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Study on historical potash-lime silicate glass corroded in the presence of volatile organic compounds

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*To Tiziana,
For her vision and passion and for her faith in me and for being the one
person who inspired me even in my dreams.*

Abstract

Transparent historical glass presents many challenges in its documentation and monitoring. Due to their chemical complexity as well as their storage conditions, many questions about their documentation and corrosion mechanisms lay unanswered. This project aimed to develop a new monitoring protocol, based on non-destructive imaging techniques. The project was concerned with the glass objects of the Swiss National Museum belonging to the 17th to 20th century. Due to inappropriate storage conditions in the past, the objects under study were in an irreversible corroded state and therefore, in order to implement the appropriate measures, research about the mechanisms of corrosion was necessary. To achieve this aim, an artificial aging protocol was setup to subject the model glasses to conditions similar to those of the historical glasses and induce corrosion for a duration of at least 18 months in the presence of VOCs namely acetic acid and formic acid as well as fluctuating or fixed relative humidity. These corroded model glass were periodically monitored to characterize the corrosion based on physical and chemical changes using various chemical analytical and imaging techniques, most of which were noninvasive.

A terminology was developed for describing the various signs of glass corrosion. The combination of chemical and imaging analyses was successful in categorizing corrosion even at an incipient stage. The chemical changes such as changes in silicate species and composition of the corrosion products were understood using FTIR and Raman spectroscopy while digital microscopy and reflectance transformation imaging proved to be helpful in quantifying the two visible signs of corrosion i.e., wet salt neocrystallizations and cracks. Hyperspectral imaging in the short-wave infra-red range was found to be the most useful to identify corrosion at an early stage. Not only it did provide visualization of features over the whole model glass, some of which could not be seen with naked eyes, but also the spectral evidence of water and hydroxyl absorption which could be used as a proxy for quantifying corrosion.

Glass corrosion was exacerbated by the presence of VOCs which formed wet formate salt neocrystallizations on the glass surface in case of corrosion in higher VOC concentrations and formed both formate and acetate salts in case of corrosion in lower VOC concentrations. Correlations were found between various parameters of corrosion such as weight changes, area covered by wet salt neocrystallizations, alteration layer thickness, Raman and FTIR peak ratios, crack density, water and hydroxyl absorbed by the glass matrix and the alkali ions leached out of the bulk glass. Some of the techniques along with few modifications such as digital photography and digital microscopy were also applied on actual historical objects and helped to validate the aging protocol which produced corrosion similar to that found on the objects. The proposed protocol in this research thus can facilitate the early identification of corrosion of glass which could help conservators and conservation scientists to apply suitable preventive conservation methods and to be able to store historical glass objects in proper conditions.

Keywords: Hyperspectral imaging, Glass corrosion, Artificial aging, Volatile Organic Compounds, Reflectance transformation imaging, Digital microscopy, Raman spectroscopy, Fourier Transform Infra-red spectroscopy

Résumé

Le verre historique transparent présente de nombreux défis en matière de documentation et de suivi. En raison de leur complexité chimique et de leurs conditions de stockage, de nombreuses questions sur leur documentation et leurs mécanismes de corrosion restent sans réponse. Ce projet visait à développer un nouveau protocole de contrôle, basé sur des techniques d'imagerie non destructives. Le projet portait sur les objets en verre du Musée national suisse datant du 17^e au 20^e siècle. En raison de conditions de stockage inappropriées dans le passé, les objets étudiés étaient dans un état de corrosion irréversible et, par conséquent, afin de mettre en œuvre les mesures appropriées, une recherche sur les mécanismes de la corrosion était nécessaire. Pour atteindre cet objectif, un protocole de vieillissement artificiel a été mis en place pour soumettre les verres modèles à des conditions similaires à celles des verres historiques et induire une corrosion pendant une durée d'au moins 18 mois en présence de COV, à savoir l'acide acétique et l'acide formique, ainsi que d'une humidité relative fluctuante ou fixe. Ces verres modèles corrodés ont été périodiquement contrôlés pour caractériser la corrosion sur la base des changements physiques et chimiques en utilisant diverses techniques d'analyse chimique et d'imagerie, dont la plupart étaient non invasives.

Une terminologie a été développée pour décrire les différents signes de corrosion du verre. La combinaison d'analyses chimiques et d'imagerie a permis de catégoriser la corrosion, même à un stade précoce. Les changements chimiques tels que les changements dans les espèces de silicate et la composition des produits de corrosion ont été compris grâce à la spectroscopie IRTF et Raman, tandis que la microscopie numérique et l'imagerie de transformation par réflectance se sont avérées utiles pour quantifier les deux signes visibles de la corrosion, à savoir les néocristallisations de sels humides et les fissures. L'imagerie hyperspectrale dans le domaine de l'infrarouge à ondes courtes s'est avérée la plus utile pour identifier la corrosion à un stade précoce. Elle a permis non seulement de visualiser des caractéristiques sur l'ensemble du verre modèle, dont certaines n'étaient pas visibles à l'œil nu, mais aussi d'obtenir des preuves spectrales de l'absorption d'eau et d'hydroxyles, qui ont pu être utilisées comme indicateur pour quantifier la corrosion.

La corrosion du verre a été exacerbée par la présence de COV qui ont formé des néocristallisations humides de sels de formate sur la surface du verre en cas de corrosion à des concentrations plus élevées de COV et ont formé des sels de formate et d'acétate en cas de corrosion à des concentrations plus faibles de COV. Des corrélations ont été trouvées entre divers paramètres de corrosion tels que les changements de poids, la zone couverte par les néocristallisations de sels humides, l'épaisseur de la couche d'altération, les rapports de pics Raman et IRTF, la densité des fissures, l'eau et l'hydroxyle absorbés par la matrice du verre et les ions alcalins lessivés du verre en vrac. Le protocole proposé dans cette recherche peut donc faciliter l'identification précoce de la corrosion du verre, ce qui pourrait aider les conservateurs et les scientifiques de la conservation à appliquer des méthodes de conservation préventive appropriées et à stocker les objets historiques en verre dans des conditions adéquates.

Mots-clés: Imagerie hyperspectrale, corrosion du verre, vieillissement artificiel, composés organiques volatils, imagerie par transformation de la réflectance, microscopie numérique, spectroscopie Raman, spectroscopie infrarouge à transformée de Fourier.

Abbreviations

AA – Acetic Acid

AL - Alteration Layer

BSED - Back-Scattered electron detector

CHANGE - Cultural Heritage Analyses for New Generations

DM - Digital Microscopy

DRH - Deliquescence Relative Humidity

EPMA - Electron Probe Microanalysis

FA – Formic Acid

FORS - Fiber Optic Reflectance Spectroscopy

FTIR - Fourier Transform Infra-Red Spectroscopy

HDR - High Dynamic Range

HD-RTI - High Dynamic Range RTI

HSI - Hyperspectral Imaging

IR - Infrared

LDR - Low Dynamic Range

LED - Light Emitting Diode

NBO - Non-bridging oxygen

P - Aging condition with high VOC concentration with fixed RH

PID - Photo Ionic Detector

PTM - Polynomial Texture Mapping

PV - Aging condition with high VOC concentration with fluctuating RH

RF - Response Factor

RGB - Red Green Blue

RH - Relative Humidity

RL - Reflected Light

TS - Transmittance spectroscopy

RSD - Relative Standard Deviation

RTI - Reflectance Transformation Imaging

SEM-EDX - Scanning electron microscopy coupled to energy dispersive X-ray spectroscopy

SN - Salt Neocrystallizations

SNM - Swiss National Museum

SNV - Standard Normal Variate

SWIR - Short-Wave Infrared

TCPL - Transmitted and Cross-Polarized Light

TL - Transmitted Light

V - Aging condition with high VOC concentration with fluctuating RH

VNIR - Visible and Near Infrared

VOCs - Volatile Organic Compounds

XRF - X-ray Fluorescence

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SECTION I

Chapter 1: Introduction

1.1. Background of the project

This project comes under the Cultural Heritage Analyses for New Generations (CHANGE) Marie Skłodowska Curie Action-Integrated Training Network (MSCA-ITN CHANGE, change-itn.eu), and was hosted at the Collection Centre of Swiss National Museum (SNM) in Affoltern am Albis. At the SNM evidence of degradation such as cracking, salt neocrystallizations primarily of methanoates (formates) and ethanoates (acetates) and delamination, was observed on historical objects dating from the 17th- 20th centuries CE, which were stored in mobile chipwood mobile shelving units for about 33 years from 1967 to 2000, without any temperature and relative humidity (RH) controls [1]. Like other types of manufactured wood and particle board, chipwood is also known to be a source of Volatile Organic Compounds (VOCs) primarily ethanoic acid (acetic acid), methanoic acid (formic acid), and methanal (formaldehyde) [2][3][4]. These compounds have been found to exacerbate the corrosion process in historical glasses kept in museums leading to the formation of formates and acetates on the surface [5][6][7]. Indeed, previous assessments of these corroded historical glass objects showed the presence of formates and acetates. Therefore, it was assumed that the long-term storage in chipwood mobile shelving units played an important part in their corrosion. Since 2000, the objects have been stored in improved conditions with added absorbing materials such as activated charcoal from 2012 onwards, however, the glass still shows evidence of corrosion products on the surface, even after cleaning.

Glass corrosion is a complex process influenced by many different factors such as temperature, relative humidity, pollutants as well as composition and manufacture process of the glass itself. Several studies have been undertaken when it comes to outdoor atmospheric corrosion of glass [8][9][10][11][12] and some studies have focused on the corrosion of historical glass, especially soda-lime silicate glass, in indoor museum environments in the presence of VOCs [4][7][13][14][6][15][16], using conventional analytical techniques such as Fourier transform infra-red spectroscopy (FTIR), Raman spectroscopy, scanning electron microscopy coupled to energy dispersive X-ray spectroscopy (SEM-EDX), X-ray fluorescence, ion chromatography, secondary ion mass spectrometry, and so on. Nonetheless, many questions surrounding their corrosion mechanisms and preservation measures lay unanswered when it comes to the corrosion of potash-lime silicate glass objects in the presence of VOCs.

Historical glass pieces were exposed to atmospheric conditions ever since they were made. According to documented assessments of glass item collections in European museums, between 15 and 30% of glass artefacts are currently corroded to varying degrees [12]. These numbers, which are based on only visual observations, may be understated because deterioration signs are not always apparent.

The over-purification of raw materials and introduction of new recipes that resulted in glass compositions containing more fluxes (Na_2O , K_2O , and PbO) and less stabiliser oxides (mainly CaO) are blamed for the low chemical durability of many of these corroded objects, most of which date from the middle-age period to the 19th century [12]. Unstable glass compositions

show visible signs of atmospheric deterioration, while stable compositions remain unaffected. Chemical stability in the atmosphere is an important quality of the glass composition.

1.2. Previous assessments

The first assessment of the historical glass objects, currently kept in the collection centre, was done by Andrea Schwarz in 2000 as part of a diploma thesis of the degree program in Conservation and Restoration at the State Academy of Fine Arts in Stuttgart. The signs of corrosion could be seen with naked eyes and thus were documented as well as the causes were investigated.

About 1300 glass objects were examined in this assessment, mainly from the 17th century till 20th century. The chipwood mobile shelving units used in the old depot are shown in fig. 1.1.



Fig. 1.1: Glass objects kept inside chipwood mobile shelving units in the old depot of SNM (Source: Andrea Schwarz [17]) (©SNM)

The climatic conditions in the depot room were already measured and recorded in 1998 with a thermohydrometer. The recorded values could be confirmed by controlled measurements using a calibrated electronic measuring device. It turned out that especially in the summer months and in the transitional months in spring and autumn a high RH, with an average value of about 65% and maximum values of up to 75% in the depot room was observed. During the heating season in the winter months, on the other hand, the RH was on average around 35%. Despite these longer-term fluctuations in RH, the daily fluctuations were relatively small in winter and could reach up to 15% in summers. The average temperature was $19^{\circ} \pm 3^{\circ}$ Celsius [1].

In addition to recording climatic conditions, indoor air measurements were carried out due to a conspicuous, intense smell in the depot. The assumption that this was a pollutant load by formaldehyde could be confirmed using passive samplers. A concentration of 0.38 mg

formaldehyde per cubic metre (about 3 times higher than the recommended upper limit of 0.125 mg/m³ by World Health Organization) was measured. In the old depot room, there was hardly any air exchange, and thus a high concentration of the harmful gas over the years had developed. Therefore, in addition to formaldehyde, measurements of the formic and acetic acid content were also carried out in the SNM old depot, but neither formic acid nor acetic acid were detected. The glass objects were also classified into four categories depending on the visible signs of corrosion (Table 1.1).

Table 1.1: Four categories of glass objects at SNM based on visual signs of corrosion

S. No.	Category	Definition	Amount
1	Stable	no visible signs of corrosion	85%
2	Unstable	deposits and/or moisture on the surface	12%
3	Attacked	deposits and/or moisture on the surface and cracking	2%
4	Severely attacked	cracking along with scales or flakes	1%

About 15% of the objects were found to be in a corroded state. Apart from classification, chemical analyses of corroded historical glasses using wavelength dispersive electron beam microprobe was also undertaken which showed the formation of a thick outermost layer from which sodium or potassium had leached out as well as had lower calcium with respect to the bulk glass composition. Additionally, glass sensors developed at the Fraunhofer Institute for Silicate Research in Würzburg were artificially corroded in the presence of chipwood to study the specific cause for the corrosion in the SNM old depot. It was found that the visible signs of corrosion were worse in the presence of chipwood. Nonetheless, the results were found to be inconclusive regarding the influence of VOCs on the corrosion of the historical glass objects [1].

This assessment was then followed by the establishment of improved storage conditions with controlled RH (40-45%) and temperature ($\approx 19^\circ\text{C}$) inside powder coated steel cabinets on ethafoam sheets (Fig. 1.2) which lasted from 2000 till 2006. From 2006 onwards, the objects were stored at an RH of $50 \pm 5\%$. The glass objects were also cleaned with lukewarm water and rinsed with a mixture of deionized water and ethanol (1:1). Further assessment was performed on selected objects before and after the cleaning using FTIR spectroscopy to understand the type of corrosion products on the surface as well as changes which might occur due to cleaning of the historical objects. This shall be discussed more in detail in chapter 5 about historical objects.



Fig. 1.2: Glass objects kept in emission-free sheet steel cabinets in the new depot from 2000 onwards (©SNM)

1.3. Terminology for visual aspects of glass corrosion

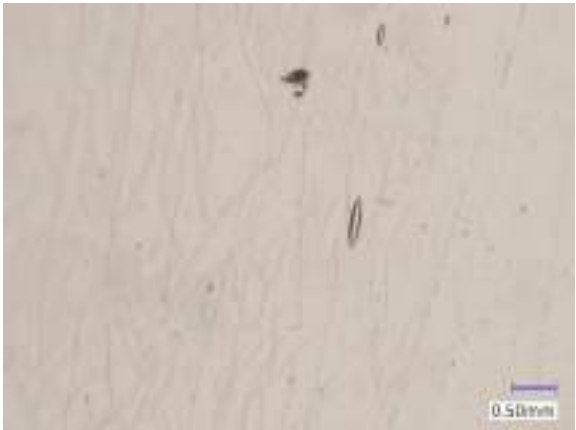
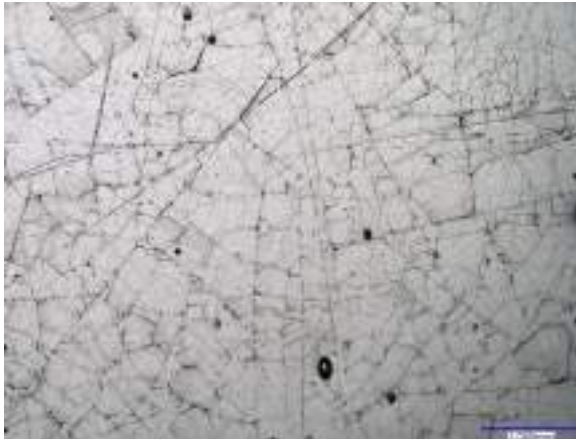
There is a lot of discrepancy when it comes to the description of visual appearance of corroded glass. Until the 19th century, general terms such as glass disease, sick glass and glass illness were used to signify glass corrosion [18] and could still be found occasionally [19]. During this research a dire need for a standardized scientific terminology was realized which would help the whole glass community if used. Therefore, the formulation of a standardized vocabulary for visual signs of glass corrosion was established as follows based on information from scientific as well as glass conservation literature inspired by the ‘glass at risk’ project (Table 1.2) [20].

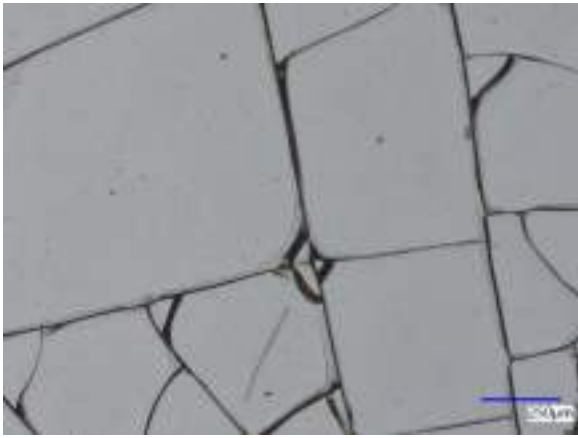
Glass corrosion features/signs have been classified, in general, under three different categories:

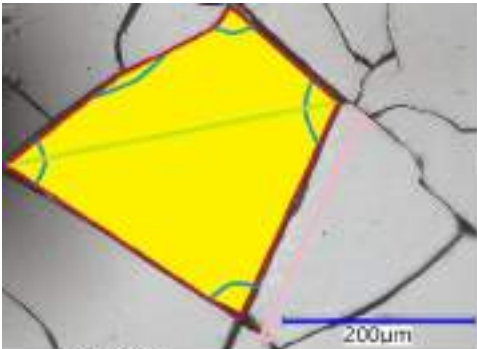
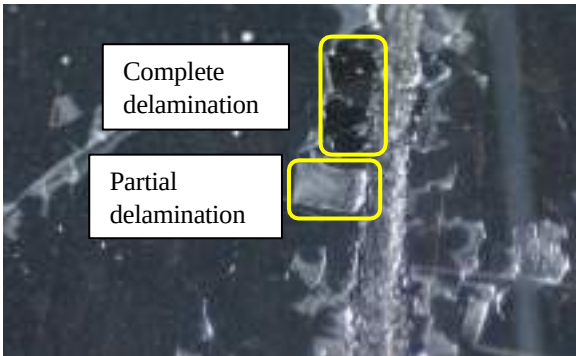
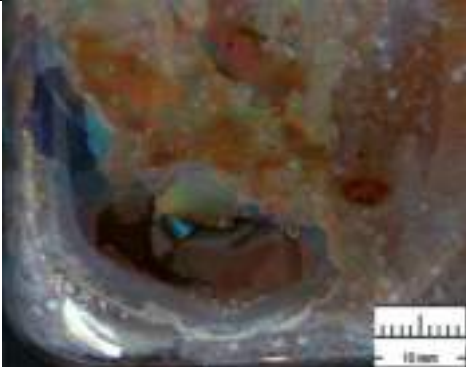
1. Little to no corrosion: Signs of corrosion only visible above 25× magnification
2. Intermediate corrosion: Signs of corrosion visible between 10× and 25× magnification
3. Advanced corrosion: Signs of corrosion easily visible with naked eyes and at less than 10× magnification

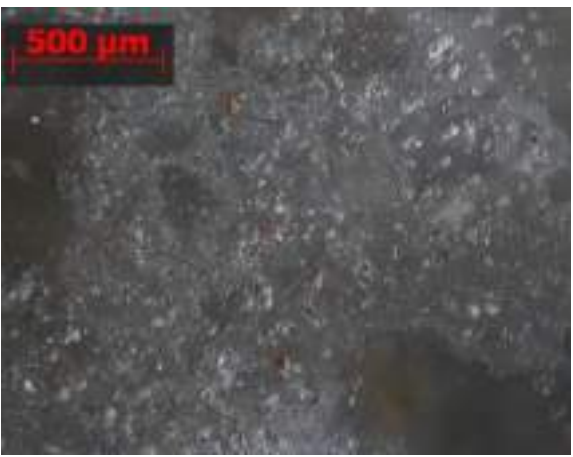
Table 1.2: Terminology for different signs of corrosion along with examples from SNM glass objects and other terms used in literature

Corrosion sign	Examples	Definition	Other terms
Opacification	 LM 7138.99, imaged using digital camera and reflected light on black background (Source: Andrea Schwartz [17]) (©SNM)	Loss of transparency because of corrosion of glass [21]. This could be quantified based on the change in light transmission percentage of the corroded glass as compared to the value of initial non-corroded glass.	Opacity [20], cloudy appearance [22], haziness, white haze [21]
Salt neocrystallizations	 LM 60578 Dry salt neocrystallizations, imaged using digital camera and reflected light on black background (Photo: Janet Schramm) (©SNM)  AG 1078, Wet salt neocrystallizations (deliquescent salts), imaged using digital camera and reflected light on black background (Photo: Janet Schramm) (©SNM)	Dry or hygroscopic (deliquescent) salts formed on the surface of glass because of corrosion when the cations leached out of the glass matrix interact with the anions in the ambient environment on the surface of the corroded glass.	Sweating [21], weeping [21], tearing [19], blooming [21], deposits [19], crying [23], moisture [19], slippery [22], alkaline deposits [19], salt crystals [19]

