

LA-UR-12-23205

Approved for public release; distribution is unlimited.

Title: Science of Signatures Workshop on Secondary Ion Mass Spectrometry (SIMS) Applications Some Nuclear and Geological Applications

Author(s): Riciputi, Lee

Intended for: LANL Science of Signatures Workshop on SIMS Applications



Disclaimer:

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the Los Alamos National Security, LLC for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

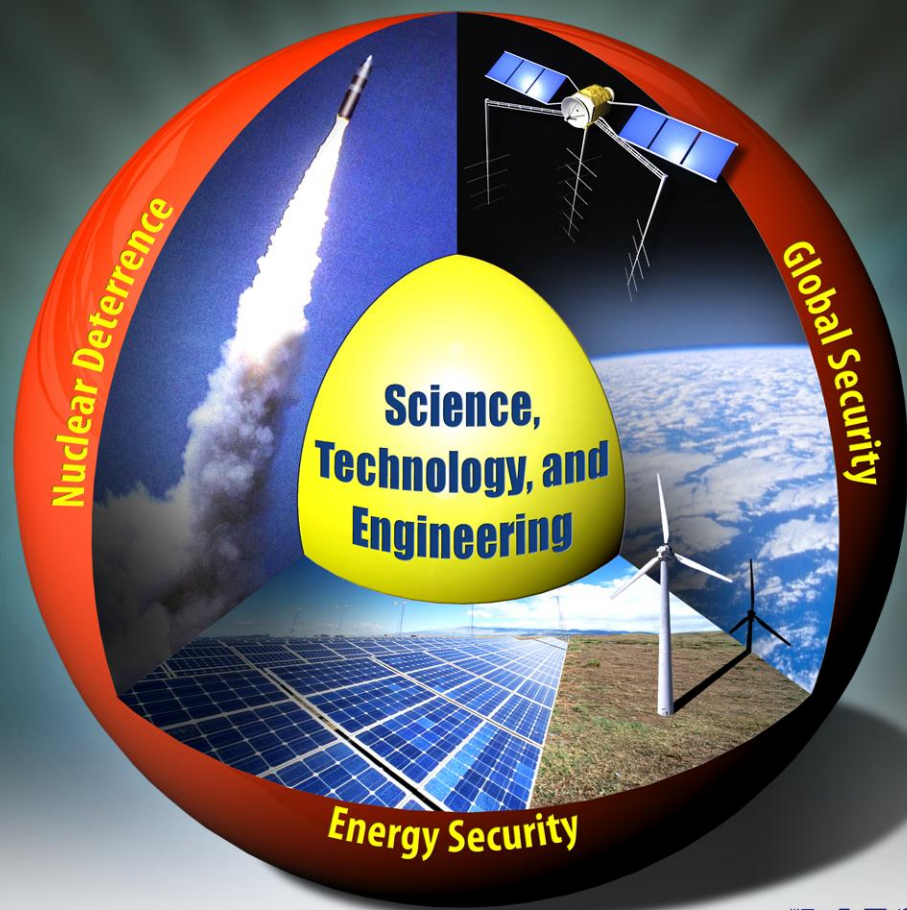
# Science of Signatures

Workshop on Secondary  
Ion Mass Spectrometry  
(SIMS) Applications

Some Nuclear and  
Geologic Applications

July 24, 2012

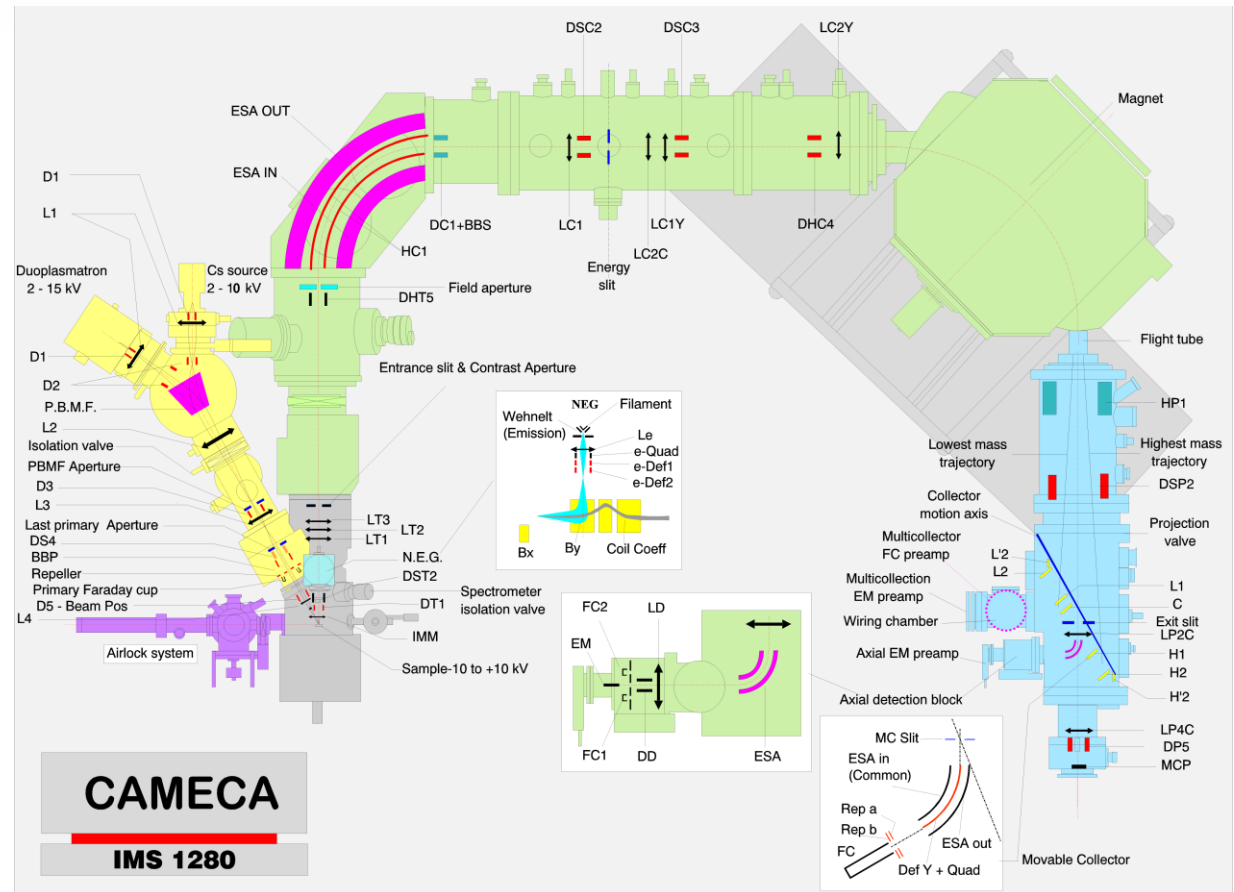
Lee Riciputi





# Nuclear Safeguards/Forensics Geology/Geochemistry/Planetary Geology

Spot analysis  
Depth Profiling  
Imaging



# Safeguards (Particle Analysis)



- “Environmental Samples” (IAEA Swipes)
- Remove, locate, separate particles of interest from sample
- Analyze particle isotopics (U, Pu) to characterize operations



IAEA inspector collecting cloth swipe samples at a nuclear facility

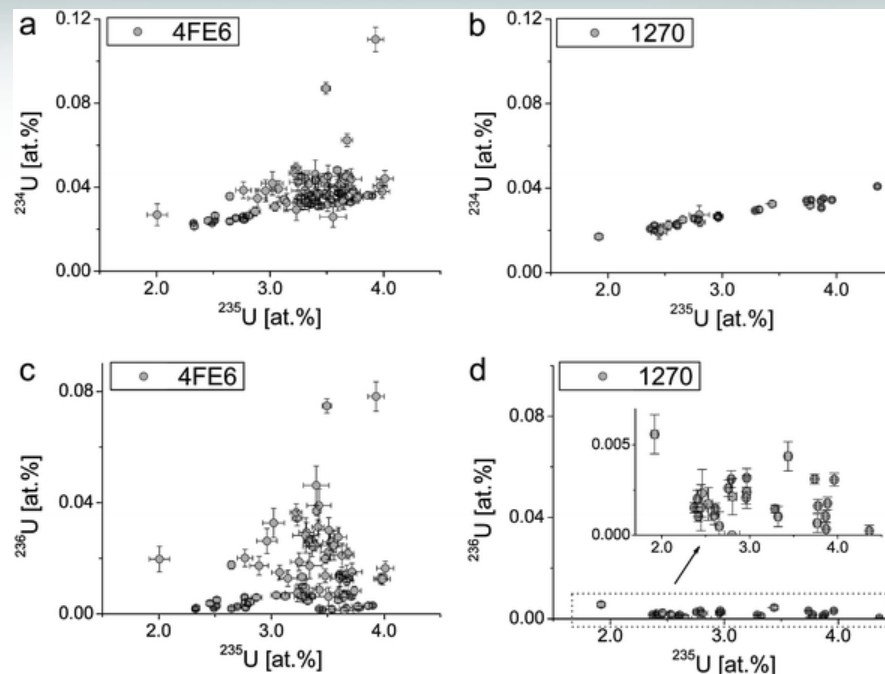
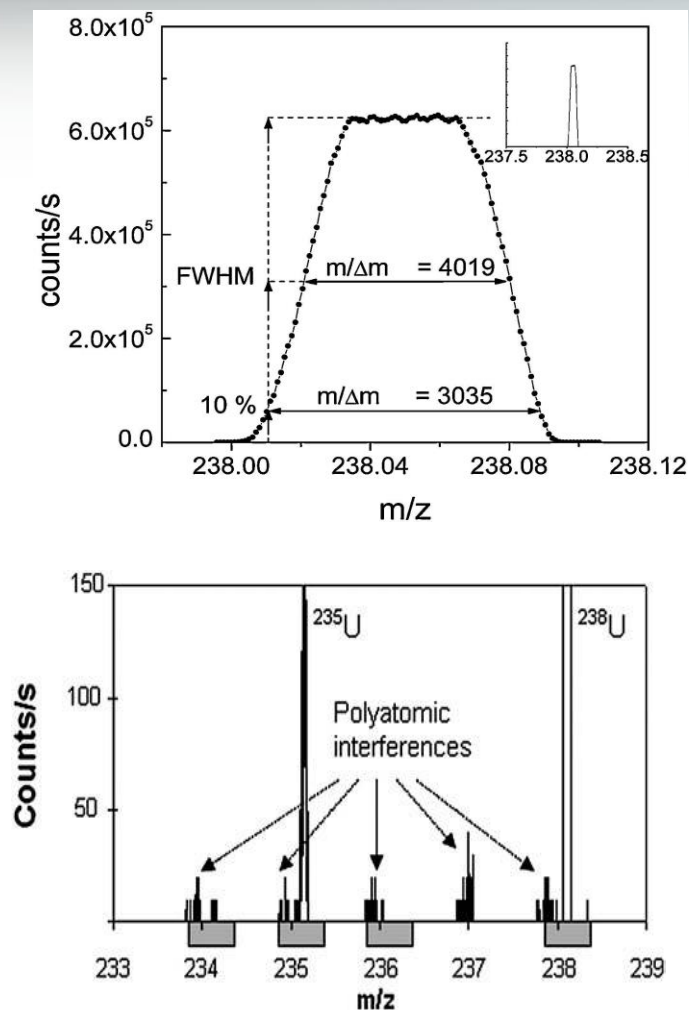
# Safeguards (Particle Analysis)



