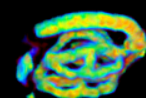
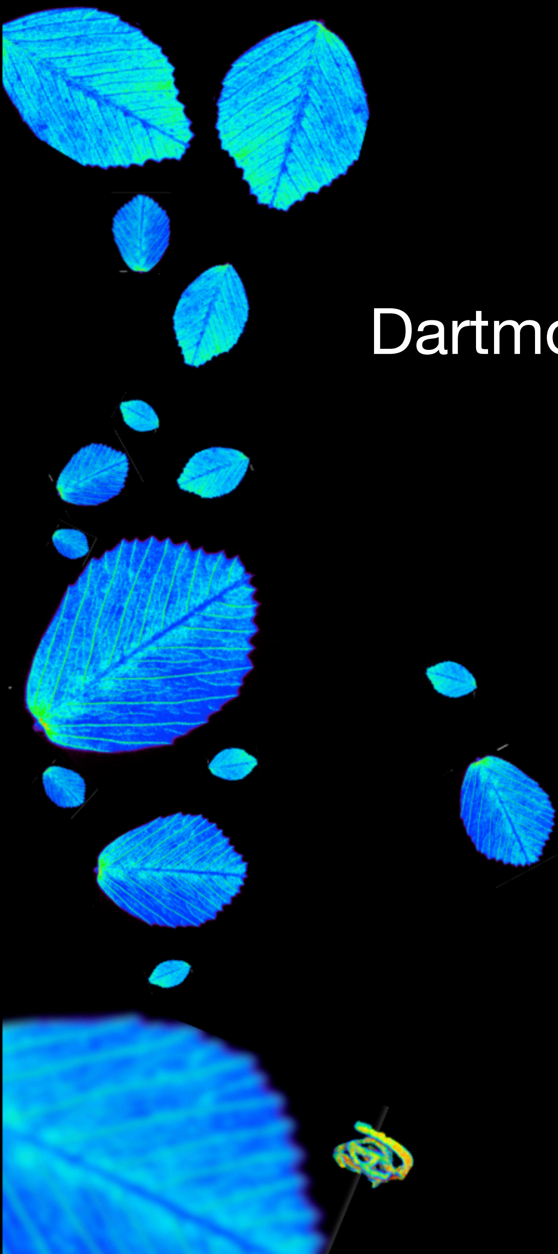
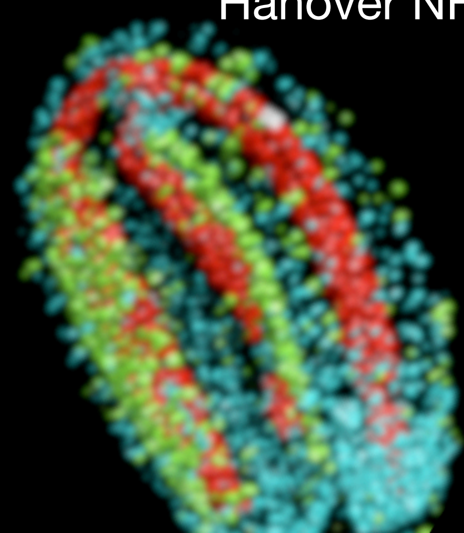
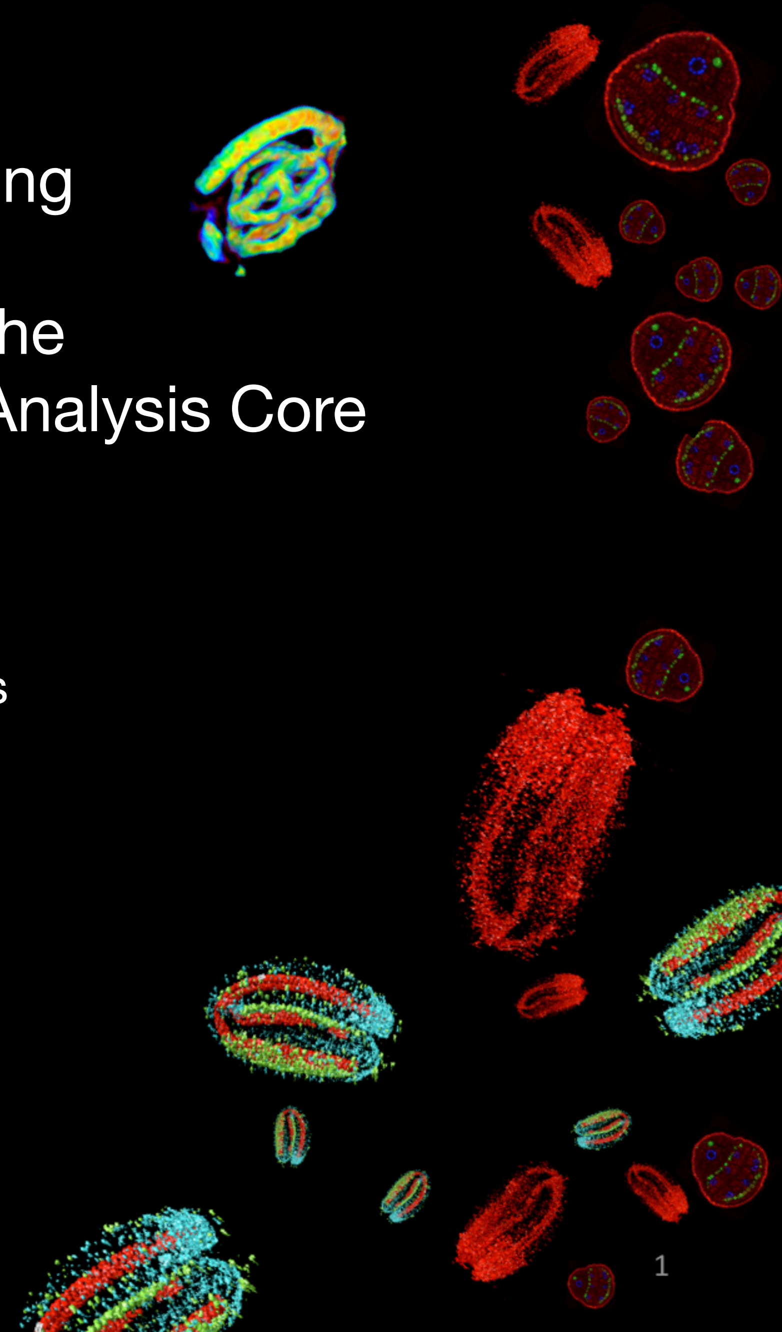
Elemental Mapping
&
Capabilities at the
Dartmouth Trace Element Analysis Core



Tracy Punshon
Biological Sciences
Dartmouth College
Hanover NH







Outline

- Elemental mapping defined
- Scientific applications – when bulk measurements are not enough
- Choosing an imaging technique
- Highlighted techniques and how they work
    - Synchrotron X-ray fluorescence mapping (SXRF)
    - Laser ablation inductively coupled plasma spectrometry (LA-ICP-MS)
- Resources and access to techniques
    - Accessing Synchrotron facilities: Beamtime proposals
    - The Dartmouth Trace Element Analysis Lab

Elemental mapping defined:

Elemental mapping is a *mode* of chemical analysis that, in addition to quantifying elements (how much), also gives spatial information (where) in the context of the sample.

Configurations:
•1D: line scans or profiles (X axis)
•2D: raster or map (X and Y axes), consisting of pixels of data
•3D: volume (X, Y, θ), consisting of voxels of data, reconstructed from multiple tomograms
•4D: volumes (X,Y, θ) integrated over time (how much, where and when)

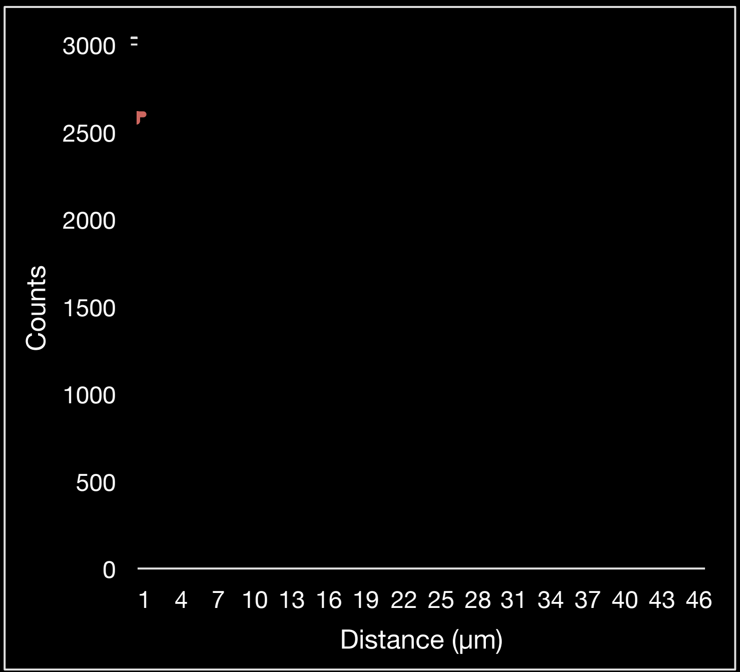
Terminology:
Volume-averaged: specimen structure is destroyed via homogenization and (if solid) dissolution prior to analysis

