

Powder Micro X-ray Diffraction of Particles

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McCrone Associates, Inc.
MAS Topical Conference
Microanalysis of Particles
April 2009

Uses of X-ray Diffraction

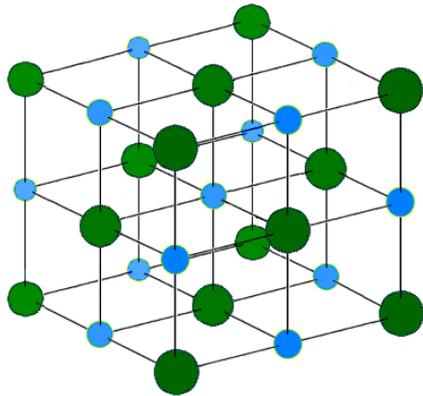
- **phase identification** of materials-
different phases of materials with
the same elemental composition
can have extremely different
properties
- degree of crystallinity

Microsamples

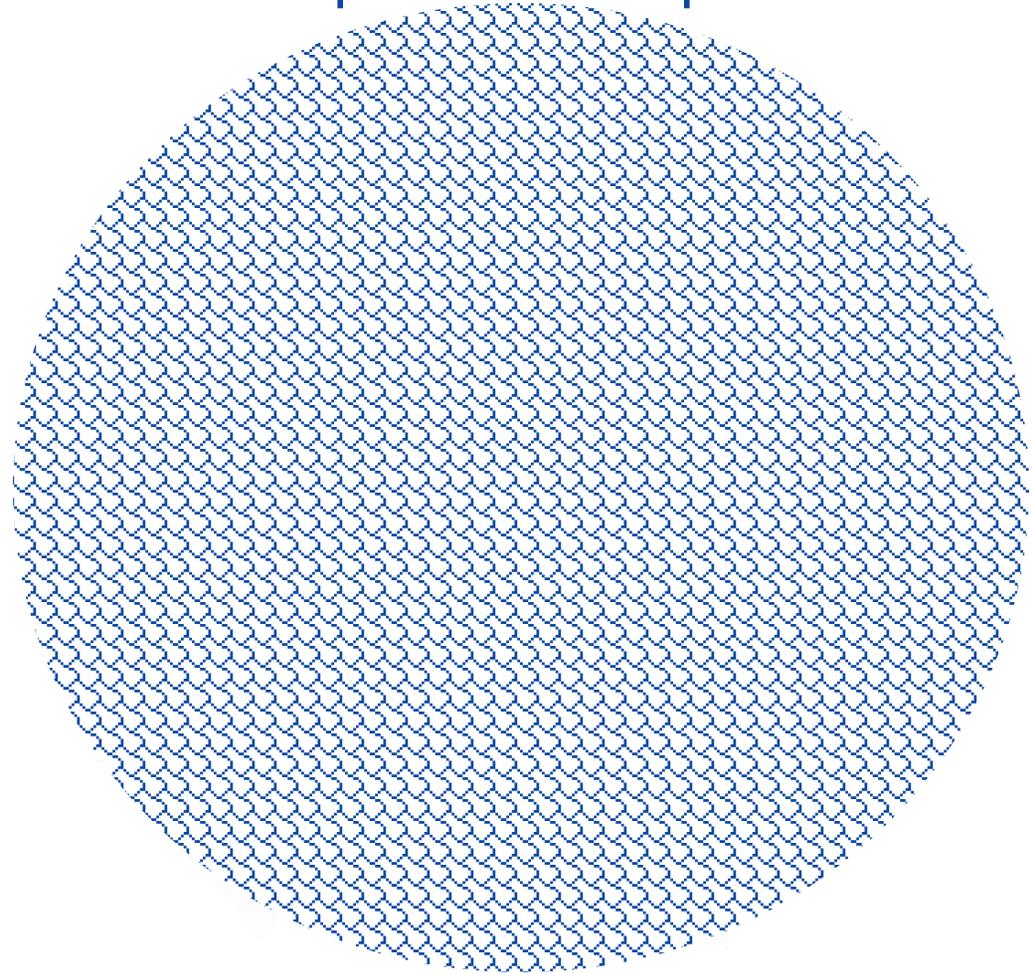
- limited amount
 - pharmaceutical trials
 - combinatorial chemistry
 - filtered material
 - removal from larger samples (i.e., artwork)
- contamination
 - extraction from pharmaceuticals
 - corrosion: circuit boards, sheet metal, outdoor metals (i.e., bronzes, steels)

Powder XRD

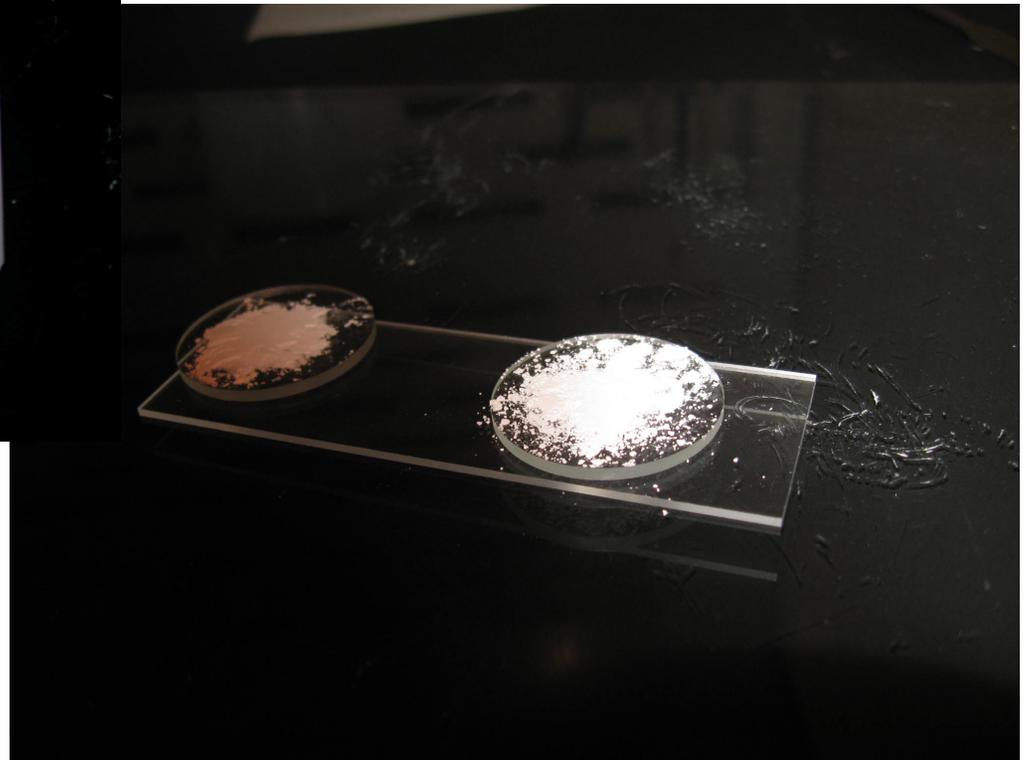
single crystal

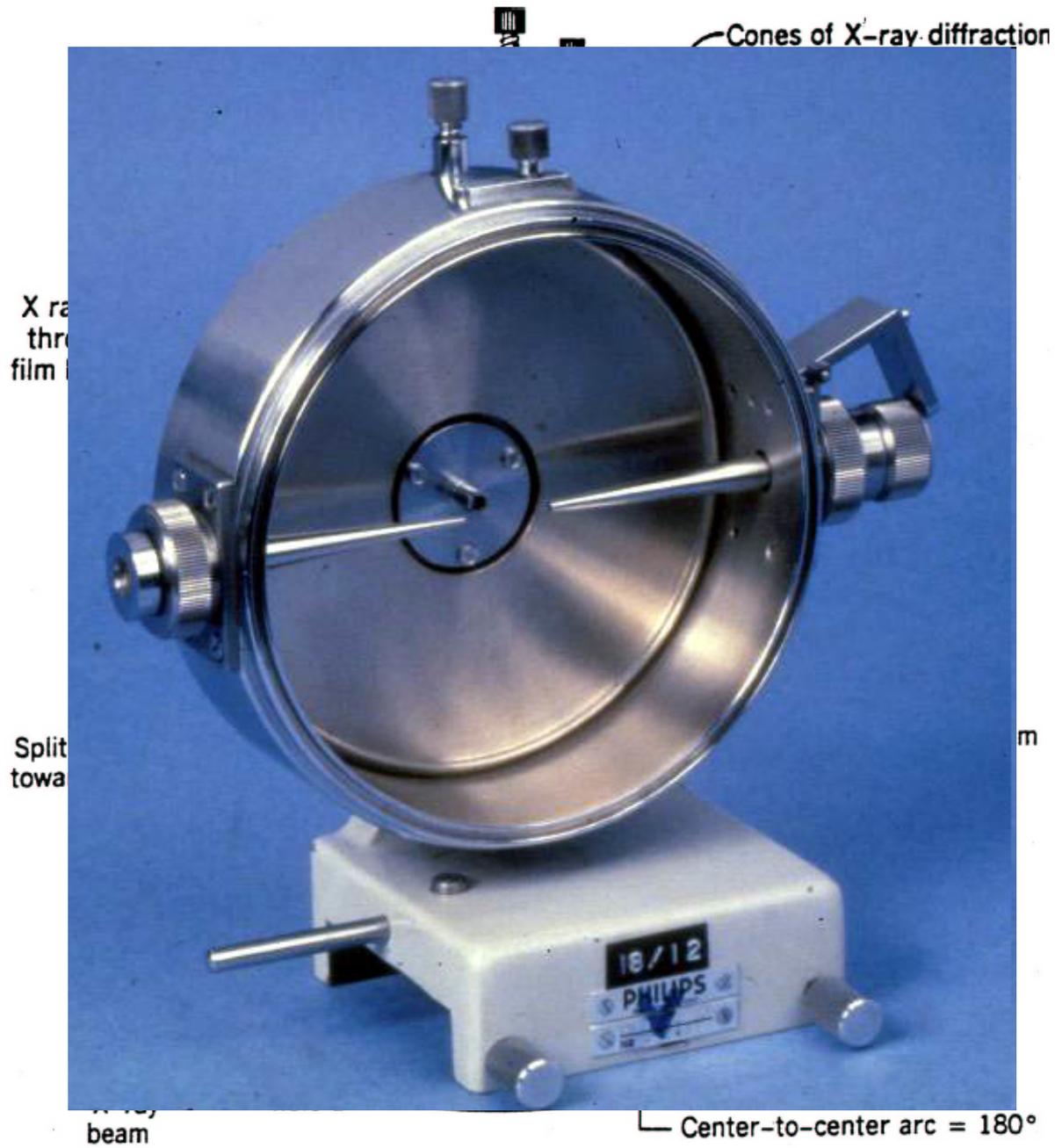


powder sample

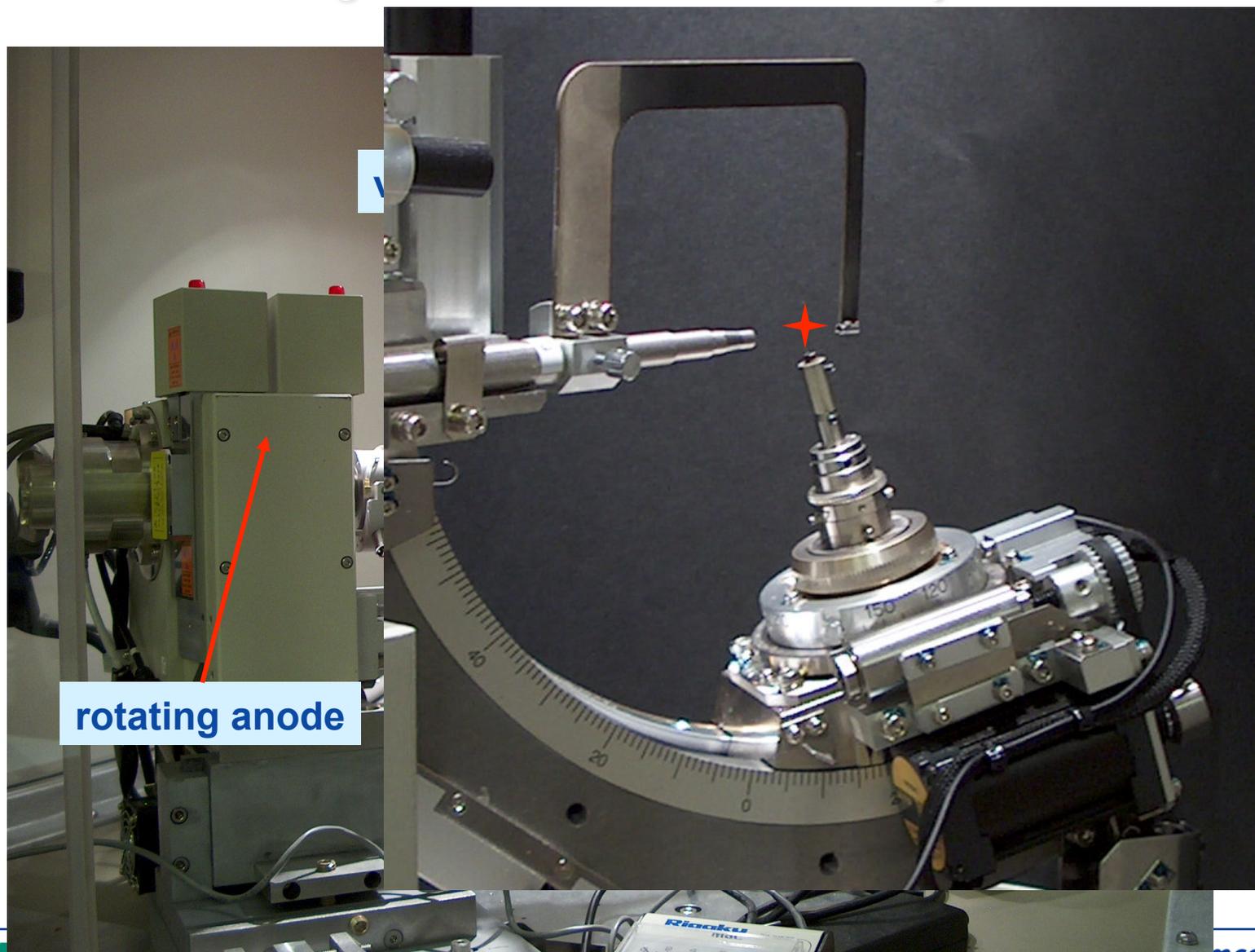


Sample Preparation Bulk-XRD





Rigaku MicroMax-007 Rotating Anode with RAPID-SPIDER Image Plate Detection XRD System



