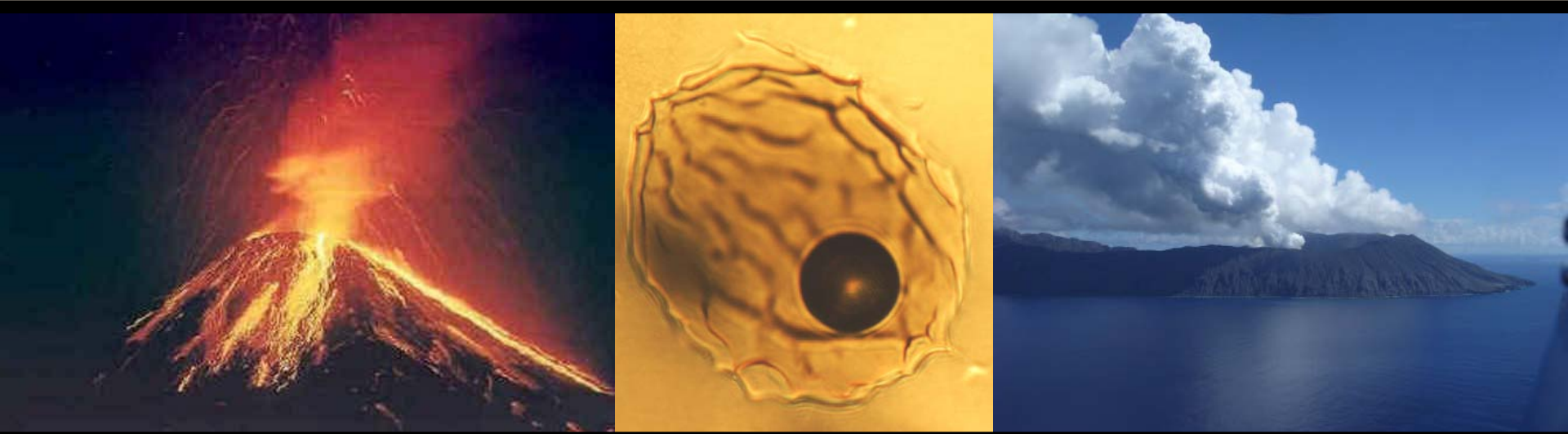


Sample Preparation and Analysis

Adam Kent, Oregon State University

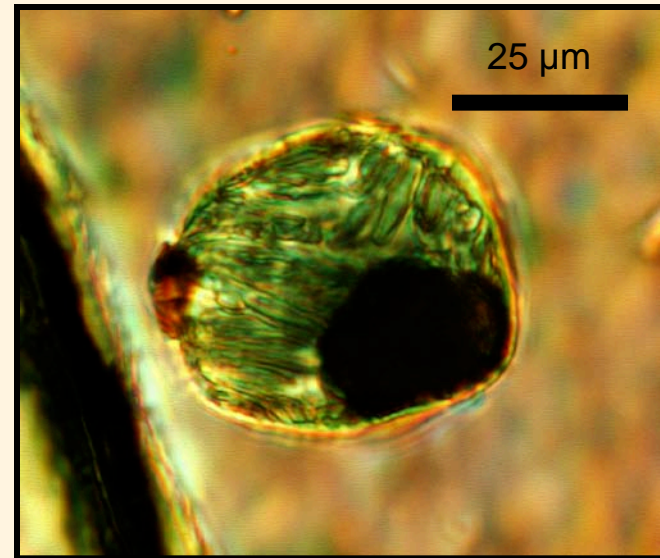
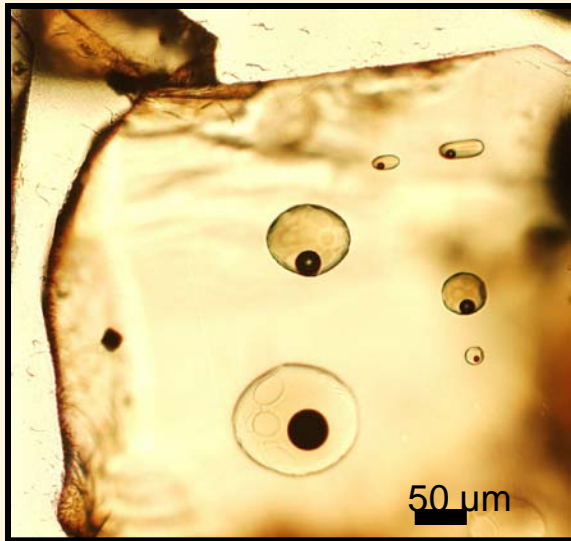


Key Questions

- How do we prepare melt inclusions for physical and chemical measurements?
- What are good sample selection strategies?
- What are the most common analytical techniques? How do these compare?
- What are the limitations to chemical analysis?

Sample Preparation and Analysis

Melt Inclusions are Small!



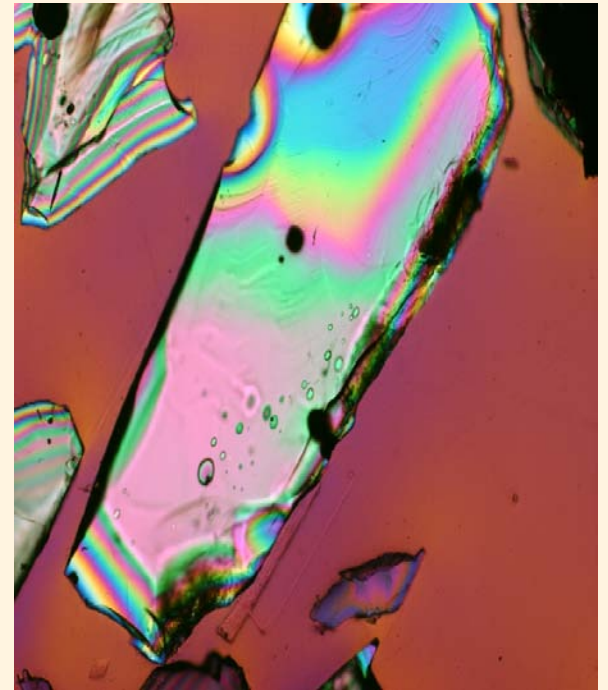
The small size of melt inclusions requires specialized techniques for analysis. This produces information that is often more limited than can be obtained from bulk samples

Sample Preparation

- Goal: To prepare melt inclusions in such a way that they can be **chemically analyzed** and **petrographically documented**
- Technique specific (c.f. FTIR, SIMS, LA-ICP-MS)
- Variable strategies

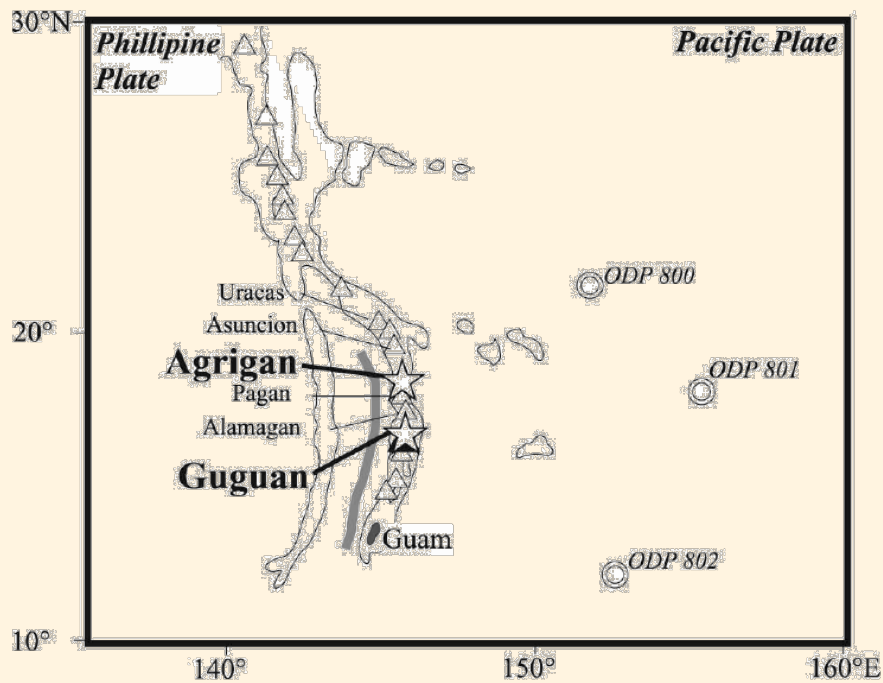
Sample Selection

- Goal specific: Sampling strategy may depend on analytical and other strategies
 - e.g. Volatiles: Rapidly cooled samples, scoria, early erupted
 - Phenocryst-bearing, glassy, primitive, representative or endmember compositions
- Geologic record: only massive lavas survive unaltered



Melt inclusions require a LOT of work: sample selection is key!

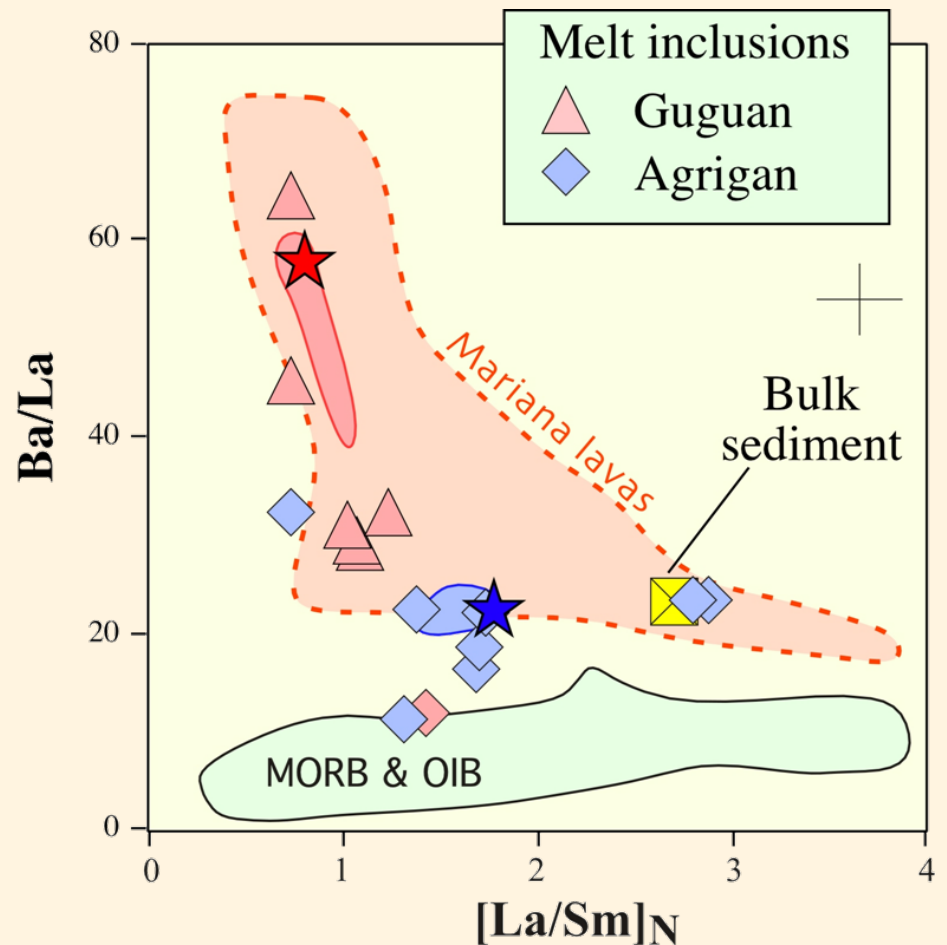
Melt inclusions are NOT a reconnaissance tool - understand the rocks you are working with first!



Mariana Arc

Kent et al. 2002

From just two selected lavas we see almost the entire variation evident in a large suite of lavas

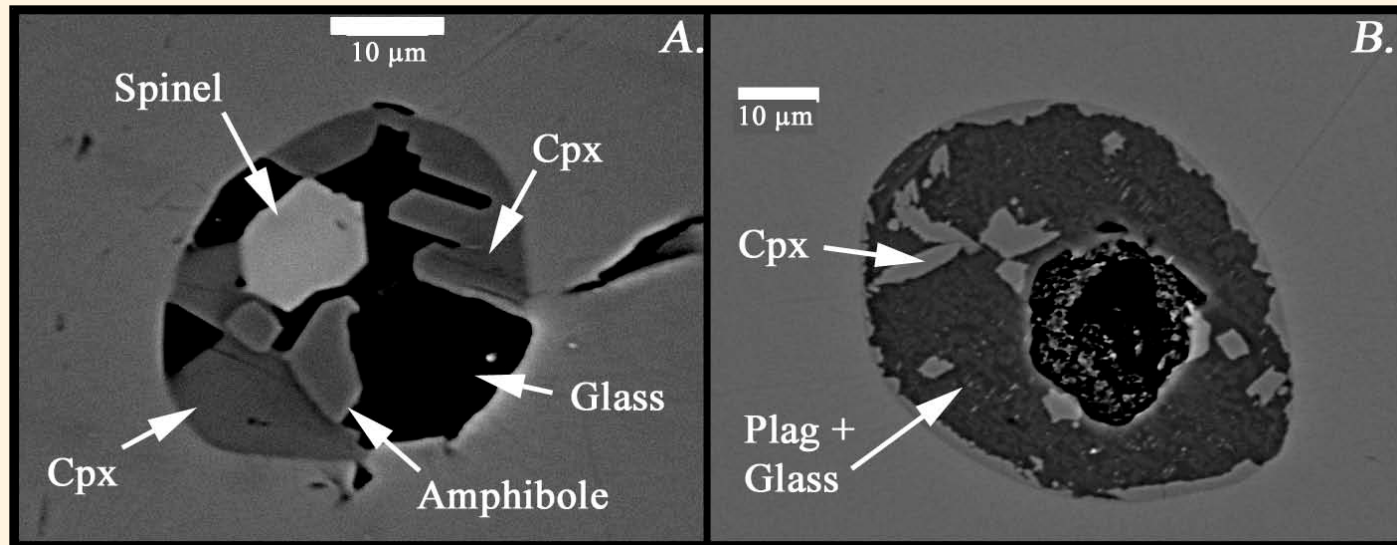


Petrographic documentation

- Make key observations through examination in 3D
 - Size, shape, crystallinity, bubbles, location within host etc.
 - Basis for subsequent sample preparation (remelt or not) and analysis
- Best done in mineral separates using **petrographic** microscope
 - Ethanol or oil
 - Fluorboric acid wash
 - Initial polish
- Thin sections are less useful except for initial reconnaissance
 - Too thin - apophyses vs. melt inclusions
 - Thick sections ($> 100\ \mu\text{m}$) better

Inclusion Rehomogenization

- For most analytical techniques crystallized inclusion need to be melted and quenched prior to analysis
 - Produces a homogenous glass for microbeam analysis
 - Where $T_{\text{heating}} = T_{\text{trapping}}$ and inclusions have been closed to exchange this can also correct for PEC
- Some minerals also require rapid quench rates to prevent mineral growth on cooling



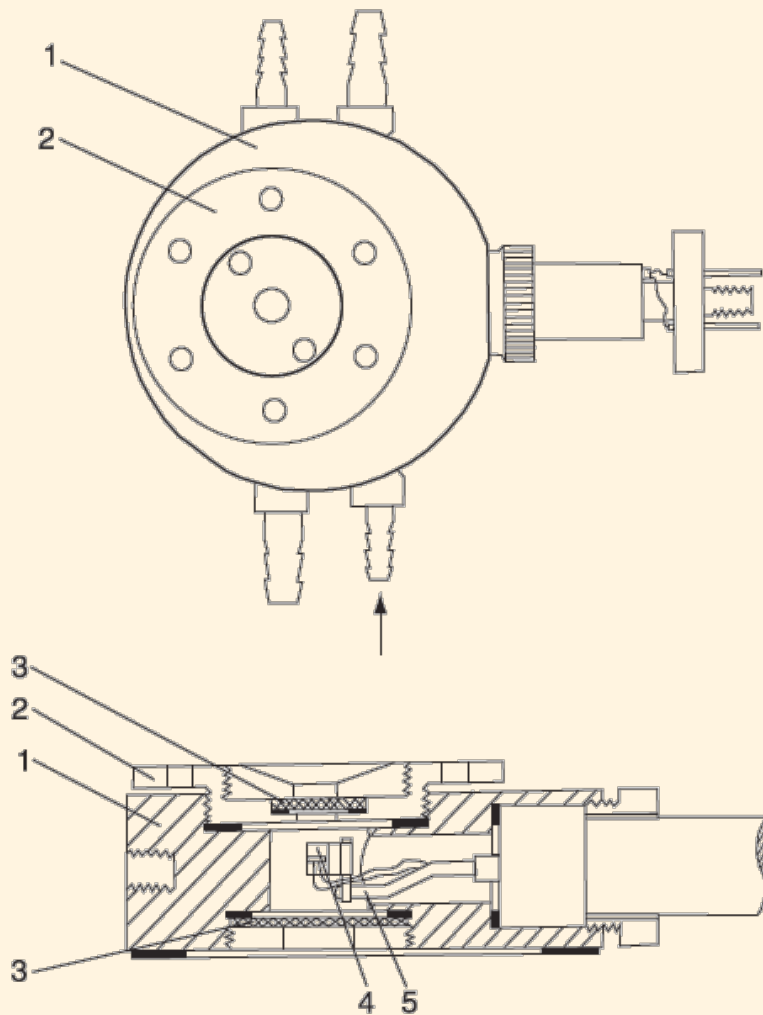
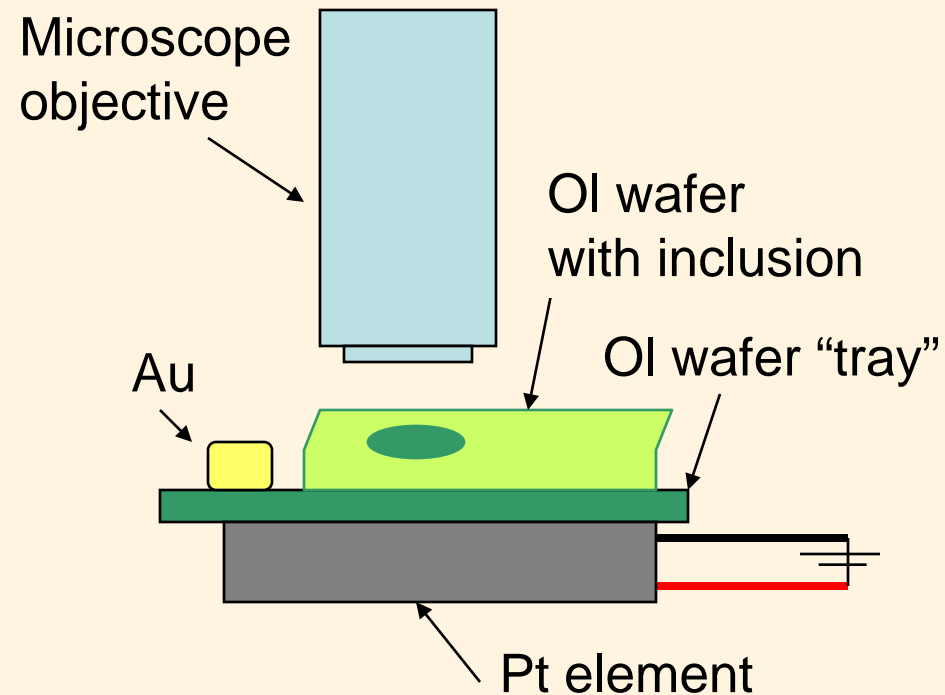
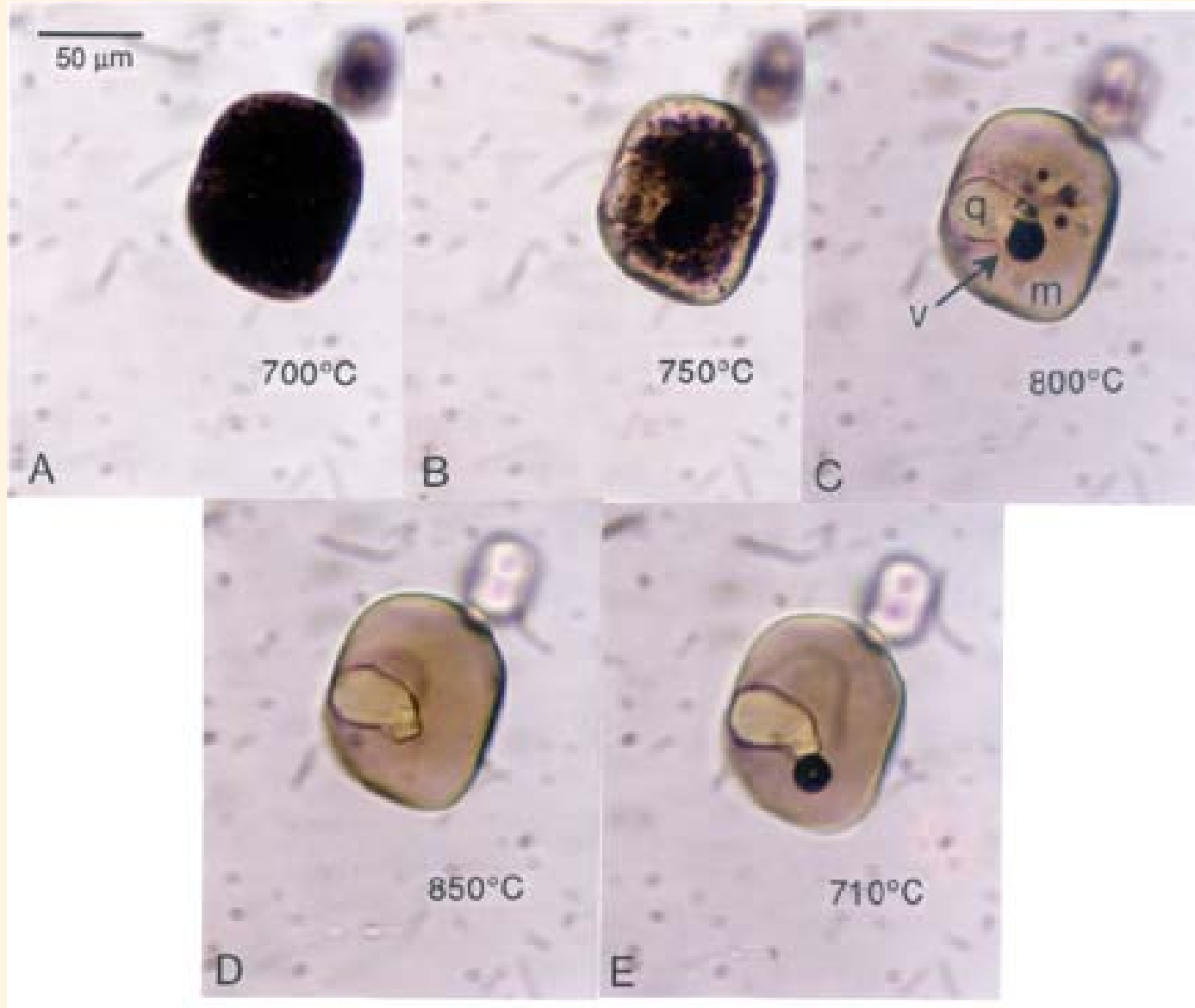