Spatially-resolved: specimen structure is preserved prior to analysis

Configurations

1D

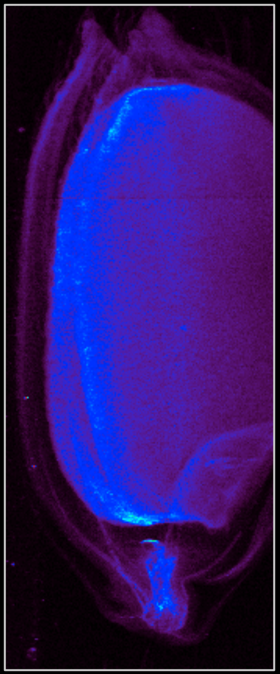
Zinc in paraffin-embedded human placenta by LA-ICP-MS



- profile
- Points:
    - Counts,
    - distance or time (X axis only)

2D

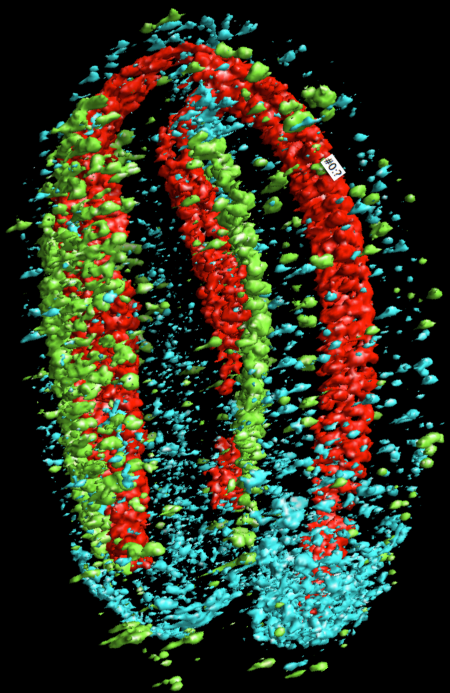
Copper in unpolished rice by SXRF



- map
- Pixels:
    - Counts,
    - X value,
    - Y value

3D

Iron, manganese and zinc in Arabidopsis seed

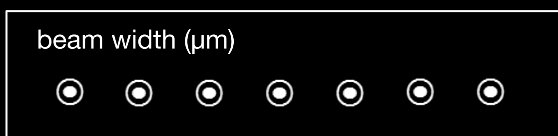


- volume
- Voxels:
    - Counts,
    - X value,
    - θ value (angle of rotation)

