Revised Report of Results: MVA9119

Progress Report on the Analysis of Red/Gray Chips in WTC Dust

Prepared for:

Classical Guide
Denver, CO

Respectfully Submitted by: _____

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Analysis of Red/Gray Chips in WTC Dust

Introduction

This revised report summarizes the results to date of the analyses of red/gray chips found in samples of dust generated by the World Trade Center (WTC) disaster of 11 September 2001. MVA Scientific Consultants was requested by Mr. Chris Mohr of Classical Guide to scientifically study red/gray chips from WTC dust that matched those presented in a paper by Harrit et al., 2009,[1] which concluded that thermitic material was present in the WTC dust. Mr. Mohr was unable to gain access to any samples used in the Harrit study so four samples were chosen from the archives of MVA Scientific Consultants. These dust samples had been collected within a month of 11 September 2001 and sent to MVA for different projects. They are identified by the sample numbers shown below and on the New York City map shown in Figure 1. The red/gray chips discussed in this report were analyzed during the period from 18 November 2011 to 20 February 2012. Some analytical results characterizing the particles in the dust from two of the samples (4808-L1616 and 9119-X0135) had been previously published in the scientific literature. [2,3]

MVA #	Date Collected	Sample Location	Fig. 1 Map No.
4808-L1616	28 September 2001	22 Cortlandt St.	1
4795-L1560	22 September 2001	Murray & Church St.	2
5230-M3451	15-16 September 2001	49 Ann St.	3
9119-X0135	07 October 2001	33 Maiden Lane	4

Methods

In order to confirm that the samples chosen had the characteristics of WTC dust, the samples were examined by stereomicroscope and by polarized light microscopy (PLM) according to the procedures described in Turner et al., 2005[4] (Figures 2 and 3). The analytical procedures used to characterize the red/gray chips were based on the criteria for the particles of interest in accordance with the recommended guidelines for forensic identification of explosives[5] and the ASTM standard guide for forensic paint analysis and comparison.[6] The criteria for the particles of interest as described by Harrit et al.[1] are: small red/gray chips attracted by a magnet and showing an elemental composition primarily of aluminum, silicon and iron as determined by scanning electron microscopy and x-ray energy dispersive spectroscopy (SEM-EDS) (Figure 4). The spectrum may also contain small peaks related to other elements. To that end, the following protocol was performed on each of the four WTC dust samples.

1. The dust sample particles contained in a plastic bag were drawn across a magnet and those attracted to the magnet were collected (Figure 5).

2. Using a stereomicroscope, particle chips showing the characteristic red/gray were removed and washed in clean water.
3. The particles were dried and mounted on a carbon adhesive film on an SEM stub and photographed (Figure 6).
4. Analysis of the surfaces of the chips was done by SEM-EDS at 20 kV without any added conductive coating (Figures 7 and 8).

Red/gray particles that matched the criteria (attracted to a magnet and an EDS Al-Si-Fe spectrum) were then considered particles of interest and subjected to additional analytical testing. The additional tests included: Fourier transform infrared spectroscopy (FTIR); SEM-EDS of cross-sections; low temperature ashing and residue analysis by transmission electron microscopy (TEM) with selected area electron diffraction (SAED) and EDS; muffle furnace ashing and residue analysis by PLM and TEM-SAED-EDS; ultra-microtome sectioning of the red layer and analysis by TEM-SAED-EDS; and solvent tests.

Stereomicroscopy was done using either an Olympus SZ-40 stereomicroscope or a Wild M5-49066 stereomicroscope.

Polarized light microscope (PLM) examination of the dusts and ashed residue was done with an Olympus BH-2 PLM or an aus Jena Jenapol PLM.

Scanning electron microscope (SEM) analysis of the surfaces of red/gray chips was done using a JEOL Model JSM-6490LV SEM coupled with a Thermo Scientific Noran System SIX x-ray energy dispersive spectrometer (EDS). Digital x-ray images and phase mapping was also done with this instrument.

Fourier transform infrared spectroscopy (FTIR) was performed with a SensIR FTIR equipped with a diamond ATR objective and attached to an Olympus BX-51 compound microscope.

Cross-sections of the chips of interest were made with clean scalpel blades. The analysis of cross-sections was done with a JEOL Model JSM-6500F field emission SEM with a Thermo Scientific Noran System SIX EDS system.

Low-temperature ashing (LTA) is an alternative to using solvents to extract inorganic constituents from an organic film or coating.[6] LTA of the chips of interest was done using an SPI Plasma Prep II plasma asher. LTA was performed for time periods of 30 minutes to 1 hour depending on the size of the chip. The gray layer remained intact and the red layer residue was collected in clean water and drops of the suspension were placed on carbon-film TEM grids. After drying, the particulate was analyzed using a Philips CM120 TEM capable of SAED and equipped with an Oxford EDS system.

Chips of interest were ashed in a muffle furnace using a NEY Temperature Programmable furnace operated at 400^{o}C for 1 hour. The gray layer remained intact and the red layer residue was prepared as described above and analyzed using a Philips CM120 TEM-SAED-EDS.

Ultra-thin sections of a red layer were cut using a Reichert-Jung Ultracut E Ultramicrotome with a diamond knife. The ultra-thin sections were placed directly on TEM grids and analyzed using a Philips EM 420 TEM-SAED-EDS.

Samples of red/gray chips were placed in several solvents overnight and then subjected to ultrasonic agitation to determine if the solvents could dissolve the epoxy binder and liberate the internal particles. The solvents included methylene chloride, methyl ethyl ketone (MEK), and two commercial paint strippers used for epoxy resins. The commercial paint strippers, Klean-Strip KS-3 Premium Stripper and Jasco Premium Paint and Epoxy Remover, contain methylene chloride, methanol and mineral spirits. One red/gray chip was subjected to 55 hours of submersion in MEK, then dried and coated with a thin layer of gold for conductivity. The red layer was analyzed by SEM-EDS analysis using an advanced x-ray phase mapping technique. The technique uses a multivariate statistical analysis program to find spectrally similar regions in a spectral image acquisition. It analyzes the spectrum at each pixel location and then groups the pixels with similar spectra into principal components or phases.[7]

Results

The composition of the four samples of dust chosen for study were consistent with WTC dust previously published [2,3] (Appendix A).

Red/gray chips that had the same morphology and appearance as those reported by Harrit et al.[1], and fitting the criteria of being attracted by a magnet and having the SEM-EDS x-ray elemental spectra described in their paper (Gray: Fe, Red: C,O, Al, Si, Fe) were found in the WTC dust from all four locations examined. The red layers were in the range of 15 to 30 micrometers thick. The gray layers were in the range of 10 to 50 micrometers thick (Appendix B).

The FTIR spectra of the red layer were consistent with reference spectra of an epoxy resin and kaolin clay (Figure 9) (Appendix C).

The SEM-EDS and backscattered electron (BE) analysis of the cross-sections of the gray layer in the red/gray chip showed it to be primarily iron consistent with a carbon steel. The cross-sections of the red layer showed the presence of equant-shaped particles of iron consistent with iron oxide pigment and plates of aluminum/silicon consistent with reference samples of kaolin. The thinnest kaolin plates were on the order of 6 nm with many sets of plates less than 1 micrometer thick. Small x-ray peaks of other elements were sometimes present. The particles were in a carbon-based matrix (Figures 10 through 15) (Appendix D).

TEM-SAED-EDS analysis of the residue after low temperature ashing showed equant-shaped particles of iron consistent with iron oxide pigment and plates of kaolin clay. Small numbers of titanium oxide particles consistent with titanium dioxide pigment were also found (Figure 16) (Appendix E).

PLM analysis of the residue from red/gray chips after muffle furnace ashing at 400^{o}C for 1 hour showed very fine red particles consistent with synthetic hematite (iron oxide) pigment particles (Figure 17). PLM also found possible clay present based on a micro-chemical clay-stain test. TEM-SAED-EDS analysis of another portion of the same muffle furnace residue showed equant-shaped particles of iron consistent with iron oxide pigment, plates of kaolin clay and some aciniform aggregates of carbon soot consistent with incomplete ashing of a carbon-based binder (Figure 18). The SAED pattern of the kaolin particles (Figure 19) matched the kaolin pattern shown in the McCrone Particle Atlas[8] (Appendix E). The values for the d-spacings determined for the diffraction patterns matched those produced by reference kaolin samples.

TEM-SAED-EDS analysis of a thin section of the red layer showed equant-shaped particles of iron consistent with iron oxide pigments and plates of kaolin clay (Figures 20 and 21). The matrix material of the red coating layer was carbon-based. Small numbers of titanium oxide particles consistent with titanium dioxide pigment and some calcium particles were also found (Appendix F).

The solvents had no effect on the gray iron/steel layer. Although the solvents softened the red layers on the chips, none of the solvents tested dissolved the epoxy resin and released the particles within. SEM-EDS phase mapping (using multivariate statistical analysis) of the red layer after exposure to MEK for 55 hours did not show evidence of individual aluminum particles (Appendix G).

In summary, red/gray chips with the same morphological characteristics, elemental spectra and magnetic attraction as those shown in Harrit et al.[1] were found in WTC dust samples from four different locations than those examined by Harrit, et al.[1] The gray side is consistent with carbon steel. The red side contains the elements: C, O, Al, Si, and Fe with small amounts of other elements such as Ti and Ca. Based on the infrared absorption (FTIR) data, the C/O matrix material is an epoxy resin. Based on the optical and electron microscopy data, the Fe/O particles are an iron oxide pigment consisting of crystalline grains in the 100-200 nm range and the Al/Si particles are kaolin clay plates that are less than a micrometer thick. There is no evidence of individual elemental aluminum particles detected by PLM, SEM-EDS, or TEM-SAED-EDS, during the analyses of the red layers in their original form or after sample preparation by ashing, thin sectioning or following MEK treatment.

Discussion

The Encyclopedia of Explosives[9] describes thermite as essentially a mixture of powdered ferric oxide and powdered or granular aluminum. There are two sets of ingredients listed for thermite in Crippen's book on explosives identification.[10] The first is iron oxide and aluminum powder and the second is magnesium powder, ferric oxide, and aluminum powder. Nano-thermite (thermitic nanocomposite energetic material) has been studied in the Lawrence Livermore National Laboratory in California. A TEM image of a thin section of that material was published by R. Simpson[11] in 2000 and

shows material that is made up of approximately 2 nanometer iron oxide particles and approximately 30 nanometer aluminum metal spheres (Figure 22).

According to the Federation of Societies for Coatings Technology, kaolin (also known as aluminum silicate or china clay) is a platy or lamellar pigment that is used extensively as a pigment in many segments of the paint industry.[12] It is a natural mineral (kaolinite) which is found in vast beds in many parts of the world.[13] Iron oxide pigments are also used extensively in paints and coatings.[13,14] Both kaolin and iron oxide pigments have been used in paints and coatings for many years.[13,14] Epoxy resins were introduced into coatings in approximately 1947[15] and are found in a number of specially designed protective coatings on metal substrates.

In forensic studies, paints and coatings often must be broken down so that the components of the entire coating product can be studied individually. Epoxy resins are formed from the reaction of two different chemicals which produces a polymer that is heavily cross-linked. Epoxy resins can be especially difficult to dissolve. Organic solvents, including those sold commercially for epoxy paint/coating stripping, were found to soften the red layer of the red/gray chips but did not dissolve the epoxy resin sufficiently so particles within the coating could be dispersed for direct examination. In this study no organic solvent was found to release particles from within the epoxy resin and it was necessary to use low temperature ashing to eliminate the epoxy resin matrix and extract the component parts of the coating. The other procedures generally used to examine component particles within a coating without extraction (cross-sections and thin sections) were also applied in this study.

Conclusions

The red/gray chips found in the WTC dust at four sites in New York City are consistent with a carbon steel coated with an epoxy resin that contains primarily iron oxide and kaolin clay pigments.

There is no evidence of individual elemental aluminum particles of any size in the red/gray chips, therefore the red layer of the red/gray chips is not thermite or nano-thermite.

Notes on the Source of the Red/Gray Chips

At the time of this progress report, the identity of the product from which the red/gray chips were generated has not been determined. The composition of the red/gray chips found in this study (epoxy resin with iron oxide and kaolin pigments) does not match the formula for the primer paint used on iron column members in the World Trade Center towers (Table 1).[16] Although both the red/gray chips and the primer paint contain iron oxide pigment particles, the primer is an alkyd-based resin with zinc yellow (zinc chromate) and diatomaceous silica along with some other proprietary (Tnemec) pigments. No diatoms were found during the analysis of the red/gray chips. Some

small EDS peaks of zinc and chromium were detected in some samples but the amount detected was inconsistent with the 20% level of zinc chromate in the primer formula.

Material Safety Data Sheets (MSDS) contain some information about product materials. According to the MSDS currently listed on the Tnemec website,[17] 55 out of the 177 different Tnemec coating products contain one or two of the three major components in the red layer: epoxy resin, iron oxide and/or kaolin (aluminum silicate) pigments. However, none of the 177 different coatings are a match for the red layer coating found in this study.

References

1. Harrit, N.H., Farrer, J., Jones, S.E., Ryan, K.R., Legge, F.M., Farnsworth, D., Roberts, G., Gourle, J.R., and Larsen, B.R., "Active Thermitic Material Discovered in Dust from the 9/11 World Trade Center Catastrophe", *The Open Chemical Physics Journal*, 2009, 2, 7-31.
2. Lioy, P.J, Weisel, C.P., Millette, J.R., Eisenreich, S., Vallero, D., Offenberg, J., Buckley, B., Turpin, B., Zhong, M., Cohen, M.D., Prophete, C., Yang, I., Stiles, R., Chee, G., Johnson, W., Porcja, R., Alimokhtari, S., Hale, R.C., Weschler, C., and Chen, L.C., "Characterization of the Dust/Smoke Aerosol that Settled East of the World Trade Center (WTC) in Lower Manhattan after the Collapse of the WTC 11 September 2001", *Environmental Health Perspectives*, Vol. 110, No. 7, 703-714, July 2002.
3. Millette, J.R., Boltin, R., Few, P. and Turner, Jr., W., "Microscopical Studies of World Trade Center Disaster Dust Particles", *Microscope*, 50(1): 29-35, 2002.
4. Turner, W.L., J.R. Millette, W.R. Boltin, and T.J. Hopen, A Standard Approach to the Characterization of Common Indoor Dust Constituents. *Microscope* 53(4):169-177. 2005.
5. TWGFEX Laboratory Explosion Group, Recommended Guidelines for Forensic Identification of Intact Explosives and Recommended Guidelines for Forensic Identification of Post-Blast Explosive Residues (Rev. 8 - 2009), Technical Working Group for Fire and Explosions, National Institute of Justice - Office of Justice Programs, U.S. Department of Justice. http://www.ncfs.org/twgfex/docs.
6. ASTM E1610-02, Standard Guide for Forensic Paint Analysis and Comparison. ASTM –International, West Conshohocken, PA. Reapproved 2008.
7. COMPASS multivariate statistical analysis software program for Noran System Six x-ray system. Minoru Suzuki, Thermo Fisher Scientific, Yokohama, Japan; Pat Camus, Ph.D., Thermo Fisher Scientific, Madison, WI, USA. Application Note: 51220. 2008.
8. McCrone, W.C. and Delly, J.G. The Particle Atlas, 2nd Ed. Ann Arbor Press. Vol. 3, p. 584. 1973.
9. Kaye, S.M. “Thermite”, Encyclopedia of Explosives and Related Items, Vol. 9, PATR 2700, US Army Armament Research and Development Command, Dover, New Jersey, 1980, (available from NTIS, US Department of Commerce, Springfield, Virginia 22161), page T189.

10. Crippen, J.B. Explosives and Chemical Weapons Identification. CRC Taylor & Francis, Boca Raton, FL, 2006, p.149.
11. Simpson, R., Nanoscale Chemistry Yields Better Explosives, *Science and Technology Review.* Lawrence Livermore National Laboratory October, 2000.
12. Smith, A. "Inorganic Primer Pigments", Federation Series on Coating Technology, Federation of Societies for Coatings Technology, Philadelphia, PA. 1988.
13. Gettens, R.J. and Stout, G. L., "Painting Materials", Dover Publications, 1966.
14. Petraco, N. and Kubic, T., Color Atlas and Manual of Microscopy for Criminalists, Chemists, and Conservators. CRC Press, Baca Raton, 2004.
15. Prane, J.A., "Introduction to Polymers and Resins", Federation Series on Coating Technology, Federation of Societies for Coatings Technology, Philadelphia, PA. 1986.
16. Sramek, T.F.: Correspondence between Pittsburgh-Des Moines Steel Co. and R. M. Monti, Port of New York Authority, giving clarification and attaching a product sheet for Tnemec 69 and 99 column paints, Nov 22, 1967. As cited in: Banovic, S.W. and Foecke, T., Assessment of Structural Steel from the World Trade Center Towers, Part IV: Experimental Techniques to Assess Possible Exposure to High –Temperature Excursions. *Journal of Failure Analysis and Prevention*. 6(5):103-120. Oct 2006.
17. www.tnemec.com [last accessed on Feb. 26, 2012].

Table 1. Composition of Primer Paint on the World Trade Center Towers according to T. F. Sramek[16]

Pigment	Iron Oxide	35.9%
	Zinc Yellow (Zinc Chromate[13])	20.3%
	Tnemec pigment (proprietary composition)	33.7%
	Diatomaceous silica	10.1%
Vehicle	Soya alkyd resin solids	16.5%
	Hard Resin	2.8%
	Raw Linseed Oil	35.1%
	Bodied Linseed Oil	6.4%
	Suspension agents	2.2%
	Driers and antiskin	4.8%
	Thinners	32.3%

Figure 1. Sample Locations.

Figure 2. Example of the WTC dust. Sample L1560 - Murray & Church St.

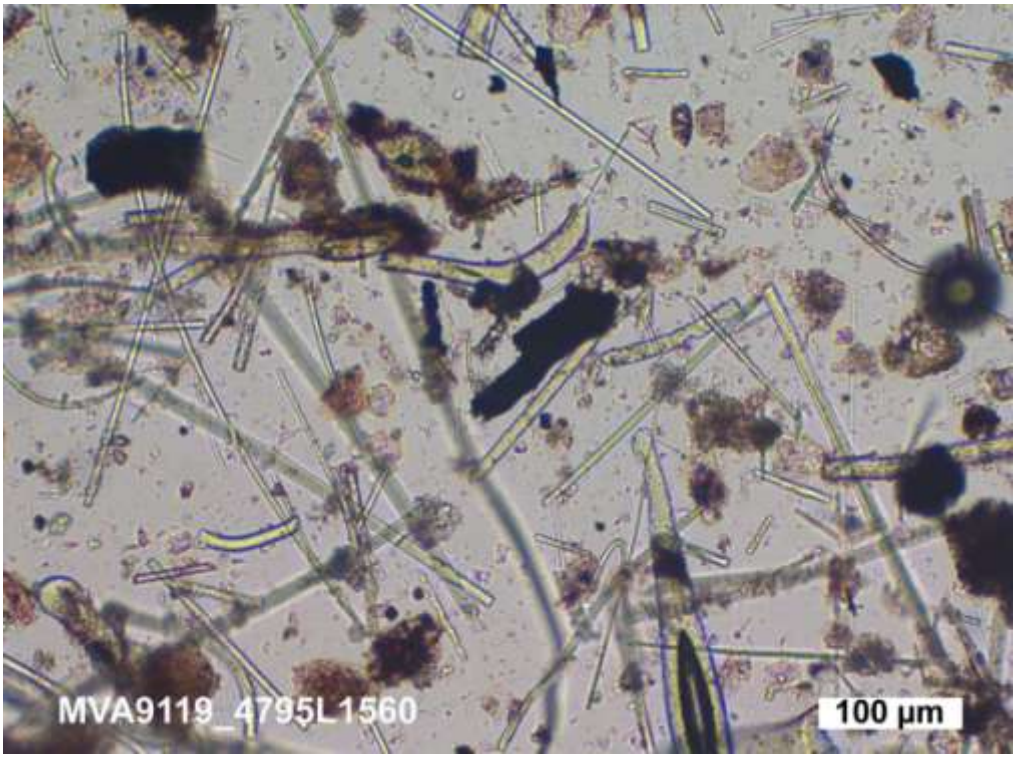


Figure 3. Example of the WTC dust as seen with PLM showing common components of glass fibers, cementitious material and soot. Sample L1560 - Murray & Church St.

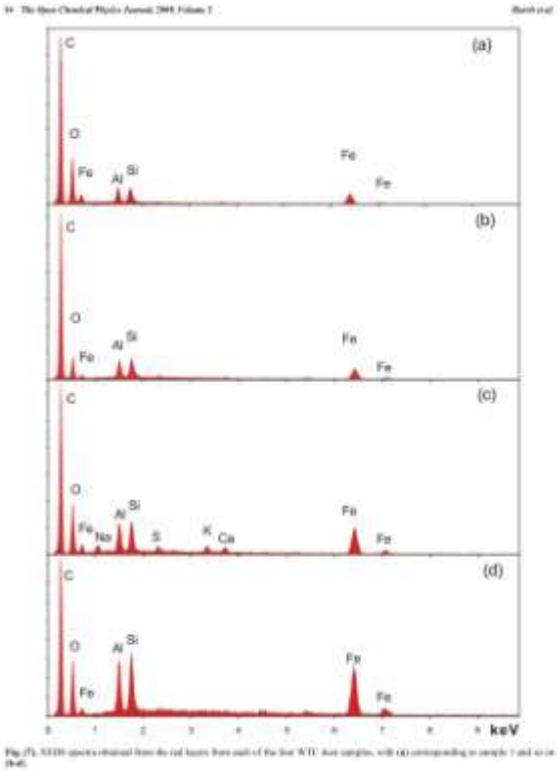


Figure 4. SEM-EDS spectral criteria for red/gray chips from Harrit, et al., 2009.

Figure 5. An example of separating particles with a magnet. Sample M3451 – Ann St.

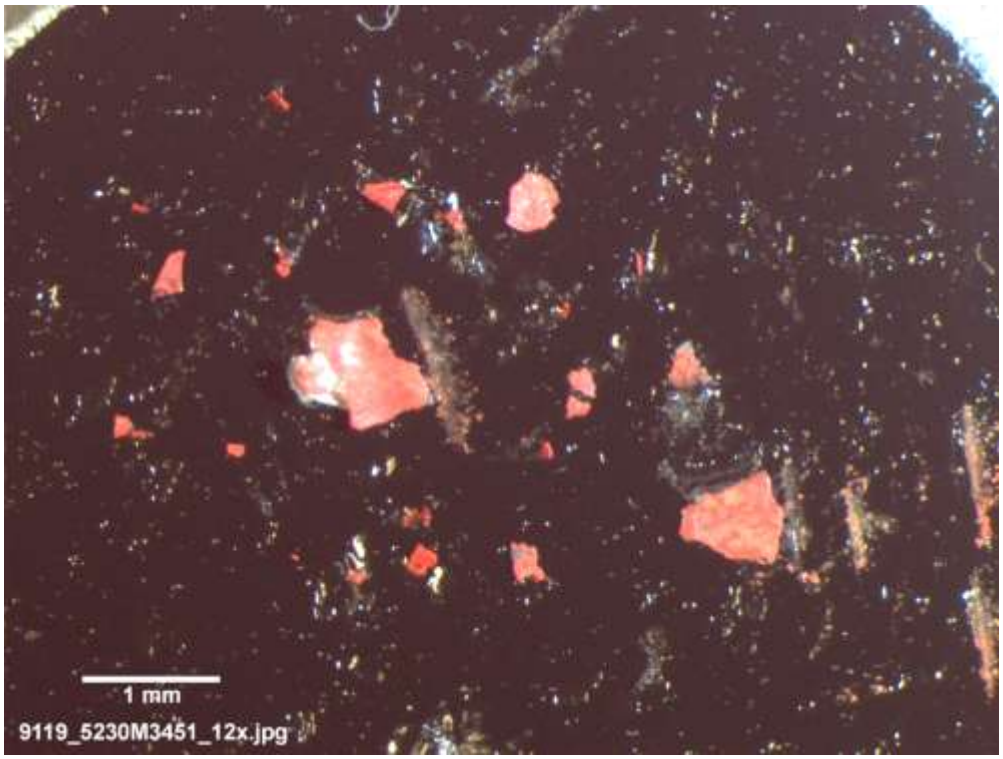


Figure 6. An example of red/gray chips mounted on a carbon stub. Sample M3451 – Ann St.