- Gold-standard method is fission-track TIMS
  - Particles extracted (typically ultrasound), mounted with LEXAN
  - Irradiated, producing fission-tracks identifying particles of interest
  - Particles extracted, analyzed using TIMS
- Small-geometry SIMS used for over a decade
  - Problems with molecular interferences (e.g.,  $^{208}\text{Pb}^{27}\text{Al} = ^{235}\text{U}$ )
  - Problems with minor isotopes  $^{234}\text{U}$ ,  $^{236}\text{U}$  (hydrocarbon, other interferences)
- Large-geometry SIMS of great interest in recent years
  - High mass resolution with transmission provides ability to remove some molecular interferences
  - Multi-collector mode? Could improve efficiency
  - Currently, 10 1280SIMS part- or full-time in this application (installed or on order)

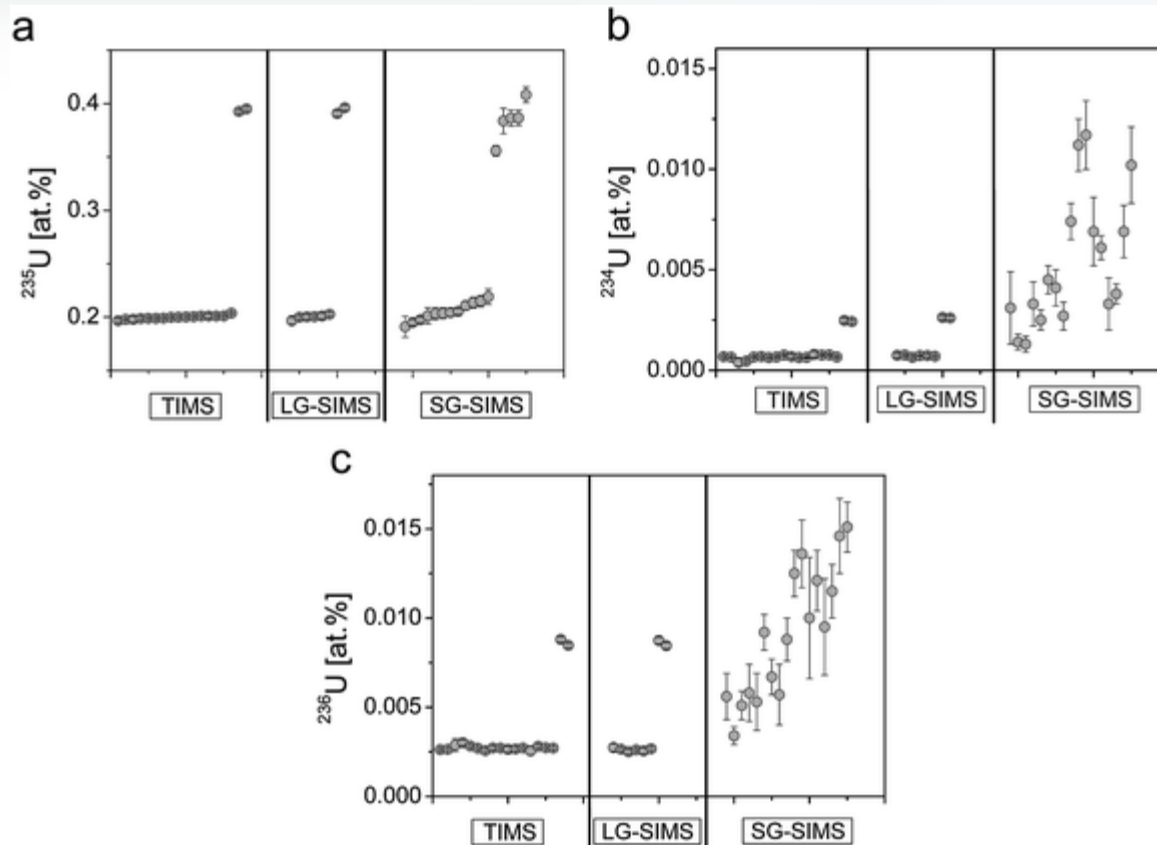


# Why the interest in LG-SIMS?



- LG-SIMS provides flat-top peak
- Resolution reveals multiple isobars at masses of interest
- Far better, more systematic isotopic analyses compared to SG-SIMS

# LG-SIMS, FT-TIMS very similar



# Challenges



## Extracting particles (wet or dry methods)

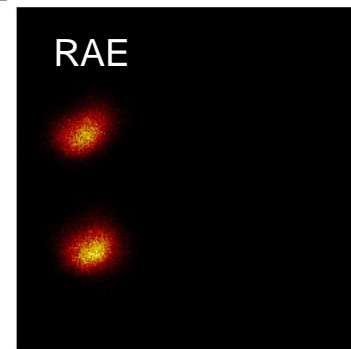
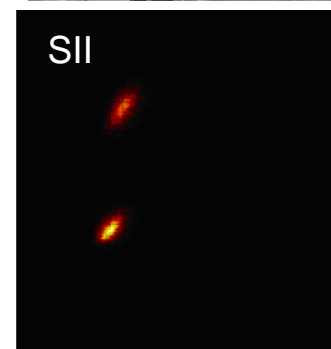
- Complex matrices pose problems (location, isobars)



Vacuum impactor extraction at ITU

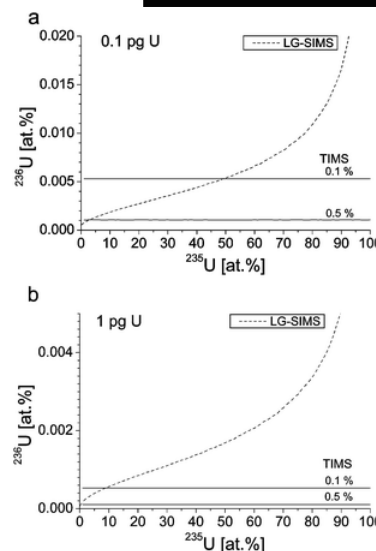
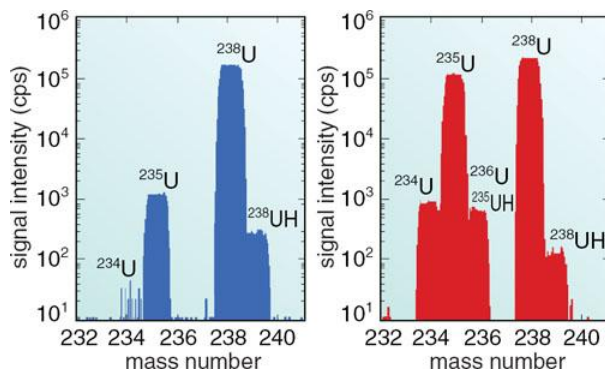
## Locating particles of interest

- Speed, sensitivity, selectivity
- Primary focus is ion imaging capability of 1280-SIMS
- FT-TIMS, SEM



## Analysis

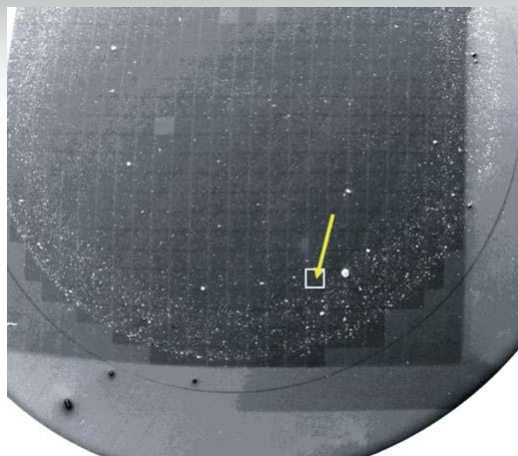
- Multi-collector vs. single detector peak jumping (speed, sample utilization)
- Matrix effects, mass bias, calibration
- Isobars (hydrides)
- Spatial resolution



Ranebo et al., J. Anal. At. Spec., 2009

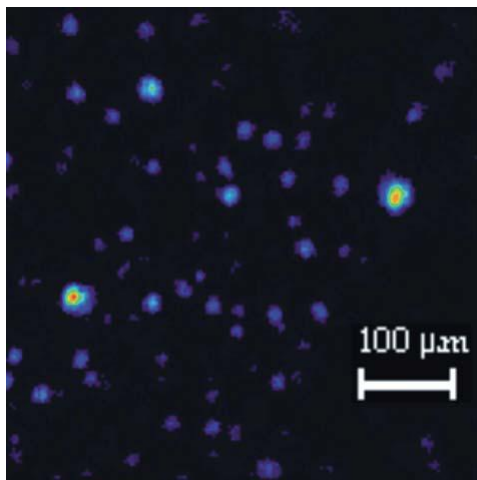
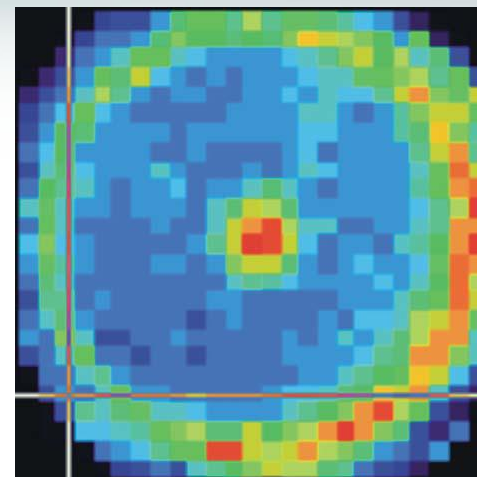


# Particle Location



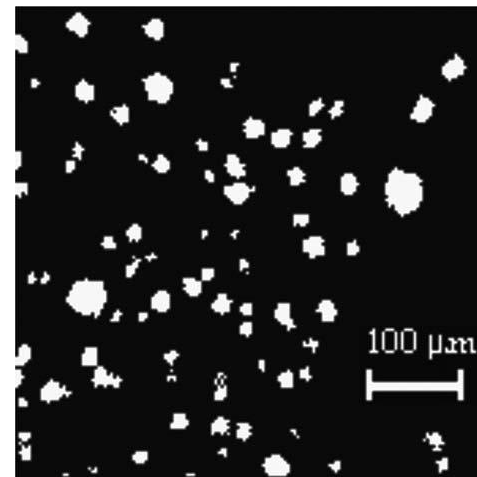
500x500 um raster areas  
25.4mm graphite planchette  
Scan for  $^{235}\text{U}$  and  $^{238}\text{U}$

