Advanced Laser Cleaning Techniques for Structural Materials:

Part I - Laser Induced Radionuclide Re-distribution on Porous Structural Materials

Part II - Laser Cleaning and Decontamination of Organic Contaminated Structural Materials

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INL

Part I - Laser Induced Radionuclide Re-distribution on Porous Structural Materials

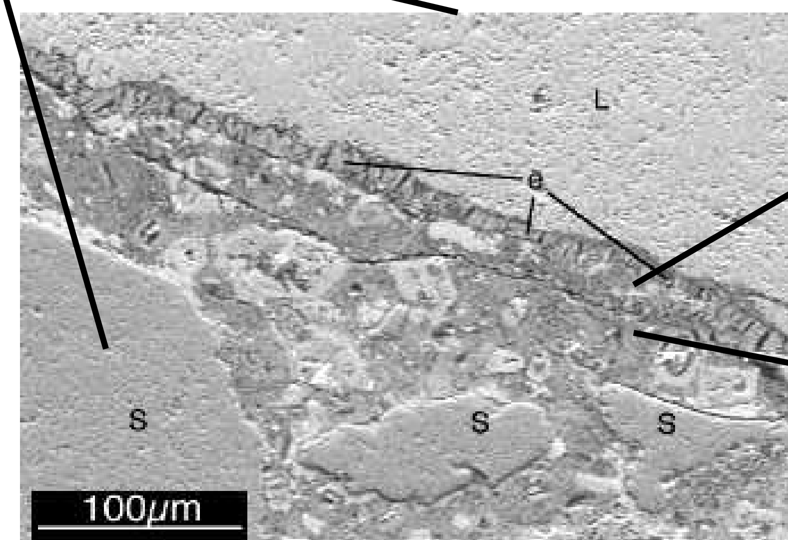
The Problem: Radionuclide Penetration into the Subsurface of Porous Solid Materials

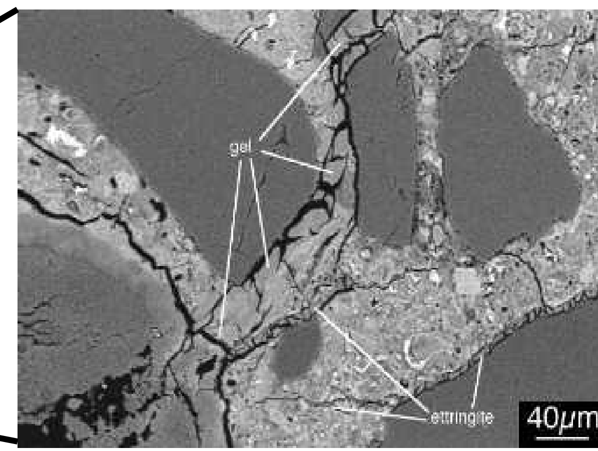
Concrete

Porous solids contain numerous air voids and cracks allowing for penetration of water and radionuclides.

<u>Depth Profile of Aqueous Spikes of CsCl</u>

Concrete	~ 1 – 20 µm
Granite	~ 1 – 200 nm
Marble	~ 1 – 50 nm

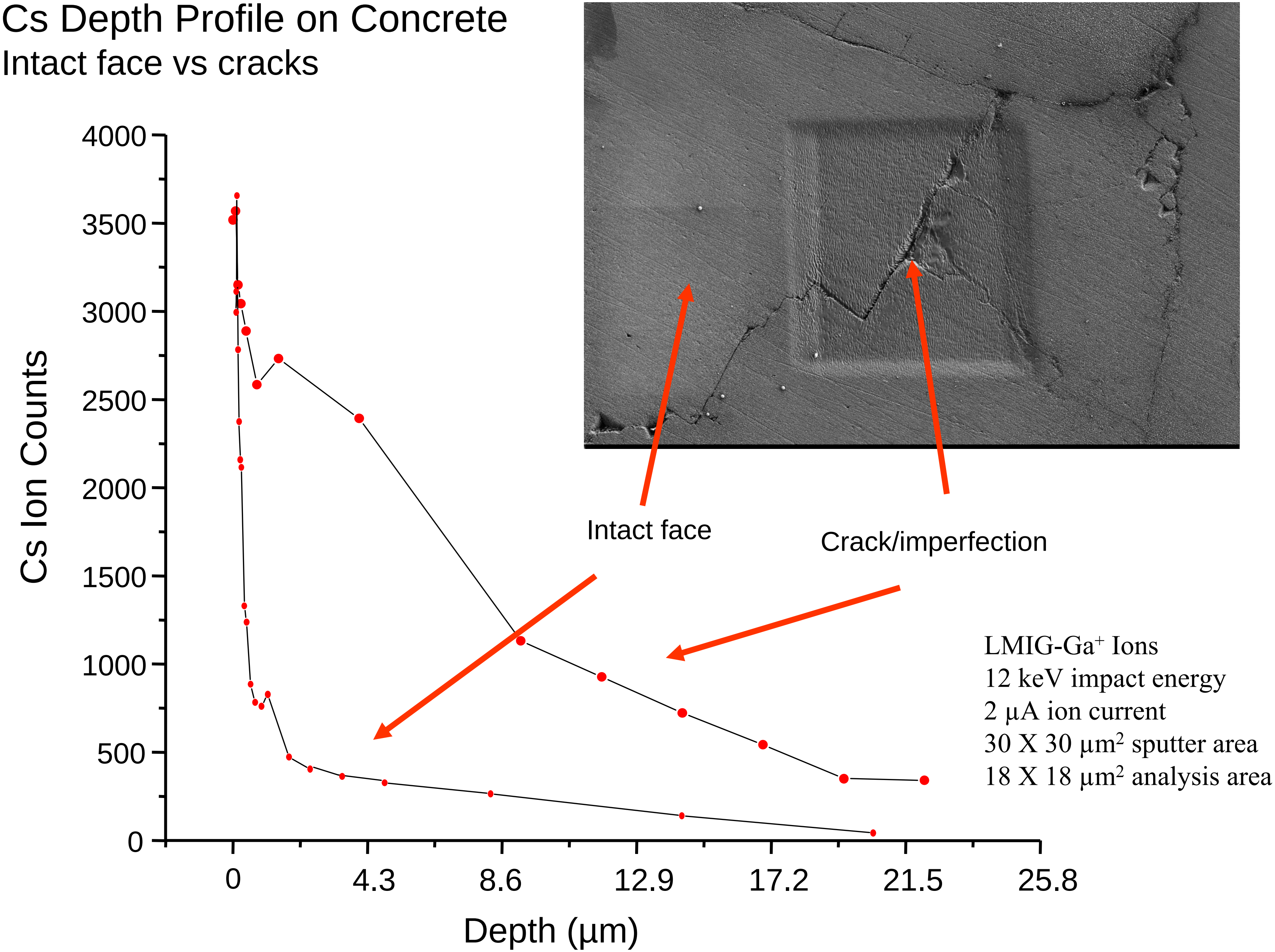




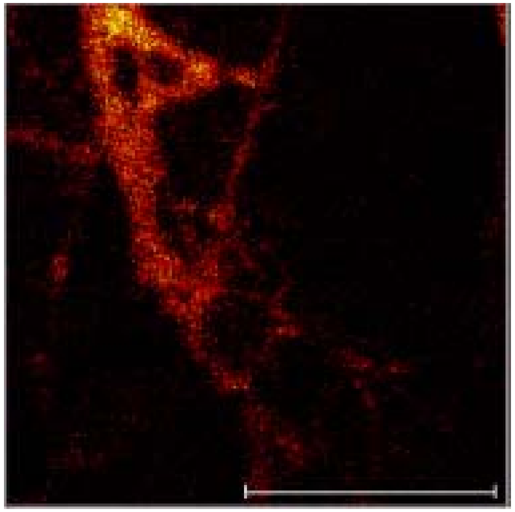
http://www.whd.co.uk/Concrete/concretebysem.html

http://ciks.cbt.nist.gov/~garbocz/nistir6399/node24.htm

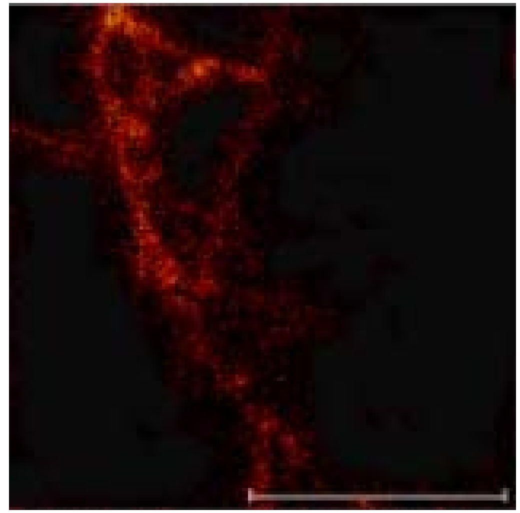
Cs Depth Profile on Concrete
Intact face vs cracks



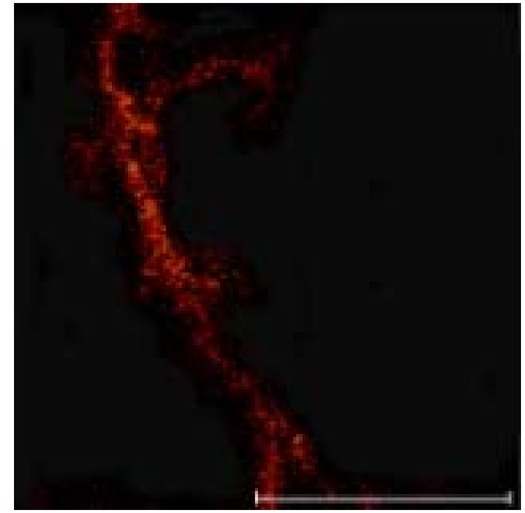
Cs Depth Profile into Concrete Surface Crack



