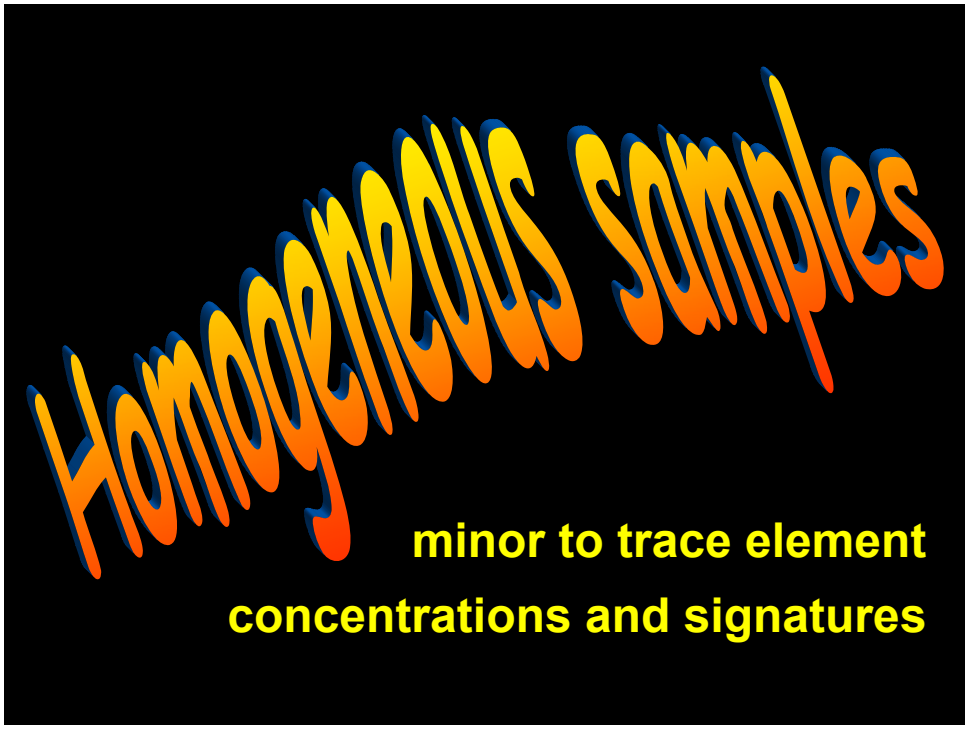
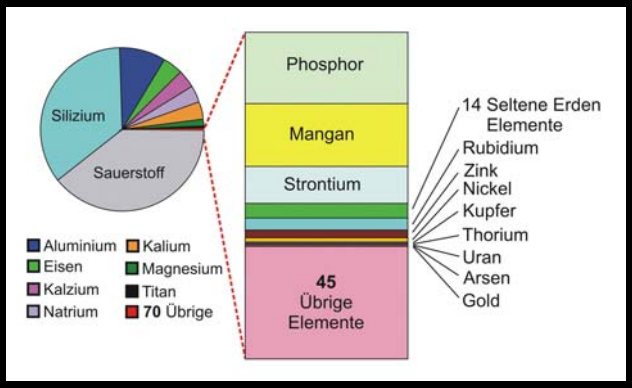
LA-ICP-MS promising, because

Thomas Pettke

- Matrix "independence" possible: Standardization "little" problematic (SRM glasses from NIST). Example: Silicate glass suitable for silicate, oxide and carbonate minerals (but recall matrix-related interferences)
- External analytical precision ca. 1% uncertainty, due to sequential recording of a flickering signal
- Limits of detection of sub-ng/g attainable
- High sample throughput (~70 spots per day)
- Enormous dynamic range of signal detection: → Major to trace elements possible within one shot!



A typical granite, there exist more than 80 elements



Of these, we can detect about 60 in a single LA-ICP-MS analysis.

→ **Petrogenetic information, ...**

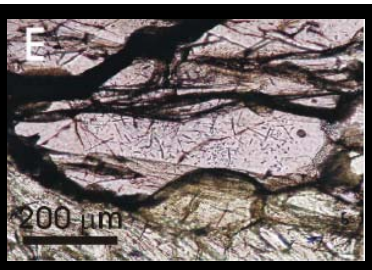
Go in-situ "on the rocks"

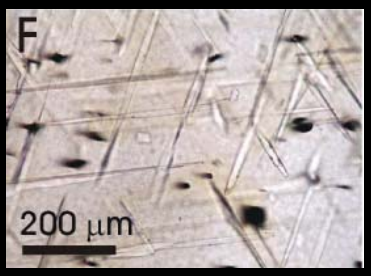
Mineral chemistry in rocks and element distribution between coexisting minerals

Hundreds of papers ...

Element (re)distribution between minerals during prograde reactions (magmatic - metamorphic - ...)

Veins cutting old opx

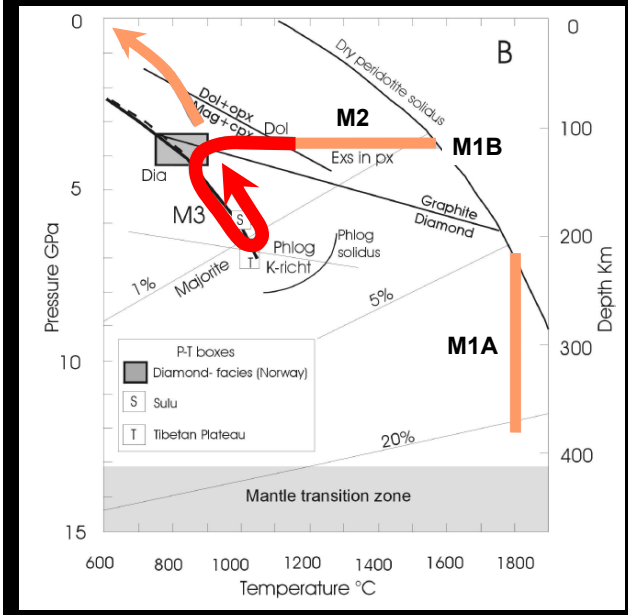




Textural difference between pre-Caledonian and Caledonian majoritic grt

Scambelluri et al. (Geology, 2008)

Petrogenetic summary of WGR genesis



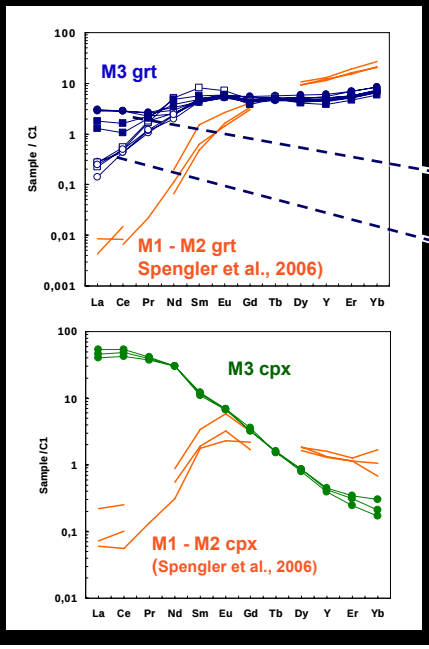
Key observations:

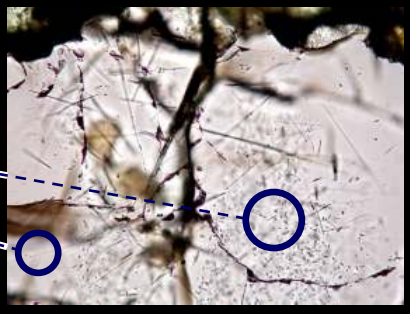
1) **M1-M2 and M3 majoritic grt texturally distinct**
2) **Phlogopite indicative of fluid presence**
3) **K-richterite absent.**
4) **Multiphase inclusion can contain diamond (Van Roermund et al., 2002)**

Ultradeep metamorphism and C-O-H - silicate fluid infiltration down to 6-7 GPa and 900-1000 °C.

Scambelluri et al. (Geology, 2008)

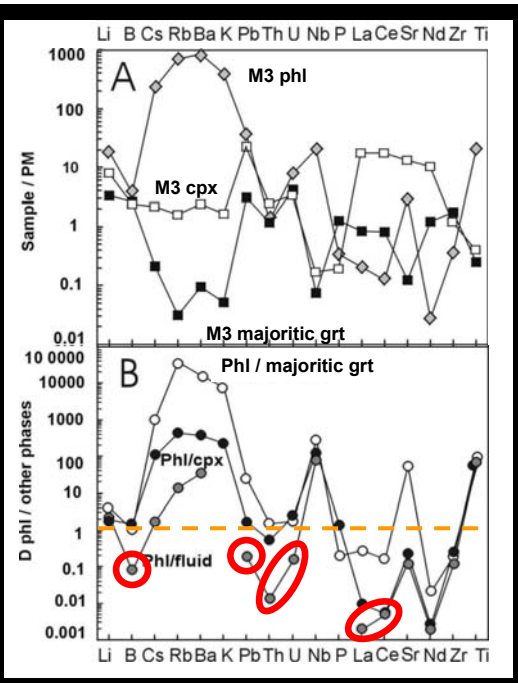
REE compositions of UHP grt and cpx





Prominent LREE enrichment points to metasomatism by a "fertile" component

Scambelluri et al. (Geology, 2008)



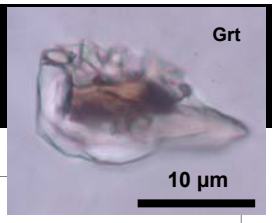
Scambelluri et al. (Geology, 2008)

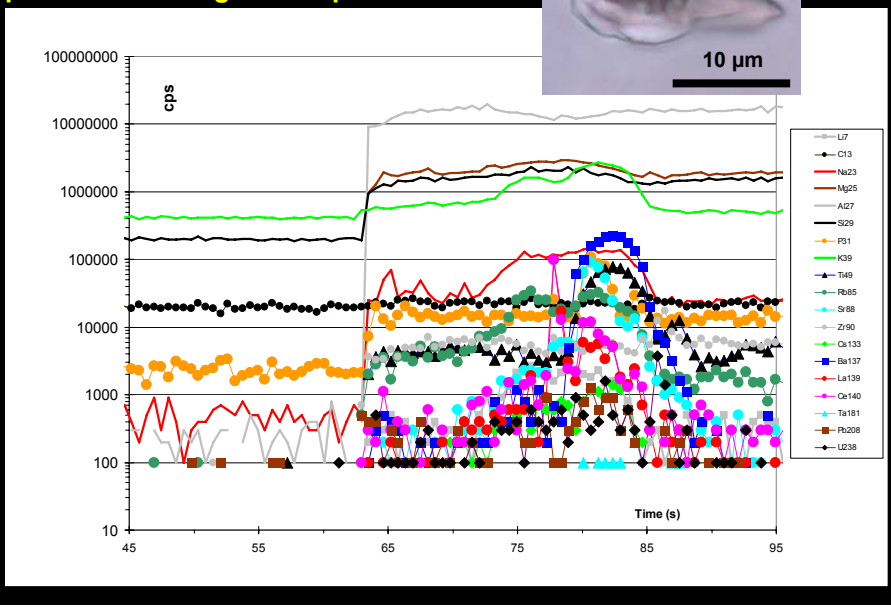
- **Phl is identified as major UHP carrier of LILE (mirrored patterns)**
- **Phl/Fluid partition coefficients calculated taking the fluid composition estimated using M3 majoritic grt and the grt - fluid partition coefficients of Kessel et al. (2005) at 6 GPa**

For the given paragenesis fluid+grt+cpx+opx+phl±carb±spl, the following elements can be expected to partition into the fluid at ca. 200 km depth: B, Pb, Th, U, ± LREE?
→ Other thought-to-be characteristic fluid elements are retained in phl!

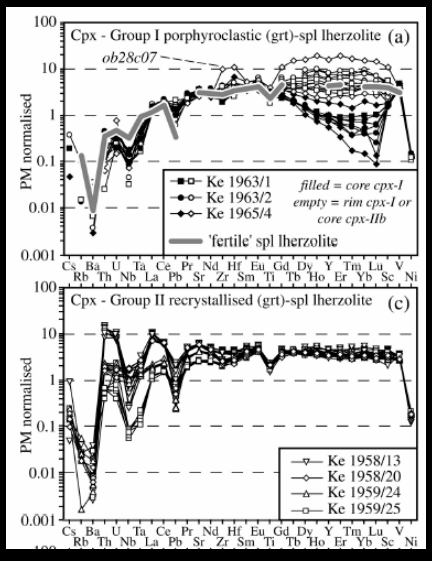
At UHP, phlogopite is a LILE repository

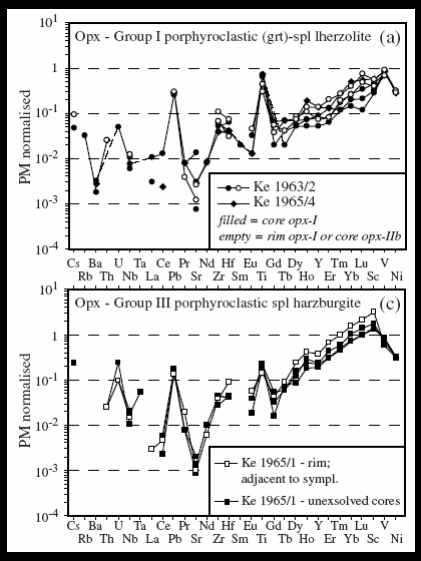
Polyphase inclusions.
Key problem: Unmix the mixed host plus inclusion signal into pure inclusion



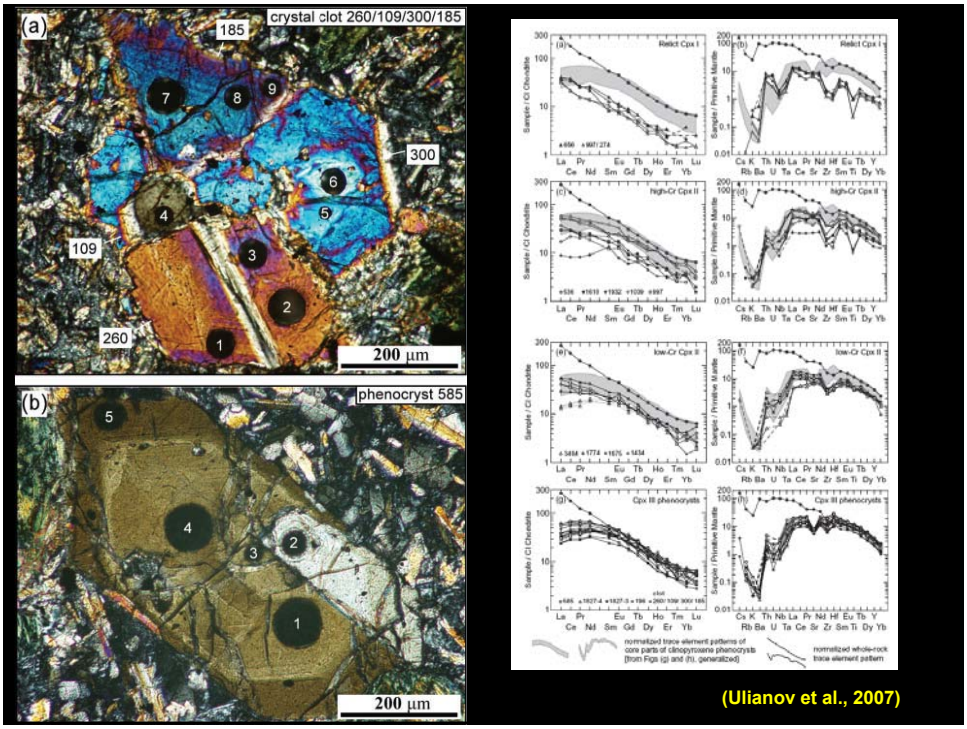


Trace elements in pyroxene, to unravel the genesis of East African rift xenoliths

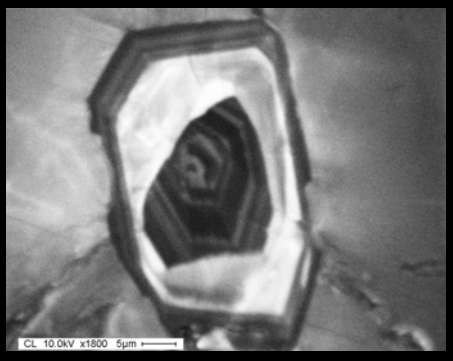




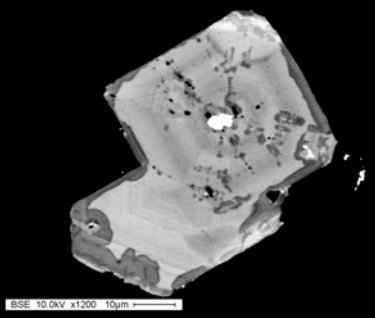
Kaeser et al., 2006, 2007, 2009



Zircon trace element systematics

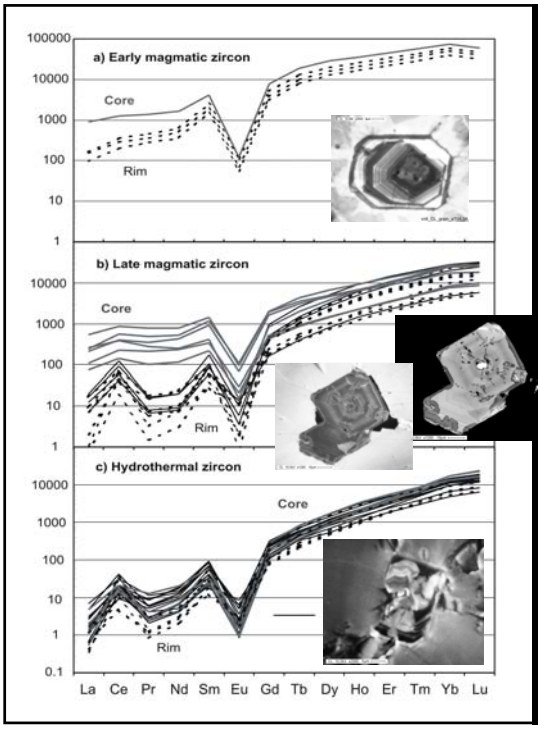


Trace element patterns of accessory minerals monitor ...



