

Applications of laser ablation
inductively coupled plasma mass-spectrometry
(LA-ICP-MS) to problems of petrology of
ultrahigh-pressure (UHP) metamorphic rocks

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LA-ICP-MS

- Powerful and versatile, but challenging, analytical tool

A combination of two instruments, each based on physical phenomena which are not yet fully understood

- Will continue to see significant instrumental and theoretical developments



Presentation

- Overview of the principal components of LA-ICP-MS systems



Leonid
Danyushevsky



Sebastien Meffre



Sarah Gilbert



Jay Thompson

- Examples of applications of the method to the UHP metamorphic rocks

LA-ICP-MS vs Raman

- Both LA and Raman use laser light source.
 - Raman use low energy and excite light
 - LA use high energy and ablate the sample
- Output of the methods also different:
 - Raman provide detailed mineralogical information
 - LA characterise composition of the samples
- Raman and LA are often used together, especially in inclusions research.

Capabilities of LA-ICP-MS

- The development of LA-ICP-MS is responsible for an ongoing revolution in geochemistry comparable to advent of electron microprobe.
- The first unique characteristic of LA is number of measured elements.

Group ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu			
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr			

- Routinely analysed elements
- Elements measured with special effort
- Elements not analysed by LA-ICP-MS

Capabilities of LA-ICP-MS

Advantages of LA-ICP-MS

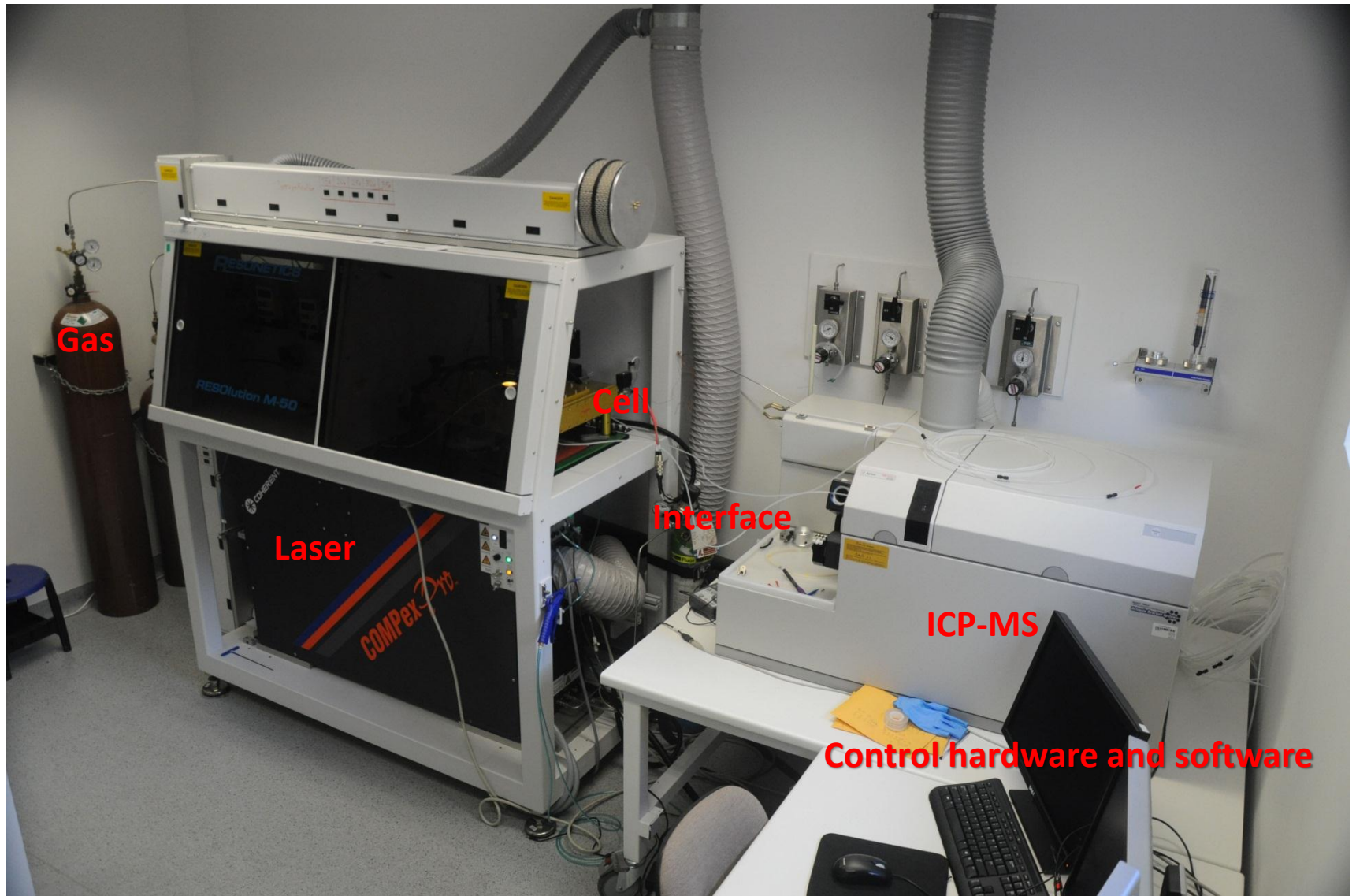
- Wide range of analysed materials:
 - Glasses
 - Silicate minerals
 - Sulfide minerals
 - Fluid and melt inclusions
 - Polyphase mixes
 - Exceptions: minerals transparent in UV e. g. quartz, fluorite are difficult to analyse, but still possible in many cases.
 - Biological, electronic, metallurgical samples.
- Sample preparation: exceptionally low requirements. Even unpolished samples can be analysed.
- Spatial resolution: range from 6 μ m to 1mm, routine analyses – 15-50 μ m
- Fast analyses: 15-20 analyses per hour is typical rate.
- Typical precision: 3-10% but matrix effects might affect accuracy.
 - Can be pushed down to 0.5% for special application like U-Pb geochronology on single collector mass-spectrometers and 0.002% for isotope ratios by multi-collector instruments.
- Wide range of concentrations: from wt.% to detection limits.
- Detection limits: depend on system, element and analyses parameters. Detection limit down to ppb levels can be achieved for many elements.
 - Detection limits are reversely proportional to the intensity of the signal. Eg. the larger the spot size the lower DLs.



LA-ICP-MS systems

Components of LA-ICP-MS instrument

- The LA-ICP-MS systems are composed of several principal components:



LA-ICP-MS systems

Lasers

Parameters to consider:

- wavelength and laser type
- pulse width
- energy distribution across the beam
- long-term / short-term stability
- unit dimensions
- working distance of the objective

Main laser types used in LA-ICP-MS

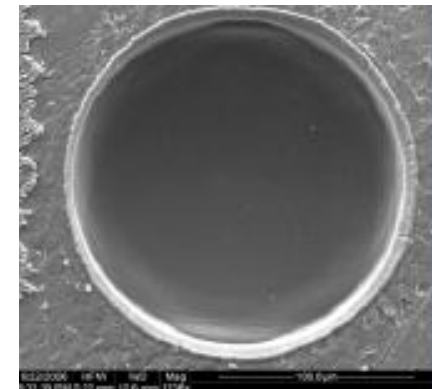
- Solid-state NdYAG lasers
- ArF excimer lasers



100 micron spots



193 nm solid state



193 nm excimer

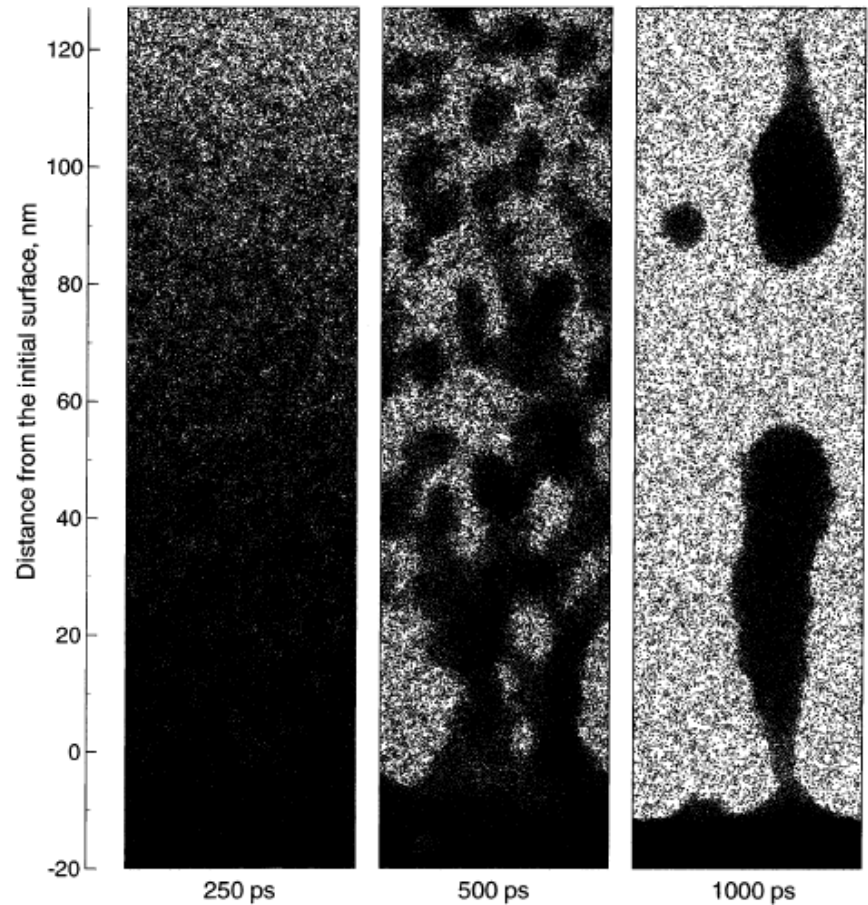
LA-ICP-MS systems

Interaction of laser with sample

Role of laser

The interaction of laser with mineral results in several different phenomena:

- Melting
 - Cracking
 - Direct vaporization: the preferred option.
 - Laser-induced breakdown radiation
-
- General rule: shorter wavelength is better
 - Poor absorption results in heating a large volume of the sample, leading to expansion and mechanical failure (cracks)
 - Shorter laser wavelength results in finer particles. Therefore larger proportion of aerosol is ionised in the plasma.



