State-of-the-science tools for measuring arsenic speciation in glacial sediments

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DNR core archive facility

Metal Partitioning in the Environment

Research

(1) Concentration

(2) Distribution

(3) Bioavailability

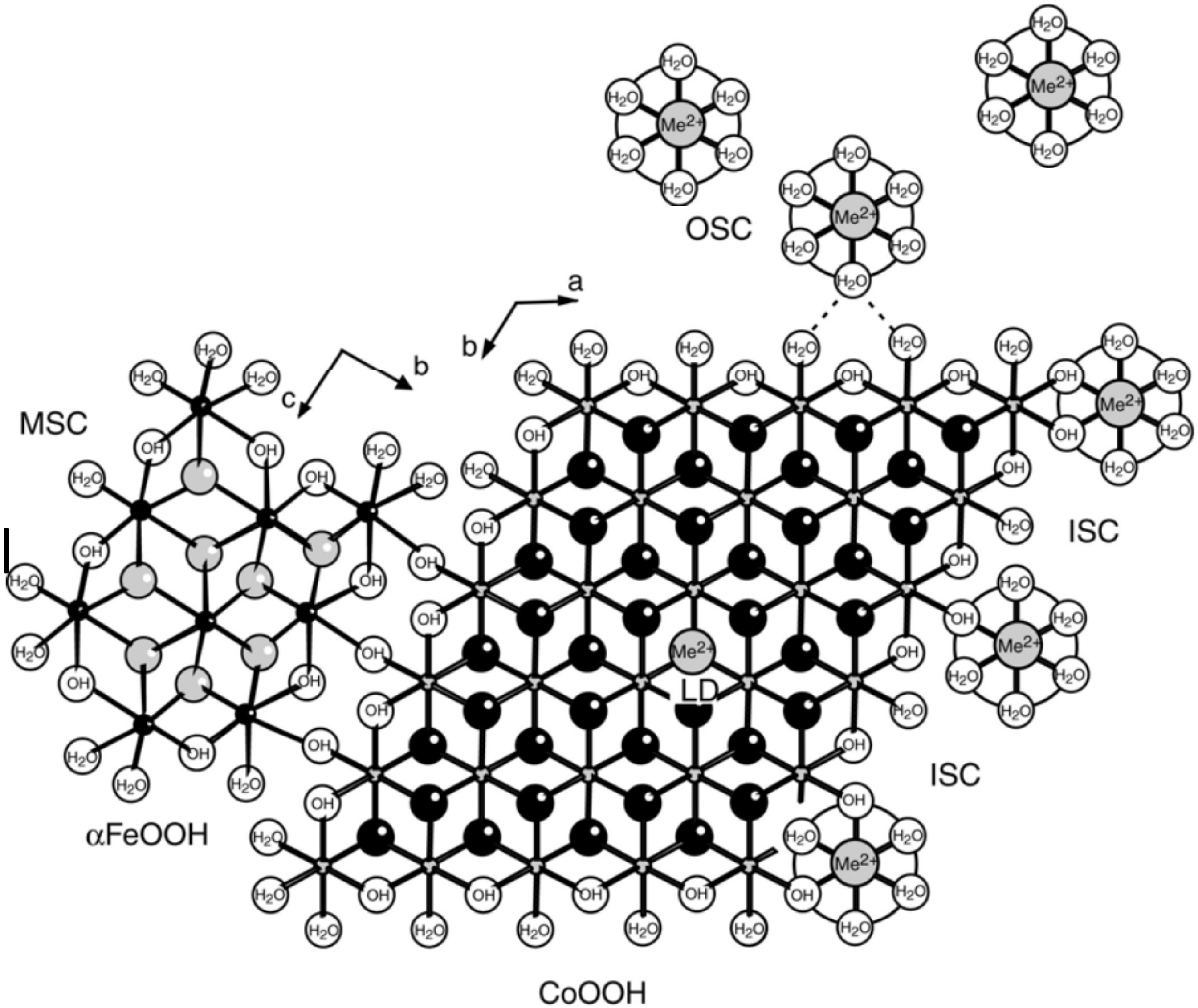
Approach

(1) Molecular-level

(2) Speciation

(3) Mechanistic

(4) Spectroscopy



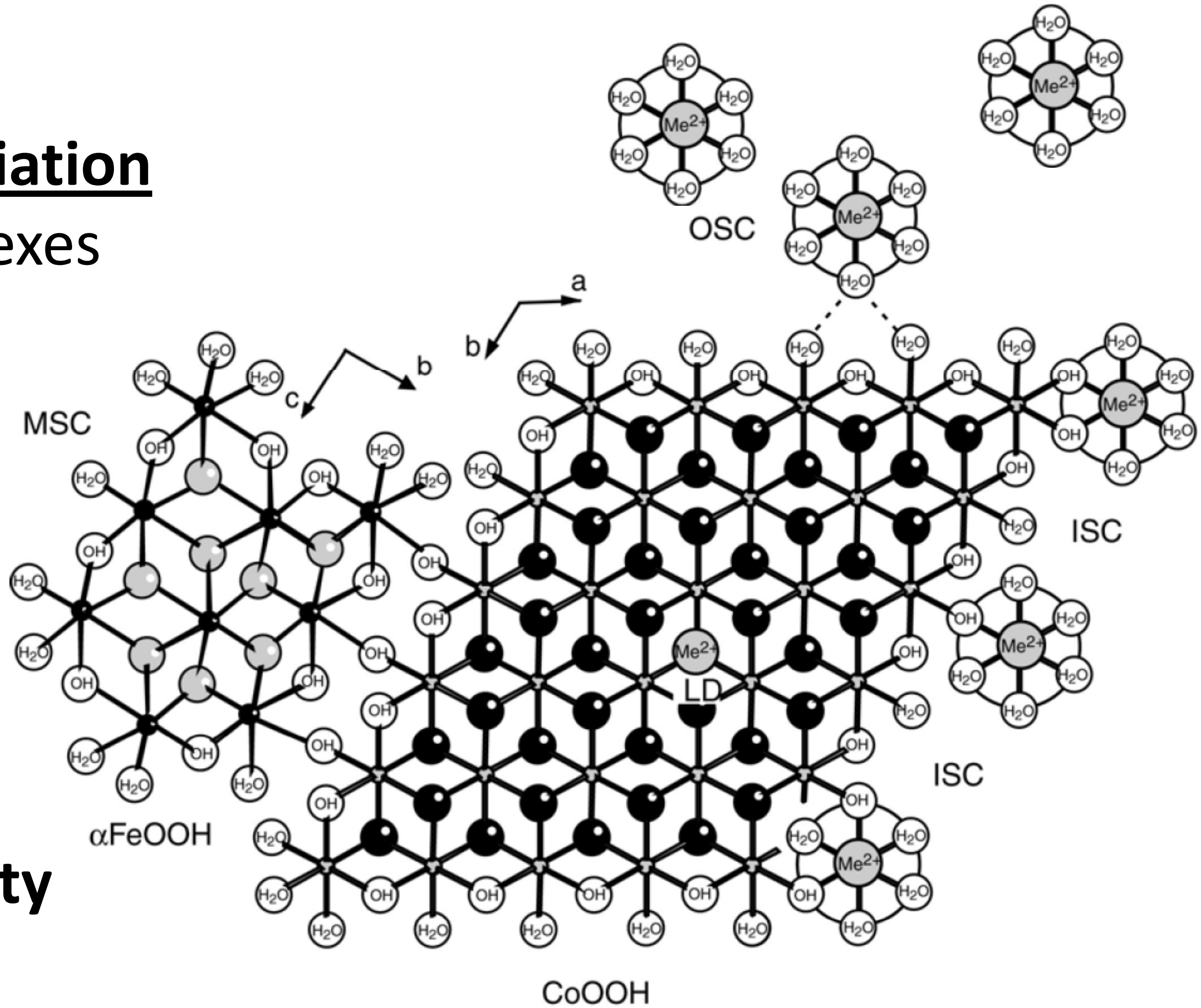
Adapted from Manceau et al., 2002

Metal Partitioning in the Environment

Examples of Speciation

- Aqueous complexes
- Adsorbed
- Precipitated

These are all influenced by **mineral surfaces** & **microbial activity**



Adapted from Manceau et al., 2002

Overview - 1

- Arsenic in domestic well water is a problem in Minnesota
- Arsenic is naturally occurring trace element
  -- values < 10 mg As / kg
- Arsenic in well water correlated with:
  -- glacial deposits
  -- well construction/placement choices
  -- Melinda Erickson