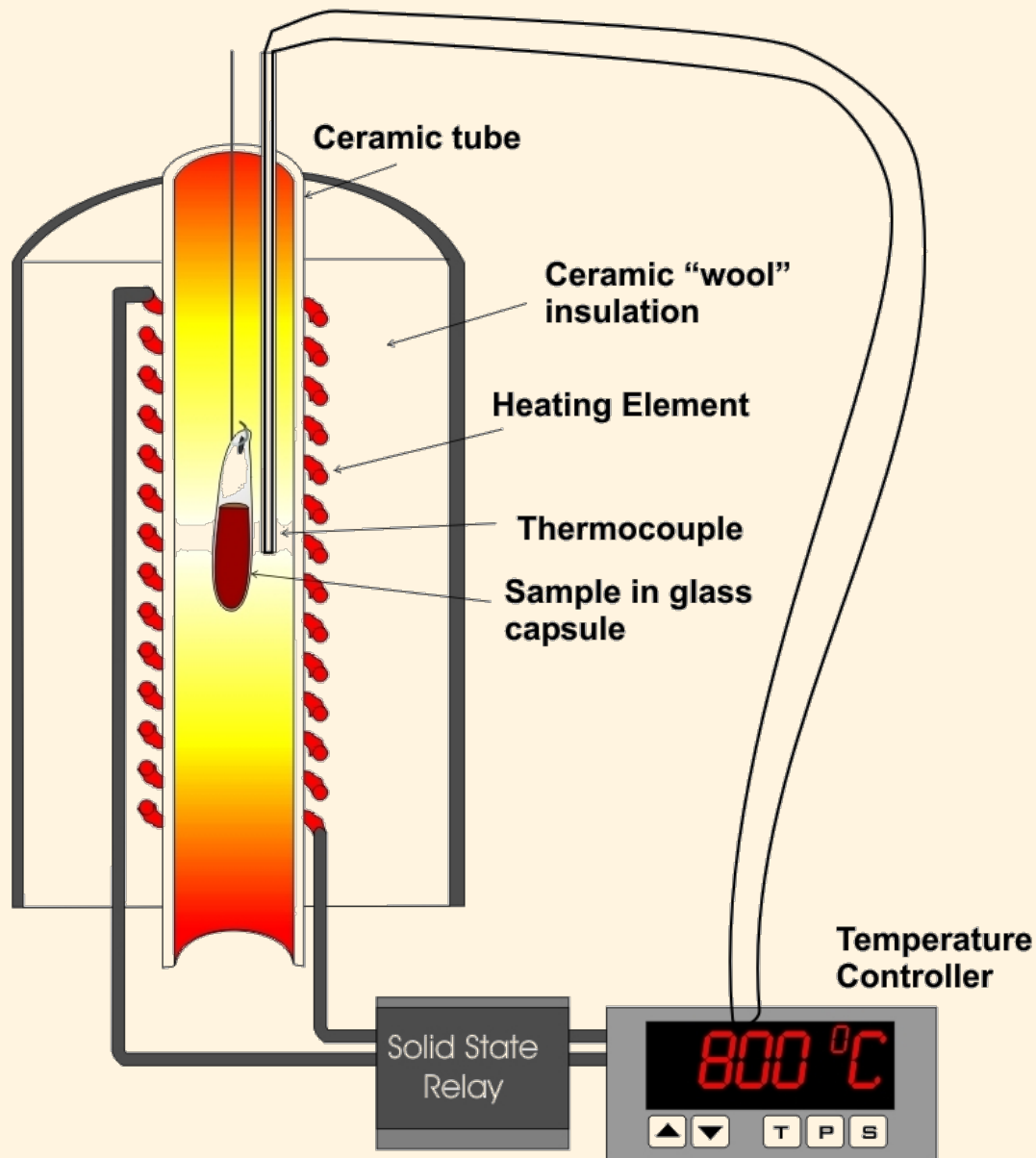
Fig. 3. Microscope heating stage designed by Sobolev et al. (1980). (1) Gas-tight sealed body cooled by water; (2) screwed lid; (3) optical quartz glass windows; (4) Pt₉₀Rh₁₀ heating element and ring-shaped metallic sample holder with Pt-Pt₉₀Rh₁₀ thermocouple; (5) electrode.



Schiano, 2003

Jake Lowenstern's USGS YVO Website

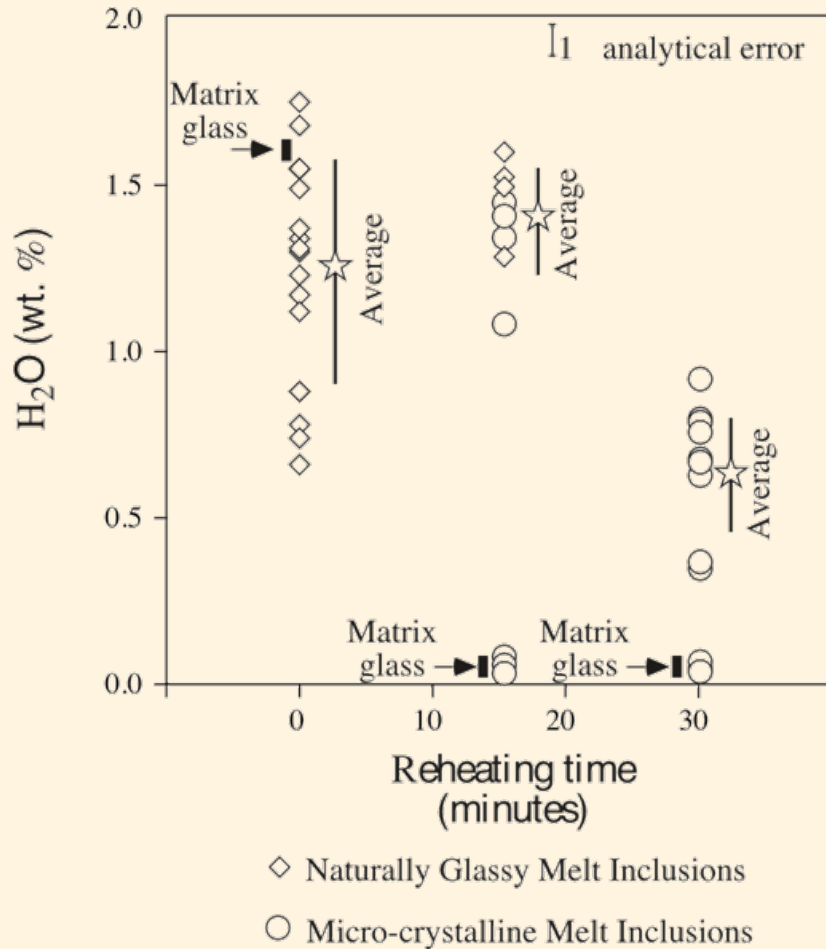




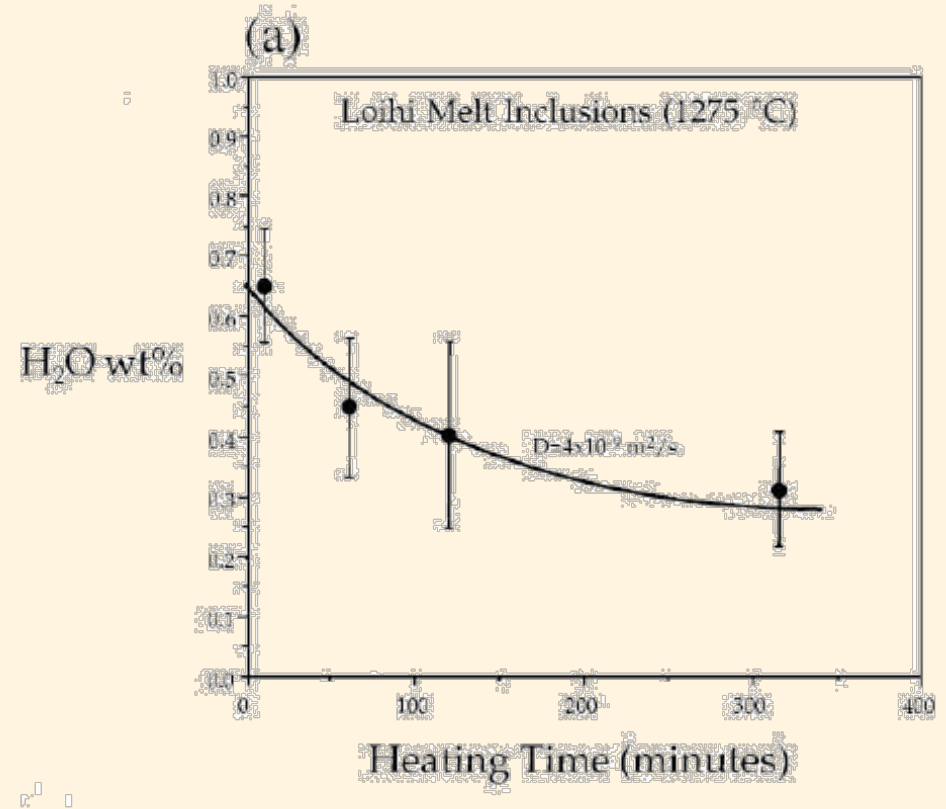
Rehomogenization of minerals in redox controlled 1 atm vertical furnace followed by water quench

	Pros	Cons
Vertical Furnace	<p>Multiple grains analyzed at a time</p> <p>Explicit redox control</p> <p>Less chance of venting/breaching</p> <p>Closer T control and rapid heating possible</p>	<p>T_{trapping} must be estimated, may require iteration</p> <p>No information obtained about homogenization process</p>
Heating Stage	<p>Observe heating</p> <p>Obtain independent measurements of T_{trapping} and temperatures of mineral dissolution</p>	<p>Slow - single crystal at a time</p> <p>No explicit redox control (He atmosphere)</p> <p>Complex in hydrous inclusions and sensitive to heating rate</p>

Unpublished data



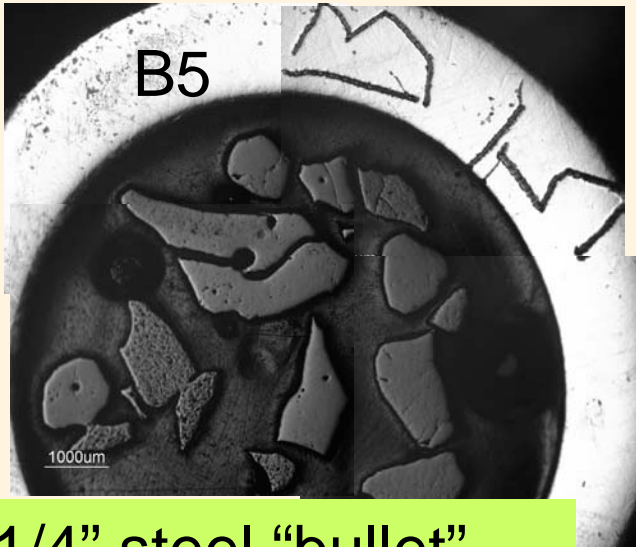
Hauri et al 2002



Excessive heating can cause H₂O loss

Sample Preparation

- Guided by analytical strategy
 - Bulk grain mounts polished to arbitrary level
 - Prepare individually selected inclusions
- Mount in epoxy, Indium, polish as wafers



1/4" steel "bullet"



Double polished FTIR wafer

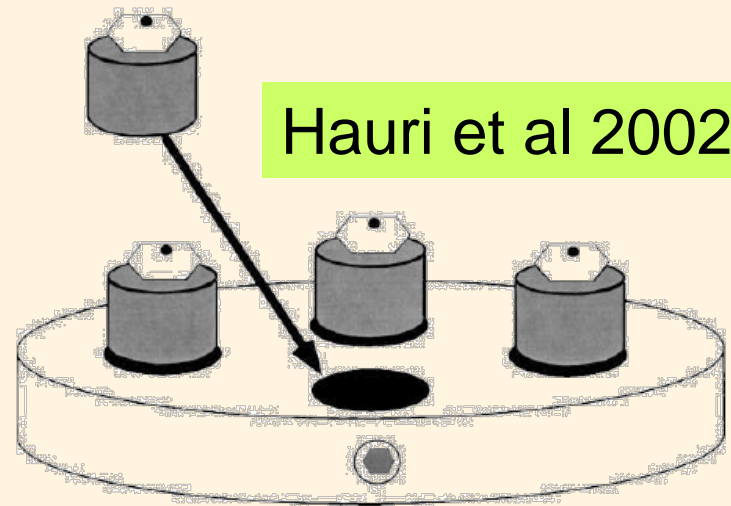
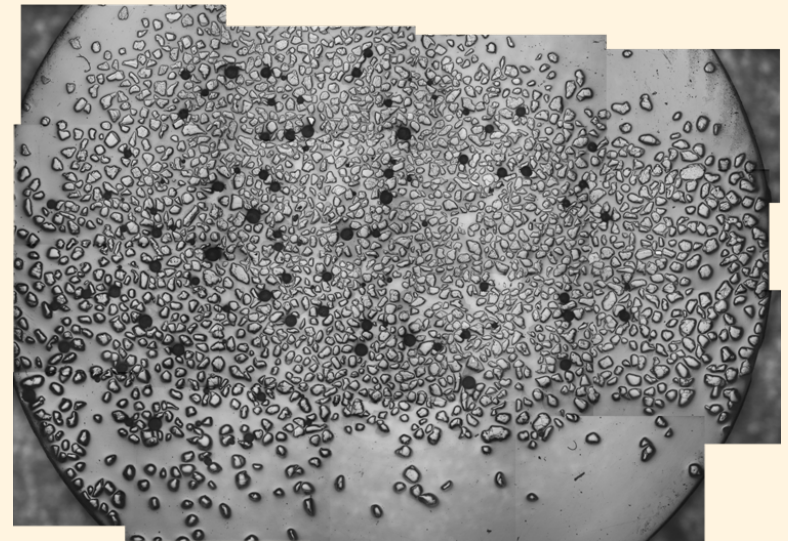
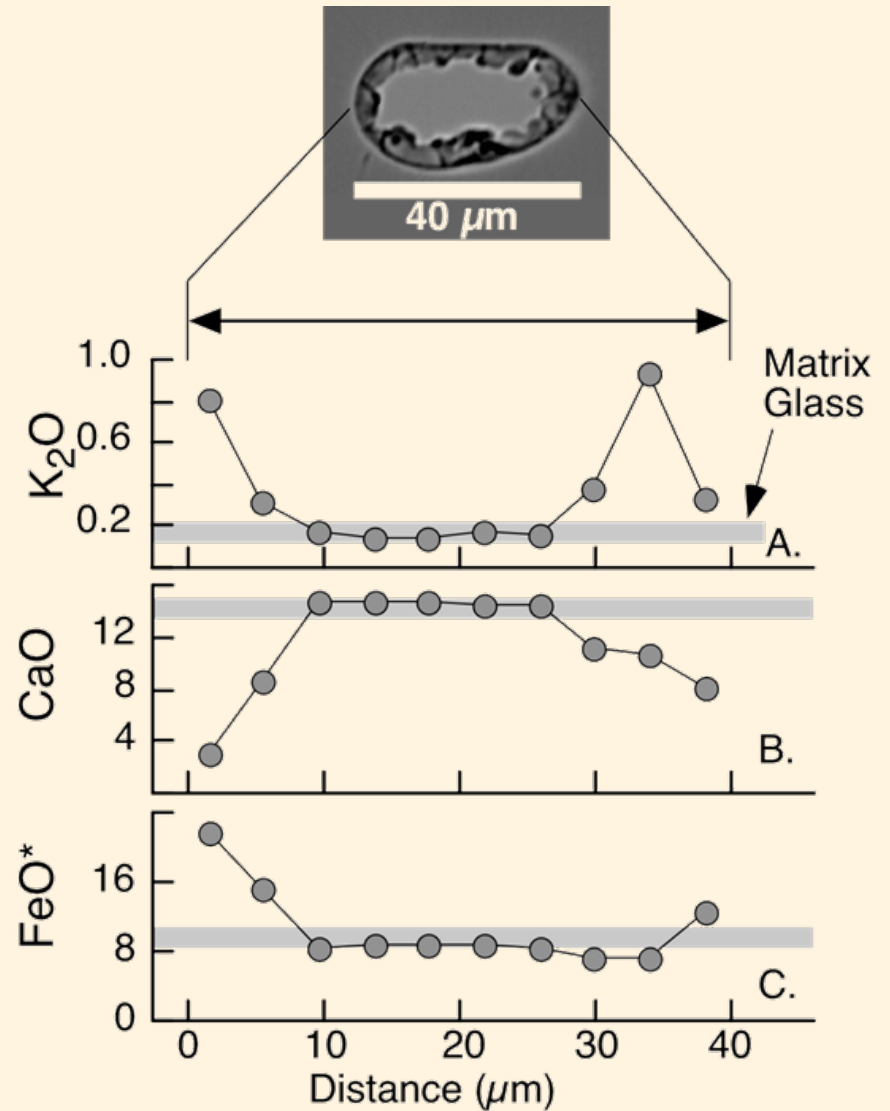
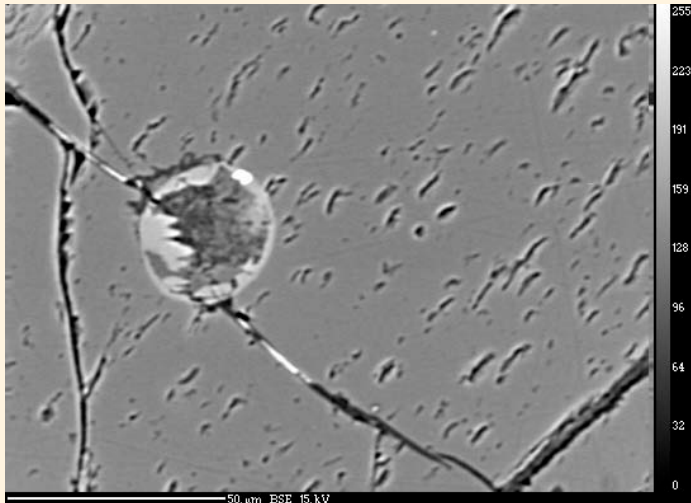
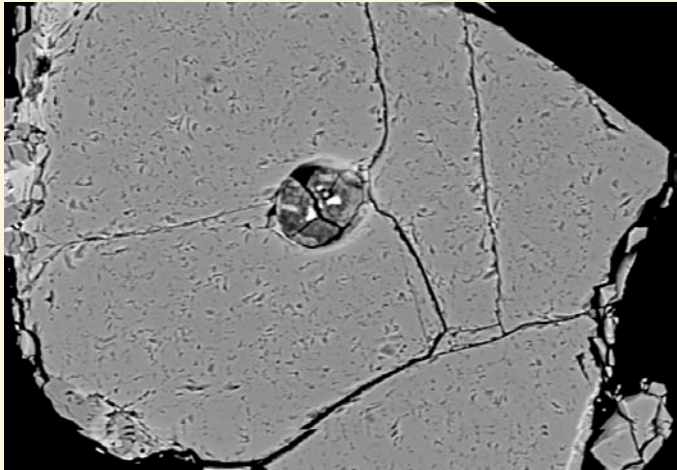