Soiling	 LM 80719.3, Dust and dirt deposited on the surface imaged using digital camera and reflected light on black background (Photo: Janet Schramm) (©SNM)	Physical deposition on the surface of glass of exogenous materials (such as dust, dirt, debris etc.), which are not a result of glass corrosion.	Deposits [22], residues [21]
Cracking	1. Fine cracking  AG 1078, Fine cracking: Fine arced micro-cracking and some T-joint and angled cracking imaged with Keyence digital microscope at 50× magnification using flexible arm and transmitted light (©SNM) 4. Coarse cracking  LM 12433, Coarse cracking, T-joint and polygonal network, imaged with Keyence digital microscope at 50× magnification using movable stage and transmitted light (©SNM) Further, under the two categories of fine and coarse microcracking, the cracks can be described based on their shapes as follows:	Cracks visible at high magnifications >25x. Two further thresholds might be defined, based on 2 parameters: -the width of the crack -the density of cracks in each area Cracks visible in low and medium magnifications <25× as well as with naked eyes. Two further thresholds might be defined, based on 2 parameters: -the width of the crack -the density of cracks in each area	kranke Gläser [1], crizzling [22][21] Incipient crizzling [24] Full-blown crizzling, advanced crizzling [24] [1]

	Linear cracking  AG 1078, Fine parallel linear cracking, some T-joint and angled cracking imaged with Keyence digital microscope at 50× magnification using flexible arm and transmitted light (©SNM) Arced cracking  AG 1078, Fine arced cracking with Keyence digital microscope at 50× magnification using flexible arm and transmitted light (©SNM) T-junction cracking  AG 1078, T-junction cracking imaged with Keyence digital microscope at 100× magnification using movable stage and transmitted light (©SNM)	Roughly straight cracks arranged in parallel series Cracks appearing as lines that arc or bend gradually Junctions where two cracks meet at nearly 90° angle, making a T shape	
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	Polygonal Network cracking  Legend: — Sides of polygon — Angles of polygon — Polygon diameter (longest diagonal) — Side length — Polygon area LM 12433, Coarse polygonal cracking imaged with Keyence digital microscope at 100x magnification using movable stage and transmitted light, showing variables of a polygon (©SNM)	In advanced micro-cracking, linear cracks join up, causing denser networks of crack, which can lead to the formation of polygons. Regular polygonal cracking patterns can be described by their number of sides and side lengths, angle, surface area, diameter.	
Delamination	 LM 40638, Complete and partial delamination imaged using digital camera and reflected light on black background (Photo: Janet Schramm) (©SNM) Complete delamination Partial delamination	When horizontal surface layers in the alteration layer separate fully or partially from the bulk glass. It is divided into two categories: When the flake is completely detached from the bulk glass When the flake is partially detached from the bulk glass	Flaking [22], scaling, spalling [20]
Iridescence	 Iridescence on apothecary bottle LM2733.76 (Source: Janet Schramm [25]) (©SNM)	This phenomenon has been described as rainbow-like with perceived colours changing as light hits the glass at different angles.	Shimmering surfaces, golden flakes, multicoloured reflections [21], opalescent layers [24]

Pitting	 Pitting on DEP-1393 (Photo: Janet Schramm) (©SNM)	Pitting results from the gathering of numerous pits or craters formed due to highly localized non-uniform dissolution of the glass matrix.	
Discolouration	Complete discolouration  Complete discolouration of glass distinguished by its pink colour LM85422 (Photo: Janet Schramm) (©SNM) Partial discolouration  DEP 1393 showing partial discolouration (Photo: Janet Schramm) (©SNM)	Any change in the colour or hue of a glass object due to corrosion. In cases such as oxidation of Manganese leading to the alteration of colour of a glass object in presence of sunlight (also known as solarisation), the whole object is influenced uniformly by colour change. In cases of non-homogenous browning, spots or stains, on specific parts of the glass.	Colour alteration [22], solarisation, browning, staining [21]

1.4. Glass chemistry

The fundamental raw materials that made up historical glass were typically network formers, network modifiers (fluxes and stabilisers), and colouring components and other components added later [26][27][28]. Sand (or other silicate materials) served as the primary raw material. Sand introduced silica (SiO_2), the major network forming component. Fluxing agents (mainly alkali and alkaline earth oxides) are added to decrease the melting temperature of the silica and viscosity of the glass mixture. In a high-temperature procedure that was occasionally carried out in multiple steps, the raw ingredients were prepared, combined, and melted. To avoid crystallisation, there was a reasonably quick cooling process after that. The glass piece was then annealed to release the tensions. Alkaline earth oxides such as calcium oxide (CaO), are network modifiers as well, but they are referred to as stabilisers since they help to increase the durability and moisture resistance of the glass. However, CaO added in glass beyond 10 mol% could even make it highly unstable [29]. However, in addition, several metals (including Cu, Co, Mn, etc.) were employed to tint the glass [19][27][30].

Due to the manufacturing method used, all unstable glasses contained chemical compositions that are not in the correct proportions. The major reasons are thought to be over-purification of some raw materials and/or inadequate batch formulation, which leads to a lack of stabilisers and an overabundance of alkali in the glass structure. Thus, it appears that the primary factor regulating instability is the total composition of the glass, and the impact of this composition on the deteriorating process is quite complex. The durability of glass can be greatly impacted by even slight compositional changes [31]. These compositional variations may be caused by the inadvertent usage of materials that are slightly different. Such forced modifications were brought on by changes in the availability of particular components or specific sources of these, or intentional alterations of materials and technology to produce new or modified features. Other factors also come into play for the durability of glass, such as the molecular makeup of the glass, which may encourage the condensation of Si-OH groups and the topology of the lattice, which may raise the activation energy for lattice hydrolysis [12].

At the atomic level, glass is a network of anions with a central silicon atom surrounded by four oxygens bonded to the silicon by strong covalent bonds in a tetrahedron. This network is formed by sharing an oxygen between two atoms of silicon, producing a bridging oxygen atom. Pure silica glass has almost all its oxygen as bridging oxygen, creating a strong network similar to crystalline silica, but with varying bond lengths and angles that make it disordered. When network modifying oxides like alkali or alkaline earth oxides are added as a flux, they introduce non-bridging oxygen atoms that disrupt the silicon-oxygen bridges, weakening the network and making it more susceptible to corrosion. The oxygen atoms in the tetrahedron usually have a second valency connecting them to neighbouring silicon tetrahedra (Si-O-Si), alkali or alkaline cations (Si-O-M), or hydrogen (Si-O-H), leading to polycondensation and the formation of a spatially linked lattice or network. The hydroxyl ions present as impurities in the glass [32][33][34] can form hydrogen bonds not only with each other but also with the oxygen atoms of normal bridging linkages [34], leading to strong or very strong hydrogen bonds as well as free hydroxyl groups (Fig 1.3). Chemically, historic glass has a small number of undissolved nuggets at the μm level, and only low concentration gradients are seen at the cm level [36].

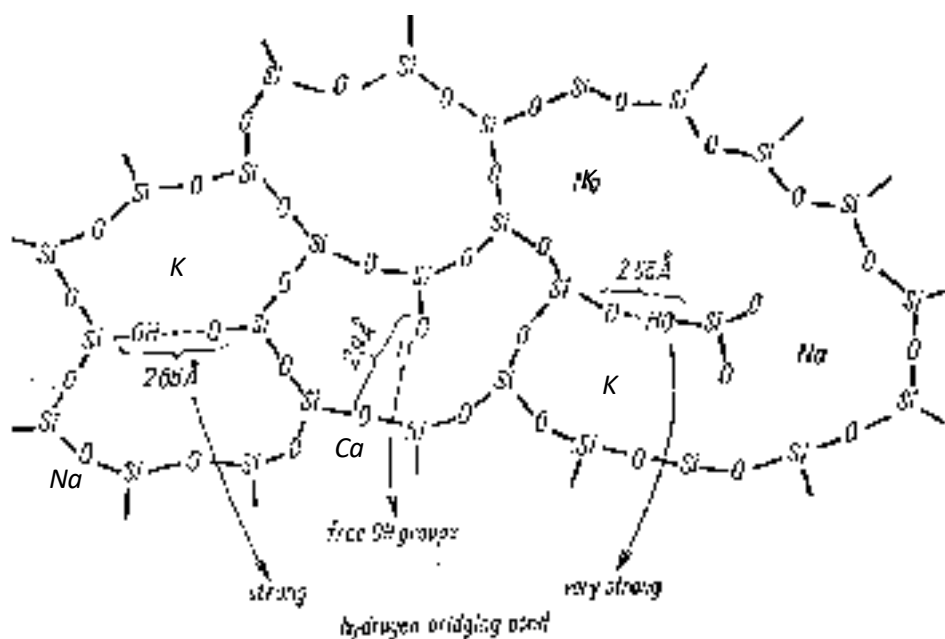


Fig. 1.3: A schematic representation of Potash-soda lime silicate glass (modified from [35])

The number of bridging oxygen atoms on a specific tetrahedral Si site is indicated by the notation Q_n with $n = 0 - 4$. For example, one Q_2 site is a Si tetrahedron linked with two bridging and two non-bridging oxygen atoms (NBOs). Q_1 , Q_2 , Q_3 , and Q_4 , is the order in which site reactivity occurs (Fig. 1.4). The network modifiers such as Na^+ and K^+ produce one NBO when attached to an Si-O- unit. The presence of Ca^{2+} ions is known to stabilise the lattice, since this allows to exhibit better bonding than Na^+ or K^+ to the oxygens non-bridged at silicon, whereas the alkali converts one Si-O-Si group into two Si-O- units (NBO). Due to the diversity of the atoms, the bond angles in the perturbed and irregular structure differ within a given range and their strength varies from one point in the structure to another.

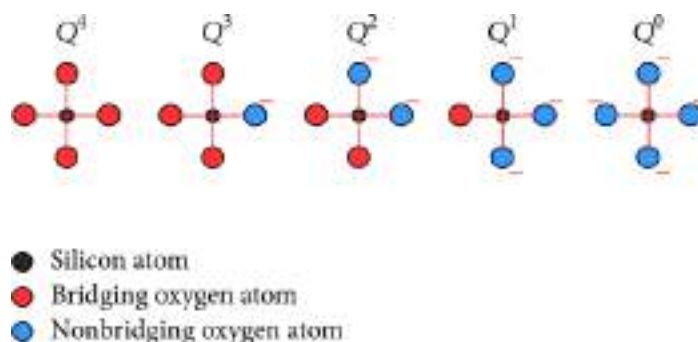


Fig. 1.4: A schematic representation of Q_n species in silicate glass [37]

Raman spectroscopy provides detailed information on Q_n silicate species. Within the $200-1300\text{ cm}^{-1}$ range, distinct vibrational bands correspond to various bridging and non-bridging Si-O bonds in the glass structure (Table 1.3). The spectral analysis of alkali silicate glasses reveals

that the range spanning from 300 to 500 cm^{-1} is predominantly linked to the bending vibrations of the polymerized structure. According to Matson et al. [38], the average angle of Si-O-Si has an impact on the position of the band between 400 and 600 cm^{-1} . A reduction in the Si-O-Si angle results in a shift towards higher frequencies.

Conversely, the range from 850 to 1300 cm^{-1} is associated with stretching vibrations primarily observed in depolymerized silicate species [5][38][39][40][41][42].

Table 1.3: Position of different Raman bands in the silicate region and their assignments according to different literature

Band position ($\approx$ wavenumber cm^{-1})	Assignment (δ =bending, ν =stretching)	References
300-400	Si-O-Si δ polymerized Q4	[5]
400-500	Rocking motion of fully polymerized Q4 units breathing modes of four- and six-membered rings of SiO ₄ tetrahedra in polymerized glasses as an independent vibrational unit Si-O-Si symmetric ν vibrations that involve bridging oxygens and four-fold coordinated cations Si-O-Si δ vibrations in glasses that contain NBOs	[39][38][43][44] [45] [41][43]
530-550	Si-O-Si δ Q3	[46]
580-606	structural defects (such as broken oxygen bridges) Mixed ν - δ vibration in Q2 structural units	[38] [47]
700	Si-O-Si δ motion	[41][43][47][48]
770-790	Q0	[39]
800	cage-like vibrations of Si atoms mainly in Q4 tetrahedra	[49]
850-950	Q1	[39]
950-990	Q2 ν	[5]
990-1020	Q2+Si-OH ν	[5] [39]
1040-1050	Si-O ν vibrations in specific Q3 or Q4 units	[50]
1080-1100	Si-O ν mode of Q3 species	[51][52][53][54]
1150	Q3' (different from Q3) + Q4 ν	[38]

The precise location and relative intensity of all these bands depend on the composition of the glass [51][52][53][54].

1.5. Chemical durability of historic potash-soda lime silicate glass

Chemical durability is a characteristic of the glass's general composition. The presence of alkali metals decreases the overall bond strength of glasses, reducing their density, refractive index, modulus of elasticity, internal bonds, and strength dependent on internal weak points. Hardness is also affected by alkali metals [35].

Potash glass has a higher density compared to soda-lime glass and solidifies faster from a molten state, making it less malleable to create intricate shapes. Nevertheless, it boasts of

greater hardness and brilliance, making it ideal for embellishing techniques like facet cutting and copper wheel engraving [55]. Therefore, it is also known as hard glass.

The literature indicates that soda-rich glasses are less vulnerable to aqueous corrosion than potash-rich glasses are [56]. Silicate glasses containing K_2O are less resilient; this fact is explained by the greater size of the K^+ ions, lower field strength of K^+ compared to Na^+ , and weaker K-NBO bond. Field strength is often used to describe the ability of a cation (positively charged ion) to attract or bind with other ions or molecules in a surrounding medium. The field strength of a cation is influenced by its charge and the size of its ionic radius.

In the case of potassium (K^+) and sodium (Na^+), both are alkali metal cations with a single positive charge, but they differ in their ionic radii. Potassium ions (K^+) are larger than sodium ions (Na^+). As a result, K^+ ions have a lower field strength compared to Na^+ ions. These two variables serve as the foundation for distinguishing between stable and unstable CH glass compositions. These glasses can therefore experience considerable corrosion involving chemical reactions with water, which can change their long-term stability [12].

Binary alkali metal silicate glasses show poor chemical durability. According to research by Alloteau et al. [57] on unstable mixed alkali-lime silicate glass, alkalis are retained adjacent to NBOs in the opposite order of their hydration energy, namely $K^+ > Na^+ \gg Ca^{2+}$, under reduced water solvation circumstances. K^+ ions are retained adjacent to NBOs more than Ca^{2+} ions are, which promotes rapid network hydrolysis in a hydrate-like environment [12].

The larger size of potassium atom makes it less mobile in the glass structure. Additionally, the larger size of the potassium ion reduces the density and increases the specific volume of the glass more than sodium does. The bond strength between potassium and oxygen in glass is one third lower than that of sodium due to the larger radius of potassium. As a result, both elements decrease the chemical durability and increase the thermal expansion of glass, but potassium has a greater effect due to its weaker bond strength. However, mixed alkali effect in case of mixed alkali glass compositions is something which affects their behaviour greatly.

The larger size of potassium ion causes more deformability compared to sodium (as indicated by ionic refraction values, $R_{Na} = 4.75$; $R_K = 8.25$), resulting in weaker Si-O-K bonds. However, K_2O promotes the formation of glass and suppresses phase separation, particularly in the presence of Na_2O .

1.6. Glass corrosion: State of art

The term "glass corrosion or deterioration" refers to a wide range of phenomena, but all deterioration involves an attack on the glass surface by water in liquid or vapor form. Assessments of previous environments and/or predictions of behaviour are difficult because of the complexity of the components that impact the type and rate of corrosion. The composition of the glass, the type of glass surface, the production history, the pH of any fluids or gases that may be present, the presence of salts, organisms, metals or organic compounds, the redox potential, O_2 levels and temperature are all important factors in the reaction of a glass to

moisture. Changes in the environment and the results of previous preservation and/or cleaning operations can aggravate the consequences of these different causes [58].

Glass modification comprises of two distinct components: the more subtle changes in glass structure and the surface-forming apparent crystalline corrosion products [5]. The process of glass alteration involves several distinct stages, as described by Frugier and colleagues [59] who described mechanistic models for the aqueous alteration kinetics of glass. Experimental observations have shown that all of the corrosion-related reactions occur simultaneously during glass corrosion but at various rates depending on the circumstances [12]. Nevertheless, the rate at which each reaction takes place is contingent upon several factors, such as glass composition [60][61][62], temperature [8][63], and pH [64], RH [15] and indoor VOC pollutants [4][5][7][65].

The composition of glass has a significant impact on its reactivity and corrosion kinetics [12]. Glass composition also affects the structure of the surface, including its porosity, size, and number of lattice voids, as well as its hygroscopicity. The distribution of exchangeable sites is determined by the glass structure, which is in turn determined by the glass composition [15]. The mixture of modifying cations affects the stability of the glass in humidity, with alkali ions being the most affected by corrosion due to their mobility and weak connections to non-bridging oxygen, resulting from their large ionic radii. As the charge to radius ratio of the cation decreases, the glass generally becomes more reactive [57].

The global scientific community has established a set of mechanisms and kinetic regimes to describe the corrosion of glass in various environments, including aqueous solutions, unsaturated atmospheres, indoor and outdoor atmospheres [15][66][67][68][69][70][71]. Unlike solution corrosion, the modification of glass in unsaturated atmospheres with water vapor involves functional surface clusters like Si-OH, which can combine with alkali ions on the glass surface. The following are the main differences [72]:

1. The glass surface contains functional surface clusters such as Si-OH, either in their acidic state or in combination with alkali ions on the glass.
2. After interdiffusion, the alkali ions leaving the glass may create compounds that concentrate on the surface.
3. The glass network is chemically attacked but does not disintegrate, which leads to the interdiffusion of alkali ions and protons without reaching an equilibrium state

Studies have shown that the texture of corroded glass can be complex and seemingly random, indicating that a single common degradation mechanism cannot explain all types [73] [74][75]. A number of mechanisms are likely responsible for the corrosion of glass, and secondary degradation processes can also occur, such as cracks created in the corroded layers being filled with precipitates [76] [78].

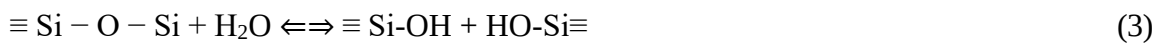
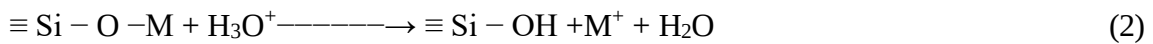
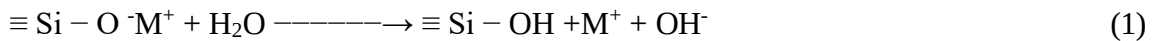
The alkali ions leaving the glass after interdiffusion form compounds that concentrate on the surface. The composition of glass, specifically the ions leached from the glass, the reaction of these latter with atmospheric pollutants, and surface deposition of ionic compounds from the atmosphere determines the nature of species present ([7] and references therein). All such ions

from within the glass and from the atmosphere can potentially produce a wide range of crystalline products or ionic solutions on the surface of unstable glass objects in museum collections, which may crystallize as dry and wet salt neocrystallizations depending on the deliquescence relative humidity (DRH) and RH of the storage or display environment.

1.7. Mechanisms of glass corrosion

The mechanisms to be discussed in this research consider the two understudied factors of glass corrosion i.e. presence and concentration of VOC pollutants (acetic acid and formic acid) in the ambient indoor atmosphere and fixed or fluctuating humidity. Silicate glasses undergo a range of interrelated processes when they encounter stagnant water at the interface between the solid and liquid phases. These processes include hydration, ion exchange or interdiffusion, hydrolysis or network dissolution, and/or neocrystal nucleation and growth, all of which operate to establish a new equilibrium or steady state.

It is widely acknowledged that water is the primary contact factor causing deterioration. The initial stage of glass corrosion occurs when water or humidity in the ambient environment adheres to the surface, forming a thin film, a few nanometers thick, which permeates it. Water molecules initially physically bind to adsorption sites on the glass surface, which are strongly reliant on the surface quality [68]. Three types of interaction between water and glass have been described in literature viz. hydration when molecular water enters the glass as an intact solvent (1), ion exchange when cations such as alkali ions are replaced by hydrogenated species (2) and hydrolysis when water breaks Si-O-Si bonds reversibly (3) [19][55].



where M^+ represents an alkali ion K^+ , Na^+ or an alkaline earth ion like Ca^{++} and so on...