Configurations

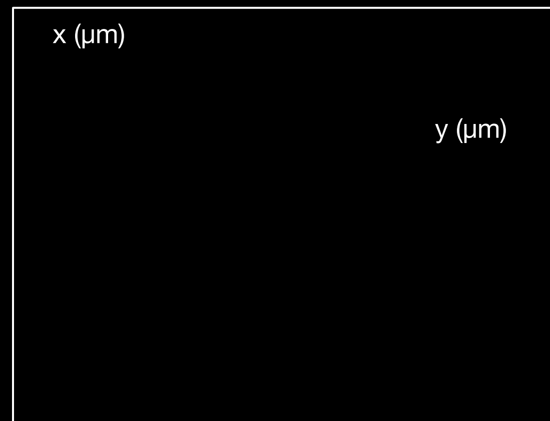
1D

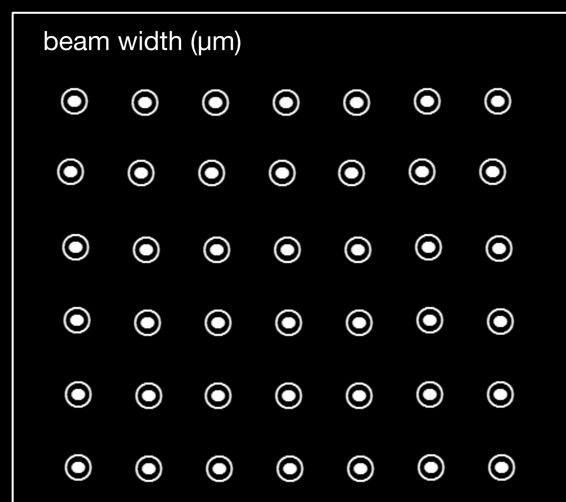
stage movement



2D

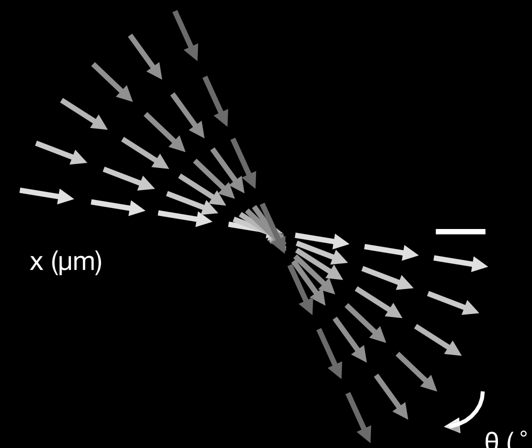
stage movement





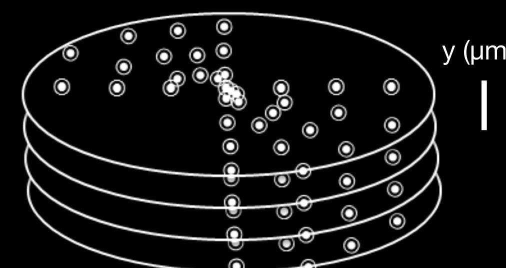
3D tomography Depth profiling

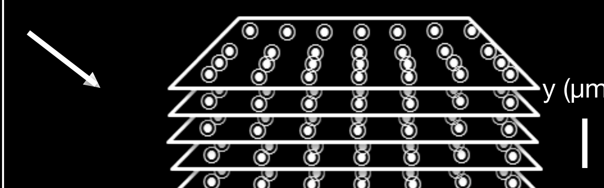
stage movement



tomogram

data



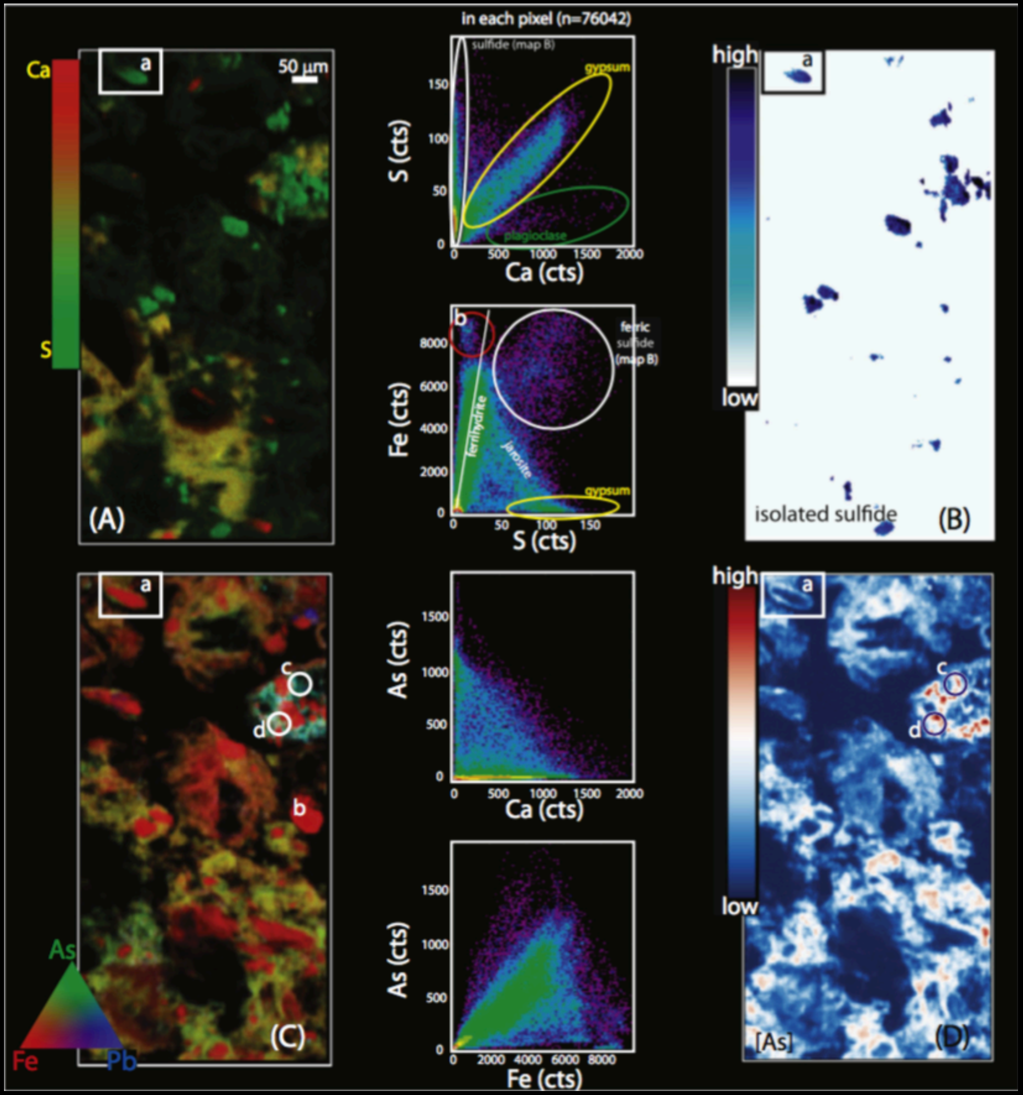


depth profile ablation

Scientific applications

- Environmental
  - Contaminant distribution in soils, mineral associations, bioreduction processes
  - Petrography
  - Entry and movement through biota
- Biological
  - Genetic control of elemental homeostasis in organisms
  - Modes of toxicity – elemental perturbations
  - Chemical signaling
- Human health
  - Time-resolved biomarkers: teeth and hair

Applications: Petrography – Toxic metals in tailing from the Iron King Mine and Humboldt Smelter Superfund Site (AZ)



- Elemental associations evident by plotting correlations between elemental abundances

Image credit: Root et al, 2015 Applied Geochem 2015

Applications: Entry and movement through biota – Elements in Daphnia

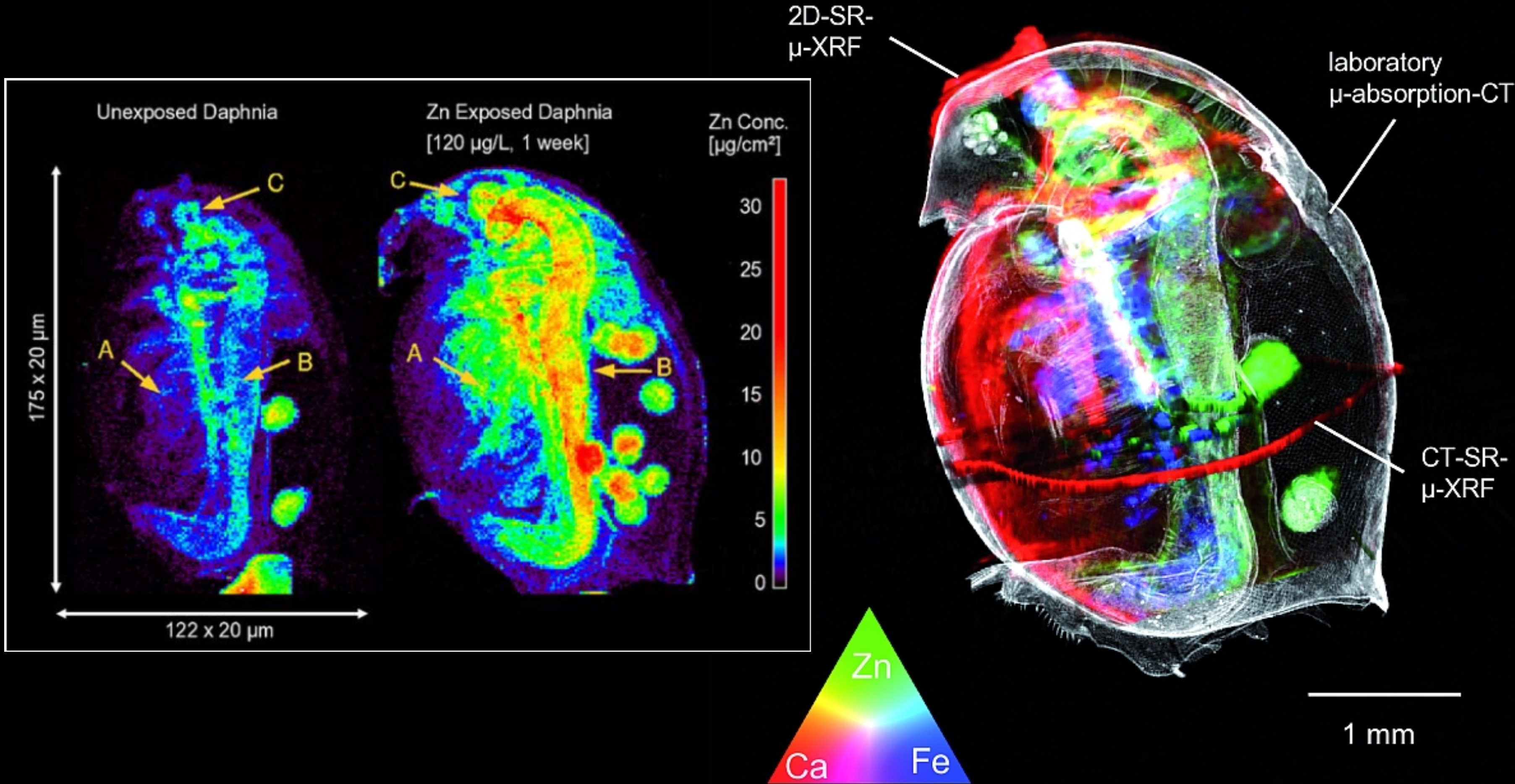
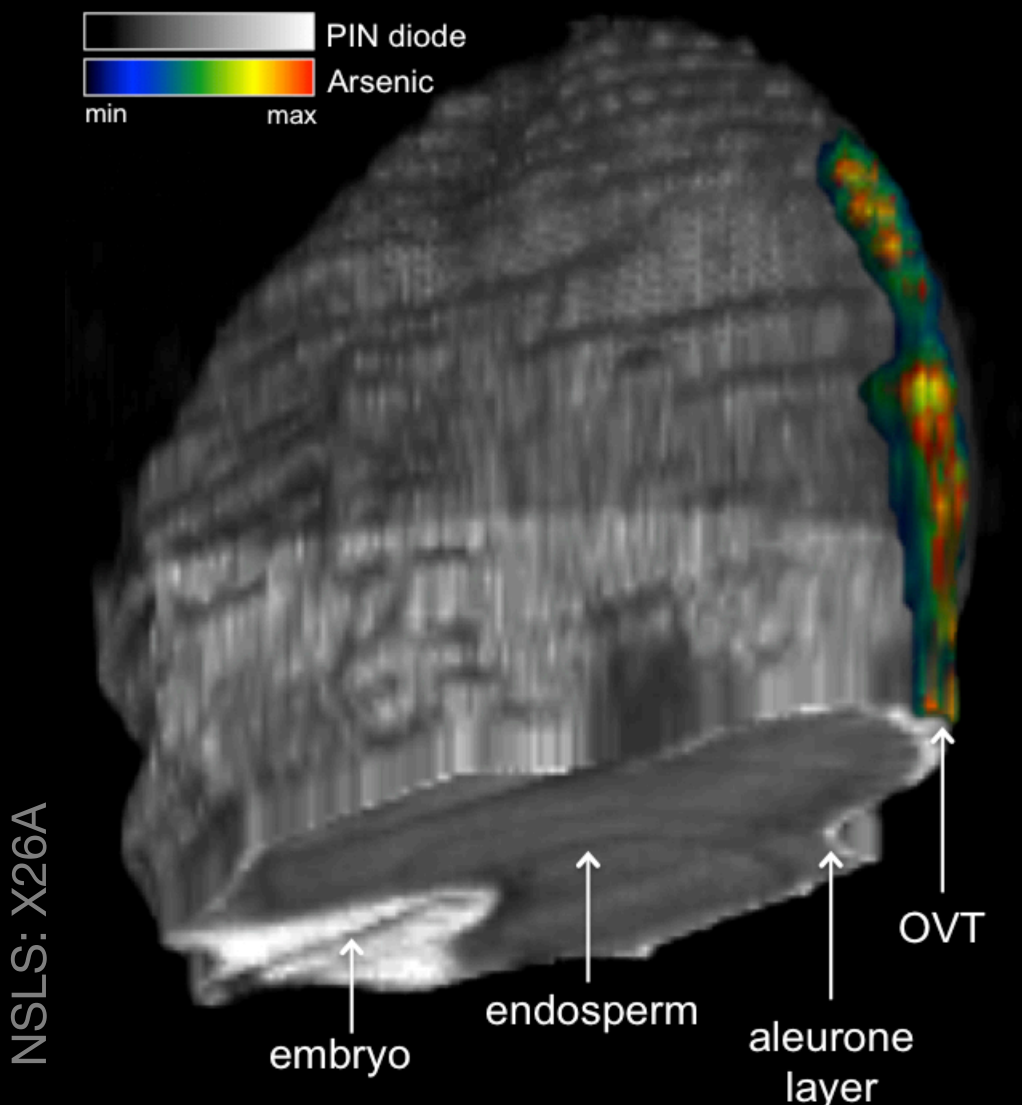


