

FINAL REPORT

Selective Atmospheric Plasma Coating Removal for Composite Substrates

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14. ABSTRACT This study investigates the application of Atmospheric Plasma Coating Removal (APCR) on composite materials prevalent in aerospace and defense assets. The technical objective was to demonstrate the efficacy of APCR on a standard aerospace coating stack and to investigate the effects of APCR on a graphite/epoxy composite substrate. Tests were completed to fulfill these objectives, including Multi-Scan Optical Microscopy, Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS), Fourier Transform Infrared Spectroscopy (FTIR), Ultrasonic C-Scans, Short Beam Shear, Differential Scanning Calorimetry (DSC), and recoating was evaluated by pull-off coating adhesion strength testing. Results indicated no adverse effects on carbon fiber composites after APCR. However, limitations in existing testing methods highlight the need for refined approaches, including advanced mechanical testing and detailed adhesion assessments. Continued research is essential to ensure APCR's efficacy and safety, guiding its implementation in practical aerospace and defense scenarios.						
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Acronyms

AFRL - Air Force Research Laboratory
APCR - Atmospheric Plasma Coating Removal
APS - Atmospheric Plasma Solutions, Inc.
ASTM - American Society for Testing and Materials
DI - de-ionized
DMA - Dynamic Mechanical Analysis
DoD - Department of Defense
DSC - Differential Scanning Calorimetry
FAA - Federal Aviation Administration
EDS - Energy Dispersive Spectroscopy
ESTCP - Environmental Security Technology Certification Program
FTIR - Fourier Transform Infrared Spectroscopy
IR - Infrared
MEK - methyl-ethyl ketone
PNNL - Pacific Northwest National Laboratory
SBIR - Small Business Innovation Research
SBS - Short Beam Shear
SE - Secondary Electron
SEM - Scanning Electron Microscopy
SERDP - Strategic Environmental Research and Development

Keywords

atmospheric plasma, Atmospheric Plasma Coating Removal, carbon fiber, composites, epoxy resin, coating removal, VOC reduction, media blasting, chemical stripping alternative, Fourier Transform Infrared Spectroscopy, FTIR, scanning electron microscopy, SEM, energy dispersive spectroscopy, EDS, C-Scan, optical microscopy, Short Beam Shear, SBS, Dynamic Mechanical Analysis, DMA, non-thermal plasma

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Abstract

Composite materials are increasingly utilized to build high performance structures used in aerospace and numerous Department of Defense (DoD) assets. Composites are usually covered in a variety of different coatings to provide protection from the elements or to impart other special properties such as radar absorption or reduced infrared (IR) signatures. When these assets require maintenance, selective removal of these coatings is required without imparting any damage or changes to the material properties of the composite. Atmospheric plasma coating removal offers a one-step process that can eliminate the need for hand sanding, traditional blast media, and toxic chemicals that are used for these maintenance activities today.

The atmospheric plasma coating removal (APCR) process uses atomic oxygen produced from compressed air to chemically etch organic coatings from substrates. In the case of many composites, an organic resin serves as the binding matrix of the composite structure. A potential concern when using atmospheric plasma coating removal on composite substrates is that the atomic oxygen or the moderate thermal energy from the plasma discharge may cause damage to this organic resin, and hence change the material properties of the composite. The goal of this project is to use APCR to selectively remove coatings over a typical graphite/epoxy composite, and study the plasma treated composite substrate material to determine what mechanical and chemical changes, if any, the plasma has imparted to the composite substrate.

Plasma coating removal was completed using Atmospheric Plasma Solutions' commercially available PB-7000 APCR system. A 3-axis robotic gantry was used to control the plasma treatment parameters. Composite samples prepared and coated by the Air Force Research Laboratory Coating Technology Team were tested in cooperation with Atmospheric Plasma Solutions, Inc., the Air Force Research Laboratory, and Pacific Northwest National Laboratory.

The suite of testing included scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS) imaging, Fourier transform infrared (FTIR) spectroscopy, 3D multi-scan optical microscopy, short beam shear (SBS) mechanical testing (ASTM D2344), C-scan ultrasonic inspection, pull-off adhesion testing (ASTM D4541), and differential scanning calorimetry (DSC) glass transition temperature determination (ASTM E1356).

This study found no evidence suggesting that the carbon fiber composite experiences any detrimental effects after the atmospheric plasma coating removal process. Additional mechanical testing is suggested to better characterize the outermost layers of the composite panels due to some limitations of the SBS analysis used in this study. Glass transition temperature measurements could also be further studied by using dynamic mechanical analysis (DMA) to achieve enhanced resolution of any transitions. Adhesion testing should also be studied further, as the pre-processing steps used in the coating re-application likely eliminated any potential benefits that the plasma treatment imparted to the surface after coating removal.

Lessons learned from this limited scope study will serve to inform future studies of the effects of APCR on composite substrates. Further studies should include other composite materials and the additional testing mentioned above. APCR shows great potential for composite materials, but further studies should be completed to ensure that optimal treatment parameters are used for each application.

Executive Summary

Introduction

Evaluation of benign coating removal processes has been of great interest to the Department of Defense. Current removal methods continue to have challenges with production rate, substrate damage, environmental impact and user safety. A previous SERDP effort, WP-1762, cited that Atmospheric Plasma Coating Removal (APCR) using a “non-thermal” plasma was an effective coating removal tool which had little effect on the uncoated steel substrates evaluated [1]. Through that SERDP effort, private and Small Business Innovation Research (SBIR) funded research, and various process improvements, the APCR process is now approved for widespread use on steel DoD assets. This limited-scope SERDP project has begun the process of understanding how APCR interacts with composite substrates and to formulate the tests required for broader approval on multiple composite systems.

APCR is a potential solution to many of the issues faced by maintenance personnel as it removes many of the hazardous conditions and chemicals involved with other coating removal methods. Non-thermal plasma processes have been traditionally used for their unique cleaning and surface activation properties that can increase the adhesion strength of new coatings or adhesives to a surface. Atmospheric Plasma Solutions, Inc. (APS) offers a commercially available APCR device, the PB-7000M seen in Figure 1, which was used throughout this study.



Figure 1: PB-7000M APCR system

High performance materials, such as carbon fiber composites, are of particular interest to the DoD due to their prevalence in mission critical assets. For example, the outer mold line of many aerospace structures is made of a graphite/epoxy composite material. These composites can be sensitive to thermal degradation and chemical damage to the matrix resin that holds the

composite structure together [2]. This Limited-Scope SERDP effort has analyzed the effect that atmospheric plasma coating removal has on these material properties critical to the functional integrity of these materials such as shear strength, resin chemistry, and surface morphology.

Objectives

The primary objective of this project was to characterize the composite substrates before and after plasma coating removal to determine their surface morphology, composition, and physical properties. Several uncoated composite samples served as controls in addition to samples that had their coating removed using a conventional method, hand sanding.

Additionally, APCR was performed on composites using a variety of operating parameters to determine the most efficient and effective parameters. Variations of standoff height, raster speed, and inter-pass spacing were evaluated for coating removal efficiency. These parameters are to serve as a baseline for future optimizations of APCR on composite substrates.

The last objective was to characterize the reapplication of coatings to the plasma treated surfaces. The primary mode of characterization was the measurement of adhesion strength. Any difference in adhesion strength compared to the control samples would warrant further study.

Technical Approach

The intention of APCR treatment is to only remove the organic coatings on the surface of the composite substrate, leaving the matrix material intact and conforming to its original material property specifications. The primer and topcoat application procedures followed standard manufacturers application instructions and the methods for testing the material properties were also performed according to standard testing requirements.

Graphite/epoxy material, IM7/977-3, was the composite selected for this limited scope project, coated in a typical coating stack for outer mold line of aircraft, one consisting of coatings conforming to MIL-PRF-23377 Type 1, Class N and MIL-PRF-85285 Type I, Class H. In addition, the coatings were applied in conformance with Technical Order 1-1-690 (General Advanced Composite Repair Process) and Technical Order 1-1-8 (Application and Removal of Organic Coatings, Aerospace, and Non-Aerospace Equipment).

Plasma processing parameters were selected by performing a small study in which standoff distance, raster speed, inter-pass spacing, and power level of the plasma system were varied. Conditions selected were optimized around the consistency of the finish, and amount of remaining primer. Three optimized plasma processing conditions, a sanded control, and an unpainted control, were analyzed to determine if any damage had occurred while removing the coating. Sanding and plasma processing conditions were completed such that a thin layer, less than 0.2 mils, of primer remained to limit the potential damage to the composite.

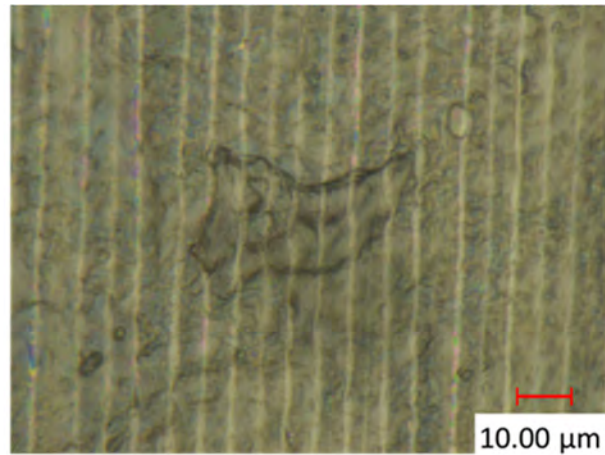
Optical micrographs were taken to image the surface at high magnification and to produce 3D scans of the surface topology. Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) maps were taken to determine the amount of coating remaining. Fourier-transform infrared spectroscopy (FTIR) spectra of the plasma stripped and sanded control specimen surfaces were collected to search for chemical changes to the resin caused by

heat or other mechanisms. C-scan ultrasonic inspection was conducted to search for voids or anomalies in the composite, and short beam shear (SBS) testing was conducted on the specimens to test their mechanical strength. Finally, the glass transition temperature was measured through digital scanning calorimetry (DSC) to detect changes, if any, to the resin crosslinking.

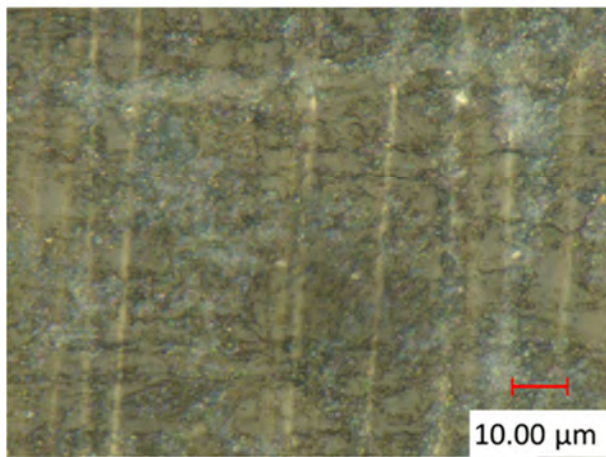
Several of the samples that had their coating removed also underwent a recoating procedure, following the same coating application specifications as the initial coating. The recoated samples then underwent the same tests as the de-coated specimens, with the addition of a pull-off adhesion test to determine the effect, if any, these coating removal methods had on the adhesion of future coatings.

Results and Discussion

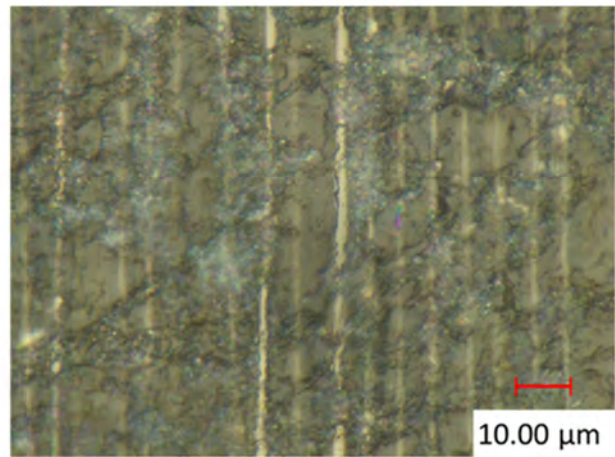
While optimizing plasma parameters, it was found that the standoff height parameter provides the largest contribution to remove coatings effectively and selectively. The plasma plume generated from the PB-7000's pen-style applicator has an effective standoff distance up to approximately 1.5" from the substrate. The composite substrate's topcoat and most of the primer were found to be effectively removed with a standoff height of 0.7" to 0.85" above the substrate. Inter-pass spacing was also adjusted from 0.04" to 0.08" to vary overlap of plasma exposure. Optical microscopy examination of the composite surface (Figure 2B and 2C) determined that no observable damage was done to the fibers, but some changes to the epoxy resin cap could be seen for both the sanded only samples and the plasma treated sample with a supplemental sanding. These changes are likely to have been caused by the preparation for the imaging where a supplemental sanding step was used to carefully remove the remaining primer and expose the bare resin cap and underlying composite.



A) Bare-Control, 3000x Optical Zoom



B) Plasma 2, 3000x Optical Zoom



C) Sanded, 3000x Optical Zoom

Figure 2: 3000x optical microscopy images / A: of bare specimen showing initial condition of fibers and resin matrix, / B: sample 13 (Plasma Condition 2, conditions given in Table 1) showing vertical lines of underlying fibers, / C: Sample 5 (Sanded) showing bright vertical lines of exposed fibers

Using a digital confocal microscope, 3D maps were taken of the surface topology, showing no difference in average peak-to-valley distance between the bare control and plasma processed panels. This would indicate the surfaces were approximately the same roughness. Again, this similar roughness could be due to the required removal of the last bit of primer via careful hand sanding. It is worth noting that the sanding control sample showed a much larger peak-to-valley distance than the other specimens.

SEM/EDS scans of the surfaces indicate that all coating removal methods left a thin layer of primer, as intended. The primer used on the composite panels contains a characteristic element that is unique to the primer, praseodymium, and was used as a marker to determine the presence of remaining primer. Praseodymium was detected in all the samples that were not recoated. The thickness of the topcoat in the recoated samples prevents the primer layer from being seen in EDS spectra.

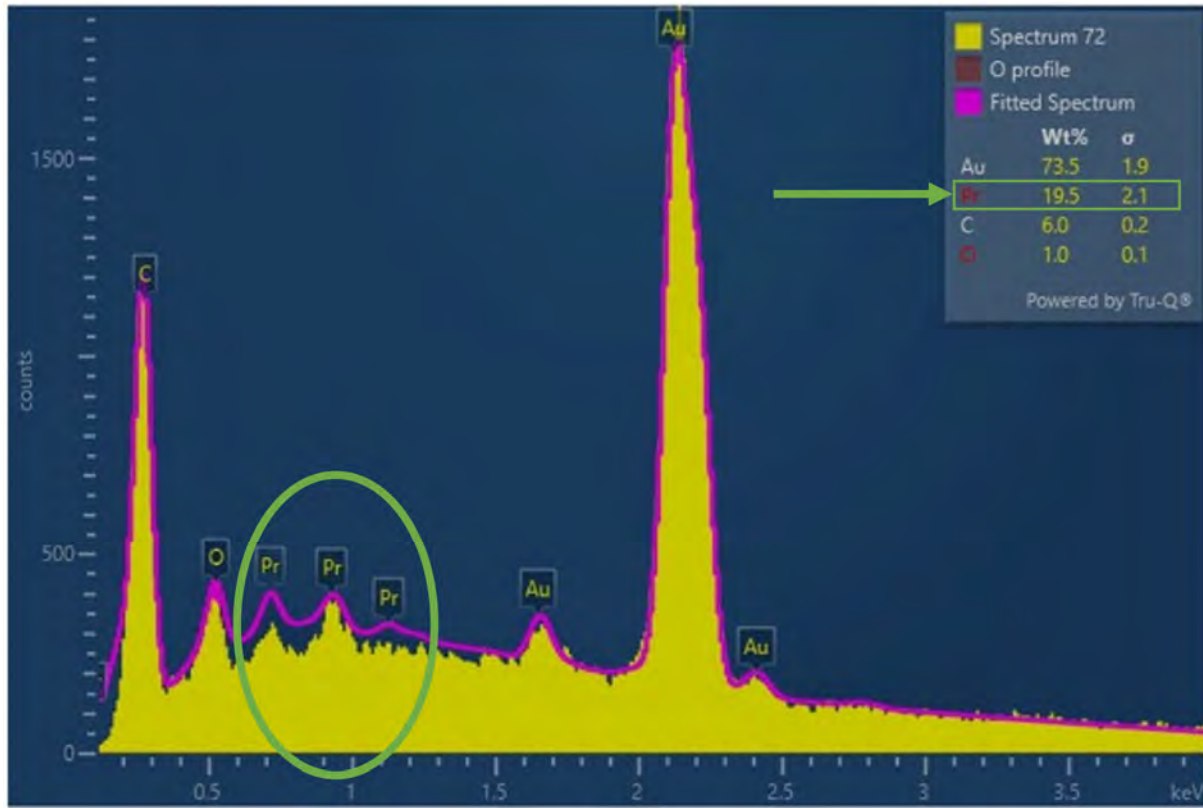


Figure 3: EDS Spectrum of a location on Sample 5, showing peaks of Pr, Praseodymium. Samples were sputter coated with gold to prevent charging which added a dominant gold (Au) peak to the spectra. The Au peaks should be disregarded.

FTIR spectra showed small increases in percent absorption in the wavenumber bands that indicate oxidation. However, the sanded specimen also showed peaks on these wavenumbers. This indicates residual coating or the procedure of removing the last layer of coating via sanding in the case of the plasma treated samples, created a nearly identical specimen that does not show any sign of being plasma treated. In all cases, the sanded and plasma treated specimens did not show FTIR peak changes that would be indicative of thermal damage to epoxy matrix of the composite in the range of 1600 cm^{-1} to 1750 cm^{-1} [3].

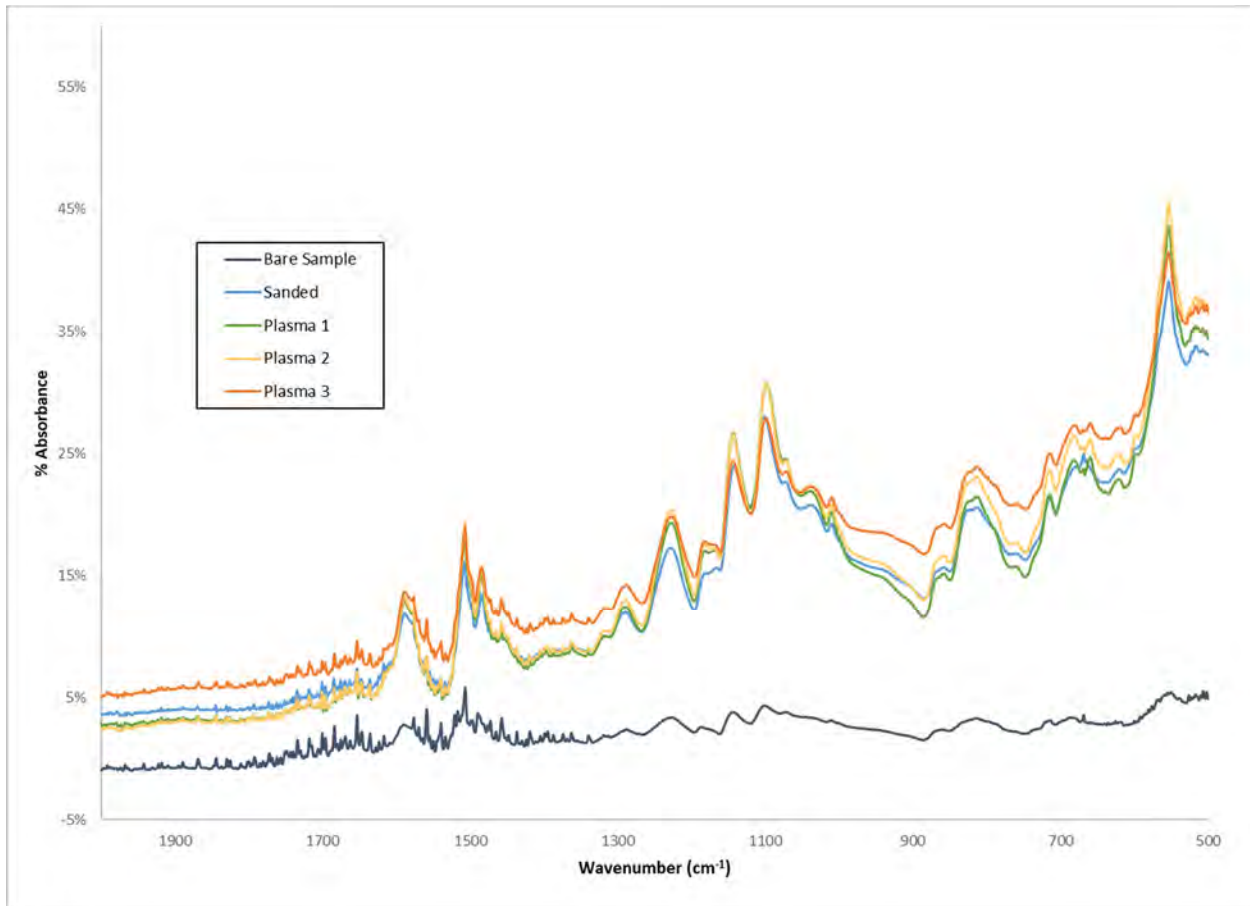


Figure 4: Average FTIR Spectra of all specimens, sample 005 being Sanded, sample 009 is condition Plasma 1, sample 013 is condition Plasma 2, sample 017 is condition Plasma 3

C-scan ultrasonic imaging showed little difference in the condition of the graphite/epoxy substrate. The test searched for voids in the bulk of the substrate that could have been caused by coating removal method [4-5]. Due to the surface-focused nature of these coating removal methods, no evidence was found that there was damage caused by either the plasma or legacy method of sanding.

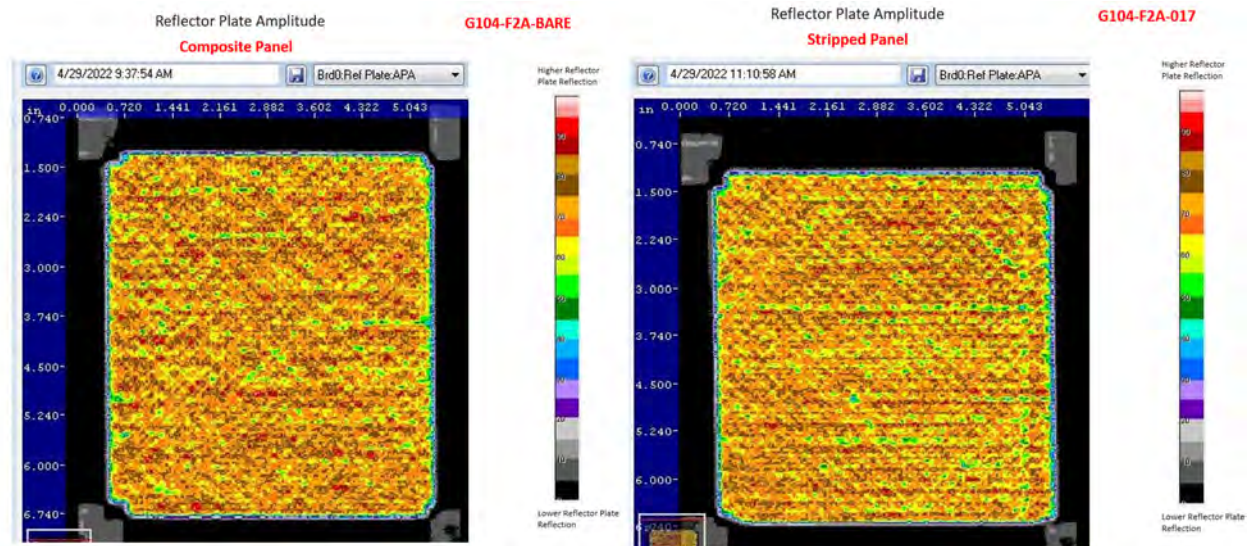


Figure 5: C-Scan image from Bare control sample (left) and Sample 17, treated with plasma condition 3 (right), showing no difference between the plasma treated samples and the untreated control samples

SBS testing conducted on the plasma samples indicated there was no difference in the measured strength of the composite when compared to the sanded and uncoated control. This destructive test also showed that the failure modes were consistent from sample to sample. Future study of the strength of these composites would be better served using thinner samples, or a modified 4-point bend or flexural test [6]. Modified testing may offer a better understanding of what effect plasma may have on the top plies only, if any.

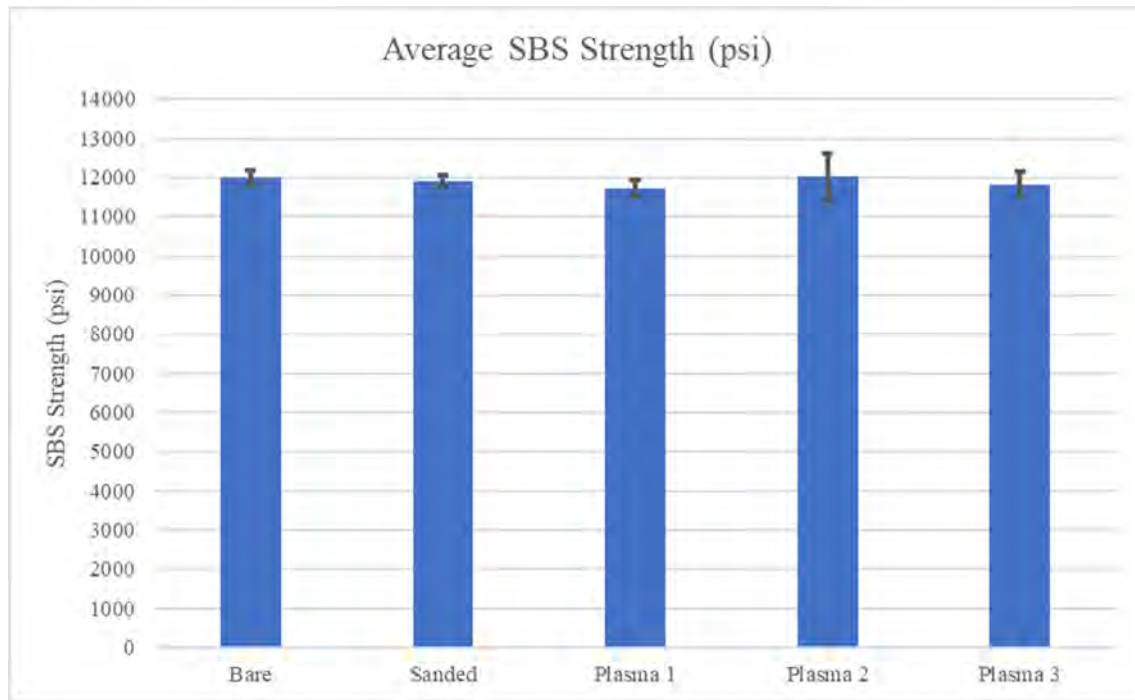


Figure 6: Summary graph of SBS strength testing; Plasma A corresponds to Plasma 1, Plasma B corresponds to Plasma 2, and Plasma C corresponds to Plasma 3

Glass transition temperature was determined using DSC. The transition temperatures were difficult to detect, suggesting DMA would be the preferred test to analyze the properties of the cured epoxy in this composite [7]. Thinner specimens would also be beneficial in pinpointing the location of any differences in the glass transition temperature. Detected glass transition temperatures were consistent from control to all treatment conditions, plasma removal and traditional sanding, which would indicate that no damage could be seen from either method.

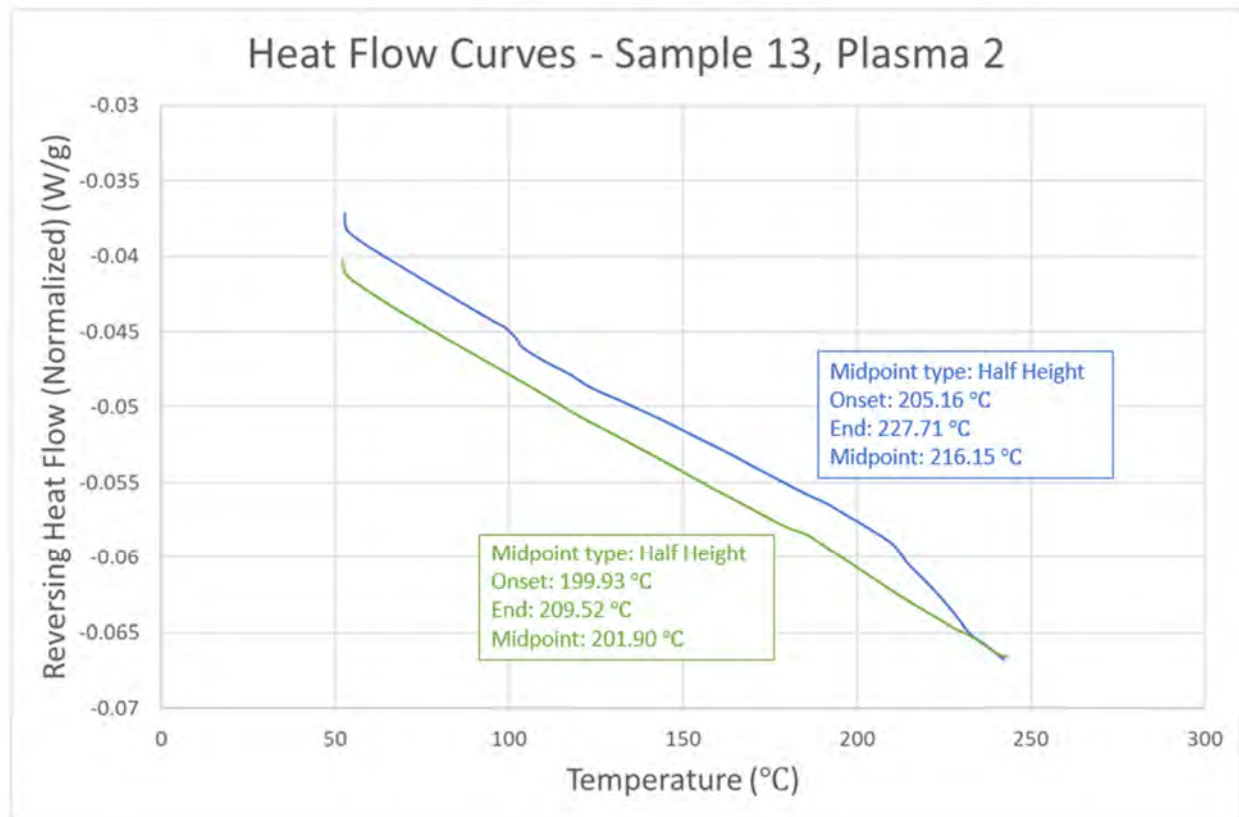


Figure 7: Heat flow curve from DSC testing on Sample 13. T_g (in °C) onset is 205, end is 227, and midpoint is 216.

Implications for Future Research and Benefits

Results from this study indicate that the benefits offered by APCR may be achieved without causing damage to the bulk of the substrate. Several of the tests performed should be re-evaluated, and alternative methods may need to be explored to evaluate the top plies of the composite material. Additional studies should be performed to determine if retained coatings like the primer in this study are truly compromised, or if plasma can be safely used to etch down to bare composite. The methods and treatment parameters found in this study serve as a baseline for testing moving forward. Determining the effect on other composites will be the focus of future efforts to ensure that optimal efficiency is achieved without affecting the integrity of the substrates.

End of Executive Summary

Objective

This project seeks to evaluate the effects of atmospheric plasma coating removal technology (APCR) on the material properties of carbon fiber composite substrates. The selected tests in this study examine the mechanical and chemical properties of carbon fiber composites before and after atmospheric plasma coating removal. Emphasis was placed on detecting potential damage mechanisms. Selective removal of topcoat and some amount of primer from a typical coating stack was achieved using a robotically controlled atmospheric plasma coating removal device.

Secondary to removing coatings and maintaining substrate integrity, surface activation of the substrate was also studied by evaluating the adhesion of a new layer of coating, applied after the initial coating was removed. This process was intended to simulate a typical maintenance cycle where a section of carbon fiber is de-painted for inspection in the event of coating failure, and the de-painted section is recoated to return to service.

The data produced from this study will form the baseline for future study of atmospheric plasma coating removal and other atmospheric plasma surface treatments on other composite substrates. The knowledge gained from completing these tests will function as a reference for future studies and inform a safe starting point for developing plasma processing parameters for future studies on composite substrates. The potential benefits of APCR have broad implications to improve equipment maintenance, lower costs and reduce impacts to the environment and the health of maintenance personnel.

Background

Composite materials throughout the DoD and commercial industries are often coated with durable organic coatings, engineered to protect the composites from some of the harshest environments. The durability of these coatings introduces significant challenges during the maintenance, repair, and overhaul cycles of these composites [8]. Current methods to remove these coatings involve toxic chemicals, large amounts of blasting media and require large amounts of labor or energy. The mixture of these issues, along with the fact that many of these durable coatings have toxic additives, creates a large risk for the environment and to human health [9]. Some of this risk can be mitigated through costly waste disposal, but other volatile components cannot be collected leaving risk for exposure to personnel, the civilian population, and the environment. Reducing the use of these hazardous chemicals and blast media has the primary effect of reducing the environmental and human health hazards, with other solutions also offering the potential to save on energy as well.

One approach to removing coatings is to utilize the fourth and most abundant state of matter in the universe, plasma. Plasma is electrically ionized, and consequently, possesses unique chemical and physical properties. One of these unique properties, especially when using plasma comprised of air, is the ability to etch organic materials such as paint or other coatings. This effort focused on only using a single-step APCR process to selectively etch one or more coating layers as well as increase surface energy and improve wettability to improve future coating adhesion. The APCR process uses a non-thermal plasma that minimizes the possibility of thermal damage to the substrate. Everyday examples of non-thermal plasmas that are more

familiar include neon signs that convert the neon gas to neon plasma or fluorescent light bulbs which use argon gas to make a plasma. While not necessarily cold to human touch, these non-thermal plasmas are cool relative to thermal plasmas. Thermal plasmas are perhaps more familiar and include arc welders, plasma cutters, and atmospheric lightning. Thermal plasma temperatures typically exceed 10,000 °C whereas non-thermal plasmas are generally on the order of a few hundred degrees °C.

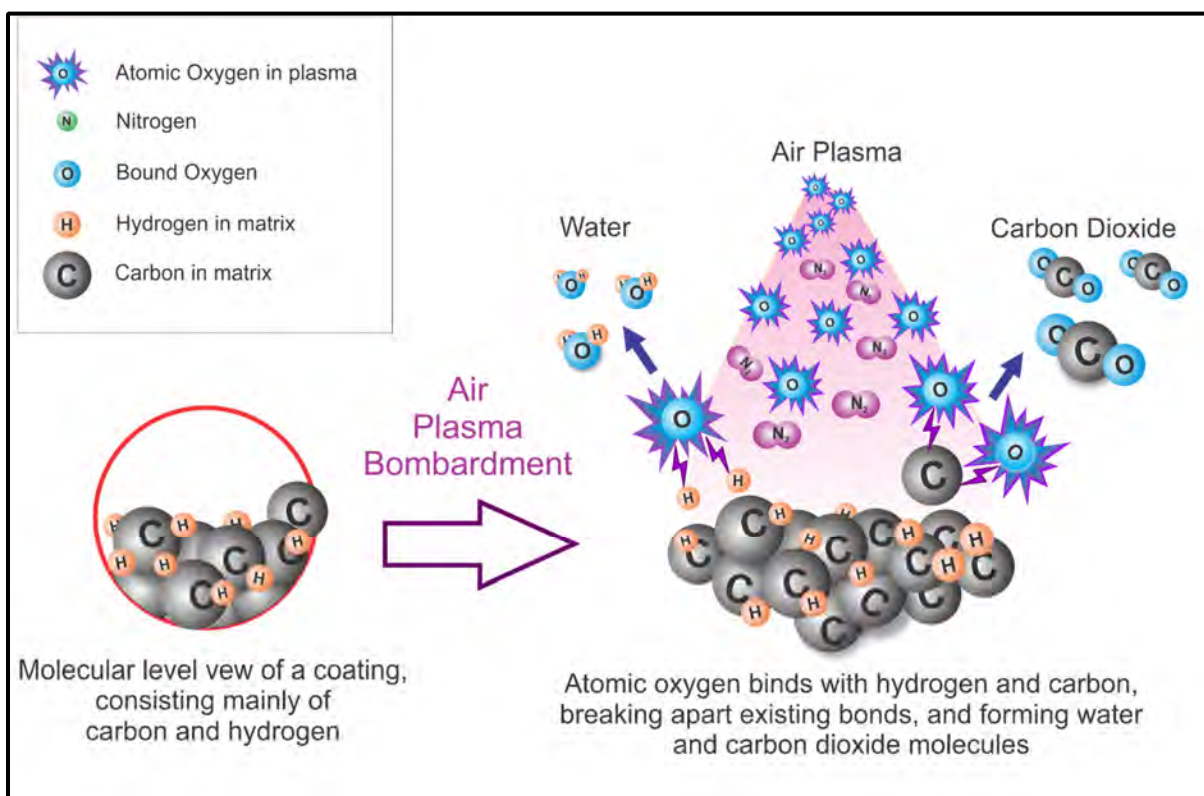


Figure 8: Diagram of plasma etching/cleaning process

The byproducts of APCR are generally benign and can easily be captured regardless of composition. In the case of air plasma (Figure 8) the plasma consists of atoms and molecules of nitrogen and oxygen, ions, electrons, free radicals, and metastables. The atoms and ions in the plasma can then react with the coating to form compounds that have high vapor pressures, such as carbon dioxide and water vapor, which escape as gases. The most economical and plentiful gas mixture available to utilize for an atmospheric plasma discharge is air. The diatomic oxygen (O₂) in the air is disassociated in the plasma to atomic oxygen (O) which has greatly enhanced chemical reactivity towards organic molecules and coatings. The atomic oxygen readily bonds with the carbon and hydrogen in the coating to form carbon dioxide and water vapor. The remaining inorganic portion of the coating, such as pigments or fillers are released as a dry dust. The atomic oxygen in concert with the radicals and metastables in the plasma removes the coating through an oxidation/etching process like that used in the semiconductor industry to etch photoresist. A major difference from the vacuum plasma used in the semiconductor industry is

the plasma is formed at atmospheric pressure and has a much higher density of active species when compared to vacuum plasmas which results in a faster etching of the organic coatings.

Materials and Methods

The carbon fiber composite substrates utilized in this research were supplied by the Air Force Research Laboratory (AFRL) and were fabricated by Lockheed-Martin to use as test specimens for the F-35 composite structure. All coatings were applied in an environmentally controlled paint booth by the AFRL Coating Technology Team. Virgin samples that did not undergo any of the coating process were set aside for controls.

The composite test specimens were IM7/977-3 graphite/epoxy composite panels. They were cross-ply continuous fiber composites designed for stiffness and strength. Panels were composed of 8 plies in a satin fiber weave with fibers oriented in 0° and 90° directions. The stacking sequence was cross-ply asymmetric [0/90]₄. The panel dimensions were 5"x 6"x 0.172" with an approximate ply thickness of 0.022".

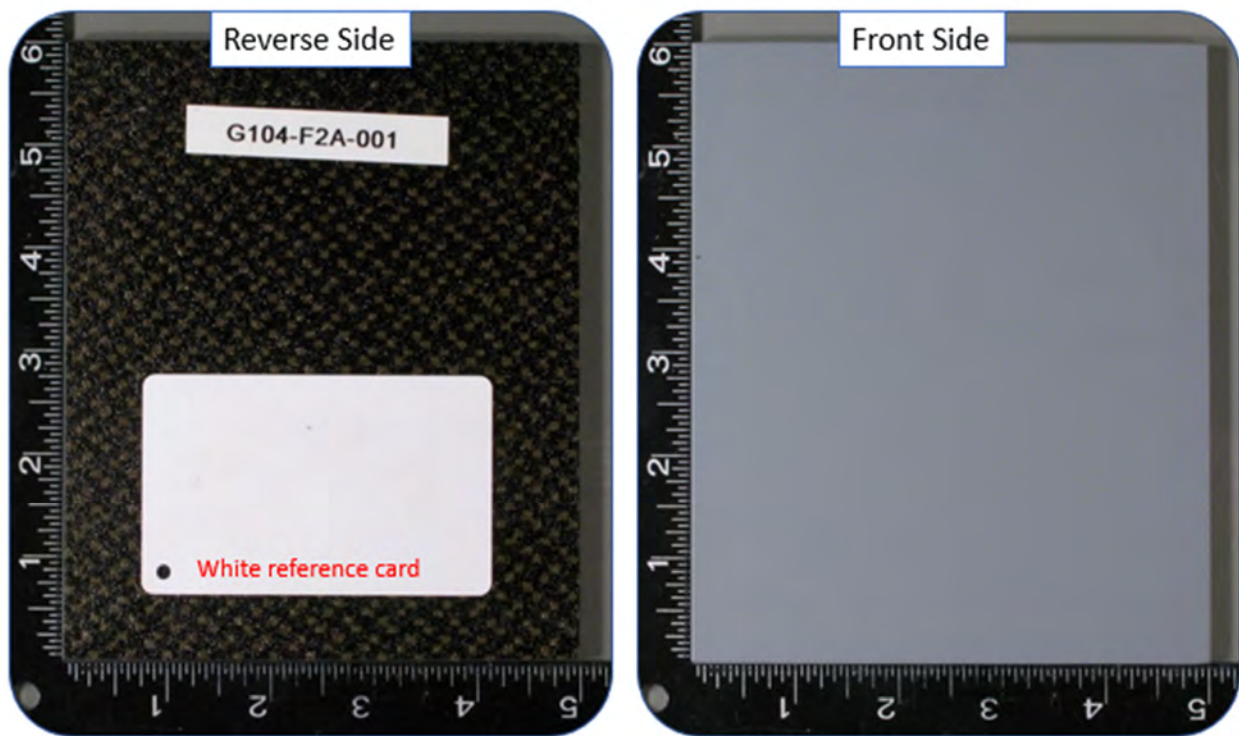


Figure 9: Exposed backside showing bare composite with sample label and white-balance reference card (left) and coated sample, frontside, that was subject to the coating removal methods (right)

All substrates were pretreated with Pantheon PreKote prior to primer application. Panels were wiped clean with a methyl ethyl ketone (MEK) solvent wipe, and then PreKote was applied liberally to the surface. Using a maroon Scotch-Brite pad (3M 7447), the entire surface was scrubbed side to side and edge to edge generating a rich lather. Once again, PreKote was applied liberally to the surface. The entire surface was scrubbed side to side and edge to edge at 90

degrees from the original direction. The entire surface was rinsed with warm tap water followed by DI water, then placed in racks to dry at ambient conditions overnight.

After the PreKote treatment, samples were then coated with 0.6-0.9 mils PPG 02GN084 conforming to MIL-PRF-23377 Type 1, Class N primer and 1.7-2.3 mils PPG 99GY001 conforming to MIL-PRF-85285 Type I, Class H topcoat. This preparation was performed by the same technician under controlled environmental conditions at 77°F and 50% humidity. Each coat was allowed to cure for the manufacturer's specified time, 5 hours for the primer and 14 days for the topcoat.

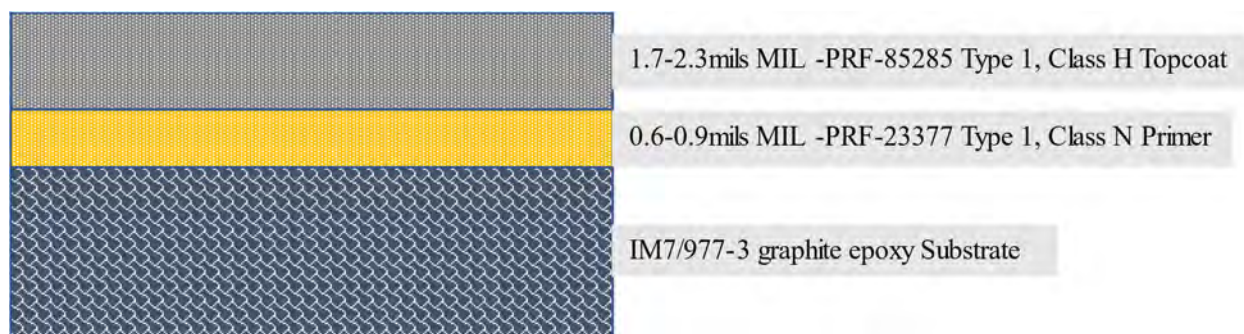


Figure 10: Coating thickness and substrate diagram

Two controls that did not undergo any coating removal and four coating removal conditions were tested; three different sets of plasma removal conditions were selected and one set of the incumbent method of sanding was chosen. APS performed all coating removal procedures.

Plasma coating removal parameters were determined through a small study based on adjustments to the system power supply and movement parameters of the plasma end-effector. Variables of system power setting, standoff distance, inter-pass spacing, and raster speed were assessed for general removal efficacy and surface finish. Power setting adjustments proved to have the least impact on removal efficacy of the variables tested, so power was kept constant at 2000 W for all plasma treated samples. Raster speed was also set to a single value of 400 inch/minute in order to reduce variables in this limited scope study. The combination of power setting and raster speed is thought to have limited heat transfer through the primer layer and into substrate, but further investigation may need to be done in order to verify the extent to which this is valid. These assessments were done to the naked eye by experienced technicians, and the best results were examined under microscopy up to 20x. The best 3 conditions were selected for further study.



Figure 11: Plasma coating removal being performed on smaller cutout piece for parameter DoE (left) and hand sanding being performed (right)

Composite panels were exposed to three different plasma conditions using a 3-axis robotic gantry in a XY raster pattern. The plasma conditions were varied by changing standoff and inter-pass spacing of the robot's path as shown in Table 1. Sanding was performed by hand using 80, 120, and 200 grit sandpaper with careful attention paid to not etch into the resin-cap or fibers of the composite, thus leaving a thin layer (0.1-0.2 mils) of primer on the surface. Plasma parameters were also selected such that a very thin layer, approximately 0.2 mils, of primer was retained. All specimens were cleaned of loose dust with a water-based alkaline cleaner and lint-free wipe, then the plasma treated samples were given a light plasma post treatment intended to re-activate the surface without removing any coating. Path parameters for the plasma coating removal as well as the plasma post treatment are provided in Table 1.

Table 1: Coating removal conditions

Performed by:	APS	APS	APS	AFRL
Condition	Removal Conditions	Post Removal Clean	Pre-Shipping Plasma Activation	Pre-coating Treatment
Sanded	P80, P120, and P200 grit aluminum oxide sandpaper	Water-based alkaline cleaner and lint-free wipe to remove loose dust	None	MEK Wipe, Pantheon PreKote Scrub
Plasma 1	APCR at 400 inch/min, 0.75" standoff, 0.08" inter-pass spacing	Water-based alkaline cleaner and lint-free wipe to remove loose dust	APCR at 700 inch/min, 1.30" standoff, 0.50" inter-pass spacing	MEK Wipe, Pantheon PreKote Scrub
Plasma 2	APCR at 400 inch/min, 0.85" standoff, 0.04" inter-pass spacing	Water-based alkaline cleaner and lint-free wipe to remove loose dust	APCR at 700 inch/min, 1.30" standoff, 0.50" inter-pass spacing	MEK Wipe, Pantheon PreKote Scrub
Plasma 3	APCR at 400 inch/min, 0.80" standoff, 0.04" inter-pass spacing	Water-based alkaline cleaner and lint-free wipe to remove loose dust	APCR at 700 inch/min, 1.30" standoff, 0.50" inter-pass spacing	MEK Wipe, Pantheon PreKote Scrub

After all required samples were de-coated at the APS facility, the de-coated samples were shipped to AFRL for recoating. Recoating followed an identical procedure to the initial coating. Once re-coated, samples required for each test were distributed to each lab to conduct testing procedures on the control uncoated samples, de-coated samples, and re-coated samples.

Pacific Northwest National Laboratory (PNNL) performed SEM/EDS analysis on 1 cm² coupons cut from the larger specimens. The testing was only conducted on the de-coated and re-coated samples to search for remaining coating constituents. Prior to SEM and EDS analysis, the samples were sputter coated with ~10 nm of gold to prevent charging from the electron beam. Note that the EDS elemental maps show a large gold (Au) peak as a result of the gold coating and should be disregarded.

AFRL took photomicrographs and generated 3D profiles using a VHX Digital Multi Scan Keyence microscope. The uncoated, de-coated, and re-coated specimens were examined for any changes to the surface structure.



Figure 12: Keyence VHX Digital Multi Scan Microscope used to take photomicrographs and generate 3D surface profiles.

Prior to imaging, the de-coated samples were subject to careful, light sanding with 400 grit sandpaper to remove the majority of the remaining primer. Only partial sanding was done to maintain the integrity of at least half the panel, although great care was taken to remove the primer without damaging the underlying composite substrate. This is displayed in Figure 13. The panels were wiped clean following sanding. Three locations were selected for optical microscopy on each panel as shown in Figure 13.

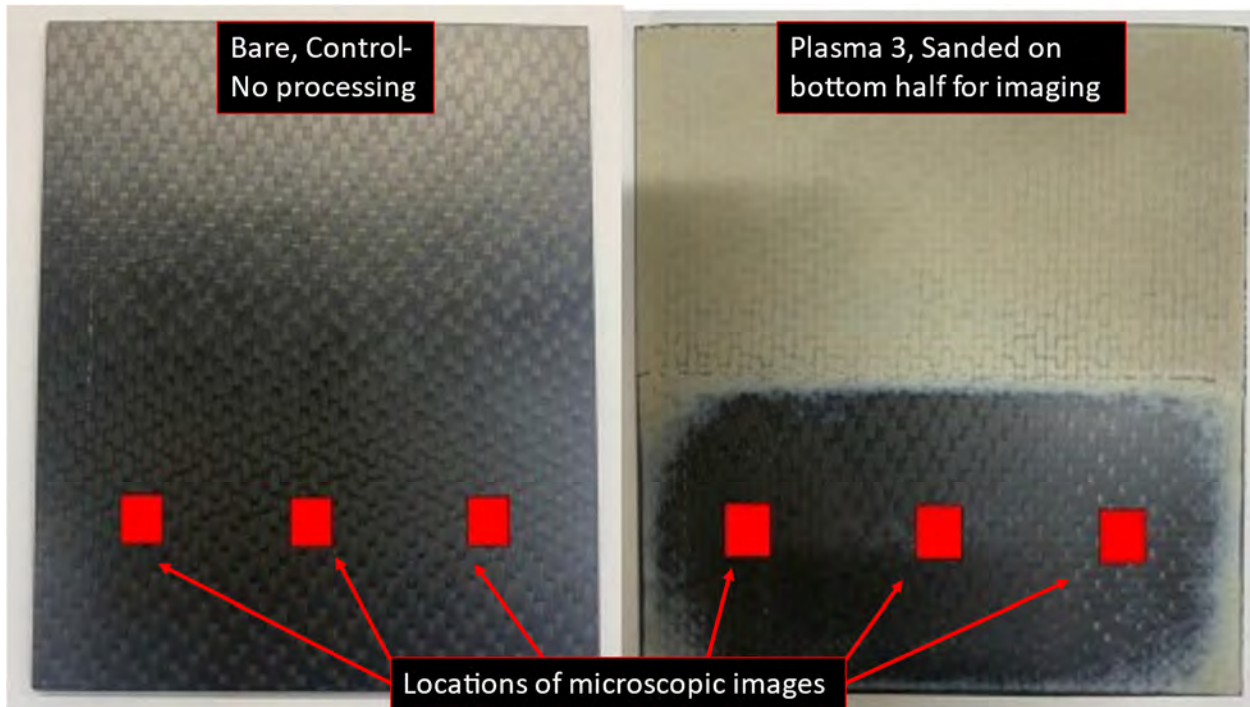


Figure 13: Bare specimen (left) and specimen 17 (right) with labeled locations of micrographs.

3D surface profiles of the untreated composite, sanded specimen and plasma treated specimens were taken with the same microscope used to take the photomicrographs. Four profiles were generated for each specimen to determine if the surface roughness had changed due to treatment.

Fourier Transform Infrared (FTIR) Spectroscopy was performed on specimens stripped with atmospheric plasma. This evaluation was completed to determine if heat transfer from the plasma caused any thermal degradation of the composite matrix was caused by the APCR process by identifying changes in the FTIR spectra indicative of oxidation.

Table 2: Condition of each specimen measured with FTIR

Condition	Specimens
None	Bare
Sanded	G104-F2A-005
Plasma 1	G104-F2A-009
Plasma 2	G104-F2A-013
Plasma 3	G104-F2A-017

A bare, untreated specimen was also examined for comparison. Table 2 identifies the specimens that were used in this evaluation. Spectra were generated using a ThermoFisher Scientific Nicolet iS5 FTIR Spectrometer pictured in Figure 14. Samples were treated in the same manner

as the samples used in microscopy, undergoing careful sanding and wiping to remove the remaining primer. Retained primer was not the focus of this test, so it was removed in all cases, sanded and plasma treated.



