LA-UR-16-23310
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Title: Determination of Volatility and Element Fractionation in Glassy Fallout Debris by SIMS

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Intended for: Internal LANL capability review

Issued: 2016-05-10

Determination of Volatility and Element Fractionation in Glassy Fallout Debris by SIMS

2016 Science of Signatures Pillar Review

Travis Tenner, Todd Williamson,
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May 17, 2016

Outline

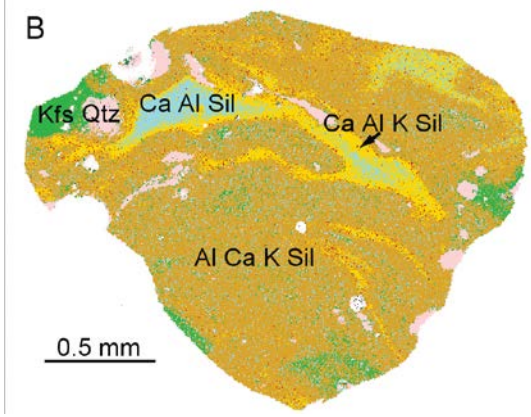
(1) Characterization of debris from the Trinity test.

- Linking chemical, isotopic, and radioactivity relationships from materials that are heterogeneous on tens of micron scales.

-Determining how materials were processed in the explosion (e.g. evaporation and condensation? Partial or complete melting?), in order to understand where specific elemental & isotopic signatures are located.

(2) Characterizing U-isotopes of U_3O_8 reference materials, as analogs of environmental samples containing materials with signatures of weaponized debris.

Forensic reconstructions of an original device, based on characterizations of its explosion debris, is a challenge.



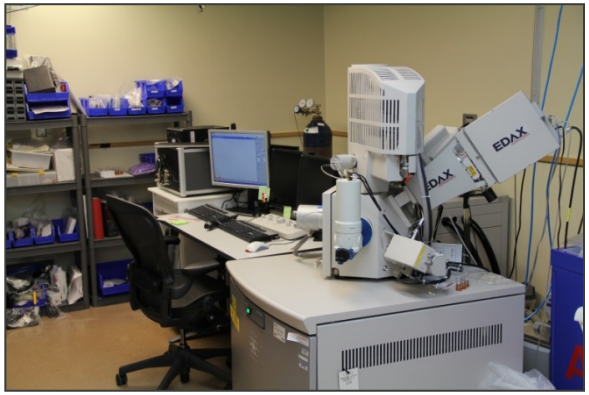
SEM map of trinitite bead *(Eby et al. 2015)*

- Amount of material from the original device is tiny. Ex: ~2 million kg of ground entrained produced from the Trinity test vs 6 kg of fissile material contained in the device = 3 ppm. *(Staritzky, 1950; LAHDRA project, Ch. 10- Trinity Test)*.
- Heterogeneous chemical and isotope fractionation occurs within the explosion cloud, on the order of microns to tens-of microns.

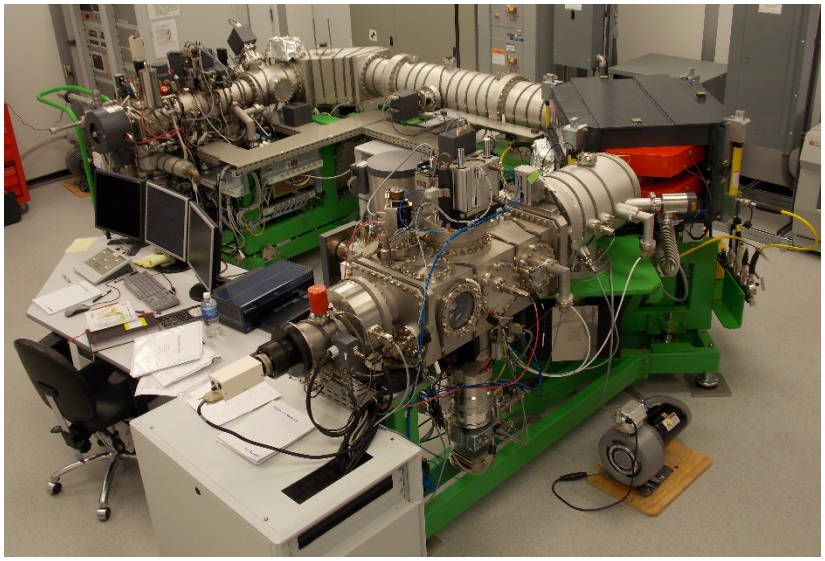
Understanding how debris was processed can help to locate device signatures.

Data relationships among multiple systems can reveal how debris was processed.

Radioactivity levels by digital autoradiography (25 µm spatial resolution)



Major element compositions and maps by scanning electron microscopy (SEM) and electron microprobe analysis (EMP). (1-5 µm spatial resolution).

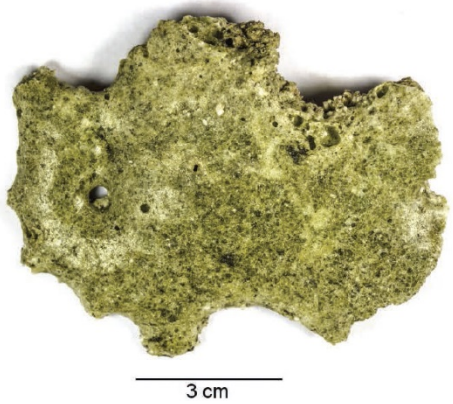


Trace element and isotope ratios by secondary ion mass spectrometry (SIMS) (~10 µm spot size per analysis with sub ppm level precision)

Background: Trinity Test

- The “gadget” was powered by ^{239}Pu fuel with large natural U tamper
- Much of of the Pu did not fission, and was dispersed in the explosion. *(Glasstone & Dolan 1977)*
- Arkosic sand ground material
  - Major minerals: quartz, alkali feldspar, calcite, olivine, pyroxene (Si, Al, Fe, Mg, Ca, Na K)
  - Trace elements: Rb, Sr, Zr, Ba, Cs, Hf, Pb, Th, U
- Produced abundant glassy debris

Morphological types of debris:

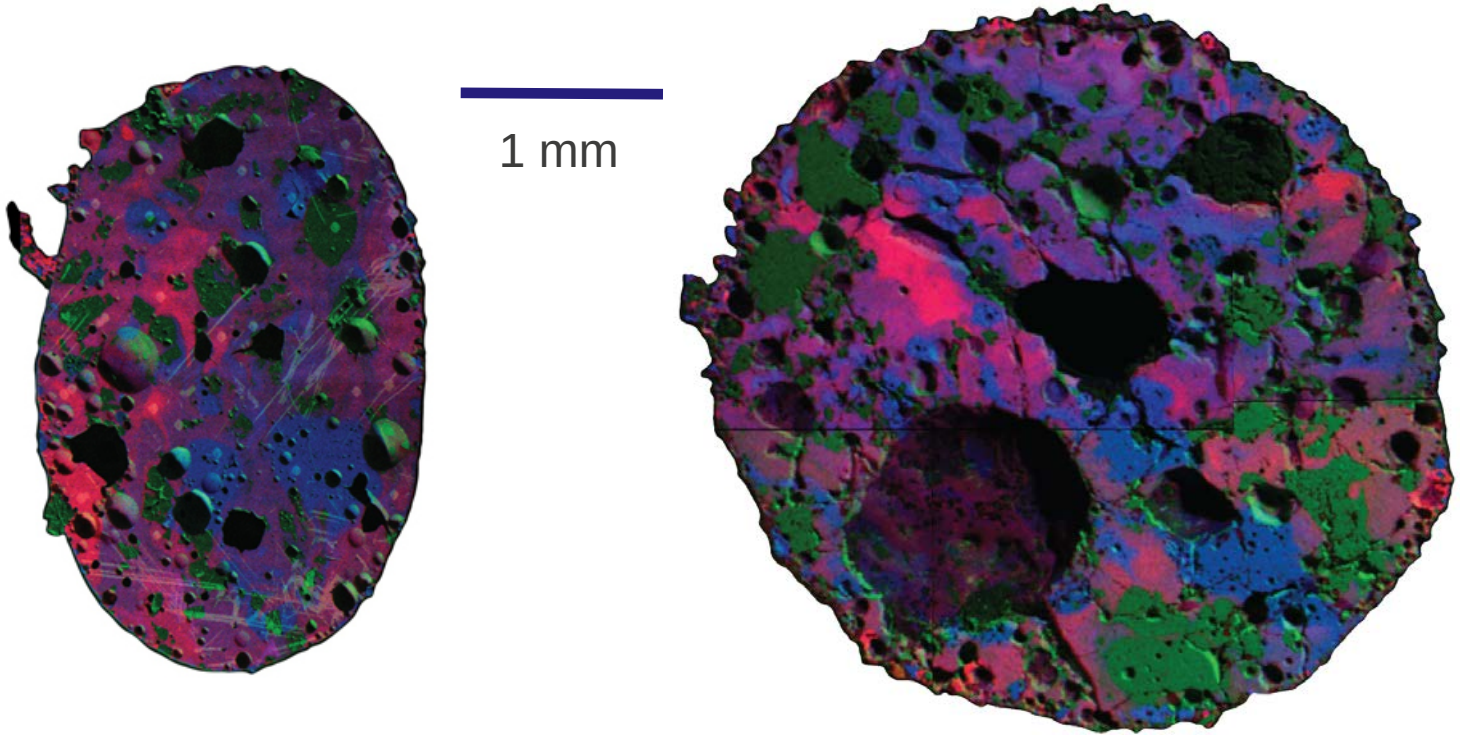


“pancake” texture: indicates a melt that puddled & glassed while on the ground.

images: Eby et al. 2015

aerodynamic beads: solidified while still in the explosion cloud = best for study

Results. SEM major element mapping reveals three types of glasses. *(Bonamici et al. submitted, Chem. Geol.)*



