Improved Analytical Characterization of Solid Waste - Forms by Fundamental Development of Laser Ablation Technology

Proposal 55318

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Purpose

Laser ablation is an advanced sampling technology viable for characterization needs within the DOE EM program.

This EMSP research endeavors to understand, develop, and improve laser ablation sampling as an accurate and sensitive analytical technology for rapid, safe, and cost effective characterization of DOE EM wastes.

- **EMSP program leverages DOE ER/BES fundamental laser ablation program:**
  - **EMSP: new studies dedicated to accurate and sensitive <u>detection</u> of ablated mass**
- **Benefits of research to EM applications:**
  - **Characterization is priority in 6 of 7 EM problem areas**
  - **Laser-induced plasmas for remote analysis**
  - **Laser ablation for decontamination**

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"Bridge the Gap"

Laser Ablation	Transport	Inductively Coupled Plasma	Mass Spectrometry
BES	BES/EMSP	EMSP	EMSP

This EMSP research benefits from a 10-year DOE Office of Energy Research Basic Energy Sciences program to study fundamental mechanisms of laser ablation:

BES: understanding laser ablation *at* the sample

EMSP: understanding *detection* of the ablated mass

BES and EMSP programs address separate issues but compliment each other in order to understand and develop laser ablation for chemical characterization.

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Laser Ablation for Characterization

» Any solid (liquid) sample

» No sample preparation

» Minimal sample quantity (μg - ng)

» No solvents or additional waste

» Direct multi-component analysis

» Spatial (micro) analysis

» Remote analysis (LIBS)

»

Laser Ablation for EM

- **Advanced characterization technology for wastes and contaminants:**
  - first step in the clean-up scenario
  - accelerate treatment and immobilization programs

- **Characterization listed as high priority in 6 of the 7 EM problem areas:**
  - High Level Waste
  - Spent Nuclear Fuel
  - Mixed Waste
  - Nuclear Materials
  - Remedial Actions
  - Decontamination and Decommissioning (including LA cleaning)

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Critical Issues

- **Accuracy:** analysis must be a true characterization of the waste sample
  - Fractionation during laser ablation (BES)
  - Transport from sample chamber to ICP (EMSP)
  - Mass Loading in the ICP (EMSP)

- **Sensitivity:** detect lowest level at which contaminants exist in the waste sample
  - Mass ablation rate (BES)
  - Particle size distribution (BES, EMSP)
  - Transport efficiency (EMSP)
  - Optimization of ICP and MS (EMSP)

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ICP/MS Sensitivity

Liquid Nebulization (LN): sensitivity is in ppt range!
Laser Ablation (LA): sensitivity is in ppm range!

Part of difference is explained in the total volume of sample introduced into the ICP. Large difference due to 'sampling' efficiency for LA

LN: 5×10^5 cps / 10ppb (10 cps = bkg)

1 L/min @ 1 ppt = 20 fg of mass (2% transport)

LA: 100 ng/pulse x 600 pulses/min = 60 mg (ablated mass amount)

If transport = 100%, should detect 0.3 ppb! (Reality is ppm)

Therefore: efficiency of 'collection' only approx. 10^{-4}

Ablated fragments in chamber too large to entrain and/or transport

Condensed mass on target, chamber, and tubing

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Particle Mass

- **Total mass related to number of particles and their diameter**
  (assumes SRS glass density = 3 g/cm^3)

2000	particles @ 0.1 μm	=	1.0 x 10^{-11} cm^3	=	30 pg
400	particles @ 0.5 μm	=	2.6 x 10^{-11} cm^3	=	78 pg
80	particles @ 1.0 μm	=	4.9 x 10^{-11} cm^3	=	125 pg
1	particle @ 5.0 μm	=	6.5 x 10^{-11} cm^3	=	196 pg

- **Large particles represent greater mass of sample**
- **Large particles not efficiently entrained and transported**
- **Particle size distribution related to laser and sample properties**
- **Composition is particle size dependent (vapor, melt, fracture)**
- **Fractionation in ICP versus particle size**

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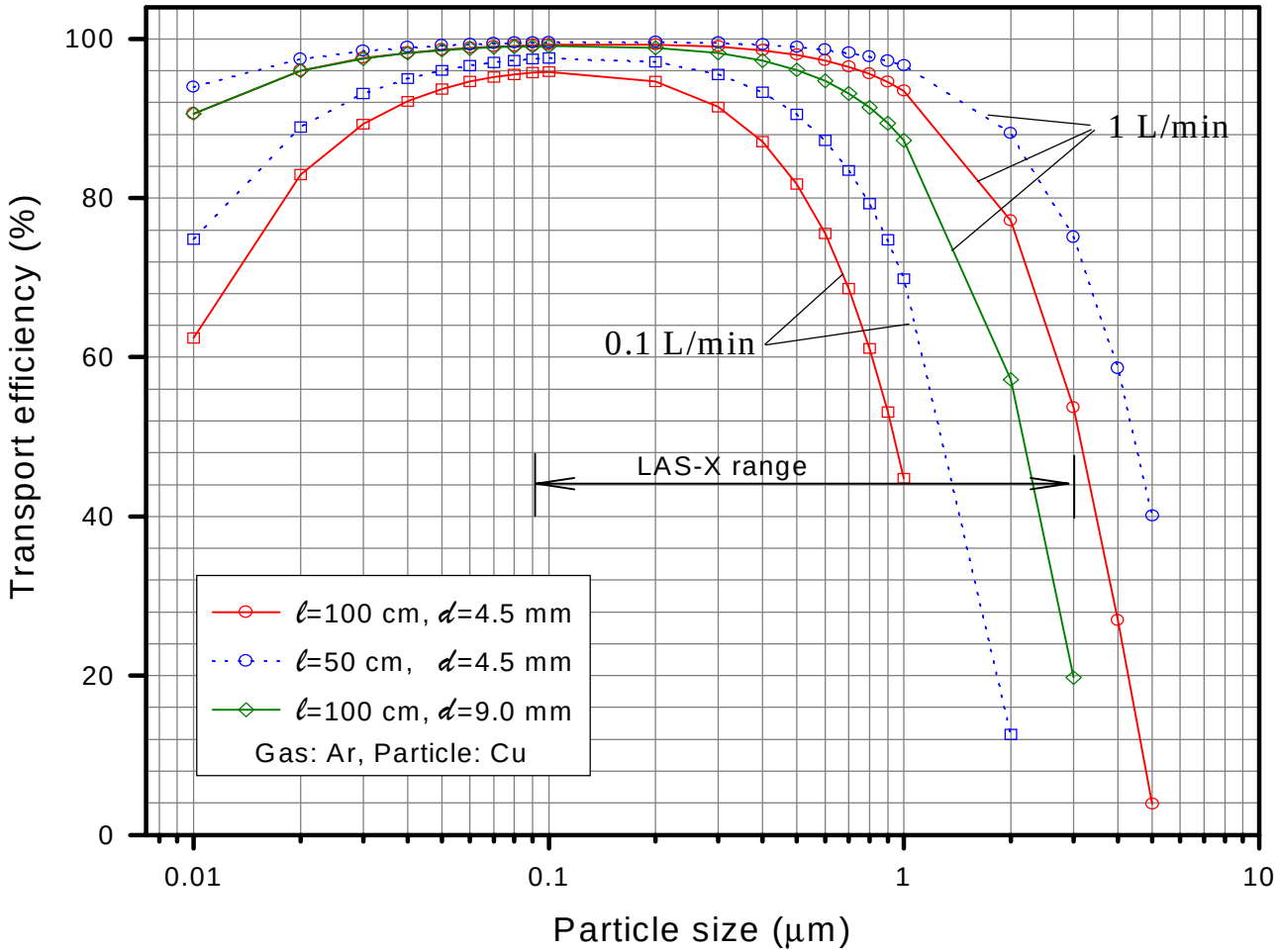
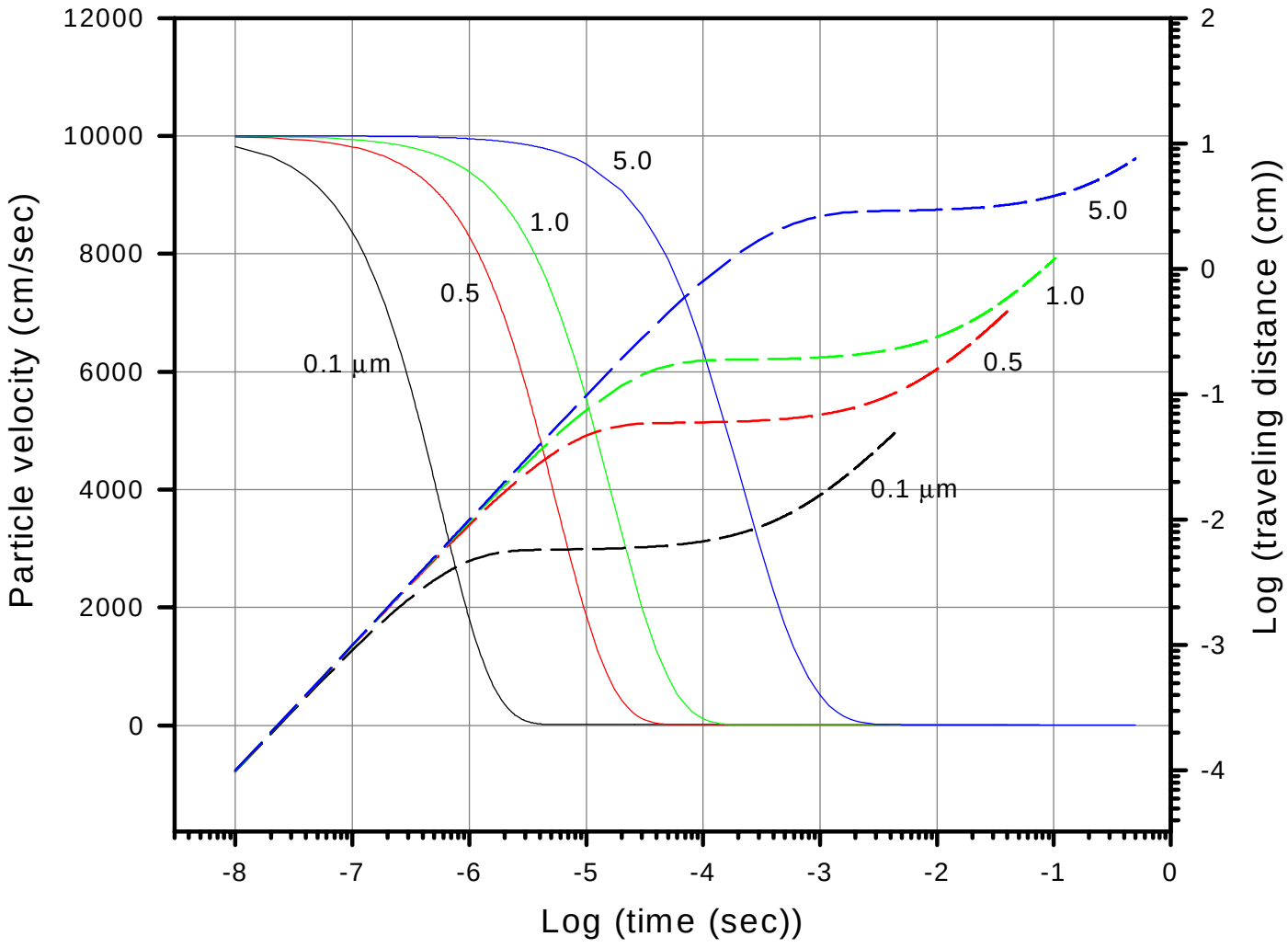
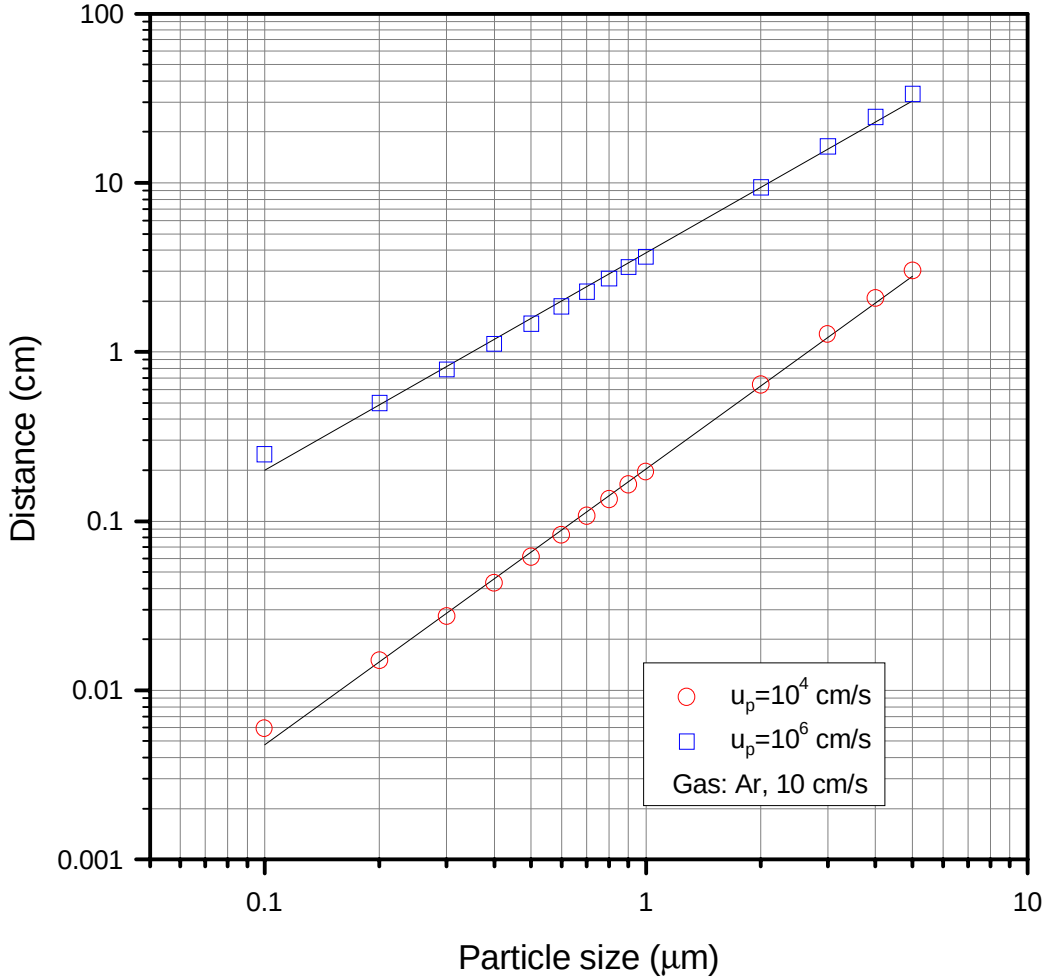
EFFECT OF GRAVITATIONAL SETTLING & DIFFUSION ON PARTICLE TRANSPORT