Ion exchange reactions are frequently held responsible for the selective leaching of modifier cations found in intricate silicate glass compositions which usually dominates in neutral and acidic solutions with pH values less than 9 [6][55][78][79]. Previous research, including studies by Scholze [80], Schreiner [81], and Melcher and Schreiner [82], has demonstrated that water diffuses into the glass through large rings of at least six silica tetrahedra. The term "interdiffusion" refers specifically to the counter-directional diffusion of positively charged water species and positively charged glass alkali and alkaline earth ions, that arise from the ion exchange process at the interface between pristine and altered glass. The mobility of the cations involved in the ion exchange process is influenced by their charge and size, as well as by the composition of the original glass. Moreover, the glass structure influences the kinetics of the exchange process and determines the distribution of exchangeable sites.

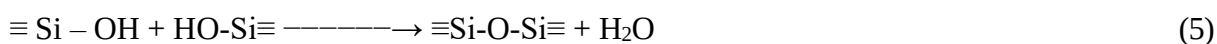
This leads to the formation of a leached glass layer with a significant decrease in network modifiers and an increase in silica concentration. According to Hench [83], the leached layer can transform into a silica-rich film with an increased number of Si-O-Si bonds. As heavier cations are replaced with lighter protons, the density of the leached layer decreases, while the

volume remains almost unchanged. However, the leached-out ions can react with water and anions in the pollutants present in the environment to form various corrosion products on the glass surface in the form of wet or dry salt neocrystallizations [84].

The leaching reaction often promotes the accumulation of a strongly alkaline hydroxyl solution. In a second phase, as the surface pH increases above 9 [85][86][87][88], network dissolution or depolymerization occurs due to hydrolysis when hydroxyl OH⁻ ions present in water break the Si-O-Si bonds (4). The ion exchange sites are removed from the leached glass surface by polymerization of the silanol (-Si-OH) groups, rendering the ion exchange reaction irreversible. Finally, the combination of hydrolysis with repolymerization can soften the surface structure and accelerate the diffusion rates of water and other species.

Additionally, some water molecules form hydrogen bonds with M⁺ ions and silanol groups. The depolymerization-induced opening of the silicate network facilitates the infiltration of more water molecules, which can activate more Si-O-M sites [57]. Network hydrolysis generally occurs at a higher rate when NBOs are present, following the Q1>Q2>Q3>Q4 pattern, but the amount of different modifying cations also affects the hydrolysis rate [15].

The silicate network can undergo a process of repolymerization (5), leading to the formation of a hydrated silicate layer which affects the release of mobile species. The numerous ion exchange sites of the original structure are removed.



The leaching process theoretically occurs before the dissolution step. However, both processes can occur simultaneously over a wide pH range which can vary based on the glass composition and the surrounding environment [19]. The formation of hydrated layers under atmospheric conditions displays a diverse range of compositions, structures, and strengths of hydrogen bonding. The resulting alteration layers can be categorized as either depolymerized hydrate-type, which contains NBO groups, or repolymerized gel-type, which lack NBOs (Q4) [12].

1.8. Research questions and Objectives

Historical glass objects are objects entirely made out of glass, or partially (as enamels), which have been produced for utilitarian or artistic purposes and have been preserved in private or museum collections in recognition of their historical and/or artistic significance. They are very fragile and challenging for imaging techniques to acquire. This is more so for the colourless and transparent glass objects. Their historical and aesthetical value is one of the main issues, which calls for development of non-destructive investigation techniques for their assessment. Moreover, the use of non-invasive and non-destructive imaging techniques has not been reported extensively in the context of historical glass corrosion in museum environments especially due to VOCs. Such techniques could provide faster and reliable monitoring and identification of the various changes in the appearance of corroded glass.

CHANGE is aimed at addressing a new generation of multi-skilled experts specialized in the study and monitoring of changes on cultural heritage objects (change-itn.eu). The main scientific objective of CHANGE is to develop a methodology to assess and monitor any modification, which cultural heritage artefacts face during their exposure to the atmosphere and

their conservation treatments. Due to inappropriate storage conditions in the past, the glass objects under study from the SNM are in problematic and unstable conservation state and therefore, it is necessary to execute precise cleaning and preventive interventions to slow down the corrosion process and to stabilize their state. The **main objective** of the present study is to establish a methodology and protocol based on non-destructive chemical and imaging techniques to identify and characterize glass corrosion in the presence of VOCs, mainly acetic acid, and formic acid in historical objects at an early stage without relying on clearly visible signs. It is also aimed to be able to monitor historical glass objects from time to time to detect any signs of corrosion or further degradation, thus leading to the exploration of imaging techniques, which can provide high-definition documentation of transparent and colourless historical glass objects. Such a study and monitoring protocol for early identification of corrosion of glass will help glass conservation stakeholders to mitigate the identified corrosive environmental conditions and to provide timely intervention for suitable preventive conservation methods and proper storage of valuable glass objects.

The main objective can be further divided into a two-fold structure along with the most important research questions given as follows:

a) Better understanding of the corrosion mechanisms:

1. What is the role of VOCs and RH in the corrosion of historical potash-lime silicate glass objects kept in museums?
2. How does VOC-induced corrosion progress with time chemically and physically?
3. What are the reactions leading to the corrosion of the potash-lime silicate glass objects kept in the SNM?

b) Establishment of a precise and reliable documentation methodology/protocol:

1. Which techniques can be successfully applied to identify glass corrosion in its early stages?
2. Which techniques are helpful for quantification of the corrosion extent either directly or by proxy?
3. Which techniques would be the most efficient and useful for regular monitoring of transparent colourless glass?
4. To which extent are the explored techniques transferable to real historical glass objects kept in museums?

1.9. Scientific Approach

The analyses to understand corrosion of actual historical museum objects was approached via artificial aging of model glass as proxy for the objects. Such an approach allowed for understanding the corrosion progression as well as in minimising intervention with the real museum objects. Ultimately, some of the useful non-invasive analytical techniques were applied on selected museum objects.

This is a well-established methodology for research on the degradation of cultural heritage materials such as paper, silk, glass, metals and so on [89][90][91][92]. As far as conservation research on historical museum glass is concerned, the use of model glasses is well-known [4][8][13][15][67][70][93][94][95] since it facilitates research related to valuable historical glass objects. These were also used in the current research to simulate the history of corroded SNM glass objects. The model glass were artificially aged in conditions mimicking the storage and therefore could be studied extensively using non-destructive as well as destructive techniques to better understand the corrosion mechanisms and corroborate the physical changes in glass with chemical changes in its structure. Model glasses also provided logistical ease for traveling around the CHANGE consortium in Europe for various analyses. A summary of the artificial aging used in glass corrosion research is given in Table 1.4.

Table 1.4: Summary of artificial aging experiments for studying glass corrosion

Reference	Material	Environment	Setup	VOCs	VOC amount	VOC measurement	Duration
[65]	Potash and soda - lime silicate glasses	40 ° C and 55 % RH climate chamber 40 ° C and 80 % RH Desiccator	Climate chamber + desiccators	acetic acid, propanoic acid, hexanoic acid and octanoic acid	400 and 1200 $\mu\text{g}/\text{cm}^3$ acetic acid	GC/MS	12-14 weeks
[65]	Glass Sensors	SO ₂ , NO _x (gaseous concentrations) and organic acid emissions 23° Celsius	Climate chamber	acetic acid	3000 $\mu\text{g}/\text{m}^3$	GC/MS	14 days
[17]	Sensors	Particle board emission source of acetic acid, formic acid and formaldehyde RH 55 % 23° Celsius	Climate chamber	acetic acid, Formic acid, formaldehyde	300 $\mu\text{g}/\text{m}^3$ acetic acid, 150 $\mu\text{g}/\text{m}^3$ formic acid, 200 $\mu\text{g}/\text{m}^3$ formaldehyde	GC/MS	3 weeks
[16]	Mixed alkali lime model glasses	70°C and 70% RH / 72% and 65°C	Climate chamber + desiccators				3 weeks
[92]	High soda/low lime model glass	40%RH & room temperature		Atmospheric pollutants			1 week
[6]	High soda/low lime	Ambient RH and temp 19 ± 0.5°C and 80 ± 1% RH	Museum cabinet + desiccators	Formic acid or formaldehyde	30 mg/m^3 formic acid 27 mg/m^3 formaldehyde	Calculated	13 months

	model glass			+ ambient air and nitrogen			
[15]	Soda rich model glass	21–24 °C, four RH 45%, 55%, 65% and about 75%	Climate chamber	Atmospheric pollutants	-	-	2 weeks to 1 year
[8]	mixed-alkali lime silicate model glass	85 RH% & T 40°C, 50°C, 60°C or 80°C	Climate chamber + hermetic box	Atmospheric pollutants			6 hrs to 9 months
[89]	high-potassium alkali silicate	90 °C and 90 %RH & 200°C and 75% RH & 90 °C & 20% and 80% RH	Climate chamber	Atmospheric pollutants			1 – 2 weeks

1.10. Outline of the dissertation

A brief description of all the chapter contents is given in this section:

Chapter 1: Introduction

The chapter discusses the background of the project, the state of the art about glass chemistry and its corrosion, the objectives and research questions and the scientific approach used in this research.

Chapter 2: Materials and experimental methods

The chapter discusses the materials studied in this research along with the aging protocols, analytical techniques employed in this study. The different imaging and chemical analyses techniques as well as trials, post-processing with software and statistical tools are also described.

Chapter 3: Results

The chapter discusses the various results obtained which describe the various aspects of glass corrosion related to the visual signs and chemical changes in the corroded glass while comparing the corrosion produced in the different aging corrosion and their temporal progression. These results were gathered from all the different experimental techniques described in chapter 2.

Chapter 4: Mechanisms of corrosion

The chapter interprets the results discussed in chapter 3 to understand the corrosion mechanisms and kinetics in the three different aging conditions. Correlations between the most important variables quantifying different aspects of corrosion were established along with a summary of the corrosion mechanisms.

Chapter 5: Application on real historical objects and proposed monitoring protocol

The chapter discusses the techniques and their modifications which were applied on actual glass objects from the SNM to establish a documentation and monitoring protocol which could be followed by glass conservators along with conclusions and perspectives of the present research.

Chapter 2: Materials and experimental methods

2.1. Historical objects

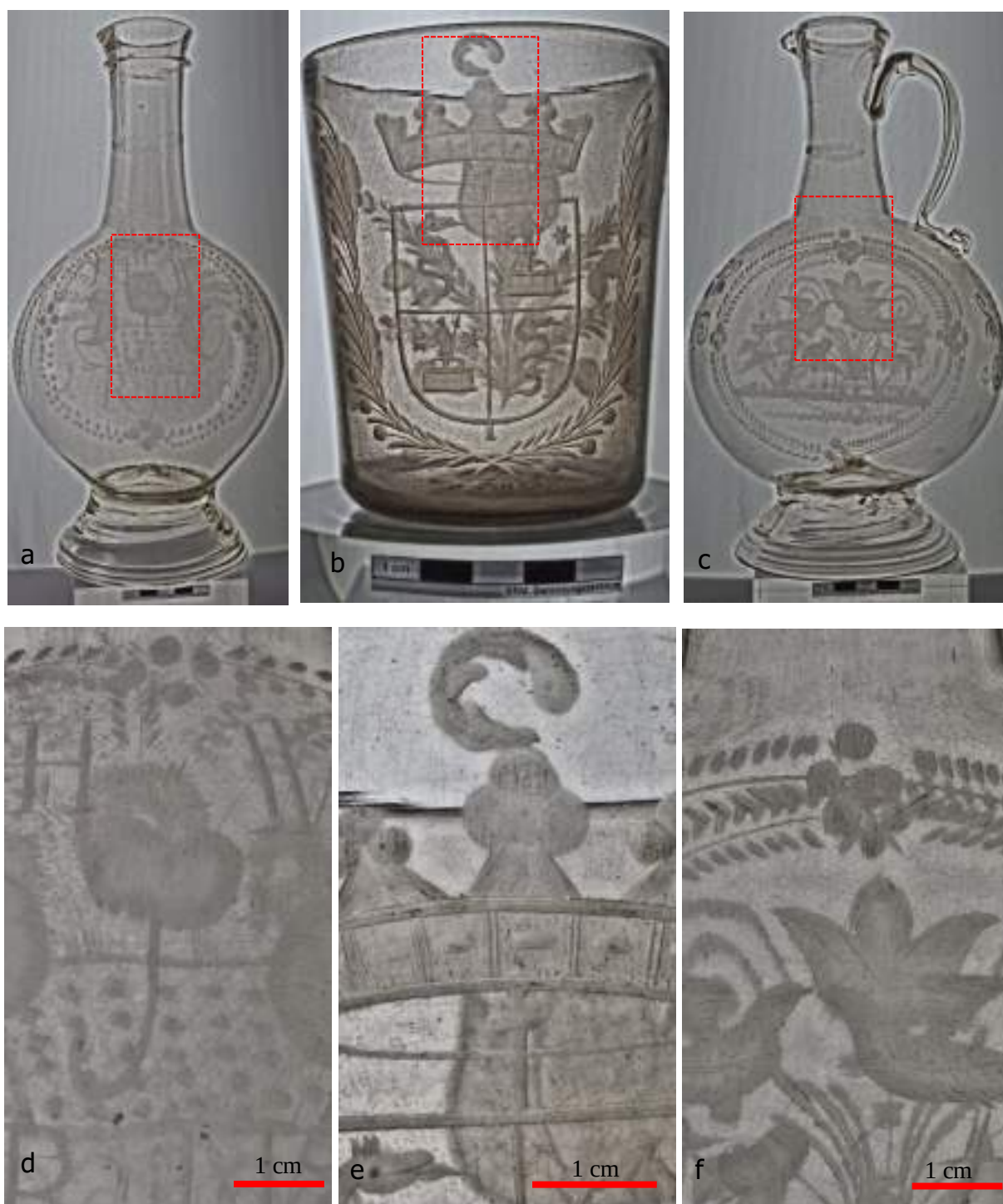


Fig. 2.1: The three ‘severely attacked’ historical glass objects examined for defining the composition of model glass a) LM15473 b) LM12433 c) AG1078 along with zoomed-in details from red rectangular area d) LM15473 e) LM12433 f) AG1078

The study commenced by investigating the composition of three of the most ‘severely attacked’ historical glass objects which also showed acetates and formates both before and after cleaning

with a 1:1 mixture of water and ethanol in 2017. These three objects (Fig. 2.1a, b and c) are described as follows:

1. LM15473: This object was manufactured in the 18th Century and was acquired by the SNM in 1920. It is long-necked transparent flask with circular body and engraved designs on both the sides made of blown glass (Fig. 2.1a). Severe corrosion on one side with coarse cracking and delamination along with fine cracking on the other side (Fig. 2.1d).

2. LM12433: This object was manufactured in the 18th Century and was acquired by the SNM in 1912. It is transparent drinking glass engraved all around with evident pink discolouration and coarse cracking all through the body along with partial delamination on the inside surface and made of blown glass (Fig. 2.1b and e).

3. AG1078: This object was manufactured in the 18th Century and was acquired by the SNM in 1891. It is long-necked transparent flask with circular body and engraved designs on both the sides along with a handle, made of blown glass (Fig. 2.1c and f). The surface was sticky due to presence of wet salt neocrystallizations on the surface as well as dry salt neocrystallizations inside the flask.

2.2. Microsamples

Microsampling is an important technique for analyses of actual historical objects. As the three historical glass objects were corroded on their surface, a precise quantitative determination of the chemical composition could only be achieved by taking small samples from the bulk glass since analyses on big samples or cross-sections were not possible. Apart from this, suitable portable X-ray Fluorescence (p – XRF) was also not available for the analyses. Microsamples also needed to be taken to address the need to minimize intervention with objects of historical importance. SEM-EDX was used to find out the composition of the bulk historical glass. Samples containing about 100 to 150 µg of glass powder could be taken from a complete object at a museum as proposed by Bronk and Freestone [96]. While they used fine grinding files coated with diamond particles, Dremel rotary tool with tapering diamond coated drill bits was found here to be a suitable alternative which is easier to handle and provides better control of the sampling.

Of course, this sampling technique is not completely non-destructive. However, the damage caused was only a small spot, which was located in a discreet area of the object i.e., the base of the object, and when possible, in correspondence with the imprint of the blowing pipe (Fig. 2.2). It seems a reasonable option, particularly for intact objects where no suitable sample for embedding can be removed.

The microsampling was carried out after cleaning the sampling area with pure ethanol. Because the historical objects are very brittle and heavily corroded, sampling was undertaken with great care and was restricted to conservators with extensive experience of vitreous materials. In a corroded glass object, the uppermost surface is usually covered with an alteration layer of varying thickness with a chemical composition distinct from the original composition of the uncorroded glass or bulk known as the bulk composition. The depth of the alteration layer may

vary from only a few micrometres to several millimetres for such unstable objects. Therefore, an initial removal of this layer was required to make sure that only the bulk glass was sampled. The particles from the alteration layer and bulk were separately collected on either sample holders consisting of an aluminium block of c. 13 mm diameter with a carbon adhesive disc (10 mm in diameter, to carry out SEM-EDX analyses afterwards) stuck on top or, alternatively on a clean sheet of paper placed underneath. The drilling tip was cleaned with ethanol after every sample removal. The extent of the damage to the object in such circumstances depends upon the thickness of corrosion product that has to be removed. For the glasses, however, the additional abrasion resulted only in negligible enlargement of the sampled area since it was carried out with caution.



Fig. 2.2: Sampling spot at the bottom of the historical glass object a) before b) after sampling highlighted by black circle

2.3. Model glass

The model glass were manufactured by a French glass blower who works with traditional techniques and recipes used for historical glass manufacture using his own recipe to achieve the required composition (Table 2.1) since it was also important to replicate the surface finish of the historical glass. The melting, working, and annealing temperatures were 1280 °C, 1150 °C and 520 °C, respectively.

The model glasses were first blown into several cylinders each measuring 11 cm in diameter, 21 cm in height, 1-2 mm thickness and then sectioned into twenty curved rectangular pieces of roughly 5 cm × 3 cm size.

Table 2.1. Ingredients used for manufacturing the model glass along with disproportionation reaction equations to calculate oxide percentage for each component in quantity of ingredient used in kilograms for producing 100 kilograms (kg) of glass [97]

Ingredient	Quantity/100 Kg	Equation for oxide	Quantity (oxide)/100 Kg
Silica (SiO ₂)	71	-	71
Sodium Carbonate (Na ₂ CO ₃)	5.25	$\text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{O} + \text{CO}_2$	3.07
Potassium Carbonate (K ₂ CO ₃)	32	$\text{K}_2\text{CO}_3 \rightarrow \text{K}_2\text{O} + \text{CO}_2$	21.81
Calcium Carbonate (CaCO ₃)	4.5	$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	2.52
Potassium Nitrate (KNO ₃)	4	$4\text{KNO}_3 \rightarrow 2\text{K}_2\text{O} + 2\text{N}_2 + 5\text{O}_2$	1.86
	116.75*		100.26

* Amounts of some components were presumably increased to account for material loss during manufacture

The edges of the model glass sample were polished to remove any sharp areas. The top surface of each sample was subsequently engraved using a drill bit coated with diamond grit and a Dremel rotary tool to recreate decorations like those observed on historical objects and to assist in locating points for analyses (Fig. 2.3a). They were then labelled individually and were then cleaned using a solution of five drops of ethanol per 100 mL of deionized water, and their weights and dimensions were recorded.

Along with them four model cups were also manufactured. The model cups were cylindrical in shape and were ≈ 5 -6 cm in diameter, 6.5-7 cm in height and 2-3 mm in thickness. The model cups were also engraved with floral decorations on four sides to replicate historical 3D glass objects (Fig.2.3b).

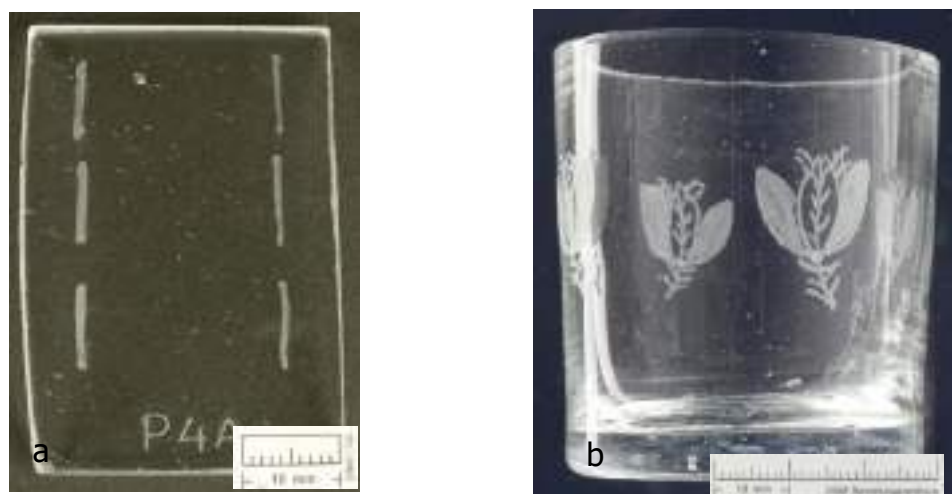


Fig. 2.3: Model glass and model cup manufactured by glass blower mimicking historical glass objects' composition showing engravings a) in form of lines on the two sides on model glass b) in the form of flowers on the model cup

2.4. Dimensions and weight measurements of the model glass

The dimensions of every model glass for artificial aging and reference sample to be kept in ambient temperature and RH were measured before starting the aging. The weights of the model glass were also recorded before the start of aging to be able to detect the slightest weight changes due to the weathering of glass.

