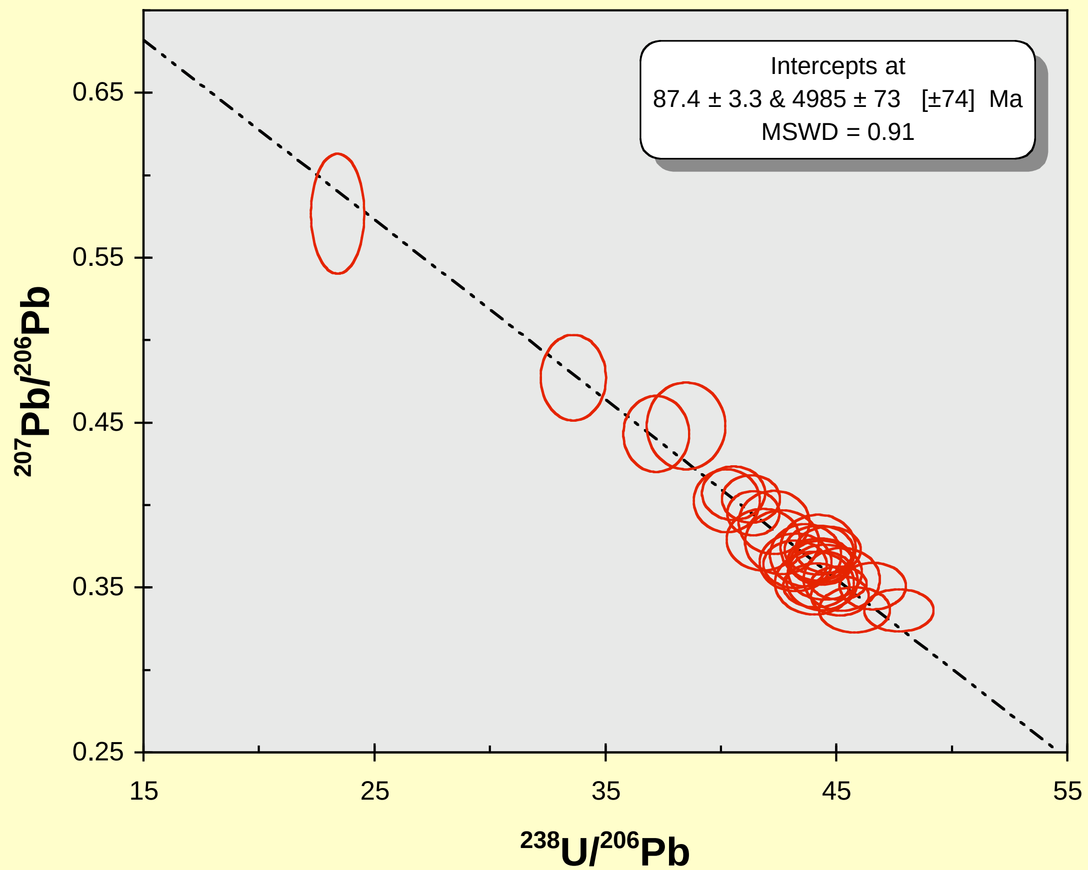
6.28±0.23 Ma

Equivalent to SHRIMP data in quality

Much faster, cheaper

Youngest yet dated = 1.2 Ma

Kimberlite Dating: U-Pb on Groundmass Perovskite



DeBeers Mine, Kimberley, RSA

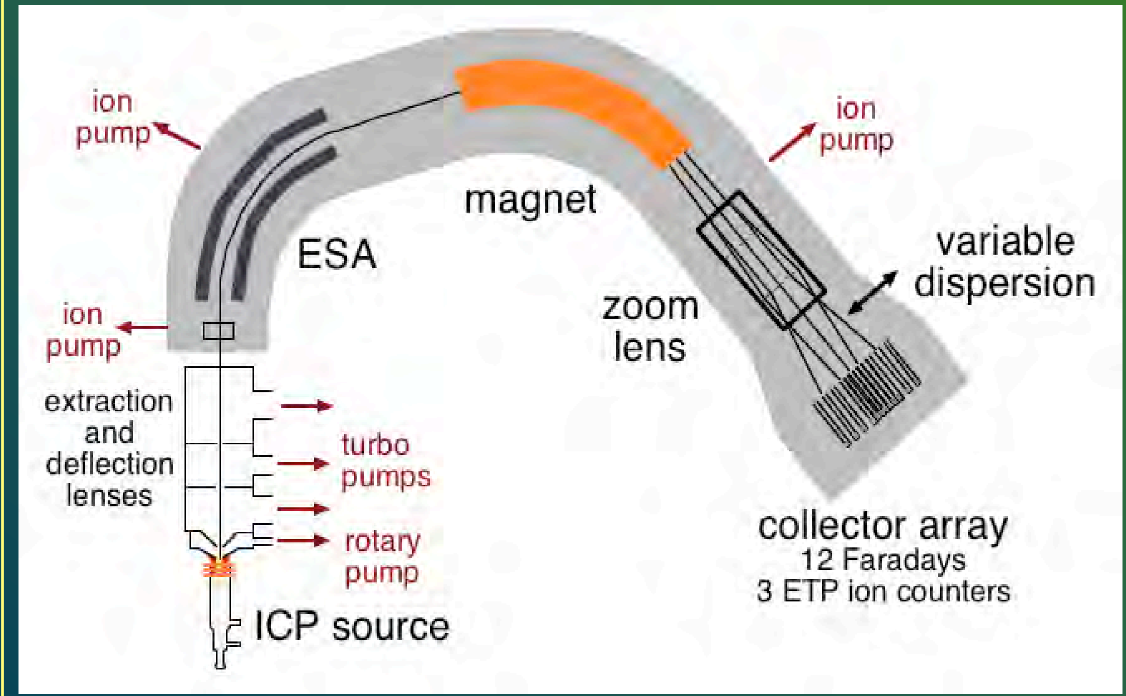
Zircon standard

Rapid -- 3-4 hours, single polished section

Typical precision ± 2-5 Ma (95% conf.)