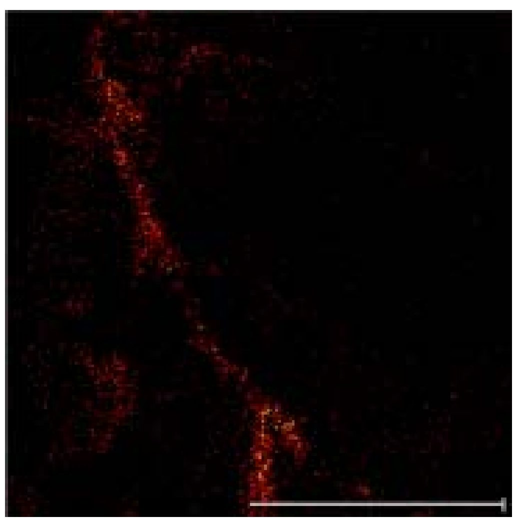
72 nm



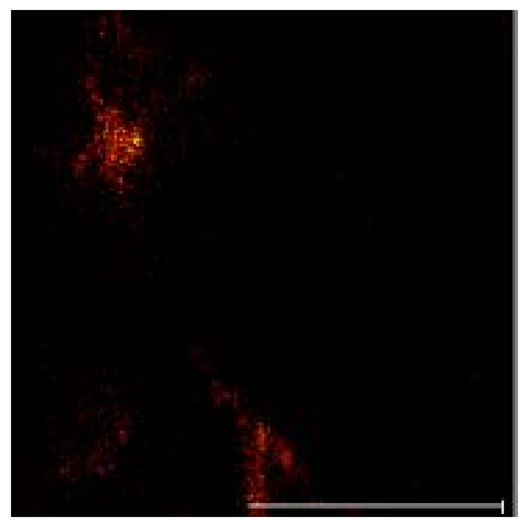
720 nm



1.44 µm

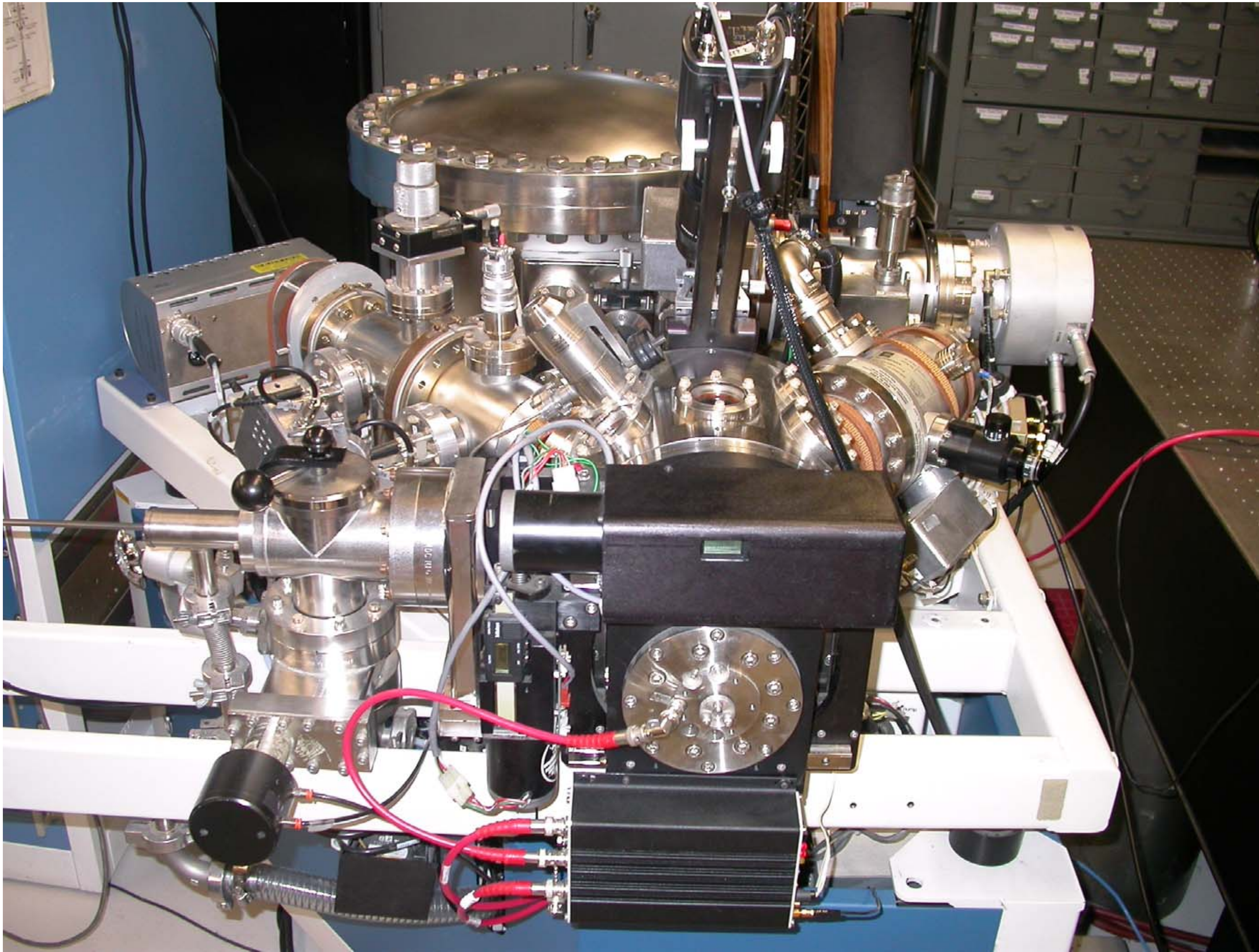


2.16 µm



2.448 µm

ToF-SIMS at MSU ICAL



Consequence: Incomplete Decontamination of Porous Solid Structural Materials

Material	Treatment		Radionuclide Activity (µCi Cs-137) Pre-Treatment	Post-Treatment	% Decontamination
Concrete	24 hr. soak in Radiac Wash	Block #1	67.2	45.9	31.7
		Block #2	5.0	4.4	12.2
		Block #3	1.45	0.821	43.4
Granite	24 hr. soak in Radiac Wash	Block #1	54.4	34.3	36.9
		Block #2	4.2	1.9	54.2
		Block #3	1.5	0.936	37.6
Marble	24 hr. soak in Radiac Wash	Block #1	53.4	18.4	65.5
		Block #2	3.9	0.3	92.6
		Block #3	1.24	0.1034	91.7

Factors Controlling The Rate of Radionuclide Decontamination from Porous Solid Media:

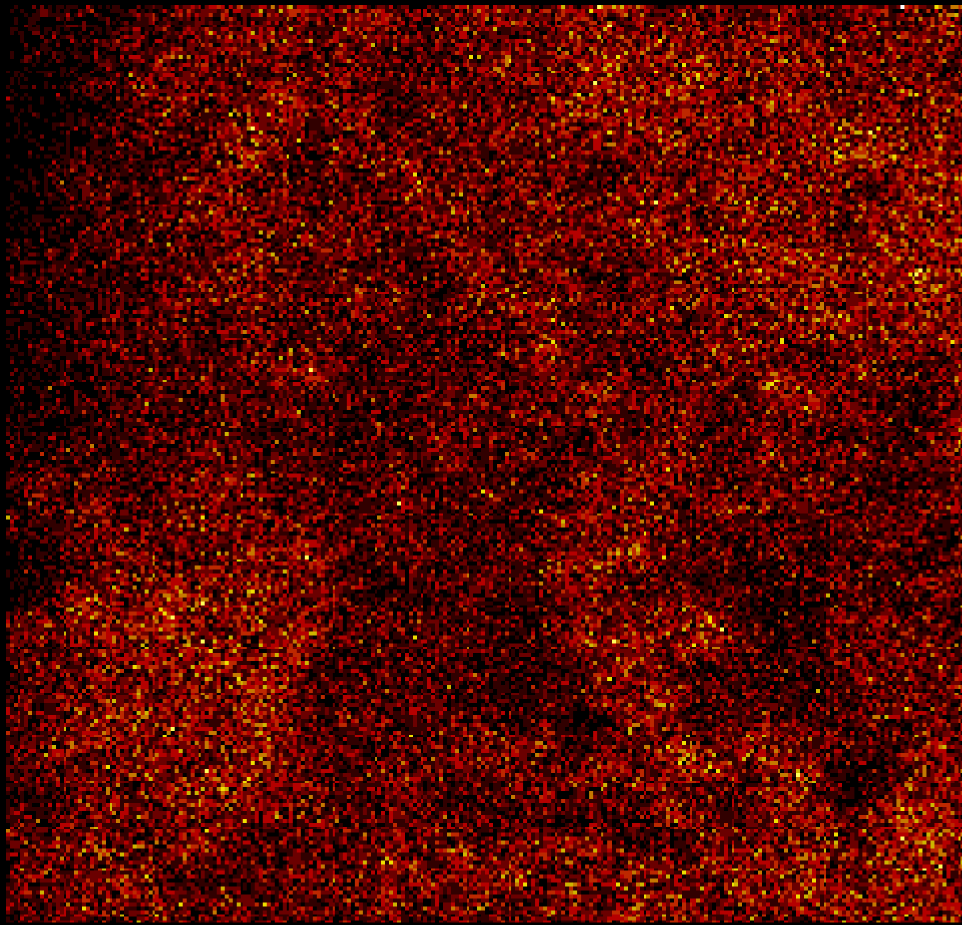
-Hydraulic Conductivity: The rate at which water moves through saturated, porous solids.

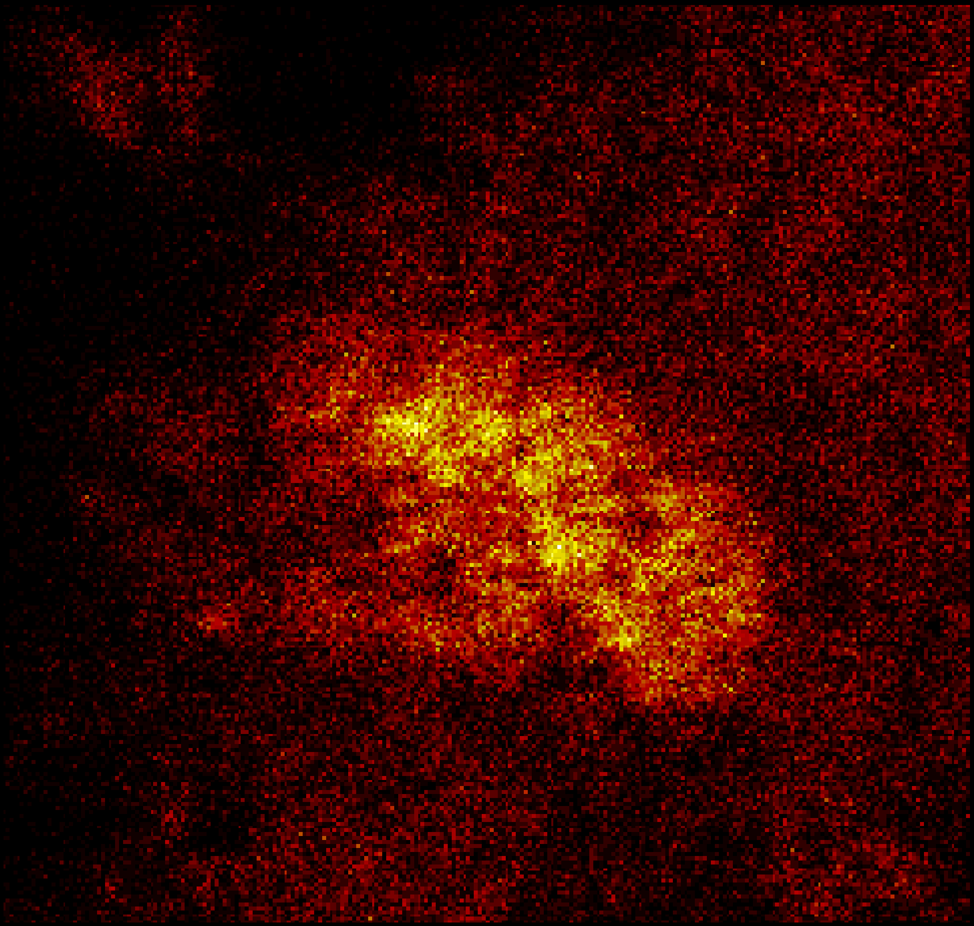
-Imbibition: The "ability" of the porous solid to absorb and adsorb water