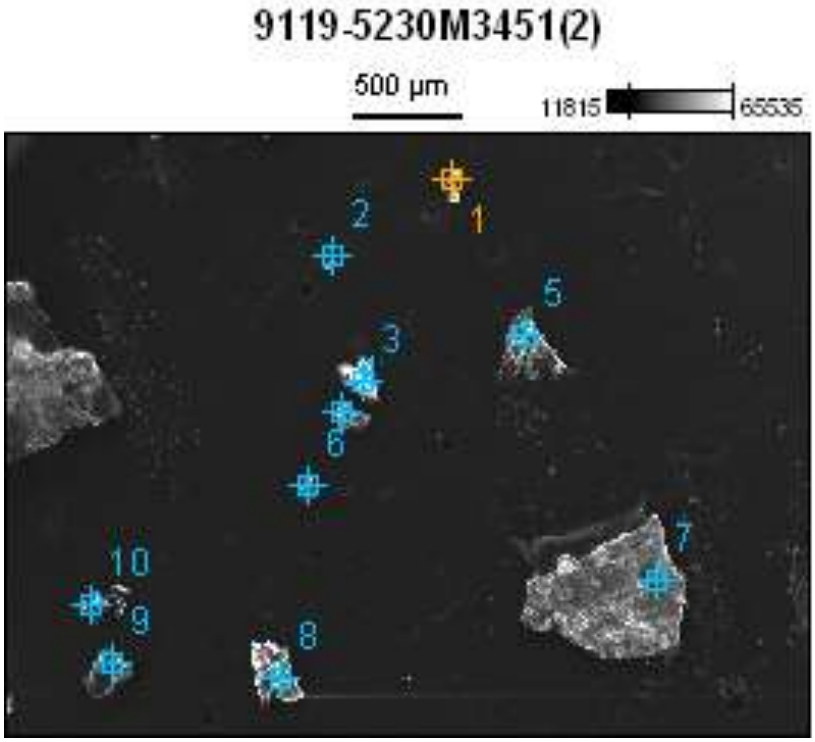


Figure 7. An example of SEM analysis of red/gray chips mounted on a carbon stub. The particle numbers are shown that correspond to EDS spectra in Figure 8.

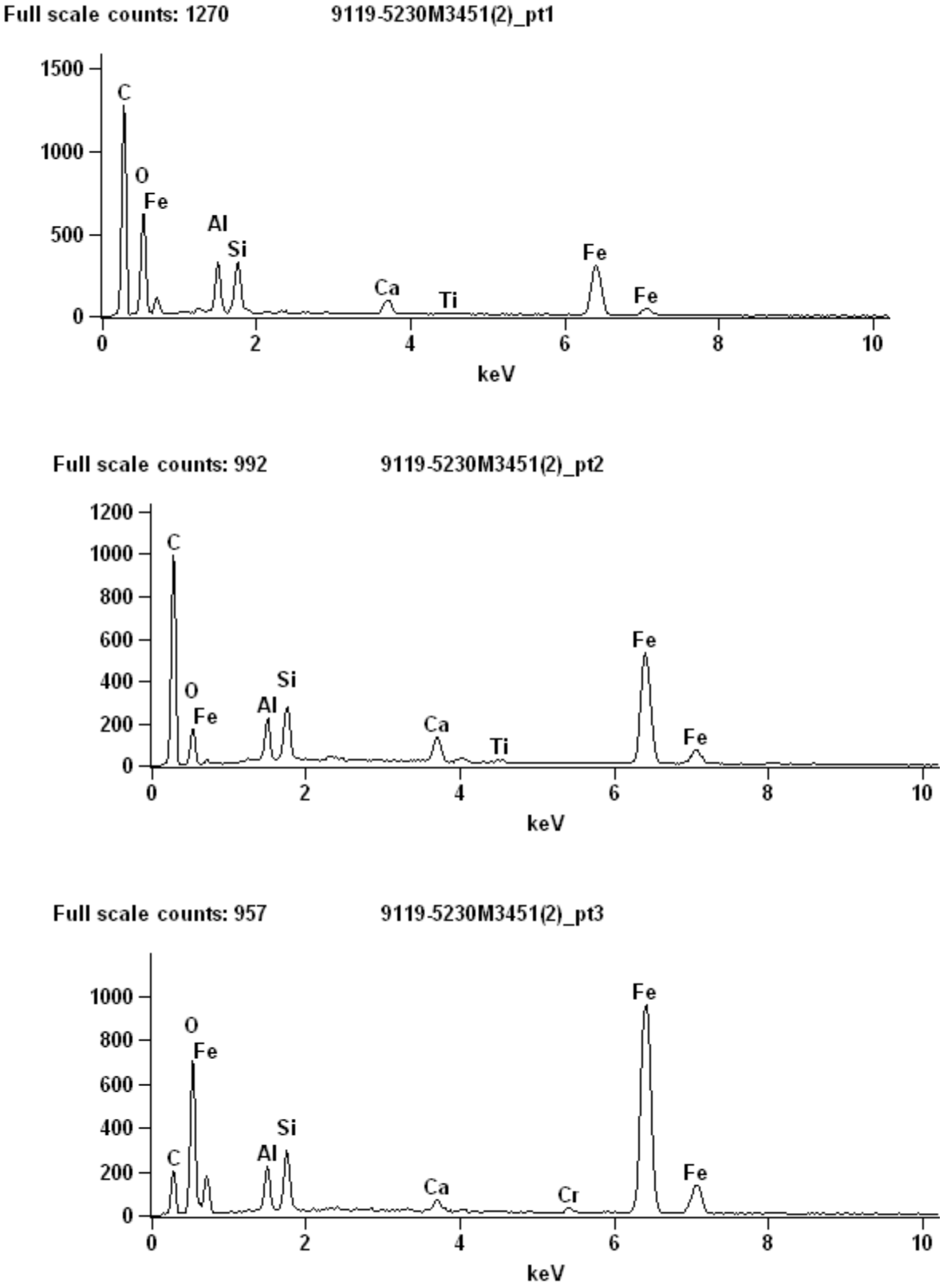


Figure 8. SEM-EDS spectra for particles 1, 2 and 3 in Figure 7.

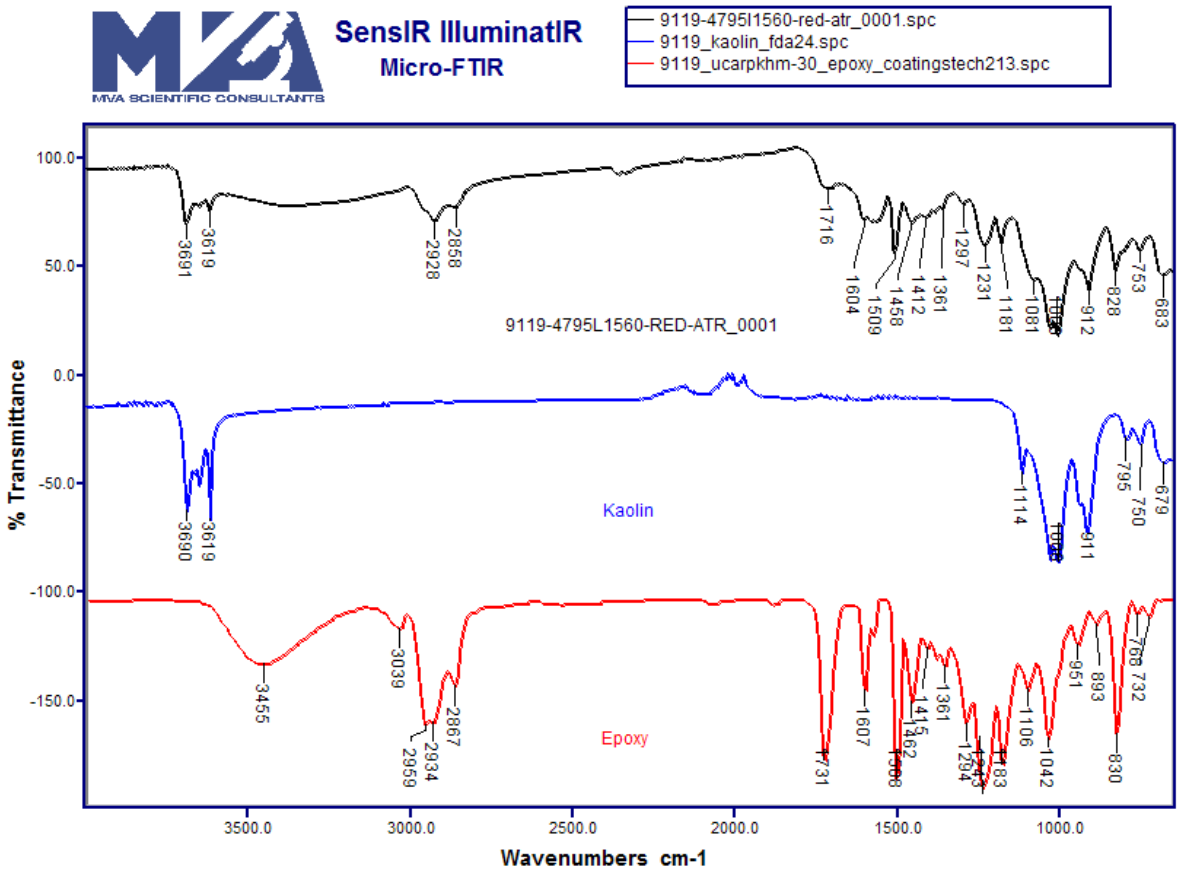


Figure 9. Comparison of FTIR spectrum from red side of a red/gray chip showing the match with kaolin and epoxy resin references. Sample L1560.

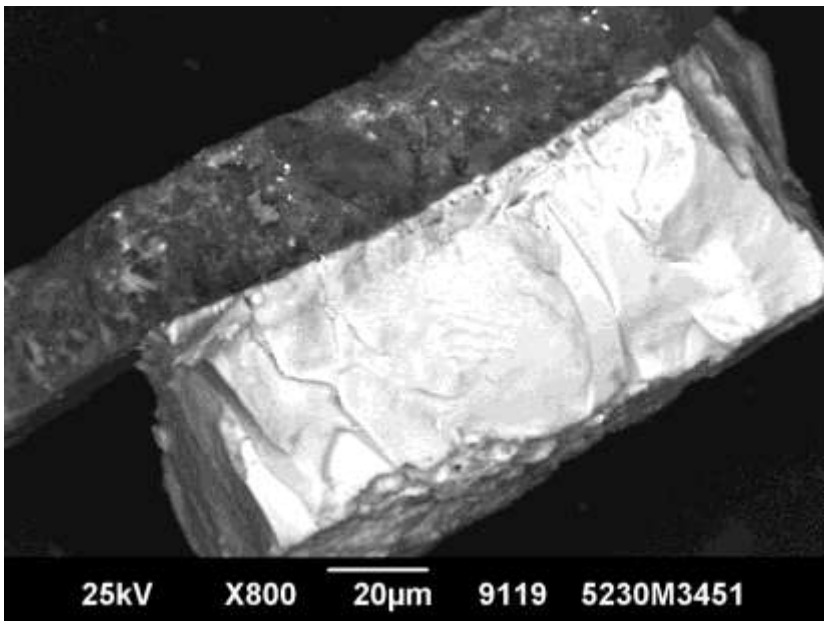


Figure 10. BE image of a cross-section of a red (top)/gray (bottom) chip.

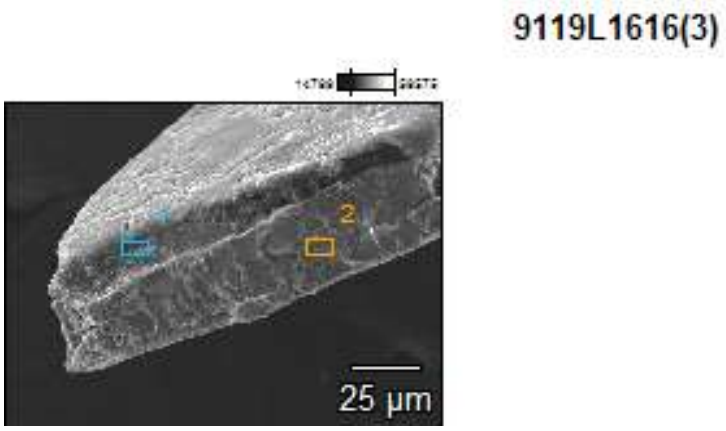


Figure 11. Secondary electron (SE) image of a cross-section of a red (top)/gray (bottom) chip.

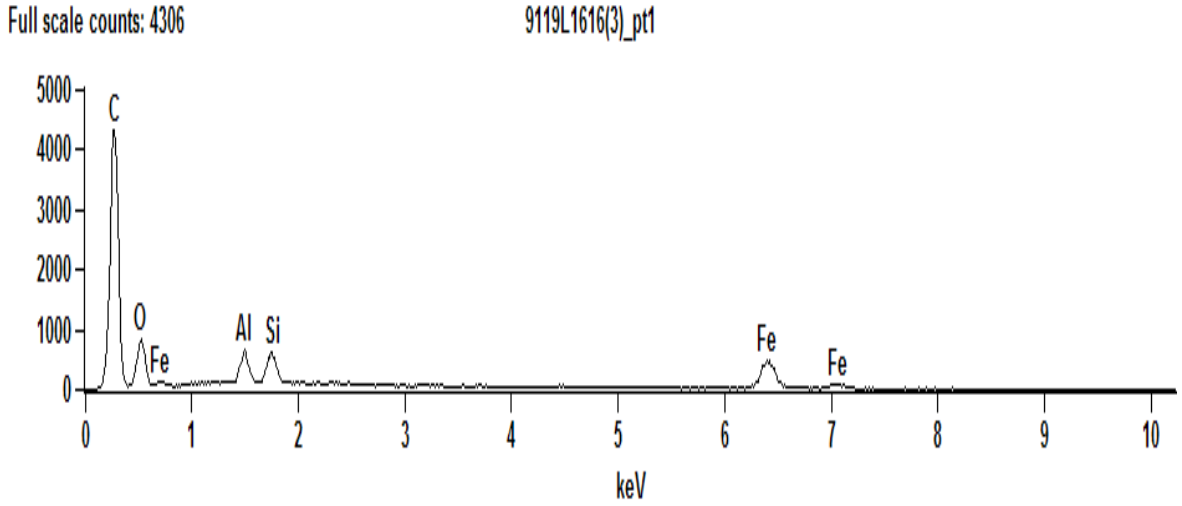


Figure 12. SEM-EDS spectrum from Spot 1 on the red layer (top) in Figure 11.

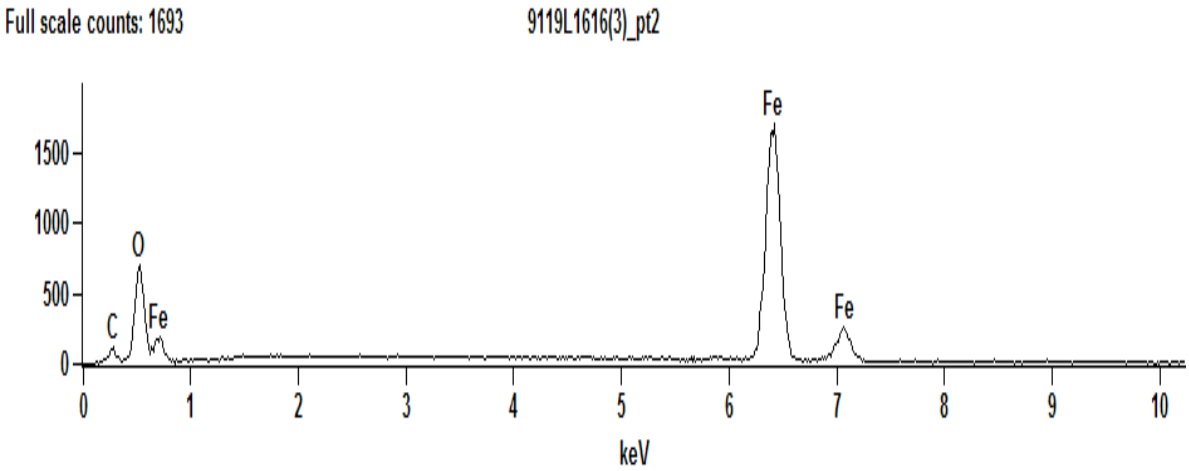


Figure 13. SEM-EDS spectrum from Spot 2 on the gray layer (bottom) in Figure 11.

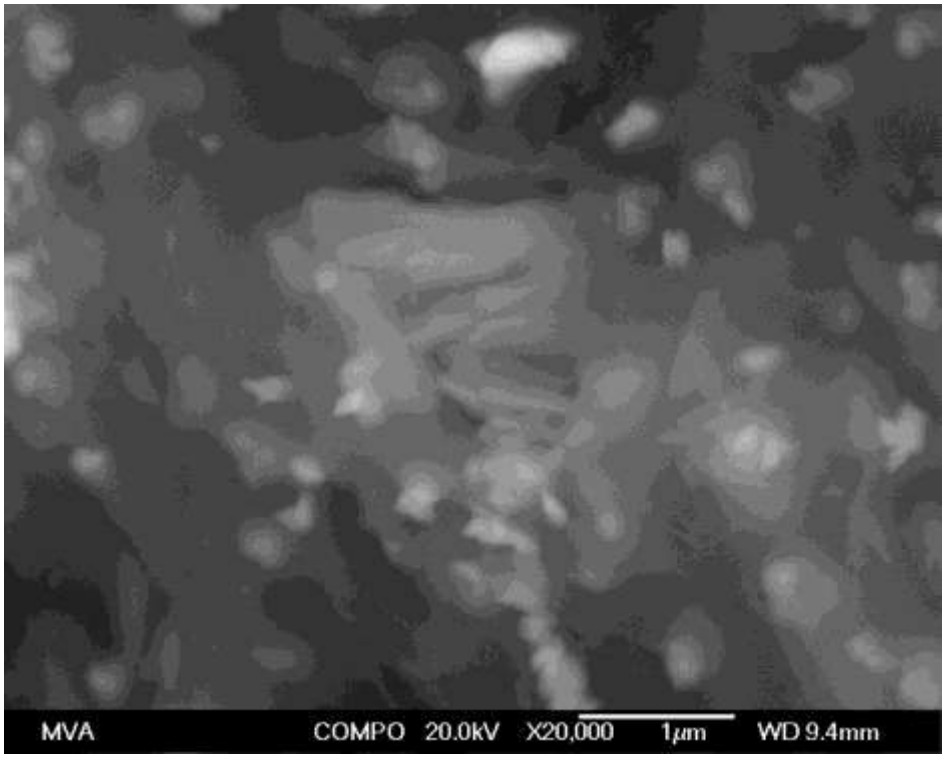


Figure 14. BE image showing bright iron particles and aluminum-silicon plates in the carbon-based matrix.

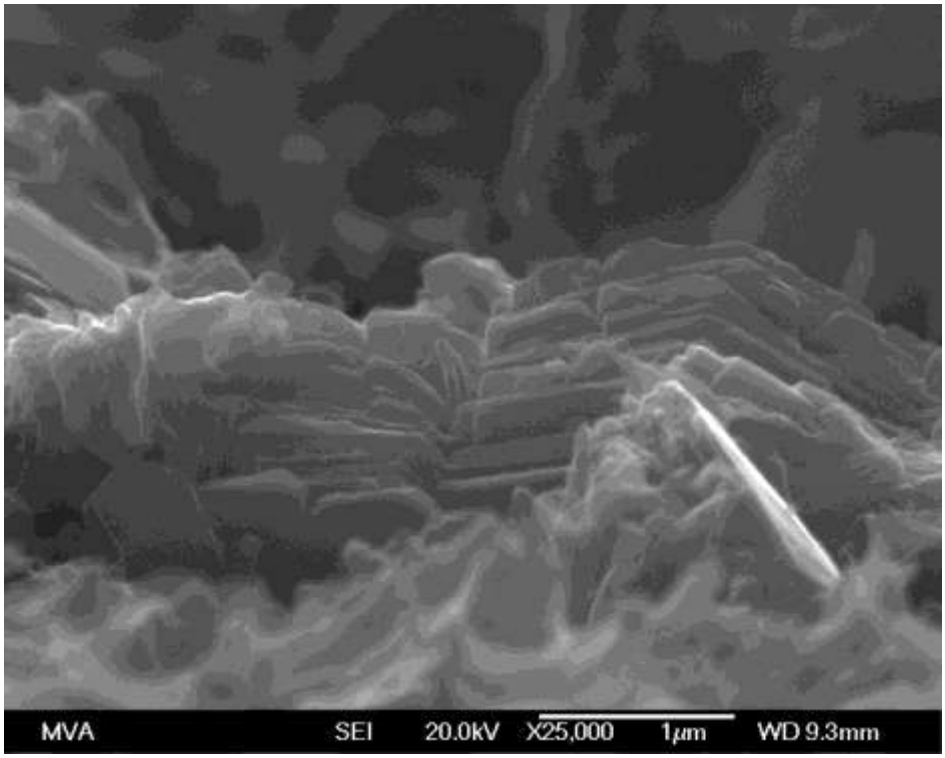


Figure 15. SE image showing books of aluminum/silicon plates.

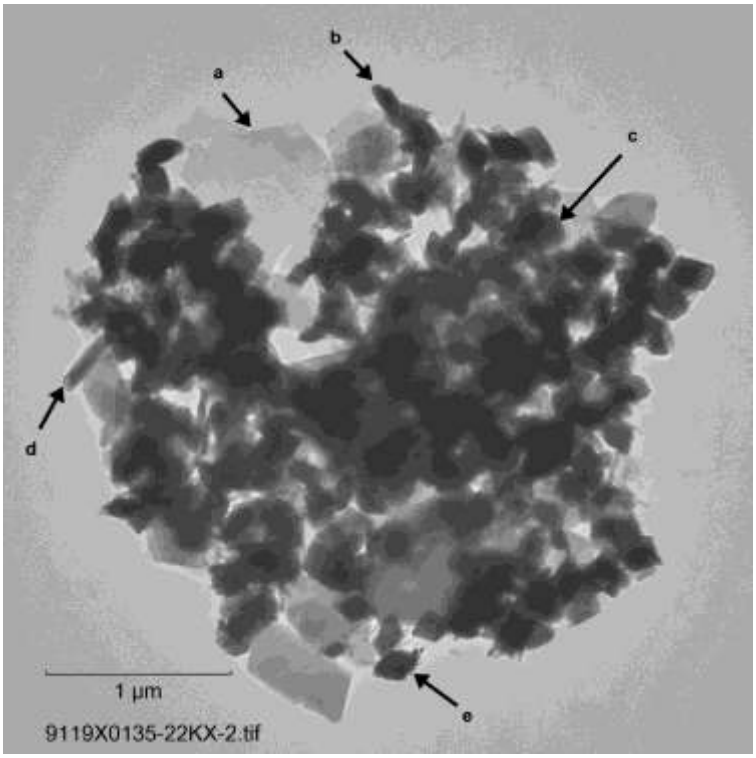


Figure 16. TEM image of residue after low temperature ashing. Particles: 'a' is kaolin, 'b' is iron oxide, 'c' is titanium dioxide, 'd' is kaolin on edge, 'e' is iron oxide.

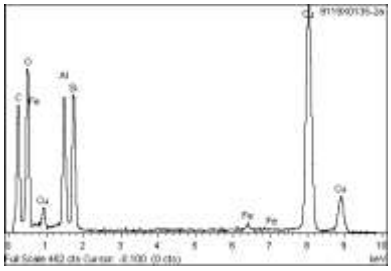


Fig 16a. EDS of 'a'.

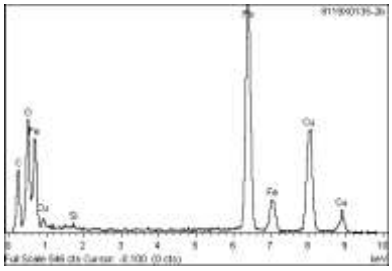


Fig 16b. EDS of 'b'

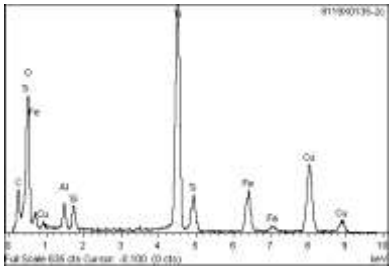


Fig 16c. EDS of 'c'

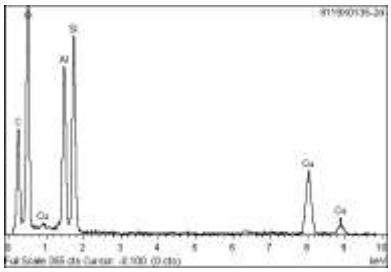


Fig 16d. EDS of 'd'.

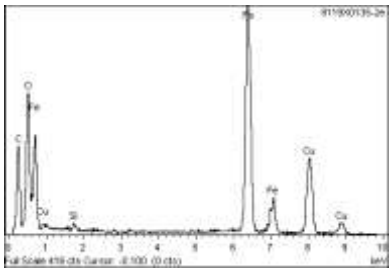


Fig 16e. EDS of 'e'.

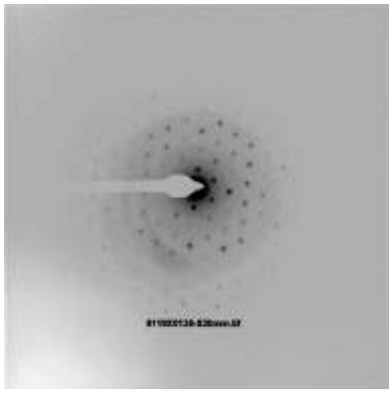


Fig16f. SAED of 'a'.