Qz/silica glass

SiO_2: 84-100 wt.%

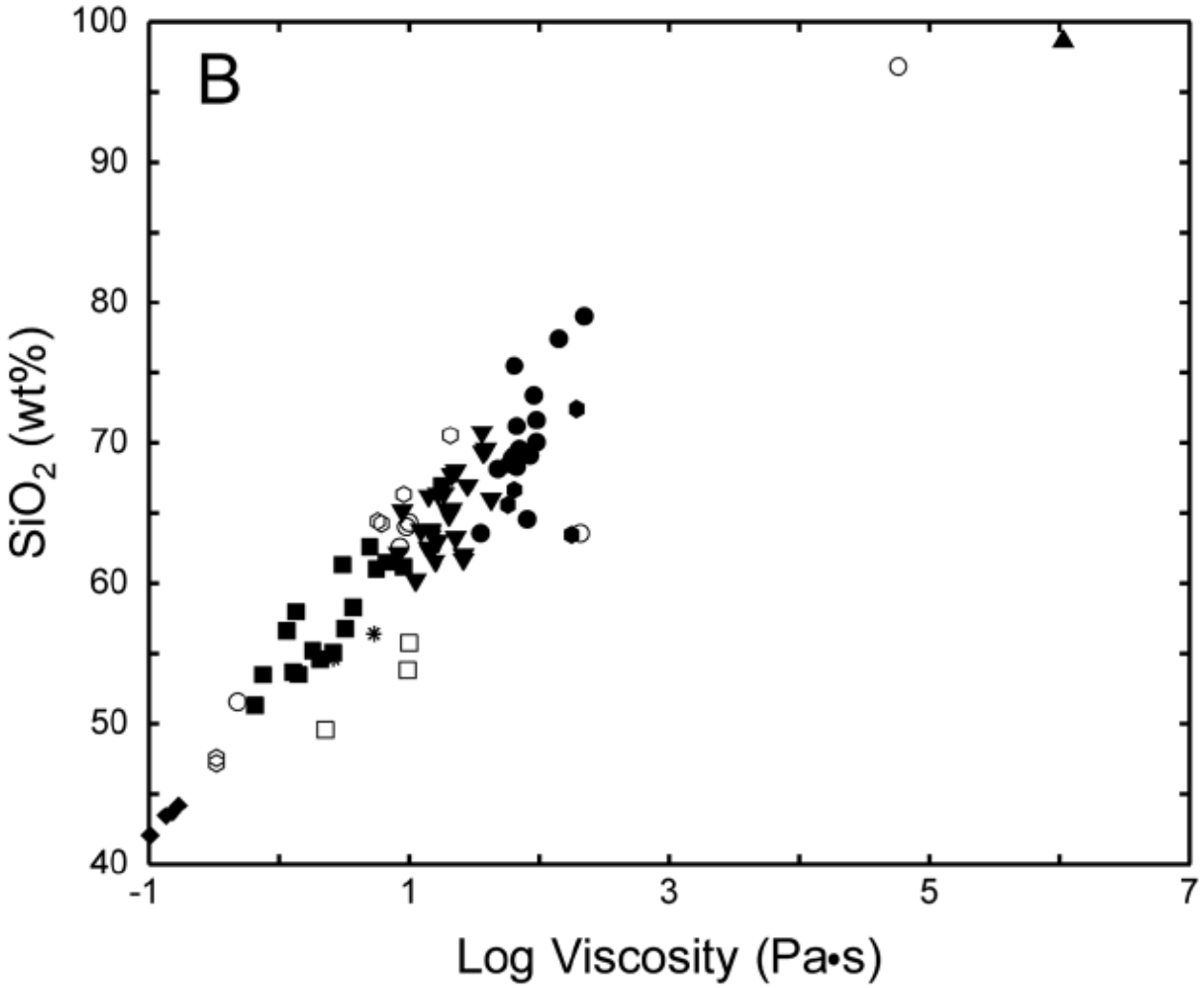
alkali-rich glass

SiO_2: 65-71 wt.%

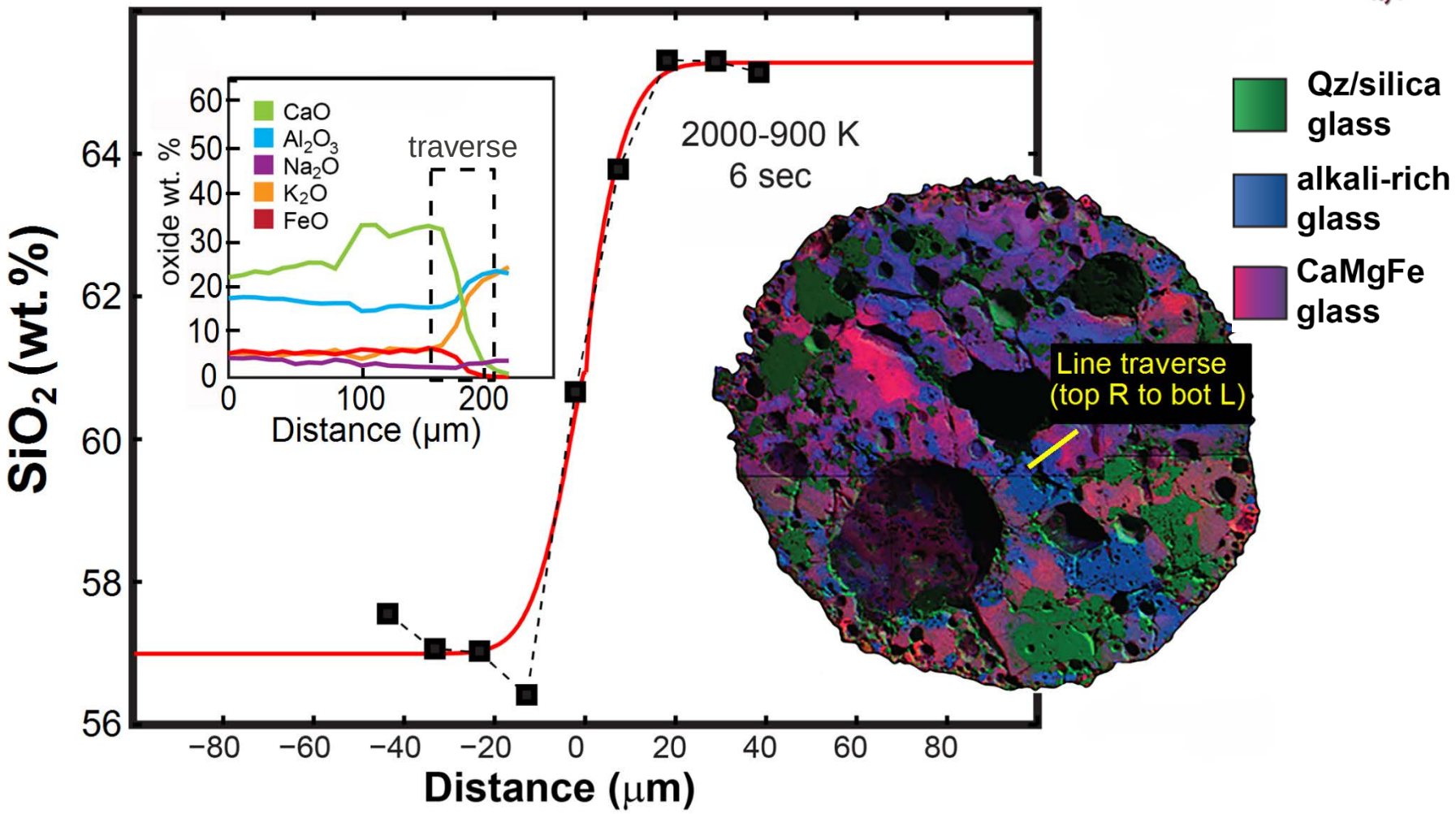
CaMgFe glass

SiO_2: 19-78 wt.%

Viscosities of trinitite compositions vs. silica content at 1700 °C *(Eby et al. 2015)*



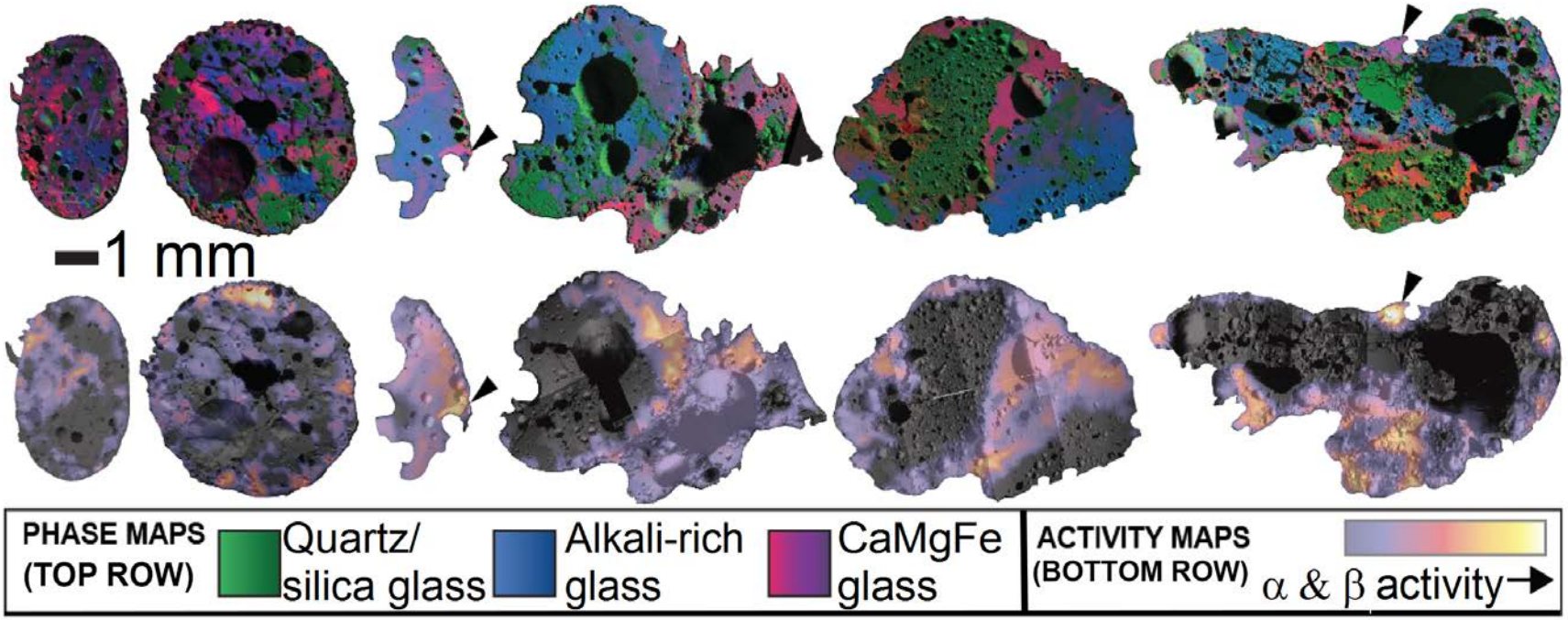
Limited glass boundary element diffusion suggests immiscibility, fast cooling. *(Bonamici et al., submitted, Chem. Geol.)*