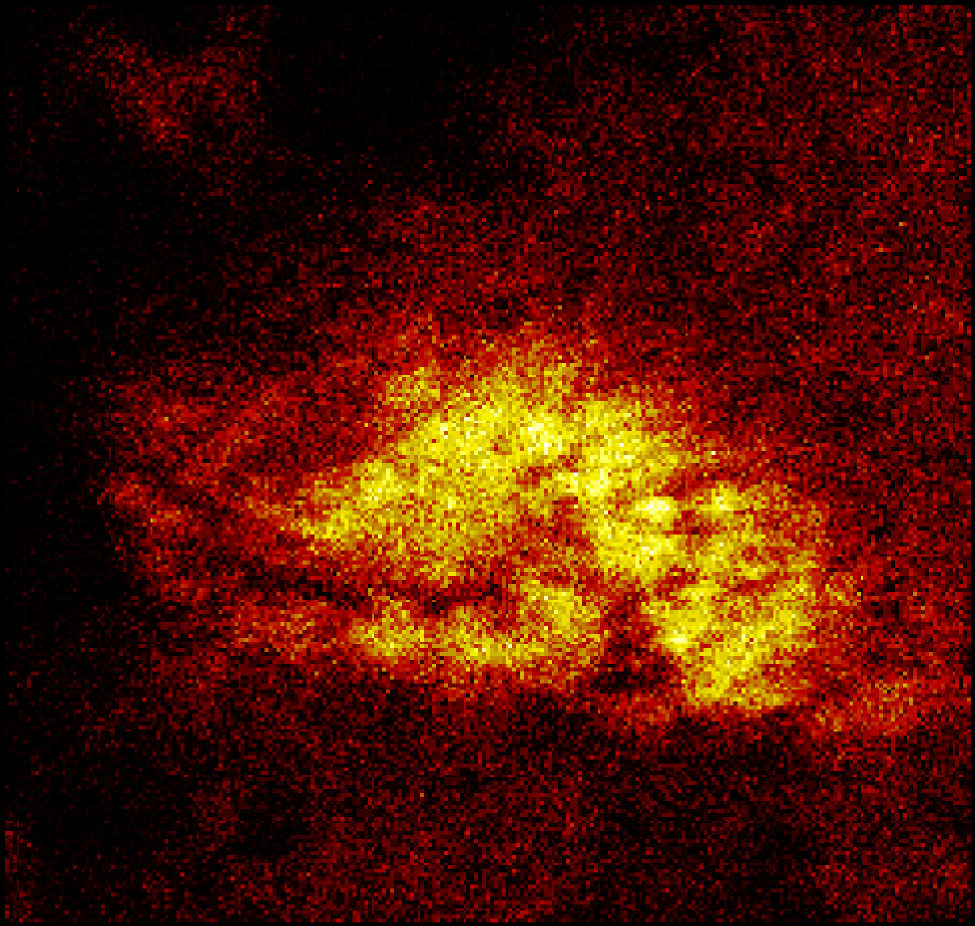
-Water Content Curve: The amount of water sorbed under saturated conditions, and the amount of water retained under various dehydration conditions (i.e., "matrix potential").

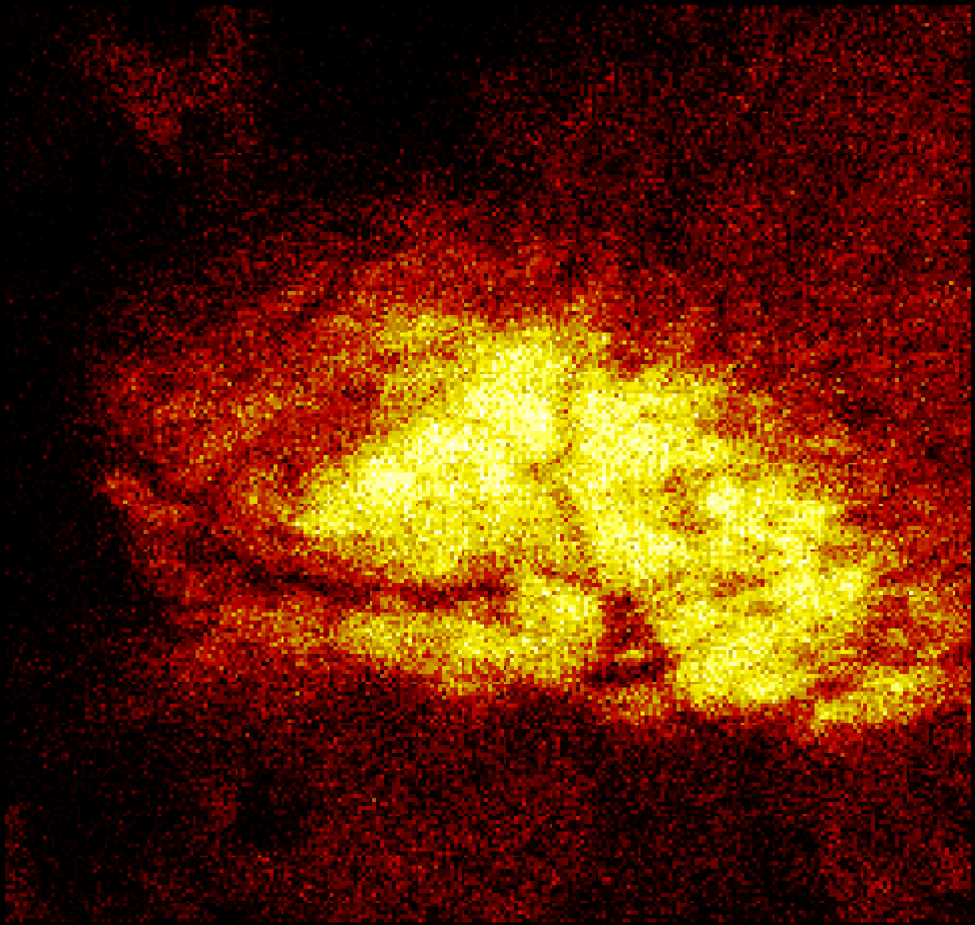
Surface Complexation Reactions (Kinetics and Thermodynamics)

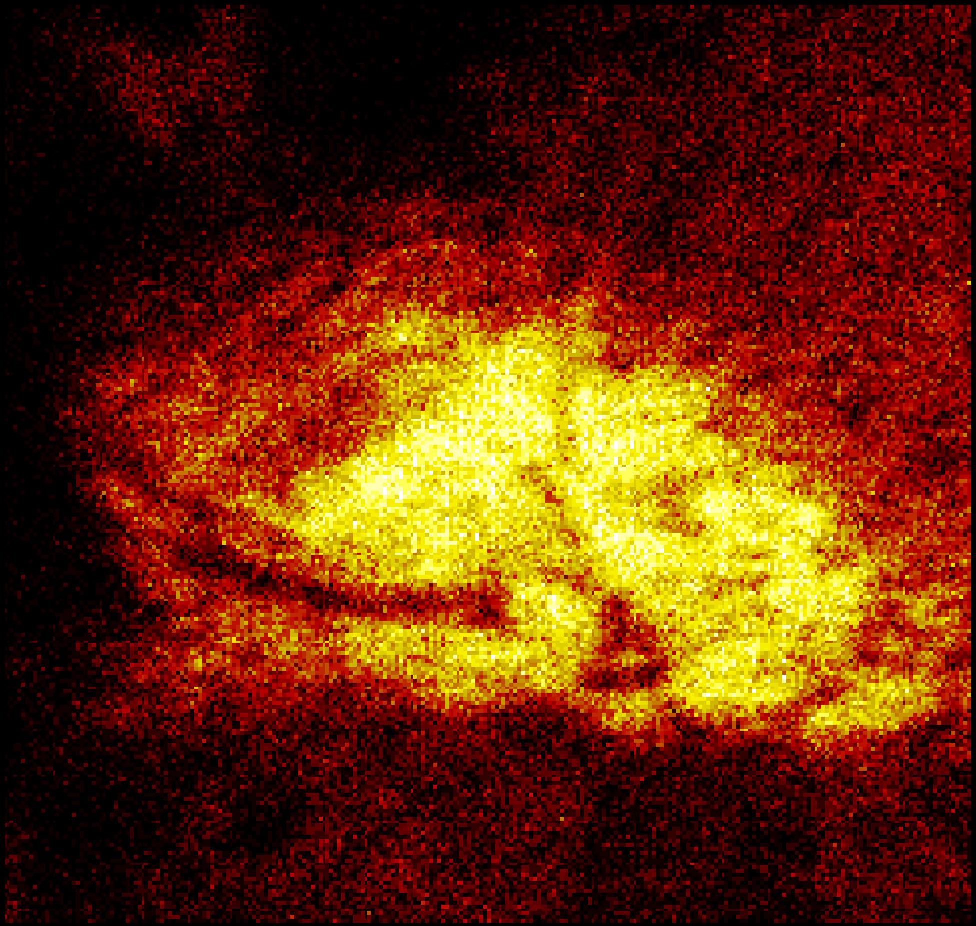
- -Low Energy Sites
- -High Energy Sites
- -Mechanical Entrapment