Cleanroom



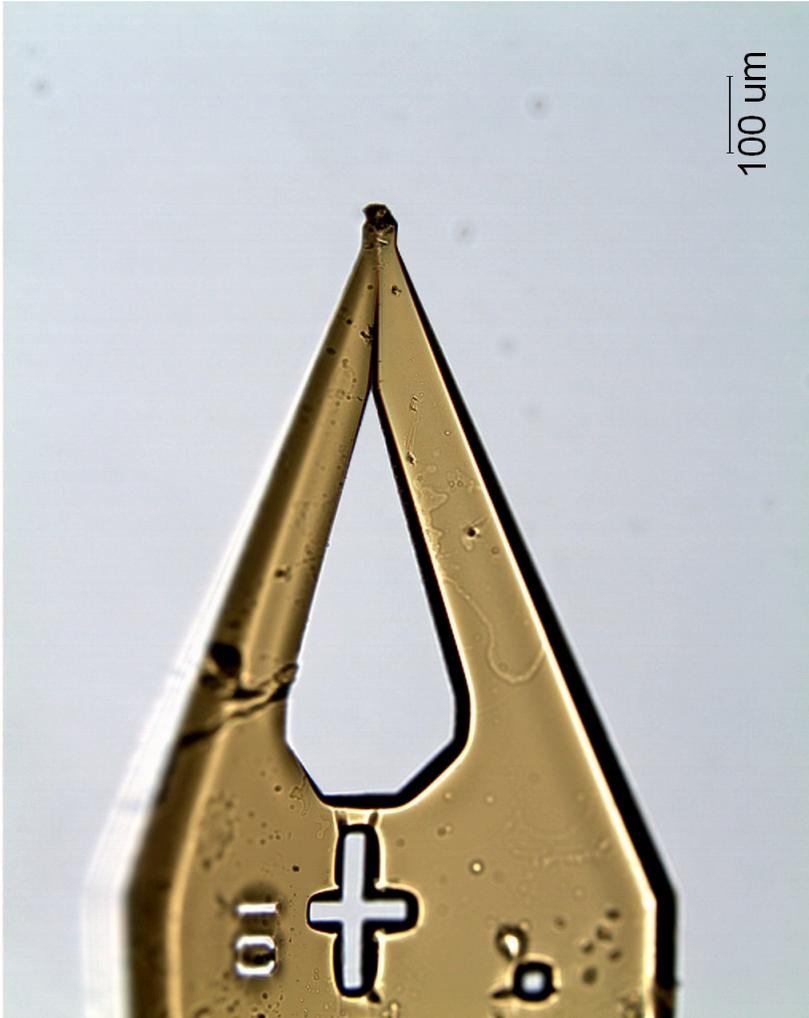
Tools for Particle Extraction



Extraction and Mounting XRD

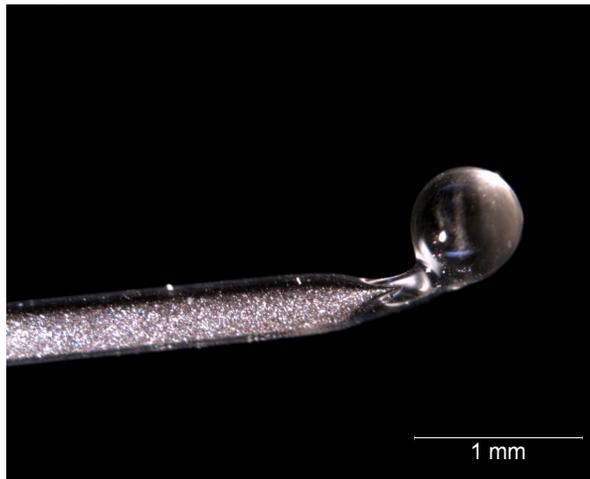


MiTeGen Mounts

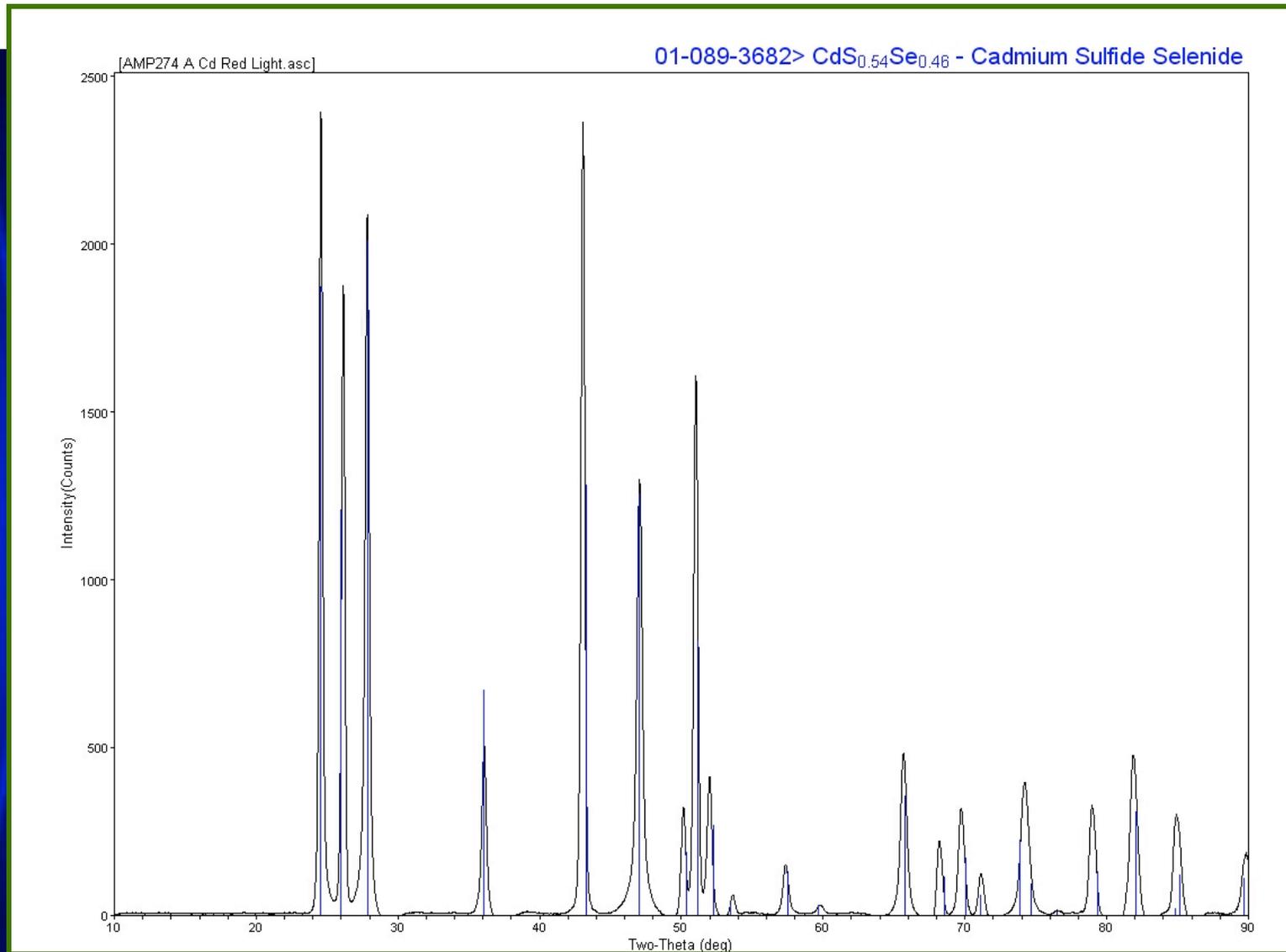


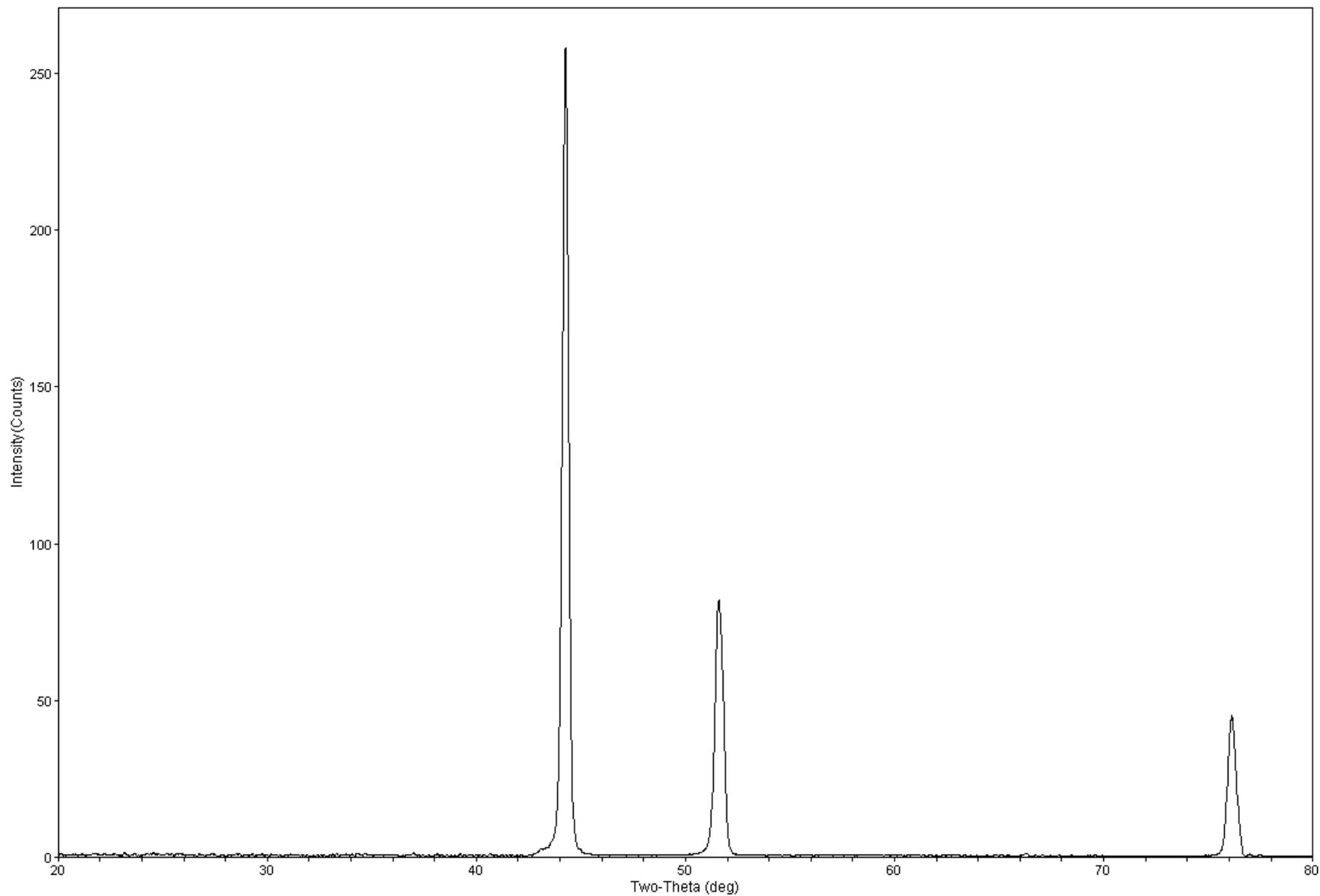
- Polyimide (Kapton)
- Low X-ray absorbance and scatter
- Easy sample mounting