TIME AND DISTANCE FOR A SPHERICAL PARTICLE TO REACH TERMINAL VELOCITY

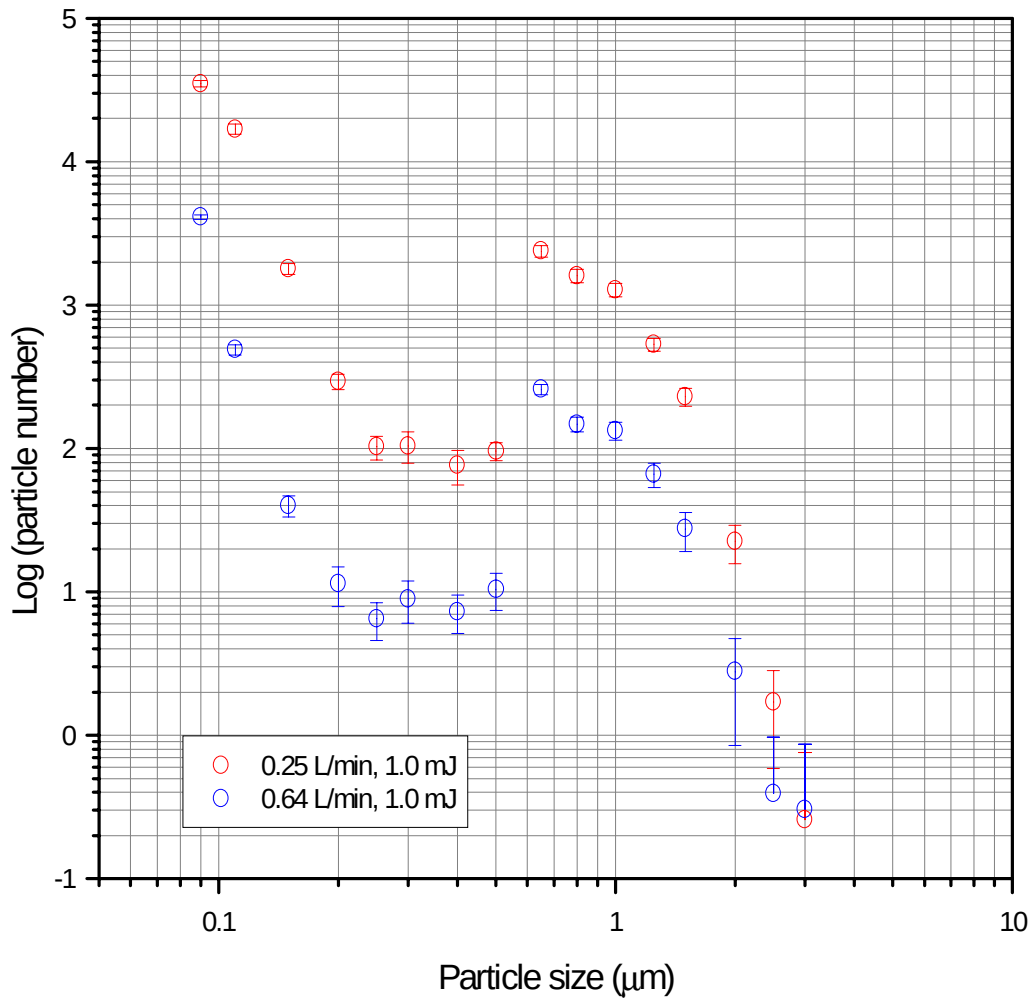


EFFECT OF PARTICLE INJECTION VELOCITY ON THE DISTANCE TO REACH TERMINAL VELOCITY



- **With an initial velocity on the order of 10^4 cm/s, all the particles below 5.0 μm diameter are entrained in the gas flow before reaching the chamber window**