... magma evolution or metamorphic processes. Example: zircon

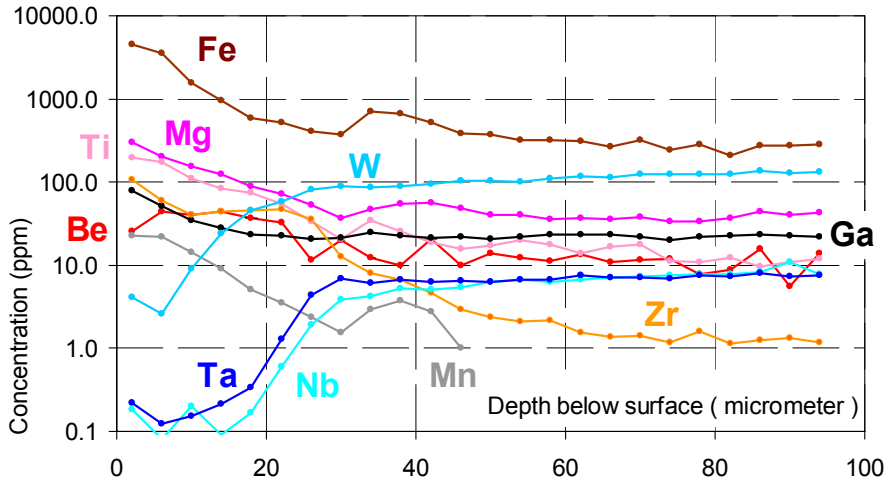
Pettke et al., 2005, Chem Geol
Schaltegger et al., 2005, Chem Geol



- Early magmatic zircon: extremely high REE contents, no Ce anomaly
- Progressive crystallization and fluid exsolution: Decrease in LREE, formation of positive Ce-anomaly; mirrored by core-rim trends
- Hydrothermal zircon uniform, indistinguishable from late magmatic zircon

(Pettke et al., 2005)

Depth profiling in sapphire perpendicular to cut surface
Each point corresponds to 3 laser pulses (i.e., ca. 0.3 µm)

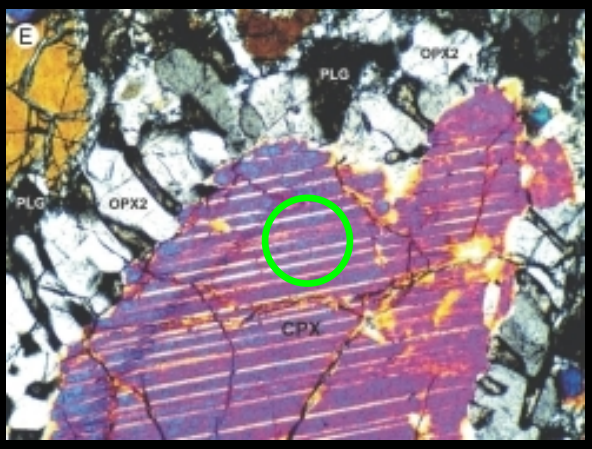


Heterogeneous samples

Reconstruction of the bulk composition of the single phase at the time of formation

Possible because we analyze a sample VOLUME

Heterogeneous phases



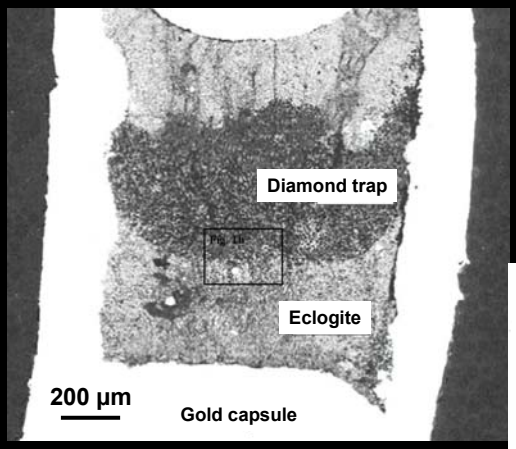
Unmixing:
OPx lamellae
in CPx

Piccardo et al. (2004)

Reconstruction of homogeneous cpx composition at formation conditions, i.e., high P and T !

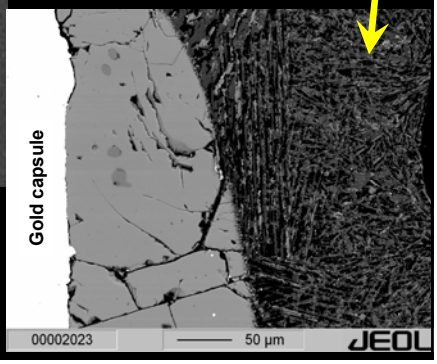
Also essential in metallurgy

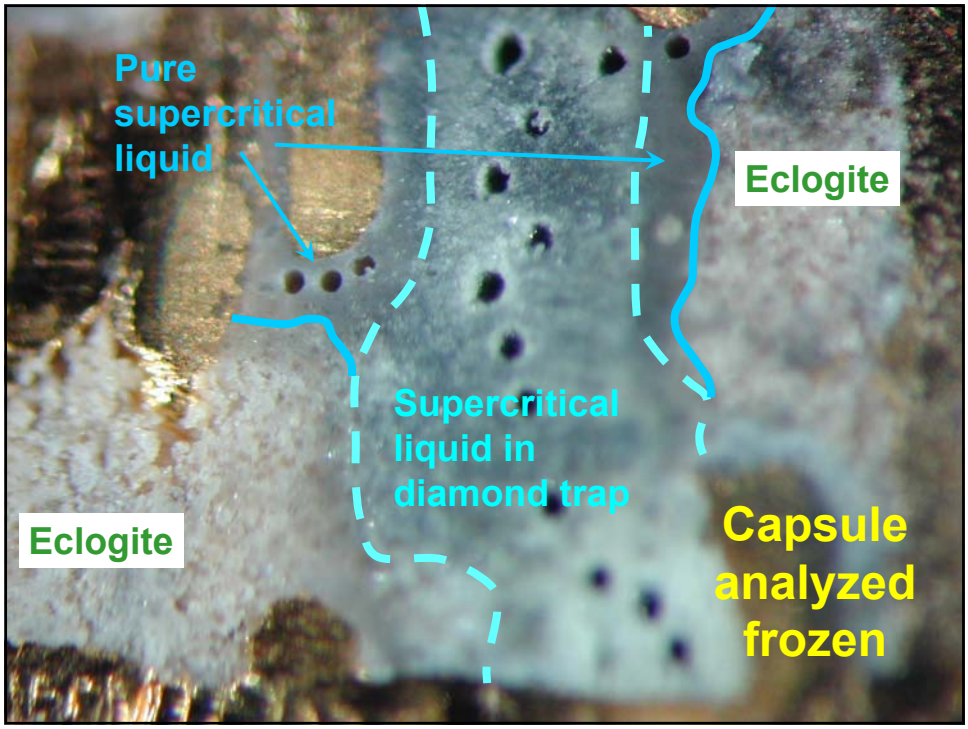
High-P experiment



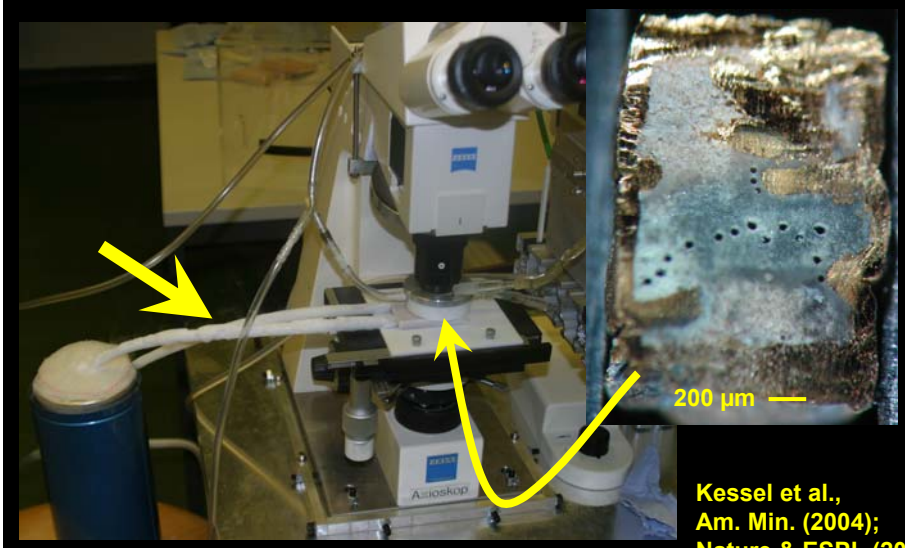
simulates fluid equilibrated with rock to depths > 300 km

Problem:
Phase unmixing (crystallization) upon quench

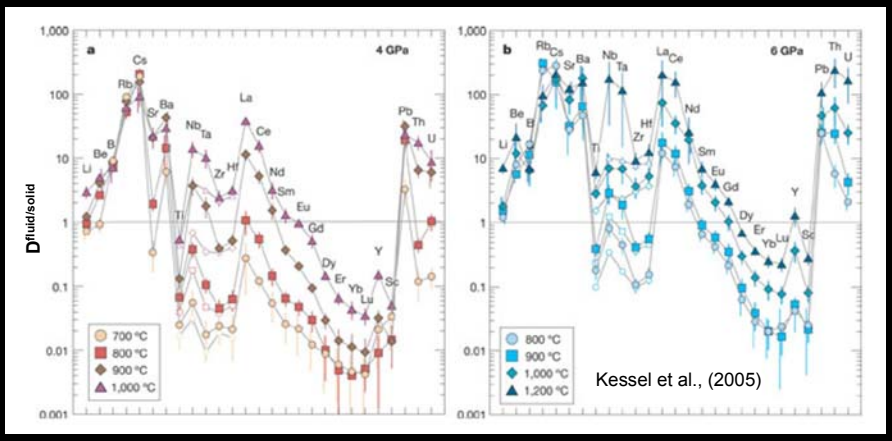




Heterogeneous phase mixture analyzed frozen



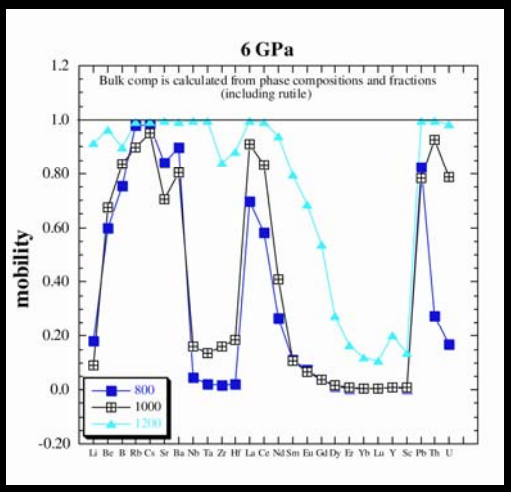
Kessel et al.,
Am. Min. (2004);
Nature & ESPL (2005)



In very much the same way as for major elements, the stable residual mineral assemblage determines which trace elements will be partitioned into the fluids. A given mineral commonly represents a sink for a suite of trace elements, e.g., garnet for the heavy REE.

Kessel et al., 2004, Am. Min.; 2005, Nature & ESPL

Transfer rate of elements from the subducting crust to the mantle wedge



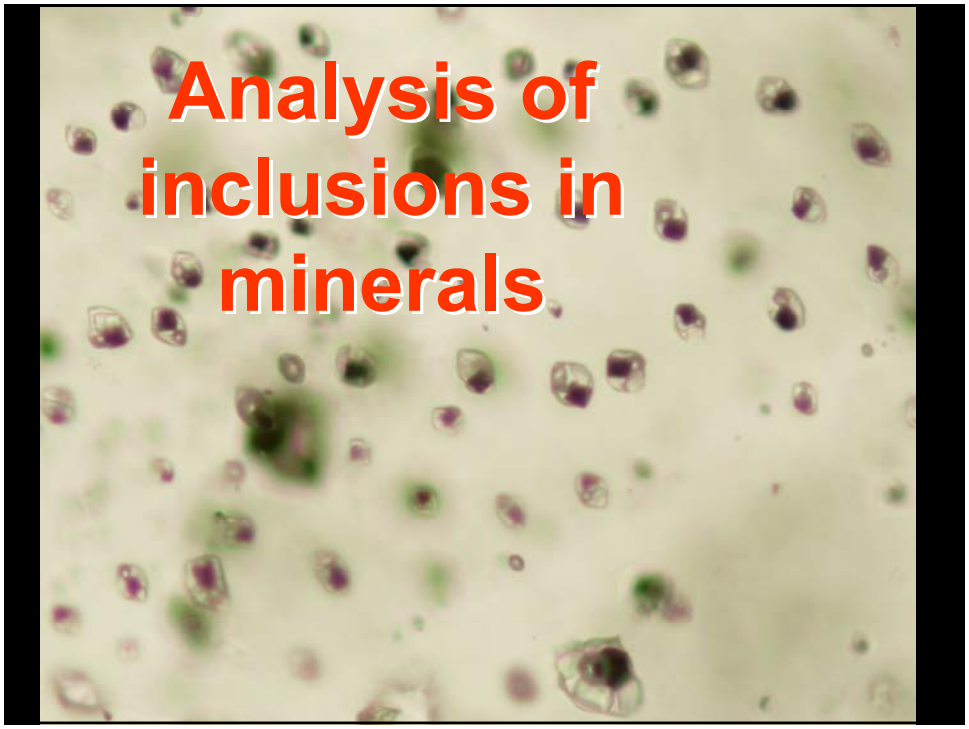
Supercritical liquids will transfer
- 60-70% Be
- extreme REE fractionation
- high Ba/La
- Th/U excess
- leave rutile in the residue and strong negative Nb/Ta anomalies

Classical fluids are distinguished by
- Low Be mobility (< 10%)
- U/Th excess
- no REE mobility/fractionation