Fig. 1. Sketch of the polishing rig used to expose melt inclusions contained within olivine crystals. This rig concentrates polishing efforts only on the olivine crystals, allowing rapid exposure of large numbers of inclusions.

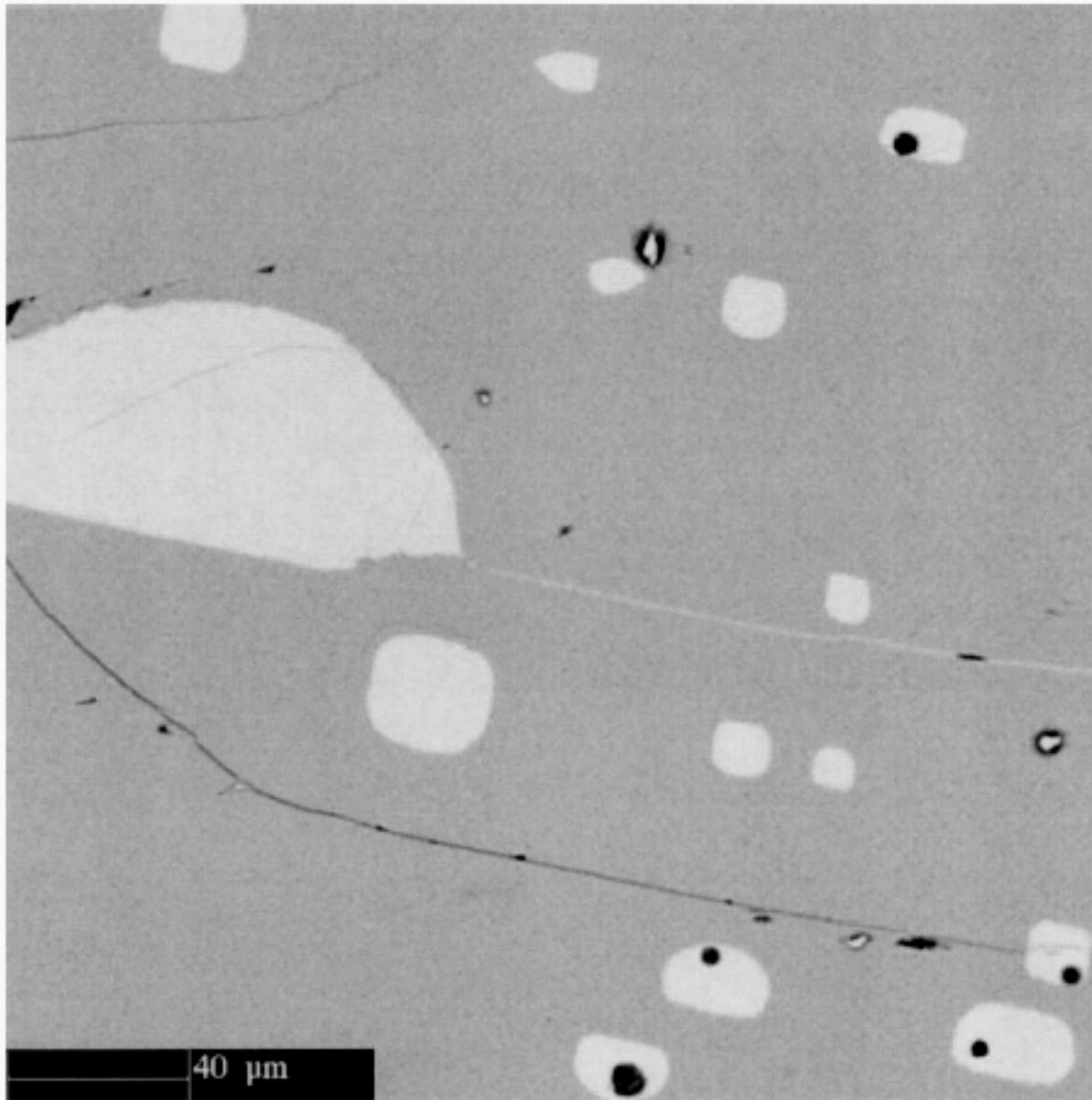


1" round epoxy grain mount

Weathering/Alteration of melt inclusion along fracture

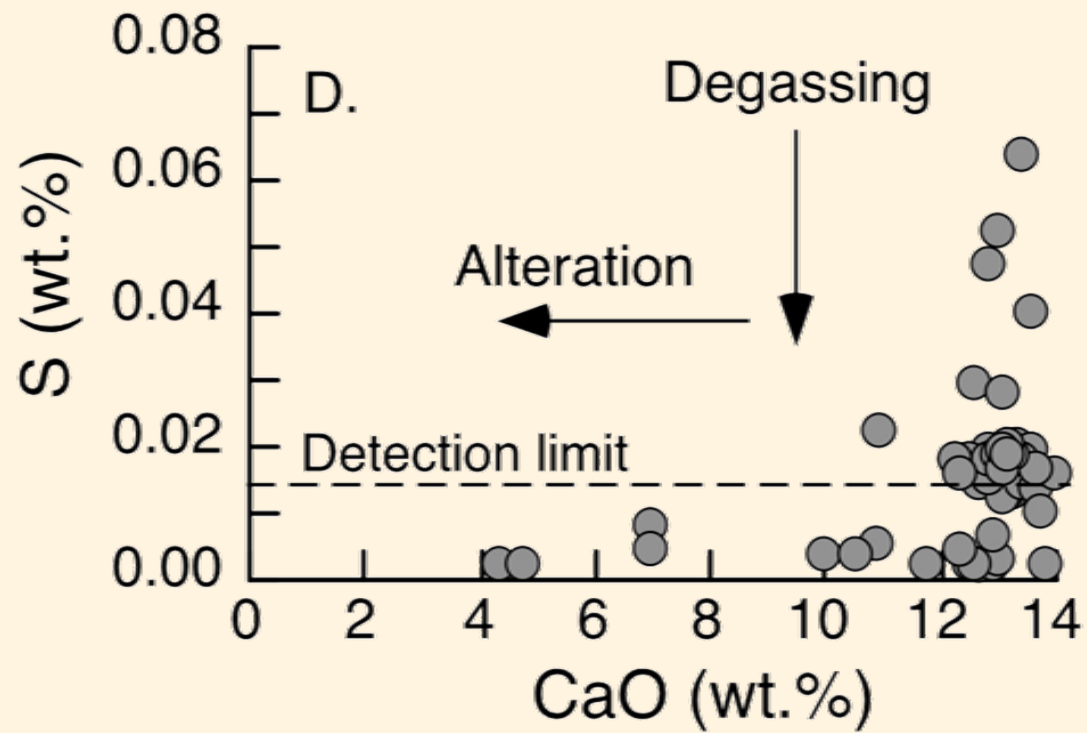


Nielsen et al 1998



	JdF O-2 intact	JdF O-2 ruptured	JdF O-2 oxidized	Gorda D9-2 intact	Gorda D9-2 ruptured	Blanco 5R intact	Blanco 5R ruptured
SiO ₂	50.03	50.39	55.39	49.75	49.42	50.00	43.75
TiO ₂	0.70	0.82	1.33	0.41	1.08	0.78	0.69
Al ₂ O ₃	17.47	17.07	16.57	16.95	16.98	17.49	18.02
FeO	8.03	7.67	0.23	7.43	8.31	8.14	5.02
MnO	0.13	0.31	0.51	0.13	0.24	0.13	10.22
MgO	9.07	8.66	9.87	10.68	9.14	8.47	6.96
CaO	13.09	13.13	14.57	13.01	12.72	12.20	12.16
Na ₂ O	1.47	1.73	0.63	1.92	1.97	2.73	2.25
K ₂ O	0.04	0.12	0.36	0.02	0.11	0.17	0.16
P ₂ O ₅	0.04	0.06	0.08	0.01	0.09	0.03	0.35
Cl (ppm)	31	0	44	23	35	43	43
S (ppm)	1020	13	21	862	28	942	13
Total	100.07	99.96	99.54	100.31	100.06	100.14	99.58
Mg#	66.8	66.8	98.7	71.9	66.2	65.0	71.2

Nielsen et al 1998



Rehomogenized

Analysis of Melt Inclusions

	Major Elements	Trace Elements	Volatiles	Isotopes
EMPA	Yes		S*, Cl	
SIMS		Yes	C,H,F,S,Cl	H, Li, B, Cl, S, O, Pb
LA-ICP-MS	Maybe	Yes		Pb, Sr
FTIR			H*,C	

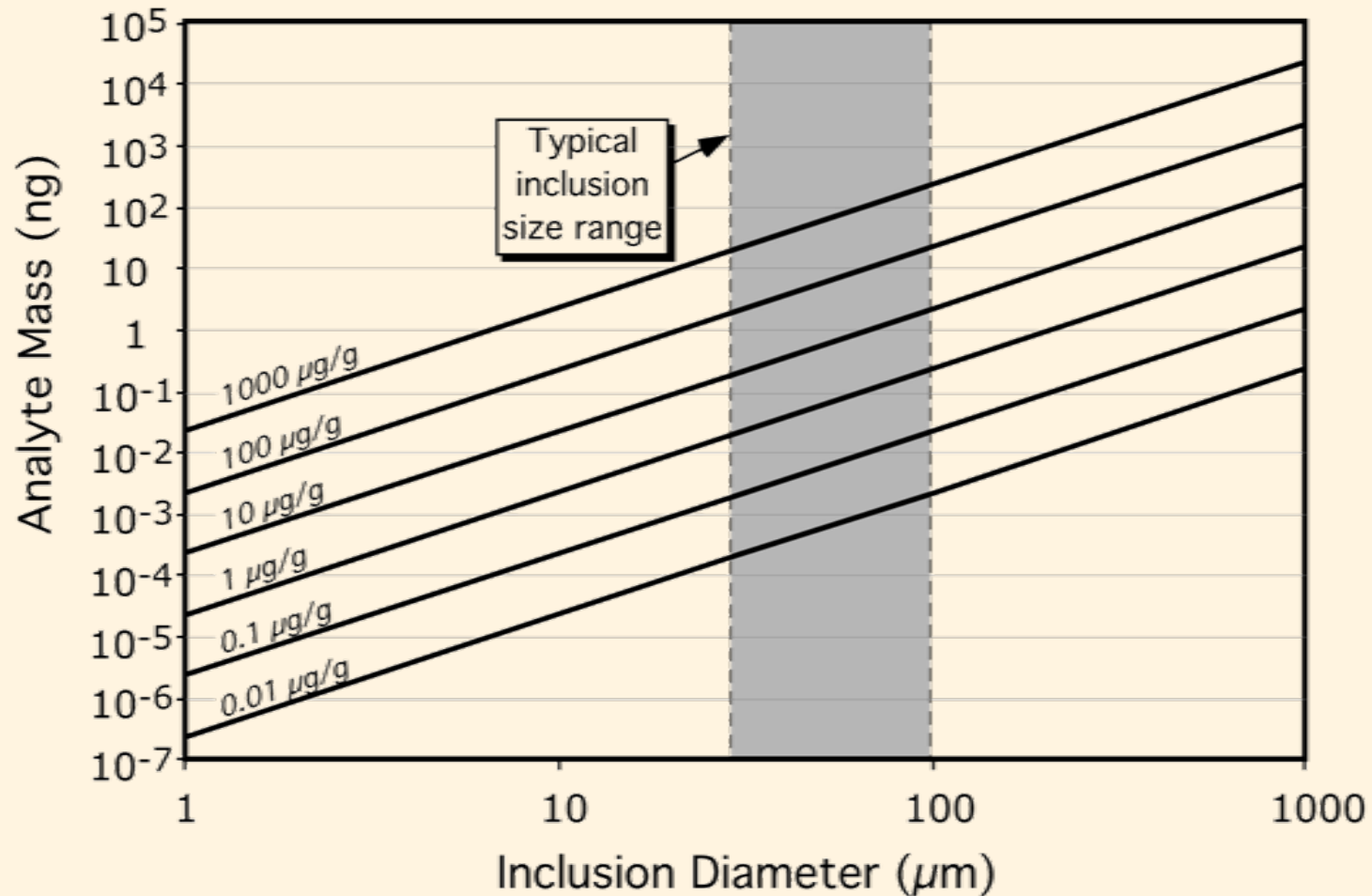
*plus speciation

Wallace

- EMPA

- FTIR

Trace Element Analysis

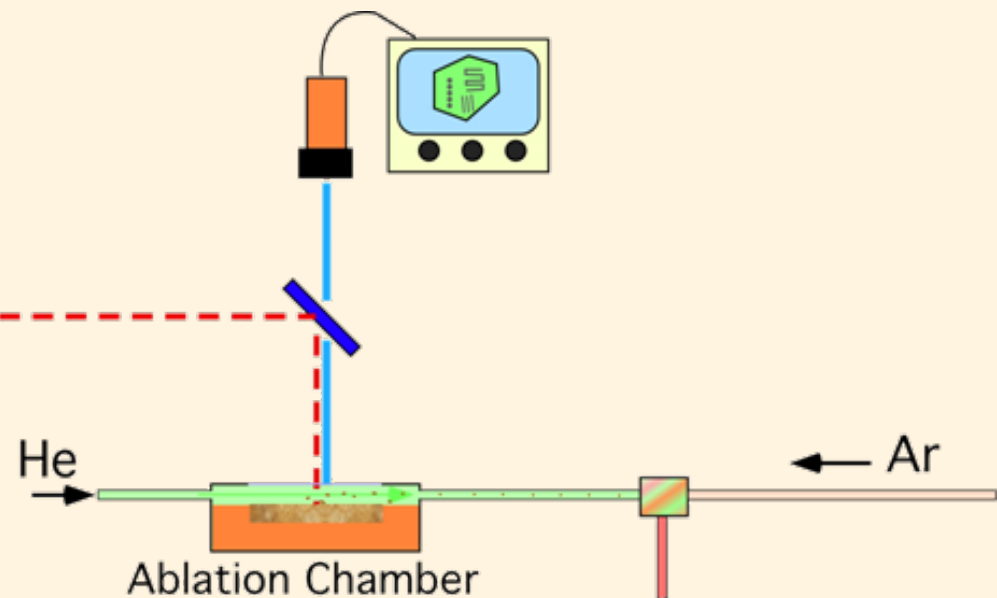
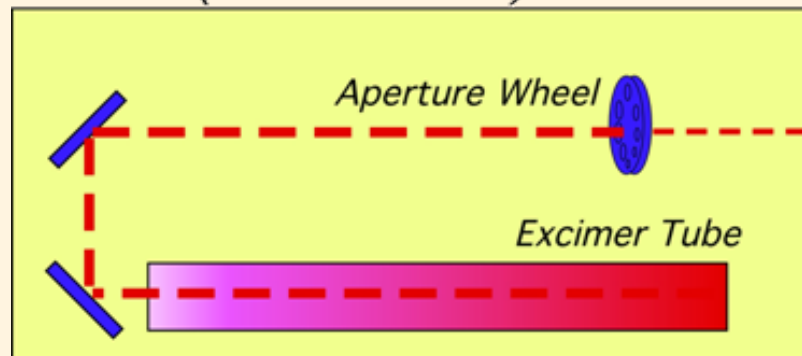


Melt inclusions are small: trace elements are present in ng-pg (10^{-9} - 10^{-12} g) quantities