Other samples in micro-XRD

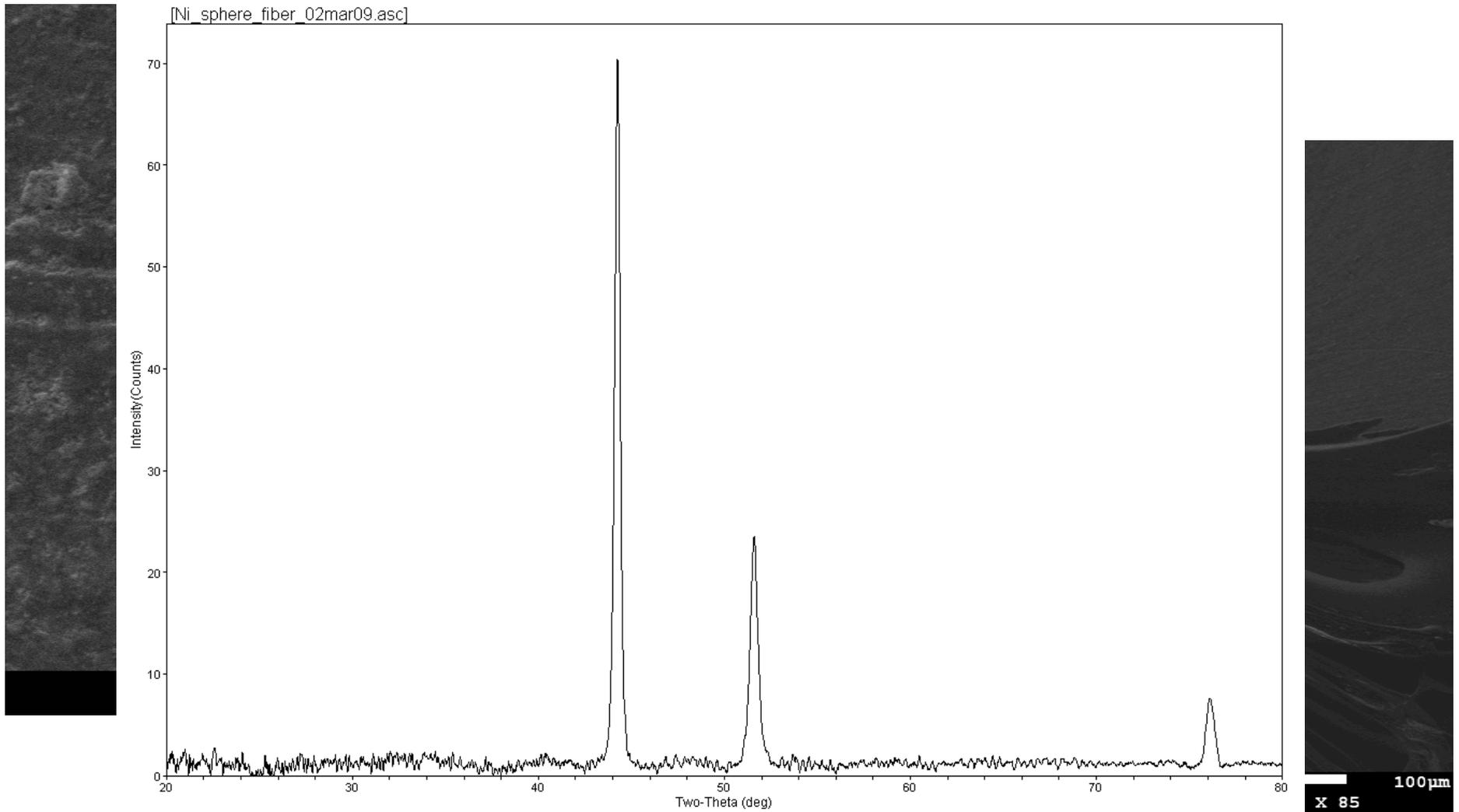


XRD Data

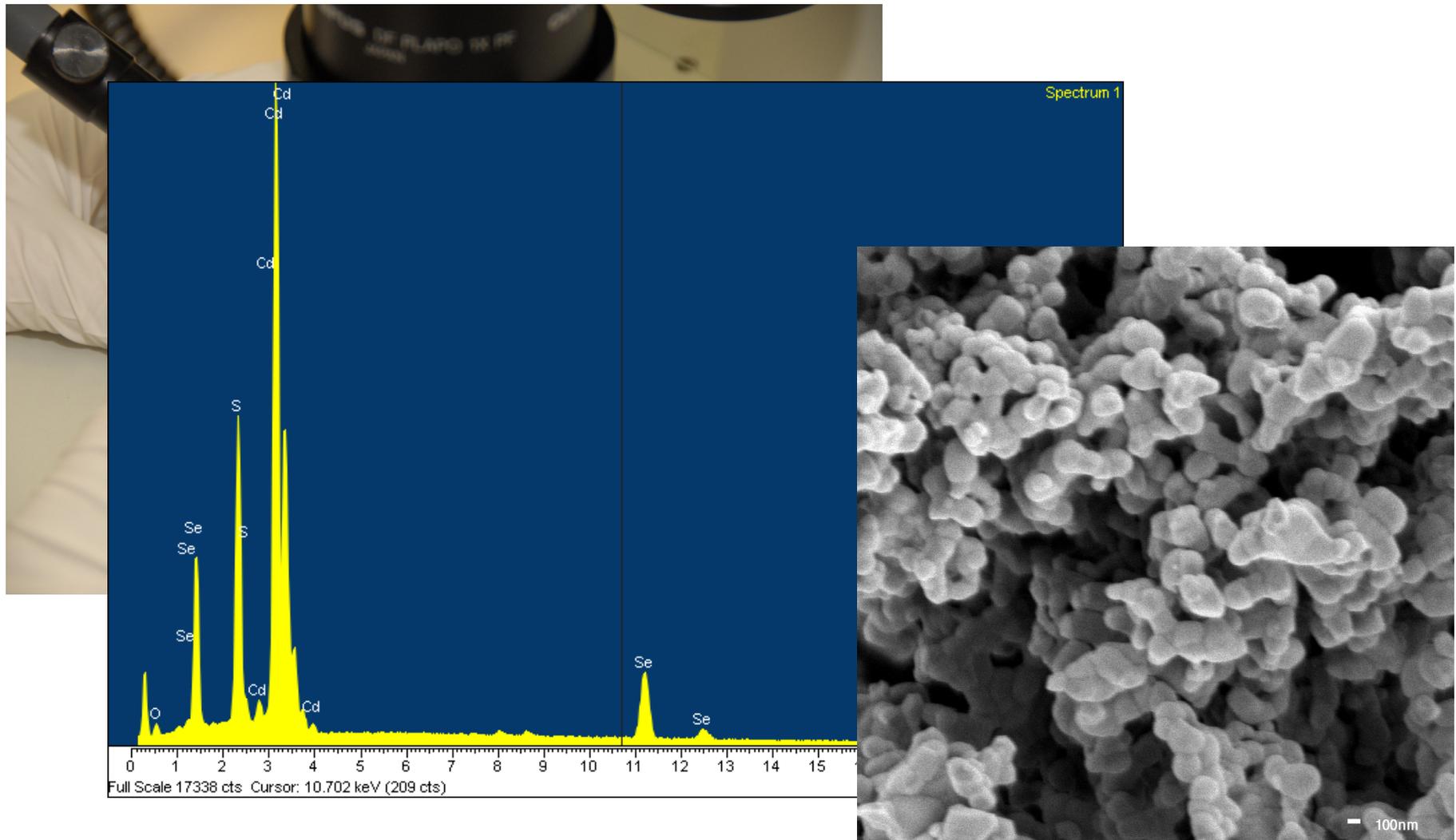


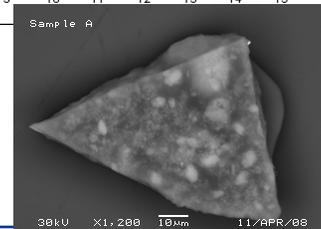
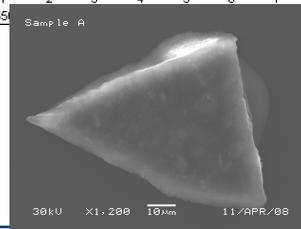
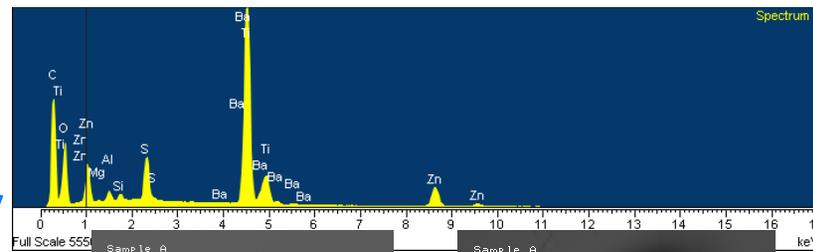
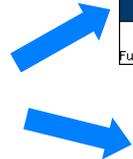
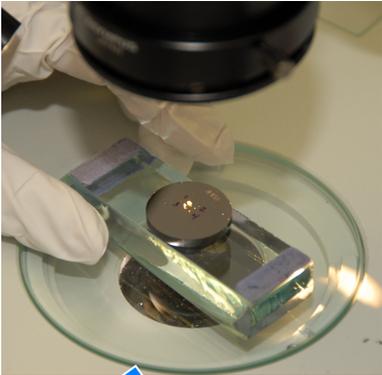
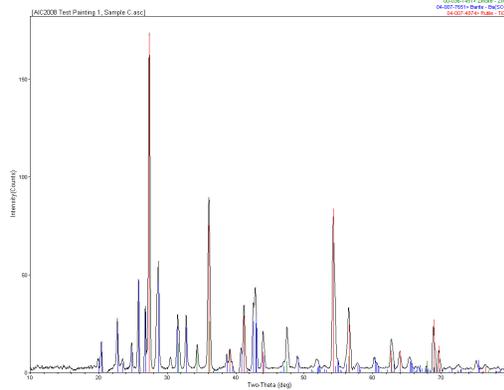
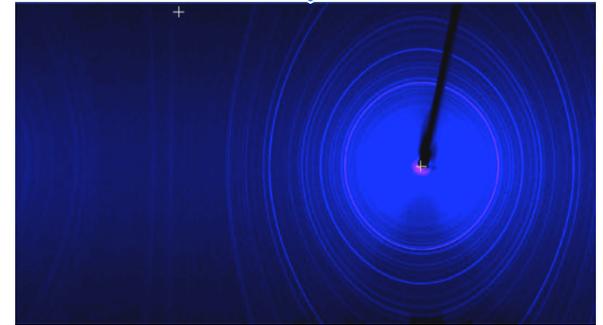
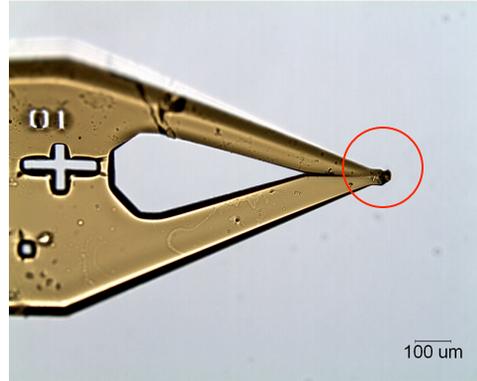


Standards



SEM/EDS of Particles

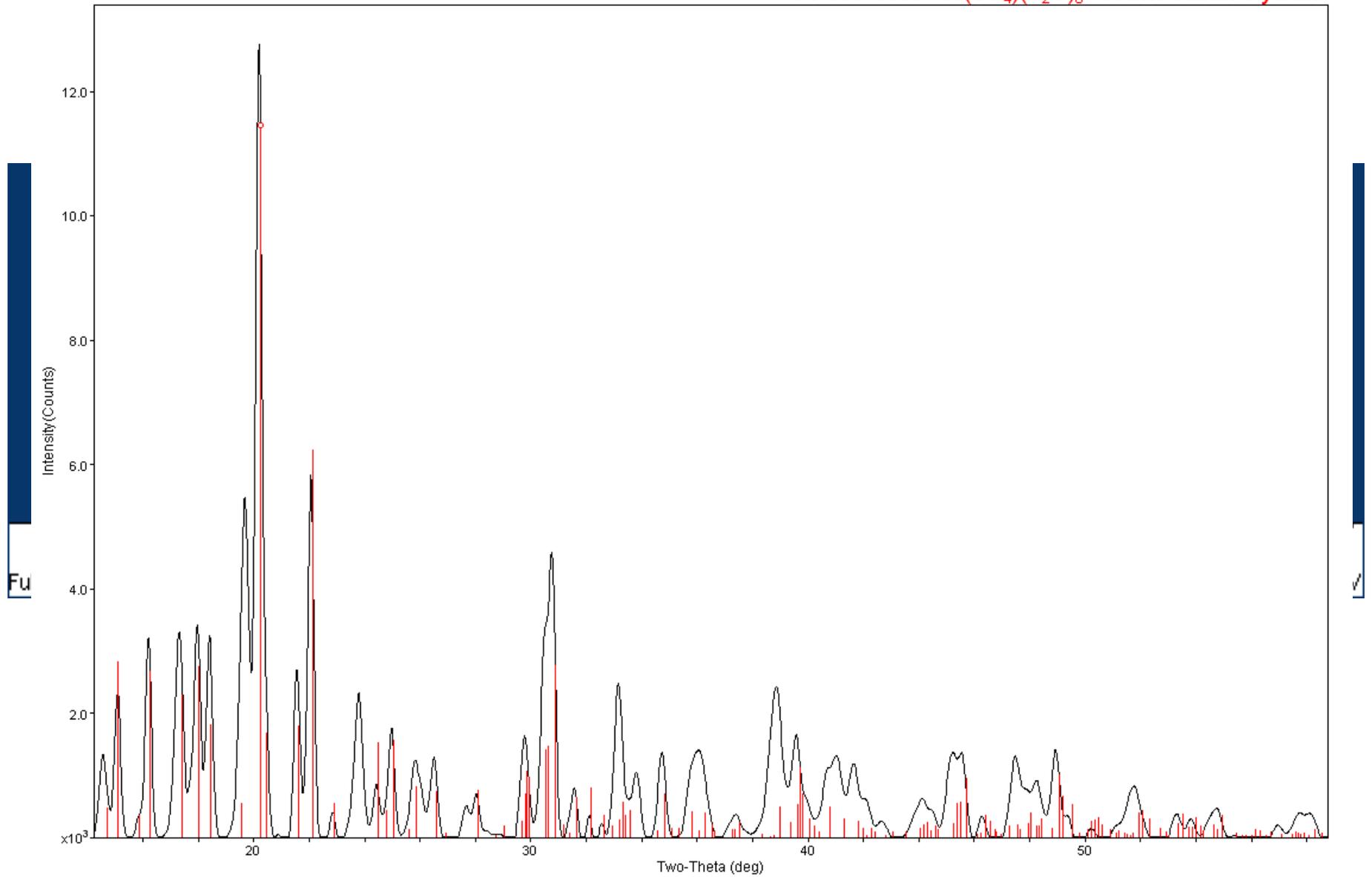




Circuit Board Corrosion

- Accelerated aging with chemicals, light, and temperature is used to test electronics
- After accelerated aging testing, a contact on a circuit board failed
 - Corrosion was evident in a contact area
- What is the corrosion?