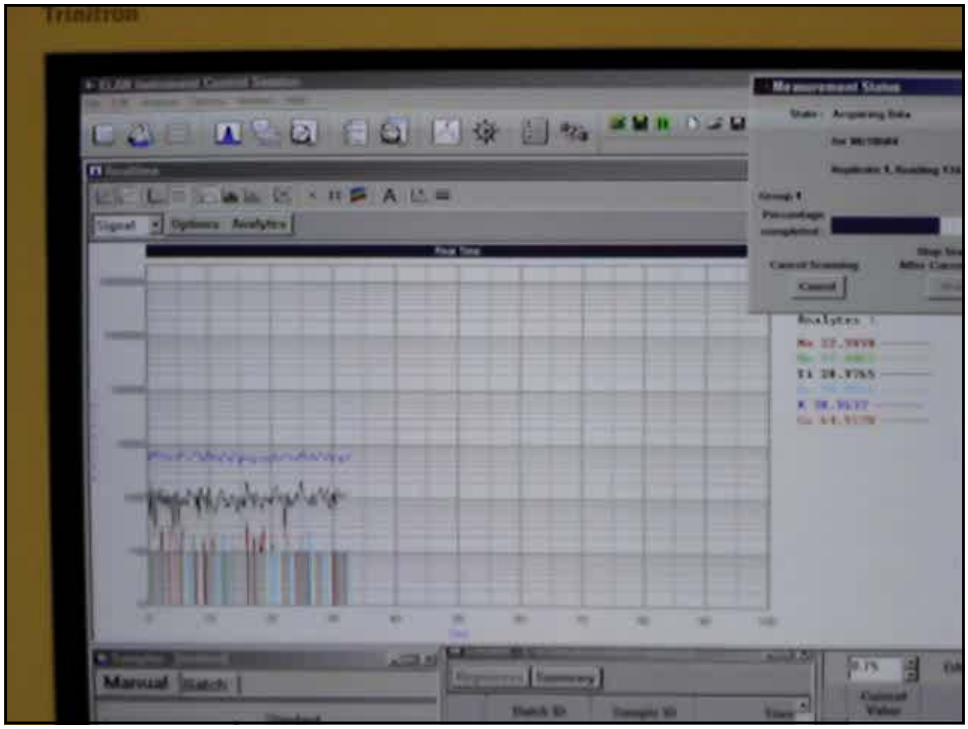
Classical melts have
- Low Ba/La
- little or no residual rutile and Nb,Ta anomaly

Supercritical liquids in the following arcs: Vanuatu, Marianas, Tonga-Kermadec

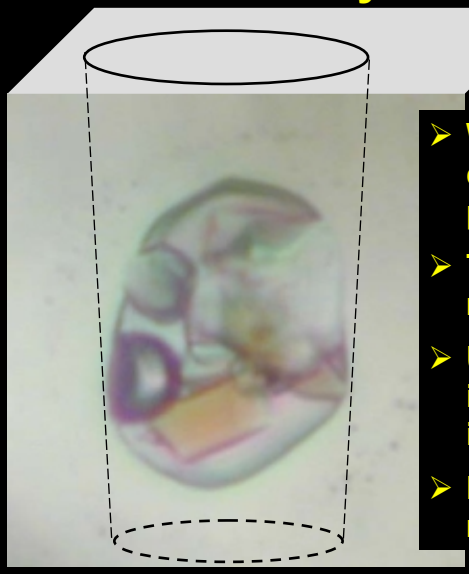
Analysis of inclusions in minerals


Analysis of
inclusions in
minerals


SONY

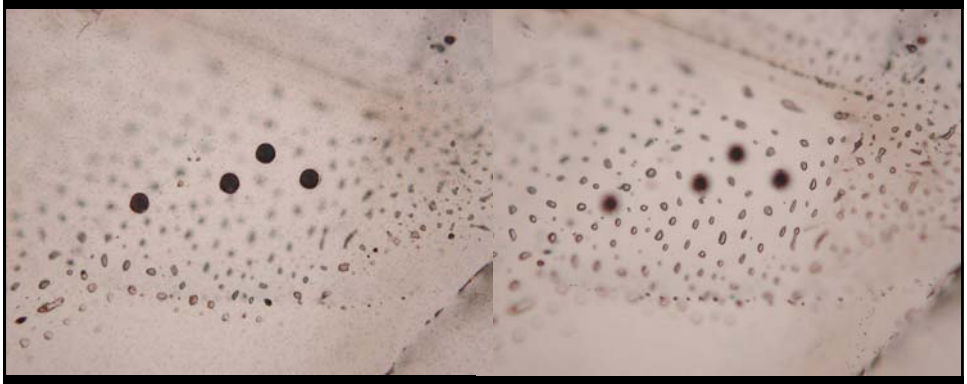


Inclusion analysis: The analytical challenge

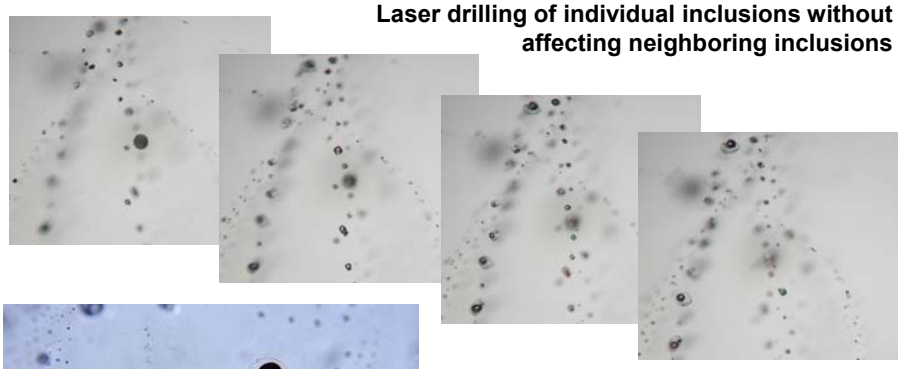


- We want to know the composition (i.e., single phase) at entrapment time
- The entire content must be analysed
- Unmix the mixed inclusion + host signal into pure inclusion
- High degree of matrix mismatch

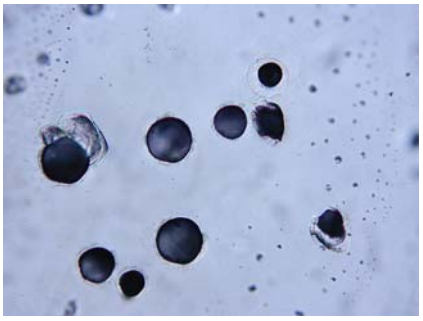
Fluid inclusions in quartz: Direct sample of the metal-transporting agent



Controlled ablation of individual inclusions

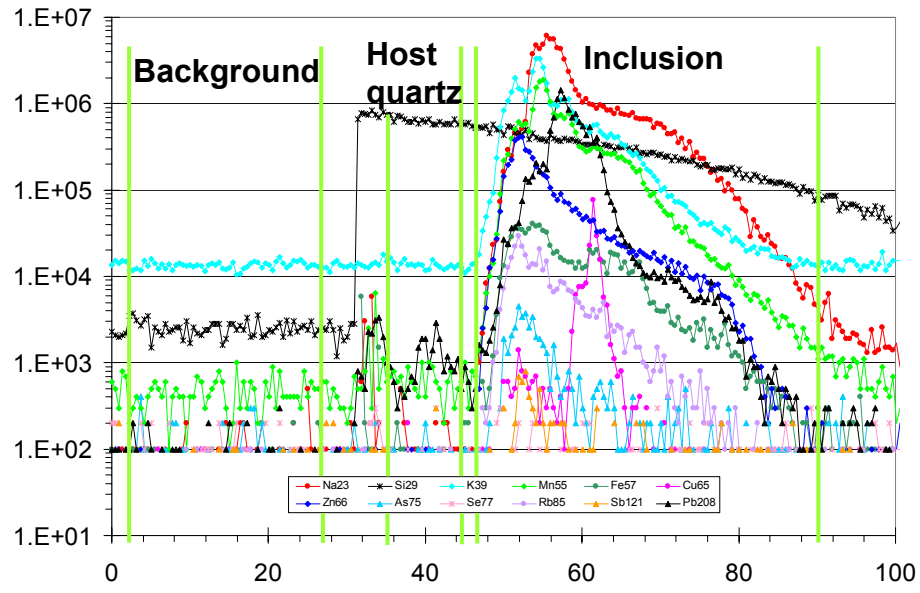


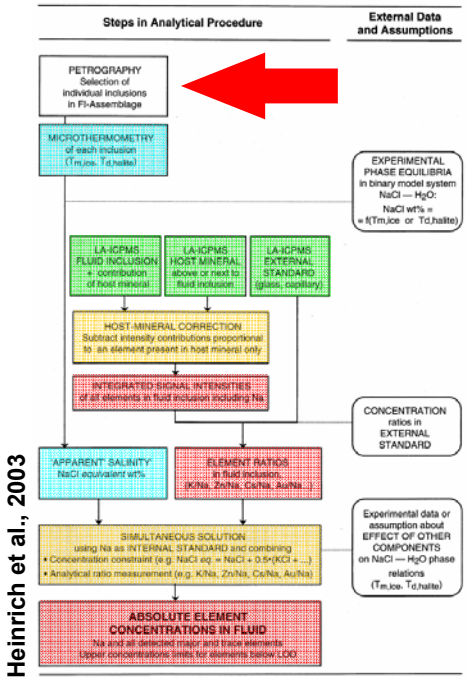
Laser drilling of individual inclusions without affecting neighboring inclusions



Analysis of inclusion assemblages, obtaining assemblage compositions by averaging individual inclusions

Complex signals





Data reduction step-by-step

1) Data are recorded as cps, i.e., COUNT RATES

2) Calculate the gross count rates for the ENTIRE FI signal

3) Correct for machine background → arrive at bkg-corr cps

4) Subtract the host mineral contribution from the FI +host signal, again all based on bkg-corr cps and normalized to an element exclusively present in the host (e.g., Si)

5) Determine for all the elements their respective sensitivities for the external standard (i.e., cps/ppm). Arrive at element sensitivity ratios

6) Use the $NaCl_{equiv}$ value from microthermometry to determine the relative sensitivity factor, RSF, between external standard and sample. Arrive at apparent element concentrations in the fluid inclusion

7) Correct the $NaCl_{equiv}$ value for the presence of Cl-complexed cations other than Na based on the LA-ICP-MS analytical data, in order to obtain the best estimate for the Na concentration in the FI

8) Recalculate the apparent FI element concentrations to the TRUE ELEMENT CONCENTRATION by using this corrected Na concentration in the fluid inclusion

9) Calculate the Limit Of Detection (=LOD) for each individual element in each FI as (3stdev bkg)/sensitivity.

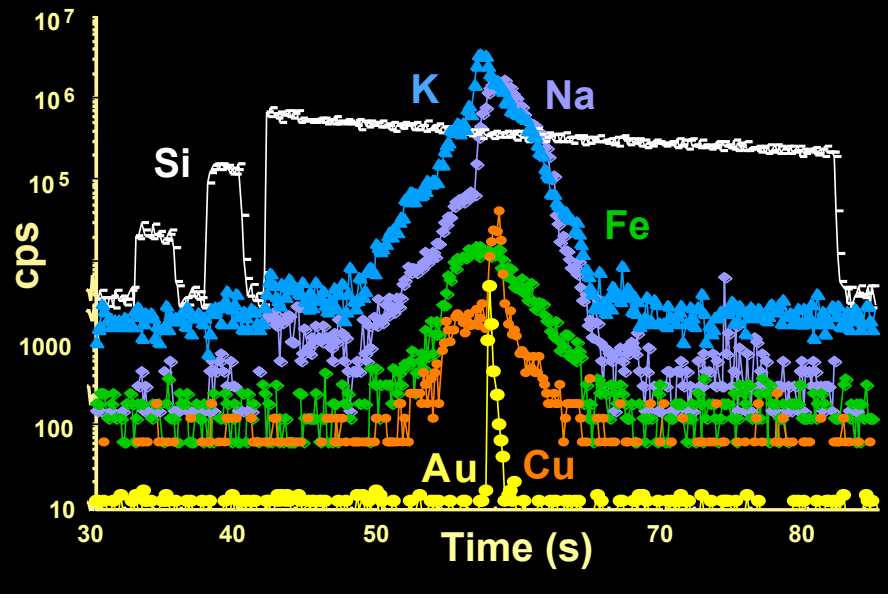
10) Filter the true element concentrations calculated above with the respective LOD

11) Report the data either as µg/g value or as < µg/g LOD

We thus need:

- Matrix INdependent external calibration
- INvariable element sensitivity ratios for standard and sample shots

Tiny daughter phases in MI, e.g., in fluid bubbles: Representative recording of fast, transient signals



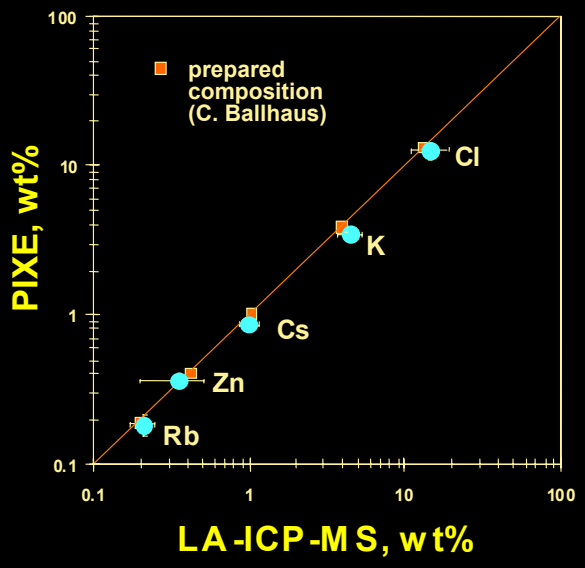
We need compromise conditions:

Fast recording protocols (short dwell times; (time per isotope and measurement),

thus "sacrificing" low LOD
(increasing dwell time lowers LOD)

Signal "smearing" is no option,
because this lowers signal / noise ratio
→ higher LOD for the analysis of inclusions

Accuracy



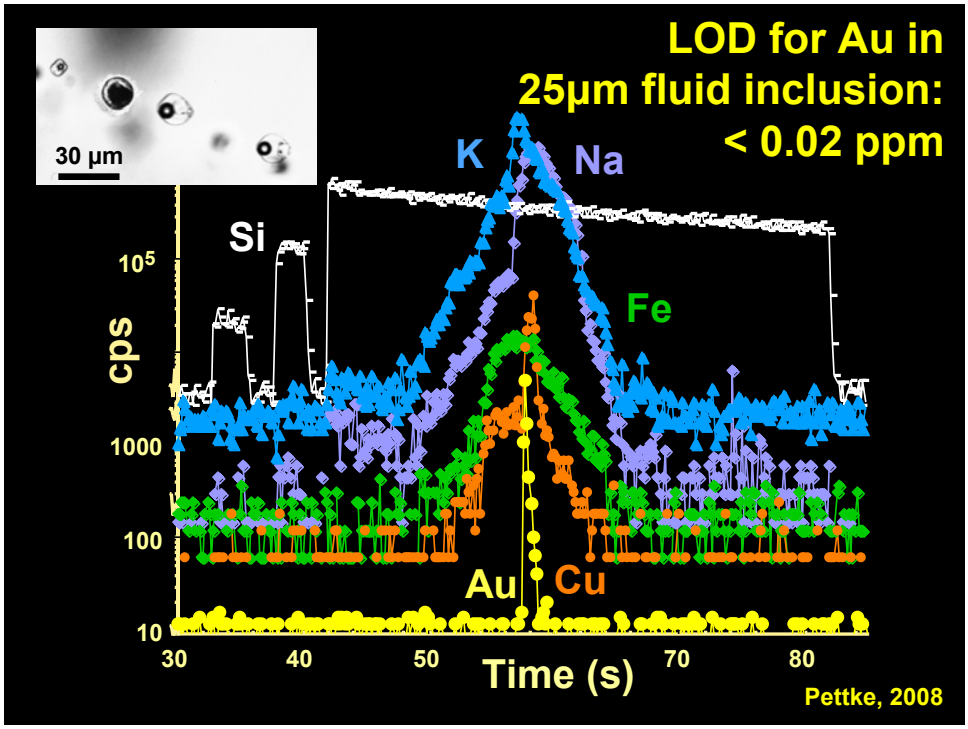
LA-ICP-MS
vs.
PIXE

(Ryan et al., 1995)

the identical synthetic inclusions analyzed

Na cannot be analyzed by PIXE

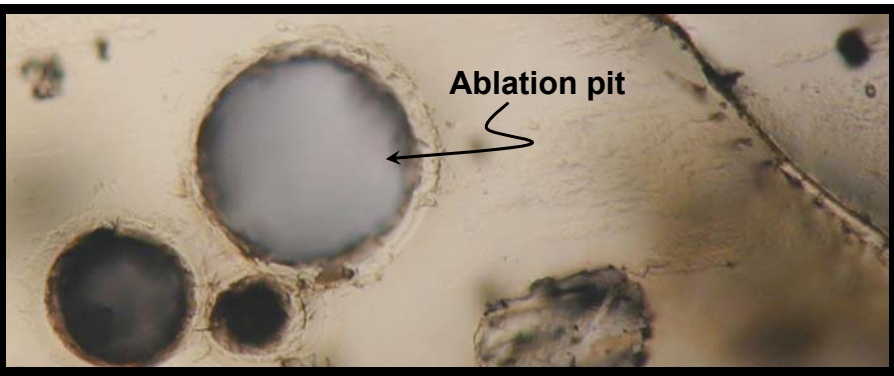
Heinrich et al., 2003, GCA



For inclusion analysis, consider

- ✓ Enough laser energy density on sample
- ✓ Homogenized energy distribution (allow for controlled inclusion ablation)
- ✓ Laser ablation in helium
- ✓ Robust plasma conditions, to maximize MATRIX INDEPENDENCE
- ✓ Low and constant gas backgrounds (LOD)
- ✓ Representative recording of transient signals
- ✓ Proper analyte isotope selection (interferences)