120 model glass samples were selected for artificial aging from about 150 model glass samples. These samples were selected based on their dimensions, shapes, thickness (ability to fit in the glass holders) and absence of any major deformities such as pits, scratches, chipping, etc. Each of the 120 model glasses was processed on automatic grinding machine to remove any chipped edges and scratches.

The glasses are semi-circular in shape with the longer edge being curved. The top and bottom edges are straight and were measured with a Toolcraft digital callipers having a precision of $0.01 \text{ mm} \pm 0.002 \text{ mm}$, while the curved edges were measured with a flexible cm scale to a precision of 1mm on the convex side. Given that the glasses did not have a homogenous thickness all throughout, the thickness of each model glass was measured at 6 points (Fig. 2.4) and then averaged. The thickness was measured with the digital callipers as well.

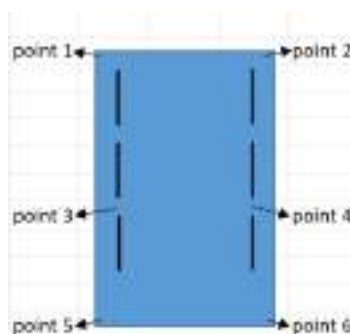


Fig. 2.4: Points for thickness measurement

The dimensions and weight of all the 120 model glass samples was summarised in Table 2.2.

Table 2.2: Average values and standard deviation for the 120 model glass samples

Variable	Mean	SD
Width (mm)	31.00	2.71
Length (mm)	47.47	2.26
Surface Area (mm ²)	1470.86	140.91
Thickness (mm)	1.98	0.35
Weight (gm)	7.17	1.24

Weight of the model glass samples ranged between 3.6353 to 10.2175 grams. A histogram for the frequency distribution of the weight of the model glass is given in figure 2.5.

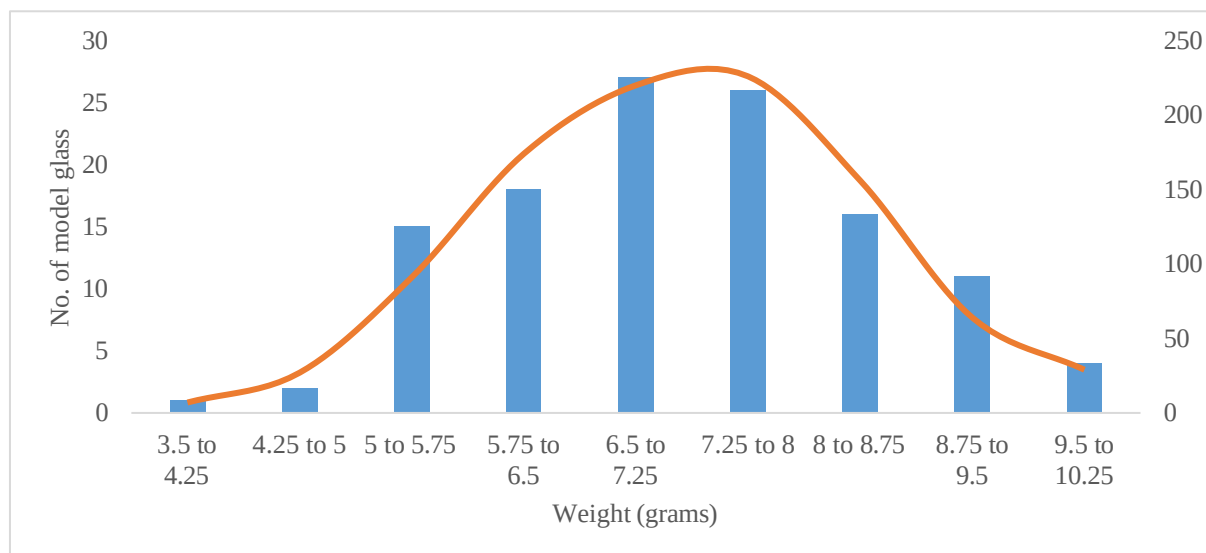


Fig. 2.5: The frequency distribution histogram of weight of the 120 model glass samples with normal curve superimposed for visual assessment (orange)

2.5. Artificial aging protocols

Environmental pollution is a component that greatly affects the rate and mechanism of change. Corrosion of glass in an indoor museum is considered with macroscopic manifestations, primarily in the form of dry and wet salt neocrystallizations, cracking, delamination that cause transparency loss and material degradation on the surface of many glass pieces held in museum collections. Glass surfaces kept in chipboard or chipwood have shown the presence of alkali formates or acetates. Chipboard or chipwood is used in the creation of showcases and are known to generate volatile organic pollutants specifically formaldehyde, acetic acid, and formic acid [4]. RH has been found to be a factor of utmost relevance inside a museum environment and is one of several elements that affect the number of water molecules. It may, in certain cases, have a more severe impact on the pace of hydration than specific amounts of pollutants [98].

For this research it was decided to artificially age the model glass in the presence of the major VOCs emitted by chipwood i.e., acetic acid, formic acid and formaldehyde, based on literature review of indoor museum pollutants in wooden enclosures (Table 2.3).

Table 2.3: Summary of VOC concentrations from different museums

SN	Museum	VOC	Max. Concentration	Reference
1.	Grünes Gewölbe in Dresden, Germany	Acetic acid	3000 $\mu\text{g}/\text{m}^3$	[99]
2.	National Museum of Scotland	acetic acid Formaldehyde Formic acid	2827 $\pm$ 35 $\mu\text{g}/\text{m}^3$ 957 $\pm$ 6 $\mu\text{g}/\text{m}^3$ 416 $\pm$ 16 $\mu\text{g}/\text{m}^3$	[6]
3.	National Museum in Kraków	Formaldehyde	175.50 $\mu\text{g}/\text{m}^3$	[4]
4.	Plantin-Moretus Museum, Antwerp, Belgium	acetic acid Formic acid	247 $\mu\text{g}/\text{m}^3$ 60 $\mu\text{g}/\text{m}^3$	[100]
5.	Statens Museum for Kunst, Copenhagen (DK)	acetic acid Formic acid	1079 $\mu\text{g}/\text{m}^3$ 161 $\mu\text{g}/\text{m}^3$	[101]
6.	National Museum of Denmark	acetic acid Formic acid	930.1 $\pm$ 37.0 $\mu\text{g}/\text{m}^3$ 507.2 $\pm$ 38.9 $\mu\text{g}/\text{m}^3$	[102]
7.	Lower Saxony State Museum Hanover	acetic acid Formaldehyde Formic acid	481 $\mu\text{g}/\text{m}^3$ 110 $\mu\text{g}/\text{m}^3$ 100 $\mu\text{g}/\text{m}^3$	[103]
8.	The Historical Museum of Crete	acetic acid	779 $\pm$ 71 $\mu\text{g}/\text{m}^3$	[104]
9.	Multiple museums	acetic acid Formaldehyde Formic acid	3282 $\mu\text{g}/\text{m}^3$ 757 $\mu\text{g}/\text{m}^3$ 782 $\mu\text{g}/\text{m}^3$	[105]
10	Multiple museums	Formaldehyde Acetic acid Formic acid	1200 ppb >500 ppb 500 ppb	[106]
11	Multiple museums	acetic acid Formaldehyde	1836.0 $\pm$ 33.8 $\mu\text{g}/\text{m}^3$ 151.6 $\pm$ 17.9 $\mu\text{g}/\text{m}^3$	[107]

For simplicity, a rounded figure for the maximum concentrations of acetic acid as found in literature i.e., 3000 $\mu\text{g}/\text{m}^3$ [99] and 3282 $\mu\text{g}/\text{m}^3$ [105] was chosen. Taking this as a base for high VOC value, a thousand times of this value was aimed as the concentration for the higher concentration aging. Accordingly, the values for other pollutants were decided.

The use of three different conditions of artificial aging on the model glass in this research helped to simulate different environmental conditions that the historical objects may have been exposed to and understand the mechanisms of corrosion in such museum conditions. By controlling the variables of VOC concentration and humidity, it was aimed to understand how these factors affect the corrosion of the model glasses.

Condition P, with a high VOC concentration and fixed humidity of 50%, to simulate a relatively stable indoor environment. This can be useful in studying the long-term effects of exposure to VOCs, such as those emitted by furniture or other objects inside a museum storage.

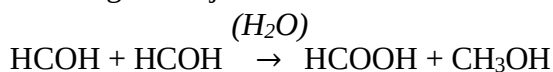
Condition PV, with a similar VOC concentration and fluctuating humidity between 35% and 70%, with changes in humidity over time to simulate an uncontrolled indoor environment.

Condition V with fluctuating humidity between 35% and 70% , supposed to be free from VOC pollutants and serve as a reference for comparison with the model glass aged in presence of VOCs. Nonetheless, later was found to have the presence of VOCs (see section 3.3) more than 1000 times lower than the pollutant concentrations in P and PV condition and thus closer to real museum concentrations.

These three different conditions of artificial aging on the model glass were designed to provide a more comprehensive understanding of how corrosion and degradation processes can be affected by environmental factors. However, it is important to recognize that the results obtained from artificial aging may not perfectly reflect the complex and varied corrosion processes that occur in actual historical objects.

Consequently, the gaseous phase concentrations in $\mu\text{g}/\text{m}^3$ decided for accelerated artificial aging of model glasses for P and PV conditions for acetic acid, formaldehyde and formic acid were 3000×10^3 , 1000×10^3 and 500×10^3 , respectively.

Out of these VOC pollutants, due to the unavailability of a controlled testing chamber and its high toxicity, formaldehyde was not used for the aging setup. Nonetheless, the compensation for formaldehyde concentration was calculated in terms of formic acid since formaldehyde attacks glass objects in the form of formic acid after oxidation in the presence of humidity [4]:



Therefore, the final total gaseous phase concentration of acetic acid and formic acid required in ppm ($\text{ppb} \times 10^{-3}$) and the volume of acids required (Table 2.4), were calculated using the equation (6)

$$\frac{\mu\text{g}}{\text{m}^3} = \frac{\text{ppb} \times 12.187 \times M}{273.15 + ^\circ\text{C}} \quad (6)$$

Where M is molar mass and $^\circ\text{C}$ is the temperature. However, the volume of pollutants used was manipulated later based on the results of the pre-aging tests (Annex XII) especially due to the absorption of VOC pollutants by the RH controlling material used during aging.

Consequently, the gaseous phase concentration in ppm calculated for P and PV conditions of artificial aging of model glass for acetic acid and formic acid was calculated to be 1209 and 670 ppm, respectively using the ideal gas law. The volume of acid required for producing the gaseous concentration was calculated to be 57 and 20.8 μL for acetic acid and formic acid respectively. The gaseous concentration of pollutants inside the desiccators were reported using PID and passive sampler results which were found to be not reliable.

Finally, an artificial aging protocol was setup to subject the model glasses to mimic conditions like those of the historical glass storage in the old depot instead of studying the individual role of acetic acid and formic acid in glass corrosion, allowing to induce corrosion for a stipulated duration of at least 20 months and to periodically monitor and characterize the corrosion of the glasses based on physical and chemical changes observed (Table 2.4).

Table 2.4: Three different aging environments decided for the research

Aging environment	Temperature + RH	Duration	Theoretical Pollutant concentration	Abbreviation
Higher VOC concentration and fluctuating	20 °C - 25 °C + 35% and 70%	20* months, equal no. of days at 35% & 70% RH	AA = 1209 ppm FA = 670 ppm	PV
Higher VOC concentration and fixed humidity	20 °C - 25 °C + 50%	20* months	AA = 1209 ppm FA = 670 ppm	P
Lower VOC concentration and fluctuating humidity	20 °C - 25 °C + 35% and 70%	20* months, equal no. of days at 35% & 70% RH	AA<15 ppm	V

*20 months is reported for the aging duration which resulted in 3 months aging using saturated salt solution as RH-controlling material. The use of saturated salt solutions inside aging desiccators introduced some major issues which were fixed after the 3 months of aging (see section below p.33). After this the model glass were aged for 17 months using preconditioned silica gel as RH-controlling material.

A total of 40 model glass were aged in each condition consisting of 5 withdrawal batches of 8 model glass each. These withdrawals were decided to be undertaken after three, six, nine, 12 and 17 months of aging in the presence of preconditioned silica gel as the RH-controlling material. The 8 different model glass were destined for different kinds of non-destructive and destructive analyses, imaging and cleaning intervention, and thus were labelled accordingly (Table 2.5).

Artificial aging experiments were carried out in new 20-liter borosilicate glass desiccators, which were cleaned with deionized water and then dried with acid-free tissue paper/microfiber prior to use. Two desiccators were used alternately to run aging cycles at 35% and 70% RH, and for every new cycle RH controlling material was renewed and kept at the bottom of the aging desiccators in ceramic dishes. Additionally, the desiccators were rinsed thoroughly with deionized water and oven-dried before the start of a new aging cycle. The petri dish used for introducing pollutants into the desiccator was kept on a steel grid and the lids were vacuum sealed using silicone-free, paraffin-based vacuum grease (Glisseal, Borer Chemie AG). The lids

of the desiccator have a small circular opening on the top which was closed using silicon rubber stoppers.

Table 2.5: Nomenclature and use for every model glass from a batch of eight model glass along with the analyses performed (some exceptions were made in special circumstances which will be explained wherever applicable)

Period A*	Imaging	Cleaning Tests	Destructive Analyses	Non-Destructive Analyses
PV#1A	HSI, RTI, Photography, DM,			Raman, FTIR, Weight changes
PV2A	DM			Weight changes
PV3A	DM			Weight changes
PV4A			SEM-EDX	Raman, FTIR, Weight changes
PV5A	HSI, RTI, Photography, DM,			Weight changes
PV6A	DM			Weight changes
PV7A	DM			Weight changes
PV8A	DM			Raman, FTIR, Weight changes

* A = 3 months, B = 6 months, C=9 months, D=12 months and E = 17 months

Abbreviation for the aging environment as given in Table 8.

Every batch of 8 model glass samples was held upright on one bar-shaped glass stands produced using a more stable glass. Such 5 batches of model glasses were kept in every aging desiccator along with a data logger for V condition and with liquid pollutants for P and PV, on a steel plate (Fig. 2.6a and b).

The data logger was used for continuously monitoring temperature and RH namely an MSR145 data logger from MSR Electronics GmbH, with accuracies of ± 0.5 °C and $\pm 2\%$ RH (MSR Electronics GmbH 2022). The ambient temperature inside desiccators ranged between 20-25 °C. Two desiccators without model glasses were also run in parallel to the aging desiccators with the same environment of higher VOC concentrations and RH to be used for calculating the quantity of VOCs being produced inside the aging desiccators.

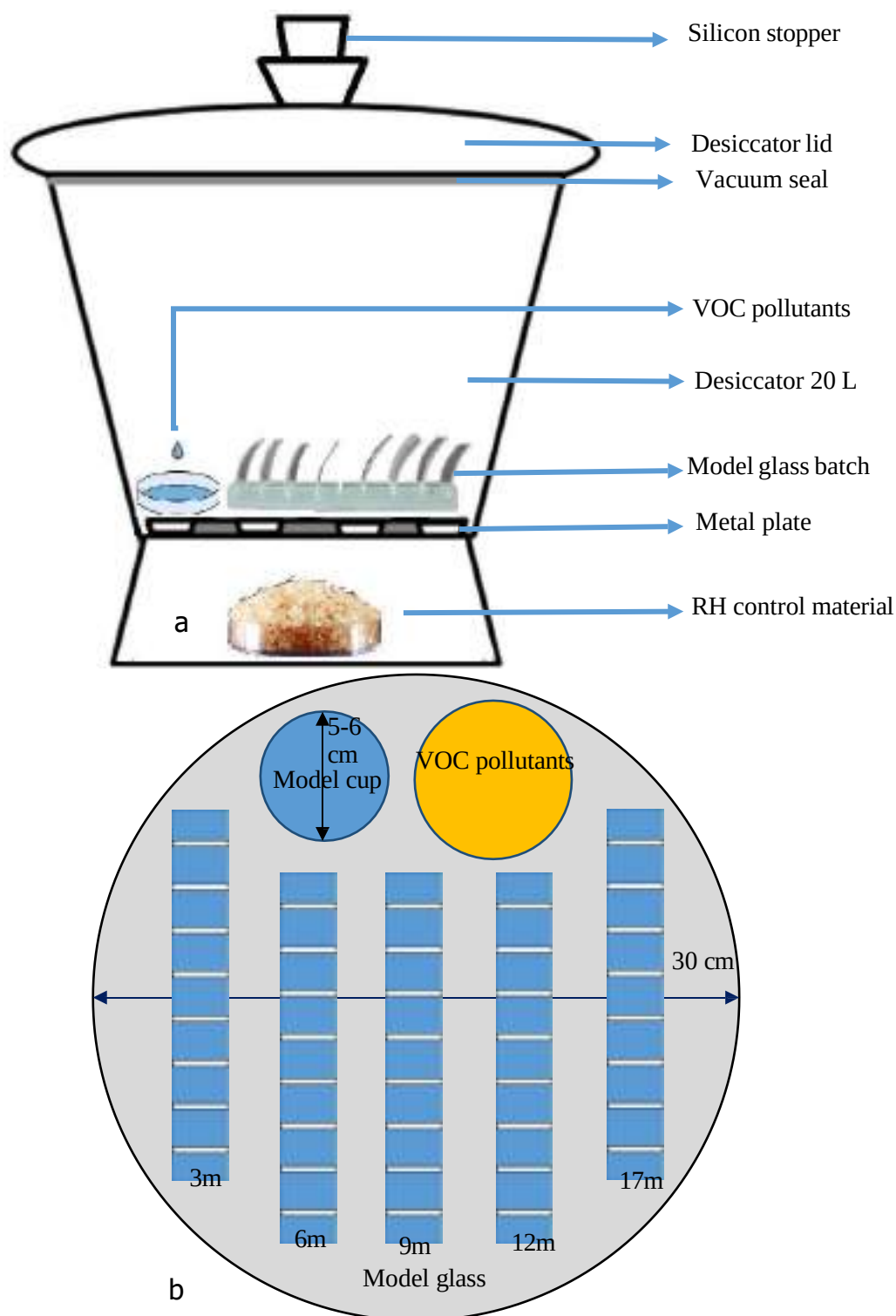


Fig. 2.6: Schematic diagram of a) aging setup in desiccator with VOC pollutants b) placement of model glass, model cup and pollutants on the metal plate inside the aging desiccators P and PV

The RH control was challenging in the presence of high concentrations of VOC. Preliminary experiments that were used to determine suitable conditions and parameters for artificial aging were first conducted in presence of saturated salt solution as the RH control material. Pre-aging tests inside desiccators were performed to understand whether the RH established by salt solution was stable over the whole aging cycle. After this, the interaction of VOCs i.e., acetic

acid and formic acid along with the salt solutions was tested in order to determine the various parameters such as the amount of saturated salt solution required and the amounts of pollutants to be injected into the desiccator for giving a specific concentration of VOC pollutants in the gaseous phase, since it was observed that pollutants were being absorbed by the salt solutions. These pre-aging tests were run for about two months before the commencement of actual artificial aging of the model glasses inside the desiccators (Annex XII, 1-12).

Consequently, aging was initiated with saturated salt solutions. Three saturated salt solutions, namely MgCl_2 (33% RH), $\text{Mg}(\text{NO}_3)_2$ (53% RH) and NaCl (75% RH) were being used in a petri dish located at the bottom of the desiccator. After running the aging cycles for three months, it was found in the first withdrawals that undesired salt crystals were formed on the surface of the P model glass (Fig. 2.7a). These crystals were examined by FTIR spectroscopy and were found to be potassium nitrate (Fig. 2.7b). Similarly, chlorides were also found on the PV and V samples using XRF spectroscopy. The source of these salts was attributed to the anions in the saturated salt solutions reacting with the alkali cations leached out from the model glass perhaps induced by the presence of VOCs. Naturally, the saturated salt solutions were discarded and replaced by preconditioned silica gel after undertaking one month of pre-aging tests with the silica gel similar to those initially performed with the saturated salt solutions in which the amount of pollutants to be introduced into the setup was determined since it was observed that the silica gel also absorbed pollutants similar to the saturated salt solutions (Annex XII, 13-16). Aging commenced after cleaning all the model glass with deionised water and ethanol (5 drops of ethanol in 500 mL water) using cotton swabs.