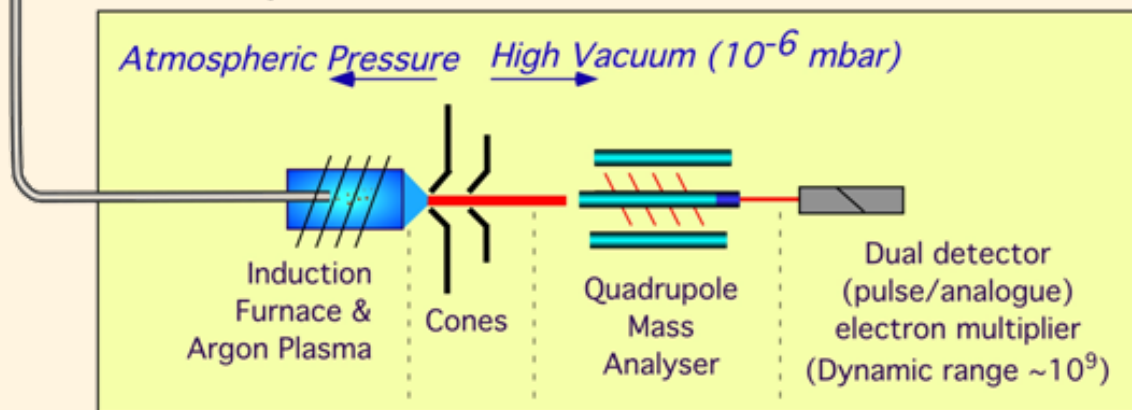
Laser Ablation ICP-MS



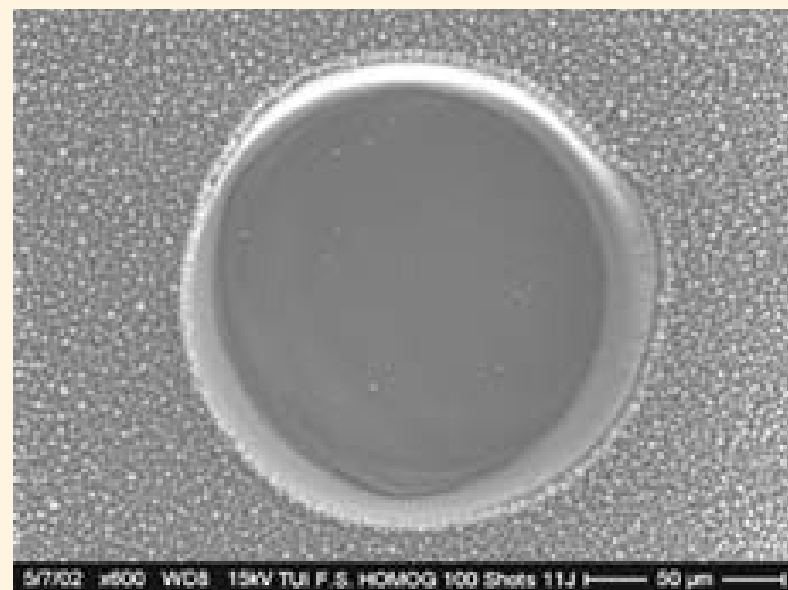
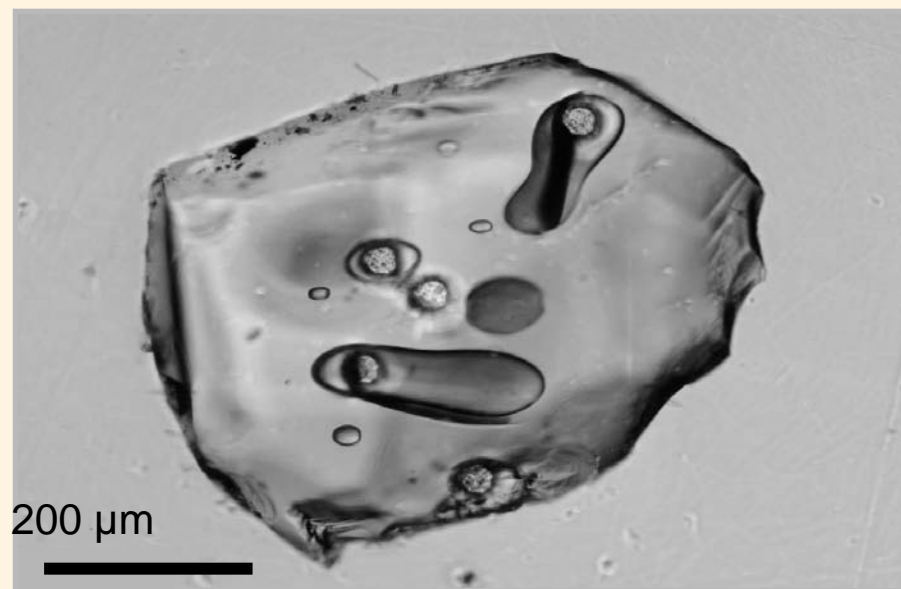
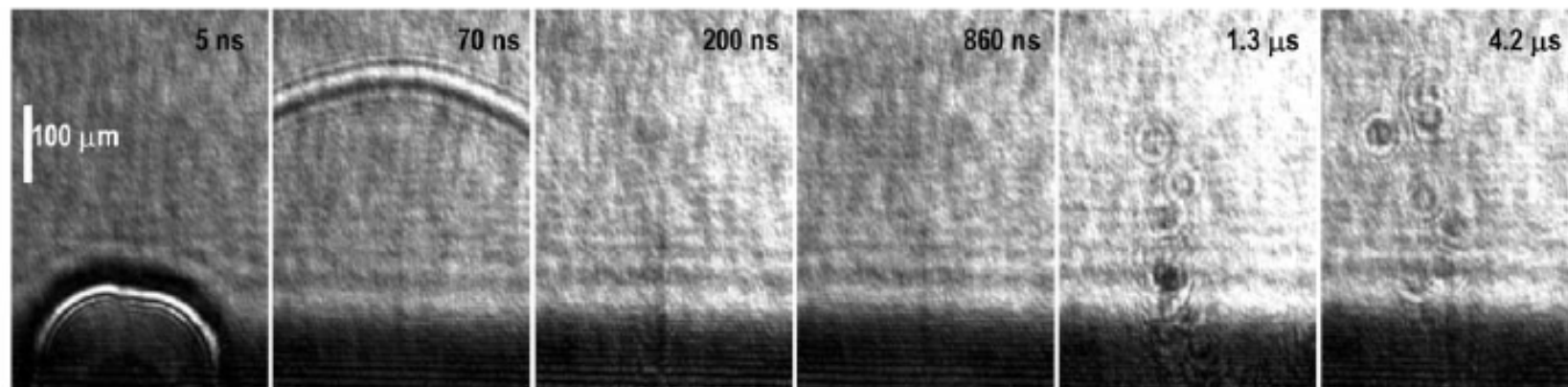
Excimer (Excited Dimer) Laser

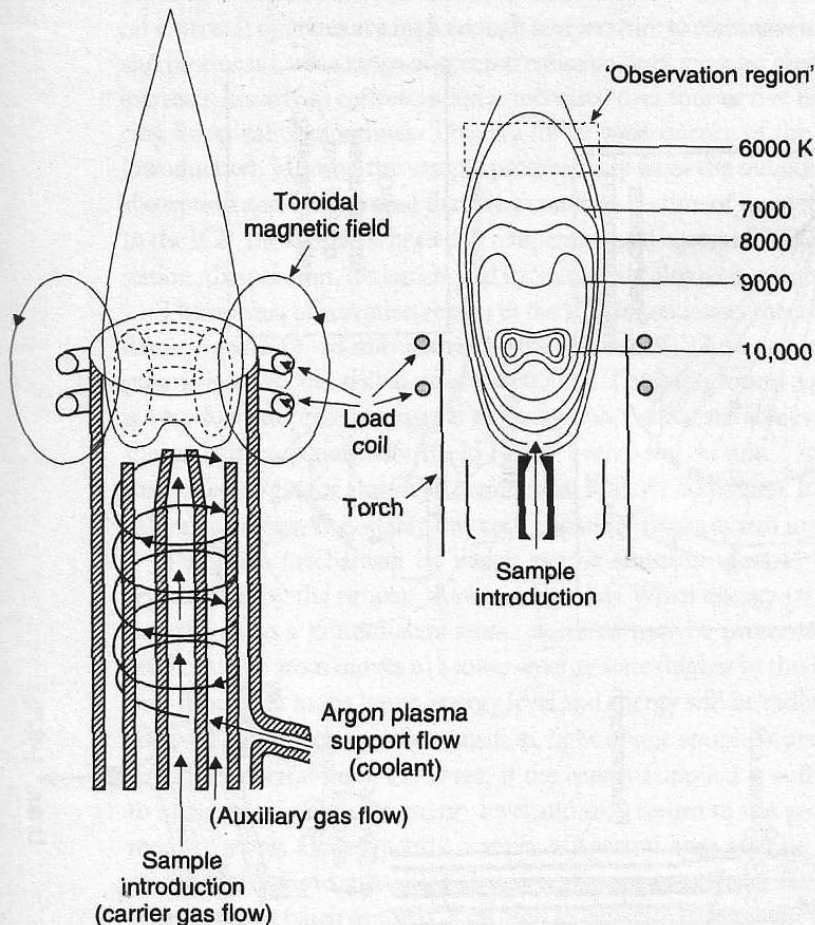


Quadrupole ICP-MS



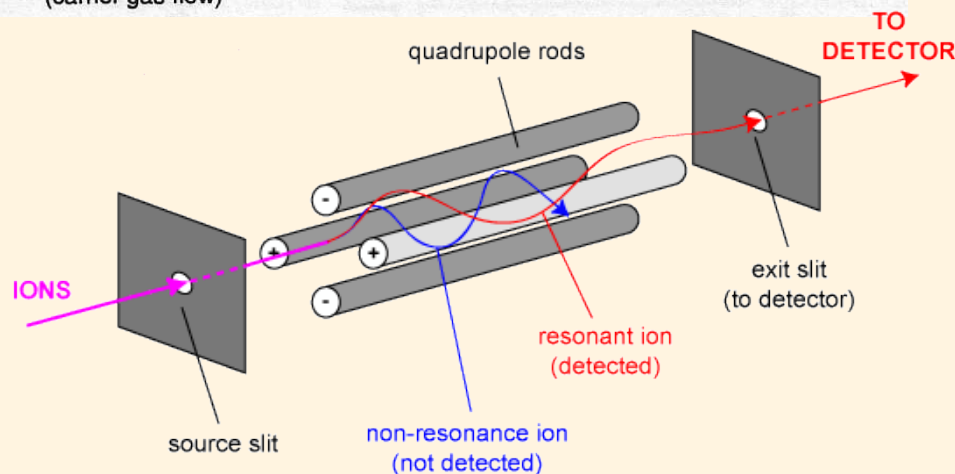
b





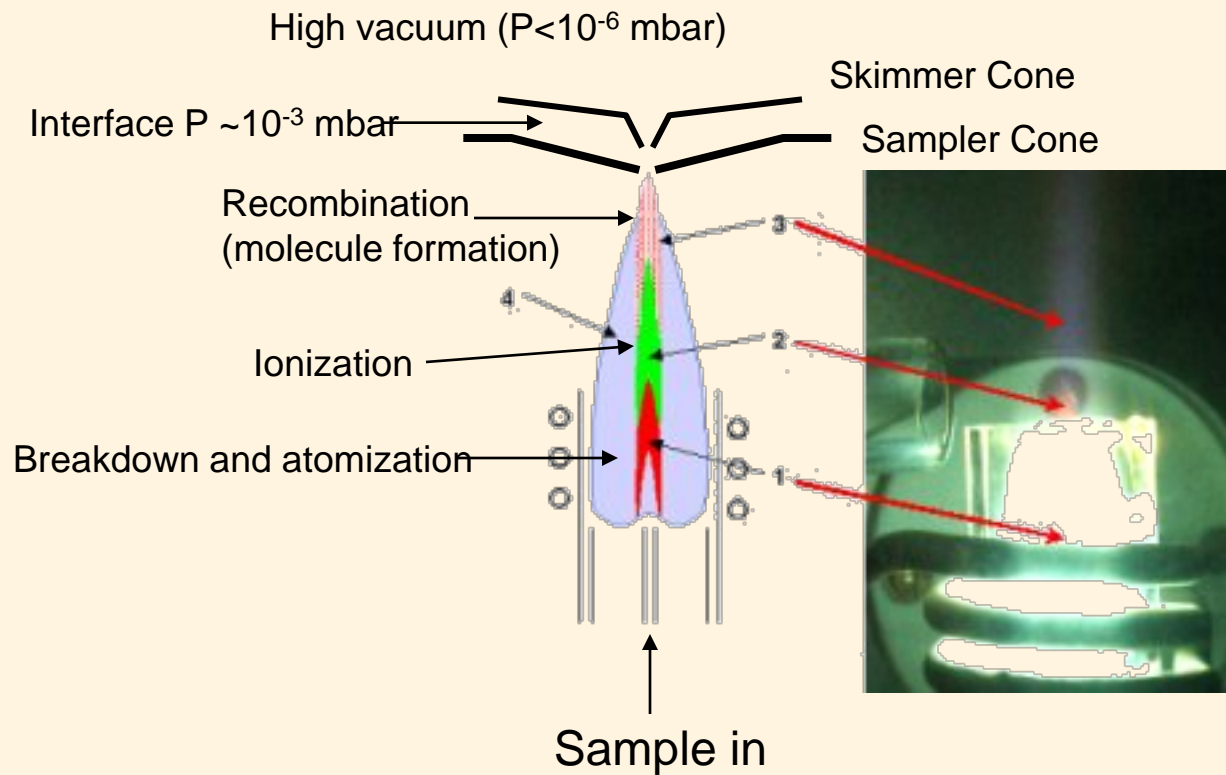
Inductively Coupled Plasma

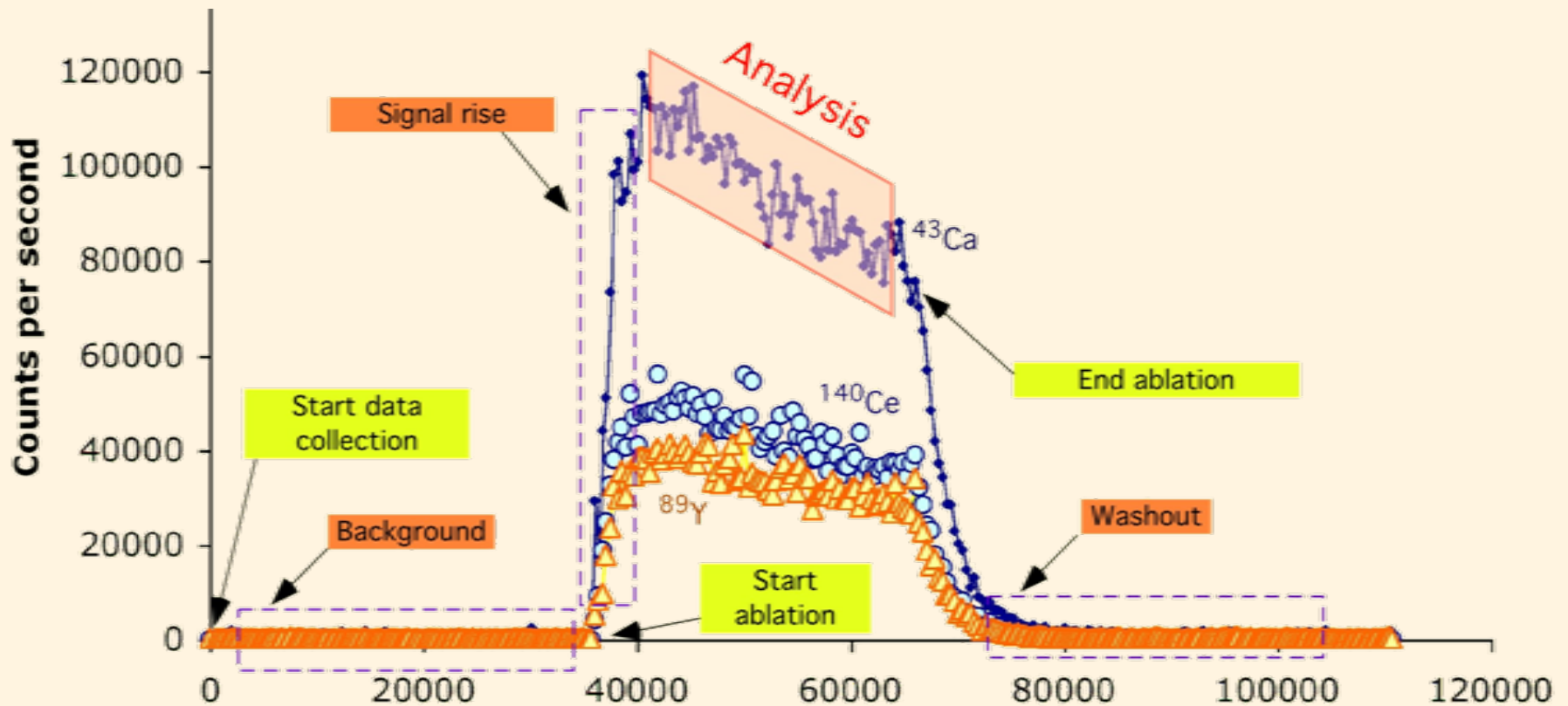
- High operating temperatures
- High atomization and ionization
- Low molecular production/survival
- Linear relation between ion intensity and response over many OOM



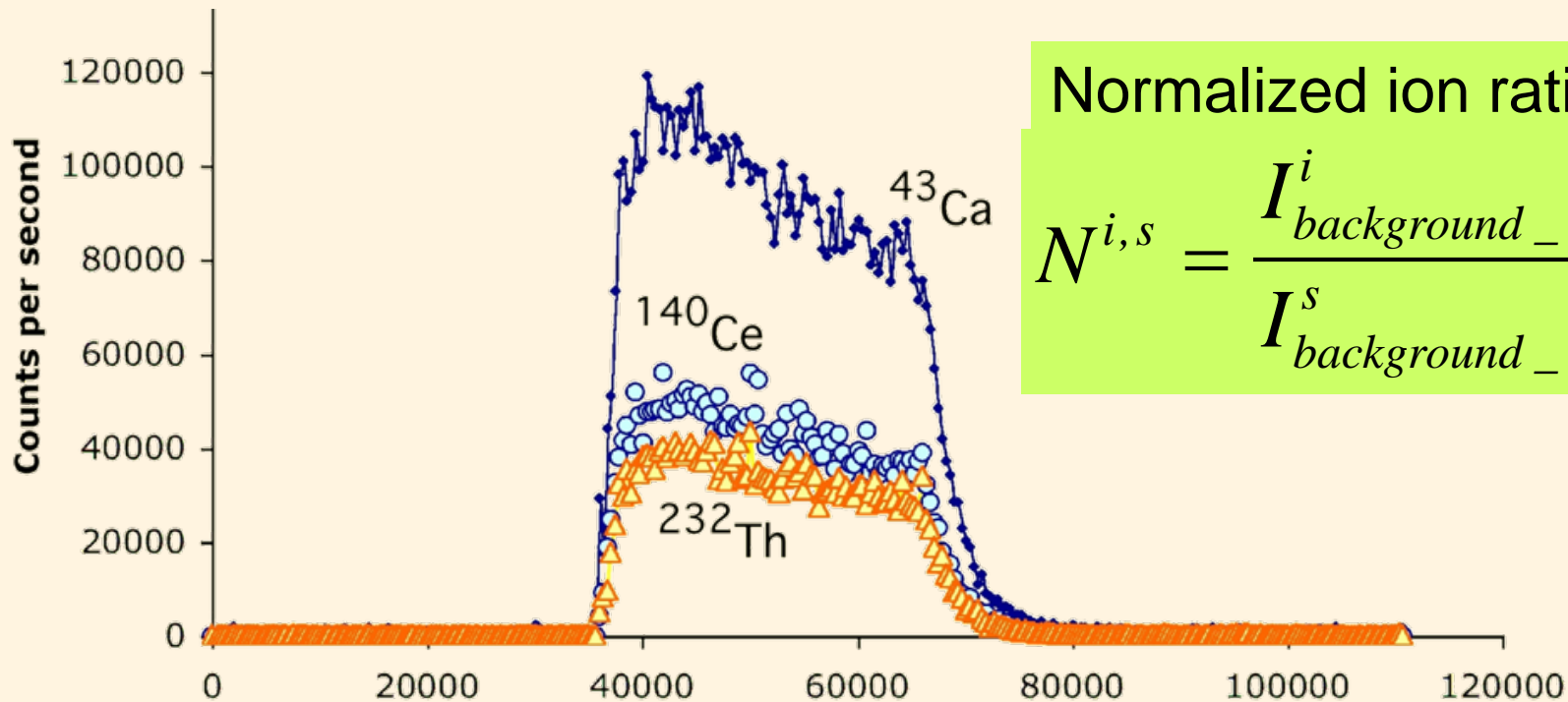
Quadrupole Mass Analyzer

- Rapid mass scanning ability (2 ms dwell, 10 ms count)
- Can monitor multiple isotopes during individual analysis
- Coupled with dual stage electron multiplier detectors with linear dynamic range of 10^8