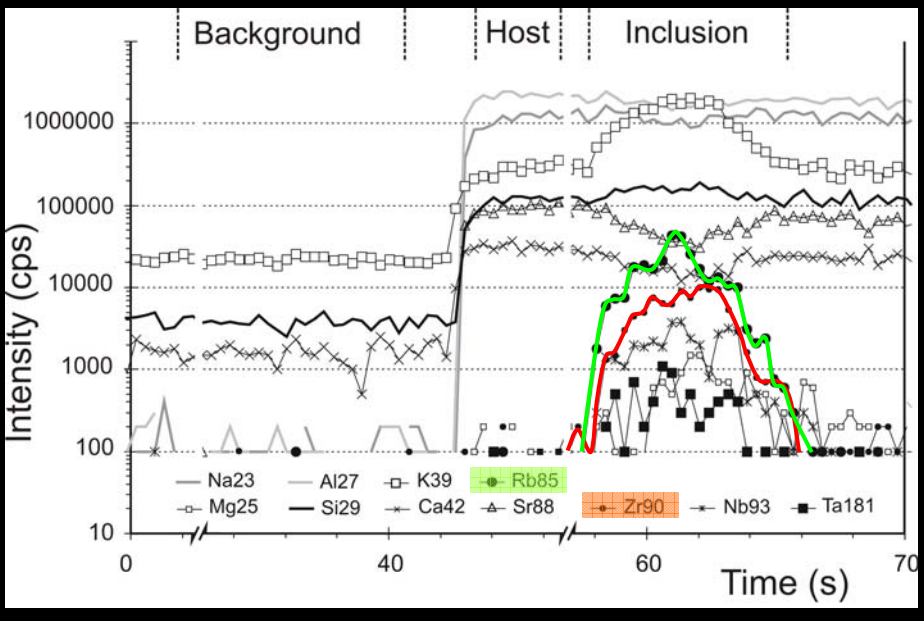
Pettke, 2006, 2008

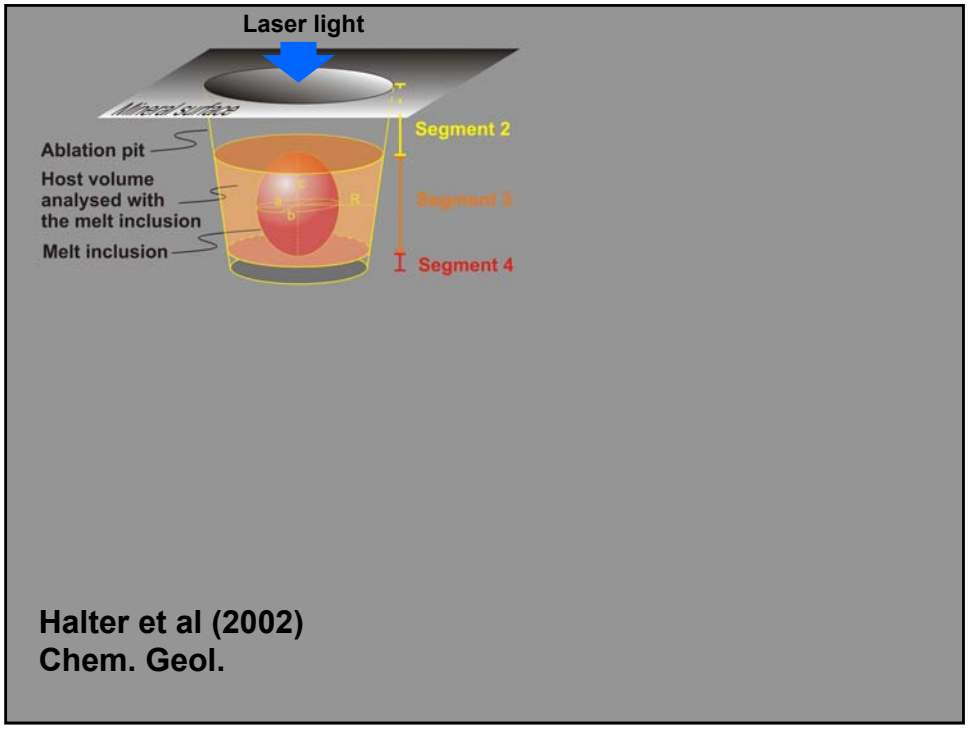


Perfect laser beam positioning required

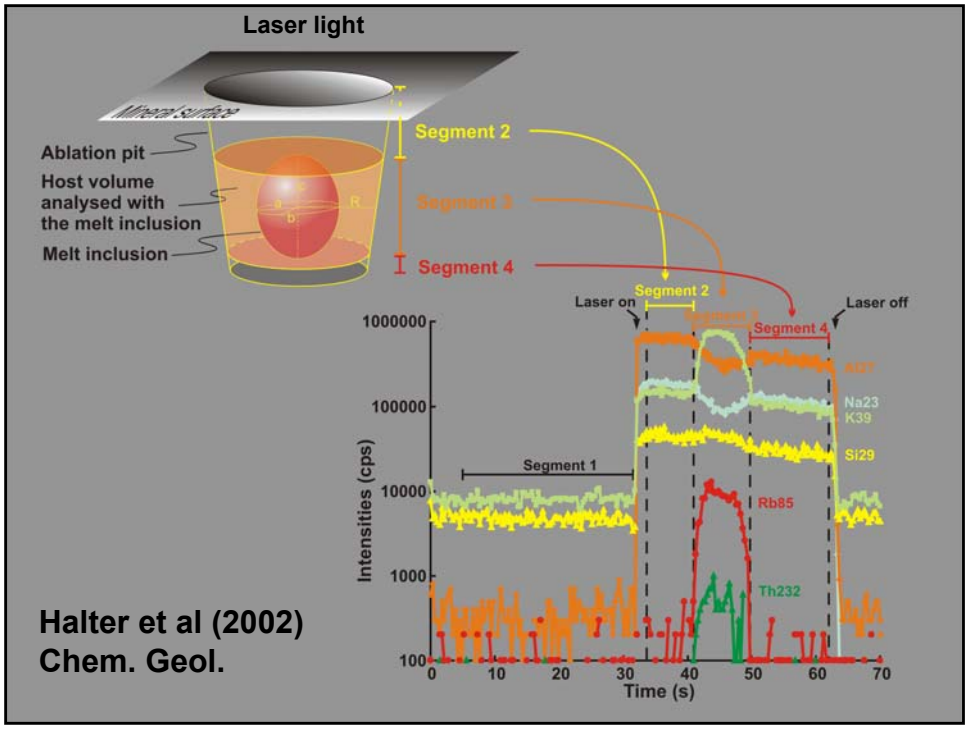
→ visual optics of LA-ICP-MS system

Signal variability in heterogeneous MI





Halter et al (2002) Chem. Geol.



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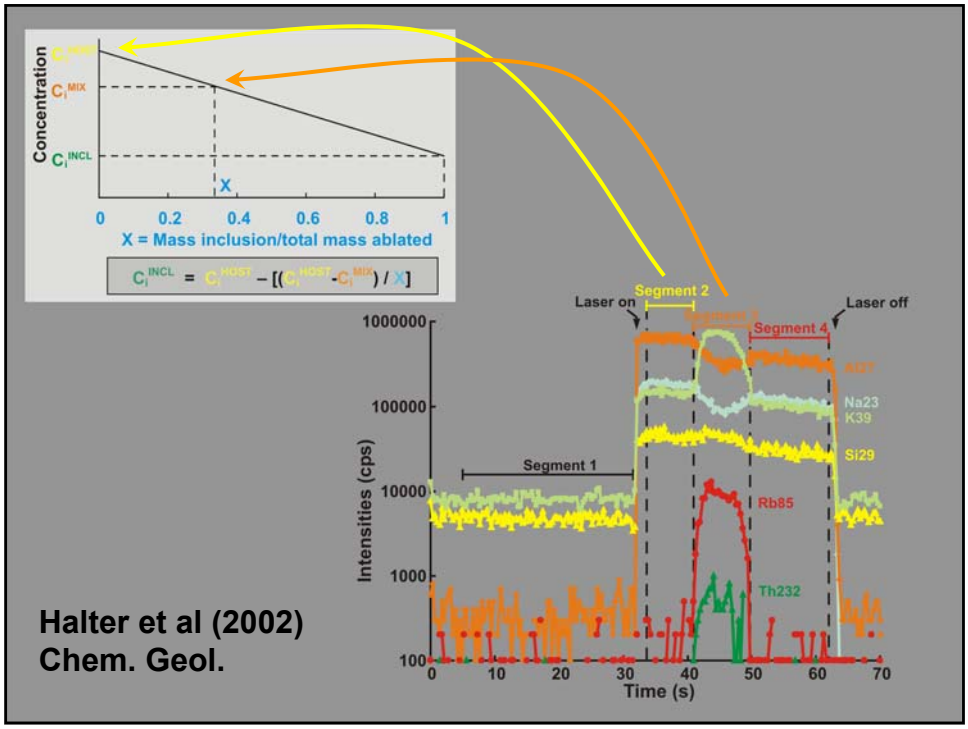
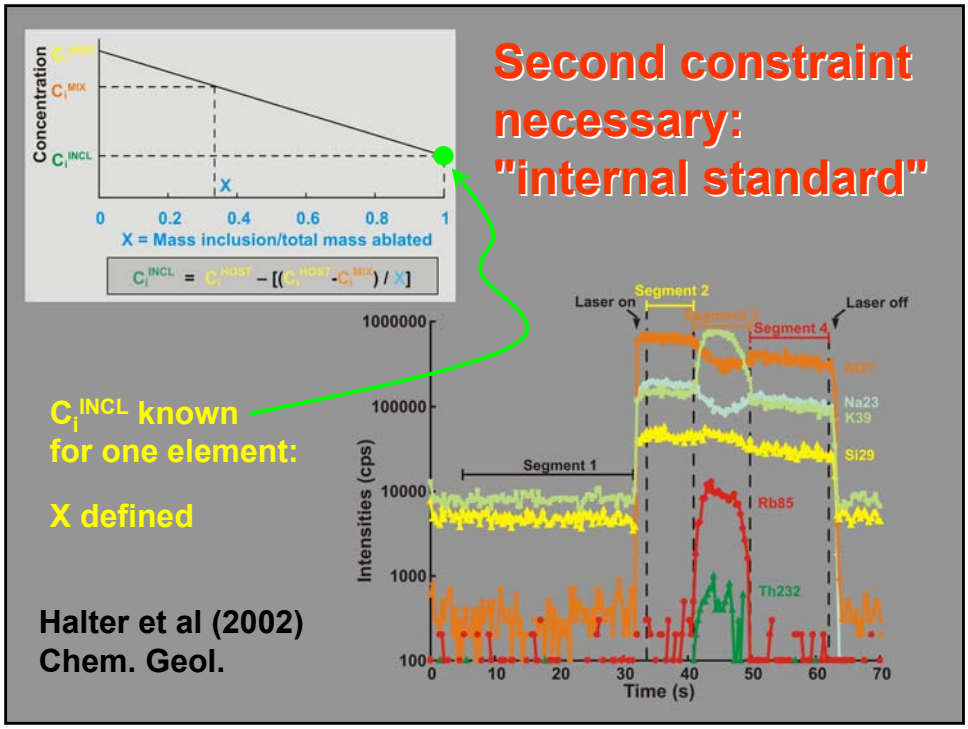


Halter et al (2002)
Chem. Geol.

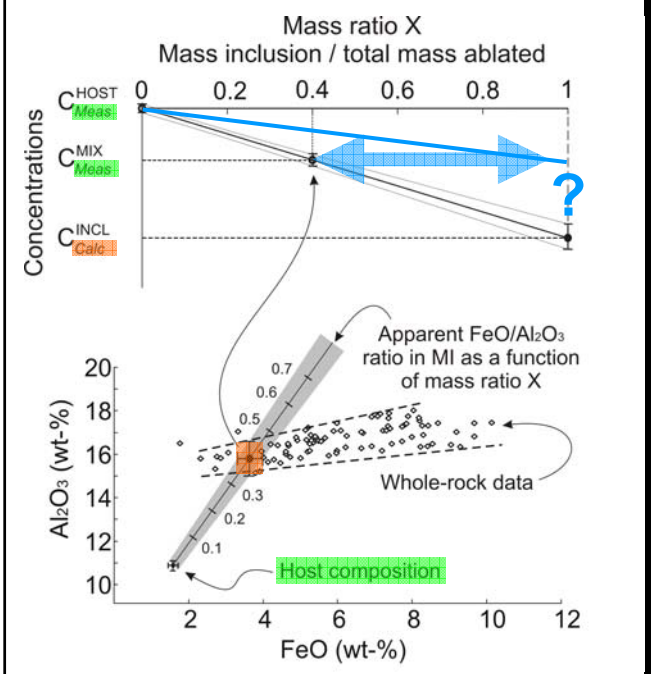


Second constraint necessary: "internal standard"

C_i^{INCL} known for one element:

X defined

Halter et al (2002)
Chem. Geol.



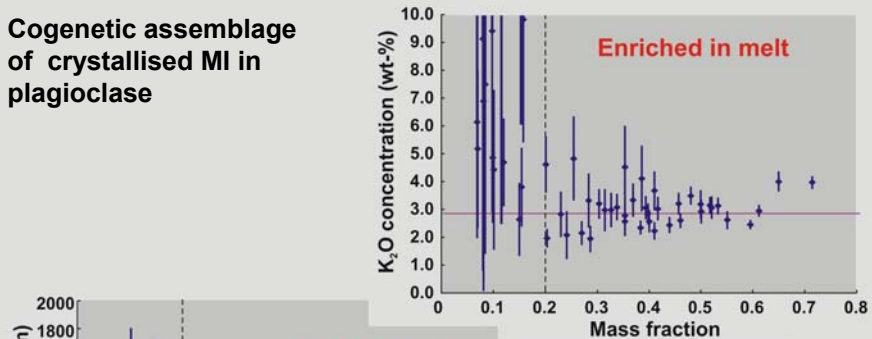
Second constraint:

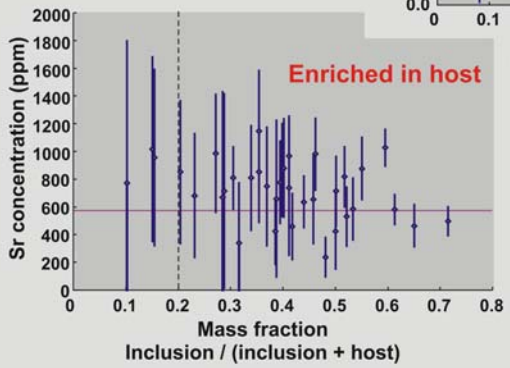
Concentration of one element or an element ratio at MI entrapment known independently to determine MI-analysis specific mass ratio, e.g., whole rock data.