Implications for analyses

- Different lasers suite different applications
- Laser energy is an important parameter for analyses and should be measured on the day of analyses. Specific energy is used for specific minerals: it helps to optimize signal, reduce melting and fractionation.

LA-ICP-MS systems

Ablation Cells

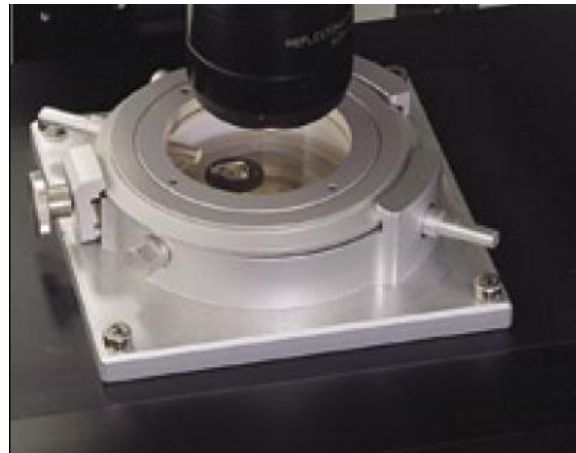
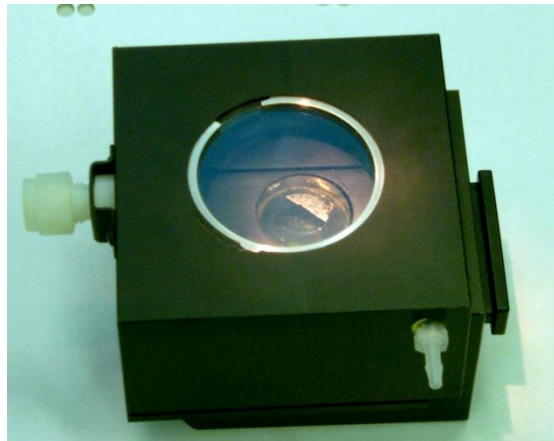
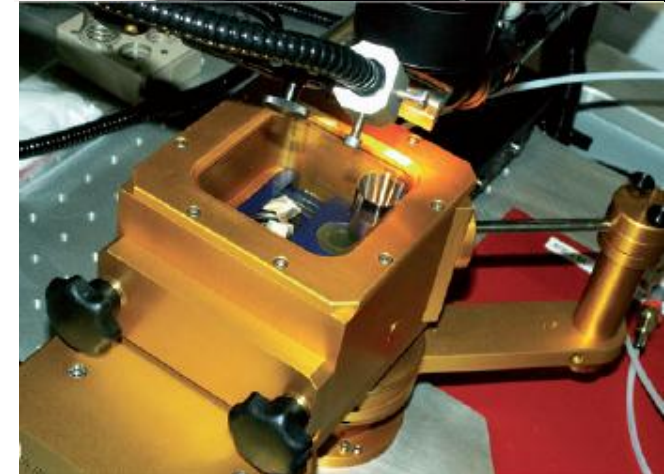
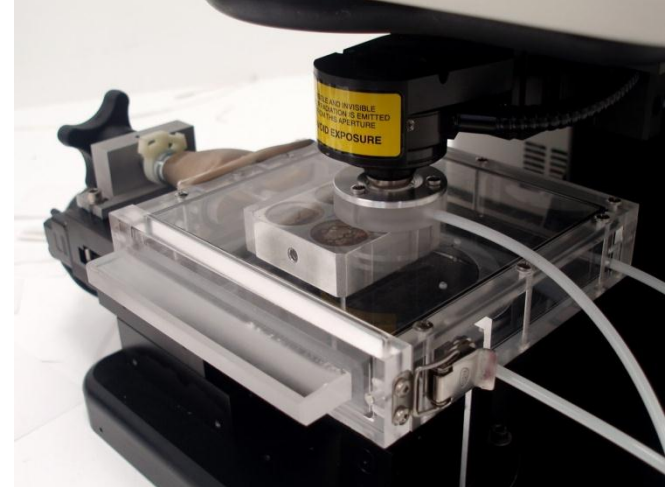
Cell design is the crucial for quantitative LA-ICP-MS.

Important cell parameters:

- Effective volume
- Purge time
- Washout time
- Geometry (gas flow configuration)

Main types

- Single volume cell
- Double volume (constant geometry cell)



LA-ICP-MS systems

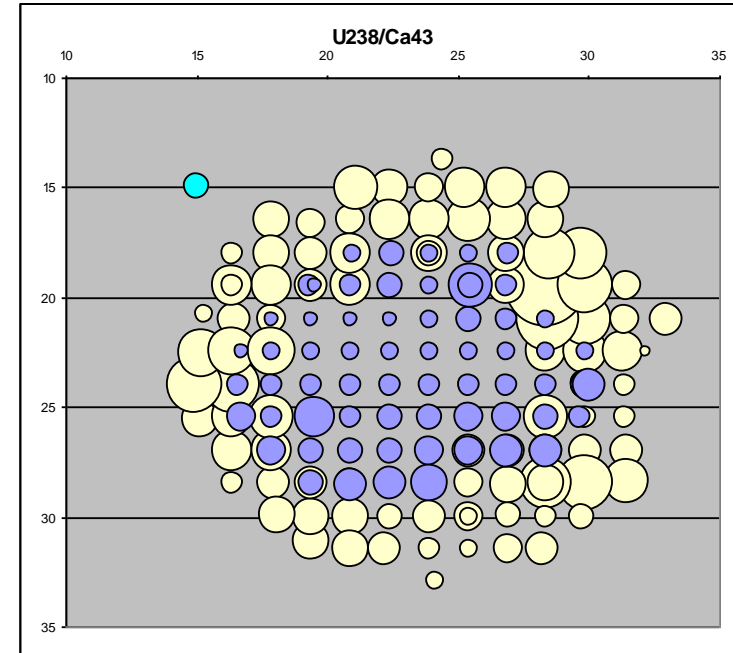
Ablation Cells



- Resonetics double volume cells allows to fit 20 mounts while no fractionation observed to correlate with location in the cell.
- Large cell is a key to efficiency:
 - 18 samples
 - 10-20 spots per sample
 - 6-8 standards per hour
 - Equals to one 24-hour session



Small-volume barrel cells

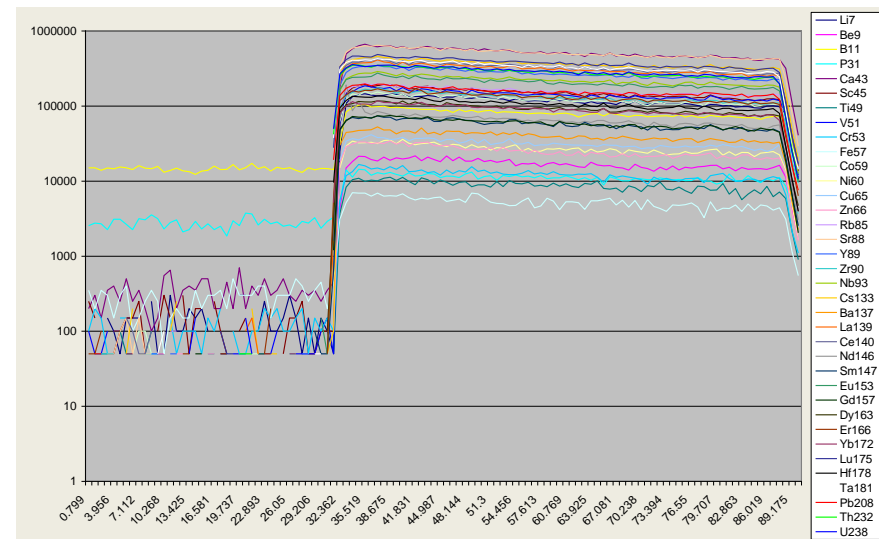
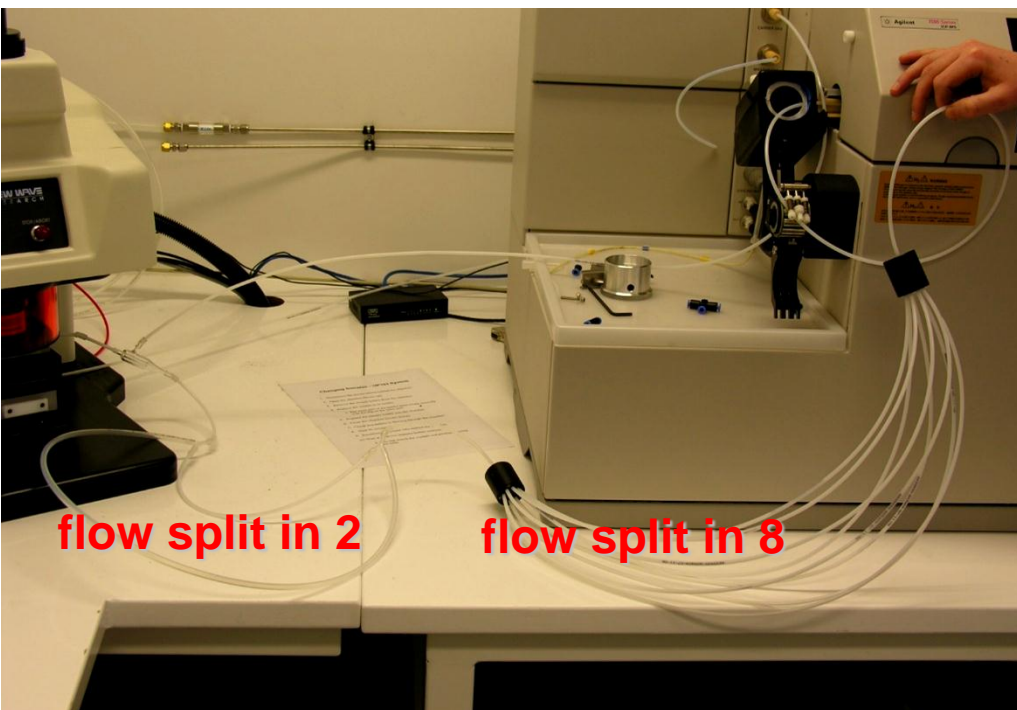
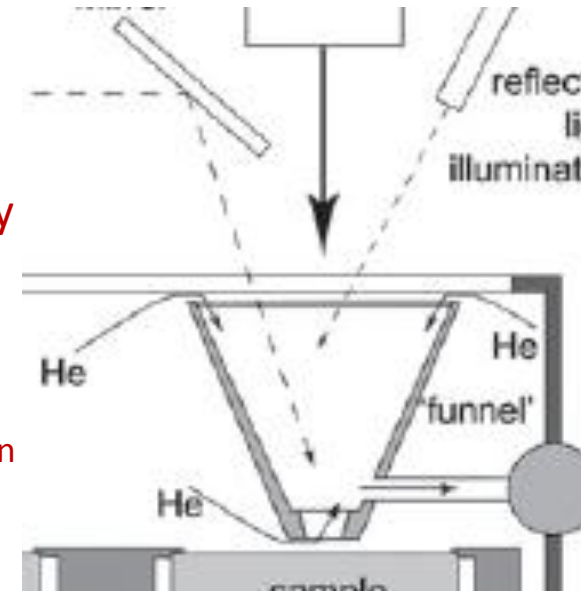


