

PIPE SCALE ANALYSES FOR CCT EVALUATION

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US EPA Office of Research and Development (ORD)

**19th Annual EPA Drinking Water Workshop: Small System
Challenges and Solutions**

Corrosion Training Session (10A)

SEPTEMBER 1, 2022



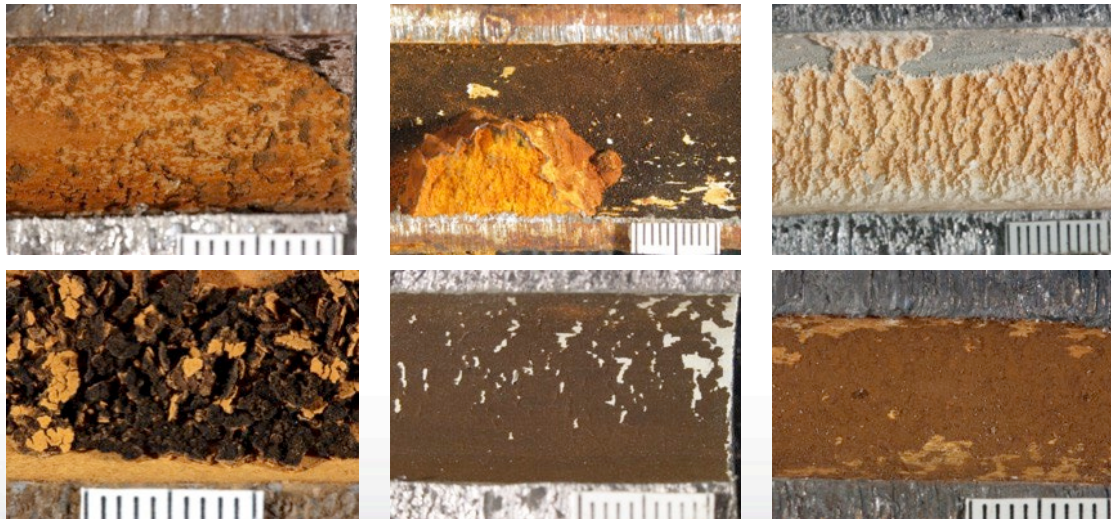
What is a Lead Service Line (LSL) pipe scale?

- The combination of lead corrosion products and deposited materials found inside a LSL
 - Crystalline lead minerals
 - Deposited materials
- Represents decades of reactions and changes in water quality/treatment



Why analyze LSLs?

- To evaluate the state of corrosion control treatment (CCT) and understand lead release
- To predict impacts of potential changes to CCT or other water treatment processes
- To address shortcomings in the ability of theoretical models to predict the lead minerals forming in the field





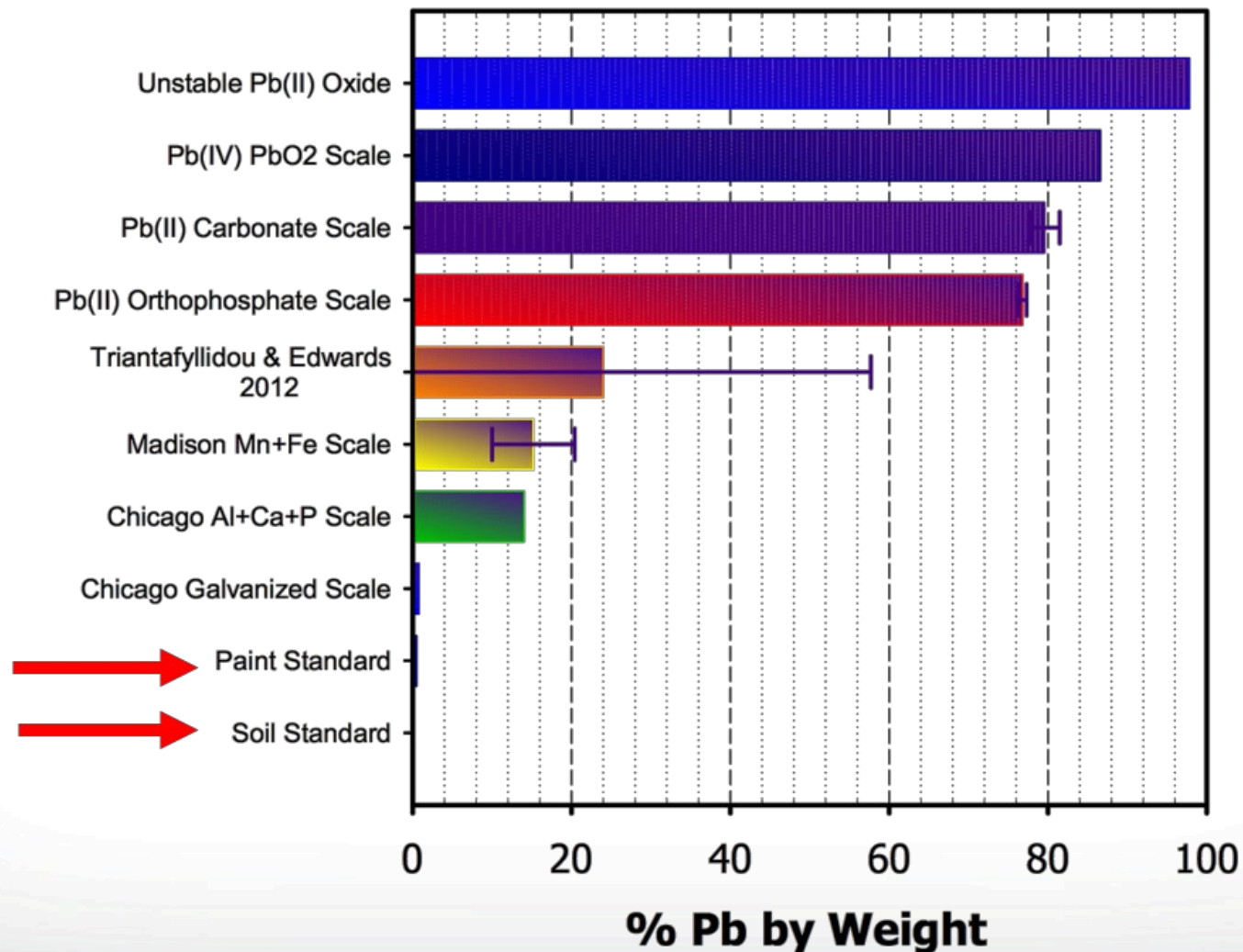
Why analyze LSLs?

- When present, LSLs are the largest source of lead to drinking water
- Still many years out from removing all LSLs in the United States
- Systems need to know by what mechanism lead release is being controlled.
 - Understanding why lead levels are low can be important too!





Lead scales contain a lot of lead...



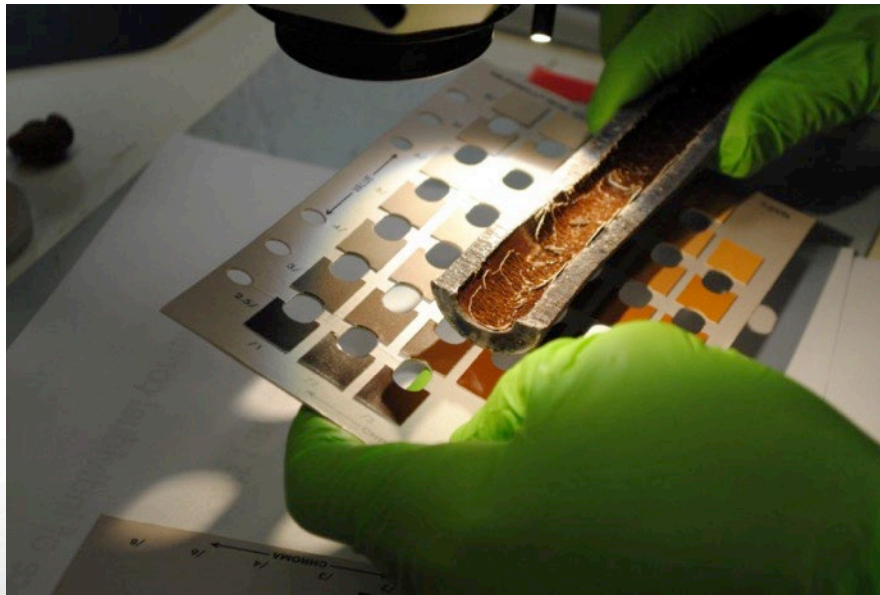
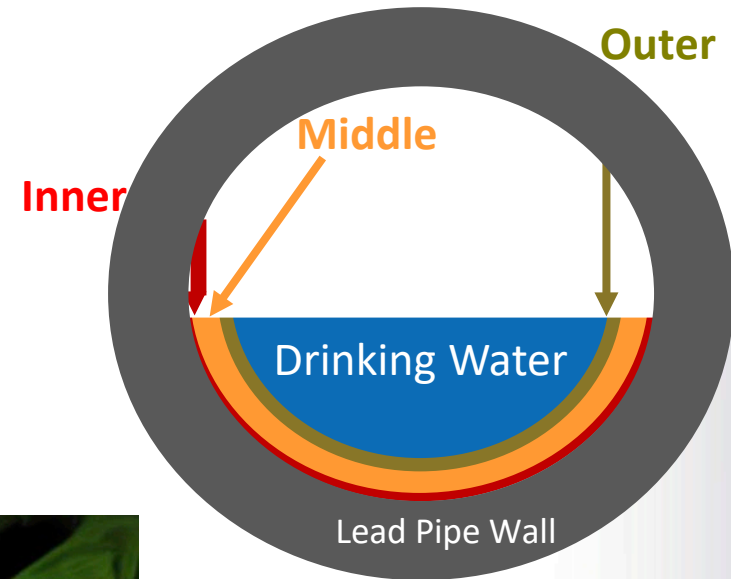
Considerations