Image credit: De Samber et al 2008 J Anal At Spectrom 23 p 829

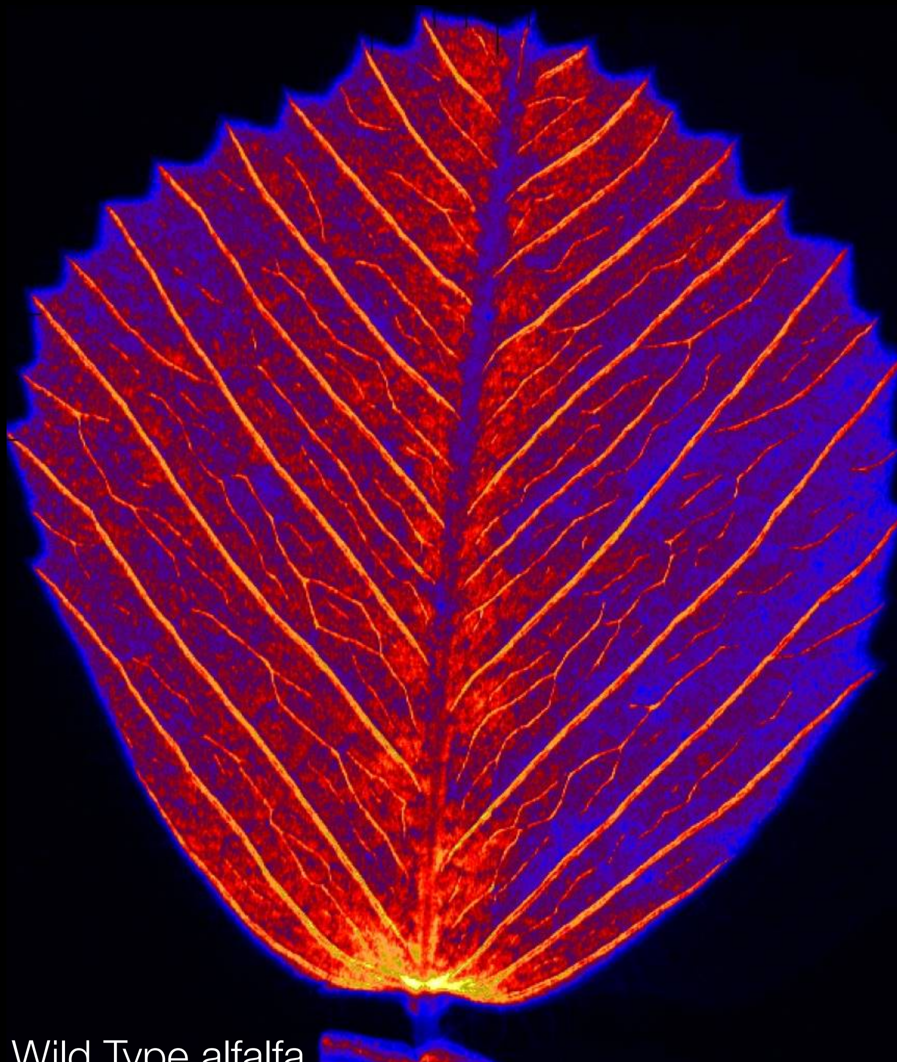
Applications: Entry and movement through biota – Arsenic in rice grains



Rice grain exposed to133 μM arsenite through the cut end of the flag leaf during grain development

Image credit: Carey et al. New Phytol. 2011;192(1):87-98

Applications: Genetic control of elemental homeostasis – Calcium in alfalfa



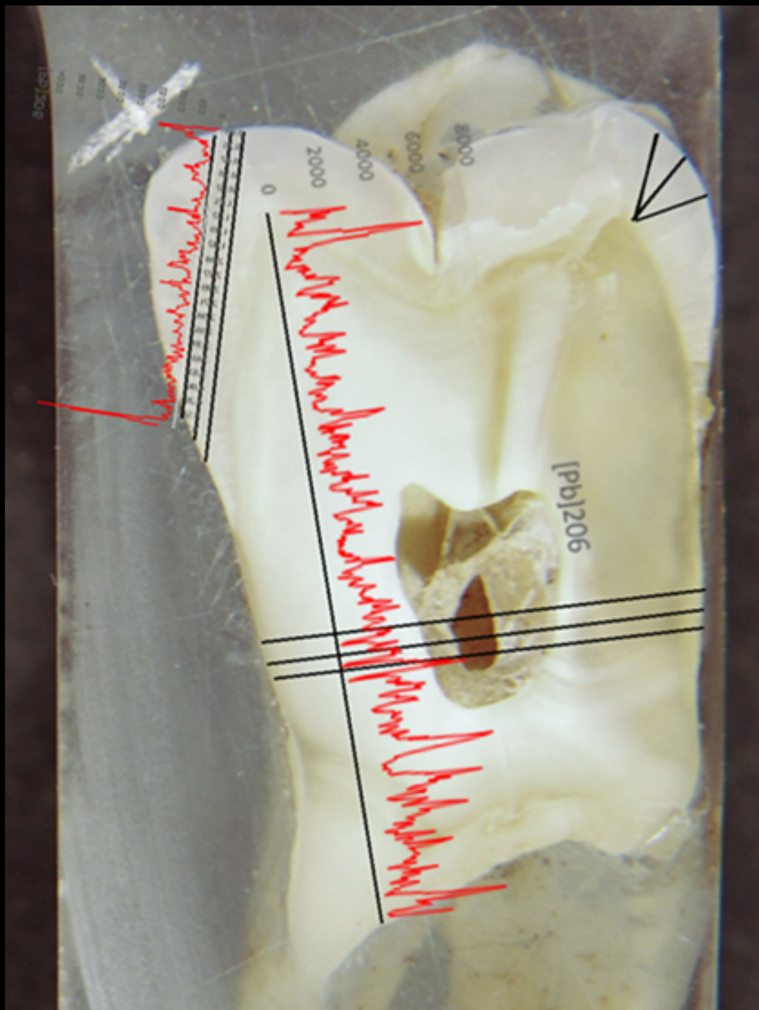
Wild Type alfalfa

Alfalfa with gene COD5 silenced

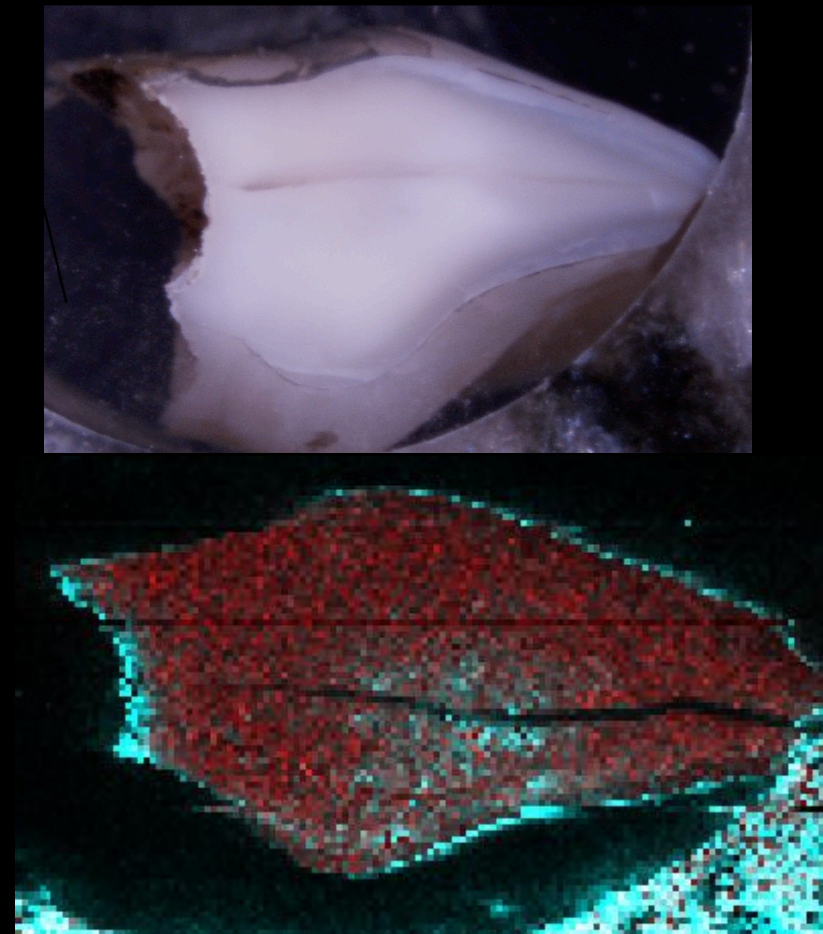
NSLS: X27A. E = 4.1 keV. 7 μm x 10 μm beam: 50 ms dwell.