Composite images showing uranium “hot-spots” on sample (cross hair marks selected sample field)



Detailed scanning ion  
image of selected  
sample field ( $^{238}\text{U}$ )

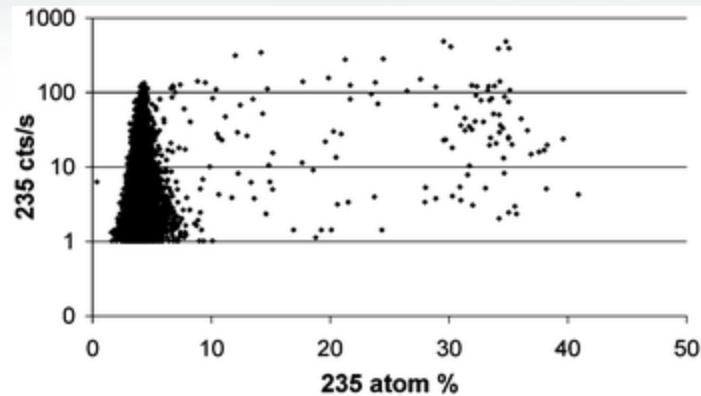
Particles defined by  
scanning ion image  
using APM software



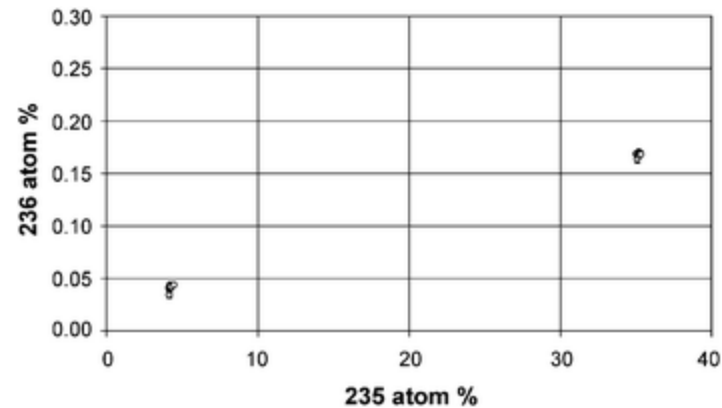
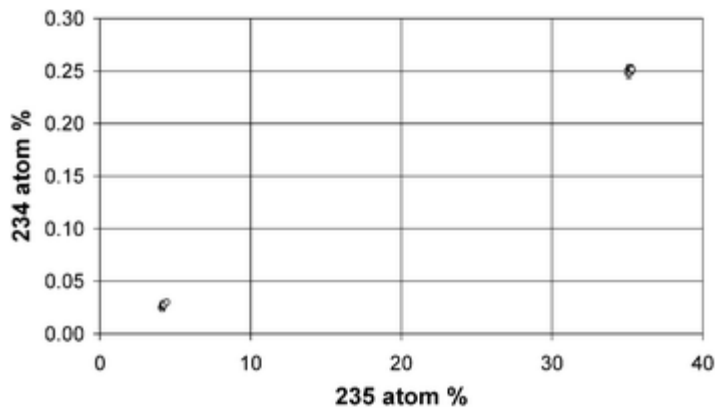
# Particle Location



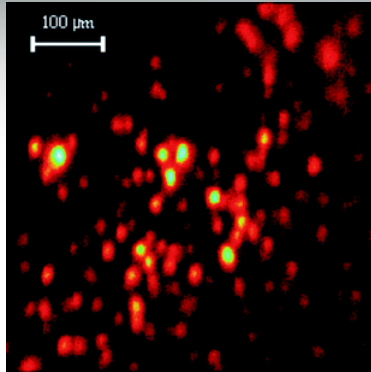
Results from screening  
QC sample, 4.5% and 35.2%  $^{235}\text{U}$   
110:1 mix  
Mixing of two particle populations  
Agglomeration, beam size, algorithm



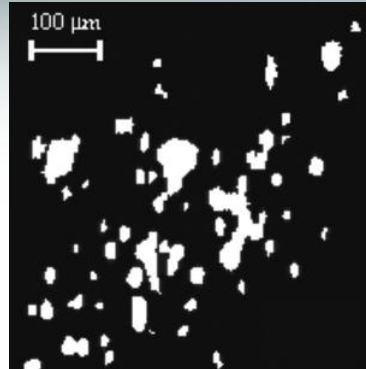
Microbeam measurements  
Clear discrimination between two populations



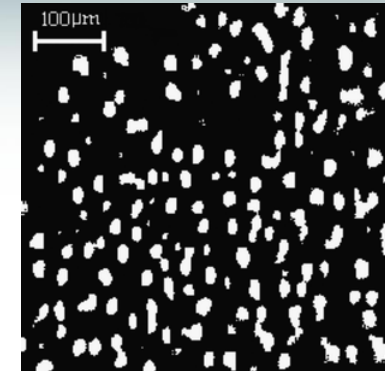
# Particle Location



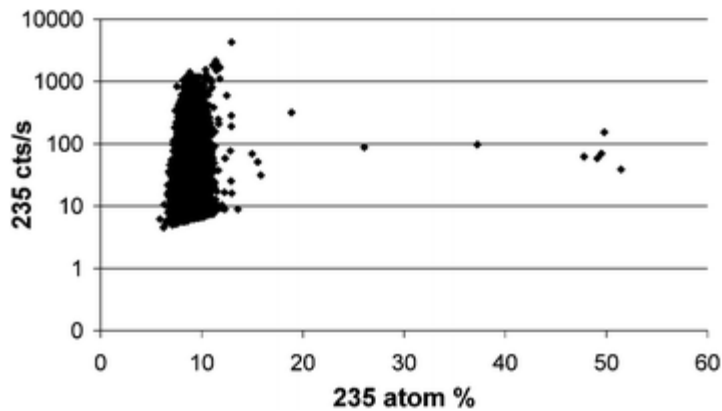
Scanning ion image



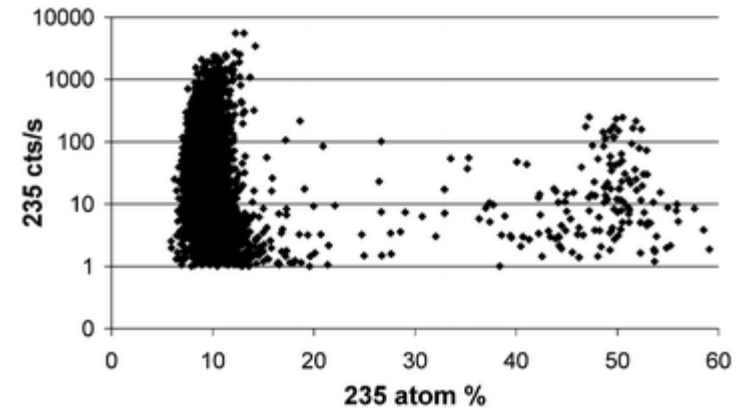
Fixed Threshold APM, 7500 particles detected



Niblock threshold, 9989 particles detected

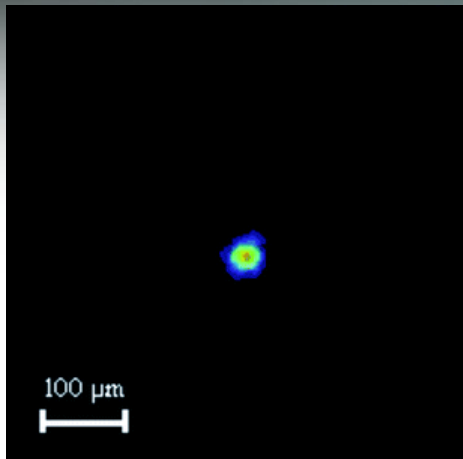


Isotopic composition using Fixed Threshold APM  
100cps to minimize clustering but still preserve detection

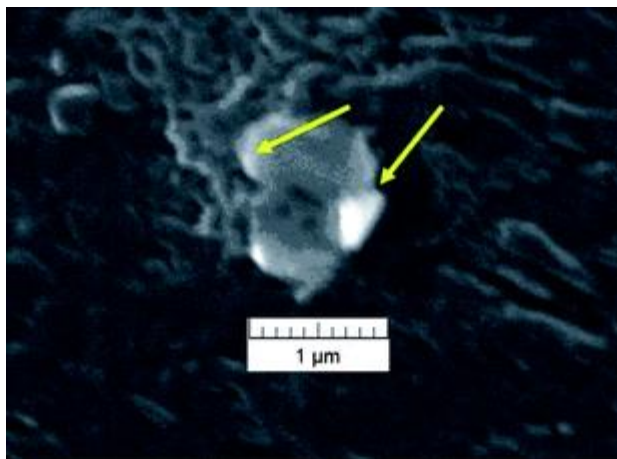


Isotopic composition using Niblock threshold  
10cps, far better detection of particles, far more showing enrichments (although still have mixing)