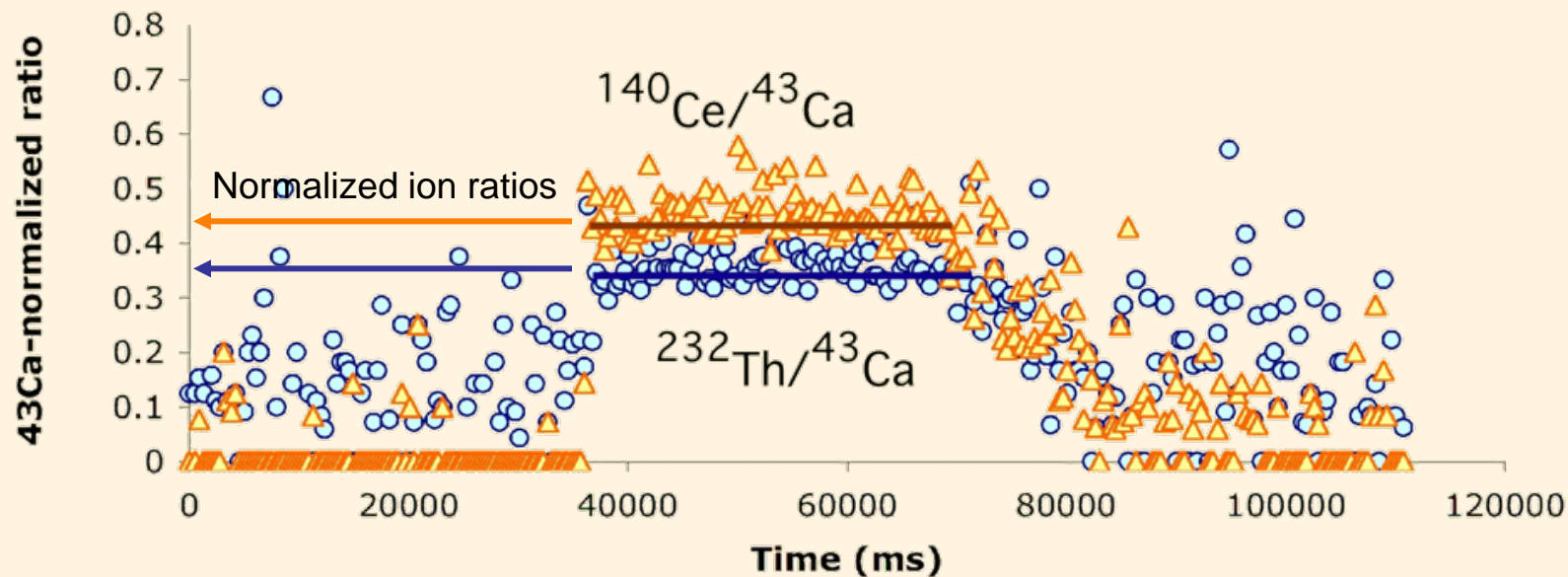


- Time resolved Analysis - TRA
- Signal intensity recorded as a function of time
- Analysis involves distinct phases
 - Background, Ablation, Washout

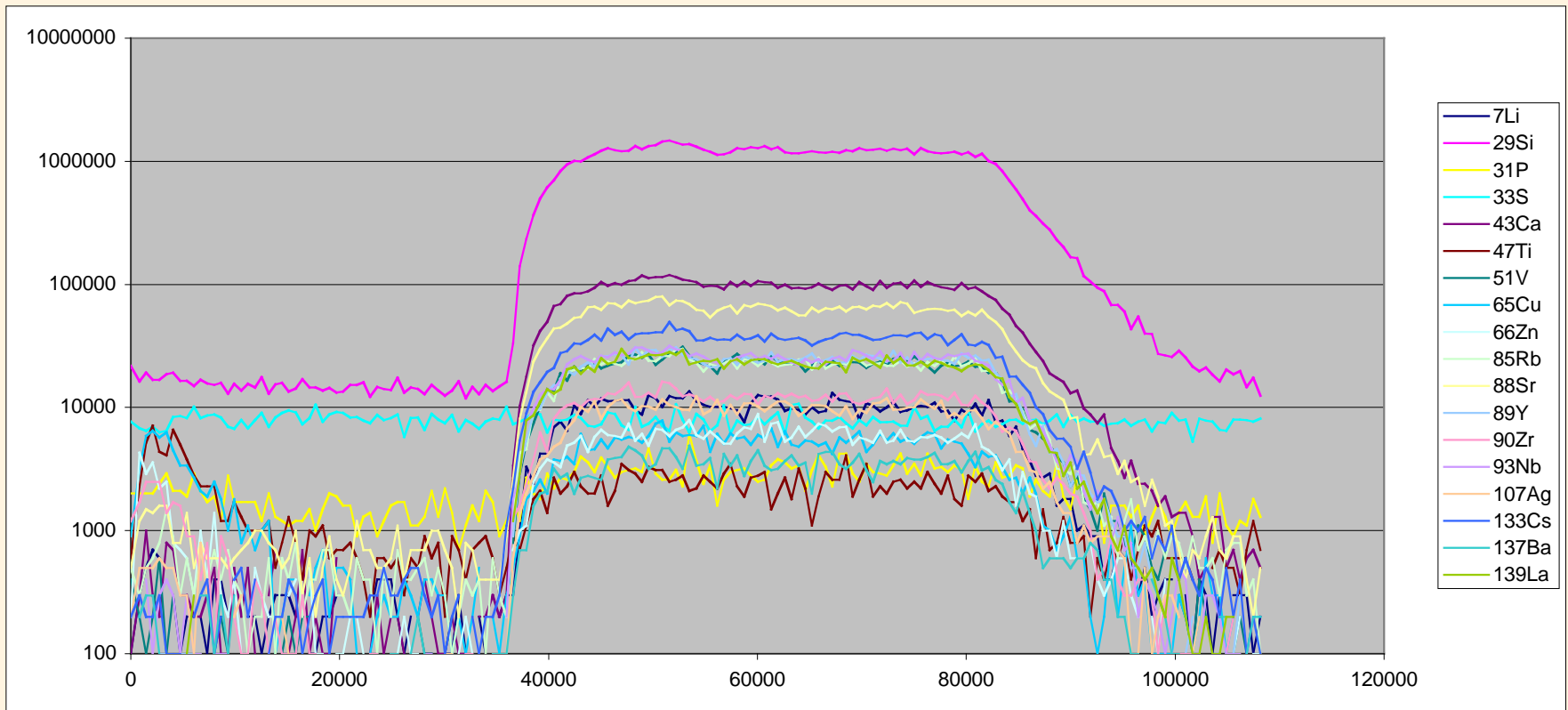


Normalized ion ratio

$$N^{i,s} = \frac{I_{background_corrected}^i}{I_{background_corrected}^s}$$

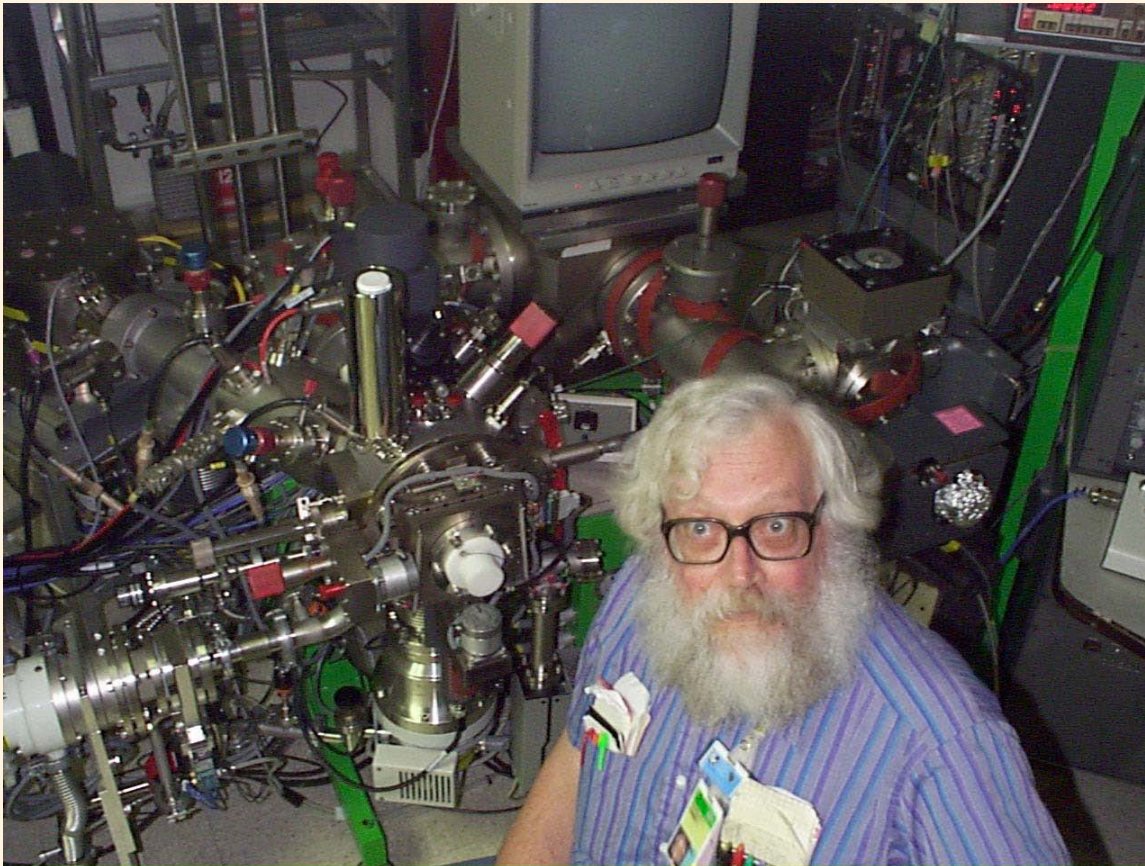


Counts vs Time

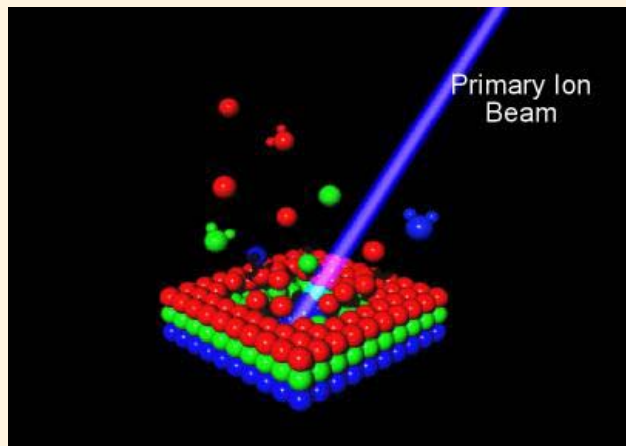
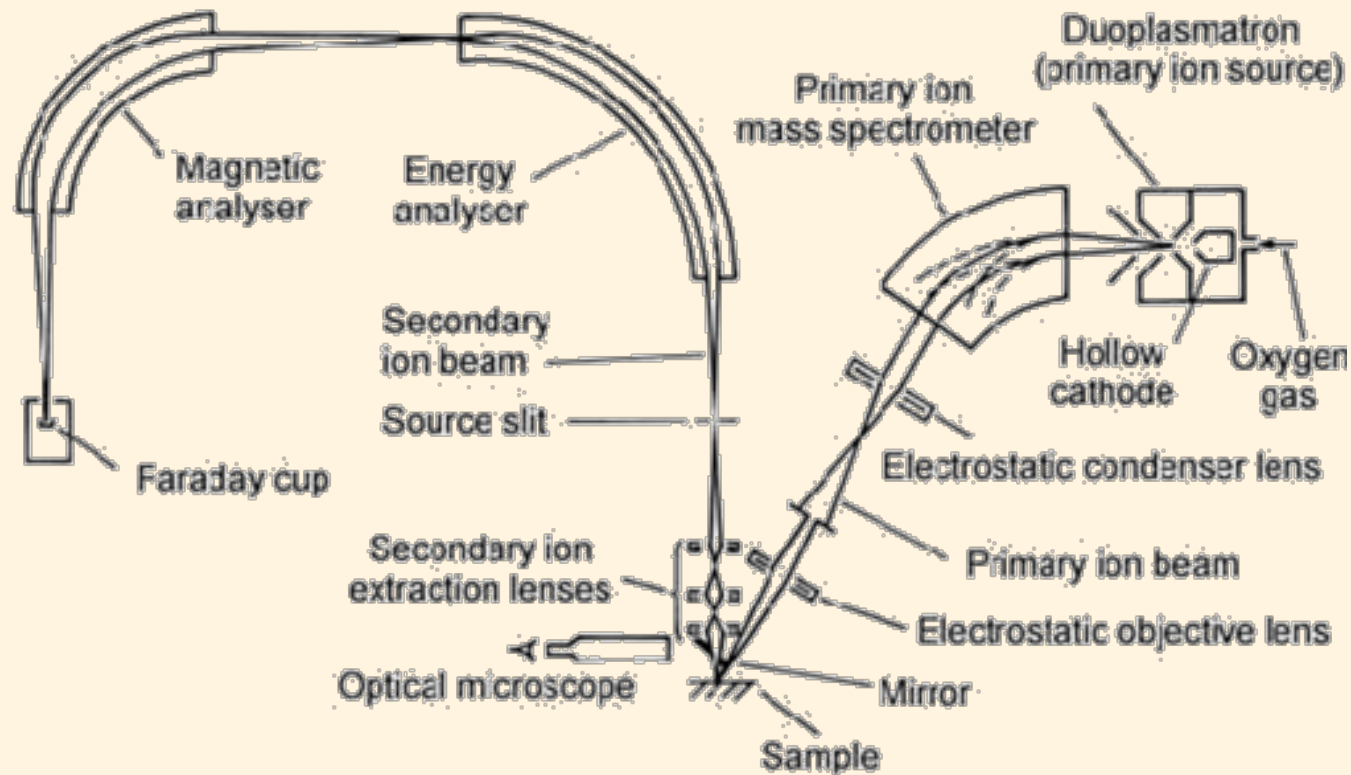


- Typically 30+ trace elements analyzed “simultaneously”

Secondary Ion Mass Spectrometry (SIMS, Ion microprobe)



BEWARE INTRUDERS!
Science in Progress



Focused beam of ions ($^{16}\text{O}^+$, $^{133}\text{Cs}^+$) coupled with double-focusing mass spectrometer



SHRIMP at Stanford

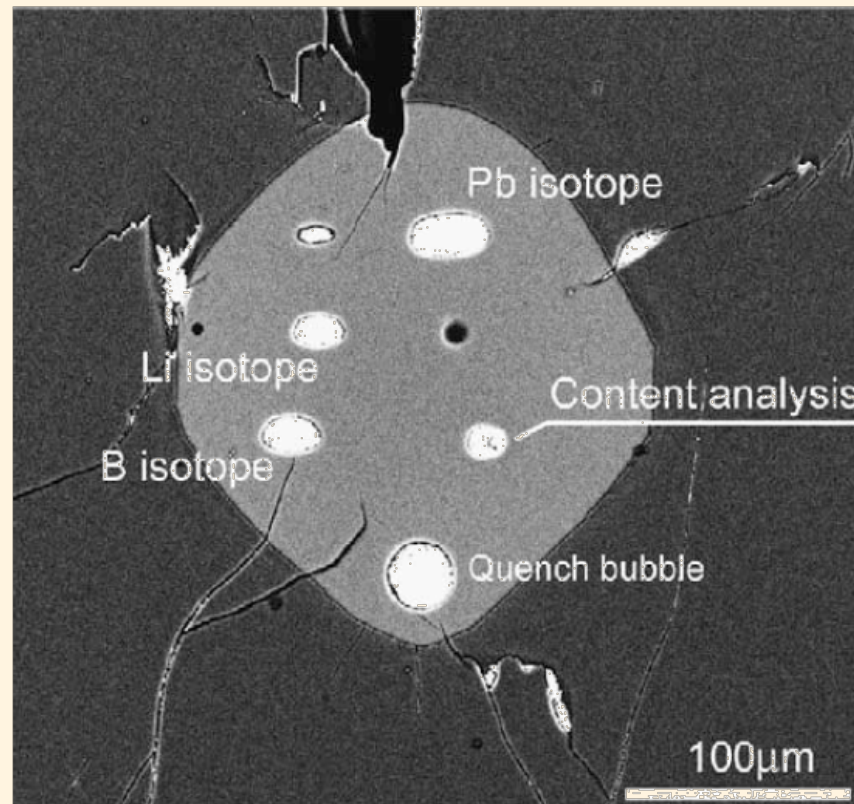
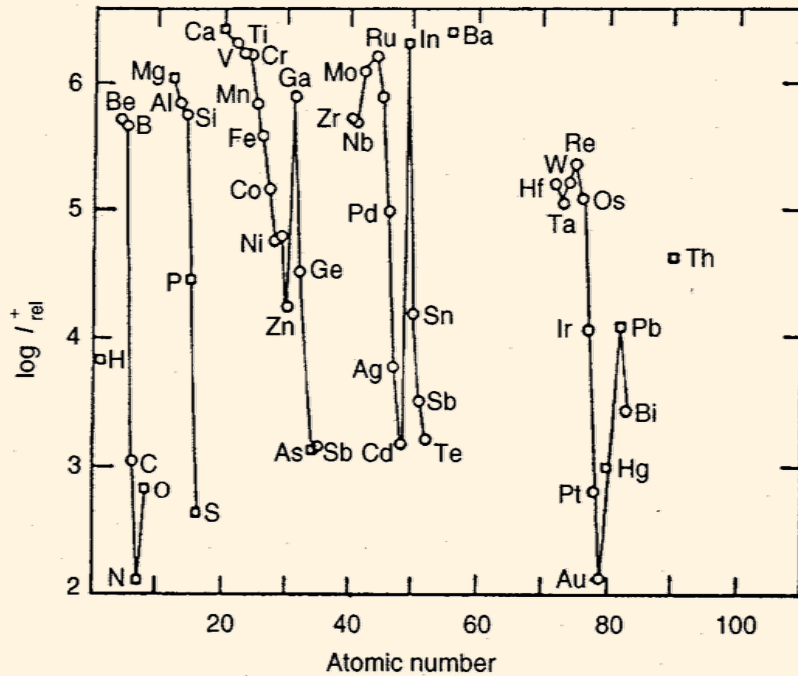
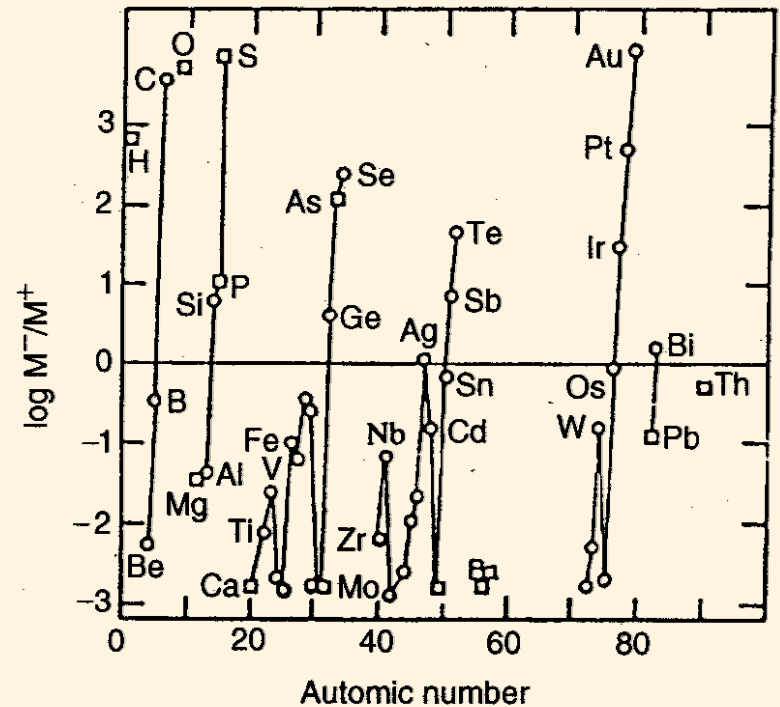


Fig. 3. Backscattered electron (BSE) image of the homogenized glass inclusion in olivine phenocryst. Dendritic crystals are eliminated after the melting experiment. Observed cracks are formed during the quenching procedure. Bright parts are remaining Au coat from the ion probe analysis. Craters of Li–B–Pb isotope analyses by Cameca ims-1270 high mass resolution ion probe and of Li–B content analysis by Cameca ims-5f ion probe are observed.