Image credit: Punshon 2013, The Plant Journal 76(4) p627

Applications: Human health and exposure – Metals in human teeth



Line profile of lead in human tooth

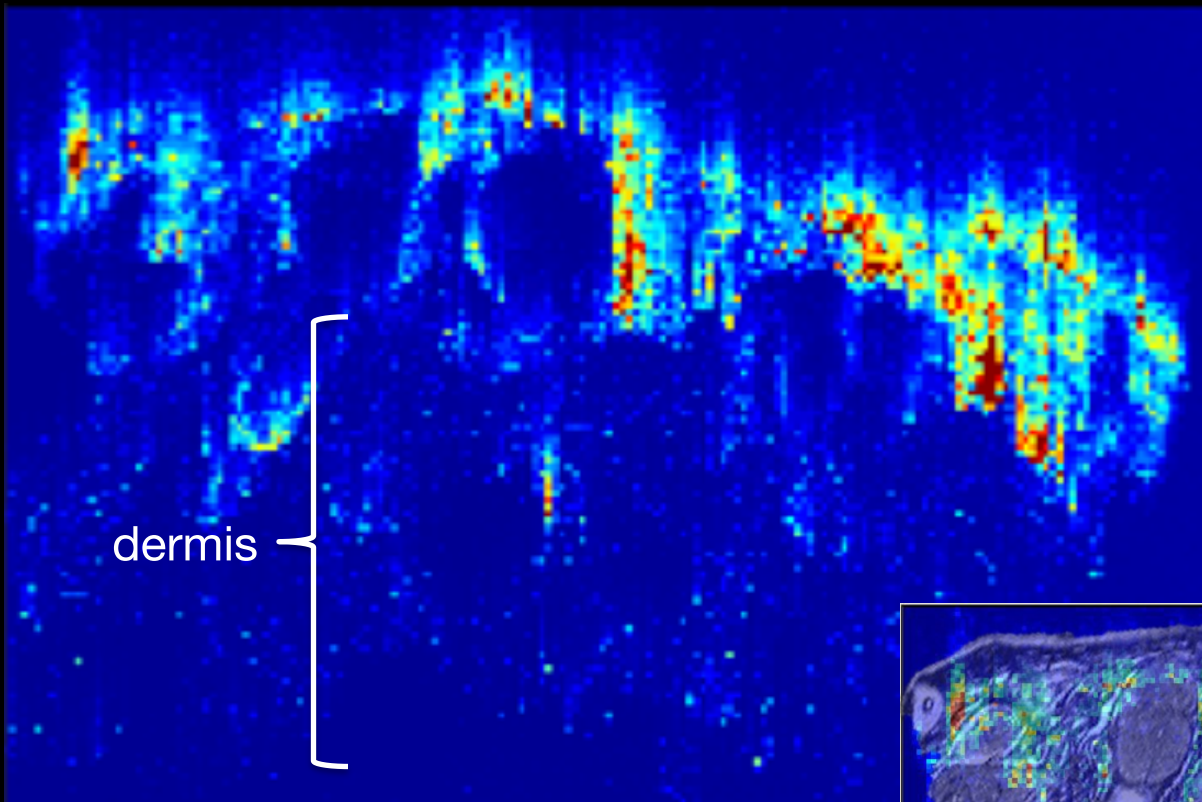


Calcium and **lead** in deciduous baby teeth as a biomarker of in utero metal exposure

Image credit: Marc Weisskopf Harvard U

Image credit: Dartmouth TEA core

Applications: Human health and exposure – silver in skin biopsy tissue



- Participant took over-the-counter colloidal silver supplements
- Skin had a blue coloration due to accumulation of silver

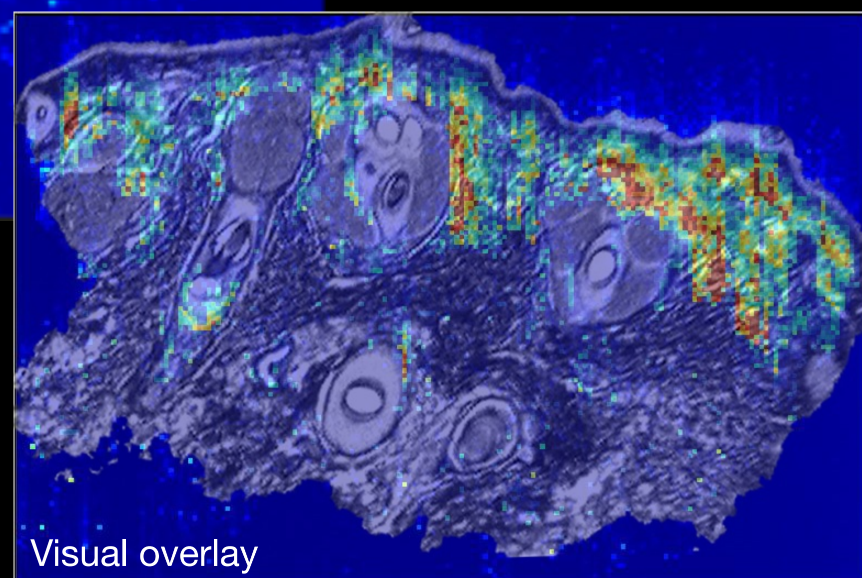
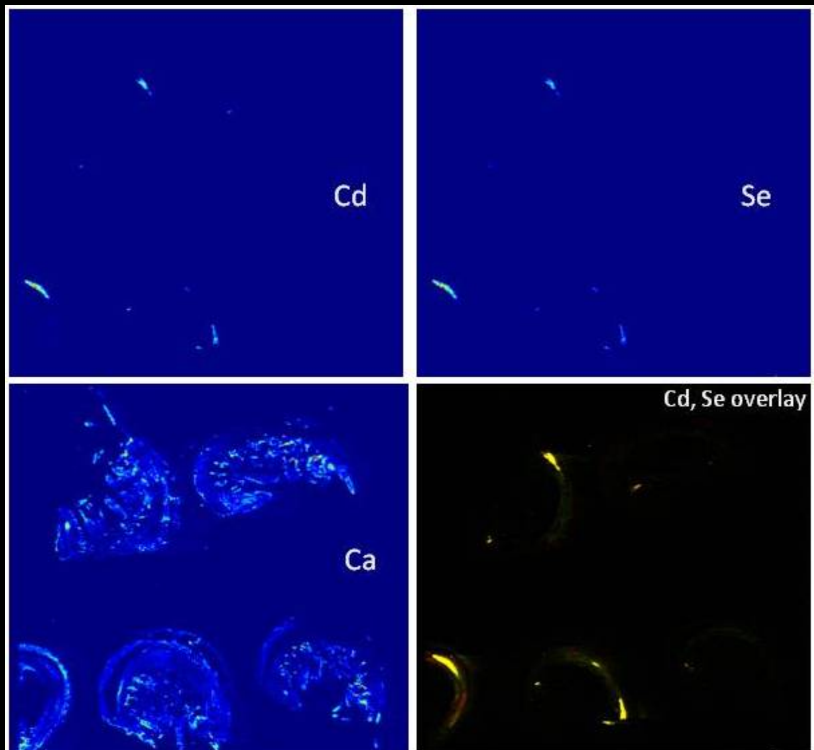
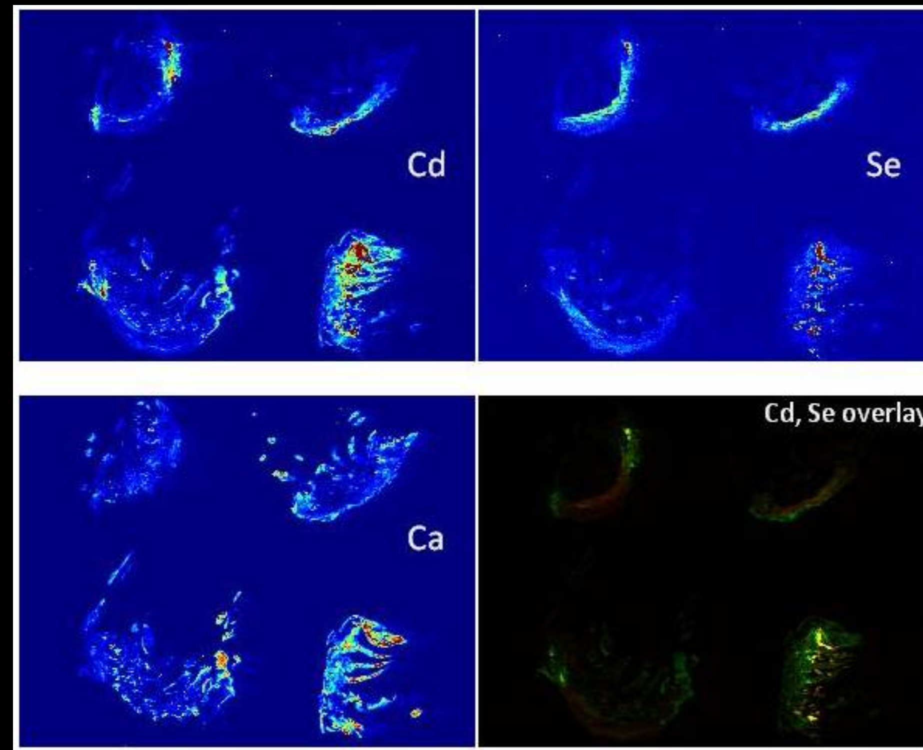