SIZE DISTRIBUTION OF ABLATED COPPER PARTICLES VS. FLOW RATE

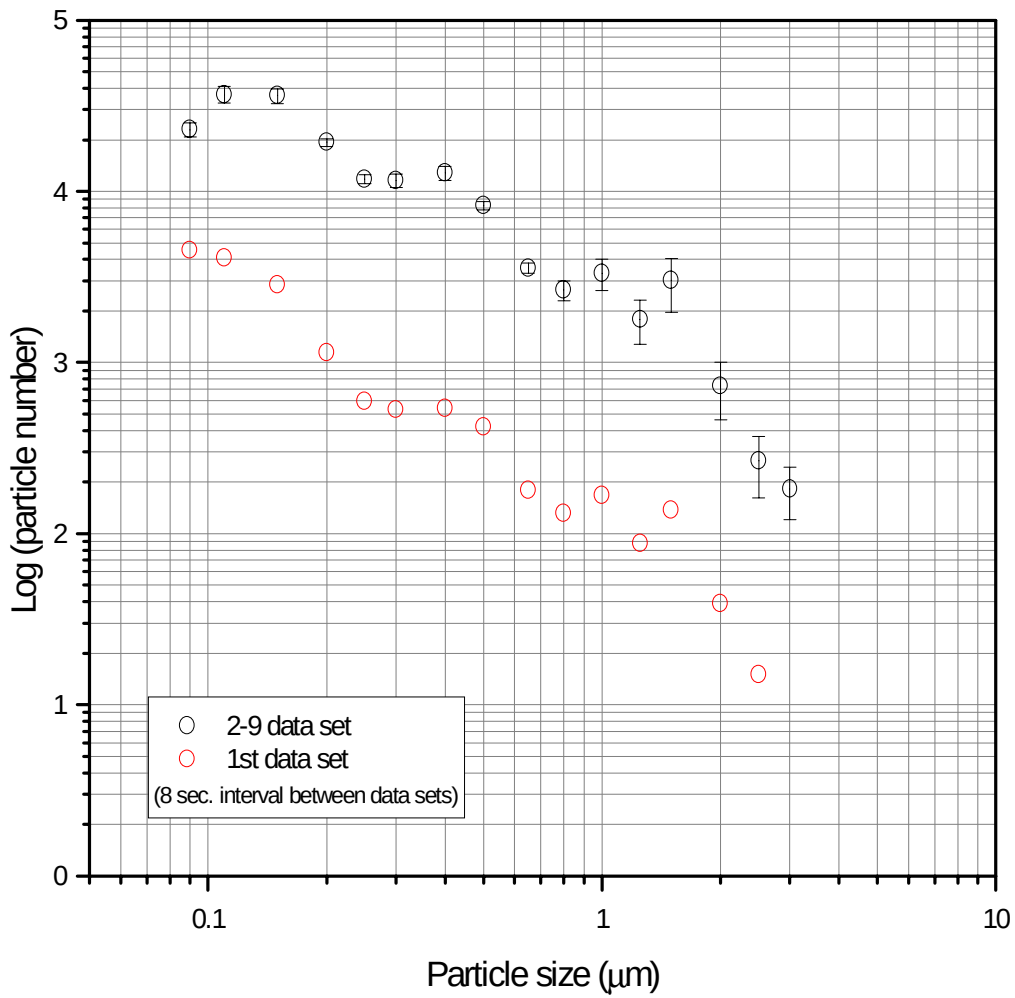


- **Unique bi-modal distribution**
- **For the same laser energy, increased particle transport was measured for lower flow rate**

Contradicts theory based on fluid dynamics

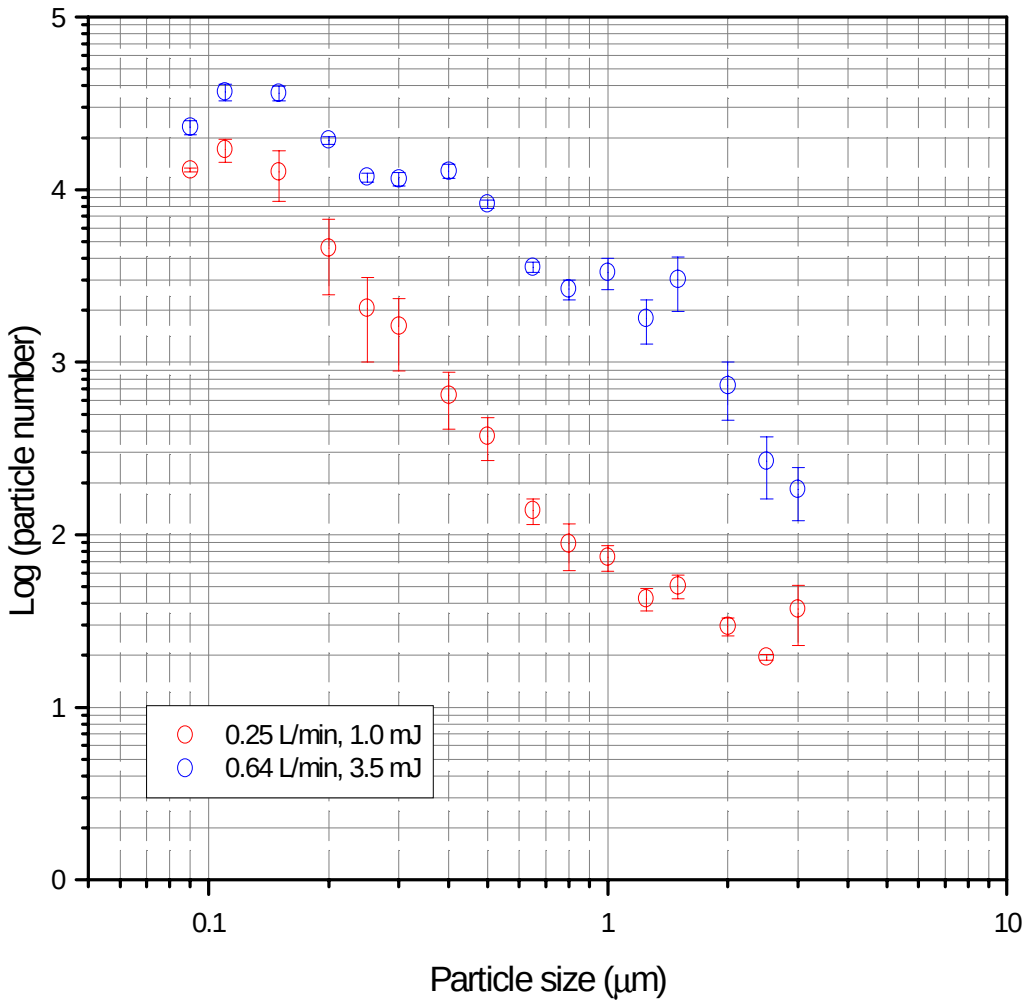
- Maybe due to entrainment and chamber effects

SIZE DISTRIBUTION OF GLASS PARTICLES DURING REPETITIVE ABLATION



- **The amount of ablated mass increased during crater formation**
- **Laser**
  λ=266 nm
  6 ns pulse
  3.5 mJ
  5 Hz

SIZE DISTRIBUTION OF ABLATED GLASS PARTICLES

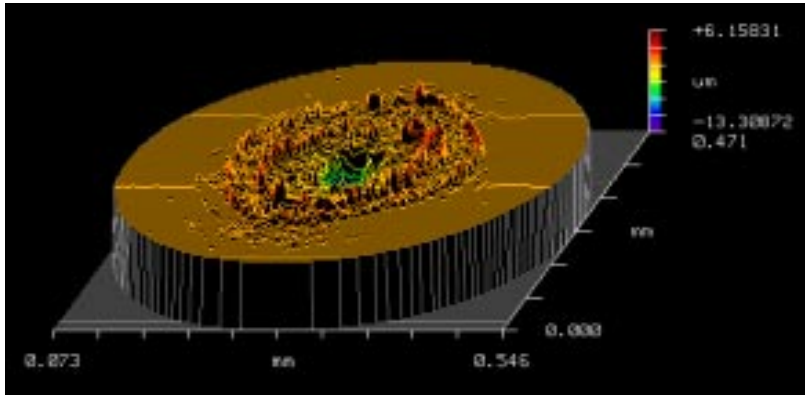


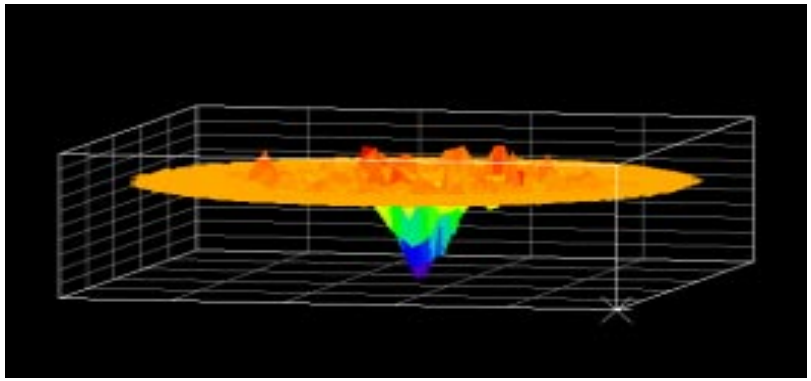
- For higher laser energy, the amount of ablated mass increased while the size distribution remains similar
- Similar to Cu ablation, number of particles decreased with increasd flow rate

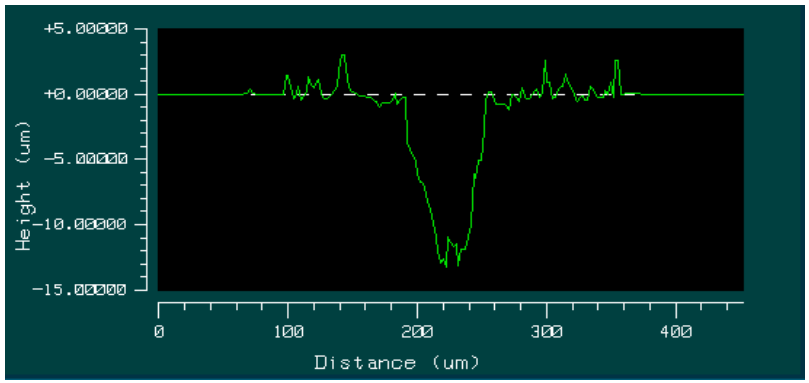
- Maybe due to entrainment and chamber effects

CRATER IN SAMPLE FROM SINGLE PULSE OF LASER ENERGY

- **Sample: Silicon**
- **Wavelength λ : 266 nm**
- **Pulse duration: 3ns**
- **Laser beam spot size: 50 μm**
- **Power density: 3.0×10^{11} W/cm^2**
- **Maximum depth: 13.3 μm**
- **Crater volume: 3.79×10^{-8} cm^3**
- **Mass removed: 90 ng/pulse**







