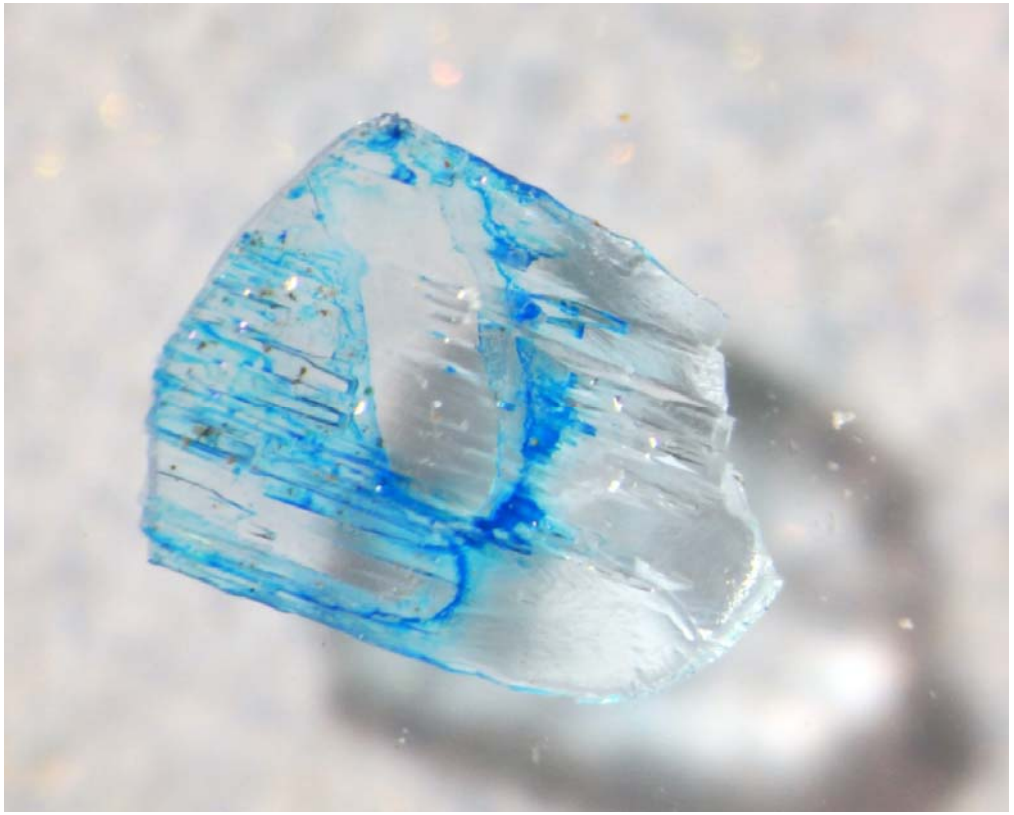
Analyses of blue hemimorphite from the Ojuela Mine, Mapimí, Mapimí Municipality, Durango, Mexico

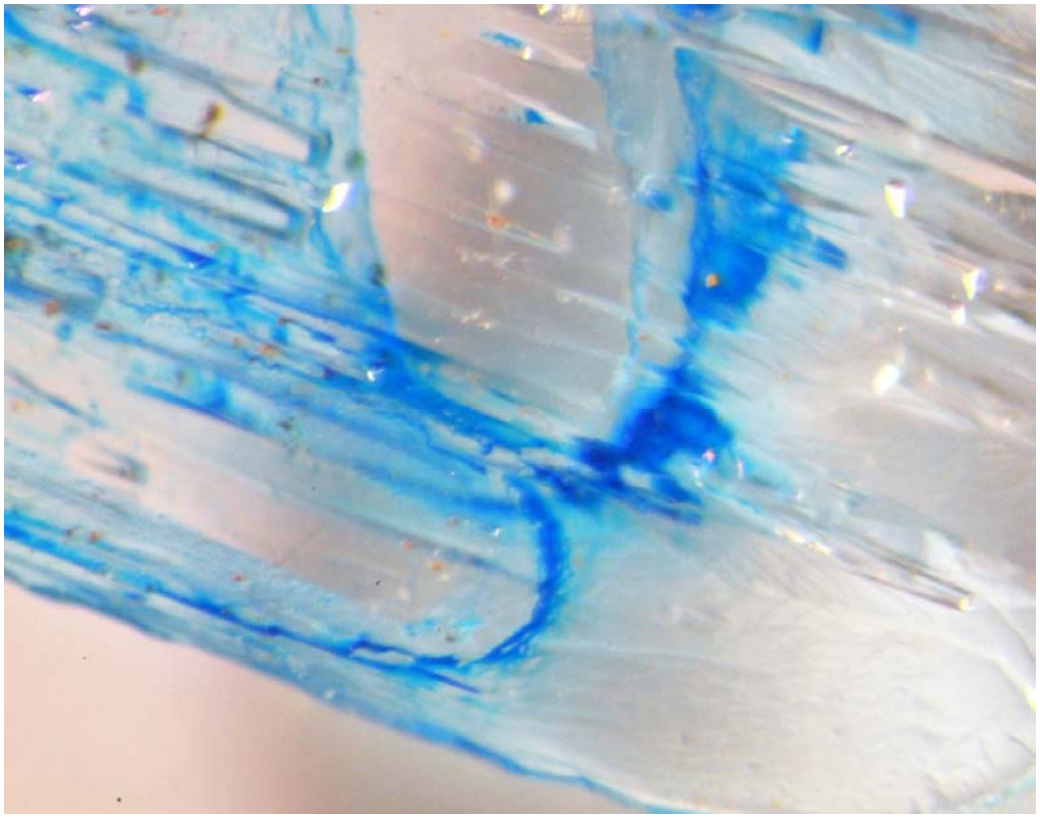
Dr. John Rakovan and research group, Miami University, Oxford Ohio September 2020