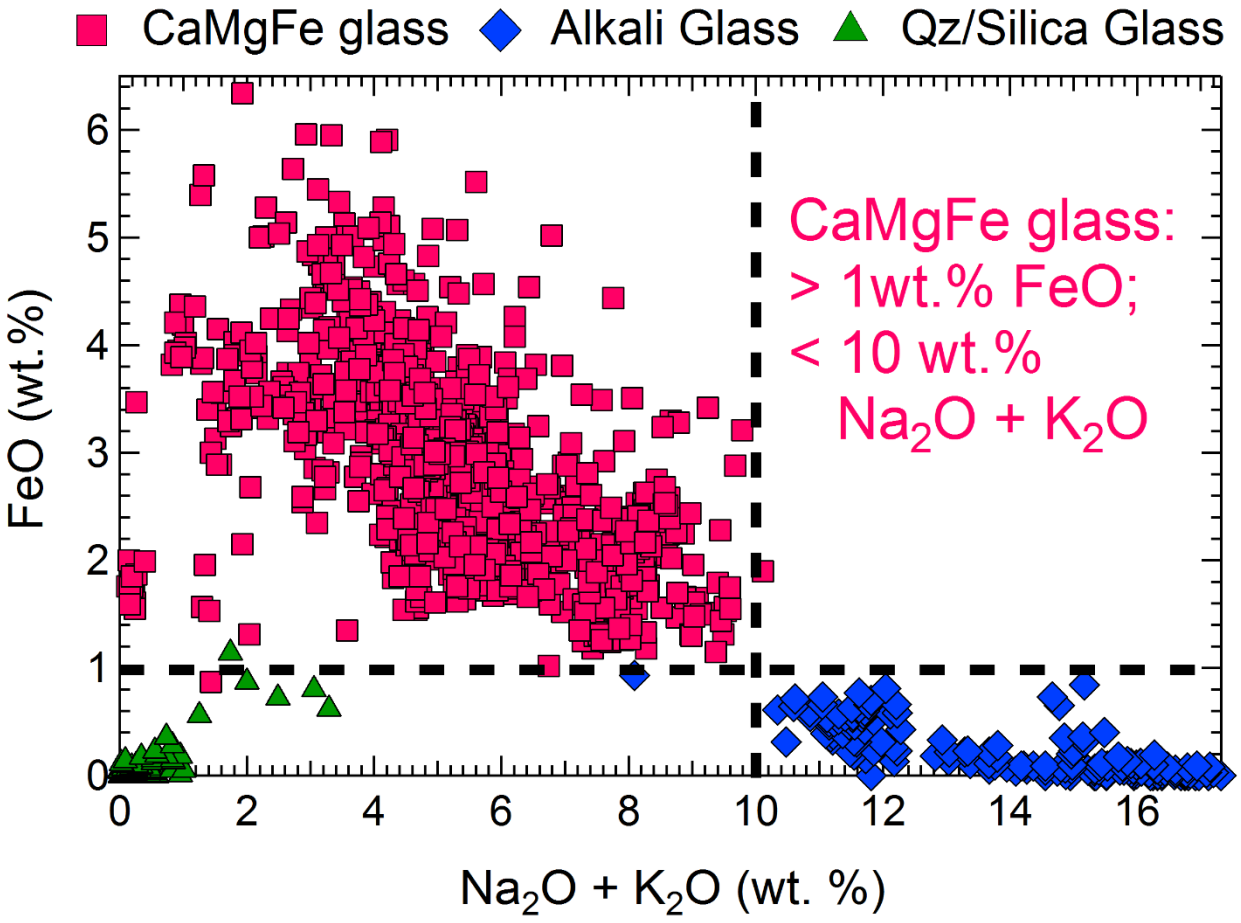
*diffusion-derived cooling rates are consistent with theoretical models & Xe isotope chronology *(e.g. Izrael, 2002; Cassata et al. 2014, respectively)*

Trinitite glass compositions vs. digital autoradiography. CaMgFe glasses contain all radioactivity.

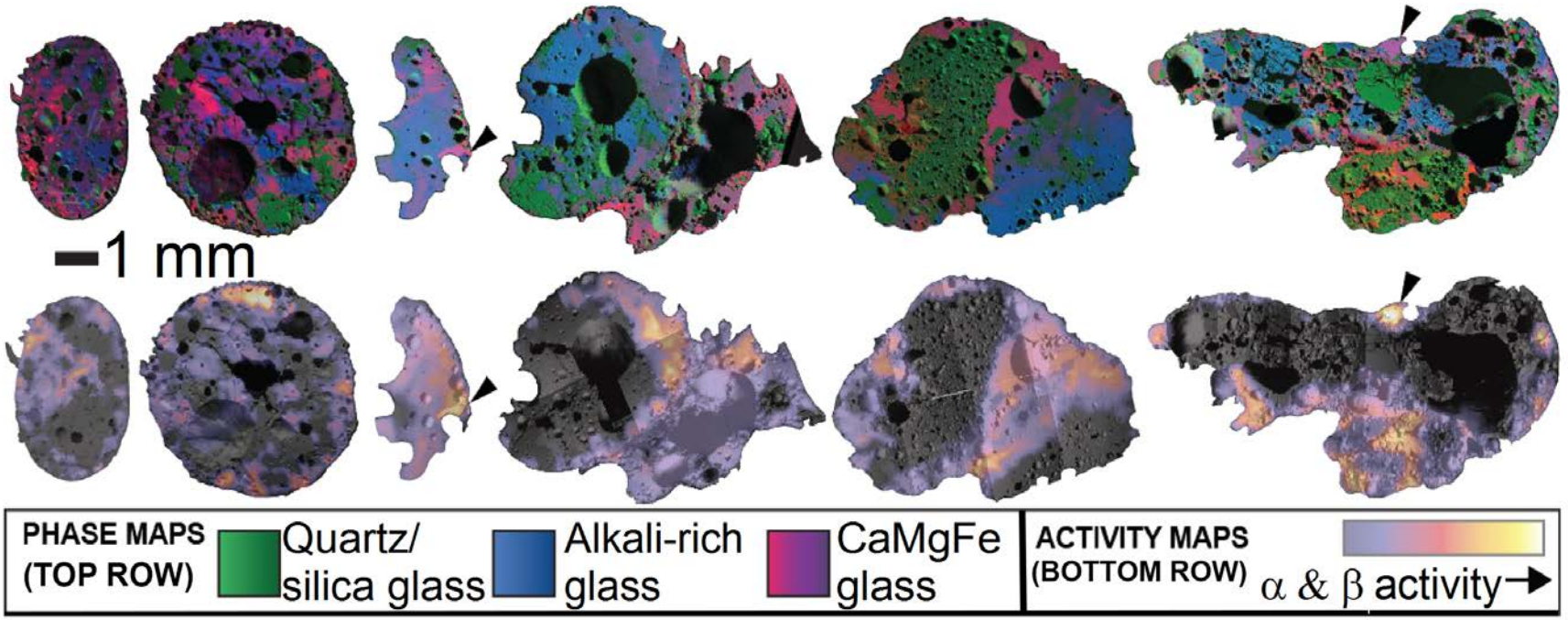
(Bonamici et al., submitted, Chem. Geol.)



A chemical proxy for field screening trinitite?

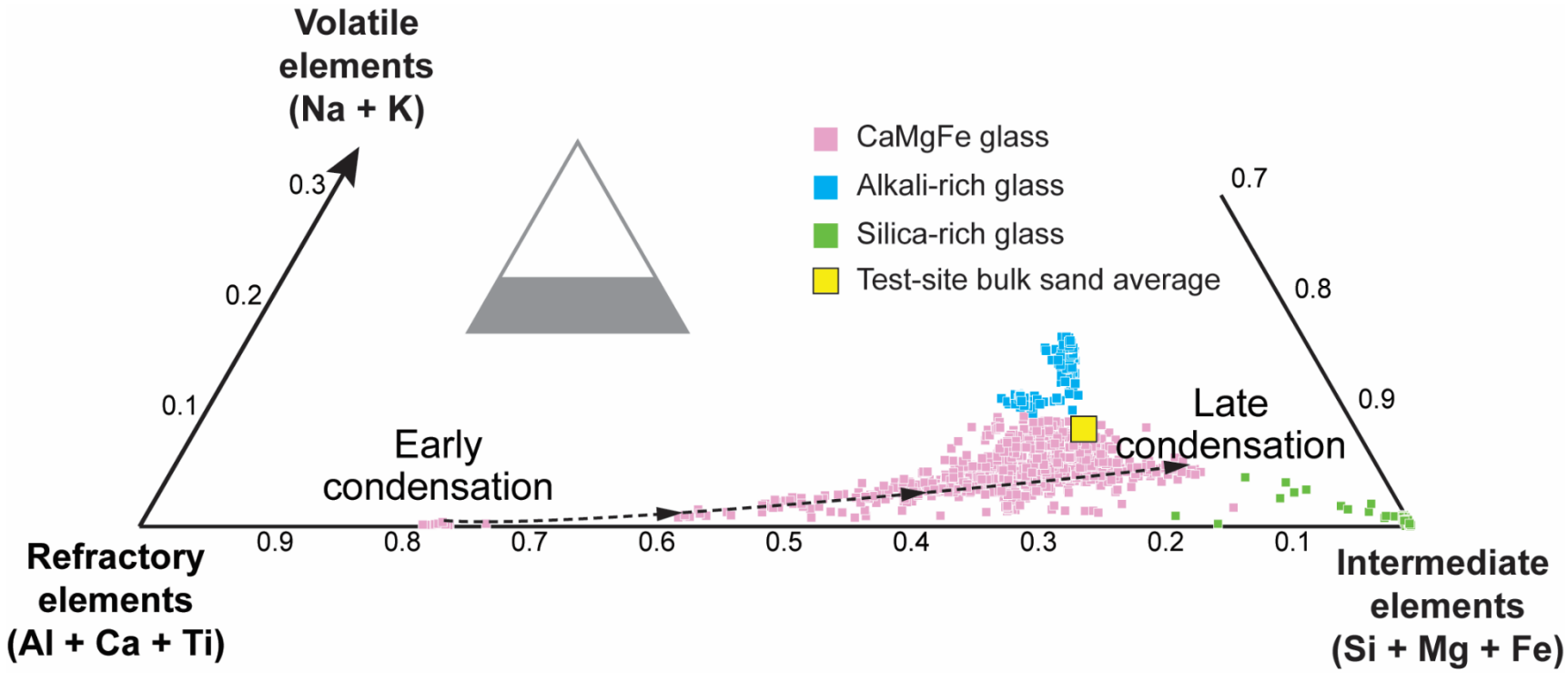


CaMgFe glass compositions and radioactivity levels are heterogeneous. *(Bonamici et al., submitted, Chem. Geol.)*



CaMgFe glass compositional trend = evaporation and condensation within the explosion. *(Bonamici et al., submitted, Chem Geol.)*

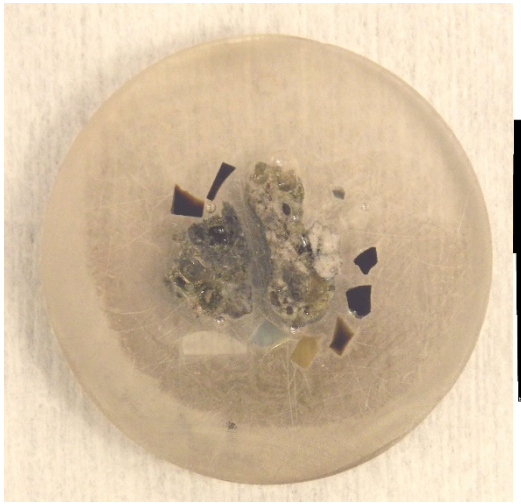
$$VolatilityIndex = \frac{volatiles}{refractories} = \frac{Na + K}{Al + Ca + Ti}$$