Ionization



Positive secondary ions

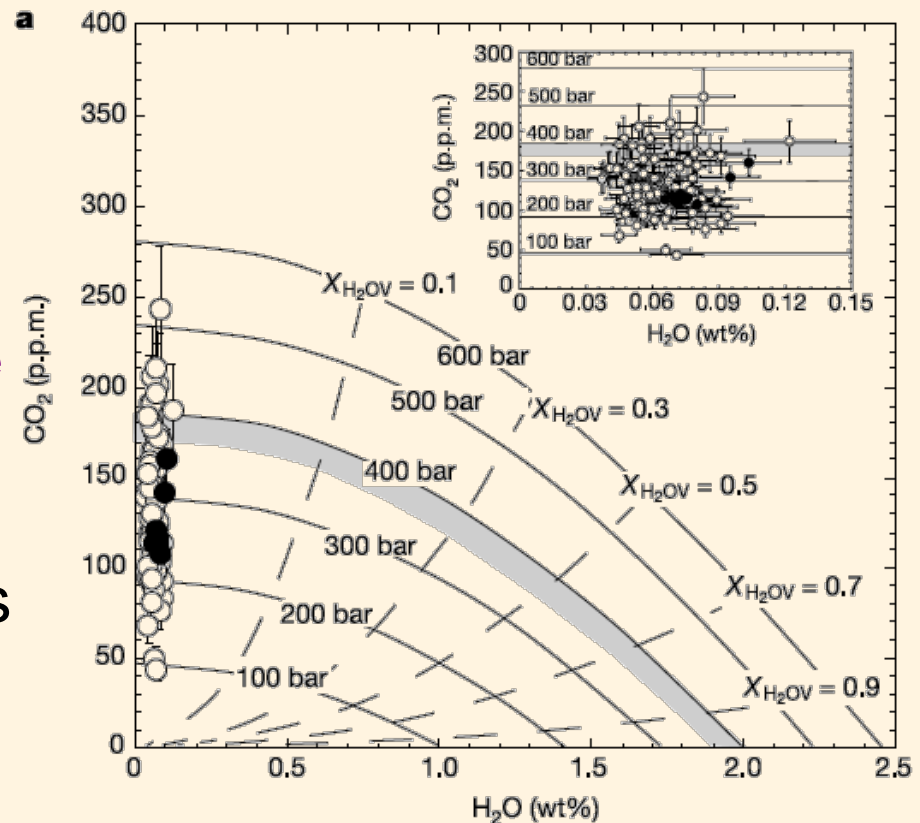


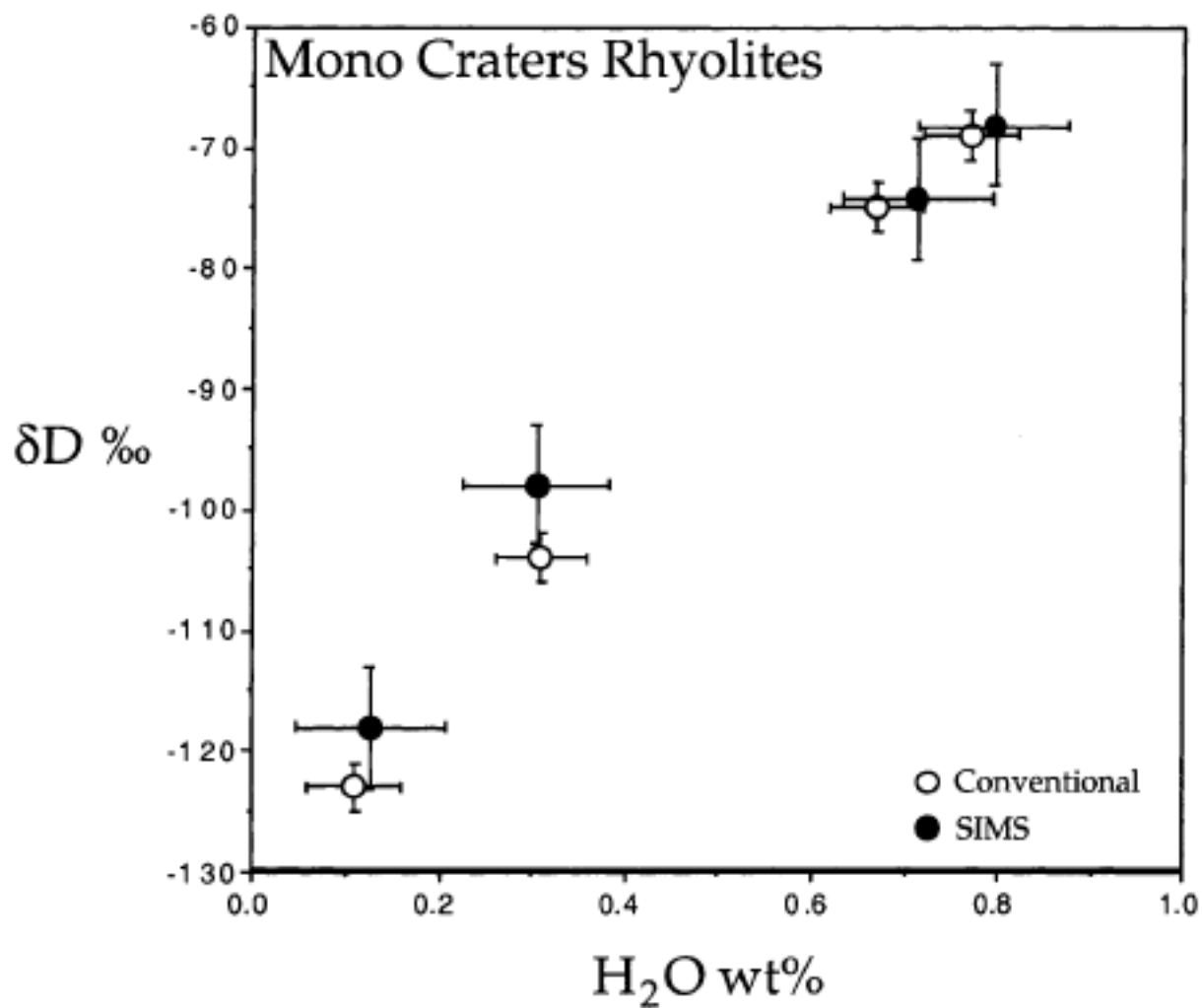
Negative secondary ions
(wrt positive)

H	<div><div><div></div><div>O₂⁺ Primary</div><div>Postive Secondary</div></div><div><div></div><div>Cs⁺ Primary</div><div>Negative Secondary</div></div></div>																He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
<div><div><div></div><div>O₂⁺ Primary</div><div>Postive Secondary</div></div><div><div></div><div>Cs⁺ Primary</div><div>Negative Secondary</div></div></div>																	
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

SIMS Volatile Measurements

- Measurement of H, C, F, Cl, S as negative secondary ions
 - Very high sensitivity due to high ionization
 - MDL are in the 1-10 ppm range
 - H^+ can also be analyzed
- Require low blank sample preparation and most mounts are now prepared with Indium metal not epoxy





Hauri et al. 2002

In-situ Analysis: Key Variables

- Precision:

$$s = \frac{\sqrt{n}}{n} = \frac{1}{\sqrt{n}}$$

R - spatial resolution

n - number of counts

B - background counts

C - concentration

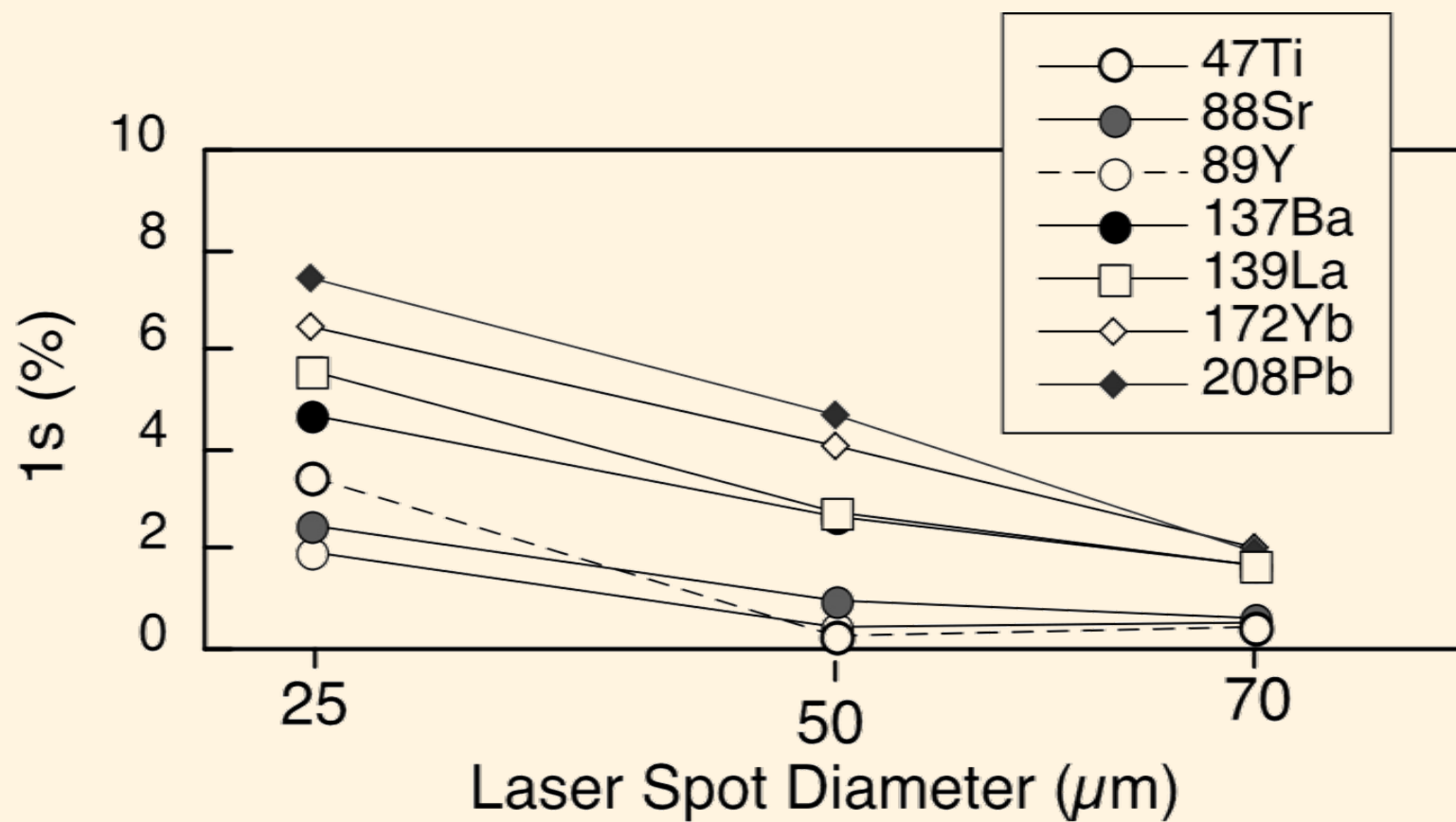
- Minimum Detection Limit:

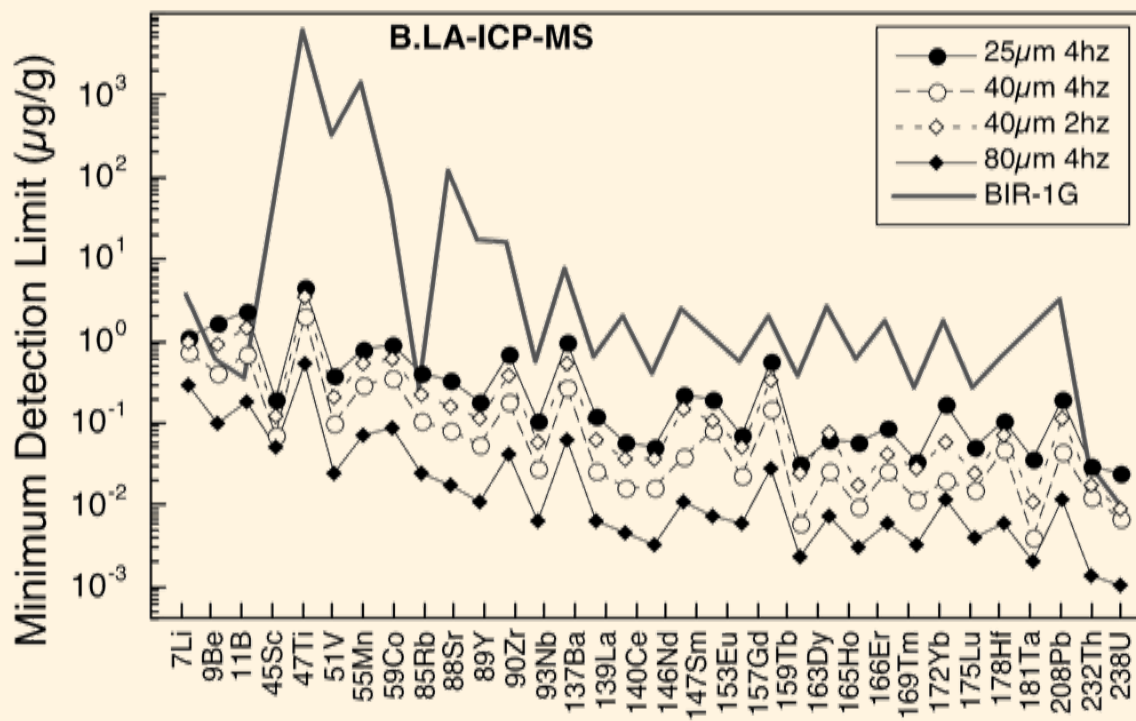
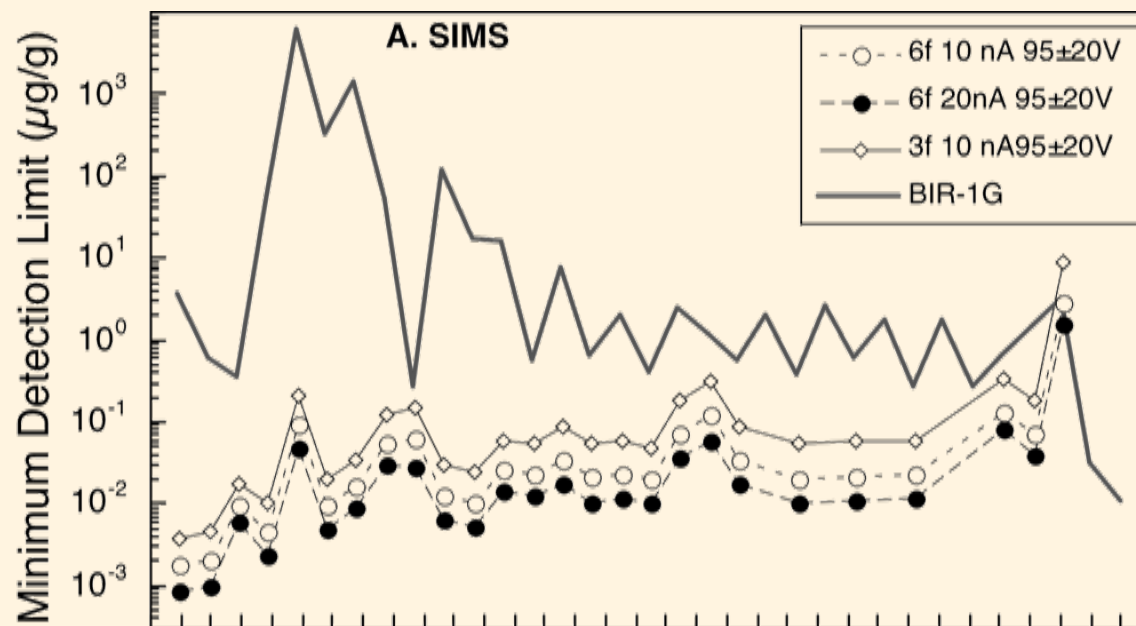
$$MDL \propto \frac{\sqrt{B}}{n} = 2\sqrt{B} \times \frac{C}{n}$$

- Spatial Resolution: $R \propto r^2 \propto n^2$

At higher spatial resolution n decreases and MDL and precision get worse

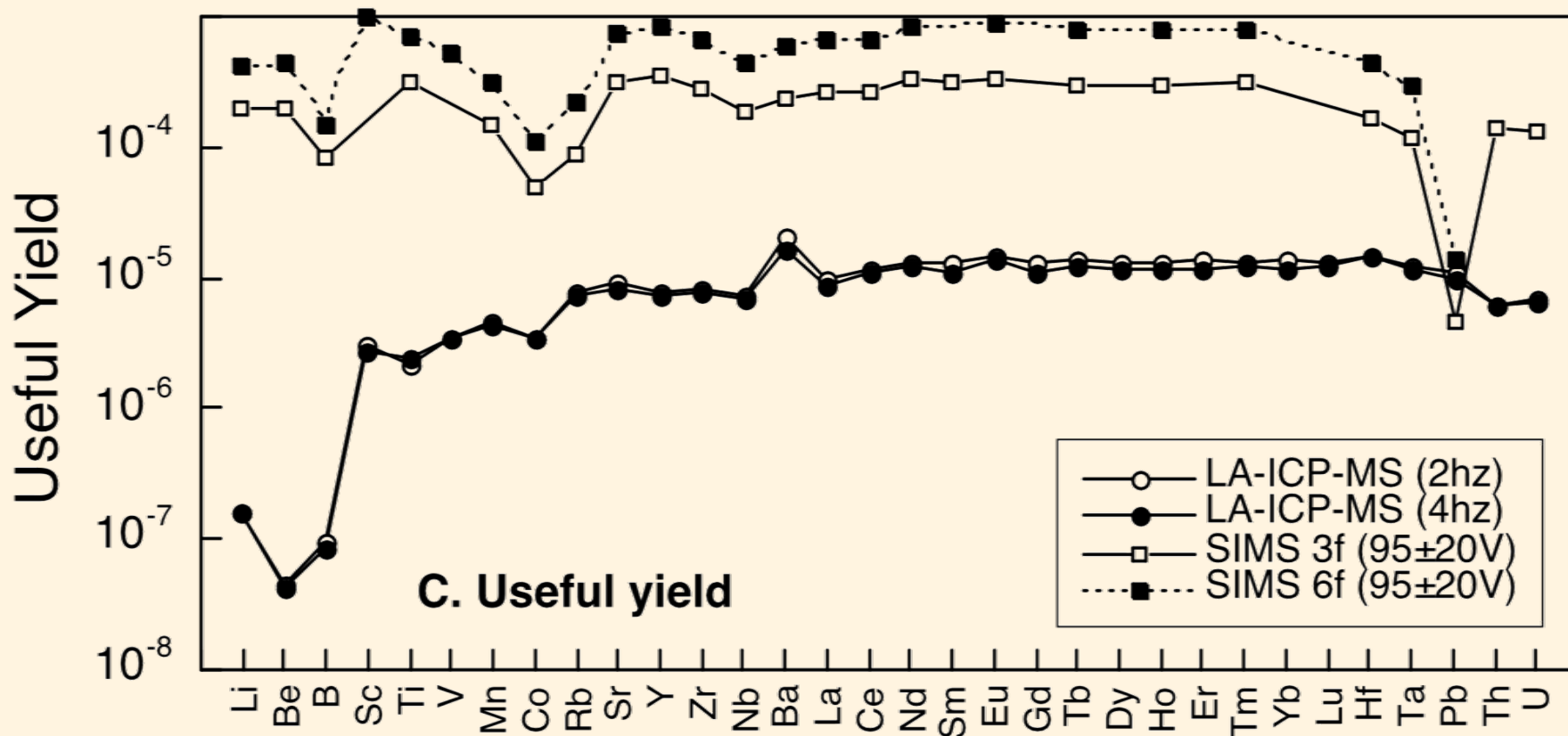
This is a fundamental limit for in situ analyses