Figure 14: ThermoFisher Scientific Nicolet iS5 FTIR Spectrometer

AFRL also performed ultrasonic C-Scans. Reflector plate ultrasound was performed on bare and treated specimens in an immersion tank with a 5 MHz transducer set to a gain of 6 dB, a voltage of 330 V, and a 3.0" water path. This scan maps a volumetric space in two dimensions using ultrasonic pulses to rapidly identify flaws, voids, and composite ply disbonding. This method is typically used to detect manufacturing defects and can also detect impact damage.

Short Beam Shear (SBS) mechanical testing was also performed by AFRL on the sanded, bare, and plasma treated specimens. This destructive test examines the strength of composites by applying pressure in a three-point bend setup that minimizes flexural (tension and compressive) stresses and maximizes the induced shear stresses at the center of the specimen. Failure modes for this test can be seen in Figure 15 and include interlaminar shear, flexure (compression and tension), and inelastic deformation.

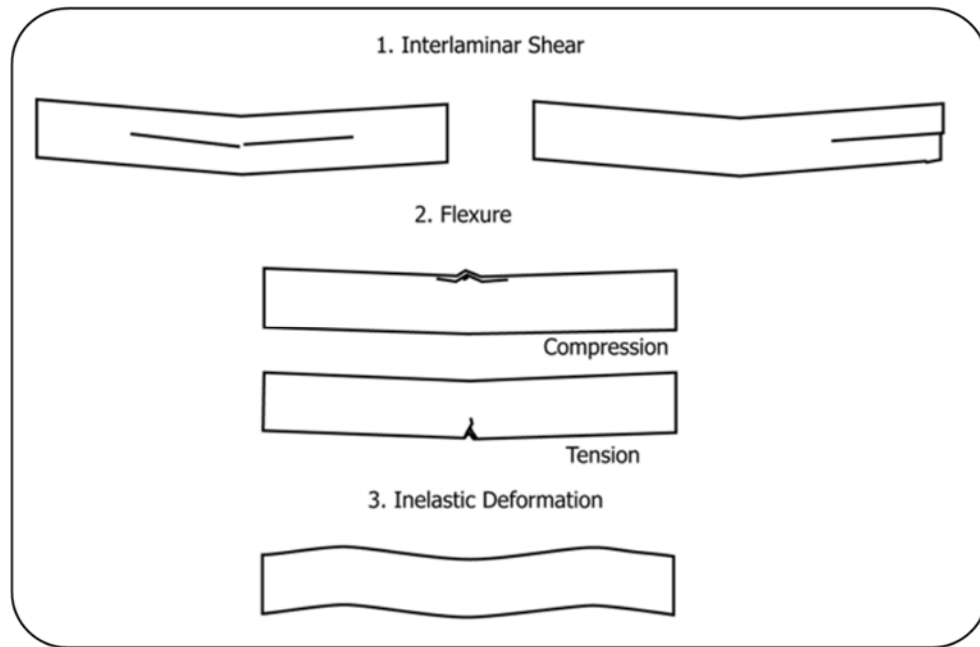


Figure 15: Failure modes for Short Beam Shear (SBS) testing

Specimen preparation and testing was done in accordance with ASTM D2344-13 [10]. Specimens were cut oversize with diamond coated, water-cooled saw, then machined to final dimensions of $1.030'' \pm 0.010'' \times 0.343'' \pm 0.003''$ with a diamond coated router bit on a Tensilkut precision milling machine. The testing was performed on a Instron test frame with 5000 lbf force transducer and three-point bend fixture. The span length-to-thickness ratio was 4.0, so, with specimen thickness between $0.170''$ and $0.173''$, the span length was $0.686'' \pm 0.010''$. Figure 16 shows the diagram for this test setup.

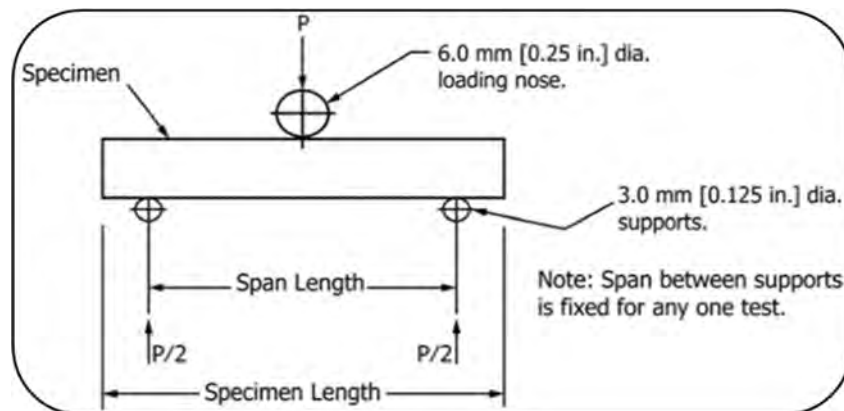


Figure 16: Diagram of the short beam shear testing setup

Differential Scanning Calorimetry (DSC) was conducted by AFRL on bare, sanded, and plasma treated samples to determine if the glass transition temperature had changed after being de-coated. The glass transition temperature is used to thermally characterize resin systems and indicate the point at which a marked difference in material properties can be seen. A modulated heating cycle was performed using a TA Discovery 2500 DSC. The temperature range was from 122 °F (50 °C) to 482°F (250 °C) with a ramp rate of 5 °F/min (3 °C/min), an amplitude of 33 °F (0.64 °C), and a period of 40.0 seconds. Samples were cut from panels using a wet wafer saw, and the bottom plies sanded to fit into Tzero Aluminum Pin Hole Hermetic Pans. Sample masses ranged from 15 to 30 mg. Table 3 shows the detailed heating profile used.

Table 3: DSC heating profile

<i>Test Name</i>	<i>Modulated Heat Cool Heat</i>
<i>Initial Temperature Stabilization</i>	Equilibrate 50.00 °C
	Modulate Temperature 0.64 °C for 40.0 s
	Isothermal 5.0 min
<i>Ramp 1</i>	Ramp 3.00 °C/min to 250.00 °C
<i>Cool Down</i>	Ramp 10.00 °C/min to 50.00 °C
<i>Ramp 2</i>	Ramp 3.00 °C/min to 250.00 °C

The characterization of the recoating adhesion strength was determined at APS by dolly pull testing performed in accordance with ASTM D4541, Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers [11]. Dolly pull testing is used to characterize the adhesive and cohesive strengths of adhesives or coatings. Analysis of the results can be used to pinpoint weak points in multi-coating systems. A Defelsko Positest AT-A was used with 20 mm dollies and Loctite E-120HP as the dolly adhesive. Pull parameters for the 20 mm dollies were 30 psi/sec, 3500 psi maximum tensile pressure, and 30 second hold at the maximum pressure.



Figure 17: Defelsko Positest AT-A used for pull-off strength adhesion testing

Results and Discussion

Multi-Scan Optical Microscopy

Photomicrographs were recorded at 50x, 500x, and 3000x magnification. Tooling marks are visible on the bare specimen which are obscured on the painted panels by residual primer. Residual primer is seen as light gray and is visible on most micrographs of prior painted specimens.

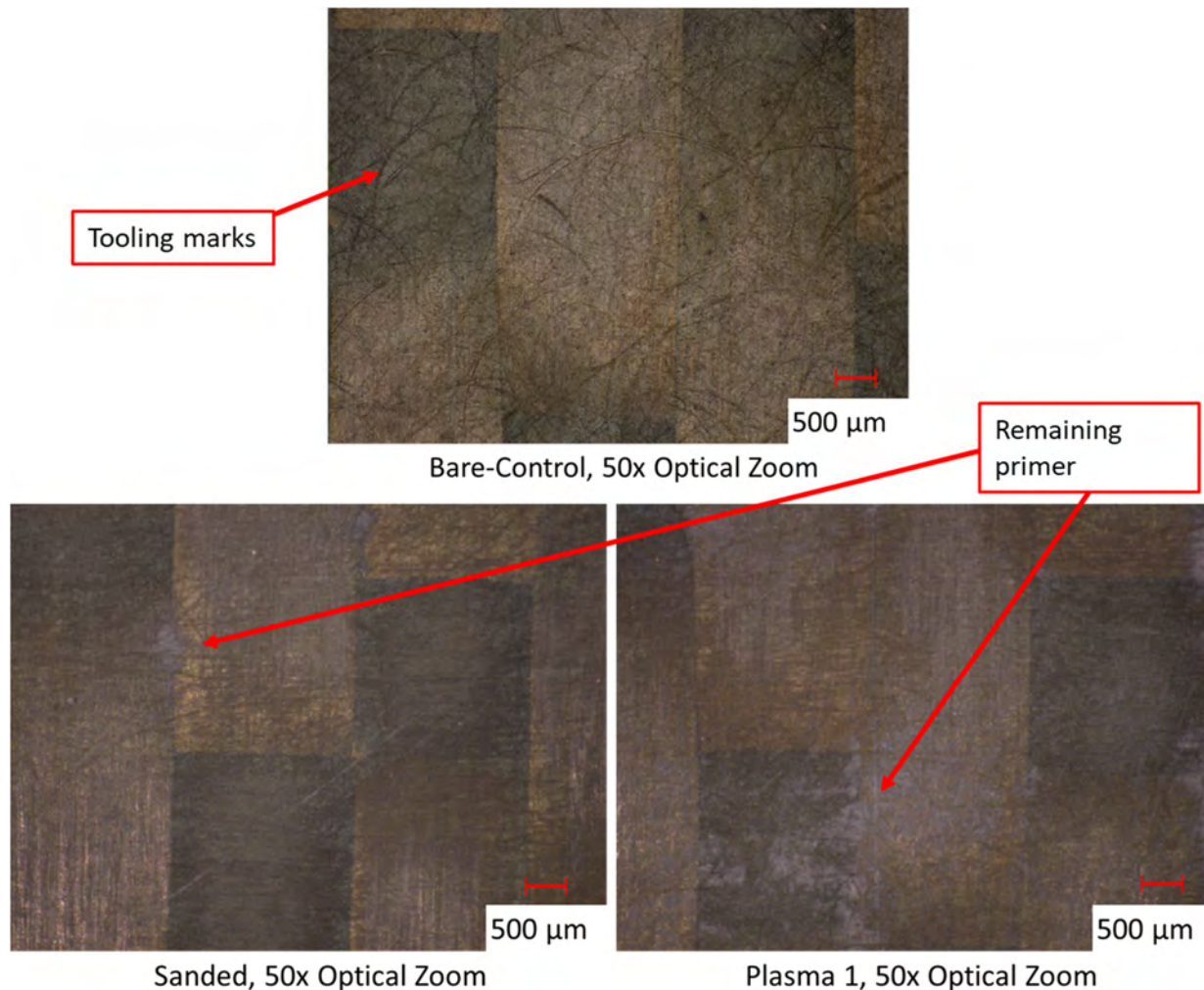
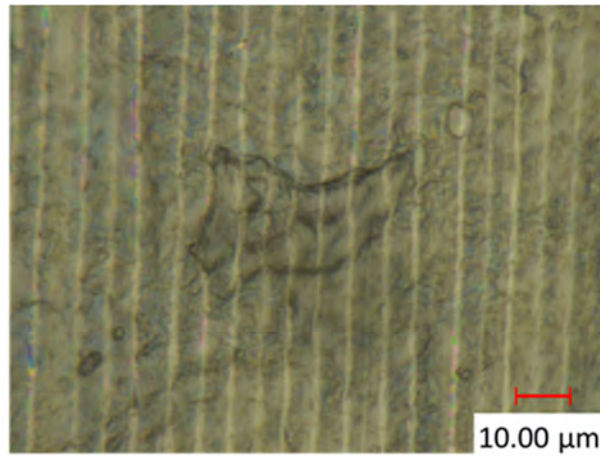


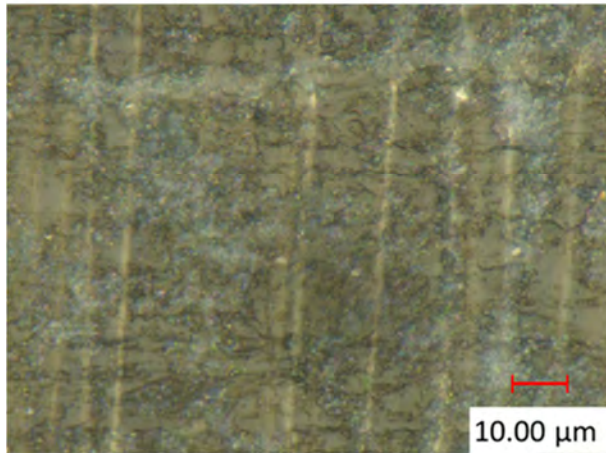
Figure 18: Bare sample surface with visible tooling marks (top), sanded sample with small patches of primer (bottom left), and plasma treated sample with small patches of primer (bottom right)

At 3000x magnification, there is a distinct visual difference between fiber rich regions and matrix rich regions of the composite. When comparing the fiber rich regions, there seems to be exposed fibers on all samples that were sanded regardless of plasma treatment which can be seen as bright lines within the resin in Figure 19. These exposed fibers do not appear to be damaged, but microscopic images indicate possible minor damage to the resin matrix surrounding the

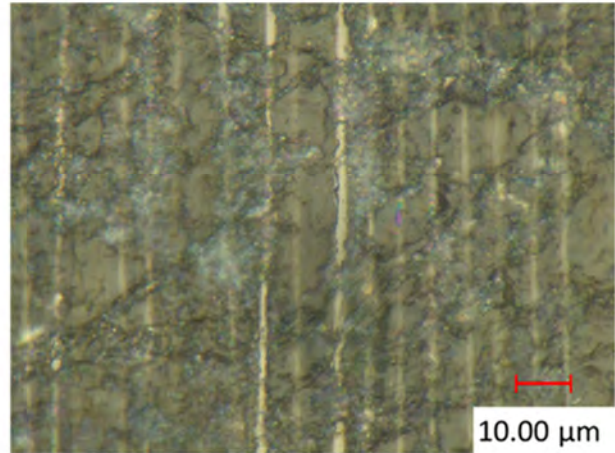
fibers. It appears that whenever a sample was sanded in either the plasma treated or sanded only case the sanding process removed the primer and caused some damage of the resin cap below.



A) Bare-Control, 3000x Optical Zoom



B) Plasma 2, 3000x Optical Zoom



C) Sanded, 3000x Optical Zoom

Figure 19: 3000x optical microscopy images of bare specimen showing initial condition of fibers and resin matrix (top), sample 13 (Sanded Plasma Condition 2, and Sample 5 (Sanded)

The average maximum difference between peak and valley as seen in the 3D surface scans has been recorded in Table 4. These profiles should not be considered for quantitative calculation of the surface roughness due to the small sample size. Measurements taken may only represent a small portion of the entire treated area, but still offer insight into roughness imparted when using these coating removal methods. Figure 20 shows a visualization of a 3D surface profile taken at 3000x.

Table 4: Surface profile measured by average max peak valley difference for specimens with treatments corresponding to descriptions in Table 1.

Specimen	Treatment	Average Max Peak-Valley Difference (micron)
Bare	No treatment; control	9.58
5	Sanded	14.57
9	Plasma 1	8.48
13	Plasma 2	6.19
17	Plasma 3	8.90

The sanded specimen and the Plasma 2 treated specimen show significantly varying results of peak-valley height difference while Plasma 1 and Plasma 3 treated specimens remain close to the bare sample. Realistically, this could be due to the small sample size or profile locations chosen as opposed to the surface treatment. Additionally, voids in the composite may already be present prior to coating removal which could produce some variation in the surface topology.

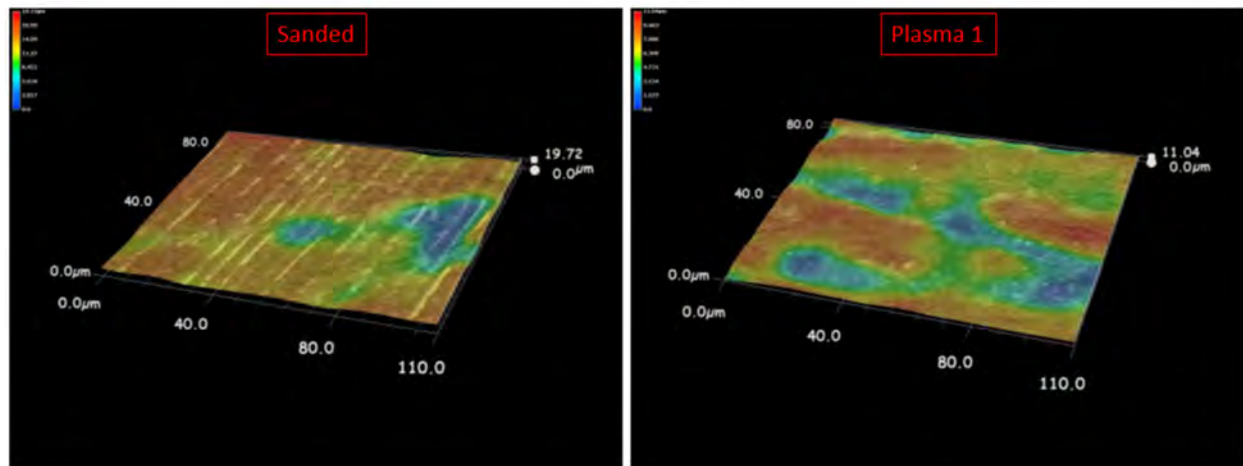


Figure 20: 3D surface profile visualization of one section of a Sanded specimen (left), and one section of a Plasma 1 specimen (right).

Fourier Transform Infrared Spectroscopy (FTIR)

Application of heat to a composite surface may lead to epoxy resin matrix degradation. Due to etching mechanisms employed by the atmospheric plasma system, it is necessary to evaluate the possible resin damage caused potential chemical reactions such as oxidation or thermal decomposition. The primary issue with resin oxidation is the associated decrease in composite strength. Thermal damage through oxidation is commonly detected in the following IR bands: carbonyl, carboxylic acid, aliphatic hydrocarbons, and esters. The carbonyl region best shows the total oxidation process, and the slow growing slope leading to the peak corresponds to the formation of organic acids. The complex progression of the epoxy resin oxidation reaction is partially indicated by a general increase in oxygen content and decrease in hydrocarbons due to water formation [12]. Due to the general increase in oxygen content, peaks were also examined that were in wavenumber bands that included oxygen. The IR bands relevant to this analysis are summarized in Table 5.

Table 5: IR bands of relevant species affected by oxidation reactions.

Species	Wavenumber (1/cm)
carboxylic acid	3300-2500
aliphatic hydrocarbons	2900
carbonyl	2000-1600
esters	1310-1050

A background spectrum (Figure 21) was generated to create a reference signal for the other spectra. FTIR uses a single beam without reference, so a background spectrum is used to remove water vapor and carbon dioxide peaks from the measured atmosphere.

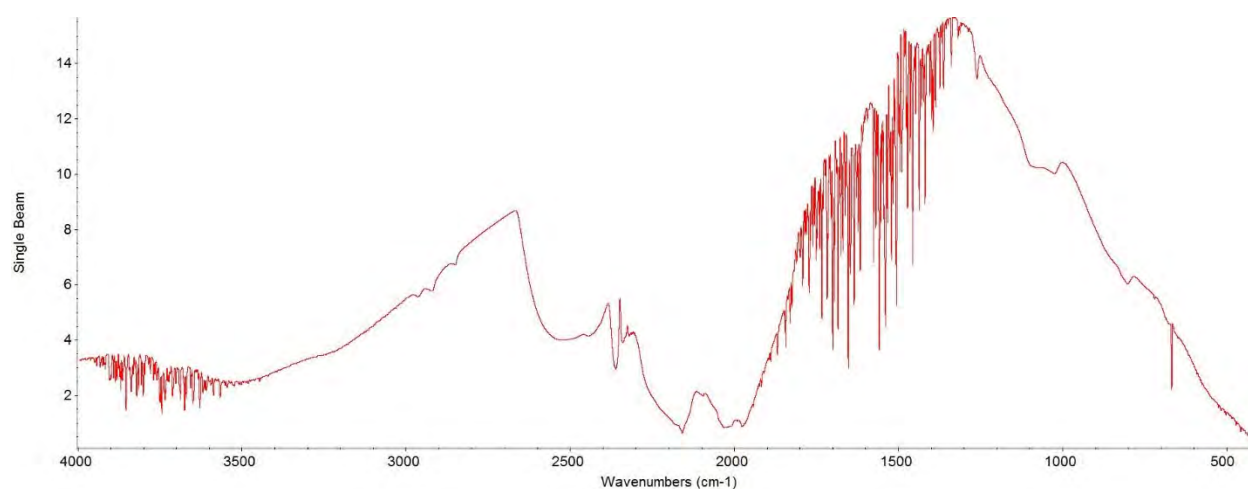


Figure 21: FTIR Absorbance Background Spectrum

Figure 22 plots the average spectrum from each examined panel for a comparative analysis. Because of the significant difference in absorbance peaks between the bare specimen and the specimen only exposed to sanding, it can be concluded that residual coating or the comparatively dull finish achieved through sanding dramatically affects the collected spectra. Due to this, comparisons will primarily be drawn between the exclusively sanded specimen and the plasma treated specimens as all four of these panels were originally painted.

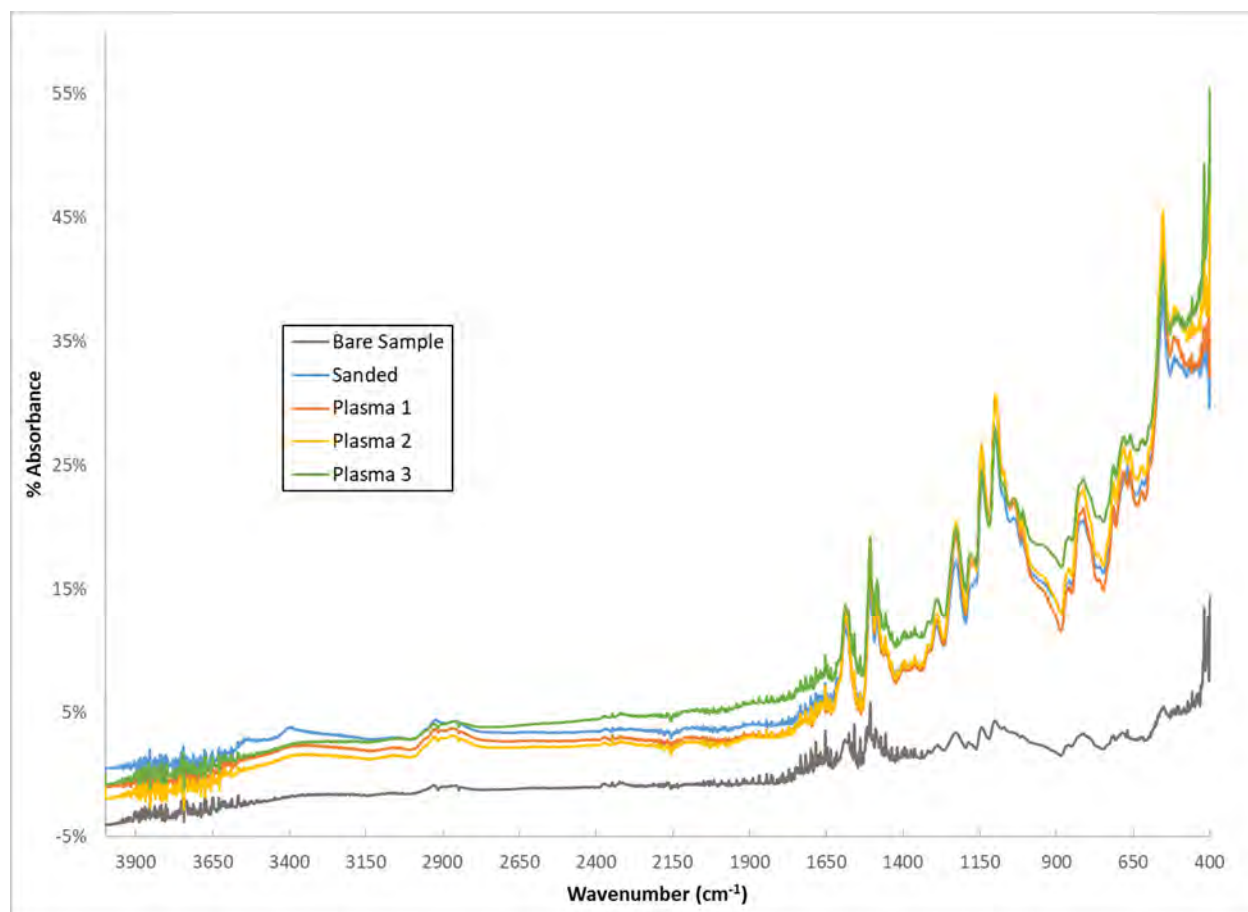


Figure 22: Combined Average FTIR Spectra of all the analyzed specimens

The carboxylic acid ($3300\text{--}2500\text{ cm}^{-1}$) and aliphatic hydrocarbon (2900 cm^{-1}) bands show minimal increase in absorbance with an increase in plasma treatment intensity although the trend is present. The gradual increase in absorbance in the carbonyl band ($2000\text{--}1600\text{ cm}^{-1}$) of sanded, Plasma 1, and Plasma 2 specimens follow closely ($\pm 5\%$) with the sanded until the peak. Plasma 3 has an increased slope in the gradual absorbance change region of the carbonyl band which may be indicative of an increased rate of organic acid formation. The maximum change of absorbance at the peak of the carbonyl band is approximately 2% between the sanded specimen and the plasma treated specimens. The ester band peaks ($1310\text{--}1050\text{ cm}^{-1}$) show a absorbance change of 3% between the sanded and plasma treated panels. Plasma 3 had the largest percent absorbance change for every peak within the carbonyl and ester IR band.

A similar study analyzing damage in aircraft composites was completed by the FAA [3]. In their study, they focused analysis on the carbonyl region, from $2000\text{--}1600\text{ cm}^{-1}$, specifically a peak around 1600 cm^{-1} . On heat-damaged specimens, they saw the sharper carbonyl peak at 1600 cm^{-1} shift to a broad peak centered on 1750 cm^{-1} . Compared to the present study, the plasma treated and sanded samples show a peak at approximately 1590 cm^{-1} , but no significant peaks appear from 1600 cm^{-1} to 2000 cm^{-1} . The findings of the FAA study, which was done on a similar carbon fiber/epoxy composite, would suggest that the plasma treated and sanded samples of this study saw no damage to the chemical integrity of the epoxy.

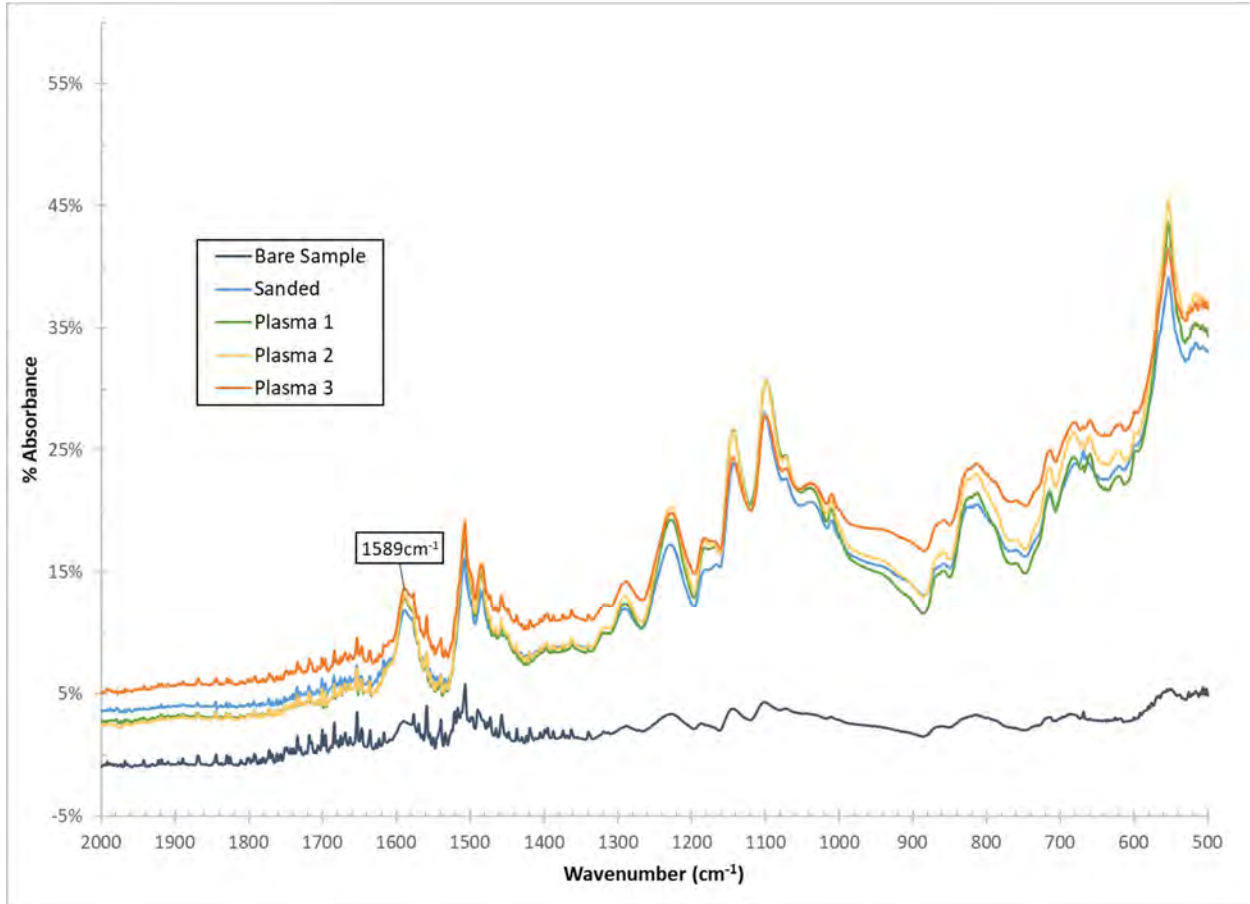


Figure 23: Lower wavenumber ($<2000\text{ cm}^{-1}$) section of Average FTIR Spectra for all Sample Conditions showing closer look at peaks of interest in carbonyl range of 1600 cm^{-1} to 2000 cm^{-1}

The difference in absorbance seen between the sanded specimens and plasma specimens are minute. It is probable that the required process of sanding the remaining coating from the plasma treated samples to take spectra of the substrate left what is essentially the same surface as the sanded only specimens.

Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM/EDS)

In some cases, it may be required that some primer is left behind for maintenance activities or inspections. In the case of this study, a thin primer layer, 0.1-0.2 mils thick, was left behind in an attempt to minimize damage to the resin cap of the composite. Sanding control samples were similarly removed down to primer to evaluate differences in techniques.

SEM and EDS maps show that while most of the coating was removed, the primer remained in a thin layer on the surface. A characteristic chemical element specific to the primer used in this effort is praseodymium, which is used to inhibit corrosion. Table 6 shows that all samples showed levels of praseodymium that were not recoated. This confirms that at least a portion of the primer layer remained intact for either sanding or plasma removal methods.

Table 6: Percentages of elements found in EDS spectra for each sample scanned

Sample ID	Sample 4	Sample 5	Sample 8	Sample 9	Sample 12	Sample 13	Sample 16	Sample 17
Removal Method	Sanded	Sanded	Plasma 1	Plasma 1	Plasma 2	Plasma 2	Plasma 3	Plasma 3
Recoating Status	Recoated		Recoated		Recoated		Recoated	
C	57.3%	84.6%	57.4%	31.3%	56.6%	45.4%	57.4%	37.0%
O	19.8%	10.0%	18.9%	33.9%	19.1%	26.9%	21.9%	28.0%
Si	6.8%	0.0%	8.1%	25.0%	7.9%	6.3%	10.0%	14.6%
N	6.3%	0.0%	6.8%	0.0%	6.6%	0.0%	0.0%	0.0%
Cl	4.7%	0.0%	4.7%	0.9%	4.6%	1.1%	5.5%	0.8%
F	3.6%	0.0%	3.4%	0.9%	3.3%	0.4%	3.5%	0.0%
Na	1.0%	0.0%	0.0%	0.0%	1.3%	0.3%	0.8%	0.4%
Al	0.5%	0.0%	0.7%	0.9%	0.7%	1.6%	0.9%	1.2%
Pr	0.0%	5.4%	0.0%	3.1%	0.0%	18.0%	0.0%	13.8%
Ca	0.0%	0.0%	0.0%	4.0%	0.0%	0.0%	0.0%	4.1%

EDS maps shown in Figure 24 and their associated spectra show evidence of praseodymium in both the samples that were sanded and samples that were plasma treated, which indicates some amount of primer remained. In contrast, the recoated and bare specimens show no praseodymium as the topcoat and bare composite have no praseodymium in their formulations.

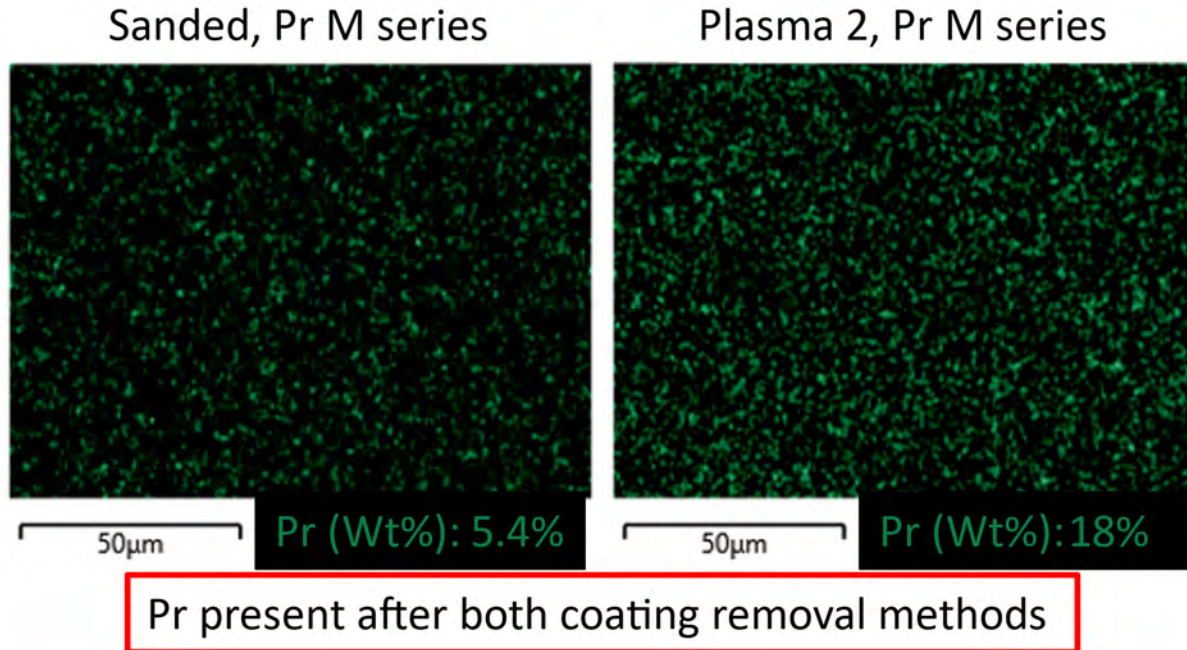


Figure 24: Praseodymium EDS maps for Sanded Sample 5 (Left) and Plasma 2 treated sample (Right), green coloring represents localized presence of Pr on the sample surface

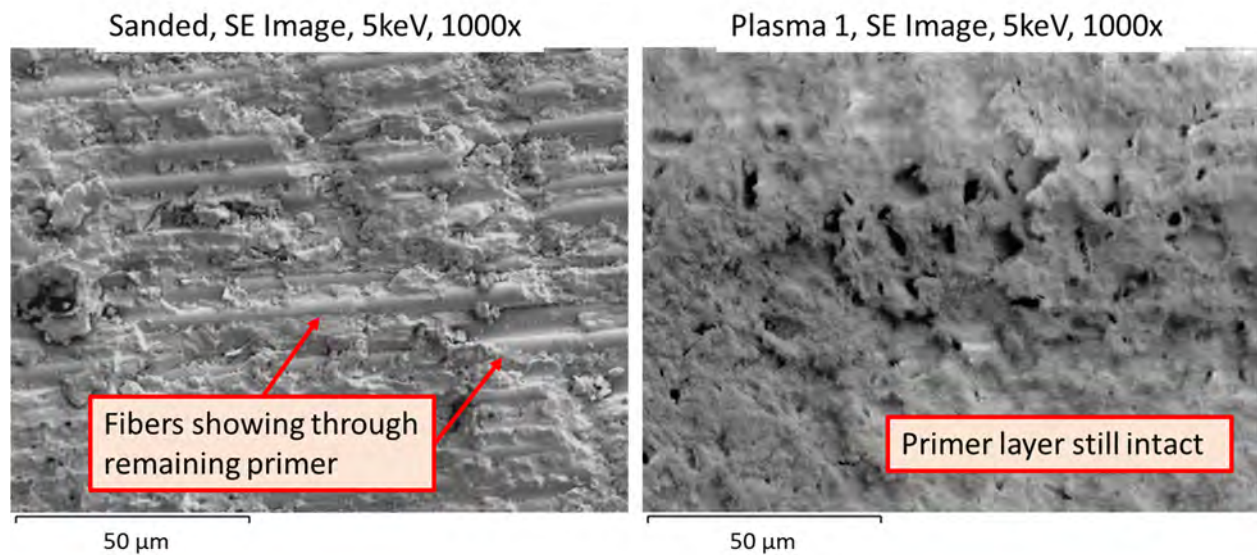


Figure 25, where the Secondary Electron (SE) image of the sanded specimen appears to show smooth, cylindrical fibers poking through the jagged remaining primer, while the plasma treated specimen shows no fibers, only the jagged remaining primer.

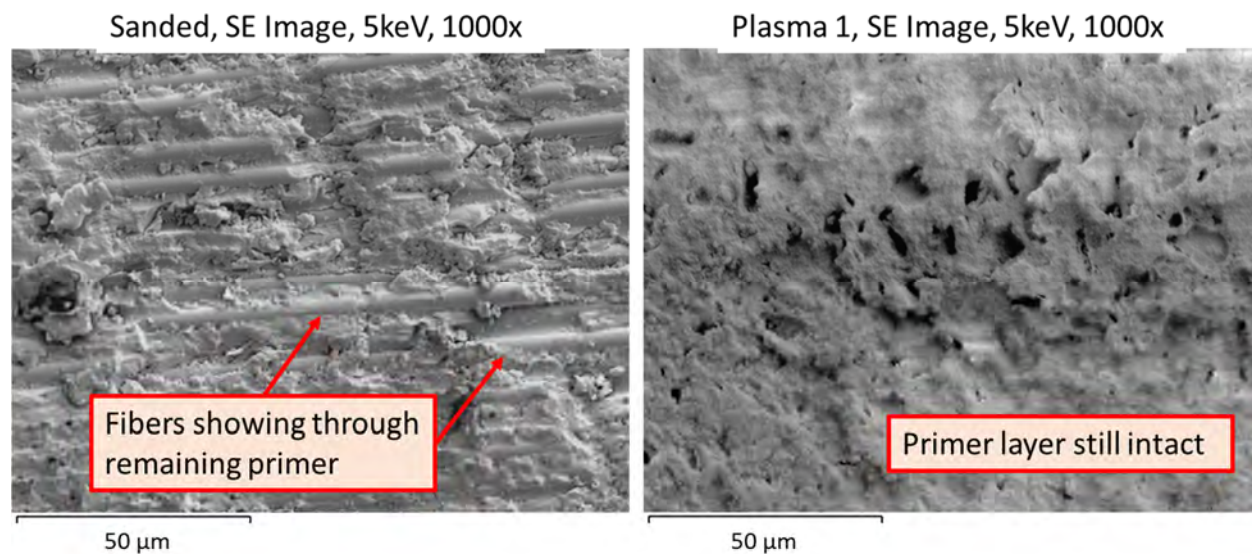


Figure 25: SE Image of Sanded sample (left) and Plasma 1 treated sample (right)

Ultrasonic C-Scan Inspection

Flaws at different depths and of varying shape are easily detected with C-scans. Abnormalities in the reflections seen in the output of these scans are evident when the pattern displayed shows inconsistencies. Ultrasonic waves that are sent through the sample that encounter voids are not reflected as strongly and show up as purple or blue areas in these images.

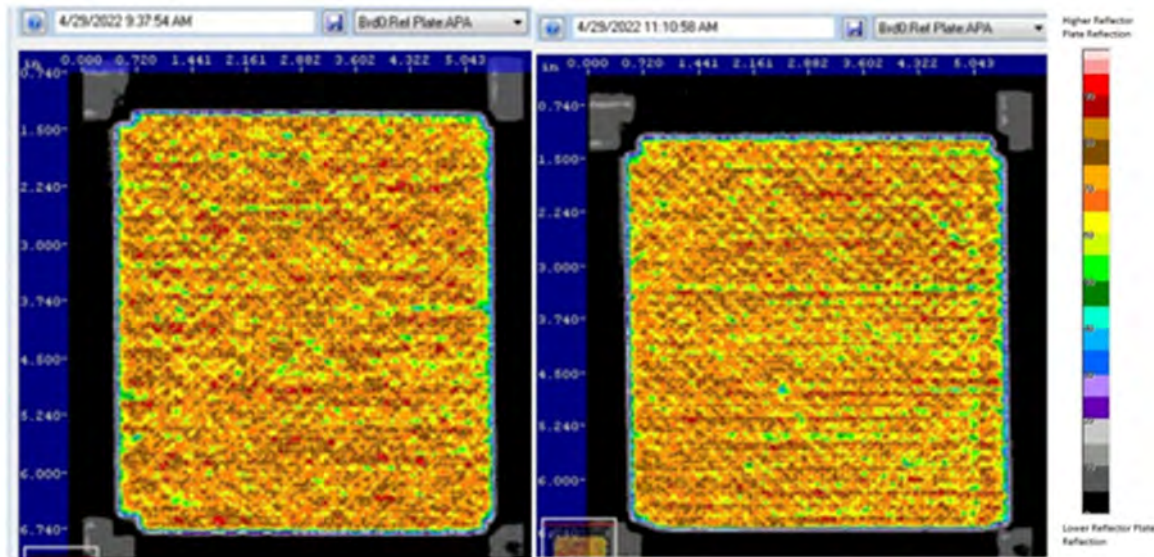


Figure 26: C-scan output of bare sample (left) and plasma-treated sample 17 (right)

Figure 26 shows the output of the ultrasonic C-Scan for the bare control specimen and one of the plasma-treated specimens, 17. The scans from the plasma treated samples showed slightly higher reflector plate reflections, but do not indicate there was any delamination of the panels.

A couple of the samples did indicate voids in the scans, but AFRL confirmed it was due to residue from the labeling or were on samples that were never coated, plasma treated, or sanded, and would indicate a manufacturing defect. Figure 27 shows what a void looks like, but for this case it was just label residue.

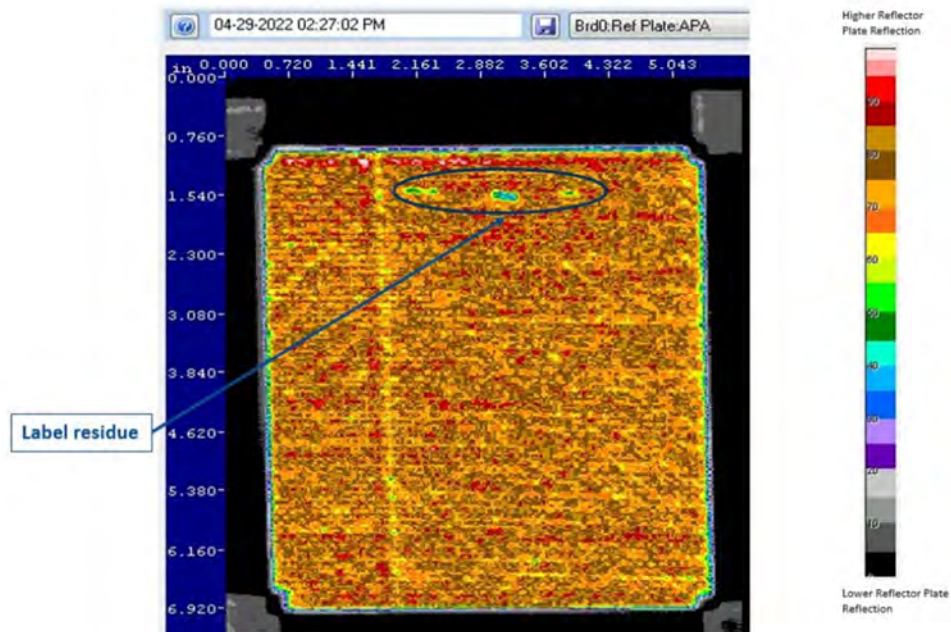


Figure 27: C-Scan of Sample 14 indicating a possible void but was actually due to label residue

Short Beam Shear (SBS)/ASTM D2344

All specimens that underwent SBS testing showed similar performance (see Table 7), indicating there is no difference in the bulk physical properties of these specimens. Average SBS strength remained within or near to being within standard deviations of each other.

Table 7: Short Beam Shear testing results and their failure modes

Coating Removal Technique	Avg SBS Strength (Psi)	Std. Dev	Failure Mode
Bare	11988	189	Interlaminar Shear
Sanded	11913	148	Interlaminar Shear & Flexure Compression
Plasma 1	11731	194	Interlaminar Shear & Flexure Compression/Tension
Plasma 2	12026	598	Interlaminar Shear
Plasma 3	11821	343	Interlaminar Shear & Flexure Compression

All samples showed interlaminar shear as the dominant failure mode. *Figure 28* shows 3 samples with the largest number of failure points for each sample type. Some of the sanded and plasma treated samples had flexure compression failures in the top plies, but the compression failures were always seen in conjunction with interlaminar shear failures. An alternative test focussing on the top plies, by using a thinner composite may give a better understanding of the effect of using these coating removal methods.

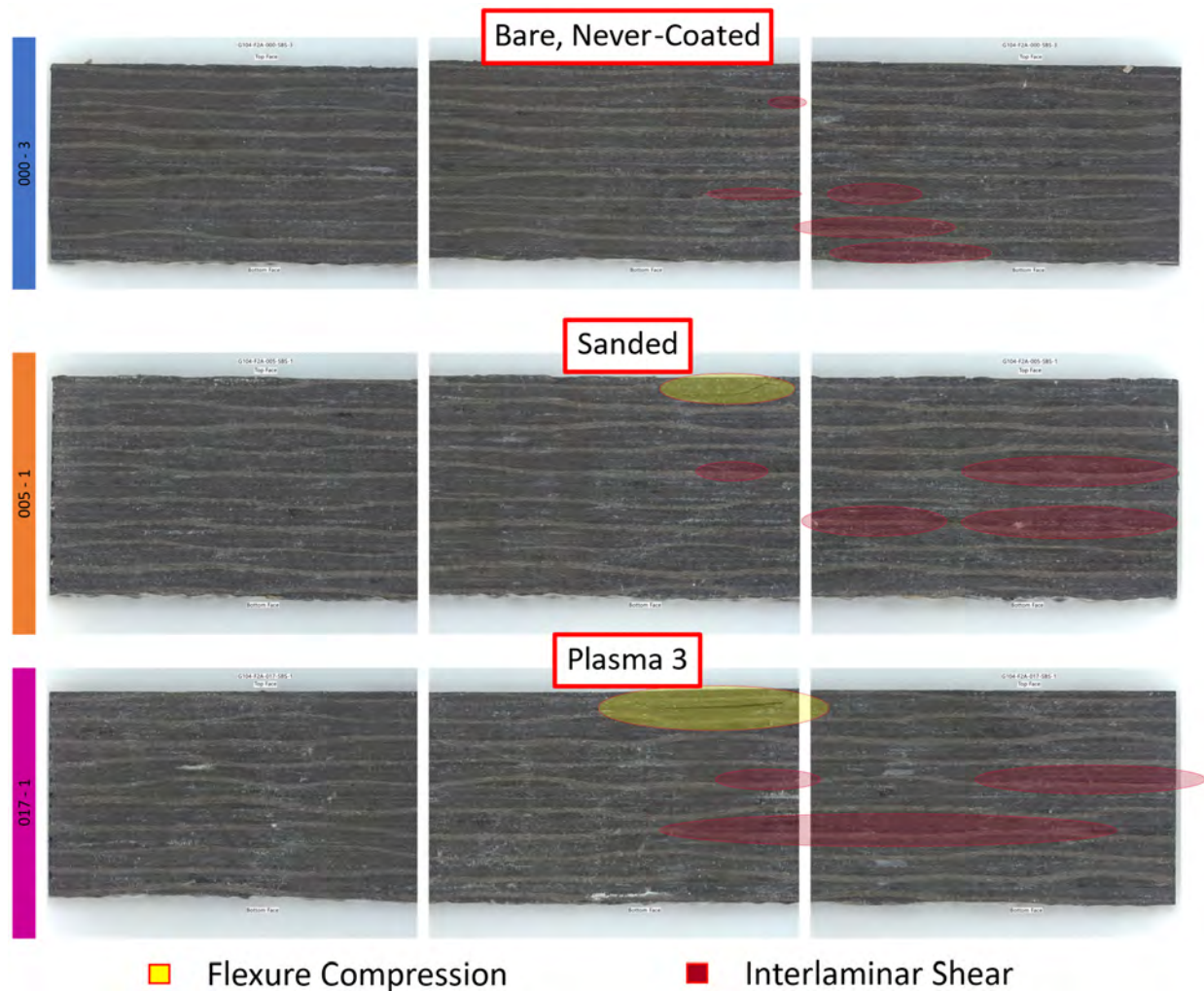


Figure 28: Cross-sections of bare (top), sanded (middle), and plasma treated (bottom) samples with highlighted indications where flexure compression and interlaminar shear failures occurred

Differential Scanning Calorimetry (DSC) / ASTM E1356 Results

DSC was used to detect possible changes to the glass transition temperature (T_g) of the composite matrix resin. A change in T_g may indicate changes and possibly damage to the material. The DSC operators noted that the specimens used for this test were likely too thick to ascertain whether the surface region exhibited any changes in T_g accurately. The relatively large thermal mass presented by the thick samples would tend to overwhelm any changes that may have been caused by the APCR process. Future studies should utilize significantly thinner composite plies to allow better resolution of the glass transition and make it easier to spot changes on the surface and near-surface regions.

In future work, Dynamic Mechanical Analysis (DMA) testing, which combines mechanical testing with thermal variations, would yield additional data to detect any difference in the mechanical properties of the composite substrates [13]. There is an expectation that DMA would show a more drastic change in the glass transition temperature than using DSC to detect the glass transition through a change in heat capacity alone. A variation of this testing could be to use varying thickness panels to help identify the point at which thermal property changes could be seen.

Table 8: DSC data - Average glass transition temperature of bare, sanded, and plasma treated specimens

Coating Removal Technique	Average Glass Transition [°C]		
	Onset of T _g	End of T _g	Midpoint of T _g
Bare	207 ± 12	217 ± 3	212 ± 5
Sanded	204 ± 10	212 ± 7	208 ± 8
Plasma 1	207 ± 8	213 ± 8	210 ± 7
Plasma 2	203 ± 8	214 ± 5	209 ± 3
Plasma 3	204 ± 6	215 ± 10	209 ± 7

With most of the DSC results, it was difficult to detect the glass transition temperature, and variations in the heat flow curves were seen. Figure 29 shows the DSC curve for the bare sample tested. It is not obvious from the shape of the curve where the glass transition is, and the detected values differ by around 50°C. The blue curve, the first heating ramp, showed a transition in the range of 80-100°C in many samples, which can most likely be attributed to water evaporation. For this reason, only the second heating ramp, in green, was taken as the reported value for all specimens.