Figures & volume measurements by Zygo NewView 200

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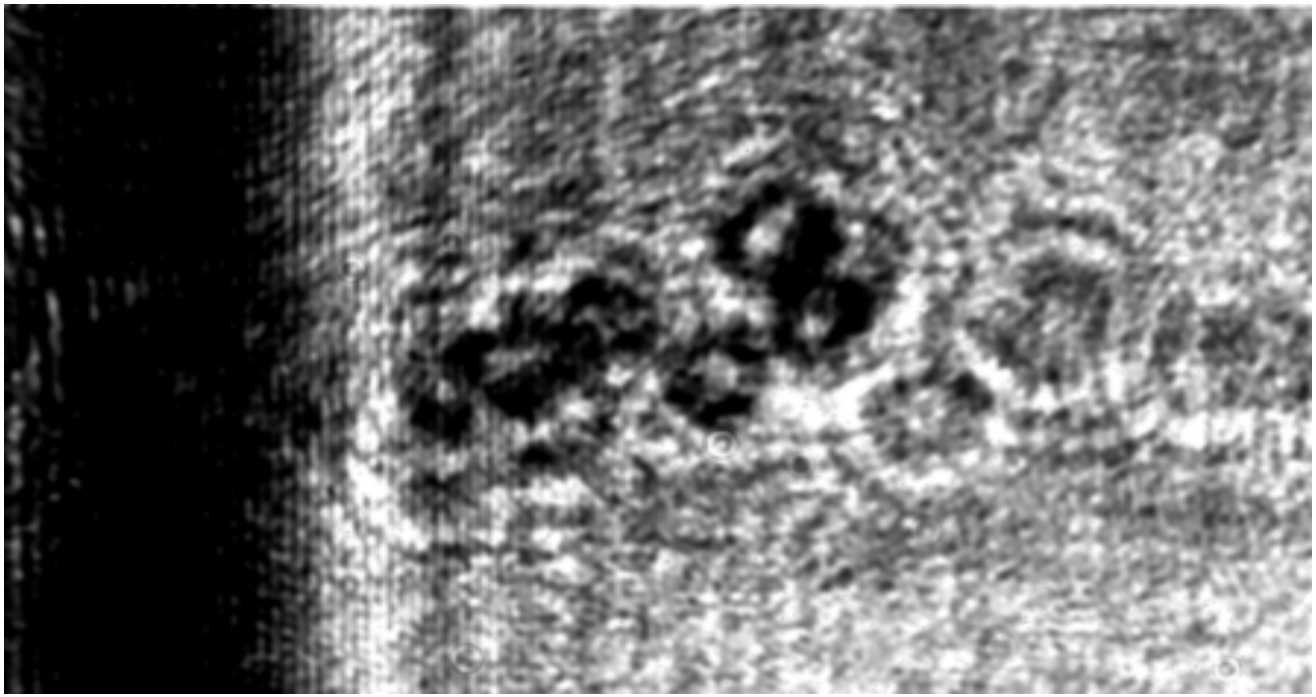
IMAGE OF EJECTED PARTICLES FOR SINGLE SHOT LASER ABLATION

Sample Surface



400 μm

-Sample: Silicon
-Wavelength: 266 nm
-Power density:
1.5X10^{11} W/cm^2
-Time delay: 9.6 μs
after laser pulse

Particles as large as 40 μm can be identified from the shadowgraphy image captured 9.6 μs after the laser pulse

Mass-loading effect in ICP

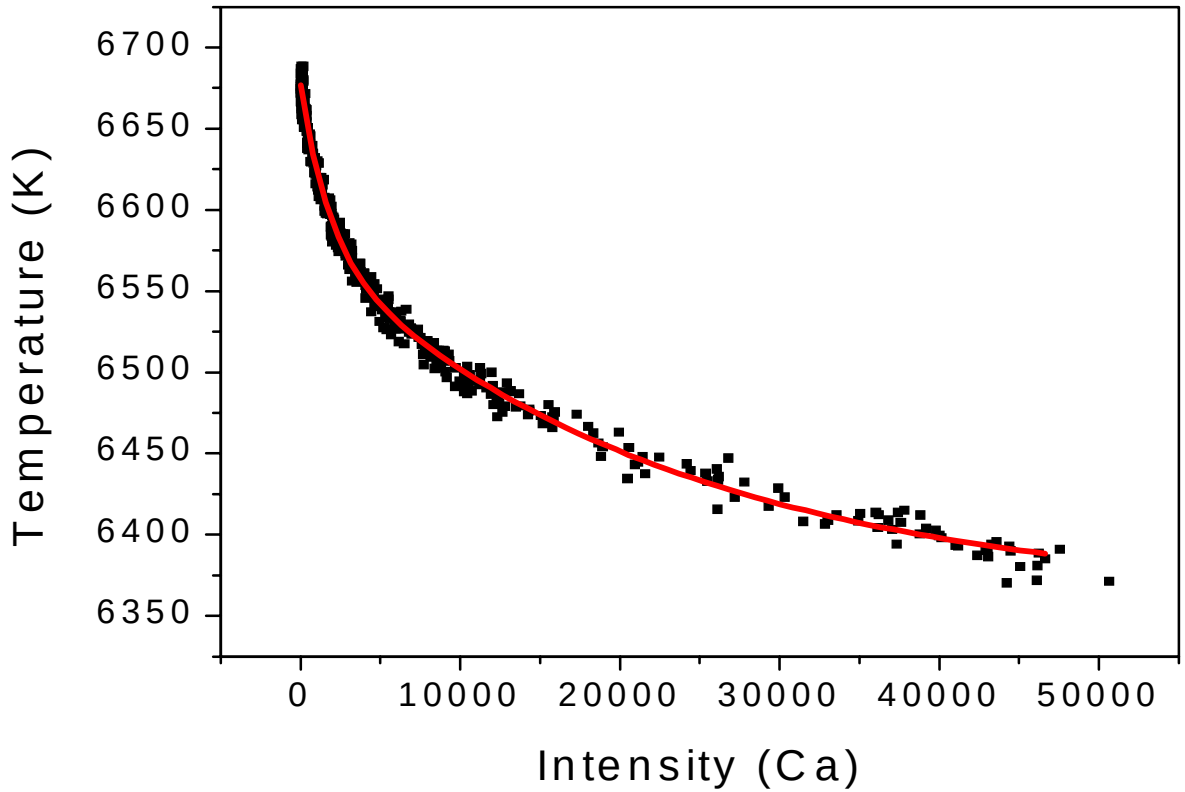
- Amount of ablated mass may influence ICP temperature and electron number density
- Intensity ratio is a function of temperature and electron number density in the ICP

$$\frac{I(ZnII)}{I(ZnI)} = \frac{4.83 \times 10^{15}}{n_e}\left(\frac{g_q A_{pq}}{\lambda_{pq}}\right)_{ZnII} \times \left(\frac{\lambda_{pq}}{g_q A_{pq}}\right)_{ZnI} T^{\frac{3}{2}} e^{-\frac{\left(E_i + E_q^+ - E_q\right)}{kT}}$$

- Zinc chosen because of its high ionization potential - very sensitive to changes in ICP conditions

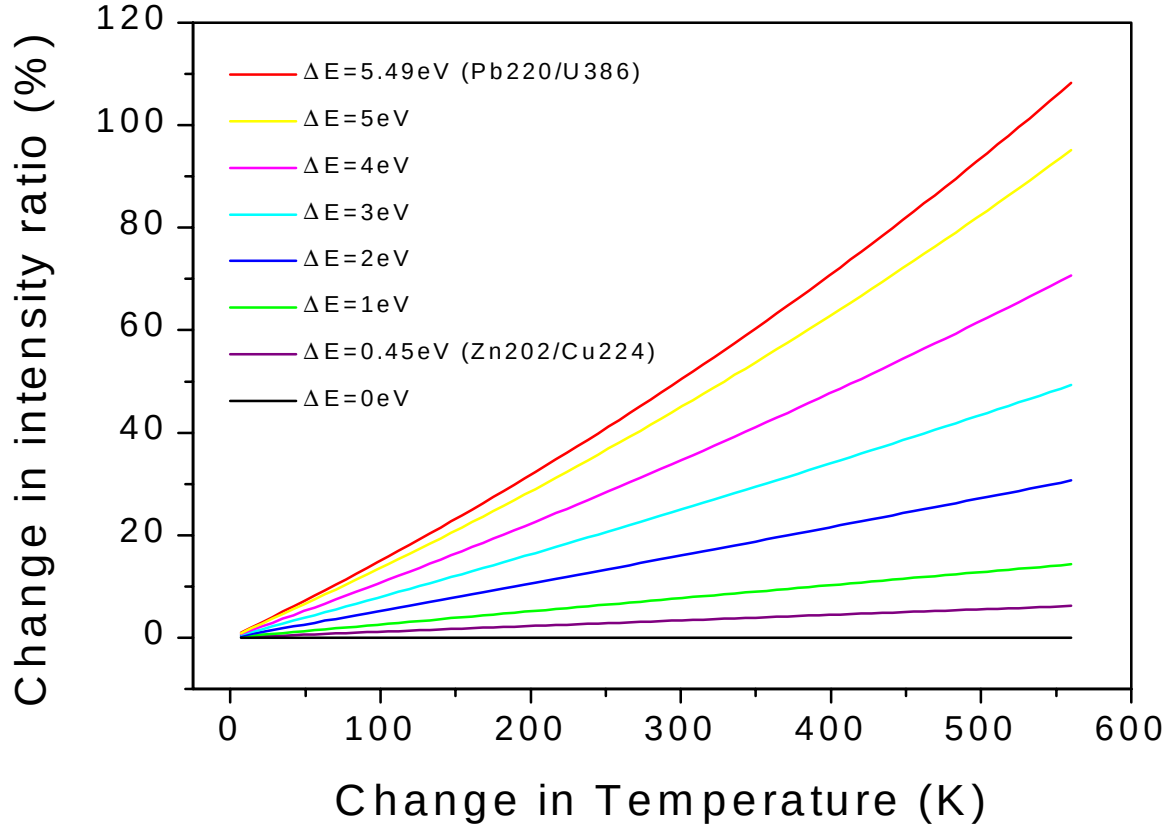
- Zinc ablated continuously in one ablation chamber
- Additional sample is ablated in separate ablation chamber
- Zinc and additional sample are simultaneously transported to the ICP - measure effect of additional sample on Zn ionic-to-atomic intensity ratio