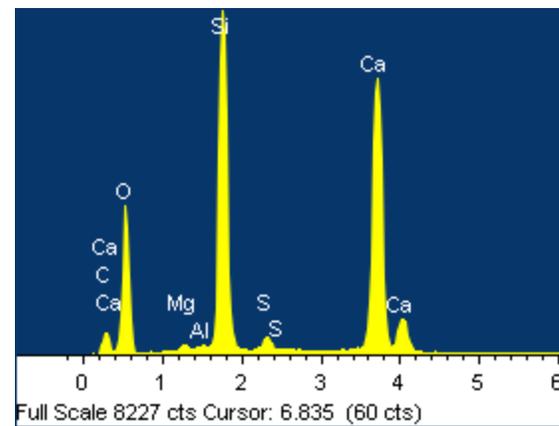
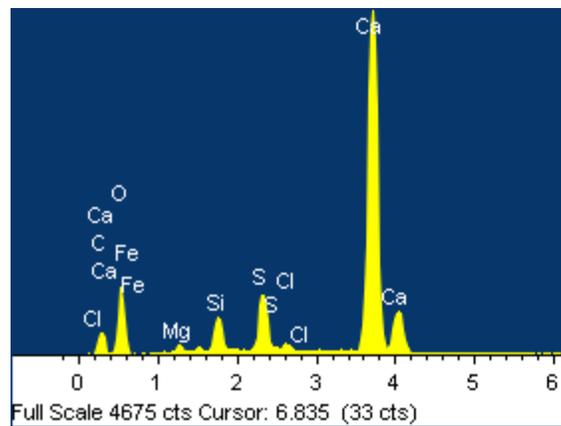
04-009-4339> Ni(SO₄)(H₂O)₆ - Nickel Sulfate Hydrate



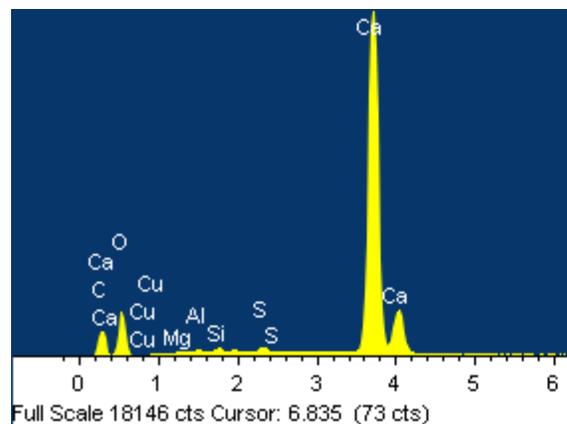
Fresco Deterioration

- Several frescoes in a university hall were cracking with numerous accretions or spall
- Architectural conservators wanted to identify the spall-this would indicate what materials were underneath the painted layer and source the problem.
- Samples of spall and from an intact fresco tested for the presence of gypsum

Sample 1
with spall

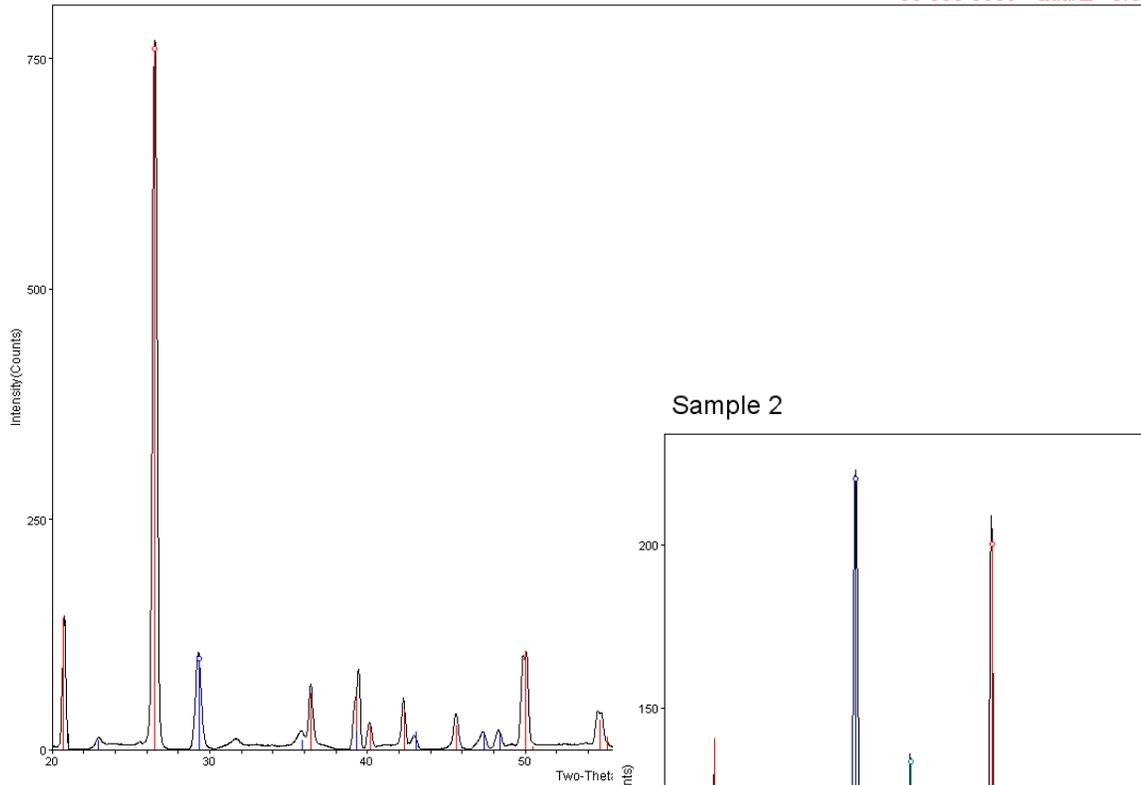


Sample 2
intact



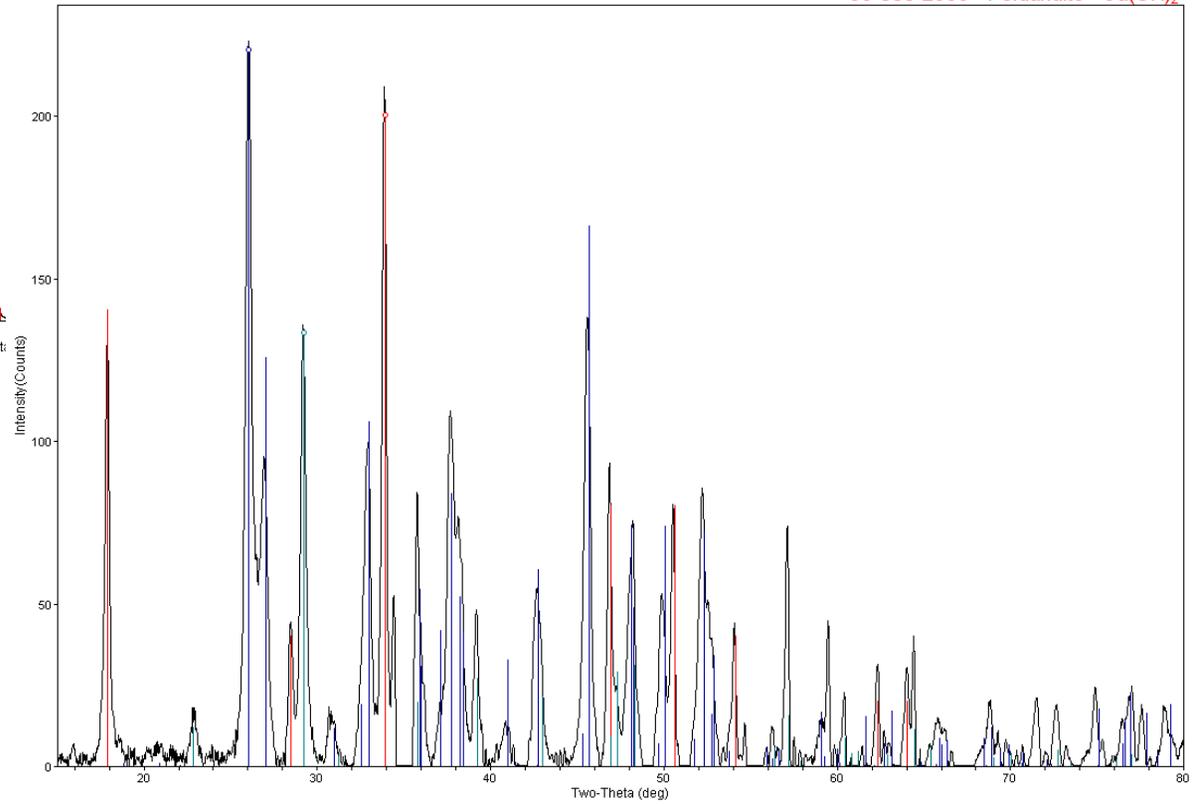
Sample 1

99-000-0548> Calcite - CaCO_3
98-000-0088> Quartz - SiO_2



Sample 2

00-047-1743> Calcite - CaCO_3
98-000-0013> Aragonite - CaCO_3
99-000-2999> Portlandite - Ca(OH)_2



Particles Removed from Cross-Section Layers

Optical Properties and Imaging

Light Microscopy (LM)

Polarized Light Microscopy (PLM)

Organic Classification

Fourier-Transform Infrared Spectroscopy (FTIR)

Raman Microscopy

High-Resolution Imaging and Elemental

Scanning Electron Microscopy with

Energy Dispersive X-ray Spectrometry (SEM/EDS)

Organic Quantification

Gas, Liquid Chromatography

Phase Identification

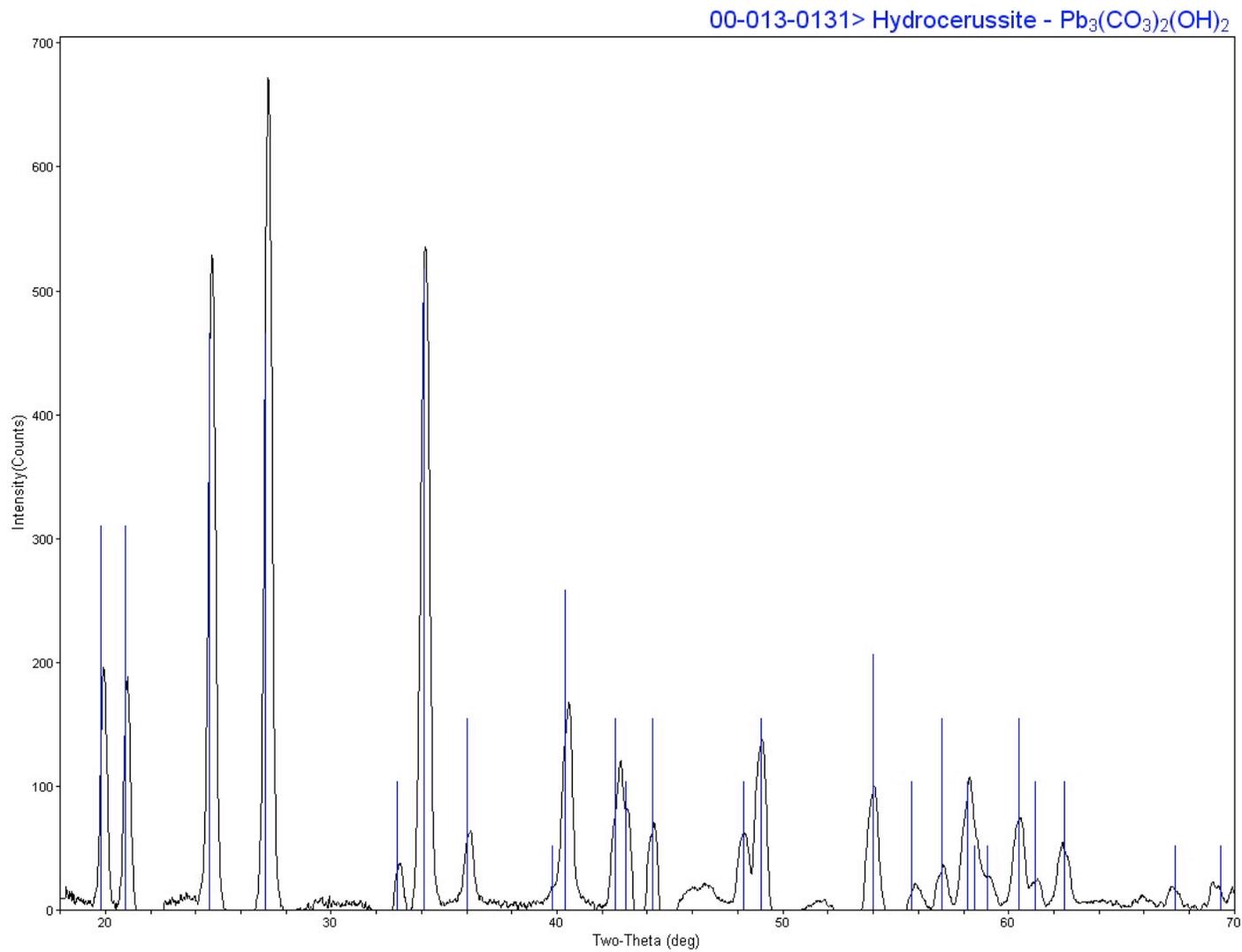
X-ray Diffraction (XRD)