- Due to the complex nature of many LSL scales there are several practical and technical considerations to take into account
- This presentation will focus on:
 - How to sample scale from LSLs
 - LSL scale analysis
 - Powder X-ray diffraction
 - Scanning electron microscopy/energy dispersive spectroscopy



Visual Characterization

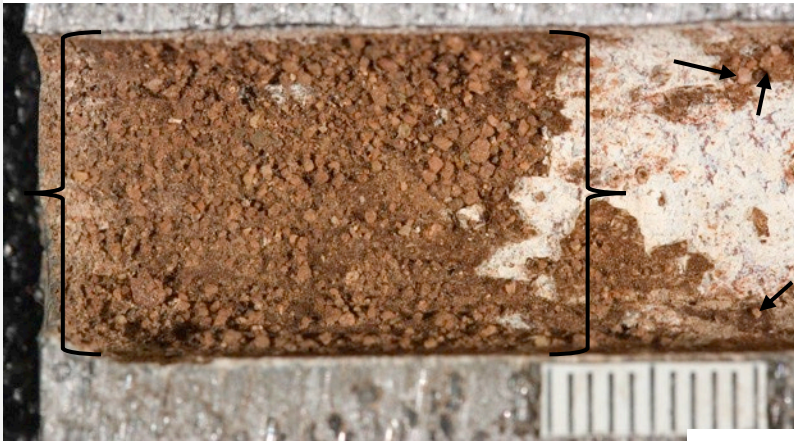
- Detailed description and documentation of the scale
 - texture, color, physical characteristics etc.
 - “Macro” and microphotography
- Designation of scale layers