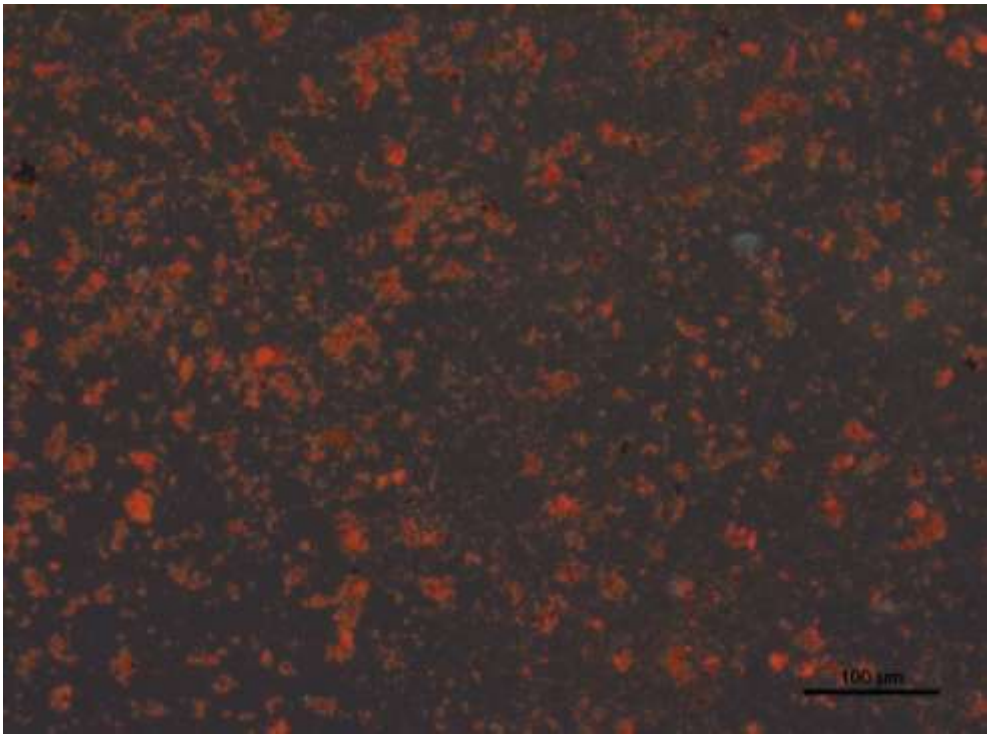


Figure 17. Reflected light microscopy image of residue after muffle furnace ashing (400^{o}C for 1 hour).

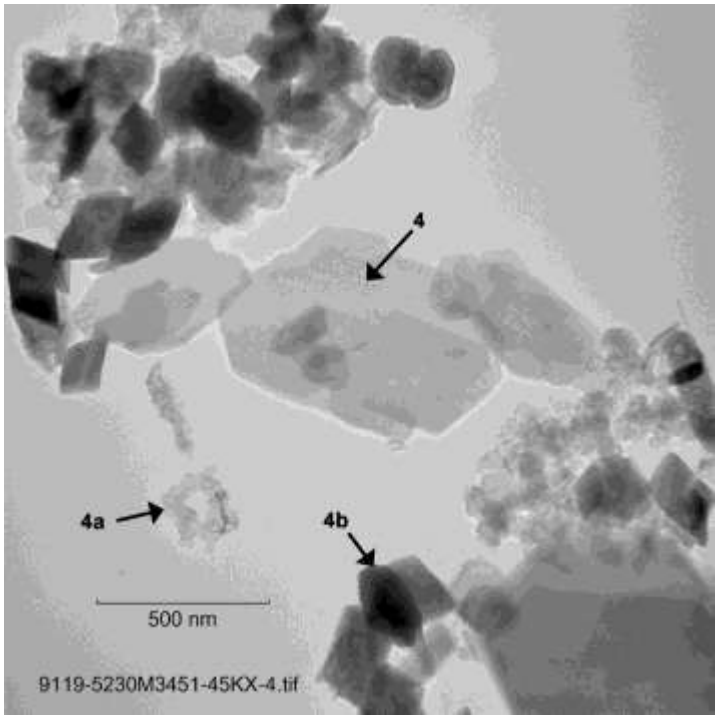


Figure 18. TEM image of residue after muffle furnace ashing. Particles: '4' is kaolin, '4a' is soot, and '4b' is iron pigment. The other dark particles are also iron pigment.

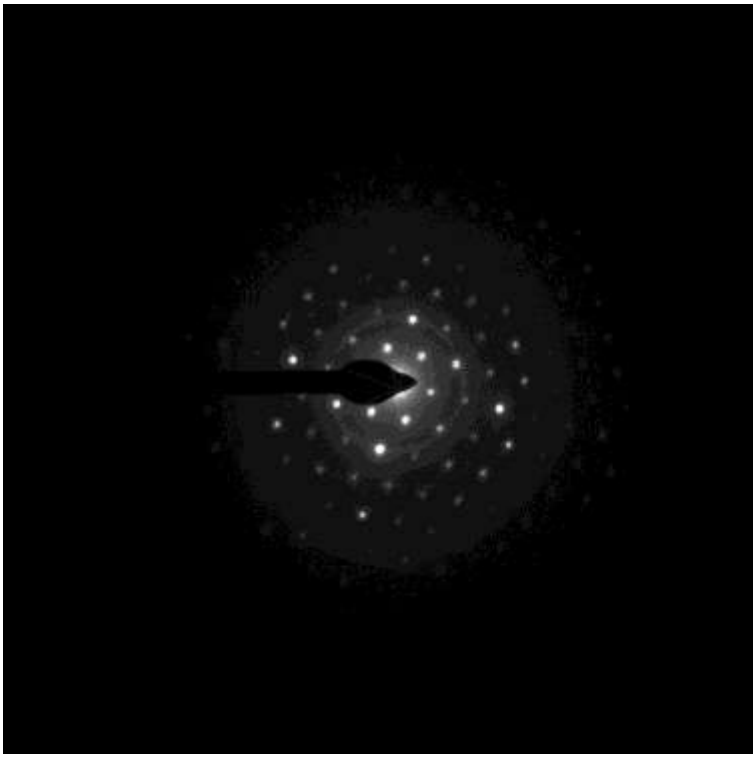


Figure 19. TEM-SAED pattern of kaolin in residue after muffle furnace ashing.

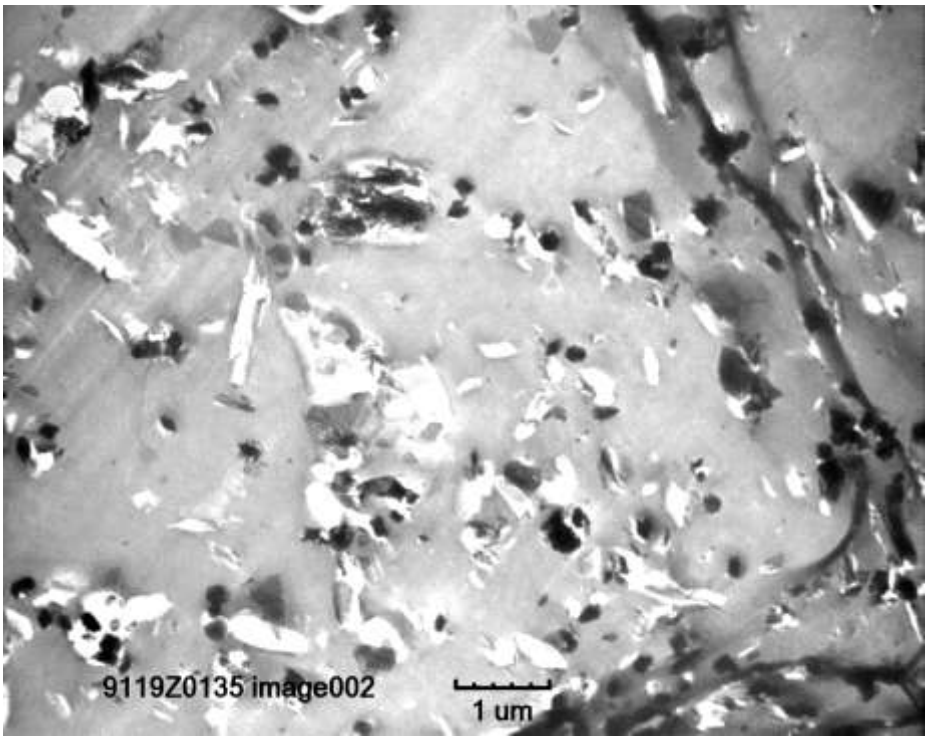


Figure 20. TEM image of an ultra-thin section of a red layer showing iron oxide faceted crystals and kaolin clay. The matrix is carbon-based.

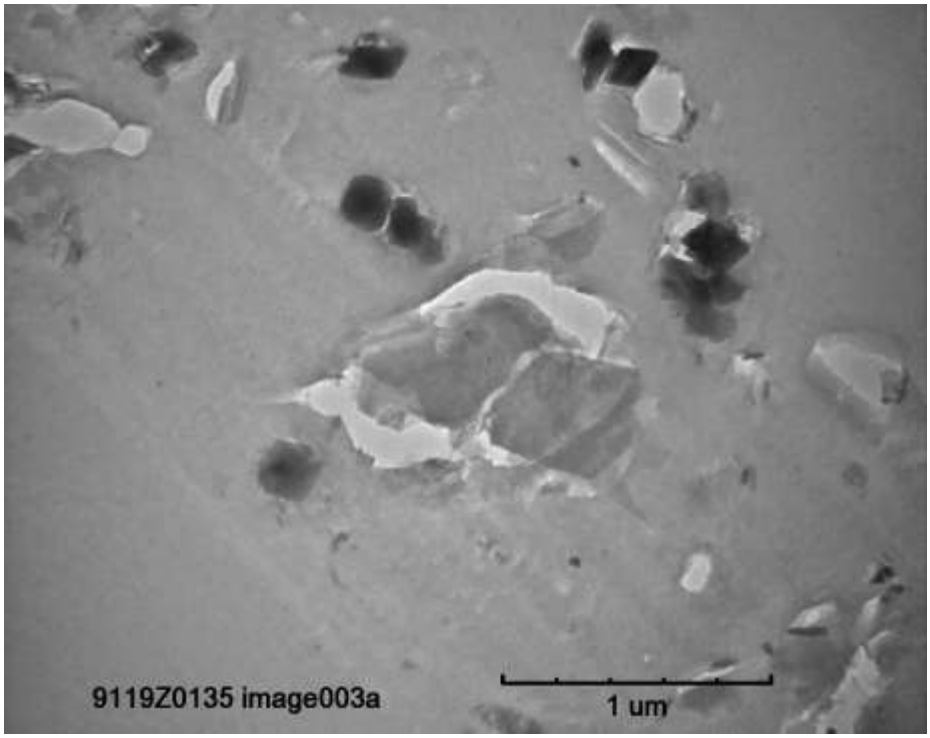
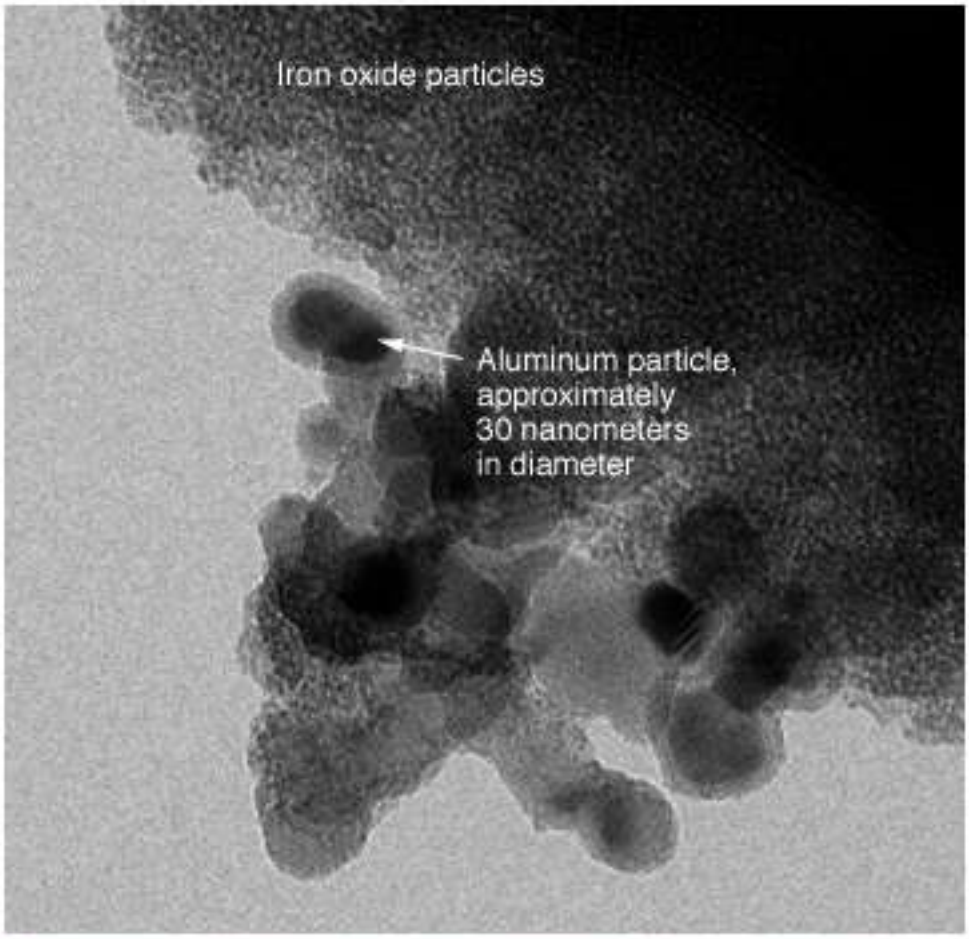


Figure 21. TEM image of an ultra-thin section of a red layer showing iron oxide faceted crystals and kaolin clay. The matrix is carbon-based.

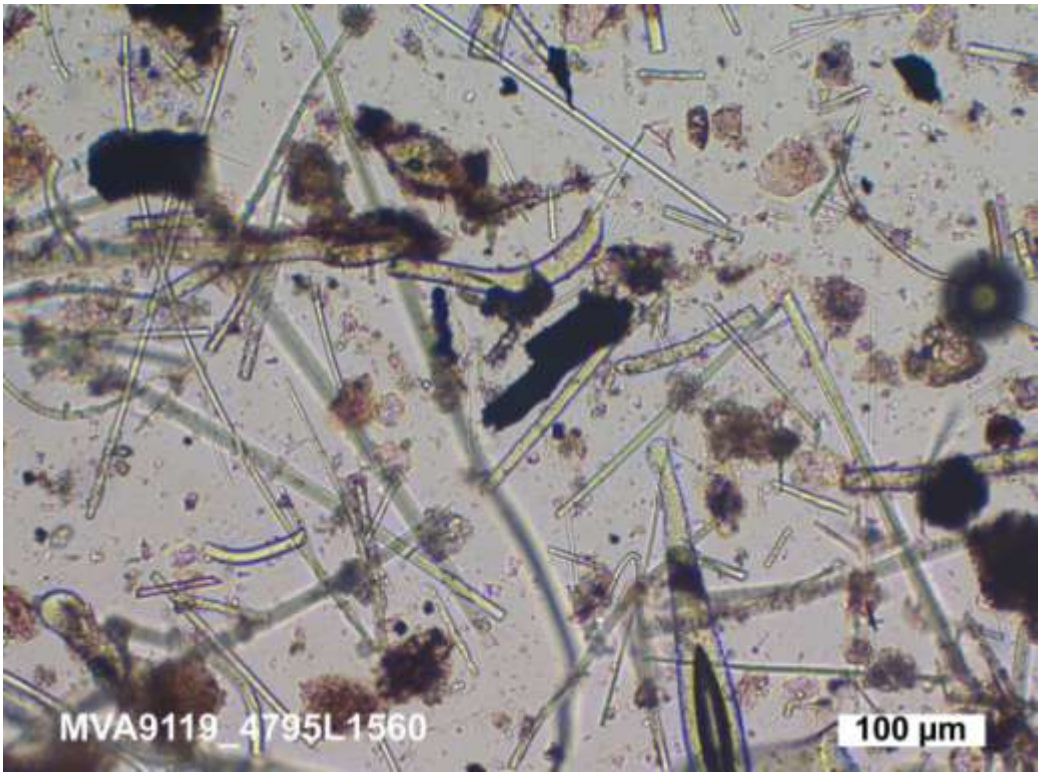


Transmission electron micrograph of a thermitic nanocomposite energetic material. The material is made up of an extremely fine iron oxide xerogel (approximately 2-nanometer particles) that has approximately 30-nanometer-diameter aluminum metal spheres (the larger globules) embedded in it.

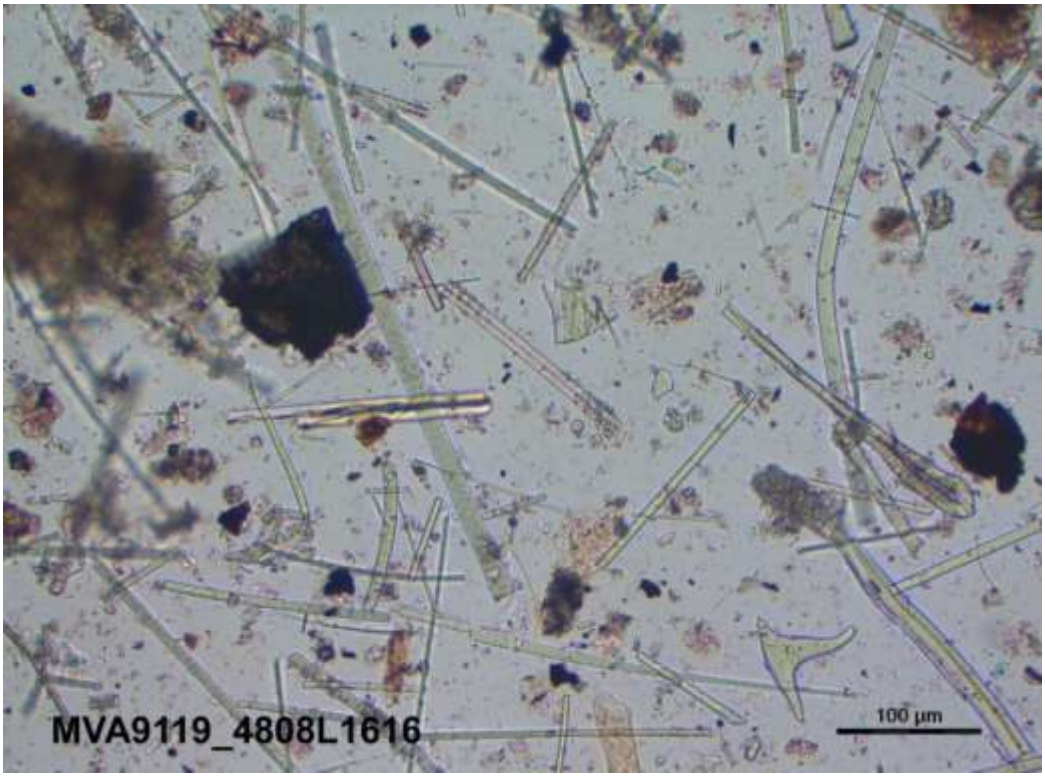
Figure 22. TEM image of nano-thermite (2 nm iron oxide and 30 nm aluminum metal spheres). Simpson, R., Lawrence Livermore National Laboratory.[11]

APPENDIX A

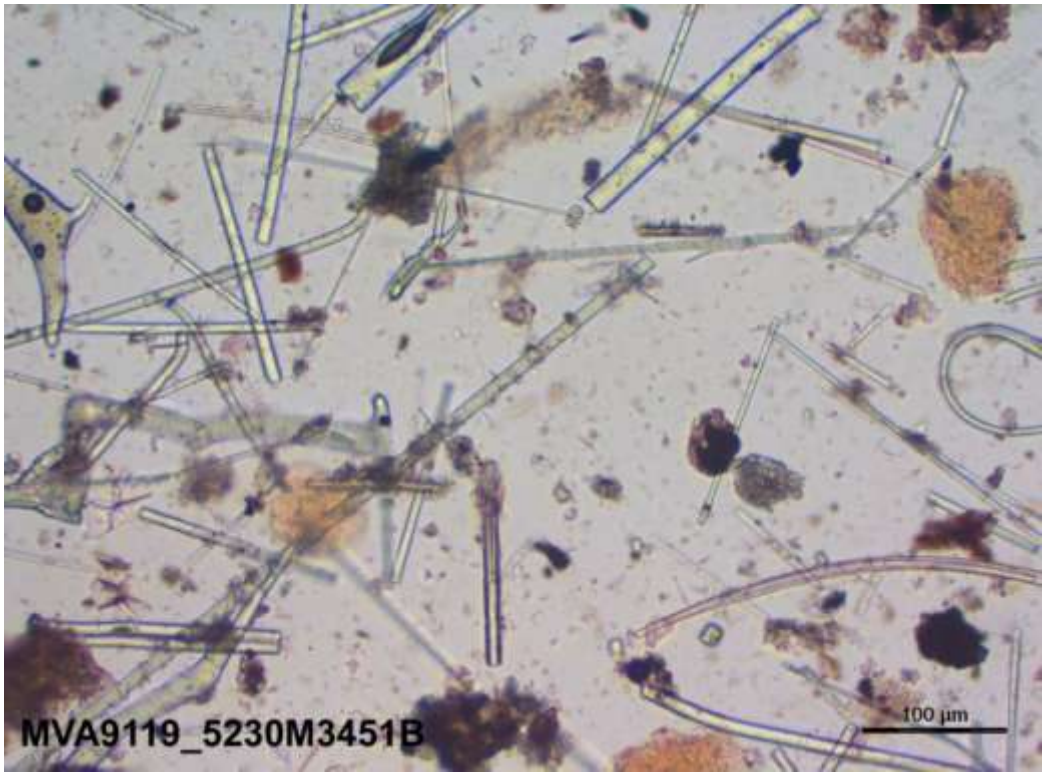
PLM Images of WTC Dust
From Four Sampling Locations



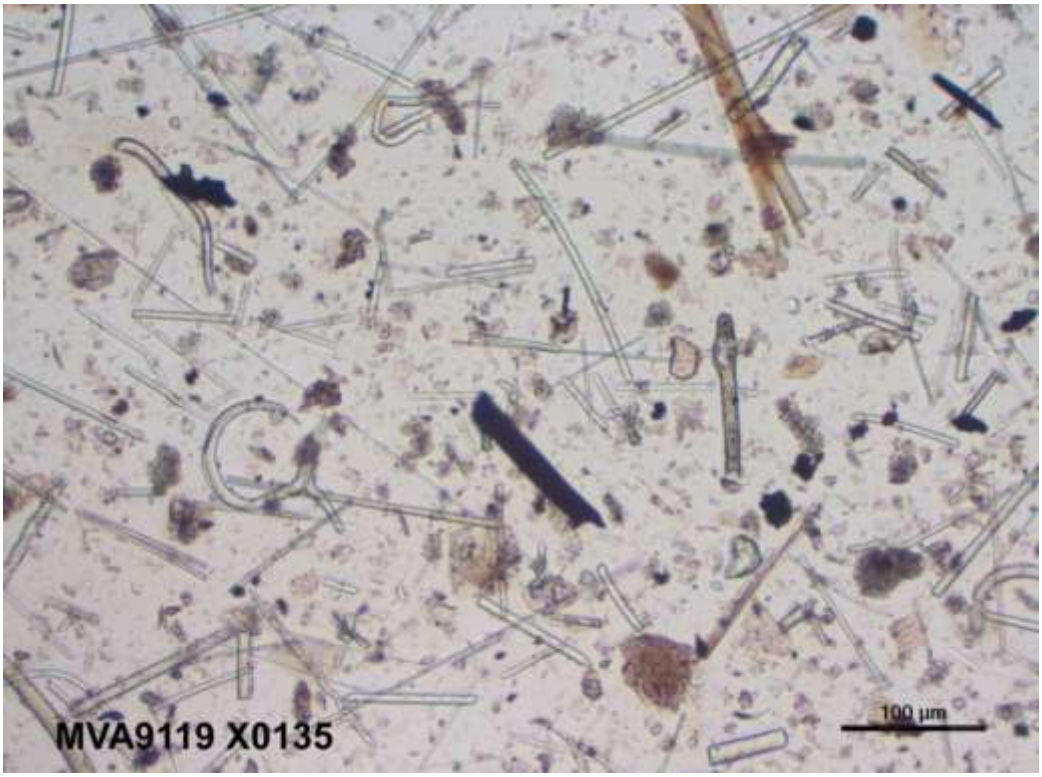
WTC dust as seen with PLM showing common components of glass fibers, cementitious material and soot. Sample L1560 - Murray & Church St.



WTC dust as seen with PLM showing common components of glass fibers, cementitious material and soot. Sample L1616 – 22 Cortlandt St.