Different spots having different gas flow results in element fractionation

LA-ICP-MS systems

Interface

- Interface transfers material from the ablation site to the ICP-MS.
- Funnel: Gas is supplied to the ablation site and then carry aerosol to ICP-MS. The geometry of He flow in funnel might affect efficiency of material extraction and reproducibility of analyses.
- Tubing connects cell to the ICP-MS. Two principal options:
 - Single tube: fast changing signal. Required for inclusions, imaging etc.
 - Multiple tubes of different length: smooth signal. Required for high precision measurements.



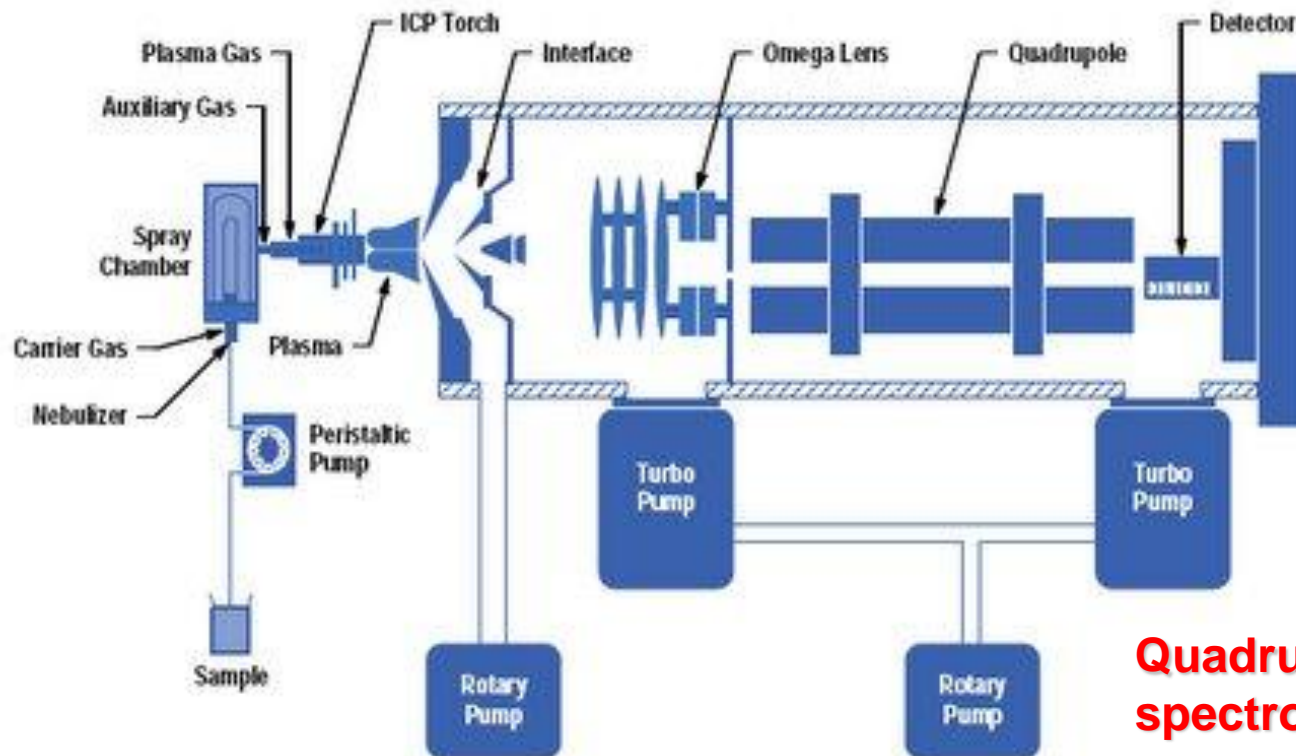
LA-ICP-MS systems

ICP-MS

- ICP-MS stands for inductively coupled plasma mass spectrometer.
- In the plasma ablated material is ionised and ions are separated by the magnet.
- The ions arrive to the detector which measures count rates .

Main types of mass spectrometers used for LA-ICP-MS

- **Quadrupole single collector:** preferred for trace elements, U-Pb geochronology.
- **Multi collector:** Sm-Nd, Lu-Hf systems.