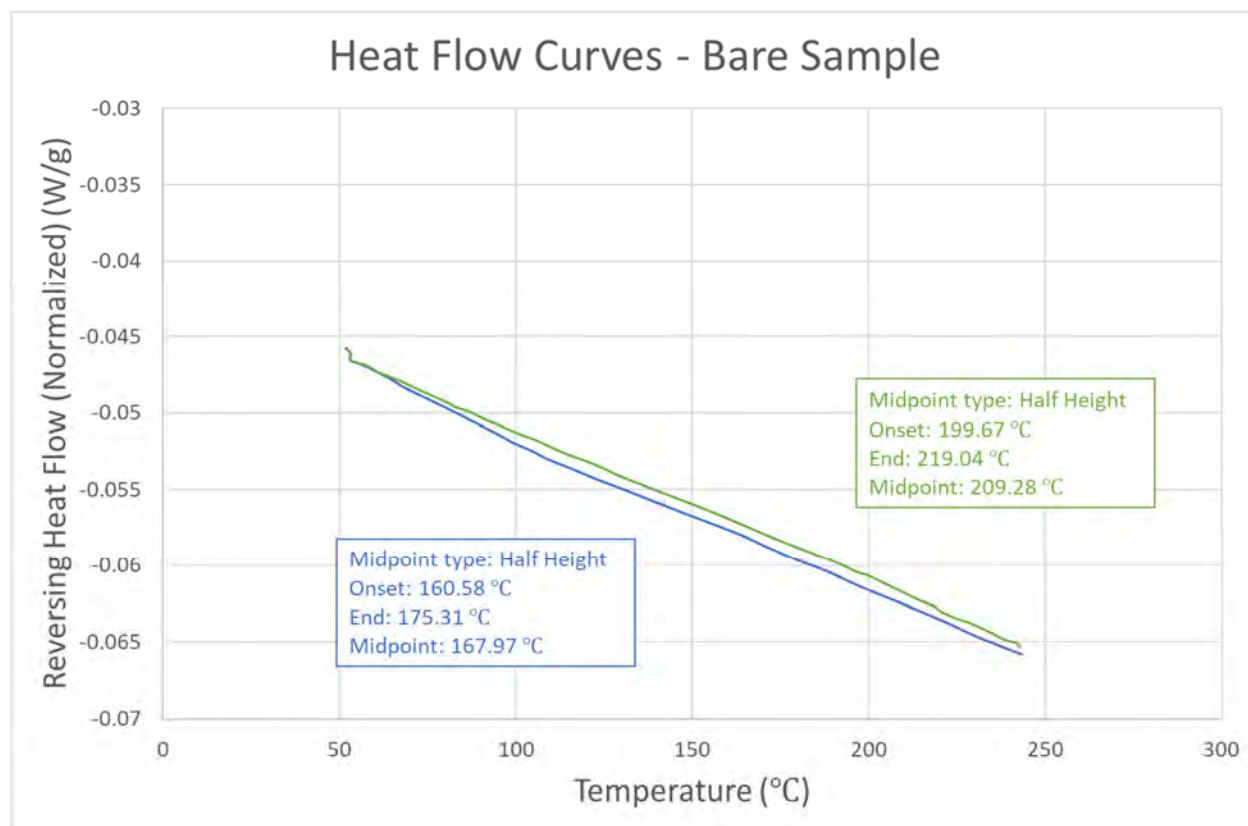


Figure 29: DSC Heating Curve for bare sample

Pull-off Coating Adhesion Strength Testing - ASTM D4541

The pull-off adhesion strengths of the painted controls, the sanded then repainted samples and the plasma treated and repainted samples was determined using the ASTM D4541 standard. Both the sanded specimens and plasma treated specimens retained a layer of the original primer coat. The highest adhesion strength was found to be the sanded and repainted samples. The improved strength appears to be due to a better adhered topcoat layer in the recoated samples, as the sanded samples show an increase in the percentage of the failures occurring between the dolly adhesive and the topcoat rather than within the topcoat layer itself. The next highest adhesion strength was the painted controls with the plasma treated panels.

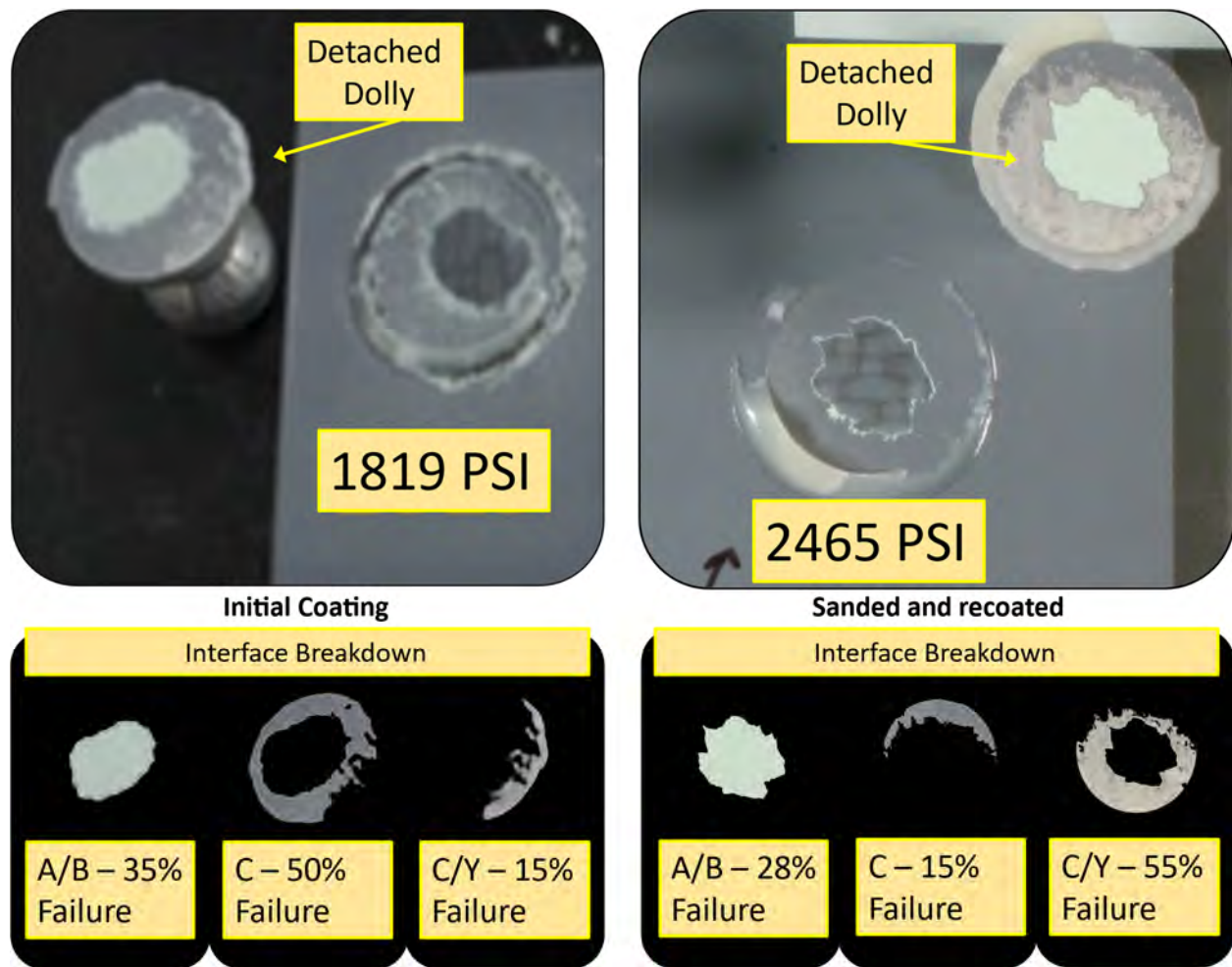


Figure 30: Coating adhesion strength (ASTM D4541) results between the control (initial coating) and incumbent method, sanding. Control with initial coating application shows significant topcoat cohesive failure, labelled “C” above, on the Interface Breakdown (left-center) and the sanded, then recoated dolly shows less of this topcoat adhesive layer failure on the surface of the dolly (right-center)

The panels that underwent plasma coating removal showed a deficit in pull-off strength, but all of these samples showed failures between the primer layer that remained after plasma treatment and the substrate. The primer used in this study experienced a marked “yellowing” effect when treated with plasma. Images in Figure 31 show the yellowed primer is completely removed with the dolly, revealing the resin and fiber pattern of the substrate.

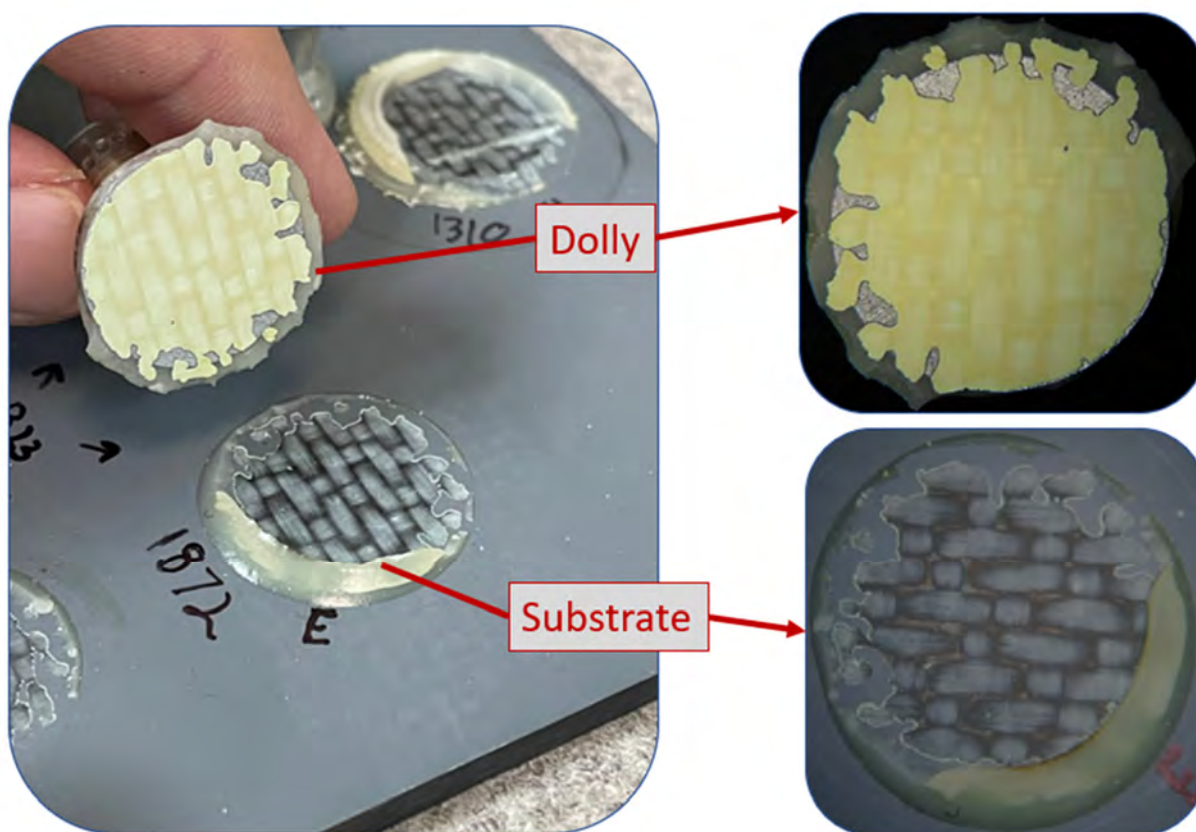


Figure 31: Dolly and substrate of repainted, plasma condition 2 treated panel (left) with close-up images of dolly and substrate (right) from ASTM D4541 adhesion strength testing

It is unknown if the initial plasma removal caused the remaining primer to be weakened, or if it was the surface reactivation plasma treatment. In all cases the effect of the plasma surface reactivation was removed by the Pre-Kote process applied to the panels during re-coating. There may also be an interaction with the plasma treated primer, MEK wipe performed prior to Pre-Kote or the Pre-Kote chemistry itself that could lead to loss of adhesion of the primer to the composite surface. There are many cases where a plasma pretreatment can be used to promote adhesion without utilizing a surface pretreatment step such as Pre-Kote. Future studies will include processing composite panels without the Pre-Kote step and recoating within a few minutes of plasma treatment to maximize the potential increase in adhesion promotion that the plasma may impart. If the direct plasma pretreatment of the bare composite increases adhesion as expected this may eliminate the need for the MEK solvent wiping and the application of the Pre-Kote pretreatment. This would significantly reduce the level of VOCs emitted during the repaint process and eliminate the additional chemicals included in the Pre-Kote formulation.

Table 9: ASTM D4541 adhesion strength and failure modes before and after re-coating. “A” represents the substrate, “B” the Primer, “C” the Topcoat, “Y” the adhesive, and “Z” the dolly. “A/B,” “B/C,” “C/Y,” and “Y/Z” represent the interface between each segment.

Sample ID	Condition	Pull	Strength (psi)	Failure Mode (% of break surface)							
				A	A/B	B	B/C	C	C/Y	Y	Y/Z
30	Control	1	1819	0	35	0	0	50	15	0	0
		2	1832	0	40	0	2	58	0	0	0
		3	2044	0	55	2	2	39	2	0	0
		4	1809	0	45	0	2	53	0	0	0
		AVG	1876	0	43.75	0.5	1.5	50	4.25	0	0
29	Control	1	1874	0	70	0	1	24	5	0	0
		2	1886	0	70	0	5	23	2	0	0
		3	1725	0	50	0	2	48	0	0	0
		4	2081	0	50	0	2	45	3	0	0
		AVG	1892	0	60	0	2.5	35	2.5	0	0
4	Sanded-Repaint	1	2645	0	45	2	0	35	18	0	0
		2	2465	0	28	2	0	15	55	0	0
		3	2192	0	55	2	0	10	33	0	0
		4	2085	0	50	2	0	8	40	0	0
		AVG	2347	0	44.5	2	0	17	36.5	0	0
8	Plasma 1-Repaint	1	1710	0	90	0	1	0	9	0	0
		2	1767	0	80	0	3	3	14	0	0
		3	1464	0	85	0	1	1	13	0	0
		4	1879	0	80	0	1	1	18	0	0
		AVG	1705	0	84	0	1.5	1.25	13.5	0	0
12	Plasma 2-Repaint	1	1188	0	70	0	2	0	28	0	0
		2	1872	0	98	0	0	0	2	0	0
		3	1544	0	97	0	0	0	3	0	0
		4	2236	0	95	0	0	0	5	0	0
		AVG	1710	0	90	0	0.5	0	9.5	0	0
16	Plasma 3-Repaint	1	1348	0	95	0	0	0	5	0	0
		2	1727	0	98	0	0	0	2	0	0
		3	1038	0	93	0	0	0	7	0	0
		4	1358	0	98	0	0	0	2	0	0
		AVG	1368	0	96	0	0	0	4	0	0

The wide range of values in the plasma treated pull-off strength values warrants further testing. Minute differences in retained coating thickness and plasma exposure over the plate may have created localized areas of high and low adhesion. Sample preparation after plasma treatment which included a solvent wipe and scouring pad application of the Pre-Kote solution eliminated

any plasma enhanced adhesion effect, as any interaction with the surface degrades the increased surface energy imparted by the plasma.

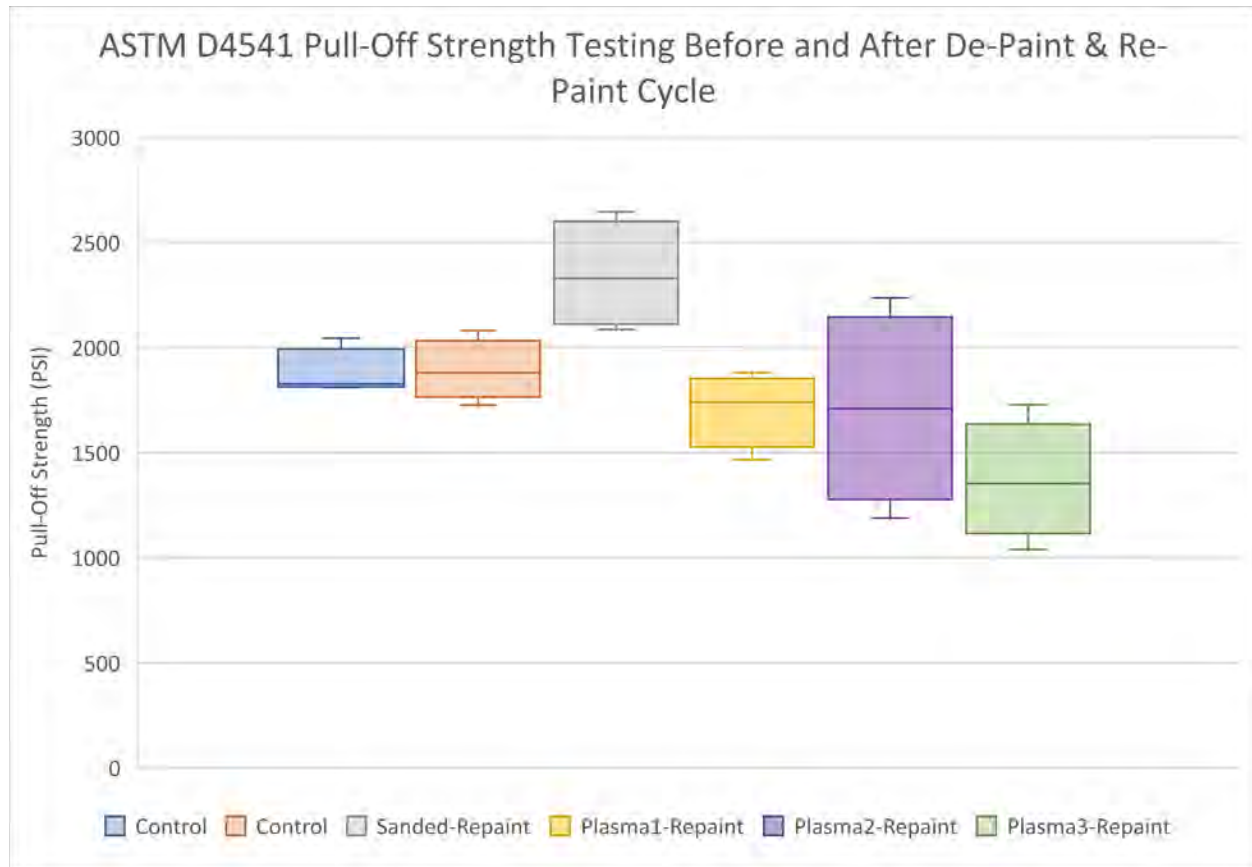


Figure 32: Box plot of Pull-off strength values for tested re-coated conditions

While ASTM D3359, Standard Test Methods for Rating Adhesion by Tape Test, is used to qualify a coating for these performance specifications, it was not considered because the chosen method using ASTM D4541 offers more objective insight into the failure mode of each part of the coating stack [14].

Conclusions, Benefits, and Implications for Future Research

Plasma treated samples in this study showed no resin damage under microscopic examination, and 3D surface profiles of the plasma samples indicate similar peak-to-valley difference to the control samples. FTIR analysis showed no shift in the characteristic carbonyl peak of the resin, indicating that APCR caused no discernable chemical change to the composite substrate. SEM and EDS images of the sanded and plasma treated samples proved both methods could retain a thin layer of primer and that plasma was able to retain a more consistent layer of the primer. C-scans of the samples indicated there were no voids in the composite caused by APCR, and the SBS testing showed a consistent shear strength from the plasma treated samples to the controls. Glass transition temperatures measured by DSC showed no change of the APCR samples from the controls. Recoated APCR samples displayed slightly lower adhesion strength, but failure modes indicate the retained primer layer was the failure initiation layer.

The results of this study build on the baseline knowledge of the effects of APCR on composites, but techniques and testing procedures were identified during the execution of this limited scope project that would improve understanding and overcome some of the challenges experienced in its execution. SBS and DSC results could be improved by using thinner samples to increase the proportion of near surface APCR treated volume to the bulk of the sample, effectively increasing the surface to volume ratio. Re-coating procedures need to be modified, removing the solvent and chemical pretreatment steps that are known to destroy the beneficial effects of plasma. New re-coating procedures will determine if plasma coating removal can also improve adhesion strength and replace solvent wiping and Pre-Kote. Other material tests such as DMA and modified SBS testing were identified, in the course of this study, which may provide more insight into the properties and near-surface areas most likely to have been affected by plasma.

APCR has numerous benefits and advantages over traditional coating removal methods that warrant further study and development. Personnel safety can be improved as the plasma generation process does not require hazardous materials, chemicals, or blast media to effectively remove coatings. Any hazardous materials present in the removed coating can be controlled with appropriate containment and personal protective equipment. Similar containment procedures for hazardous coatings are required regardless of coating removal method, but APCR produces far less waste, often over 99.9% less waste compared to media blasting techniques. For these same reasons, APCR could prove to have a significant environmental safety benefit.

The precision of APCR also affords advantages and new possibilities. As shown in this study, APCR can be controlled to remove coatings, layer by layer, to prevent over treatment and damage to underlying surfaces. In multi-layer coating systems, upper layers of coatings can be removed if it's beneficial for the lower layers to be retained. APCR's precision is also beneficial on parts with complex geometry where other coating removal methods may find difficulty providing consistent results or in accessing confined spaces with narrow geometries.

One of the beneficial side-effects of the APCR process is the surface energy enhancement of the plasma treated surface after the plasma has removed the coating. This effect can be used, in many cases, to replace the use of solvent wiping to clean surfaces. Many coating procedures currently include multiple solvent wiping steps that could be eliminated altogether. Some of the

sol-gel surface treatments solutions and other pre-Kote type chemical solutions could be replaced by a rapid plasma treatment, further reducing the use of chemicals and reducing the number of process steps. Future research to determine how a plasma pretreatment could eliminate the use of solvents in the coating process should be investigated.

It is evident from these results that the effects of APCR are predominantly, if not entirely, superficial to the surface of the composite substrate when a thin layer of primer is left on the surface. Changes, if any, to the material properties of the composite happen at the surface and thus do not alter the bulk properties of the material. The lack of any material property effects may be in part due to the thin remaining primer layer acting as a protective barrier or sacrificial layer. Future testing should include residual coating integrity testing to determine if it is suitable for the APCR process to leave remaining coating, and it should include more aggressive plasma treatments to determine when damage from overtreatment will occur to create appropriate process limits for the APCR technology.

Future work should also include the testing of additional composite materials and resin chemistries to determine if certain composites may be more or less susceptible to damage from APCR. These suggested future studies will expand APCR's benefits to a broad range of other areas involved in the maintenance of existing assets as well as new construction while reducing the environmental impacts and increasing user safety.