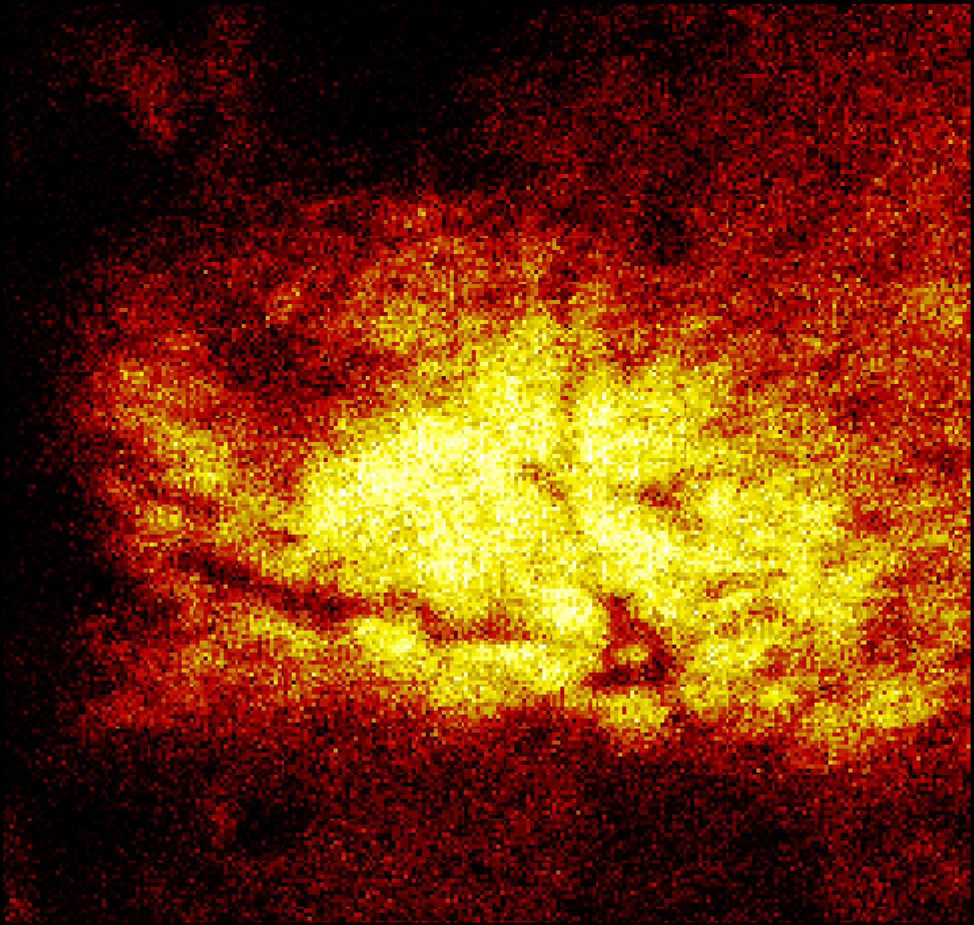






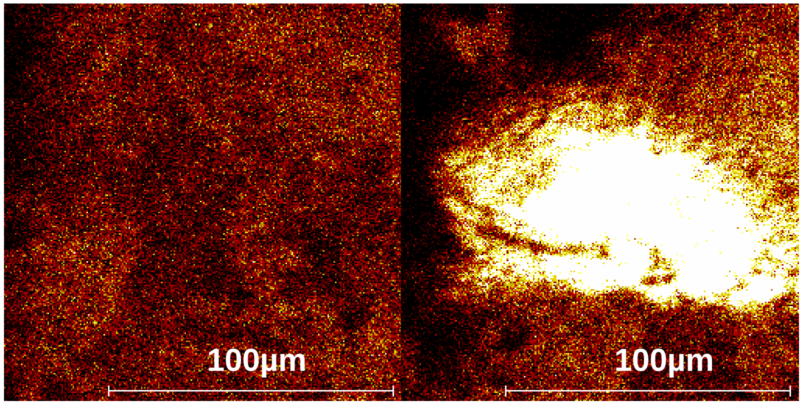






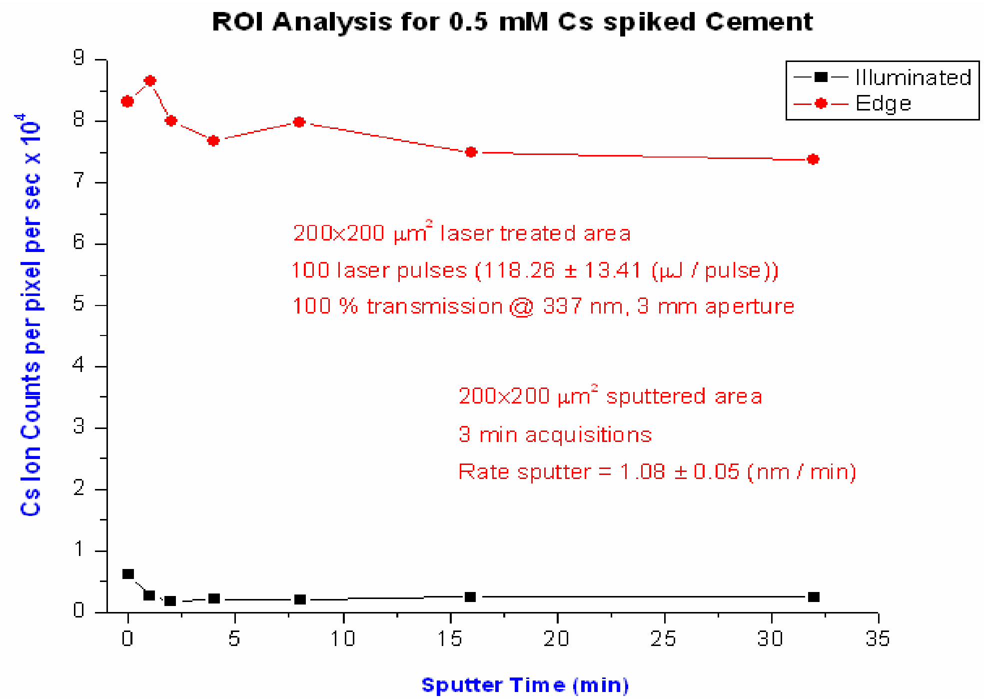
Laser Redistribution of Radionuclides

Cesium on Cement

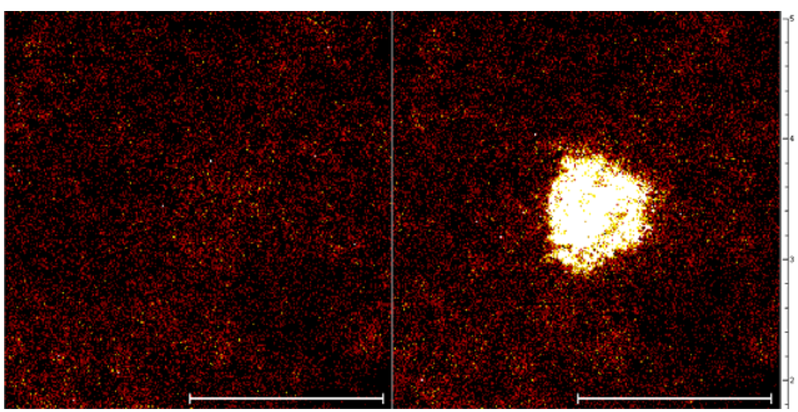


Before Laser

After 100 Laser Pulses at ~50 mJ/cm^2

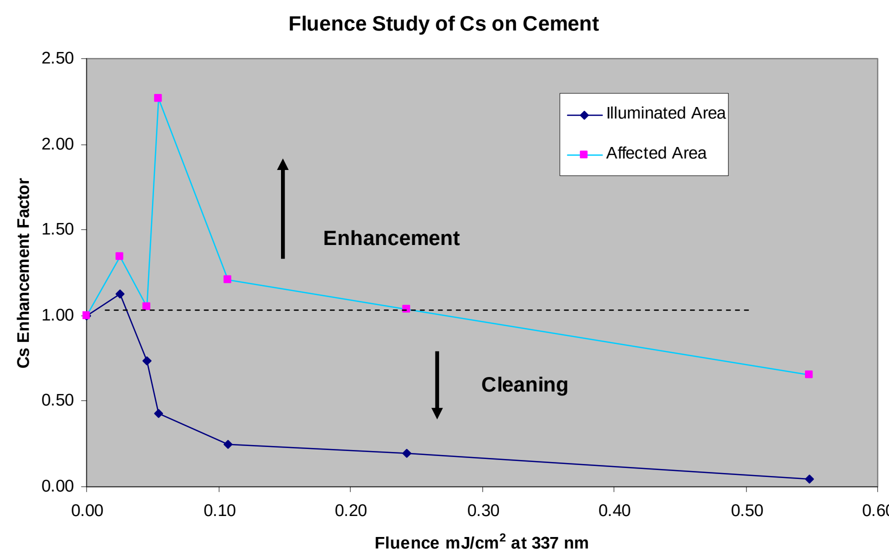


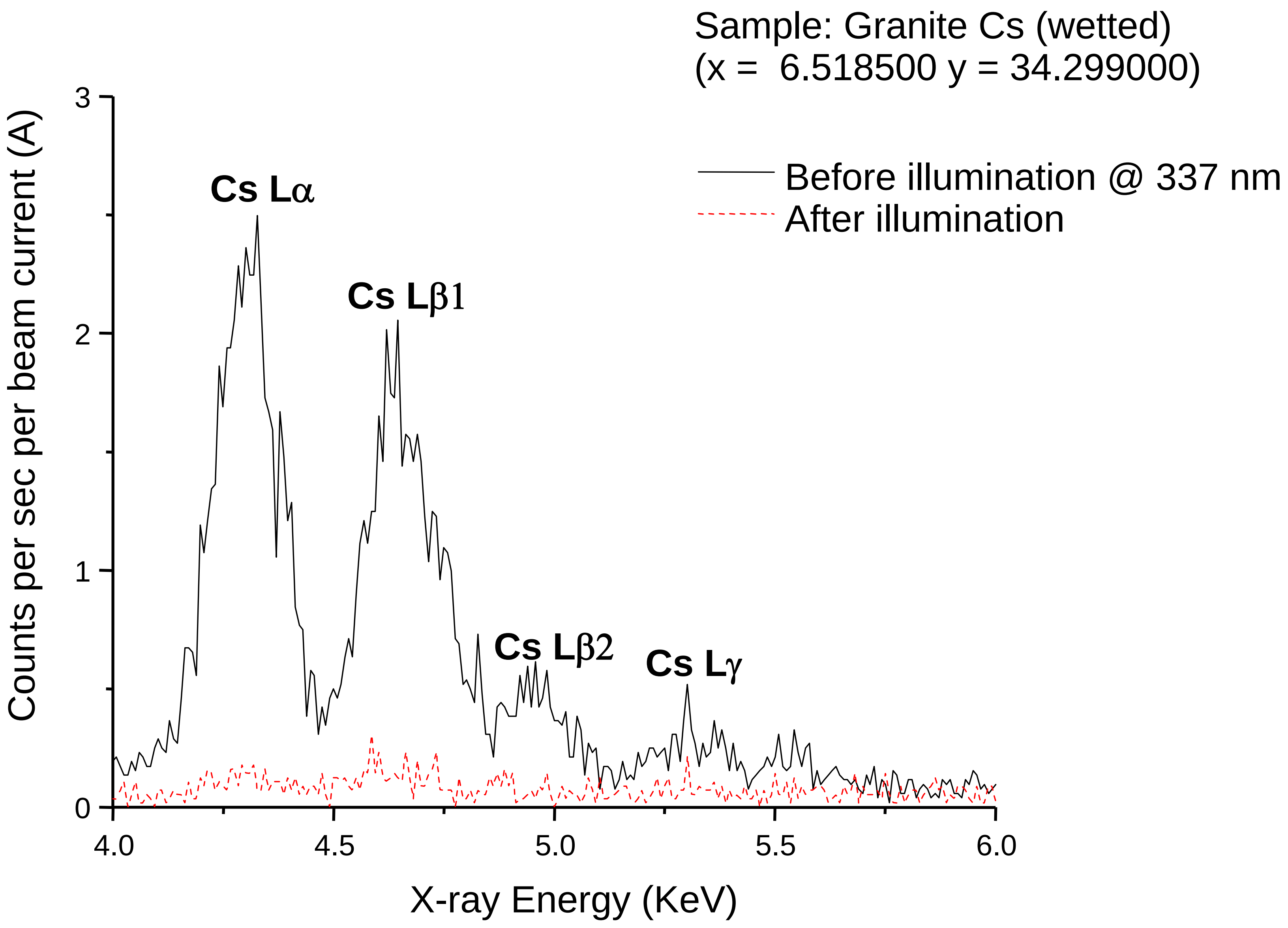
Cobalt on Cement



Before Laser

After 100 Laser Pulses at ~50 mJ/cm^2





Sample: Granite Cs (wetted)
(x = 6.518500 y = 34.299000)
Before illumination @ 337 nm
After illumination
Cs Lα
Cs Lβ1
Cs Lβ2
Cs Lγ
Counts per sec per beam current (A)
X-ray Energy (KeV)
0
1
2
3
4.0
4.5
5.0
5.5
6.0

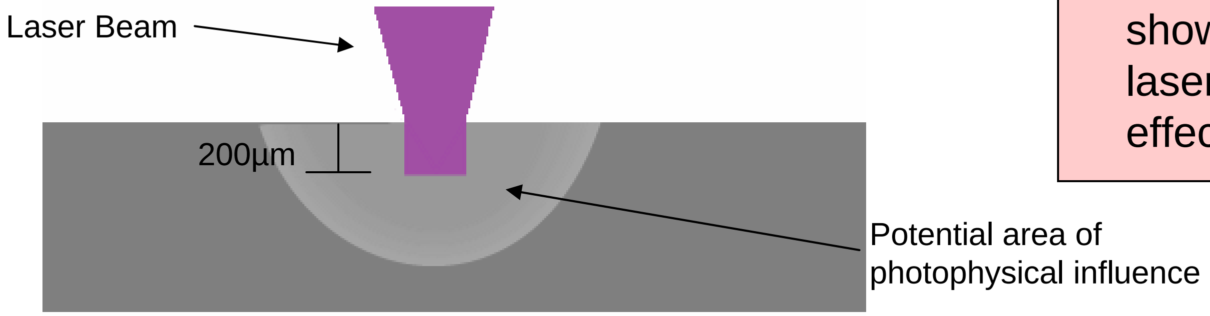
Laser Induced Phenomena

Photophysical Phenomena

- *Rapid localized heating*
- Formation of a thermal shockwave
- Formation of an acoustic shockwave
- Rapid expansion and contraction of the surface lattice structure
- Formation of phonons (thermally excited vibrational modes in a crystalline lattice

Photophysical Effects

- *Changes in matrix-adsorbate bonds*
- *Changes in the matrix binding sites*
- Kinetic energy changes in the adsorbate molecule and in the crystalline lattice where it resides
- *Bond rupture*
- Phase changes in matter (e.g., solid to vapor, or liquid to vapor)
- *Hydraulic mass transport to the surface*



Photochemical Phenomena

- Electronic transitions
- Bond polarization
- Bond rupture and creation of ionic species
- Creation of singlets and electron hole pairs
- Increased Coulombic repulsion
- Dielectric breakdown