This mass ratio is then used to calculate the element concentrations of this MI

Halter et al. (2002)
Pettke, (2006)

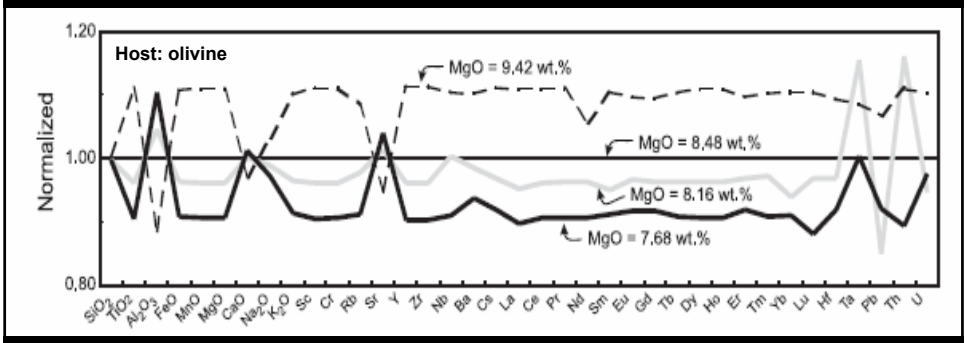
Cogenetic assemblage of crystallised MI in plagioclase





Uncertainties and detection limits depend on relative concentrations, X , and size of inclusion

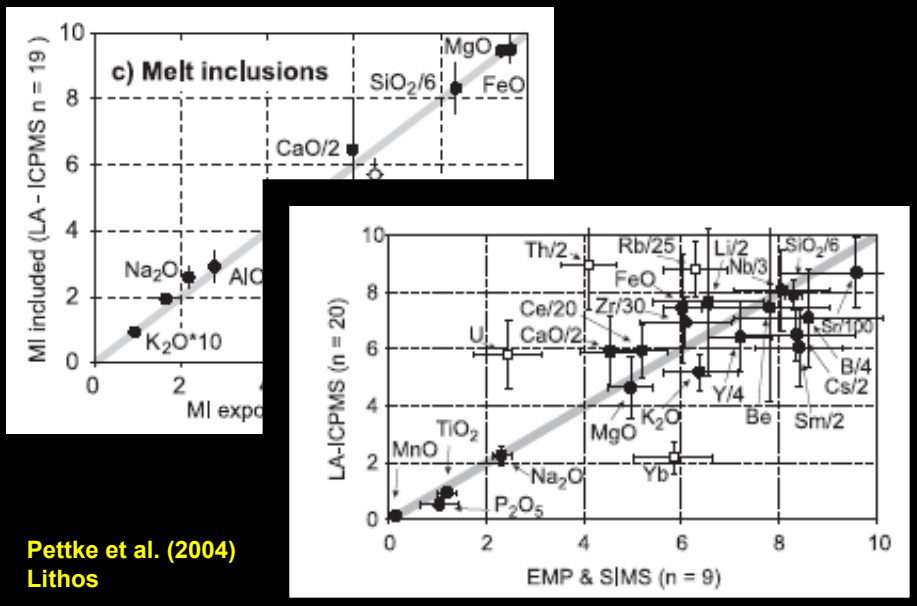
Effect of "wrong" mass ratio X



Pettke et al. (2004) Lithos

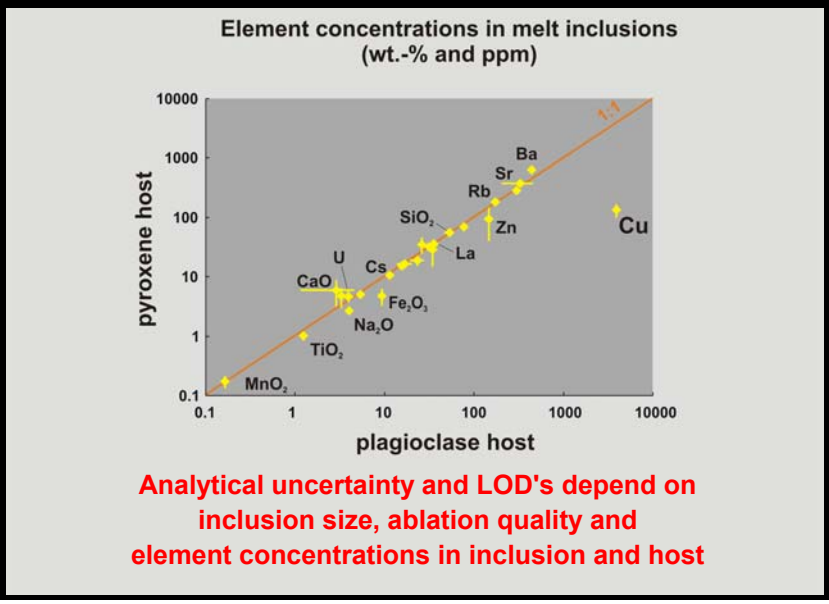
MI homogenization in the lab as required for EPMA and SIMS analysis:
Exactly the same effects caused by insufficient or excessive host remelting!

Accurate LA-ICP-MS MI data



Pettke et al. (2004) Lithos

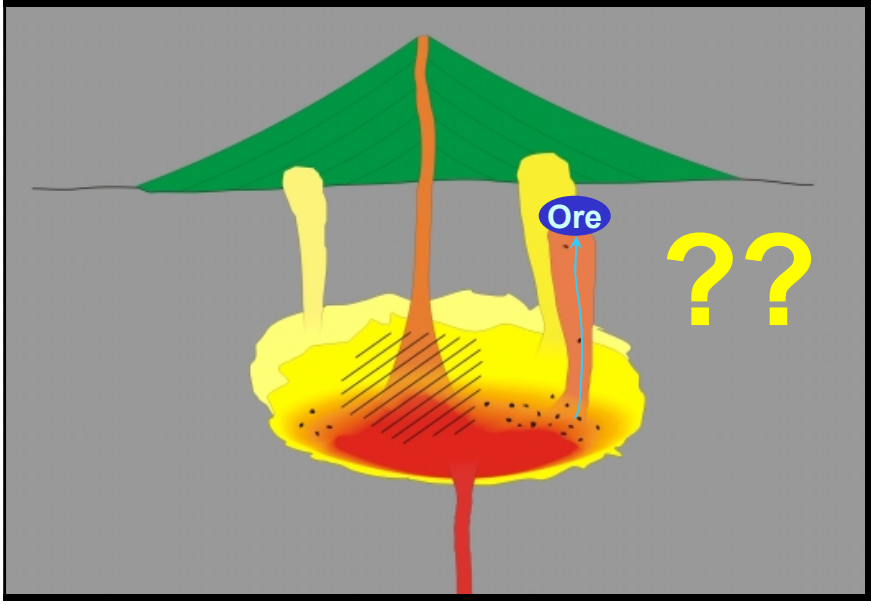
Co-existing clinopyroxene & plagioclase host compositionally identical MI



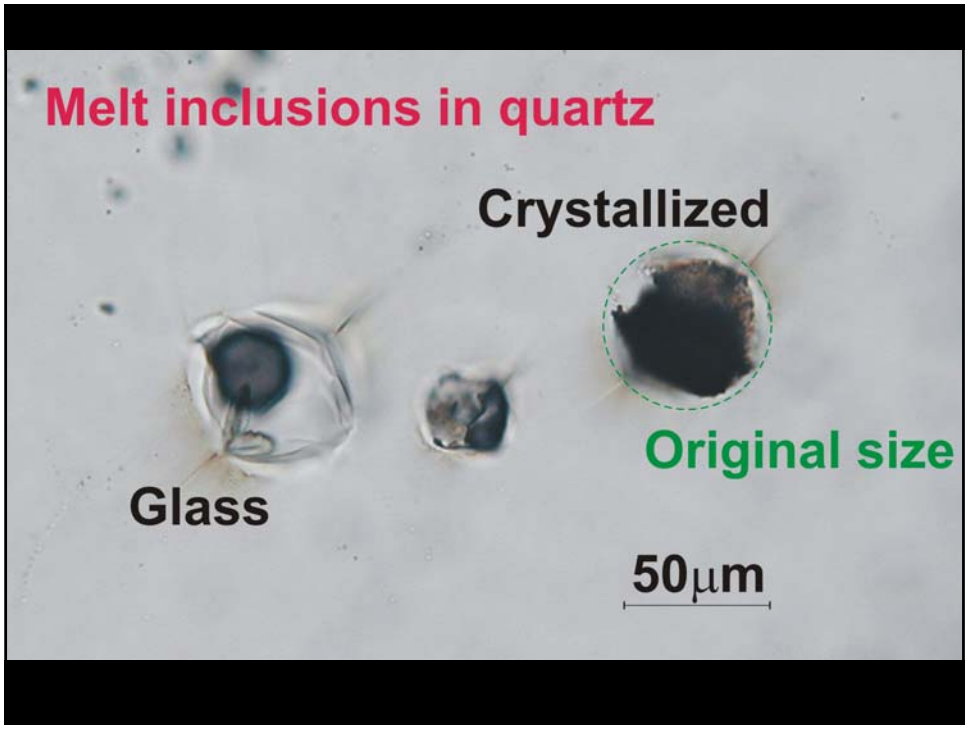
Analytical uncertainty and LOD's depend on inclusion size, ablation quality and element concentrations in inclusion and host

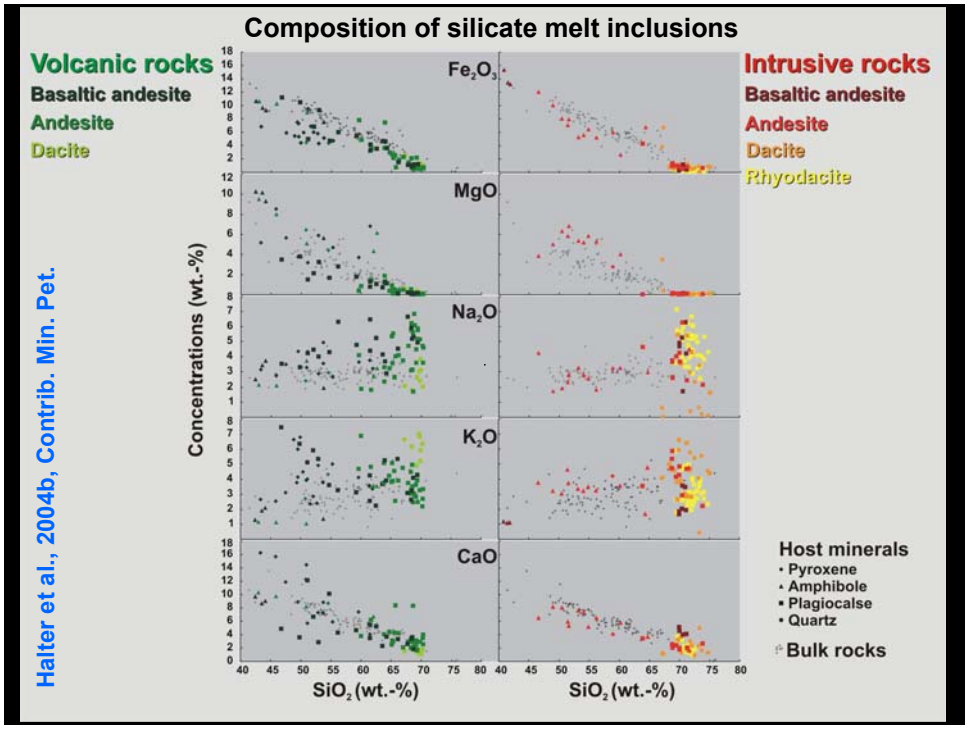
Halter et al., 2004a, Contrib. Min. Pet.

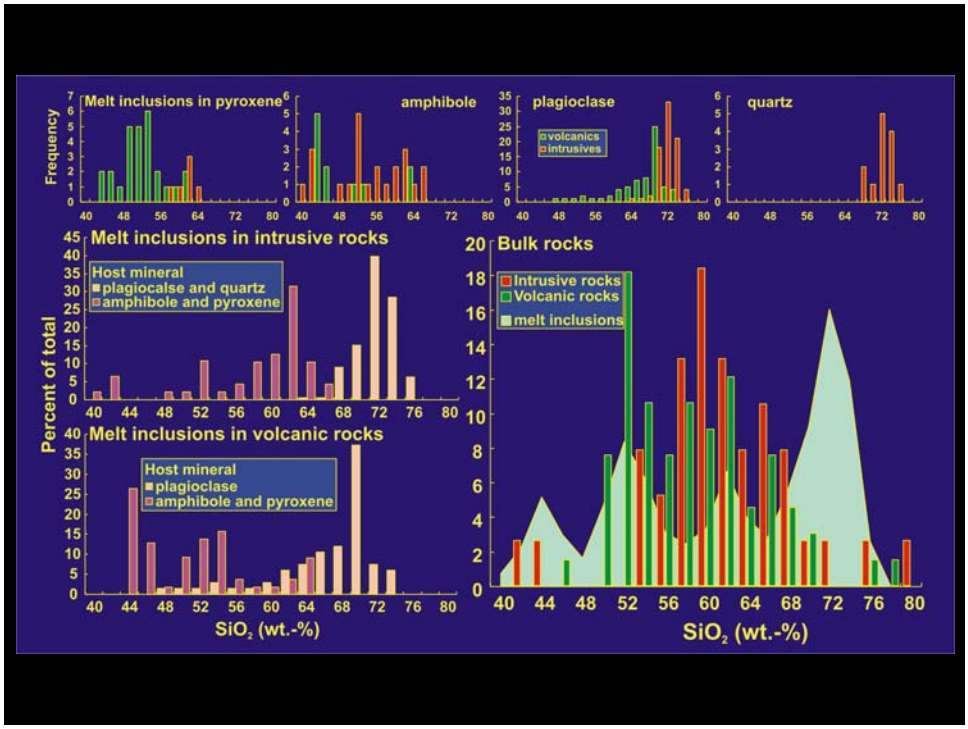
Magmatic-hydrothermal activity atop subduktion zones

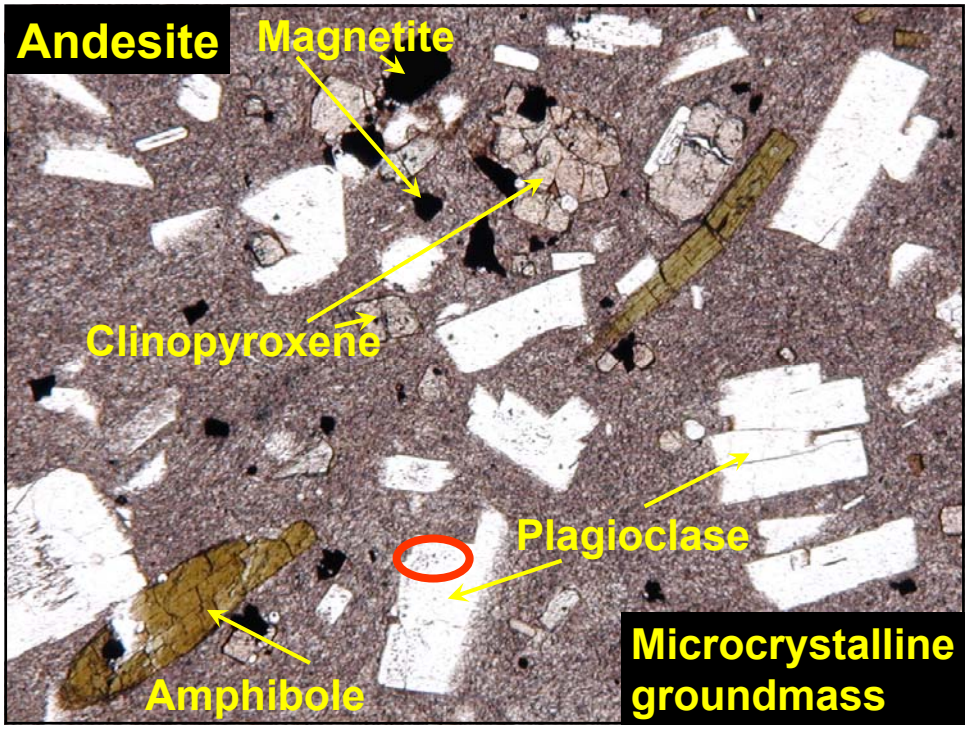


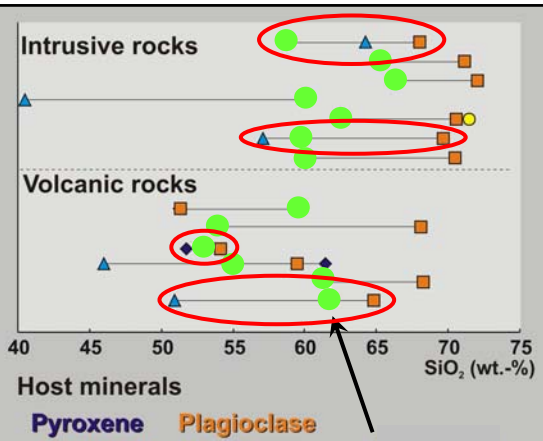
Halter et al., 2002, 2004, 2005


Melt inclusions in quartz
Crystallized
Original size
Glass
50μm


Composition of silicate melt inclusions
Volcanic rocks
Basaltic andesite
Andesite
Dacite
Intrusive rocks
Basaltic andesite
Andesite
Dacite
Rhyodacite
Fe2O3
MgO
Na2O
K2O
CaO
Concentrations (wt.-%)
SiO2 (wt.-%)
SiO2 (wt.-%)
Host minerals
Pyroxene
Amphibole
Plagiocalse
Quartz
Bulk rocks
Halter et al., 2004b, Contrib. Min. Pet.