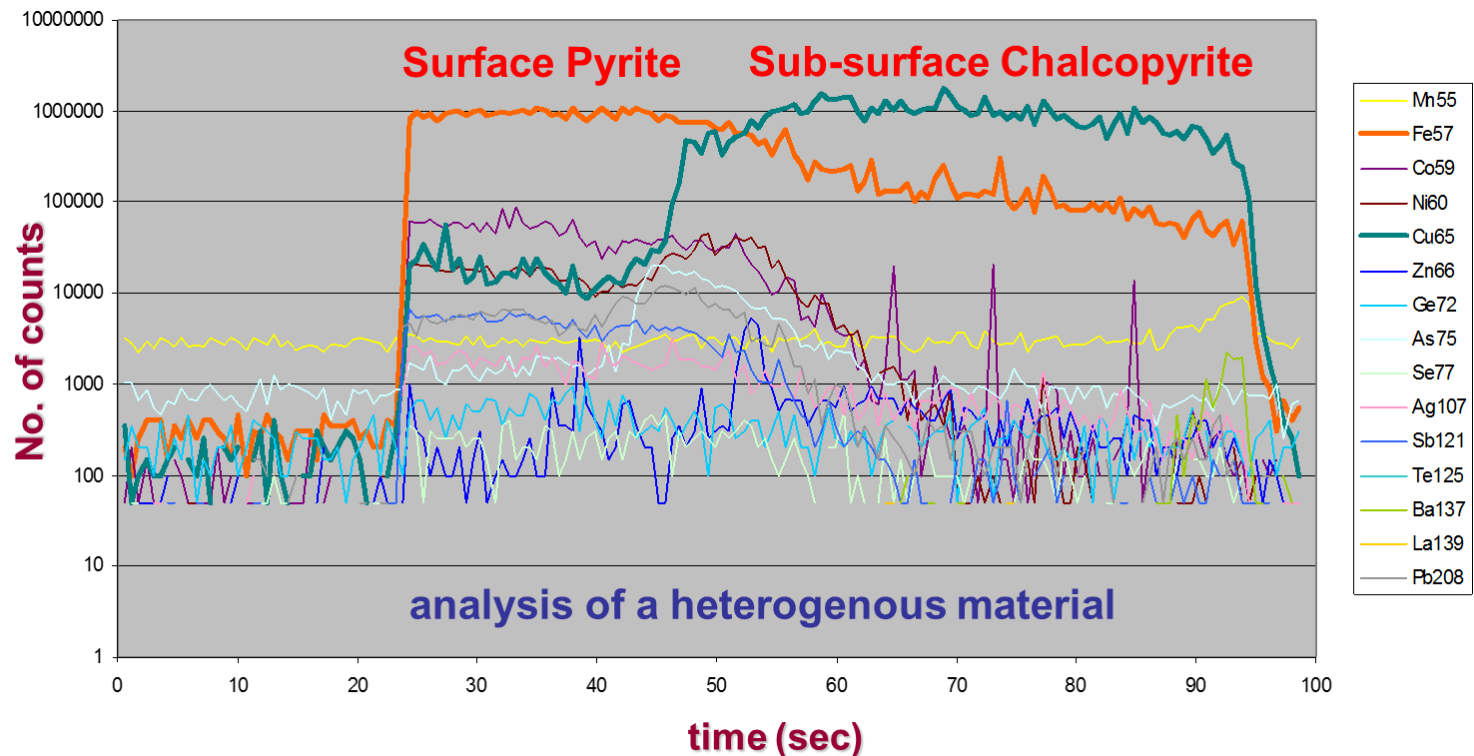


Quadrupole mass spectrometer

Reduction of data obtained by LA-ICP-MS

Analytical set up

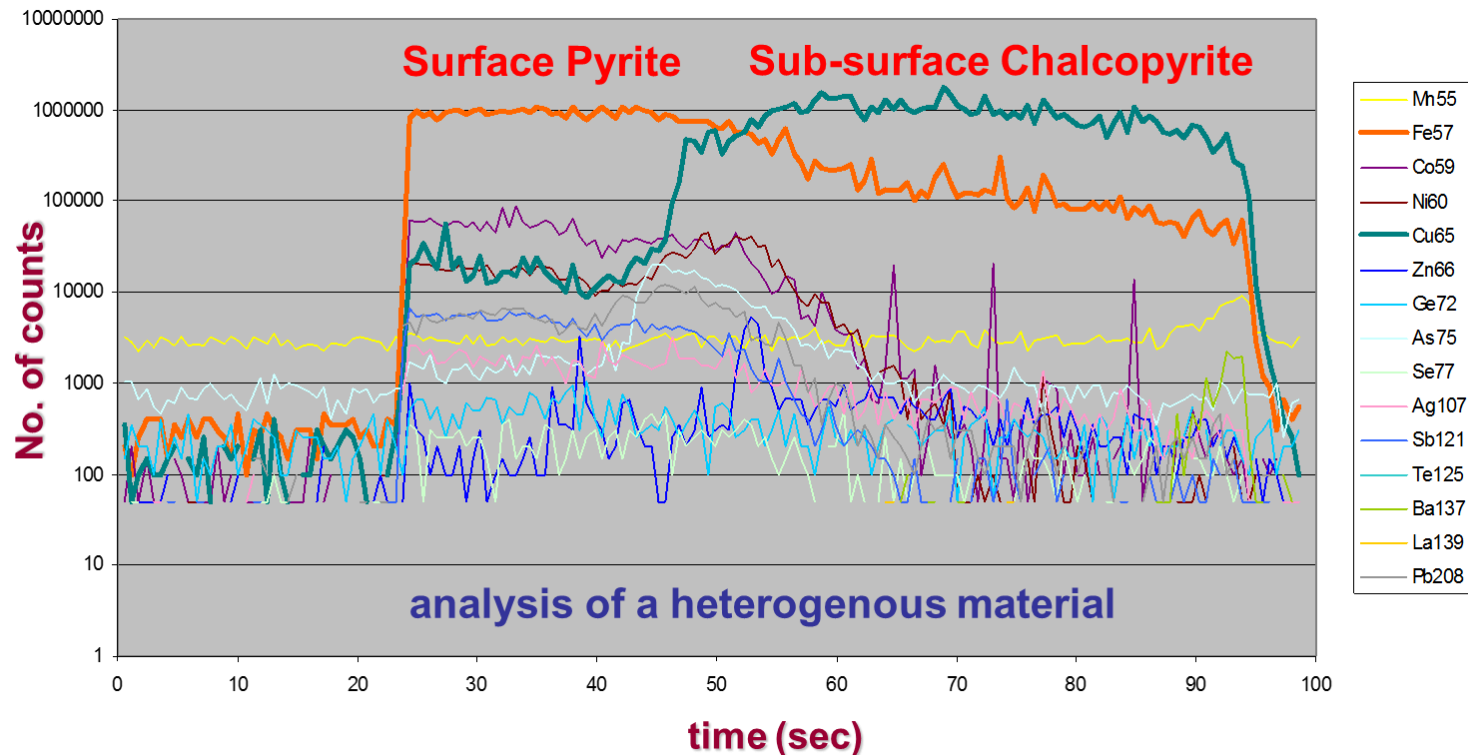
- Before the analyses decision is made about the characteristics of analyses:
 - Masses
 - Standards
 - Dwell times
 - Duration of analyses and background



Reduction of data obtained by LA-ICP-MS

Data reduction

- Data reduction is an important step in collection of LA-ICP-MS data.
- During data reduction things to look after:
 - Background
 - Drift
 - Interferences
 - Stability of primary and secondary standards



Reduction of data obtained by LA-ICP-MS

Interferences

- Ions of the mass not distinguished by mass-spectrometer are called interferences. They can be either monoatomic or polyatomic particles. Polyatomic ions with O and Ar are the most common.
- Generally LA-ICP-MS has low level of interferences: thanks to the efficient decomposition of the particles in the plasma and tuning of oxide production to low levels.
- However the possibility of interferences never should be overlooked: significant interferences occur for major elements e. g. Ca but they are most pronounced for elements of low abundance eg. Pb, Ag and Au.

Reduction of LA-ICP-MS data

Standards

- The signal collected by LA-ICP-MS system represents measurements of count intensities measured over time. These need to be recalculated to concentrations. For this we use standards.

$$\frac{\left(\frac{CPS}{PPM}\right)_{STD}^{IS}}{\left(\frac{CPS}{PPM}\right)_{STD}^{EL}} = \frac{\left(\frac{CPS}{PPM}\right)_{SAMP}^{IS}}{\left(\frac{CPS}{PPM}\right)_{SAMP}^{EL}} * X$$

$$X = C_{SAMP} / C_{ANAL}$$

X – correction factor,
a function of all analytical parameters +
matrix dependent

Primary (calibration) standards

1. Contain as many elements as possible *at reasonable* concentrations;
2. Large volume (can be used by different labs);
3. Homogenous

It is a glass

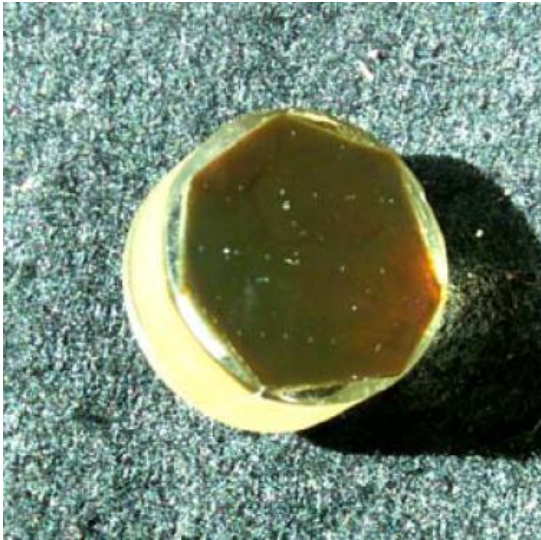
Reduction of data obtained by LA-ICP-MS

Secondary standards

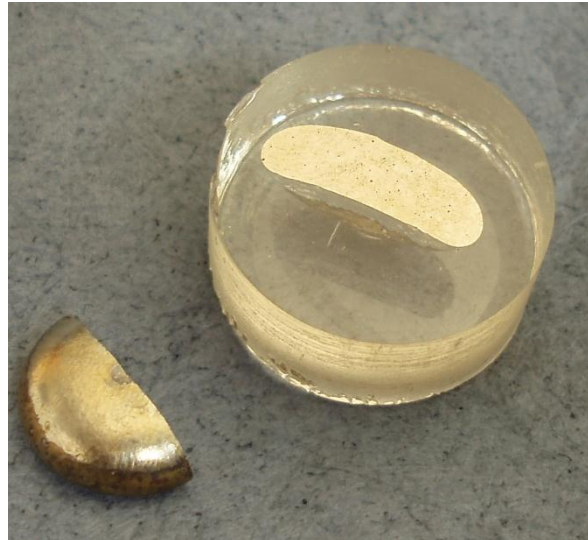
If NIST glass is used as the Primary Standards, then

1. Secondary matrix-matching standards are required, and
2. Identical ablation parameters should be used for the secondary standards and samples.

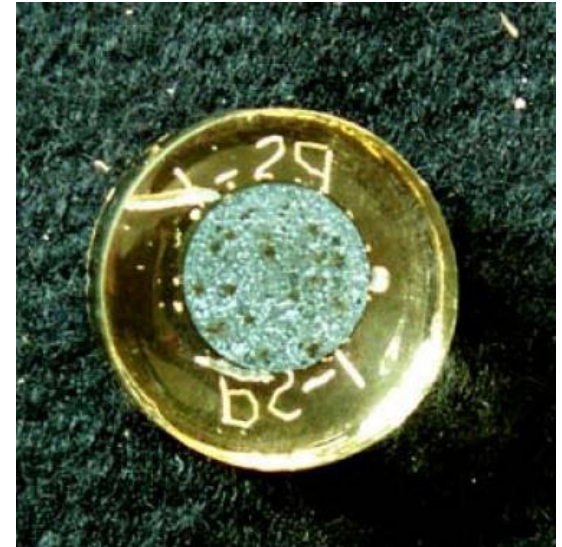
NIST glass is not suited for analysis of sulphides, as it has high Ca/Fe value; also, no secondary standards are available (lack of homogeneous sulphides)



Sphalerite-pyrite mix doped with trace elements fused into XRF Li-borate glass disc; STDGL2b2