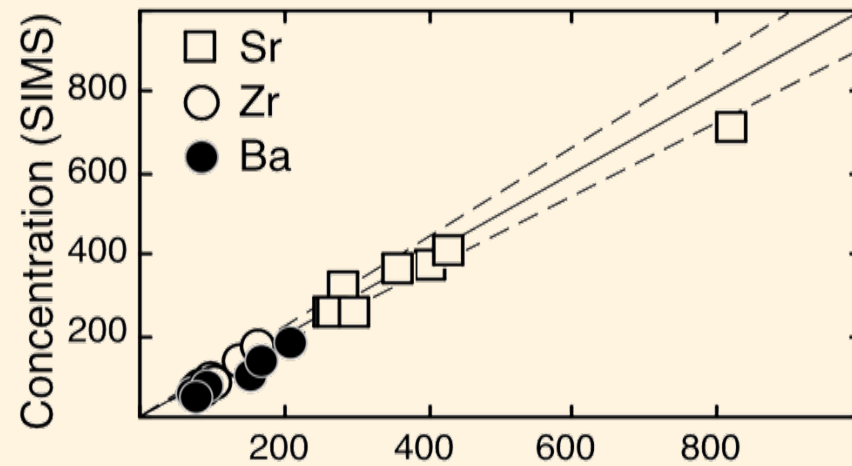
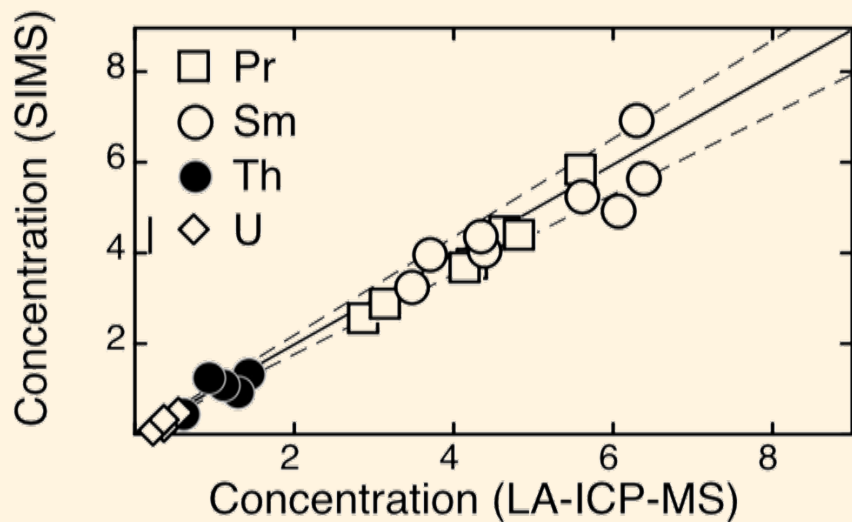
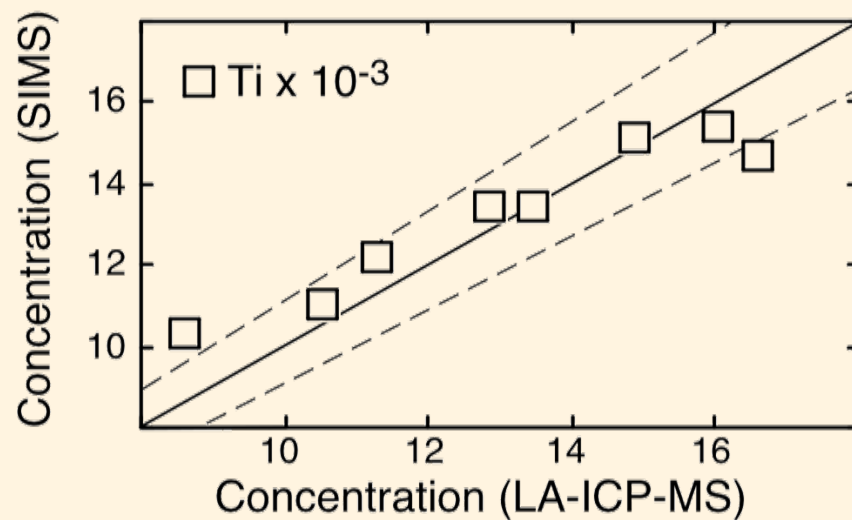
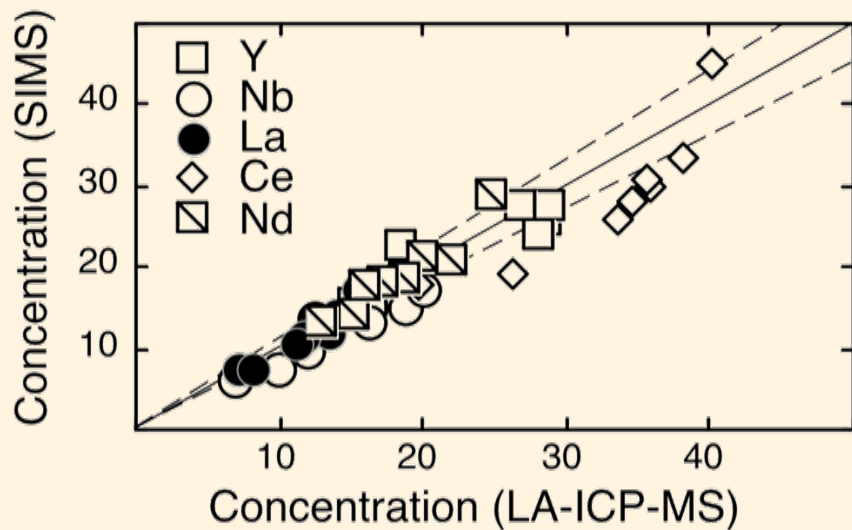
$$UY = \frac{\text{counts detected}}{\text{atoms removed}}$$

$$UY_{\text{SIMS}} \gg UY_{\text{LA-ICP-MS}}$$



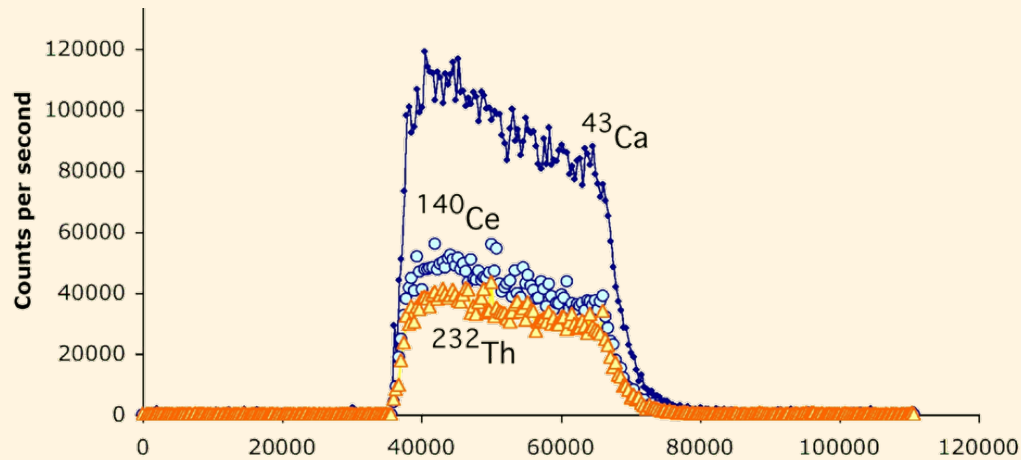
SIMS vs LA-ICP-MS

	SIMS	LA-ICP-MS
Resolution	5-30 μm	5-300 μm
Accuracy	5-15%	5-15%
Precision	2-20%	2-20%
Removal rate	$\mu\text{m}/\text{hour}$	$\mu\text{m}/\text{second}$
Useful Yield	10^{-2} - 10^{-3}	10^{-4} - 10^{-6}
Analysis Time	30-60 min	1-2 min
Destructive?	Yes, can be minor	Very
Problematic elements	Transition metals, Rb, Pb, HREE, low masses, oxides	As, halogens, LLE, argides, oxides
Cost	US\$2-5 million	\$300-600K

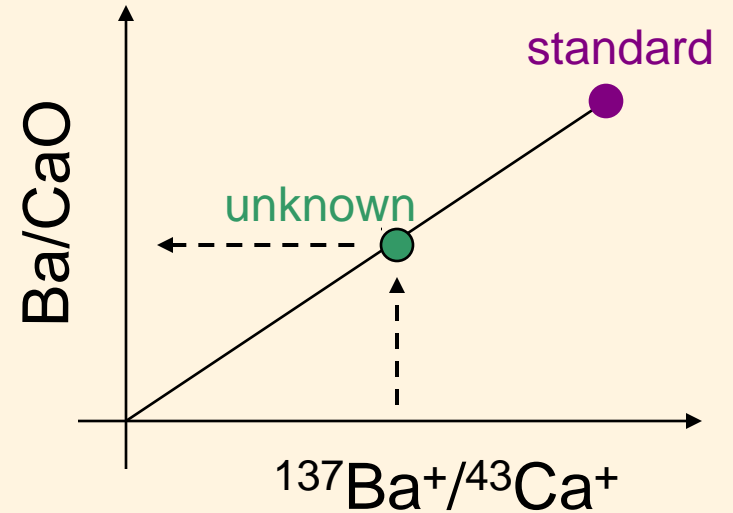
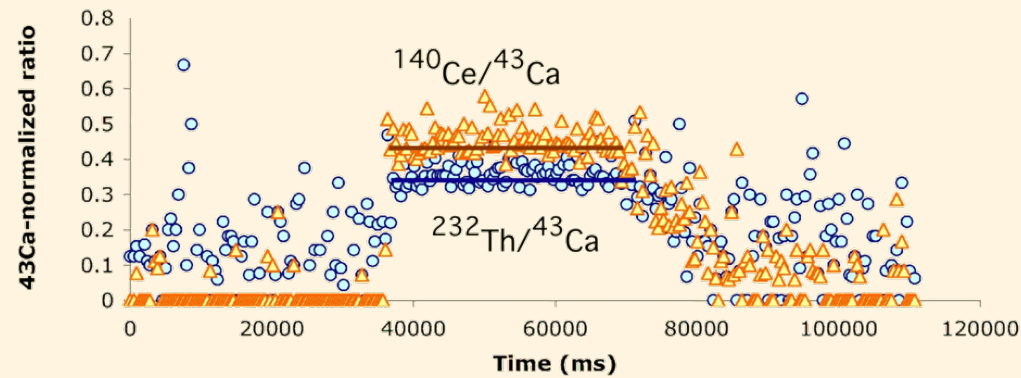


Standardization

- **Problem 1:** Physics of laser ablation or ion sputtering are not sufficiently well understood to allow calculation of concentrations directly from measured ion intensities
- **Problem 2:** Intensity of counts will vary depending on tuning and instrumental parameters as well as with the efficiency of laser/ion beam “coupling”
- Solution 1: Calibrate by comparison to standard materials
- Standard 2: Use internal standard based calibration
 - Requires knowing the composition of an *internal standard* element (Ca, Si, Ti, Mg)



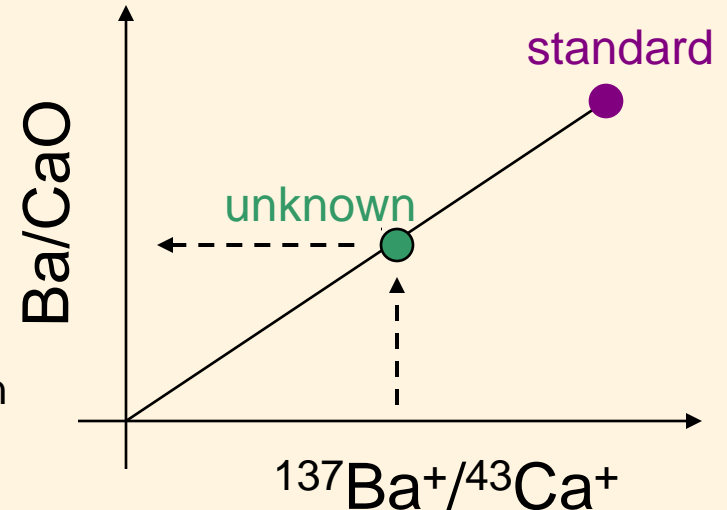
$$N^{i,s} = \frac{I_{corrected}^i}{I_{corrected}^s}$$



$$C_i^U = C_s^U \frac{\left(\frac{C_i^R}{C_s^R} \right)}{\left(\frac{I_{ij}^R}{I_{Sk}^R} \right)} \left(\frac{I_{ij}^U}{I_{Sk}^U} \right)$$

Mini Exercise

- Write an equation for the gradient (m)
- Write an equation for the straight line
Assume the intercept = 0
- Using Ba/CaO as the y value
write your equation so you
relate $\text{Ba/CaO}_{\text{unknown}}$ to
 $^{137}\text{Ba}^+ / ^{43}\text{Ca}^+_{\text{unknown}}$
- Rearrange to calculate $\text{Ba}_{\text{unknown}}$



C_i^U = the concentration of trace element i in unknown material U

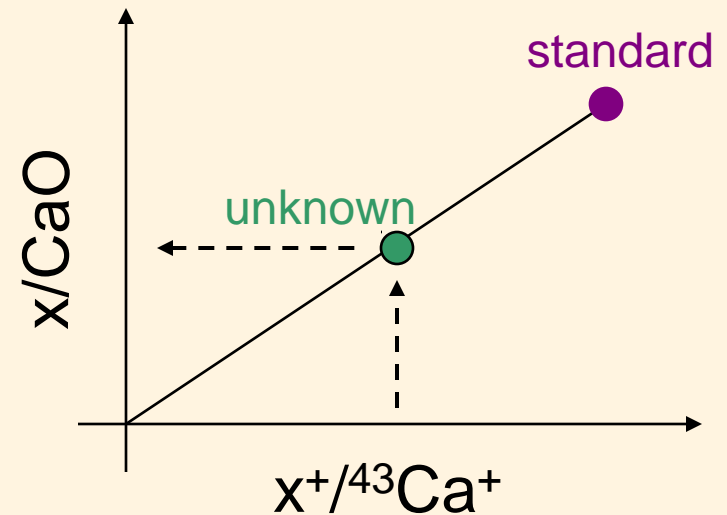
C_S^U = the concentration of the internal standard element S in the unknown material U .

C_i^R / C_S^R = the ratio of the known concentrations of trace element i to the internal standard element S in reference standard R .

I_{ij}^R / I_{Sk}^R = normalized ion yield (the ratio of measured ion beam intensities) for isotope j of trace element i and isotope k of the internal standard element S in the reference standard

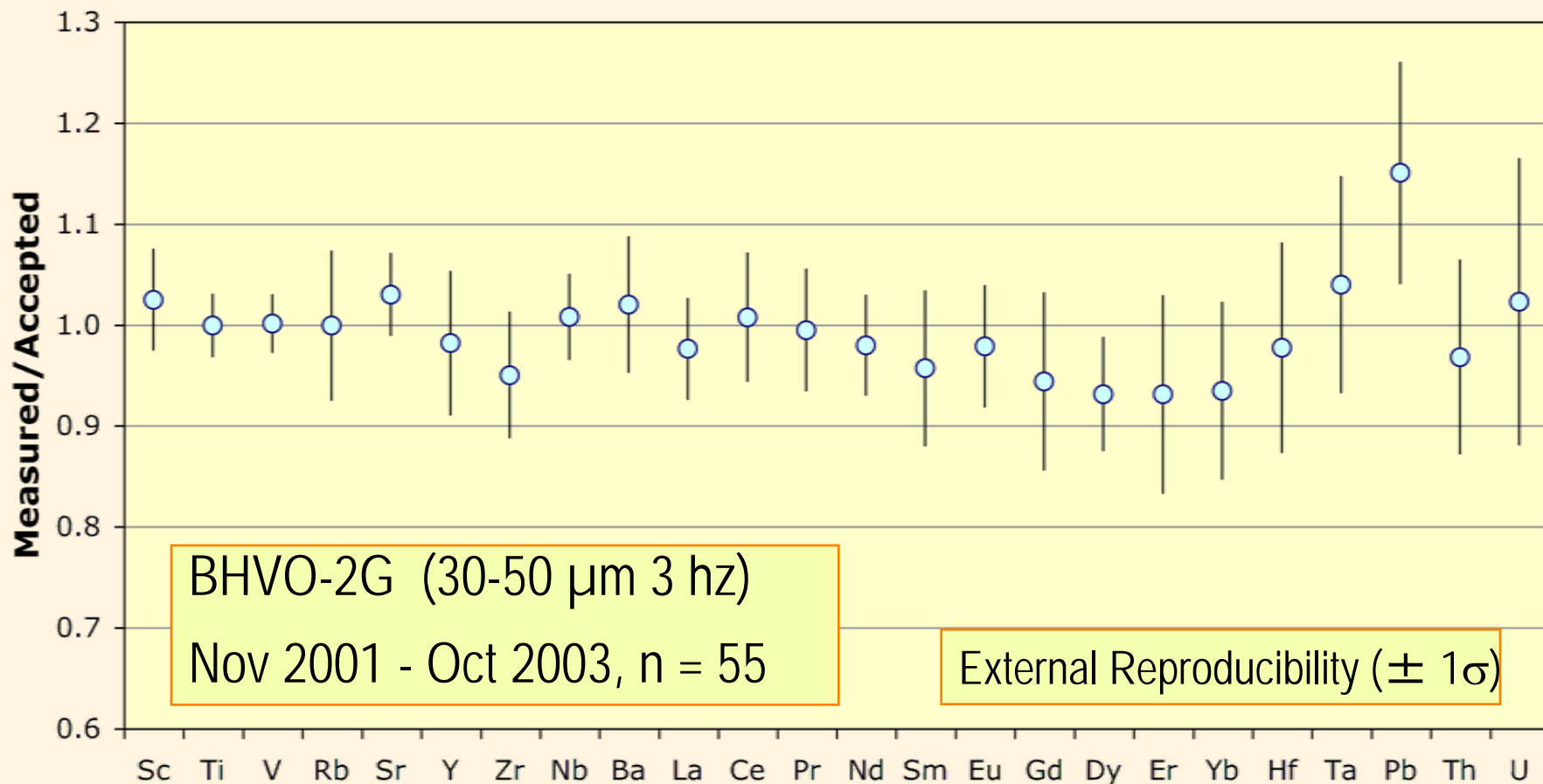
I_{ij}^U / I_{Sk}^U = normalized ion yield for isotope j of trace element i and isotope k of the internal standard element S in the unknown material

$$C_i^U = C_S^U \frac{\left(\frac{C_i^R}{C_S^R} \right)}{\left(\frac{I_{ij}^R}{I_{Sk}^R} \right)} \left(\frac{I_{ij}^U}{I_{Sk}^U} \right)$$