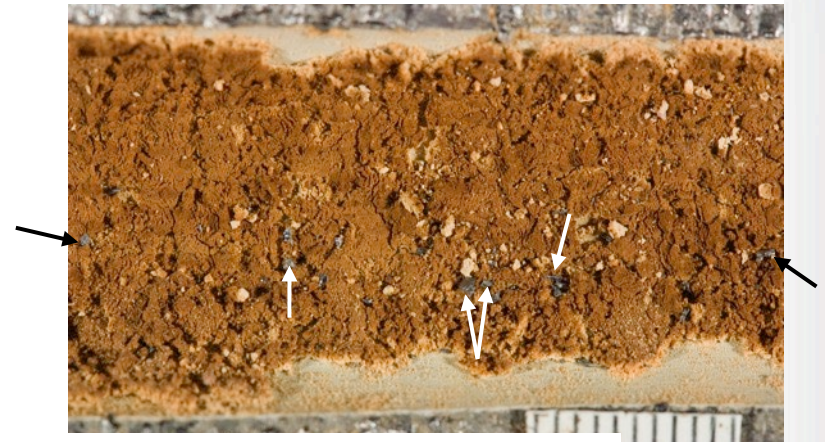
Cautions and Caveats

- Contamination/Disturbances

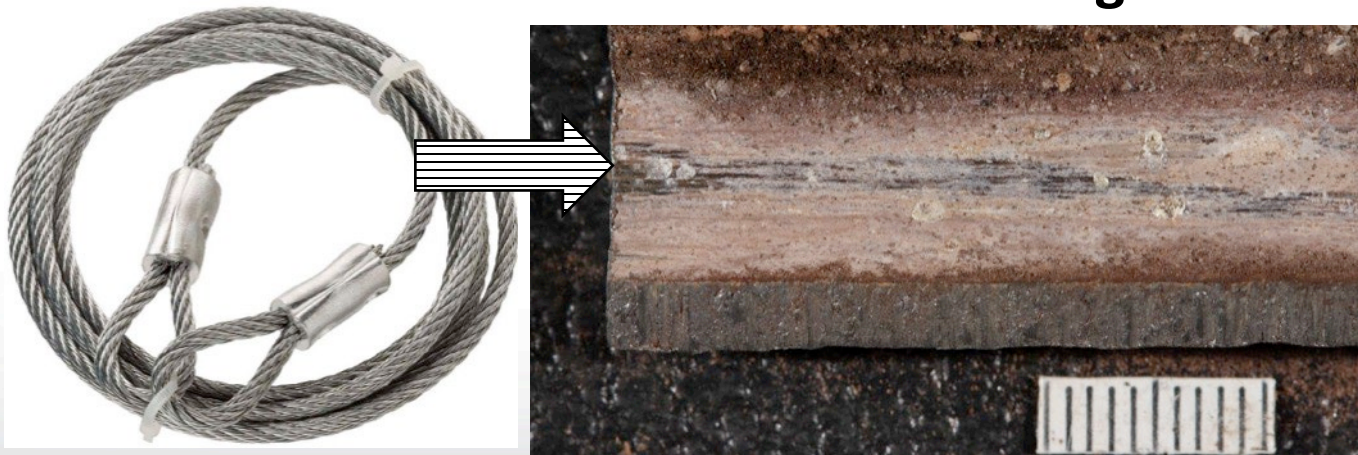
Trench Sediment



Lead Shavings



Cable Tooling

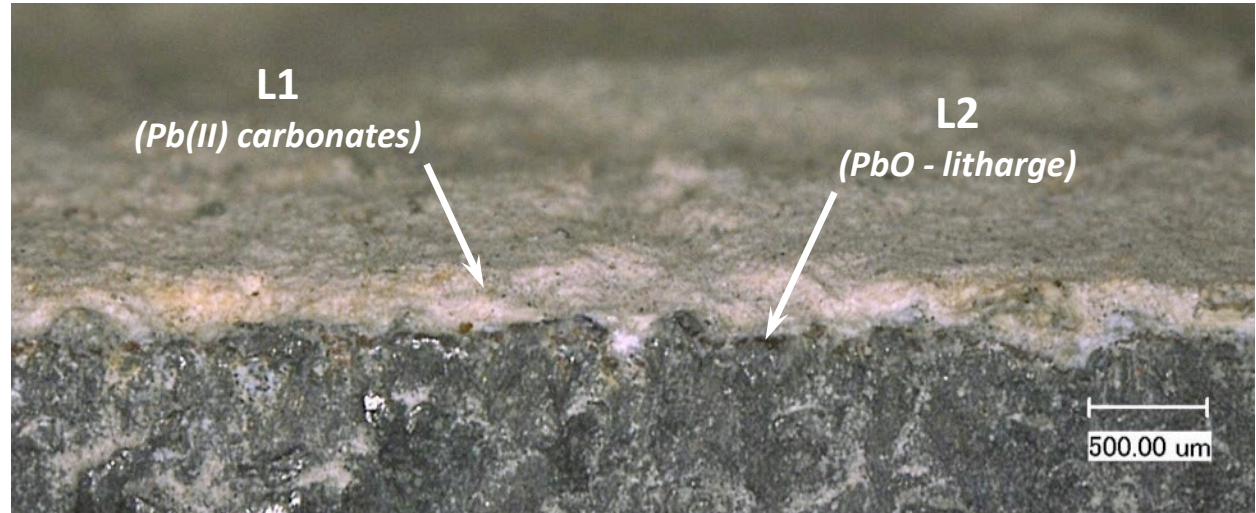




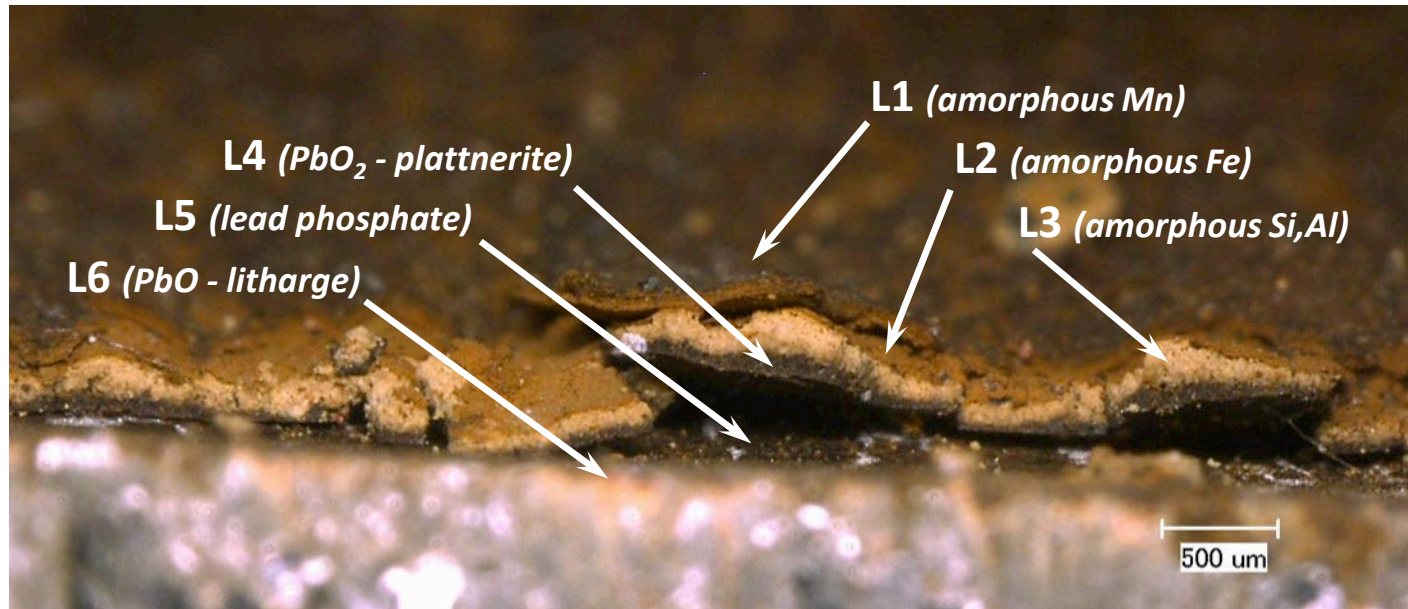
Scale Layers

Depending on treatment history and distribution system nuances

Can be simple...

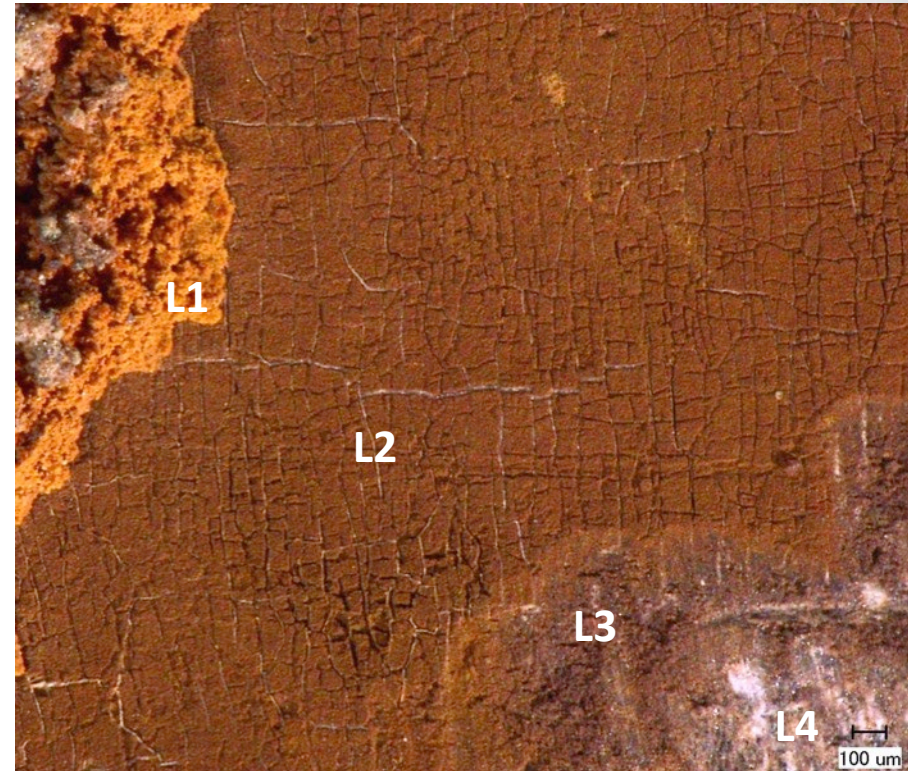


Or complex...



Sampling by layer

- Once the layers are defined the process of carefully subsampling the identified layers can begin
- Can be time consuming, depending on complexity of the scale
- In some cases may not be able to separate very thin or very friable materials



- Experience has taught that there can be distinct differences in the mineralogy of the layers due to varying reaction fronts, redox gradients, etc.
- Spatial position of different scale components is important for assessing risk of lead (& other metals) release.
- **Bulk sampling of whole scale loses information!!**

Resulting Material

- Separated layers are then individually crushed and passed through a 75 μm sieve
- One of the drawbacks of subsampling layers will be a low yield (~ 200 mg or less in some cases)
- Some LSLs will provide plenty of material for certain layers whereas other layers can be difficult to obtain enough sample





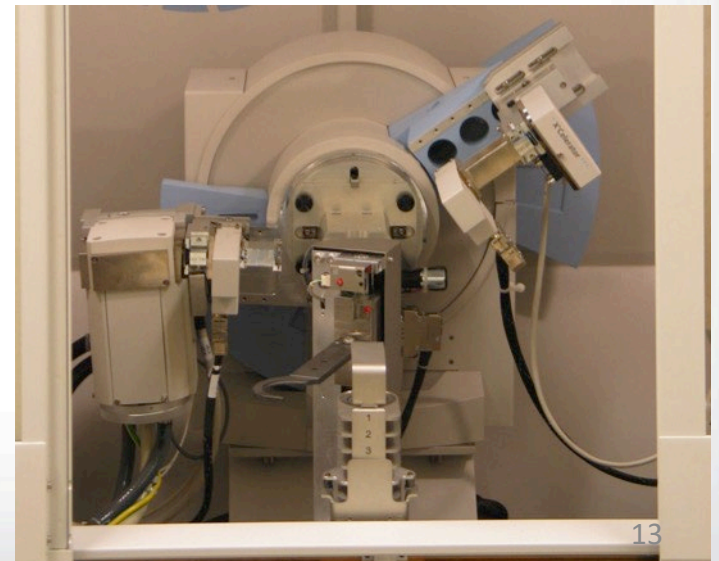
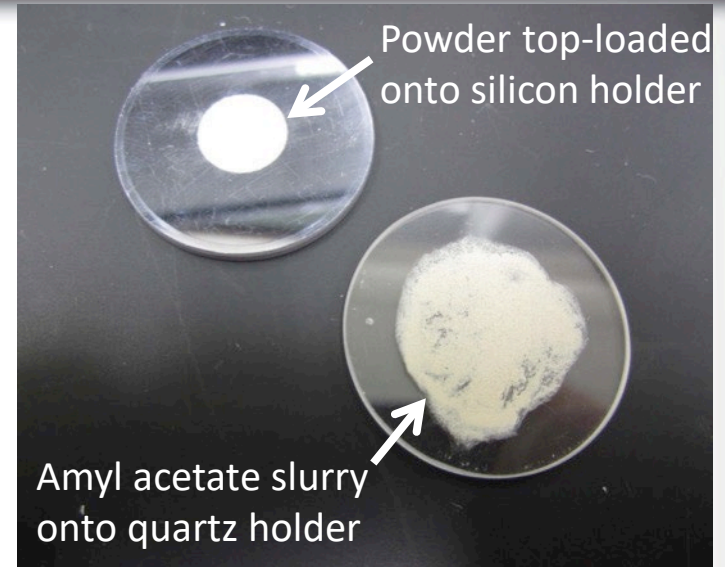
ORD's main components of scale analysis