- Oxidation/reduction reactions
- Generation of plasmons and polarons

These phenomena are more pronounced in metallic and semi-conductor materials; however, even large band-gap insulator materials have been shown to be susceptible to laser-induced non-thermal effects

Summary of Laser Decontamination of Radionuclides

- When coupled with a chemical decontamination technique, the laser shows promise of being able to achieve high levels of radionuclide decontamination for Cs and Co.

- Both thermal and photochemical phenomena appear to exist with photochemical phenomena being more predominant at wavelengths in the UV.

- UV wavelengths appear to be optimal for redistribution.

- Laser power is optimal for radionuclide redistribution at ~ 50 - <300 mJ/cm^2.

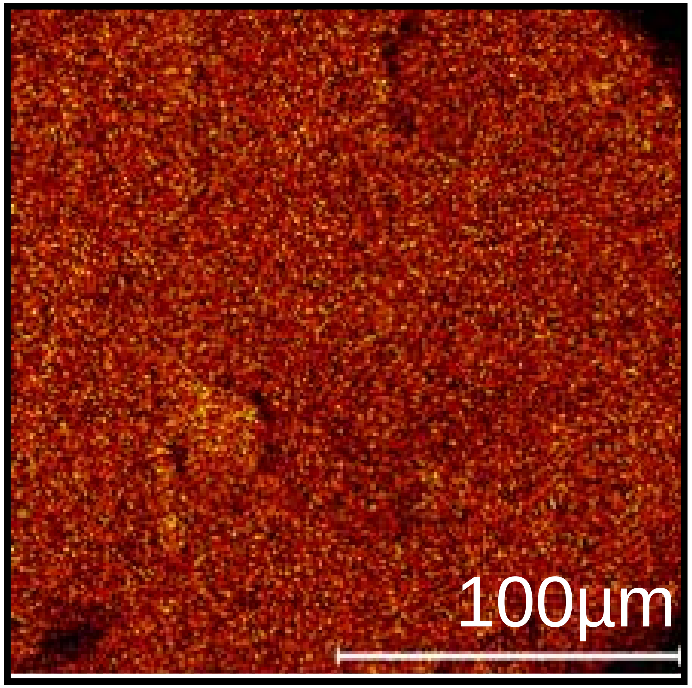
- Laser damage threshold is >300 mJ/cm^2 for cement, granite, and marble.

- Both Cs and Co are affected as well as Group I and IIA metals.

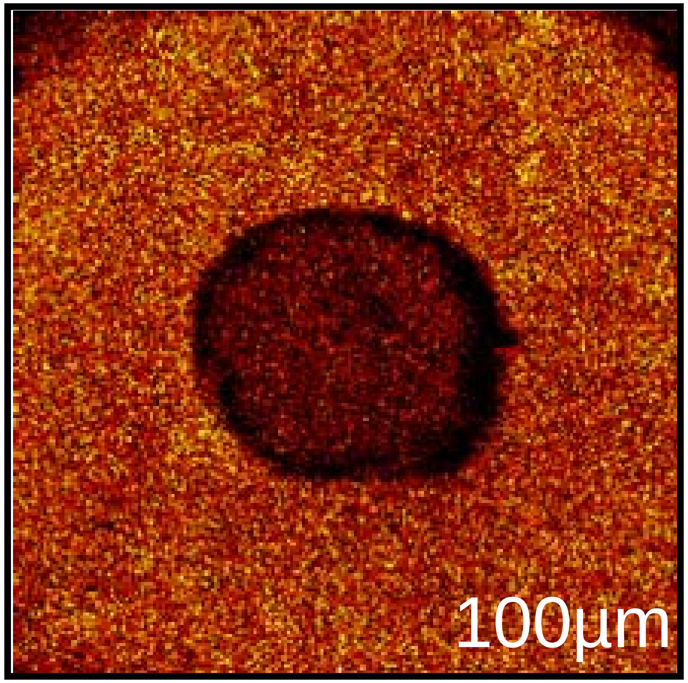
- It is plausible to assume that other sources of non-damaging energy (e.g., microwave) may promote the same effects.

Part II - Laser Cleaning and Decontamination of Organic Contaminated Structural Materials

Laser Cleaning of Chem/Bio Contaminants on Surfaces



Granite coupon ToF-SIMS image of $C_3H_7^+$ organic ubiquitously present on surfaces before laser fire.



Granite coupon after laser fire.
The dark spot shows that $C_3H_7^+$ organic has been removed from the surface by 50 mJ/cm^2 laser light at 337 nm without **without** damaging the substrate.