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Appendices

Appendix A: Optical Microscopy Images

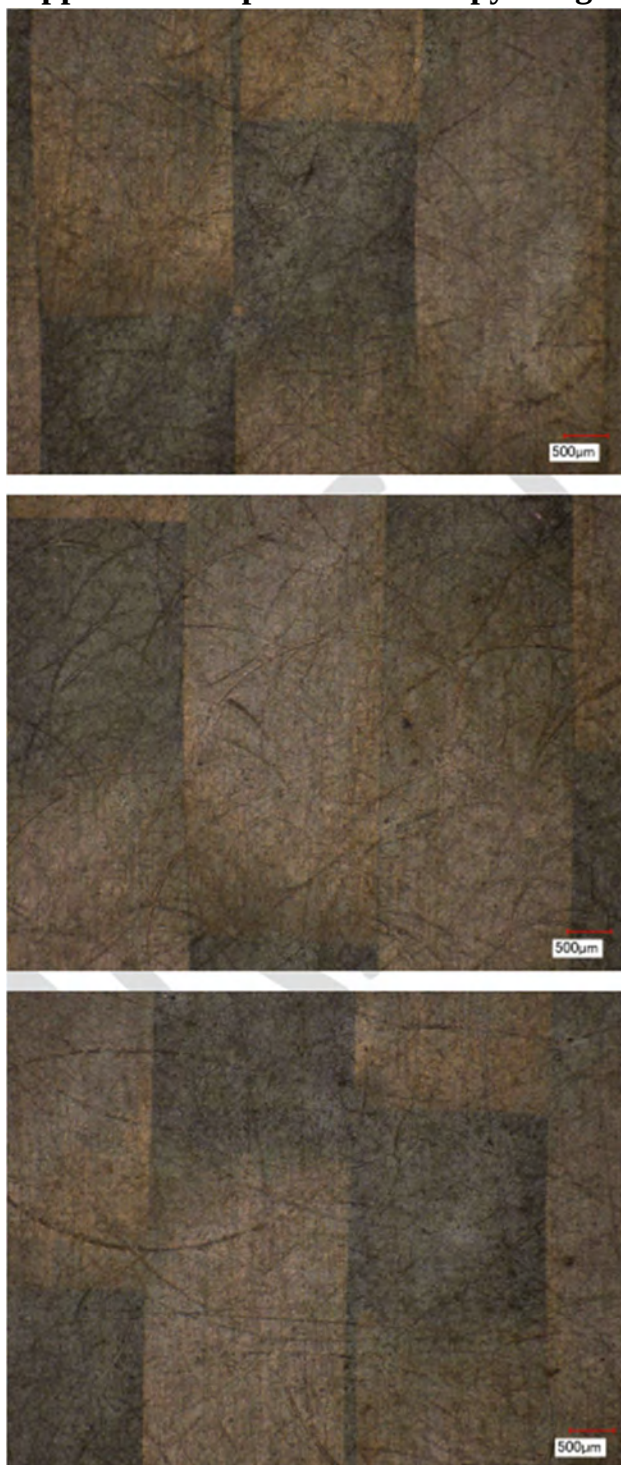


Figure A1: Bare Carbon Fiber Control Specimen 50x



Figure A2: Bare Carbon Fiber Control Specimen 500x

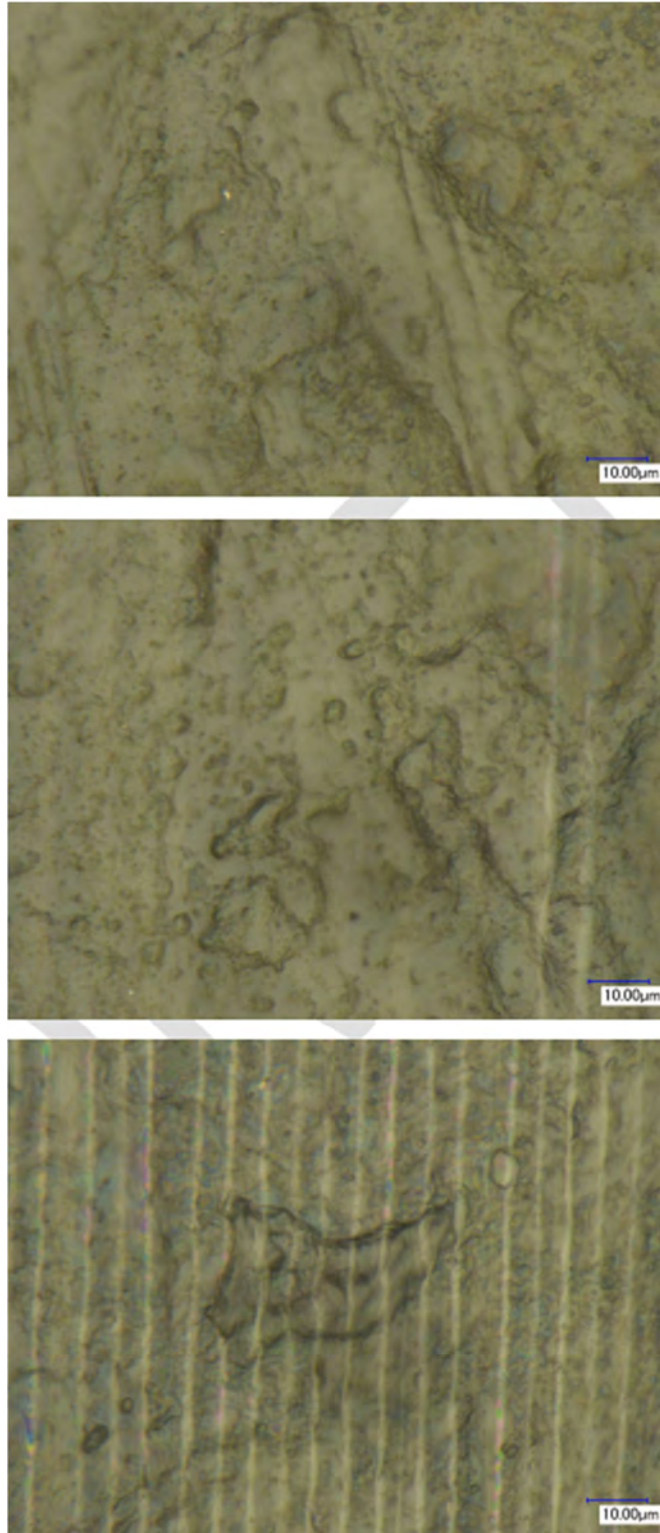


Figure A3: Bare Carbon Fiber Control Specimen 3000x



Figure A4: Sample 5, Sanded, 50x

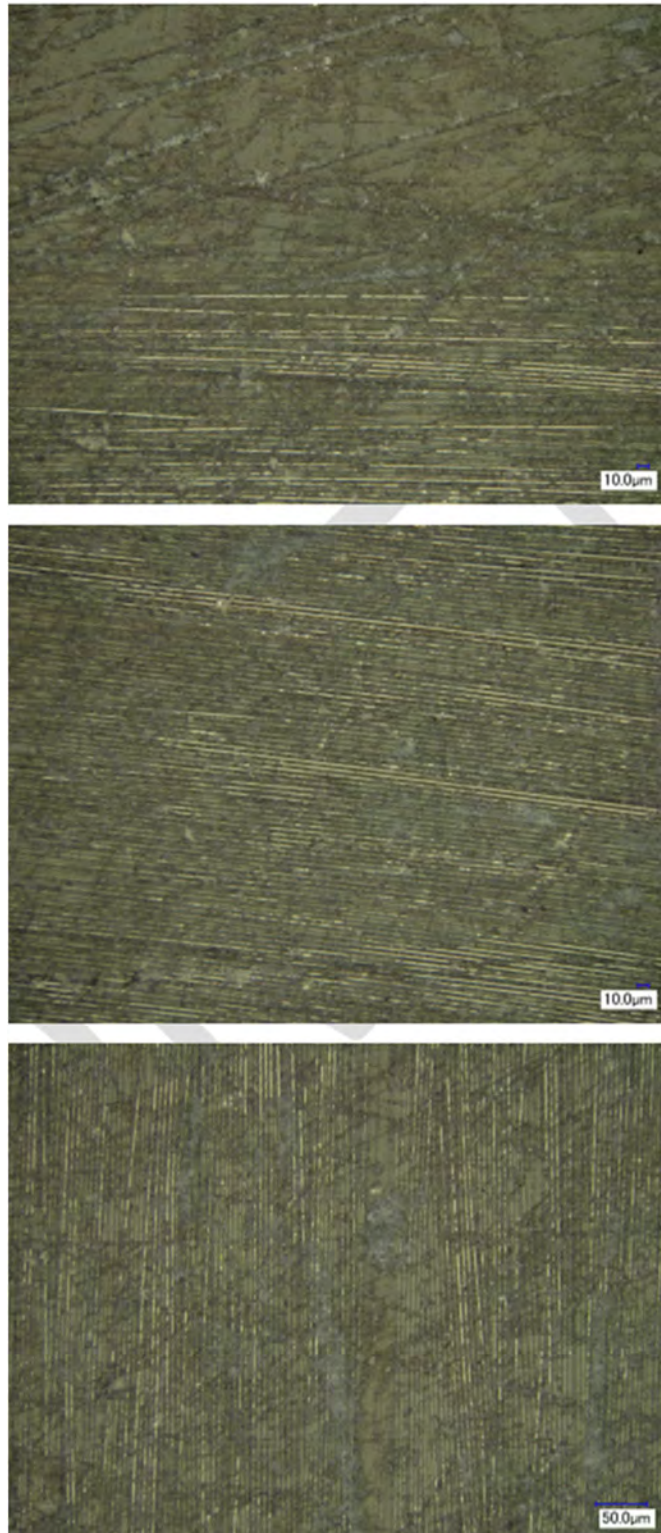


Figure A5 : Sample 5, Sanded, 500x

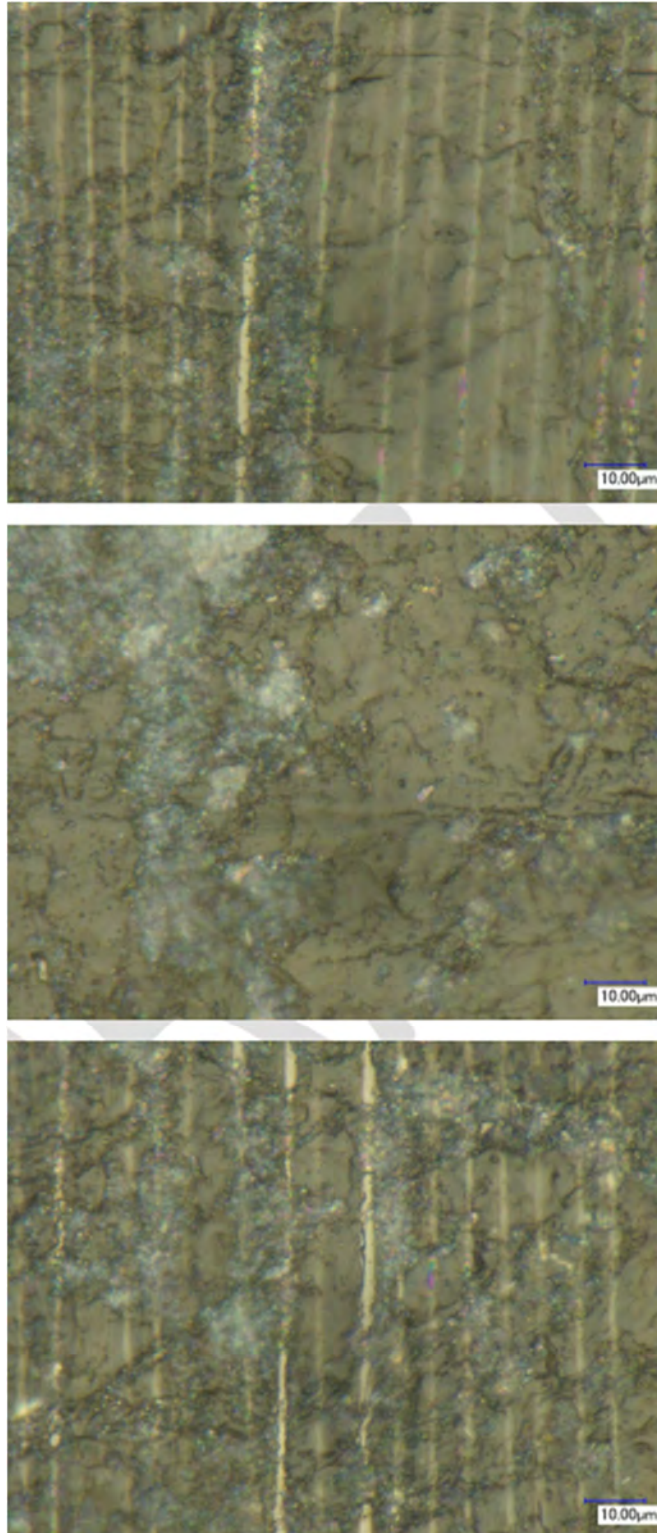


Figure A6: Sample 5, Sanded, 3000x



Figure A7: Sample 9, Plasma 1, 50x

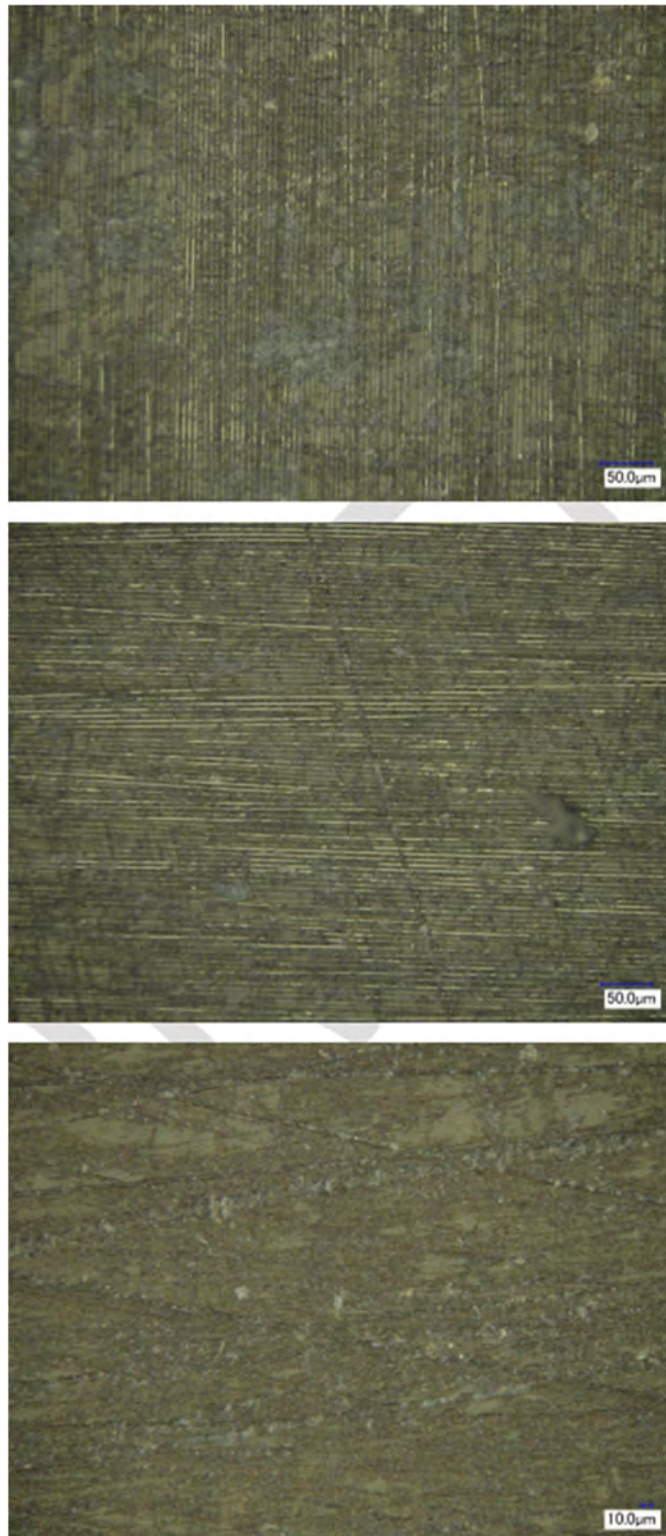


Figure A8: Sample 9, Plasma 1, 500x

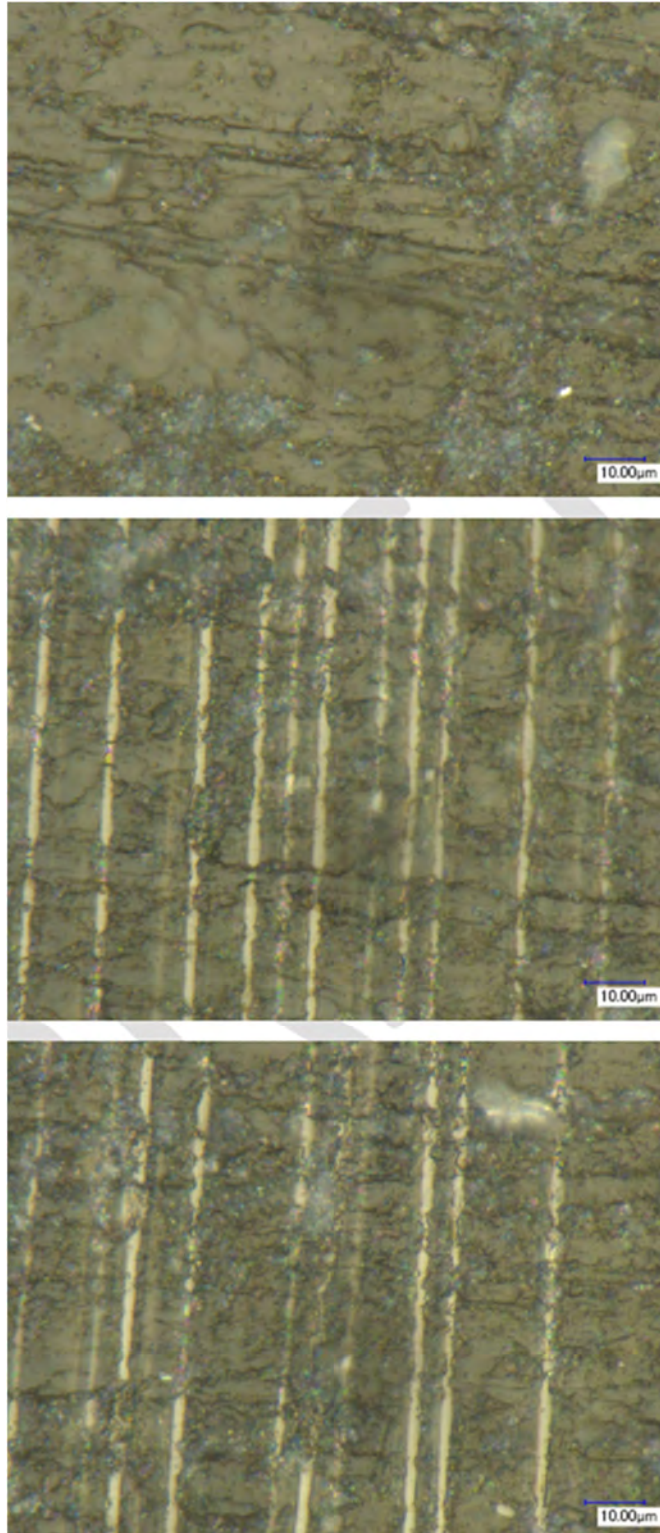


Figure A9: Sample 9, Plasma 1, 3000x

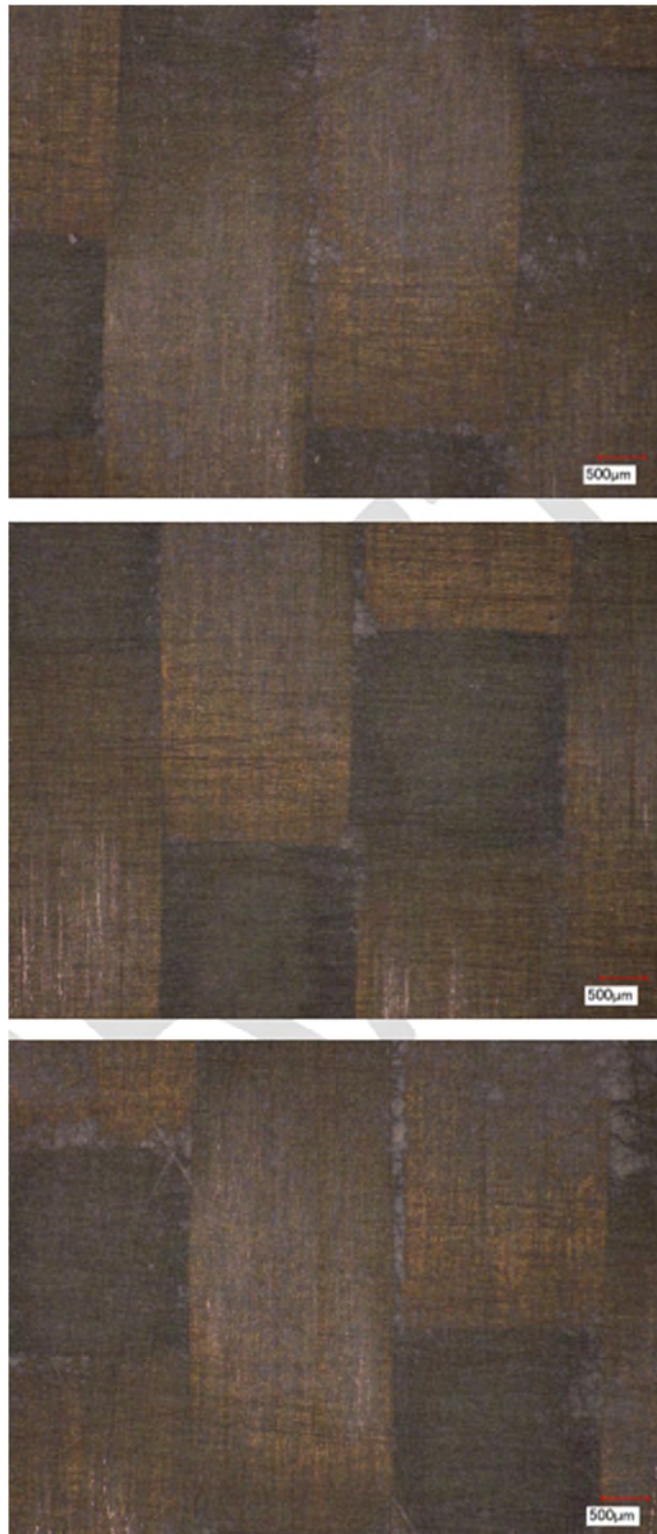


Figure A10: Sample 13, Plasma 2, 50x

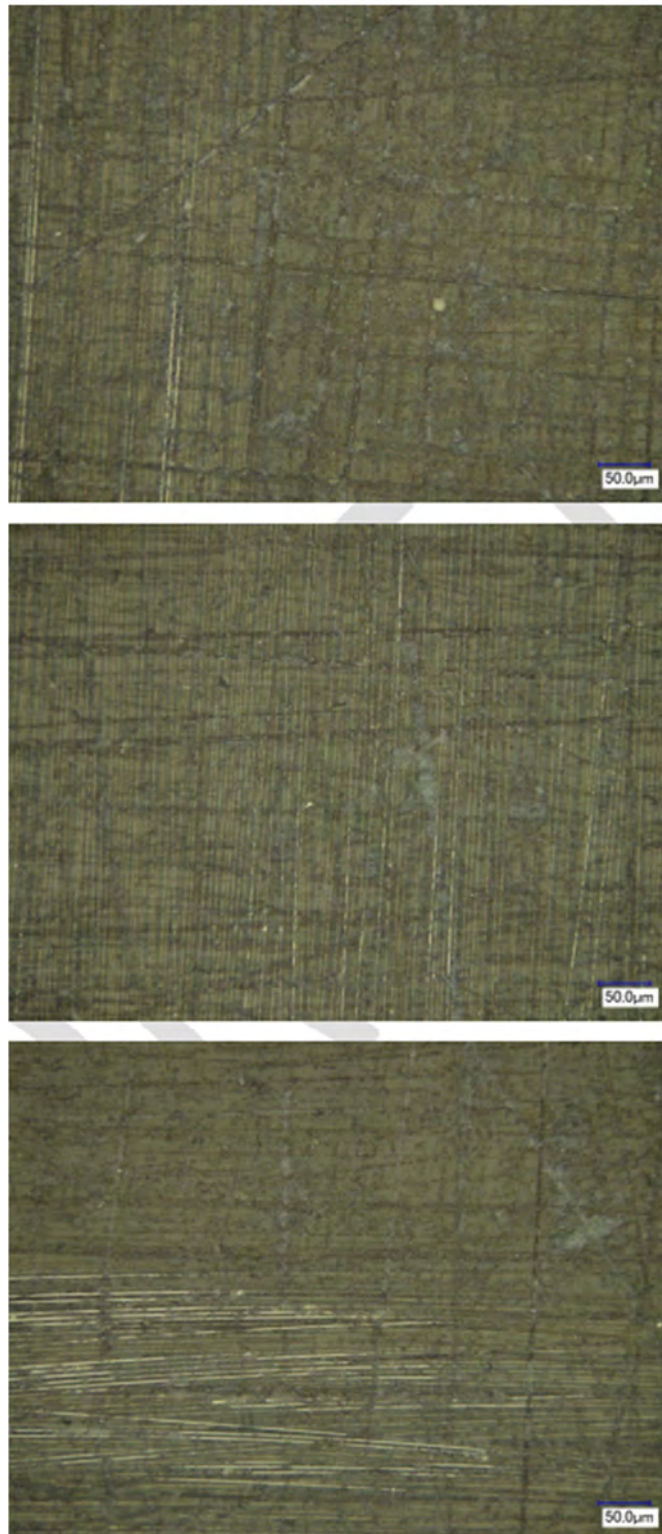


Figure A11: Sample 13, Plasma 2, 500x

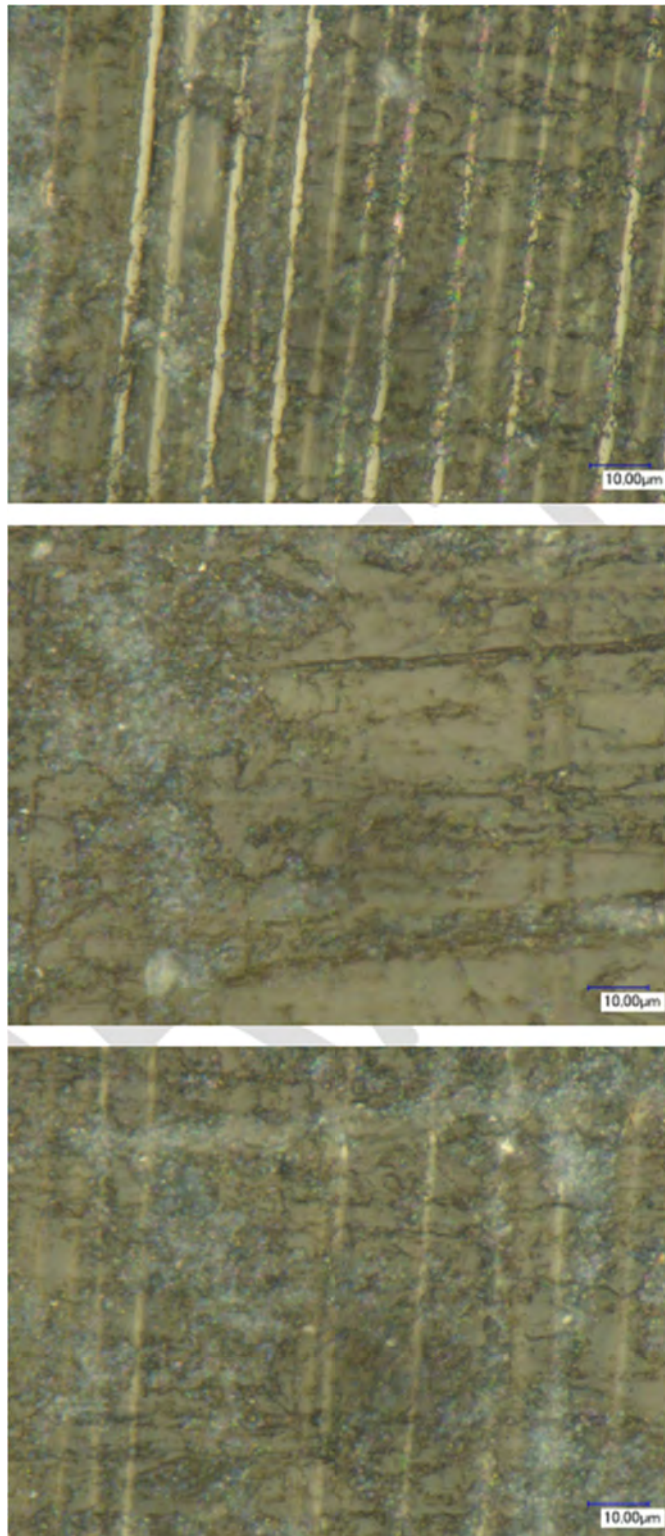


Figure A12: Sample 13, Plasma 2, 3000x

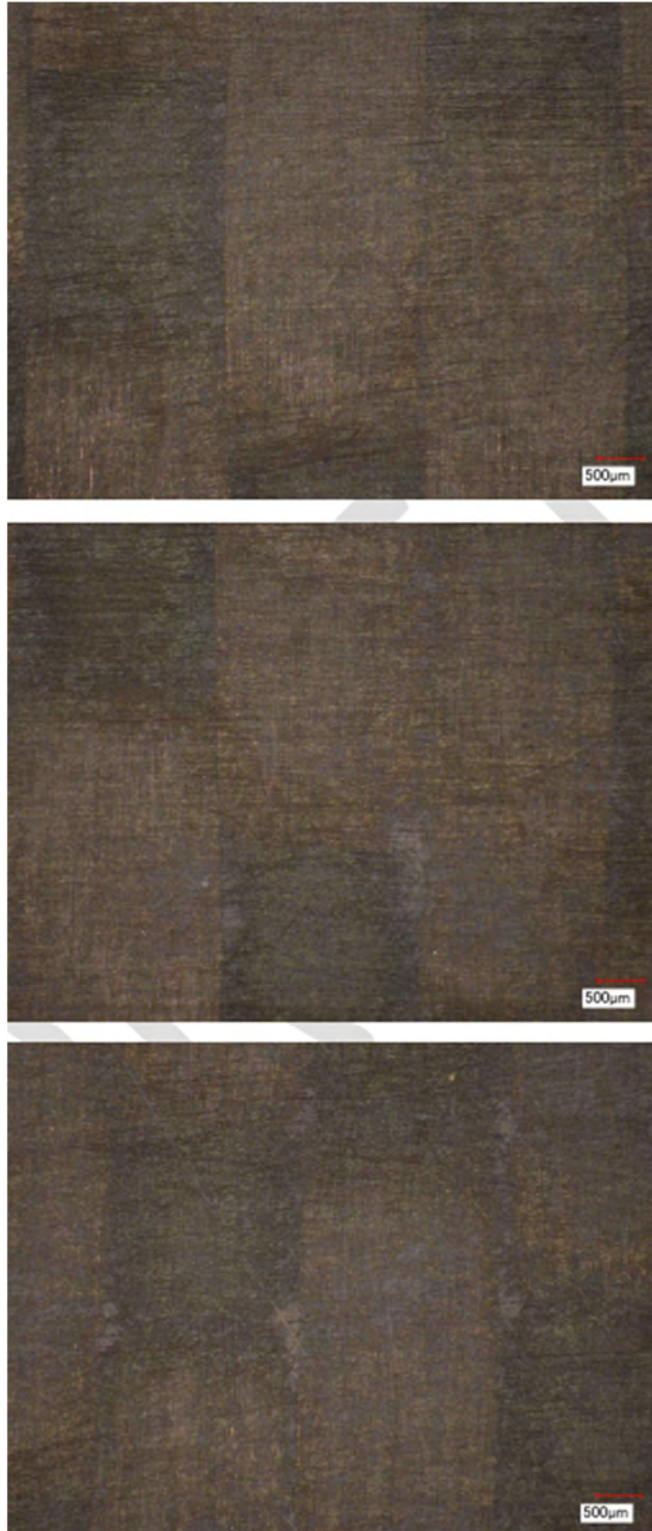


Figure A13: Sample 17, Plasma 3, 50x



Figure A14: Sample 17, Plasma 3, 500x

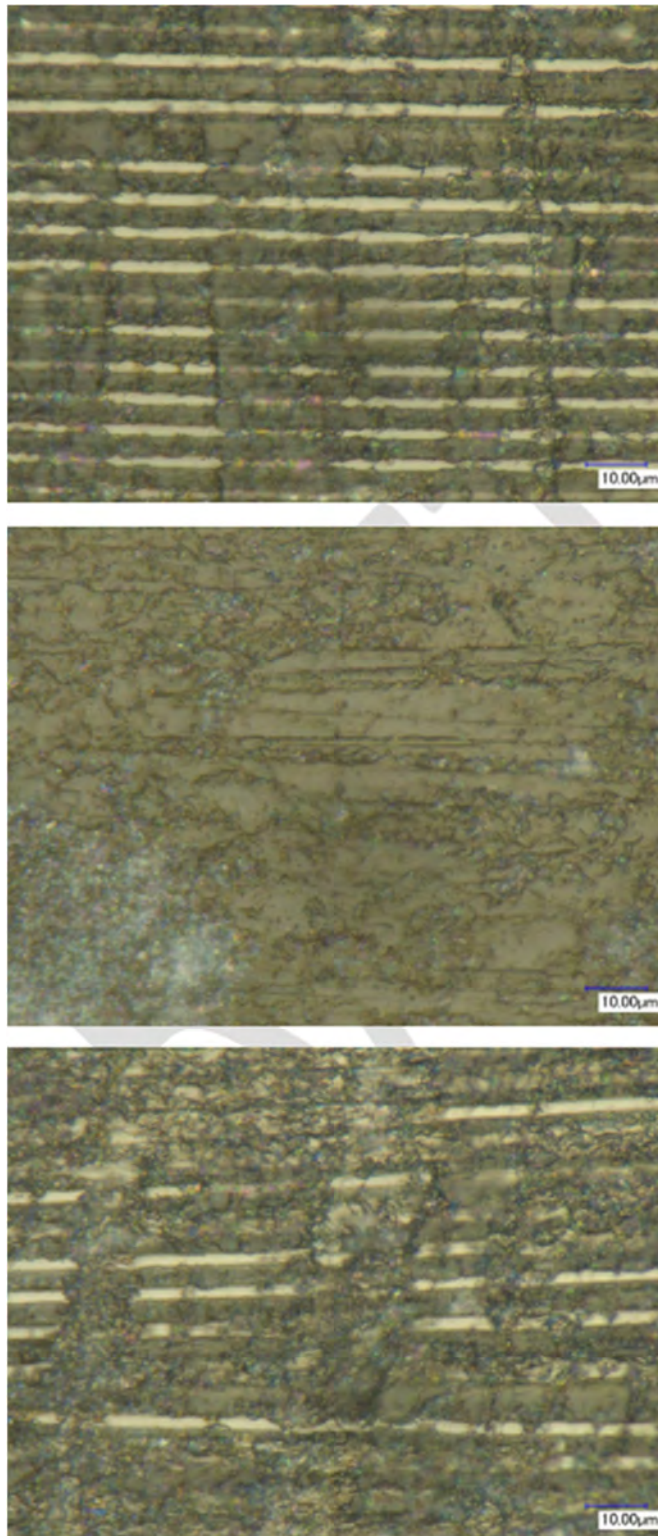


Figure A15: Sample 17, Plasma 3, 3000x

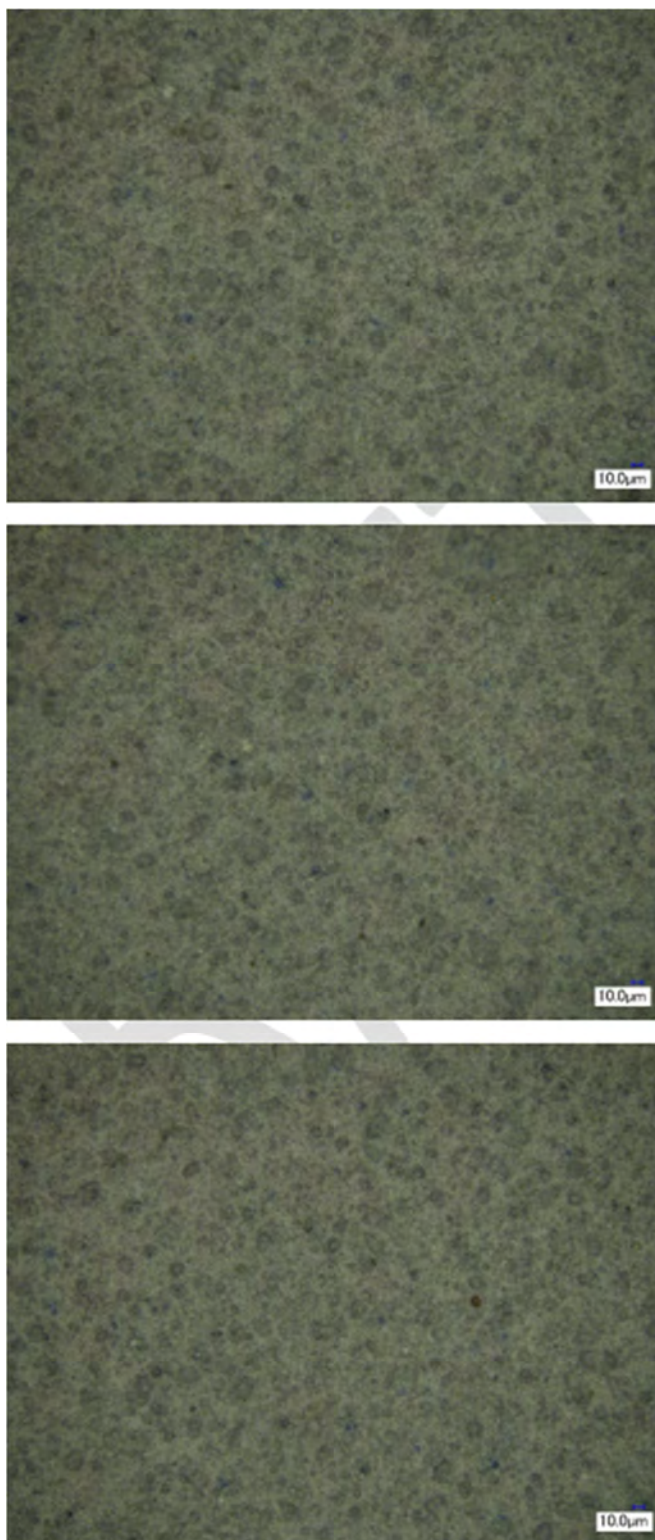


Figure A16: Sample 1, Sanded, Repainted, 500x

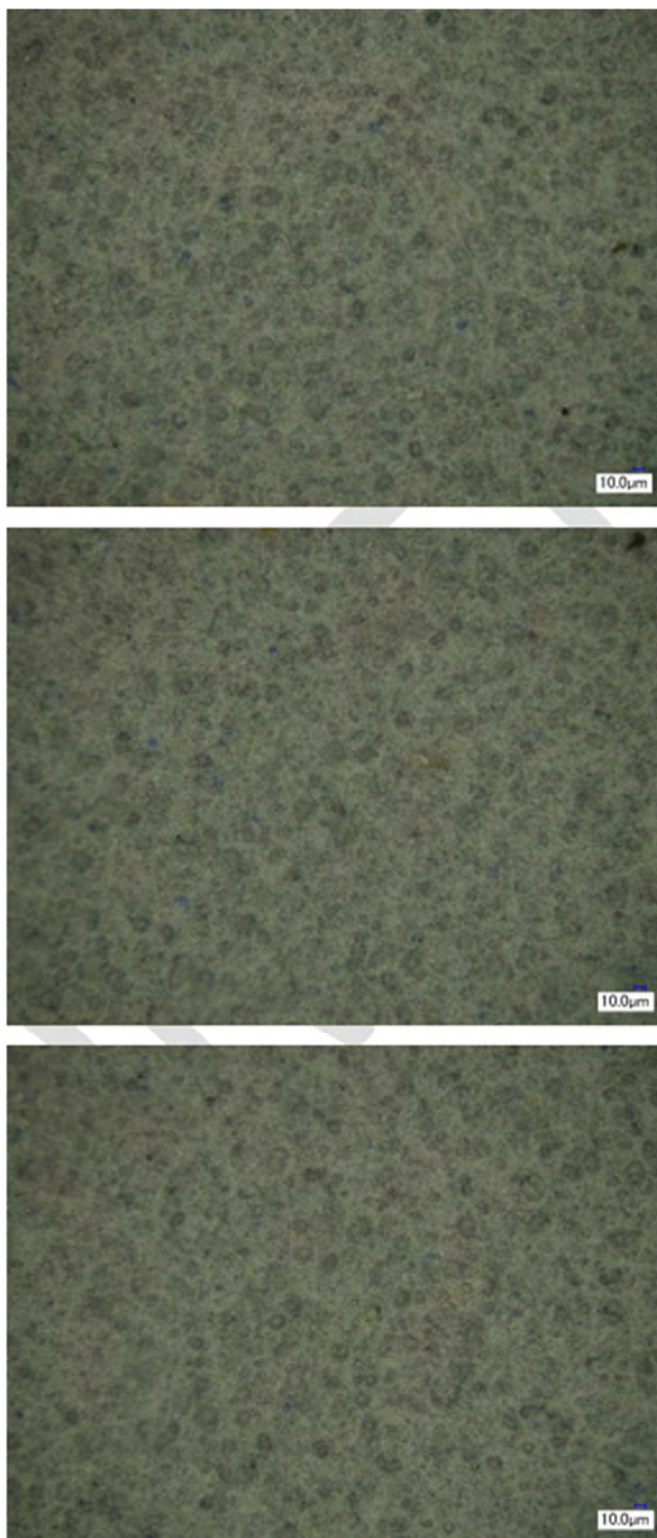


Figure A17: Sample 6, Plasma A, Repainted, 500x

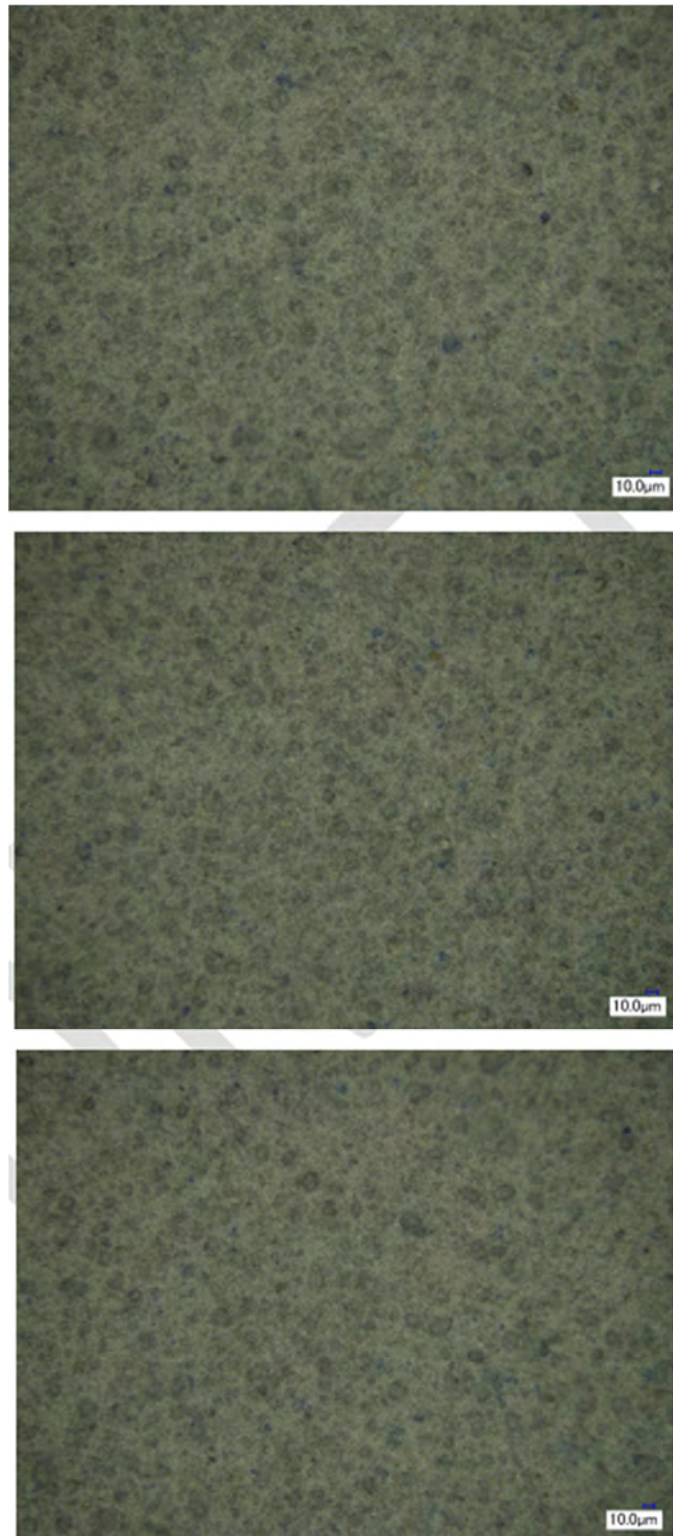


Figure A18: Sample 10, Plasma B, Repainted, 500x

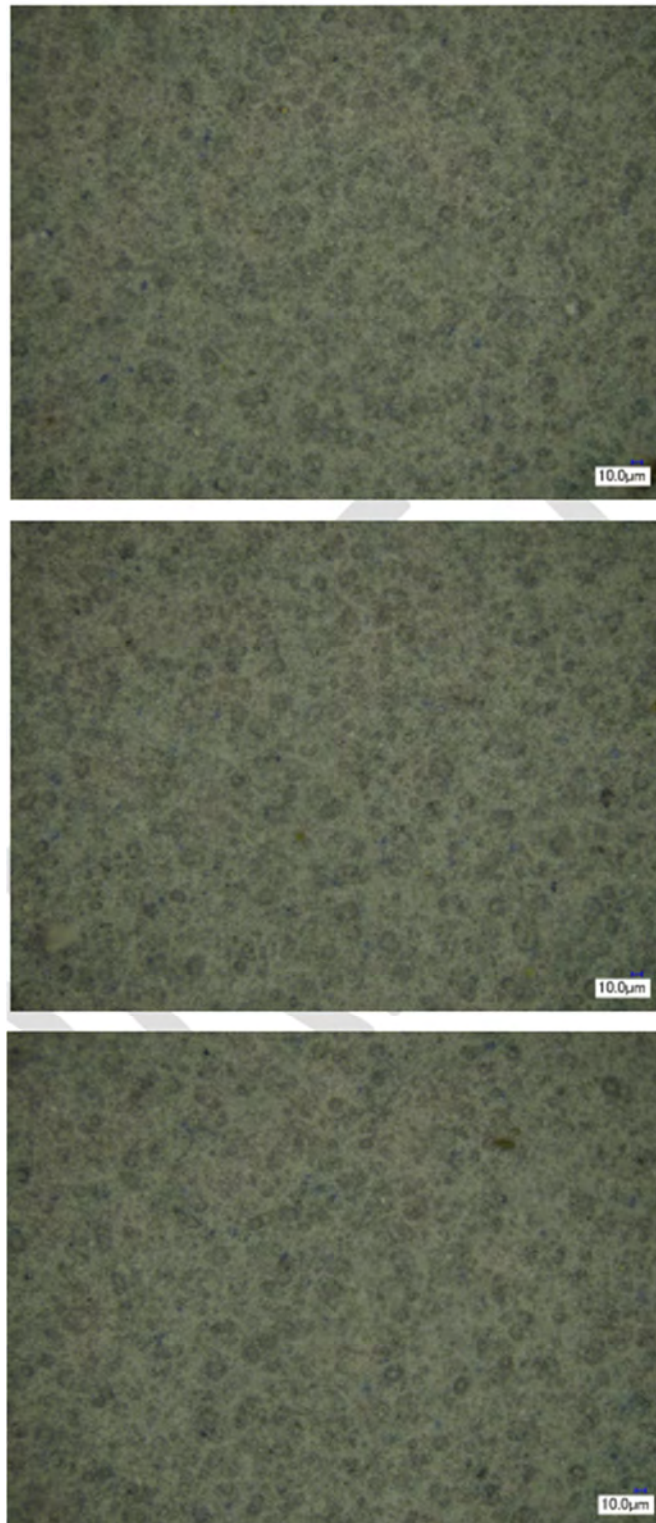


Figure A19: Sample 14, Plasma C, Repainted, 500x

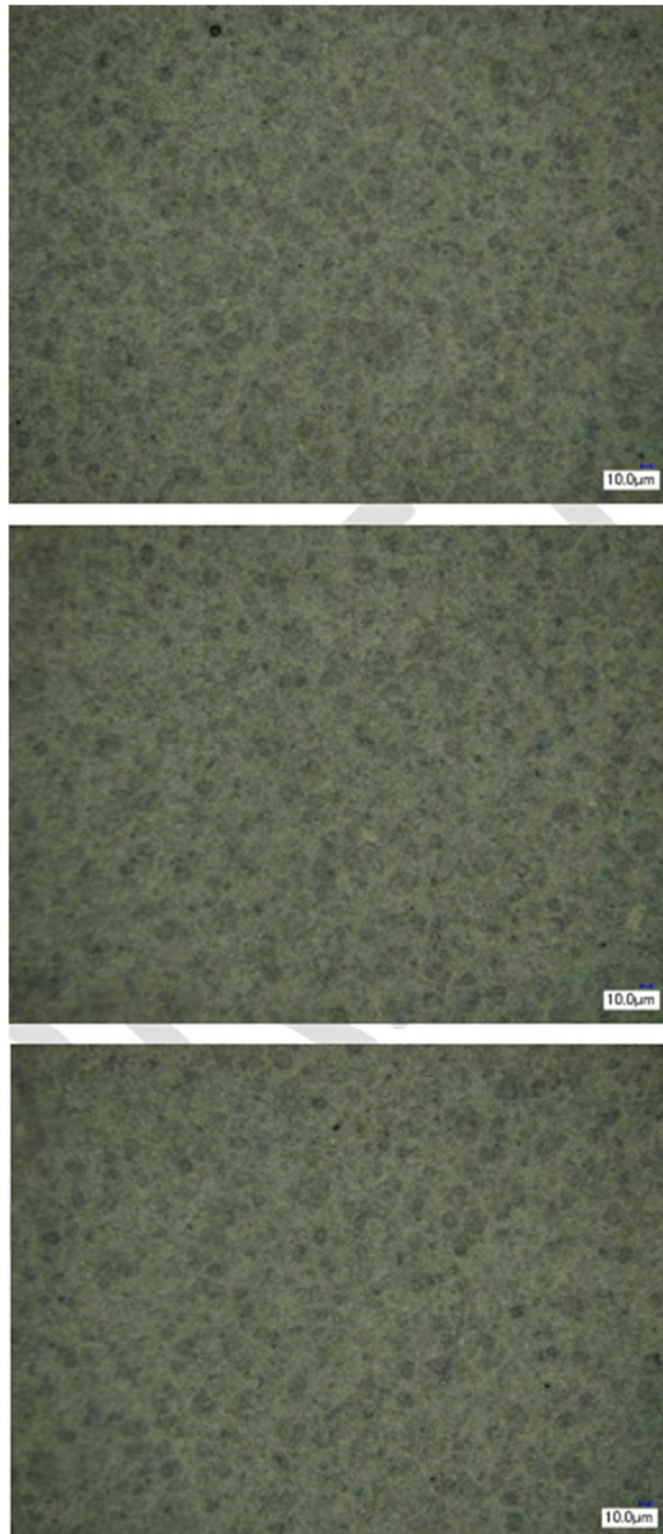
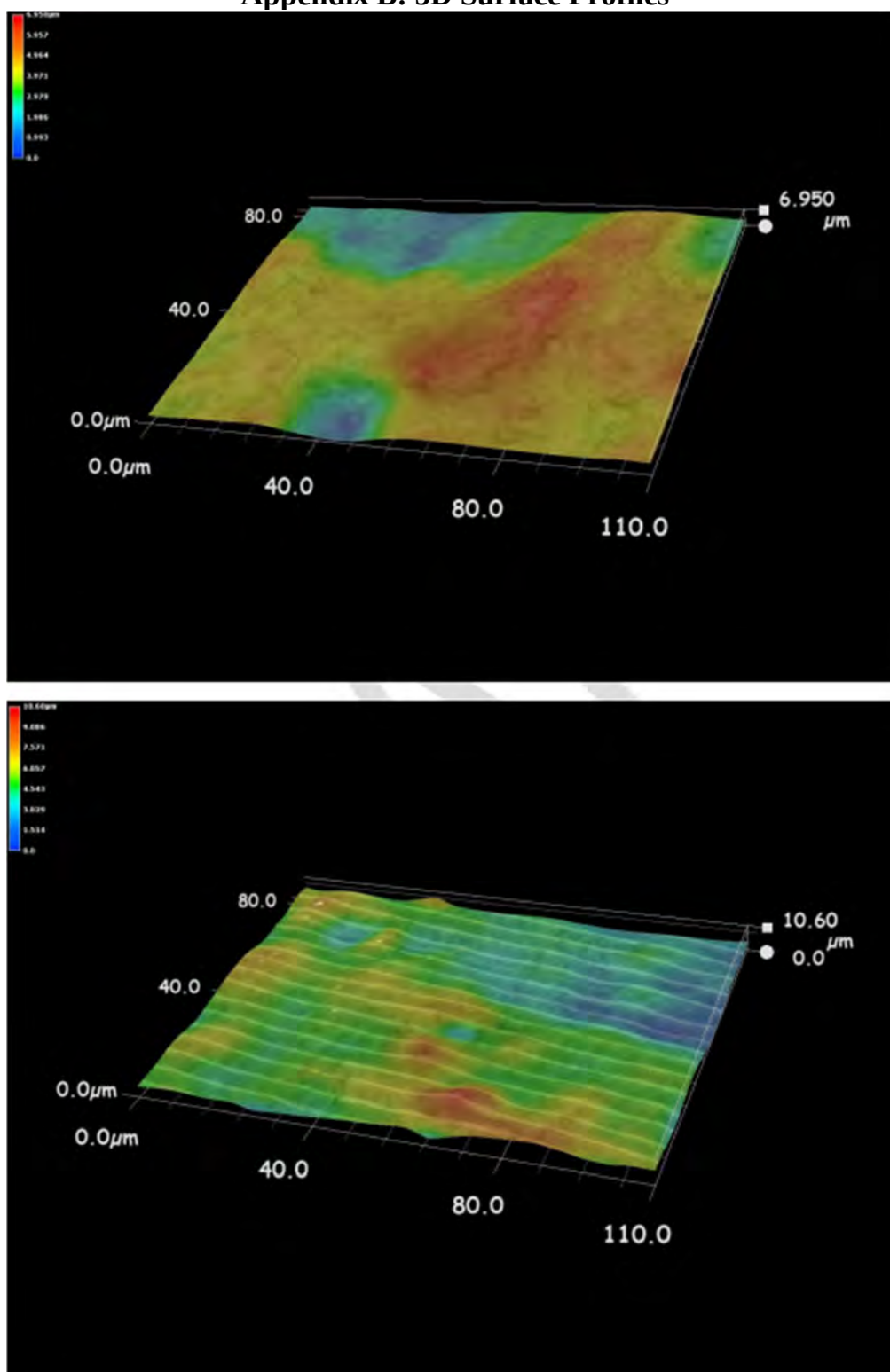


Figure A20: Sample 27, Original Paint, 500x

Appendix B: 3D Surface Profiles

*Figure B1: Bare Specimen 3D Surface Profile*

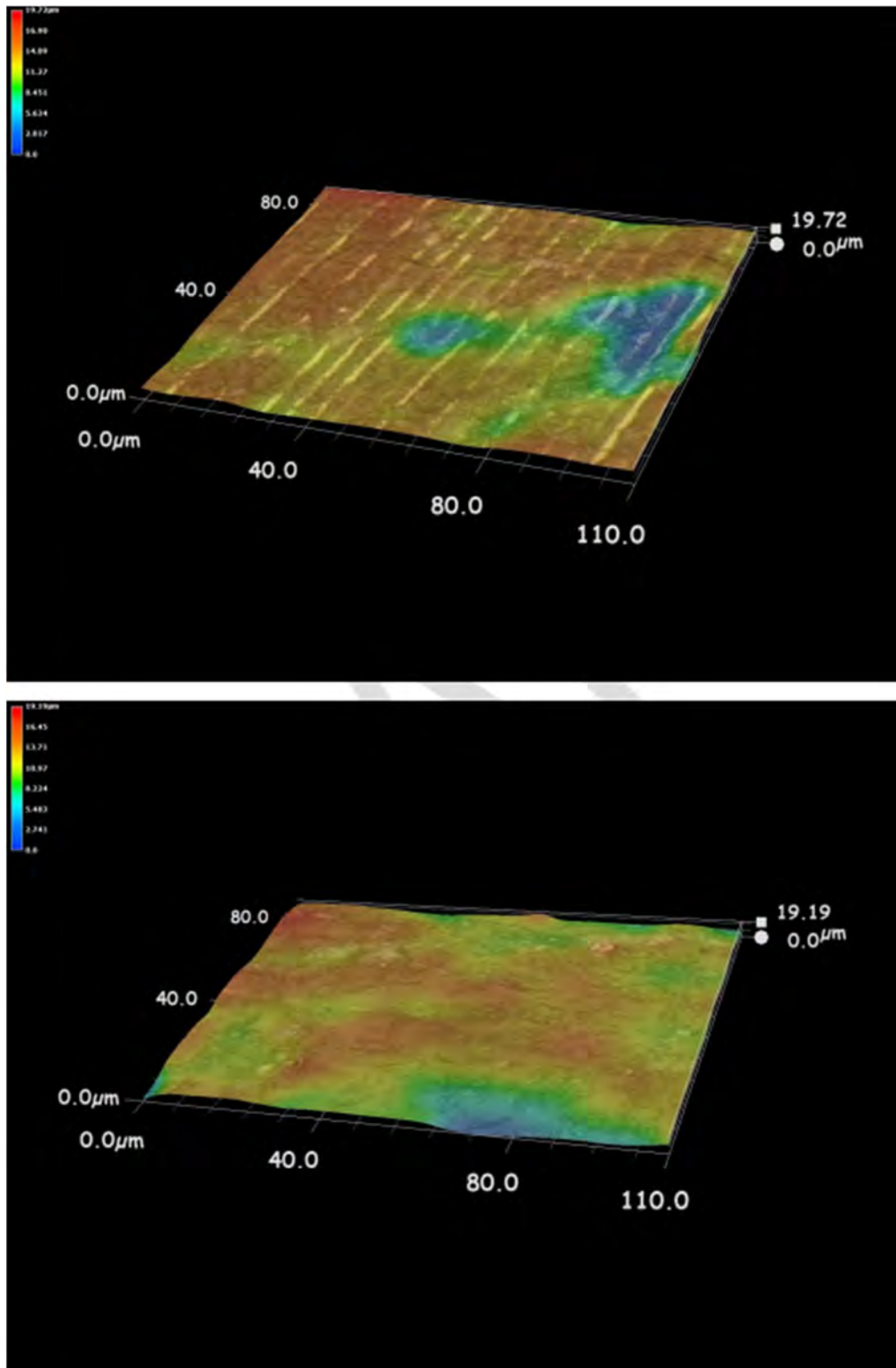


Figure B2: Sample 5, Sanded, 3D Surface Profile

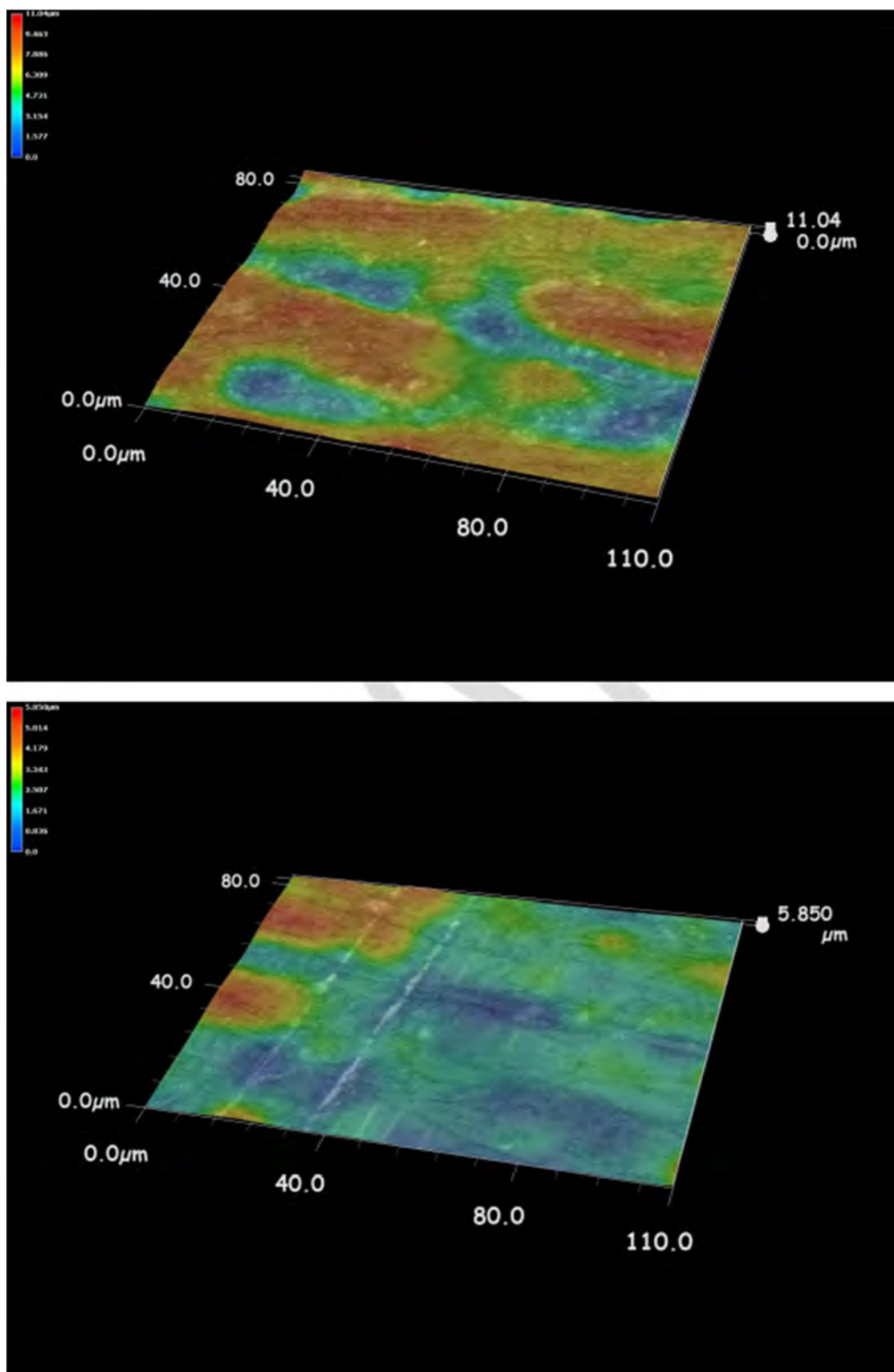


Figure B3: Sample 9, Plasma 1, 3D Surface Profile

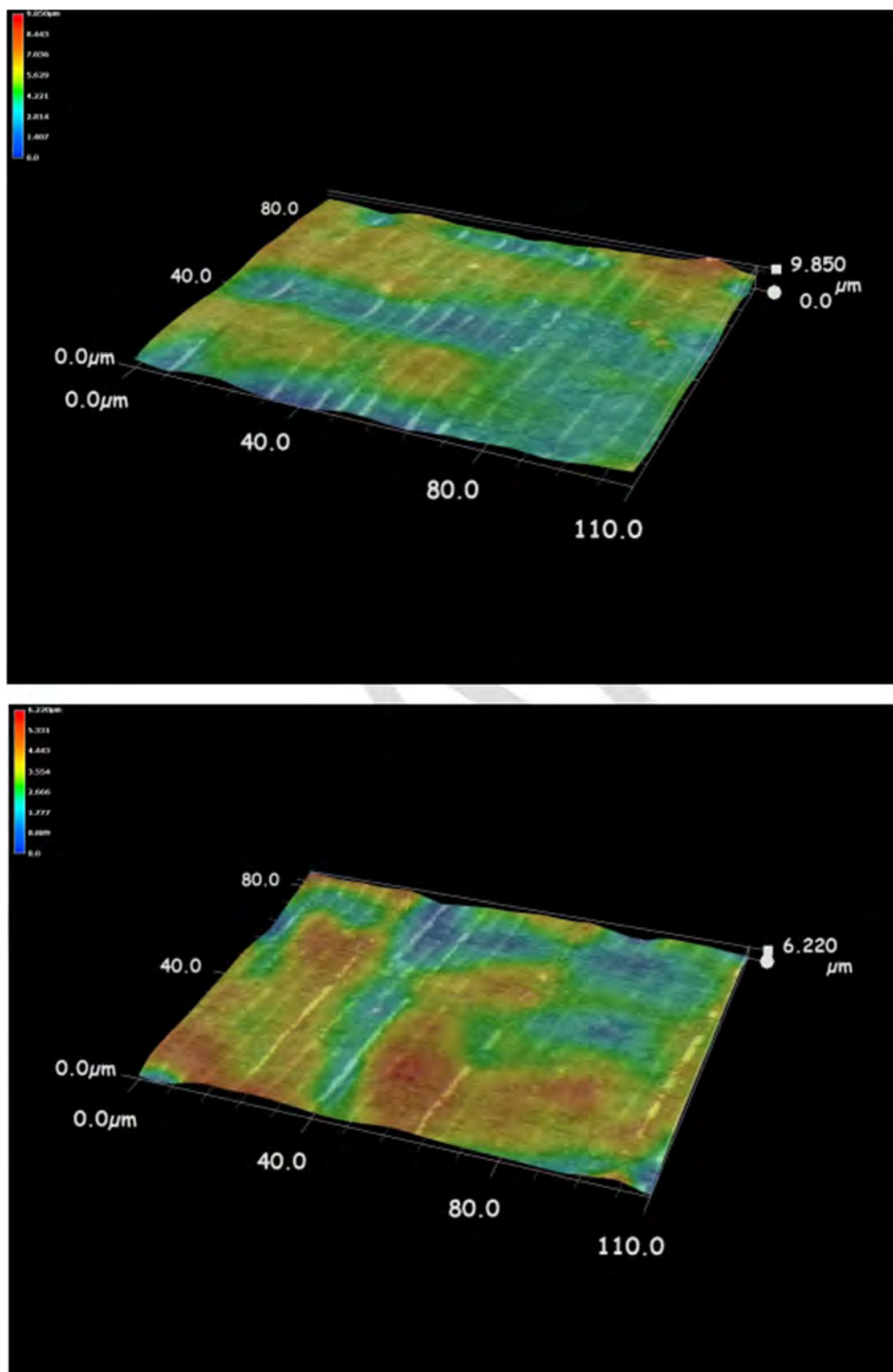


Figure B4: Sample 13, Plasma 2, 3D Surface Profile

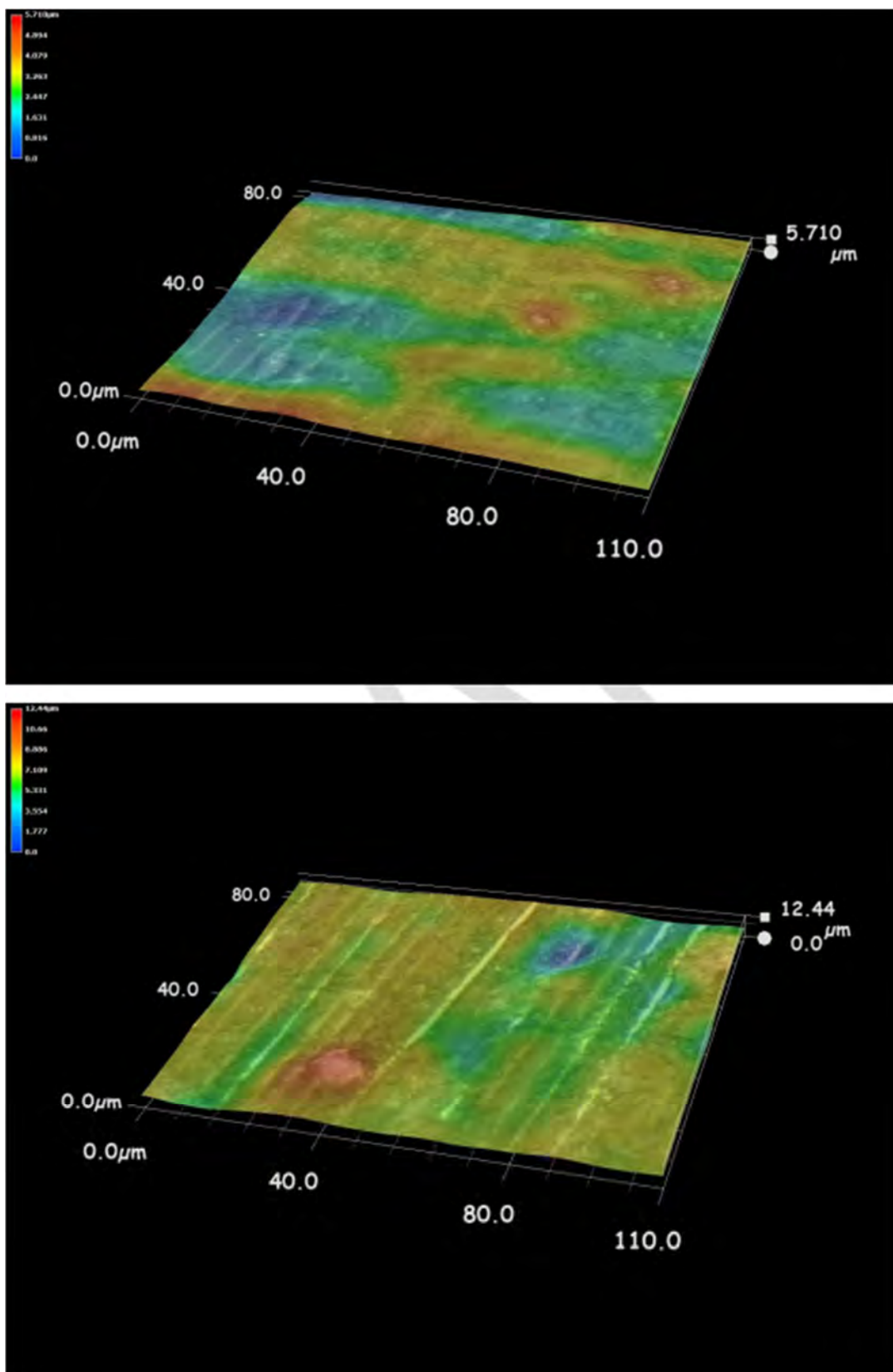


Figure B5: Sample 17, Plasma 3, 3D Surface Profile

Appendix C: SEM and EDS Graphs and Maps

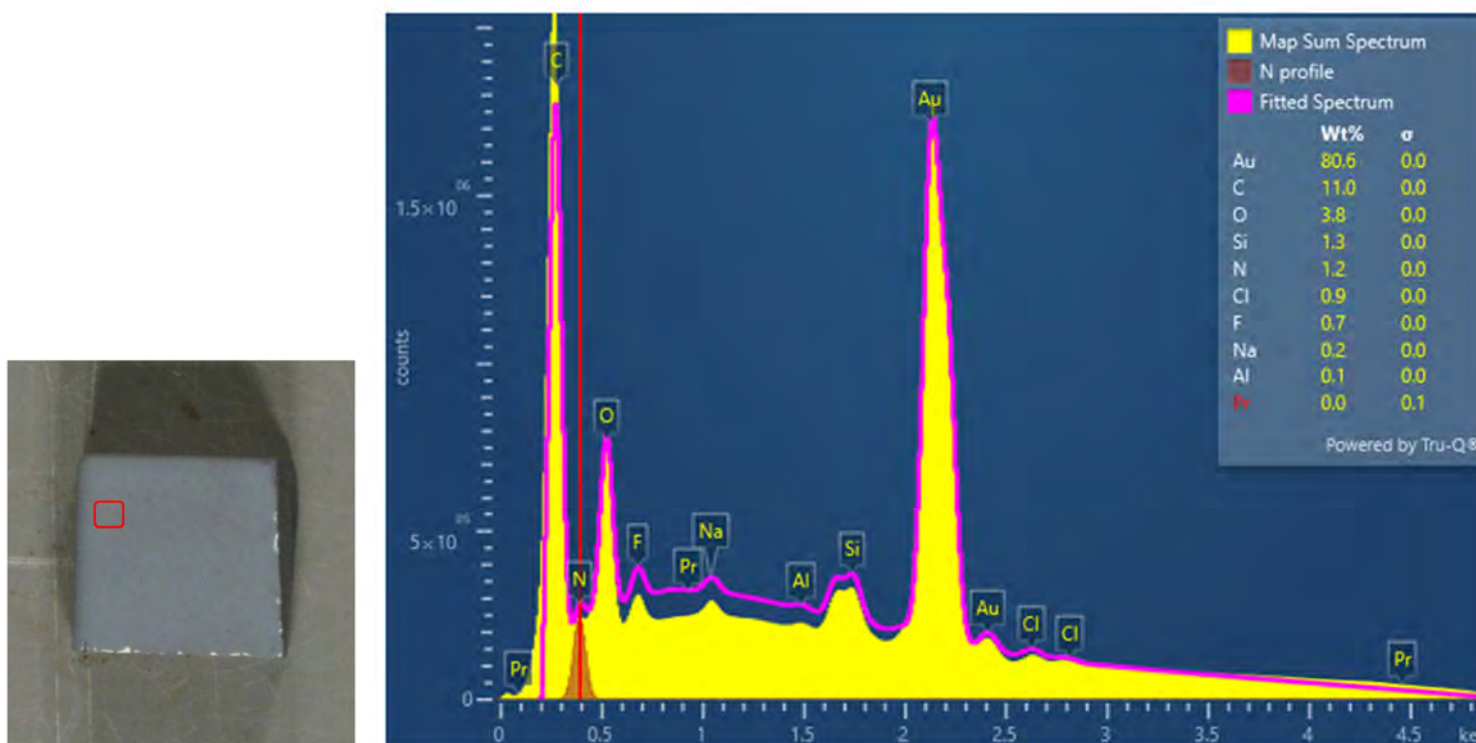


Figure C1: Piece of sample 4 used for SEM and EDS analysis (left), and Elemental Analysis of Entire Surface Area (right)

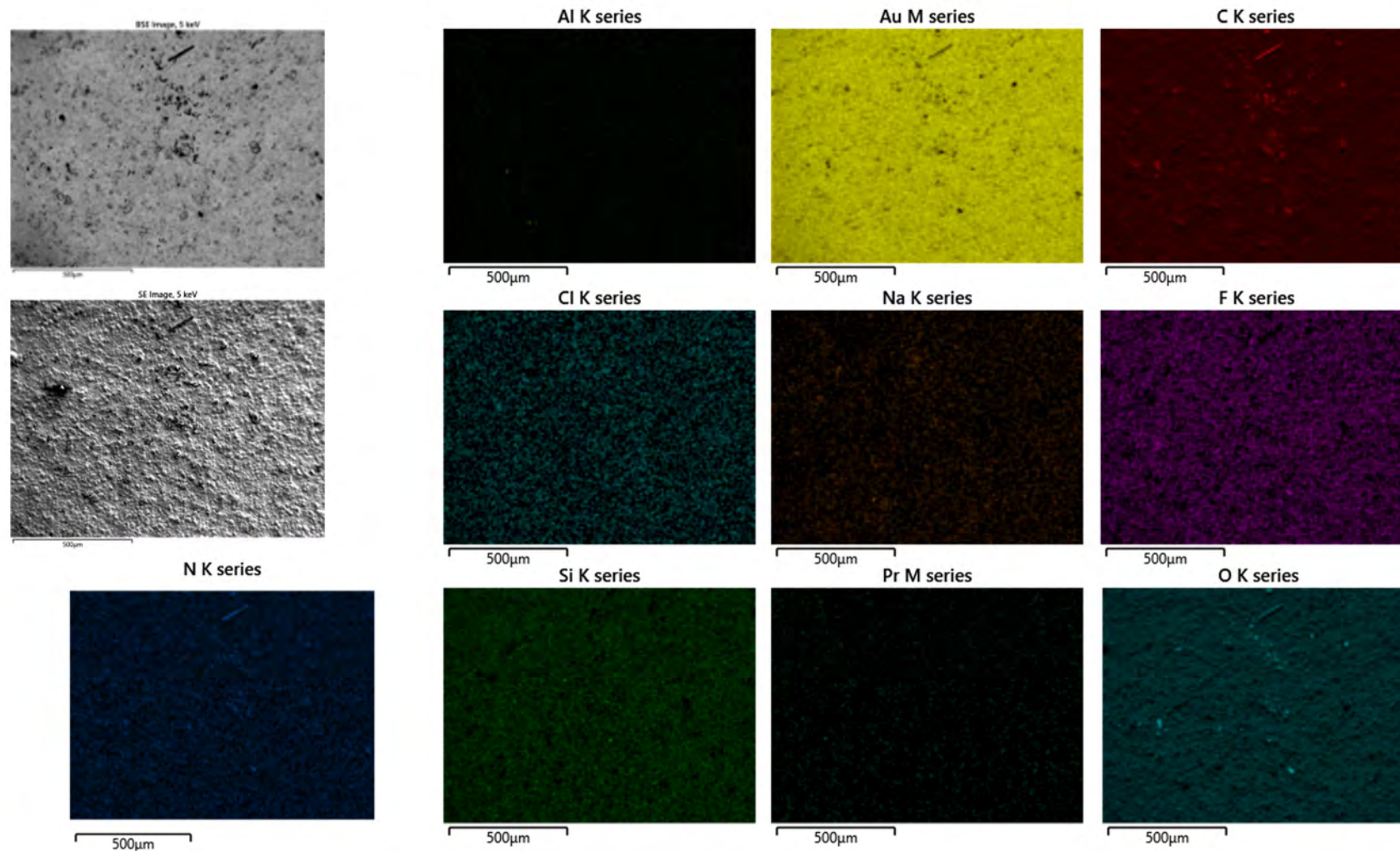


Figure C2: Sample 4, 100x SEM and EDS maps, 5 keV

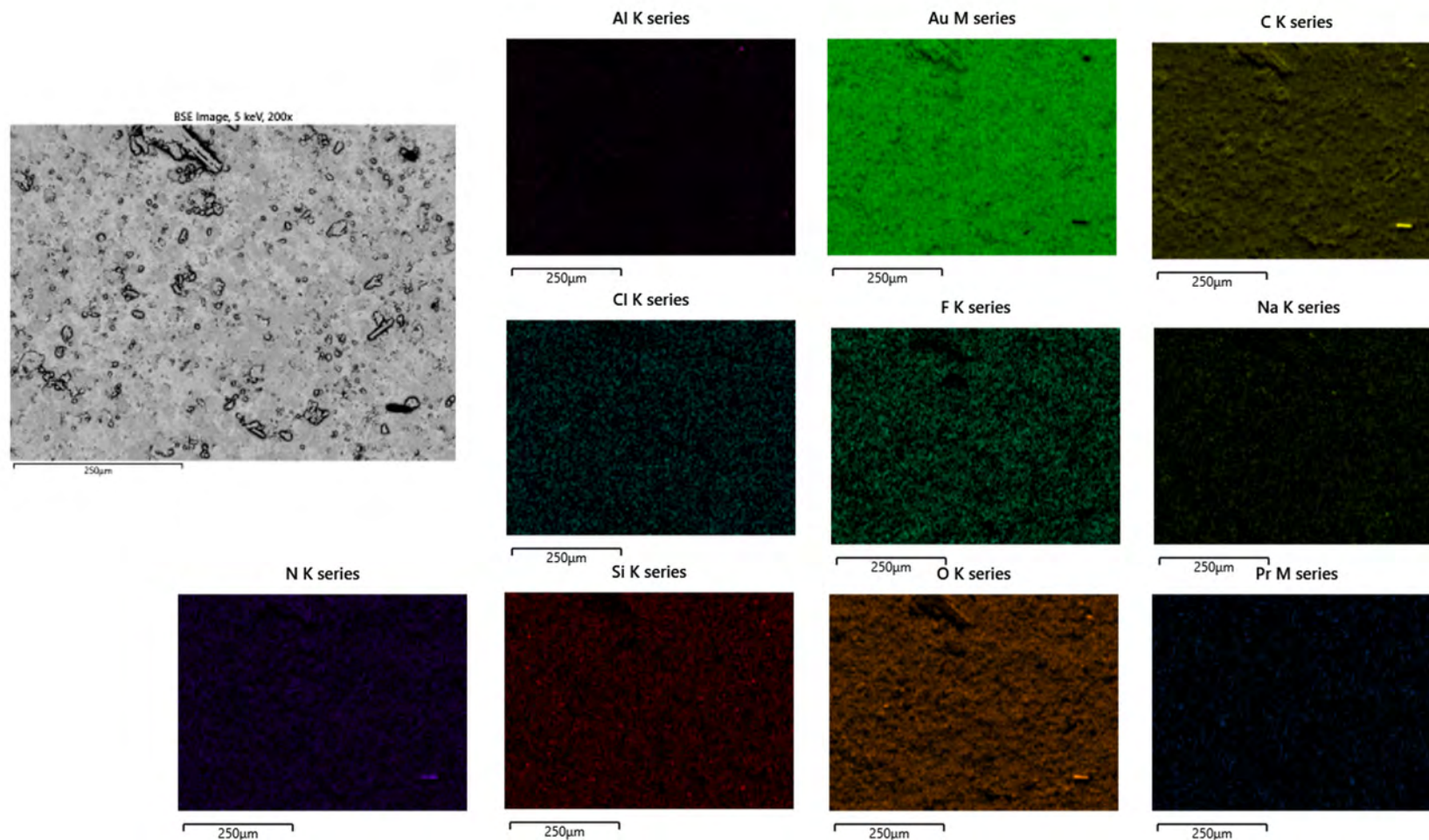


Figure C3: Sample 4, 200x SEM and EDS maps, 5 keV

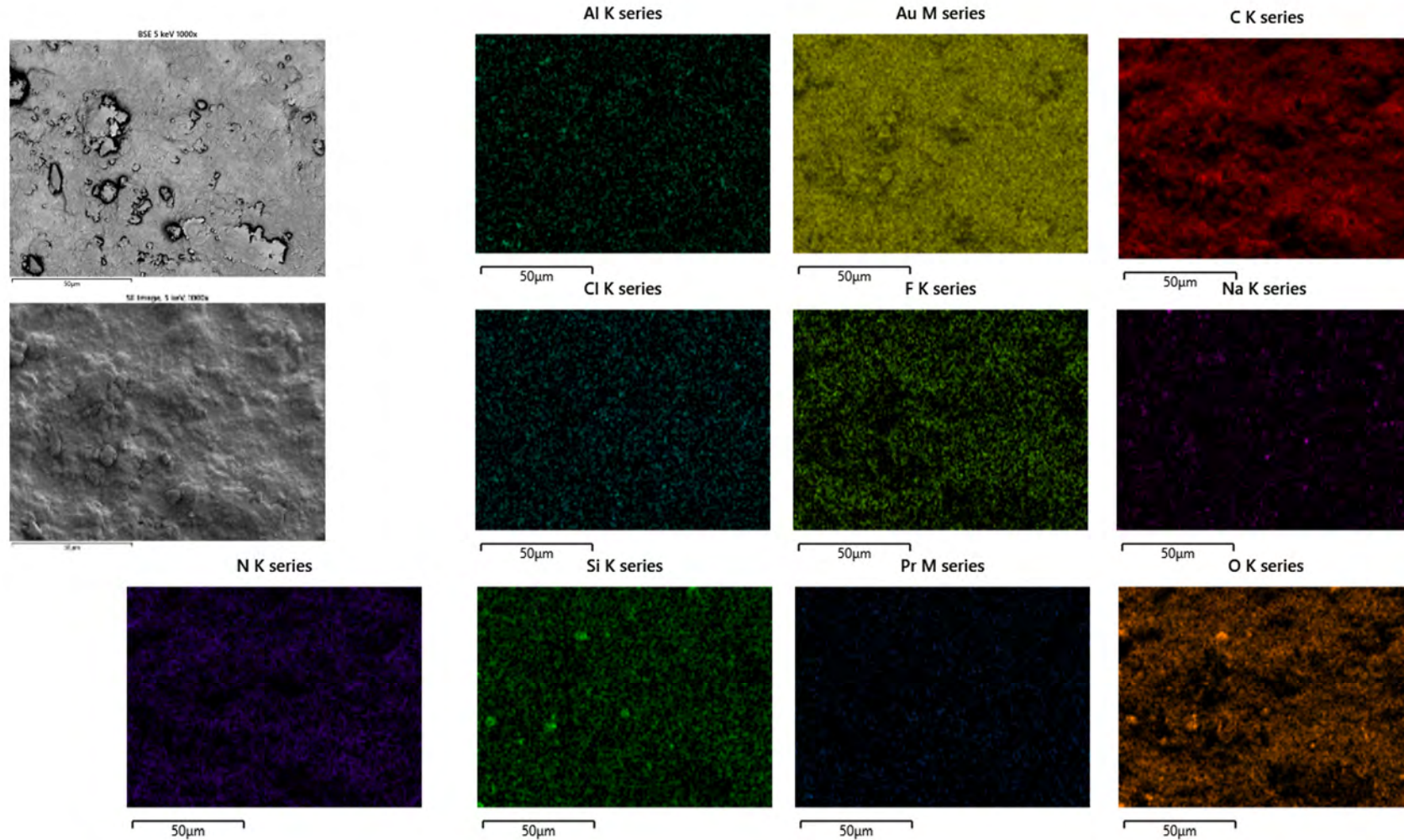


Figure C4: Sample 4, 1000x SEM and EDS maps, 5 keV

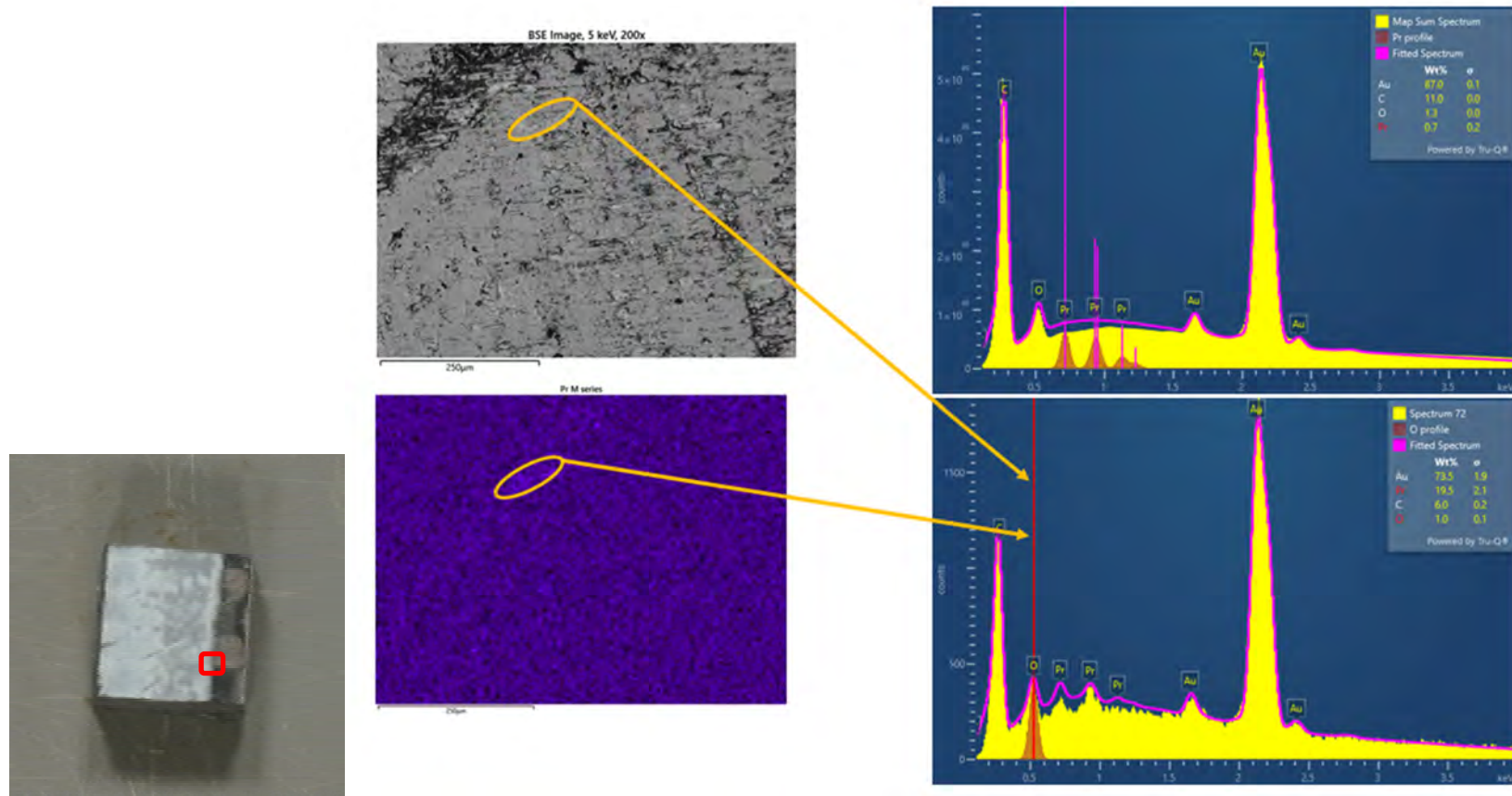


Figure C5: Piece of sample 5 used for SEM and EDS analysis (left), and Elemental Analysis of Entire Surface Area and SEM/EDS scans with indication of Praseodymium (right)