Melt inclusions in pyroxene
amphibole
plagioclase
volcanics
intrusives
quartz
Frequency
Melt inclusions in intrusive rocks
Host mineral
plagiocalse and quartz
amphibole and pyroxene
Melt inclusions in volcanic rocks
Host mineral
plagioclase
amphibole and pyroxene
Percent of total
SiO2 (wt.-%)
Bulk rocks
Intrusive rocks
Volcanic rocks
melt inclusions
SiO2 (wt.-%)


Andesite
Magnetite
Clinopyroxene
Plagioclase
Amphibole
Microcrystalline groundmass



Melt inclusions in various host minerals

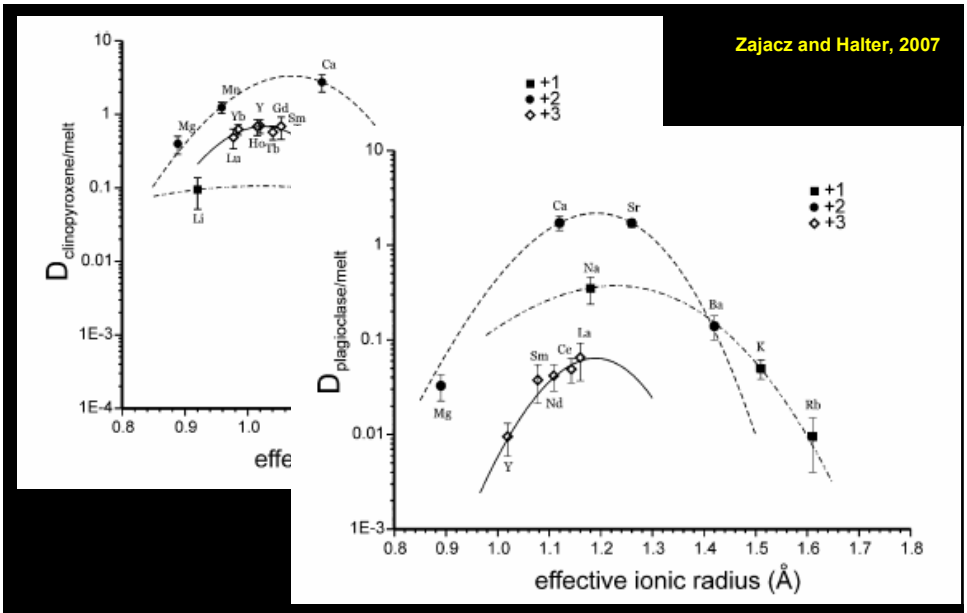
Bulk rock composition

Halter et al., 2004

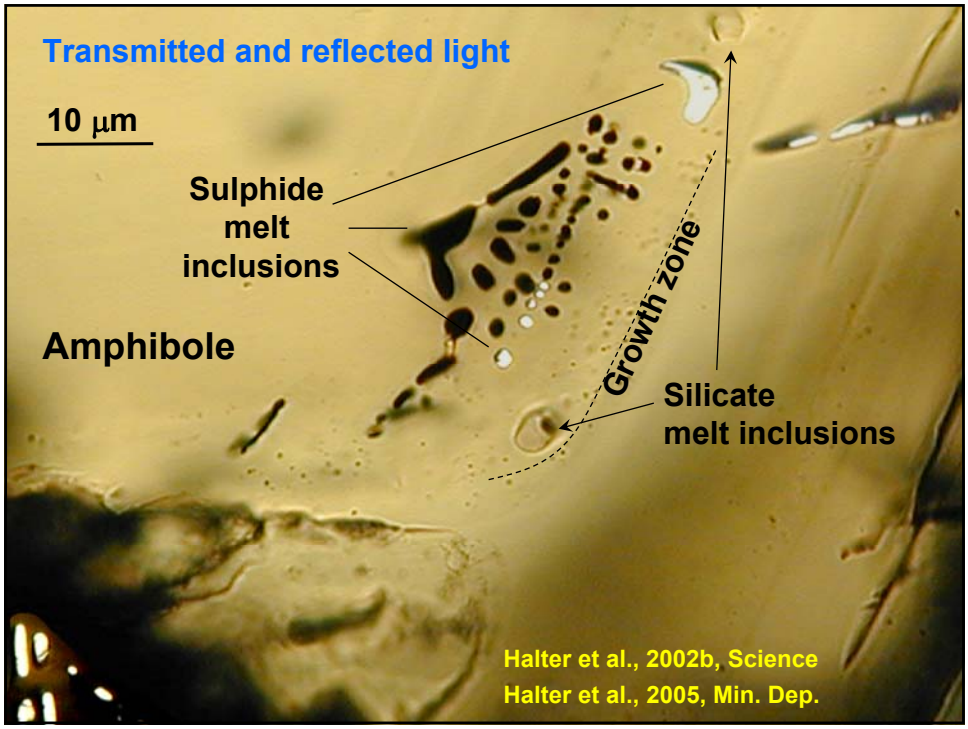
Melt inclusions of vastly different compositions occur in different minerals AND in different crystals of the same mineral: Disequilibrium conditions

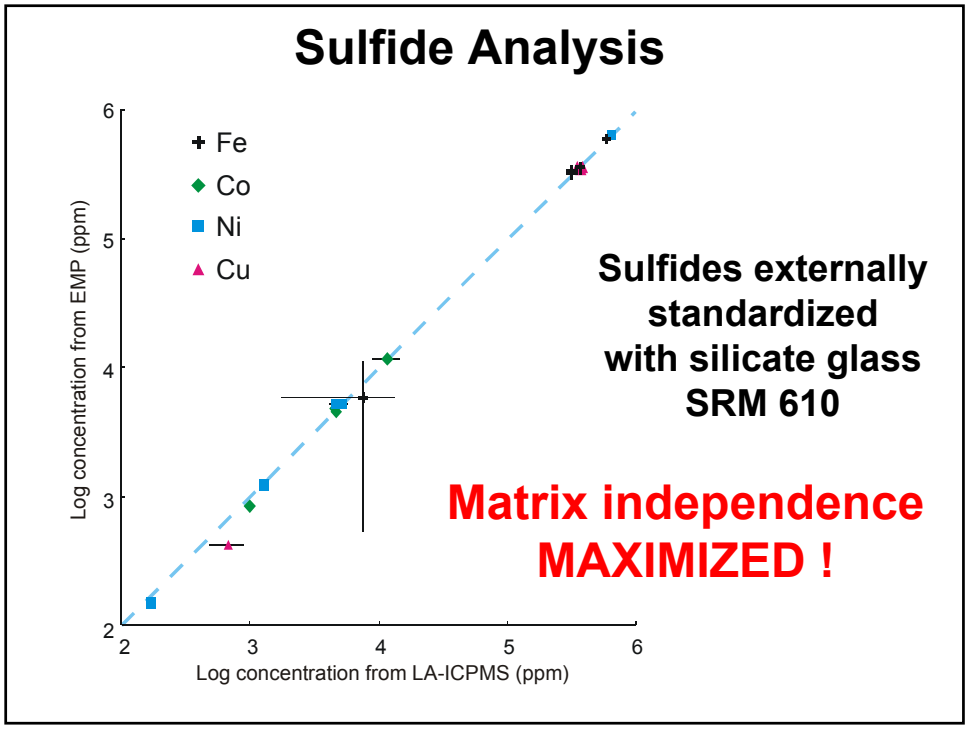
MAGMA MIXING

Zajacz and Halter, 2007

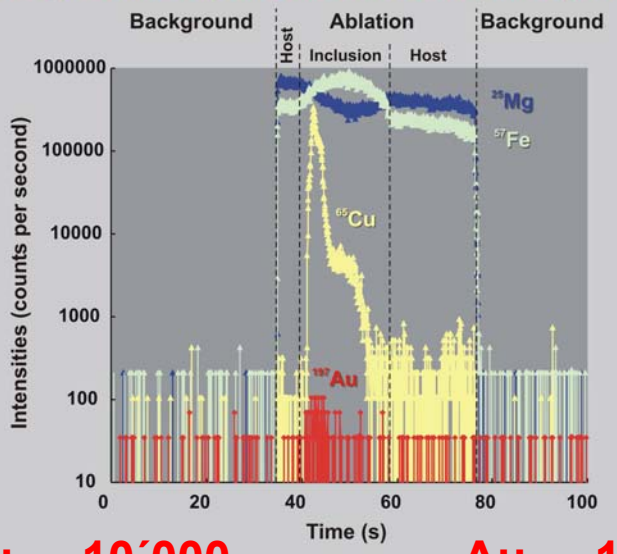


Mineral/melt partitioning data calculated using the SMI and host mineral compositions as a function of effective ionic radius. Lines represent the fit obtained by the theoretical model of Blundy and Wood (1994).


Transmitted and reflected light
10 μm
Sulphide melt inclusions
Amphibole
Growth zone
Silicate melt inclusions
Halter et al., 2002b, Science
Halter et al., 2005, Min. Dep.

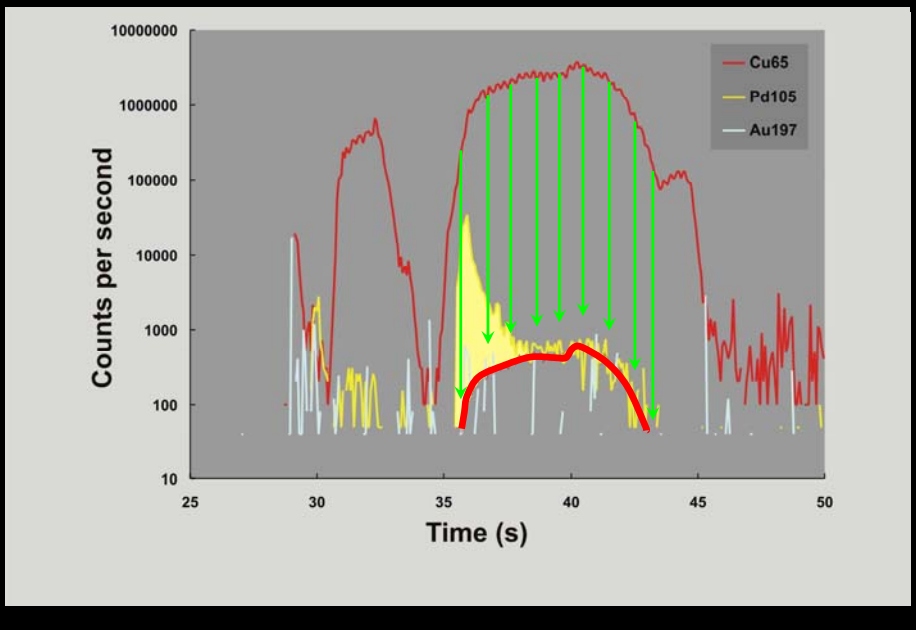

Sulfide Analysis
Fe
Co
Ni
Cu
Log concentration from EMP (ppm)
Log concentration from LA-ICPMS (ppm)
2
3
4
5
6
Sulfides externally standardized with silicate glass SRM 610
Matrix independence MAXIMIZED !

Analysis of a sulphide melt inclusion in amphibole

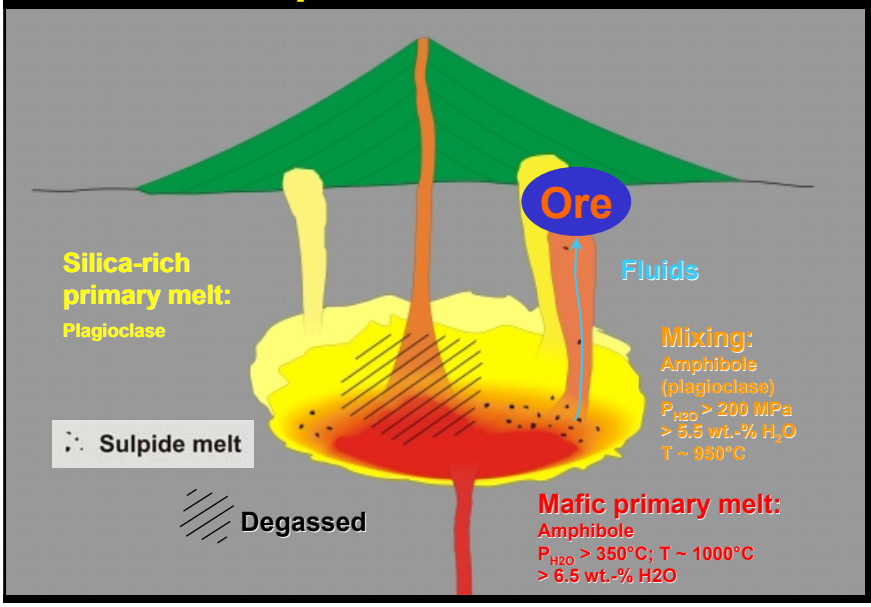


Cu/Au ~ 10´000 **Au ~ 1 µg/g**

$(^{65}Cu^{40}Ar)^{+}$ interference on $^{105}Pd^{+}$



Magmatic-hydrothermal activity atop subduktion zones



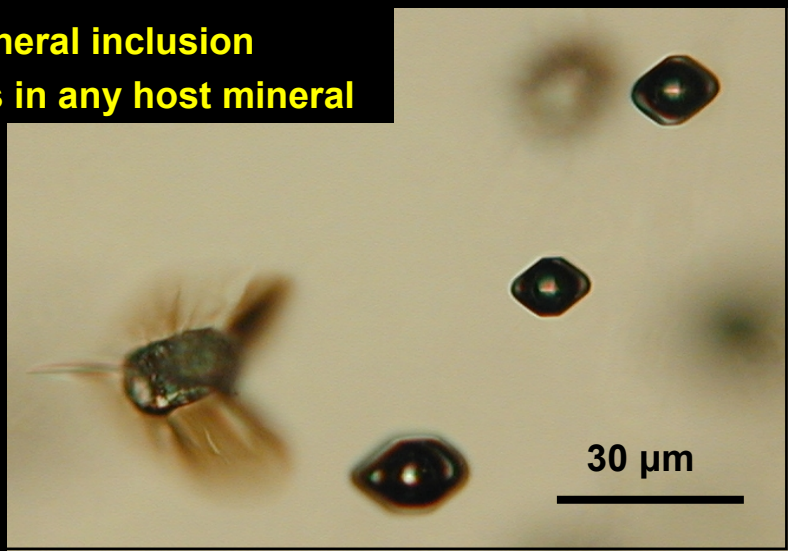
Fluids and ore deposits group of Prof. Heinrich.