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Laser cleaning of *Prestige* tanker oil spill on coastal rocks controlled by spectrochemical analysis

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Cleaning graffitis on urban buildings by use of second and third harmonic wavelength of a Nd:YAG laser: a comparative study

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Laser cleaning of parchment: structural, thermal and biochemical studies into the effect of wavelength and fluence

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Achievement of optimum laser cleaning in the restoration of artworks: expected improvements by on-line optical diagnostics☆

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Laser cleaning of printed circuit boards

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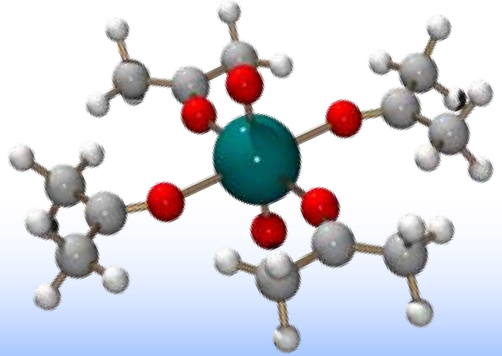
Possible Organic Contaminants

- ***m/z* 29**
  - C2H5+
  - CHO+
- ***m/z* 43**
  - C3H7+
  - C2H3O+
  - C2H5N+
- ***m/z* 73**
  - C4H9O+
  - C3H5O2+
- ***m/z* 101**
  - $C_6H_{13}O^+$
  - $C_5H_9O_2^+$
  - $C_4H_5O_3^+$
- ***m/z* 147**
  - $C_{11}H_{15}^+$
  - $C_9H_7O_2^+$
  - $C_5H_{15}OSi_2^+$
- ***m/z* 149**
  - $C_8H_5O_3^+$
  - $C_5H_9O_5^+$
  - $C_8H_9N_2O^+$



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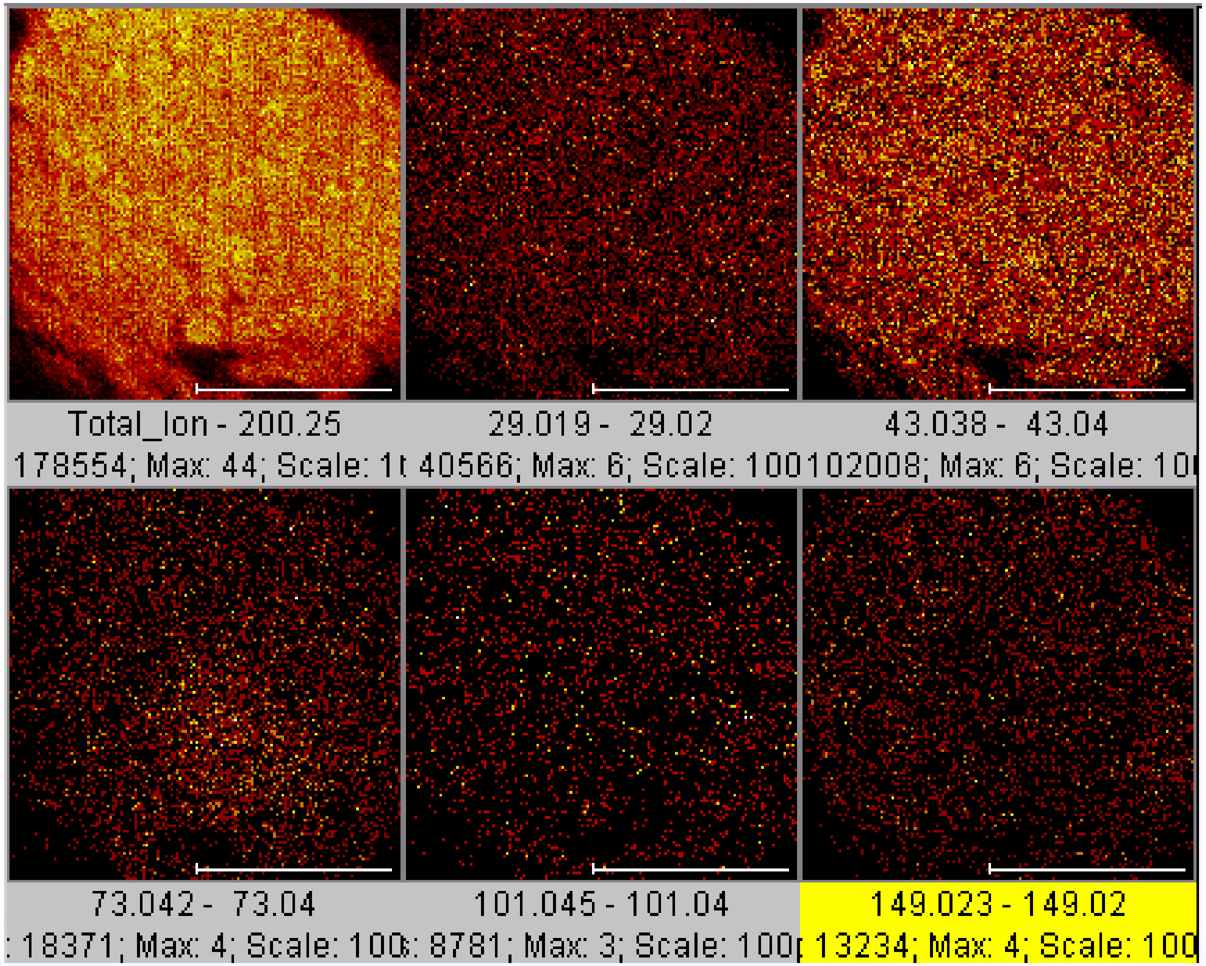
Concrete Images
No Laser Illumination



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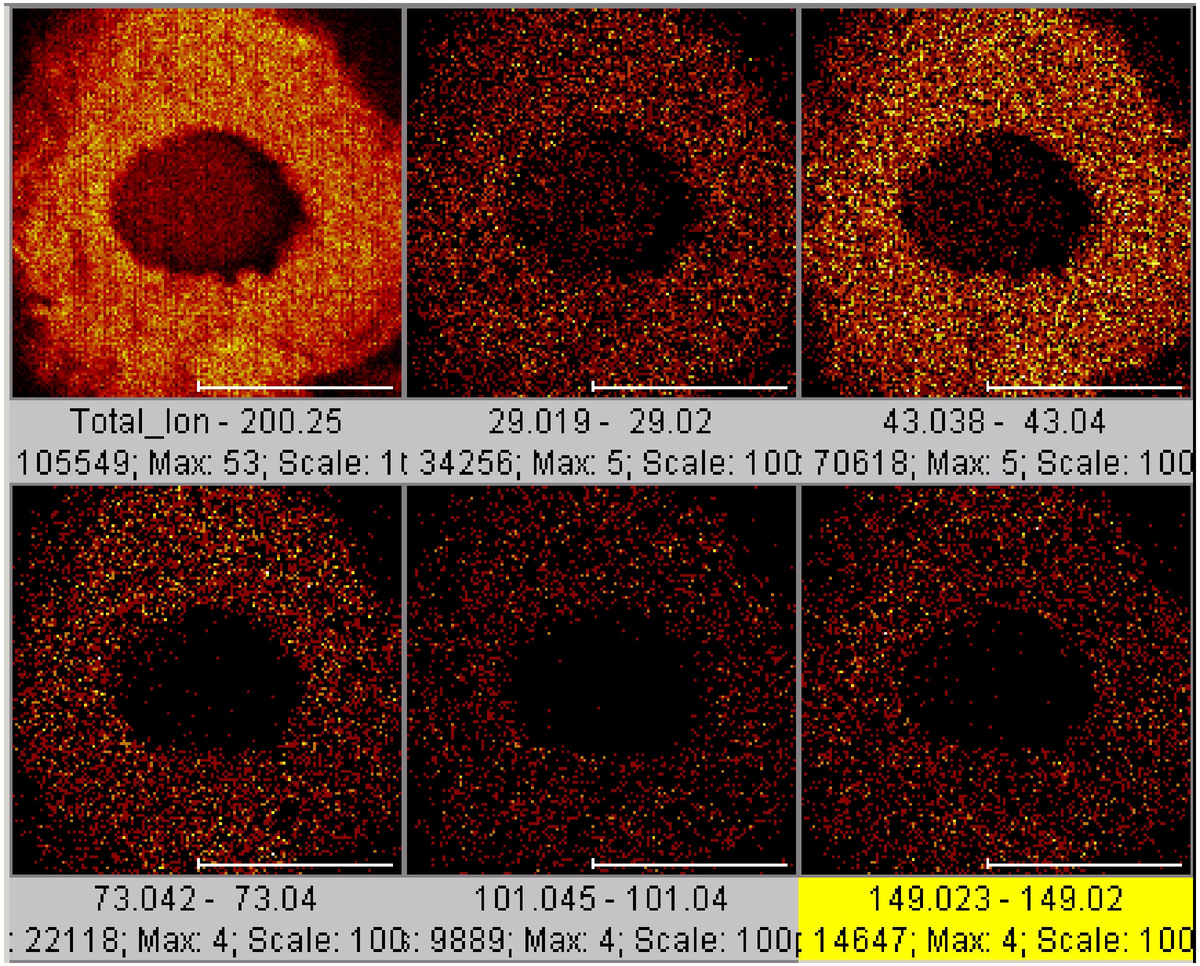
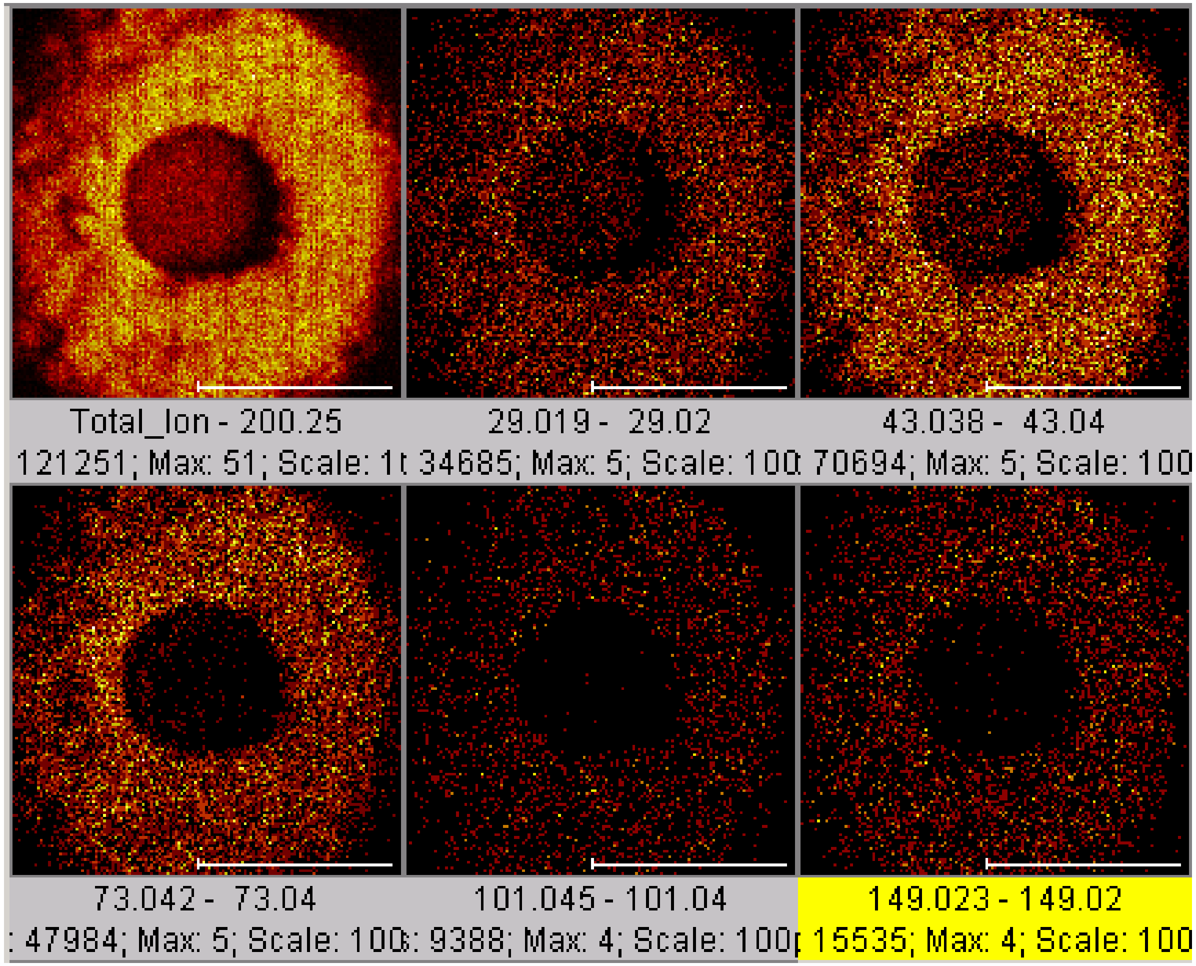
Illumination at 230 nm