Good agreement with "known" ages

Isotopic Analysis: LAM-MC-ICPMS



Nu Plasma MC-ICPMS: schematic

High ionisation efficiency -- can analyse difficult elements like Hf

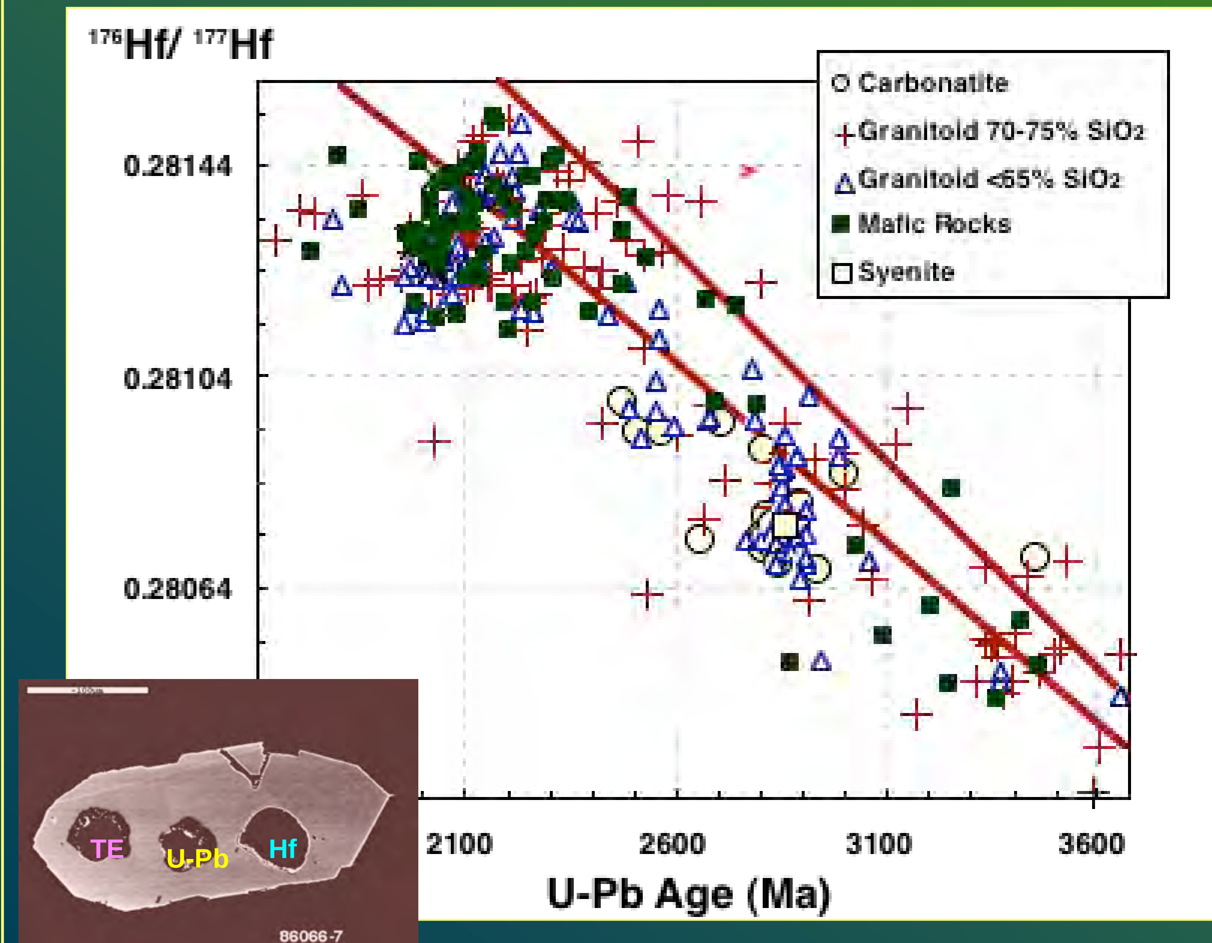
Multiple collectors, static measurement = high precision

Element spiking by injection of solutions (Tl in Pb, Ir in Os....) = improved precision

In-situ Isotopic Analysis: LAM-MC-ICPMS

- Rb-Sr, Sm-Nd, Lu-Hf, Re-Os: more precision required relative to element abundance -- use LAM-MC-ICPMS
- Peak overlap corrections essential for LAM applications (eg Rb on Sr) -- but very difficult on some instruments --
- These corrections limit “dating” applications
- Best for measurement of *initial ratios* (Sr, Hf, Os, Nd, etc…)
- Major applications: Hf in zircons, Os in sulfides, Sr in carbonates and feldspars
- GEMOC: Nu Plasma ICPMS + Nd:YAG laser (266 or 213 nm) or Excimer laser (193 nm). Hf in zircon >80 analyses/day