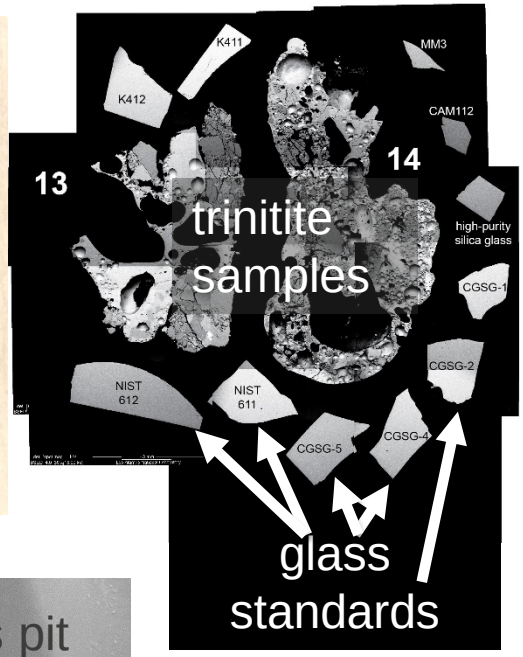
Trace element analysis by Secondary Ion Mass Spectrometry (SIMS)

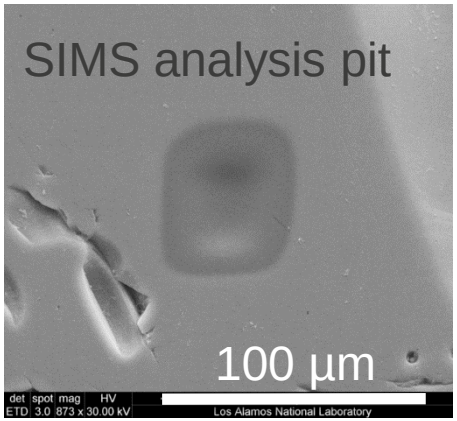
- Instrumental Mass fractionation is calibrated with multiple glass standards.
- Spot size: ~15 µm
- Count duration: ~10s per element
- ^{238}U count rate on NIST 611 glass (461 ppm U): 1.6×10^5 cps; on NIST 612 glass (37 ppm): 1.4×10^4 cps.
- Typical measured U concentrations in trinitite: 2-53 ppm; (unc. ± 0.1-2.1 ppm 2SD, respectively)

1” epoxy mount



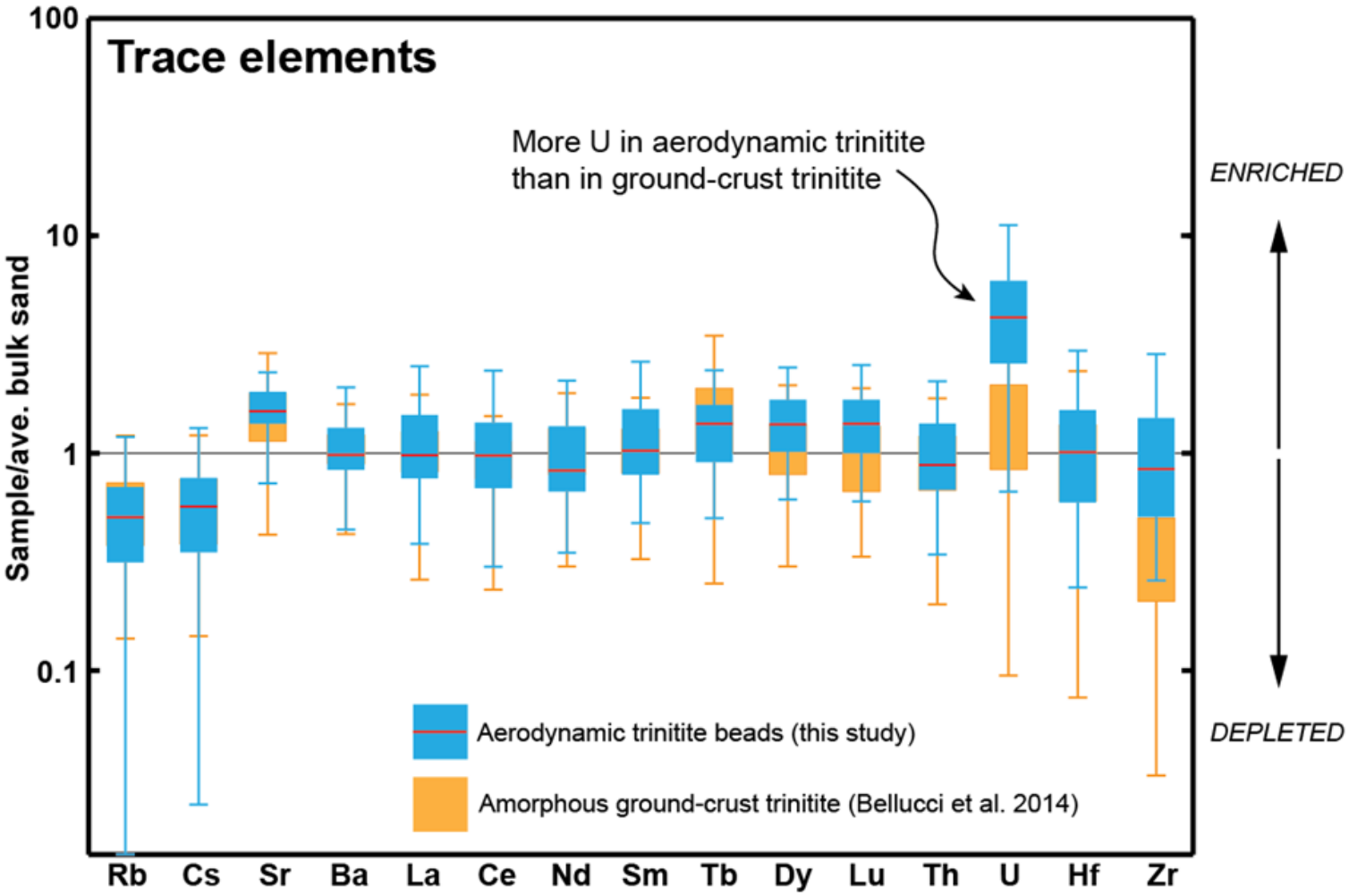
SEM map of mount



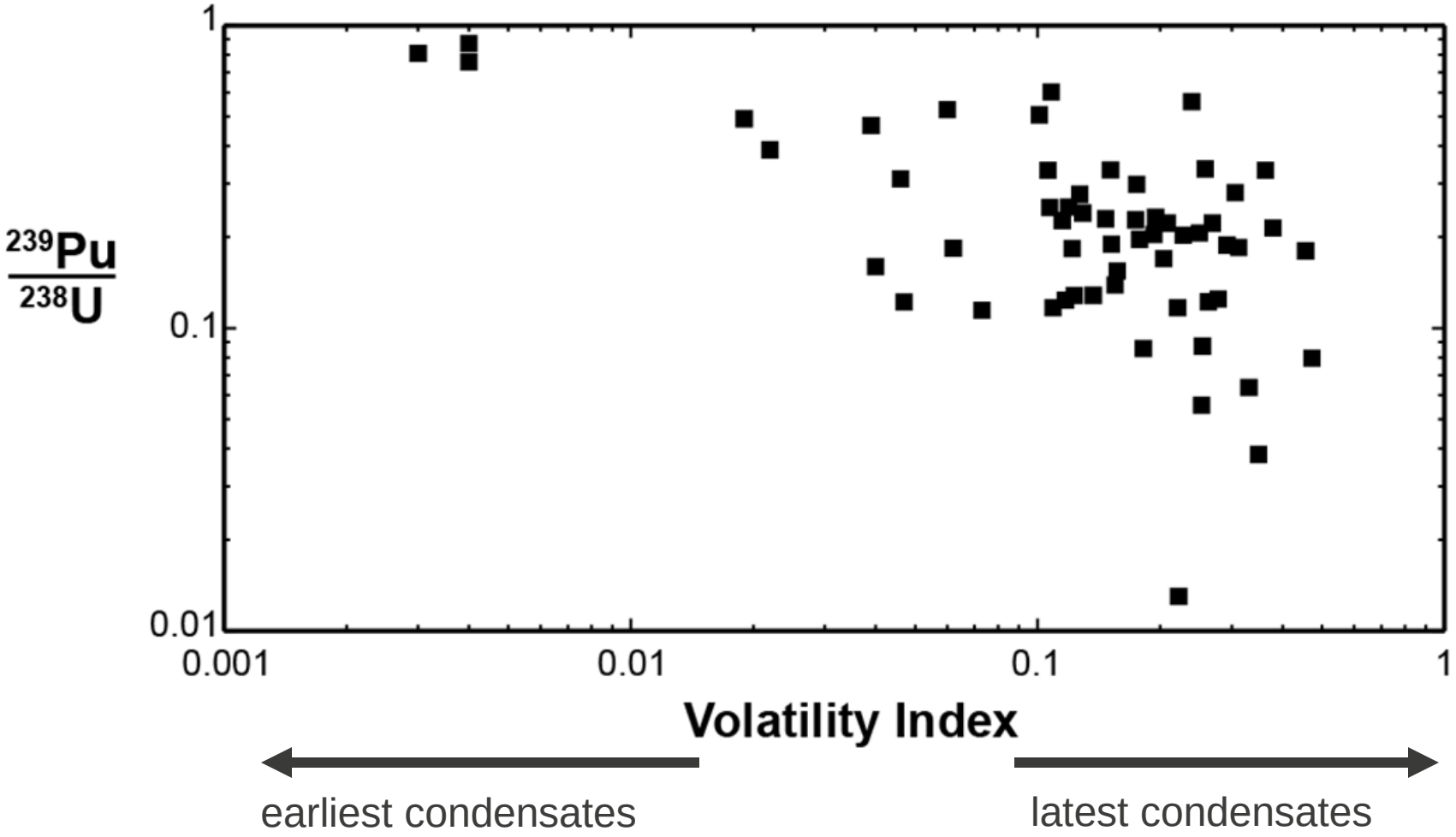


Aerodynamic beads vs. ground crust trinitite trace elements.