Fire-assay NiS doped with PGEs and Au



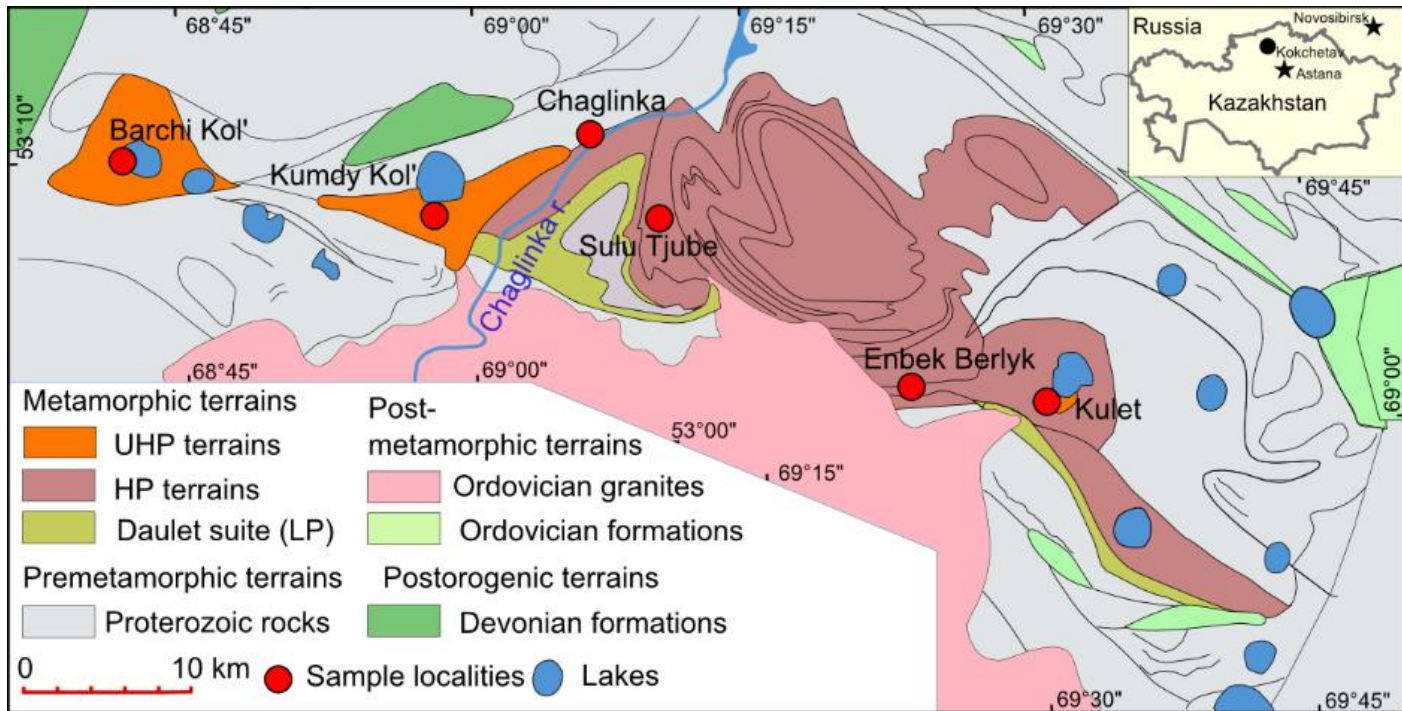
tested on natural sulphides

Applications of LA-ICP-MS to UHP metamorphic rocks

Applications of LA-ICP-MS to UHP metamorphic rocks

The Kokchetav complex

- The Kokchetav complex in Kazakhstan is a classic example of ultrahigh pressure metamorphism.
- The Kokchetav massif contains the rocks recorded the highest PT conditions (1000 °C, >45 kbar) of metamorphism of crustal rocks.
- The UHP metamorphism dramatically affected compositions of the Kokchetav rocks and depleted the gneisses in several key elements, particularly LREE, Th and U.



Mikhno, A. O. & Korsakov, A. V. (2012). K₂O prograde zoning pattern in clinopyroxene from the Kokchetav diamond-grade metamorphic rocks: Missing part of metamorphic history and location of second critical end point for calc-silicate system.

Stepanov, A. S., Hermann, J., Korsakov, A. V. & Rubatto, D. (2014b). Geochemistry of ultrahigh-pressure anatexis: fractionation of elements in the Kokchetav gneisses during melting at diamond-facies conditions. *Contributions to Mineralogy and Petrology* 167, 1–25.

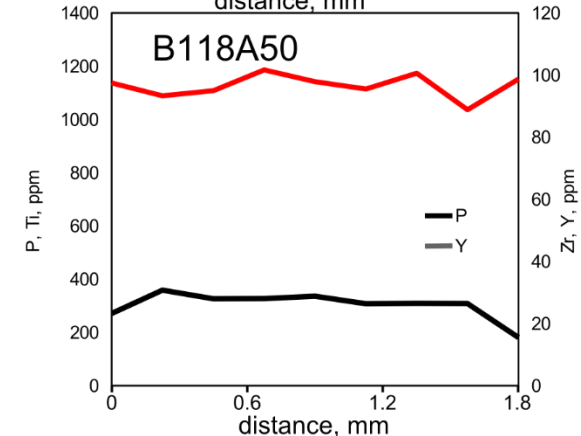
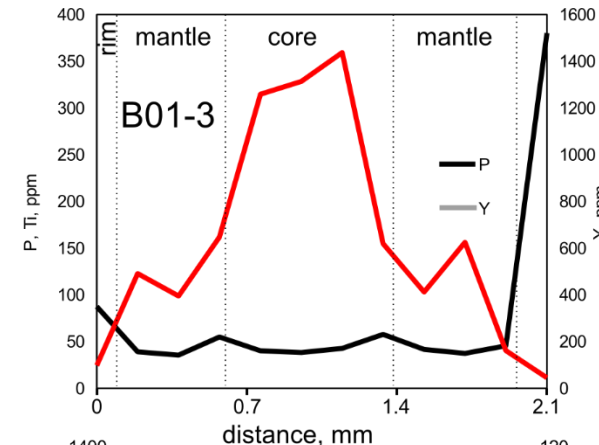
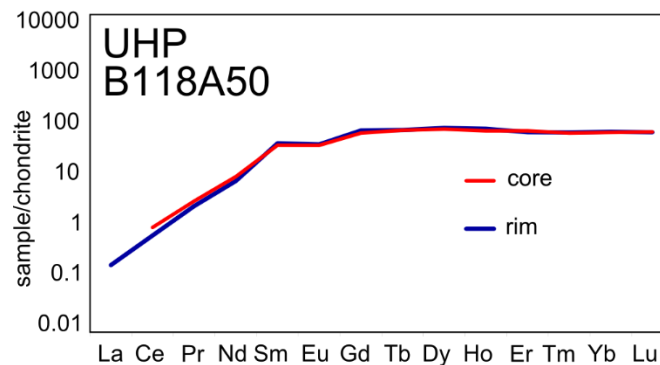
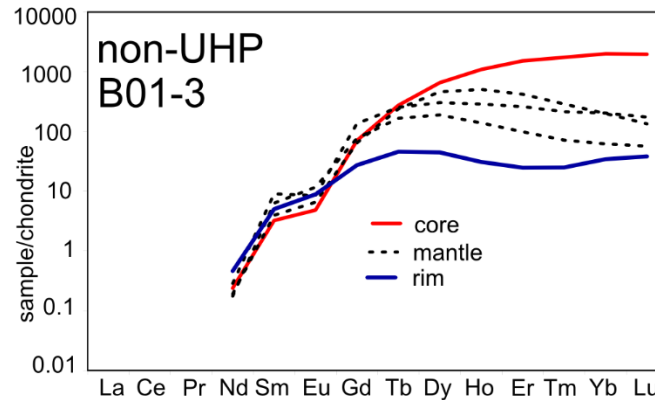
Applications of LA-ICP-MS to UHP metamorphic rocks

Trace element in garnet

- Several samples from the Barchi Kol unit from the Kokchetav complex showed variable zonation in garnet. We used LA-ICP-MS to study trace element zonation.

Analytical set up

- Analyses with 20 μm spot
- NIST610 standard
(sufficiently high P and K)
- Si as internal standard

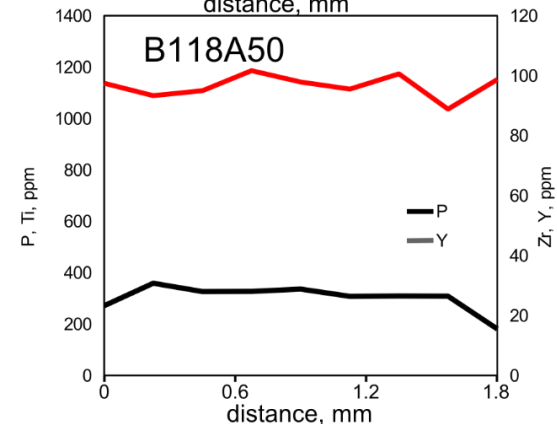
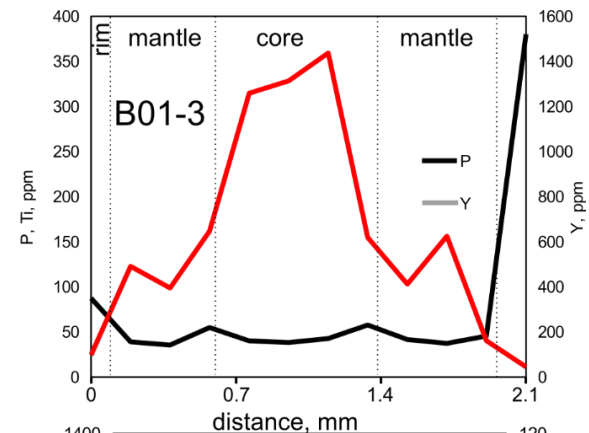
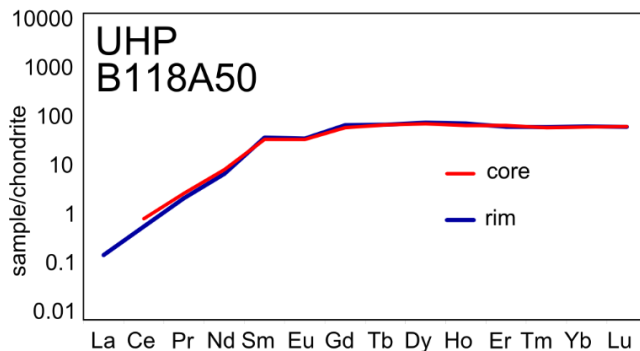
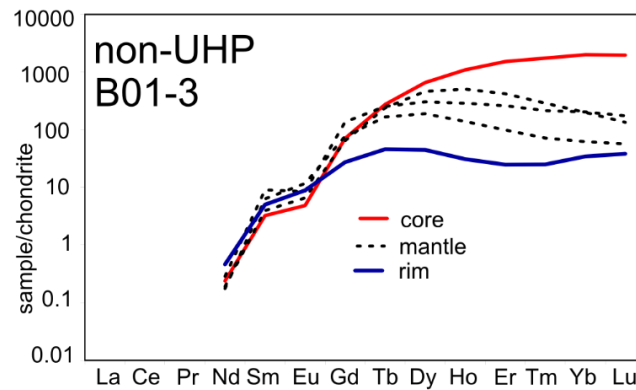


Stepanov A. S., Rubatto D., Hermann J., Korsakov A. V., Association of rocks with different P-T paths within the Barchi-Kol UHP terrain (Kokchetav Complex): Implications for subduction and exhumation of continental crust, *American Mineralogist*, 101 (4), p. 788-807.