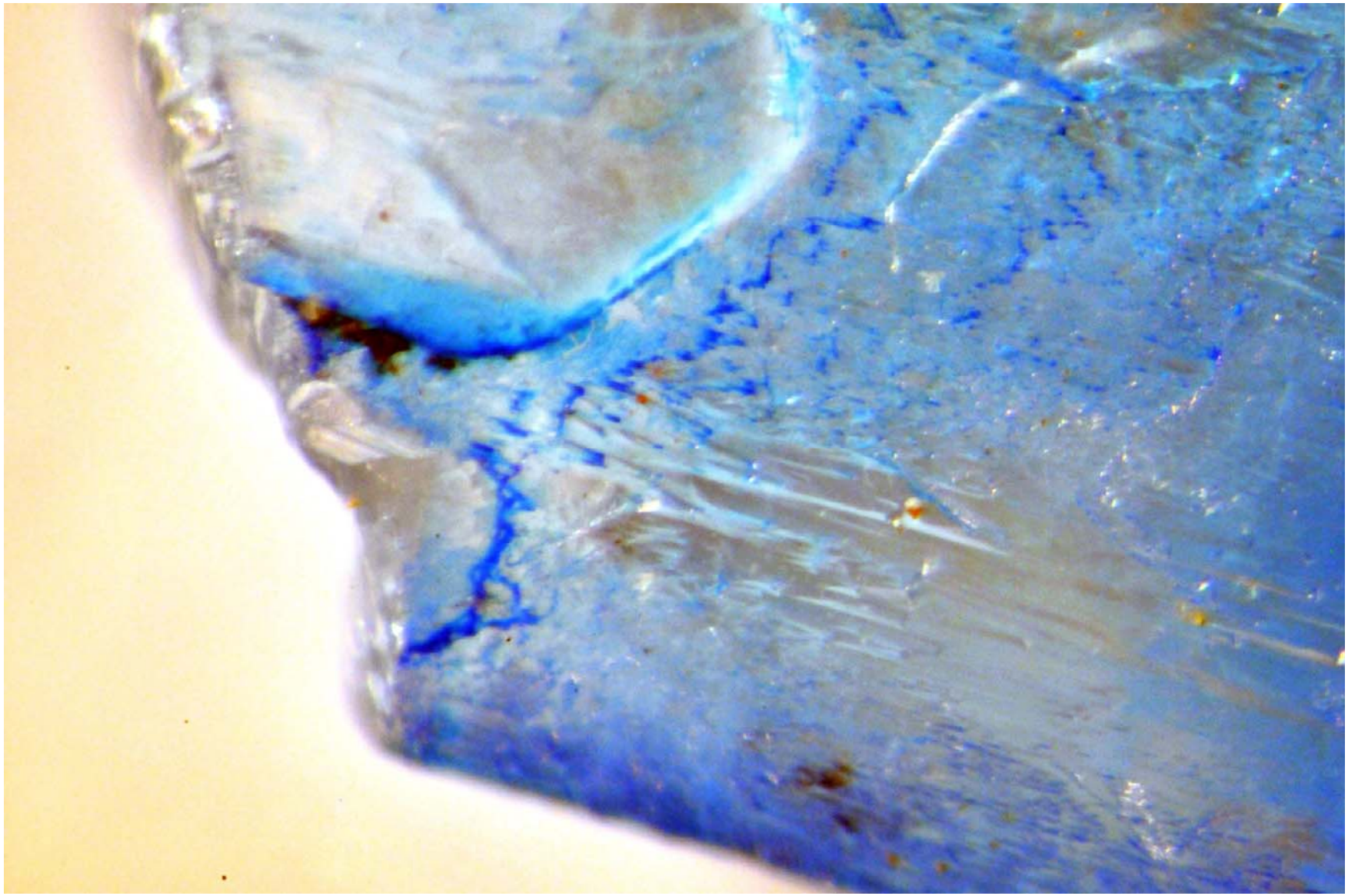
Analyses: A flat of specimens with varying characteristics was viewed.
Representative examples of hemimorphite crystals were removed and analyzed by powder X-ray diffraction (PXRD), Raman Spectroscopy, Scanning Electron Microscopy, X-ray fluorescence via EDS, and optical microscopy. Numerous crystals of hemimorphite show an uneven distribution of a blue surface coating (film), which on larger crystals appears to concentrate in crystal surface depressions (e.g. striation troughs, around the edges of intergrown crystals, etc.). In some places the coating is much thicker than in most areas. It is these ticker coatings that were analyzed most closely because they are the most highly concentrated with the material. Several complete crystals that appeared to have a thicker than typical coating were powdered for PXRD. Both an area of thick coating and an seemingly clean portion of hemimorphite were analyzed by Raman using a 633nm wavelength laser.