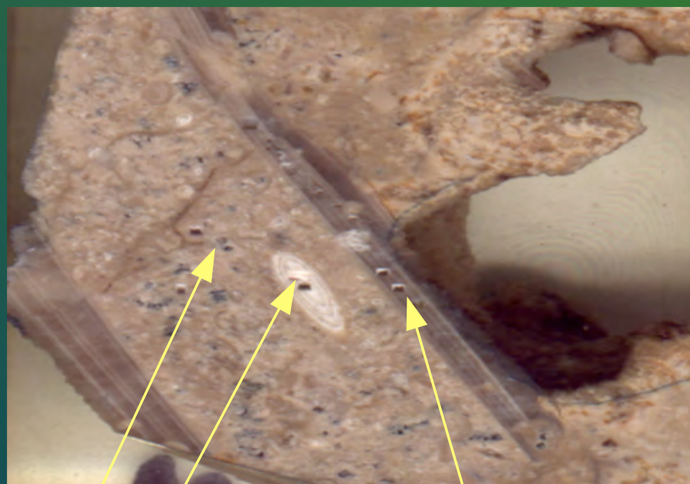
TerraneChron®:
Integrated analysis of detrital zircons



W. Carajas area, Amazon Craton

- U-Pb dating = age
- Hf isotopes = magma source
- Trace elements = magma composition
- Integration = crustal history in drainage area
- Terrane-scale studies of crustal evolution
- Extra dimension to sediment-provenance studies

In-situ Isotopic Analysis: Sr in carbonate, feldspar



Worm tube: $^{87}Sr/^{86}Sr$= 0.708087±10

(TIMS = 0.708079±20)