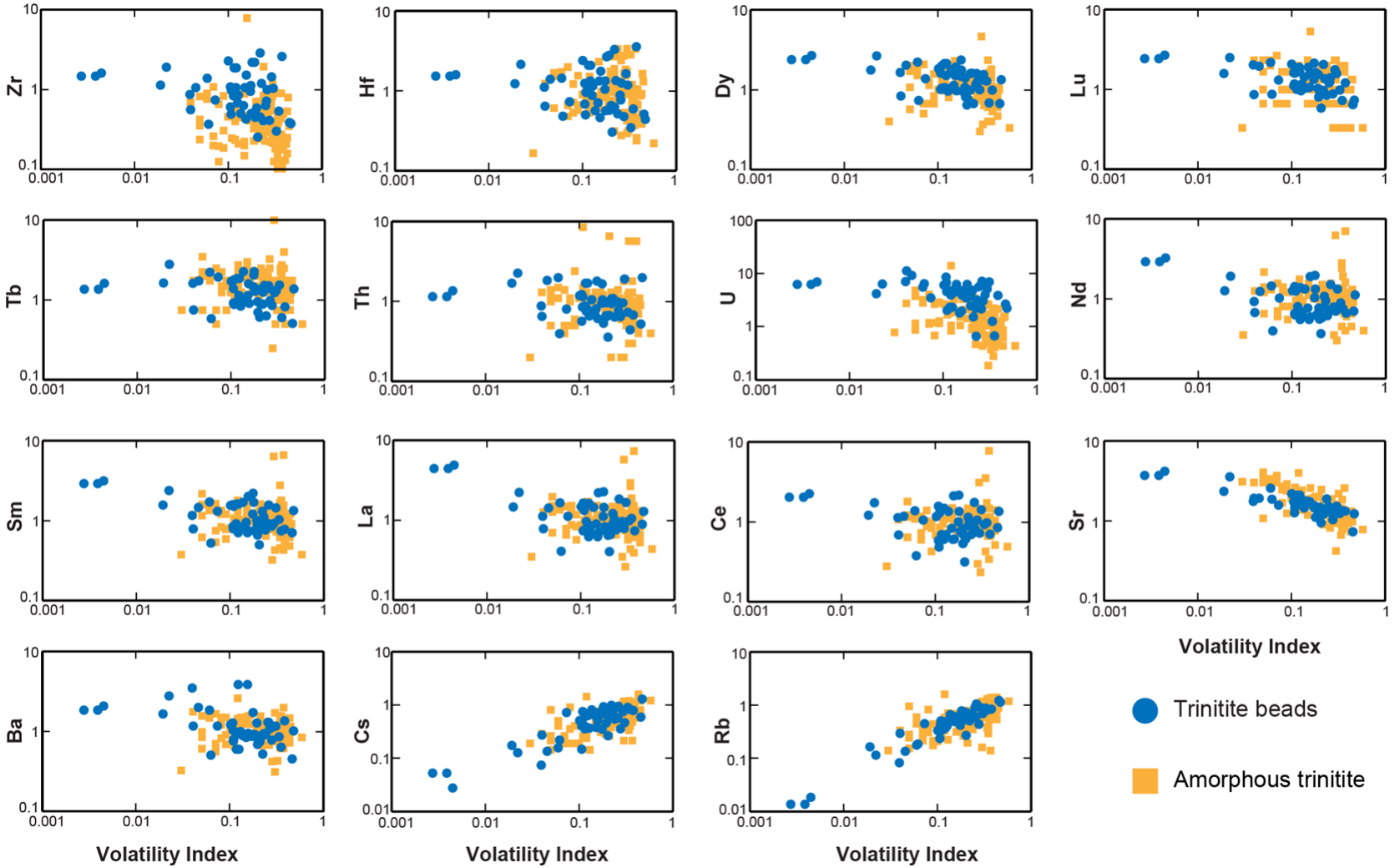
(Bonamici et al. submitted, Chem. Geol.)



Pu was more refractory than U in the explosion cloud.
It is more concentrated in the earliest condensates.



most refractory



most volatile

Trace element ordering: Bland et al. 2005; Gaboardi and Humayun 2009

Part I Summary

(1) The combination of micro-analytical techniques in chemical, isotopic, and radioactivity systems is a powerful tool to investigate fine-scale heterogeneous debris, with respect to nuclear forensic investigations.

(2) Using trinitite as an analog, we find heterogeneous glass compositions, due to viscosity differences related to SiO_2 concentrations. Limited major element diffusion across compositional boundaries indicates cooling from 2000K to 1000K in a matter of seconds.

(3) Trinitite CaMgFe glass sequesters all radioactivity. Distinct glass characteristics (high FeO and low $Na_2O + K_2O$) could be used to field-screen the best samples of interest.

(4) CaMgFe glass compositional variability is consistent with evaporation and condensation processes within the explosion. As such they are appropriately categorized by their volatility index.

(5) Trace element concentrations are also consistent with evaporation and condensation. e.g. refractories sequester into low volatility index glasses; volatiles concentrate into high volatility index glasses.

Part I Future Directions

(1) Investigate glassy debris from other types of test settings.

(2) How do compositions of entrained materials influence chemical, isotopic, and radioactive behavior of debris?

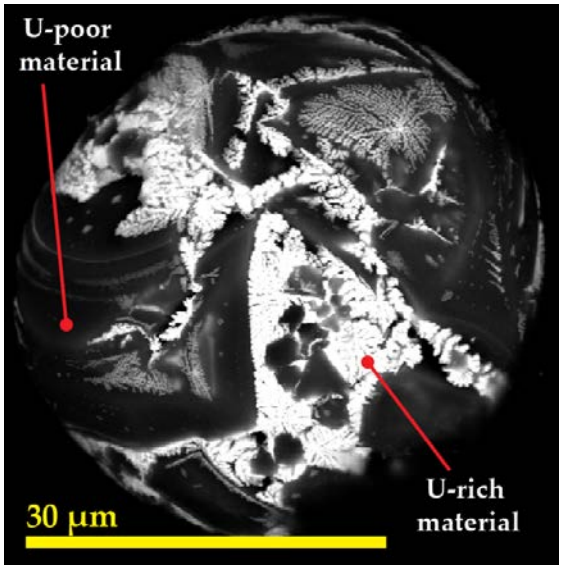
(3) How do yields influence the type of processing that occurs within an explosion? e.g. Do lower yields produce more products of partial melting? Do higher yields cause more evaporation and condensation?

(4) How do the above variables fit in with regard to the volatility index? Will we discover other indices that are better suited for other explosion scenarios?

(5) Ultimately, future investigations of analogs closer to real-world scenarios (urban environment) will be beneficial.

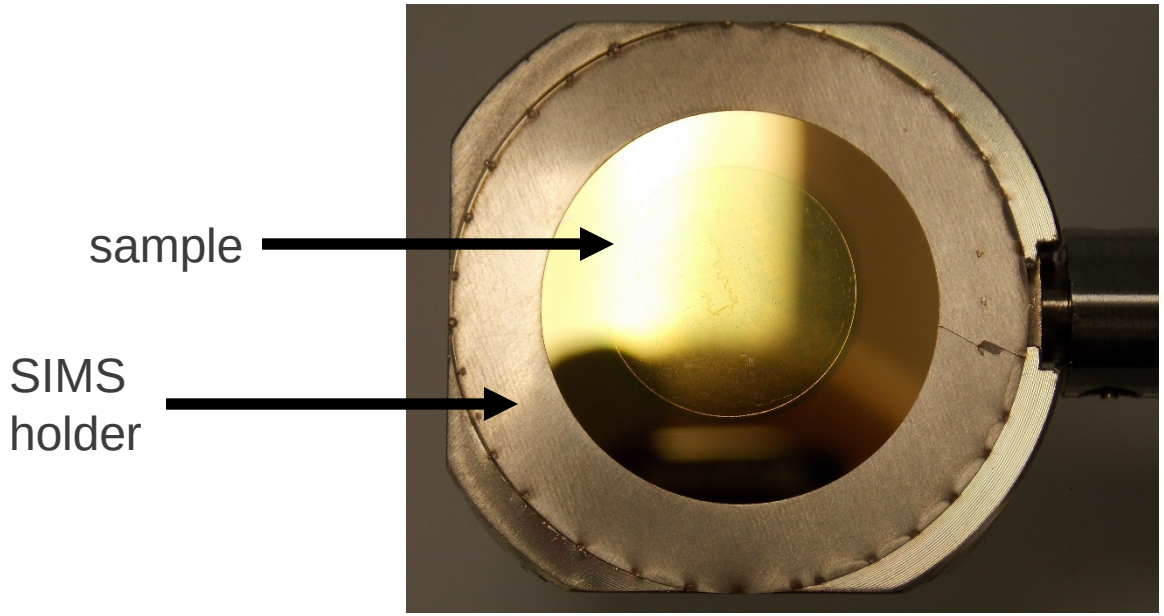
Part II Objectives

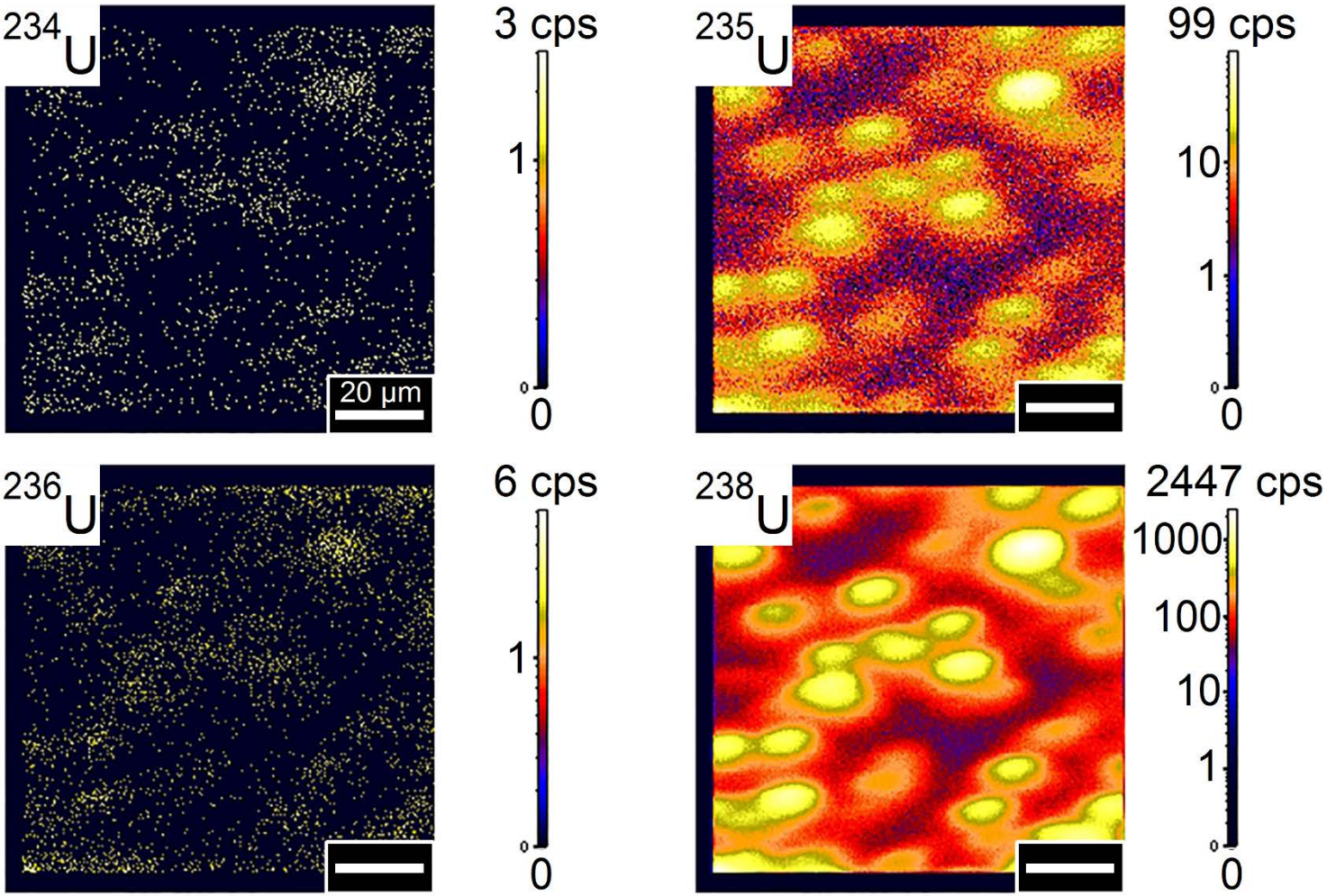
(1) Identify materials among small grains that contain signatures of weaponization activities.
(2) Example: Detect materials with unique U-isotope ratios relative to ground material, among swipes/filters of environmental samples.
(3) Preliminary approach: SIMS analysis of U_3O_8 reference materials, with known isotope ratios, as analogs.
    (3a) Determine the extent of SIMS instrumental mass fractionation.
    (3b) Distinguish U-isotope ratios from mixed reference materials.