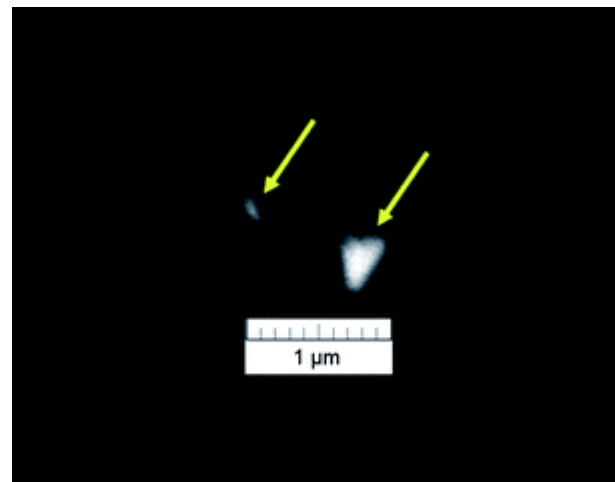
# Particle Location



Scanning ion image of one of 3 uranium particles located in sample

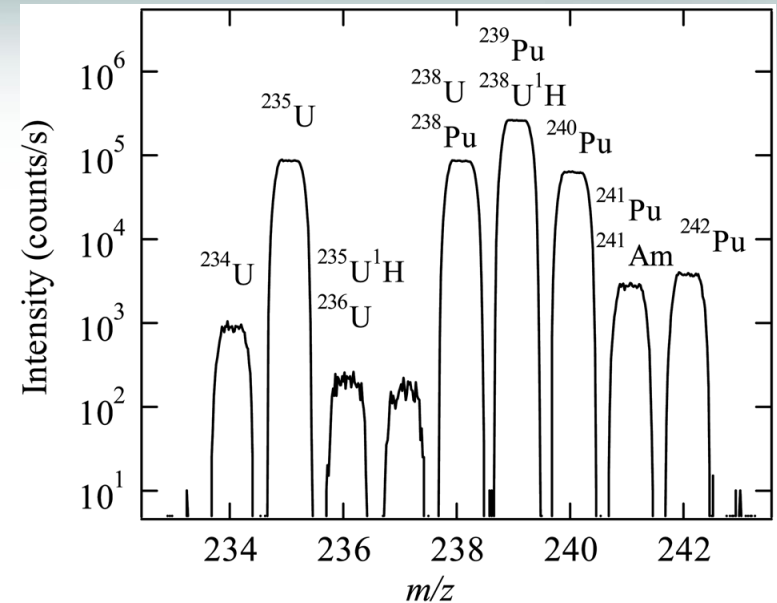
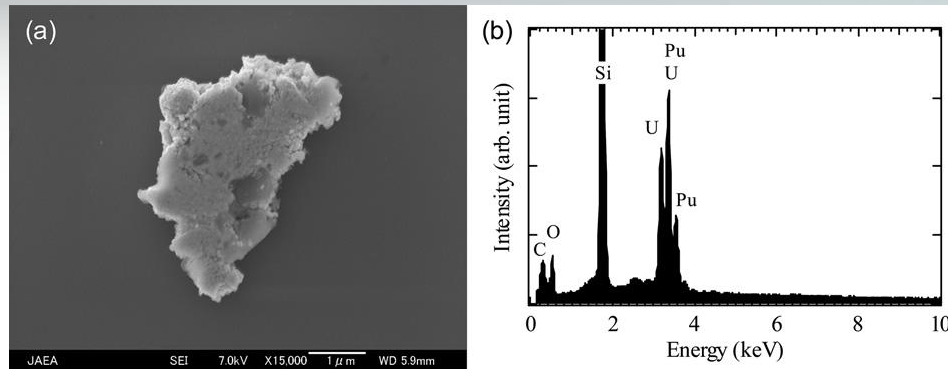


Secondary electron (SE) image of uranium particle (2 particles on surface of another material)



Backscatter electron (BSE) image of uranium particle(s)

# Mixed U-Pu Particles



	$^{235}\text{U}/^{238}\text{U}$	$^{240}\text{Pu}/^{239}\text{Pu}$	$^{241}\text{Pu}/^{239}\text{Pu}$	$^{242}\text{Pu}/^{239}\text{Pu}$
Particle 1	$1.00 \pm 0.02^*$	$0.238 \pm 0.006$	$(1.03 \pm 0.06) \times 10^{-2}$	$(1.52 \pm 0.15) \times 10^{-2}$
Particle 2	$0.988 \pm 0.008$	$0.240 \pm 0.002$	$(1.01 \pm 0.02) \times 10^{-2}$	$(1.54 \pm 0.03) \times 10^{-2}$
Certified value	1.00	0.241	$0.900 \times 10^{-2}$	$1.56 \times 10^{-2}$

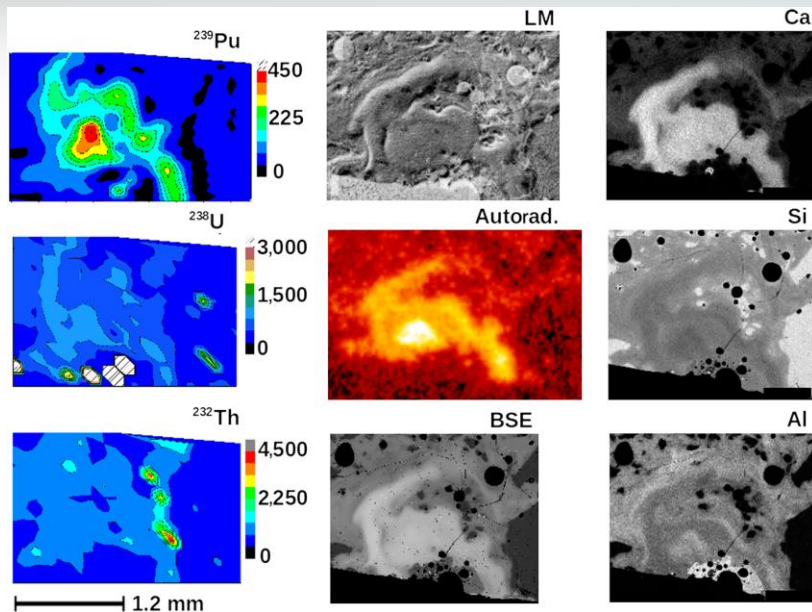
Good results for all but  $^{241}\text{Pu}$  ( $^{241}\text{Am}$  unable to be resolved)

However, higher U/Pu ratios will lead to major issues with  $^{239}\text{Pu}$

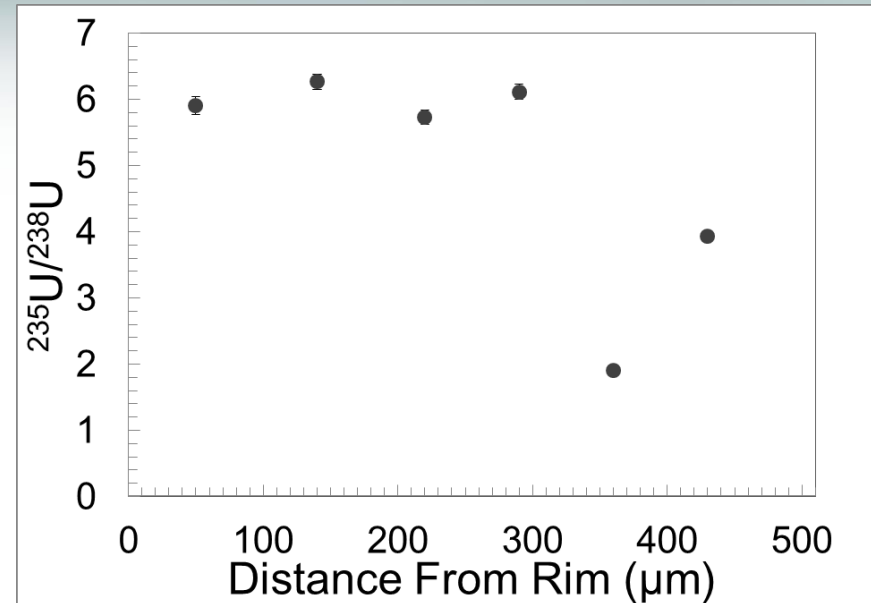
Did not measure  $^{236}\text{U}$  – complicated due to inability to measure UH production



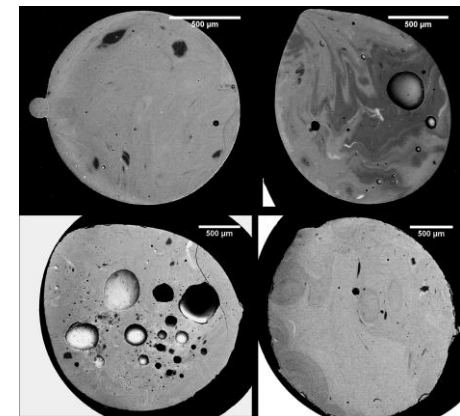
# Materials from Nuclear Tests



Images of isotopic (SIMS) and elemental (SEM) distributions in ground glass from the Trinity test.



BSE and uranium isotopes from NTS glass spherules.

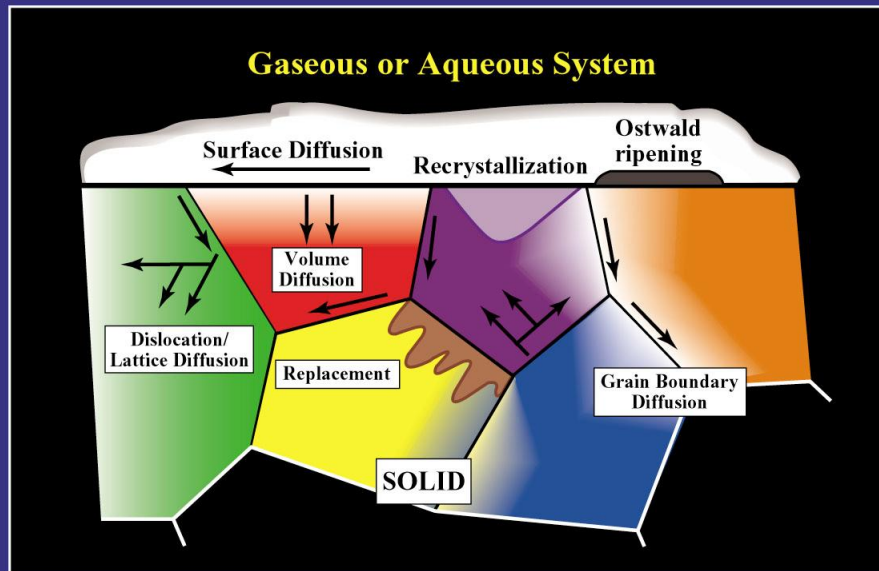


**Elemental and isotopic heterogeneity preserved in both types of material.**

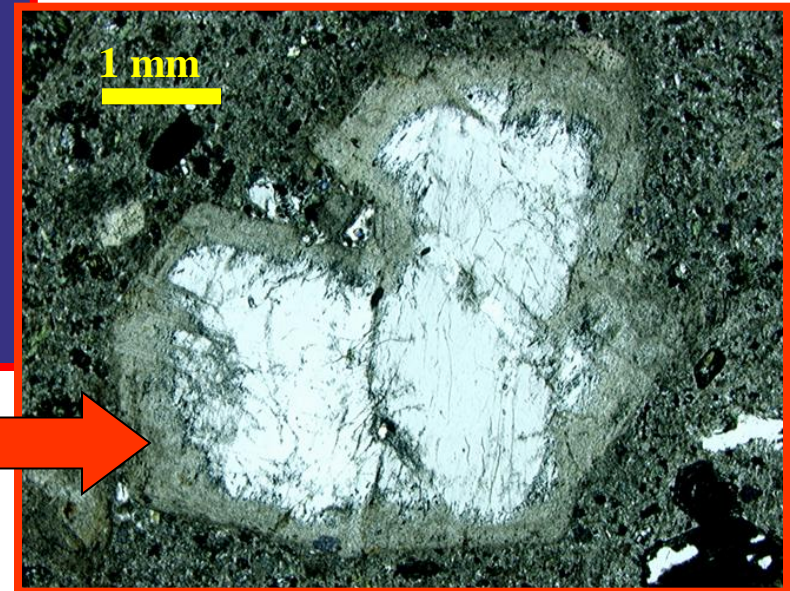
# Exchange Pathways in Mineral-Fluid Systems