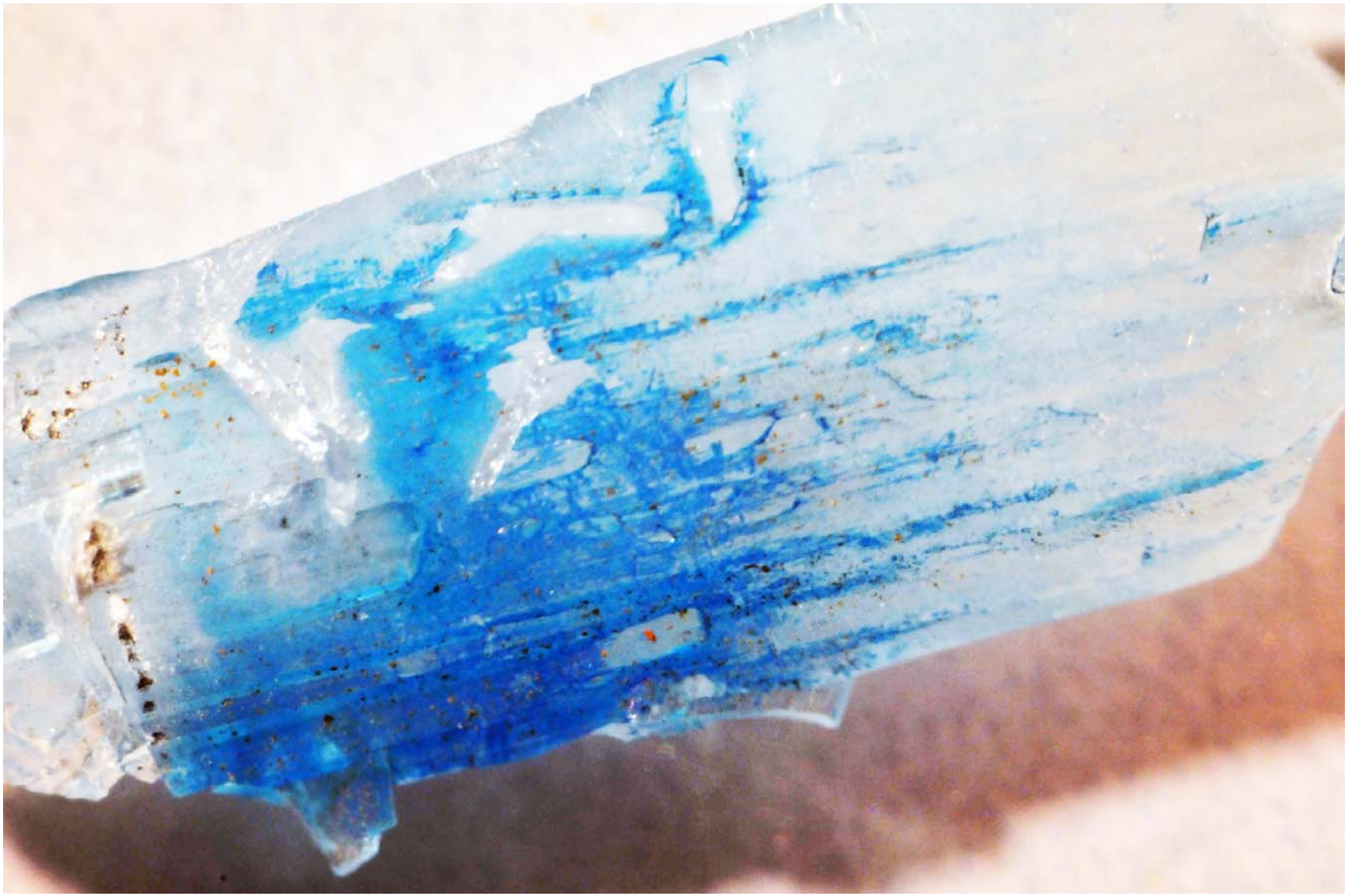
Results: PXRD shows only the presence of hemimorphite. This may be the result of the concentration of the blue coating material (i.e. too little) or lack of crystallinity. Raman spectroscopy, which has a much greater spatial resolution compared to the PXRD, was able to isolate the blue material in the analysis signal. The Raman pattern from the blue film shows a perfect match with the dye/pigment Phthalocyanine Blue BN. Interestingly, the strongest Raman bands from Phthalocyanine Blue BN are observed in the data collected on the white portion of the same crystal (i.e. where the film is not visible). It is believed that this is the result of resonance enhancement of the Raman signal associated with use of A 633 nm laser and detection of a very thin film that is not optically detectable. EDS data shows the presence of Cu but spectra are dominated by the underlying hemimorphite. The Kα peak intensity ratio of Cu:Zn is approximately 1:8.