Fusilinid: $^{87}Sr/^{86}Sr$= 0.708121±15

Bryozoan: $^{87}Sr/^{86}Sr$= 0.708302±17

$^{87}Sr/^{86}Sr$ -- information on isotopic composition of fluids

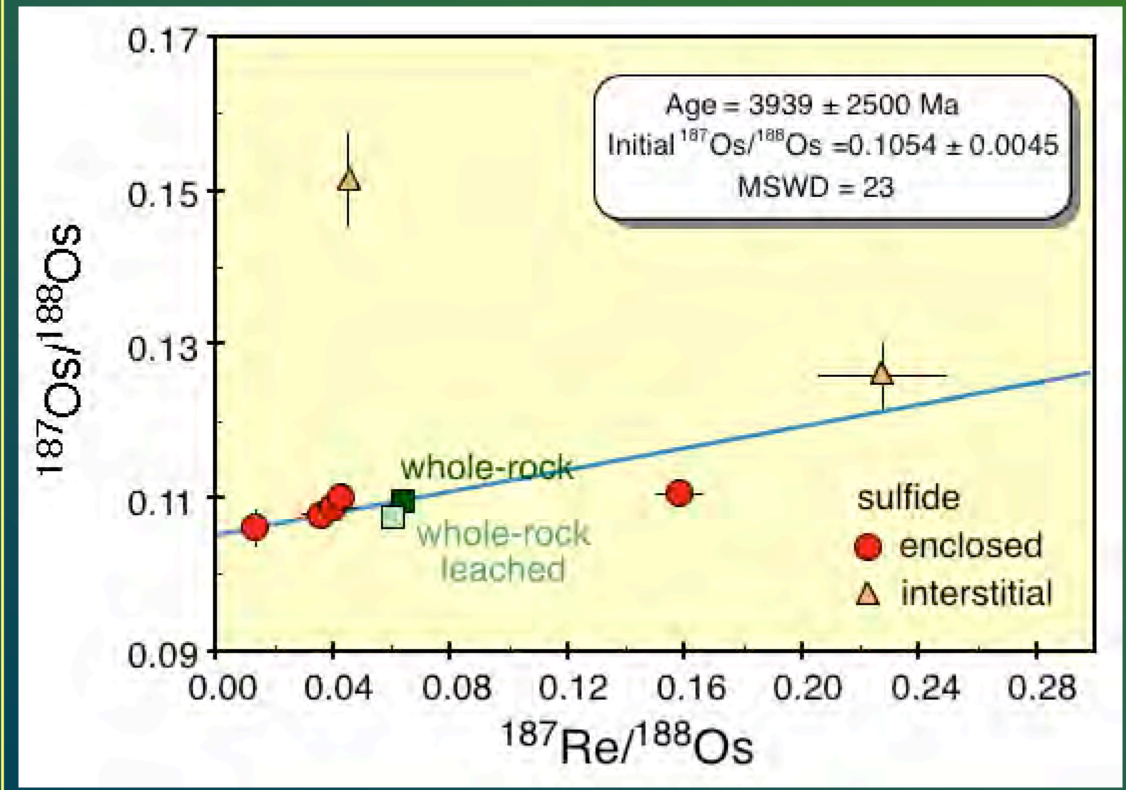
1000 ppm Sr = 10-20 ppm precision

Tracer of diagenesis in sediments, fluid changes in hydrothermal systems

Dating of fossils relative to sea-water Sr-isotope curves

Isotope stratigraphy in feldspar -- magma evolution

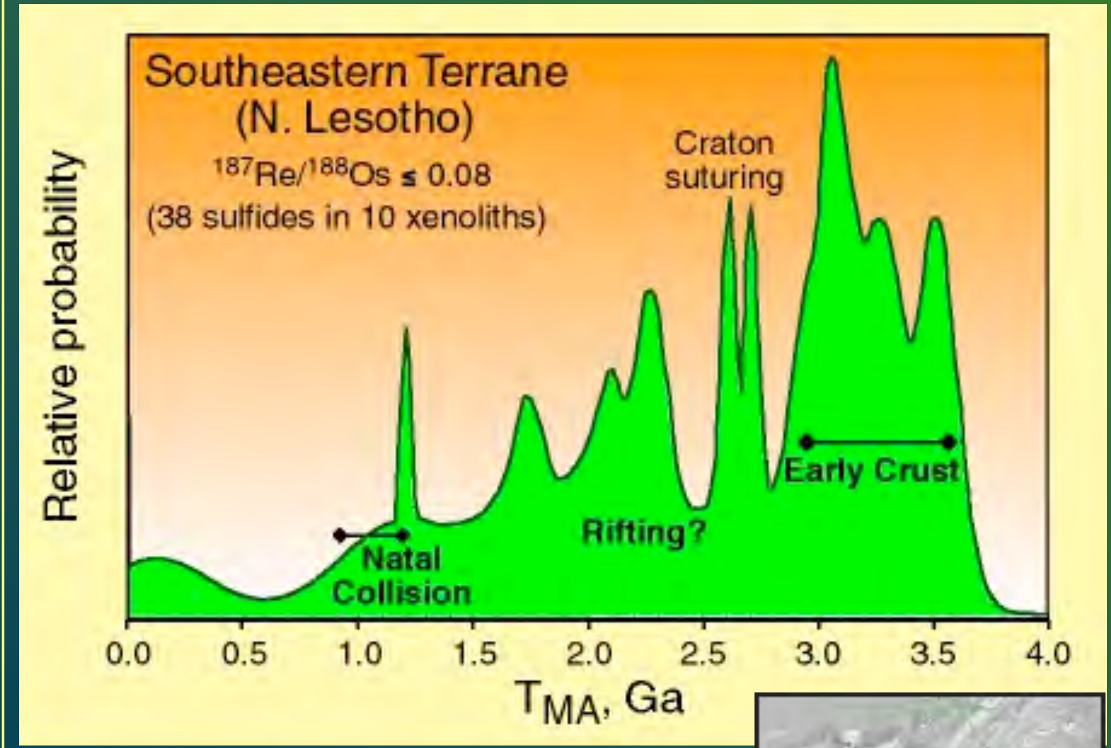
In-situ Isotopic Analysis: Re-Os in mantle sulfides



Kaapvaal Craton peridotite xenolith: sulfides + whole rock

- Mantle Os resides in sulfides, can give model ages
- >1 generation sulfide in rocks; whole-rock model ages = mixtures
- Analyse single sulfide grains; model ages resolve different events
- 50 ppm Os = 0.01% precision

In-situ Isotopic Analysis: Re-Os in mantle sulfides



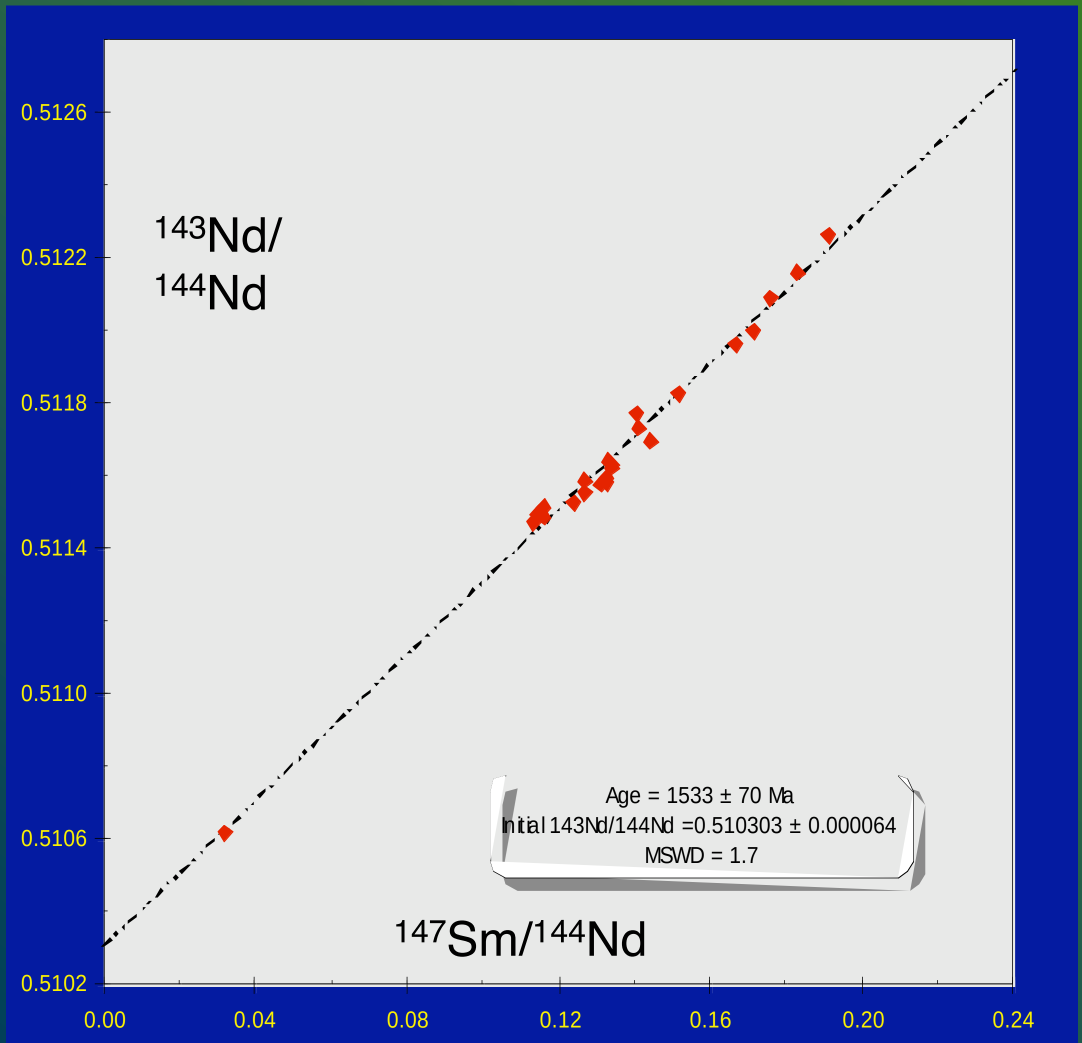
Analyse single sulfide grains; model ages resolve different events