Mechanism and degree of reaction:  $f(T, P, X, W/R, t)$



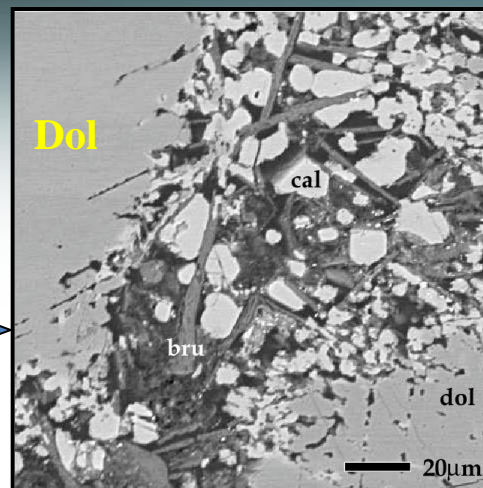
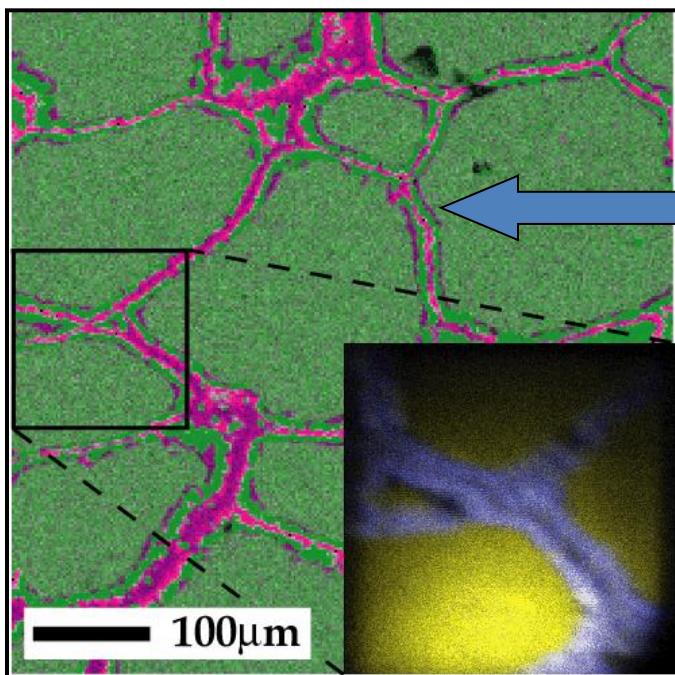
Pseudomorphic Replacement of Andesine by Albite  
Rico, CO hydrothermal system



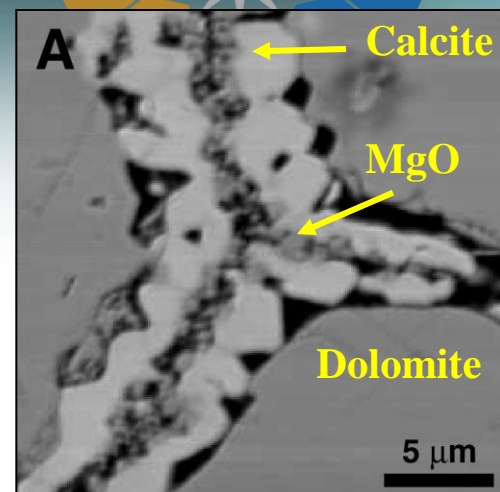


# Oxygen Isotope Imaging of Fluid Transport and Reaction

**Reaction Textures:** Two domains were observed, one at the core exterior and a second long grain boundaries or fractures (shown here)



Reaction along a fracture



Pore formation

**Reaction Products:** Calcite, periclase, and brucite (breakdown of MgO) form along grain boundaries and fractures as revealed by X-ray mapping (Mg in purple).

**Ion imaging** (NanoSIMS) of  $^{18}\text{O}$  rich zones (inset) provides direct evidence for fluid infiltration along grain boundaries. Isotopic zoning within reaction zones is also observed (shades of blue).

# Oxygen Isotope Imaging of Reaction Zones



**Objective:** Document the rate of chemical and isotopic reaction rim formation, geometry, structure.

## Hydrothermal Reactions:

Albite + KCl = K-feldspar + NaCl

K-Feldspar + NaCl = Albite + KCl

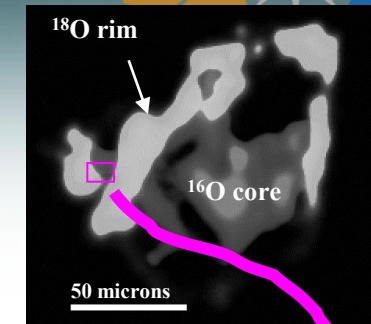
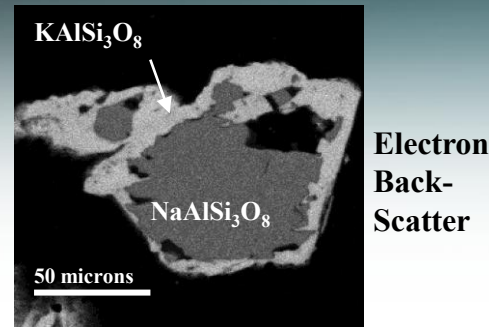
## Experimental Conditions:

T = 300 - 600°C, P = 200 MPa

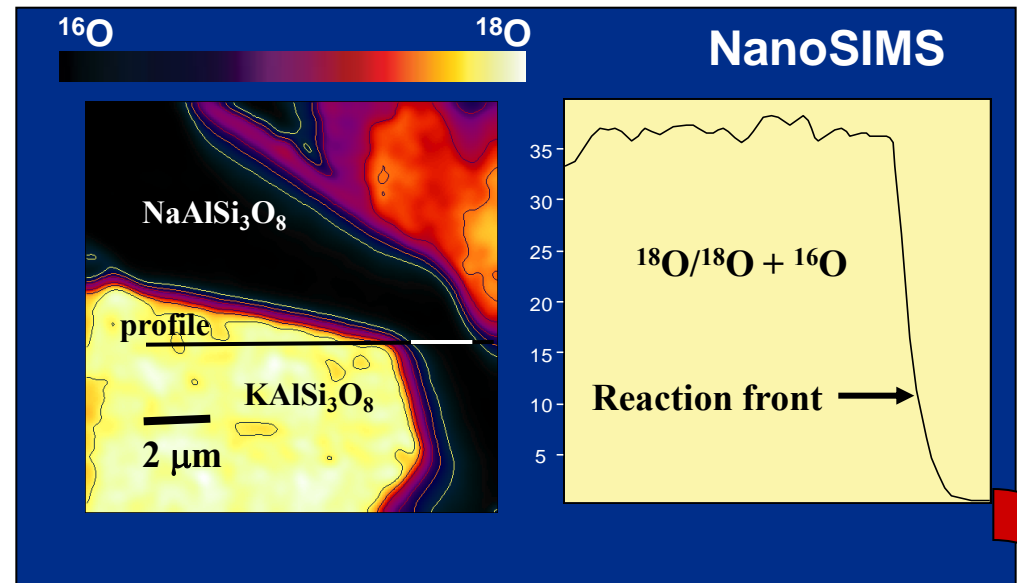
Durations: 4 – 90 days

The pattern of  $^{18}\text{O}$  matches the cation distribution within the resolution of the ion probe.

NanoSIMS results reveal a very steep  $^{18}\text{O}$  profile at the reaction front.



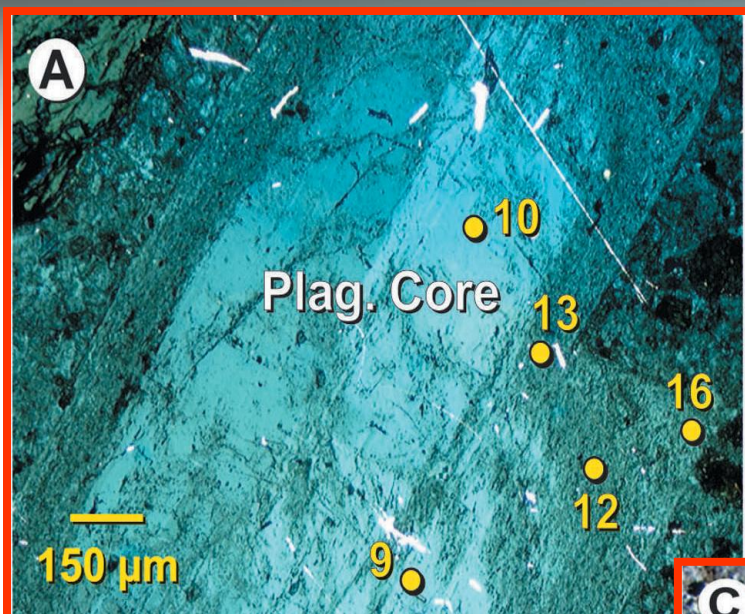
Na-feldspar reacted with  $^{18}\text{O}$  rich 2 *m* KCl at 600°C, 200 MPa for 6 d; note  $^{18}\text{O}$  rich halo penetrating solid.