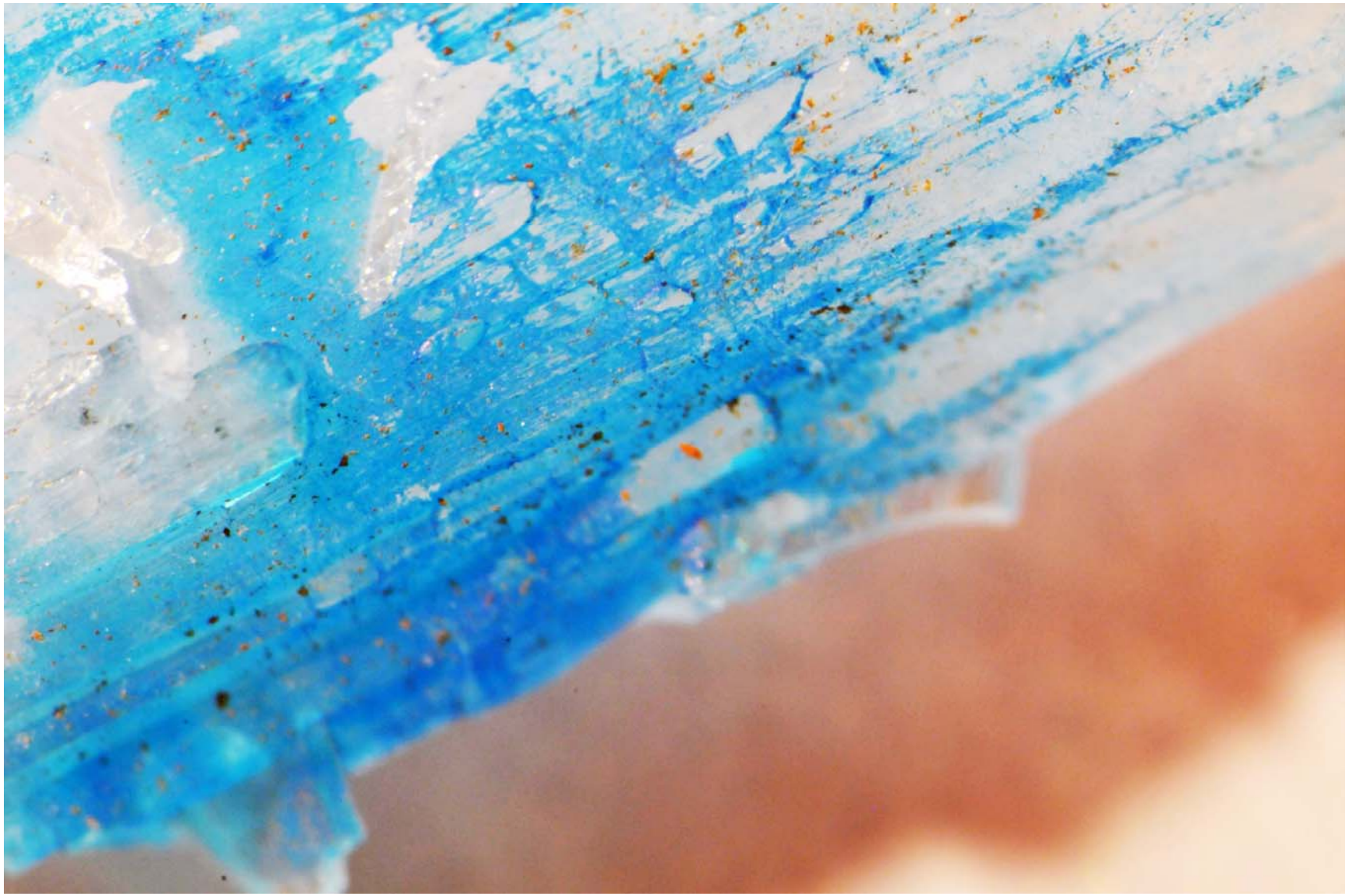
Another group working with these samples found that a solution of sodium bicarbonate and detergent removed some of the coating. It is unknown if it dissolved a portion of the coating or dispersed it into a colloidal suspension.