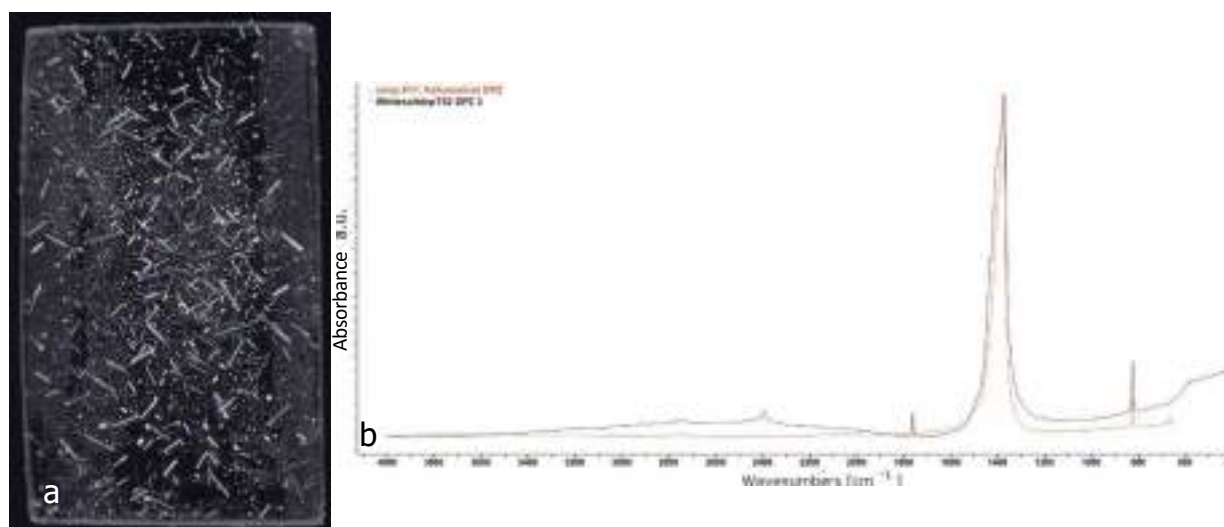


Fig. 2.7 a) Transmitted and Cross Polarized Light image of P model glass ($\approx 5\text{cm} \times 3\text{ cm}$) aged for 3 months showing needle-like salt formation b) FTIR spectrum of the precipitates (black) along with a reference spectrum of potassium nitrate (red)

At each new cycle, 60 g of previously unused preconditioned silica gel was placed in a ceramic dish at the bottom of the desiccator. The product was selected for the absence of chlorides, present in some other brands, and was purchased from the supplier preconditioned to 35%, 50%, and 70% RH. After reception, the silica gel was stored in enclosures comprising four

layers of different materials – polyethylene bag, RP ESCAL bag, aluminium foil, and plastic box – to prevent contamination and exchange with the ambient atmosphere.

Model glass from the last withdrawal batches at 17 months of all the three aging conditions were also oven-dried to produce coarse cracking on the surface. A trial was achieved with one model glass from each condition withdrawn at 15 months and then dried in the oven at 100°C for one week. This produced severe cracking and complete delamination on P and PV glasses and no visible cracks on the V glasses. Thus, the remaining model glasses (five in total, excepting the two model glasses for imaging) were withdrawn after 17 months aging from P, PV and V batches and were dried in the oven for 15 minutes at 100°C. These five model glasses were also then used for imaging along with the two imaging model glasses, not exposed to 100°C.

2.6. VOC measurements

The concentrations of acetic acid were measured every working day using a Photo Ionic Detector (PID). A photoionization detector uses a vacuum ultraviolet light source to ionize chemicals to positive and negative ions that can be easily counted with a detector. Ionization occurs when a molecule absorbs the light energy produced by the PID lamp. The gas becomes electrically charged. These charged particles produce a current that is then amplified and displayed, after internal calculation, on the meter as "ppm" or even "ppb". For the PID sensor to respond to a volatile compound, the photon energy of the lamp must be greater than its ionisation energy. The response factor (RF) relates to the sensitivity of PID to a volatile compound to the standard calibration gas isobutylene. RFs are inverse to sensitivity, the higher RF, the lower the sensitivity. Isobutylene is used to calibrate PID, and RF is used to convert the isobutylene calibrated measurement to a measurement of the target volatile compound.

A 10.6 eV lamp is the most commonly used detector for a PID. This is able to detect acetic acid but not formic acid, which would be detected by a 11.7 eV lamp. However, this latter is known for being easily damaged in humid conditions. Being too expensive to be often replaced, it was decided to use the 10.6 eV lamp and to follow up on the acetic acid only.

The PID detector was calibrated at 0, 100 and 1000 ppm using carbon filter for zero point and isobutylene cylinders of 100 and 1000 ppm concentrations. The PID was inserted into the small opening on the top of the desiccators and the measurements were recorded along with the time taken in seconds. A silicon pipe was attached to the pump outlet so that the air from the desiccator could be reinjected into the desiccator without losing the pollutants. The measurement was recorded when the PID readings stop changing rapidly, for acetic acid (RF= 28). The pH of the salt solutions was measured every time they were taken out of the desiccator after the aging test using single colour pH strips.

Given the high correction factor for acetic acid (RF= 28) using the PID, it might not be highly accurate. Additionally, high humidity environment affects the accuracy of the readings of the PID whichever lamp might be used. The higher the humidity of the environment, the less accurate the readings. Therefore, the readings of the PID need to be corroborated with more accurate methods of determining concentration such as passive sampler, which is lengthier

and time taking process. Passive sampling was done using acetic acid and formic acid diffusion type passive samplers developed by IVL Swedish Environmental Research Institute. Diffusive sampling is based on using the molecules' thermal diffusion (heat movement) and thus does not require a pump. Stainless steel samplers with an adsorbent (Tenax-TA) were used for sampling. However, the absorption of volatile acids such as acetic acid and formic acid on Tenax is generally poor. The reason for this poor absorption lies in the chemical properties of Tenax and the specific interaction mechanisms between the adsorbent and the analytes. Tenax is typically effective at adsorbing organic compounds with lower polarity and smaller molecular sizes, but volatile acids, being relatively polar and smaller, do not interact as strongly with Tenax. Instead, they may pass through or desorb quickly from Tenax columns and thus may not be ideal for capturing and retaining volatile acids like acetic acid and formic acid due to their distinct chemical properties.

During storage and transport, the tubes were sealed at both ends and the sampling was started by replacing one seal with a diffusion cap. The analyses were performed with an automated thermal injector connected to a high-resolution gas chromatograph with a flame ionization detector according to IVL's accredited method that follows SS-EN ISO 16017-2:2003 and SS-EN 14662-4:2005. During sampling the samplers were introduced in the aging desiccator hanging by a thread for 8 hours along with parallel recording of the acetic acid using PID. Nine such measurements were performed. The results from both were compared.

VOC pollutant acetic acid (AA) was measured in both aging desiccators P and PV along with parallel running desiccators with the same amount and type of preconditioned silica gel and VOC pollutants as used in P and PV but without putting any model glass. This was done using PID to find the amounts of pollutants being produced inside the desiccators.

PID readings were taken twice on the first day of the aging cycle or parallel empty desiccator and then consequently once every 24 hours on working days for acetic acid in ppm. As a serious limitation of PID, the readings cannot be trusted in high humidity because water vapour scatters and absorbs photons, reducing the PID output called 'quenching', resulting in higher than actual readings [107]. However, for the current research, it was seen as the readily available and affordable method for regular monitoring. The results of the VOC measurements in the aging setup will be discussed in the following chapter.

2.7. pH measurements

pH measurements were undertaken on the surface of the corroded model glass right after withdrawal using Hydriion Brilliant dip sticks manufactured by MicroEssentialLab. This was done on 3 model glass from each aging batch by touching the surface while keeping in mind to minimize the contact and impact.

2.8. Weight Changes

The weight of each sample was measured on a Mettler Toledo digital scale with a precision of 0.1 mg and repeatability of 0.08 mg. Five measurements per sample were recorded, both before

and after aging and then averaged to calculate the percentage weight change using the formula (7):

$$\text{Weight change in percent} = \frac{(\text{Weight after aging} - \text{weight before aging})}{\text{Weight before aging}} \times 100 \quad (7)$$

2.9. Scanning Electron Microscopy with energy dispersive X-ray spectroscopy (SEM-EDX)

Owing to the high lateral resolution in the SEM and the fast and non-destructive manner of EDX, a complete determination of the main constituents could be obtained. Additionally, SEM-EDX enables the analysis of Na, Mg, Al and Si, which are the main constituents in glasses. However, the determination of the minor constituents or even of traces in glasses is limited by the high background in an energy dispersive system leading to low signal to noise ratios. In this research, SEM-EDX was used for three main objectives:

1. Historical glass objects' composition to find the composition of bulk glass and alteration layer (AL) using SEM A
2. Initial bulk composition of model glass using SEM B
3. Chemical modification of corroded model glass in terms of composition and alteration layer thickness using SEM C

SEM A: An ESEM Quanta 600 Field Electron and Ion Company (FEI) equipped with EDAX dual back scatter detector operated in high vacuum. The particles from the alteration layer and bulk collected from the glass objects were placed on sample holder consisting of an aluminium block of c. 13 mm diameter with a carbon adhesive disc (10 mm in diameter) stuck on top. The samples were carbon-coated to give conductivity before performing SEM-EDX measurements. Samples were placed on a stage inside the chamber and were viewed using the back-scattered electron detector (BSE) to determine the most appropriate points to analyse. Points were selected to be analysed in the flat looking glass particles of the samples (Fig. 2.8a-c). The EDX was set at an operating voltage of 20 kV and a current of 0.6 -1.6 nA based on a fixed spot size of 4.5 μm . The working distance was set to 14.5-15 mm. The point was analysed for until 3000 counts or up to a live time of 200 seconds. Each sample was analysed 10 to 15 times, choosing a different point for each analysis. The analysis was run standardless and quantification was carried out using the ZAF correction software in the Genesis utility software. Oxide weight percentages were calculated stoichiometrically and normalized to totals of 100%. The average and standard deviations for all the measurements were calculated. The accuracy of the measurements by this sampling method was assessed by comparison with the measurement of glass standards of known elemental composition (Corning B, Lead glass, BRU7, NIST620) (Fig. 2.8d-f) and potash lime glasses of well-characterized composition (Fig. 2.8g-h) after having taken micro samples with the same procedure.

The performance of the SEM-EDX system A under the defined operating conditions was initially evaluated for ten repeated measurements of the standard glasses along with potash lime

glasses of known composition. For these conditions, the error percentage was determined to be less than 20% for all the major oxides (present in concentrations above 2%: SiO_2 , Na_2O , CaO , K_2O , CuO and MgO) except for Al_2O_3 (Table 2.6 and 2.7).

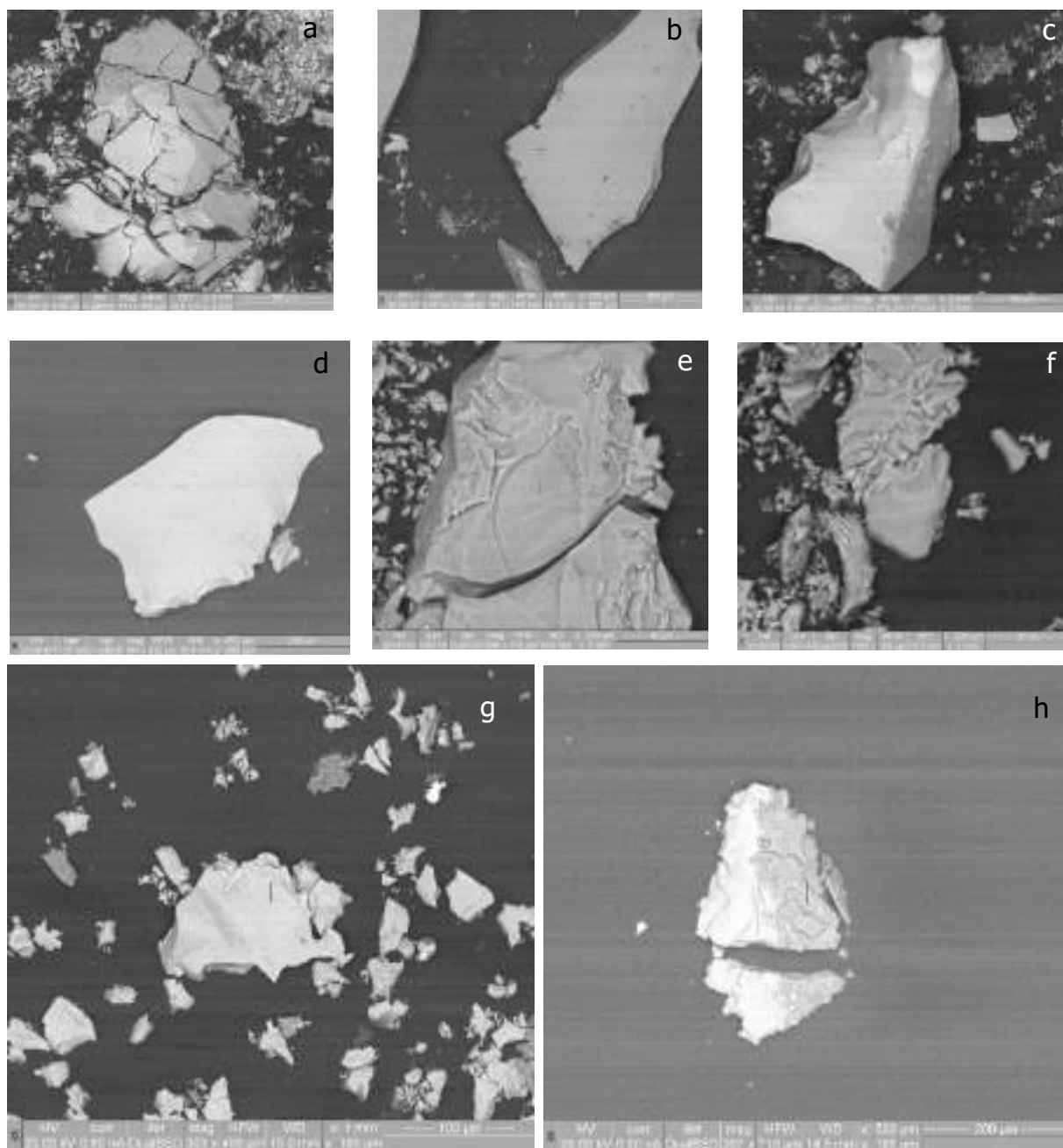


Fig. 2.8: Backscattered image of glass particles from historical objects: a) LM12433 Bulk b) AG1078 Bulk c) LM15473 Bulk; and from glass standards: d) Corning B e) BRU7 and f) NIST620 and potash lime glasses of known composition: g) K31M Bulk h) K10M Bulk

Table 2.6: Average values of glass composition and percentage error for the glass standards BRU7 and Corning B

	BRU7				Corning B			
Element oxide	Average values	Theoretical values	Error%	RSD	Average values	Theoretical values	Error%	RSD
Al ₂ O ₃	9.32	7.10	31.28	3.17	4.61	4.22	9.27	4.70
CaO	3.40	3.60	-5.47	14.02	8.09	8.71	-7.11	8.68
Cl-	0.56	0.60	-6.33	21.22	0.20	0.20	-1.50	32.81
F-	2.66	2.80	-5.04	22.89				
Fe ₂ O ₃					0.62	0.35	76.57	22.73
K ₂ O	4.10	5.10	-19.71	10.09	1.07	1.10	-2.82	11.23
MgO					1.04	1.19	-12.94	10.23
MnO					0.44	0.28	58.21	23.77
Na ₂ O	9.75	11.50	-15.19	9.76	15.17	17.26	-12.10	8.34
P ₂ O ₅	1.71	2.50	-31.68	11.99	0.64	0.84	-23.69	13.53
SiO ₂	68.35	65.07	5.04	1.38	62.78	61.55	2.00	1.78
SO ₃					0.73	0.54	35.93	13.78

Table 2.7: Average values of glass composition and percentage error for the glass standards BRU7 and Corning B

	NIST 620				Lead glass			
Element oxide	Average values	Theoretical values	Error%	RSD	Average values	Theoretical values	Error%	RSD
Al ₂ O ₃	2.38	1.80	32.37	6.08	0.94	0.128	637.11	6.56
BaO					1.10	1.04	6.63	9.14
CaO	6.44	7.11	-9.43	6.43	0.90	1.03	-12.77	10.66
K ₂ O	0.50	0.41	21.30	9.72	8.32	10.00	-16.85	1.15
MgO	3.65	3.69	-0.96	3.23	0.56	0.512	10.04	14.19
Na ₂ O	13.18	14.39	-8.41	4.70	3.42	3.58	-4.35	7.13
PbO					25.57	23.98	4.73	50.76
Sb ₂ O ₃					0.10	0.29	-66.06	126.03
SiO ₂	73.28	72.08	1.66	0.54	57.82	57.80	0.03	0.99
SO ₃	0.57	0.28	103.57	20.39				
ZnO					1.26	1.02	23.78	14.42

In case of the potash lime glasses of known composition, error percentage was determined to be less than 10% for all the major oxides (SiO₂, CaO, K₂O, MgO) except Al₂O₃) (Table 2.8).

Table 2.8: Average values of glass composition and percentage error for aged potash lime glasses with known composition

Element oxide	K10M Bulk				K31M Bulk			
	Average values	Theoretical values	Error%	RSD	Average values	Theoretical values	Error%	RSD
Al ₂ O ₃	2.784	2	39.20	12.79	2.52	2	-26.00	11.23
CaO	16.601	18	-7.77	6.16	18.596	18	-3.31	8.35
K ₂ O	22.645	25	-9.42	7.04	24.133	25	3.47	10.60
MgO	2.791	3	-6.97	14.86	2.738	3	8.73	19.42
P ₂ O ₅	1.186	2	-40.70	17.44	1.204	2	39.80	10.12
SiO ₂	53.994	50	7.99	4.51	50.81	50	-1.62	6.45

SEM B: The model glass samples were analysed using a FEI SEM equipped with EDX detector. The SEM was operated in high vacuum. The samples were placed on a stage inside the chamber and were viewed using the BSE detector to determine the most appropriate areas to analyse. The EDX probe was set at an operating voltage of 20 kV and a current of 0.8 -1.6 A. The working distance was set to 7 mm. The areas were analysed with a live time of 30 seconds and a resolution of 124.1 eV. Each sample was analysed five times, choosing a different area for each analysis. The analysis was run standardless and quantification was carried out using the eZAF smart quant correction software. Oxide weight percentages were calculated stoichiometrically. The average and standard deviations for all the measurements were calculated.

Ten glasses were selected randomly, cleaned with ethanol and water (1:1) mixture and left to dry under fume hood. Around 1 cm square pieces were cut using an oiled wheel glass cutter. The pieces were stuck directly on the adhesive carbon tape on to the sample-holder. The sample-holder used consisted of a circular aluminium block of c. 13 mm diameter with a carbon adhesive disc (10 mm in diameter) stuck on top. The samples were carbon coated without grinding or polishing. Mean compositions were determined for 5 arbitrarily selected areas (approx. 50 × 60 µm) and normalized to totals of 100%.

SEM C: The imaging and characterization of the cross-section of corroded model glass samples was done using a FEI Quanta 200F FEG-SEM equipped with EDAX Octane super and BSE detector in high vacuum, an operating voltage of 20 kV and a current of 0.6 -1.6 nA based on a fixed spot size of 4.5 µm. The working distance was 10 mm. The analysis was run using Electron Probe Microanalysis (EPMA) results as standards and quantification was carried out using the eZAF smart quant correction software in Ametek-EDAX Team software. This was done to analyse the depth morphology of the corrosion layer by taking series of pictures of the model glass cross-section samples. The samples were cut from the top middle part of the model glass. One sample each from all the aging periods was analysed producing 20-50 images per sample (Annex X). Table 2.9 gives a full summary of all the SEM-EDX analyses.

Table 2.9: SEM-EDX analyses along with the type of samples

	Glass object		Model glass		
	Bulk composition	Alteration layer composition	Bulk composition	Alteration layer composition	Alteration layer thickness
SEM A	Microsamples	Microsamples			
SEM B			Broken pieces		
SEM C				Cross-section	Cross-section

2.10. Electron Probe Microanalyses (EPMA)

EPMA is a widely employed analytical technique in various scientific fields, including materials science, geology, and environmental science. This method enables researchers to determine the elemental composition of solid materials with exceptional precision and sensitivity. EPMA operates by bombarding a sample with a focused electron beam, resulting in the emission of characteristic X-rays from the sample's constituent elements. These X-rays are then measured and analyzed to deduce the elemental composition by recording Wavelength Dispersive Spectroscopy spectra. EPMA offers distinct advantages, such as the ability to analyze small sample areas, non-destructive elemental analysis, and high spatial resolution.