Transmission Electron Microscopy (TEM)

Architectural Lead Paint Identification

- Elemental (EDS or XRF) will identify Pb in paint structures or layers from samples but will not determine if it is white lead carbonate, the white pigment discontinued from industrial paints and known to be a health hazard
- Received samples as polished mounts with EDS map and Pb-rich layers to sample for identification of white lead carbonate
- Particles removed from chips or dust wipes can confirm the presence of white lead carbonate

Polished Mounts



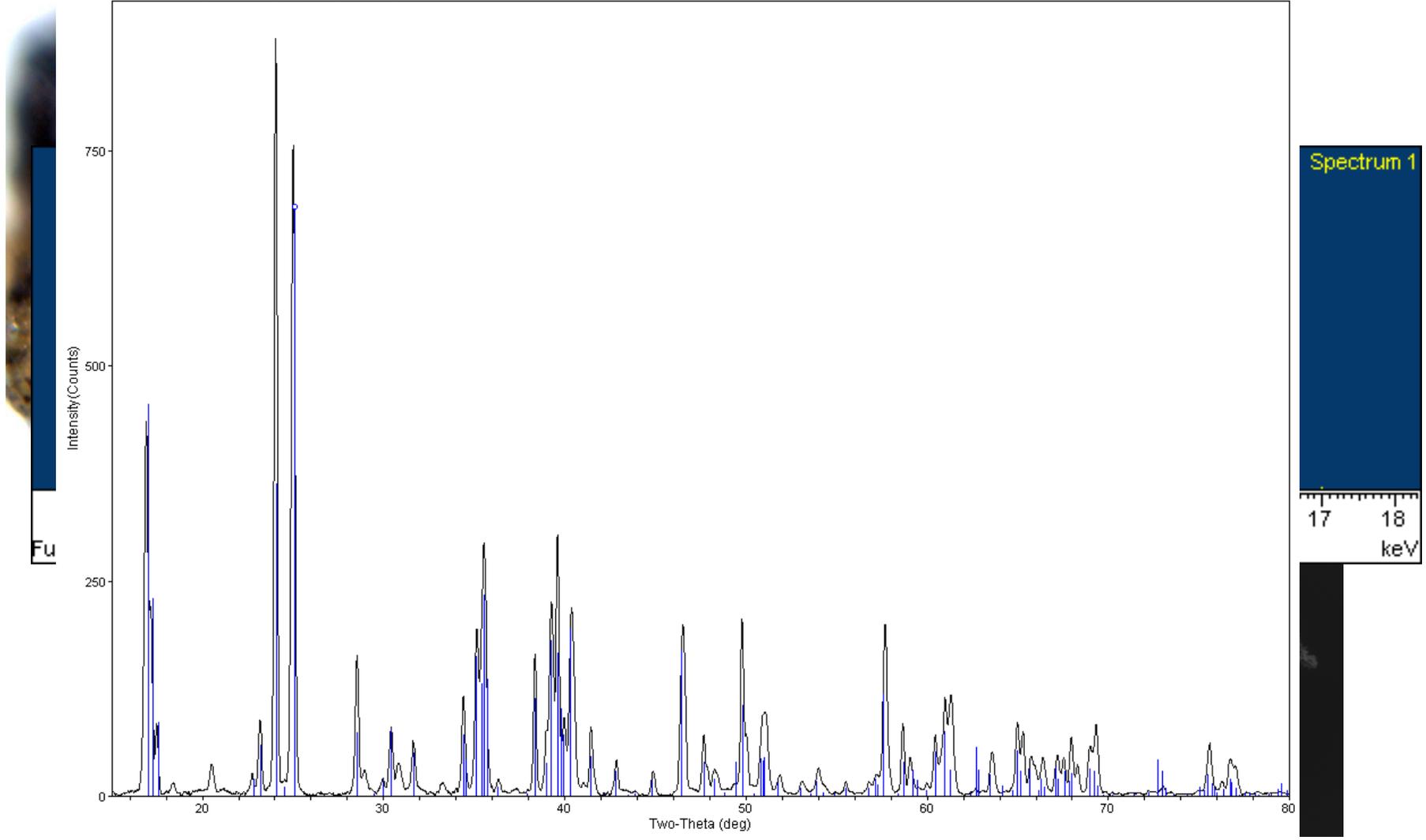
15th century Spanish panel painting



Sample 1, Layer 2

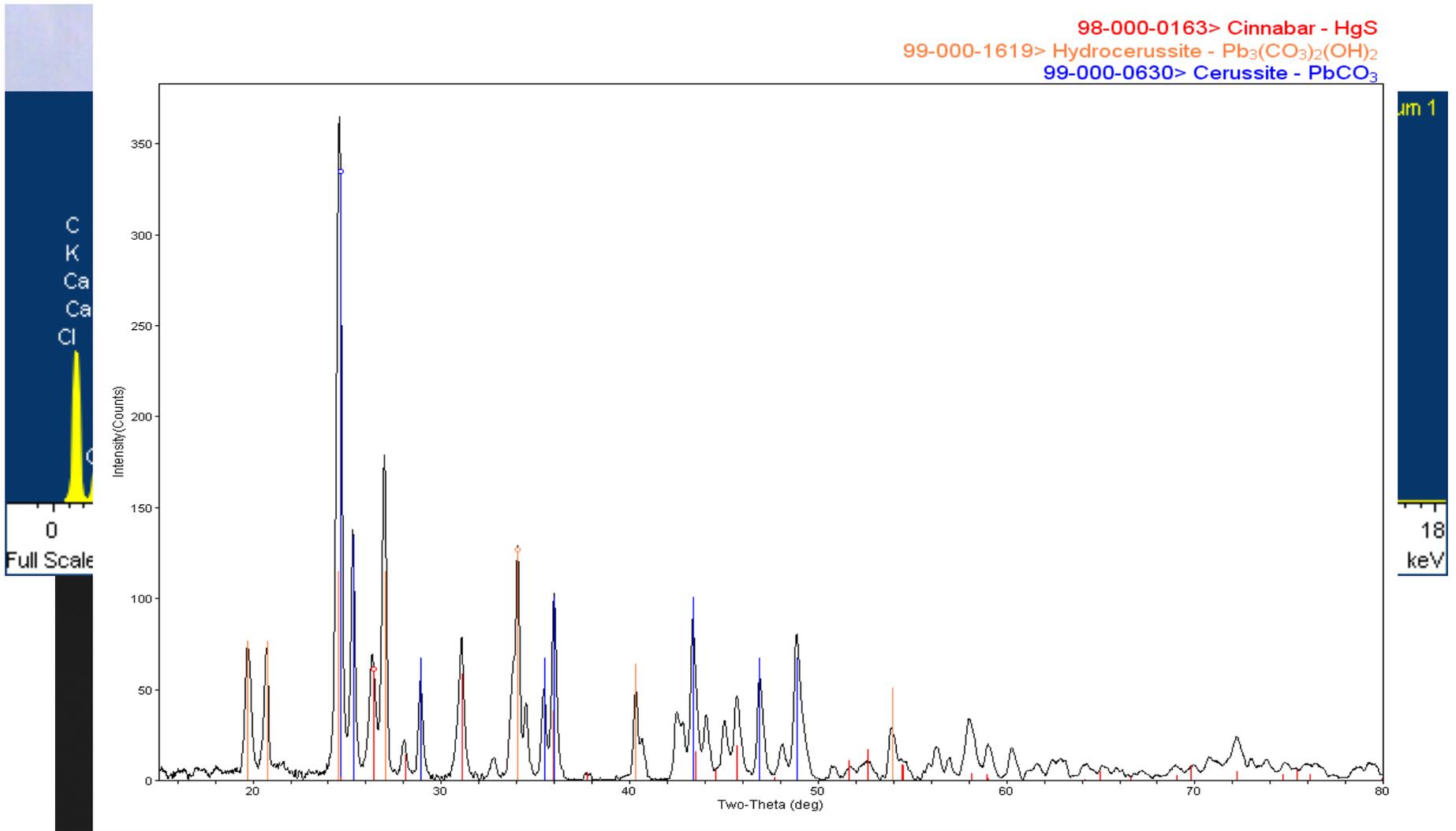
[MA47297_Sample_1_Top_Layer_2 run1 sub1.asc]

01-070-1579> Azurite - $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$

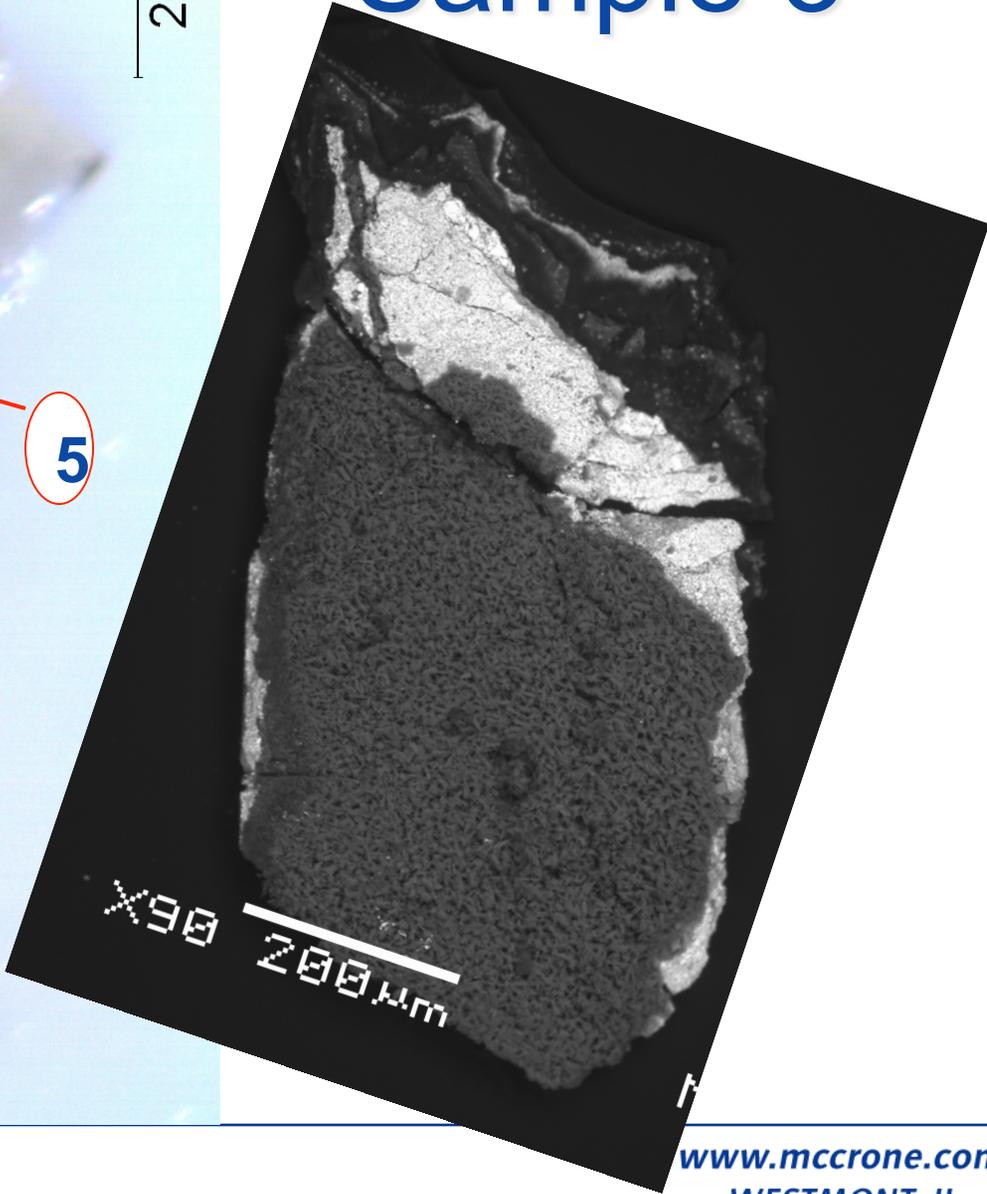
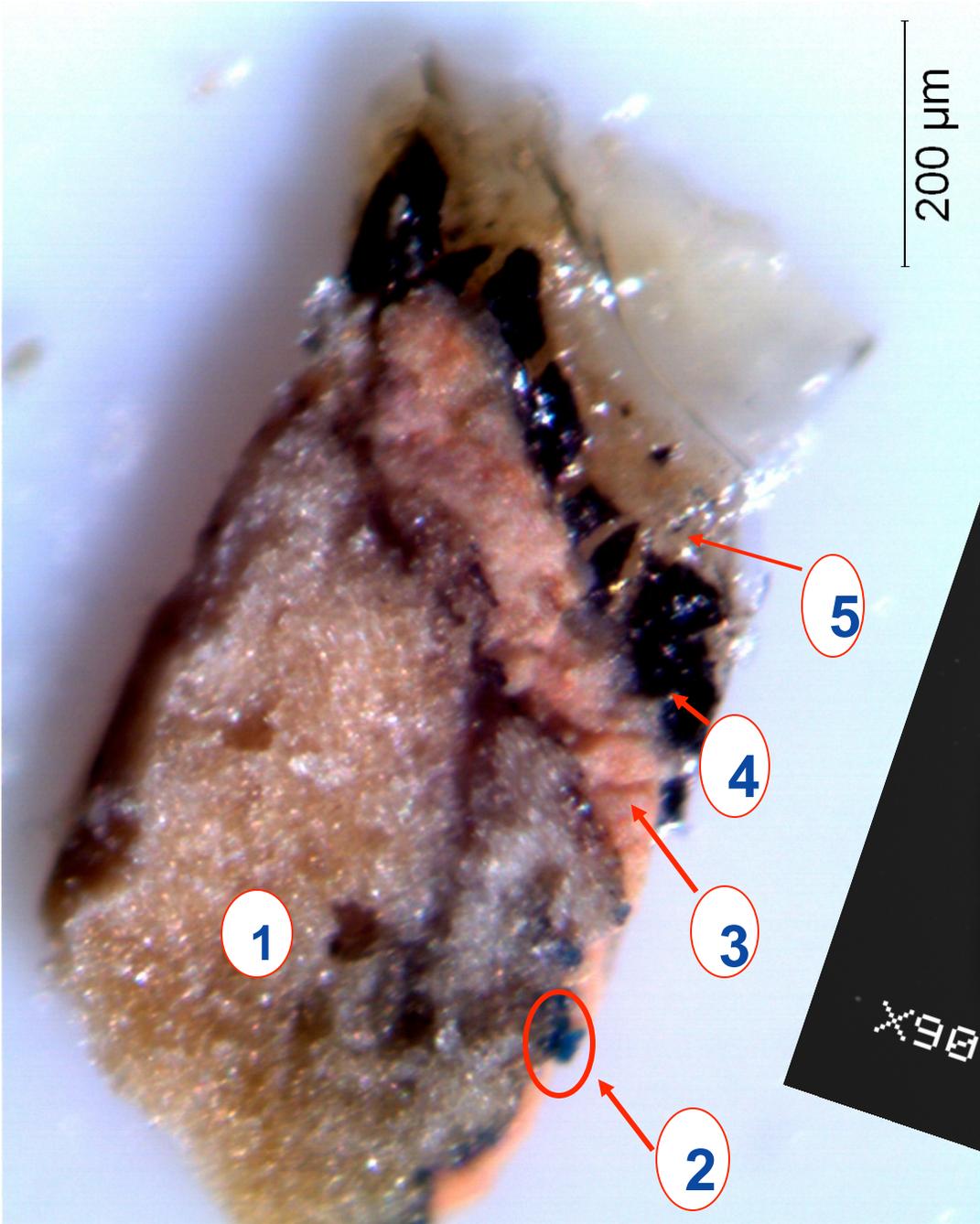