Mantle events = crustal events, in detail

Lithosphere formed 3.6-2.9 Ga; modified at 2.6-2.7 Ga, ca 2.2 Ga, 1.7-1.8 Ga

More precise tool for analysis of crust/mantle evolution

In-situ Isotopic Analysis: Sm-Nd in titanite



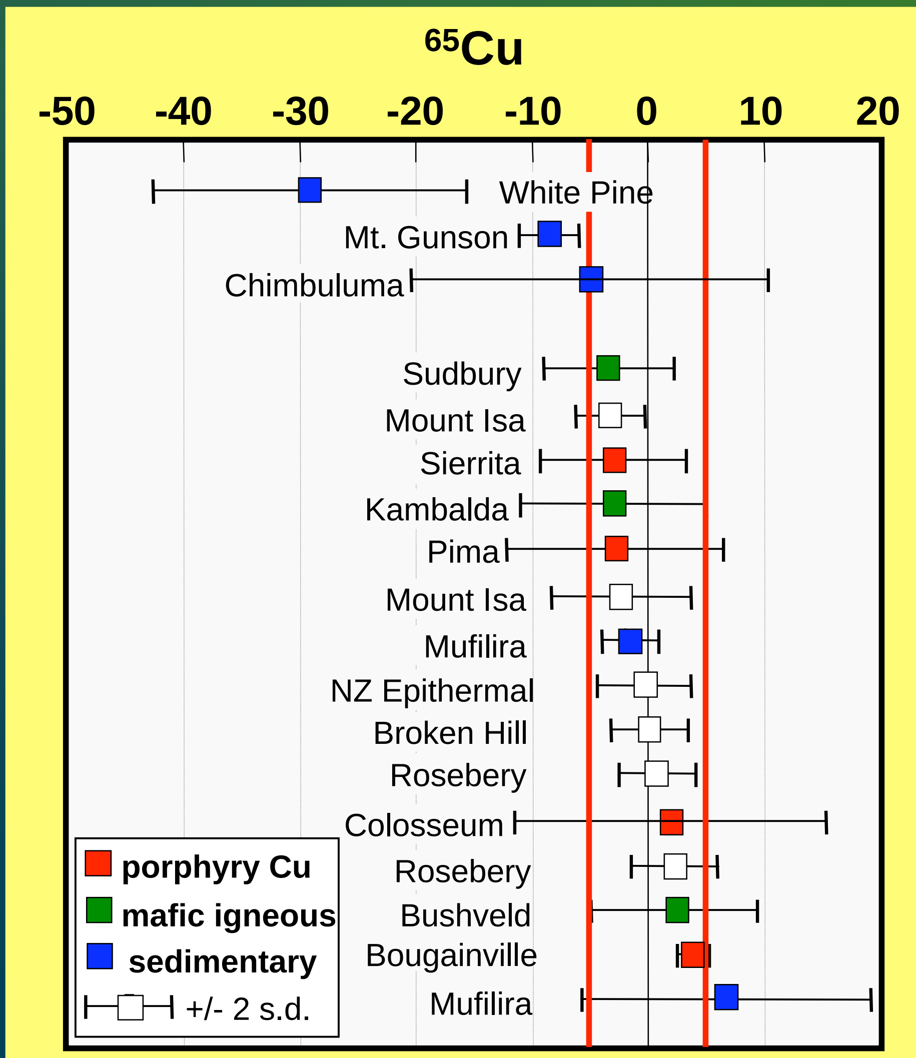
- Measure $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ simultaneously
- Titanite: 1000-4000 ppm Nd, range in Sm/Nd
- Sm-Nd = 1533±70 Ma
- Granite zircon age = 1525 Ma
- 20 analyses = 2 hours
- Rapid survey tool, good for altered rocks

Stable Isotope Analysis: New Developments

Metal Isotopes (Cu, Fe, Zn, Mo, Sb, Ni….)

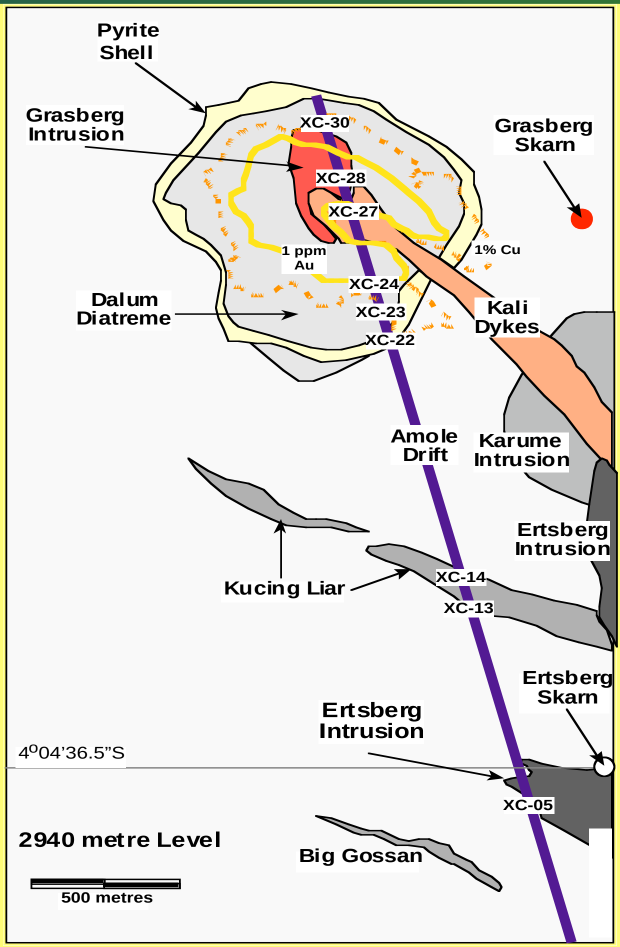
- New field, made possible by MC-ICPMS (better ionisation)
- Rapidly expanding into LAM-MC-ICPMS
- Ore deposit studies -- direct data on sources of metals
- Light elements -- Mg, Li, B -- data on other processes