ICP temperature during laser ablation of $CaCO_3$



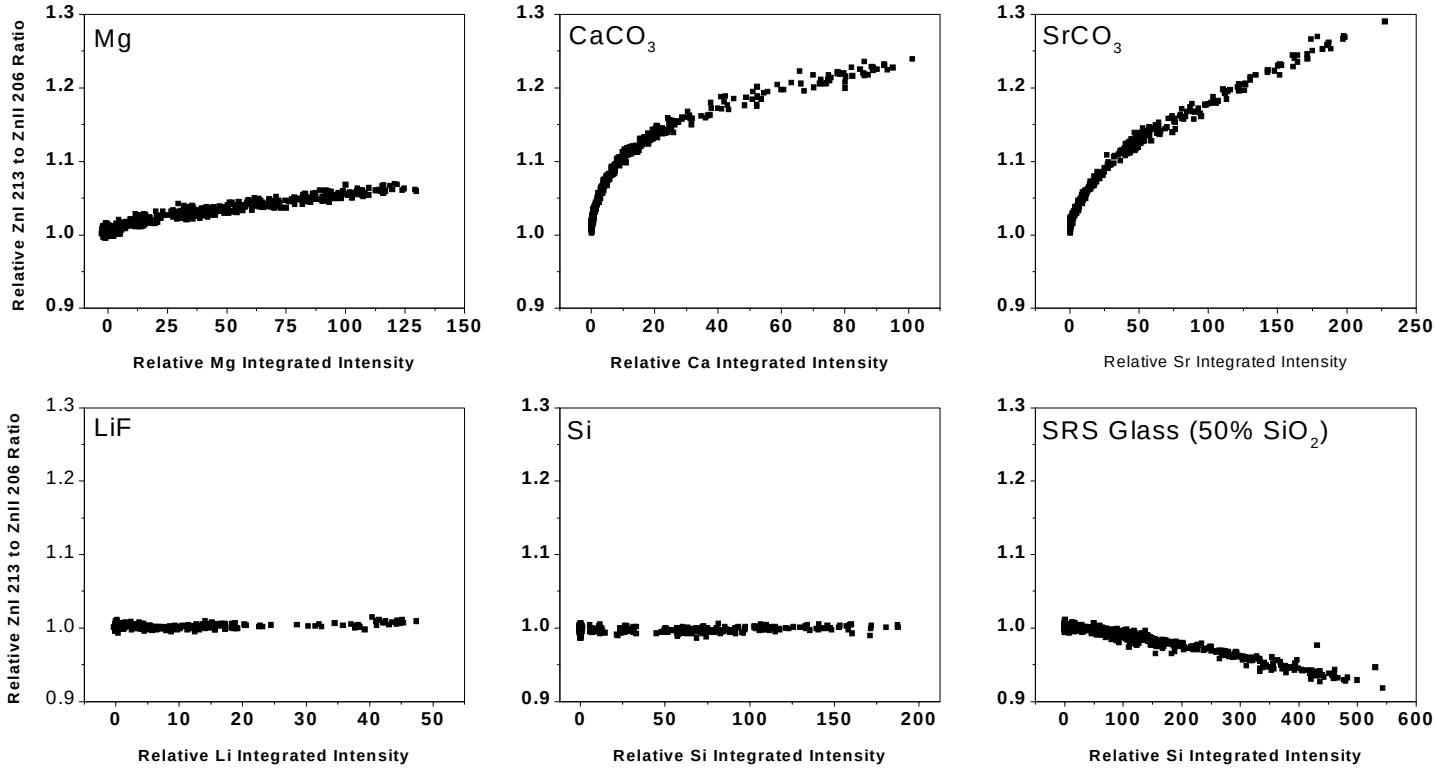
- Excitation temperature dropped about 300K during ablation of $CaCO_3$
- Temperature calculation is based on ZnI (213nm) to ZnII (206nm) ratio assuming LTE

Theoretical calculation for the effect of temperature change on ICP-AES intensity ratios



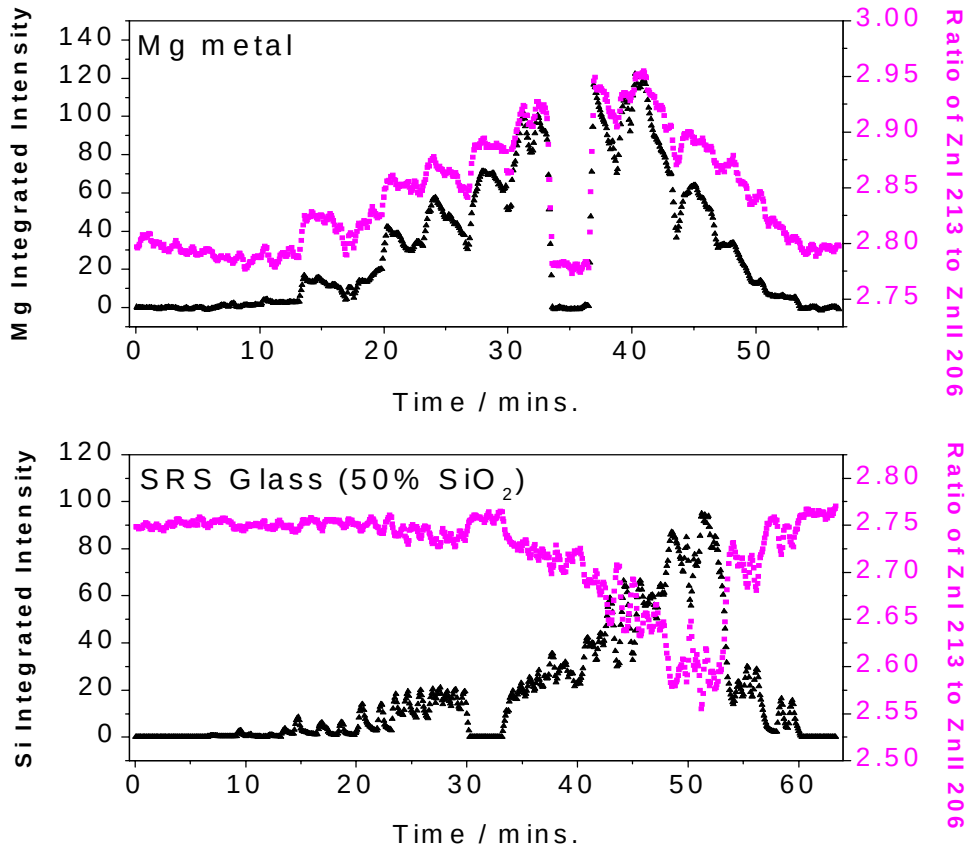
- Intensity ratio for two emission lines depends on ICP temperature and difference in their energy levels
- Change in temperature of ICP affects analytical accuracy !

Effect of sample on ICP conditions



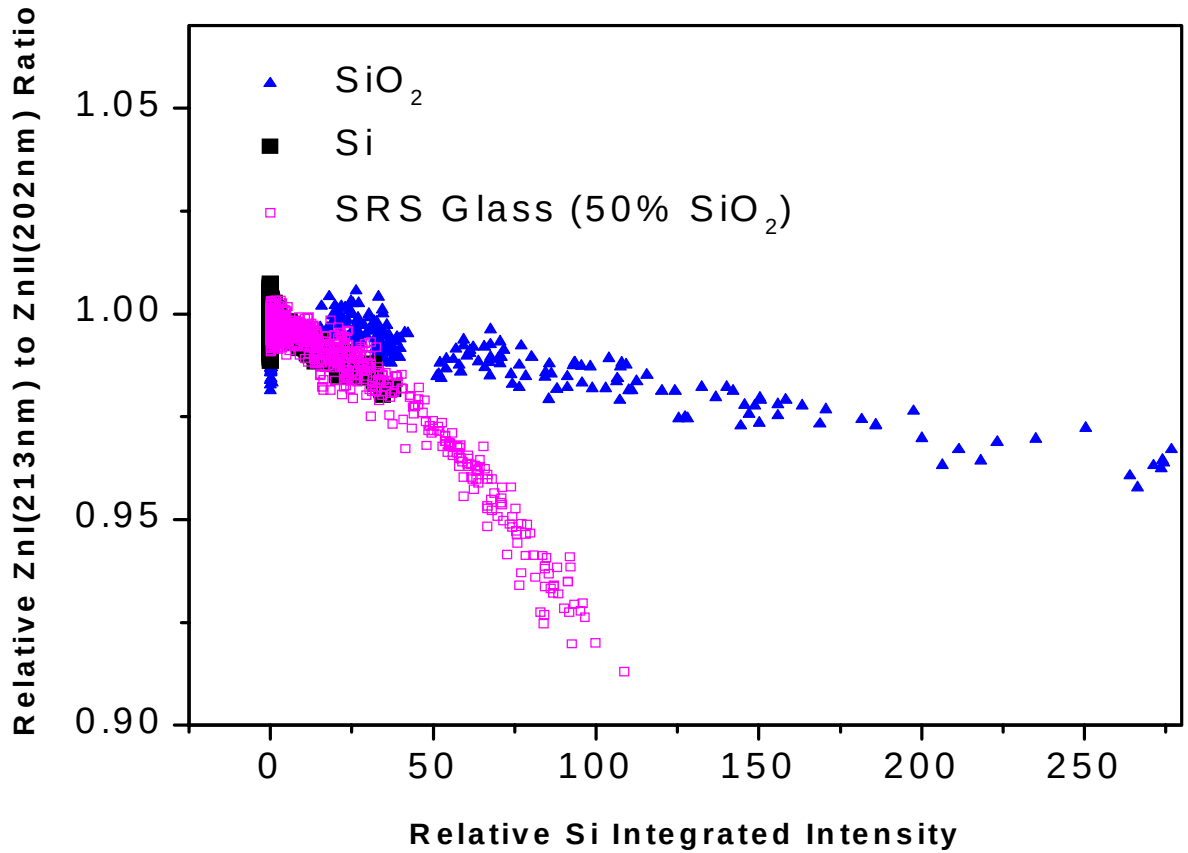
- The amount of each species in a sample <u>may</u> change the ICP conditions
- No general trend is observed (yet)
- Major composition of SRS Glass sample is : 50% SiO_2, 12% Fe_2O_3, 9% Na_2O, 4% Li_2O, 3% K_2O, 1% CaO, and others

Time profile of ICP conditions



- Ratio of ZnI (213nm) to ZnII (206nm) changes with amount of ablated mass
- Change in plasma conditions (temperature and/or electron number density) caused by the ablated mass