Analyses performed on individual layers:

Analytical Technique	Information	Destructive / Nondestructive	Sample amount needed
Powder X-ray Diffraction (XRD)	Mineralogy of crystalline material	Nondestructive	As little as 10 mg <i>(more is better)</i>
X-ray Fluorescence (XRF)	Elemental composition	Destructive	100 - 200 mg
ICP-AES w/ multi-acid digestion or fusion bead preparation			
Total Carbon/Total Sulfur (TC/TS)			50 mg
Total Inorganic Carbon (TIC)			10-20 mg
Scanning Electron Microscopy (SEM) / Energy Dispersive Spectroscopy (EDS)	Images and spatial distribution of elements	-NA-	-NA-

Powder XRD

- Non-destructive method
- Ability to analyze small amounts of material
- Provides information regarding the crystalline and (to some extent) poorly-crystalline components (“phases”) of the analyzed material
- Semi-quantitative to quantitative measure of relative proportions of scale phases based on peak intensity measurements



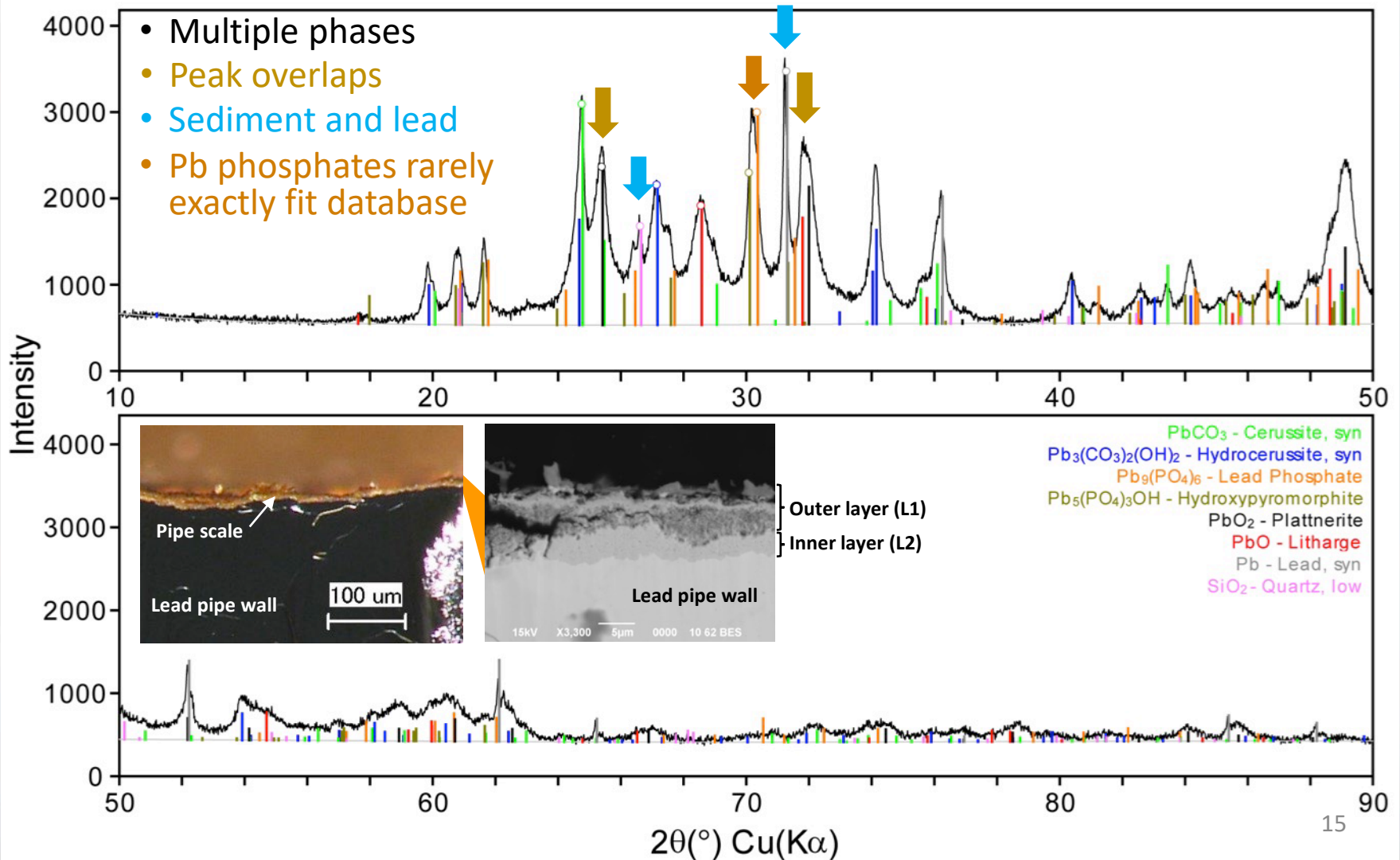


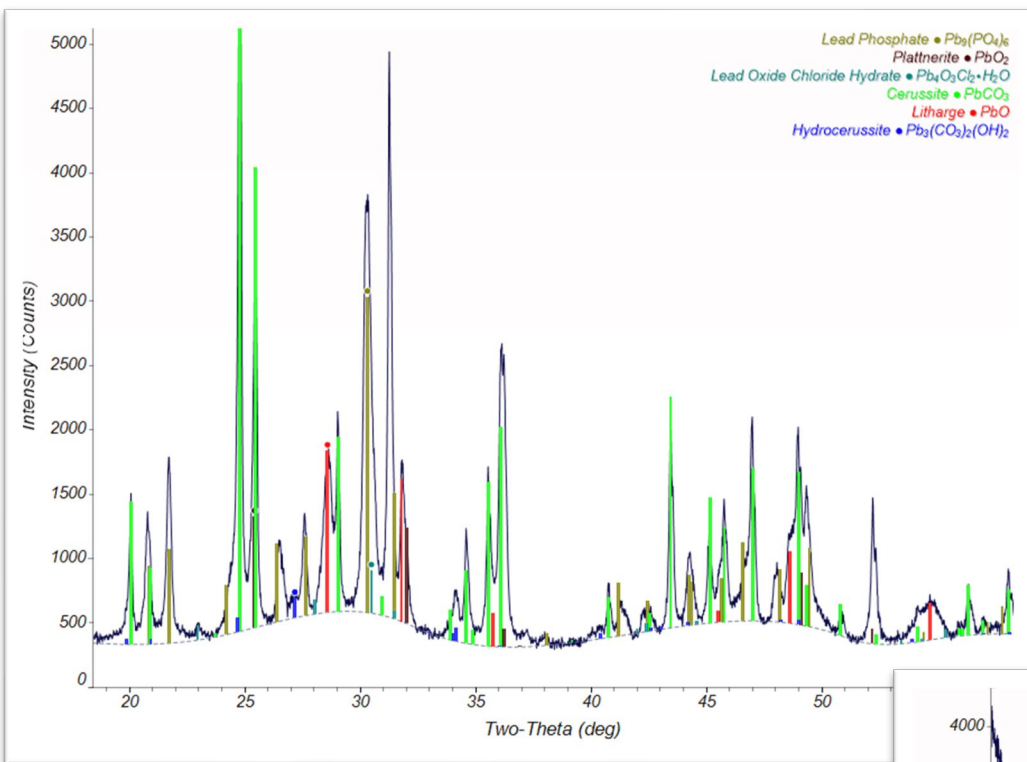
Phase identification: Cautions and Caveats

- Pipe scales are rarely composed of a single mineral phase
=> Peak overlaps
- Auto-ID feature in pattern fitting software should be used with caution
- Some practical knowledge of expected (and improbable) minerals in a drinking water environment is useful
- Ideally want phase identifications to be based on multiple peaks in the diffraction pattern
 - Generally not an issue for major phases
 - Minor/trace phases may only have the strongest 1 or 2 peaks visible above background/not hidden by peak overlaps