LAM-MC-ICPMS data: Cu isotopes



- Cu + Fe isotopes measured *in situ*: chalcopyrite grains from range of ore deposit types
- Analytical precision: ±2sd ≈ $1\varepsilon^{65}$Cu
- Large ranges in some ore deposits - fluid flow, deposition episodes
- "Magmatic band"; deviations related to redox processes
- New tools for ore deposit studies, mineral exploration

Grasberg Intrusive Complex
Irian Jaya (3 Ma)

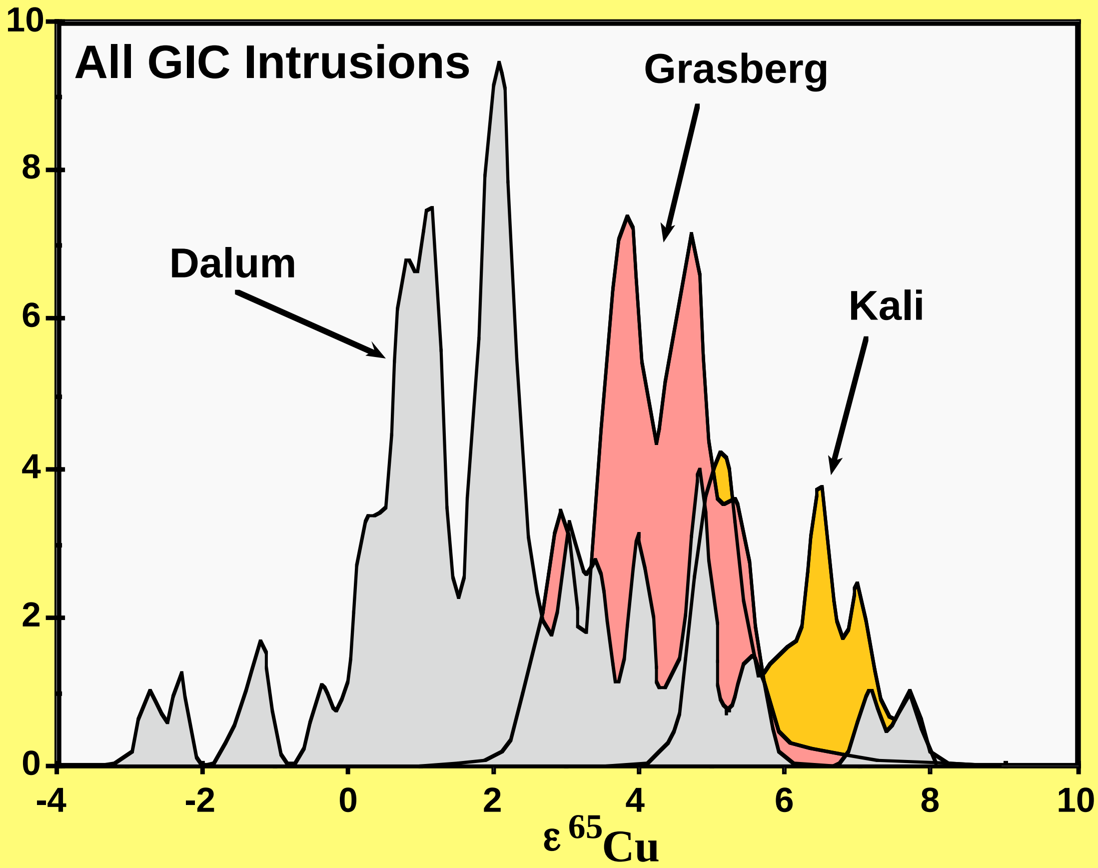


2 models:

(1) 3 episodes of mineralisation associated with 3 intrusive phases (MacDonald and Arnold, 1994)

(2) Bulk of ore post-magmatic (Kavalieris & Pennington, 1999); (Pollard and Taylor, 2002)

Grasberg Intrusive Complex
Irian Jaya (3 Ma)