Image credit: Whitney High

Applications: Environmental – Food chain transfer of Cd Se Quantum Dots in benthic amphipod *Leptocheirus pulmunosa*



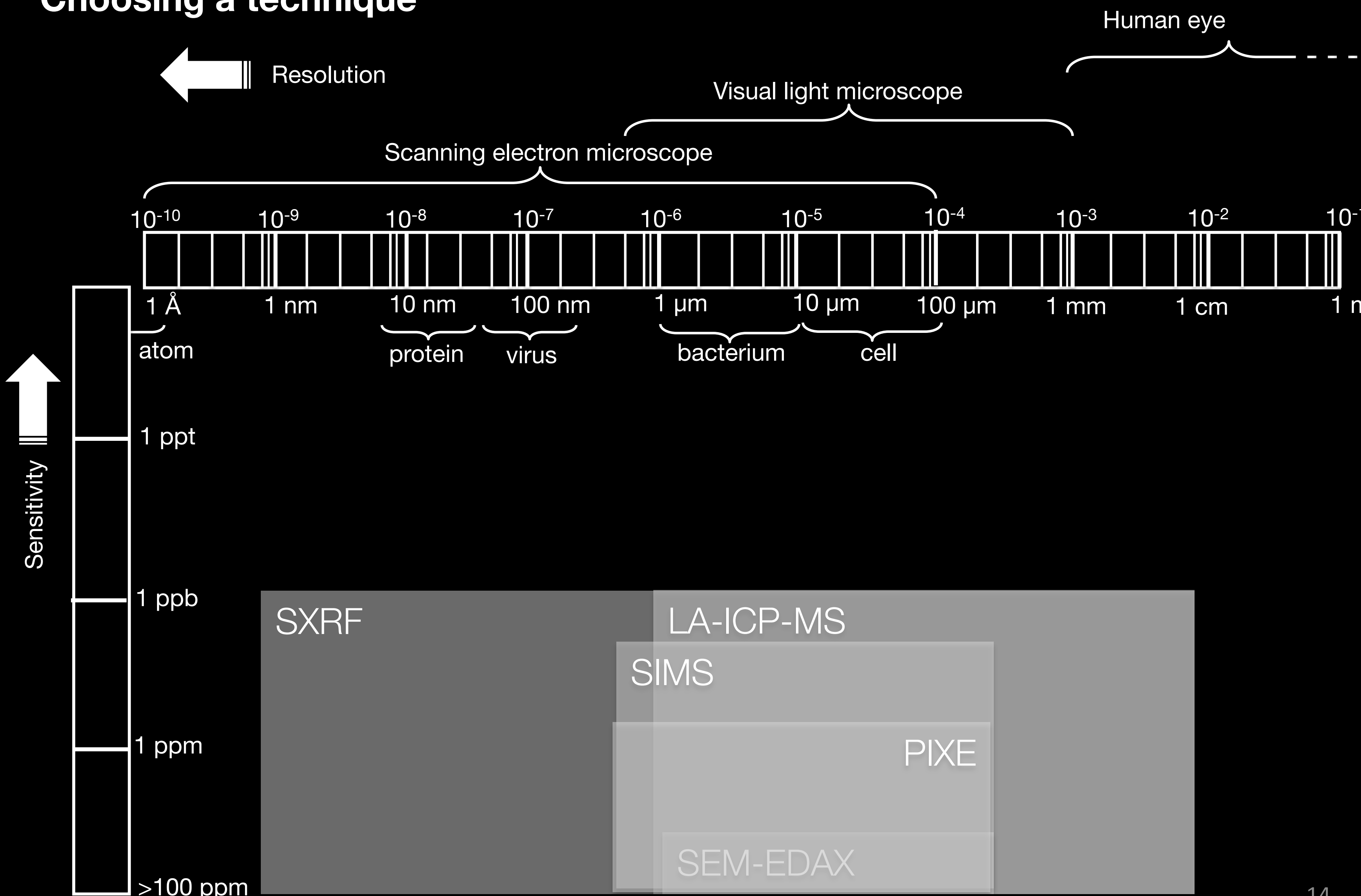
Aqueous exposure: Cd and Se closely co-localize



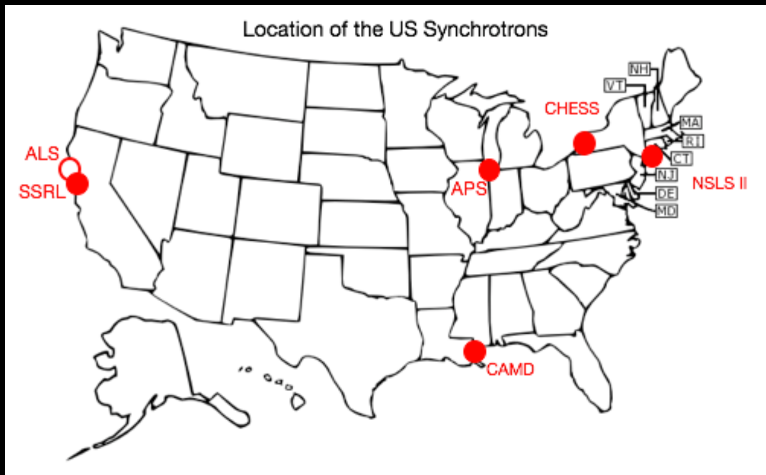
Exposure via algae: Cd and Se disassociation evident