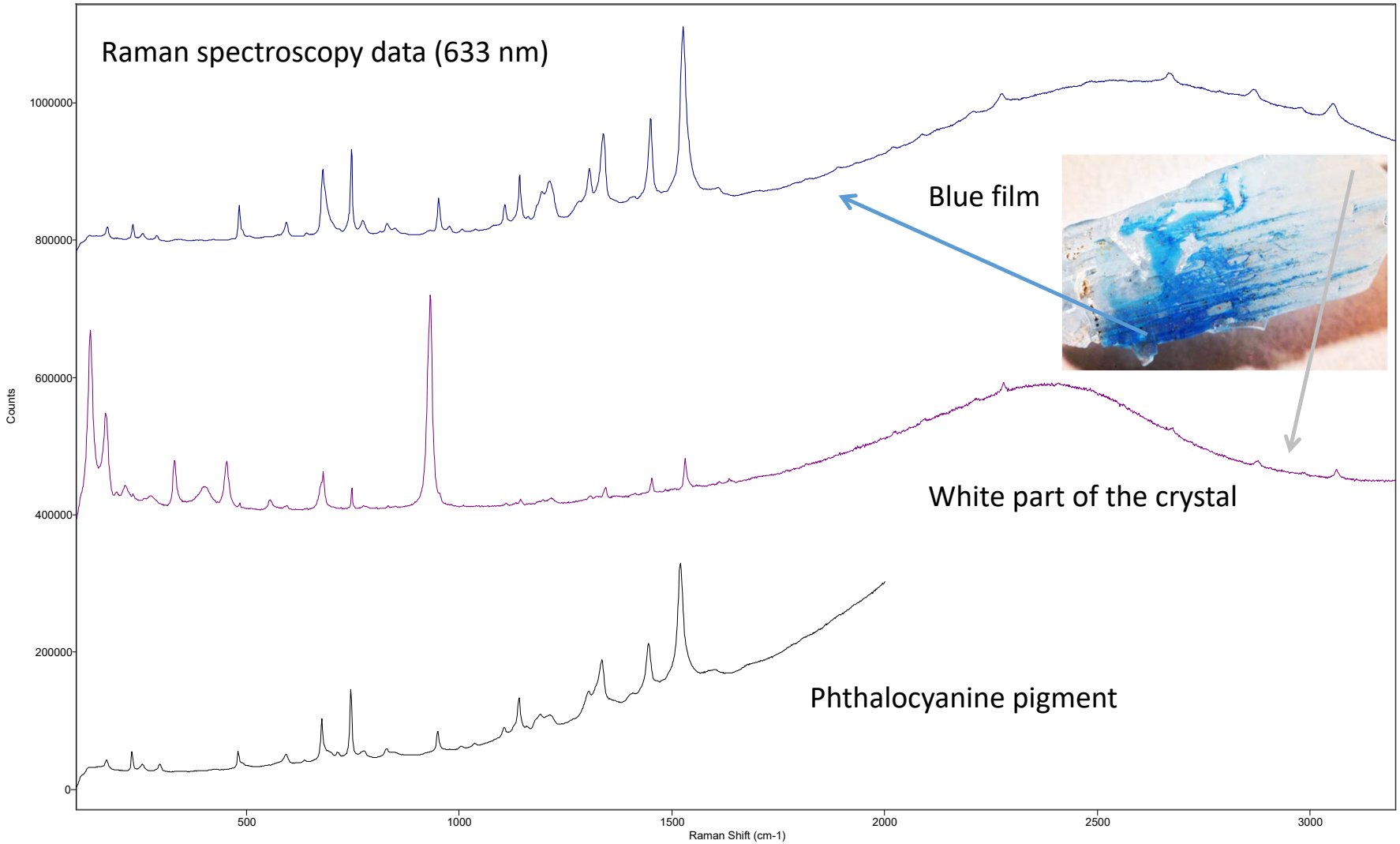


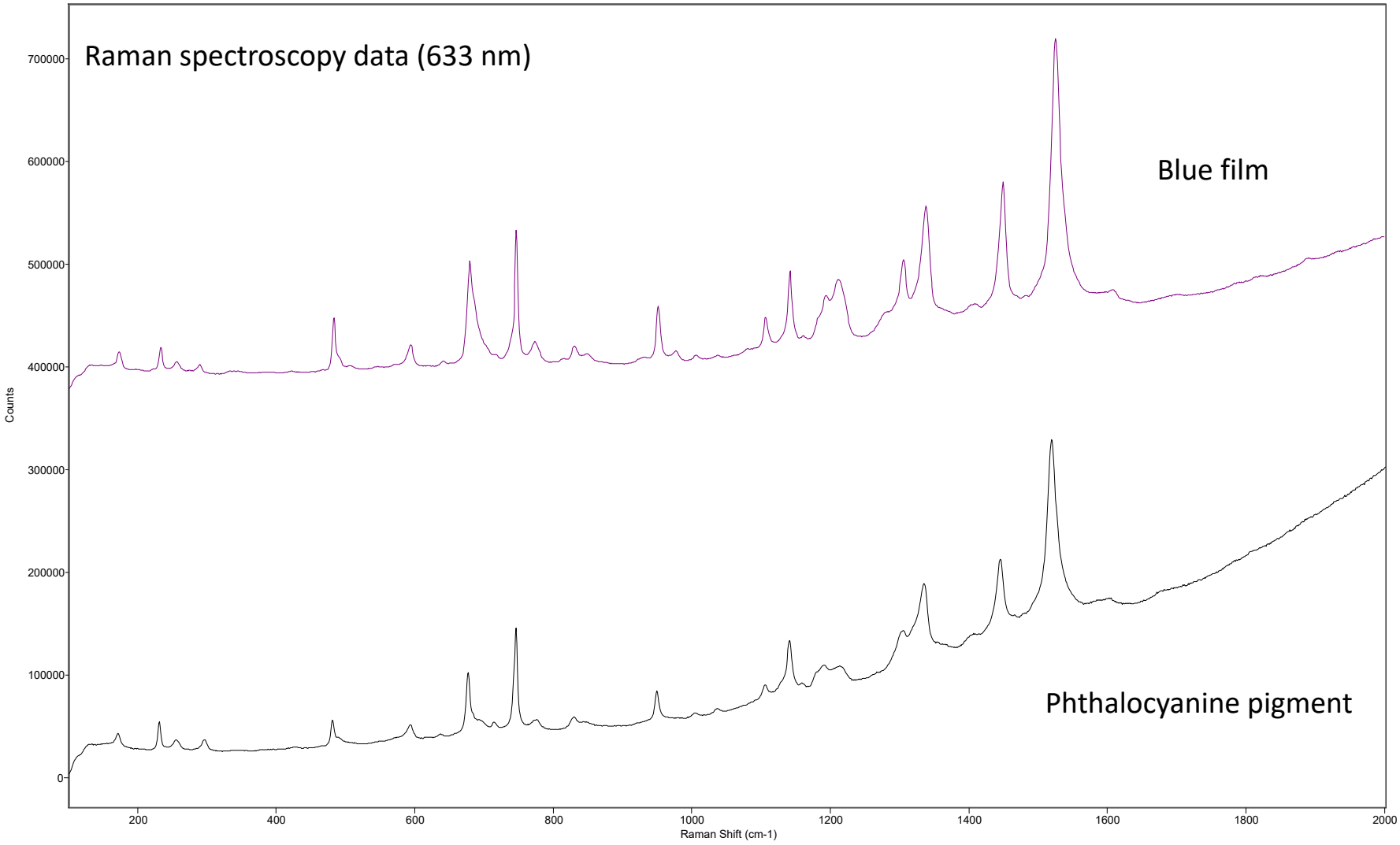


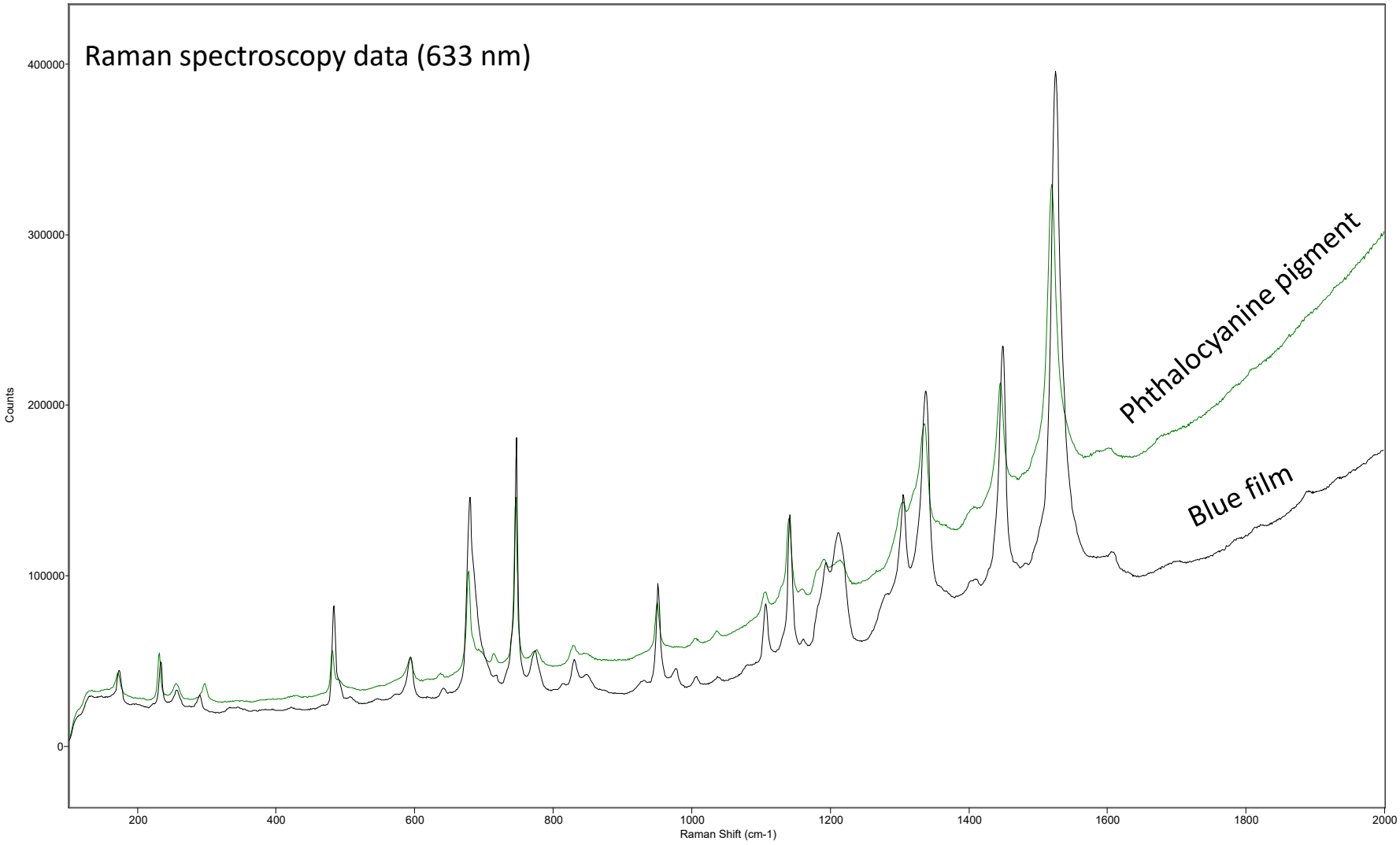