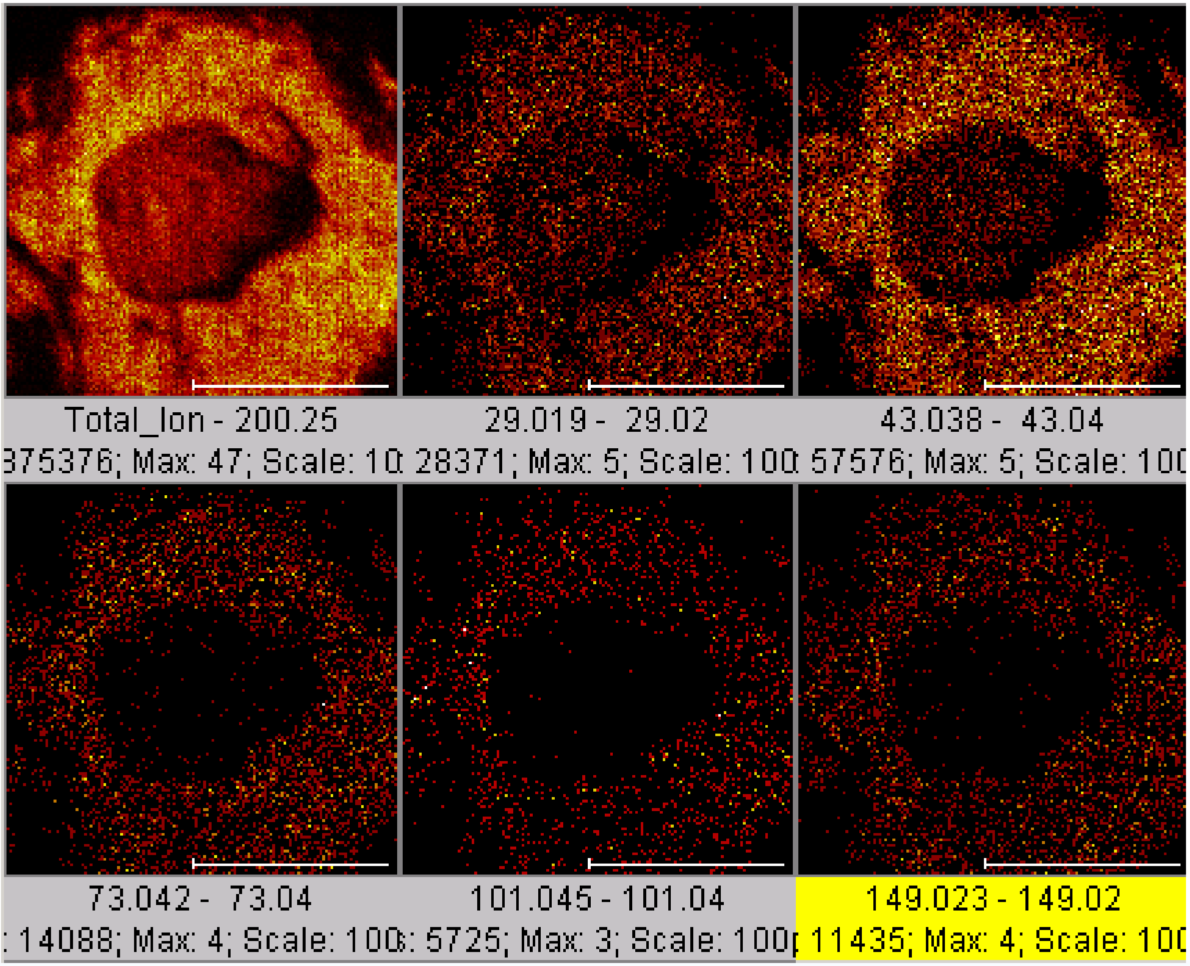
Average Fluence = $0.09 J/cm^2$

Illumination at 337 nm



Average Fluence = 0.09J/cm^2

Illumination at 355 nm



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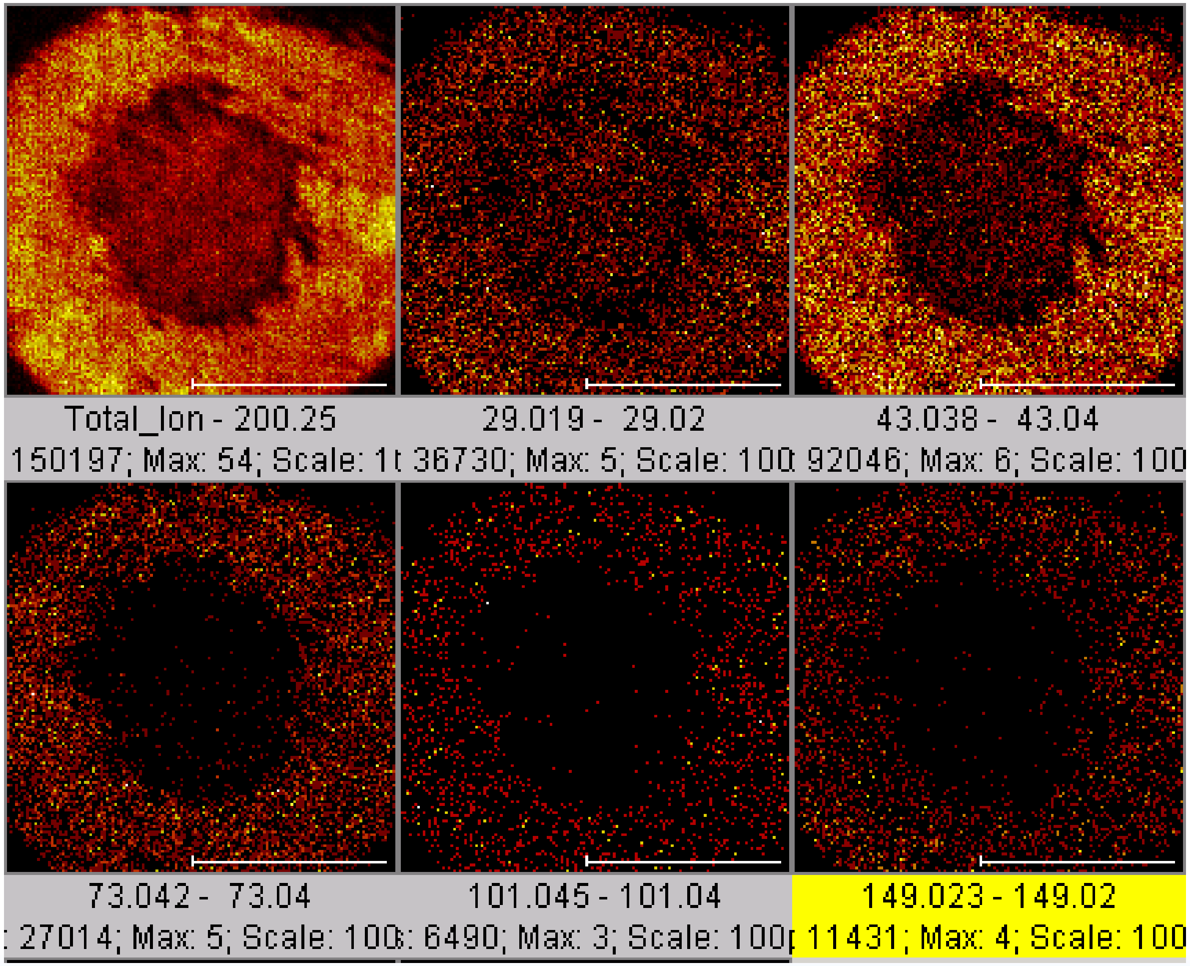
Average Fluence = 0.09J/cm^2

Illumination at 532 nm



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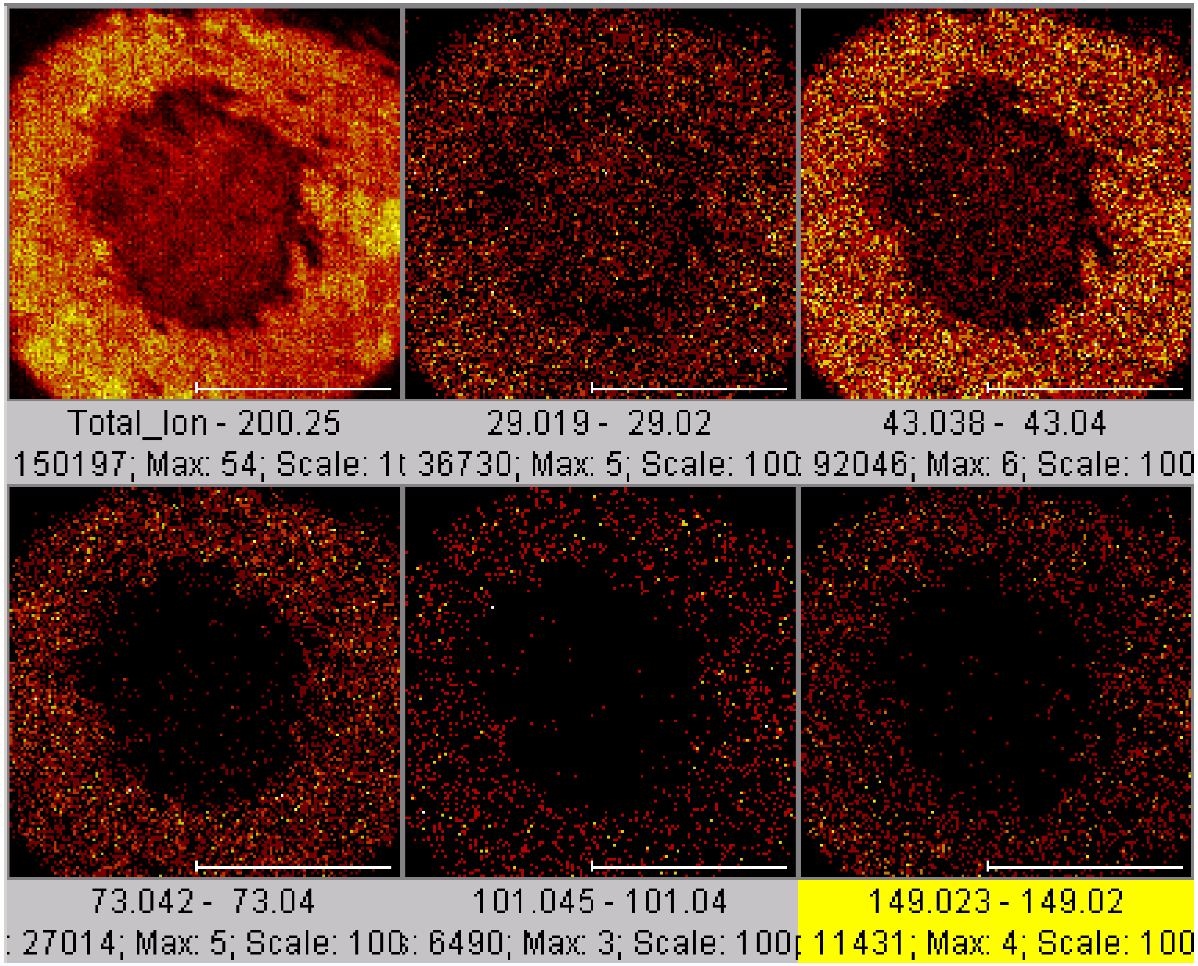
Average Fluence = 0.09J/cm^2