WTC dust as seen with PLM showing common components of glass fibers, cementitious material and soot. Sample M3451, 49 Ann St.

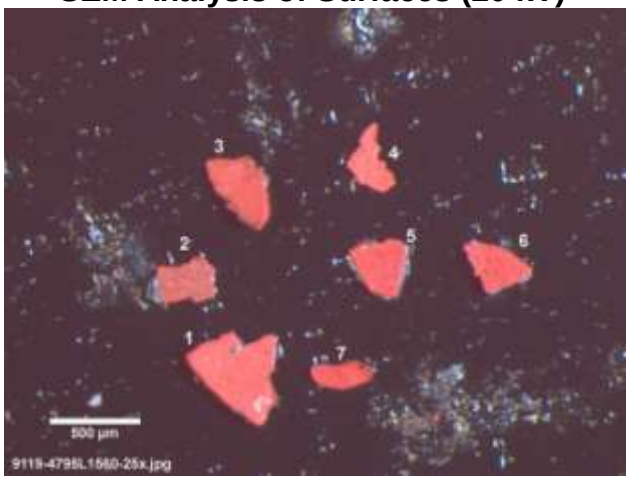


WTC dust as seen with PLM showing common components of glass fibers, cementitious material and soot. Sample X0135, 33 Maiden Ln.

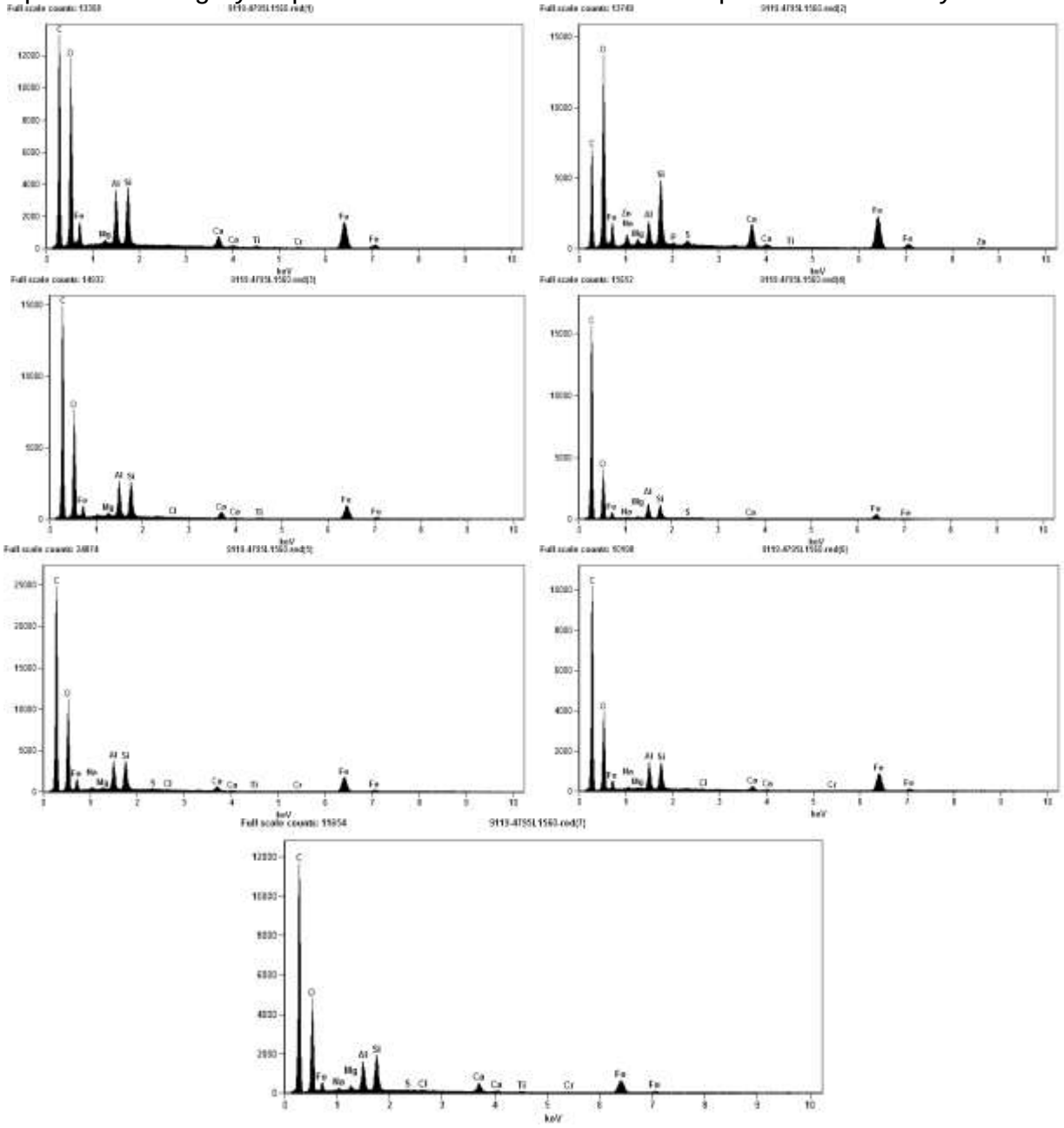
APPENDIX B

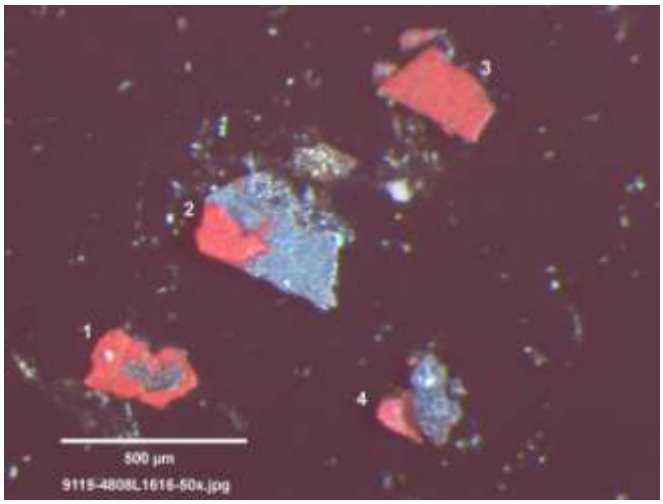
Red/Gray Chips From Dust From Four Sampling Locations

SEM Analysis of Surfaces (20 kV)

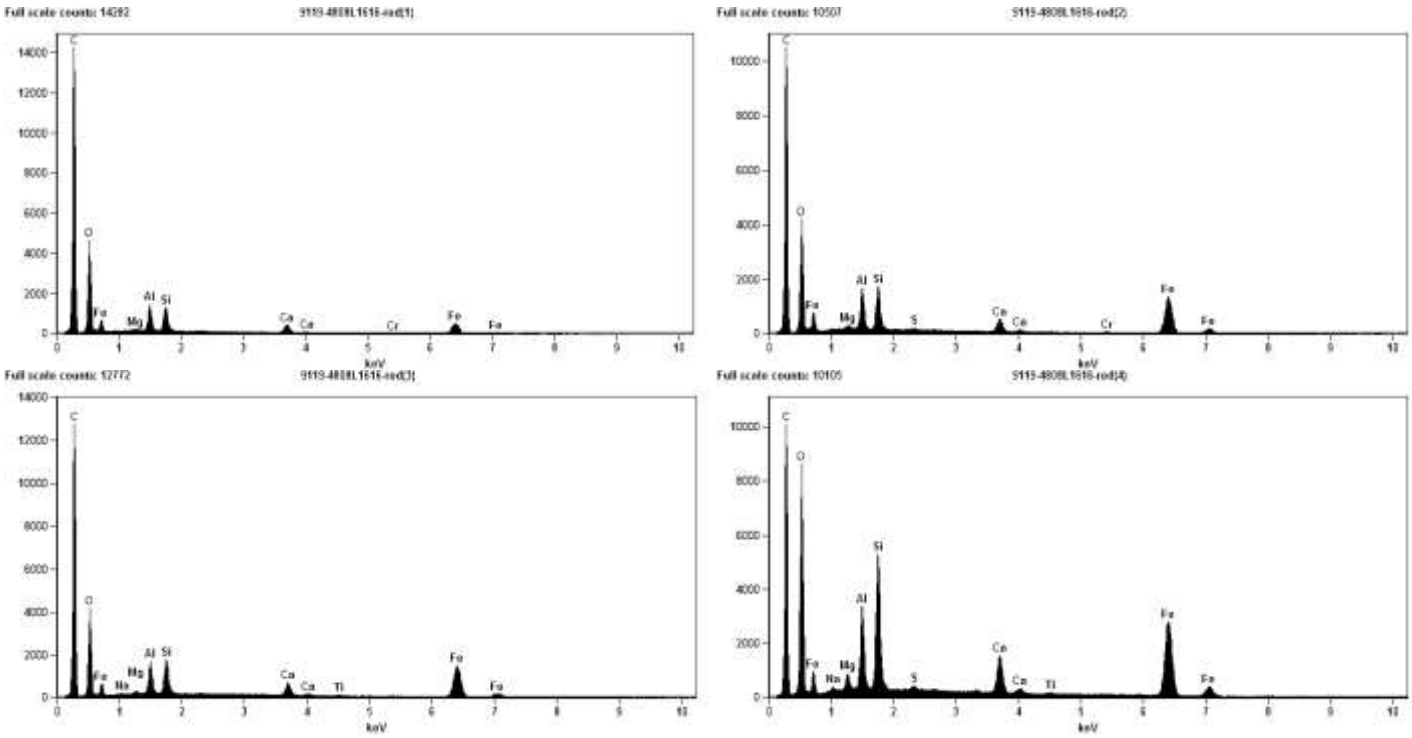


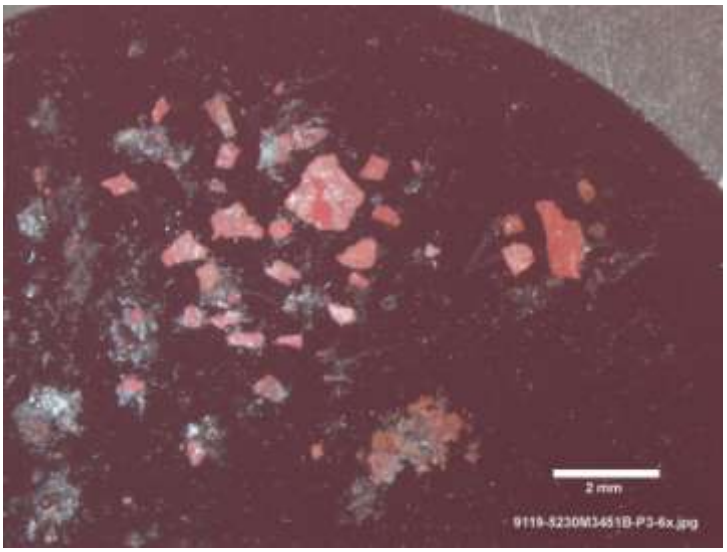
Example of the red/gray chips mounted on a carbon tab. Sample L1560 - Murray & Church St.



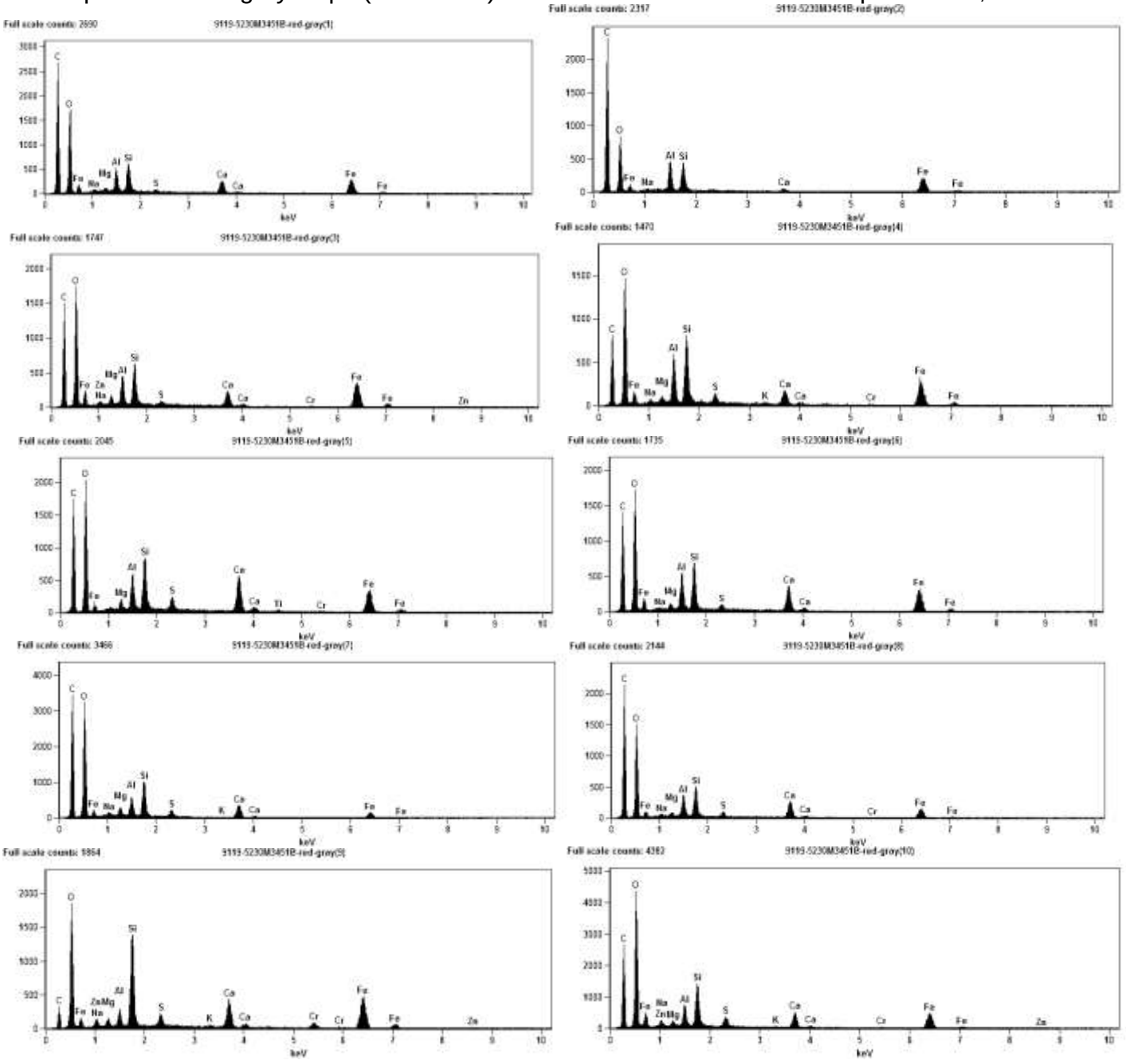


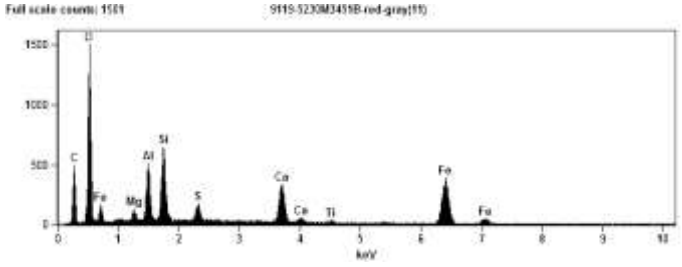
Example of the red/gray chips mounted on a carbon tab. Sample L1616 – 22 Cortlandt St.

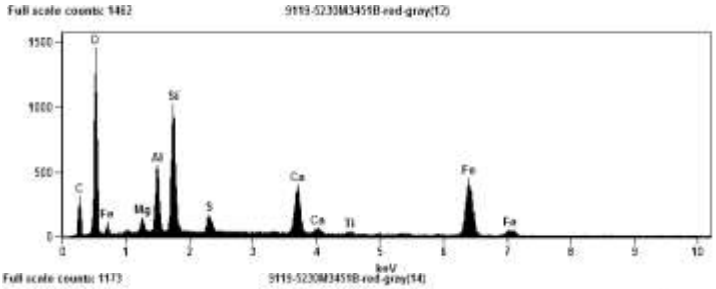


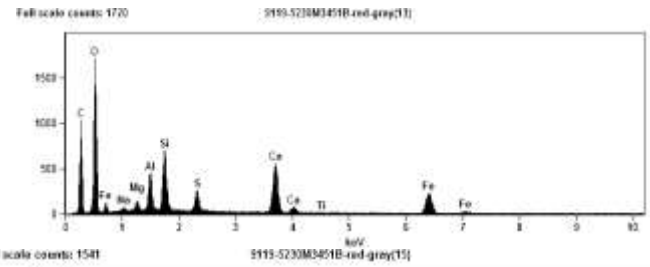


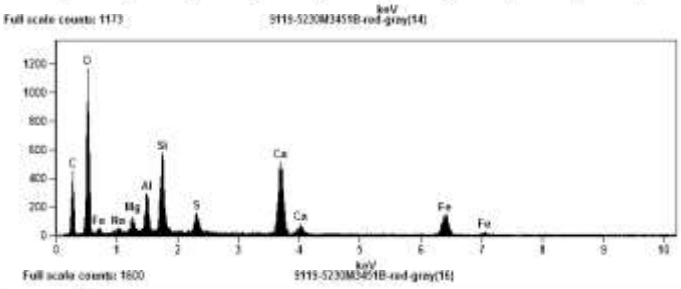
Example of the red/gray chips (unwashed) mounted on a carbon tab. Sample M3451, 49 Ann St.

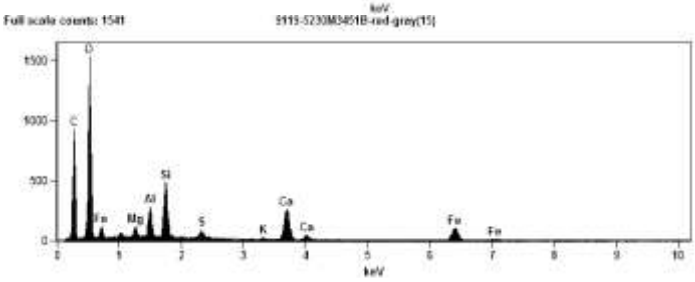


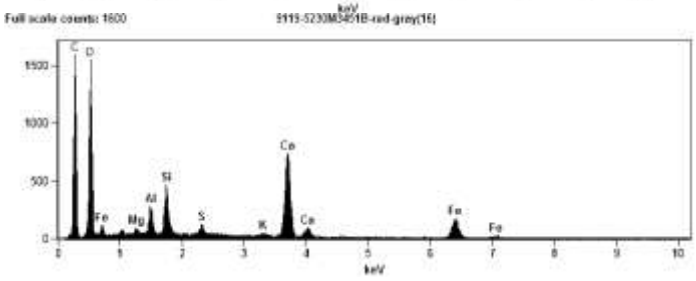

Full scale counts: 1501
9119-5230M3455B-red-gray(11)
O
C
Fe
Mg
Al
Si
S
Ca
Ce
Ti
Fe
Fe
keV

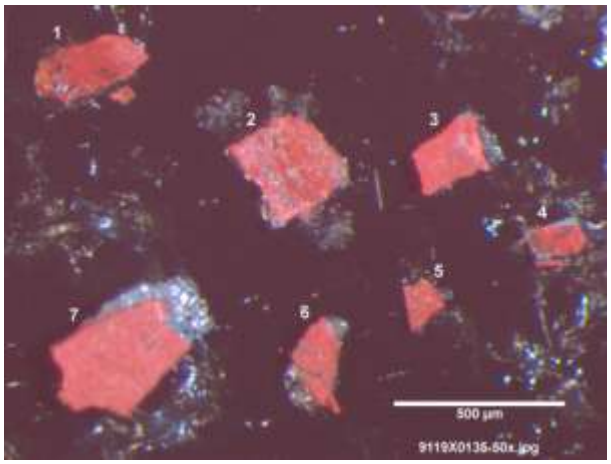

Full scale counts: 1462
9119-5230M3455B-red-gray(12)
O
C
Fe
Mg
Al
Si
S
Ca
Ce
Ti
Fe
Fe
keV


Full scale counts: 1720
9119-5230M3455B-red-gray(13)
O
C
Fe
Mg
Al
Si
S
Ca
Ce
Ti
Fe
Fe
keV

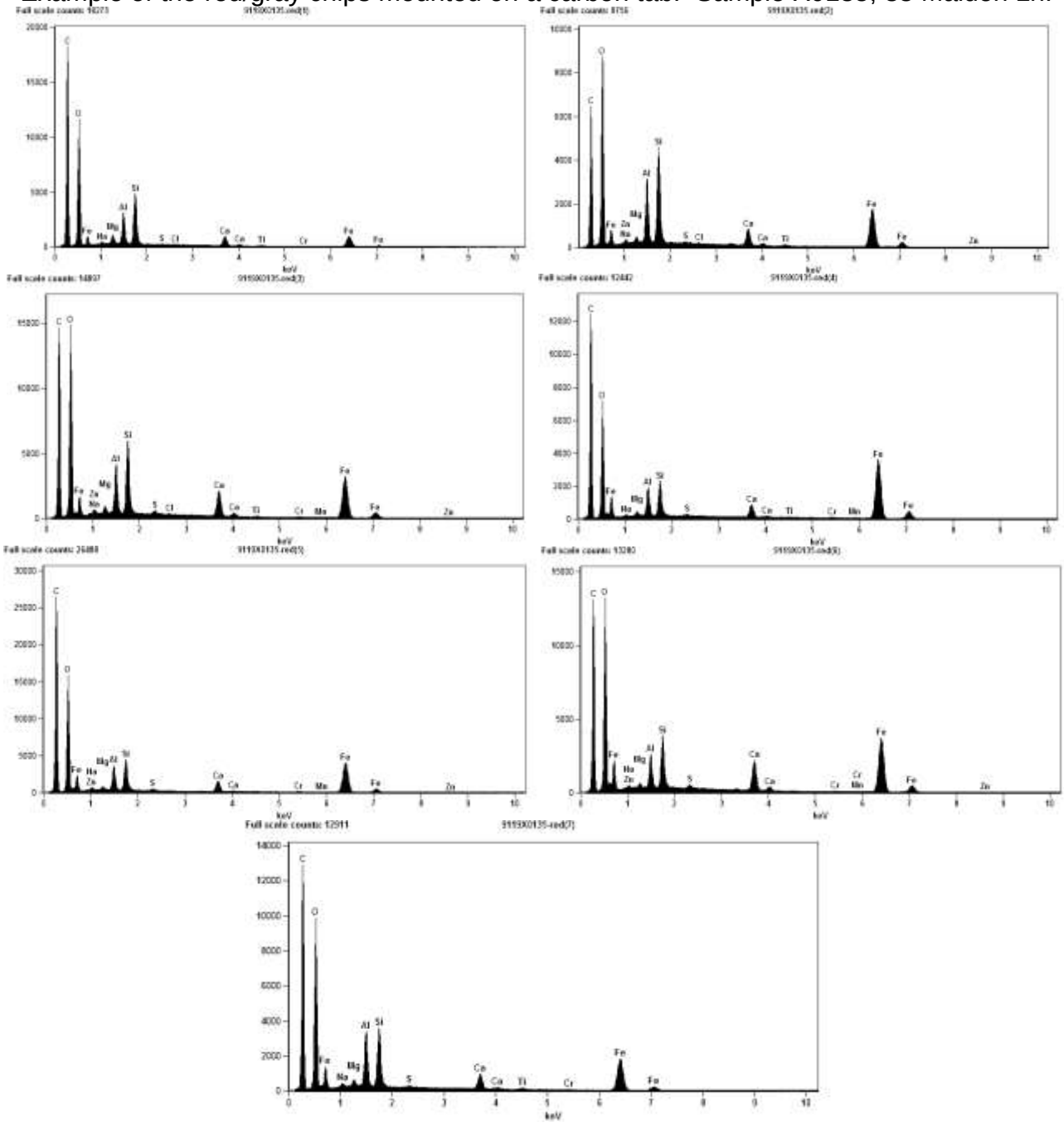

Full scale counts: 1173
9119-5230M3455B-red-gray(14)
O
C
Fe
Mg
Al
Si
S
Ca
Ca
Fe
Fe
keV


Full scale counts: 1541
9119-5230M3455B-red-gray(15)
O
C
Fe
Mg
Al
Si
S
K
Ca
Ce
Fe
Fe
keV


Full scale counts: 1600
9119-5230M3455B-red-gray(16)
C
O
Fe
Mg
Al
Si
S
K
Ca
Ce
Fe
Fe
keV



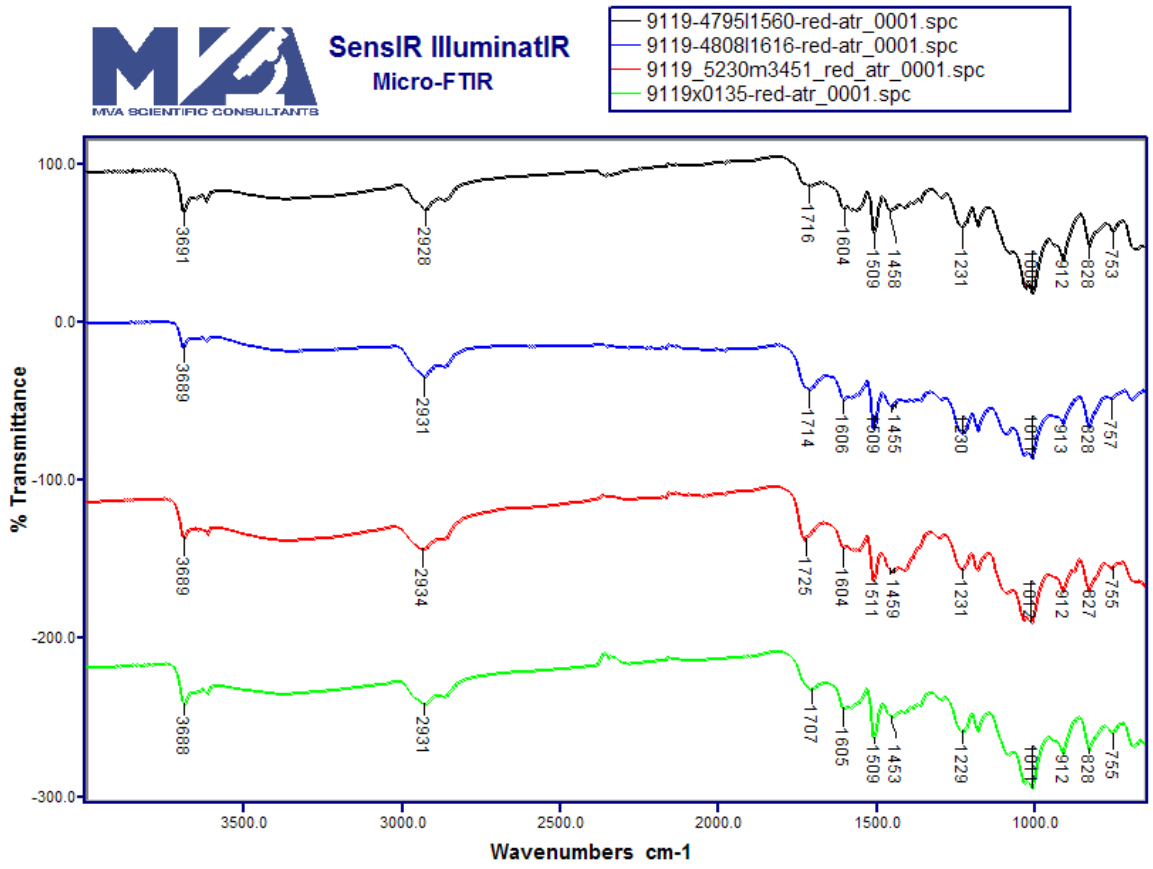
Example of the red/gray chips mounted on a carbon tab. Sample X0135, 33 Maiden Ln.