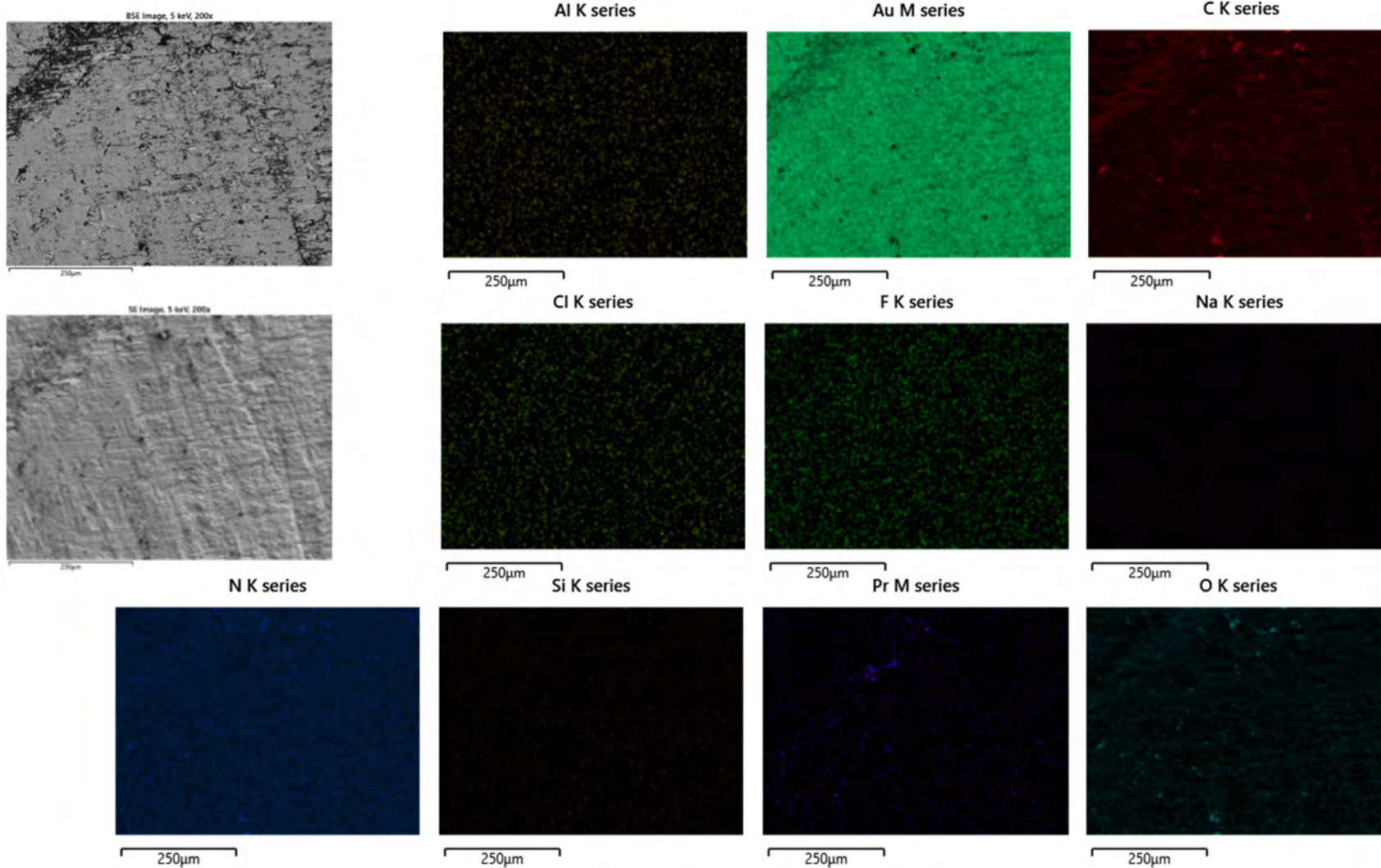


Figure C6: Sample 5, 200x SEM and EDS maps, 5 keV

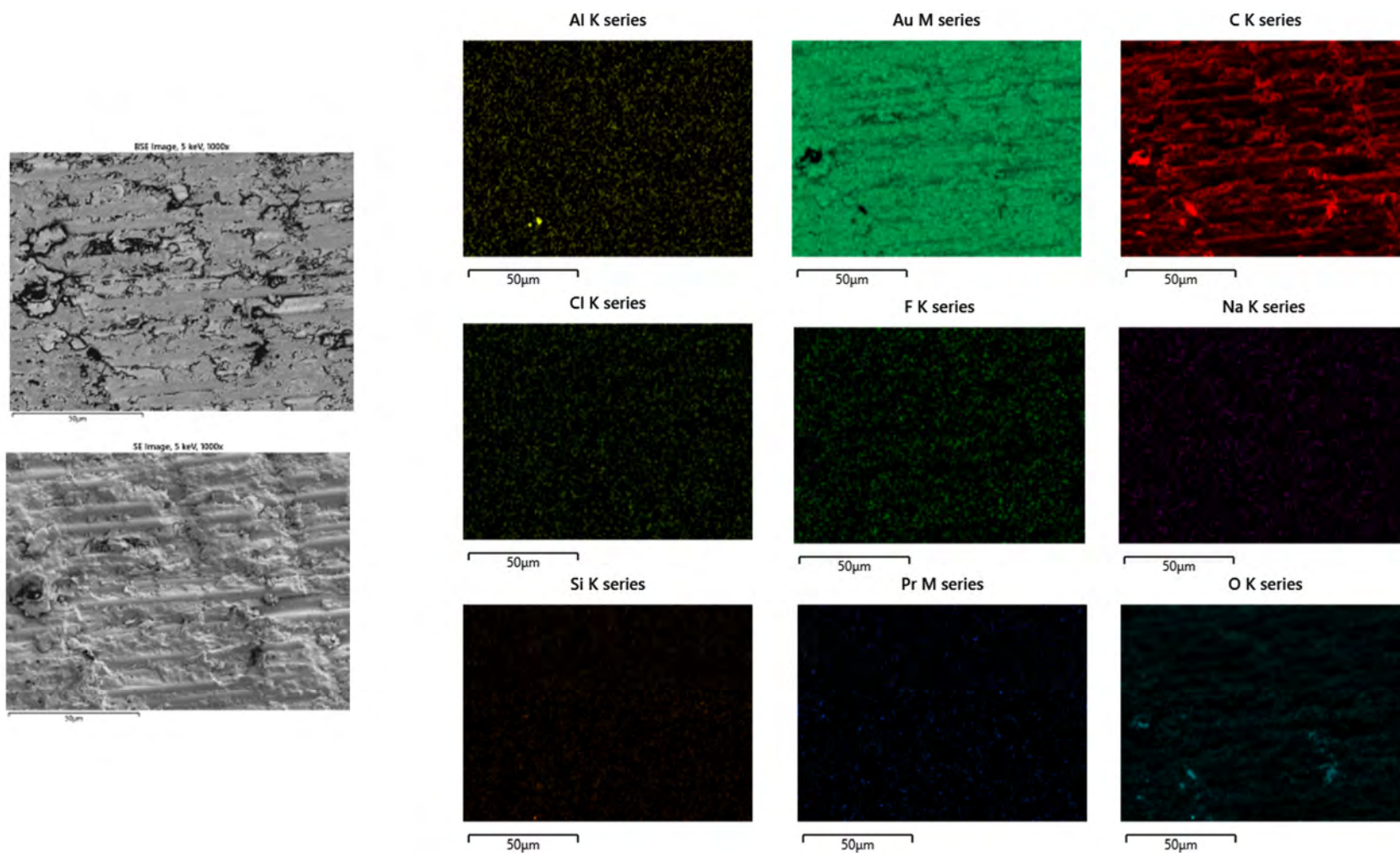


Figure C7: Sample 5, 1000x SEM and EDS maps, 5 keV

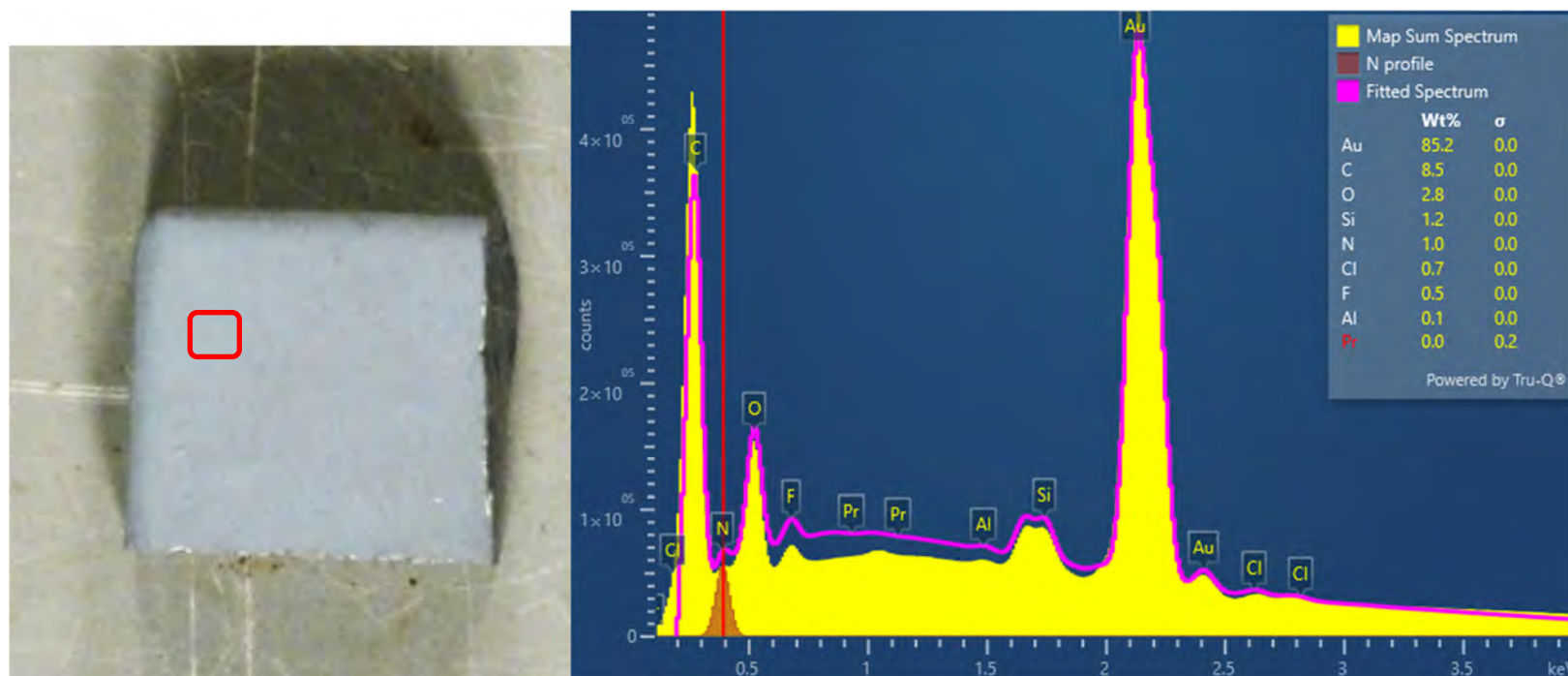


Figure C8: Piece of sample 8 used for SEM and EDS analysis (left), and Elemental Analysis of Entire Surface Area (right)

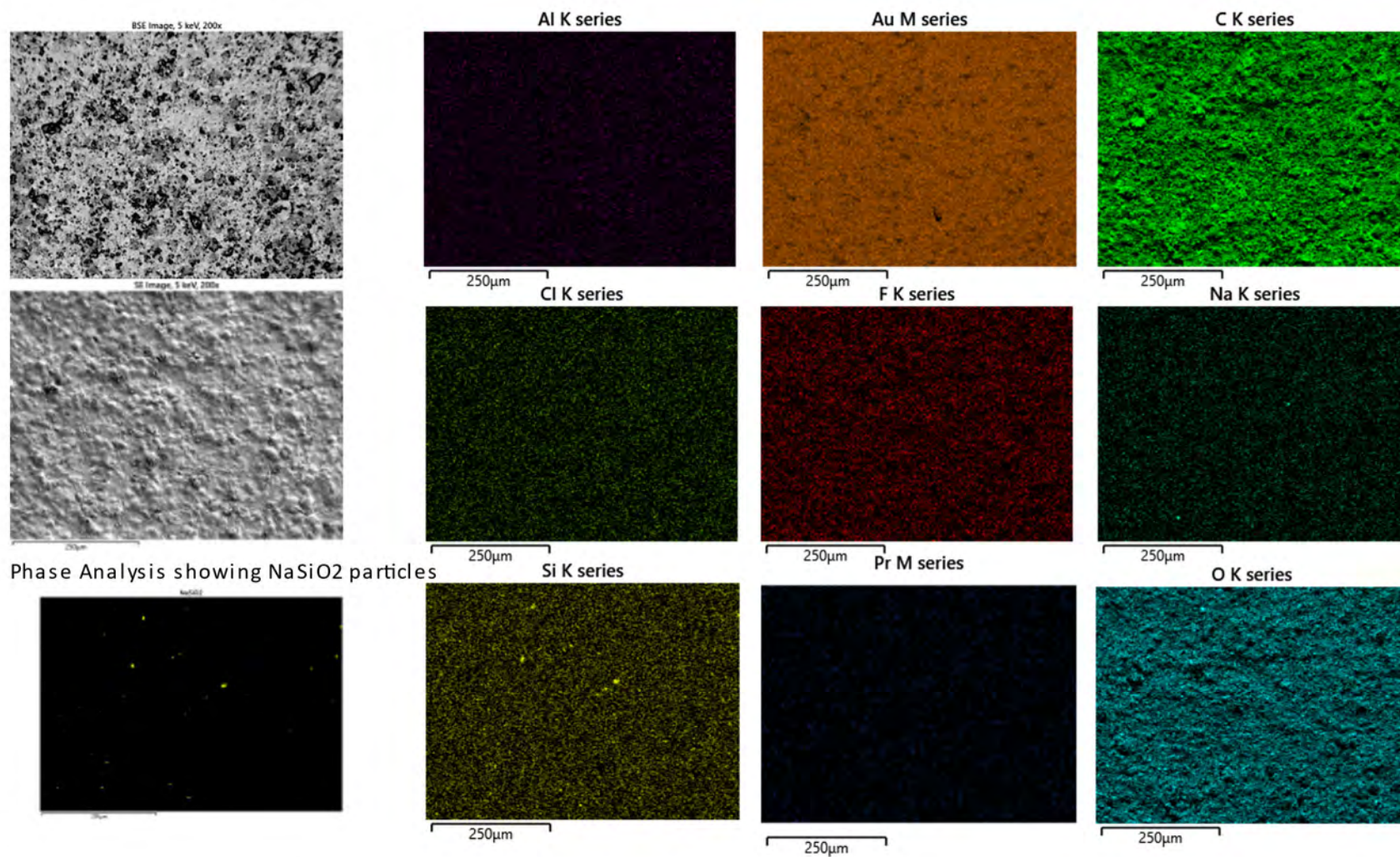


Figure C9: Sample 8, 200x SEM, EDS maps, and Phase Analysis showing NaSiO₂ particles, 5 keV

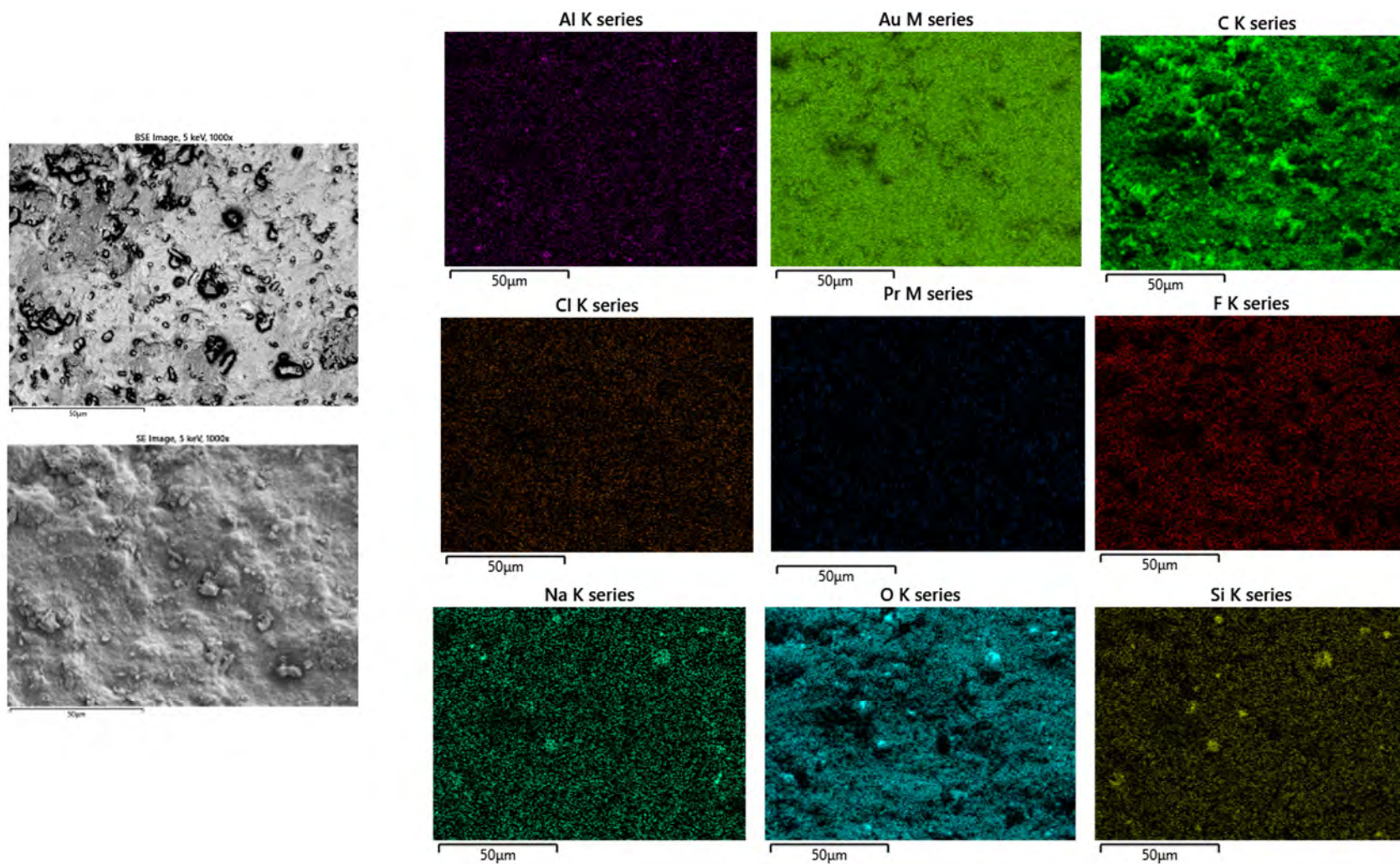


Figure C10: Sample 8, 1000x SEM and EDS maps, 5 keV

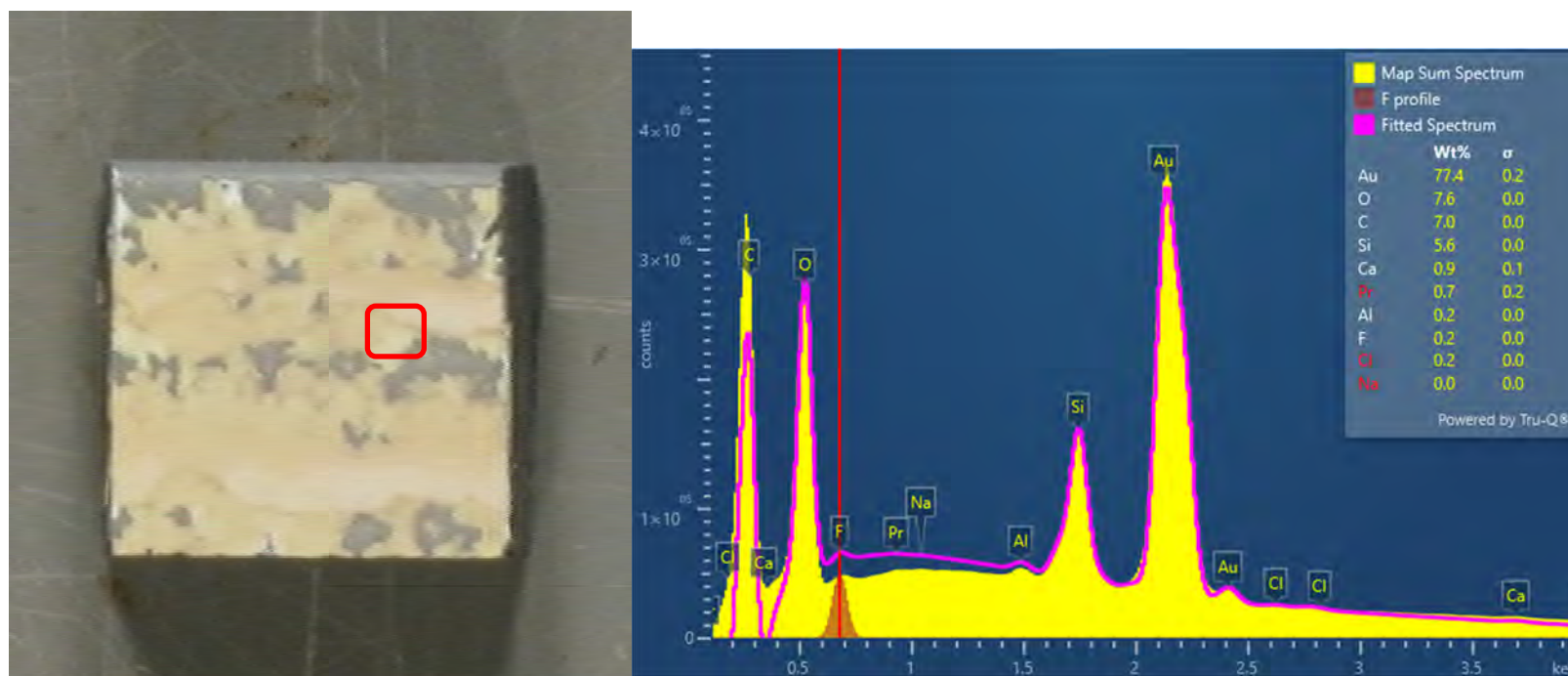


Figure C11: Piece of sample 9 used for SEM and EDS analysis (left), and Elemental Analysis of Entire Surface Area (right)

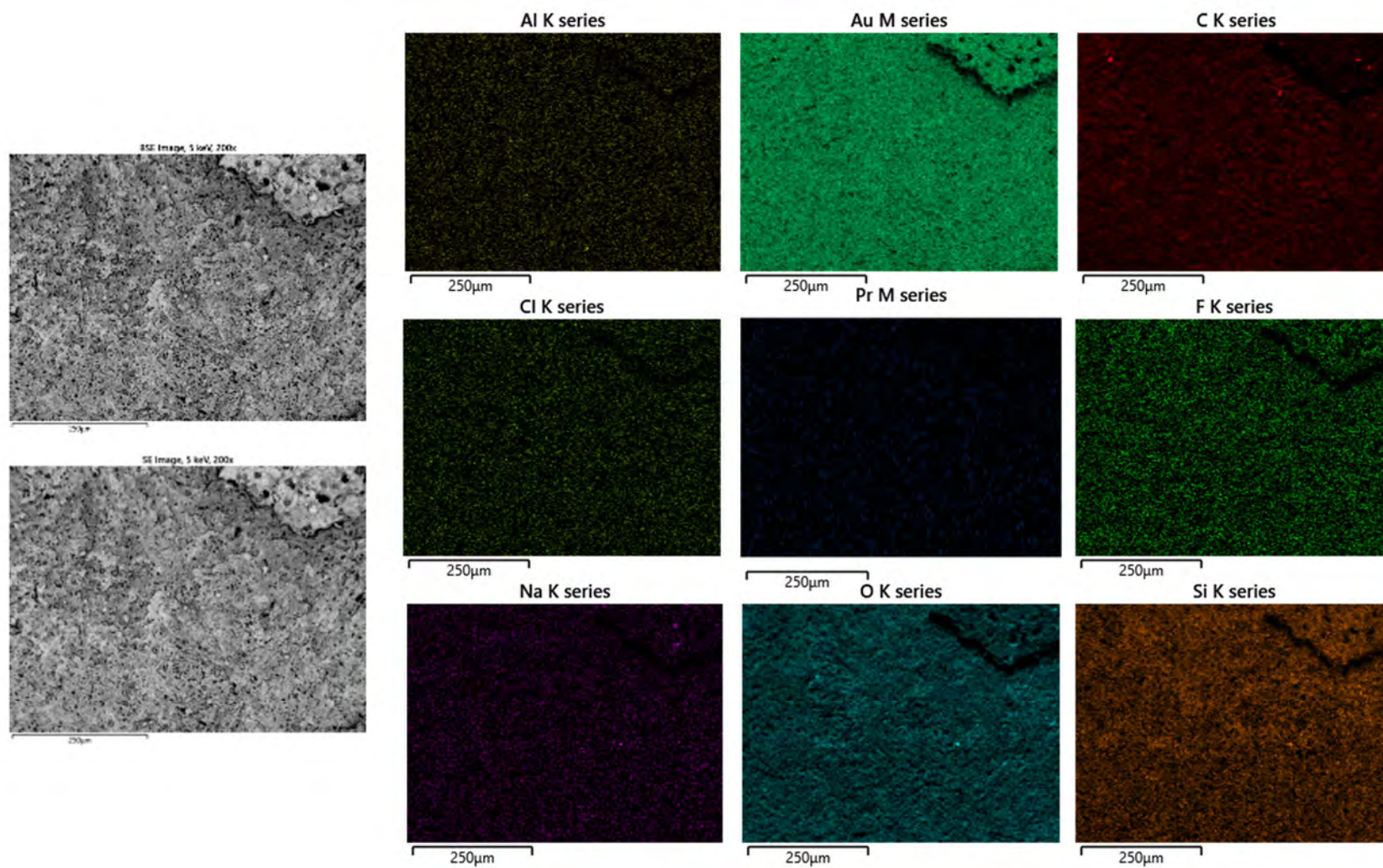


Figure C12: Sample 9, 200x SEM and EDS maps, 5 keV

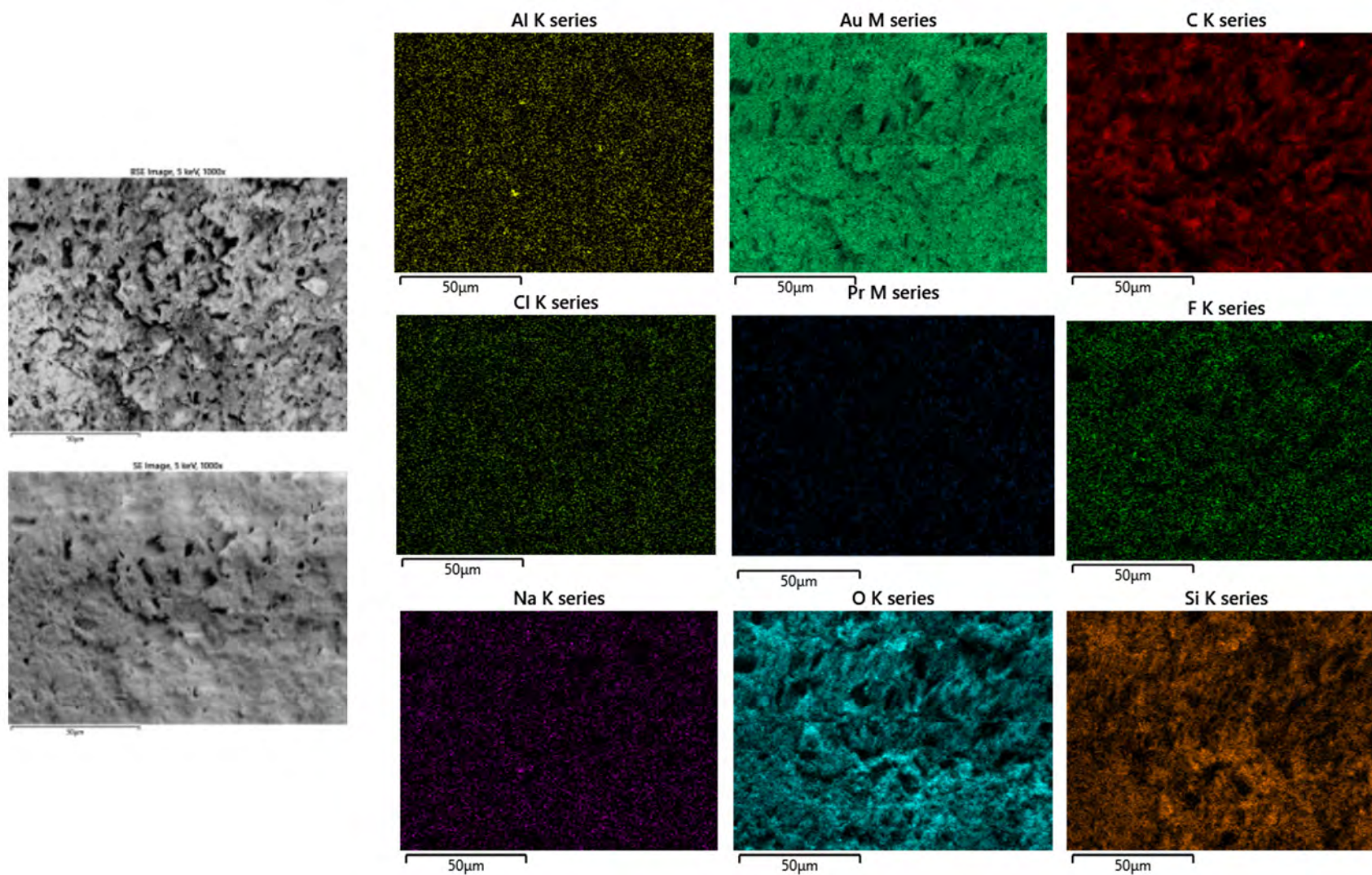


Figure C13: Sample 9, 1000x SEM and EDS maps, 5 keV

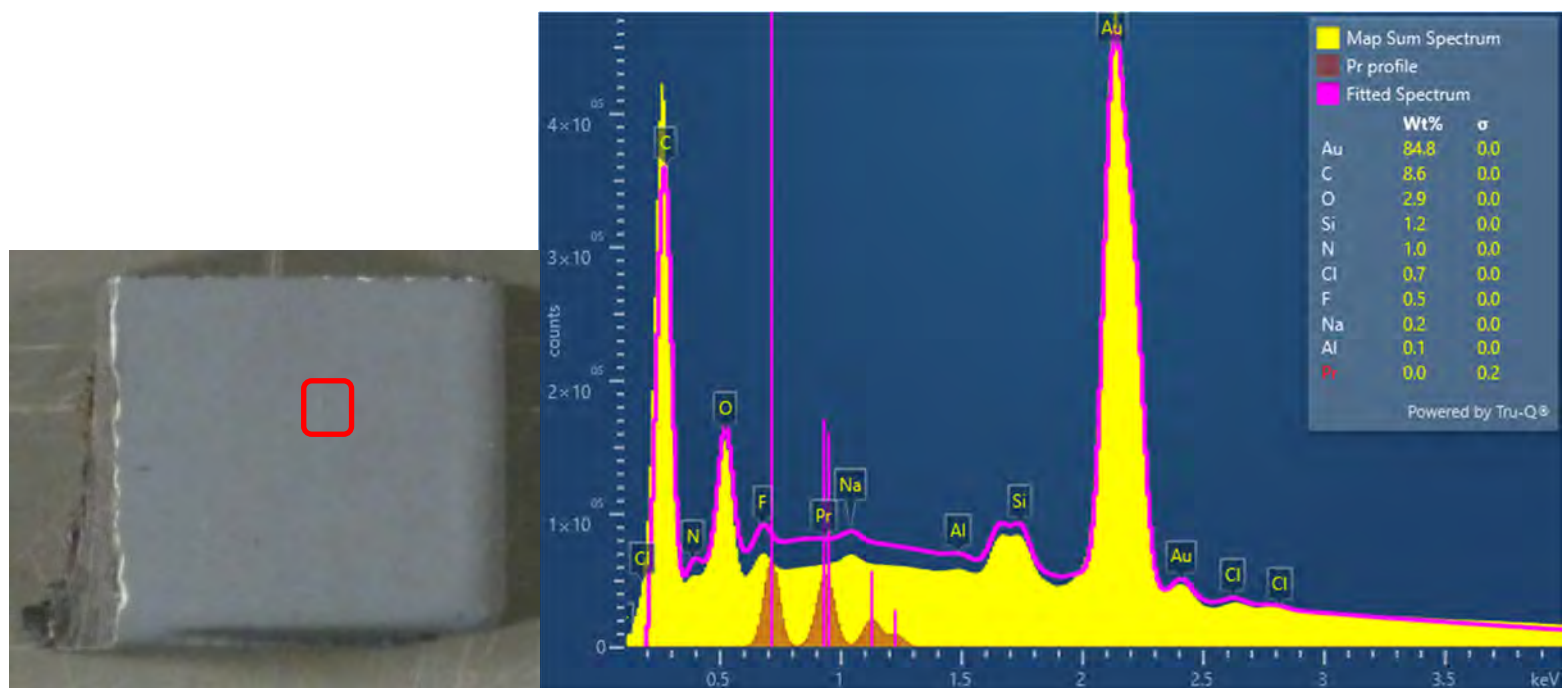


Figure C14: Piece of sample 12 used for SEM and EDS analysis (left), and Elemental Analysis of Entire Surface Area (right)

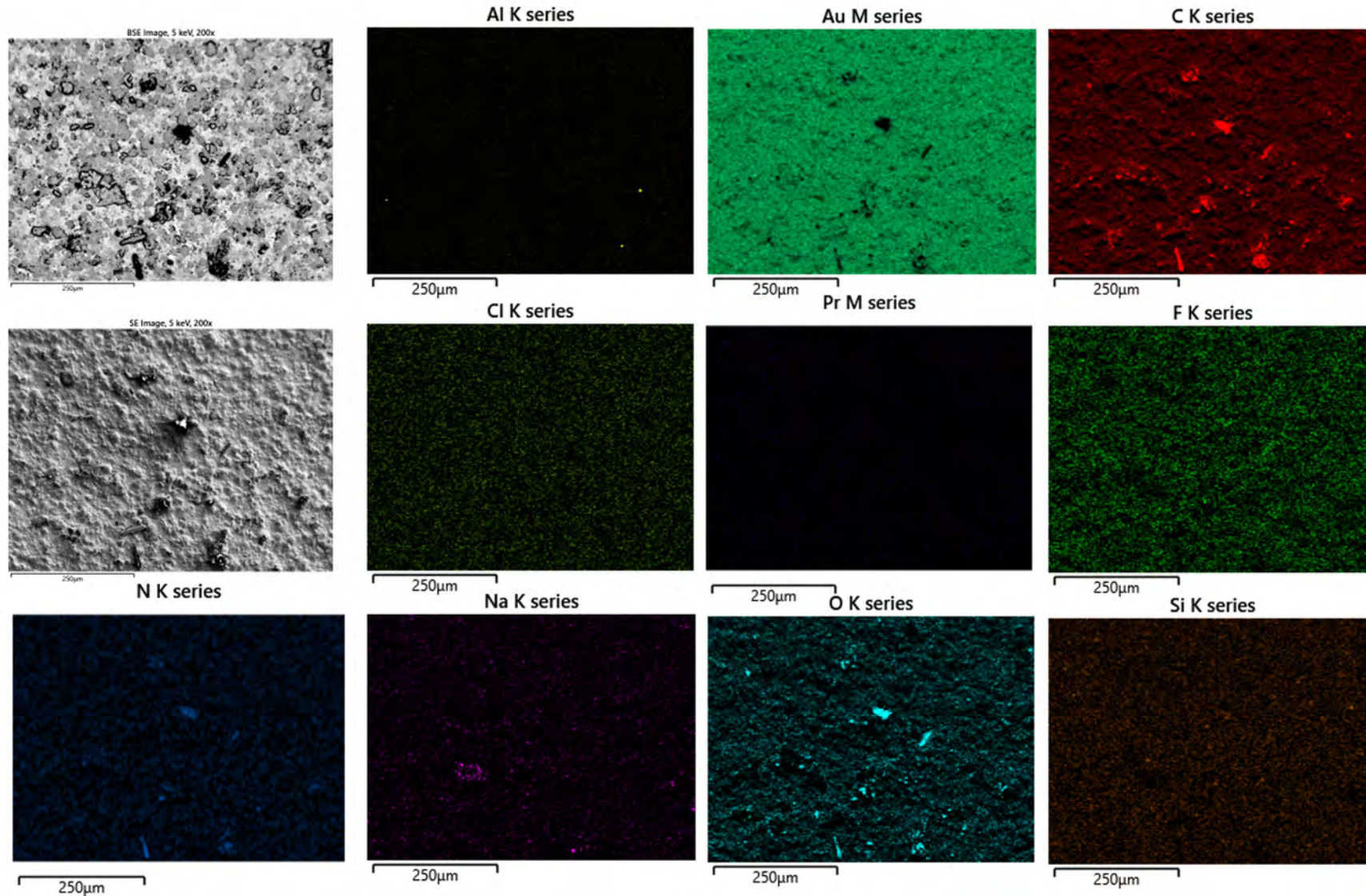


Figure C15: Sample 12, 200x SEM and EDS maps, 5 keV

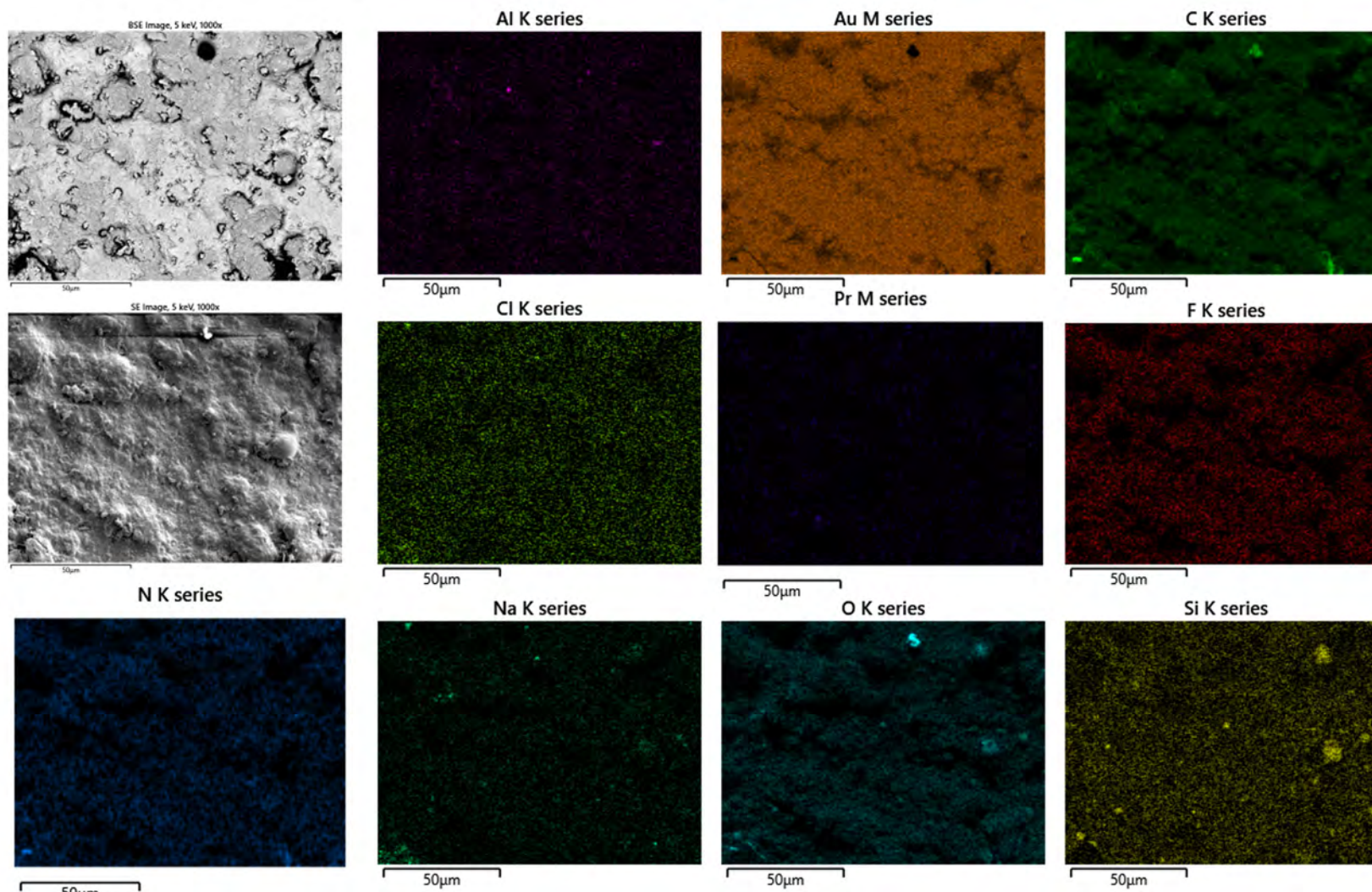


Figure C16: Sample 12, 1000x SEM and EDS maps, 5 keV

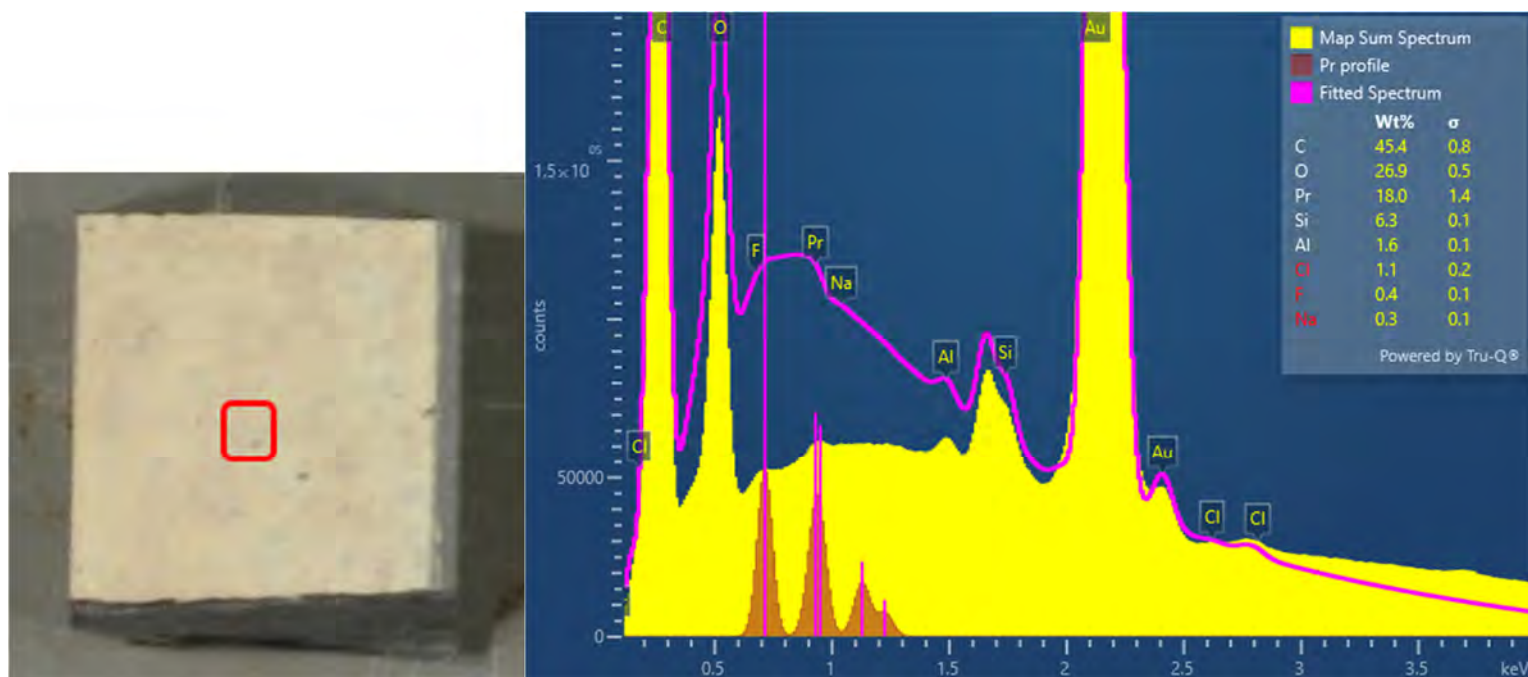


Figure C17: Piece of sample 13 used for SEM and EDS analysis (left), and Elemental Analysis of Entire Surface Area (right)