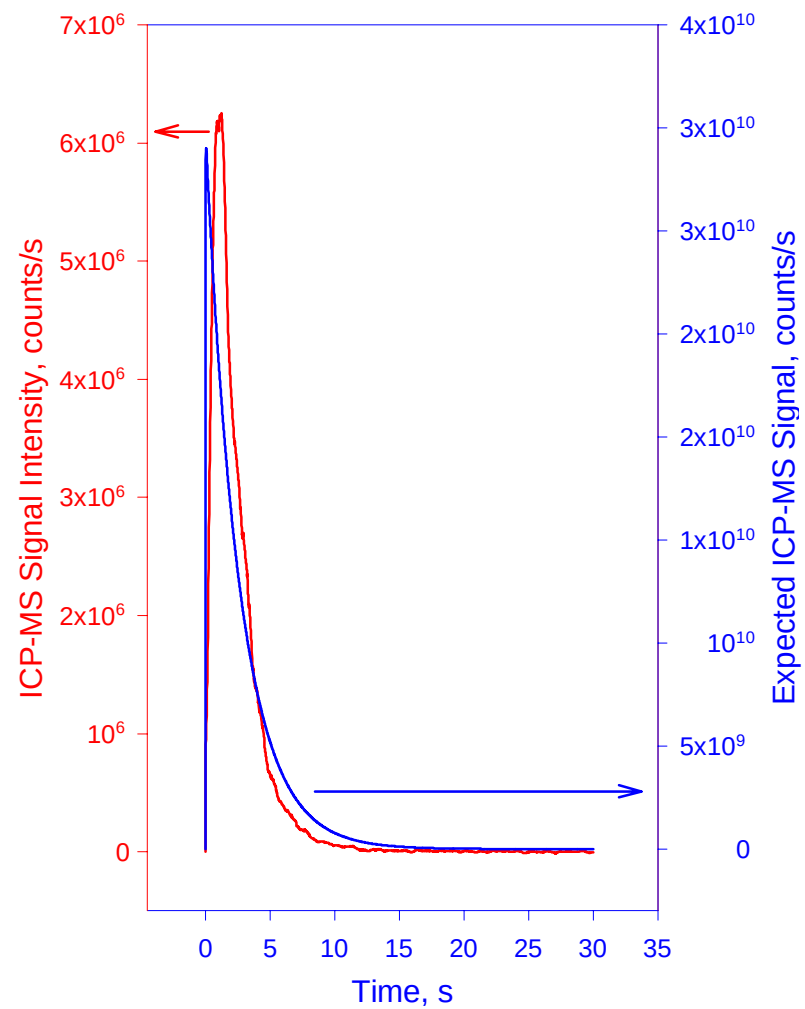
Effect of Si, SiO_2 and SRS Glass on ICP conditions



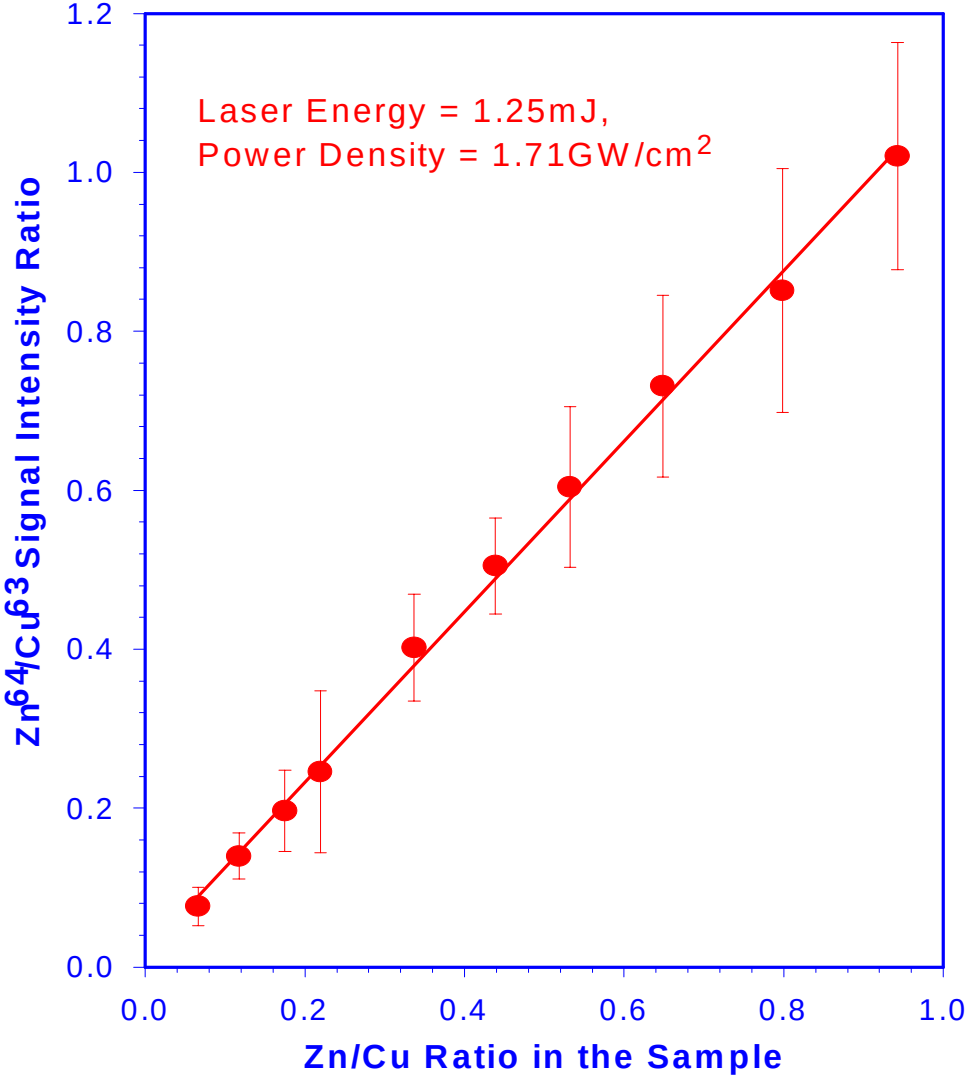
- The effect of pure silicon, quartz (pure SiO_2) and SRS Glass sample (50% SiO_2) on ICP conditions is different
- Decreasing ratio for glass sample is not caused by Si or SiO_2 alone

LA-ICP-MS Efficiency

- ICP-MS Detection Efficiency Estimation:
  - 1 count per $7*10^4$ ions entering the torch
- Laser Ablation of Silicon; Single Shot:
  - 100 ng of mass per pulse are sampled
  - corresponds to $2*10^{15}$ silicon atoms
- ICP-MS Detected $2*10^6$ Ions.
- Assuming Low Ion Transmission in ICP-MS:
  - $2*10^6$ counts are produced by $2*10^{11}$ ions
- Transport Efficiency of Ablated Mass:
  - Out of $2*10^{15}$ atoms sampled, signal equivalent to $2*10^{11}$ atoms was detected
  - Out of **100 ng** of laser sampled mass, only **10 pg** reached the ICP
- Transport Efficiency of Ablated Mass is **0.01%**



Calibration Curves for Brass Samples



- Good standards are required
- Concentration of an internal standard must be known
- Accuracy and precision depend on laser ablation parameters:

Calibration Curves:

$log\left(\frac{Zn^{64}}{Cu^{63}}\right)$ Intensity Ratio *vs.* $log\left(\frac{Zn}{Cu}\right)$ wt. % Ratio.

Power Density, GW/cm^2	Intercept	Slope	Correlation Coefficient
0.041	0.92	1.43	0.958
0.27	1.18	1.52	0.963
1.71	$4 * 10^{-3}$	1.03	0.998

- Higher laser power density provides more accurate calibration

ICP-MS Tuning: Laser Ablation *vs.* Liquid Nebulization

Wet *vs.* Dry ICP Plasma:

- Temperature
- Electron number density

↓

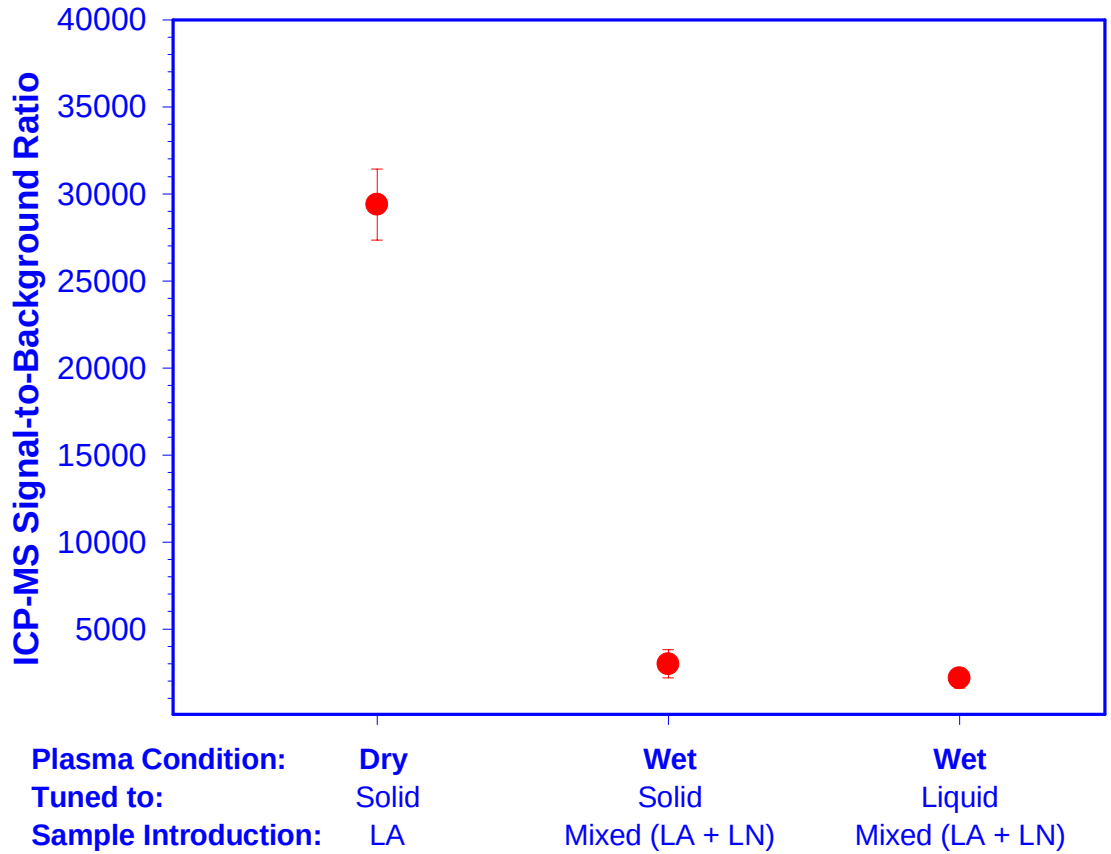
- Ionization efficiency
- Ion kinetic energy