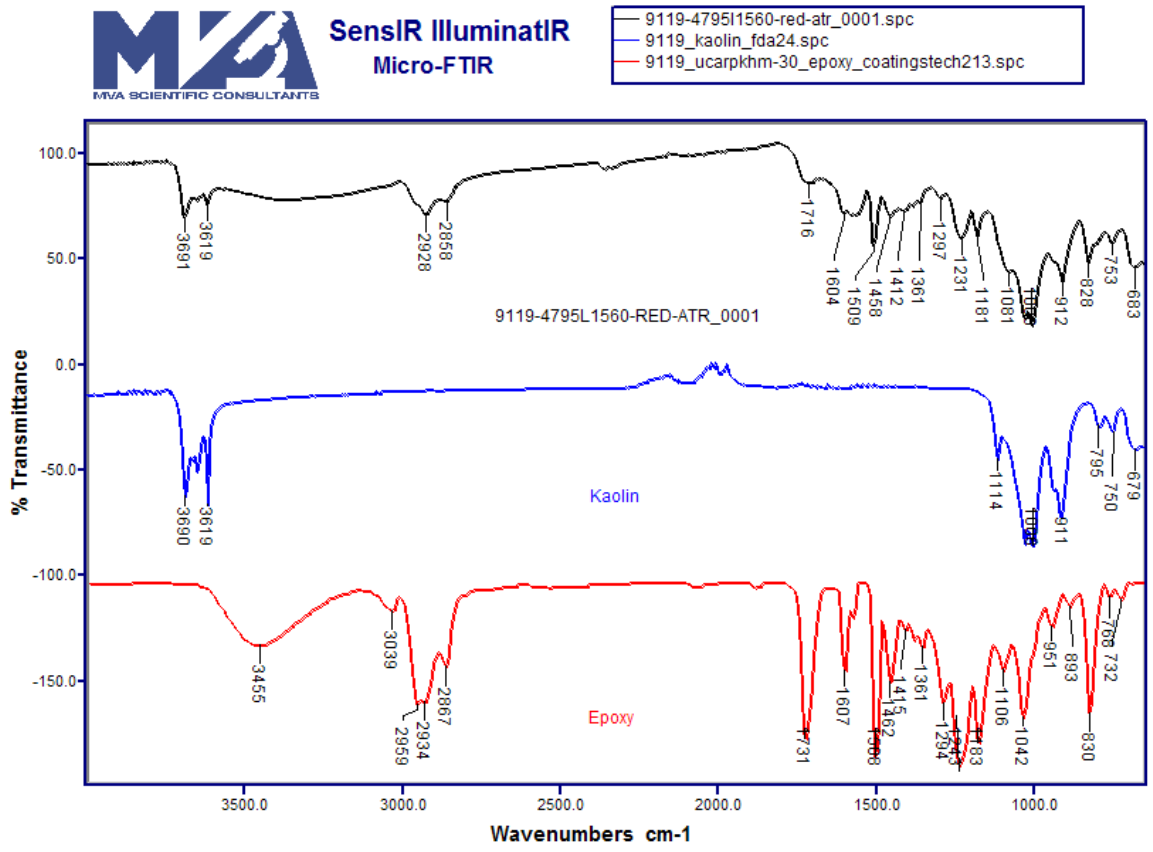


APPENDIX C

FTIR Spectra

FTIR Analysis of Red Layers





APPENDIX D

SEM Cross-Section Images and Spectra

SEM Analysis of Cross-Sections (20 kV)

9119L1560(1)

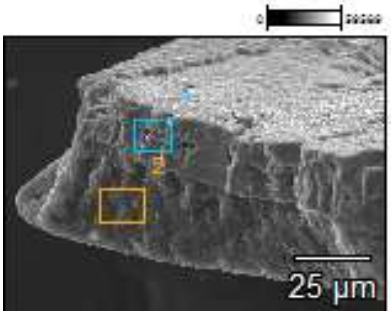
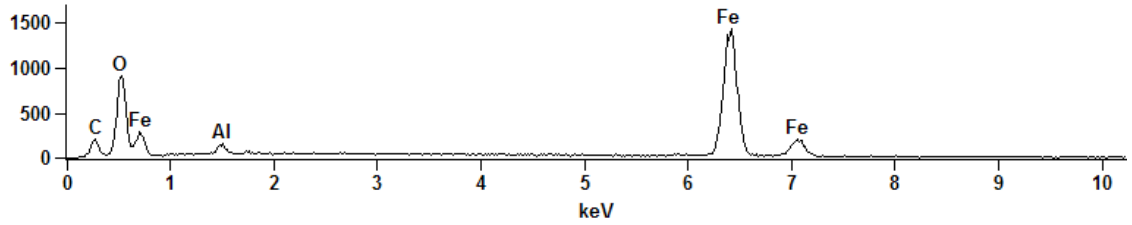
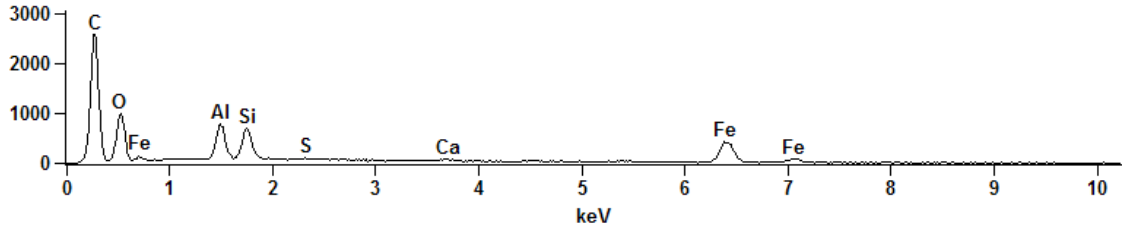


Image Name: 9119L1560(1)
Accelerating Voltage: 20.0 kV
Magnification: 950

Full scale counts: 1423 9119L1560(1)_pt1



Full scale counts: 2567 9119L1560(1)_pt2



9119L1560(2)

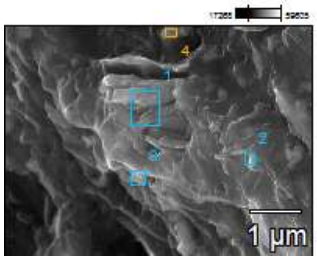
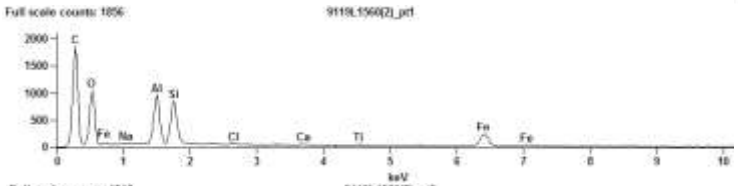
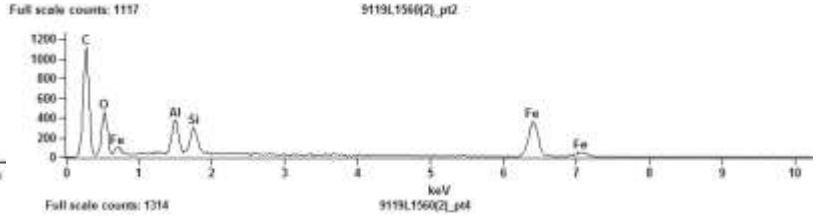
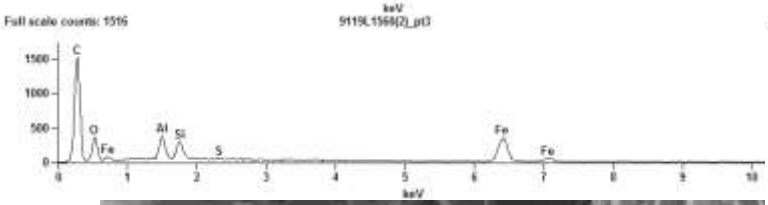
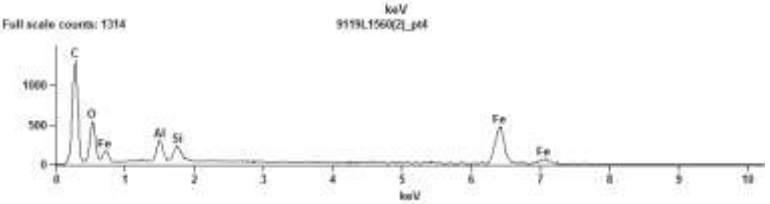


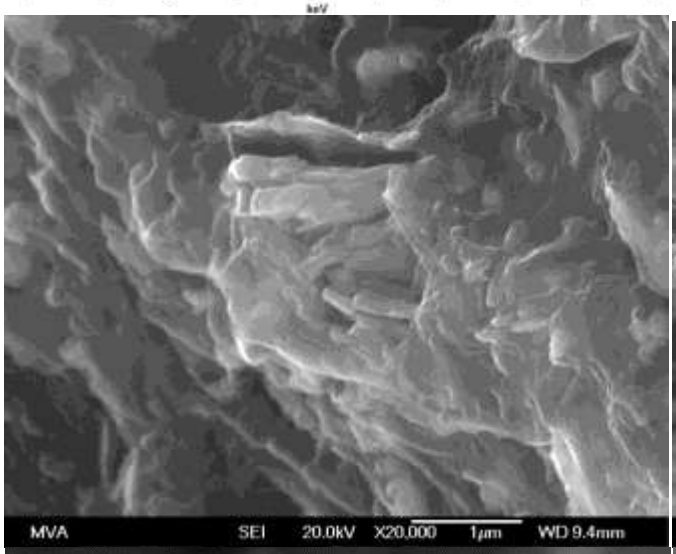
Image Name: 9119L1560(2)
Accelerating Voltage: 20.0 kV
Magnification: 20000

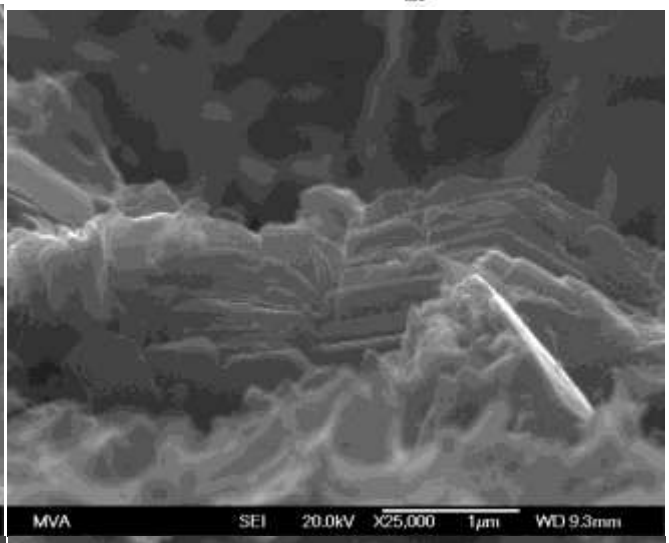


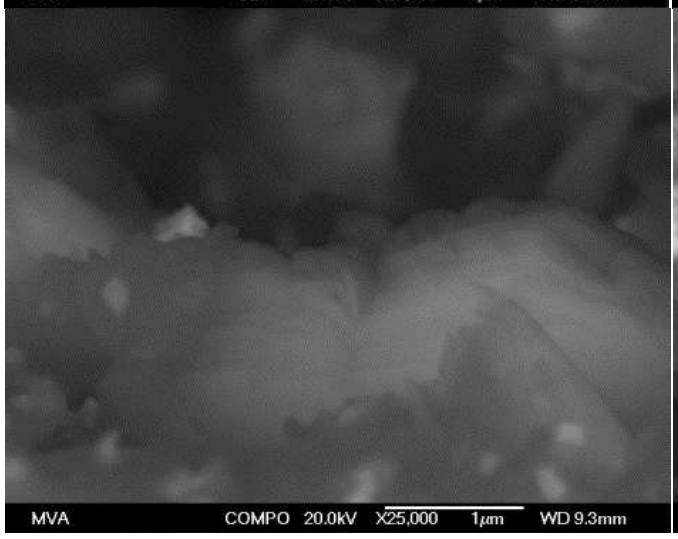


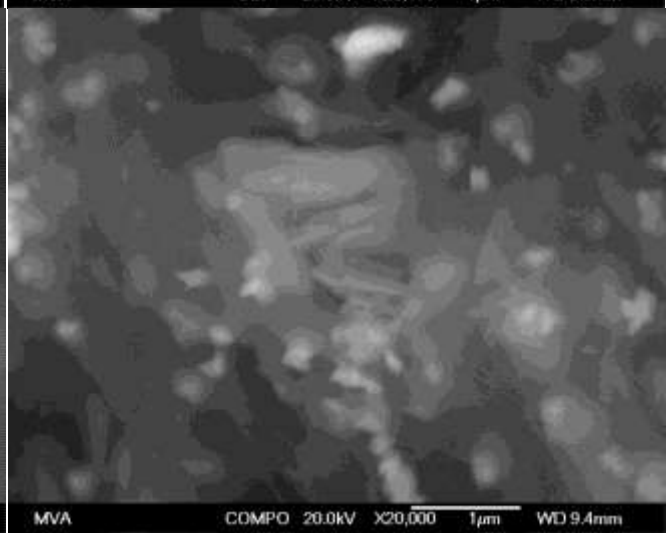












9119L1560(3)

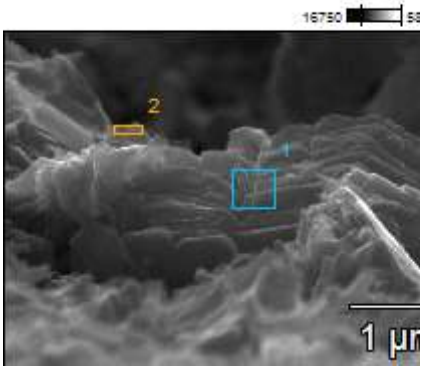
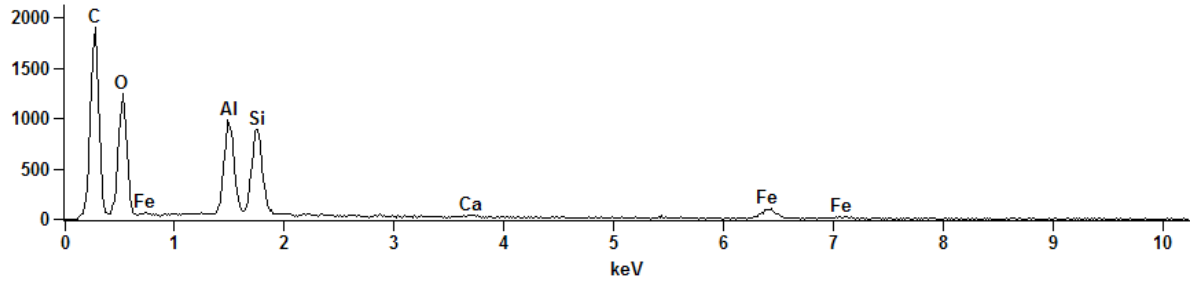


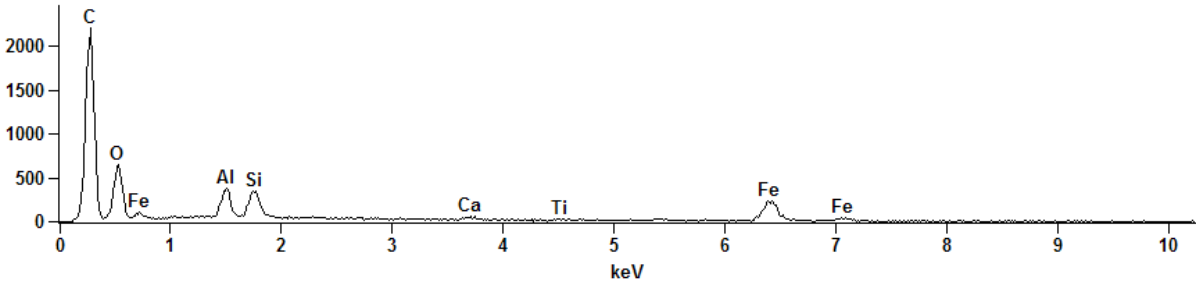
Image Name: 9119L1560(3)
Accelerating Voltage: 20.0 kV
Magnification: 25000

Full scale counts: 1903



Full scale counts: 2204

9119L1560(3)_pt2



9119L1616(3)

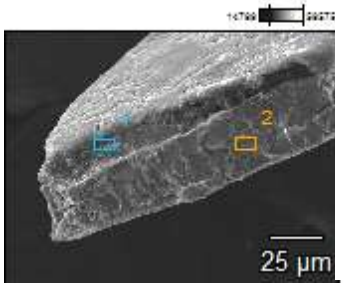
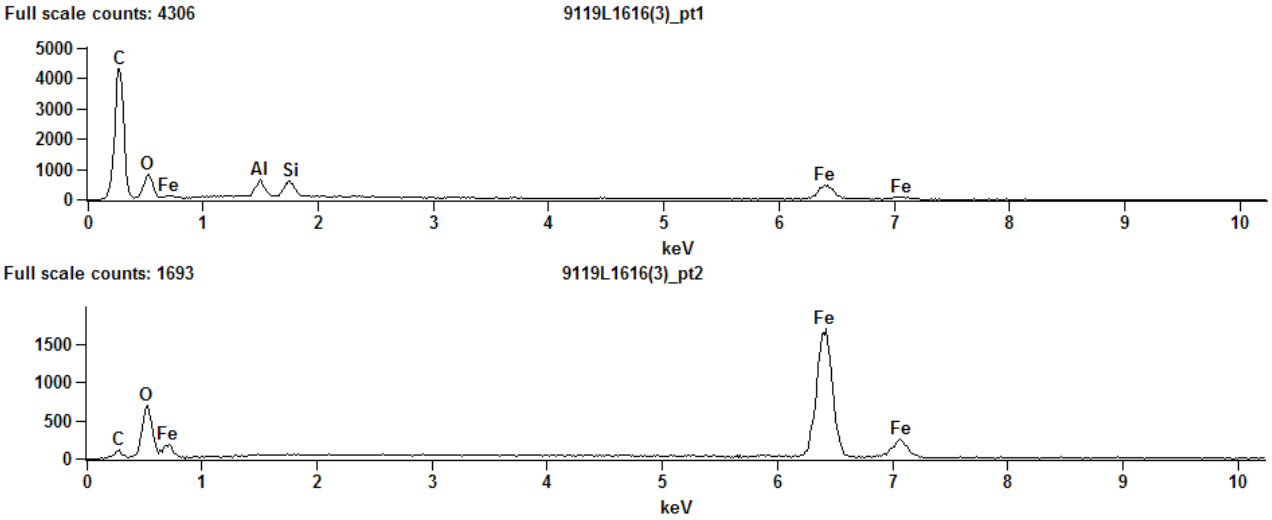


Image Name: 9119L1616(3)
Accelerating Voltage: 20.0 kV
Magnification: 750



9119L1616(1)

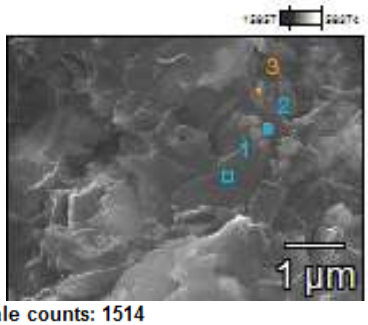
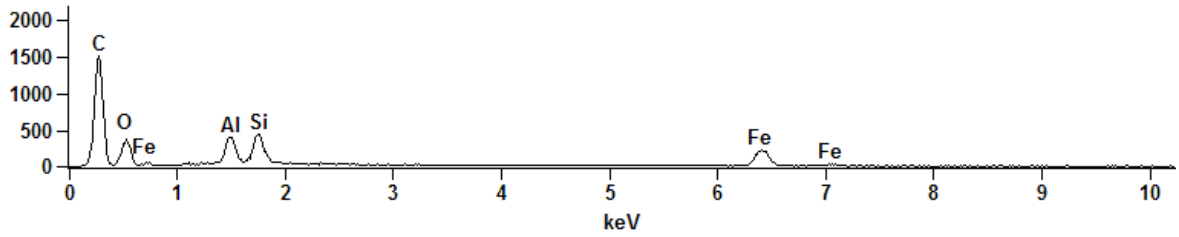
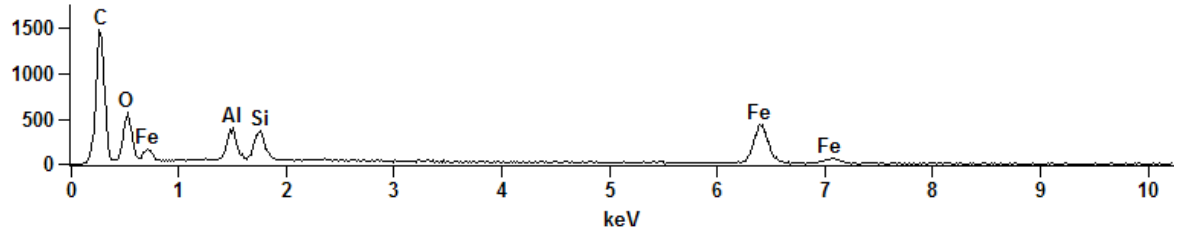


Image Name: 9119L1616(1)
Accelerating Voltage: 20.0 kV
Magnification: 20000

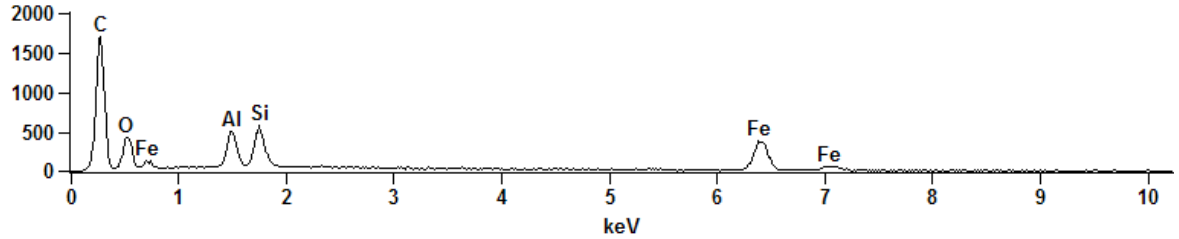
Full scale counts: 1514 9119L1616(1)_pt1