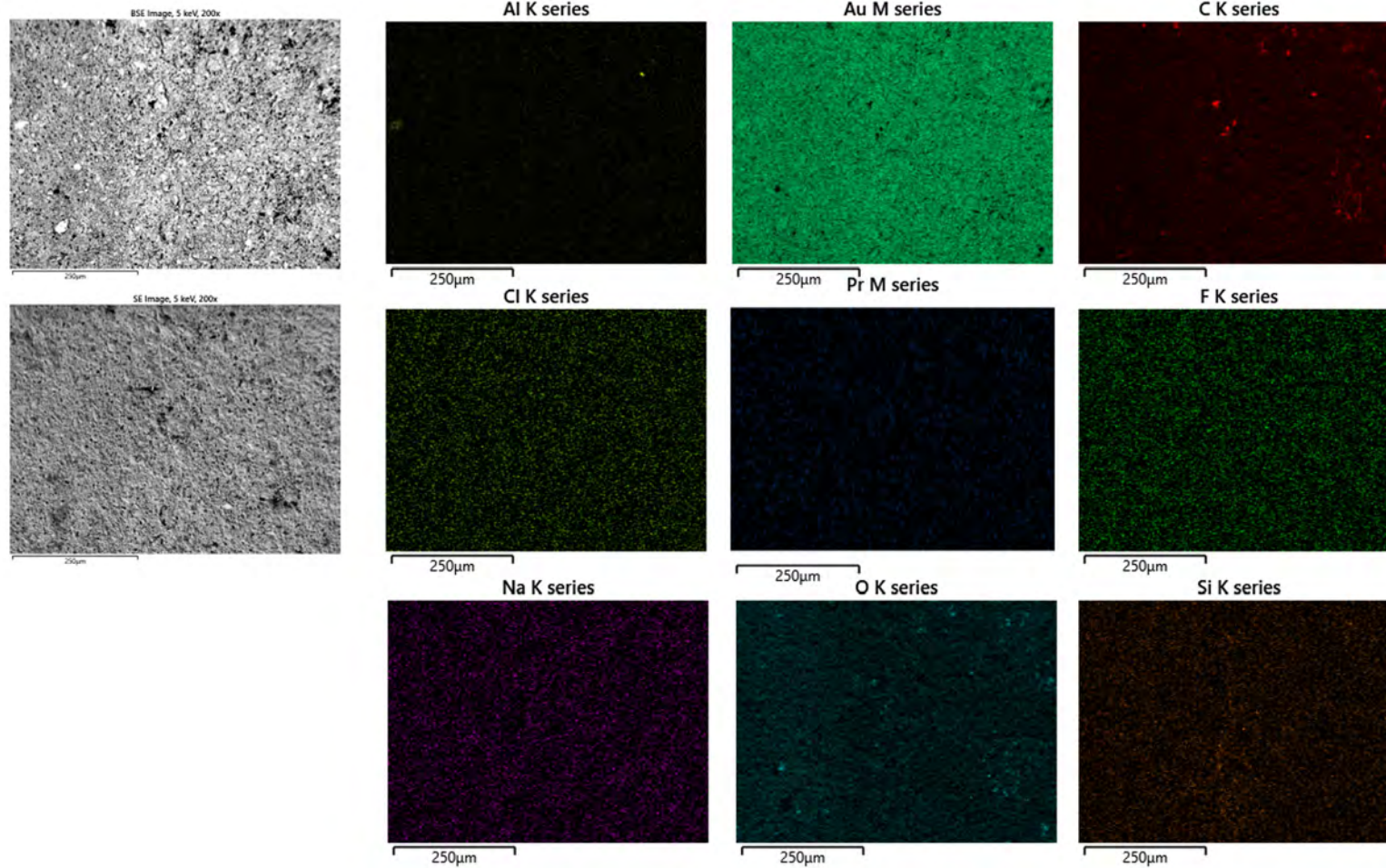


Figure C18: Sample 13, 200x SEM and EDS maps, 5 keV

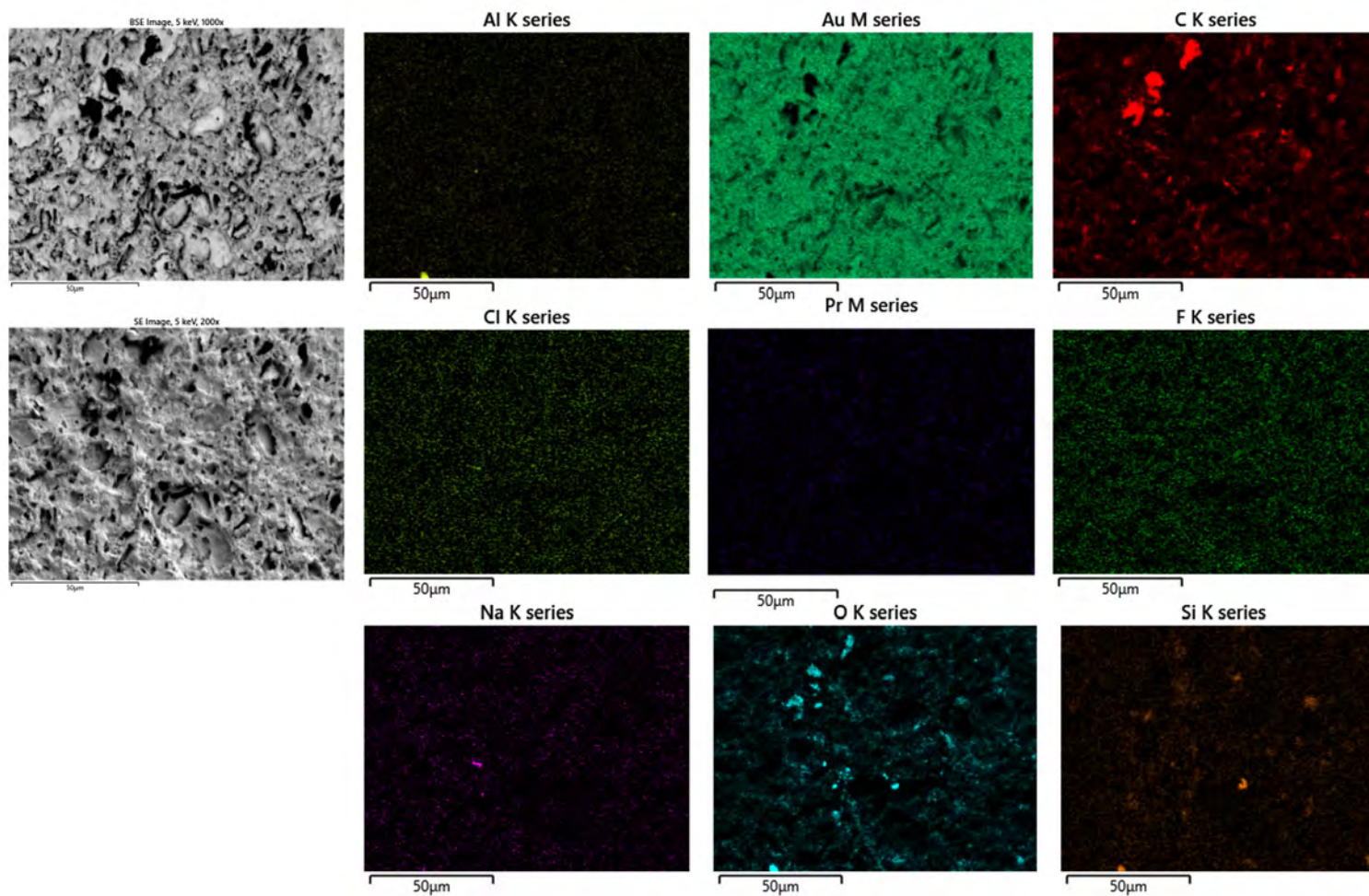


Figure C19: Sample 13, 1000x SEM and EDS maps, 5 keV

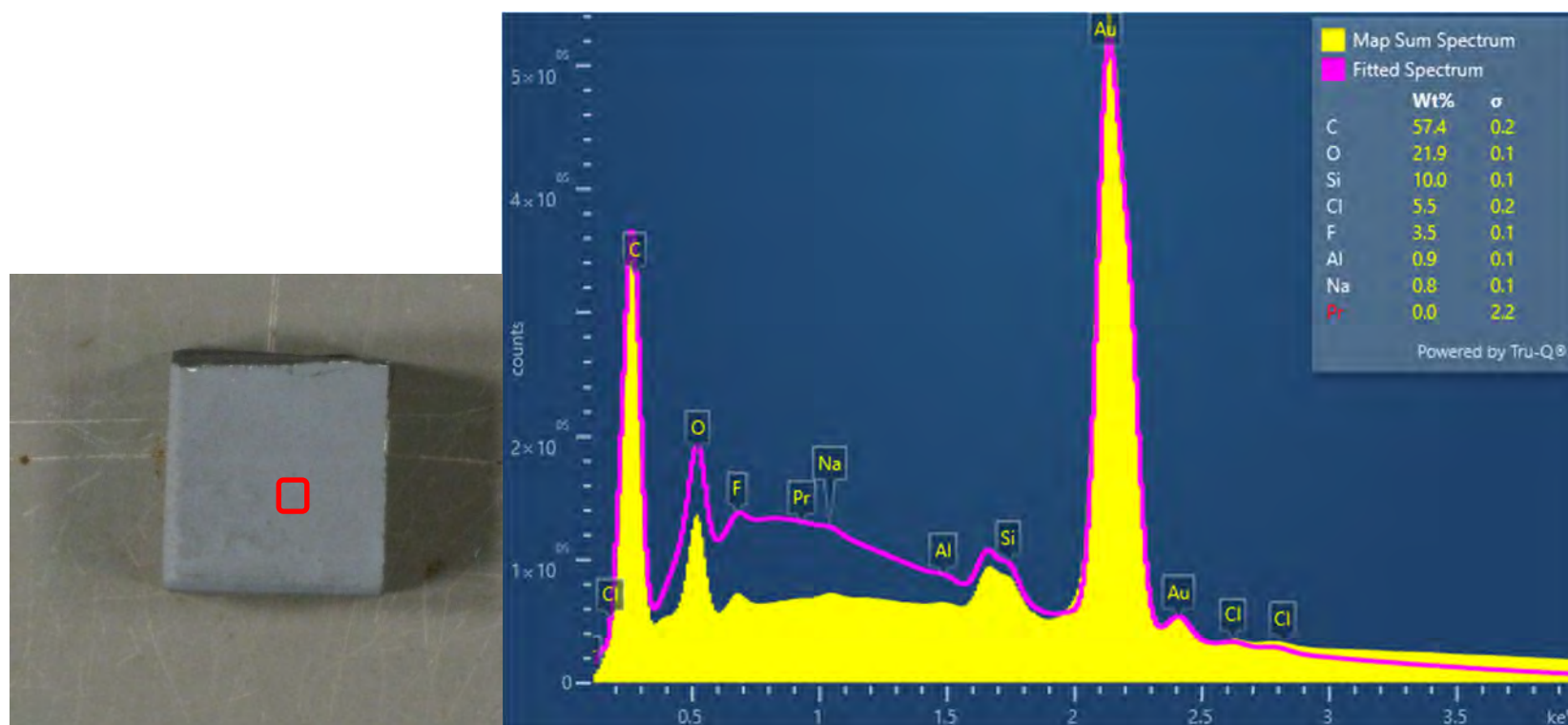


Figure C20: Piece of sample 16 used for SEM and EDS analysis (left), and Elemental Analysis of Entire Surface Area (right)

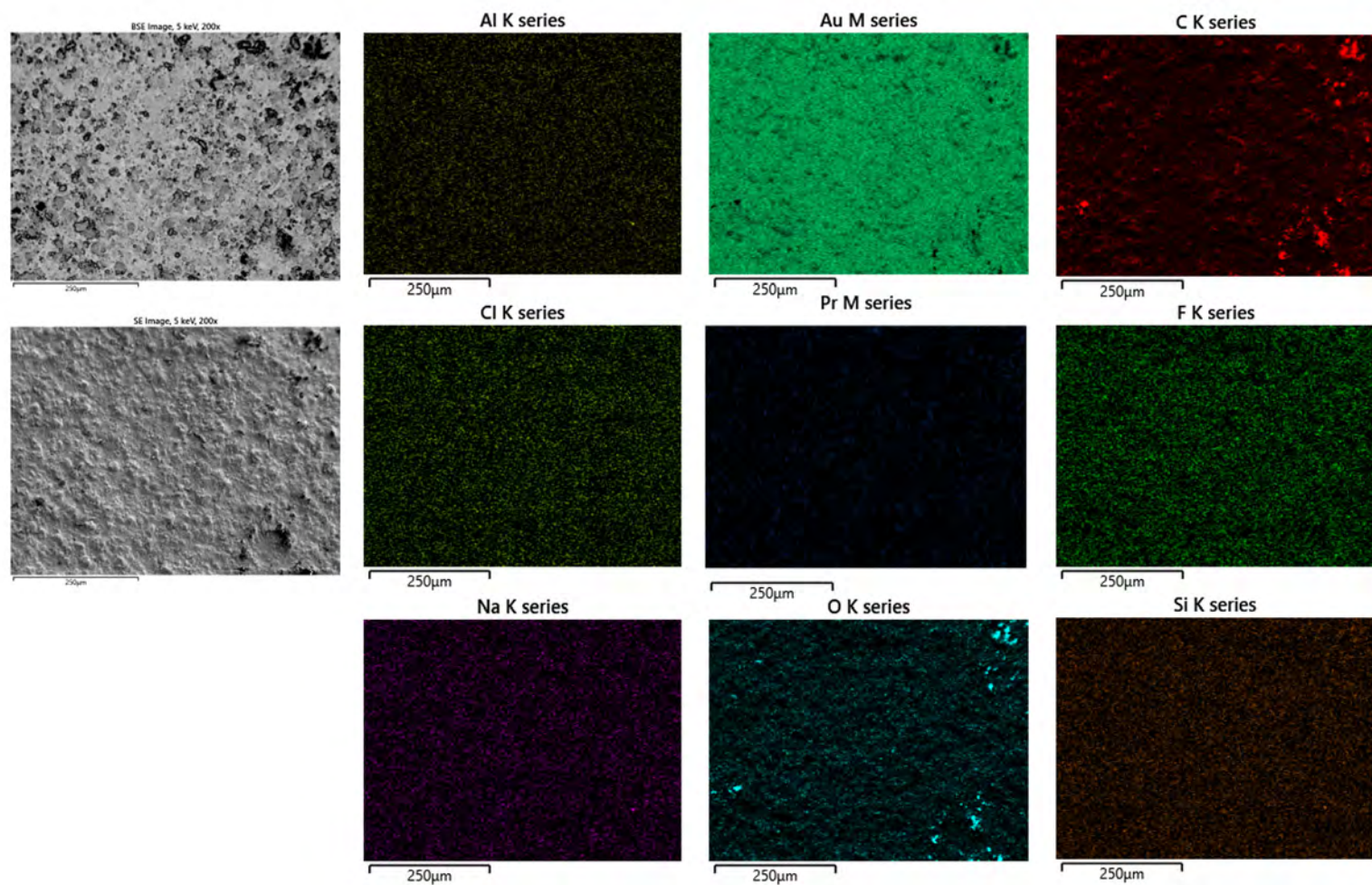


Figure C21: Sample 16, 200x SEM and EDS maps, 5 keV

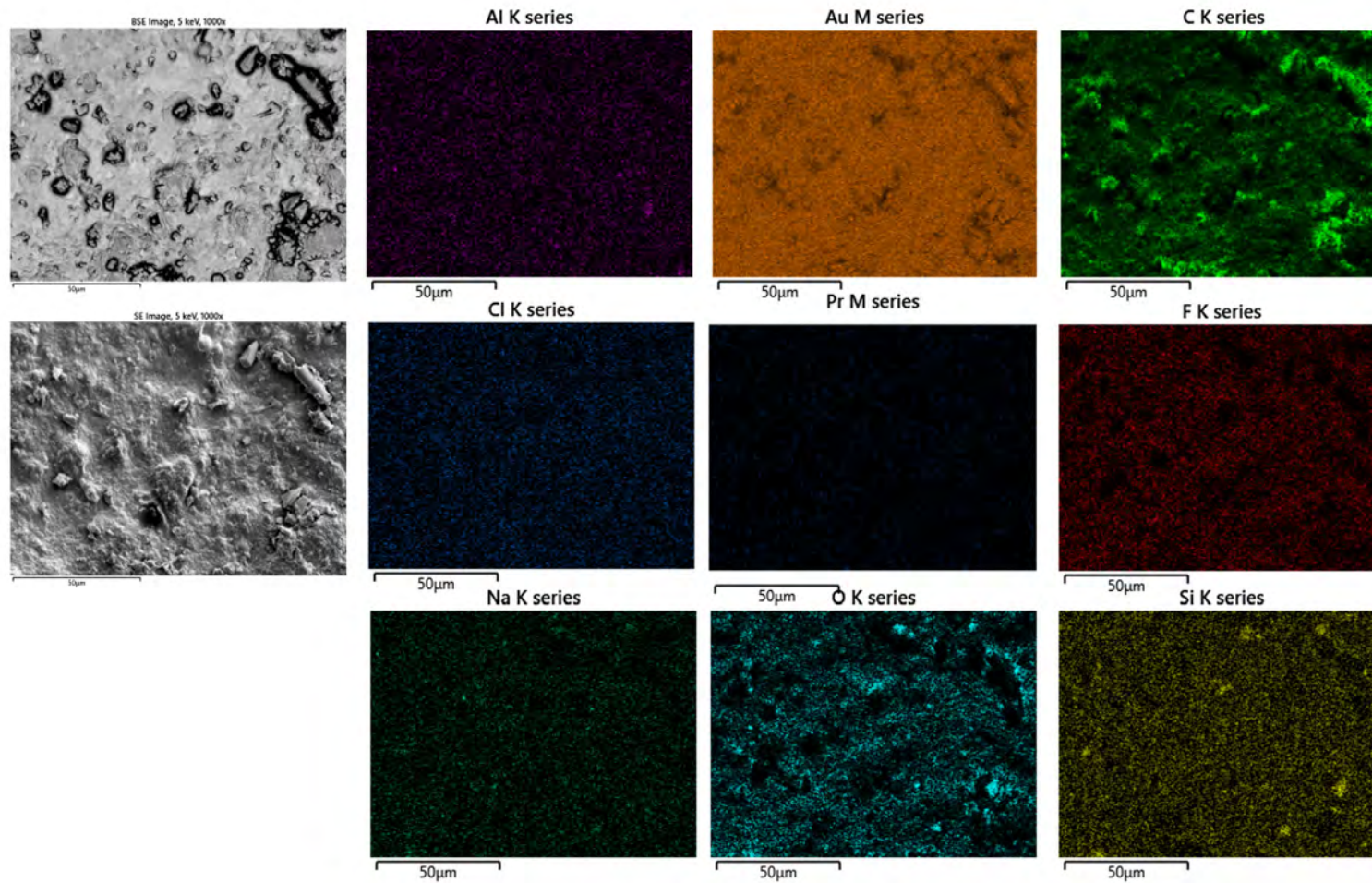


Figure C22: Sample 16, 1000x SEM and EDS maps, 5 keV

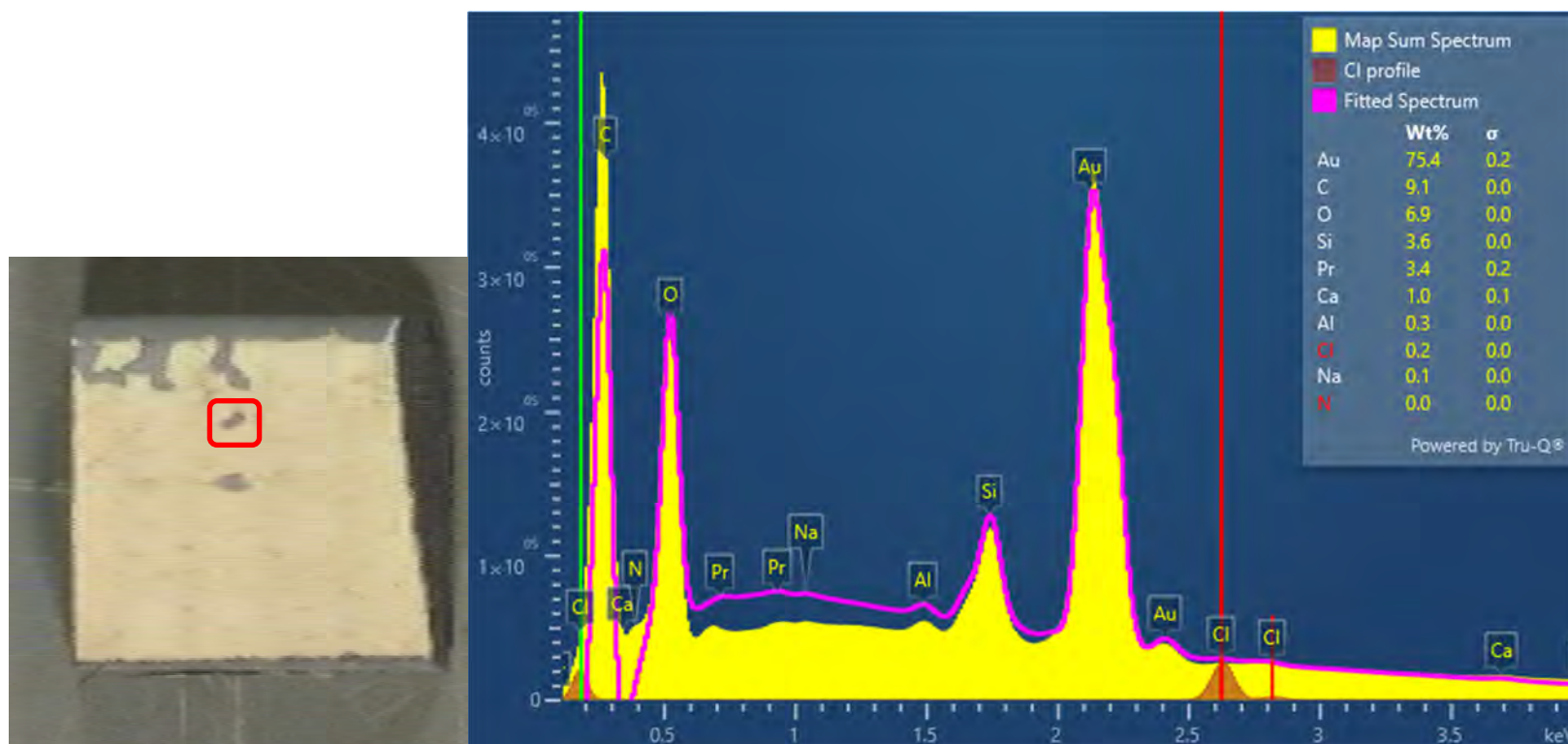


Figure C23: Piece of sample 17 used for SEM and EDS analysis (left), and Elemental Analysis of Entire Surface Area (right)

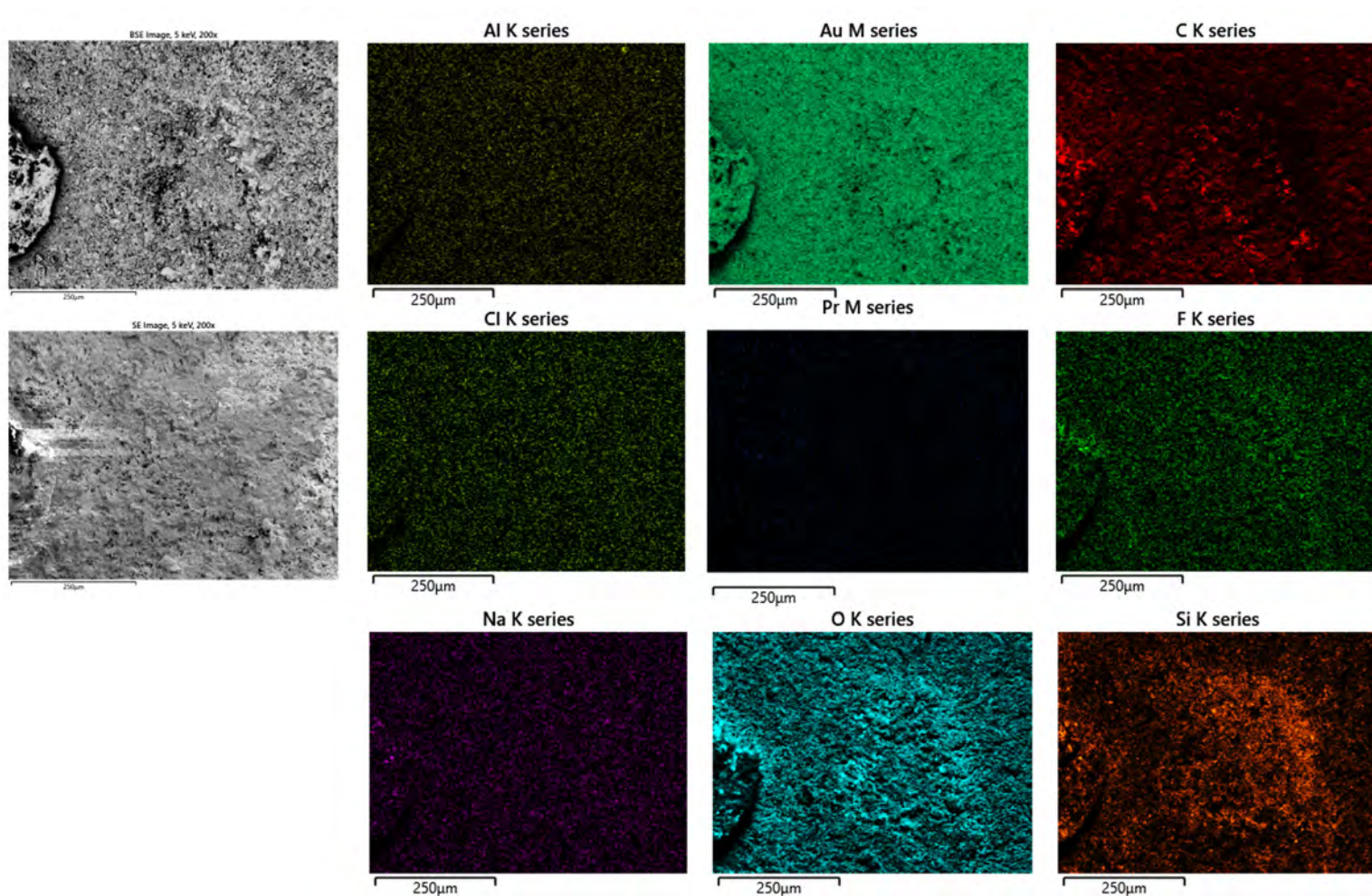


Figure C24: Sample 17, 200x SEM and EDS maps, 5 keV

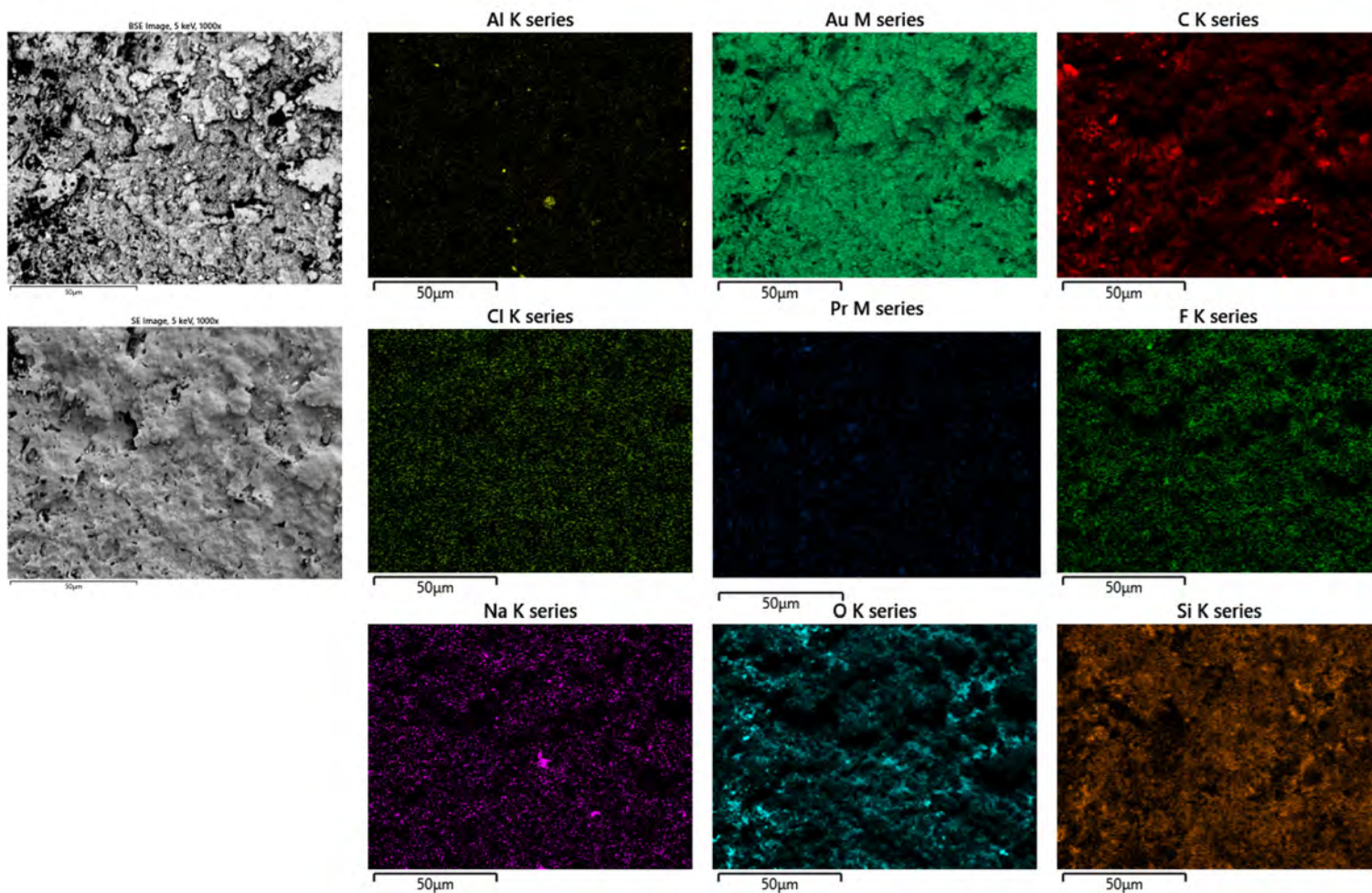


Figure C25: Sample 17, 1000x SEM and EDS maps, 5 keV

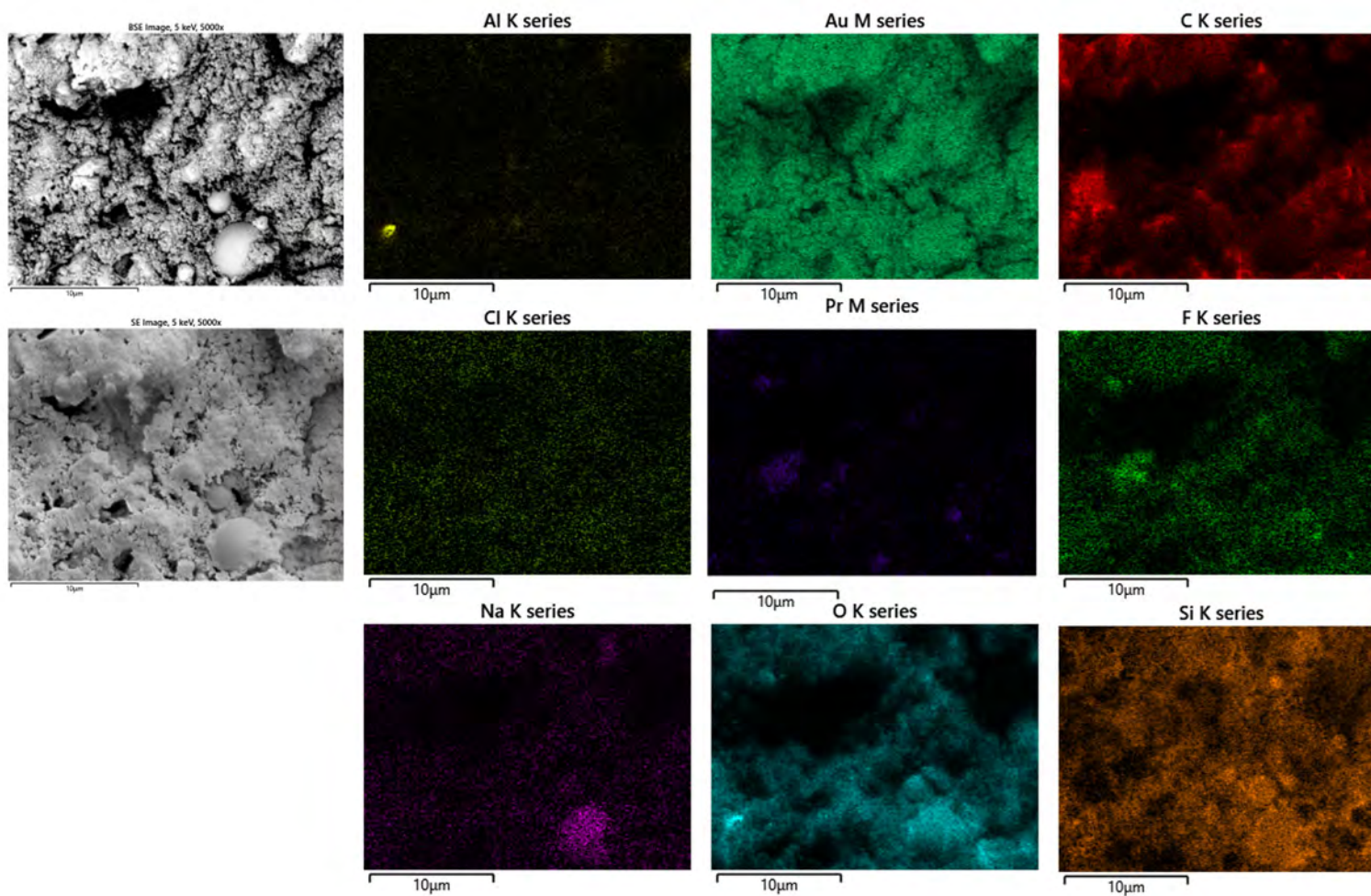
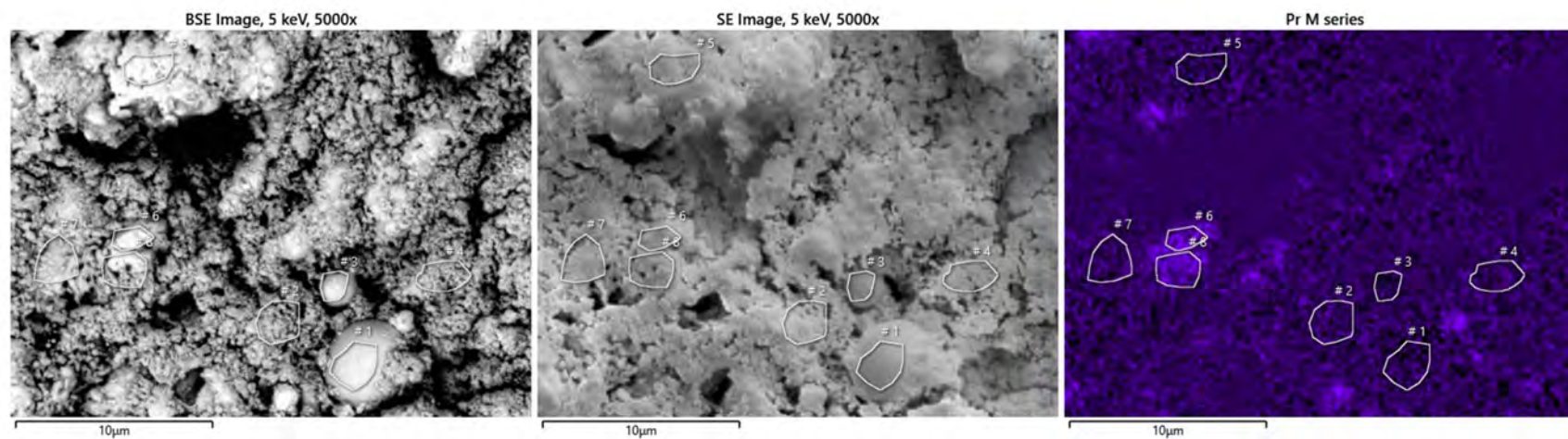
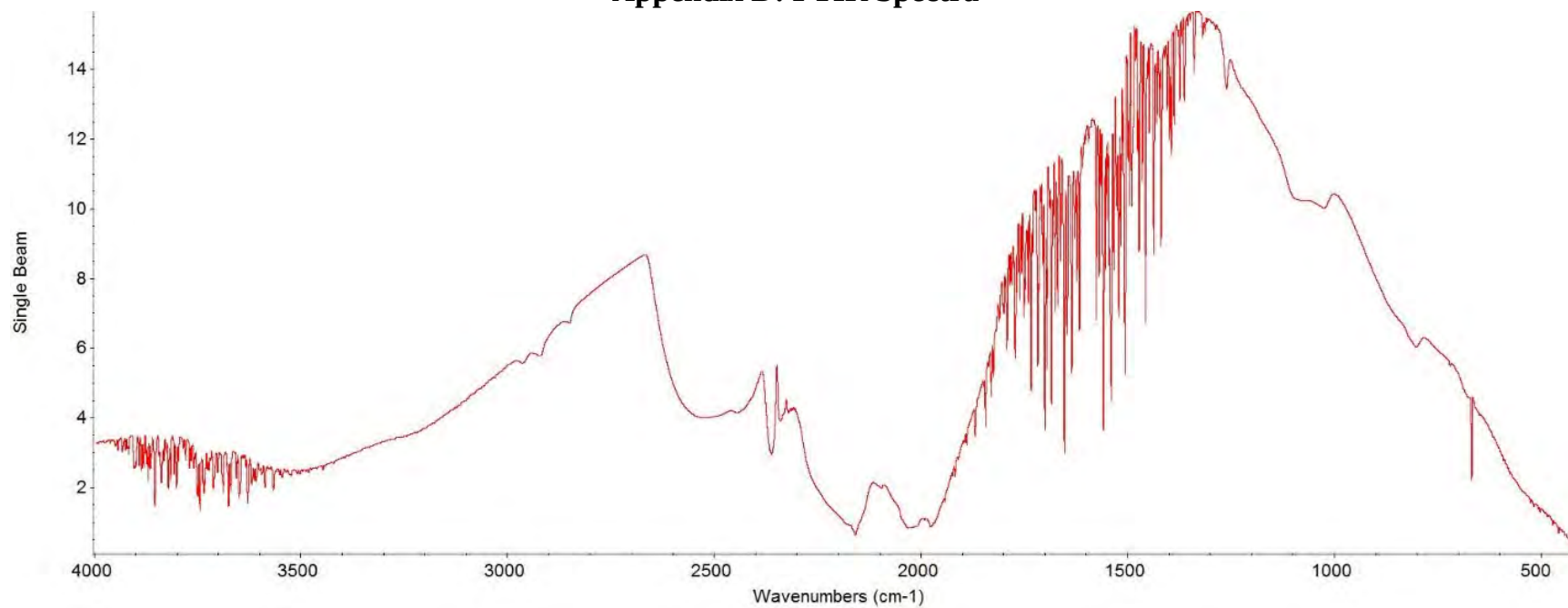


Figure C26: Sample 17, 5000x SEM and EDS maps, 5 keV



Spectrum Label	C	O	Na	Al	Si	Cl	Pr	Au
Map Sum Spectrum	4.56	6.63	0.17	0.39	6.56	0.24	4.80	76.66
# 1	1.98	10.95	1.88	0.18	8.30	0.09	0.38	76.25
# 2	4.08	9.64	0.17	0.83	6.07	0.00	5.84	73.37
# 3	2.14	12.90	0.55	0.24	10.16	0.16	0.00	73.86
# 4	7.18	6.34	0.00	0.25	5.66	0.00	1.34	79.23
# 5	5.56	4.65	0.04	0.10	4.06	0.53	1.67	83.39
# 6	1.19	3.93	0.00	0.00	1.20	0.00	34.62	59.05
# 7	14.04	4.04	0.08	0.10	2.07	0.32	1.99	77.36
# 8	1.68	4.62	0.00	0.13	2.07	0.39	32.71	58.41

Figure C27: Sample 17, 5000x SEM and EDS maps, 5 keV, with Elemental analysis of several selected spots