Sample 2, Layer 2

98-000-0163> Cinnabar - HgS
99-000-1619> Hydrocerussite - $Pb_3(CO_3)_2(OH)_2$
99-000-0630> Cerussite - $PbCO_3$



Sample 3

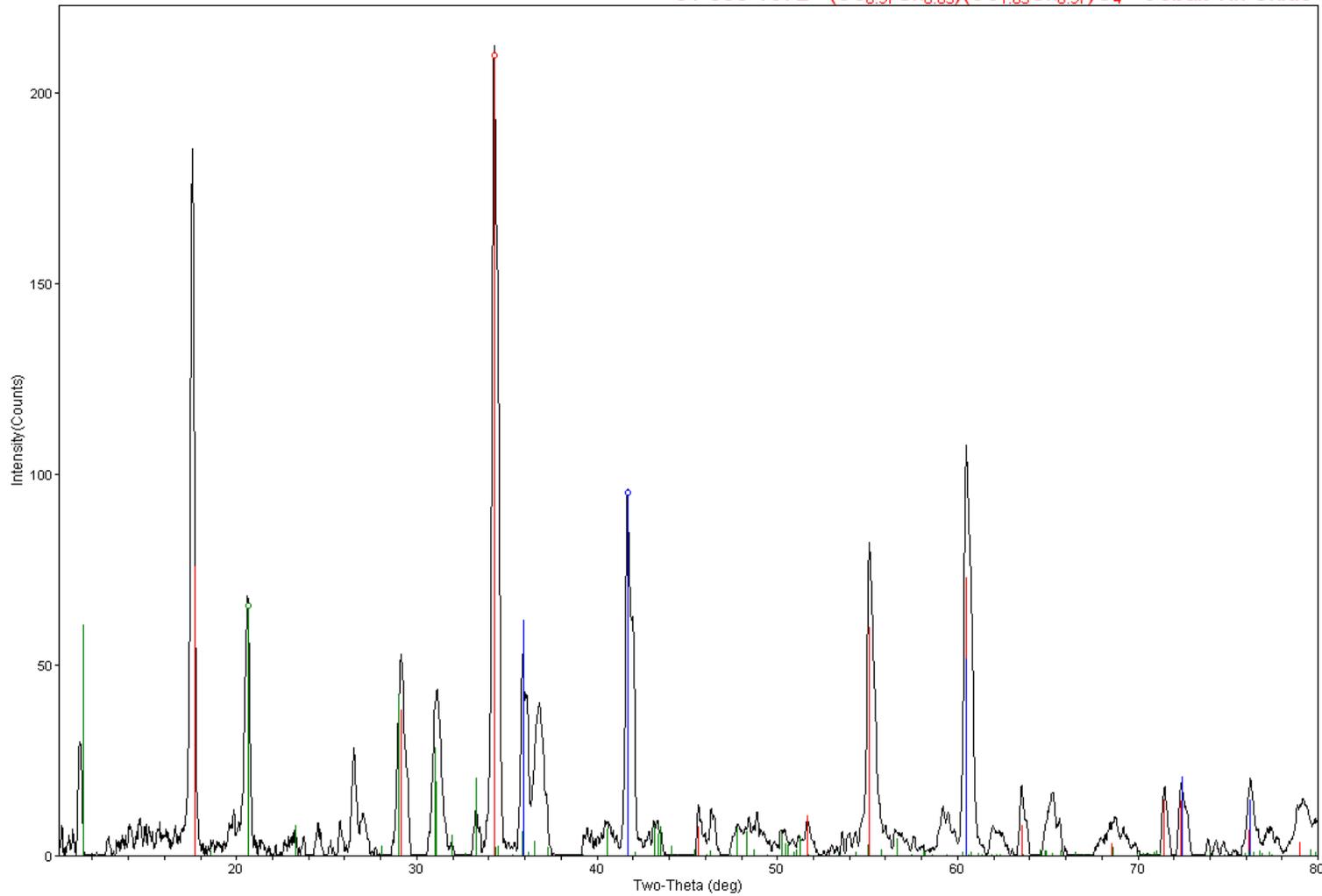


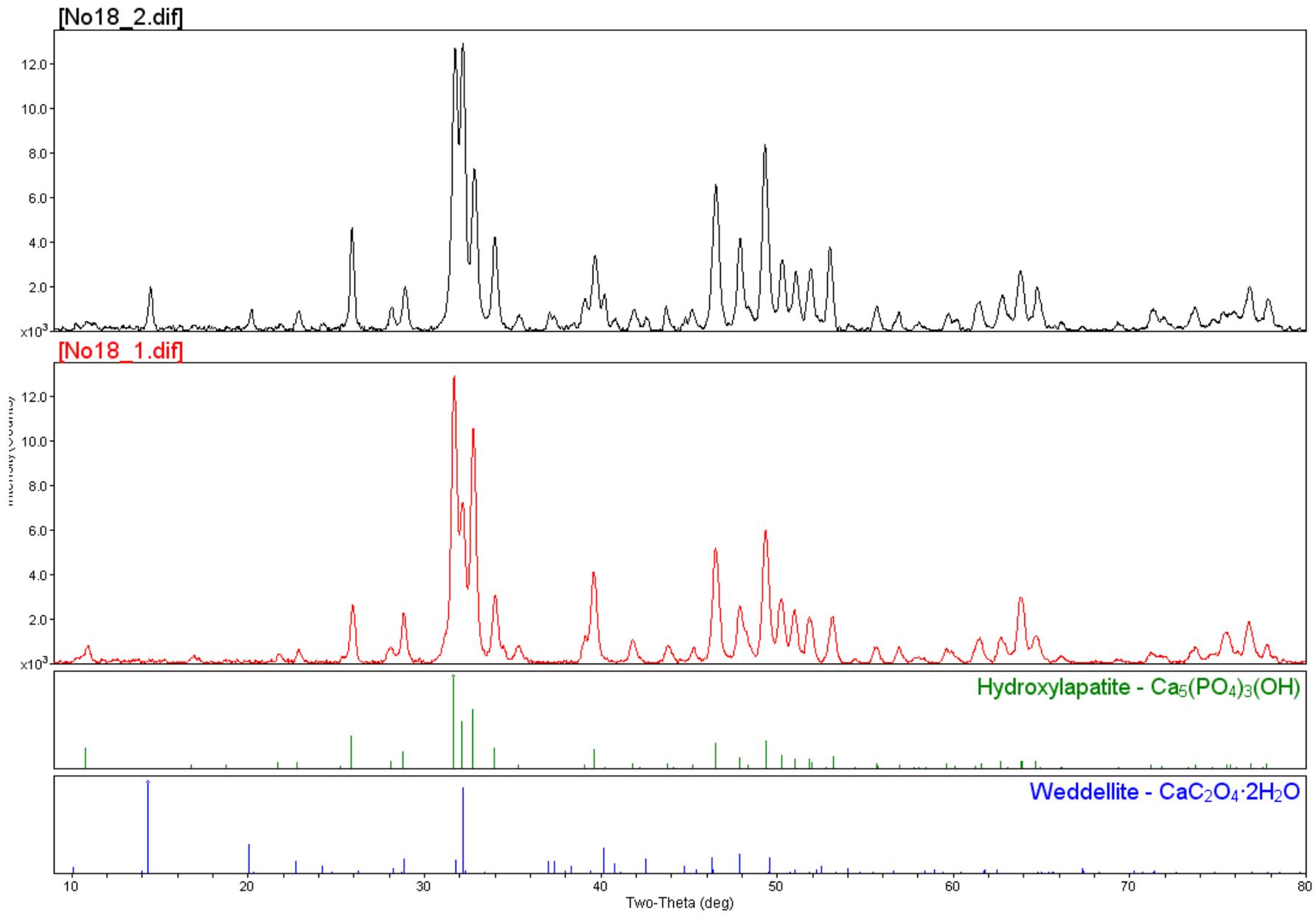
Sample 3, Layer 4

04-009-3817> Gypsum - $\text{Ca}(\text{SO}_4)(\text{H}_2\text{O})_2$

98-000-0464> Wuestite - FeO

01-080-1672> $(\text{Co}_{0.97}\text{Sn}_{0.03})(\text{Co}_{1.03}\text{Sn}_{0.97})\text{O}_4$ - Cobalt Tin Oxide





Acknowledgements

McCrone Associates Staff

Cynthia Kuniej Berry, Conservator

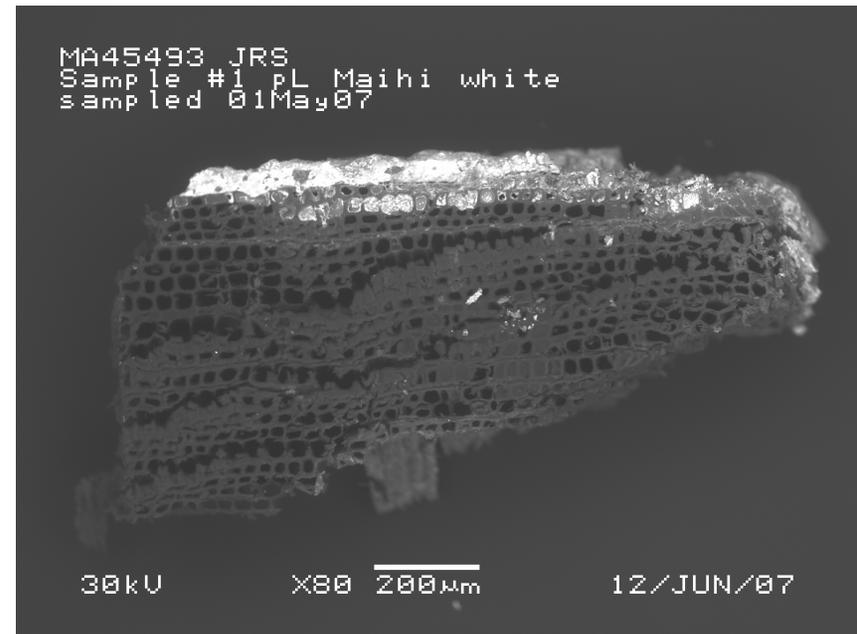
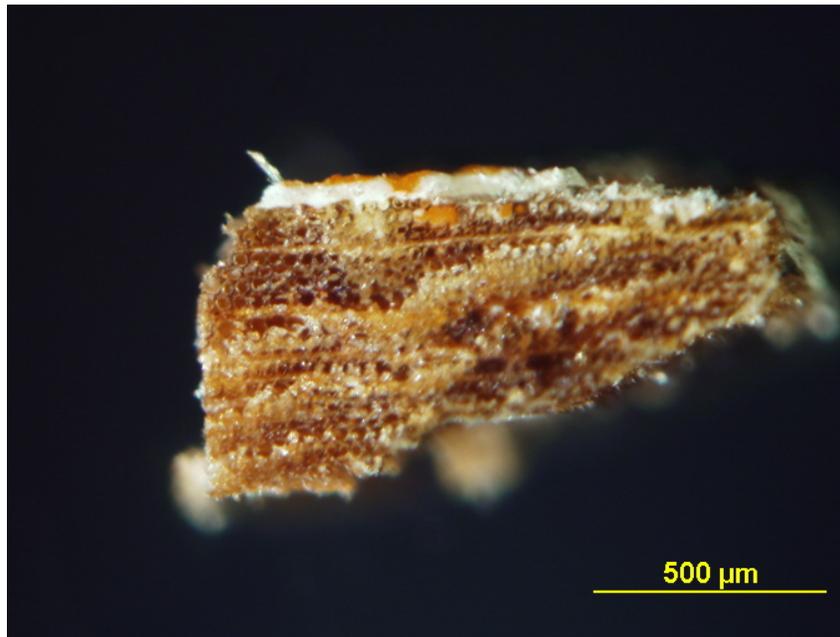
Robert LaFrance, University of Illinois
Museums