The EPMA instrument used was a JEOL Electron Probe Microanalyser model featuring five wavelength dispersive spectrometers (WDS) and one silicon-drift EDX spectrometer, operating at 15 kV voltage and employing a 20.82 nA current. The instrument's working distance was set at 11 mm, and the probe diameter was 10 μm . Calibration of the EPMA system was carried out using standard minerals, namely anorthite, albite, periclase, apatite, and microcline. These calibration materials were utilized to ensure the accuracy and precision of the elemental composition of the manufactured model glass.

2.11. Fourier Transform Infrared spectroscopy (FTIR)

FTIR is a widely used analytical technique used to determine the chemical composition of a sample based on its interaction with infrared (IR) light. As it passes through a sample, some of the light is absorbed, while the rest is transmitted. The absorbed wavelengths correspond to the characteristic vibrational frequencies of the chemical bonds present in the sample. FTIR spectroscopy utilizes a Michelson interferometer, which splits a beam of IR light into two paths and then analyzed using a mathematical technique called Fourier transform to obtain the sample's IR spectrum. The resulting FTIR spectrum provides valuable information about the functional groups and molecular structure present in the sample.

FTIR was performed using a Bio-Rad Infra-red Spectroscope. It was used in the analyses of the structural modification occurring on the model glass. Ten points each were recorded for 3 model glass from each batch at the same locations, before and after aging. Spectra were acquired in reflection mode on $250 \times 250 \mu\text{m}^2$ area taken as an average of 512 scans on the same spot, in the range of $650\text{--}4000 \text{ cm}^{-1}$. Additionally, corrosion products produced on the glass during the aging with saturated salt solution as well as with preconditioned silica gel were also analysed using

diamond press cell and transmittance mode on smaller areas of $20 \times 20 - 50 \times 50 \mu\text{m}^2$ depending on the amount of salt neocrystallizations collected using the same range and number of scans.

FTIR spectra were processed using Agilent resolutions software for baseline correction and calculating derivatives. Spectragryph software [109] was used for smoothing, calculating average spectra and peak area calculation. The peak ratios calculated using FTIR spectra averaged by spectragryph could not be reported along with standard deviation. Chemometric Agile Tool was used for statistical data processing. Deconvolution of the FTIR spectra was performed using Labspec 6 software.

2.12. Raman Spectroscopy (Raman)

Raman spectroscopy is an analytical technique that offers non-destructive insights into chemical structures, phases, polymorphism, crystallinity, and molecular interactions. It operates on the principle of light interacting with the chemical bonds present in a substance. The key process involved is the inelastic scattering of photons, referred to as Raman scattering. By examining the resulting scattered light, Raman spectroscopy provides detailed information about a material's molecular composition and properties.

Raman spectroscopy was performed to characterize two sample features i.e. changes in glass structure and salt neocrystallizations. Information about glass structure in terms of Qn silicate species can be obtained at the Raman shift range of $150\text{-}1650 \text{ cm}^{-1}$ known as the alumino-silicate region ([6] and references therein). A modification in the glass structure due to corrosion will result in the shifting of Raman bands towards lower wavenumbers. For characterizing the silicate species modifications in the alumino-silicate region, 20 points (ten accumulations of ten seconds) were acquired on three samples per withdrawal duration at power measured lower than 12 mW on the glass surface. All the spectra were normalized using standard normal variate (SNV).

Corroded glass might also display a broad band at the high frequency range of $2800\text{-}3800 \text{ cm}^{-1}$ corresponding to the stretching of -OH and H_2O molecules (hereafter called water band). The -OH group can be present in the glass as part of molecular water dissolved in the glass matrix or silanol species (-Si-OH) formed because of corrosion. Therefore, the area of this band can be used to characterise the extent of corrosion [4][110]. For characterizing the water band, three points each (ten accumulations of 60 seconds) were acquired on three samples from every withdrawal batch at power less than 6 mW, before and after aging. All the spectra were baseline corrected and integrated to calculate the water band area using Spectragryph software [109].

Salt neocrystallizations form on glass surfaces due to the interaction between alkali components (cations) leached from the glass and atmospheric pollutants (anions) [110]. To characterize the neocrystallizations, ten points (ten accumulations of ten seconds) were acquired on three model glass from each withdrawal in the range of $150\text{-}1650 \text{ cm}^{-1}$ and $2050\text{-}3050 \text{ cm}^{-1}$. All the spectra were normalized using SNV in the alumino-silicate region.

Raman mapping was performed initially to provide a spatial visualization of the different neocrystallizations. One model glass sample from each withdrawal batch was mapped over an

area of $400 \times 400 \mu\text{m}^2$. The Raman mapping was performed in swift mode (400 points with ten accumulations of two seconds), over a range of $150\text{--}3800 \text{ cm}^{-1}$. Each acquisition lasted for eight hours.

Raman point analyses and mapping were performed using a LabRAM ARAMIS instrument from HORIBA Jobin Yvon, GmbH, with a 532 nm laser, $100\times$ objective (numerical aperture of 0.9), 1800 lines/mm grating, $1000\text{-}\mu\text{m}$ confocal pinhole, and $100\text{-}\mu\text{m}$ spectrometer entrance slit. Data were collected and interpreted using HORIBA LabSpec 6 Spectroscopy Suite software.

Raman depth profiling was also performed on actual historical objects for understanding the extent of corrosion. This was done using a Renishaw VirsaTM Raman Analyser equipped with $100\times$ magnification objective was employed using a 532 nm P2-HiSens laser with a grating of 2400 lines/mm. Depth profile measurements were recorded in the spectral range of $50\text{--}1650 \text{ cm}^{-1}$ until a depth of $300 \mu\text{m}$ by automatically adjusting the focal plane along the z-axis starting from the surface and incrementally moving deeper into the material with a step size of $15 \mu\text{m}$. Each of the measurement was with 5 accumulations of 10 sec each. The data were post-processed using spectragryph software.

Deconvolution of the Raman spectra in the alumino-silicate region $250\text{--}1400 \text{ cm}^{-1}$ was required to characterize the changes in glass structure in the context of Qn silicate components and salt neocrystallizations. Consequently, the Raman spectra at 18 different points from each aging batch were deconvoluted after subtracting a baseline using Labspec 6 using gaussian curve fitting. An example of the deconvolution is shown in figure 2.9 with the specific bands deemed important for the analyses.

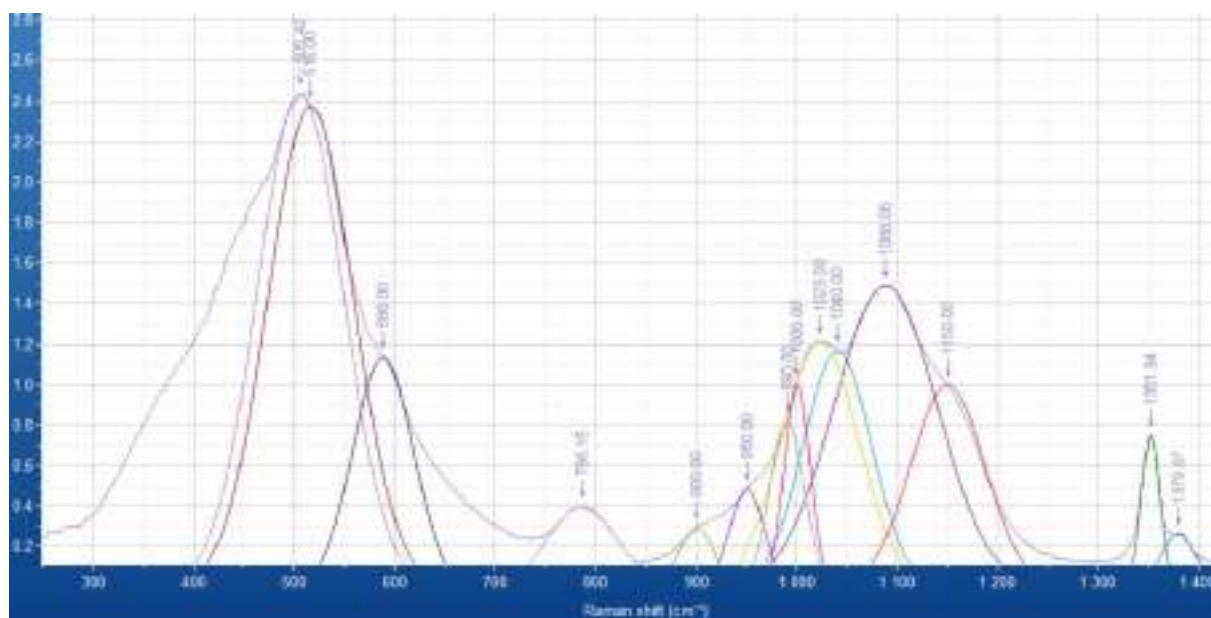


Fig. 2.9: Deconvolution and peak fitting for a Raman single-point measurement of P model glass aged for 12 months using Labspec 6 software

To determine the water content in an unknown glass sample, integrated area (AH_2O) of the water band between $2800\text{--}3800 \text{ cm}^{-1}$ was studied. However, quantifying the water content requires normalization of the water band with an internal standard. The process of internal

calibration relies on the connection between the water content in glass and the combined intensities of the water and alumino-silicate Raman bands ($\approx 500 \text{ cm}^{-1}$) [50][110]. After normalizing the water peak area, it is possible to calibrate it using samples that have known water contents.

The software, LaGa systems OriginPro was used to perform spectral deconvolution in order to compare the spectral components of the water band (as shown in Fig 2.10a-c). The deconvolution process involved several steps, including identifying a specific number of peaks based on previous research findings [50][110][111], performing an initial set of iterations with fixed peak positions until the quality of the fit (measured as χ^2) no longer changed, and then conducting a second set of iterations in which peak position and areas were allowed to freely evolve to obtain the best possible fit (i.e., the lowest χ^2). The Levenberg-Marquardt algorithm in OriginPro was used to iteratively adjust the fitting parameters until convergence was reached, and both algorithms produced similar results. The simulations were conducted with a χ^2 tolerance value of 10^{-9} (as shown in Fig 2.10d).

Previous studies [110][112][113][114] have found that to accurately analyze the entire water band, at least four Gaussian components are necessary. These components are located at specific positions within the band: I) $2930\text{--}3160 \text{ cm}^{-1}$, II) $3200\text{--}3390 \text{ cm}^{-1}$, III) $3410\text{--}3500 \text{ cm}^{-1}$, IV) $3510\text{--}3590 \text{ cm}^{-1}$, and V) $3600\text{--}3650 \text{ cm}^{-1}$. It should be noted that component I is only visible in water-rich glasses and is much weaker than the other components. The first three components indicate molecular water while the last two indicate OH^- species [50]. To obtain accurate results, a linear baseline was subtracted from the water band.

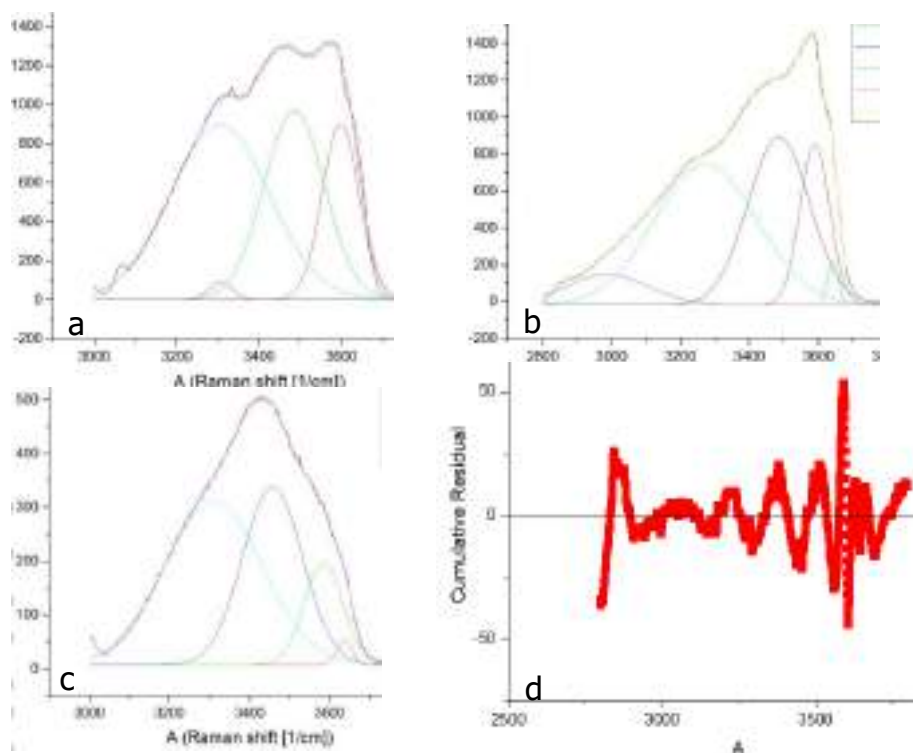


Fig. 2.10: Different shapes of the water band from 2800 to 3800 cm^{-1} subjected to peak fitting using a finite number of Gaussian components in OriginPro software a) and b) P model glass aged for 9 months c) V model glass aged for 6 months d) The randomness of the residuals indicated a good fit quality (colours were randomly assigned to all the peaks identified by peak fitting)

Spectragryph [109] was used on all the Raman spectra for smoothing, SNV, averaging spectra and integral of peak area, wherever applicable. The peak ratios calculated using FTIR spectra averaged by spectragryph could not be reported along with standard deviation. Statistical analyses were performed using Microsoft office excel and Origin pro. The software used for peak fitting in the alumino-silicate region and in the water band region were Labspec 6 and Origin pro, respectively.

2.13. Transmittance Spectroscopy (TS)

Transmittance spectroscopy (TS) is a significant technique for assessing the absorption spectra and various characteristics of solids. One of its key advantages is the ability to perform measurements without directly contacting the sample.

TS on selected model glass was performed to validate the acquired hyperspectral imaging data. PV model glass aged for 3, 6, 9 and 12 months along with one reference (unaged model glass) were measured using the LAMBDA 1050 UV/Vis/NIR spectrophotometer from PerkinElmer, which is a double beam, double monochromator, ratio recording UV/Vis/NIR spectrophotometer (250-2500 nm) with a wavelength accuracy of ± 0.080 nm in UV/VIS and ± 0.300 nm in NIR range. The data was treated to remove the noisy region beyond 2100 nm.

2.14. Digital Photography

Digital photography of transparent glass is best achieved with transmitted light to avoid stray reflections in the photographs. Although reflections from glass surface at different angles can give a lot of information about its surface and therefore reflected light (RL) photography with a standardized setup will add to the information. RL on glass surfaces from different fixed angles can also be studied through reflectance transformation imaging (RTI) with a standardized setup.

All the model glasses were photographed with and without a polarizer filter before starting the artificial aging of the samples, so that the changes in visual appearance can be detected by comparing the pictures before aging and those taken after aging. Apart from this, they can be compared with the reference glasses kept at ambient humidity in the laboratory.

Three different setups were used for photography of the samples using transmitted light (TL), transmitted and cross-polarized light (TCPL) and RL. Additionally, TCPL photography should provide visualization of mechanical strains developed as colourful anisotropic patterns on corroded glass. It is well-known that colourful an-isotropic patterns (equivalent of birefringence for minerals) develop when glass is badly annealed, or subjected to compression, bending or stretching [27]. This can be understood using the photoelasticity theory [115]. Our hypothesis is that strain-producing inhomogeneities might be developed because of weathering and corrosion as well.

Every batch of eight model glasses was photo-graphed together and in sets of two, at different exposures of shutter speed with fixed aperture, on manual mode using a digital camera with white LED light source.

The photography setup consists of a Nikon D800 Digital Single-Lens Reflex (DSLR) camera fitted on a camera stand with a light table (60 × 60 cm) at the bottom of the stand kept in a dark room with windows covered by thick black paper to avoid any stray lights. The lens used was a Nikon aspherical micro lens of 60 mm focal length.

For TL photography, the glasses were placed on printed and labelled grids on acetate sheets, which were cut to create windows to ensure consistent positioning of the glass samples and clearly visible labels. This acetate sheet was placed on the light table. The photography was done at manual mode with aperture F16, ISO 100 and four different shutter speeds at 1/20, 1/30, 1/50 and 1/80 of a second.

For TCPL photography (Fig. 2.11), the same setup was used with a Hama© circular polarization filter fitted on the camera lens along with a ROSCO© linear polarization sheet with the labelled acetate sheet placed on top of it. Once the glasses were set in their right place, the polarization filter on the camera was rotated to find the darkest back-ground under the glass samples (which is the angle of total extinction) and then photos were taken at manual mode with aperture of F16, ISO 100 with five different shutter speeds at 1/1.3, 1/1.6, 1, 1.3 and 2 seconds.

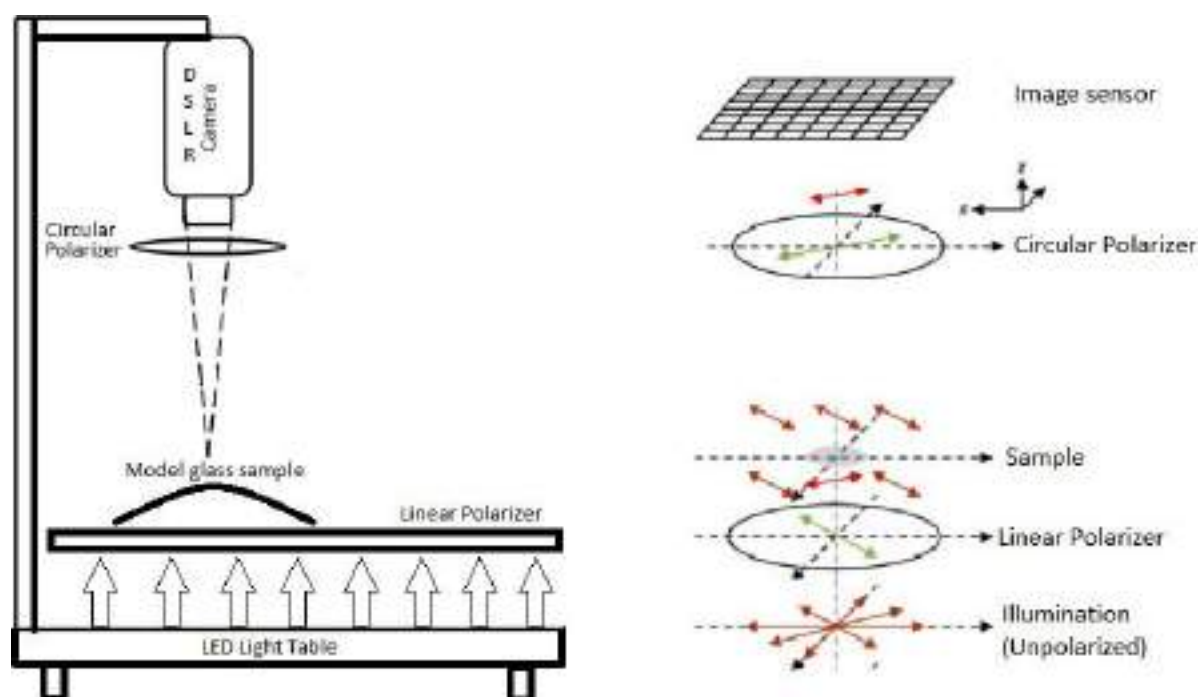


Fig. 2.11: Schematic diagram of the TCPL photography setup showing incident light directions with red arrows and polarizing direction with green arrows

For RL photography, light from two standing studio lights (diffused white LED lights) kept on either side of the sample were used and the samples were placed on a black cardboard background. Photos were captured at aperture F16, ISO 100 and shutter speeds at 1/1.3, 1/1.6, 1, 1.3 and 1.6 seconds, in manual mode. In very few cases, intense white torch lights were also used fixed on vertical stands.

2.15. Digital Microscopy

A digital microscope, also referred to as a digital scope or digital inspection system, replaces the traditional eyepiece with a digital camera to perform microscopic observations. It enables the examination and analysis of minuscule objects and samples that are not easily observable with the naked eye.

Digital microscopy (DM) was done using Keyence VHX 6000 with movable stage (Fig. 2.12a) and at magnifications from 20 $\times$ - 100 $\times$ using RL and TL. The microscope is manipulated using VHX communication software provided by the manufacturer which also provided digital stitching, optical shadow effect mode and high dynamic ratio mode.

The digital microscope also offered a flexible arm which could be used for the imaging of historical 3D glass objects in TL mode using a white light source (Fig. 2.12b).