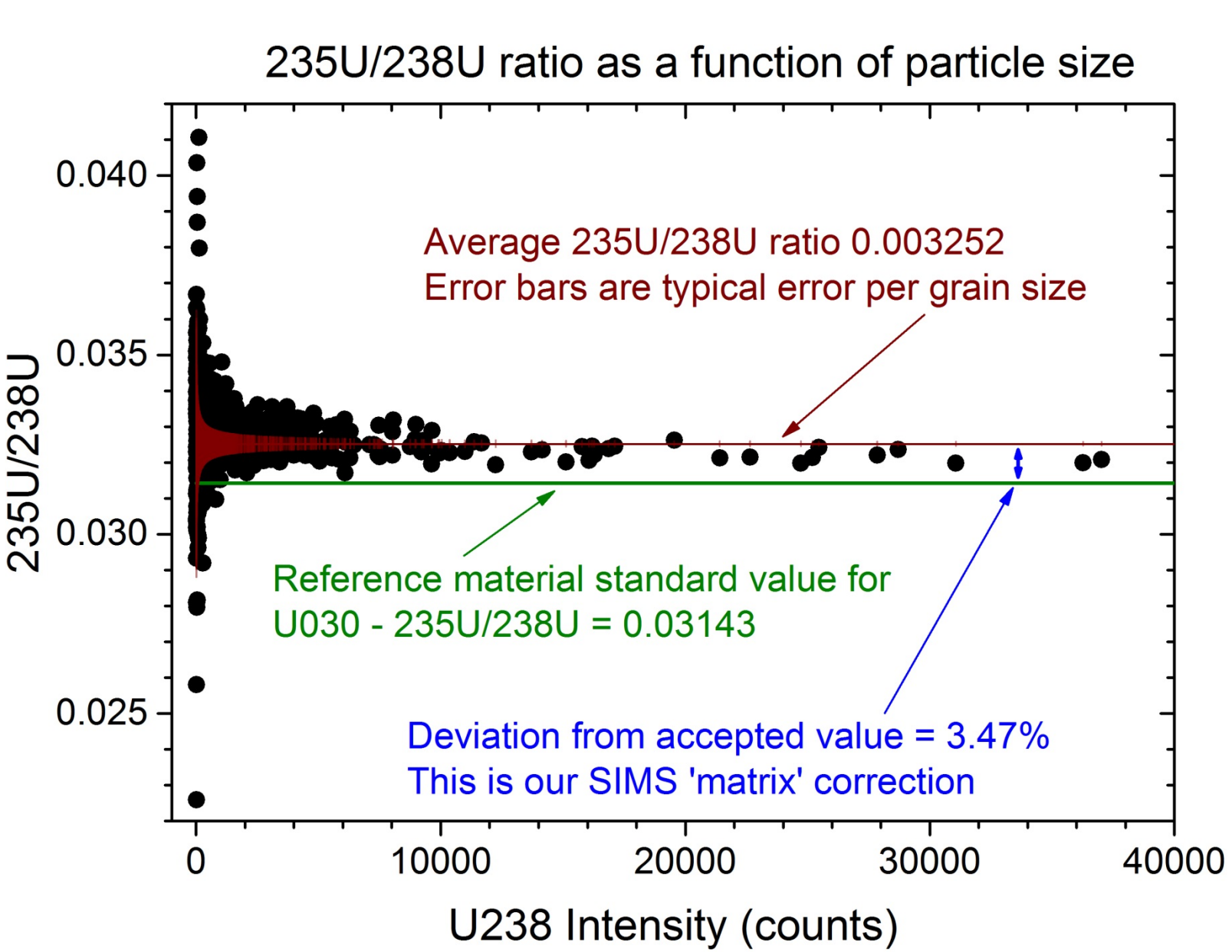


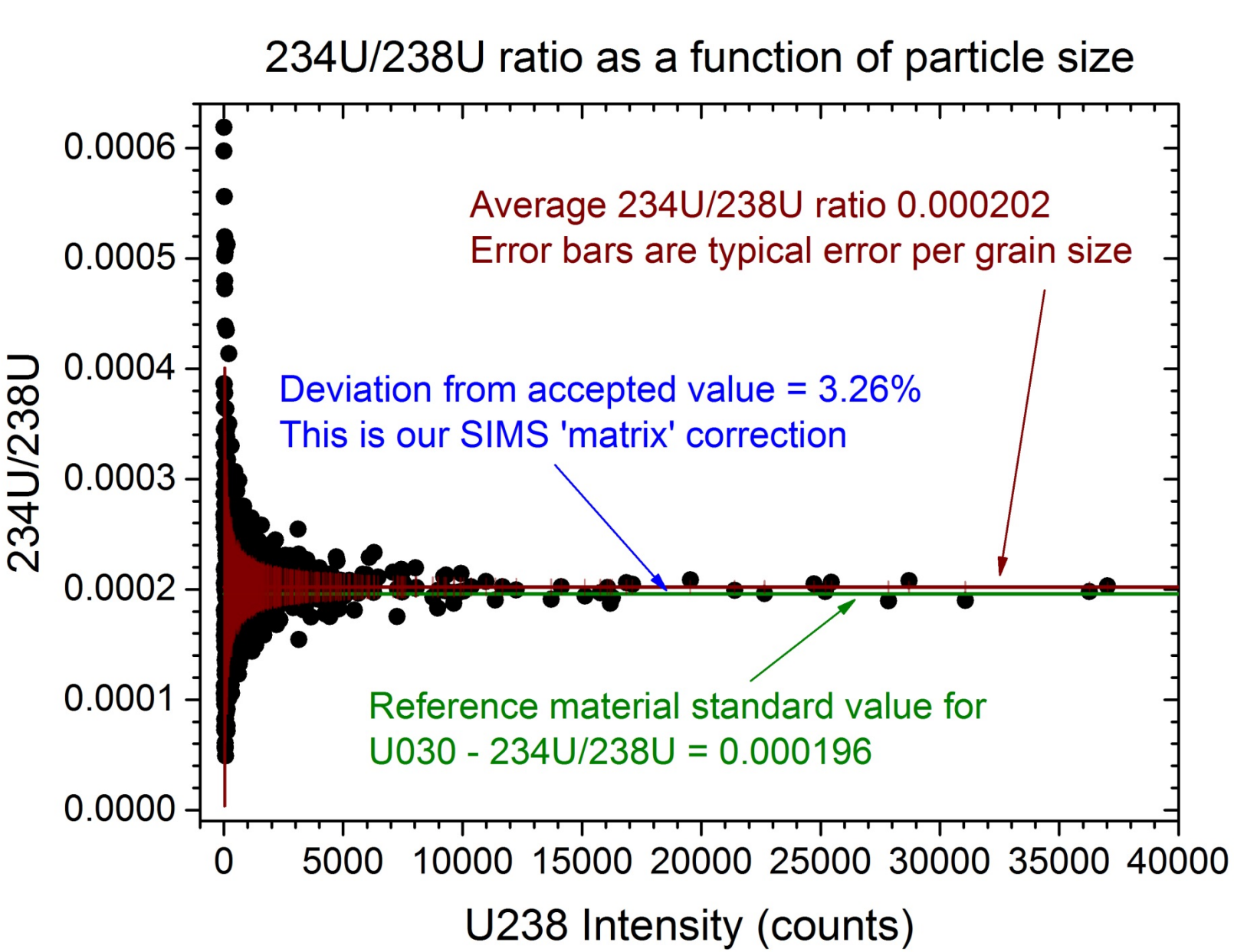
Materials & Sample Preparation

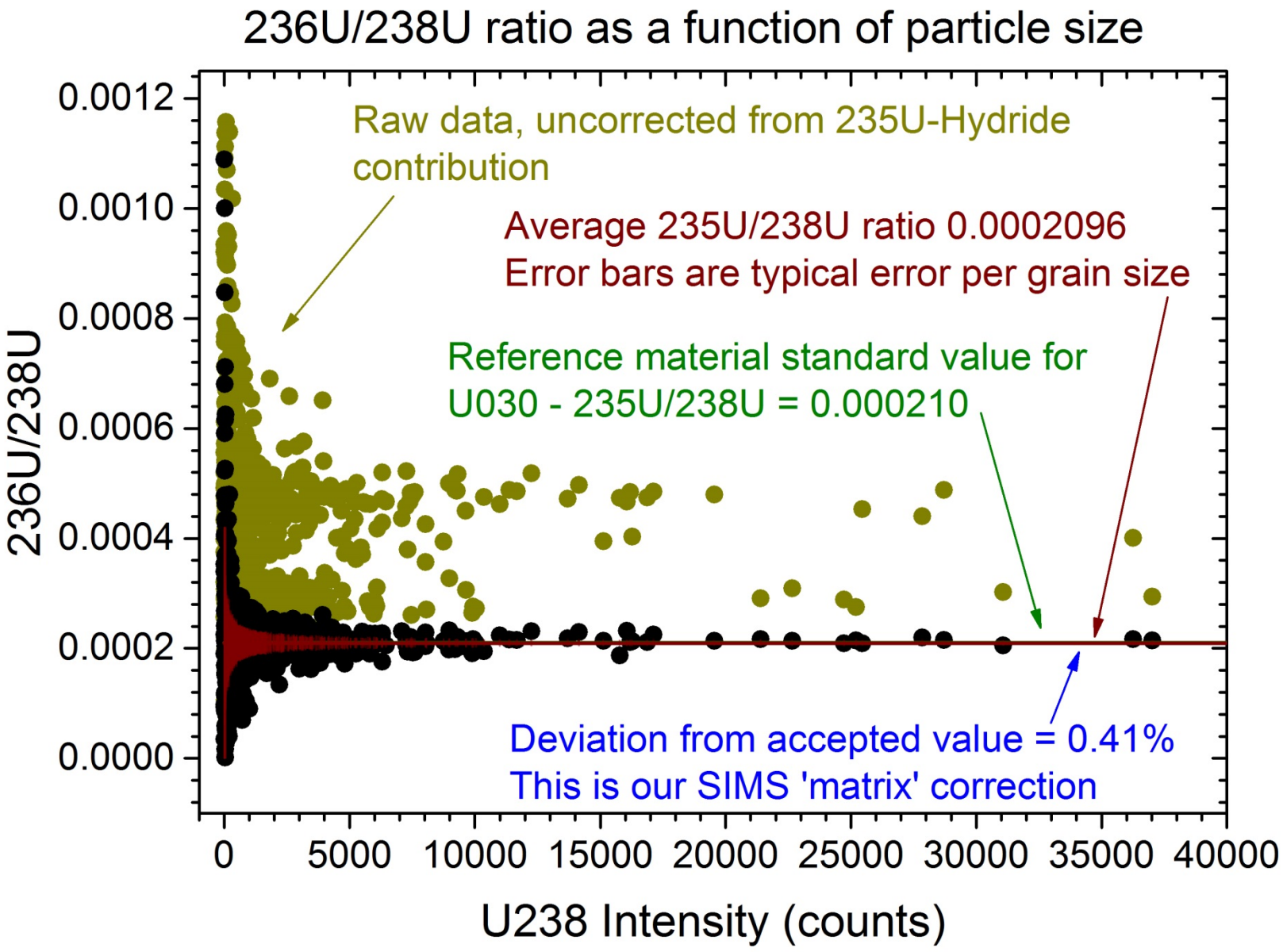
- U_3O_8 reference powders from New Brunswick National Laboratory: U030, U005, U0002.
- Powders suspended in containers filled with acetone and ultrasonicated.
- Suspensions pipetted onto Au-coated Si wafers and dried.