↓

- Sampling efficiency
- Ion transmission efficiency

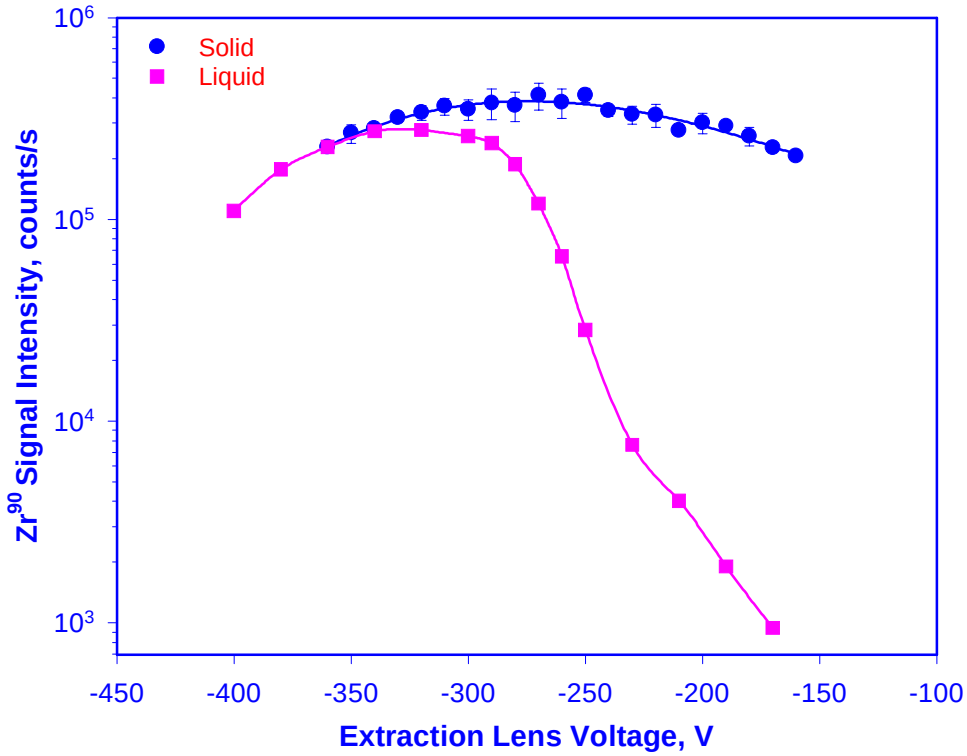
↓

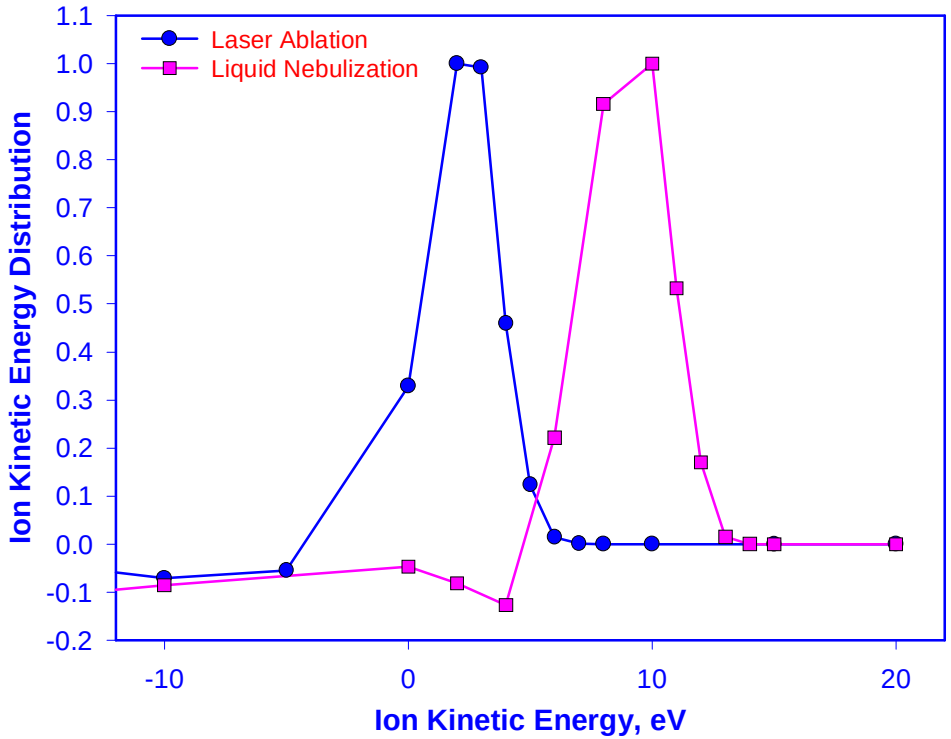
- ICP-MS optimization



- ICP plasma conditions influence optimization and performance
- Dry ICP plasma offers higher signal-to-background ratios due to lower background levels
- Dry plasma is characterized with fewer interferences from polyatomics

ICP-MS Optimization: Laser Ablation *vs.* Liquid Nebulization





- Careful ion-optics tuning is required when plasma conditions change
  - Preliminary measurements indicate higher ion energies in wet ICP
- Different ion kinetic energy distributions are characteristic for dry and wet plasmas
- Ion kinetic energy determines ion optics performance

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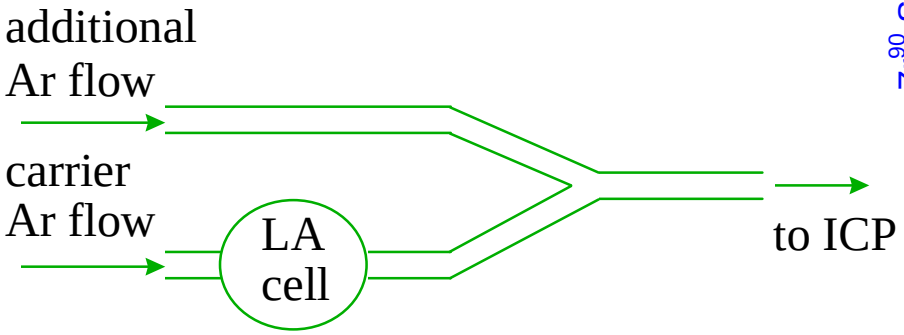
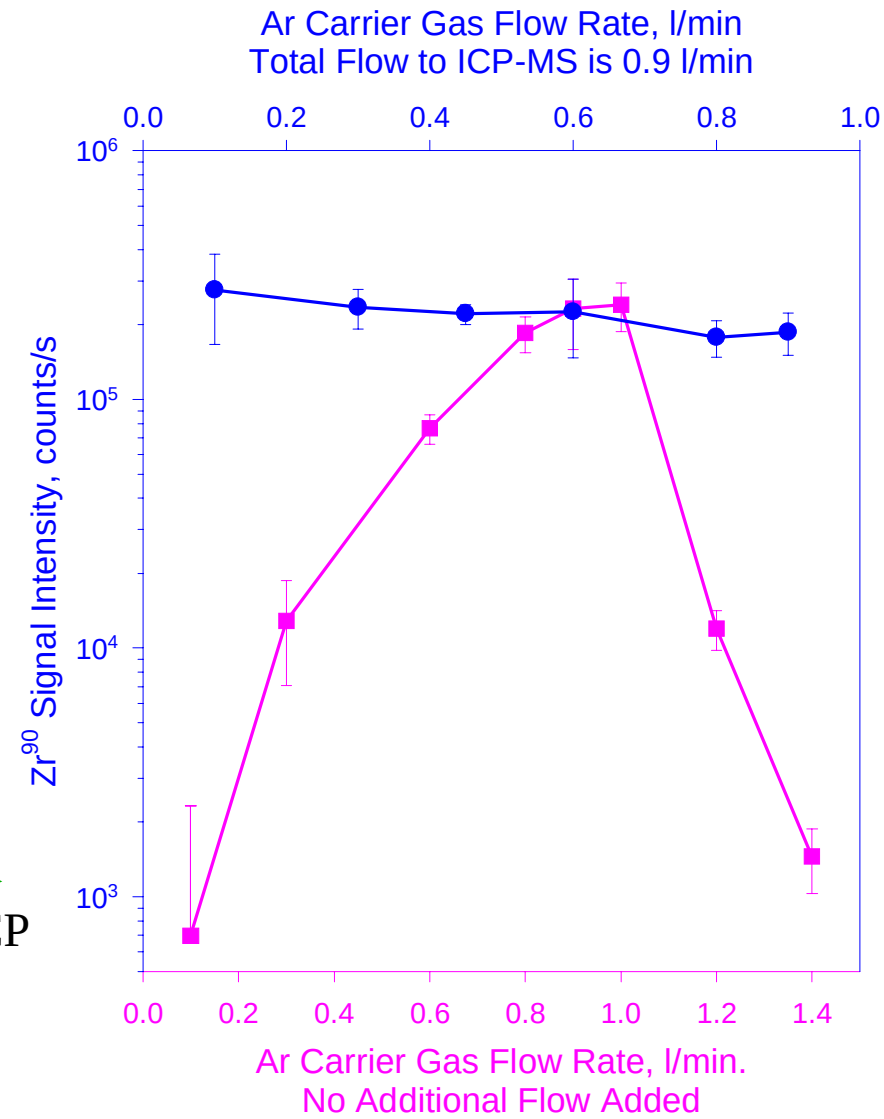
ICP-MS Ar Carrier Gas Flow Optimization

- Flow Optimization
  - ICP-MS sensitivity
  - Transport efficiently
  - 0.9 l/min total flow rate provides optimum performance
  - 0.1 l/min flow is sufficient to carry ablated material from ablation chamber to ICP





ICP-MS Semi-Quantitative Analysis of Savannah River Site Prototypic Glasses (Mg as an Internal Standard).