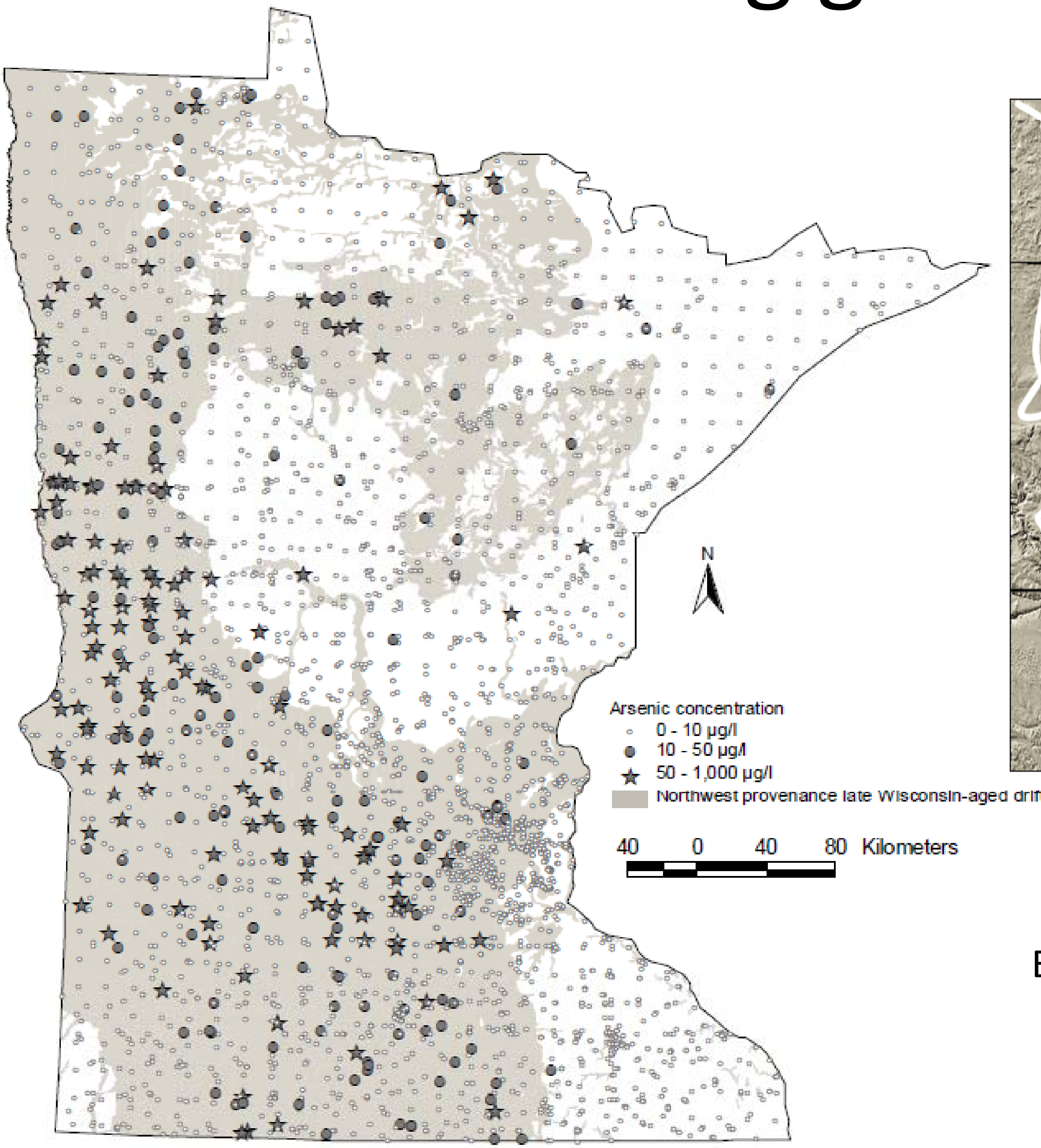
Overview - 2

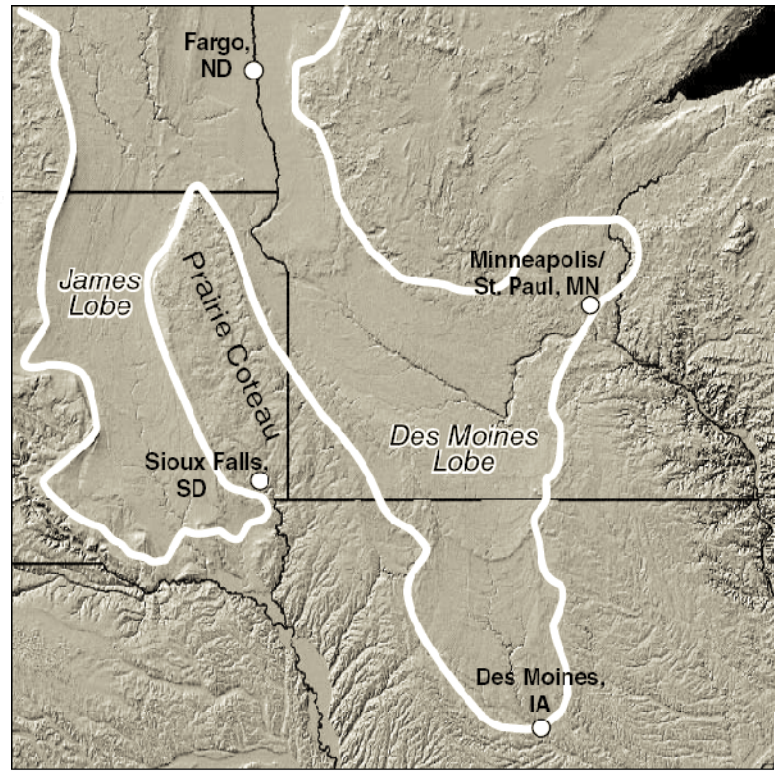
- Mineral phases hosting arsenic are not known
- Correspondence between stratigraphy and geochemistry not known
- Start at the beginning:
  - -- mineralogy
  - -- arsenic speciation

Arsenic
Trace Element & Contaminant

- Drinking water is the primary exposure
- [As] = 10 - 50 μg/L increases risk of cancer
- EPA definition of "elevated" [As] > 10 μg/L