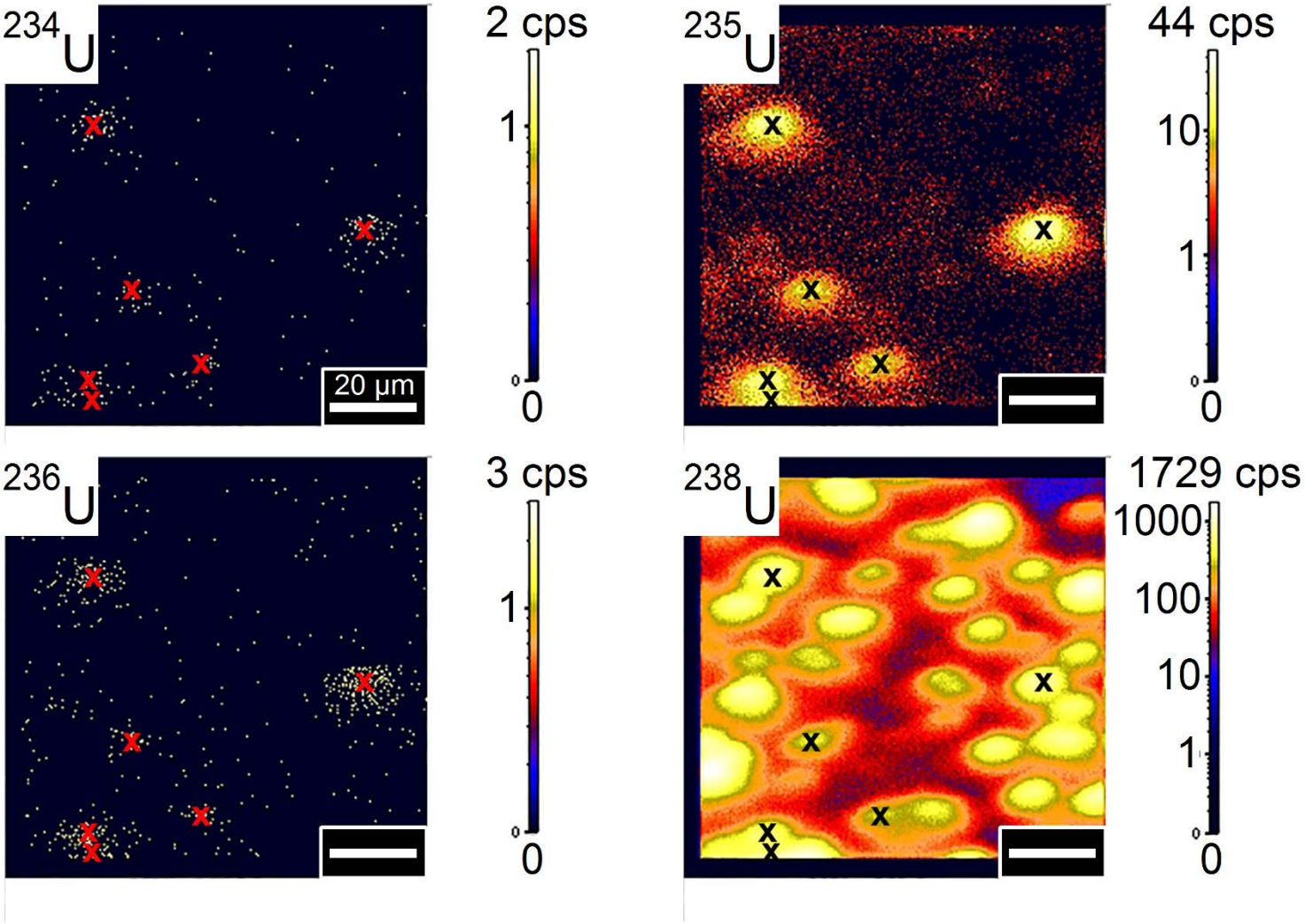


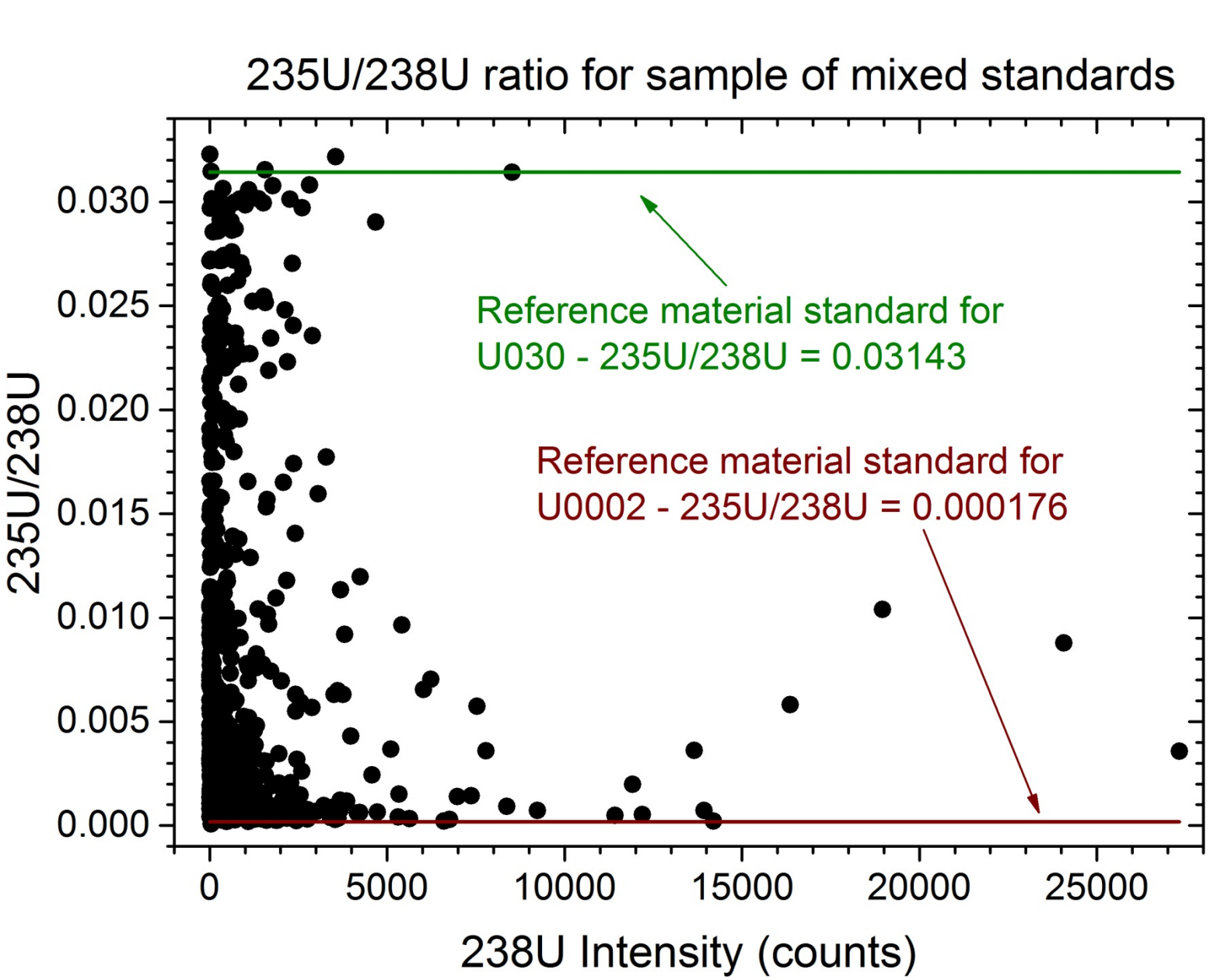

234 U
20 µm
3 cps
1
0
235 U
99 cps
10
1
0
236 U
6 cps
1
0
238 U
2447 cps
1000
100
10
1
0

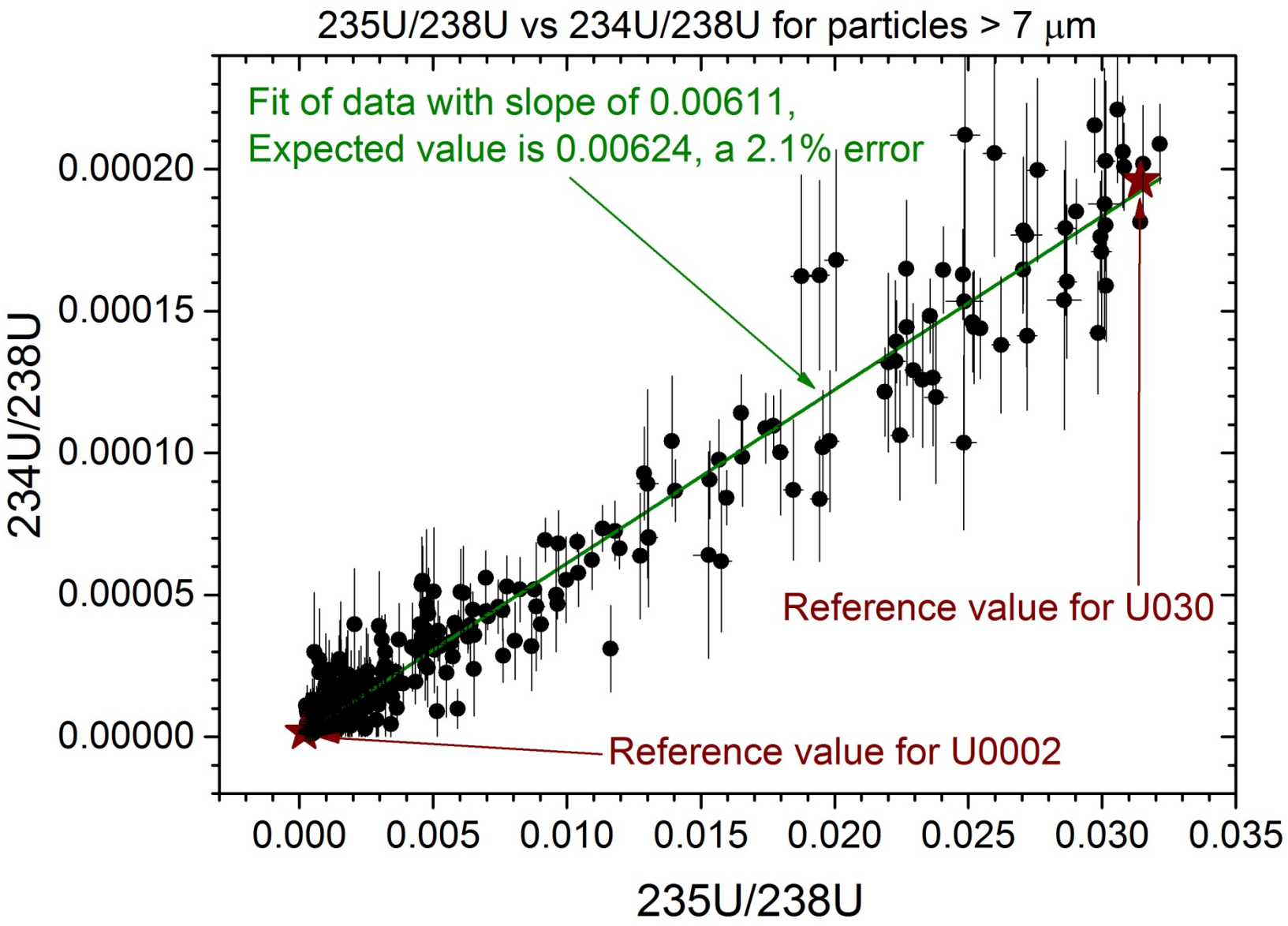

235U/238U ratio as a function of particle size
Average 235U/238U ratio 0.003252
Error bars are typical error per grain size
Reference material standard value for
U030 - 235U/238U = 0.03143
Deviation from accepted value = 3.47%
This is our SIMS 'matrix' correction
235U/238U
0.040
0.035
0.030
0.025
0
10000
20000
30000
40000
U238 Intensity (counts)


234U/238U ratio as a function of particle size
Average 234U/238U ratio 0.000202
Error bars are typical error per grain size
Deviation from accepted value = 3.26%
This is our SIMS 'matrix' correction
Reference material standard value for
U030 - 234U/238U = 0.000196
234U/238U
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0.0000
0
5000
10000
15000
20000
25000
30000
35000
40000
U238 Intensity (counts)


236U/238U ratio as a function of particle size
Raw data, uncorrected from 235U-Hydride contribution
Average 235U/238U ratio 0.0002096
Error bars are typical error per grain size
Reference material standard value for U030 - 235U/238U = 0.000210
Deviation from accepted value = 0.41%
This is our SIMS 'matrix' correction
236U/238U
0.0012
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000
0
5000
10000
15000
20000
25000
30000
35000
40000
U238 Intensity (counts)


234 U
20 µm
2 cps
1
0
235 U
44 cps
10
1
0
236 U
3 cps
1
0
238 U
1729 cps
1000
100
10
1
0


235U/238U ratio for sample of mixed standards
Reference material standard for
U030 - 235U/238U = 0.03143
Reference material standard for
U0002 - 235U/238U = 0.000176
235U/238U
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0
5000
10000
15000
20000
25000
238U Intensity (counts)


235U/238U vs 234U/238U for particles > 7 μm
Fit of data with slope of 0.00611,
Expected value is 0.00624, a 2.1% error
Reference value for U030
Reference value for U0002
234U/238U
235U/238U
0.00020
0.00015
0.00010
0.00005
0.00000
0.000
0.005
0.010
0.015