(and clients who know who they are)

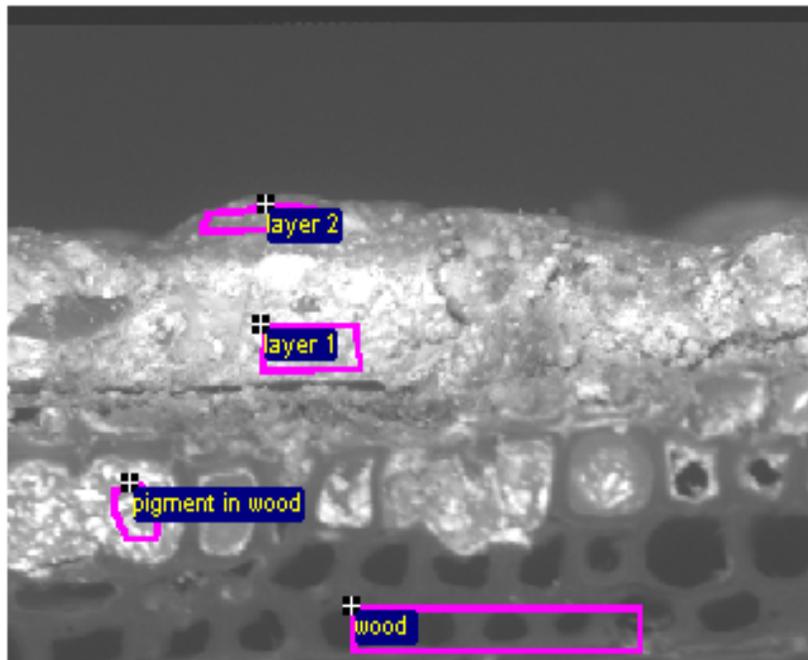
Maori House The Field Museum



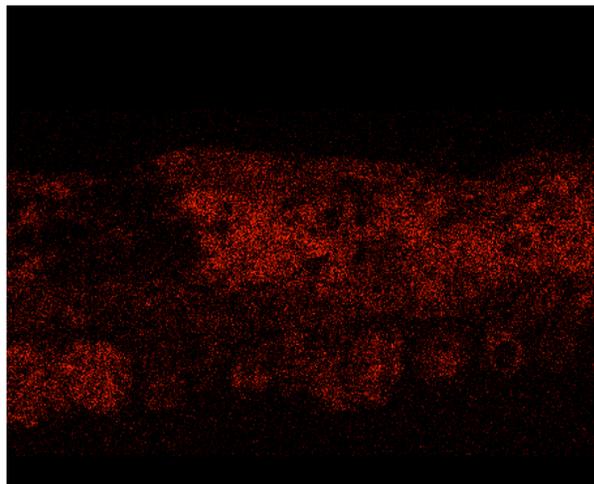
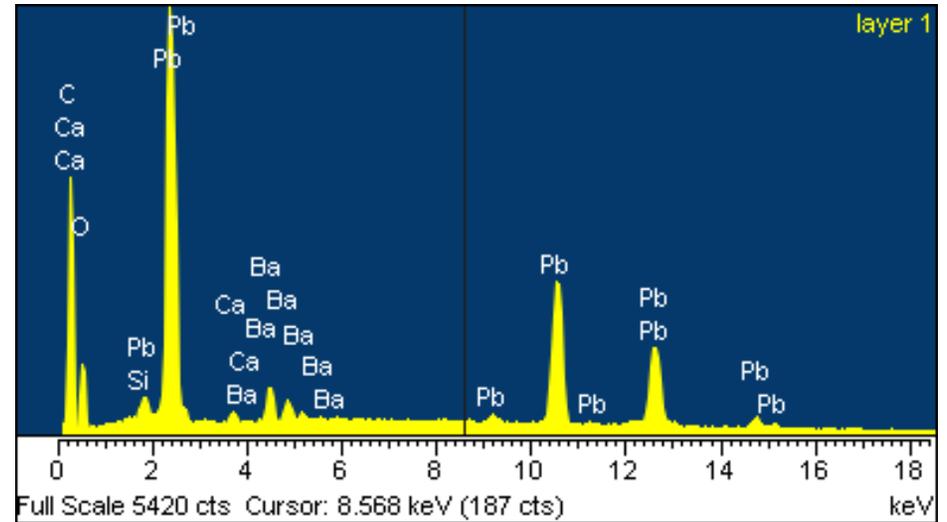
Cross-Section Evaluation



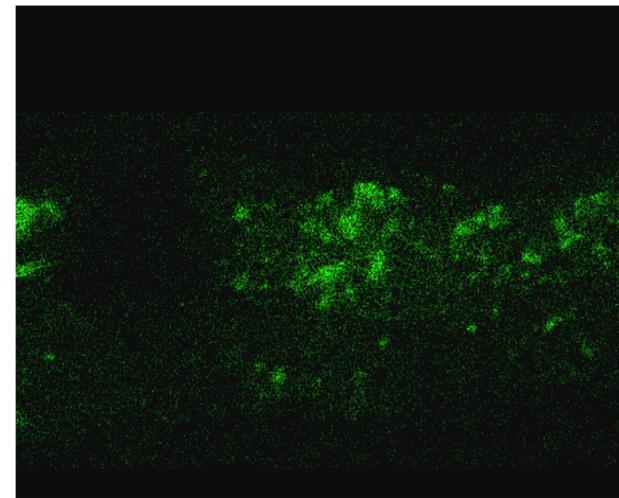
Not embedded in epoxy!



Electron Image 1



Pb La1



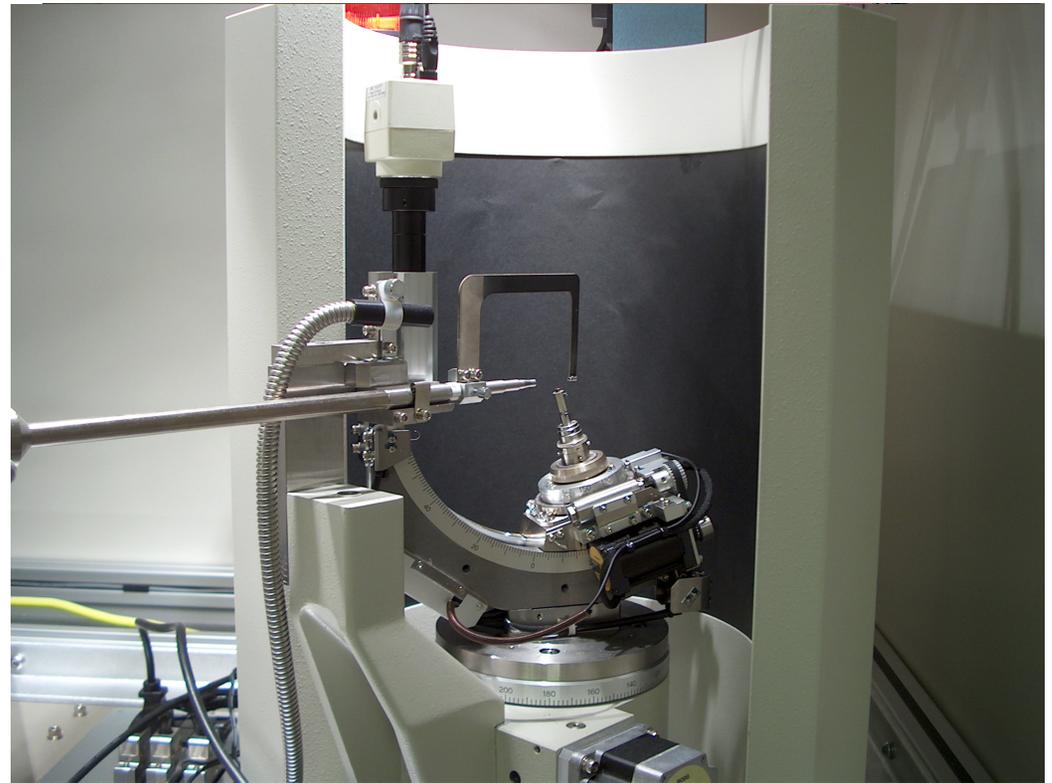
Ba La1

Microanalysis



Micro-XRD

- Rotating anode
- Image plate detection
- Particles in the 10 μm size range
- Beam size 300 μm or 100 μm



Phase Identification

How are the atoms in a sample arranged?

Calcium carbonate



calcite



aragonite



Phase Identification

rutile



anatase



brookite

Corrosion or
patina?



What type?

Particle Approach to Material Identification

- Multi-technique instruments versus micro-instrumentation
- Major obstacle is removing particles for analysis and using the same particle for multiple instruments
- “particle” ~ micron size range

Standards

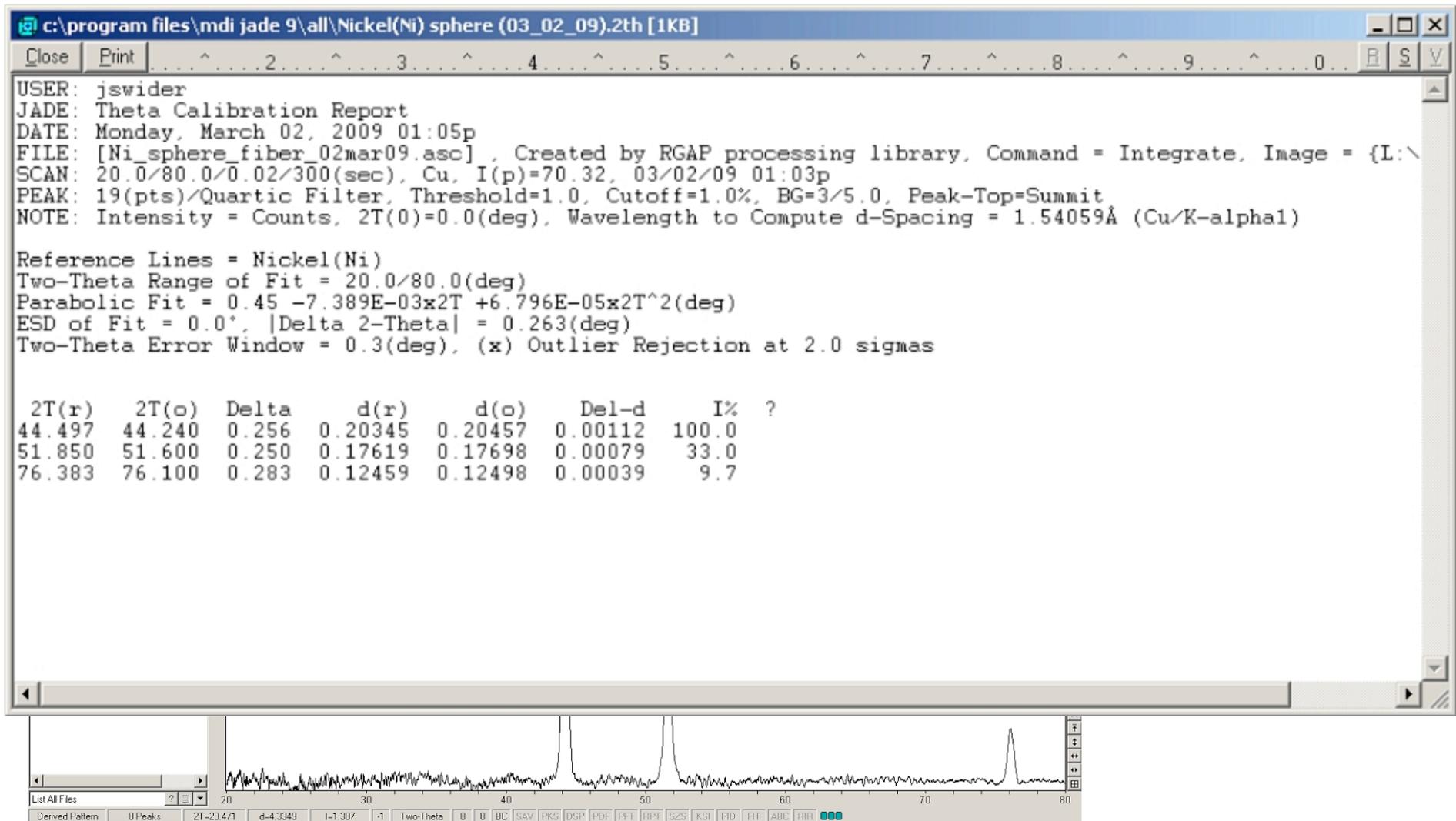
- Powders in capillary
 - Corundum, silicon
- Wires
 - 50 μ m Ni, 100 μ m Au
- Ni spheres