Arsenic-bearing glacial sediments

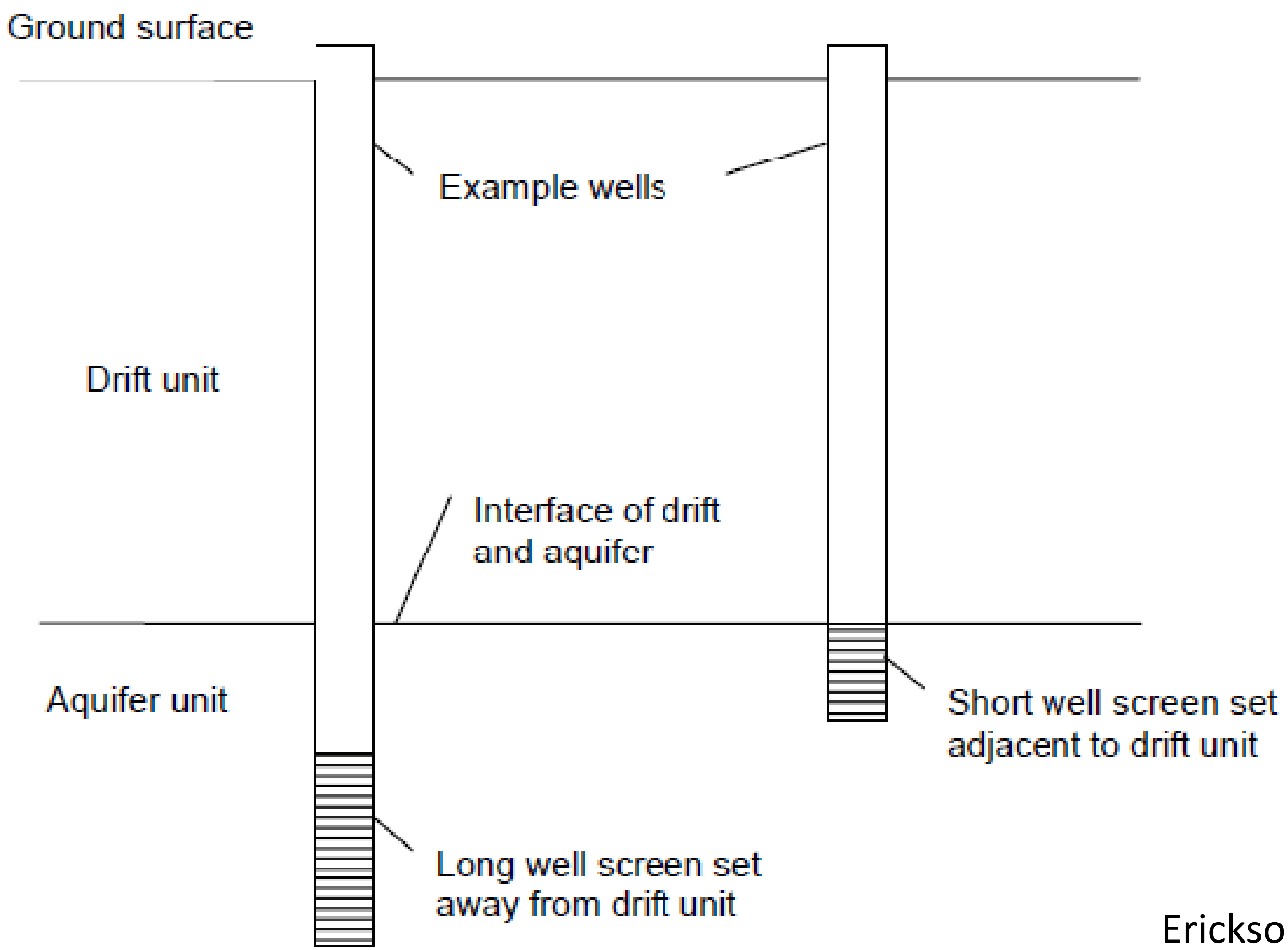




Erickson 2005; Jennings 2009

Risk Factors

Well screen placement/construction
Proximity to glacial contacts



Erickson 2005

(1) Arsenic in glacial sediments

(2) Risk Factors: well screen proximity to glacial contacts

Little nagging question…

…why is arsenic still a problem in new wells?

Complexity – Heterogeneity - 1

Distribution of elevated [As] wells enigmatic:

- -- wells in close proximity
- -- wells with similar depth
- -- wells with similar properties aqueous geochemistry
- -- ***different*** [As]

Complexity – Heterogeneity - 2

Des Moines Lobe tills = complex group of glacial deposits

-- variable source materials

-- not all strata have elevated [As]

Some elevated [As] wells screened in older, pre-Wisconsin age tills

Open Questions

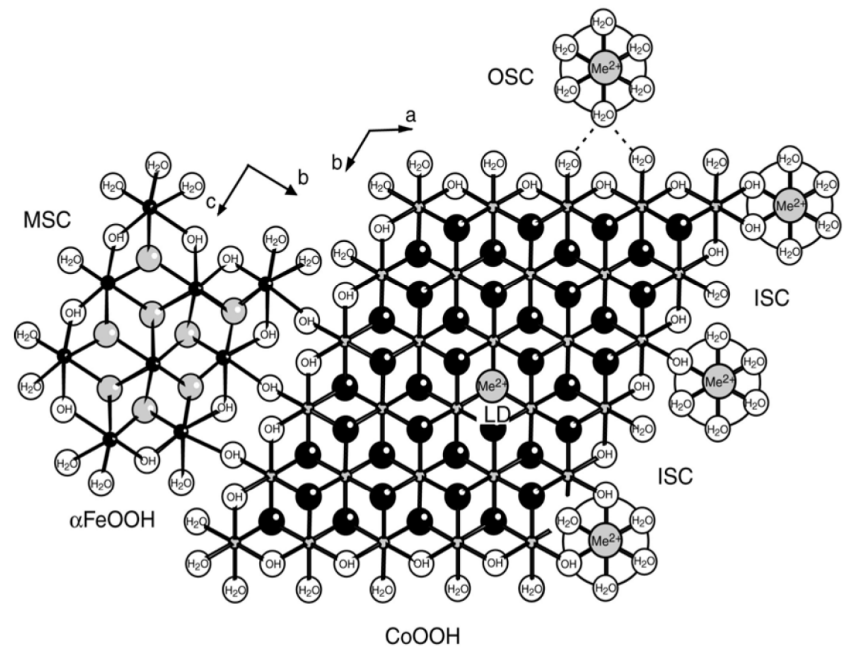
- Which formation(s) are the source of the arsenic?
- What are the primary mineral phase(s)?
- Do stratigraphy and geochemistry correspond in formations?
- Can we predict arsenic vulnerability in west-central Minnesota?

New Focus

- All evidence -- source of arsenic to ground-water is naturally occurring ***minerals***
- Shift focus from aqueous phase to solid phase
- Start by identifying the source(s) of arsenic

Solid Phase Speciation

- A single element may exist in many different chemical forms
- Chemical form or ***speciation*** determines its behavior in environment