Applications of LA-ICP-MS to UHP metamorphic rocks

Trace element in garnet: Conclusions

- Some rocks preserve prograde zonation in major and elements and REE (B01-3) while others show constant composition due to diffusional homogenisation of garnet.
- Together with other indicators LA-ICP-MS data demonstrated that sample B01-3 have experienced much lower peak T than the UHP gneiss and also constraint temperature of garnet core formation at 500°C.



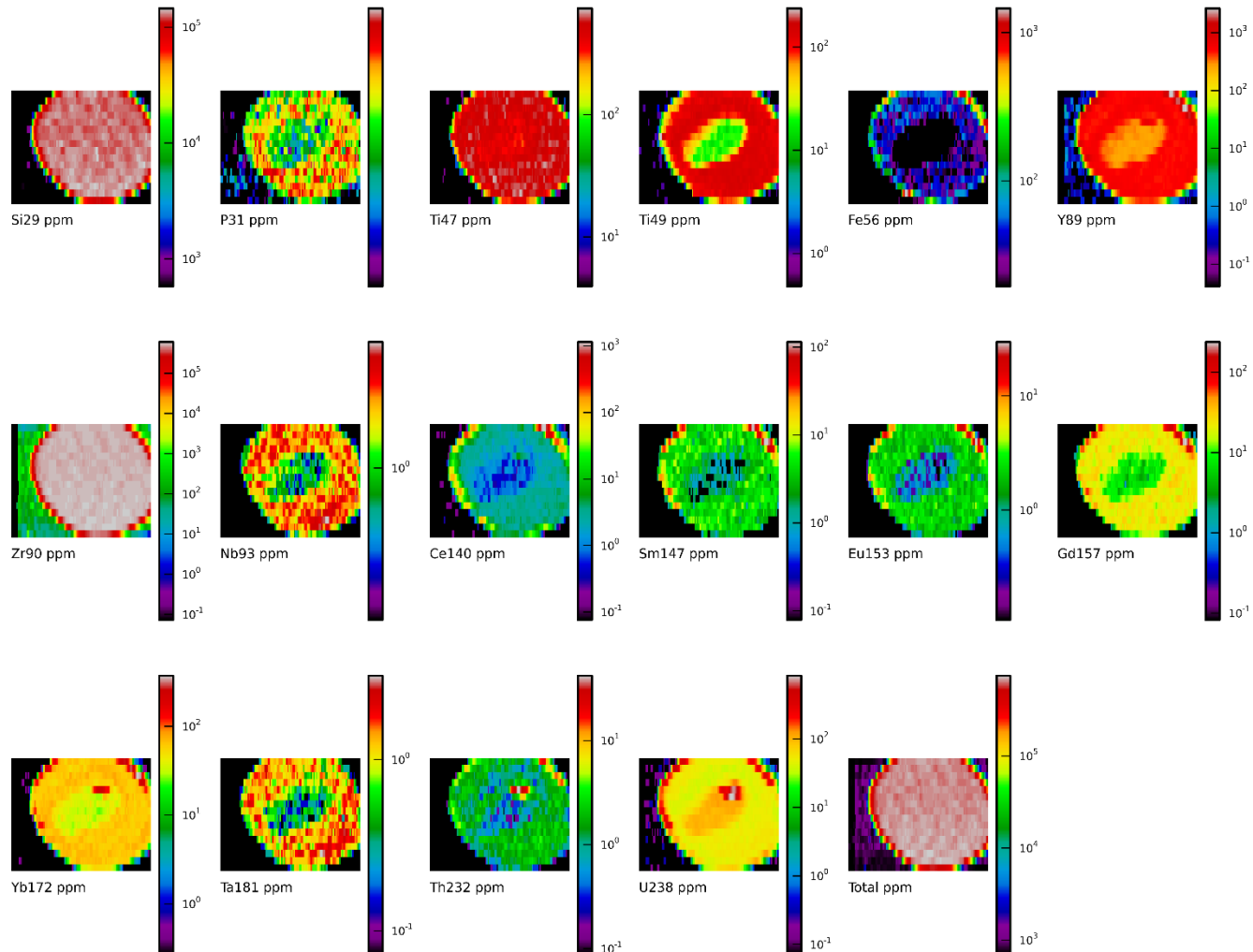
Applications of LA-ICP-MS to UHP metamorphic rocks

LA-ICP-MS imaging:

- Zircon is an essential mineral in UHP rocks because it preserves record of number of trace elements and also can be dated.

Analytical set up

- Single tube for interface to record zonation
- NIST612 standard
- Si content in zircon for internal standard.
- Ti^{49} isotope selected to avoid interference of doubly charged Zr^{94} on Ti^{47}
- The sequence is programmed where lines are measured between standards

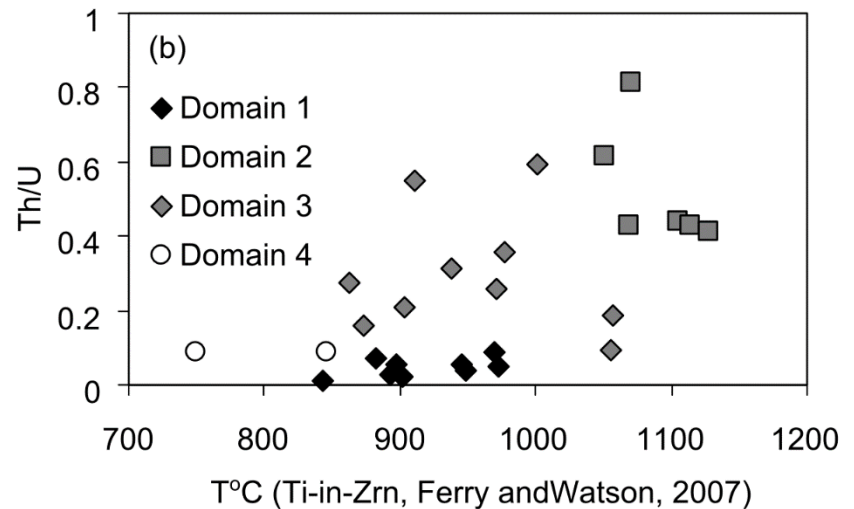
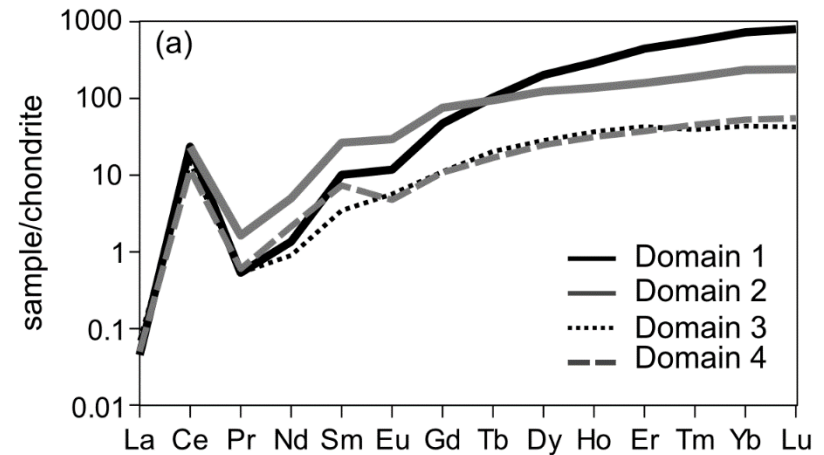


Applications of LA-ICP-MS to UHP metamorphic rocks

LA-ICP-MS imaging and trace elements in zircon: Conclusions

Trace element compositions of zircons record prolonged metamorphic evolution.