Element, %	168AV		200AL		202G	
	Corning	LBNL	Corning	LBNL	Corning	LBNL
Al	2.95	2.51	7.09	5.70	2.79	2.34
Ba	____	0.012	____	0.0050	0.18	0.13
Ca	0.49	0.63	0.39	0.55	1.01	1.28
Cr	____	0.0014	____	0.0026	0.075	0.091
Cs	____	____	____	____	0.085	0.054
Cu	____	0.0006	____	0.0012	0.33	0.34
Fe	7.83	9.19	3.12	3.85	9.49	9.87
K	____	0.081	2.59	2.87	3.04	3.24
Li	1.97	1.52	1.23	1.08	2.00	1.68
Mn	2.04	2.72	1.93	3.09	1.29	1.46
Na	7.49	6.97	7.86	7.98	6.94	7.70
Ni	0.80	0.70	0.48	0.49	0.68	0.62
Si	24.1	27.79	22.6	23.81	23.2	25.6
Ti	____	0.034	1.02	1.11	0.37	0.38
Zr	0.51	0.52	0.021	0.013	____	0.0070

- Semi-quantitative analysis possible because concentration of one element (internal standard) known
- ICP-MS response curve was generated using 10 ppb multi-element standard during mixed sample introduction (LA and LN)

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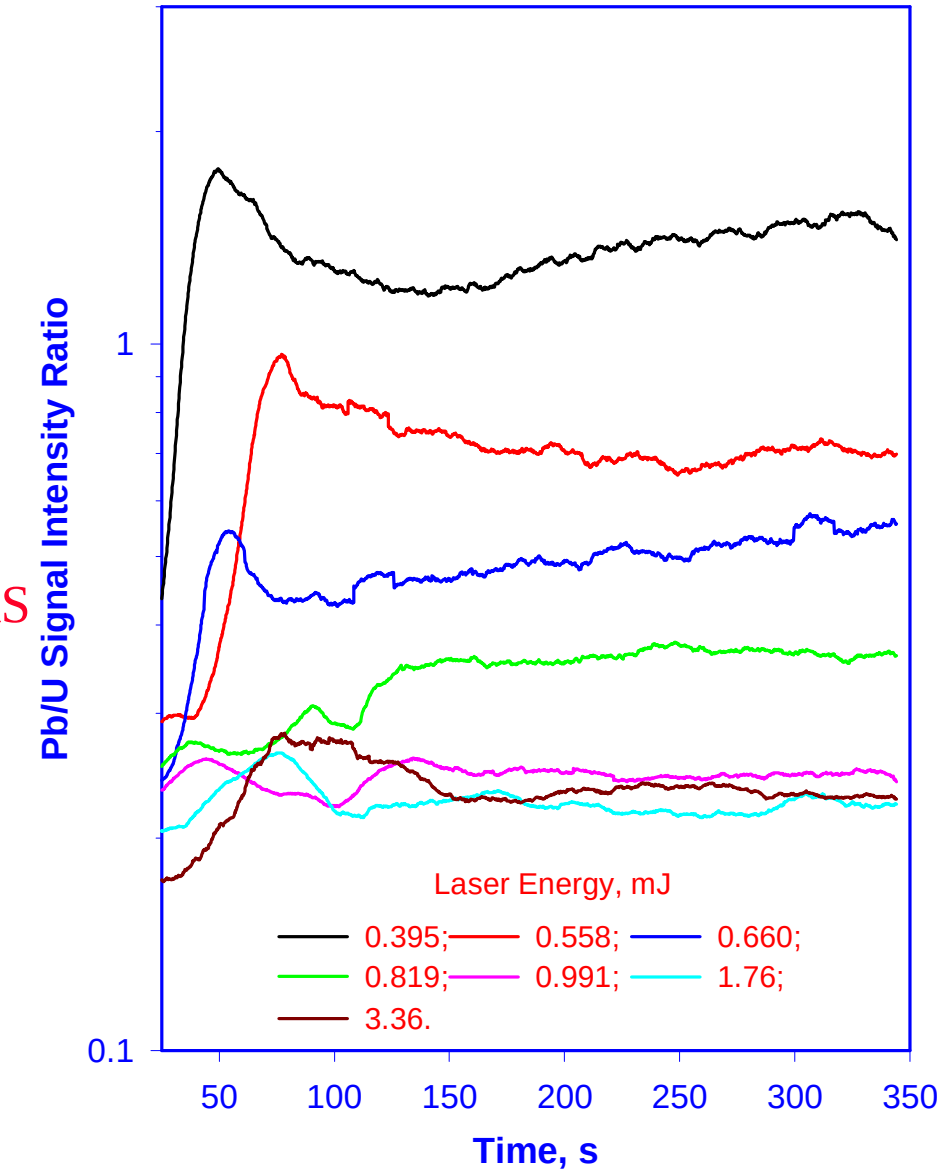
Effect of Laser Energy on Pb/U Ratio During Ablation of SRS Glass Sample

- Time-Resolved ICP-MS Measurements:
  - Time-dependent changes in laser ablation:
    - » **Stiochiometry**
    - » **Ablated mass**
  - Fractionation changes due to:
    - » **Laser ablation**
    - » **During transport**
    - » **ICP mass loading**
- Pb/U Ratio During Laser Ablation of SRS 168AV
  - Low Laser Energy:
    - » **Ratio depends on energy**
  - High Laser Energy:
    - » **More stable with time**
    - » **Relatively independent of laser energy**



Summary

Laser ablation (LA) is an advanced sampling technology viable for characterization needs within the DOE EM program.

Research endeavors to understand, develop, and improve LA sampling as an accurate and sensitive analytical technology for rapid, safe, and cost effective characterization of DOE EM wastes.

LA issues addressed are important because of the nature of EM waste samples: samples are unique - no standards!

- **Accurate characterization:**
  - » **semiquantitative analysis when calibrate to liquids and known internal standard (SRS prototypic glass samples)**
  - » **concentration of constituent can change ICP performance**
  - » **fractionation may exist during transport and in ICP - particle size dependence**
- **Sensitivite characterization:**
  - » **ablated mass not efficiently transported to ICP (10^{-4})**
  - » **understand and optimize ICP/MS conditions for LA sample introduction**

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Continued Efforts

Continue studies to understand and develop laser ablation for accurate and sensitive characterization of EM waste samples.

- **Transport studies to improve sampling**
  - **model of transport**
  - **new chamber design based on enhanced transport**
  - **chemistry of particles**
  - **gases (thermal conductivity)**
- **ICP studies to improve accuracy**
  - **mass loading**
  - **temperature**
  - **electron number density**
  - **EIE (easily ionizable energy)**
- **MS studies to improve sensitivity**
  - **throughput efficiency for dry conditions**
  - **ion optics related to energies**
  - **space charge**

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EMSP Publications and Interactions

- 8 Publications
- 3 Refereed Proceedings
- 6 Presentations (3 Invited)
- 2 PhD Students
- 1 Post Doc
- Visiting Scientists:
  - Univ of Caracus, Venezuela
  - Univ of Hong Kong, Hong Kong
  - Guangzhou Institute of Geochemistry, China
- Collaborations/Interactions:
  - Universities
    - » UC Berkeley, U. of Illinois, WSU, HKU
  - National Labs
    - » PNNL, ANL (West), LANL, SRS

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Scientific Reporting

PUBLICATIONS:

Optimization Conditions for ICP/MS Laser-ablated Mass Sampling: Relevance to Ion Energies, O.V. Borisov, X.L. Mao, and R.E. Russo, *to Appl. Spectrosc., August 1998.*

Laser Ablation ICP/MS calibration based on binary Cu/Zn alloy standards, O.V. Borisov, X.L. Mao, and R.E. Russo, *submitted to Spectrochimica Acta B, July 1998.*

Effects of Gas Atmosphere on Laser Ablation Sampling and ICP-AES, A.P.K. Leung, W.T. Chan, X.L. Mao, and R.E. Russo, *accepted in Analytical Chemistry, July 1998*.

Particle Size Distribution and Transport Effects during Laser Ablation Sampling into an ICP/MS, S.H. Jeong, J. Yoo, X.L. Mao, and R.E. Russo, *submitted to J. Analy. Atom. Spectrom. June 1998.*

Laser Ablation Sampling, R.E. Russo, X.L. Mao, and O.V. Borisov, *accepted in Trends in Analytical Chemistry, April 1998.* **(Invited Paper)**

Time Resolved Parametric Studies of Laser Ablation Using ICP-AES, O.V. Borisov, X.L. Mao, A.C. Ciocan, and R.E. Russo, *Applied Surface Science* ***129****, 315 (1998).*

Optical Emission Spectroscopy of the Influence of Laser Ablated Mass on Dry Inductively Coupled Plasma Conditions, A.C. Ciocan, X.L. Mao, O.V. Borisov, and R.E. Russo, *Spectrochimica Acta,* ***53B****, 463 (1998).*

Effects of Gas Environment on Pico-Second Laser Ablation, W.T. Chan, A.P.K. Leung, X.L. Mao, and R.E. Russo, *Applied Surface Science* ***129****, 269 (1998).*

PROCEEDINGS:

Effects of Gas Atmosphere on Pico-Second Laser Ablation Sampling for ICP-AES, W.T. Chan, A.P.K. Leung, X.L. Mao, and R.E. Russo, *proceedings of the Fourth International Conference on Laser Ablation (COLA 97), July 1997, Asilomar CA.*

Time Resolved Parametric Studies of Laser Ablation of Brass Using ICP-AES, X.L. Mao, A.C. Ciocan, O.V. Borisov, and R.E. Russo, *COLA proceedings, July 1997, Asilomar CA.*

Optical Emission Spectroscopy Studies of the Influence of Ablated Material on Dry Inductively Coupled Plasma Conditions, A.C. Ciocan, X.L. Mao, O.V. Borisov, and R.E. Russo, *COLA proceedings, July 1997, Asilomar CA.*

PRESENTATIONS:

Laser Ablation Solid Sample Chemical Analysis: Dream or Reality, R.E. Russo, X.L. Mao, A.C. Ciocan, and B.V. Borisov, *Twenty-Fourth Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, (FACSS), October 1997, Providence, RI* **(Invited).**

Effect of Gas Medium on Laser Ablation Sampling for ICP-AES, W.-T. Chan, A.P.K. Leung, X.L. Mao, and R.E. Russo, *Twenty-Fourth Annual FACSS meeting, October 1997, Providence, RI.*

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