Illumination at 1064 nm



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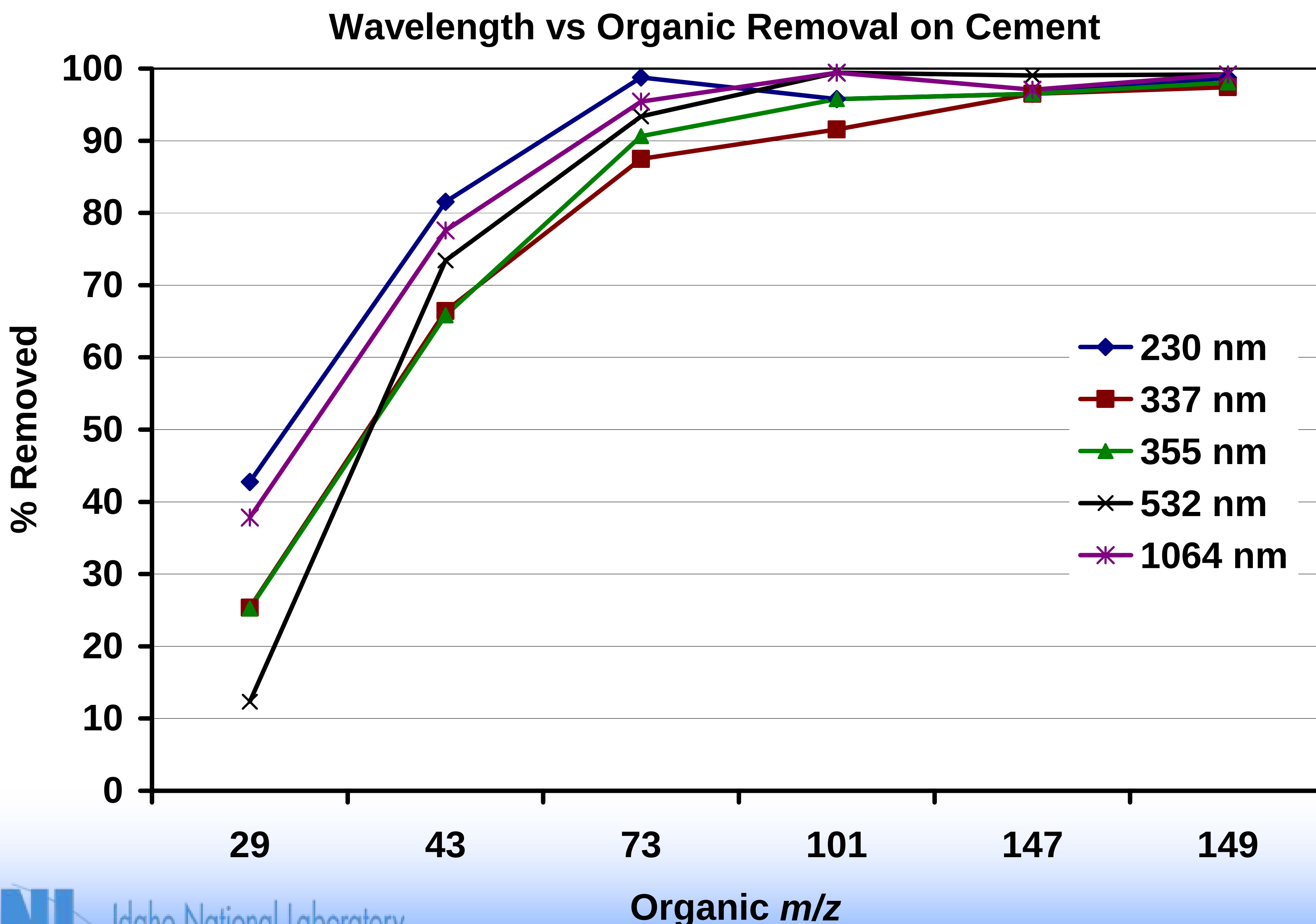
Average Fluence = 0.18J/cm^2

Organic Trends on Cement



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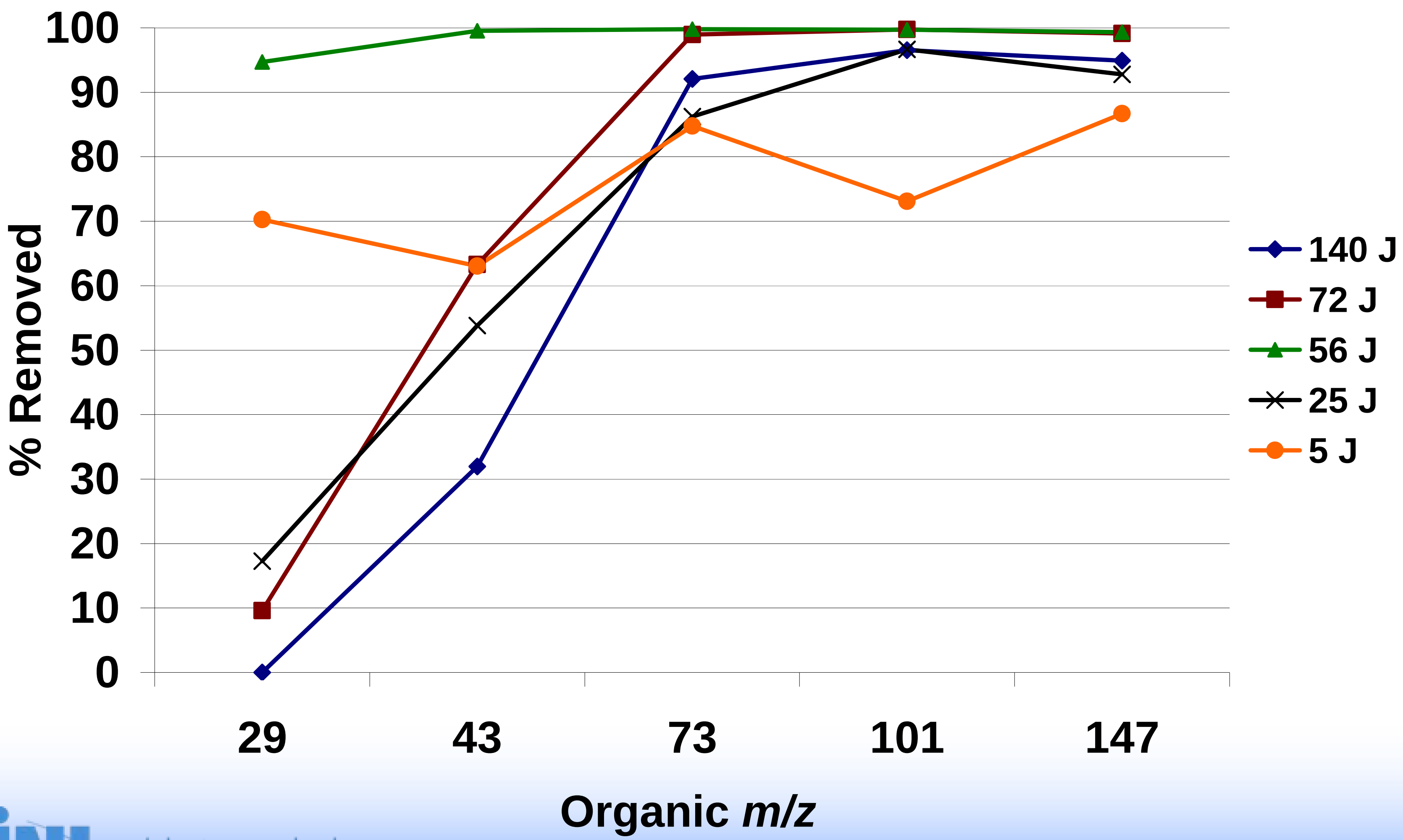
Average Fluence = 0.09J/cm^2 except 1064 nm=0.18J/cm^2

Energy vs Organic Removed on Cement



A Single Laser Platform for Chemical and Radionuclide Detection and Decontamination ?

Key Technical Challenges:

- Laser based 4-wave mixing and thermal lensing techniques are currently under development for standoff (100+ meter) detection, but face a significant challenge with precision delivery/retrieval of interrogation/signal beams to buildings/walls w/o significant degradation of beam quality arising from environmental "noise".

- Non-damaging laser cleaning is currently under development for Cs and Co radionuclides on porous matrices, but the data are limited and the technique may display variable results for different radionuclides on different surfaces.
  - Capture coatings which are transparent to the laser will be needed.
  - The laser can work standalone for some radionuclides (e.g., Cs), but ideally works with an existing chemical decon method for most applications.
  - Use of the laser may become obsolete if a better energy source is found.

- Laser destruction of CWA is currently being investigated on porous structural materials and common polymeric materials, but may not be compatible with all urban surfaces. Conditions which balance agent volatilization versus *in-situ* destruction may still give rise to some amount of volatile materials, mandating the laser head include a vacuum cowling for capture of emissions.
  - Photoactivated catalytic "aids" also being developed.

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