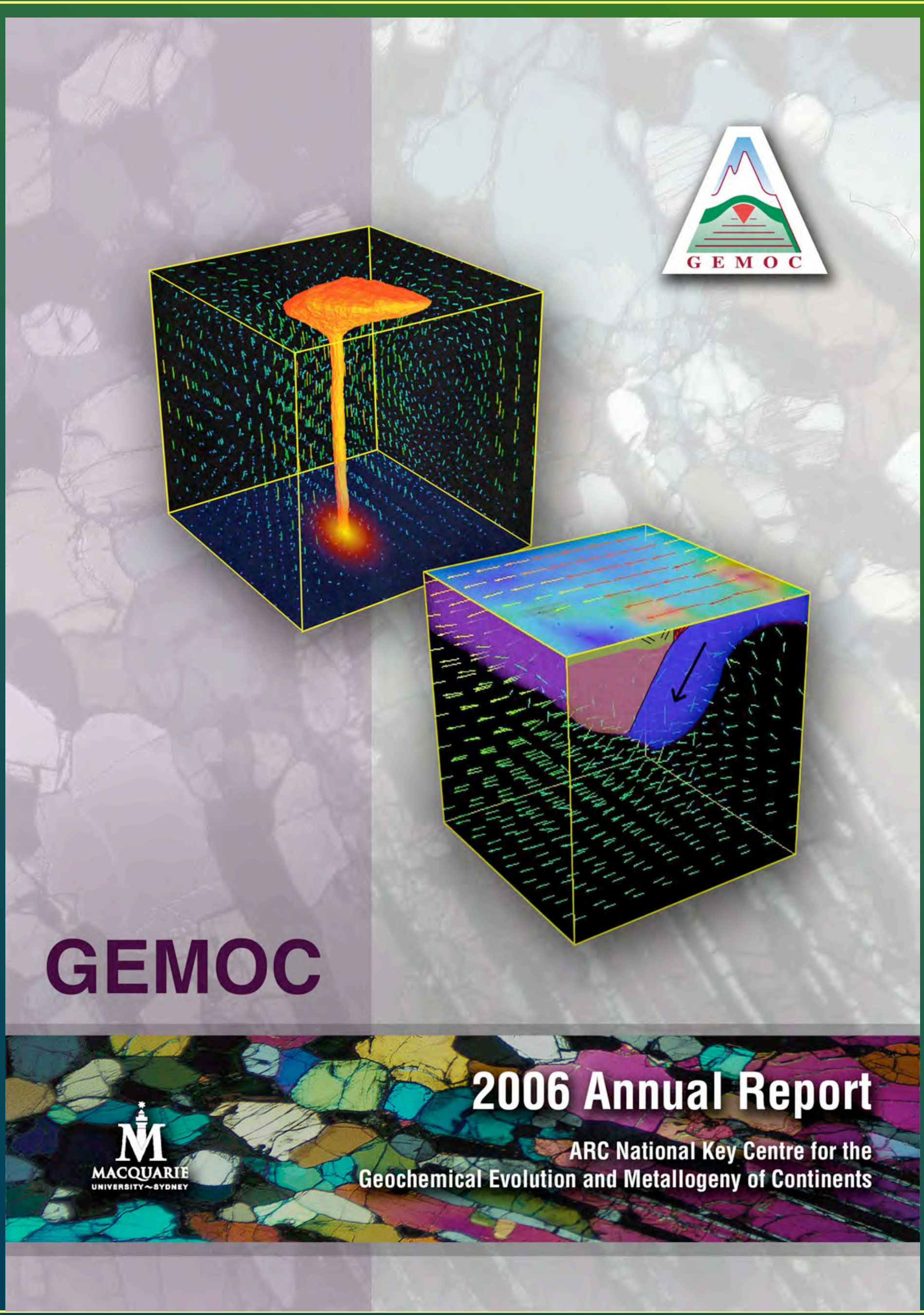
3 bodies have different Cu- (and Fe-) isotope signatures in Cpy

Supports model of MacDonald and Arnold, 1994)

Can use to identify ore sources in drilling programs

Summary

- *In-situ* microanalysis: Essential for applications of RIM technology to mineral exploration
- EMP (major and minor elements) -- data quality depends on counting time -- cutting corners may be wasting $$$
- Trace elements: LAM-ICPMS is most rapid, cost-effective
- U-Pb dating: LAM-ICPMS best for 90-95% of work!
- LAM-MC-ICPMS isotope analysis -- many new applications (Hf, Sr, Nd ……) for tracers
- Stable isotopes of metals -- new and promising field for applications to mineral exploration