Measuring Solid Phase Arsenic Speciation

(1) Synchrotron Radiation
X-ray Absorption Spectroscopy

(2) Sequential Extractions

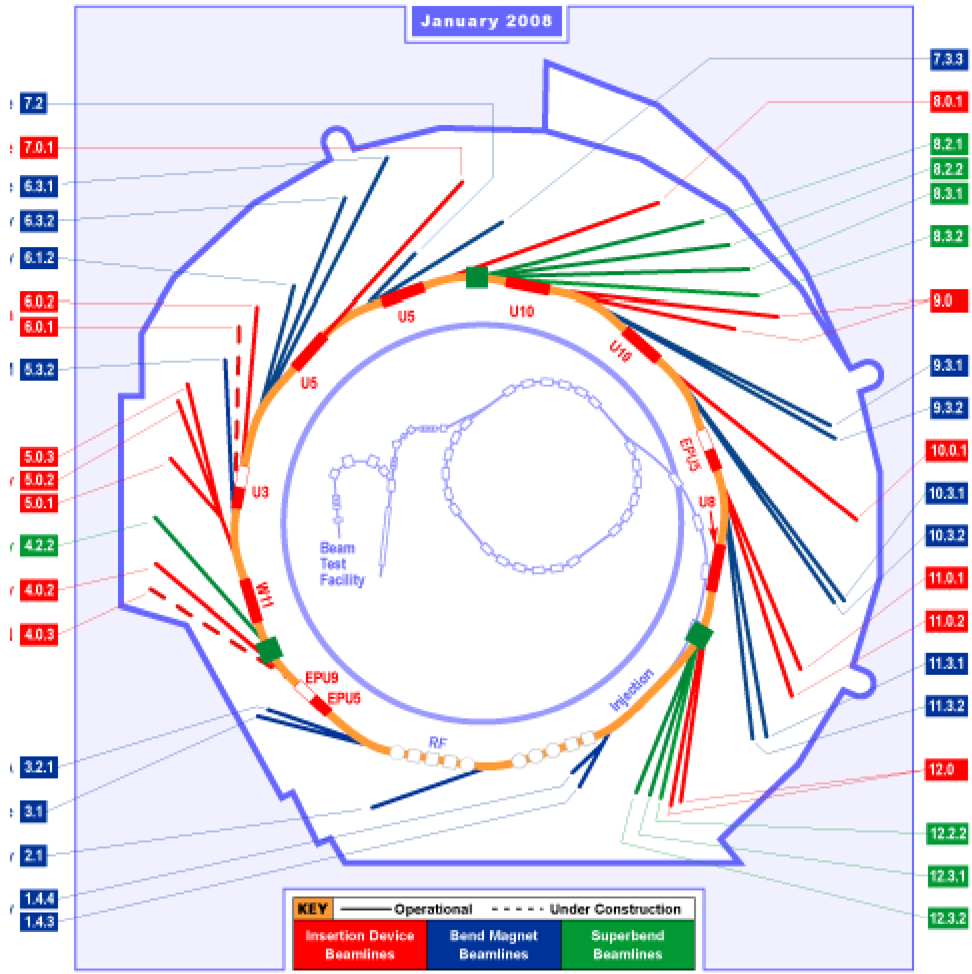
(3) Glacial sediments
-- aquifers (sand-gravel)
-- confining layers (tills)
-- interfaces (contacts)

X-ray Absorption Spectroscopy (XAS)

Advantages – Capabilities

- Elementally specific
- Sensitive to valence state
- Sensitive to the local bonding environment
- Choices in spatial resolution
- Environmentally relevant conditions

Where to get X-rays?



- Synchrotron Facilities
- Department of Energy
- Berkeley, CA
- Argonne, IL

Photo credit: Roy Kaltschmidt
http://www.als.lbl.gov/als/als_users_bl/bl_layout.html

Samples

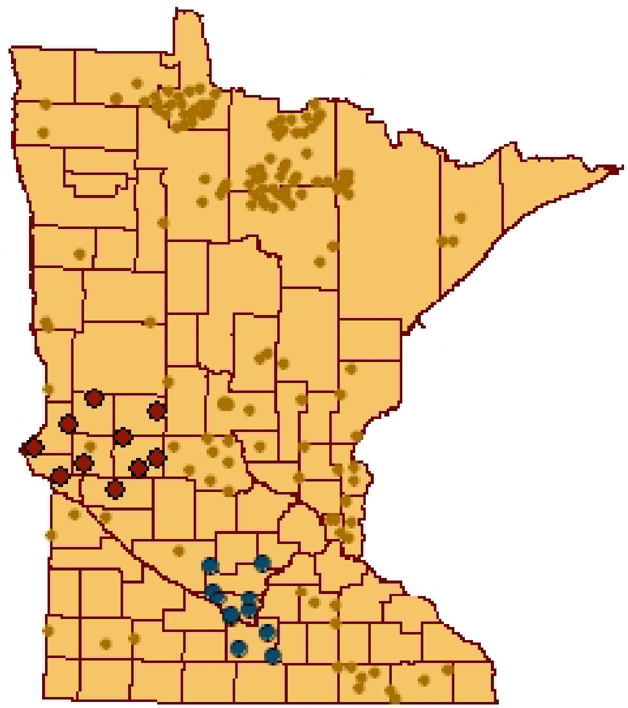
(1) Begin with archived rotary sonic drill cores (RED)

DNR, Lands and Minerals Drill Core Library, Hibbing, MN

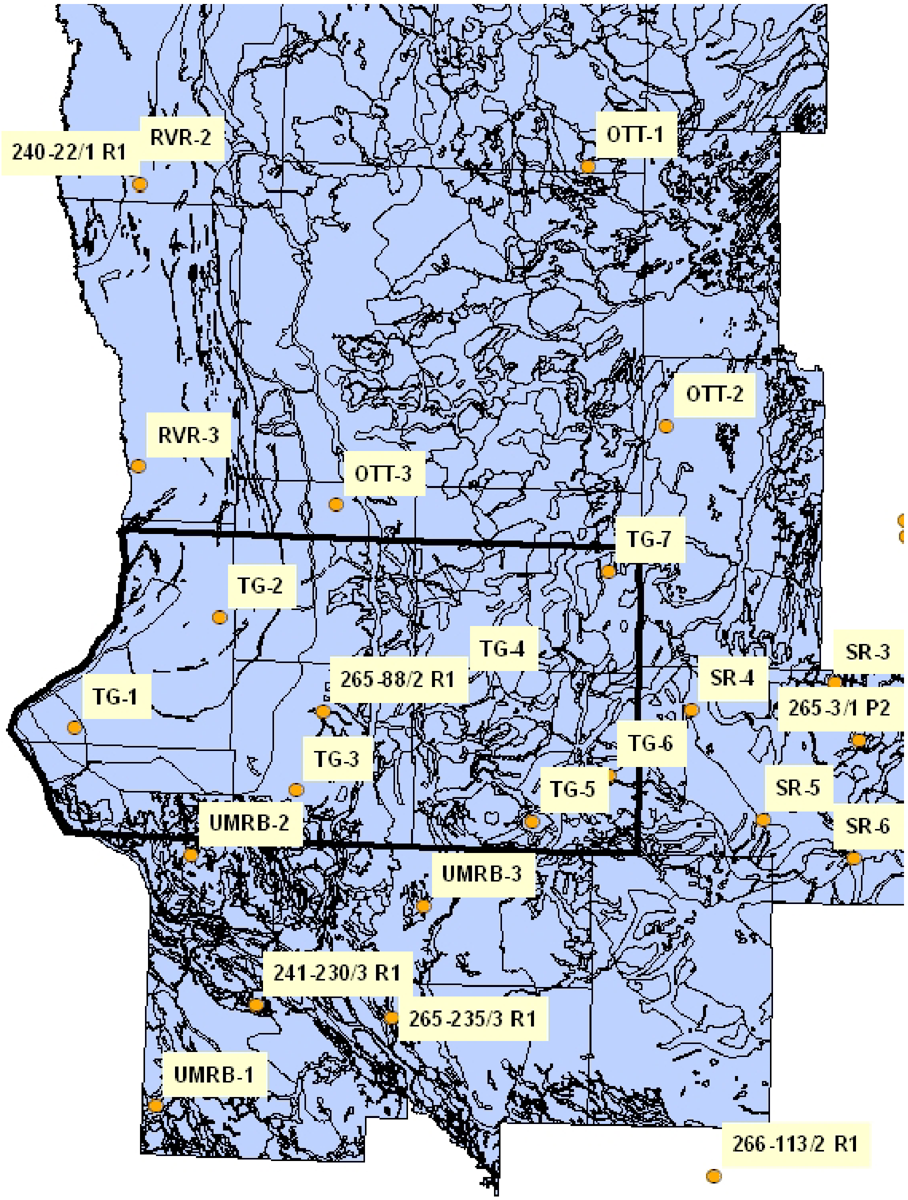
Thanks to Rick Ruhanen and Jordan Goodman

(2) Participate in new drilling

Minnesota Geological Survey (BLUE)