Some XRD Pattern Complications

Outer layer of ~10 μ m thick scale

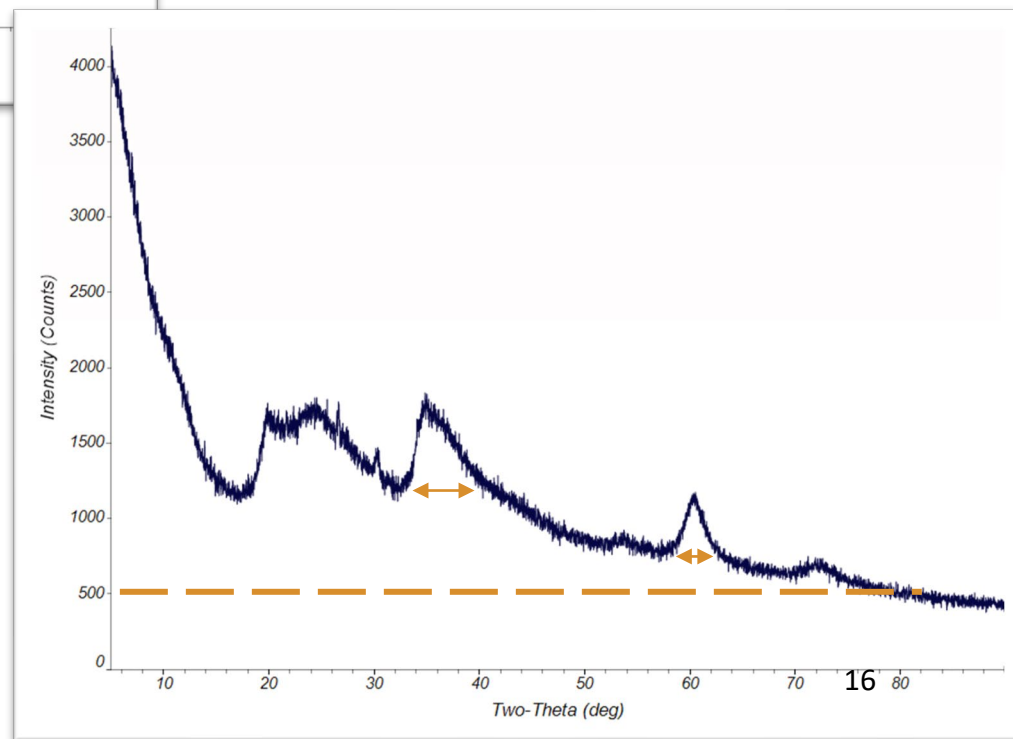




Crystalline

vs.

Amorphous





PXRD Quantitative Analysis

- Semi-quantitative to quantitative measure of relative proportions of scale phases based on peak intensity measurements
 - Generally: higher proportion of phase => more intense diffraction peaks
- Two common methods: Reference Intensity Ratio (RIR) and Rietveld Refinement
 - RIR: Comparison of a measured peak intensity/integrated area from each phase, scaled to a standard reference (typically corundum) => **RIR VALUES MUST BE AVAILABLE FOR EVERY PHASE!!**
 - Rietveld: Model of entire diffraction pattern, iteratively fit from crystal structure data for phases previously identified in the sample. => **CRYSTAL STRUCTURE DATA MUST BE AVAILABLE FOR EVERY PHASE!!**



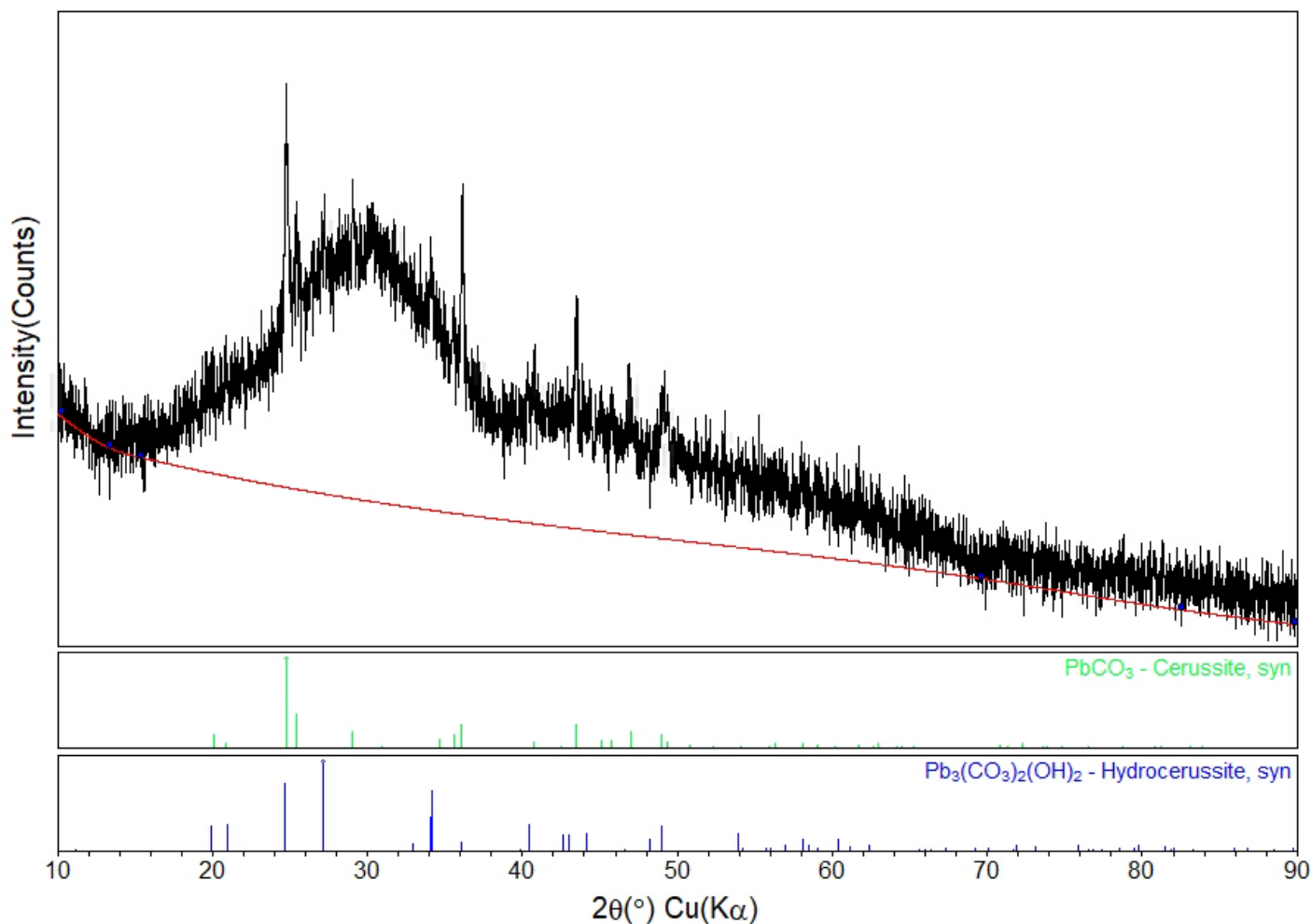
PXRD Quantitative Analysis: Cautions and Caveats

What do reported percentages of scale minerals in a sample actually represent?

- Automated programs calculate based on identified (crystalline) phases, with the assumption that they add up to 100% of the sample
- What if there are unidentified materials present in the sample?
- Amorphous component(s) are not quantified, unless specifically accounted for by spiking the sample with a known amount of a crystalline reference material.