Full scale counts: 1482 9119L1616(1)_pt2



Full scale counts: 1697 9119L1616(1)_pt3



9119L1616(2)

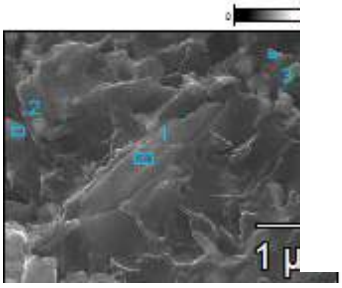
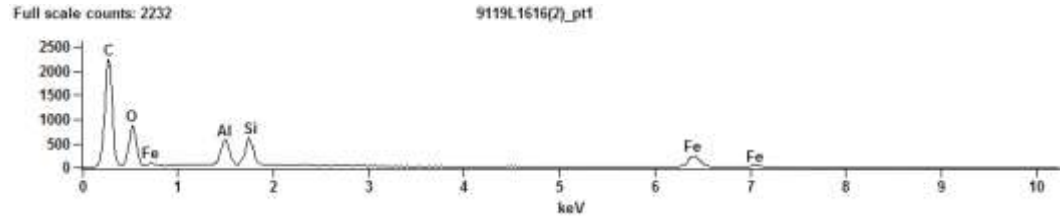
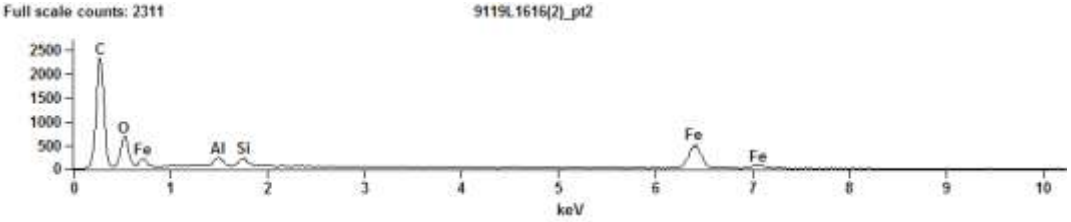
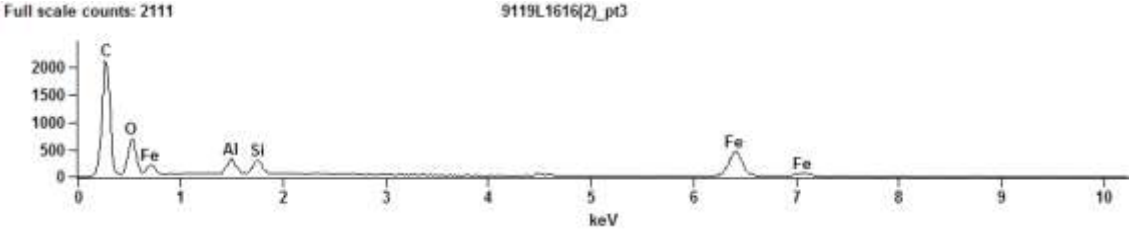
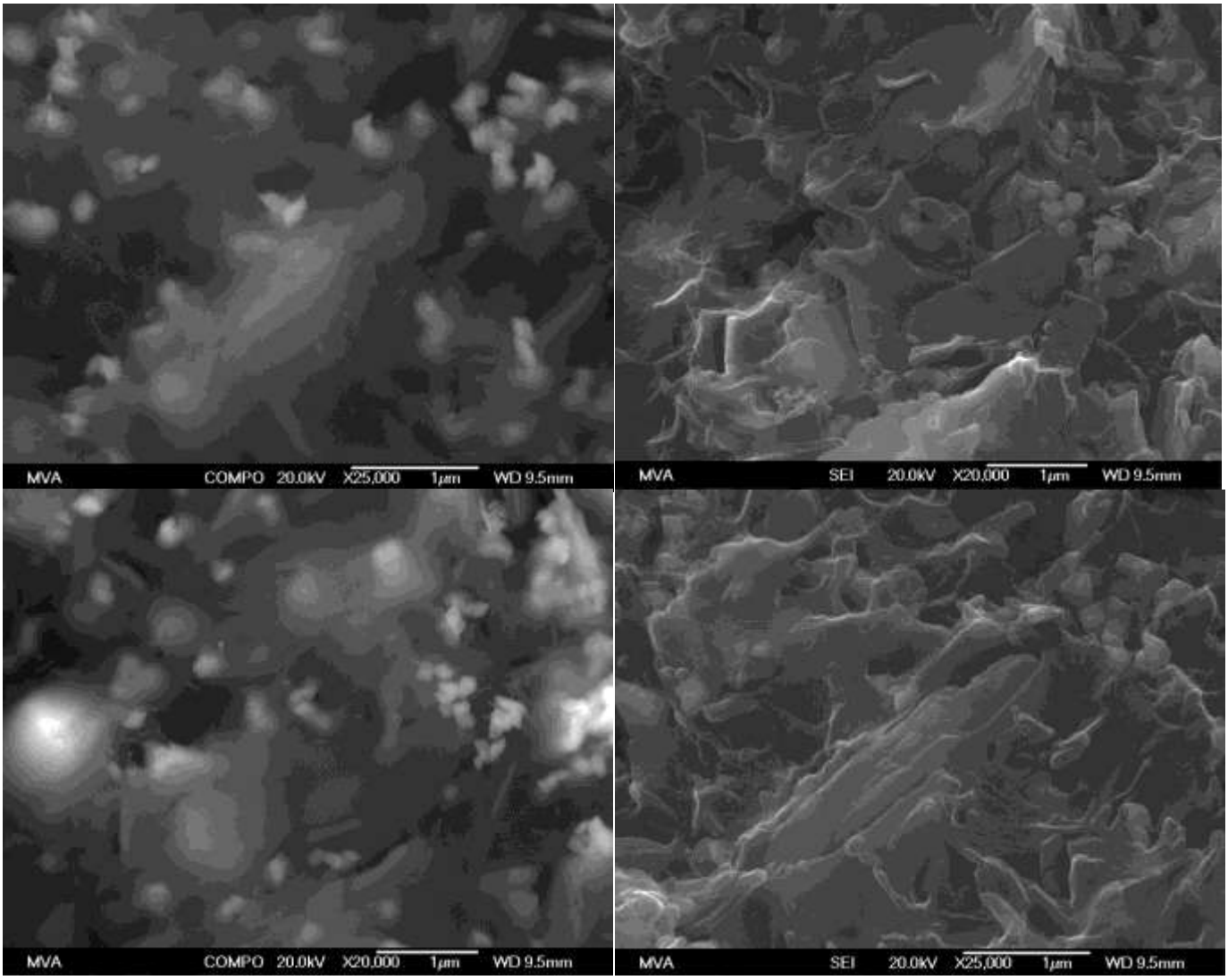


Image Name: 9119L1616(2)
Accelerating Voltage: 20.0 kV
Magnification: 25000



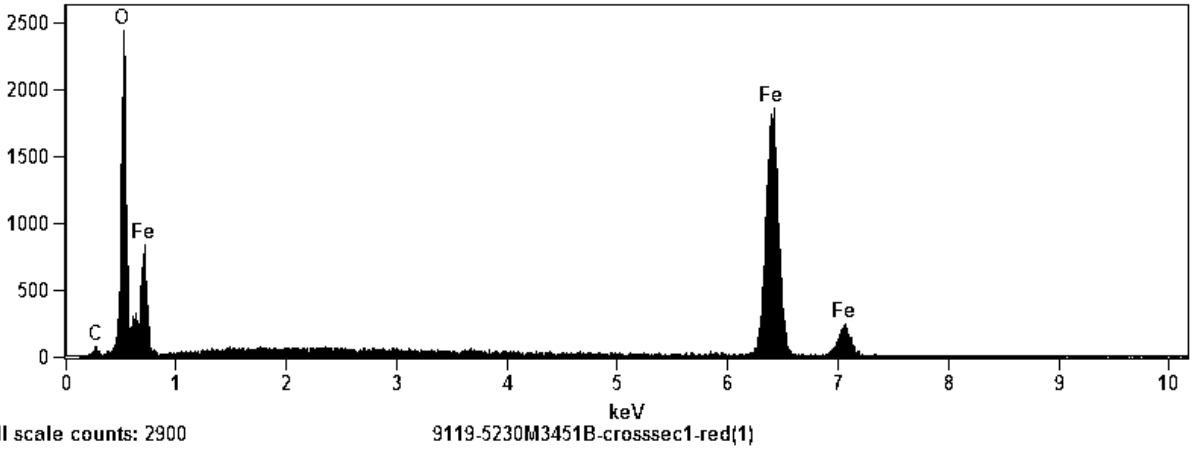




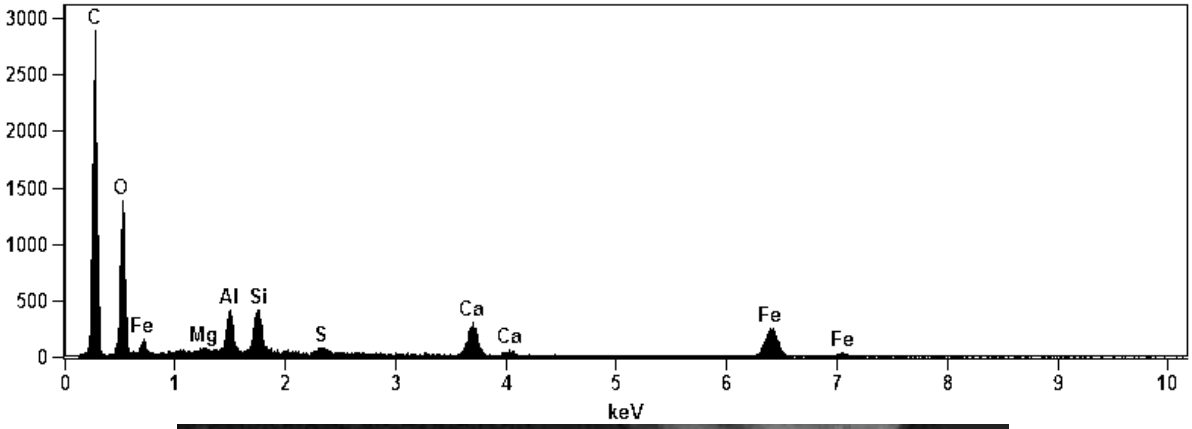

MVA COMPO 20.0kV X25,000 1μm WD 9.5mm
MVA SEI 20.0kV X20,000 1μm WD 9.5mm
MVA COMPO 20.0kV X20,000 1μm WD 9.5mm
MVA SEI 20.0kV X25,000 1μm WD 9.5mm

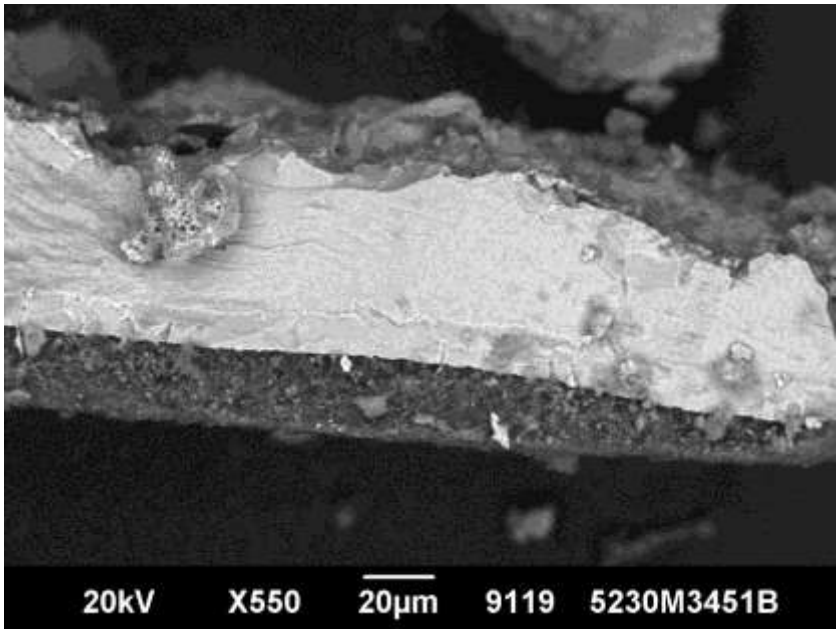
9119L1616

Full scale counts: 2454 9119-5230M3451B-crosssec1-gray(1)

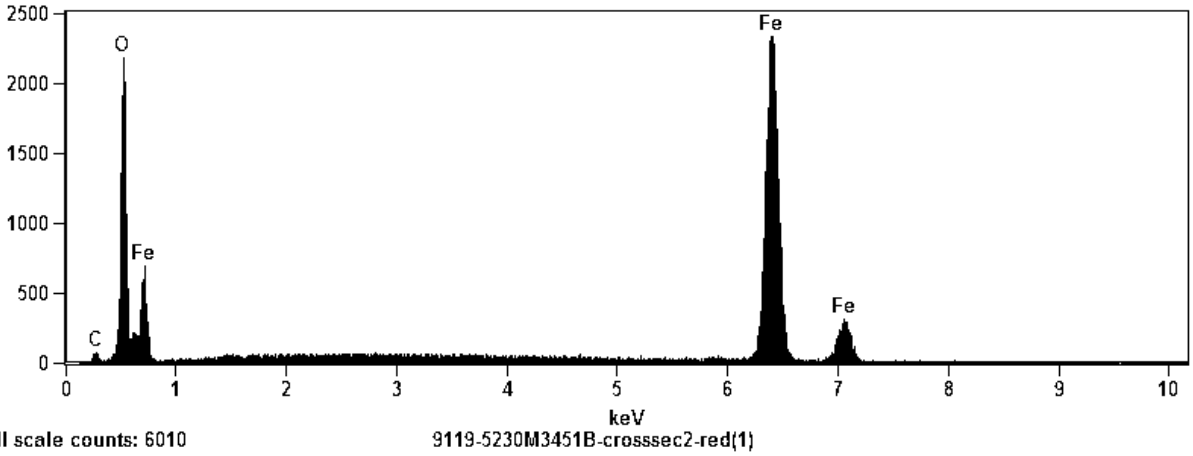


Full scale counts: 2900 9119-5230M3451B-crosssec1-red(1)

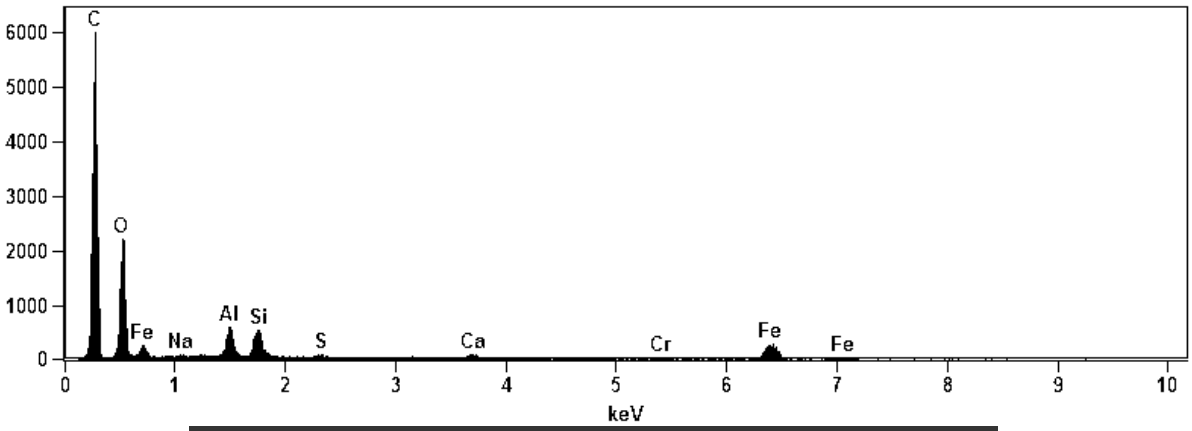


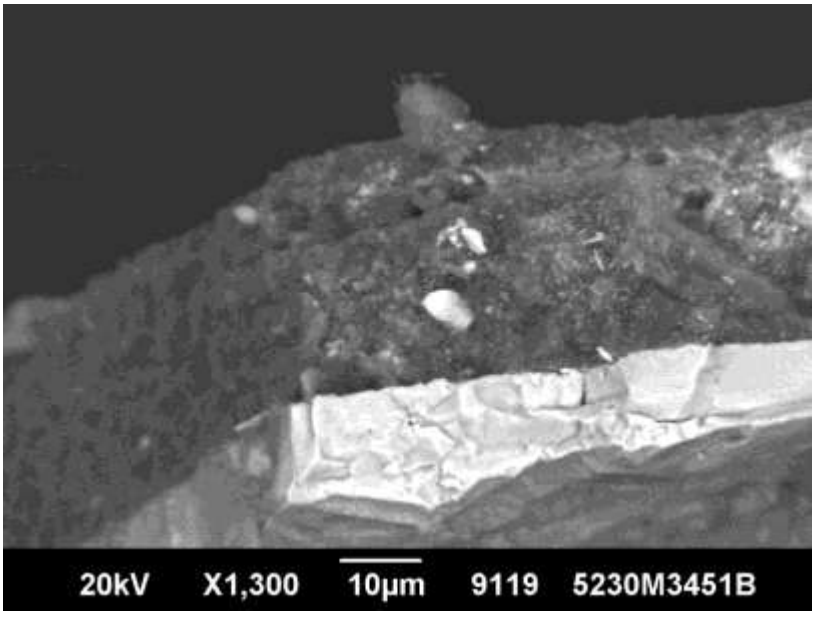


Full scale counts: 2342 9119-5230M3451B-crosssec2-gray(1)



Full scale counts: 6010 9119-5230M3451B-crosssec2-red(1)





9119X0135(3)

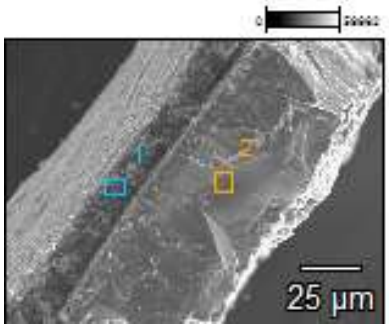
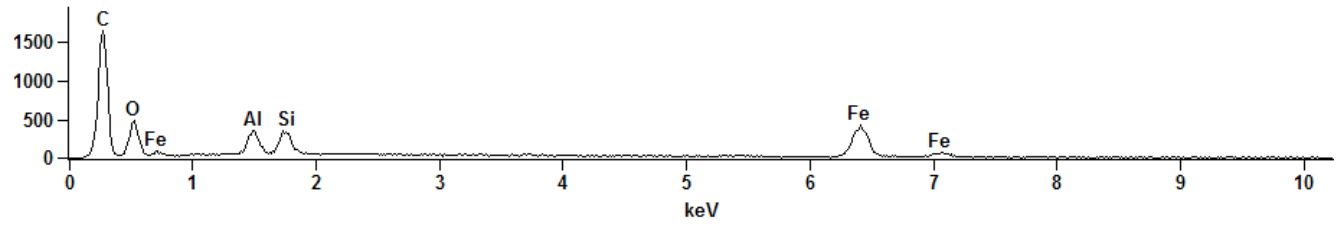


Image Name: 9119X0135(3)
Accelerating Voltage: 20.0 kV
Magnification: 750

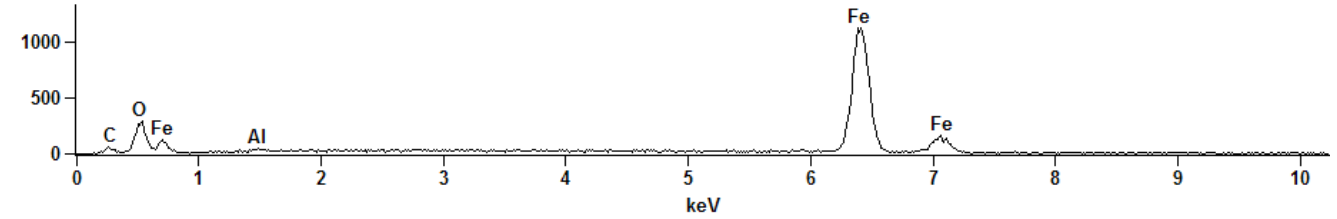
Full scale counts: 1644

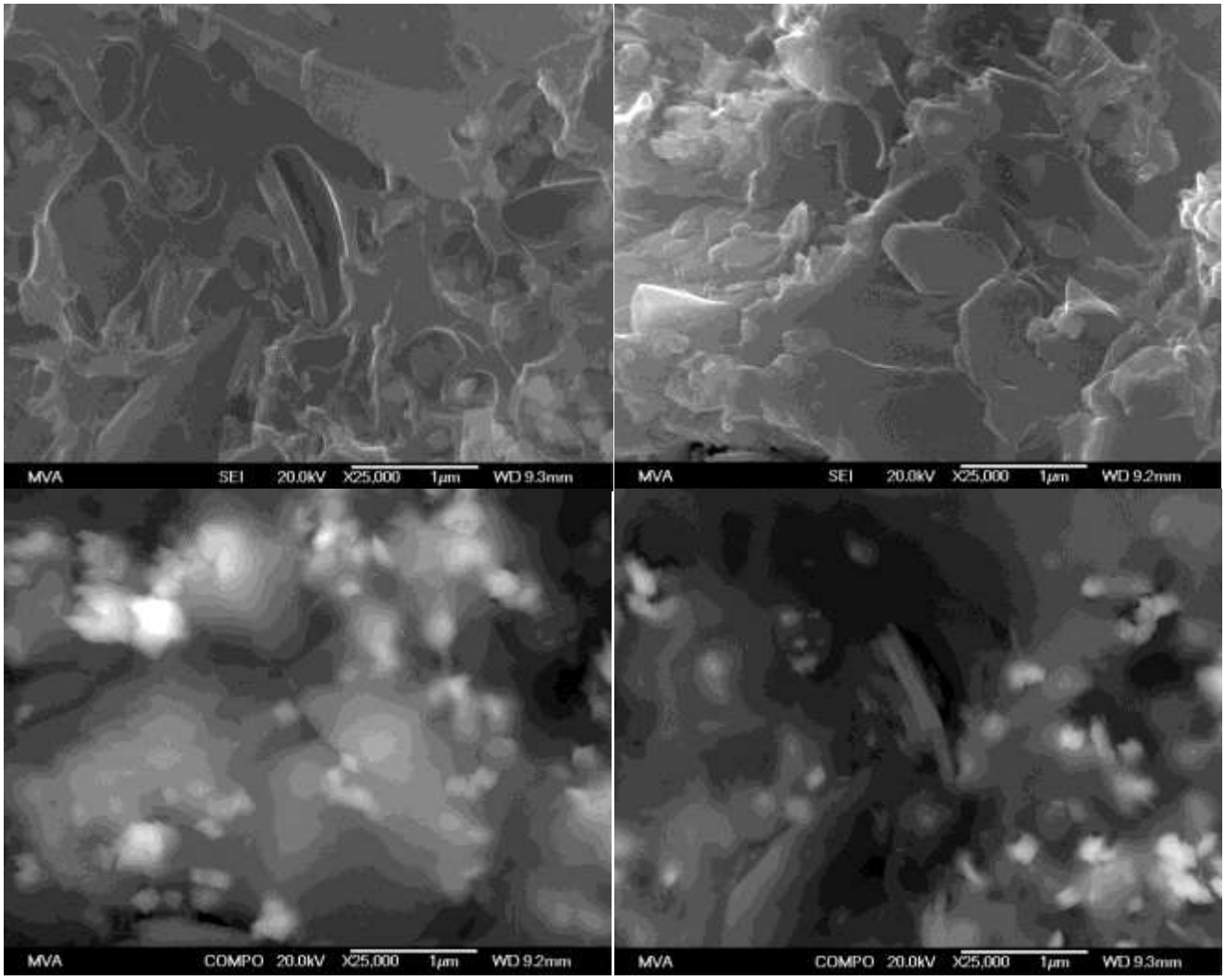
9119X0135(3)_pt1



Full scale counts: 1121

9119X0135(3)_pt2




MVA SEI 20.0kV X25,000 1μm WD 9.3mm
MVA SEI 20.0kV X25,000 1μm WD 9.2mm
MVA COMPO 20.0kV X25,000 1μm WD 9.2mm
MVA COMPO 20.0kV X25,000 1μm WD 9.3mm

9119X0135

9119X0135(1)