Image credit: Jackson et al ES&T 2012 46(10) 5550

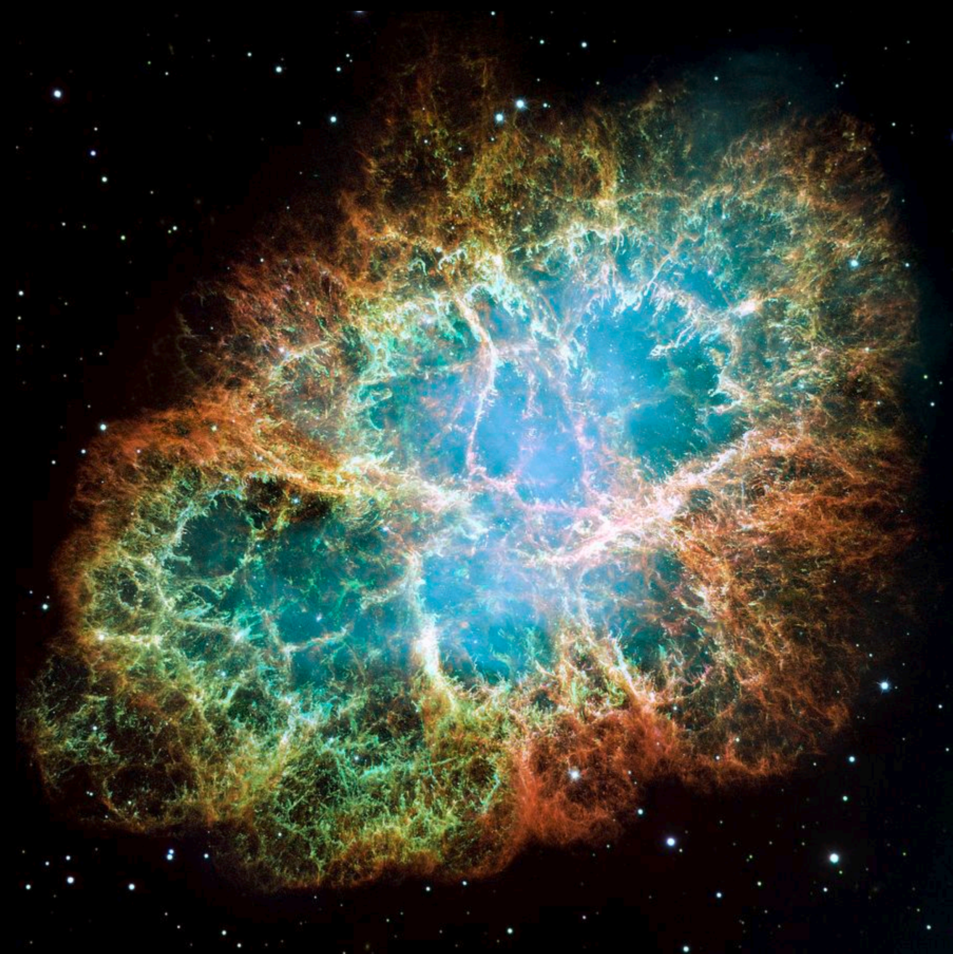
Choosing a technique



Synchrotron based techniques

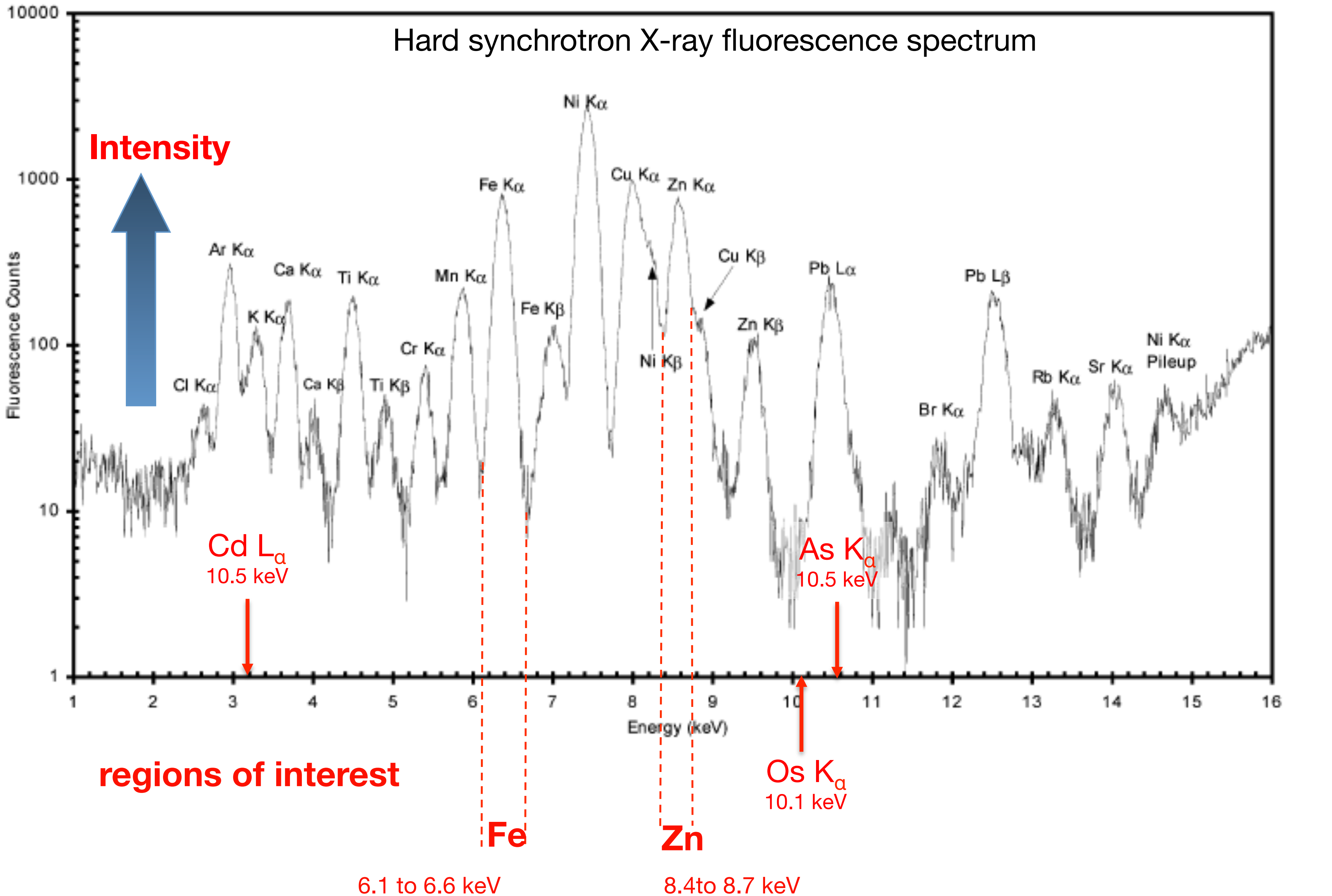


- Involves writing a peer-reviewed proposal for your experiment
- Involves travel to and accommodation at the facility
- 24-hour availability of the synchrotron beam
- Training, technical assistance and support provided
- Simultaneously multi-elemental
- Can be non-destructive (less so with newer, more powerful facilities)

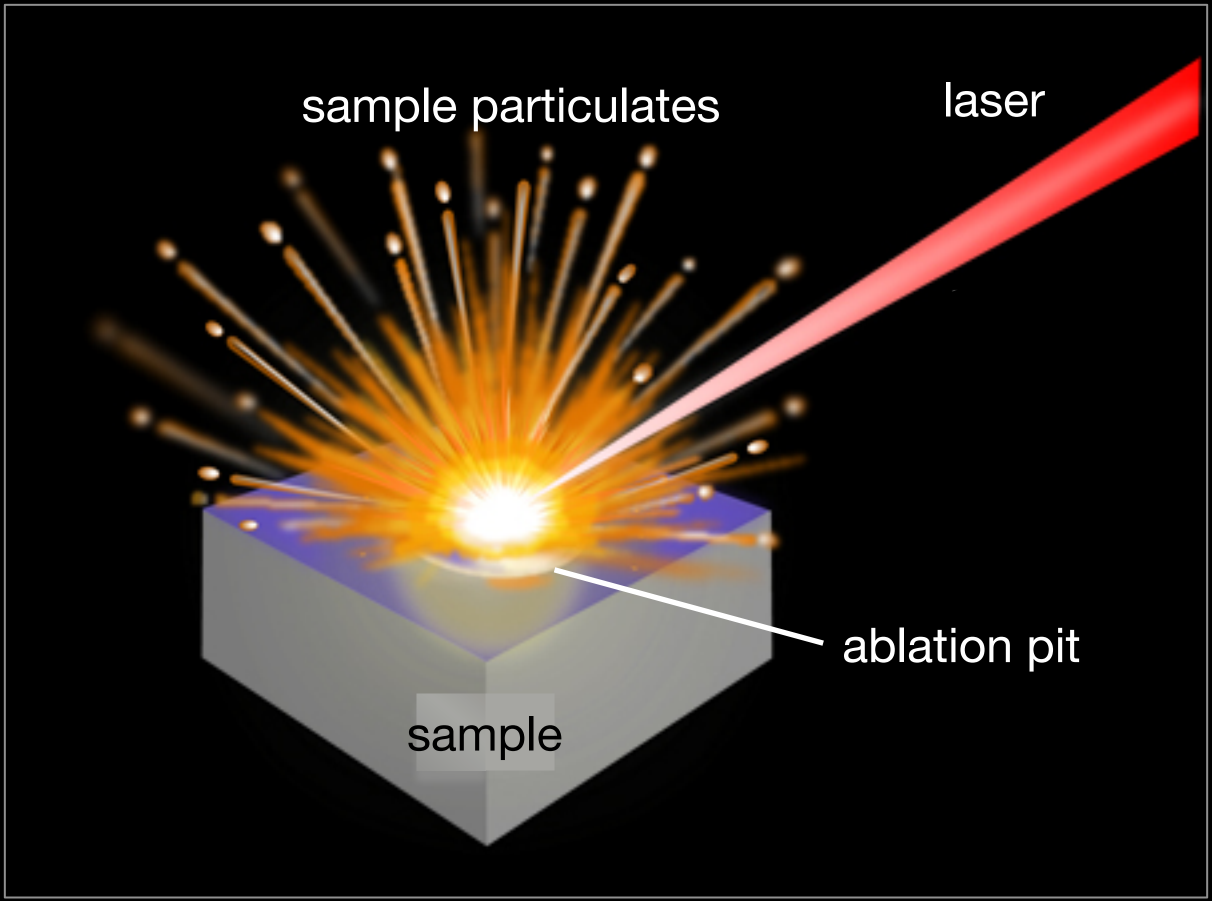


Synchrotron (blue) light emanating from the crab nebula

By NASA, ESA, J. Hester and A. Loll (Arizona State University) - HubbleSite: gallery, release., Public Domain, https://commons.wikimedia.org/w/index.php?curid=516106