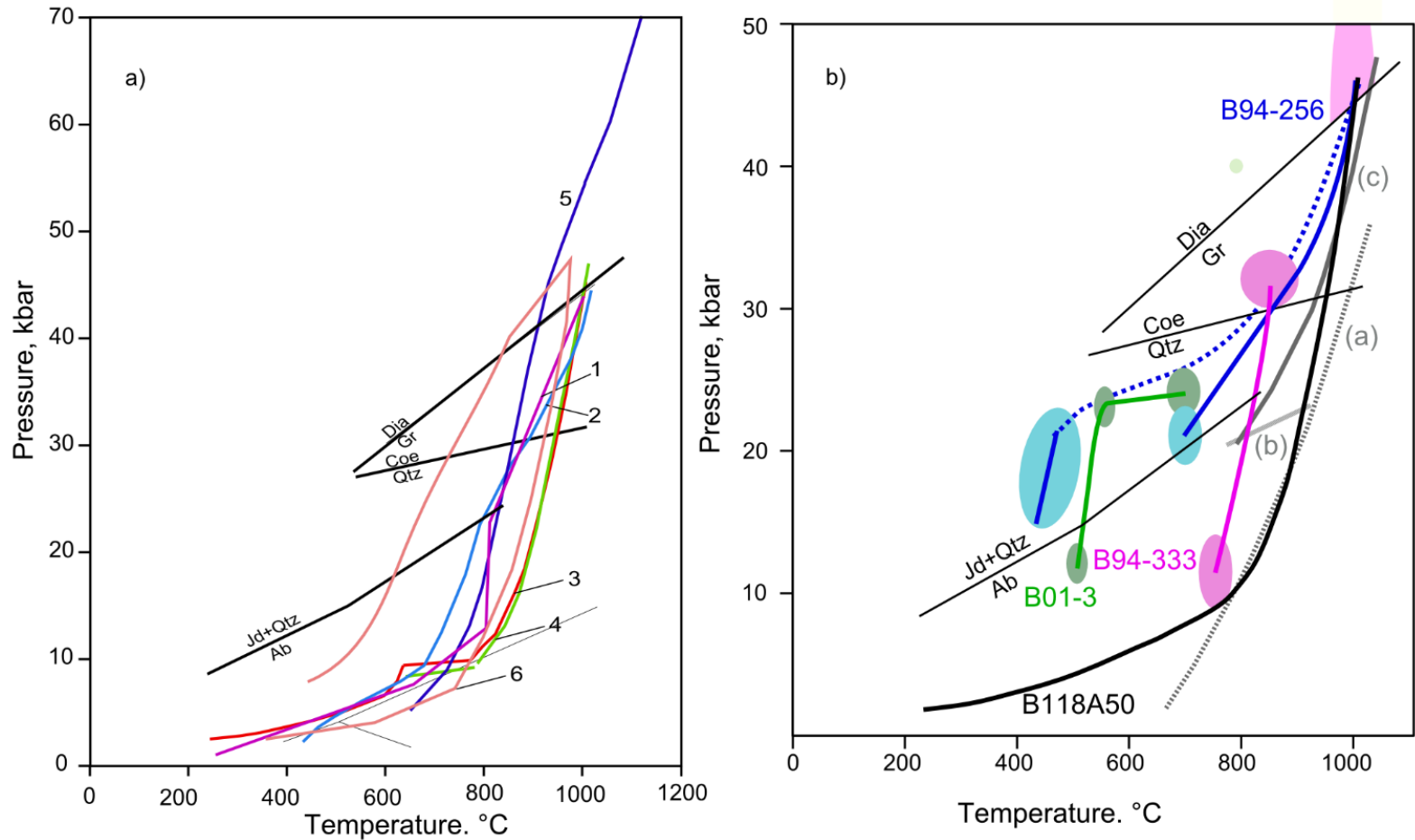
- Domain 1: prograde zircon: formed before metamorphic peak when monazite was in the rock.
- Domain 2: Highest T, peak UHP conditions.
- Domain 3: exhumation.
- Domain 4: crystallization of exhumation melt.



Applications of LA-ICP-MS to UHP metamorphic rocks

Trace element in garnet and zircon: Conclusions

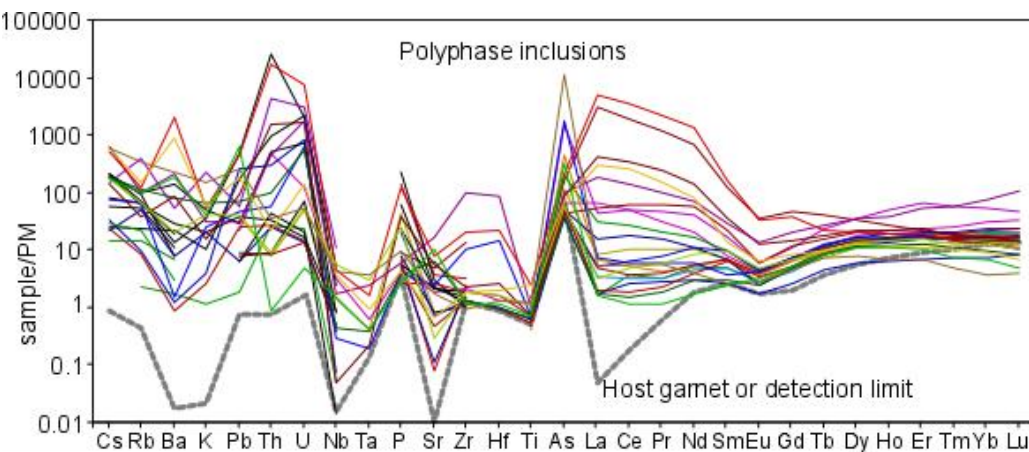
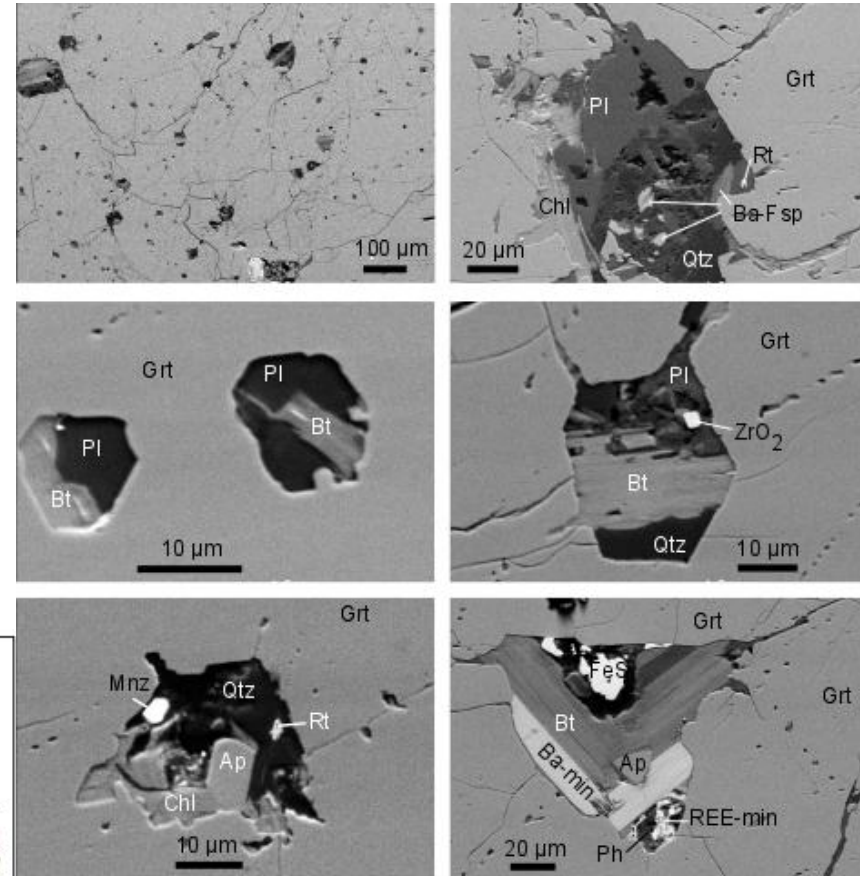
- The combination of data from the conventional geothermobarometers and trace element data allow new constraints on PT evolution of the rocks of the Kokchetav complex.



Applications of LA-ICP-MS to UHP metamorphic rocks

Melt inclusions: multi phase solid inclusions

- The sample of UHP gneiss from the Kokchetav complex, Kazakhstan contains garnet with abundant multi phase solid inclusions (MSI).
- The inclusions are composed of more than 30 minerals and record disequilibrium assemblages.
- LA-ICP-MS of the multi phase solid inclusions is possible but the result is of little use: the heterogeneity is too great.



Stepanov A. S., Hermann J., Rubatto D., Korsakov A. V., Danyushevsky L. D. Melting history of the Kokchetav ultrahigh-pressure gneiss revealed by polyphase inclusions in garnet, under review at Journal of Petrology.

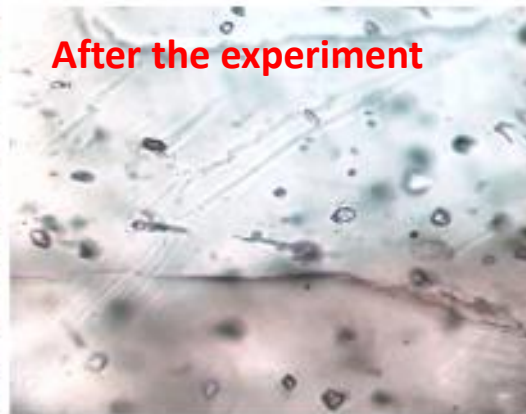
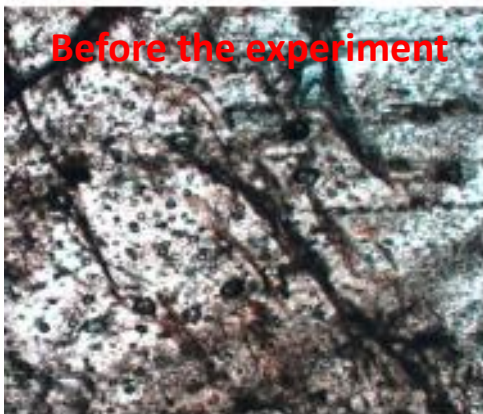
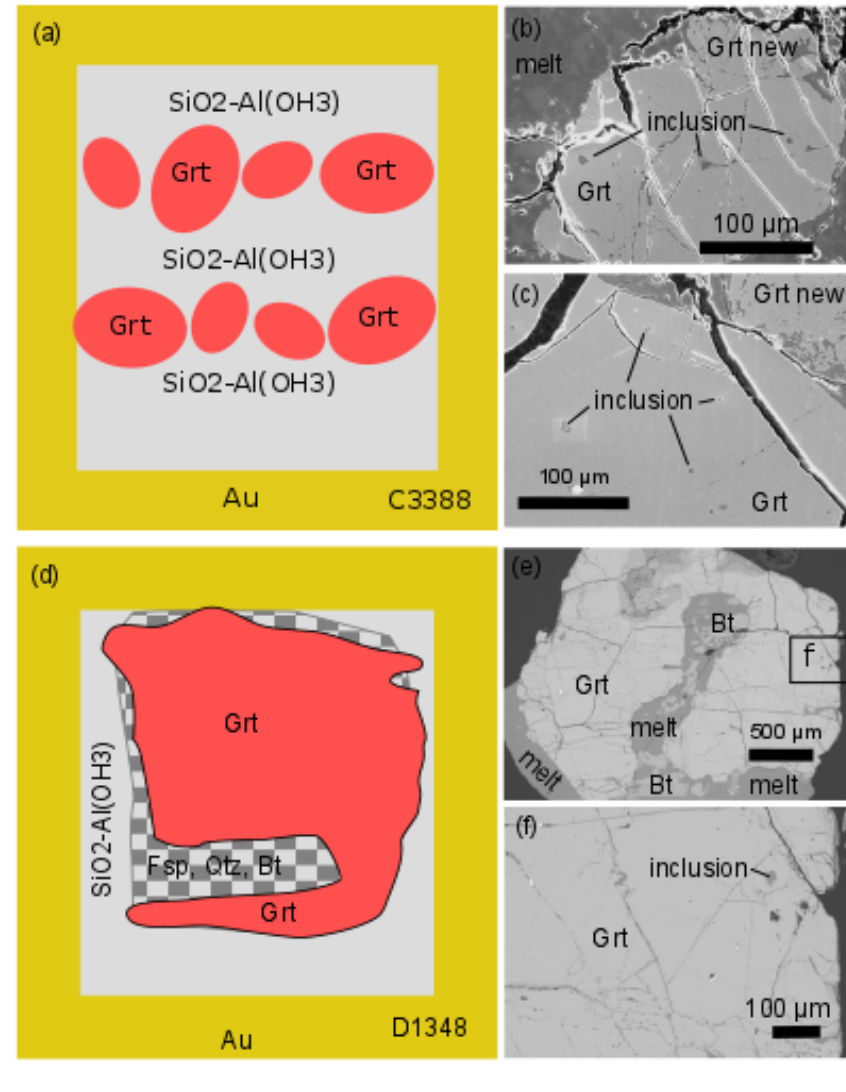
Applications of LA-ICP-MS to UHP metamorphic rocks