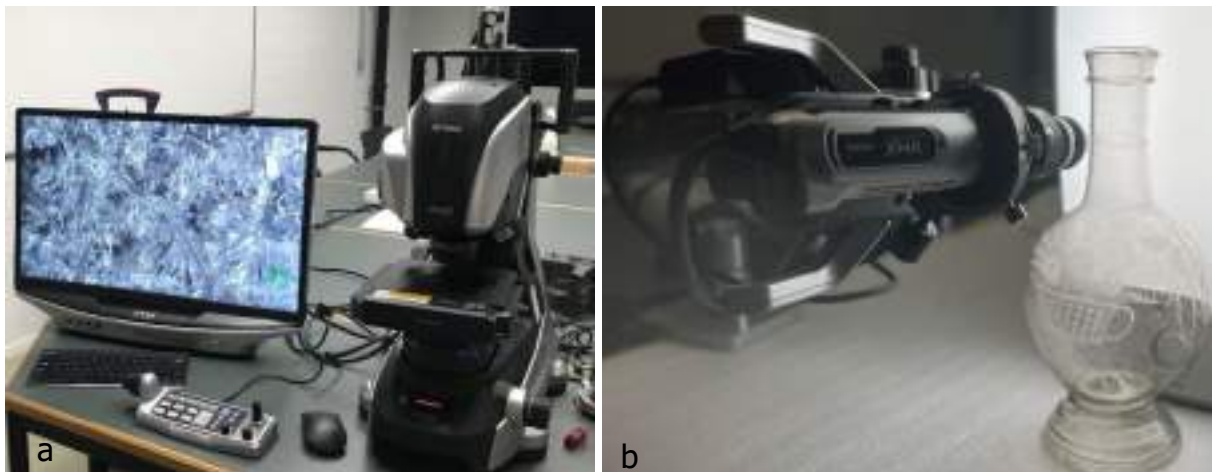


Fig. 2.12: Digital microscopy Keyence VHX 6000 a) with movable stage b) analysing glass object with flexible arm

Photomicrographs were processed using open-source Fiji distribution of ImageJ software [116] and the relevant plugins along with the software provided by the microscope manufacturers.

Areas of 5 mm x 5 mm were extracted from all the photomicrographs for quantification of cracks and SNs using ImageJ (Fig 2.13a). These were then changed into binary images using thresholding for dark grey colour over lighter background (Fig 2.13b). This resulted in black and white images indicating SNs (black rectangles), and cracks (red rectangles) along with scratches (blue rectangles), dust particles (yellow rectangles) and shadows of bubbles (green rectangles) in the model glass (Fig 2.13).

The centre of the SNs usually remained empty due to the shiny lighter region which were then filled with ImageJ plugin of ‘fill holes’ (Fig. 2.14a). Then all the thresholded images were treated with MatLab© to extract the cracks and other noisy specks from the images (Fig. 2.14b).

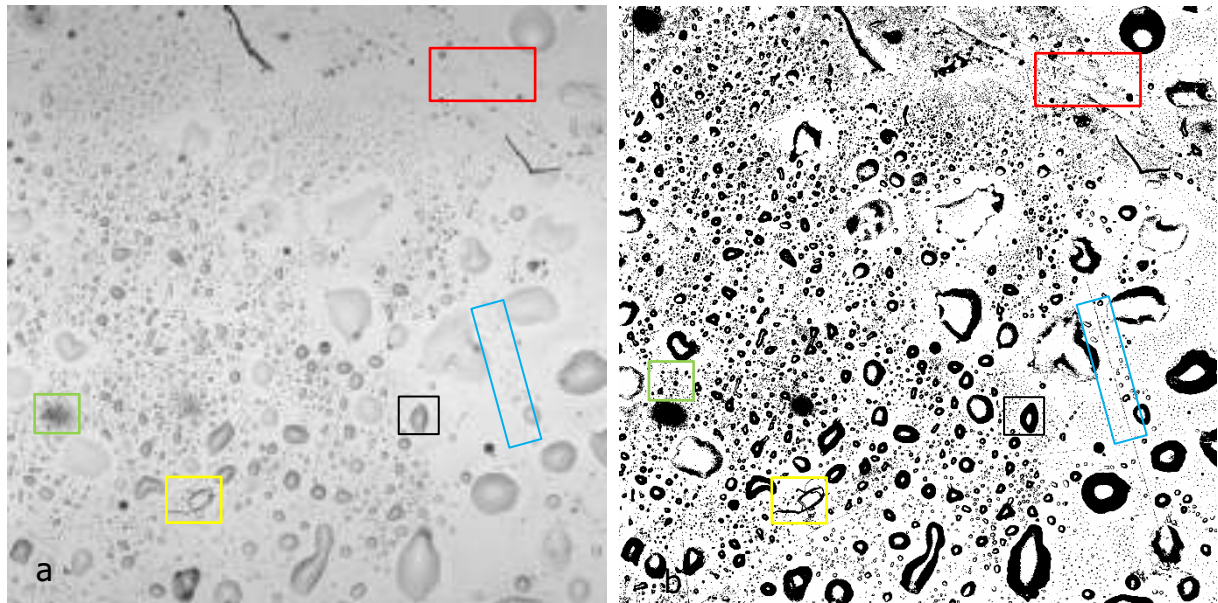


Fig. 2.13: a) Photomicrograph at 100 $\times$ original magnification of extracted area from P model glass aged for 3 months showing SNs (black rectangles), and cracks (red rectangles) along with scratches (blue rectangles), dust particles (yellow rectangles) and shadows of bubbles (green rectangles) b) the same area after greyscale thresholding (Field of view: 5 mm $\times$ 5 mm)

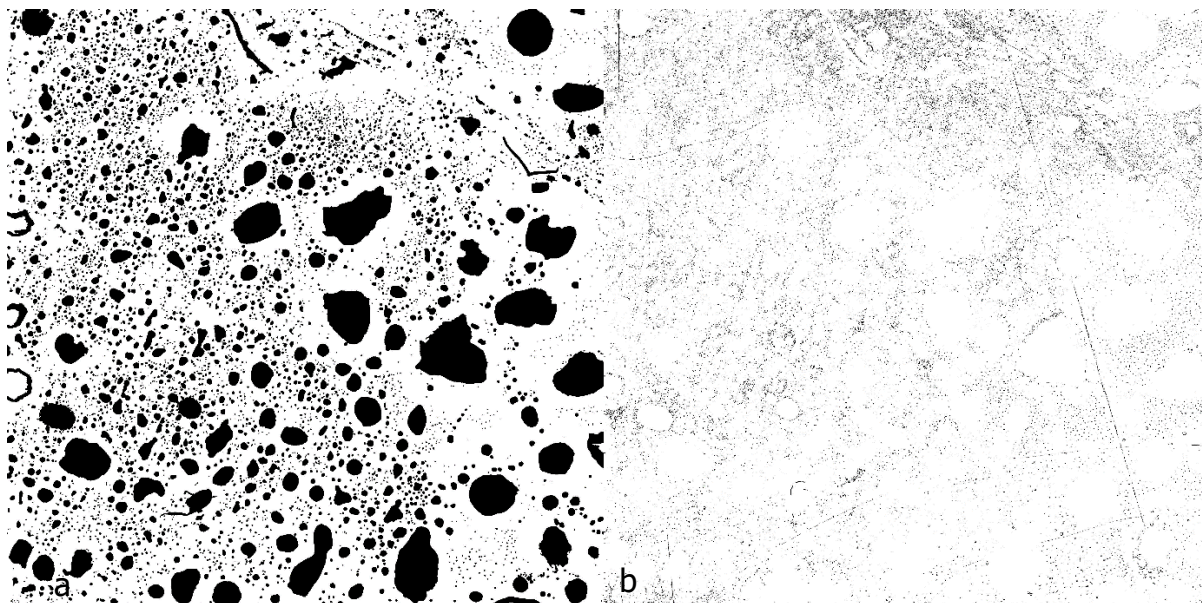


Fig. 2.14: Binary image of photomicrograph at 100 $\times$ original magnification of extracted area from P model glass sample aged for 3 months a) after greyscale thresholding and filling holes b) the noise and cracks extracted using MatLab $^{\circledR}$ (Field of view: 5 mm $\times$ 5 mm)

This treatment reduced a lot of noise from the images which was useful for quantifying the SNs. However, the noise from the shadows of bubbles present in some of the images, could not be removed without manual intervention. Since these shadows were mostly in circular or elliptical shape, they interfere with the SN calculations and thus were removed manually as much as possible (Fig 2.15).

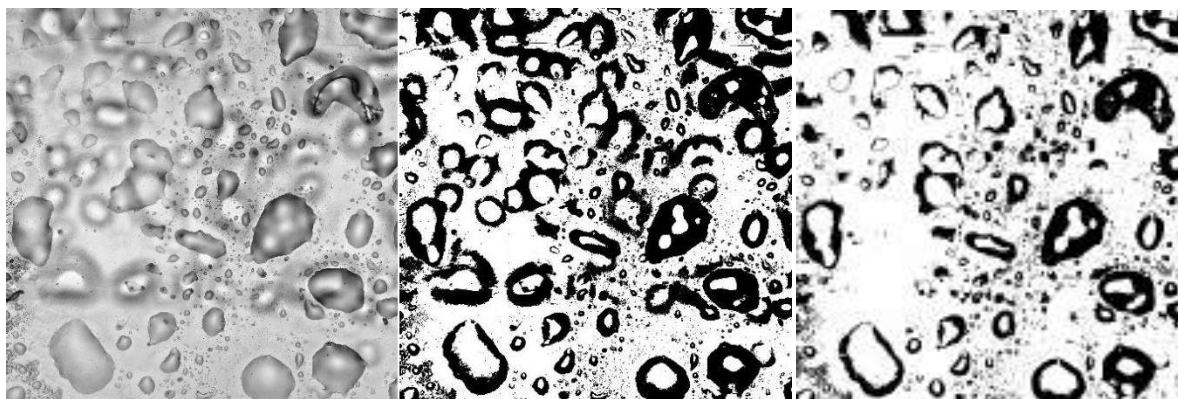


Fig. 2.15: Manual removal of bubble shadows which could interfere with the SN results on P model glass sample aged for 12 months (Field of view: 5 mm × 5 mm)

Ultimately, SNs were then automatically measured for number and percentage area covered using ImageJ ‘Analyse particles’ plugin on 15-30 sample areas from each aging period.

2.16. Hyperspectral Imaging (HSI)

Hyperspectral imaging is a technique based on the high-resolution recording of spectral reflectance at every spatial point (pixel) of the object throughout a contiguous range of wavelengths within the electromagnetic spectrum [117]. This technique records both spectral and spatial data for an object at the same time and therefore has been applied to several research areas. Throughout a specific spectral range, spectral reflectance (i.e., reflectance per unit of wavelength) can be transformed into a spectral reflectance curve and it depends on various factors such as the illumination, the viewing geometry, the detector sensitivity as well as the material properties of the object being examined [118]. Originally developed for geological and mineralogical research and remote sensing [119], HSI is relatively new in the field of cultural heritage and has already given promising results on historical artworks and documents [118][120] ([121] and references therein). Physical (e.g., colour) as well as chemical information (composition) of the material being analysed can be obtained by the detection of the vibrational absorption bands observed at different wavelengths on their reflectance spectrum. The visualisation of the distribution of specific compounds is also possible. Glass, as a material, has not been extensively investigated by HSI. Studies by [122][123][124] showed the use of HSI to identify the chromophores in stained glass using visible and near infrared (VNIR) range. A recent work was done on glass fibre composites to map their degradation due to thermal loading using HSI [125]. A patent, by Hong Jin Gwang, for an HSI system to detect defects on mobile cover glass, bare glass and film was published in 2016 [126]. These are the closest to any approach towards detecting degradation signs on transparent glass using HSI. Nonetheless, there is no other reported work on characterization of glass corrosion using HSI. Therefore, it is important to ascertain the potential of HSI for the assessment and monitoring of historical glass objects that are undergoing continuous degradation.

The physics of light propagation in glass, particularly in the context of 3D transparent glass objects, involves several key aspects:

Refraction: When light passes from one medium (e.g., air) into another (e.g., glass), it undergoes refraction. This is due to the change in the speed of light as it travels through different materials. The extent of bending (refraction) depends on the refractive index of the glass mostly determined by its composition.

Dispersion: Glass materials typically exhibit dispersion, which means that the speed of light and its refractive index can vary with the color or wavelength of the light.

Absorption: Some wavelengths of light may be absorbed by the glass material, leading to a reduction in the intensity of the transmitted light. The extent of absorption depends on the specific properties of the glass.

Scattering: Microscopic imperfections and irregularities in the glass can cause scattering of light. This effect can result in a diffuse appearance or the creation of a frosted or translucent look in some 3D glass objects.

Optics and Lens Effects: Transparent glass objects can act as lenses, both converging and diverging light, depending on their shape and curvature.

Polarization: Glass can affect the polarization state of light. Some types of glass may selectively transmit or block polarized light, making them useful in applications like 3D movie glasses or polarized sunglasses.

As discussed in section 1.6.1 already, glass corrosion leads to the changes in H_3O^+ and OH^- ions present in glass could be useful for characterizing corrosion. Rice et al. [127] shows that short-wave infrared (SWIR) range could provide various information about water molecules present in silica, which could also be detected in silicate glass matrix because of water uptake during corrosion. The most important bands are ≈ 1410 nm showing OH^- overtone, ≈ 1470 nm showing H_2O overtone or combination, ≈ 1910 nm indicating H_2O molecules in silica cages (almost free from hydrogen bonding) and $\approx 1940 - 1960$ nm indicating hydrogen-bonded H_2O molecules in voids or films on silica surfaces (Table 2.10). Indeed, the prominent bands around ≈ 1415 nm and ≈ 1905 nm were successfully used by Zaleski et al. [94] and Brostoff et al. [89] for the characterization of glass corrosion using Fiber Optic Reflectance Spectroscopy (FORS). However, FORS provides single point measurements without comprehensive spatial information.

Table 2.10: Position of bands in SWIR range, providing various information on glass corrosion [127]

Position (nm)	Assignment
1410	OH^- overtone
1470	H_2O overtone/combination
1910	H_2O molecules in silica cages (almost free from hydrogen bonding)
1940-1960	Hydrogen-bonded H_2O molecules in voids or films on silica surfaces

Experiments were conducted at Colourlab, NTNU Norway with two cameras operating in the SWIR and VNIR range (Table 2.11). Trials were performed with different imaging parameters

to identify the best configuration for the acquisition of corroded glass. The desired value for detector saturation is between 60-75% of the (Fig. 2.16a and c, yellow green to orange colour on the scale). To get best results, it is reasonable to choose a configuration that takes light conditions into consideration and neither causes overexposure (saturation) nor generates signals that are too weak which will lead to a poor signal-to-noise ratio (Fig. 2.16b). Moreover, the light distribution should be as homogenous as possible within the area captured by the cameras (Fig. 2.16c).

Table 2.11: Hyperspectral imaging cameras used for the study

Camera from Norsk Elektro Optikk As	Wavelength range	Spatial resolution (Pixels across track)	Spectral Sampling	No. of wavelength bands/images
HySpex VNIR-1800	400 - 1000 nm	1800 pixels	3.26 nm	186
HySpex SWIR-384	1000-2500 nm	384 pixels	5.45 nm	288

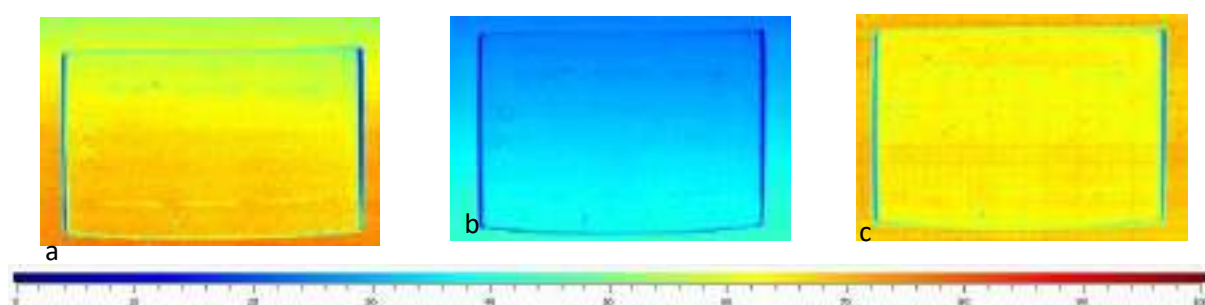


Fig. 2.16: Trials for best configuration for HSI of model glass samples a) non-homogenous light distribution between 60-75% b) non-homogenous light distribution between 30-45% b) homogenous light distribution between 60-75 % (scale showing detection saturation percentage)

The optimum configuration was affected by various factors which needed to be ascertained for capturing useful HSI data for this kind of initial study, based on the detector saturation level and the homogeneity of the light distribution in the region captured by the camera.

1. **Lighting mode:** Lighting in transmission mode and reflection mode were used to acquire hyperspectral images of the corroded glass. It was found that acquisitions in transmission mode were useful for gathering data about the transparent glass matrix while the reflection mode produced shadows due to the geometry of the model glass samples which would lead to noise in the data and hence was found impractical (Fig. 2.17).

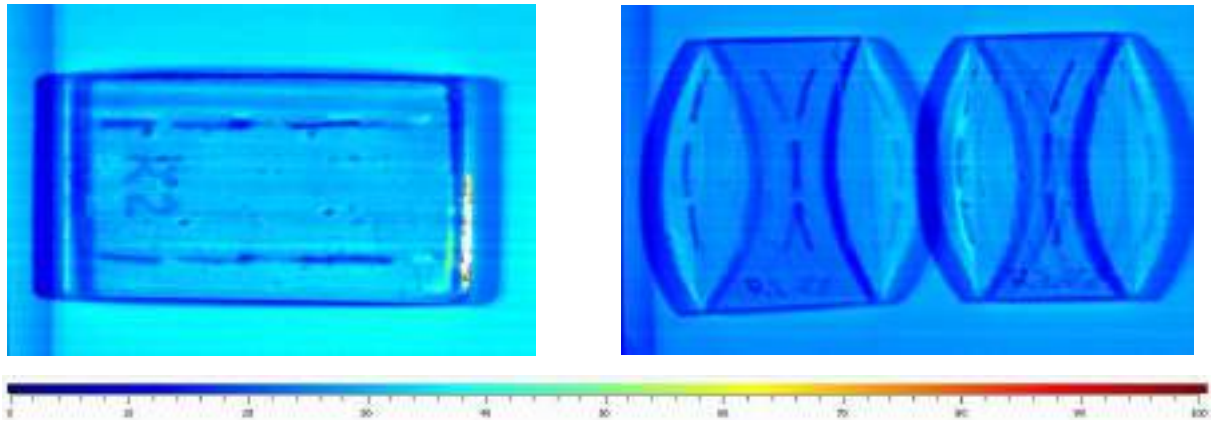


Fig. 2.17: HSI trials with reflected light on white background showing very low detector saturation along with shadows of the samples on the background (scale showing detection saturation percentage)

2. **Type of lights:** Light sources to be used for acquisition should be able to produce spectral reflectance in the specific range of the camera (VNIR/SWIR). Four different types of light sources were used for the trials i.e., halogen circular and cylindrical bulbs and tubes of different radiation intensity (Fig 2.18).



Fig. 2.18: Different light sources used for the HSI trials

3. **Light positions:** Two light sources were positioned at 45° angle to the vertical on both sides of the two cameras for reflectance mode, which was abandoned after few trials. For transmission mode, the two light sources were placed under the translational stage at different distances from each other during trials. In case of model cups, the two light sources were placed at different distances behind the diffuser plate to produce the desired light distribution and intensity.
4. **Diffuser plate:** A frosted glass diffuser plate along with a plastic diffuser plate were used individually and together during the trials to choose the best configuration for acquisition.
5. **Integration time:** The integration time is defined as the time in which the spectral camera captures the photons. This can be flexibly set by the acquisition software provided by the camera manufacturer. Eventually, the optimal configuration was defined as followed.

For model glass samples:

The two HSI cameras were mounted on vertical stands. The HSI data was collected in transmittance mode (Fig. 2.19). Two circular halogen bulbs (150 watts, Philips spotline) were used as the light sources and were placed below a moving translation stage; one directly under each camera. They were placed in a way that radiation from the light source will be transmitted through a glass (sometimes along with plastic) diffuser plate with enough intensity to reach the camera through the model glass sample to be studied. The camera focused on the top of the glass sample and images were acquired with two lenses of focal distance 3 and 30 cm (distance between the camera and the object) in both VNIR and SWIR. Equalizer was used in the case of VNIR camera with 3 cm focus lens. Acquisition parameters such as integration time, frame averaging, etc. were set and were synchronized with the speed of the moving stage controlled using a computer software provided by the camera manufacturer. All the image acquisitions were performed in a dark room to avoid any stray light recorded in the sensor.

The acquisition time for a whole model glass sample was approximately two minutes and the temperature at the sample surface generated by the heat produced by halogen lamps was constantly monitored using a thermal camera during acquisition. Small table fan directed towards the sample was also used to reduce the heat at the sample surface. This way it was ensured that the temperature during light exposure was not more than $\approx 30^{\circ}\text{C}$, which was considered to be safe for the model glass (and eventually for the historical glass objects) [128].

For model cups:

The SWIR camera was mounted on a rotating stand. The HSI data was collected in transmittance mode (Fig. 2.20). Two circular halogen bulbs (150 watts) were used as the light sources and were placed behind a stationary stand at a suitable distance which produced a homogenous light distribution at 60-75% detector saturation. They were placed in a way that radiation from the light sources will be transmitted through a glass and plastic diffuser plate with enough intensity to reach the camera through the model glass sample to be studied. The camera focused on the front wall of the model cup and images were acquired with the lens of focal distance 30 cm in SWIR. Acquisition parameters such as integration time, frame averaging, etc. were set and were synchronized with the speed of the rotating stand controlled using the computer software provided by the camera manufacturer. All the image acquisitions were performed in a dark room to avoid any stray light recorded in the sensor. The temperature was monitored as mentioned previously.