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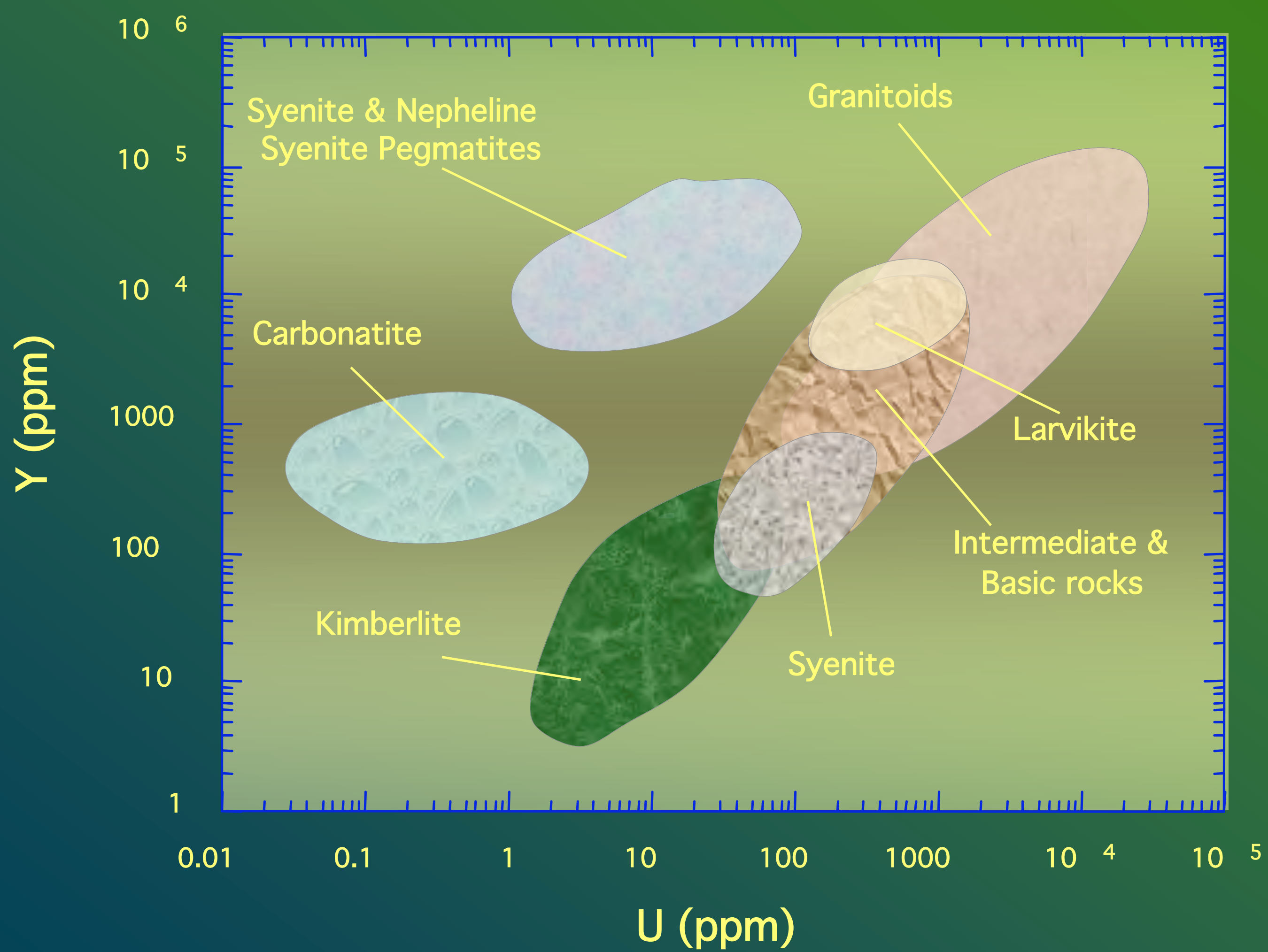
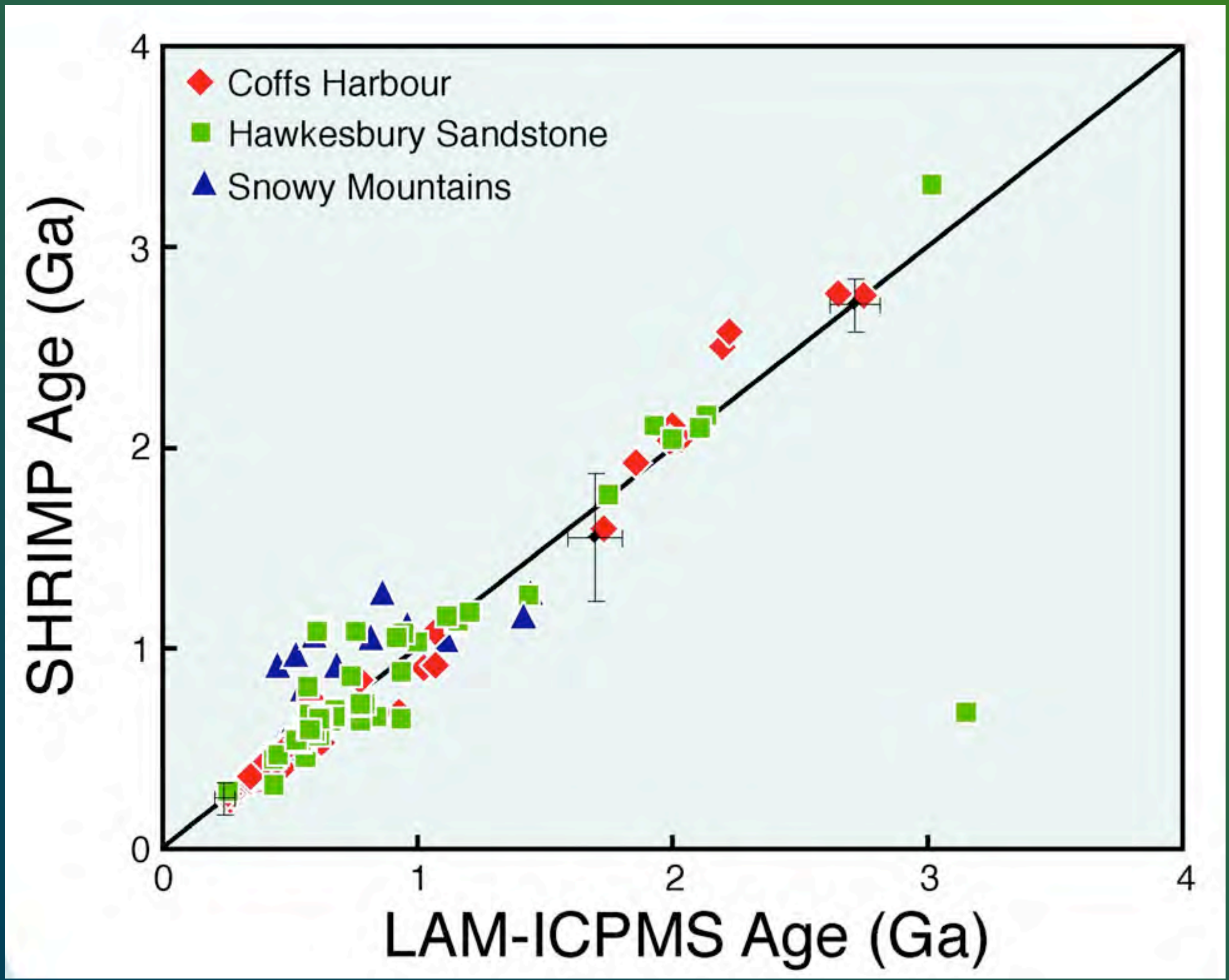
Zircon Trace Elements: Recognition of Host Rock Type



LAM-ICPMS vs SHRIMP:
U-Pb ages of detrital zircons



- comparable in accuracy and precision
- LAM more rapid (5 minutes/grain)
- significantly lower unit cost w/ LAM
- but slightly lower spatial resolution
- scatter of ages = more complex grains