Melt inclusions: homogenisation experiments

- Inclusions were homogenised using piston cylinder experimental presses.

Analytical set up

- Analyses with 15-20 μm spot
- NIST610 standard (sufficiently high P and K)
- Short dwell time for better resolution of inclusion signal



Applications of LA-ICP-MS to UHP metamorphic rocks

Melt inclusions: Calculation of inclusion compositions

- The LA analyses produced mixtures of inclusion and host garnet. We need to extract inclusion signal from the mixed signal. The main equation of LA-ICP-MS:

$$\left(\frac{cps_{STD}^{EL}}{ppm_{STD}^{EL}} \right) / \left(\frac{cps_{STD}^{IS}}{ppm_{STD}^{IS}} \right) = \left(\frac{cps_{unk}^{EL}}{ppm_{unk}^{EL}} \right) / \left(\frac{cps_{unk}^{IS}}{ppm_{unk}^{IS}} \right)$$

- For mixed signal of inclusion and host garnet this can be transformed to:

$$\left(\frac{cps_{STD}^{EL}}{ppm_{STD}^{EL}} \right) / \left(\frac{cps_{STD}^{IS}}{ppm_{STD}^{IS}} \right) = \left(\frac{cps_{inc}^{EL}}{x \cdot ppm_{inc}^{EL} + (1-x) \cdot ppm_{Grt}^{EL}} \right) / \left(\frac{cps_{inc}^{IS}}{x \cdot ppm_{inc}^{IS} + (1-x) \cdot ppm_{Grt}^{IS}} \right)$$

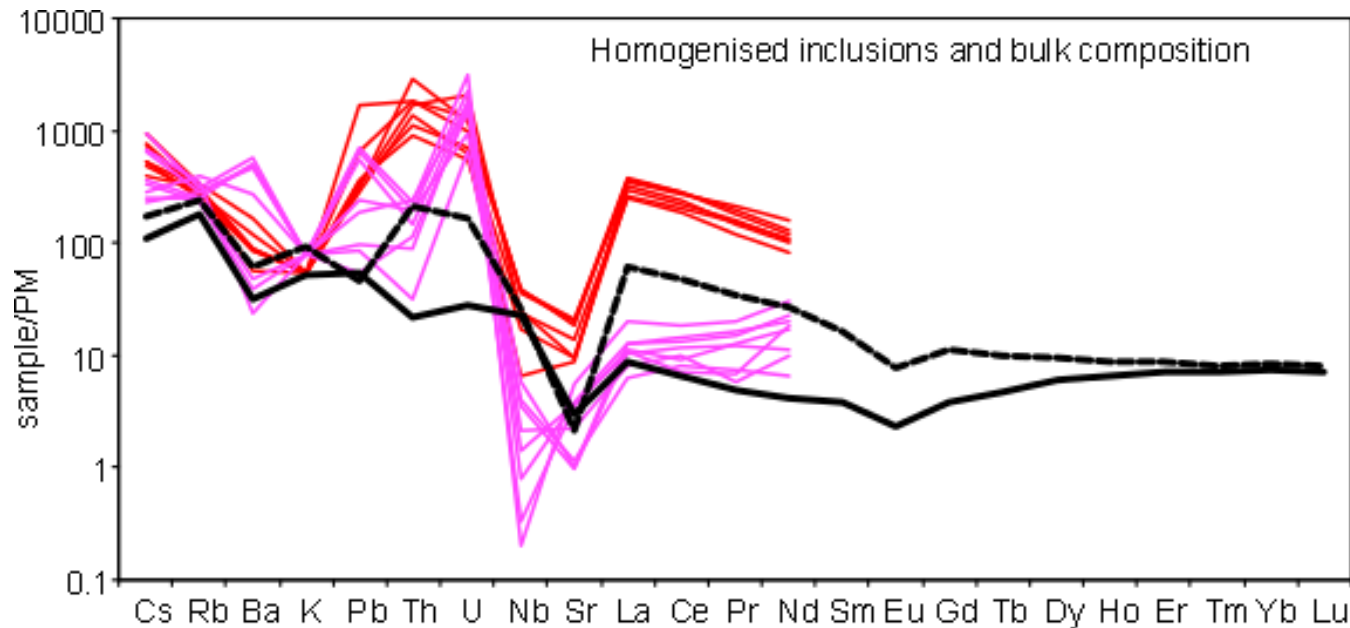
- Where x is amount of host garnet in the mixed analysis. x can be calculated when two elements are known.
- The difference between this formula and equation by Pettke is that it allows to reduce the mixed LA data without making assumptions about composition of the mix however it requires to know concentration of 2 elements in inclusions.

Applications of LA-ICP-MS to UHP metamorphic rocks

Melt inclusions: Results

We found two types of melts in inclusions:

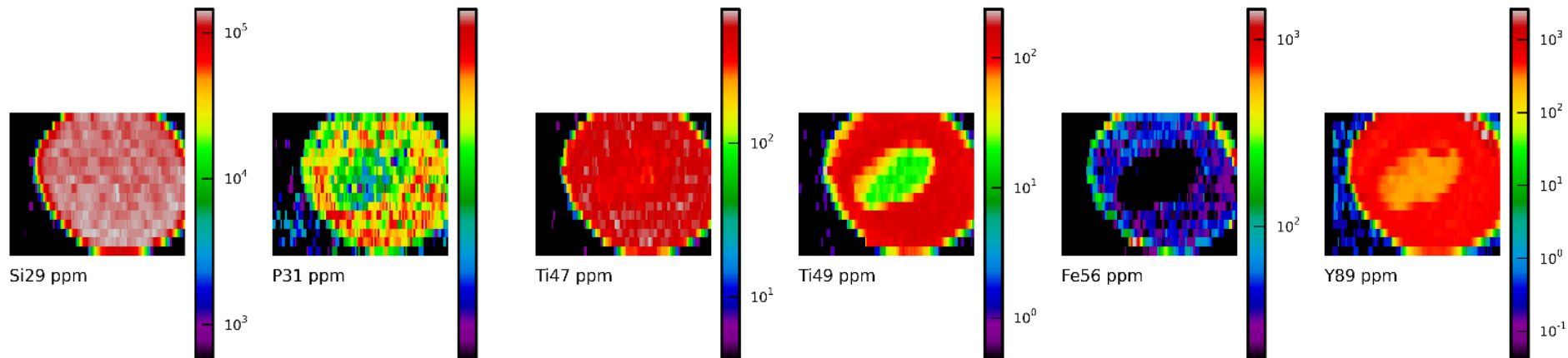
- Type-M melt inclusions occur in garnet from melanosome part. Have very high LREE, Th and U contents. These inclusions are interpreted to form at peak conditions.
- Type-L melt inclusions occur in garnet from leucosome part of the rock. These inclusions have low LREE and elevated U. These melts formed during rock exhumation.



Applications of LA-ICP-MS to UHP metamorphic rocks

Conclusions

- LA-ICP-MS is an extremely powerful tool capable to resolve numerous problem in petrology of UHP metamorphic rocks:
- T constraints can be obtained with several powerful geothermometers
- Link different minerals to each other and events in the rock:
 - Equilibrium-disequilibrium between minerals
 - Depletion of the system in some components
- LA-ICP-MS is currently the best method for measurement of multy-element composition of metamorphic fluids and melts



Applications of LA-ICP-MS to UHP metamorphic rocks

Future developments

- Femto second lasers: more homogeneous signal, less fractionation.
- Laser induces breakdown spectroscopy (LIBS): Raman spectroscopy of light emitted during ablation. Possibility to analyze the last elements remaining inaccessible.
- Time of flight ICP-MS : measure all (almost) masses at the same time. Improved limits of detection, sensitivity and spatial resolution.
- Developments in the processing of mixed laser signal
- ??

LA-ICP-MS systems

LA-ICP-MS systems at the University of Tasmania

- Four laser ablation instruments
 - 193 and 213 lasers
 - Agilent 7700 and 7900 mass spectrometers
- Dedicated instruments for:
 - U-Pb geochronology (low Pb backgrounds)
 - Silicate trace element analyses (low Li and B backgrounds)
 - Sulfide trace element analyses
- Clean lab for wet chemistry



Thank you for your attention