Samples - 1



Archived Rotary Sonic Cores

TG-1	255368
TG-2	255369
TG-3	255370
TG-4	255371
TG-5	255372
TG-6	255373
TG-7	255374
OTT-3	251486
UMRB-2	20341
UMRB-3	20343
SR-4	249857
TR-3	256716

Samples - 1

10 Cores / 250 samples

Counties

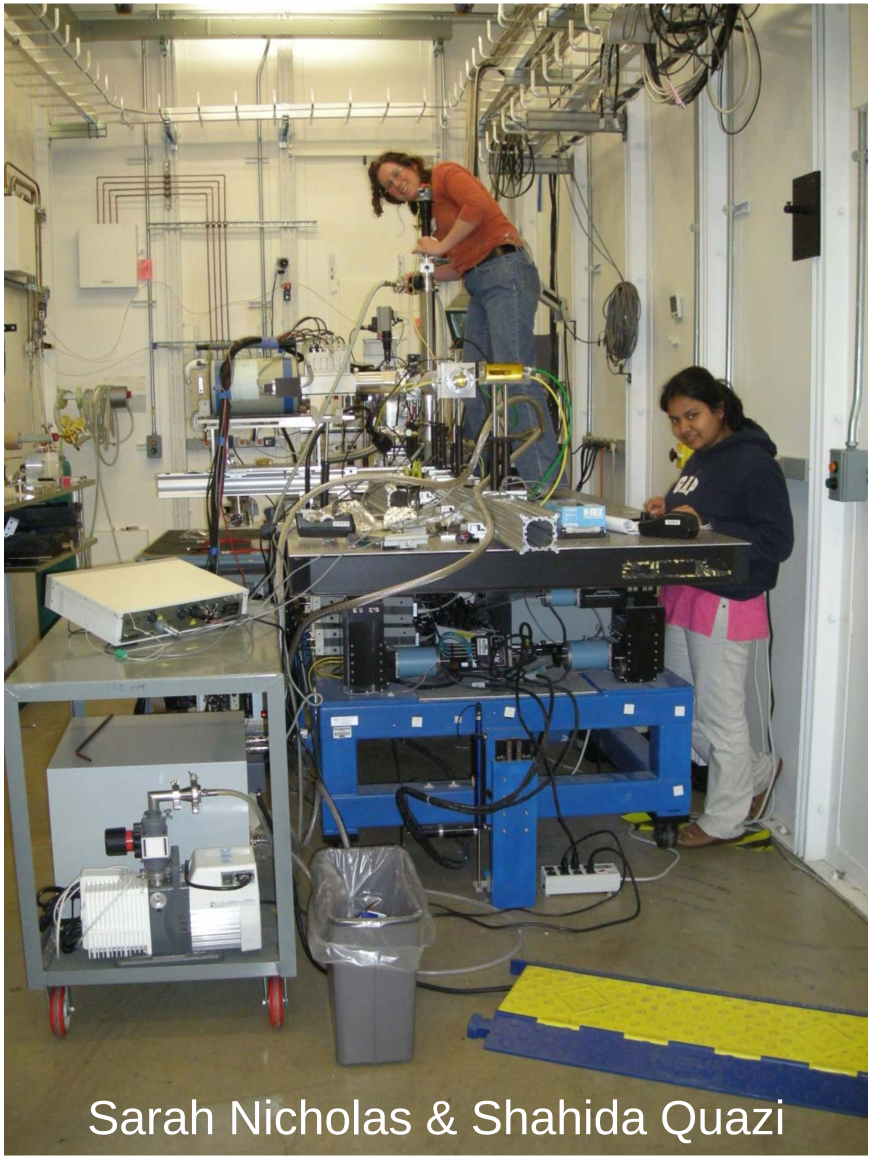
Traverse, Grant, Stevens, Douglas, Pope, Big Stone, Swift

Samples - 2

10 ***fresh*** cores / 426 samples

Counties
Sibley, Nicollet, and Blue Earth

Useful Tools: “bulk” XAS



Glacial sediments

aquifers (sand-gravel)
confining layers (tills)
interfaces (contacts)

Method Question

Can we measure As < 10 mg/kg?

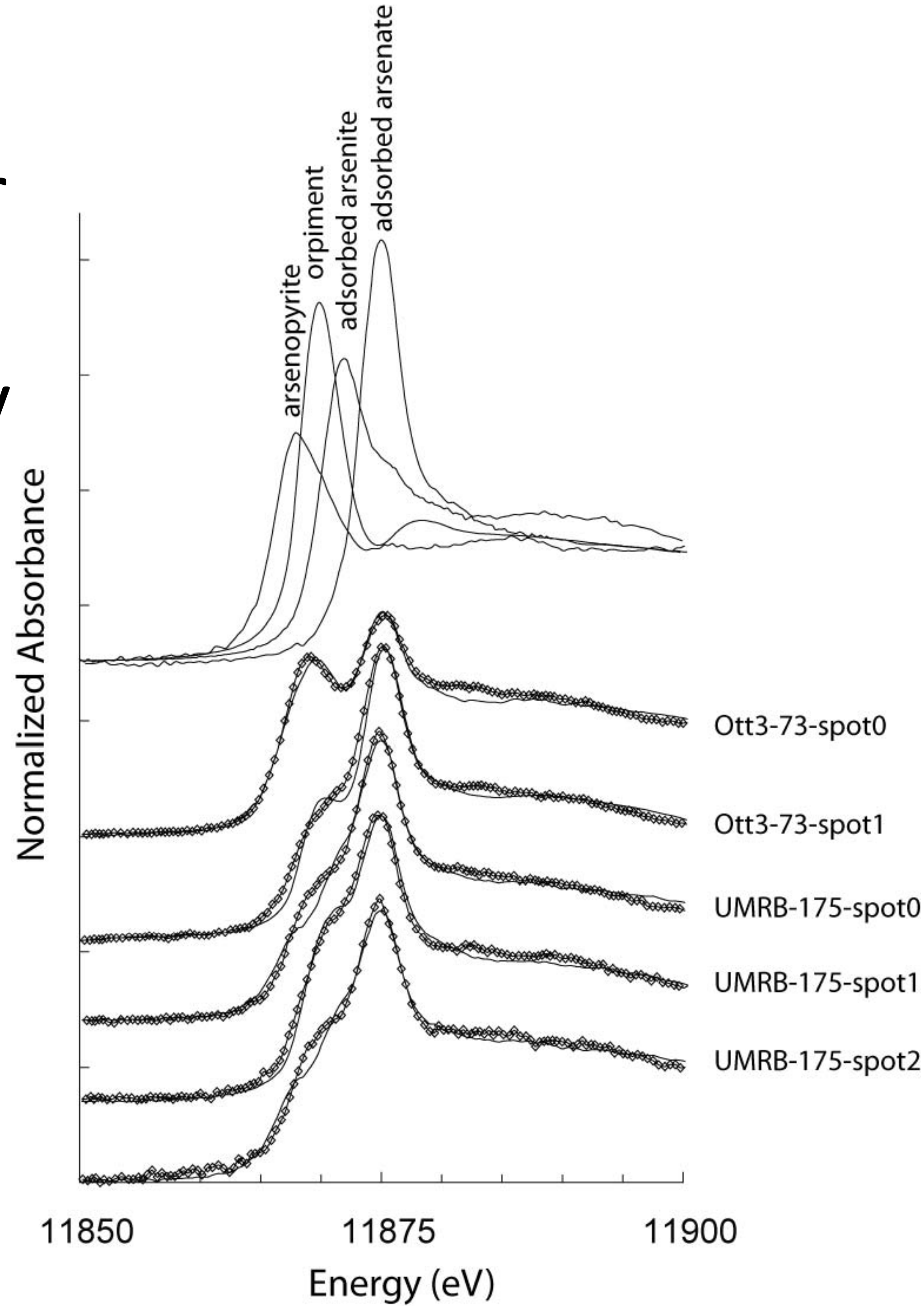
Facility

Advanced Photon Source
Argonne National Laboratory

Answer

Yes we can!