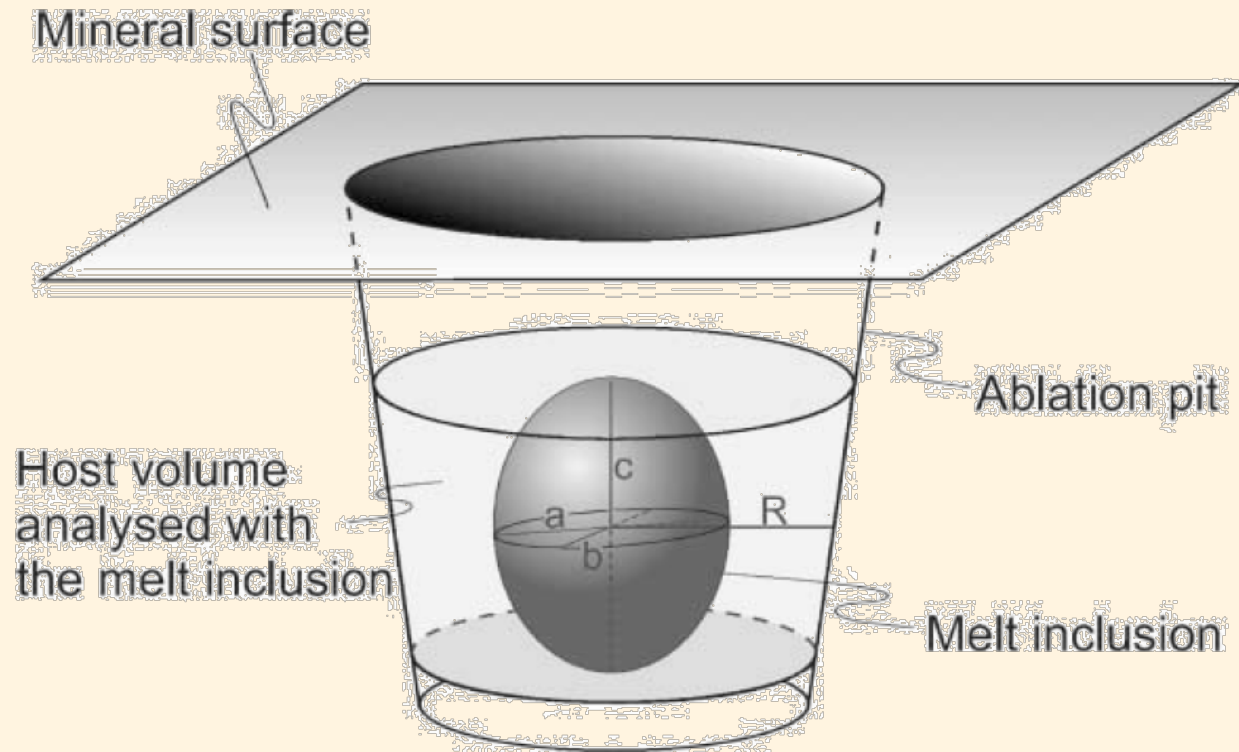
For unknown element x , with measured isotope x^+

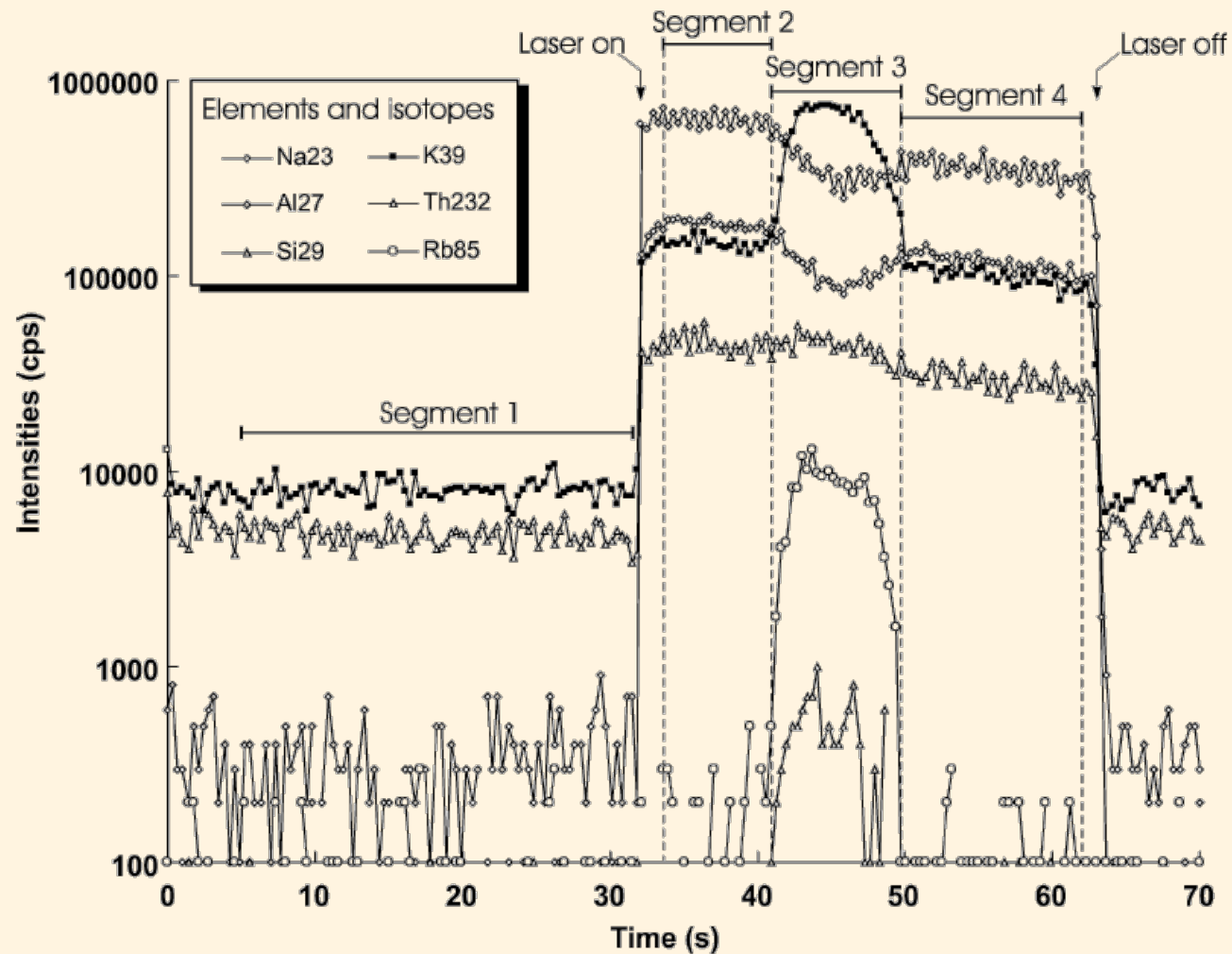
LA-ICP-MS: Long term precision and accuracy



Summary of BHVO-2G LA-ICP-MS analyses over 11 month period at OSU. All concentrations calibrated by BCR-2G glass.

Whole Inclusion Ablation Technique

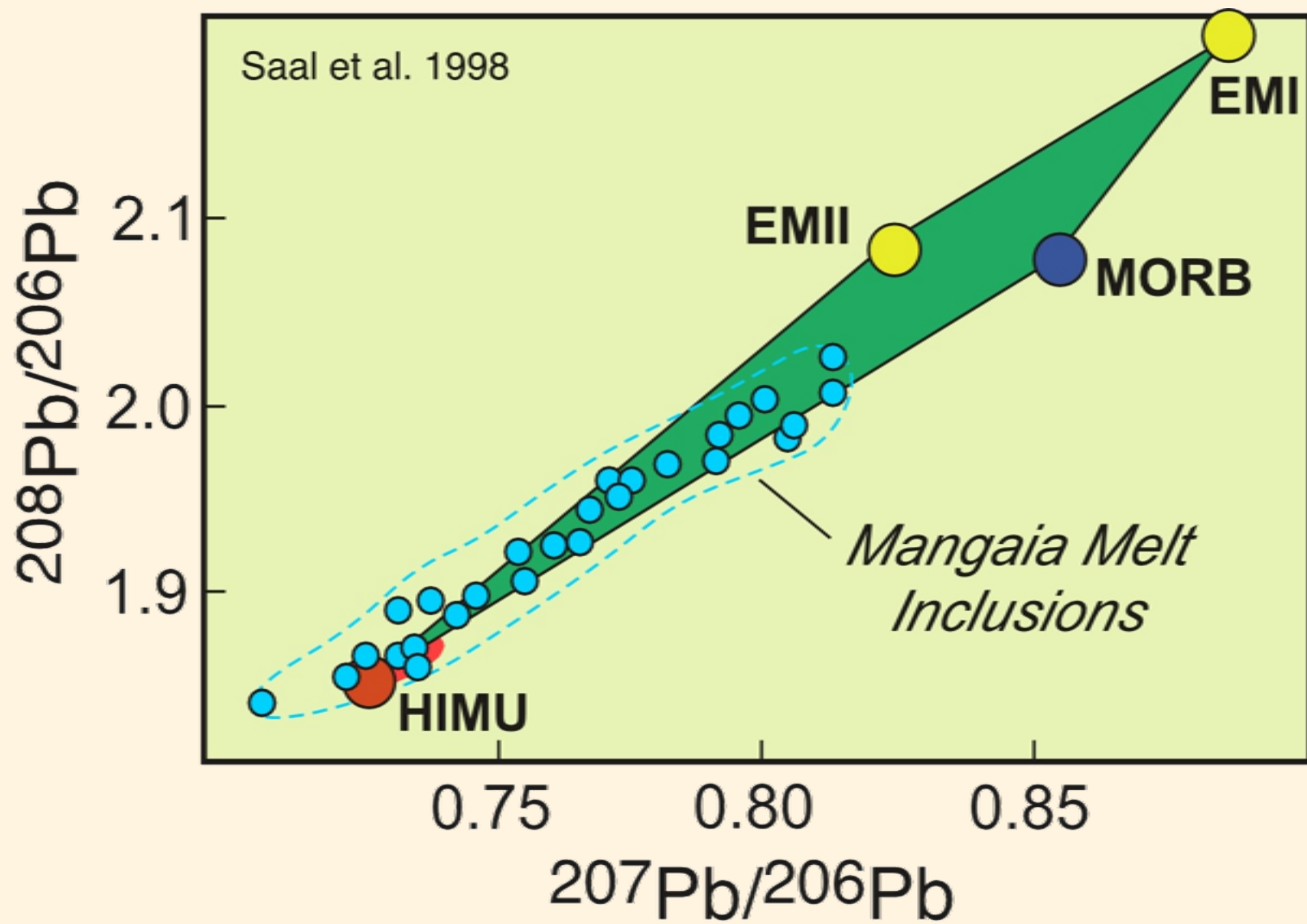


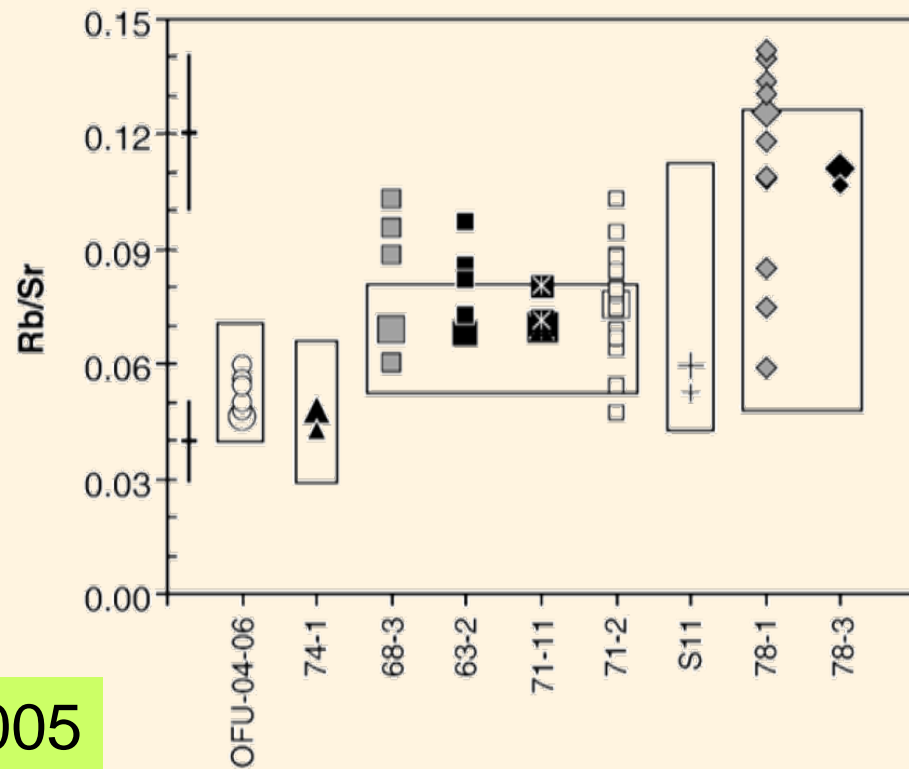
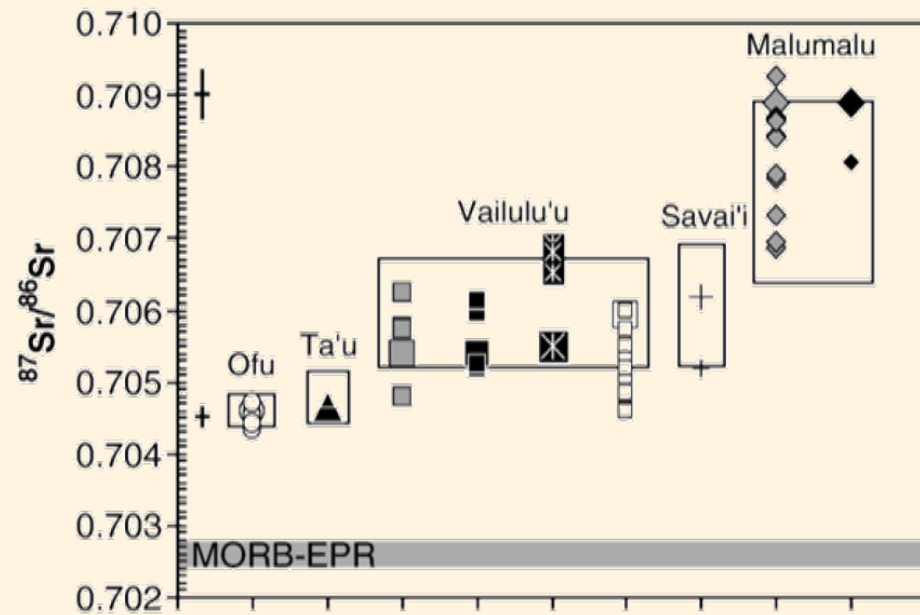


$$x = \frac{m^{\text{INCL}}}{m^{\text{MIX}}} = \frac{C_i^{\text{HOST}} - C_i^{\text{MIX}}}{C_i^{\text{HOST}} - C_i^{\text{INCL}}}$$

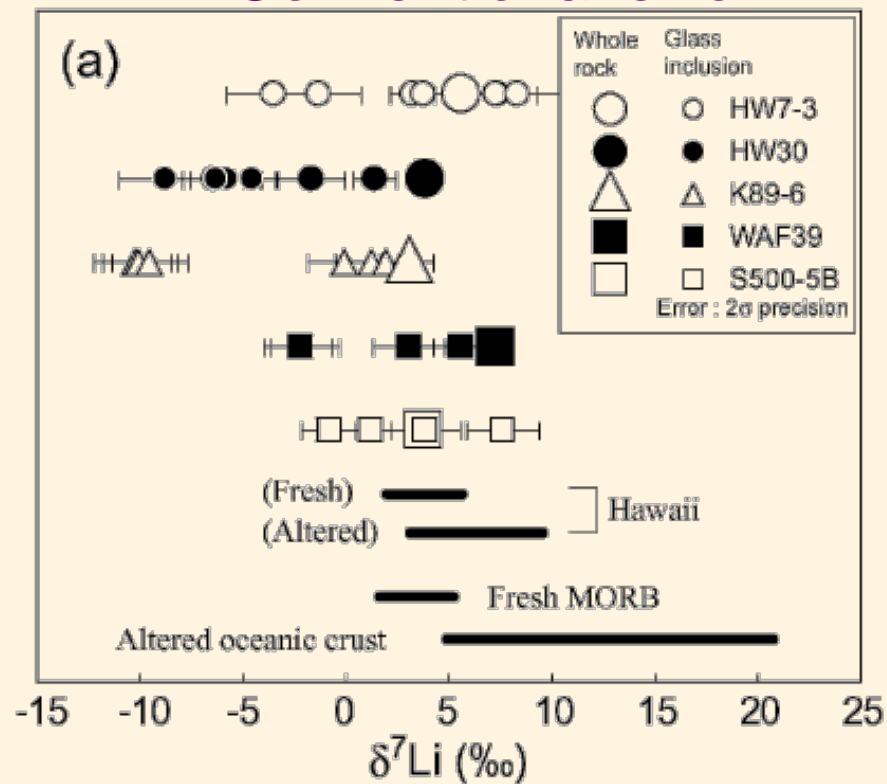
Isotopic Measurements

- SIMS: Light stable isotopes (H, Li, B, C, O, Cl, S) and Pb
 - Somewhat reduced precision (0.1-1 per mil)
 - No ^{204}Pb
- LA-ICP-MS (Sr, Pb)

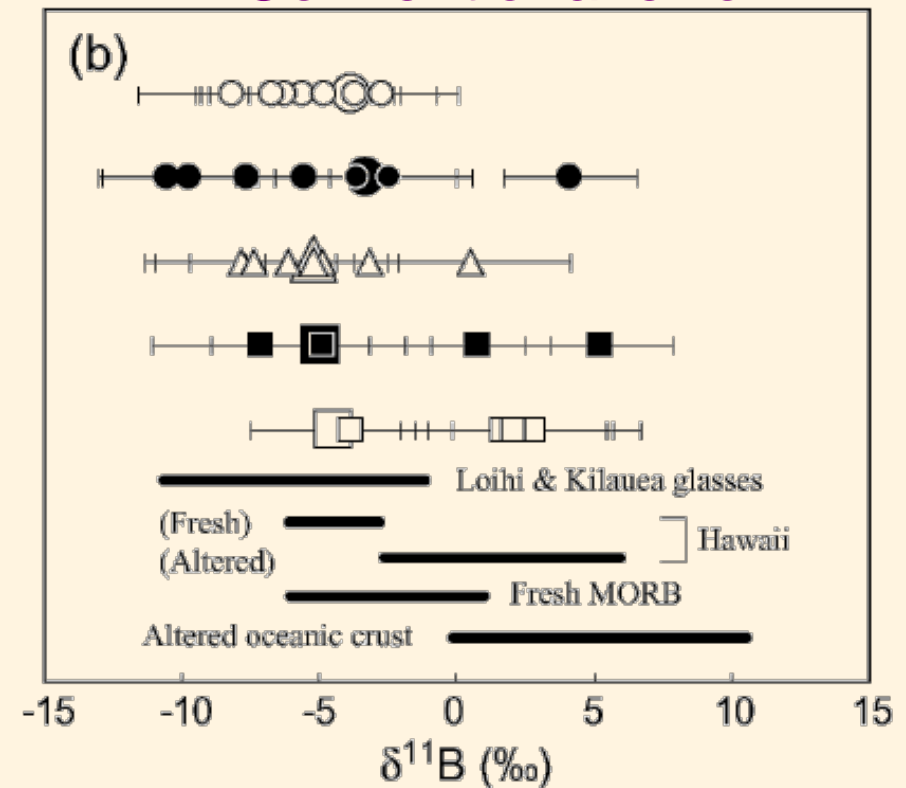




– Conventional error



– Conventional error



Points to remember

- Sample preparation for melt inclusion analysis is labour intensive - works best as part of a focused study
- Accurate trace element analyses are possible using in situ techniques, but there are some limitations
- Some isotopic measurements are also possible.
- The larger uncertainties in melt inclusion measurements are often offset by greater chemical variability