Mineral inclusions are all the same

Hydrothermal zircon

- hosted in freegrown hydrothermal quartz

Bulk mineral inclusion analysis in any host mineral



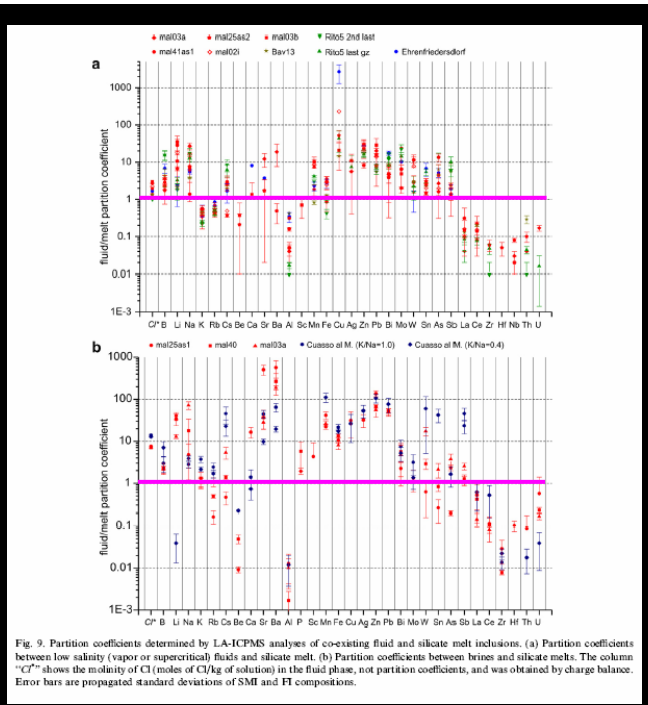
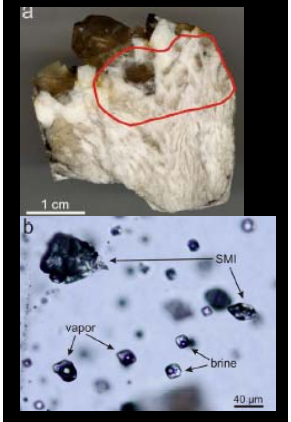


Fig. 9. Partition coefficients determined by LA-ICPMS analyses of co-existing fluid and silicate melt inclusions. (a) Partition coefficients between low salinity (vapor or supercritical) fluids and silicate melt. (b) Partition coefficients between brines and silicate melts. The column "*Cl**" shows the molinity of Cl (moles of Cl/kg of solution) in the fluid phase, not partition coefficients, and was obtained by charge balance. Error bars are propagated standard deviations of SMI and FI compositions.

Fluid / melt element distribution coefficients measured from co-existing silicate melt - aqueous fluid inclusion assemblages

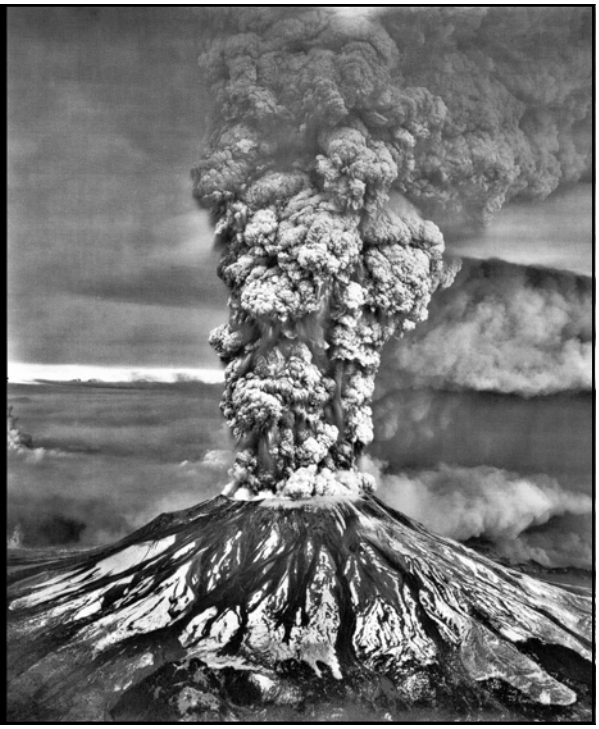


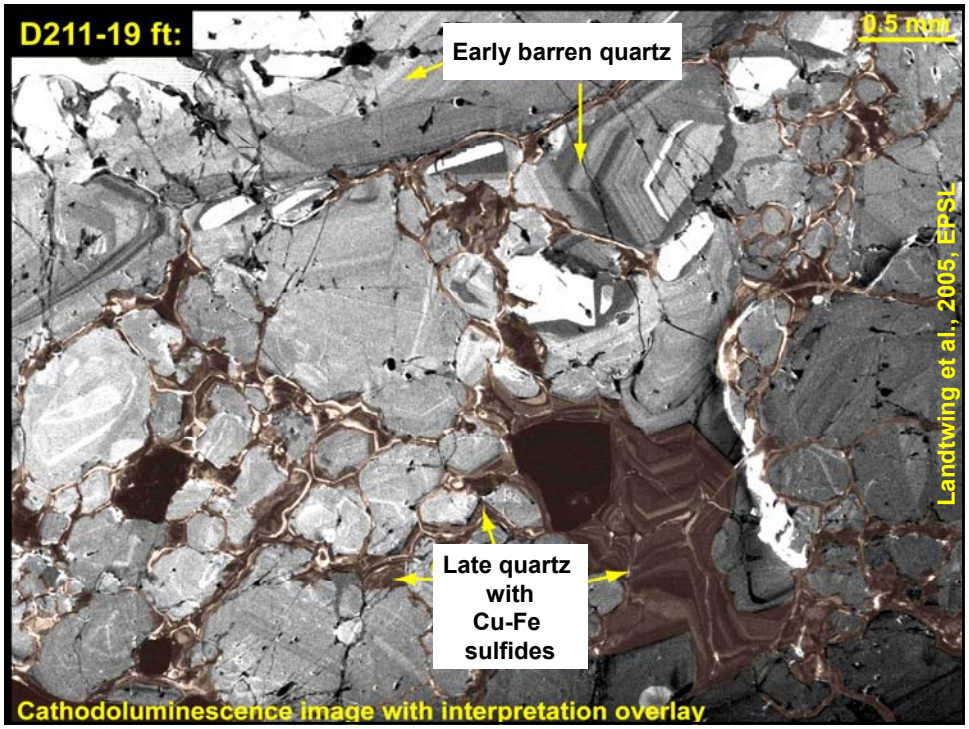
Zajacz et al., 2008, GCA

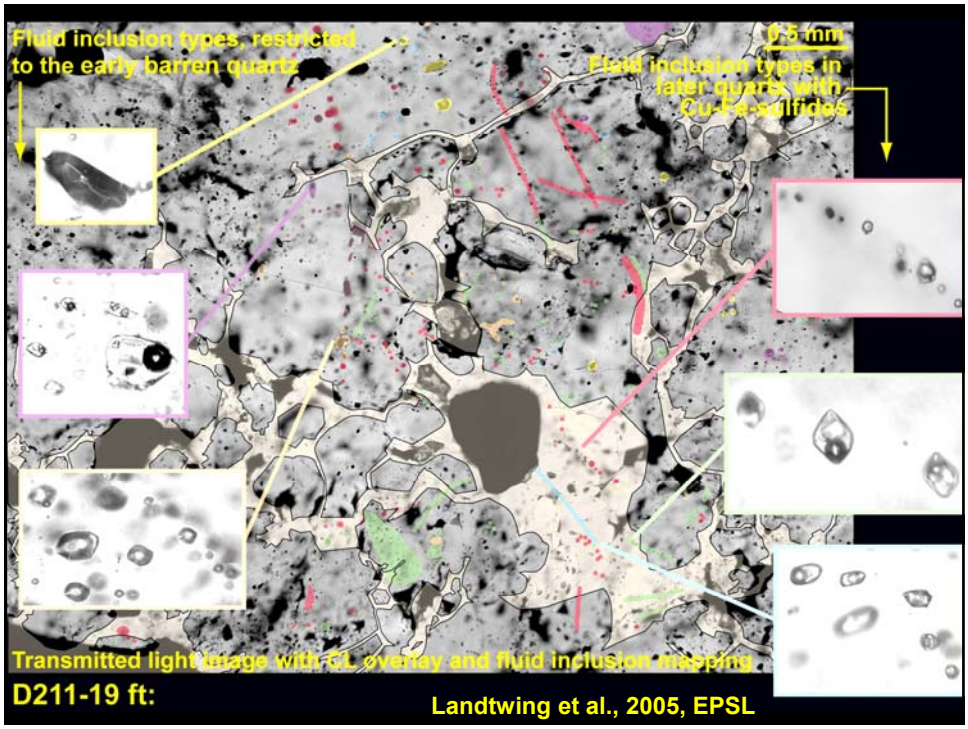
Bingham porphyry-Cu-Au deposit formed beneath something like this - but how?

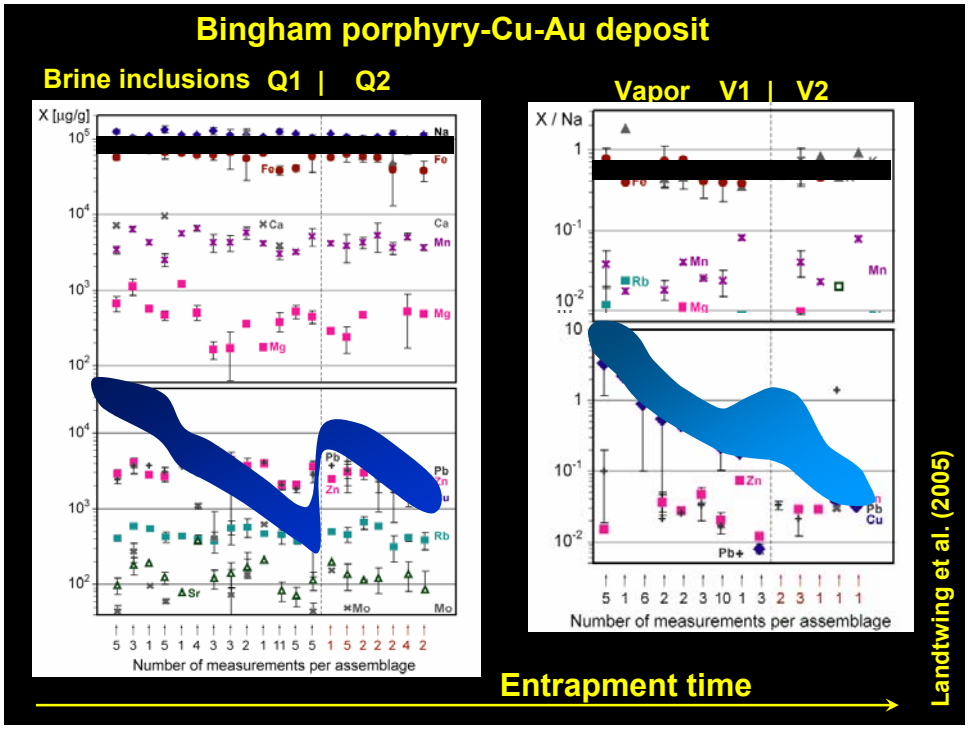
see Landtwing et al. (2005)

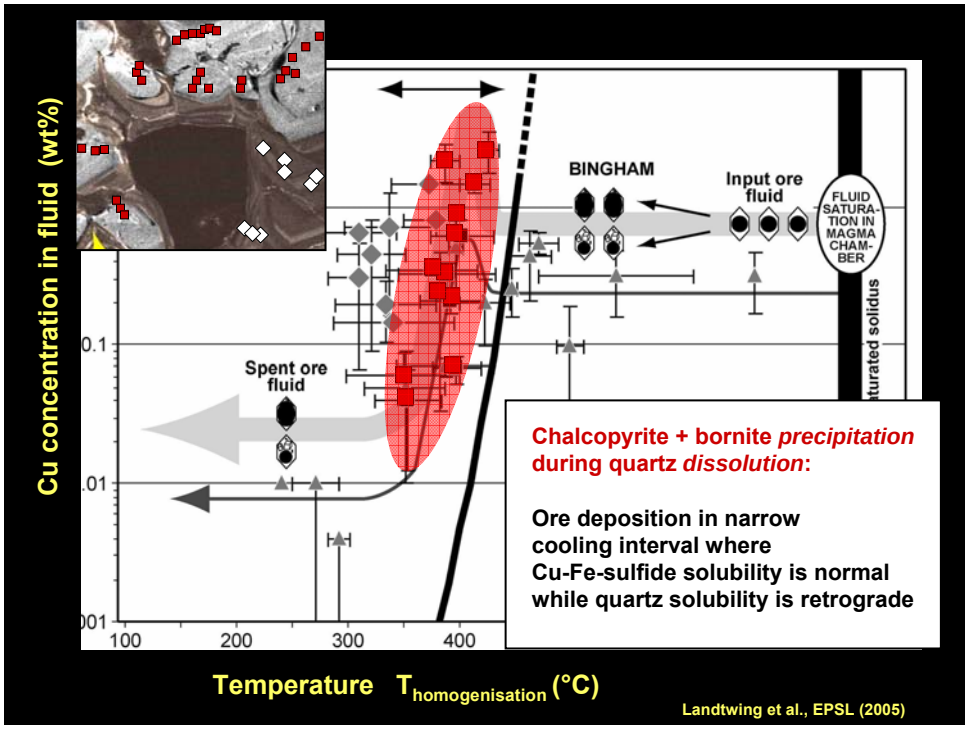
Mt. St. Helens
18. Mai 1980



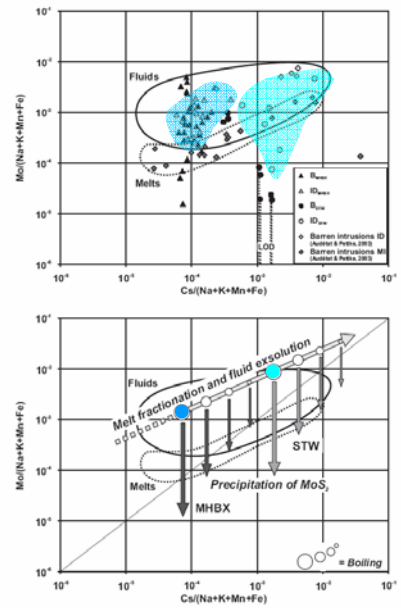



Fluid inclusion types, restricted to the early barren quartz
0.5 mm
Fluid inclusion types in later quartz with Cu-Fe-sulfides
Transmitted light image with CL overlay and fluid inclusion mapping
D211-19 ft:
Landtwing et al., 2005, EPSL

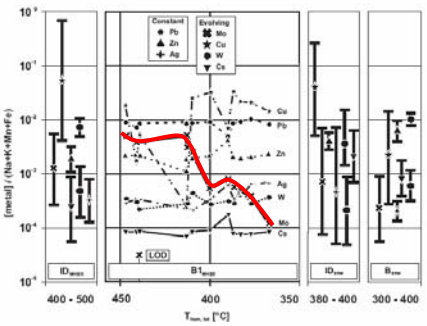

Bingham porphyry-Cu-Au deposit
Brine inclusions Q1 | Q2
Vapor V1 | V2
X [µg/g]
X / Na
Number of measurements per assemblage
Number of measurements per assemblage
Entrapment time
Landtwing et al. (2005)