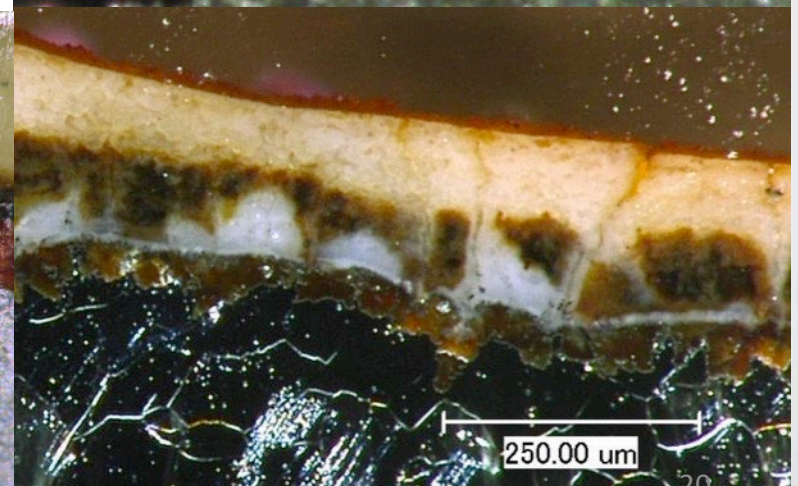
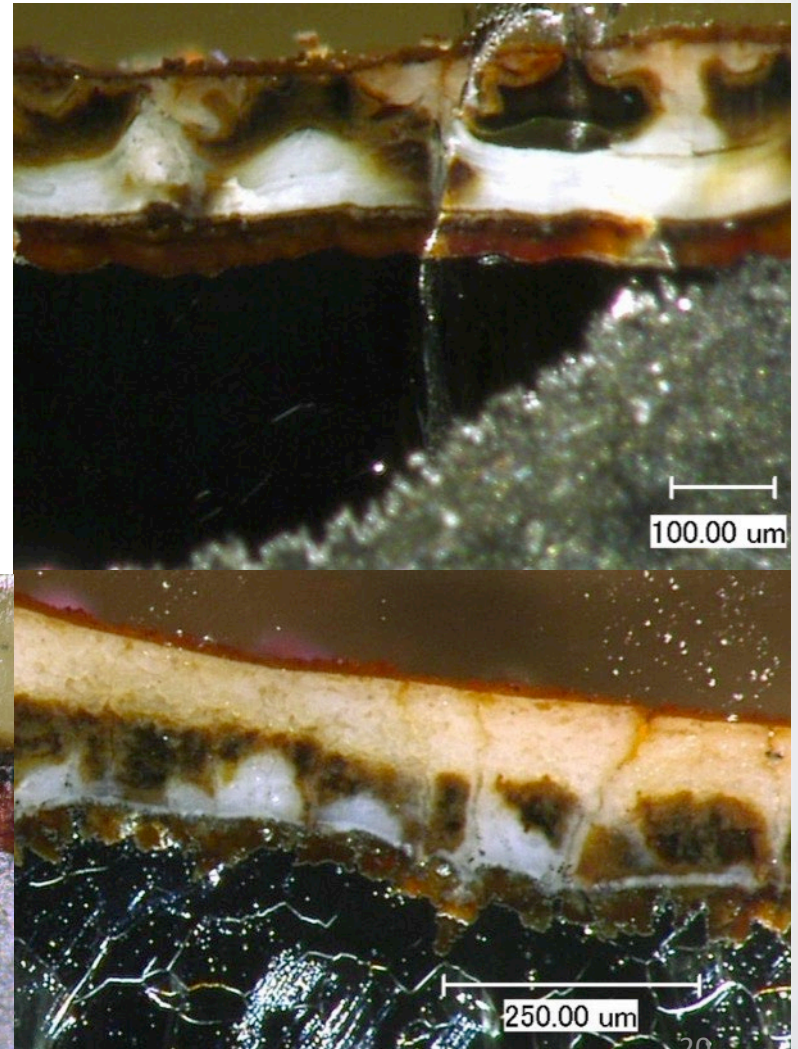
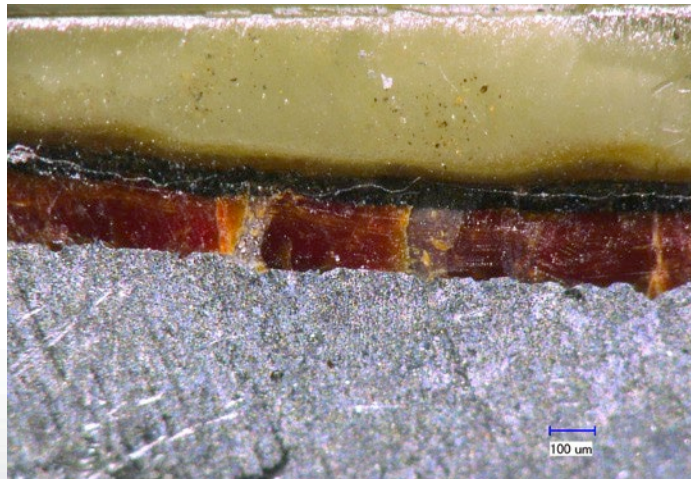


PXRD Quantitative Analysis: Cautions and Caveats



SEM/EDS Analysis

- Preservation of *in-situ* layer relationships from a representative undisturbed section of the LSL
- Cross-sectional view
- Useful for understanding complex layering