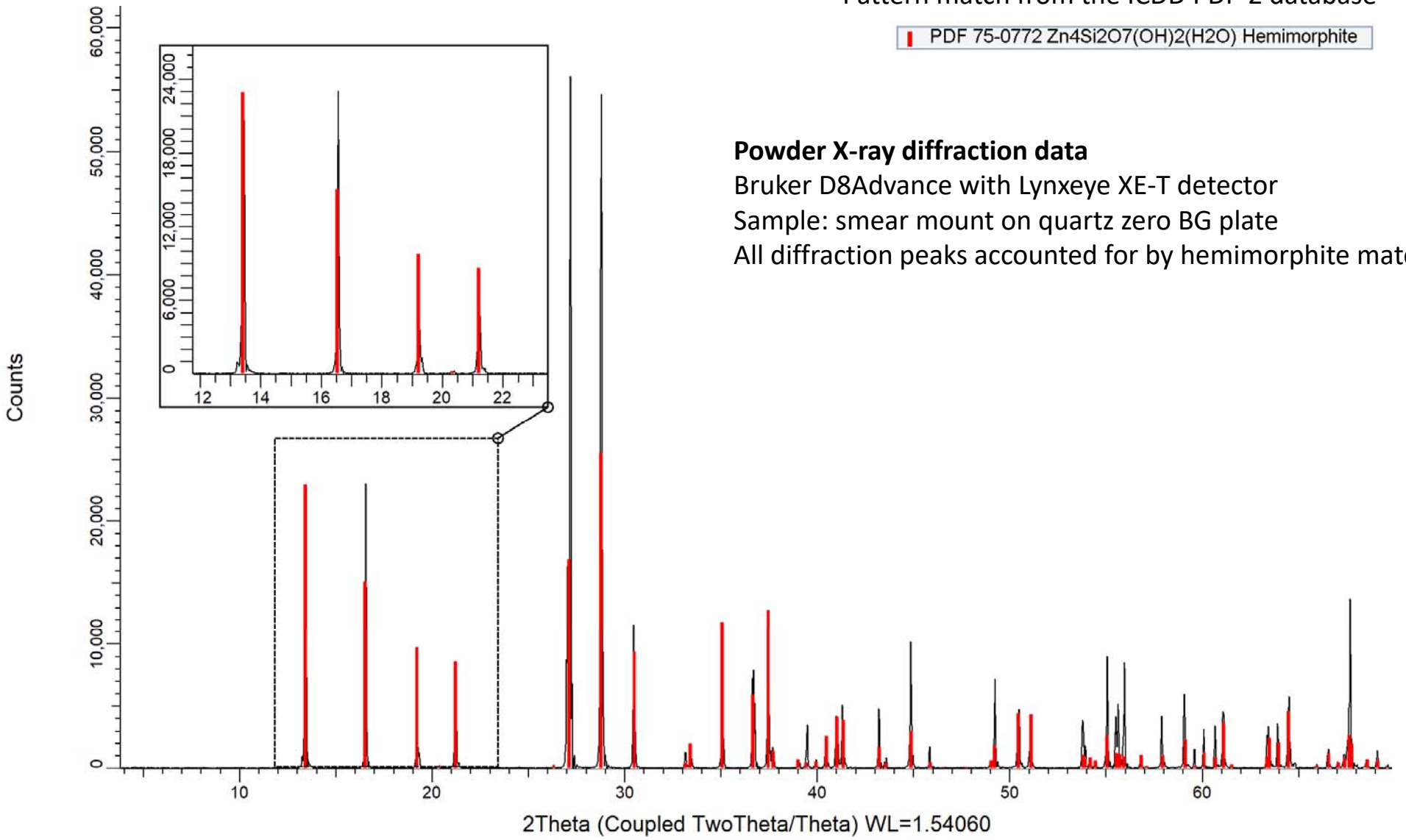



Raman spectroscopy data (633 nm)
Blue film
White part of the crystal
Phthalocyanine pigment
Counts
1000000
800000
600000
400000
200000
0
500
1000
1500
2000
2500
3000
Raman Shift (cm-1)