Appendix D: FTIR Spectra*Figure D1: FTIR Background Spectrum*

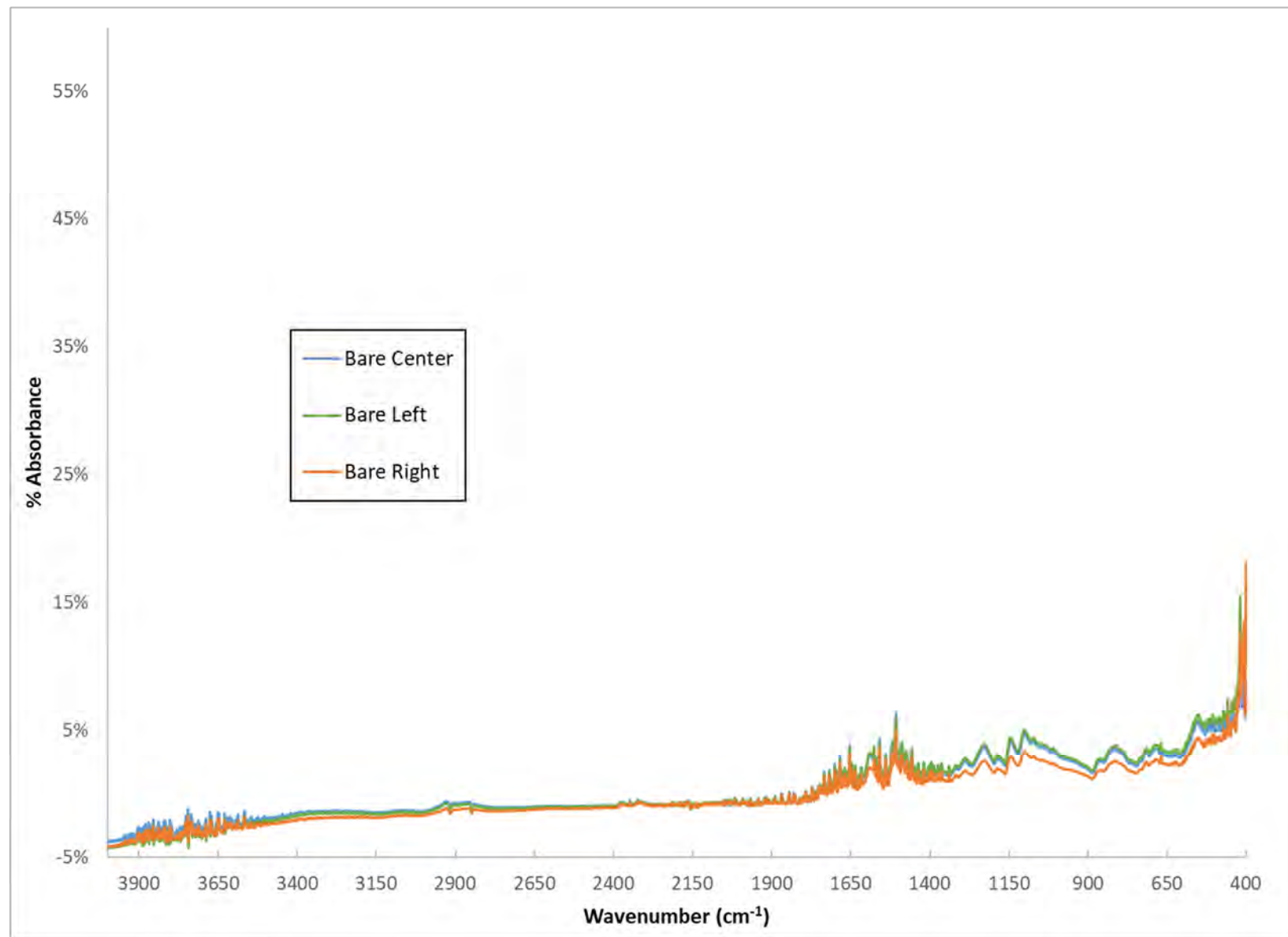


Figure D2: FTIR spectra of Bare Specimen

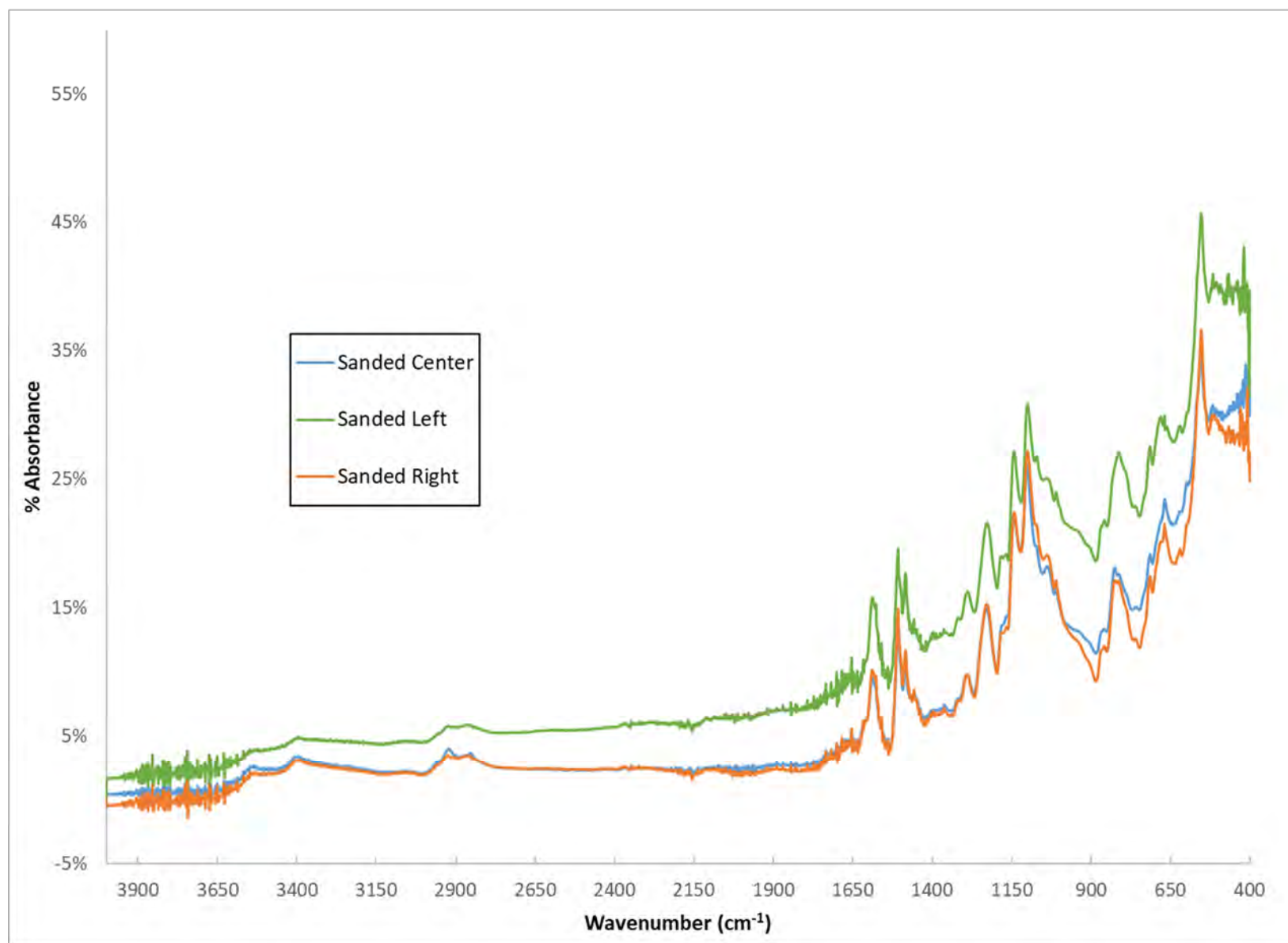


Figure D3: FTIR spectra of Sanded, Sample 5

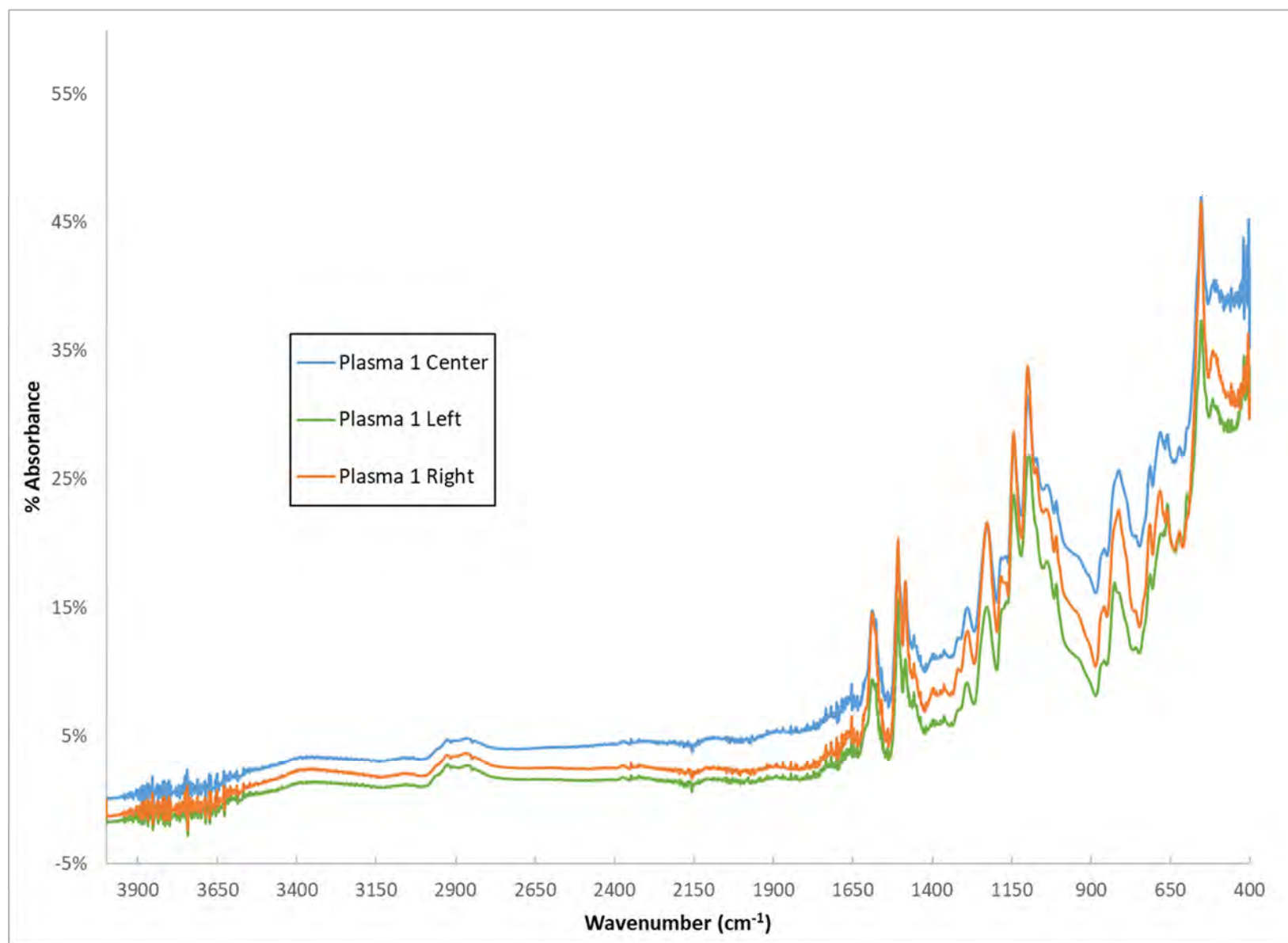


Figure D4: FTIR spectra of Plasma 1, Sample 9

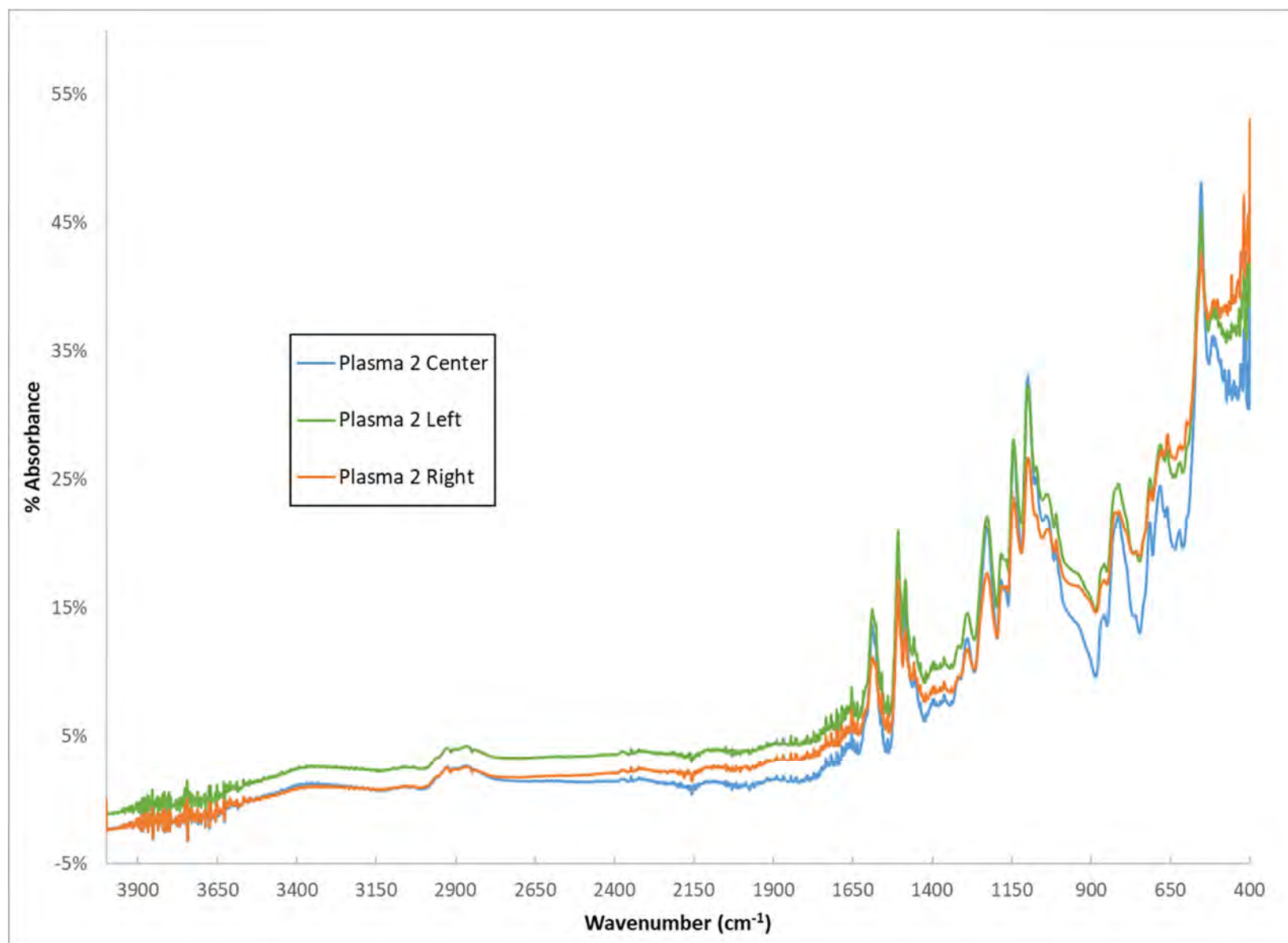


Figure D5: FTIR Spectra of Plasma 2, Sample 13

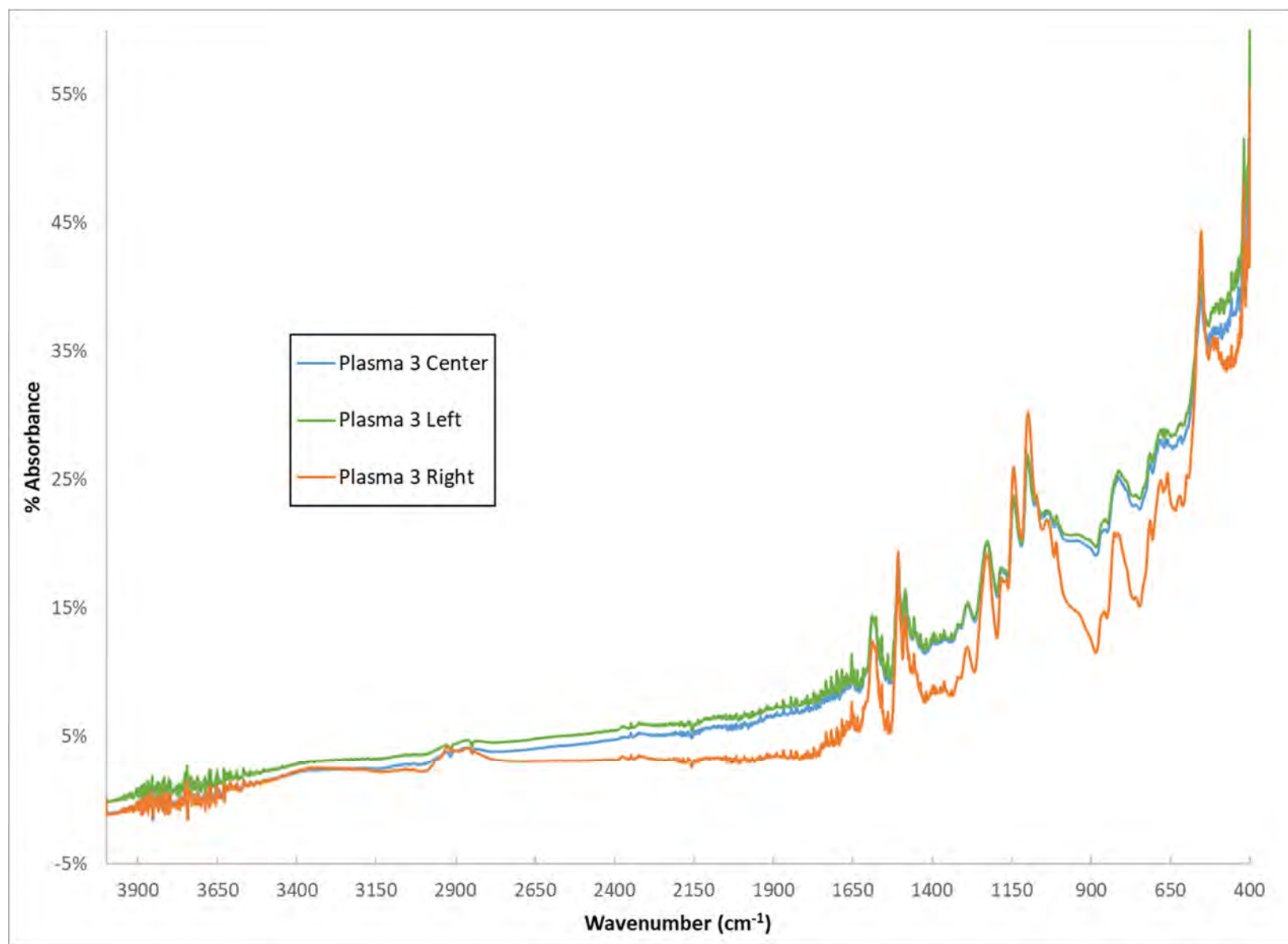
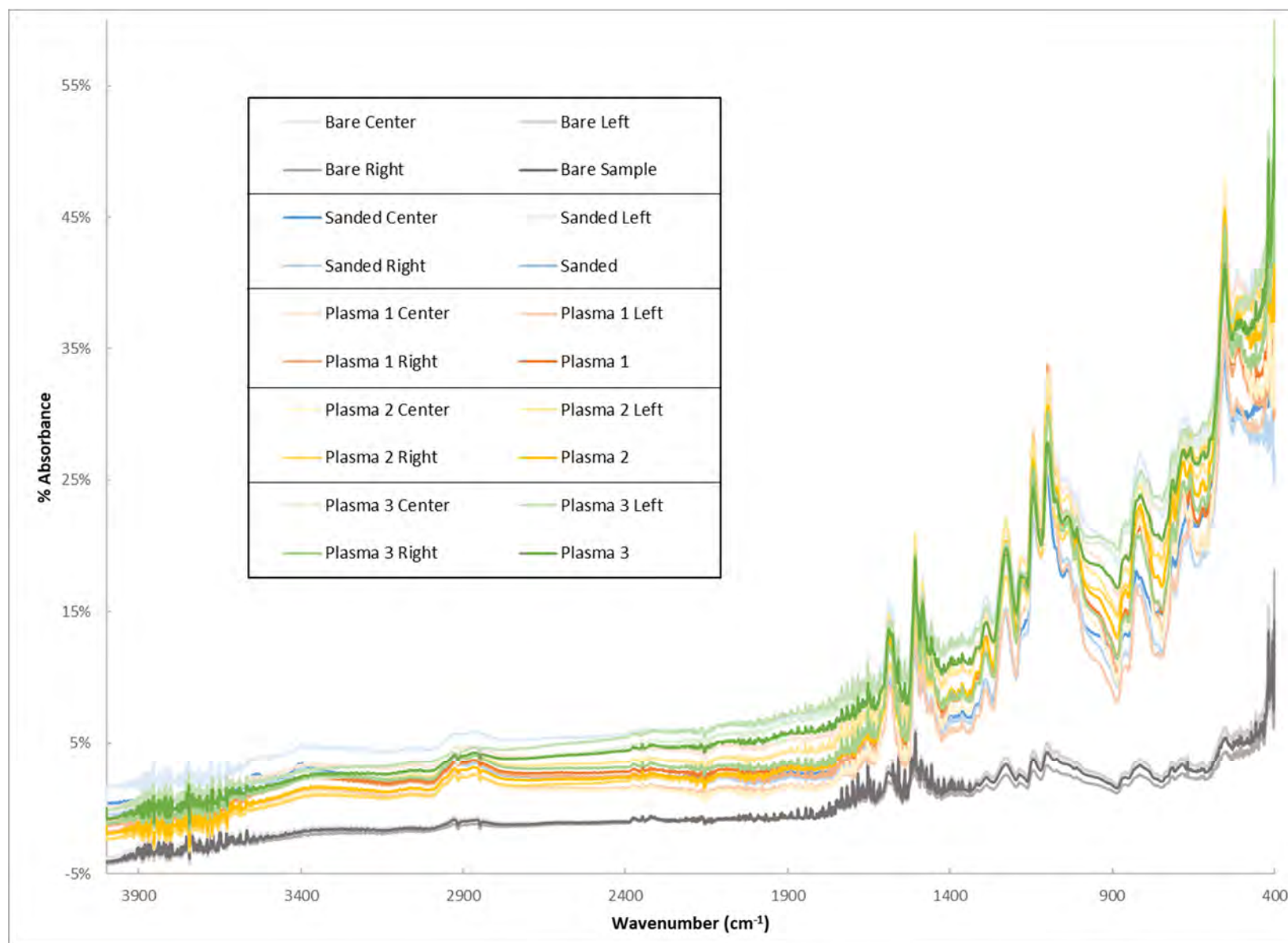


Figure D6: FTIR Spectra of Plasma 3, Sample 17

*Figure D7: FTIR Spectra of all Samples*

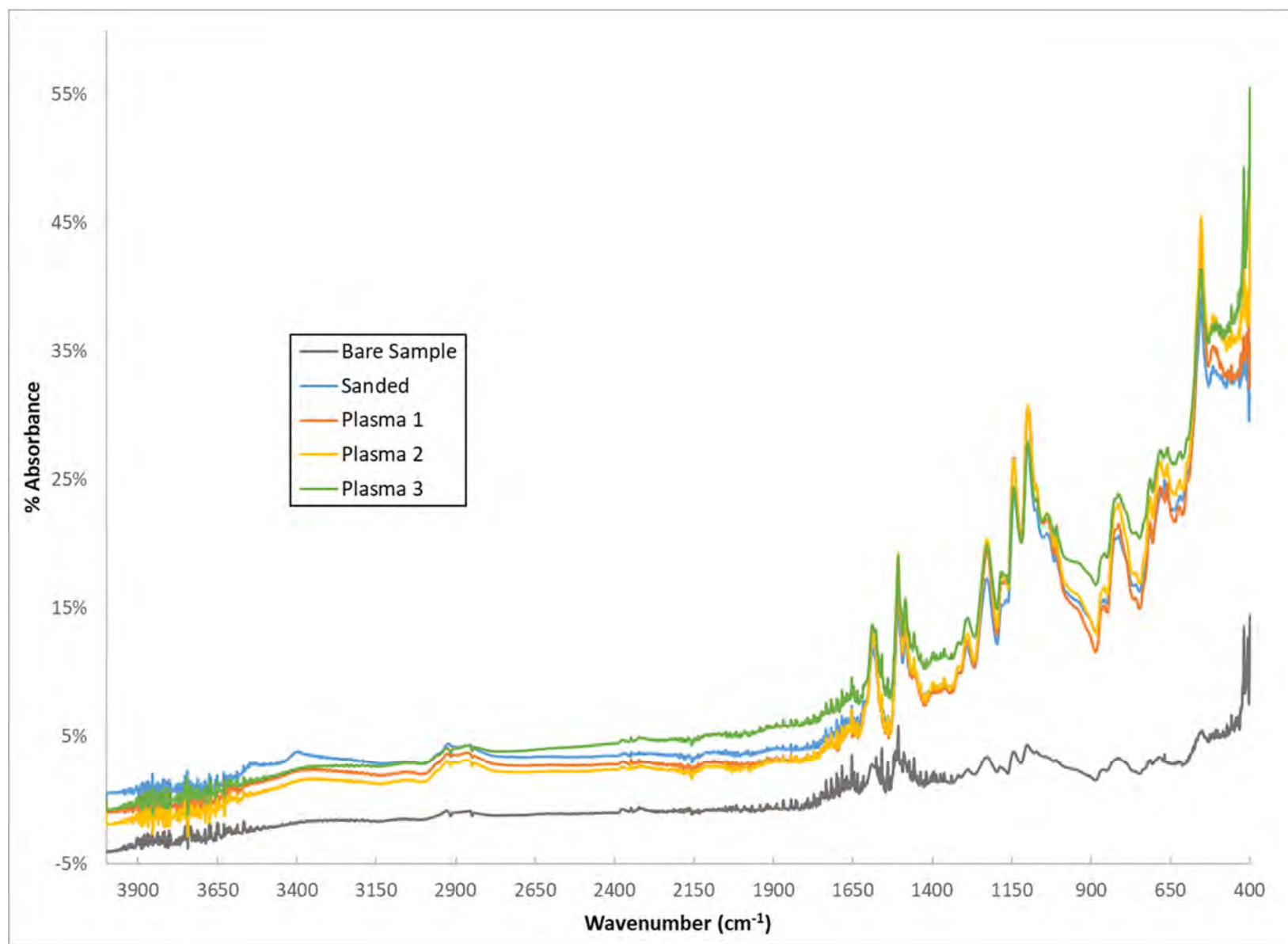


Figure D8: Average FTIR Spectra of all Treatment Conditions

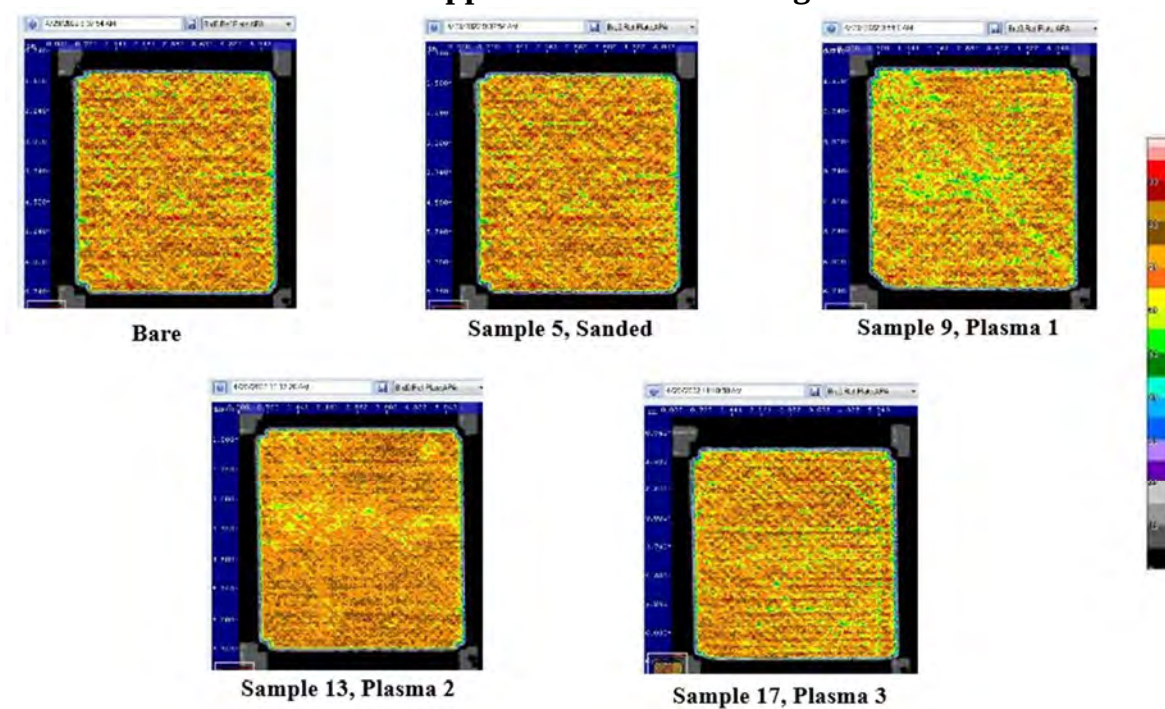
Appendix E: C-Scan Images

Figure E1: C-Scan of bare, sanded and plasma treated specimens

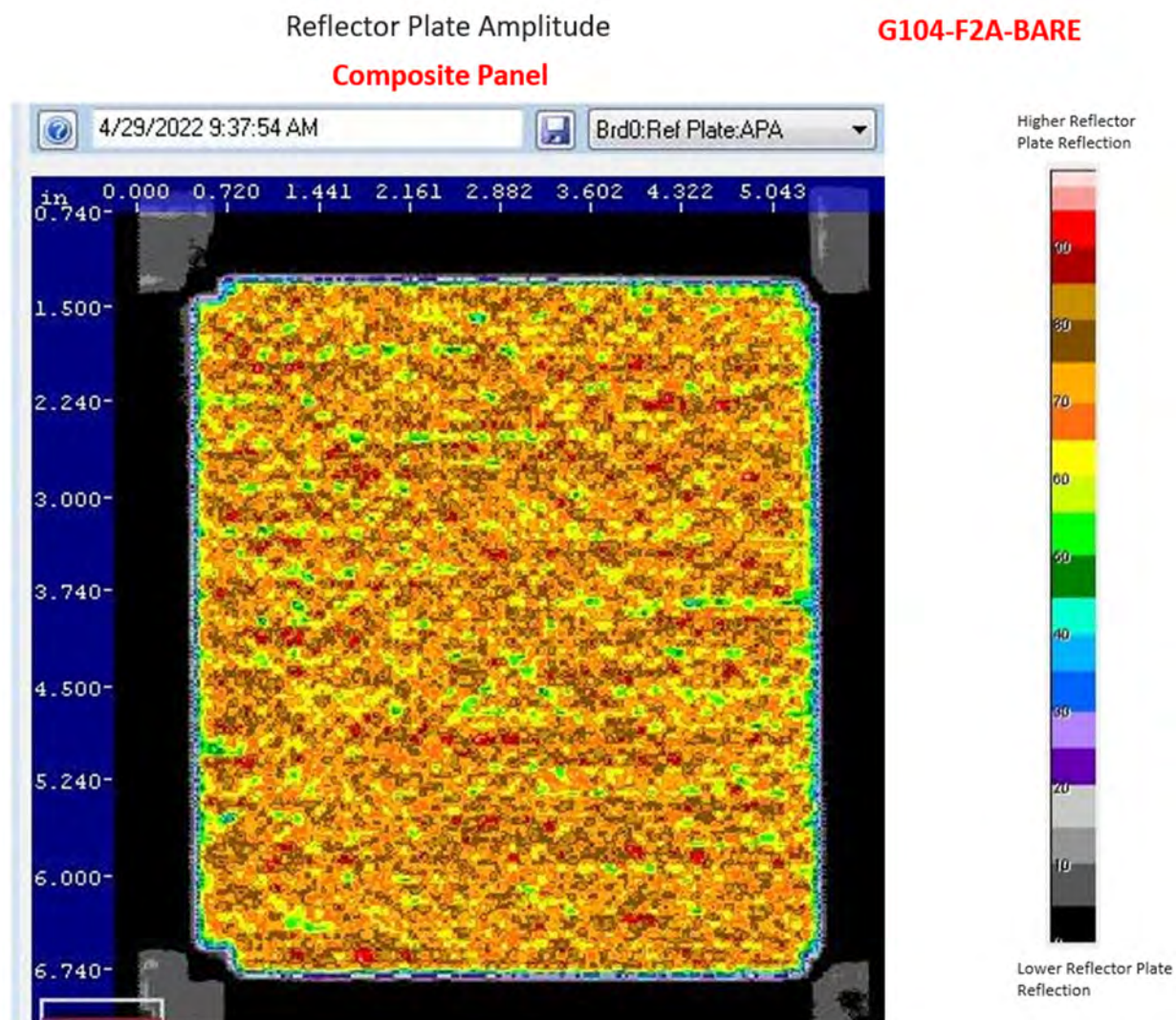


Figure E2: C-Scan of bare specimen, 5 MHz transducer, 6 dB gain, 330 V, and 3" wafer path

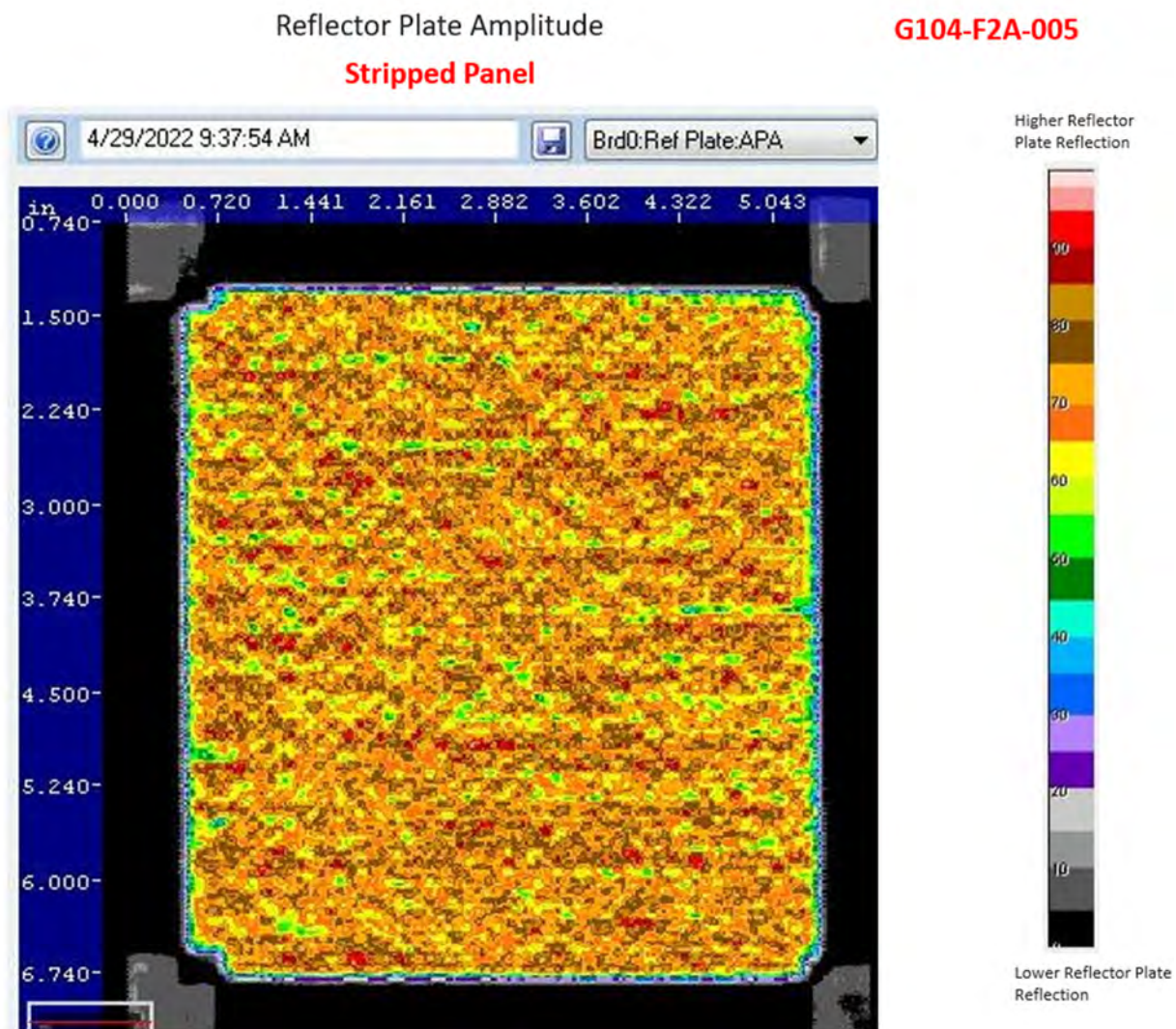


Figure E3: C-Scan of specimen 5, 5 MHz transducer, 6 dB gain, 330 V, and 3" wafer path

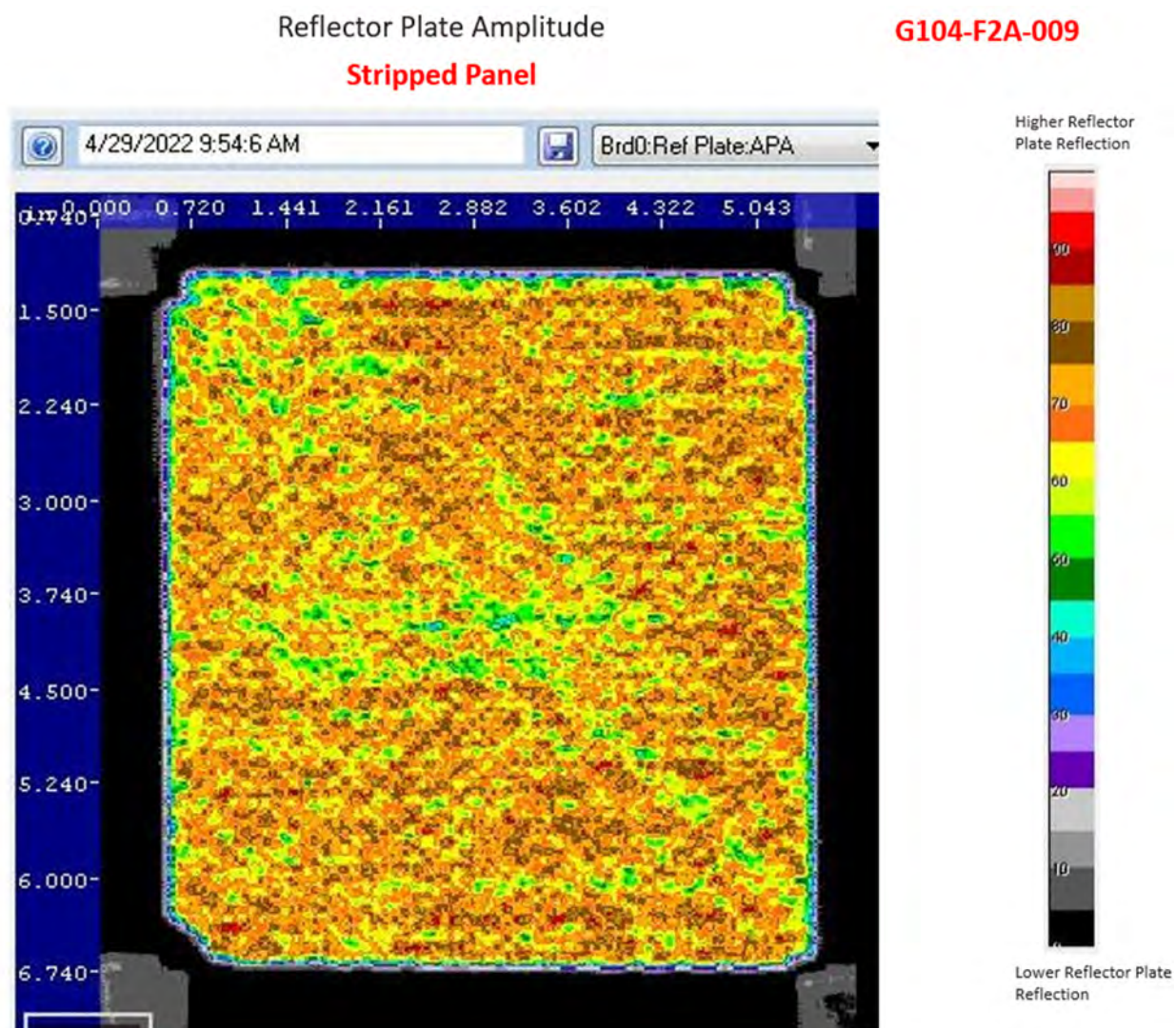


Figure E4: C-Scan of specimen 9, 5 MHz transducer, 6 dB gain, 330 V, and 3" wafer path

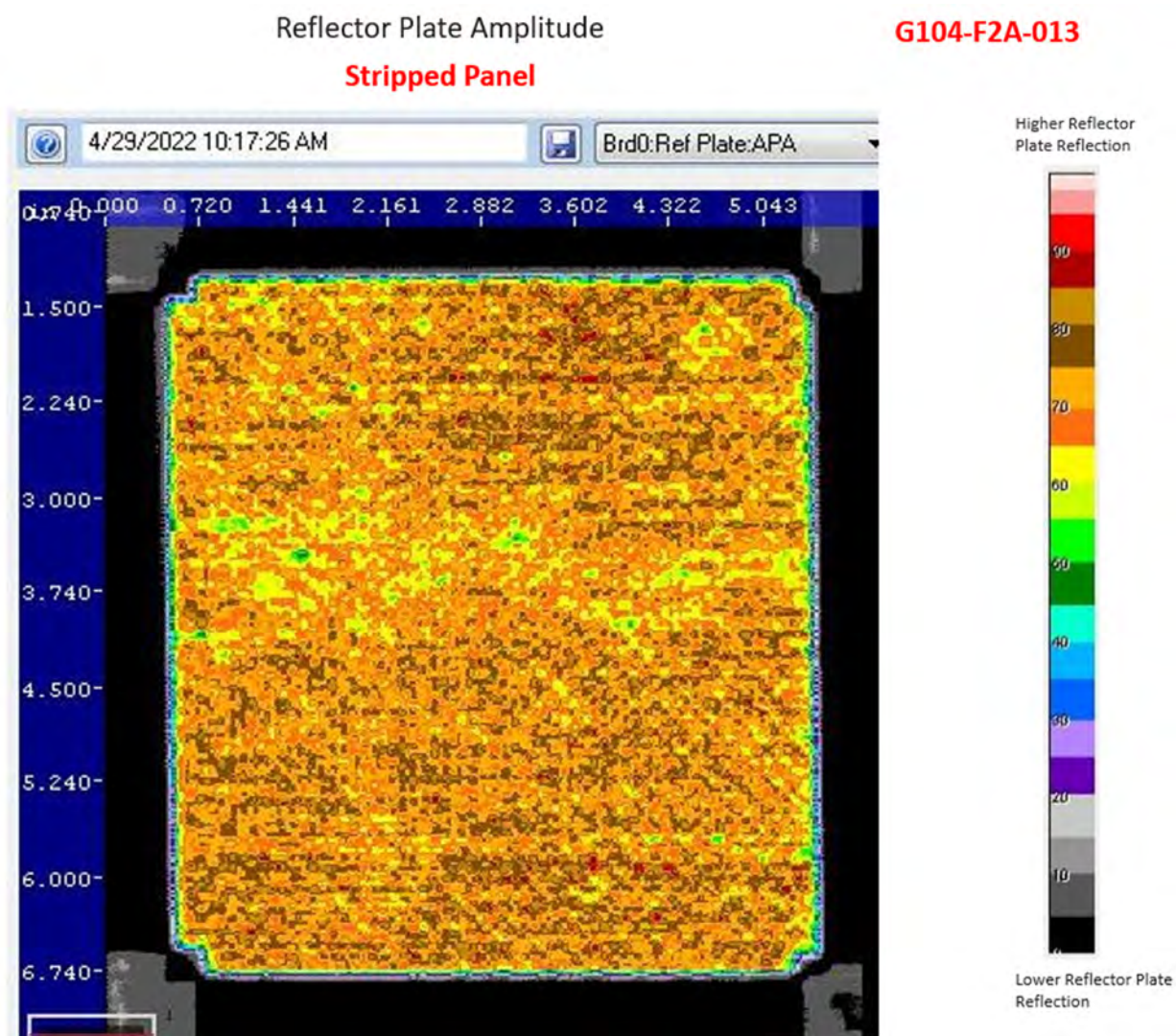


Figure E5: C-Scan of specimen 13, 5 MHz transducer, 6 dB gain, 330 V, and 3" wafer path

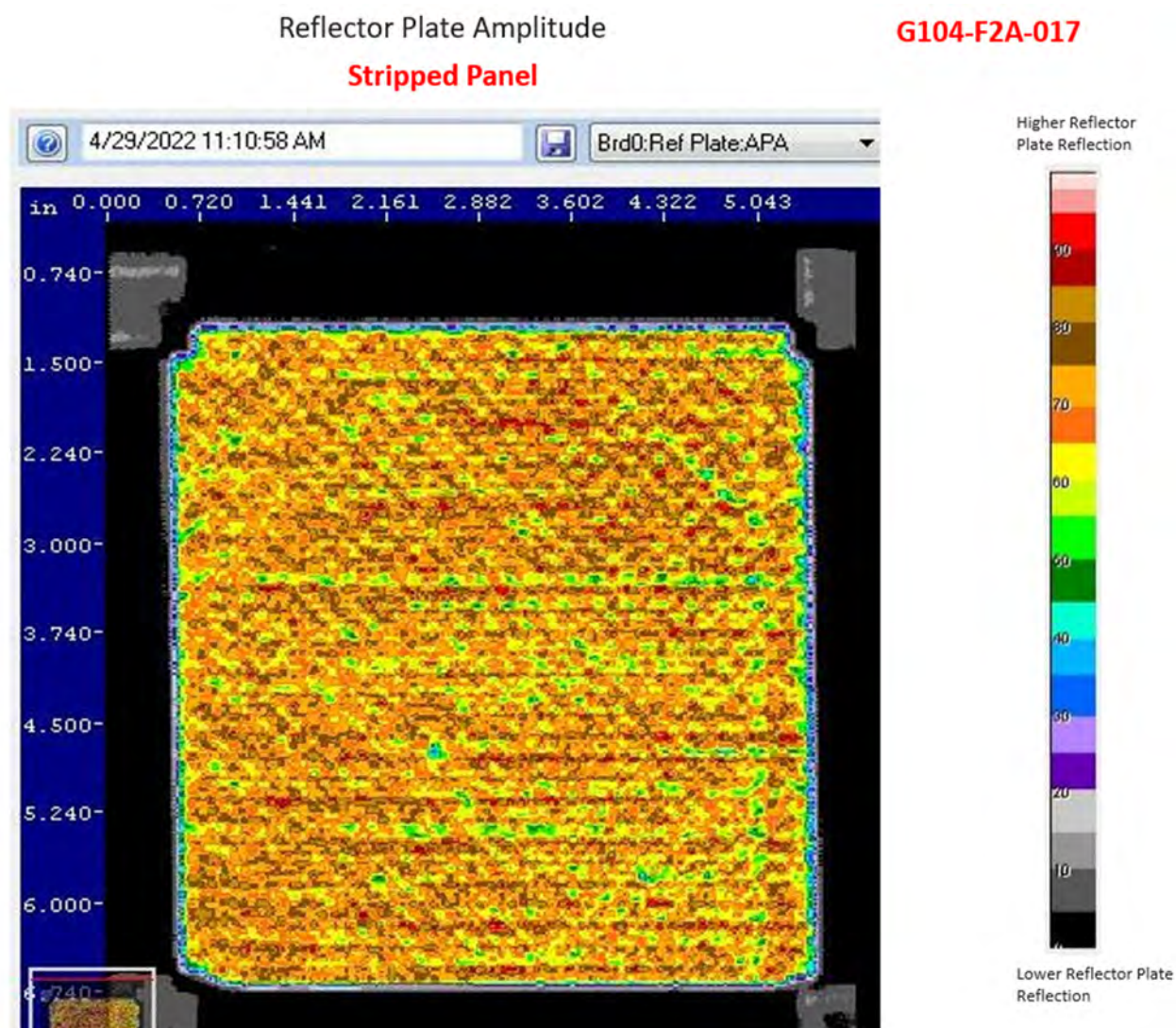


Figure E6: C-Scan of specimen 17, 5 MHz transducer, 6 dB gain, 330 V, and 3" wafer path

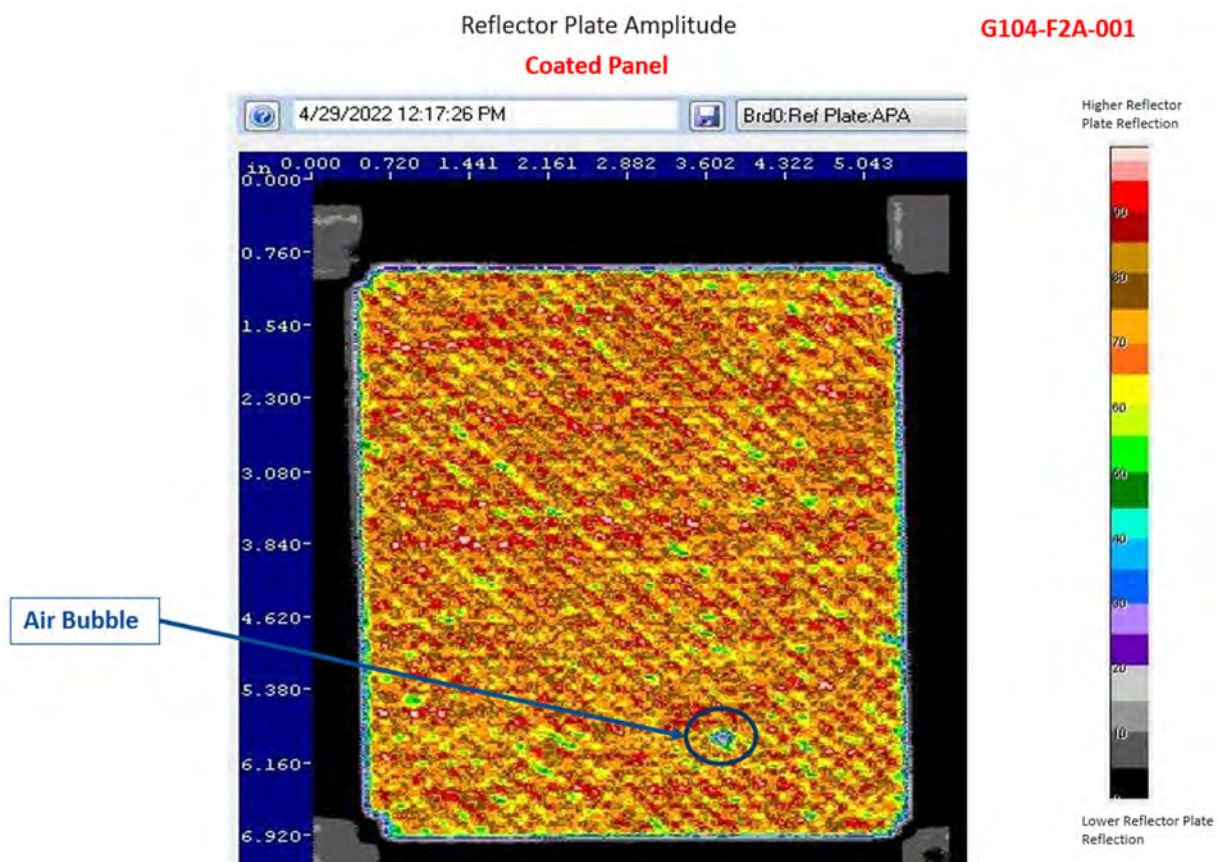


Figure E7: C-Scan of specimen 1, 5 MHz transducer, 6 dB gain, 330 V, and 3" wafer path, with noted air bubble

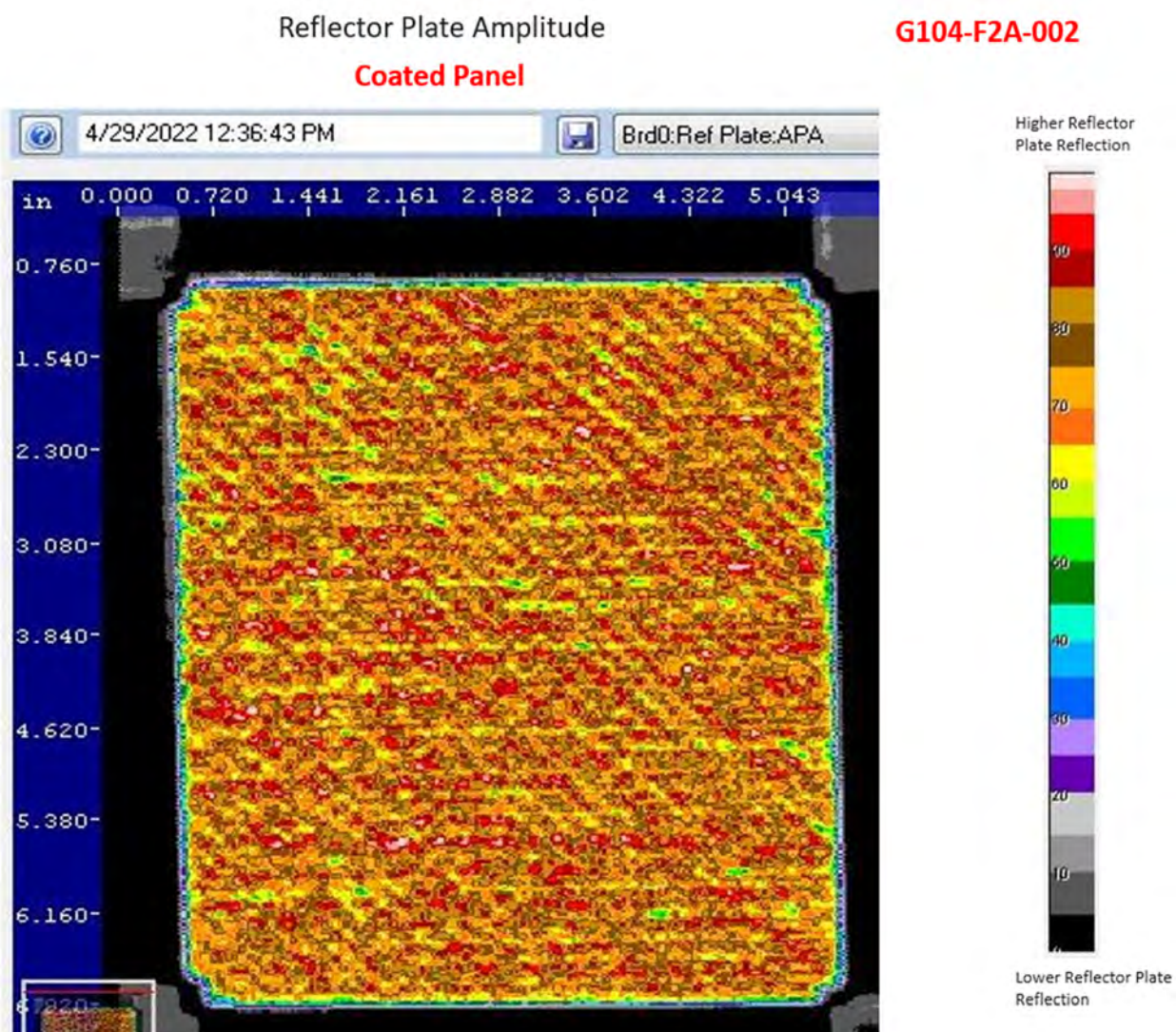


Figure E8: C-Scan of specimen 2, 5 MHz transducer, 6 dB gain, 330 V, and 3" wafer path

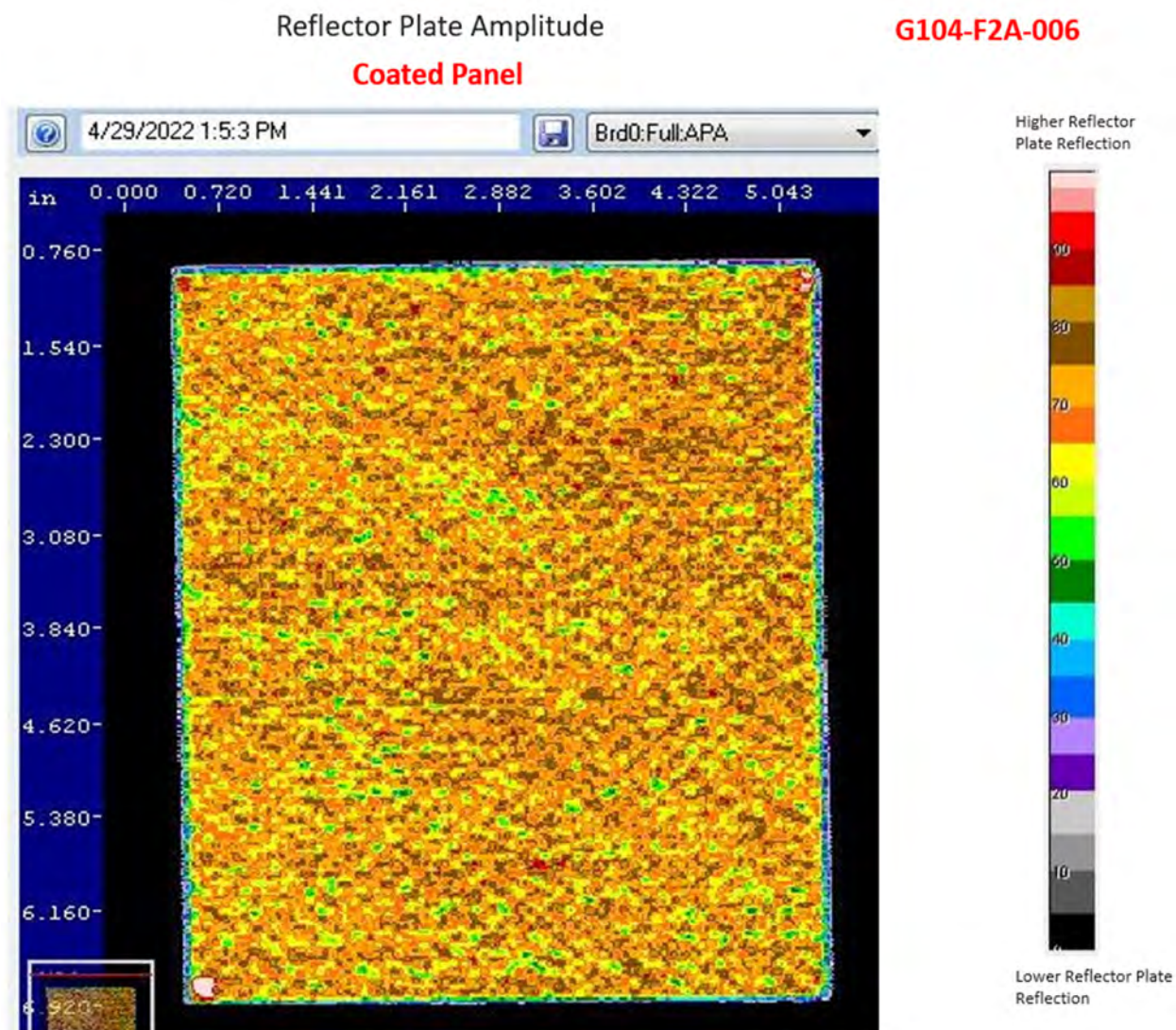


Figure E9: C-Scan of specimen 6, 5 MHz transducer, 6 dB gain, 330 V, and 3" wafer path

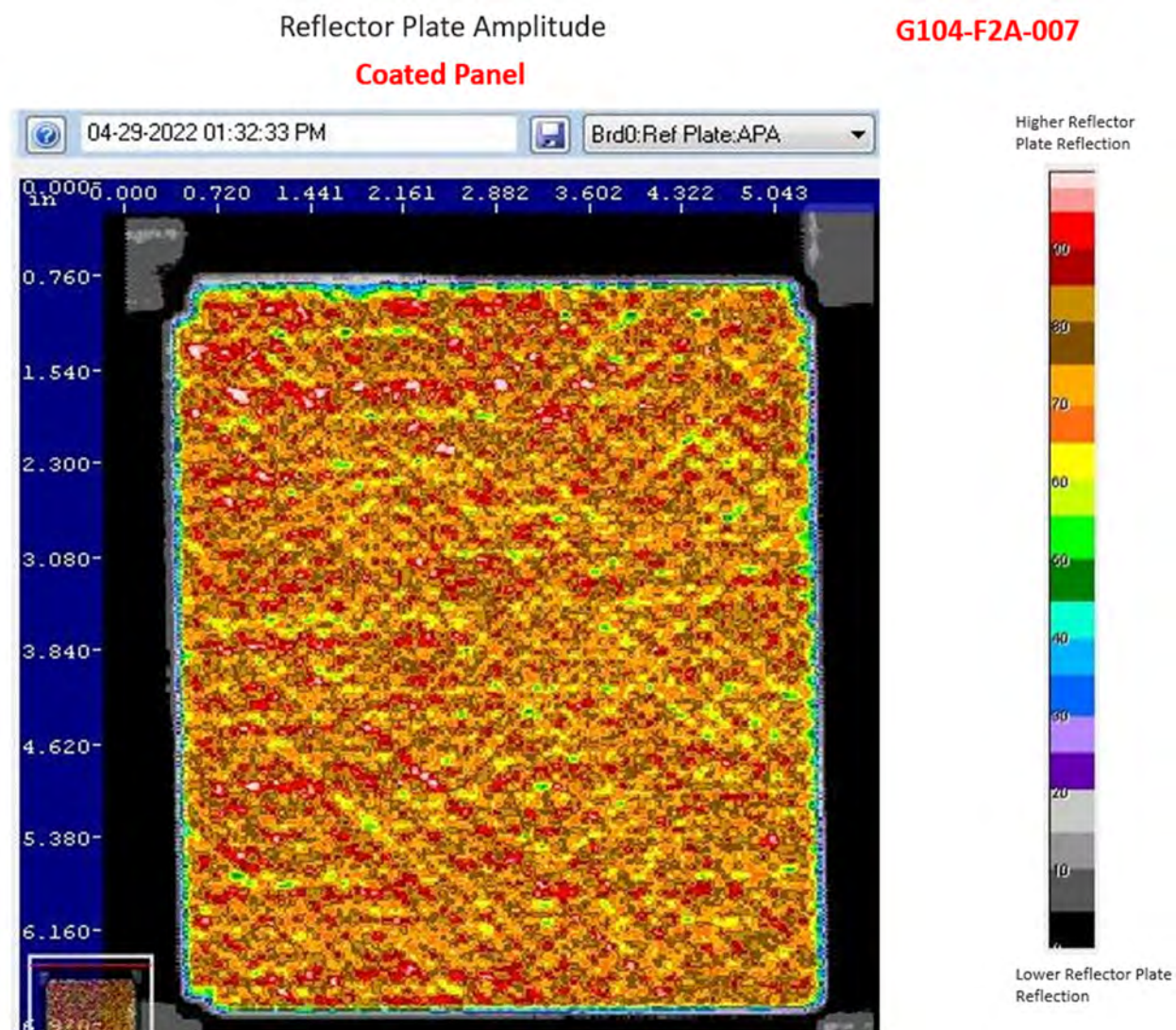


Figure E10: C-Scan of specimen 7, 5 MHz transducer, 6 dB gain, 330 V, and 3" wafer path

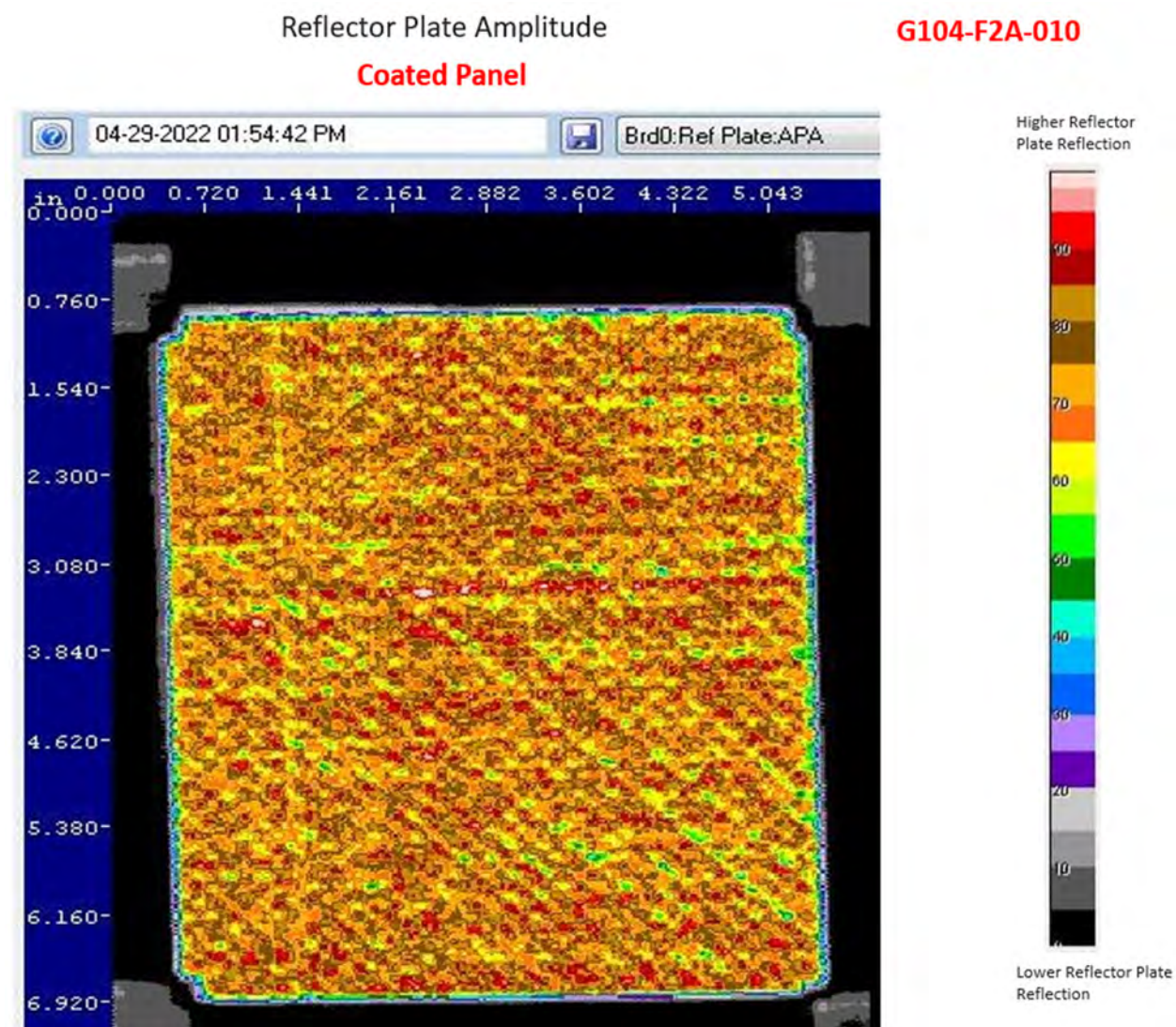


Figure E11: C-Scan of specimen 10, 5 MHz transducer, 6 dB gain, 330 V, and 3" wafer path