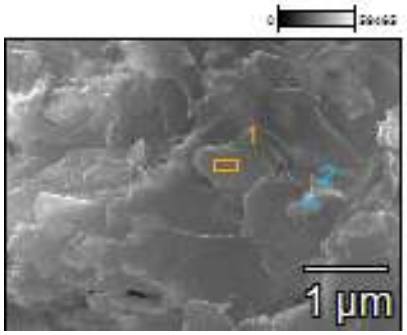
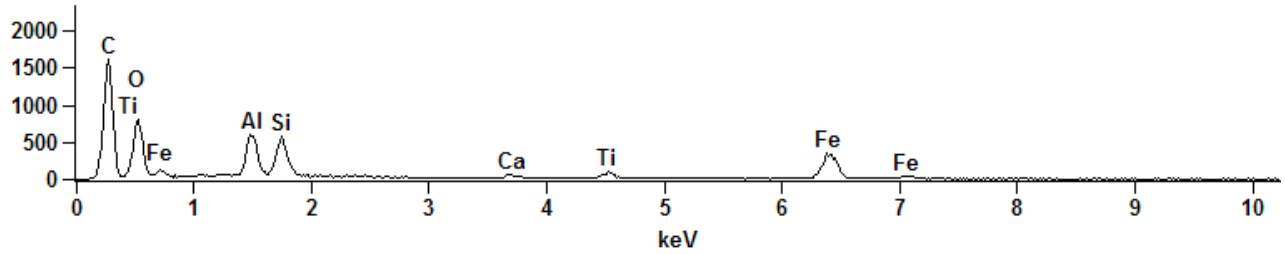
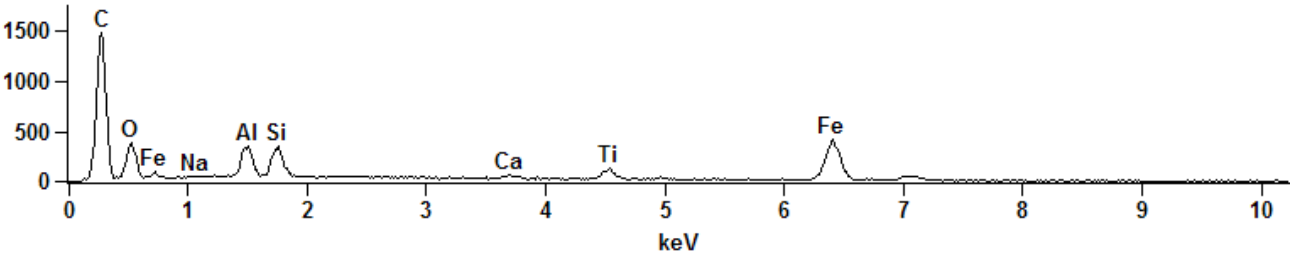


Image Name: 9119X0135(1)
Accelerating Voltage: 20.0 kV
Magnification: 25000

Full scale counts: 1606 9119X0135(1)_pt1



Full scale counts: 1481 9119X0135(1)_pt2



9119X0135(2)

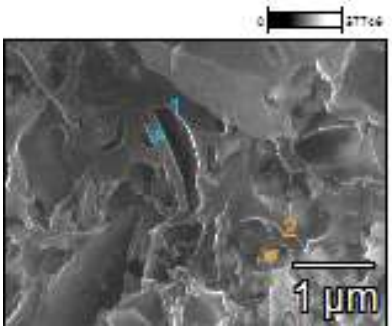
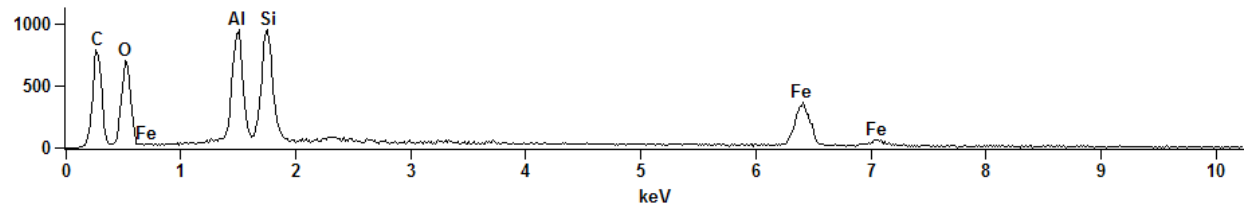


Image Name: 9119X0135(2)
Accelerating Voltage: 20.0 kV
Magnification: 25000

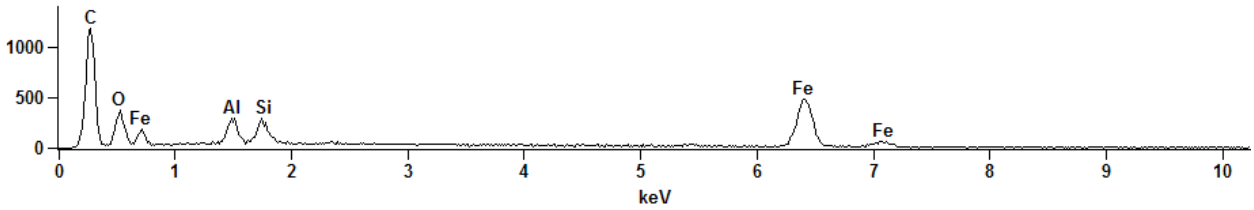
Full scale counts: 955

9119X0135(2)_pt1



Full scale counts: 1179

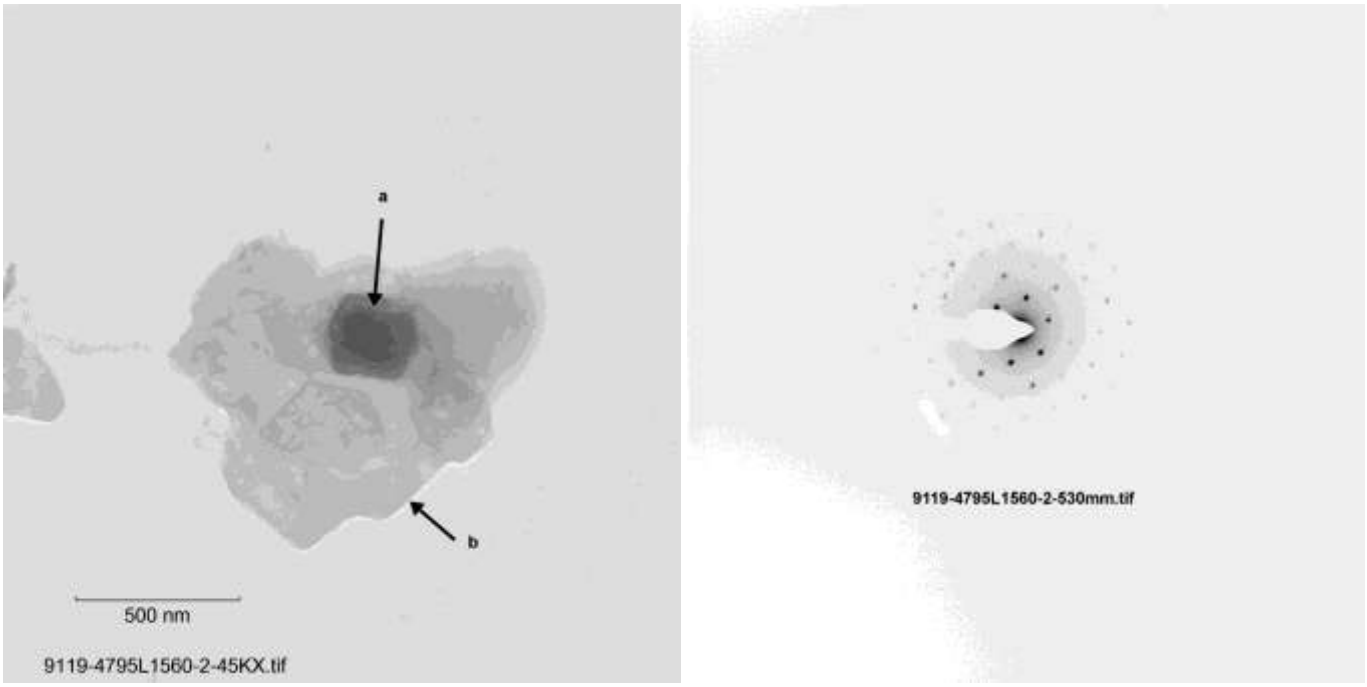
9119X0135(2)_pt2

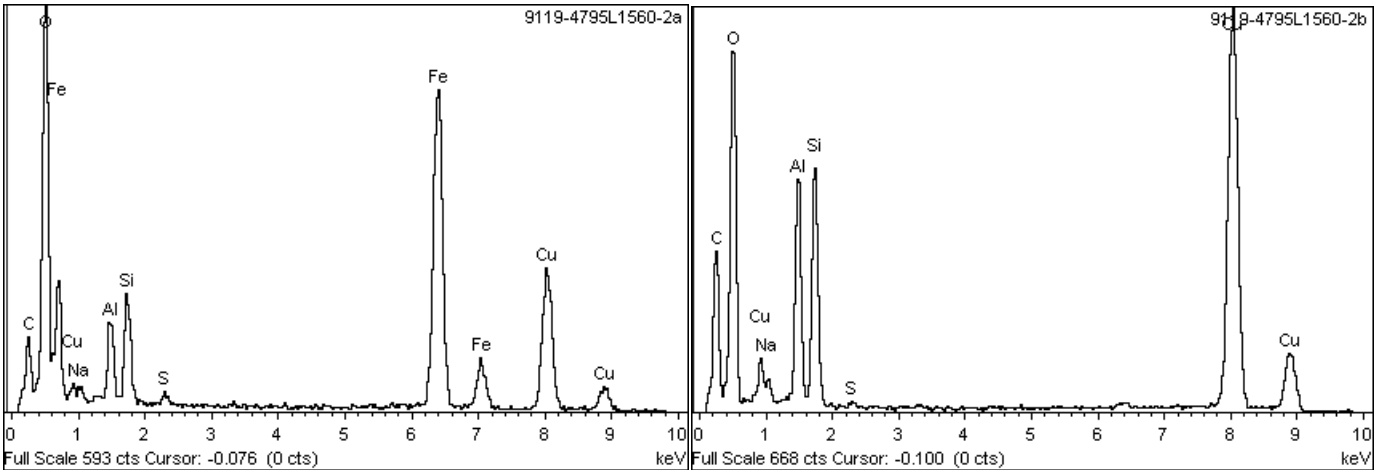


APPENDIX E

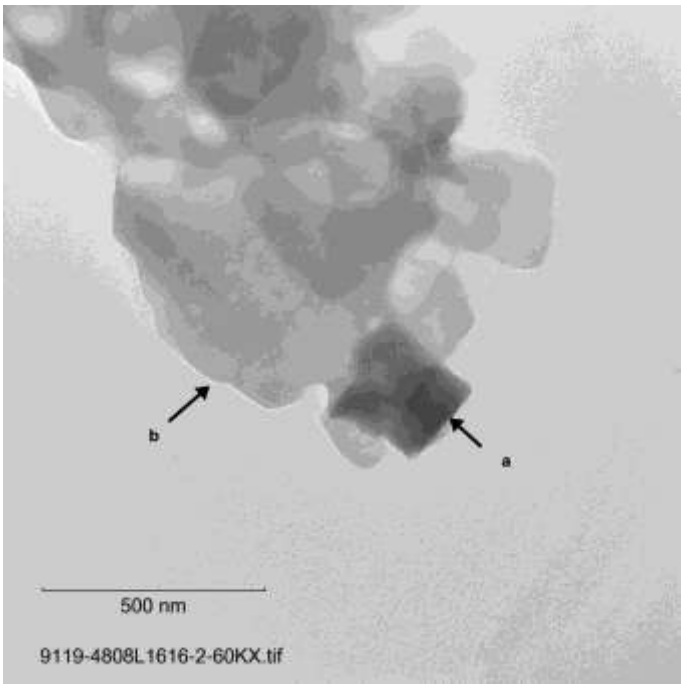
TEM Images, Data After Ashing

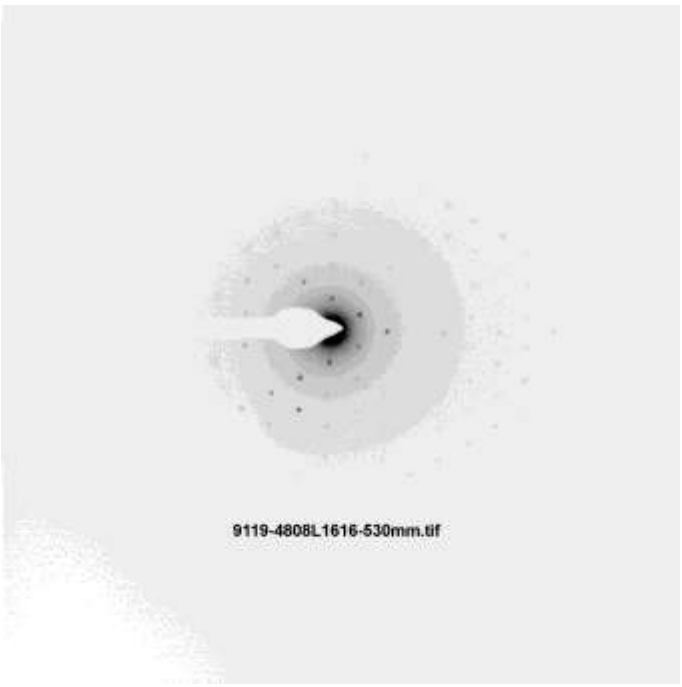
TEM-SAED-EDS analysis of the residue after low temperature ashing showed equant-shaped particles of iron consistent with iron oxide pigments and plates of kaolin clay.

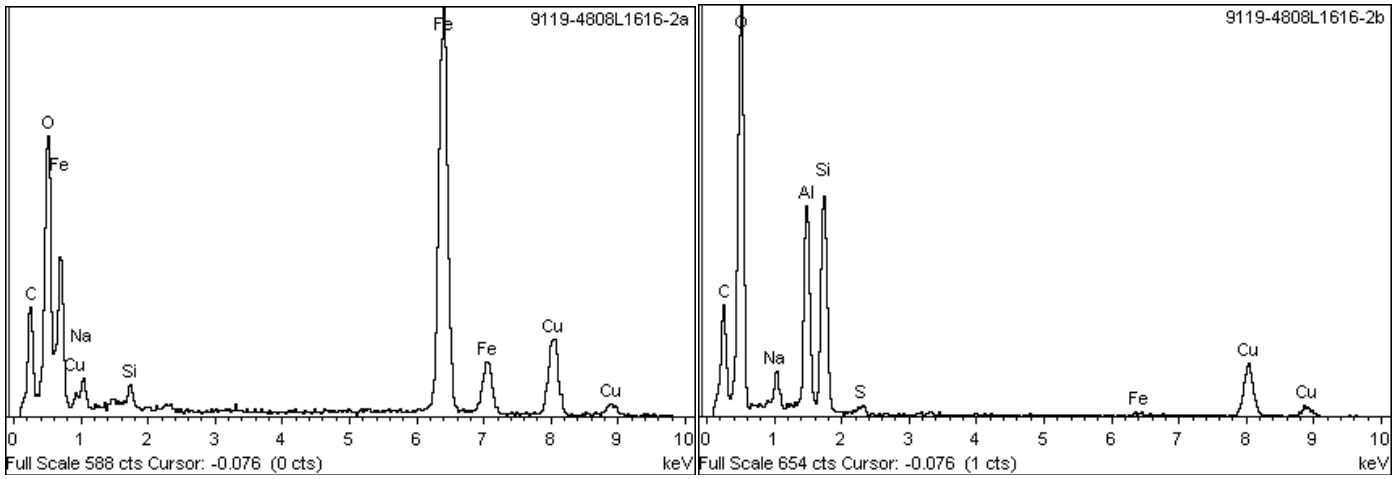




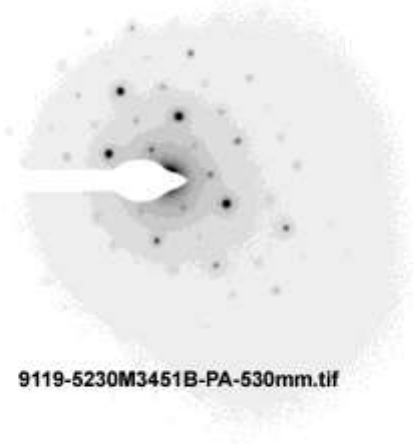
Sample L1560 – Murray & Church St.

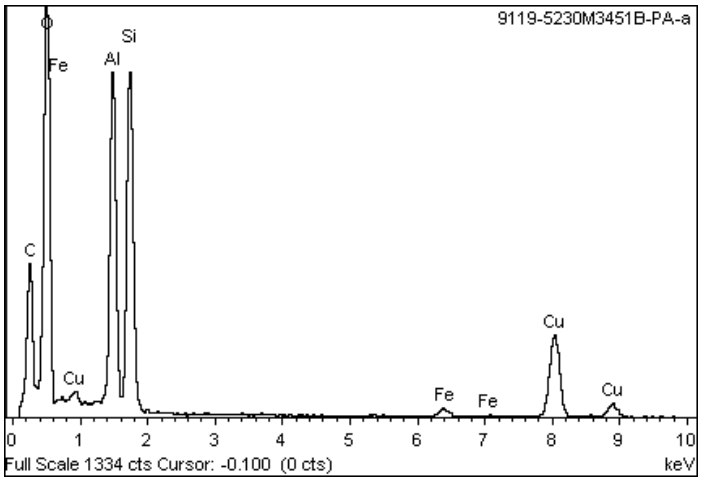


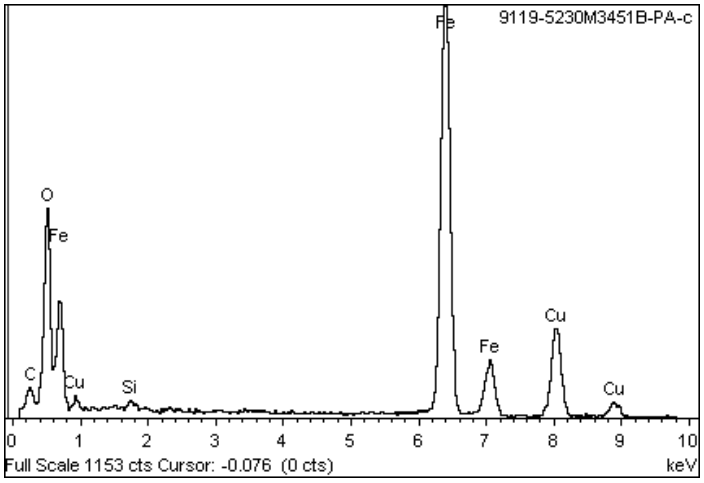


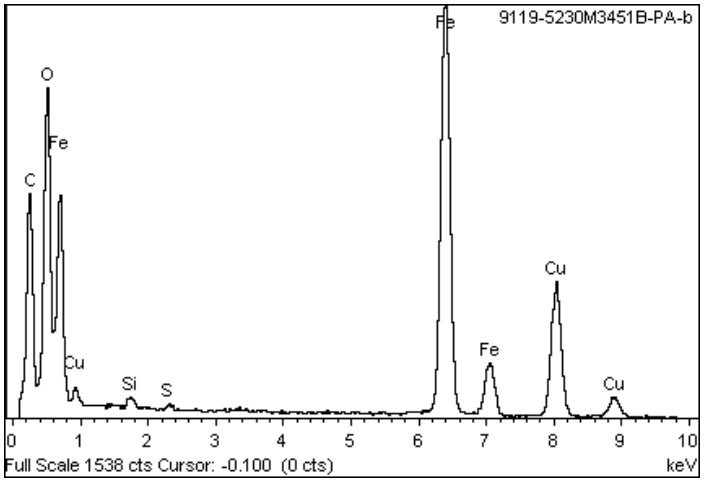


Sample L1616 – 22 Cortlandt St.

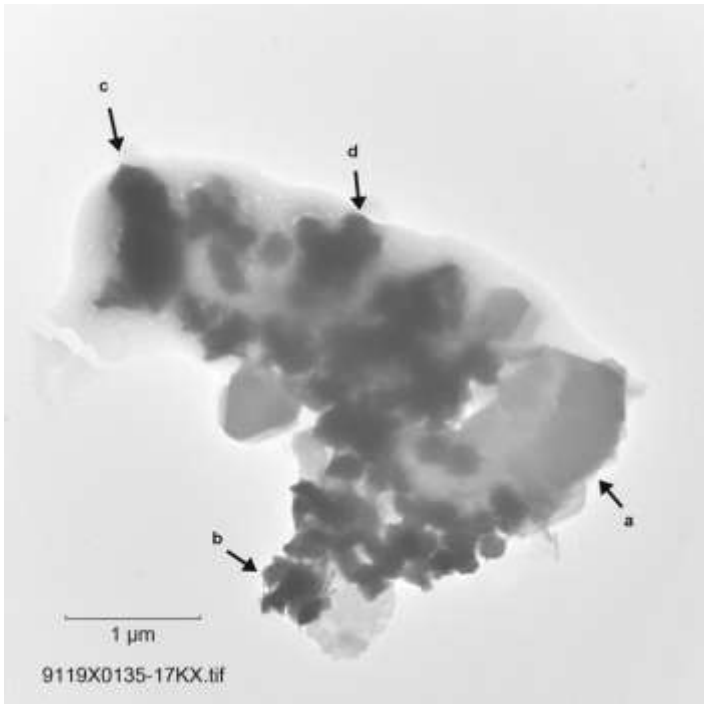


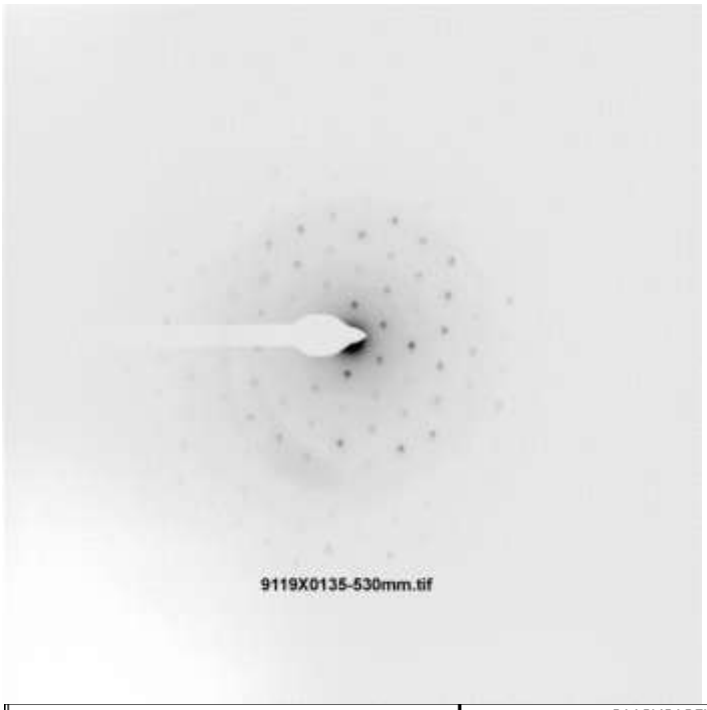


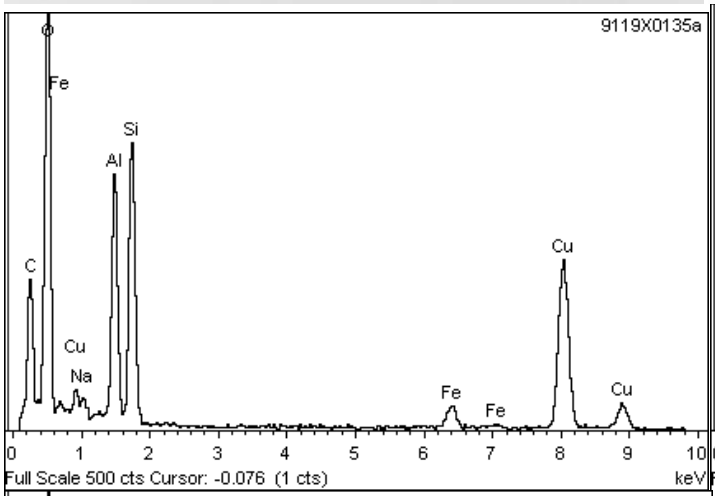


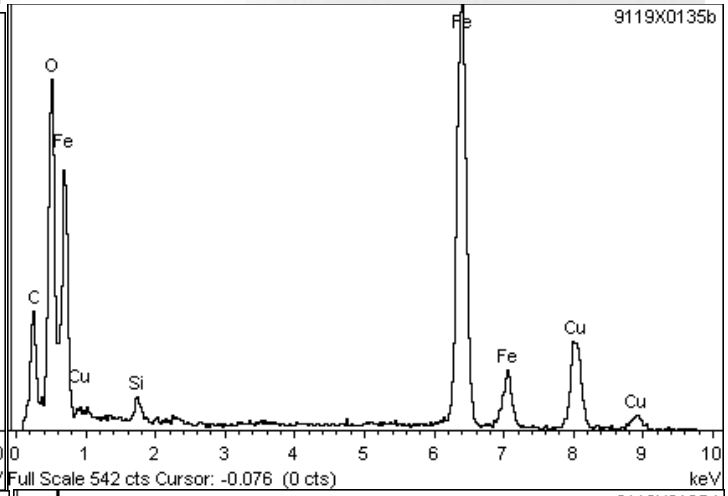


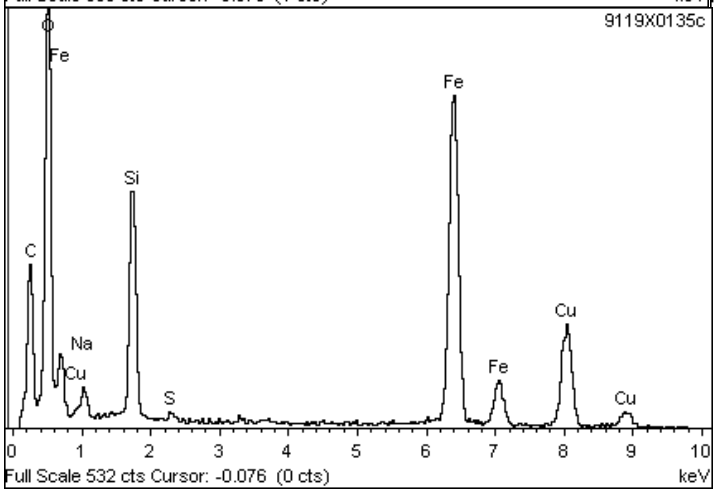
Sample M3451 – 49 Ann St.