**This capability opens up the door for imaging geochemical processes at the nanoscale.**

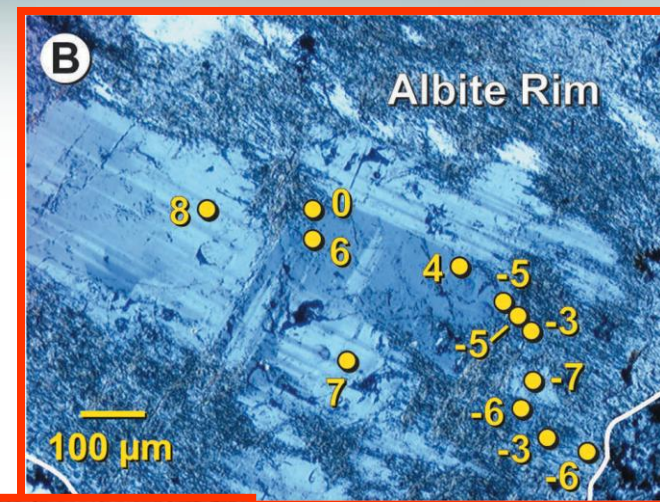


# Mineral Zoning and $^{18}\text{O}$ Variations

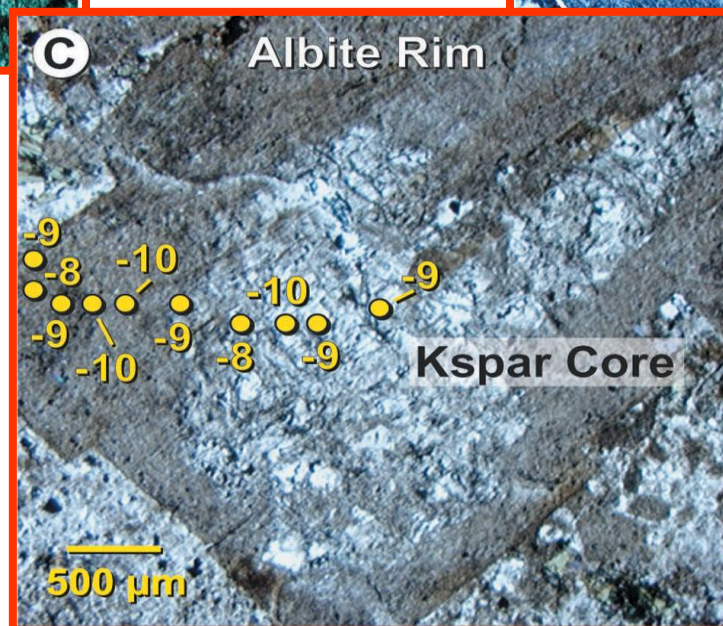


Distal: 150-200°C

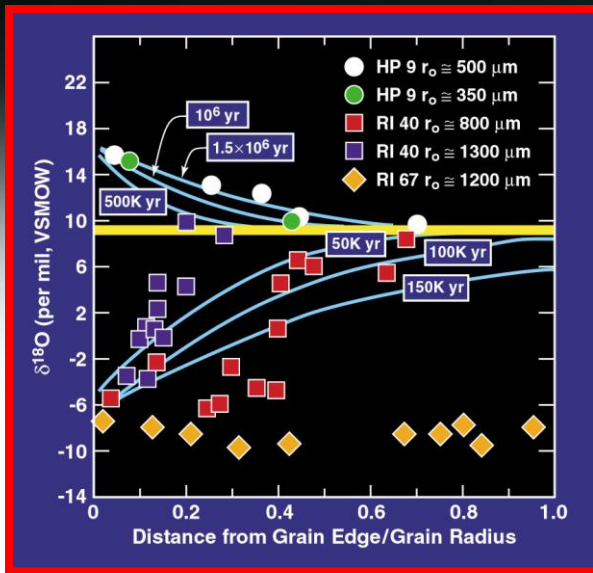
Proximal: 300-350°C



Intermediate:  
250°C







Reaction rim thicknesses measured for grains 500 to ~1,200  $\mu\text{m}$  in radius.

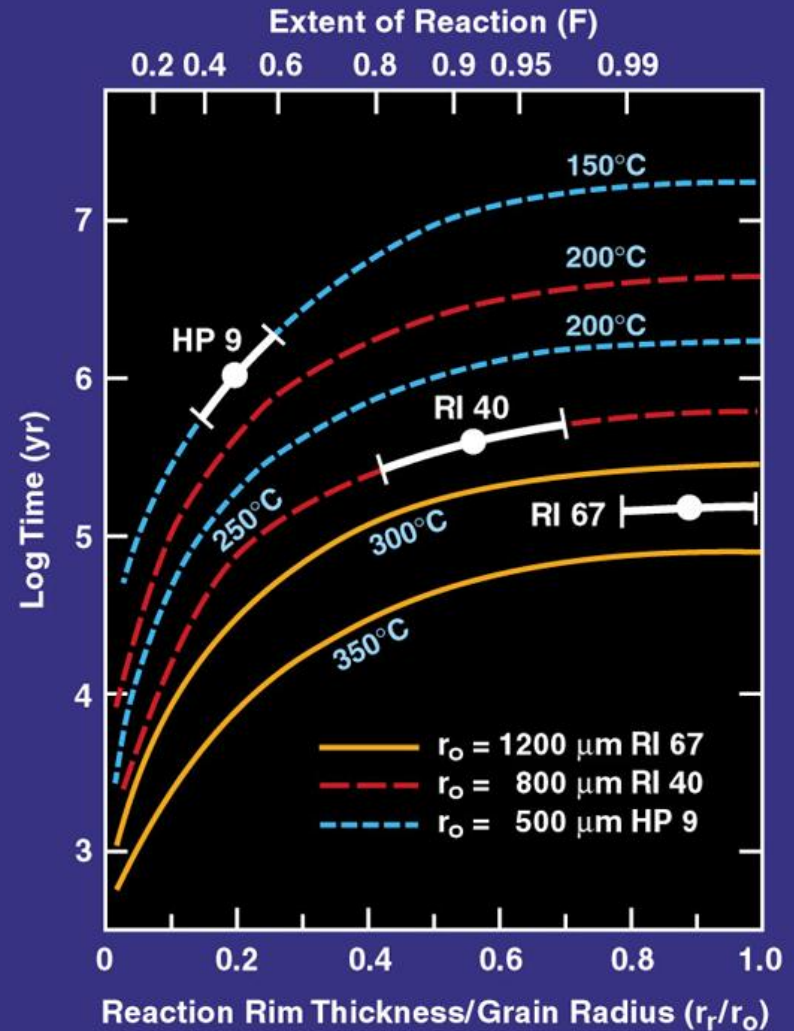
Shrinking core model used to calibrate rim thicknesses for temperatures between 150 and 350°C.

Distal:  $\sim 1 \times 10^6$  yrs

Intermediate:  $\sim 2 - 5 \times 10^5$  yr

Proximal:  $\sim 140,000$  yr

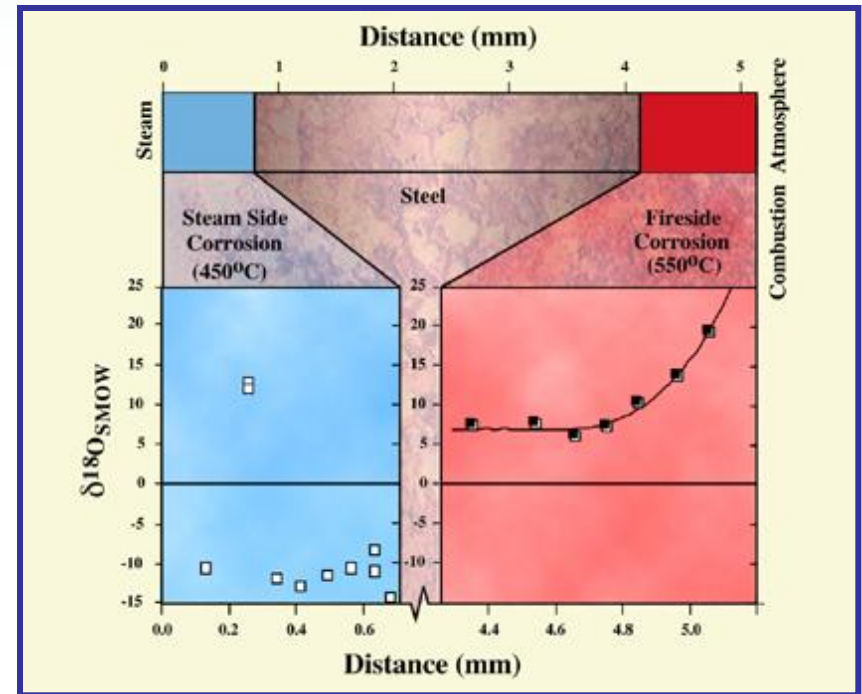
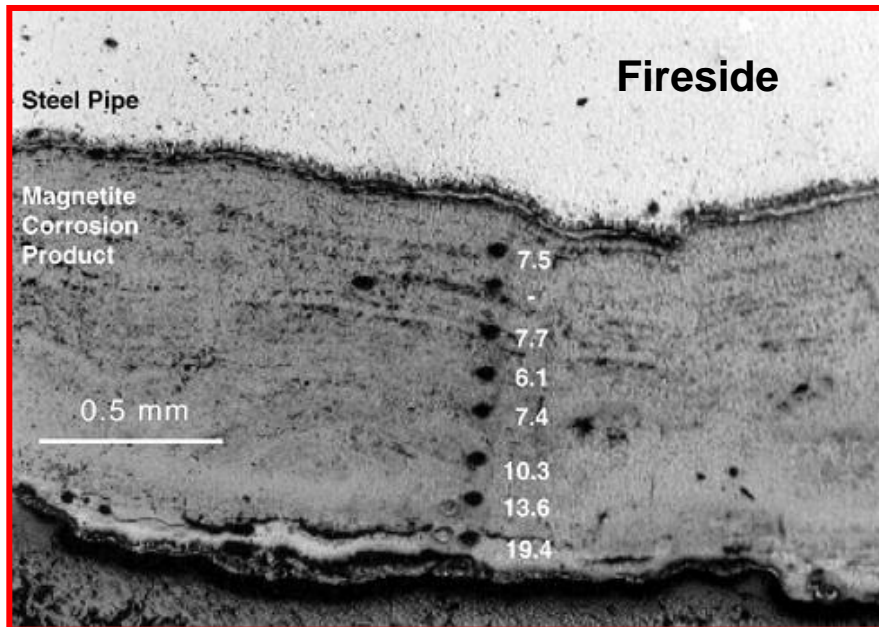
Durations for high T reactions comparable to those estimated from heat and fluid flow models



# Corrosion in Power Plant Boiler Tubes



Photomicrograph of magnetite growth layer (~1mm thick) formed at ~550°C on steel tube. Black spots are pits made during SIMS analyses for  $^{18}\text{O}/^{16}\text{O}$  ratios.