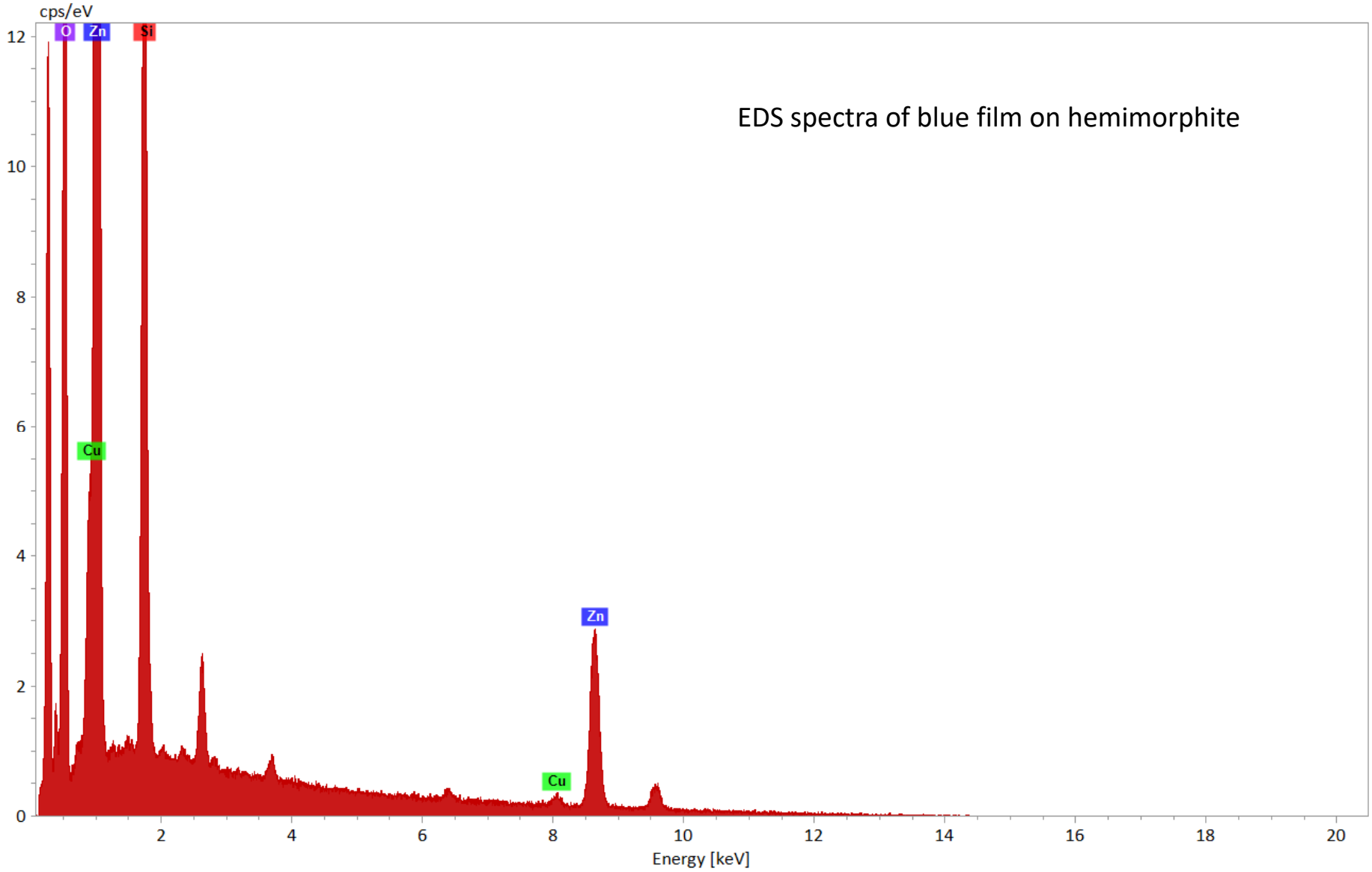

Raman spectroscopy data (633 nm)
Blue film
Phthalocyanine pigment
Counts
Raman Shift (cm-1)
0
100000
200000
300000
400000
500000
600000
700000
200
400
600
800
1000
1200
1400
1600
1800
2000


Raman spectroscopy data (633 nm)
Counts
400000
300000
200000
100000
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Raman Shift (cm-1)
Phthalocyanine pigment
Blue film

Pattern match from the ICDD PDF-2 database

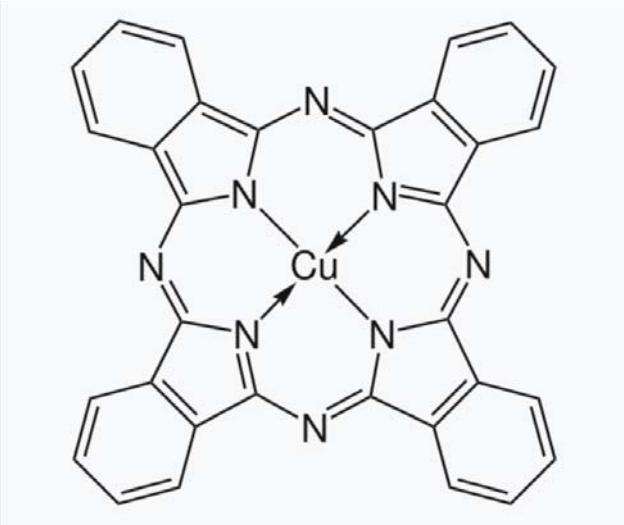


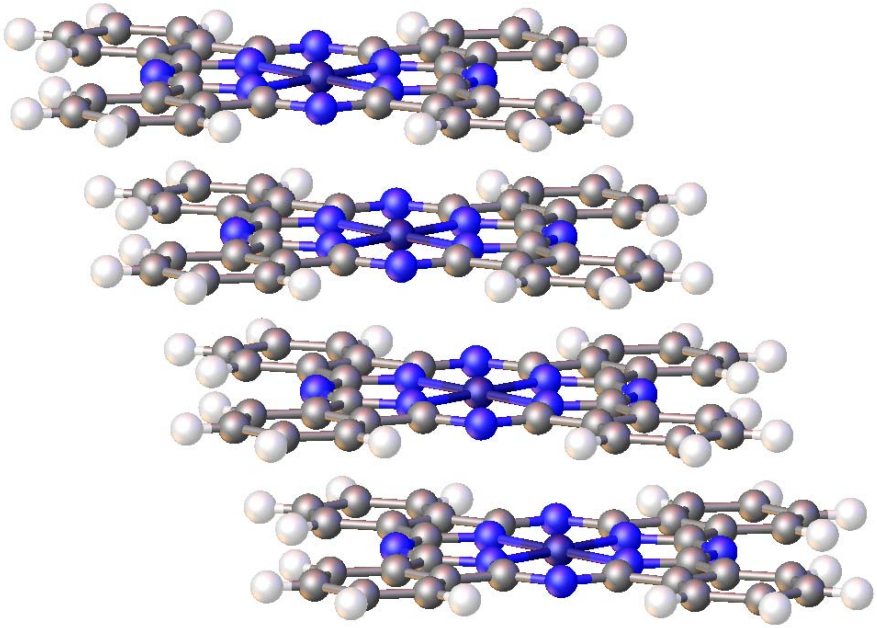
Powder X-ray diffraction data
Bruker D8Advance with Lynxeye XE-T detector
Sample: smear mount on quartz zero BG plate
All diffraction peaks accounted for by hemimorphite match



EDS spectra of blue film on hemimorphite

“Phthalocyanine Blue BN, (EINECS 205-685-1), is a bright, crystalline, synthetic blue pigment from the group of phthalocyanine dyes. Its brilliant blue is frequently used in paints and dyes. It is highly valued for its superior properties such as light fastness, tinting strength, covering power and resistance to the effects of alkalis and acids. It has the appearance of a blue powder, insoluble in most solvents including water” Source: https://en.wikipedia.org/wiki/Phthalocyanine_Blue_BN





$C_{32}H_{16}CuN_8$

Sample in a Na-bicarbonate and detergent solution (video)