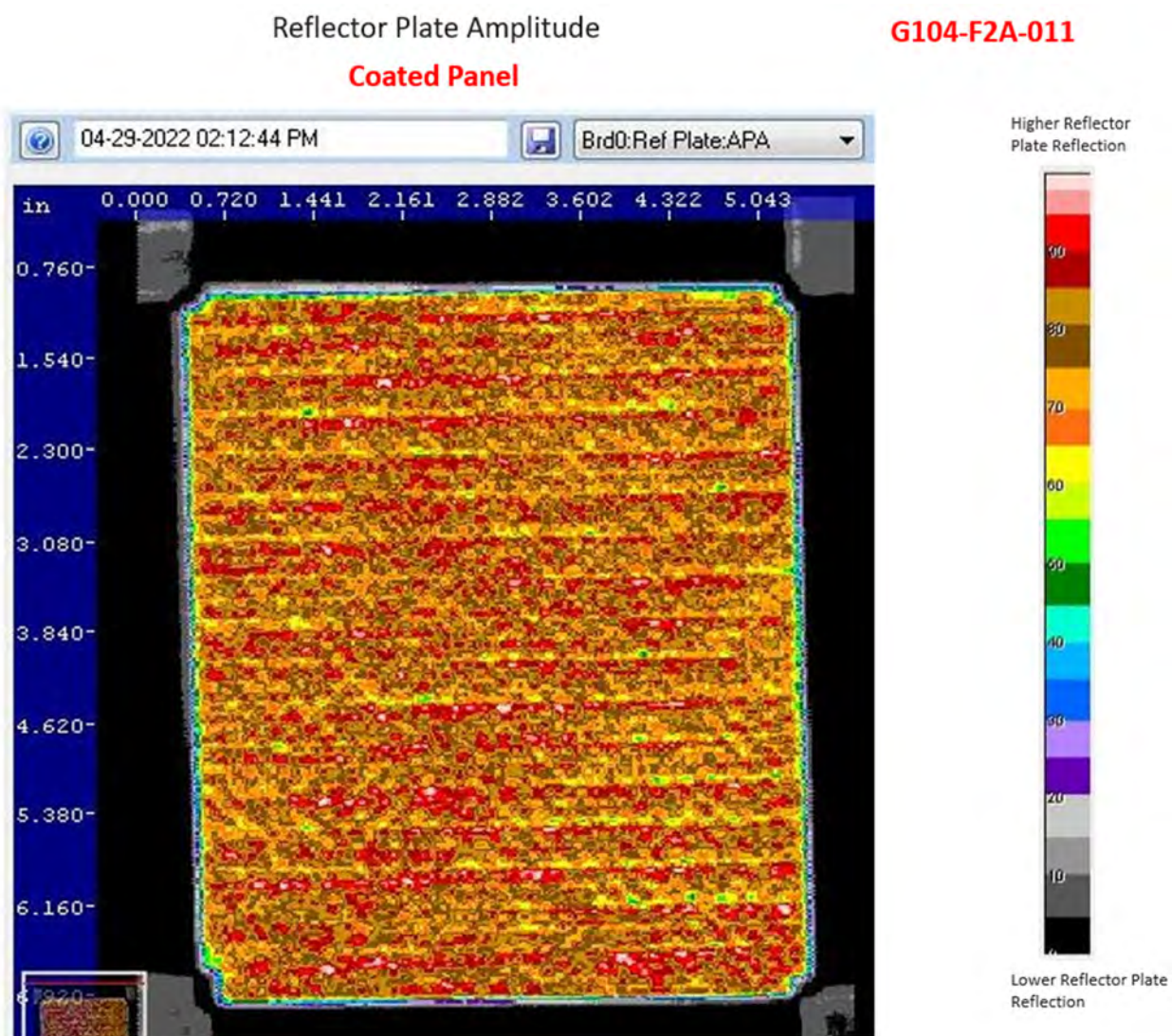


Figure E12: C-Scan of specimen 11, 5 MHz transducer, 6 dB gain, 330 V, and 3" wafer path

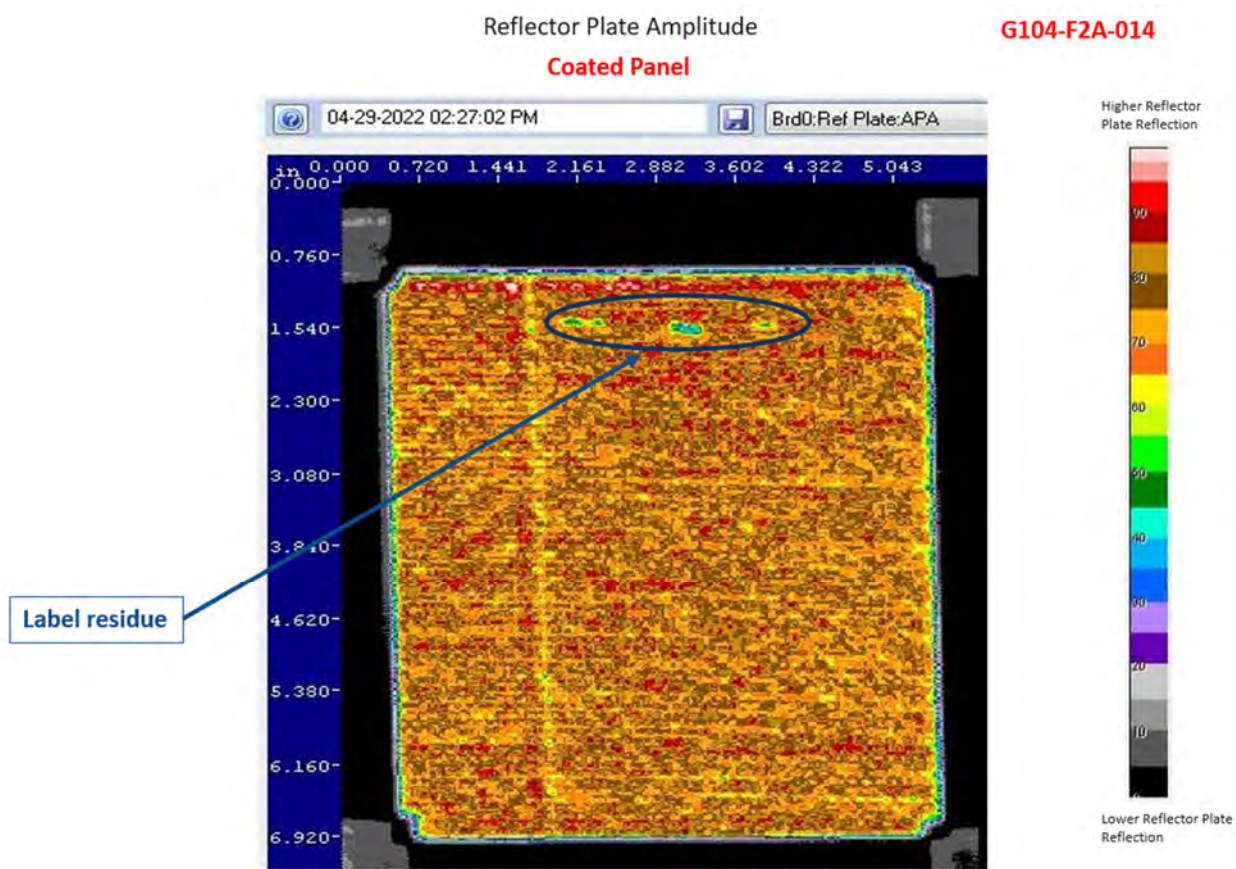


Figure E13: C-Scan of specimen 14, 5 MHz transducer, 6 dB gain, 330 V, and 3" wafer path, with indication of label residue

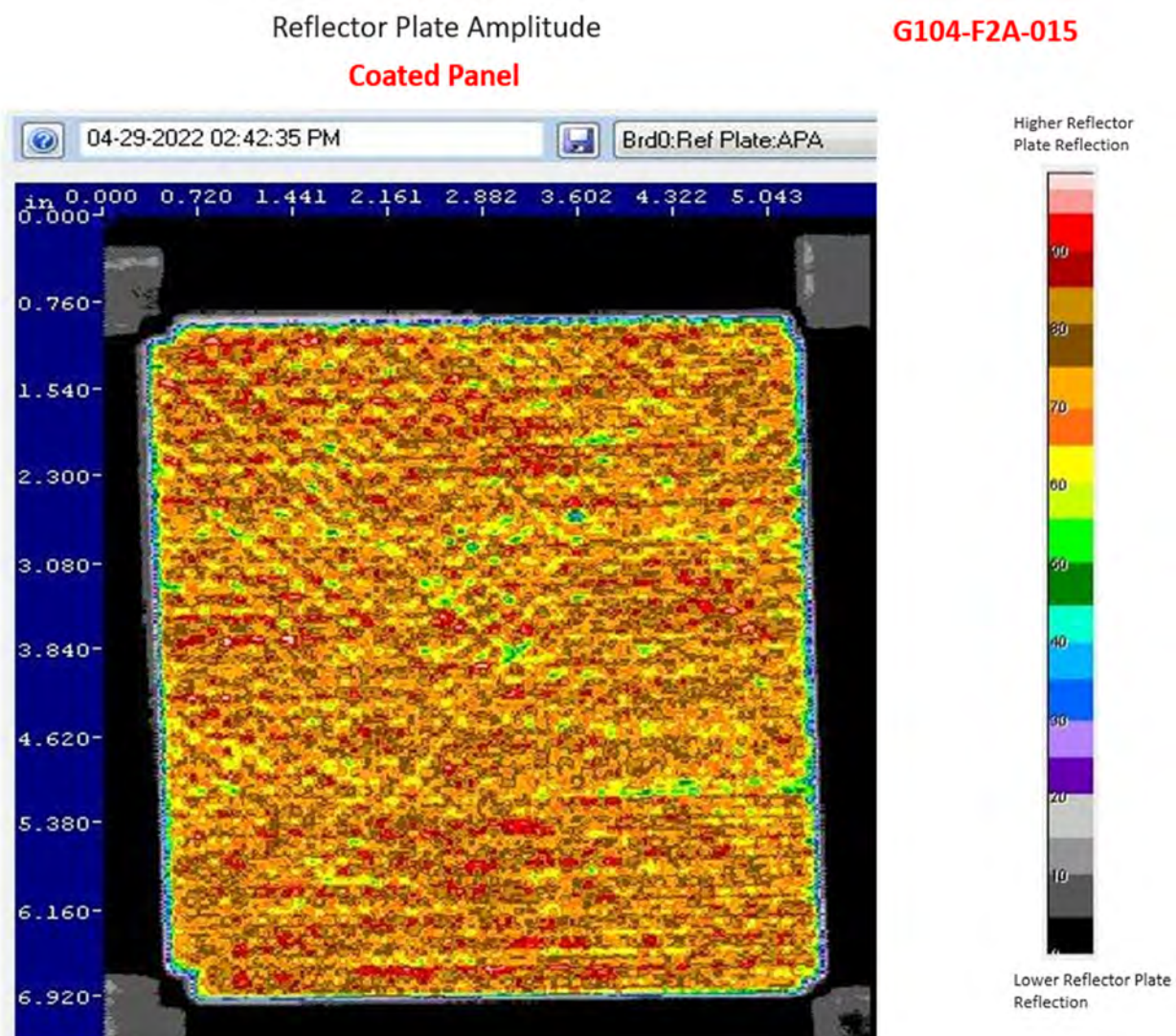


Figure E14: C-Scan of specimen 15, 5 MHz transducer, 6 dB gain, 330 V, and 3" wafer path

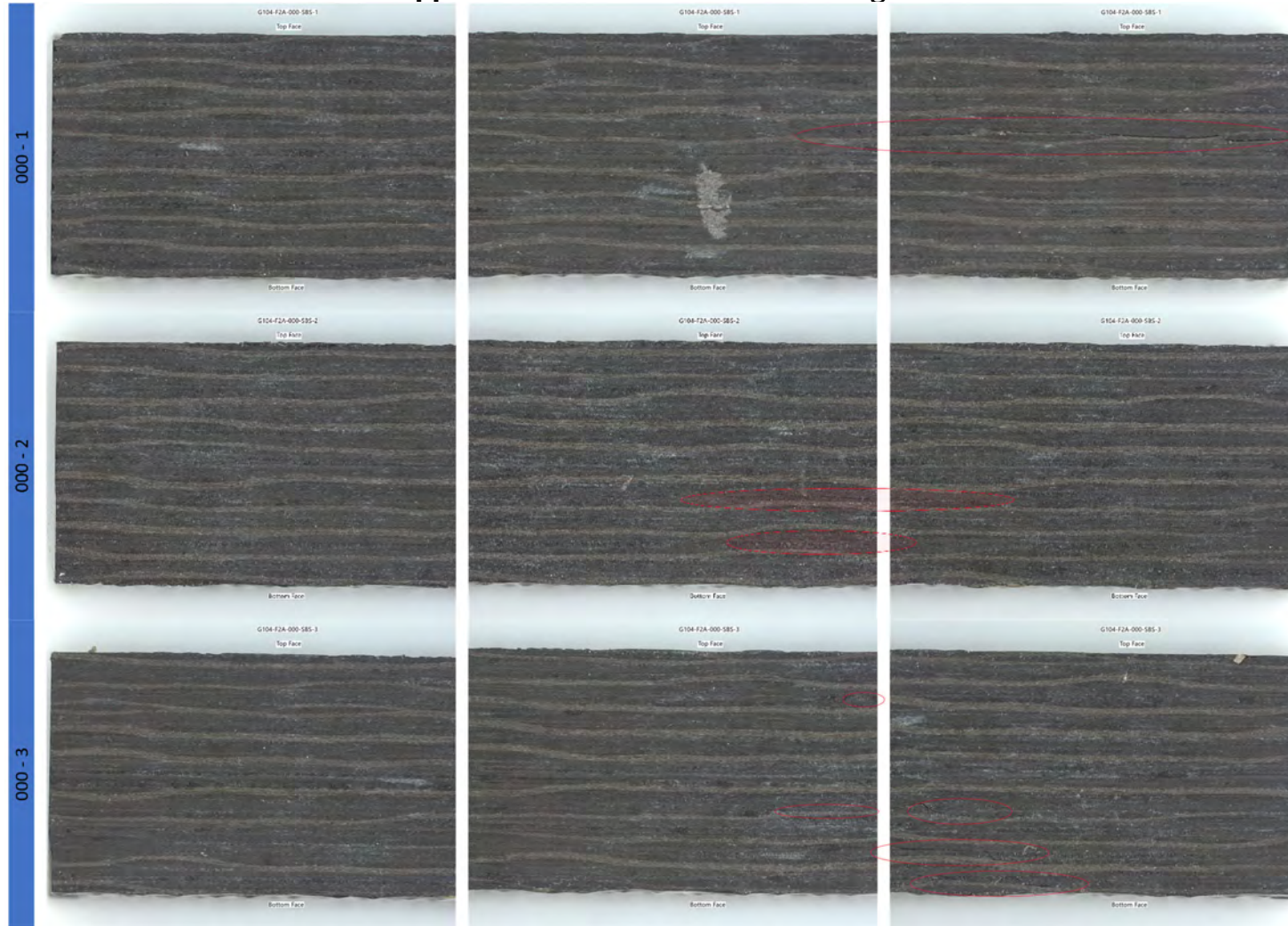
Appendix F: SBS Cross-Section Images

Figure F1: Cross Sections of SBS results for bare sample, with locations of failures circled in red

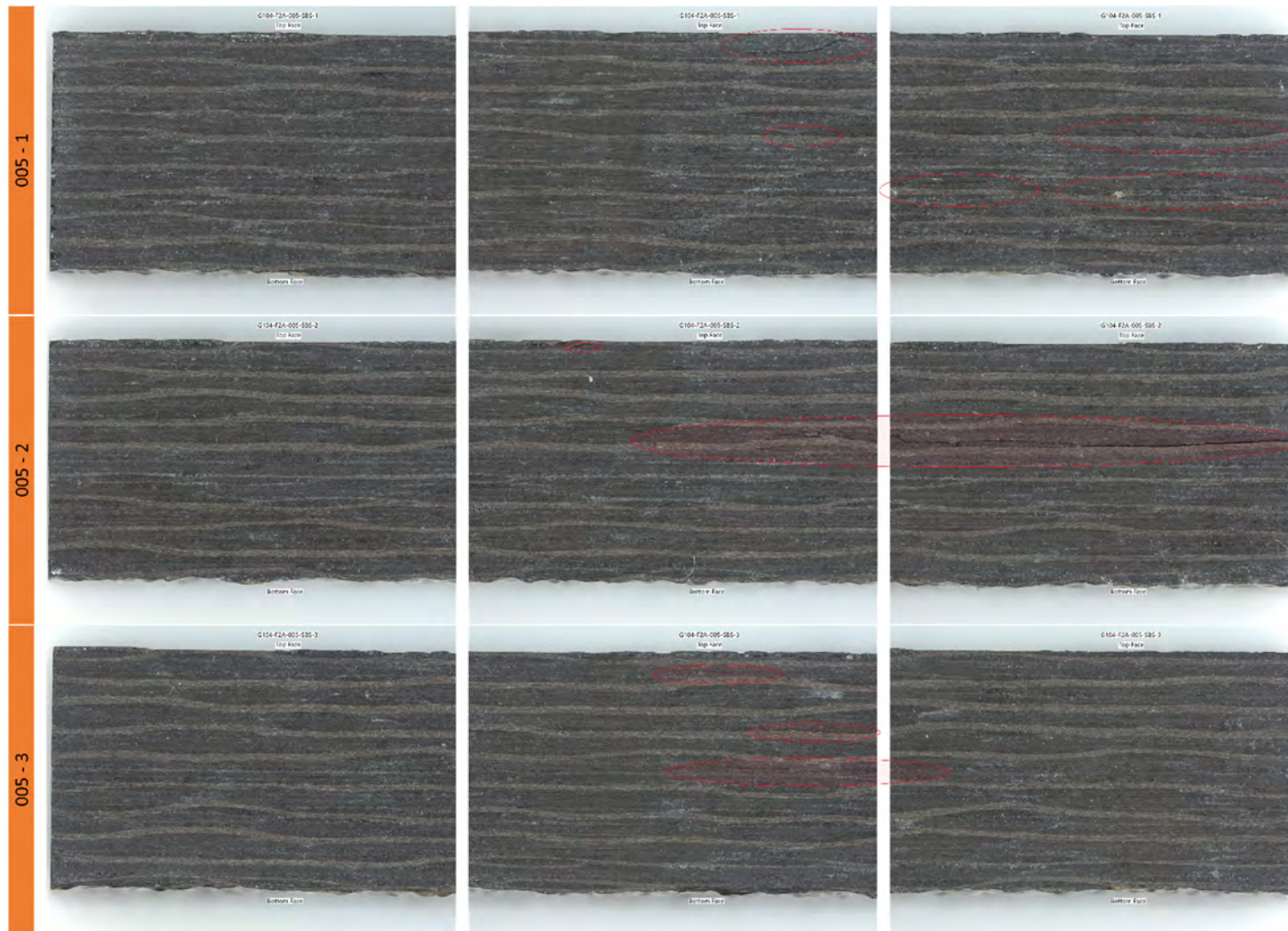


Figure F2: Cross Sections of SBS results for sample 5, with locations of failures circled in red

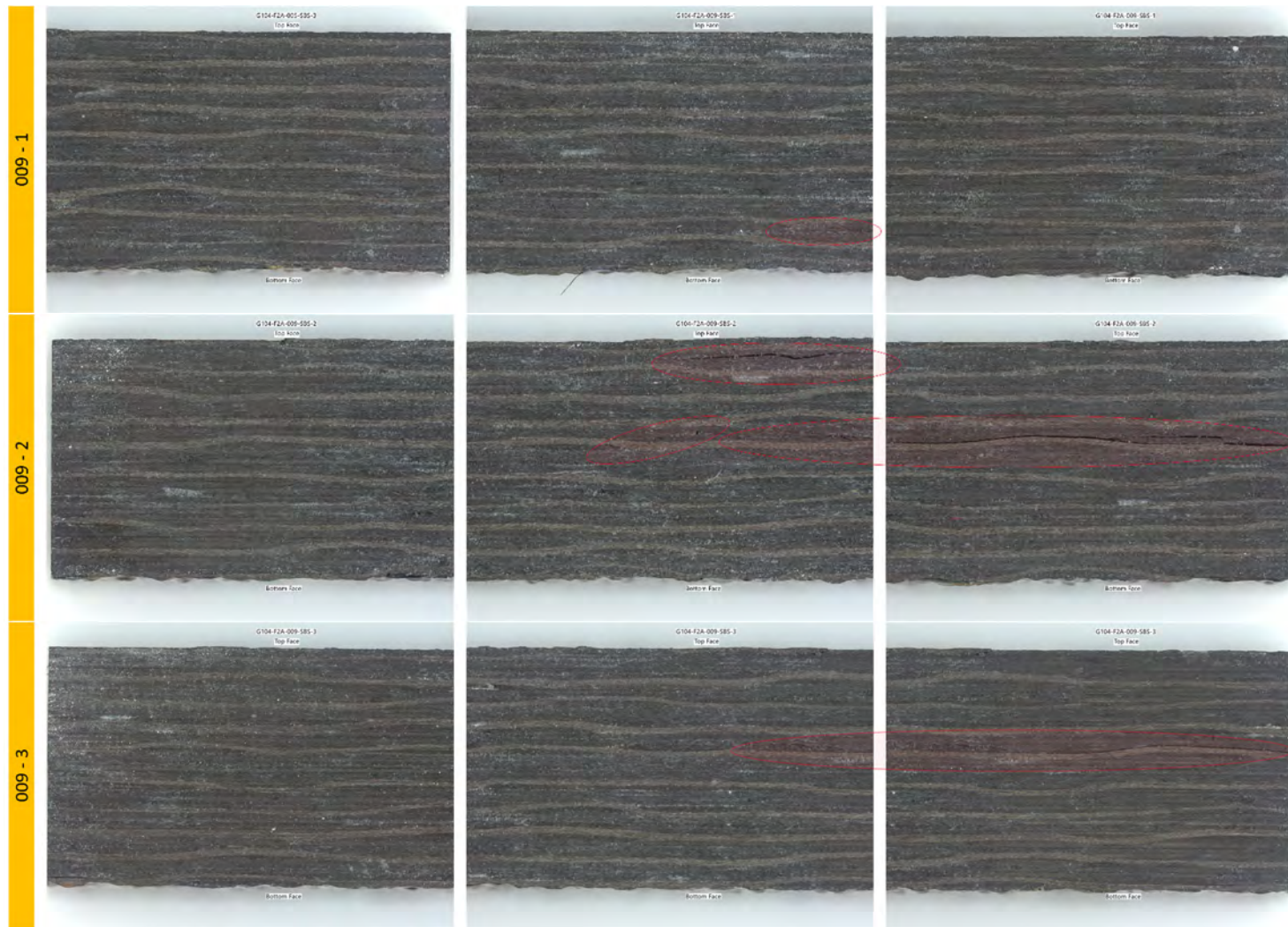


Figure F3: Cross Sections of SBS results for sample 9, with locations of failures circled in red

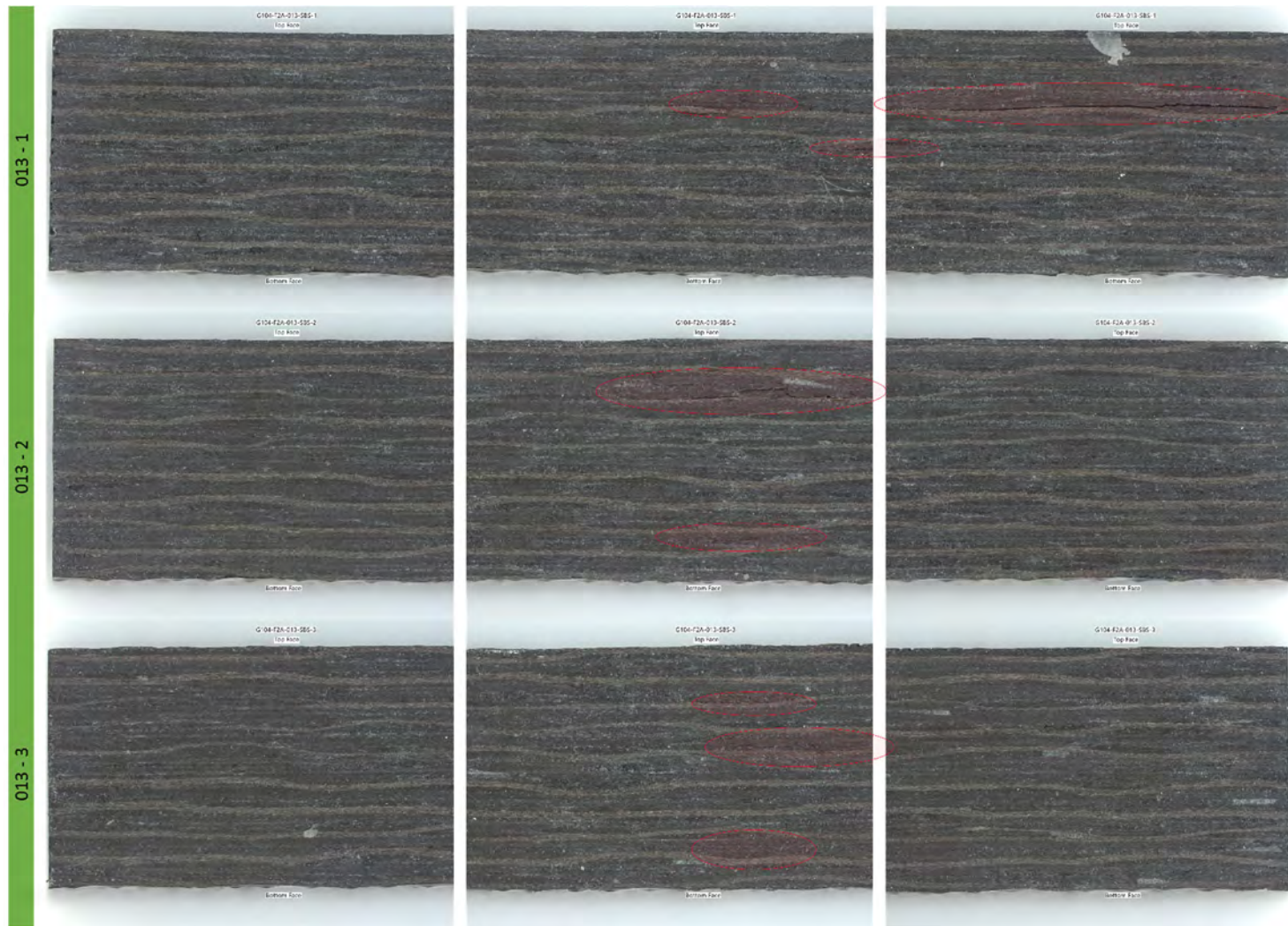


Figure F4: Cross Sections of SBS results for sample 13, with locations of failures circled in red

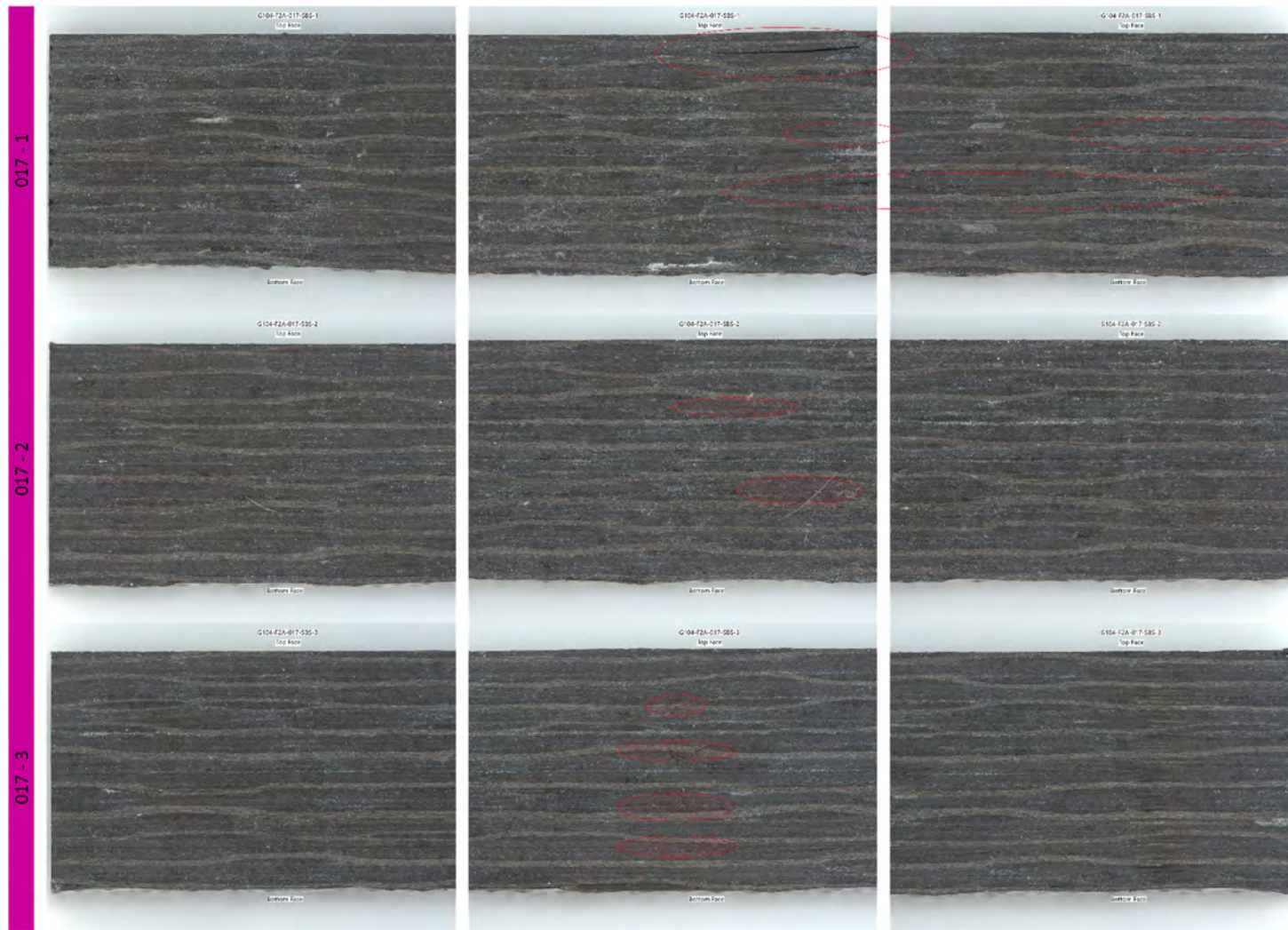


Figure F5: Cross Sections of SBS results for sample 17, with locations of failures circled in red

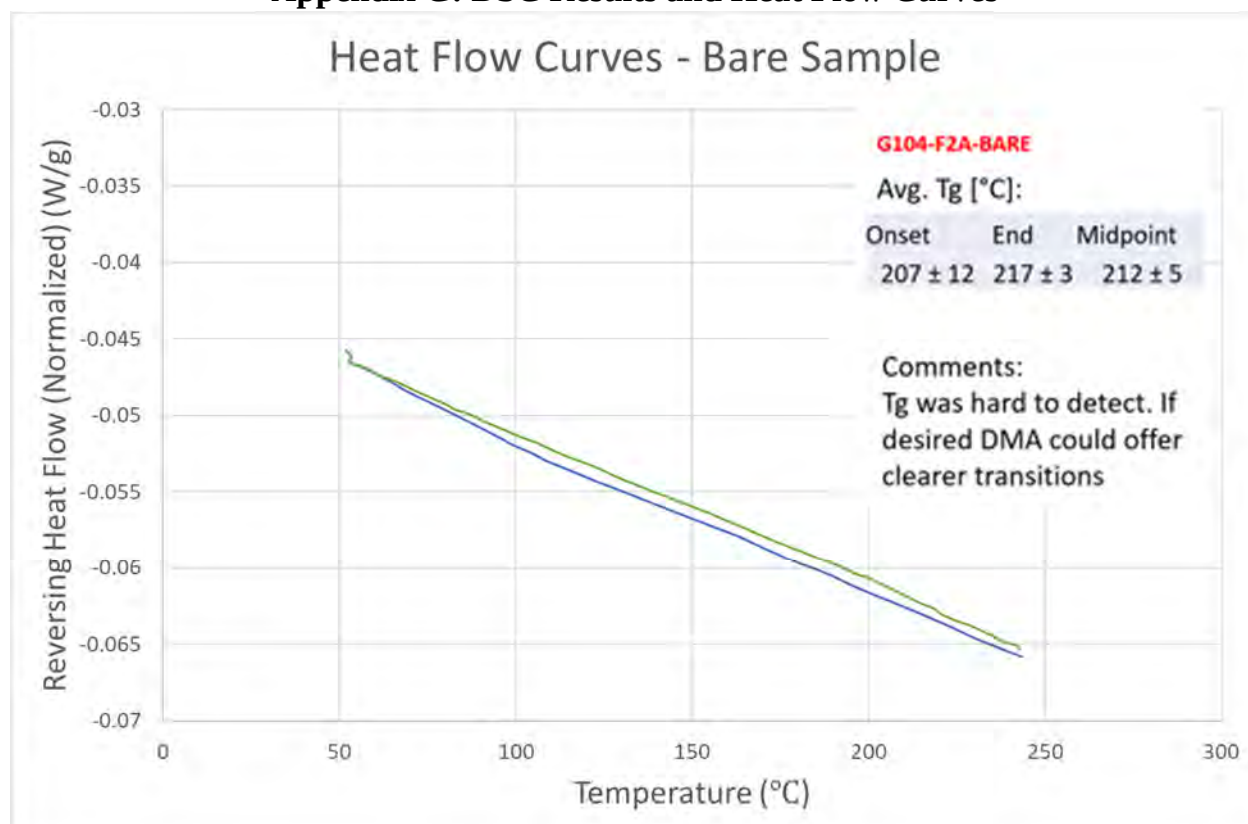
Appendix G: DSC Results and Heat Flow Curves

Figure G1: DSC results for bare specimen, with graph of heat flow vs. temperature

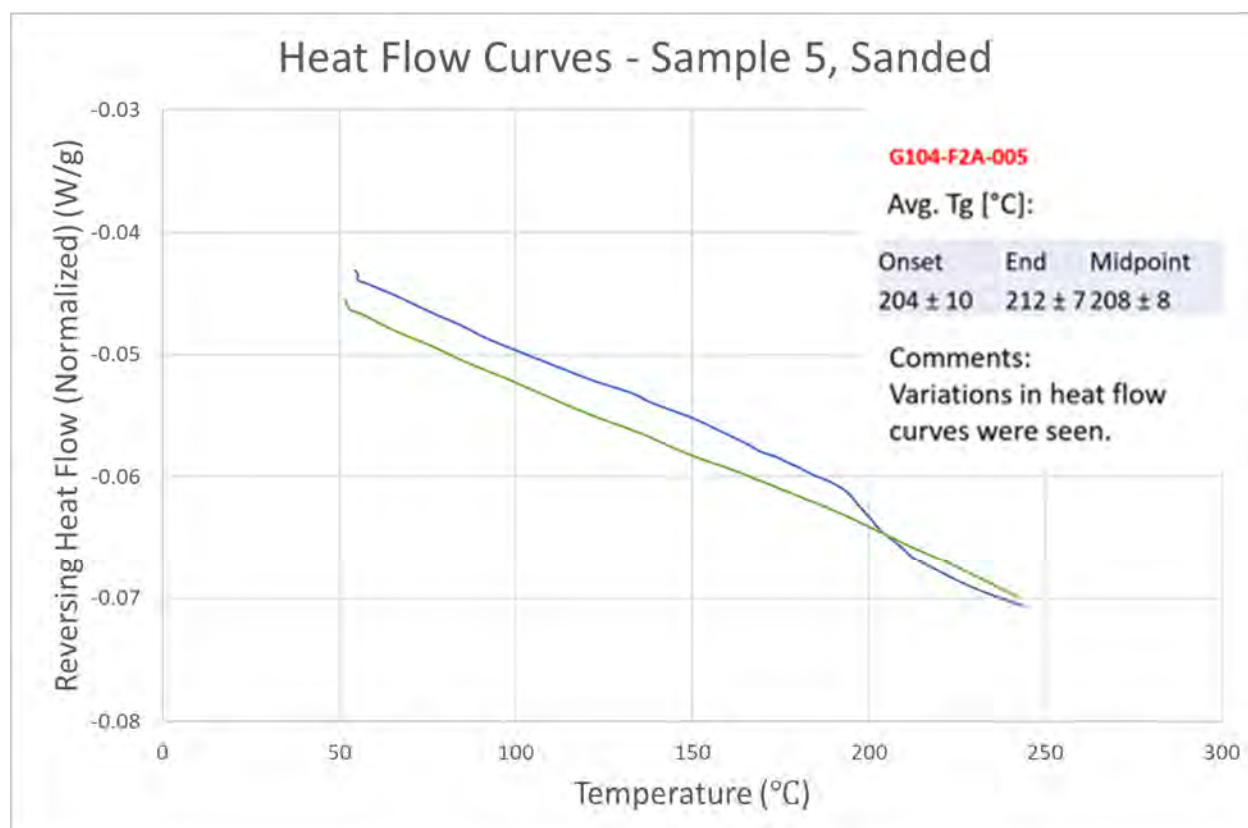


Figure G2: DSC results for specimen 5, with graph of heat flow vs. temperature

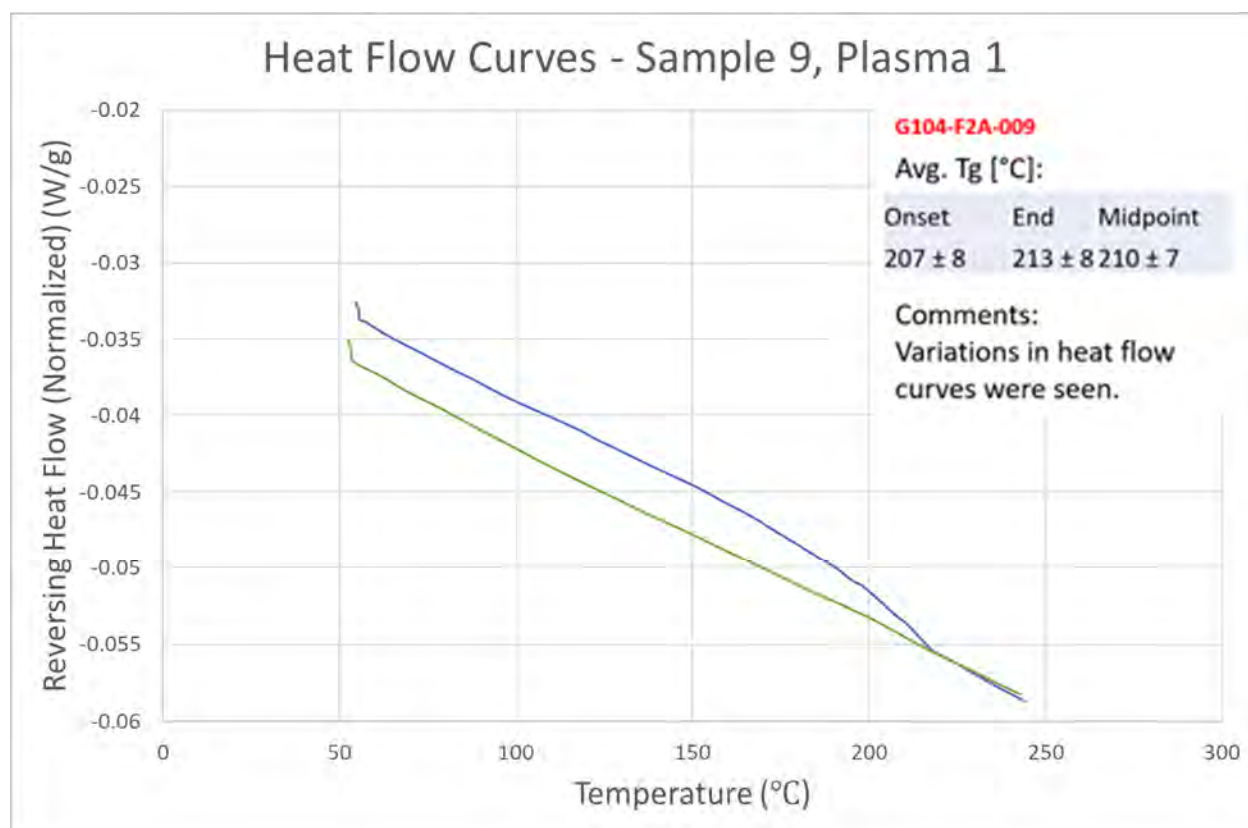


Figure G3: DSC results for specimen 9, with graph of heat flow vs. temperature

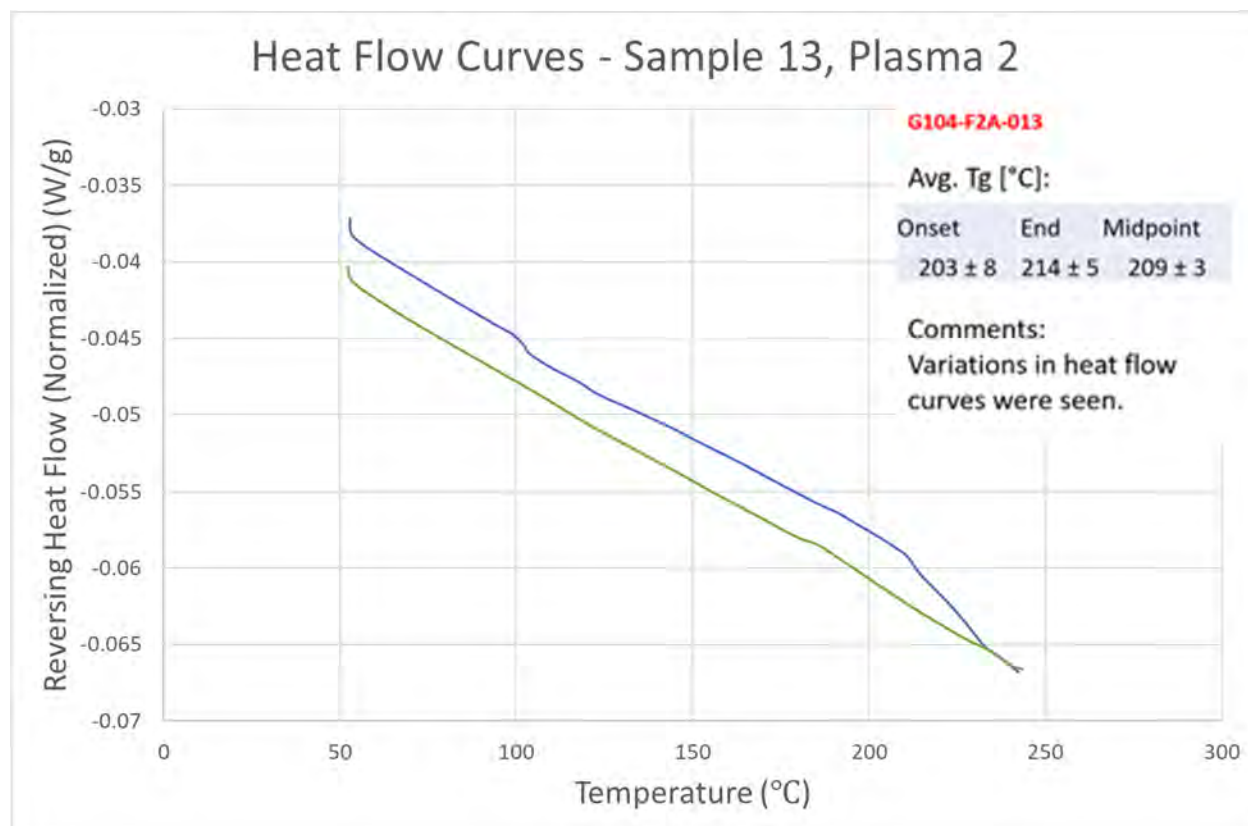


Figure G4: DSC results for specimen 13, with graph of heat flow vs. temperature

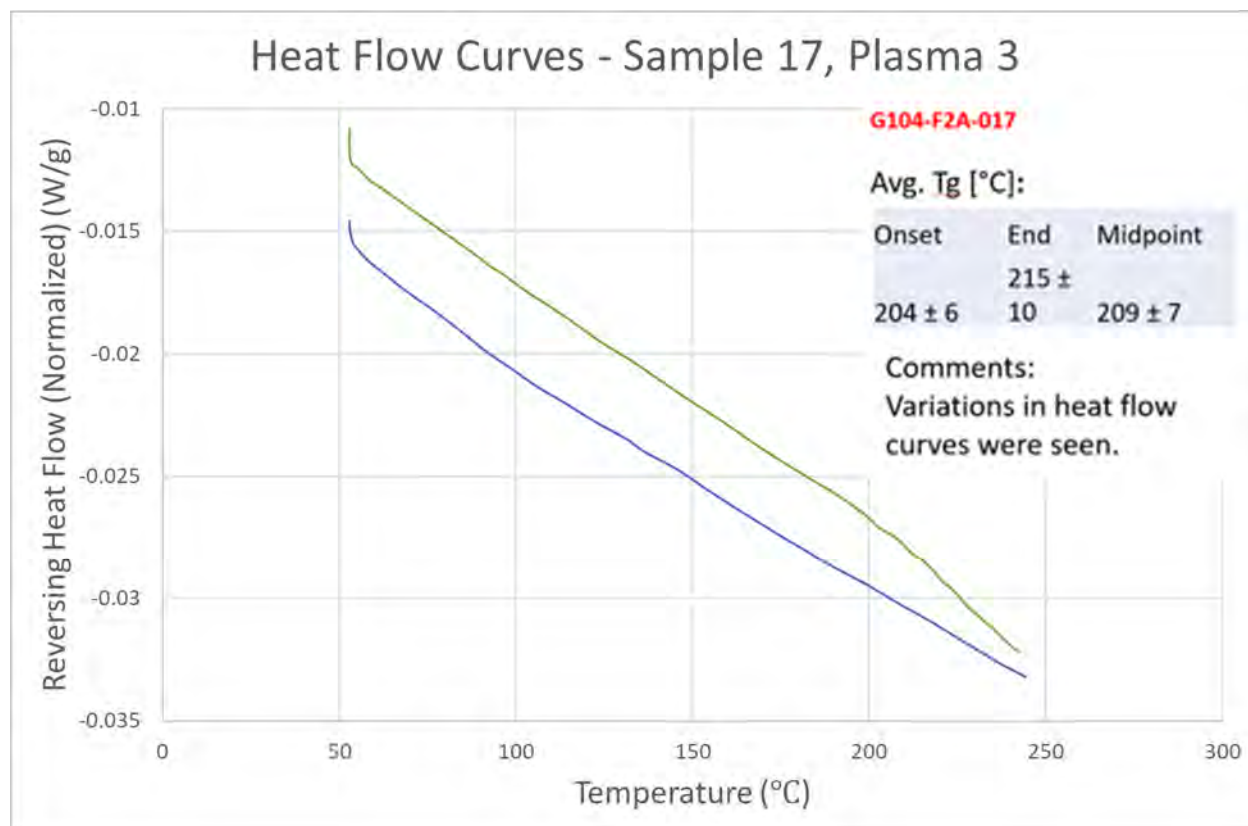
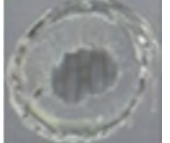
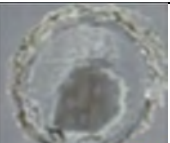
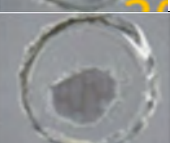
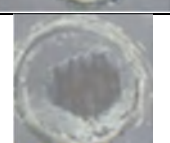
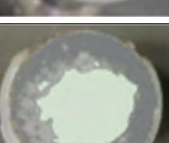
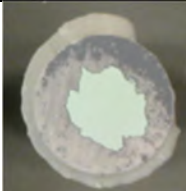
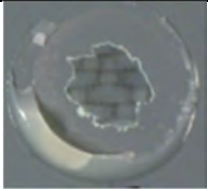
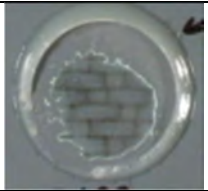
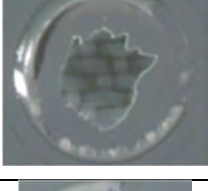
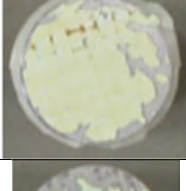
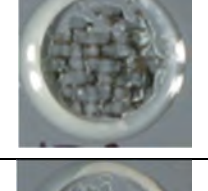
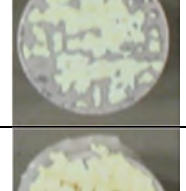
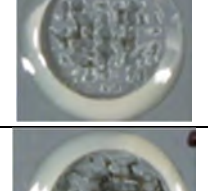
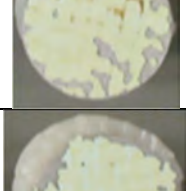
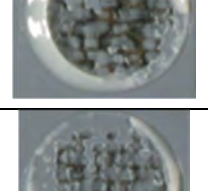
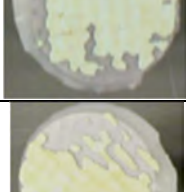
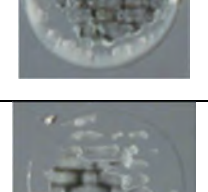
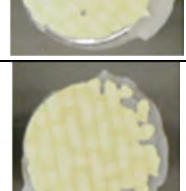
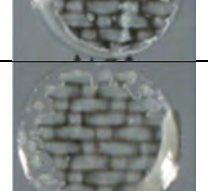
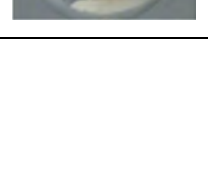
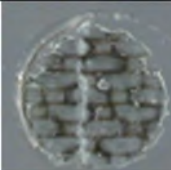
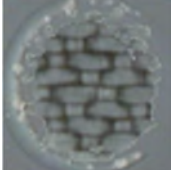
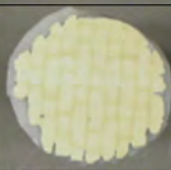
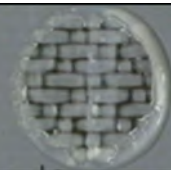
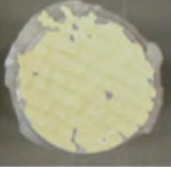


Figure G5: DSC results for specimen 17, with graph of heat flow vs. temperature

Appendix H: Pull-off Adhesion Results and Images*Table H1: Images of dolly pull results*

Sample ID	Condition	Pull	Strength (psi)	Dolly Face	Substrate
30	Control	1	1819		
30	Control	2	1832		
30	Control	3	2044		
30	Control	4	1809		
29	Control	1	1874		
29	Control	2	1886		
29	Control	3	1725		
29	Control	4	2081		
4	Sanded-Repaint	1	2645		

4	Sanded-Repaint	2	2465		
4	Sanded-Repaint	3	2192		
4	Sanded-Repaint	4	2085		
8	Plasma1-Repaint	1	1710		
8	Plasma1-Repaint	2	1767		
8	Plasma1-Repaint	3	1464		
8	Plasma1-Repaint	4	1879		
12	Plasma2-Repaint	1	1188		
12	Plasma2-Repaint	2	1872		

12	Plasma2-Repaint	3	1544		
12	Plasma2-Repaint	4	2236		
16	Plasma3-Repaint	1	1348		
16	Plasma3-Repaint	2	1727		
16	Plasma3-Repaint	3	1038		
16	Plasma3-Repaint	4	1358	