Siemens 5000 Bulk XRD

- Bulk powder XRD
- Pharmaceuticals
- Asbestos
- USP methods
- Automated sample changing



2-theta calibration



International Centre for Diffraction Data (ICDD)



A screenshot of the PDF Card software interface. The main window displays a diffraction pattern for PDF # 00-003-0593. The pattern shows a series of peaks at various 2θ angles. The software interface includes a menu bar (File, Edit, d-Spacings, Tools, Window, Help), a toolbar, and a main display area with a grid of d-spacings and intensity values. A table of results is visible, listing PDF #, QM, and Chemical Formula. The search results table is as follows:

PDF #	QM	Chemical Formula	Calc
00-001-0229	O	Ca (N O3)2 4 H2 O	Calc
00-001-0770	I	Ba Ca (C O3)2	Bar
00-001-0837	B	Ca C O3	Calc
00-002-0604	O	(Ca, Mn) C O3	Calc
00-002-0623	I	Ca C O3	Calc
00-002-0629	I	Ca C O3	Calc
00-002-0630	O	(Ca, Mn) C O3	Calc
00-002-0643	O	(Ca, Mn) C O3	Calc
00-002-0670	O	(Ca, Mn) C O3	Calc
00-002-0714	O	(Ca, Mn) C O3	Calc
00-003-0569	O	Ca C O3	Calc
00-003-0593	O	Ca C O3	Calc
00-003-0596	O	Ca C O3	Calc
00-003-0612	O	Ca C O3	Calc
00-003-0670	O	Ca C O3	Calc
00-004-0636	B	Ca C O3	Calc
00-004-0637	B	Ca C O3	Calc
00-005-0586	S	Ca C O3	Calc
00-014-0177	I	Ca C O3 · 0.65 H2 O	Calc

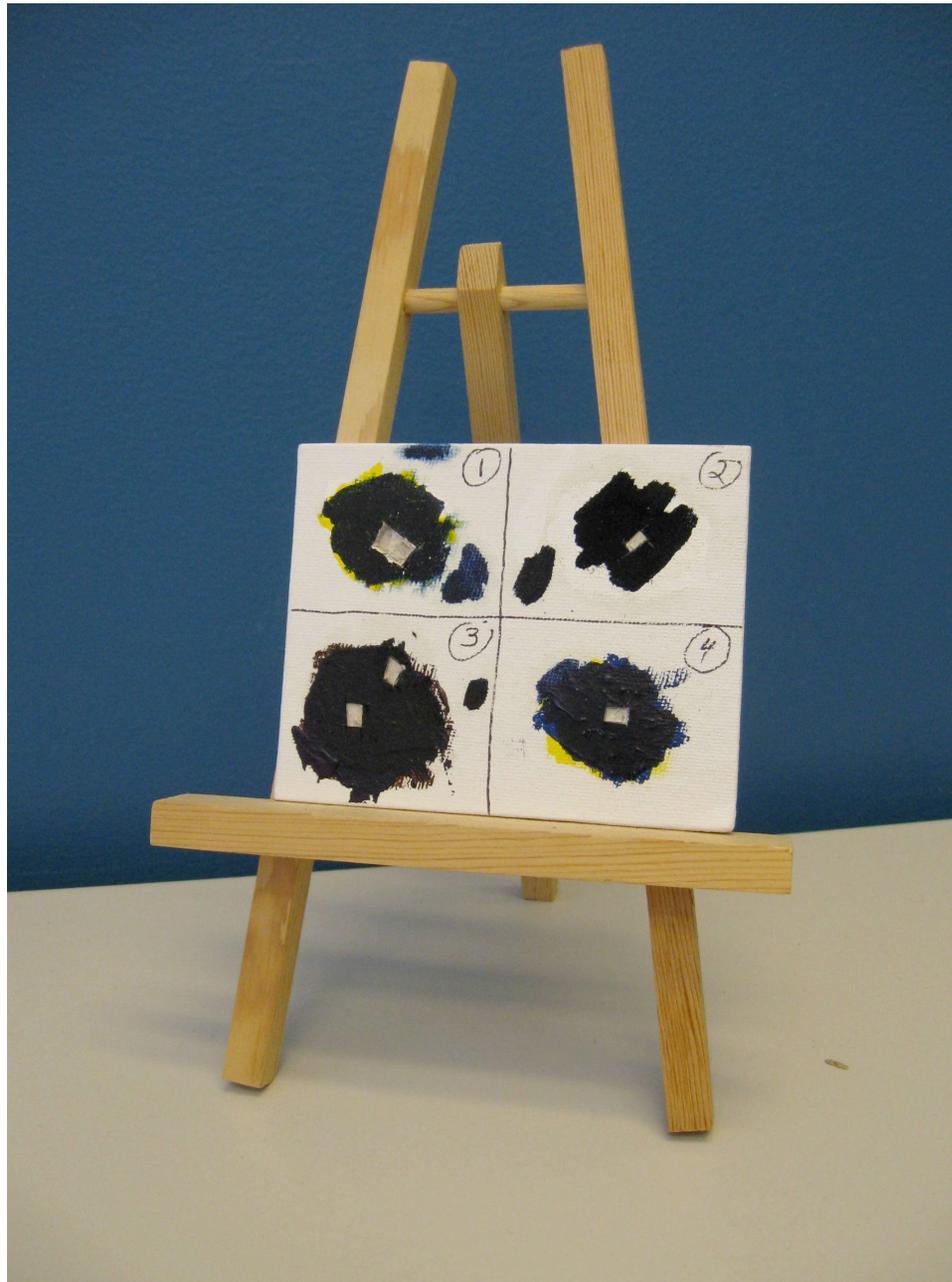
The interface also shows a search description: '[All Names Contains Words 'calcite']'. The bottom status bar indicates the system is running Windows XP with the taskbar showing various open applications like XRay Gener..., Jade 7, and ICDD DDView... at 8:51 AM.

Cross-Section Studies

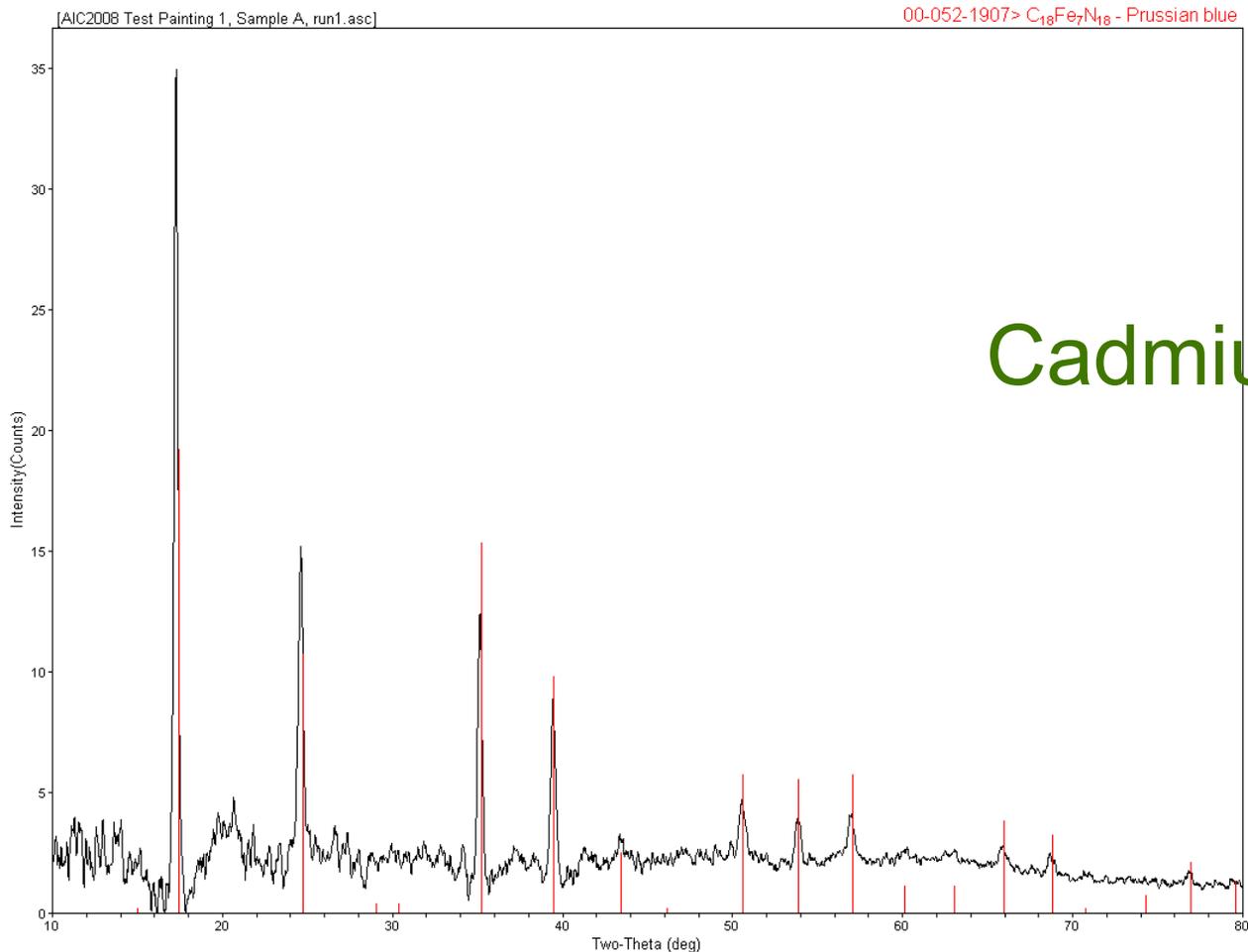
- test paintings
- architectural lead paint identification
- 15th century Spanish panel painting

Test Painting

- Simple primed canvas with three layers of known pigment and media or commercial paint
- Sections taken and the layers analyzed for pigment and media by particle
- Not embedded in epoxy



Test Painting Area 1



Prussian Blue

Cadmium Yellow Light

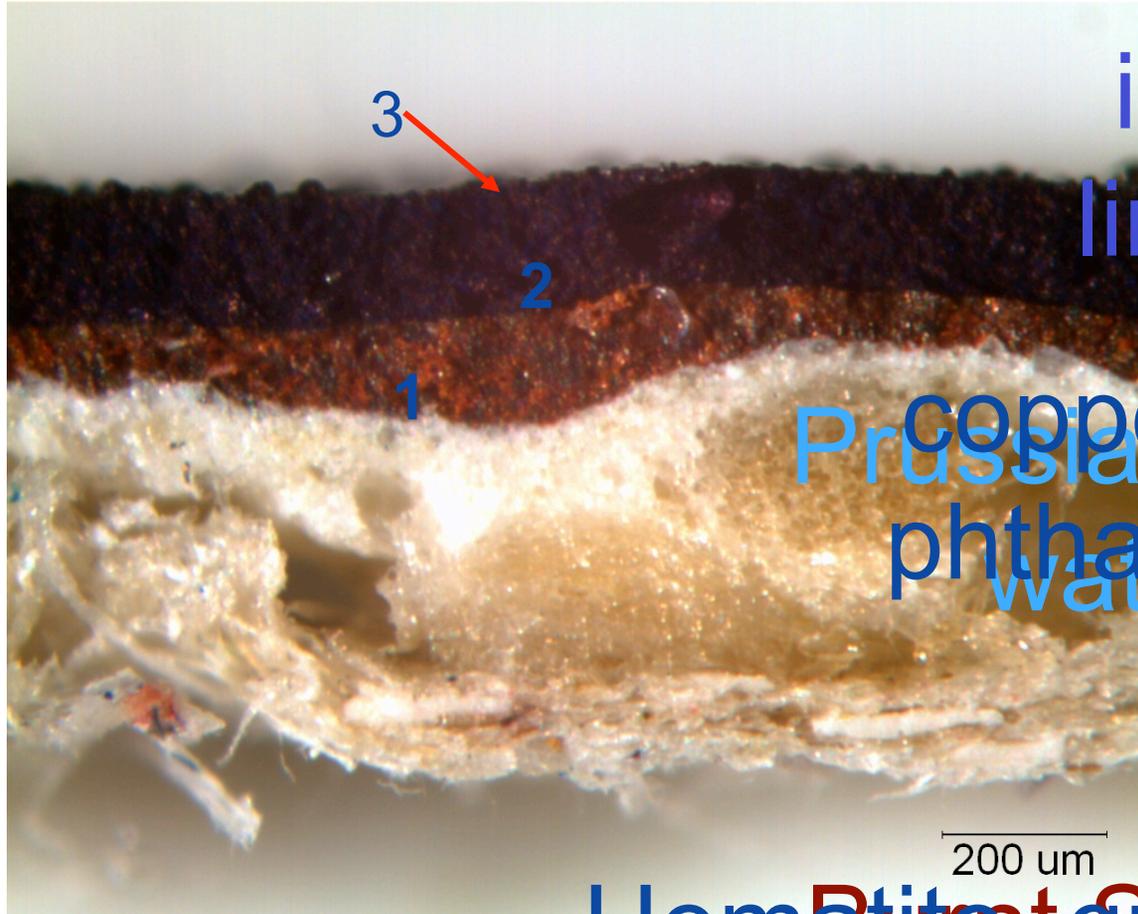
Zincite

Barite

Rutile

tanium white

Test Painting Area 3



indigo in
barite
linseed oil

copper and iron
Prussian Blue Hue
phthalocyanines
watercolor

Hematite, Quartz, barite