Hard synchrotron X-ray fluorescence spectrum
Intensity
Fluorescence Counts
10000
1000
100
10
1
Ni Kα
Fe Kα
Cu Kα
Zn Kα
Ar Kα
Ca Kα
Ti Kα
Mn Kα
Cu Kβ
Pb Lα
Pb Lβ
K Kα
Fe Kβ
Zn Kβ
Cr Kα
Ni Kβ
Ni Kα
Pileup
Cl Kα
Ca Kβ
Ti Kβ
Rb Kα
Sr Kα
Br Kα
Cd Lα
10.5 keV
As Kα
10.5 keV
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
Energy (keV)
regions of interest
Os Kα
10.1 keV
Fe
Zn
6.1 to 6.6 keV
8.4to 8.7 keV

How it works: Laser ablation



- Power and frequency of the laser
- Sample specific interactions
- Efficiency of collection and transport of particulates into the ICP-MS
- Availability of matrix-matched standards
- Multi-elemental collection is sequential, not simultaneous

Interferences in ICP-MS

1. Polyatomics: Two- or three-atom clusters formed in the plasma with the same molecular weight as the analyte ion:

    Phosphorus (31) or ON (16 + 15)

    Sulphur (32) or O_2 (16 + 16)

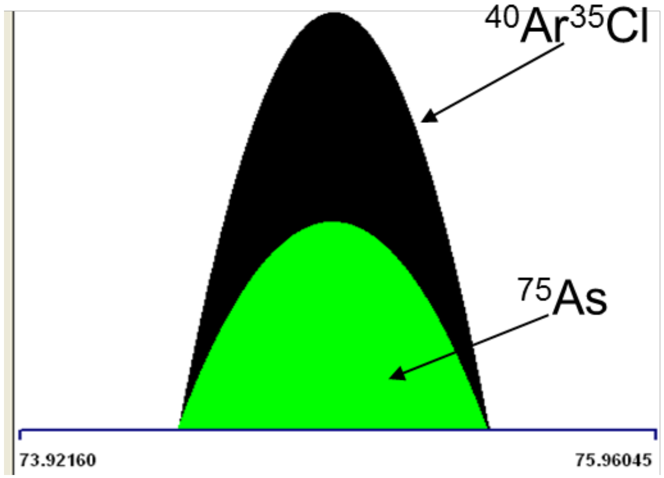
    Vanadium (51) or OCl

    Chromium (52) or ArC

    Iron (56) or ArO

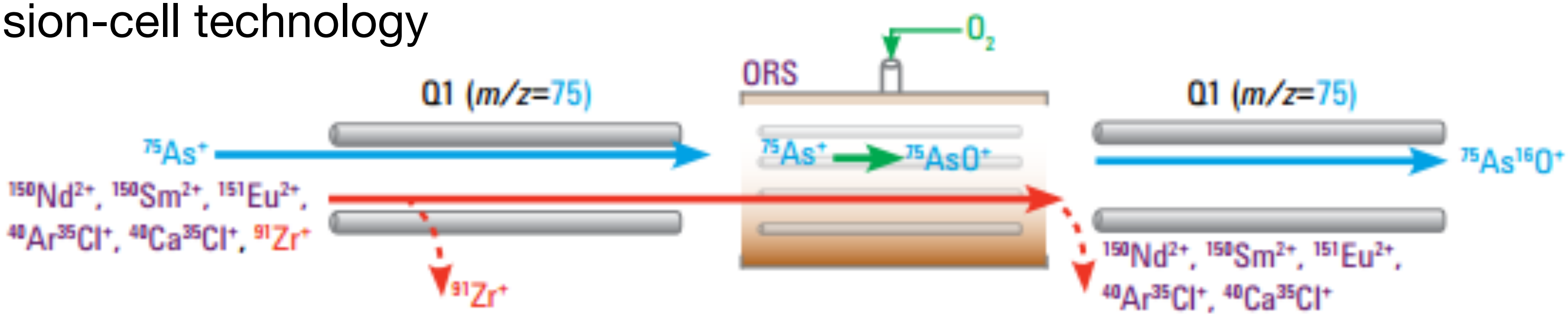
    Arsenic (75) or ArCl

    Selenium (78), Se 80 or Ar_2



2. Doubly charged ions
    - MS separates based on mass to charge ratio, we just assume that z = 1+
    - Proportion of 2+ ions formed can be ca. 2 %

Collision-cell technology



Access to elemental mapping techniques

For synchrotron access:

1. Visit the web pages of beamlines you see in papers of interest (or ask the Dartmouth TEA)

2. **Email the Beamline Scientists with your experimental details to discuss feasibility**

3. Write a Beamtime proposal short web form – abstract, significance, experiment

4. Include number of samples you have, and how long it will take

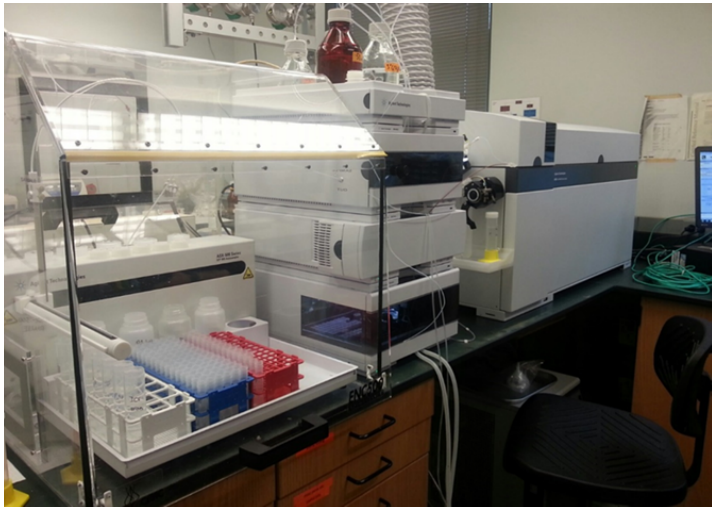
5. Consult synchrotron websites for submission deadlines

6. Fill out online form

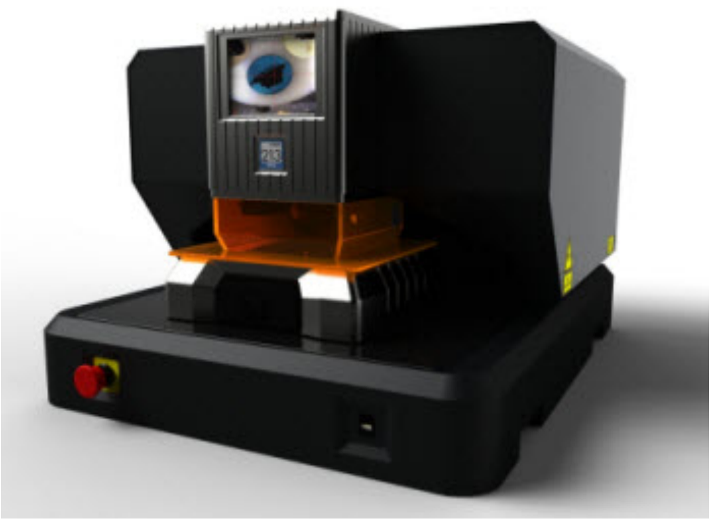
For Laser Ablation access

1. Contact Dartmouth TEA

Dartmouth TEA Core Services and Instrumentation



- Quantitative analysis
  - Water, soils, sediments
  - Biological: urine, serum, blood, tissue,
- Speciation analysis
  - Arsenic in water, urine, food
  - Mercury in water, tissues, sediments
- Spatial analysis
  - Laser ablation ICP-MS



- Agilent 7900 and 8900 ICP-MS
- Agilent 1260 LC
- Brooks Rand MERX-T, MERX-M Mercury Analyzer
- Milestone Dissolved Mercury Analyzer
- New Wave Research Laser Ablation 213 system

National Institute of Environmental Health Sciences

Your Environment. Your Health.

Dartmouth Superfund Research Program