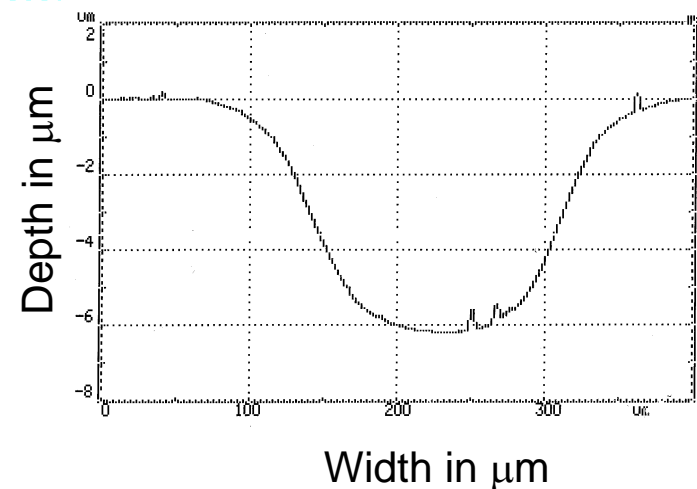
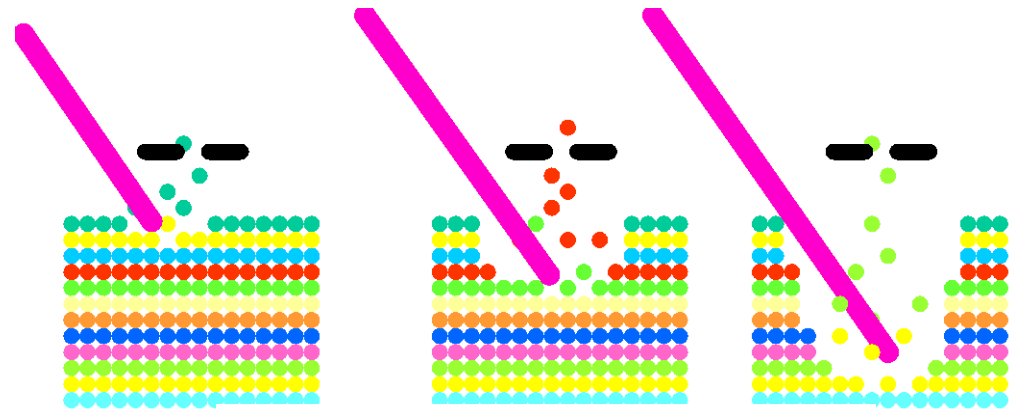
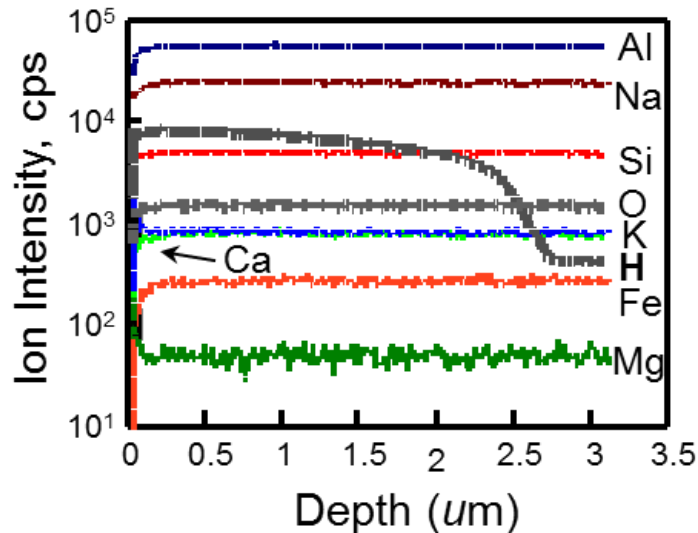
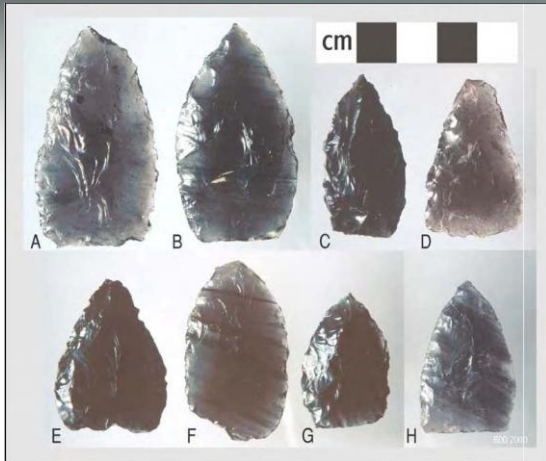


Schematic representation of a cross-section through steel tube that has undergone both steamside and fireside corrosion.  $\delta^{18}\text{O}$  values for magnetite for each type of corrosion are plotted a function of distance.

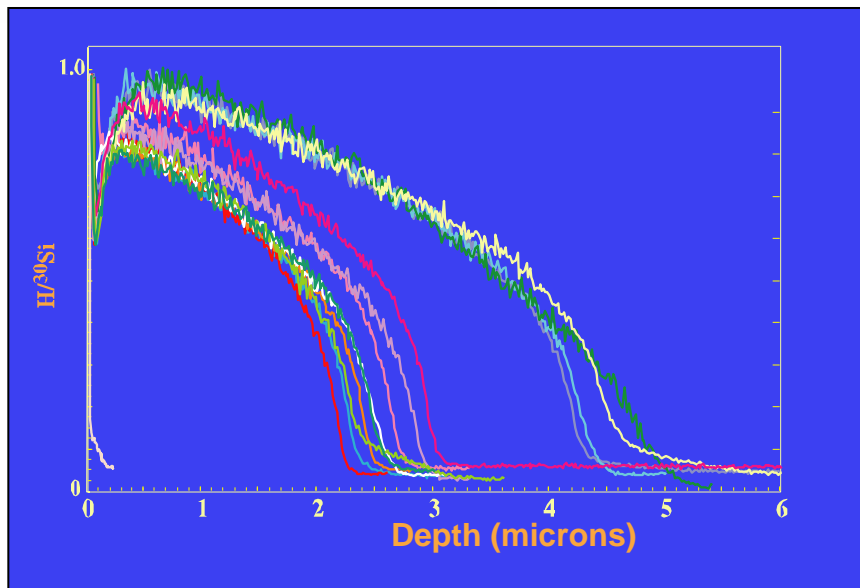
# Dating Obsidian Artifacts



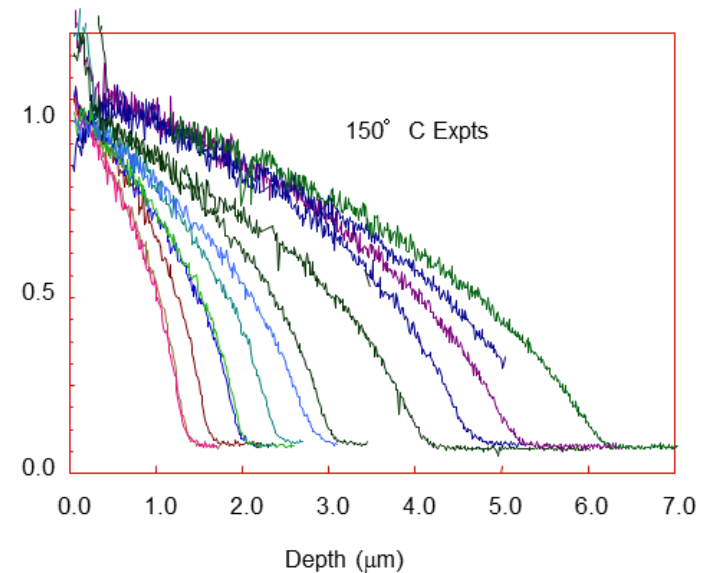
Freshly flaked obsidian begins to hydrate.  
Can calibrate rate using experiments.  
Use SIMS in depth-profile mode to get depth-concentration distribution.



# Dating Obsidian Artifacts – Chalco, Mexico

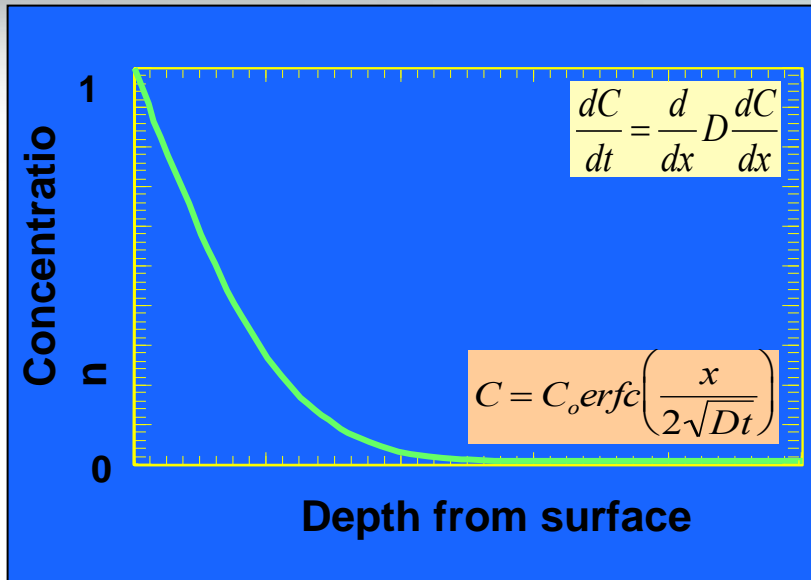


Hydrogen profiles in obsidian artifacts



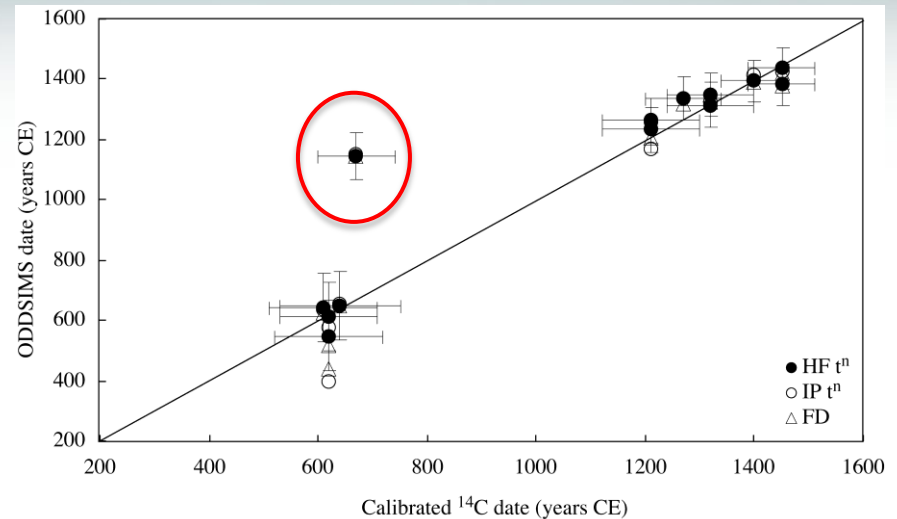
Hydrogen profiles in obsidian hydration experiments

# Dating Obsidian Artifacts



Hydration rate can be modelled using transport laws

$$\vec{J} = \vec{J}_0 \left[ \frac{C_{\max} - C}{C_{\max}} \right] \left( 1 - \left( S \left[ \frac{C - C_{\text{init}}}{C_{\max}} \right] \exp [Rt] \right) \right)$$