X-ray absorption near edge structure (XANES) spectroscopy



Results

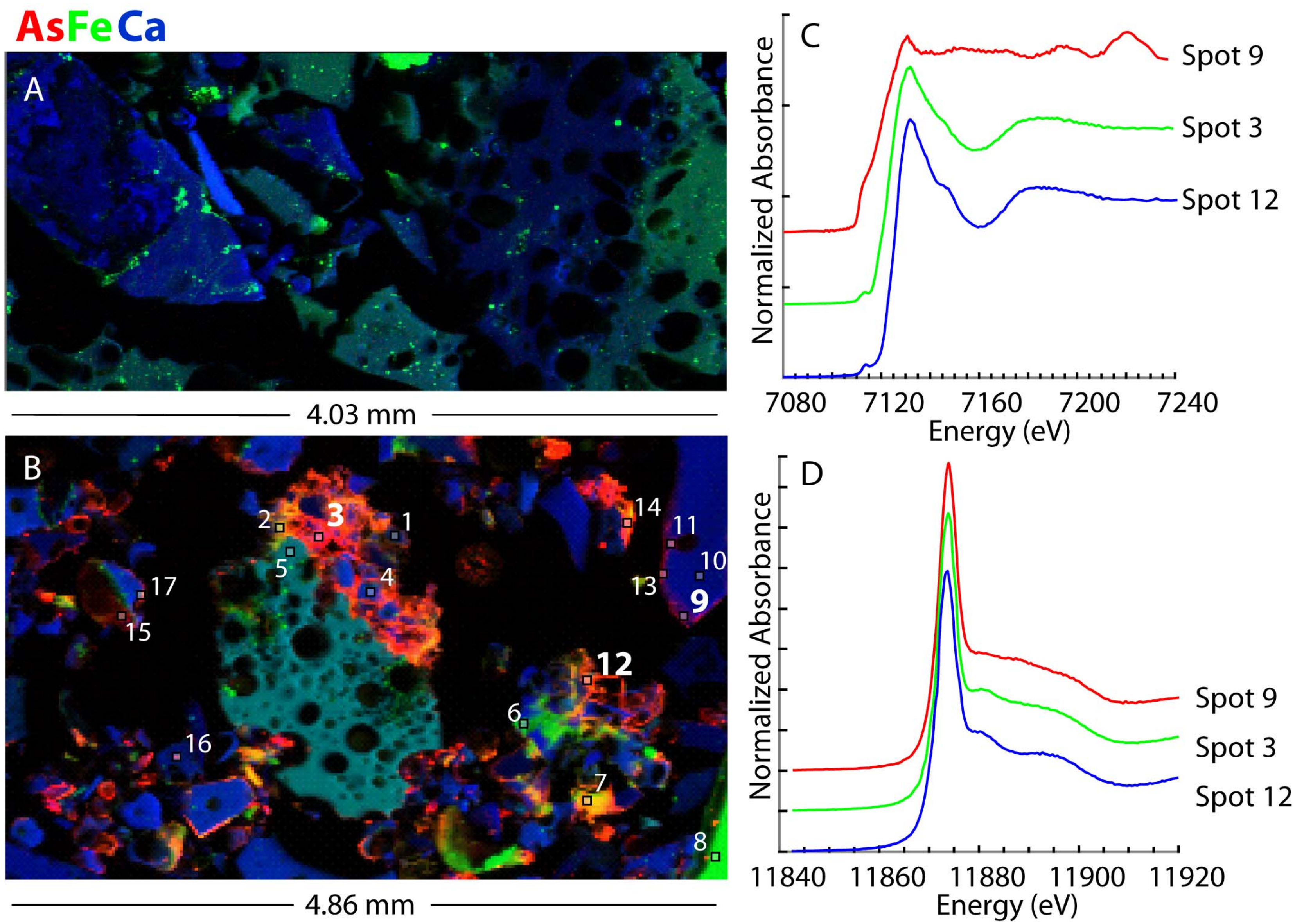
-- Can detect 4 mg As/kg

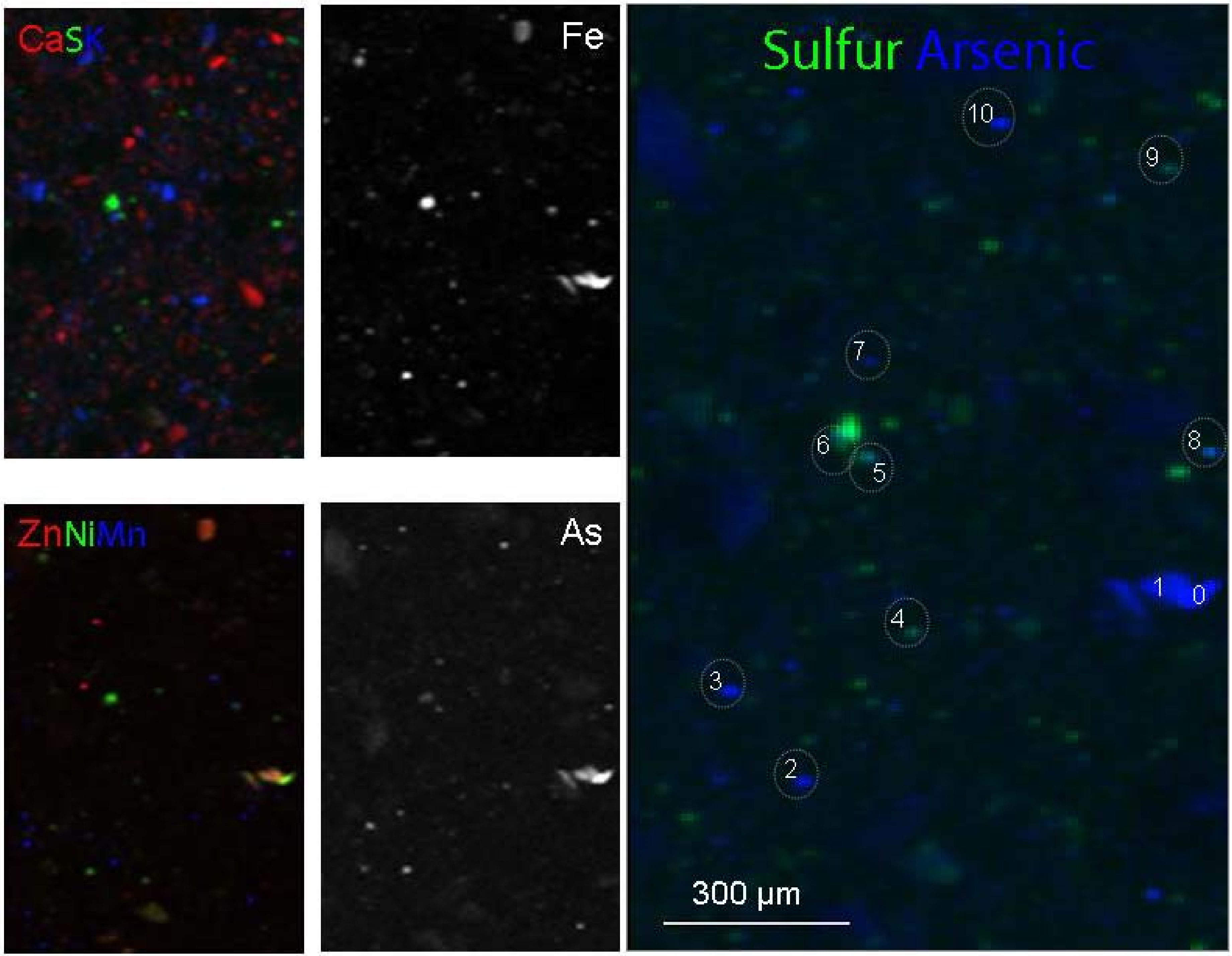
-- See spatial heterogeneity

-- Reduced As present

Nicholas & Toner (unpubl)