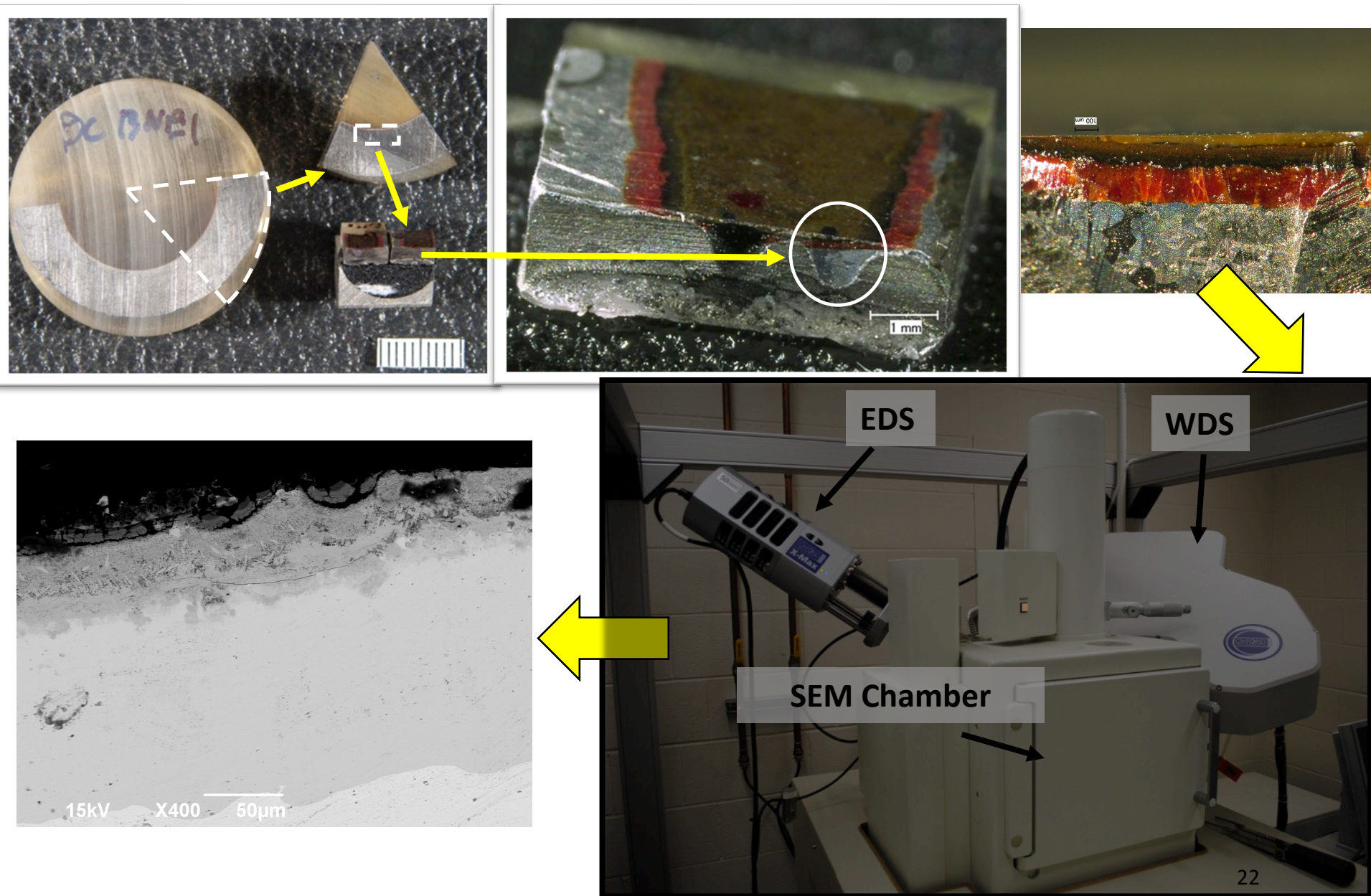




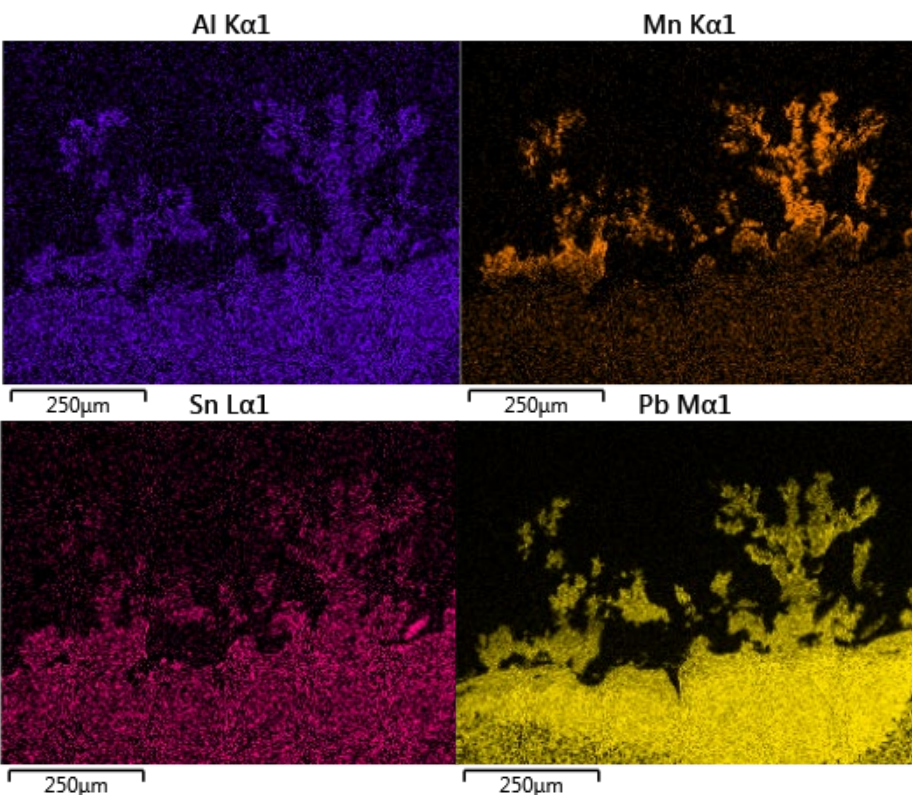
Cross Section equipment



Cross Section Preparation

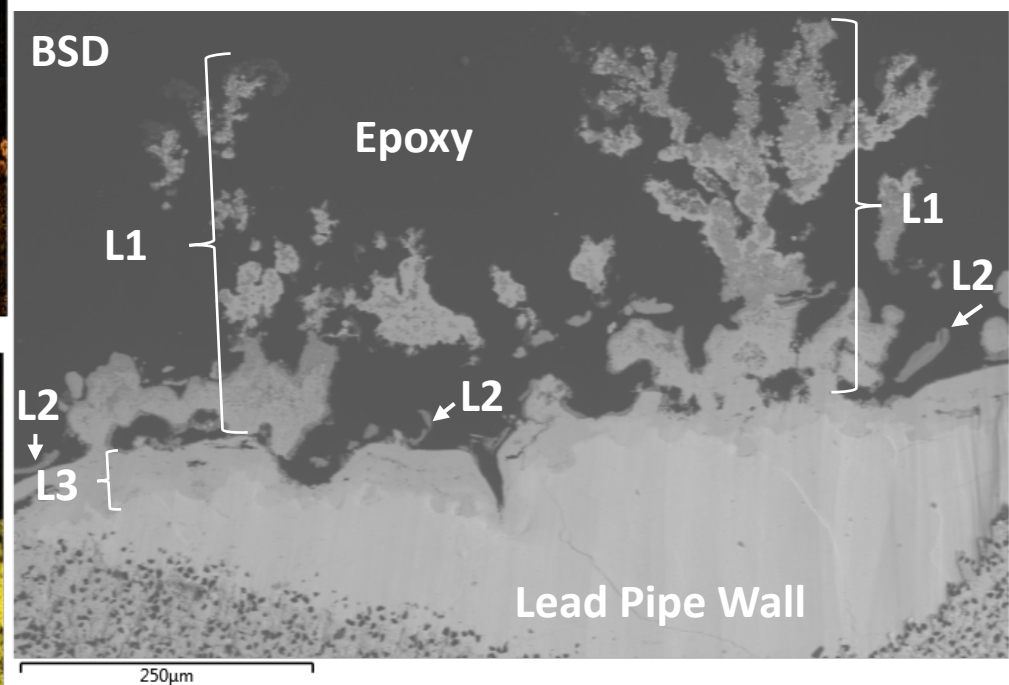


Elemental Maps are Useful for General Spatial Relationships



EDS results from a spectrum taken over an entire area

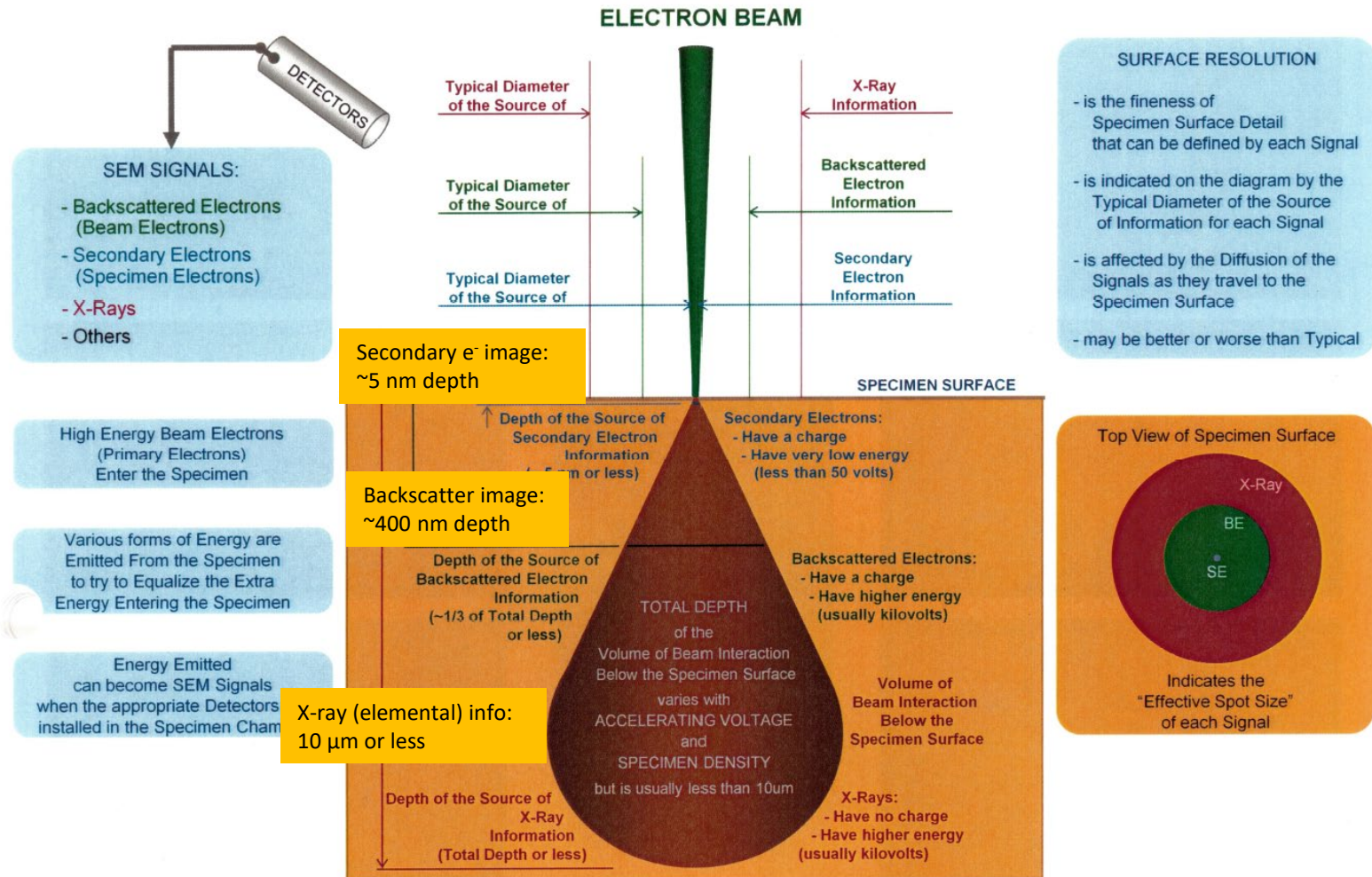
Element	Weight %
Al	0.37
Mn	2.05
Sn	1.05
Pb	78