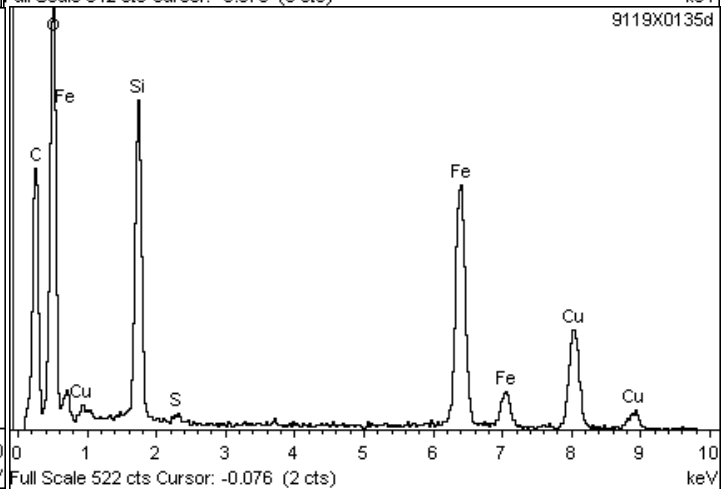








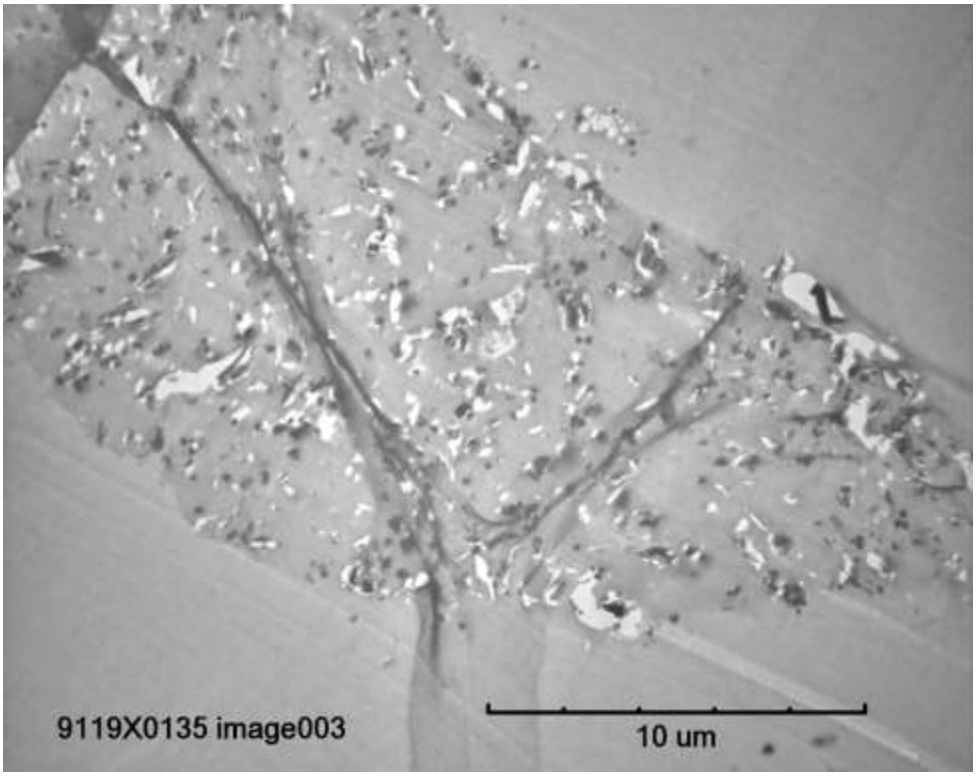


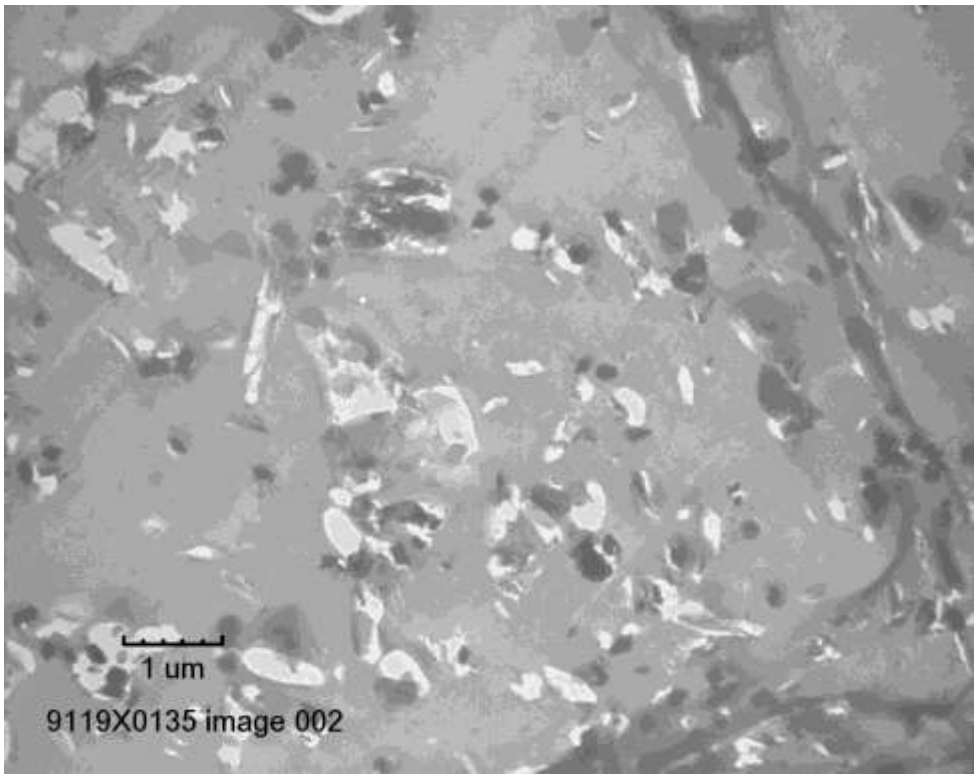


Sample X0135 – 33 Maiden Ln.

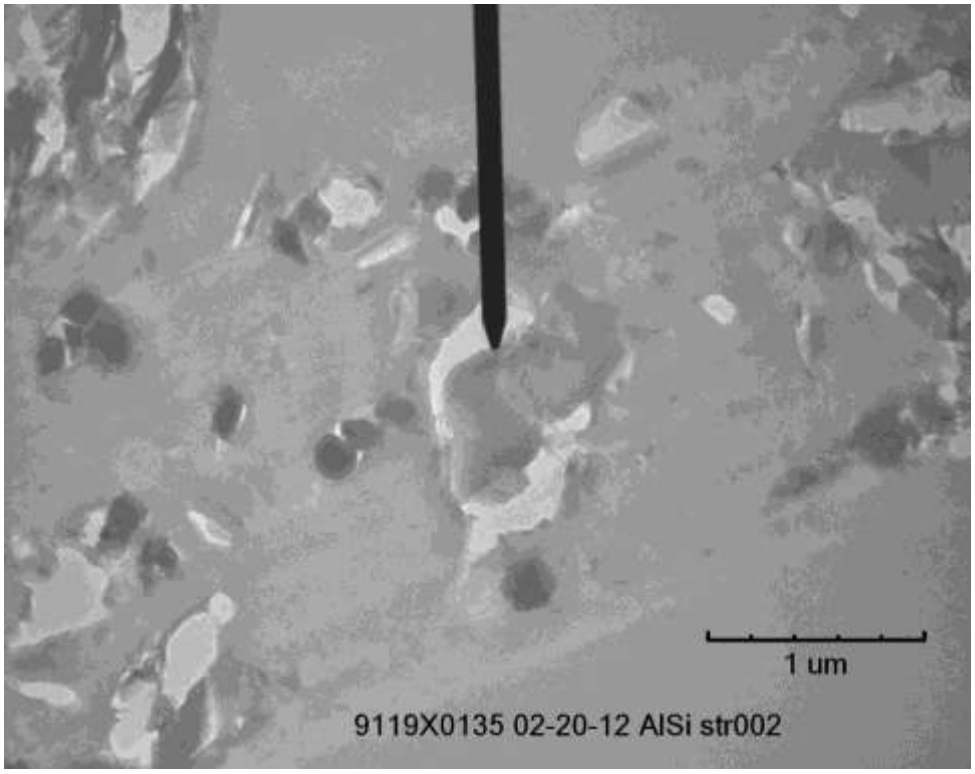
APPENDIX F

TEM Images, Data From Thin Section

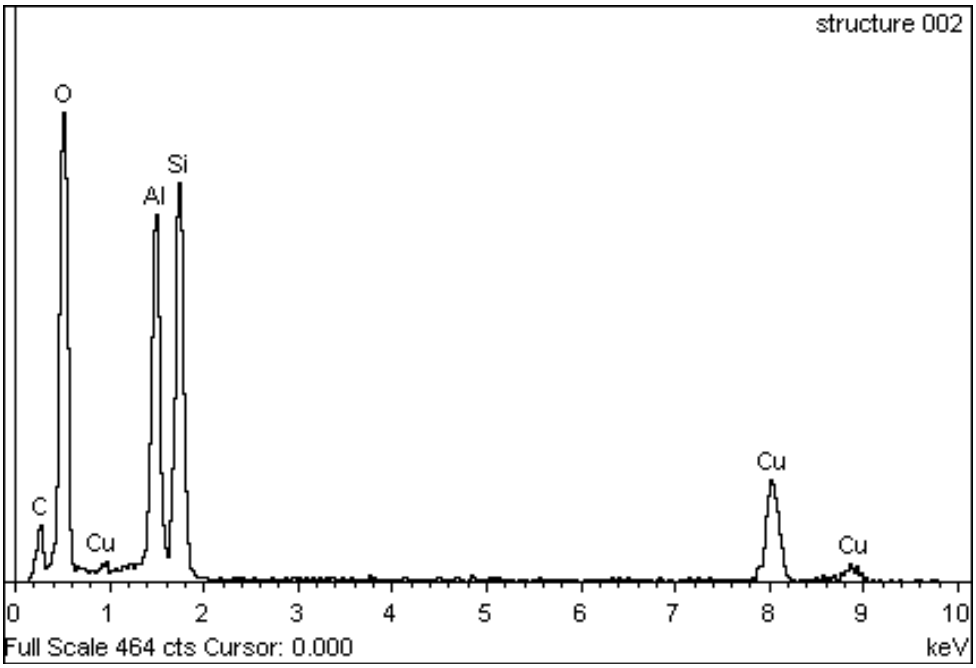


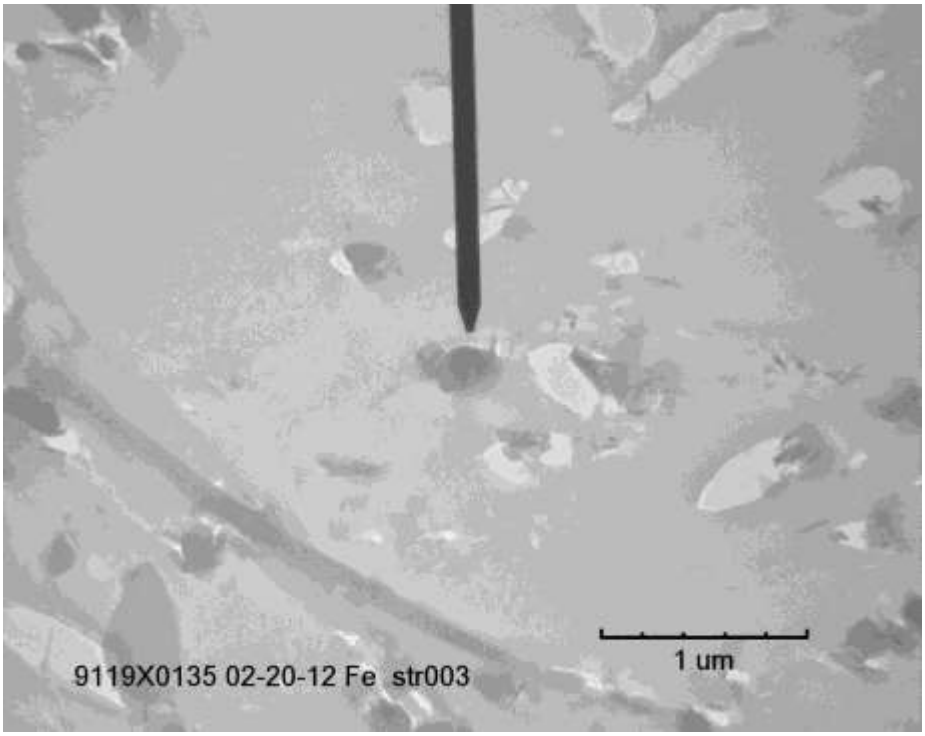


TEM images of an ultra-thin section of a red layer showing iron oxide faceted crystals and kaolin pigments. The matrix is carbon-based. Sample X0135, 33 Maiden Ln.

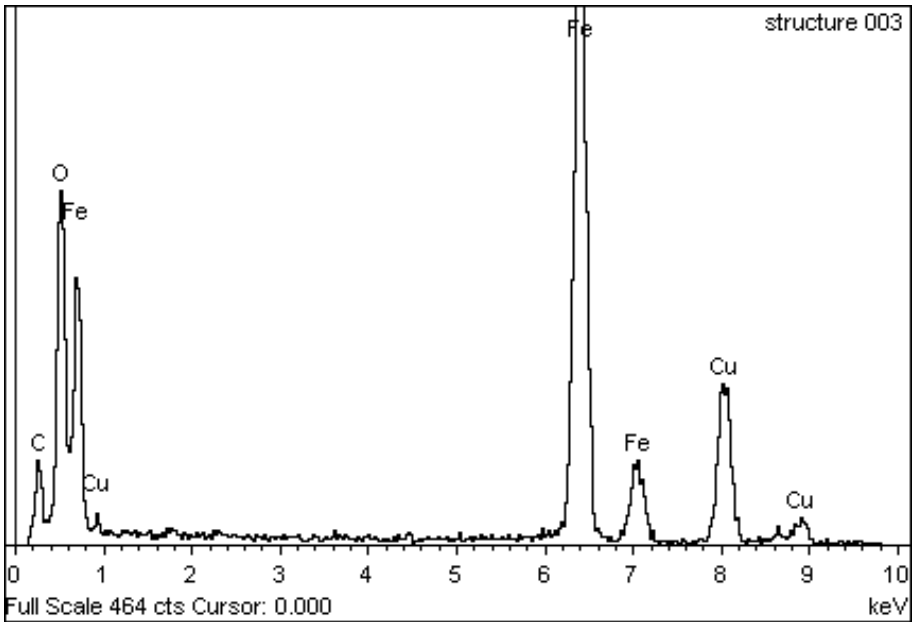


TEM image (above) and x-ray spectrum (below) of kaolin in an ultra-thin section of a red layer.





TEM image (above) and x-ray spectrum (below) of an iron oxide faceted crystal and an ultra-thin section of a red layer.

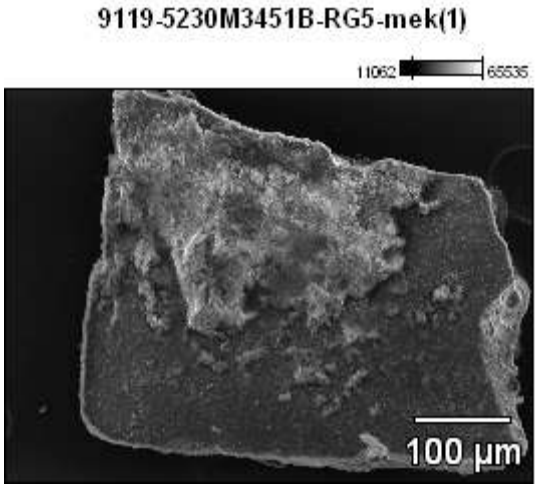


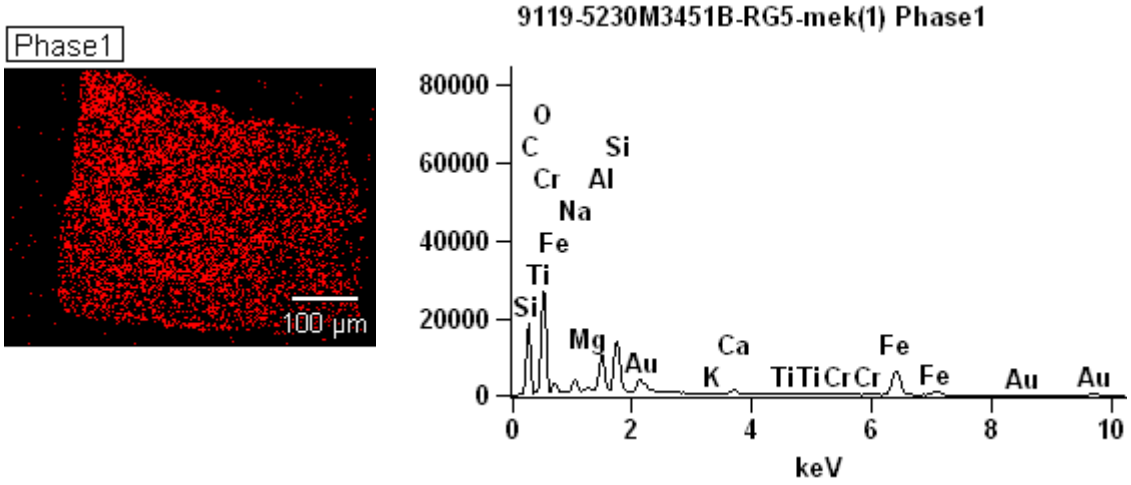
APPENDIX G

Statistical Phase X-ray Mapping of a Red Layer After MEK Treatment

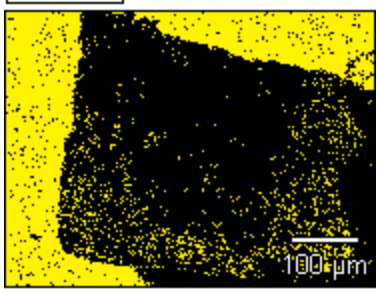
Auto-Phase Mapping after MEK (20kV) light gold coating to eliminate charging.
No aluminum-only phase detected.

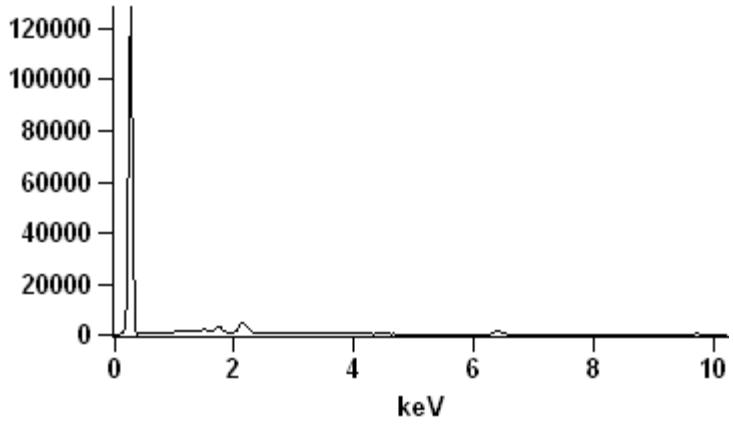
Phase	Elemental Composition	% of Area Covered
1	Primary: Al nearly equal Si >Fe	24.10
2	Primary: C	33.02
3	Primary: High Si	7.92
4	Primary: Si>Fe>Al	11.57
5	Primary: Fe>Si>Al	3.24
6	Primary: Al nearly equal Si &Fe	20.15



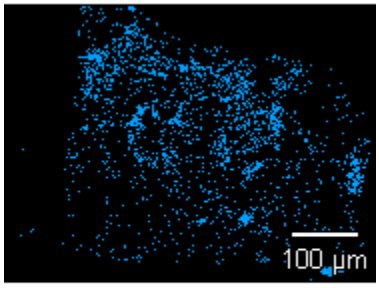


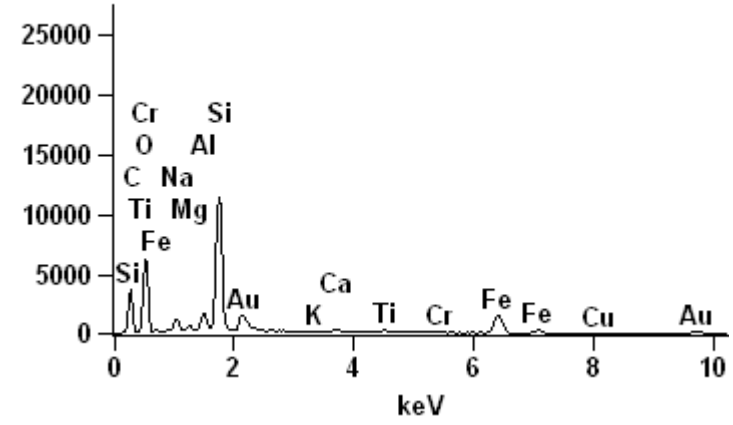
Phase2



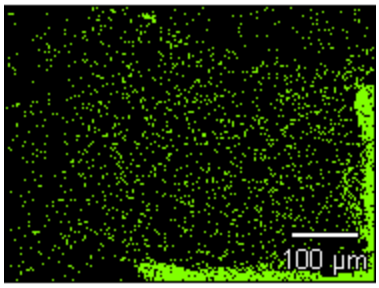


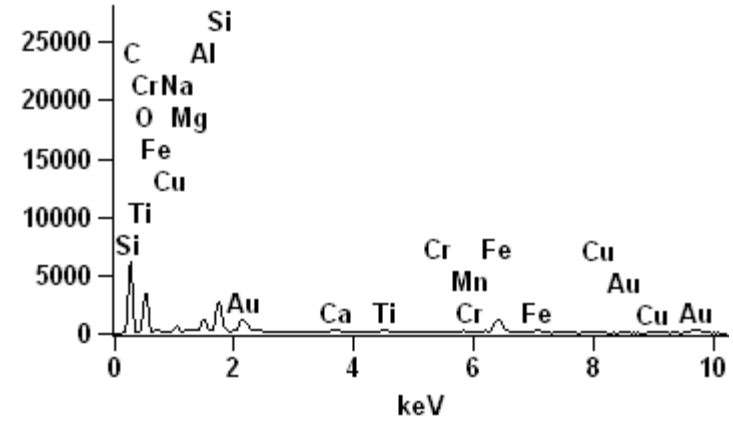
Phase3



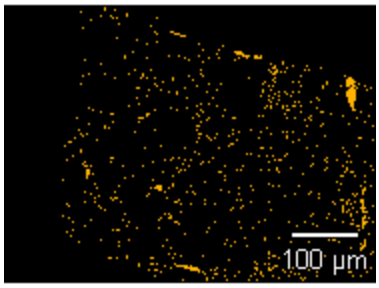


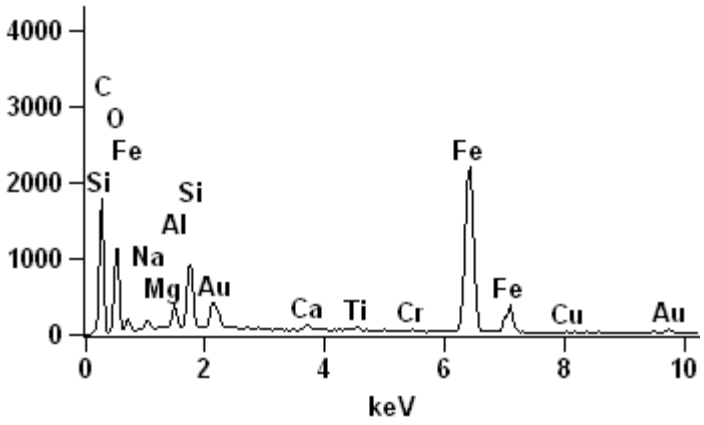
Phase4





Phase5





Phase6