Useful Tools: Microprobe XAS





CaSK
Fe
Sulfur Arsenic
10
9
7
6
5
8
1
0
4
3
2
300 µm
ZnNiMn
As

Microprobe XANES spectroscopy

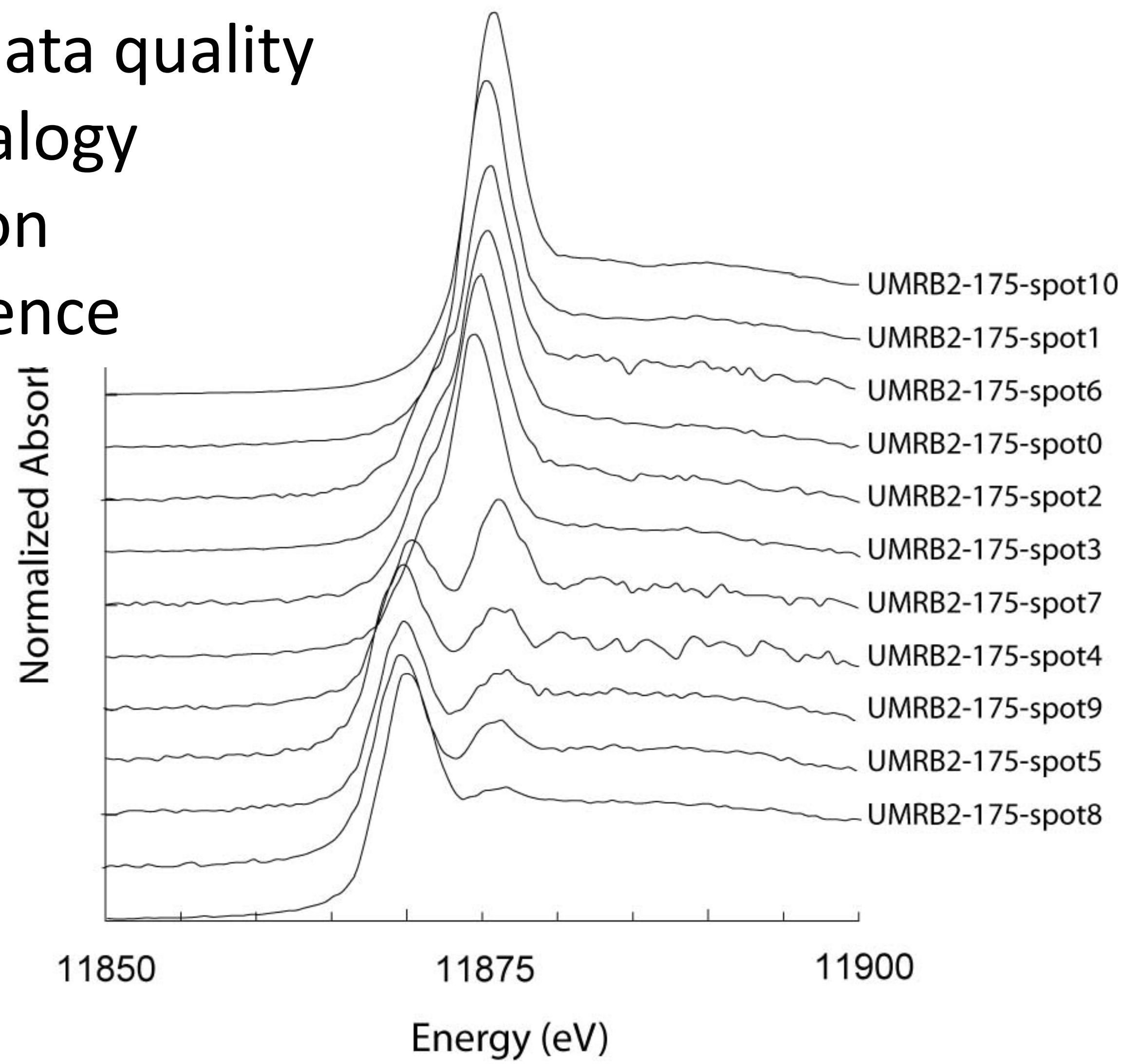
Results:

Microprobe improves data quality

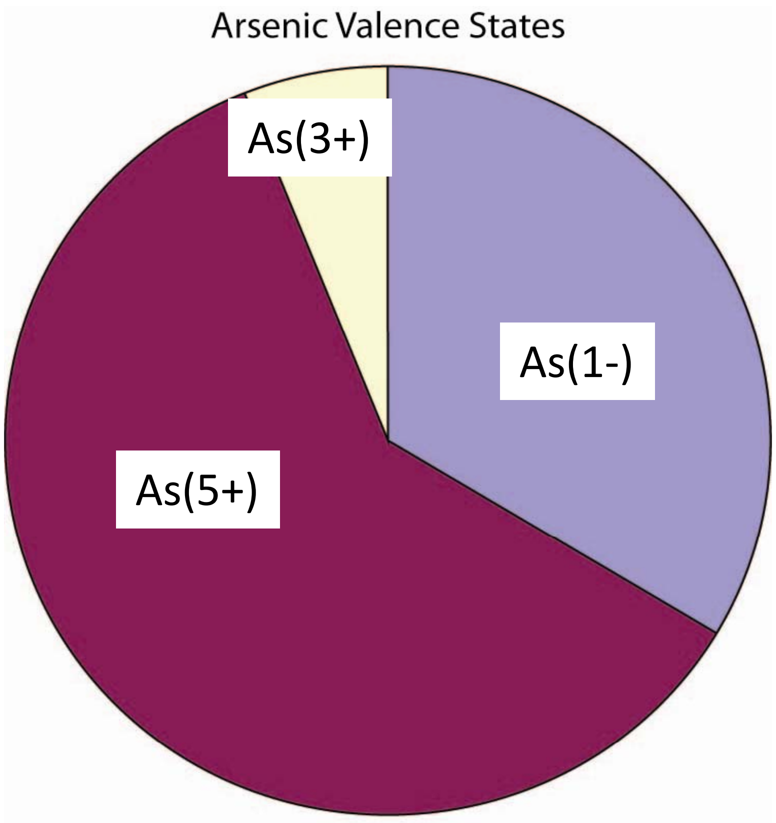
Begin to unravel mineralogy

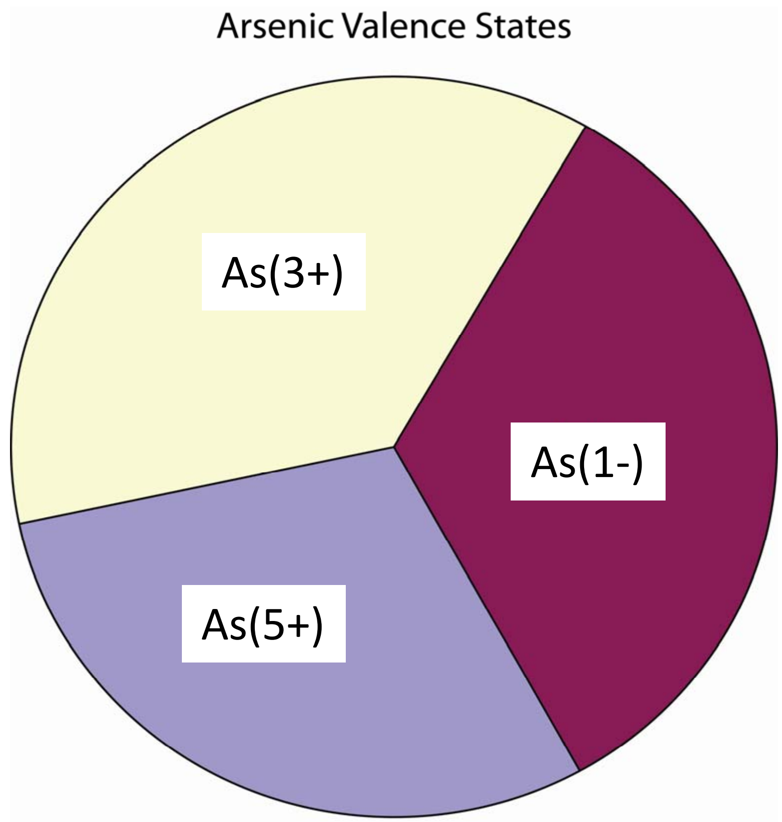
-- X-ray diffraction

-- X-ray fluorescence



Proportion of Arsenic Valence States
Microprobe XANES spectroscopy





Notes:
(1) From linear least squares fitting
(2) Distribution of valence states in archived cores
(3) Upper Minnesota River Basin, core 2, 175 ft depth
(4) Ottertail County. Core 3, 73 ft depth

Next Step

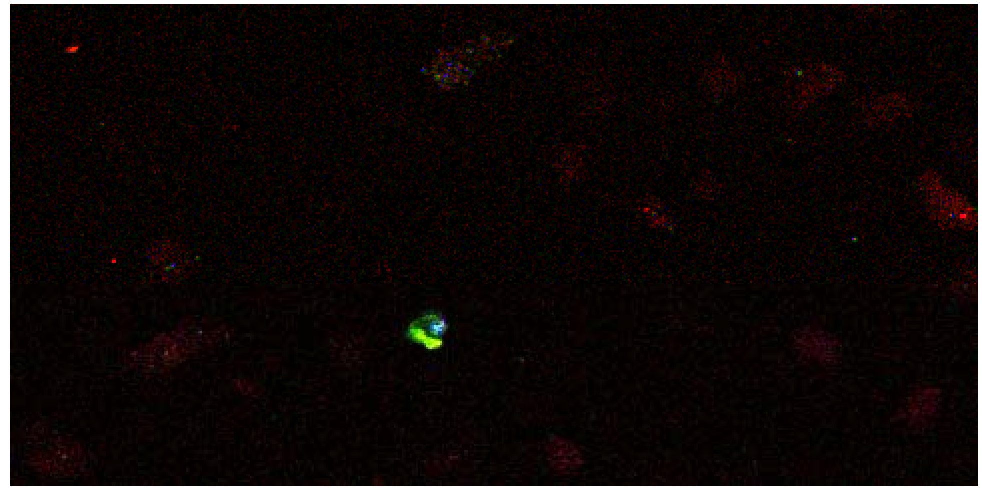
Improve Sample Coverage

-- Point-to-Point

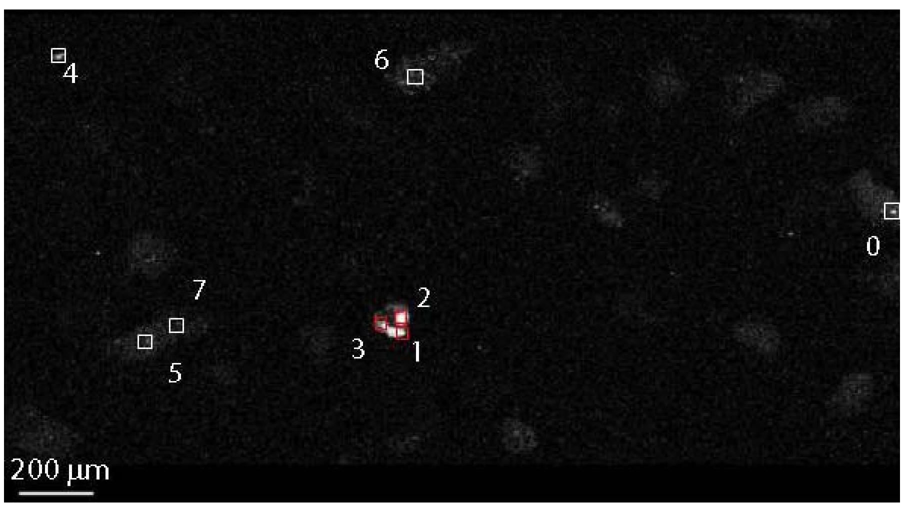
-- Pixel-by-Pixel

-- “Chemical Mapping”

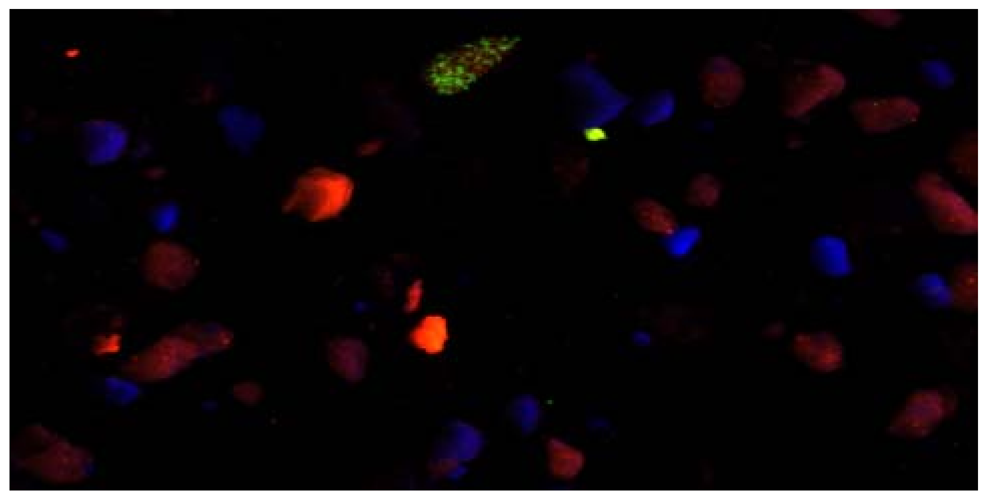
As(5+)As(3+)As(1-) Chemical mapping



Pixel-by-pixel



FeMnCa



Conclusions

- Using As XAS spectroscopy we can
  - Identify (and quantify) As valence states in archived tills
  - As(5+), As(3+), As(1-)

- Detection limit is appropriate for trace As in solid phase

- Archived rotary sonic cores are valuable for the study of As geochemistry

- We have a lot of work to do!

Integration Steps - 1

- All samples by sequential extraction
- Sub-set of samples by XAS
- Add speciation data to GIS database
- Geospatial analysis
- Mapping

Integration Steps - 2

Dream 1

Sub-surface arsenic speciation mapped with stratigraphy

Dream 2

Arsenic vulnerability map for regions of MN

Acknowledgments

Center for Urban and Regional Affairs

Faculty Interactive Research Program

http://www.cura.umn.edu/

“Arsenic Vulnerability Maps for New Domestic Wells in West-Central Minnesota”

Thank you!




Understand Distribution of Arsenic

Best Practice

- Strategic placement of wells
- Probability of clean water is highest

To achieve this goal we must understand

- Arsenic source(s)
- Bio-geo-chemical processes
- Human choice/activity

Measuring Solid Phase Arsenic Speciation

Arsenic speciation in the solid geological materials will be accessed with three different techniques:

(1) total arsenic and associated geochemical composition in the solid phase;
(2) distribution of arsenic forms among species that are defined operationally to estimate arsenic *lability* – the likelihood of release to groundwater from solids; and
(3) direct spectroscopic measurements at the micron spatial scale to define exactly the arsenic speciation in particles composing the sediments.