0.020
0.025
0.030
0.035

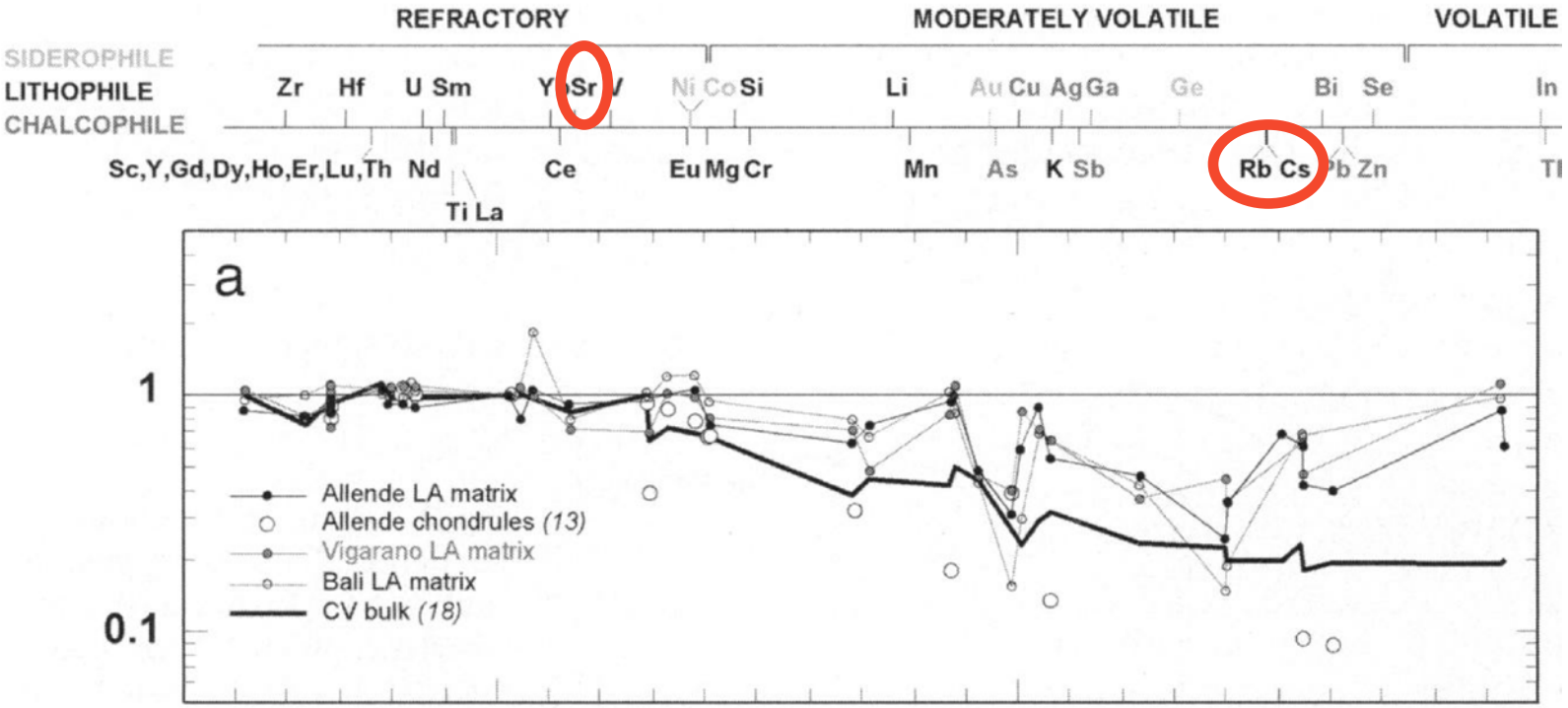
Summary for Part II

Accomplishments:

- **Demonstrated state-of-the-art spatial resolution with the LG-SIMS at LANL.**
- **Shown low 'matrix' effect for U_3O_8 materials with reasonable precision down to small sample sizes.**
- **Differentiated particles with different U isotope compositions.**

Future Work:

- **Differentiate particles with smaller differences in their U isotope compositions.**
- **Look at mixes of samples with 3 or more components.**
- **Analyze samples composed of UO_2.**
- **Compare matrix effects between UO_2 and U_3O_8.**


REFRACTORY
MODERATELY VOLATILE
VOLATILE
SIDEROPHILE
LITHOPHILE
CHALCOPHILE
Zr Hf U Sm Y Sr V Ni Co Si Li Au Cu Ag Ga Ge Bi Se In
Sc,Y,Gd,Dy,Ho,Er,Lu,Th Nd Ti La Ce Eu Mg Cr Mn As K Sb Rb Cs Pb Zn Tl
a
1
0.1
Allende LA matrix
Allende chondrules (13)
Vigarano LA matrix
Bali LA matrix
CV bulk (18)

Larger Laboratory Context

- **What work is taking place at LANL in this general area? Yours and everybody else's**
- **Roughly what is the scale in terms of personnel and number of projects?**
- **Where does the work you're talking about today fit into that larger picture?**

Introduction/Background

- **Significance of work**
- **Why LANL?**
- **Two or three key take away messages**

Current status of work

- Where is the work today?
- Past/current funding?
- What's the follow on plan for funding?
- Provide LDRD involvement here and/or last slide
- Customers?
- Assess the competitive landscape by providing an assessment of who else is working in this field, their approach, and why your approach will make an impact

Problem statement

- **What is the problem to be solved? E.g., why are you doing this work?**

Approach

- **What is the approach you're taking to solving this problem?**

Results

- **What have you achieved so far?**

Path Forward

- **Provide both technical and program development path forward**

Acknowledgements

- **Provide ties to LDRD program – previous support, etc.**
- **Remember to leave plenty of time for questions.**