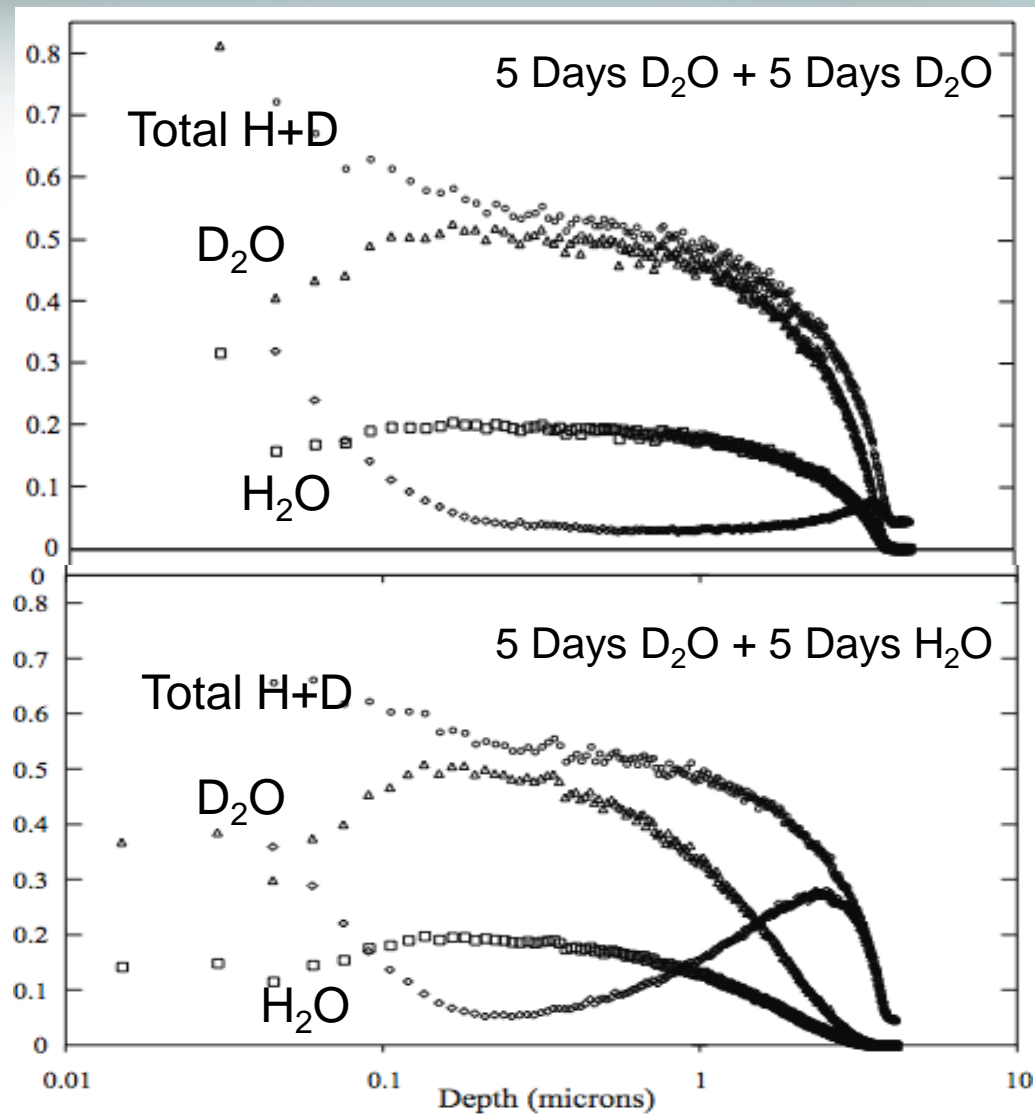
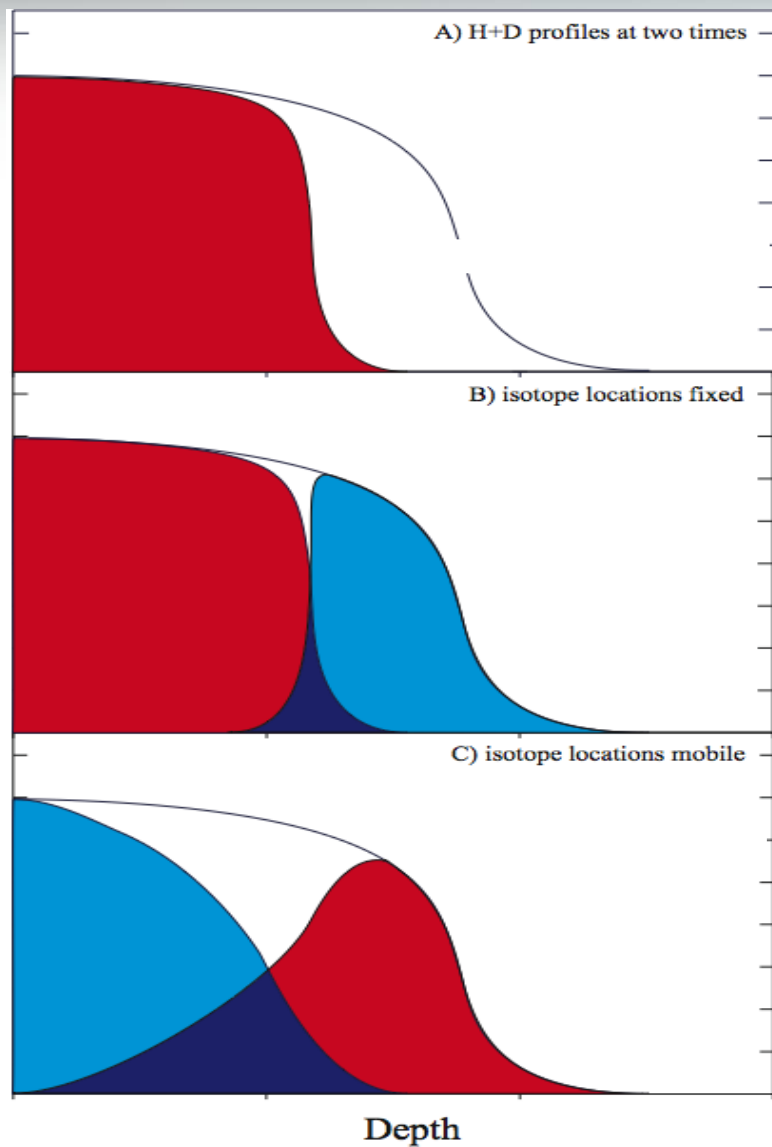


Calculated age compares very well with associated radiocarbon.  
Intrinsic measurement – no uncertainty regarding integrity of material association.

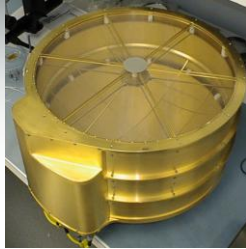
Figure 11 b



# Labeled Isotope Exchange – Hydrogen Mobility

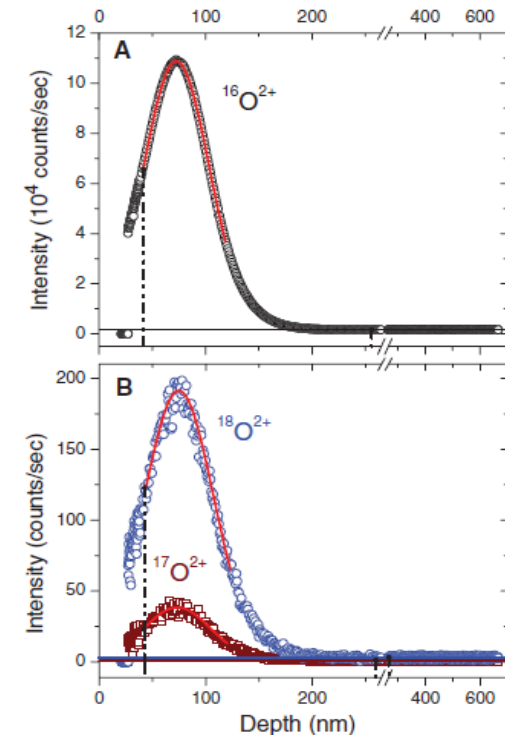
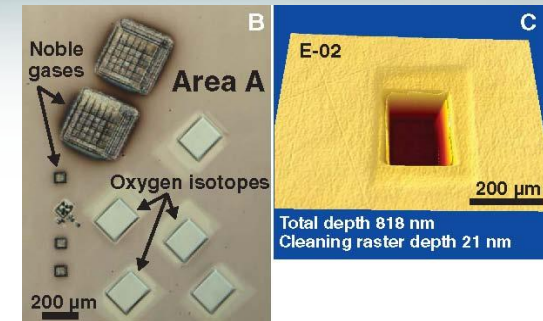


# Shallow depth profiling – Stardust Mission



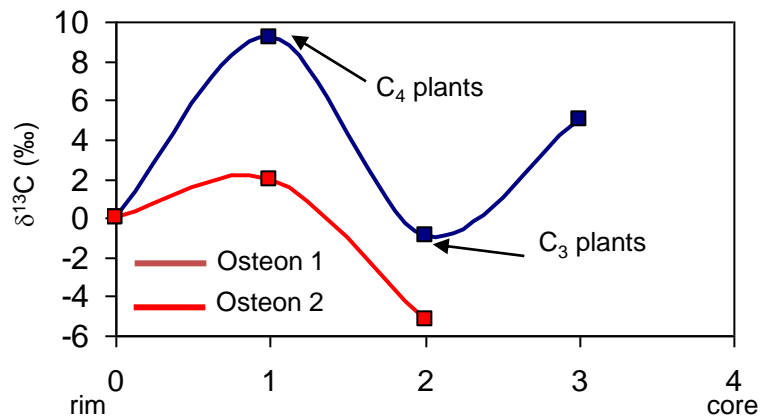
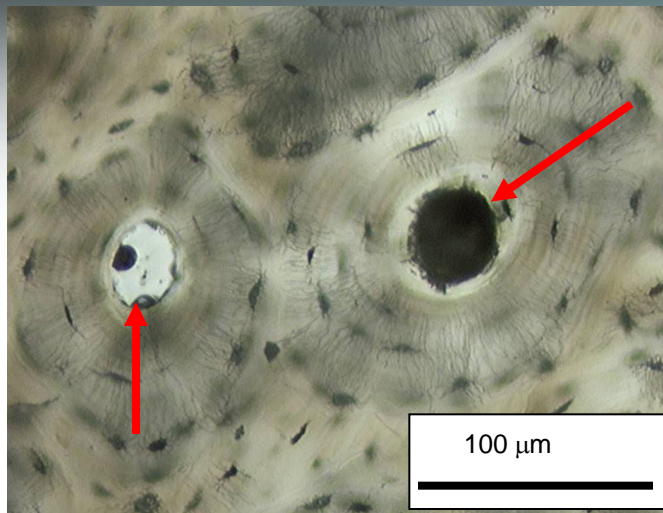
LANL-developed solar wind concentrator for GENESIS mission (Wiens et al.)

- Exposed to solar wind
- Very shallow implants (<200nm)
- First direct measurement of the sun's oxygen isotope composition (Marty et al., 2011, also measured nitrogen isotopes via SIMS)
- Results unexpected, indicate photochemical self-shielding during early T-Tauri phase
- Altered oxygen and nitrogen isotopic composition of all terrestrial planet material (6 and 38%)



Oxygen Isotope Profiles

# Biological Applications



Optical image of human bone. Variations of up to 10‰ in  $^{13}\text{C}/^{12}\text{C}$  occur within a single osteon in mineralized bone. The variation in  $^{13}\text{C}/^{12}\text{C}$  corresponds to winter and summer periods when  $\text{C}_3$  and  $\text{C}_4$  plants were consumed, respectively.