XRF results from subsampling the individual layers

Element	L1	L2	L3
Al	1.4	0.8	0.3
Mn	7.4	2.7	0.2
Sn	2.8	3.1	1.4
Pb	58.6	71.3	83.6 ²³

SEM/EDS Interaction Volume

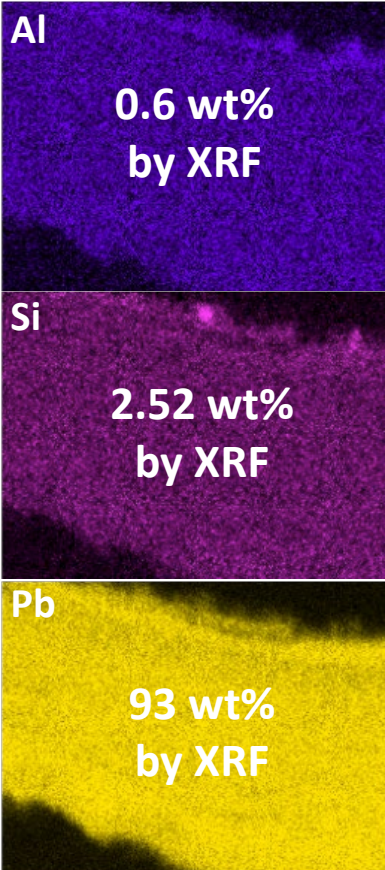


ELECTRON BEAM - SPECIMEN INTERACTION:
CHARACTERISTICS OF THE INTERACTION / DEPTH OF SEM SIGNALS / SURFACE RESOLUTION

Caution Required When Evaluating SEM/EDS Results

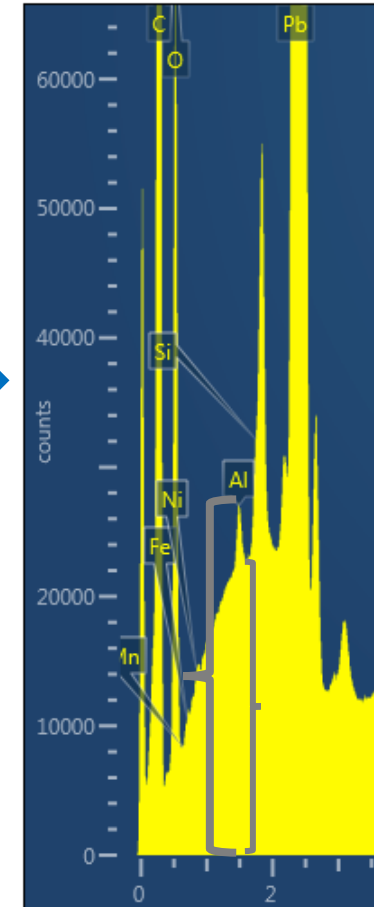
Common output for SEM/EDS analysis

Elemental Maps



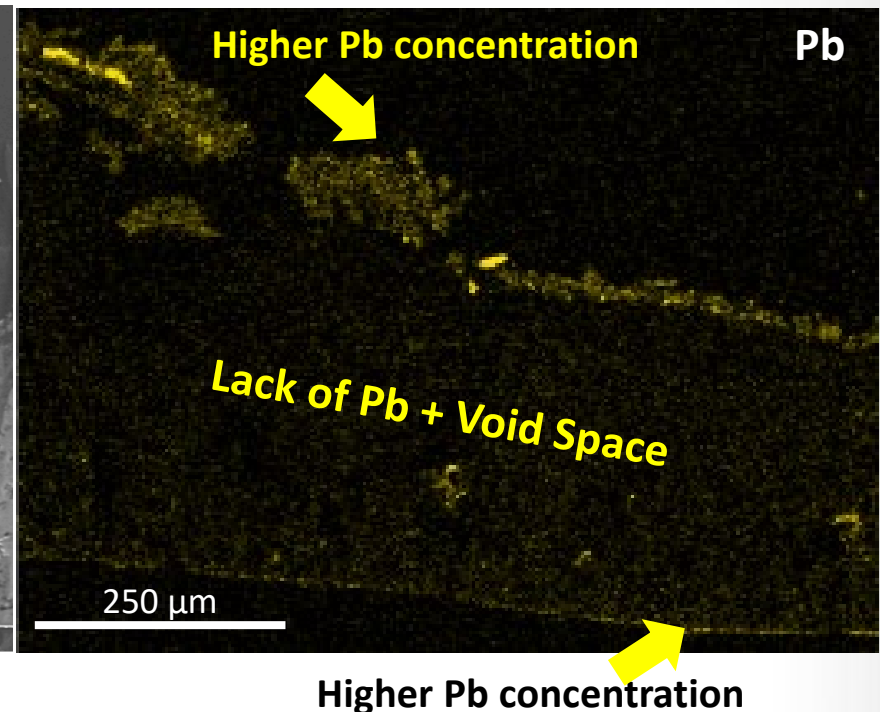
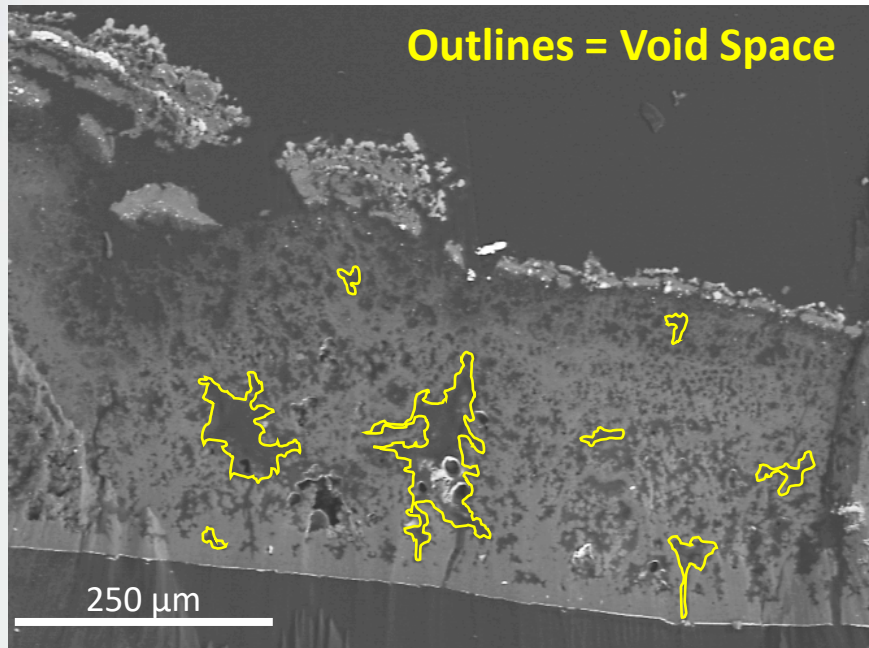
However, to truly interpret the elemental maps the associated spectrum needs to be evaluated

EDS Spectra



While Al appears across the entire map and at a comparable brightness to that of Pb and Si this cannot be interpreted as the elements are present in equal concentrations to one another

One Final Caution: Chemistry Context and Experience Matters



Interpretation A

Porous, poorly-adherent scale of non-crystalline Mg, Al, Si, Ca, P material, consistent with other observations in systems with phosphate and blended phosphate treatments

Interpretation B

Void spaces left by dissolution of highly crystalline Pb (II) orthophosphate solids, like hydroxy- or chloro-pyromorphite



Conclusions

- Scale analysis is a complicated undertaking that is labor intensive
- Experience, robust methodology, and an attention to detail are needed; otherwise wrong conclusions may be drawn
- Results of various analyses are best interpreted holistically and with historic system water quality parameters when possible
- Information learned from scale analysis can provide insight into the potential impacts of water quality or CCT changes



Questions?

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