Selected applications: Questa Mo-deposit

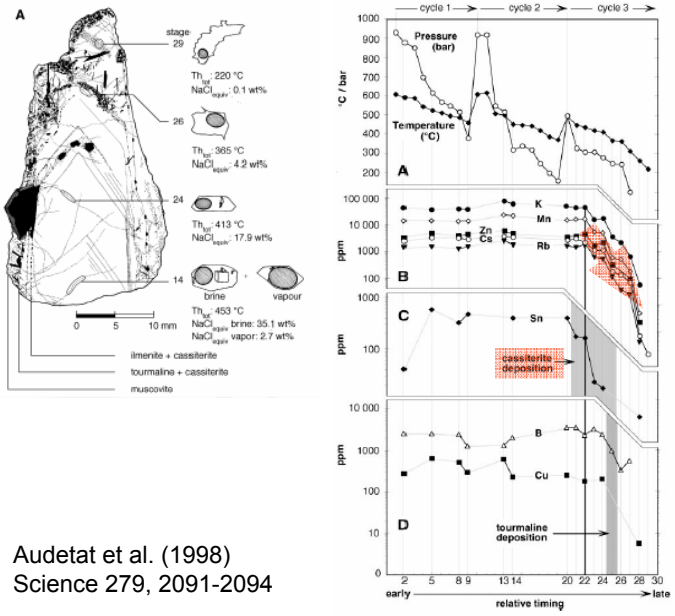


- Two petrographic molybdenite-forming stages sourced by progressively evolved magmas as monitored by fluid Cs contents
- Molybdenite precipitation in response to fluid cooling



Klemm et al. (2008) Min Dep

Selected applications: Mole Granite Sn-W-deposit



Audetat et al. (1998)
Science 279, 2091-2094

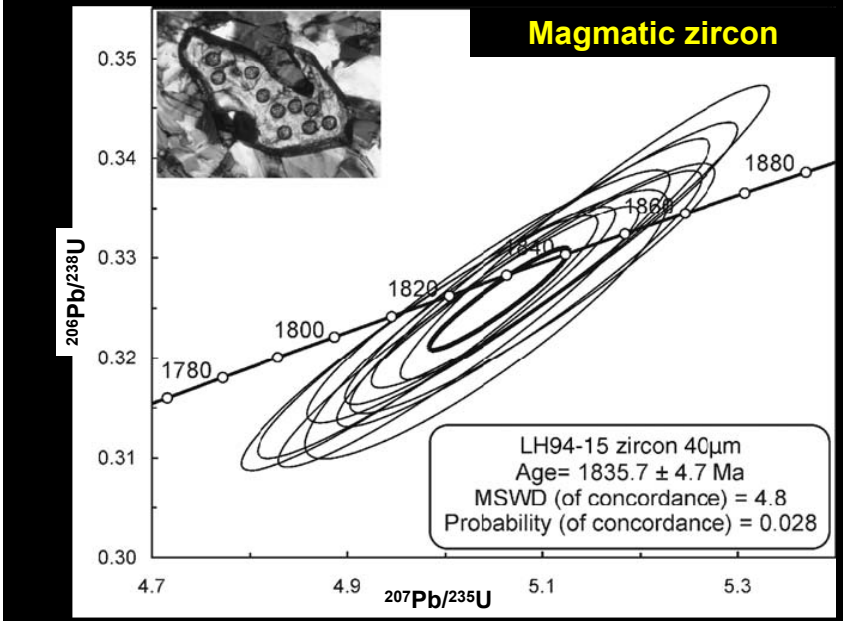
Cassiterite precipitation recorded in progressively entrapped fluid inclusion assemblages, interpreted to monitor admixture of ground-water to the ore-forming fluid.

In-situ isotopic analysis by LA-ICP-MS:

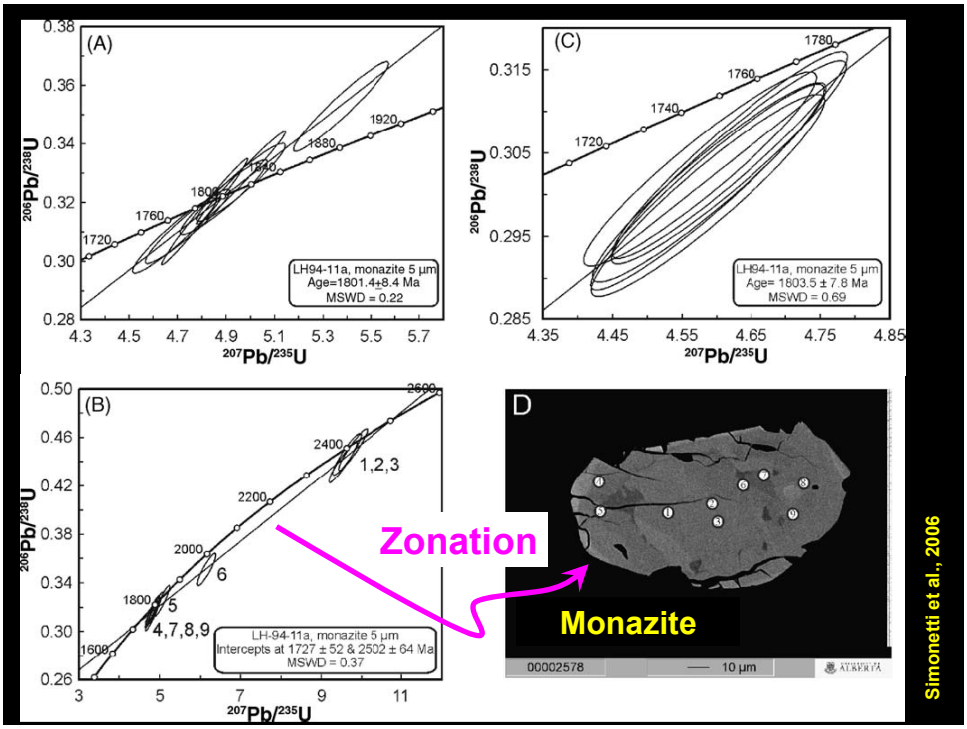
Age dating

Source tracing

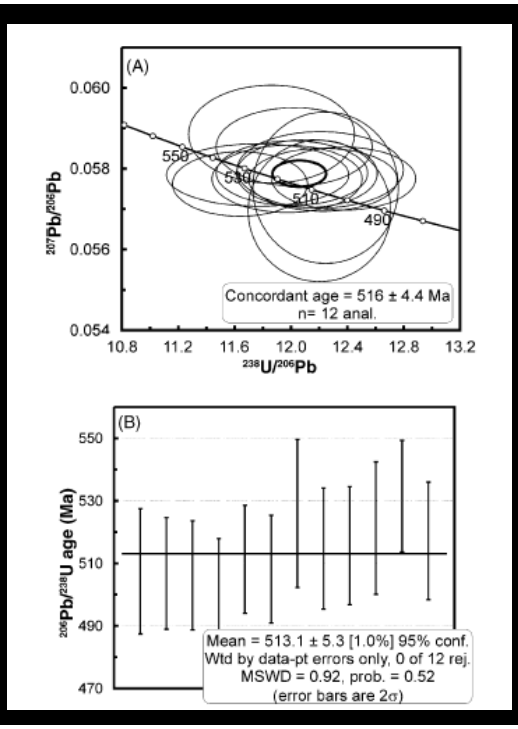
LA-MC-ICP-MS U-Pb dating



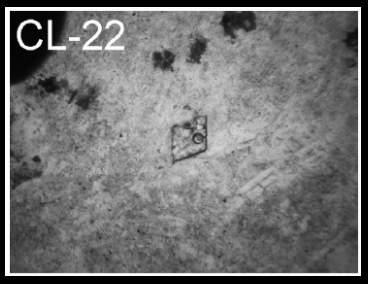
Simonetti et al., 2006



Simonetti et al., 2006



Ages obtained on titanite standard



NOTE:
All these data were obtained by using matrix-matched external standardization !!!

Simonetti et al., 2006

Pb isotopes in fluid inclusions: Motivation

- **Fluids effect significant and fast mass and heat transfer in the Earth's interior:**

  → Fluid origin and migration paths?

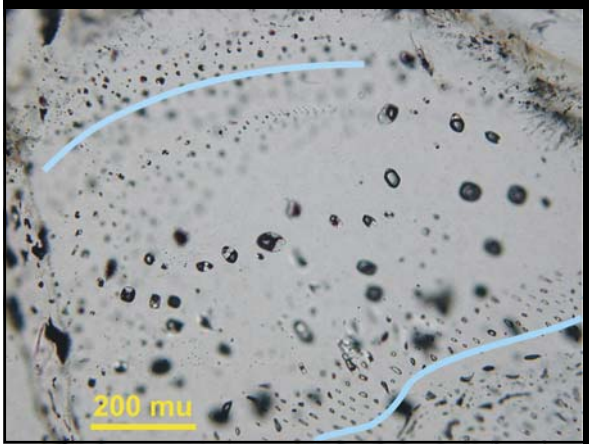
- **Samples of ancient fluids are preserved as inclusions in minerals**
- **Pb isotopes are an excellent tracer of aqueous fluid-based geological processes**

Bulk crush leach Pb isotope approach: PhD

Multiple generations of fluid inclusions:
→ MIXTURES ...

Feasibility ?

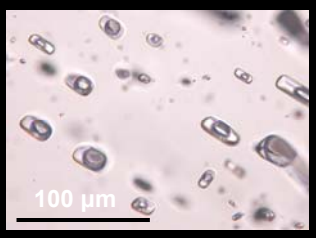
- ✓ Brine inclusions often contain 5000 ppm Pb
- ✓ Element concentrations of individual fluid inclusions are accurately quantified by LA-ICP-MS



- ➢ Enough sample?
- ➢ Analytical precision?
- ➢ Are Pb isotopic measurements accurate?
- ➢ Which ICP-MS?
- ➢ Transient signal acquisition

The reference materials

- SRM610 from NIST:
  426 ppm Pb of known isotopic composition
- Synthetic fluid inclusions (700 °C, 180 MPa, 144h)
  - (Na,K,Pb)Cl
  - (Na,K,Tl,Pb)Cl

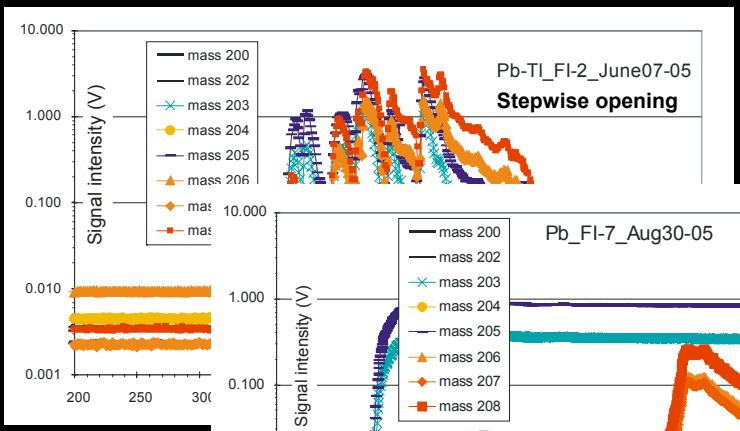


Concentrations:

N: 11.7 wt-% NaCl
N: 6.2 wt-% KCl
M: 5000 µg/g Pb (SRM 981)

N: 10.5 wt-% NaCl
N: 5.9 wt-% KCl
M: 4200 µg/g Pb (SRM 981)
M: 1600 µg/g Tl (SRM 997)

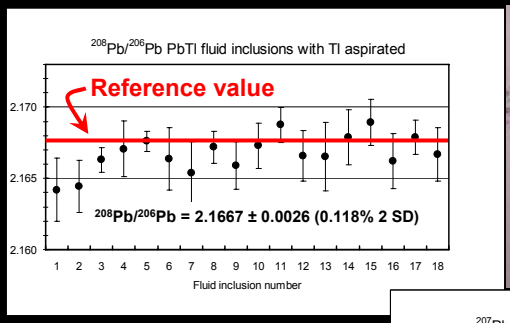
Fluid inclusion signals

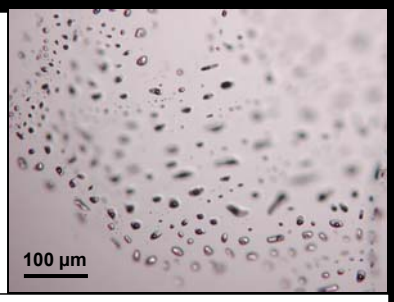


Where to set …

the signal borders ?!?

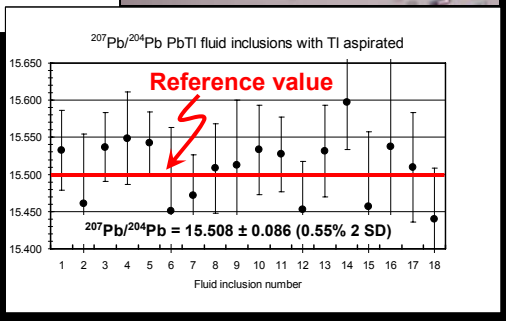
Accuracy on fluid inclusion standards



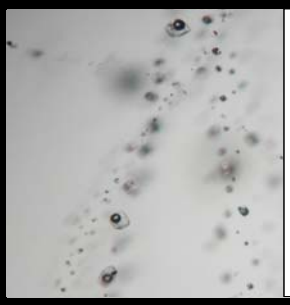


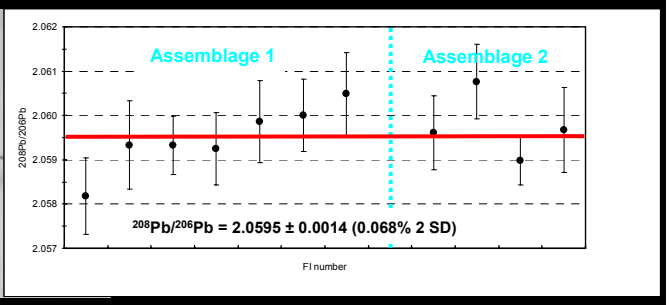
Average size of isometric fluid inclusions is 25 µm; SRM981 reference values from Baker et al. (2004)

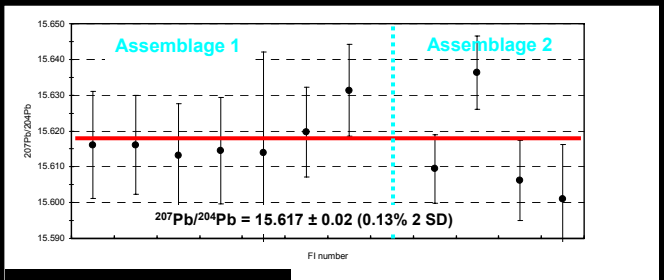
NU-1700 data



Rosia Poieni, porphyry-type Cu-Au deposit



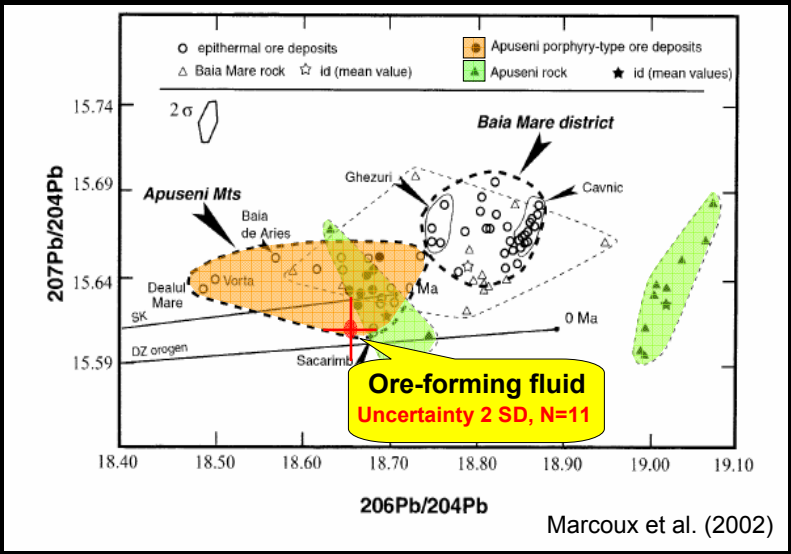




NU-Plasma data

Inclusion to inclusion (~40 µm) reproducibility much better than for the standard inclusions (larger size, higher Pb concentration)

The result



Marcoux et al. (2002)

PhD Harris, 2007; in prep.

Develop an idea for analysis.
Define the strategy and do it.

It will likely be successful,
at least partially.

Thanks!