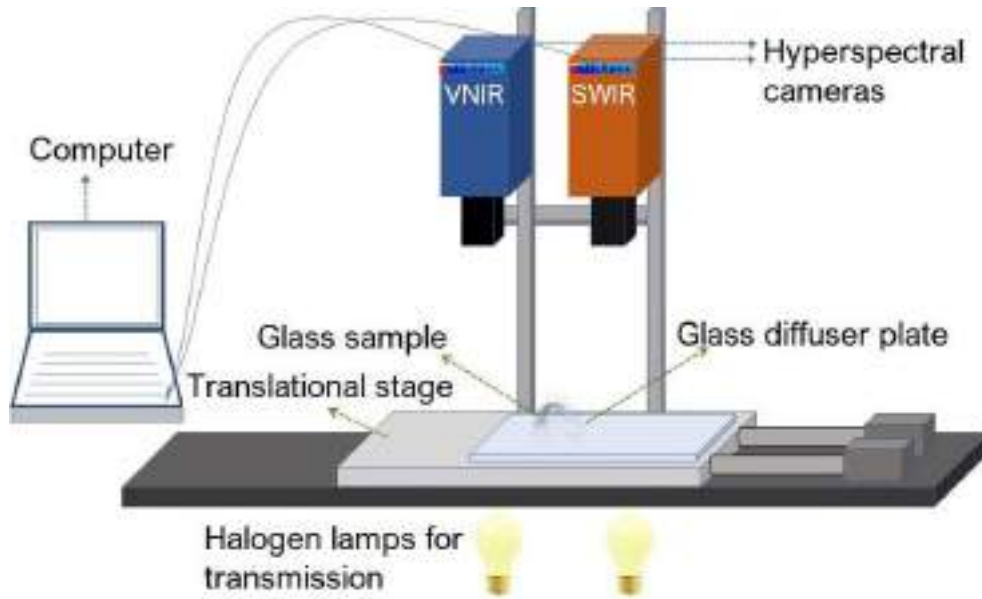


Fig. 2.19: A schematic diagram of the Hyperspectral Imaging setup in transmission mode using both VNIR and SWIR cameras [129]

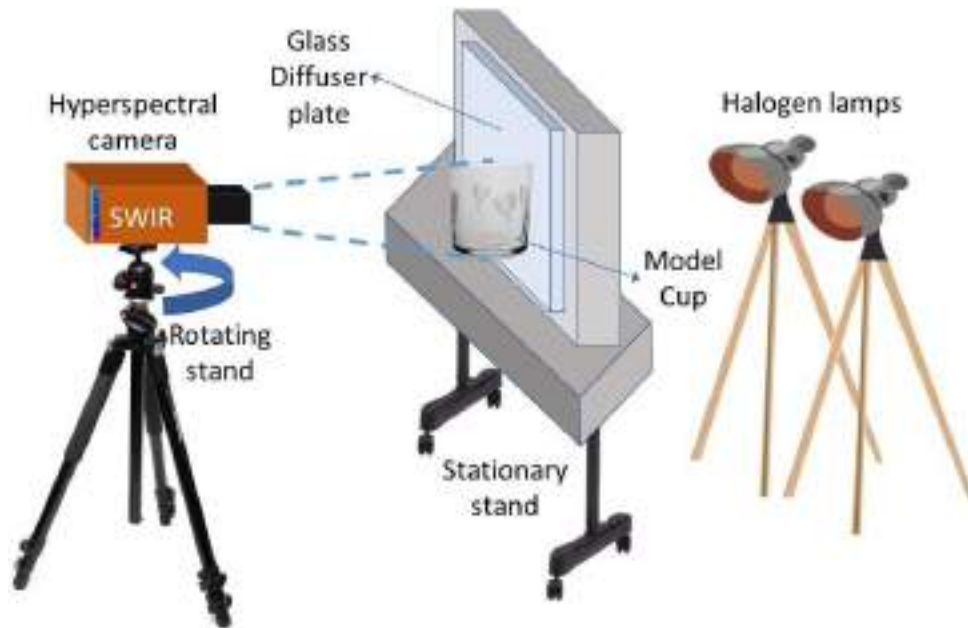


Fig. 2.20: Schematic diagram of the HSI setup in transmission mode for model cups using SWIR camera [129]

The HSI setup was tested and verified with both curved and flat glass samples to understand how the curvature of the samples studied might have influenced the results. There was no noticeable difference due to the small curvature of the glass samples studied in this research. The software provided by the manufacturer automatically corrected the factors like quantum efficiency of the sensor, dark current etc. which were the same irrespective of the sample shape, the radiance correction of the HSI data was unaffected. With some preliminary testing and analysis, it was verified that the curvature of the samples used in this study didn't affect the transmittance measurement. The presented study focused on the specific spatial points that were not influenced by the features in the global geometry.

The visualization using 3 cm and 30 cm lens both could cover the whole sample for VNIR camera (Fig. 2.21a and b) and only a part of the sample for the SWIR camera with 3 cm ($\approx 5 \times 2$ cm) (Fig. 2.21c). On the spectral processing side, average spectra from the whole sample region for every acquisition with 30 cm lens was used for the quantification of the corrosion extent since it covered the whole sample (Fig. 2.21b and d). It was found that there was no significant difference in the spectral data acquired from the two lenses.

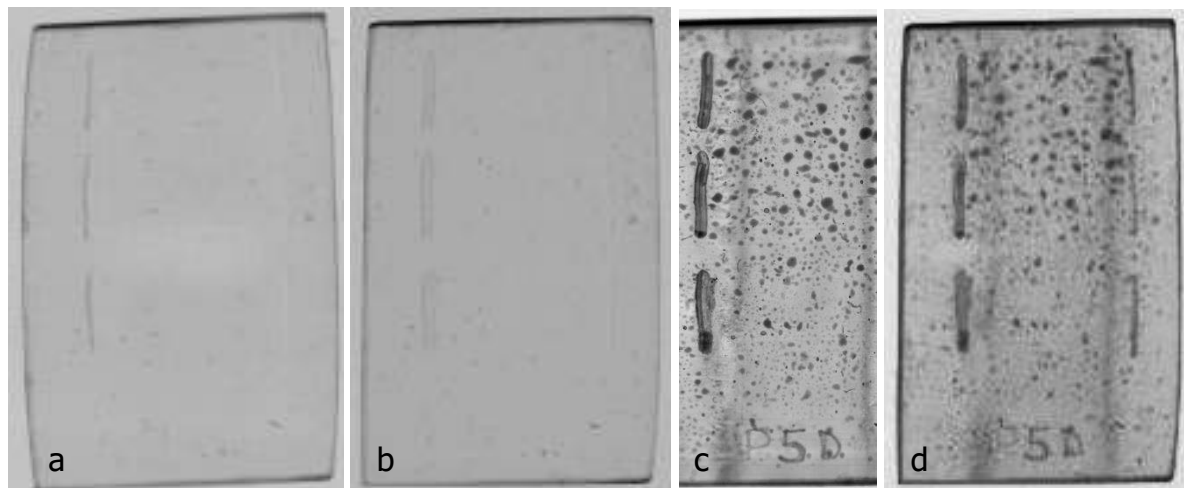


Fig. 2.21: Hyperspectral image of P model glass sample aged to 12 months at 700 nm (VNIR) with a) 3 cm ($\approx 5 \text{ cm} \times 3 \text{ cm}$) and b) 30 cm lens ($\approx 5 \text{ cm} \times 3 \text{ cm}$) and at 1906 nm (SWIR) with c) 3 cm ($\approx 5 \text{ cm} \times 2 \text{ cm}$) and d) 30 cm ($\approx 5 \text{ cm} \times 3 \text{ cm}$) lens

The VNIR spectra of unaged and aged model glass P were found to lack any special features between 400 – 1000 nm (Fig. 2.22) in accordance with existing literature [130]. Additionally, since in the present case the curves obtained for both unaged and aged model glass are very similar, it was concluded that the spectral information in VNIR is not relevant to identify corrosion.

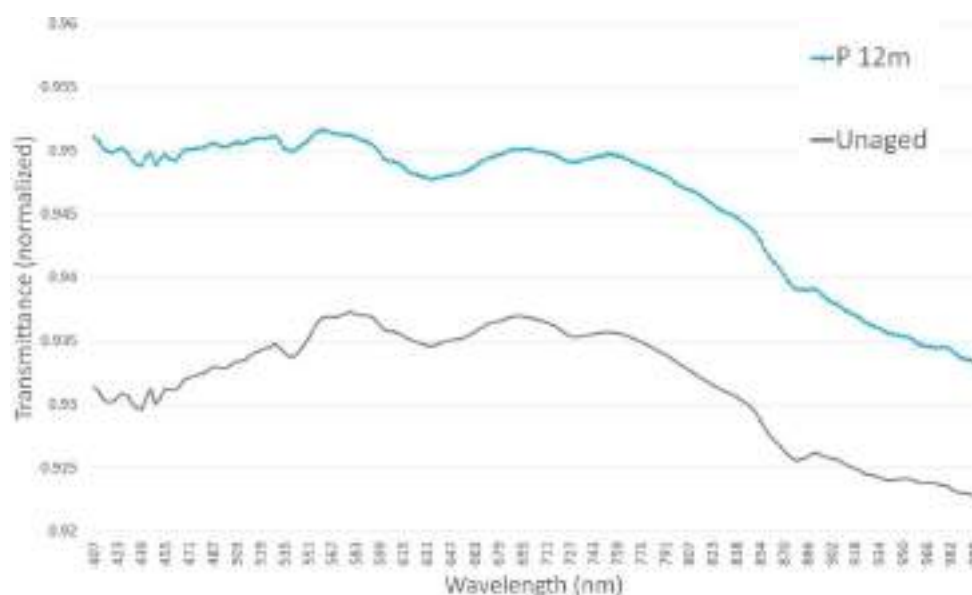


Fig 2.22: VNIR average spectra of model glass samples from P aged for 12 months compared (blue) with unaged reference (grey) glass acquired using 3cm focal length lens

Averages of data from ten unaged reference model glass samples along with two model glass samples from each of the aging condition and aging periods are presented in the results along with three model cups and one reference model cup. The raw data initially need to be corrected to radiance using HySpex-RAD software provided by the camera manufacturer. Sensor corrections and dark current subtraction were automatically done by the software. After the radiance correction, the acquired 3D data cubes were transformed into transmittance, by dividing each of them by an image of the diffuser alone, with the same size of the image and illumination condition as that of the sample. Transmittance then was calculated by the formula (8):

$$T = \frac{S_{x,\lambda}}{W_{x,\lambda}} \quad (8)$$

where $S_{x,\lambda}$ is the light signal transmitted by the object and $W_{x,\lambda}$ is the light signal transmitted by the diffuser alone, at pixel location x , λ . Indices x , λ indicate respectively pixels across the track and the number of bands (1800 and 186 for VNIR; 384 and 288 for SWIR) [123].

HSI images were processed for spatial and spectral data using open-source Fiji distribution of ImageJ software. HSI spectra averaged by ImageJ could not be reported along with standard deviation. Statistical analyses were performed using Microsoft office excel and Origin pro. Spectragryph software was used to calculate the integral (area under the peak) of the significant vibrational bands identified in the spectra collected.

2.17. Reflectance Transformation Imaging (RTI)

RL on glass surfaces can also be studied through Reflectance Transformation Imaging (RTI). RTI combines many photographs of the same artefact taken from a camera on a fixed position, while varying the light position at each picture. Different methods are used to process RTI data such as the polynomial texture mapping (PTM), hemi-spherical harmonics and discrete modal decomposition [131]. The most popular method to process RTI data is PTM, which was initially developed by Tom Malzbender [132]. One of the most known features allowed by the RTI data, is the creation of a relightable file, which allows an interactive visualisation of the imaged object under different lighting positions. RTI acquisition of transparent surfaces are complicated due to the various possible interactions between the surface and its light environment [133]. Although, there have been some previous works on re-lighting visualizations of glass objects [134][135].

Besides the relighting, RTI data can be used to produce normal maps using local geometry as well as statistical maps using local reflectance [136]. Both maps are generated using descriptors which can characterise different local reflectance features and in turn different degradation phenomena on corroded glass surfaces. This is possible because light is reflected differently from isotropic or anisotropic features on the surface. Reflectance response of an isotropic geometry is homogenous and does not vary with the angle of incident light, while for an anisotropic geometry, it varies depending on whether the angle of incident light is parallel (low response) or perpendicular (high response), so the scale of variation is large.

The RTI datasets presented in this paper were acquired using a custom designed dome-based system [136]. This is a completely automated system, with a single light source held on a motorized arc that allows the light source to be placed at any desired position of the angular space defined between 0° to 360° for azimuth (ϕ) and 0° to 75° for elevation of the dome (θ) with a radius of 220 mm. The system is equipped with a 12.4-megapixel monochrome camera, which along with a motorized zoom and focus forms an optical system that offers high quality images. A white light emitting diode (LED) light was used as the light source designed to be integrated into the acquisition system (Fig. 2.23). Thanks to the synergy between motorized hardware and custom-made control software, this robust system ensures highly accurate and repeatable RTI acquisitions [136].

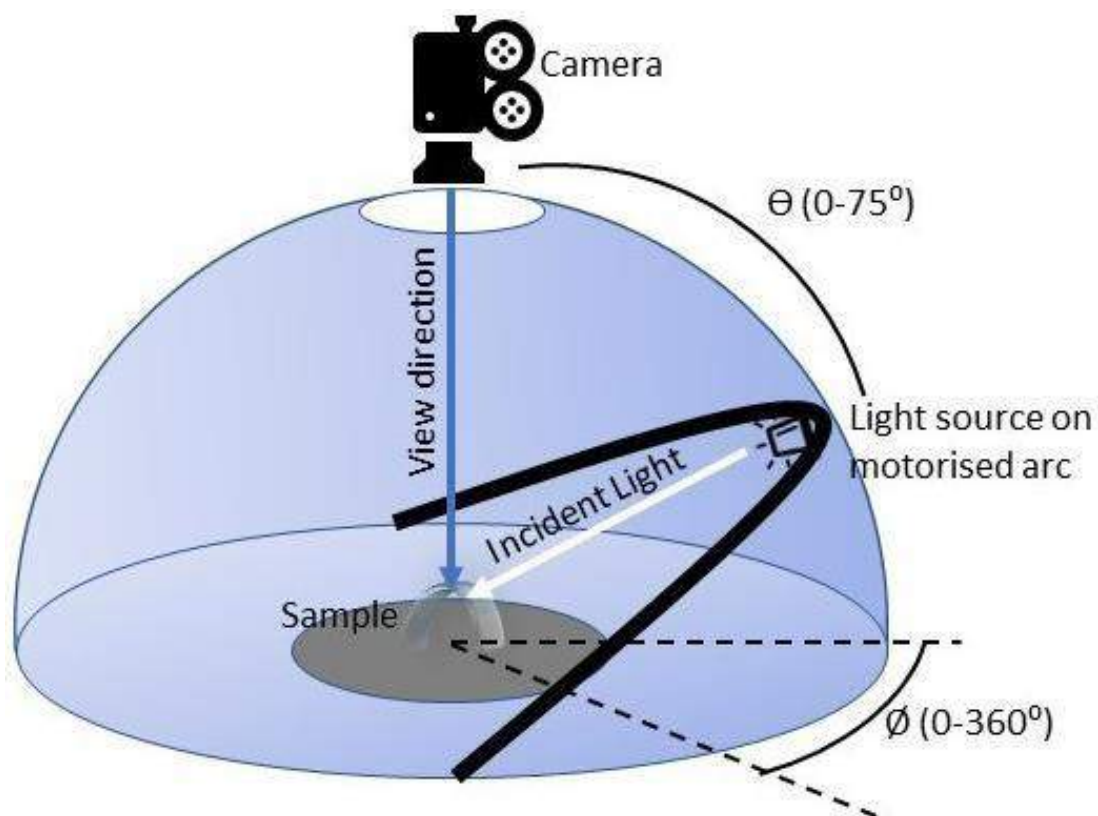


Fig. 2.23: Schematic diagram of the RTI dome setup [137]

Various trials were undertaken with lights of different wavelength within the visible light range but white light was chosen for the final acquisitions since the different wavelength lights did not add any new information. Apart from this, various homogenous and non-homogenous patterns of lighting positions were explored at different exposure levels as well as the type of exposure i.e., low dynamic range (LDR) or at high dynamic range (HDR). The greatest challenge for a transparent material like glass in RTI is the elimination of unnecessary information from the background. The background should be able absorb as much light as possible without reflecting it back. Therefore, materials such as black velvet were also used which created noise in the RTI images (Fig. 2.24). The tests done for producing re-lighting visualizations and RTI maps produced results which were in agreement with previous studies by Dittus [138]. His research made use of free form RTI setup which was successful in producing re-lighting visualizations of transparent and colourless historical glass objects.

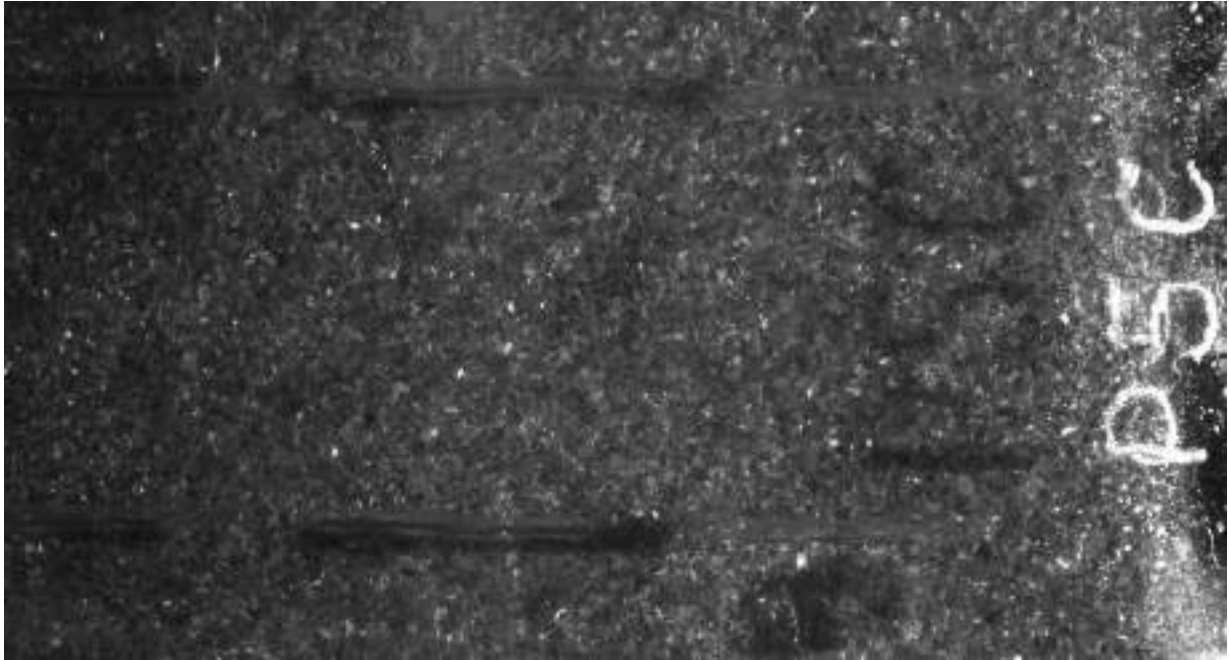


Fig. 2.24: RTI image of model glass aged to 9 months showing texture of the black velvet background (Field of view: $\approx 5\text{ cm} \times 2.5\text{ cm}$)

This led to the designing of a black plastic platform which could be fit on the acquisition area inside the dome (Fig. 2.25). This platform was designed based on light traps with a dome-shaped double walled form having an oval rectangular opening on the top for keeping the model glass sample. There is space between the inner and outer wall with inner wall bearing holes to trap more light within this space. The opening on the top defined the maximum area which could be acquired on each sample without disturbance from the background. This platform was then 3D printed using matte black plastic.



Fig. 2.25: Black plastic background designed for RTI acquisitions of model glass.

In the process of surface characterization, the presence of "artifacts" can be notably influenced by a few instances of exceptionally high responses. Consequently, employing a larger number of light positions serves to diminish the occurrence of these artifacts. Therefore, the selection of the specific quantity of light positions was a strategic decision aimed at striking a balance between encompassing a maximal range of positions while concurrently optimizing the acquisition time to its lowest feasible duration. Two different lighting configurations were used

for capturing the data. The data from these two configurations is described and compared in this section (Fig. 2.26a and b):

1. Homogenous 500 lights distributed around the RTI dome in LDR
2. Homogenous 250 lights in a ring ($\emptyset = 0$) in HDR

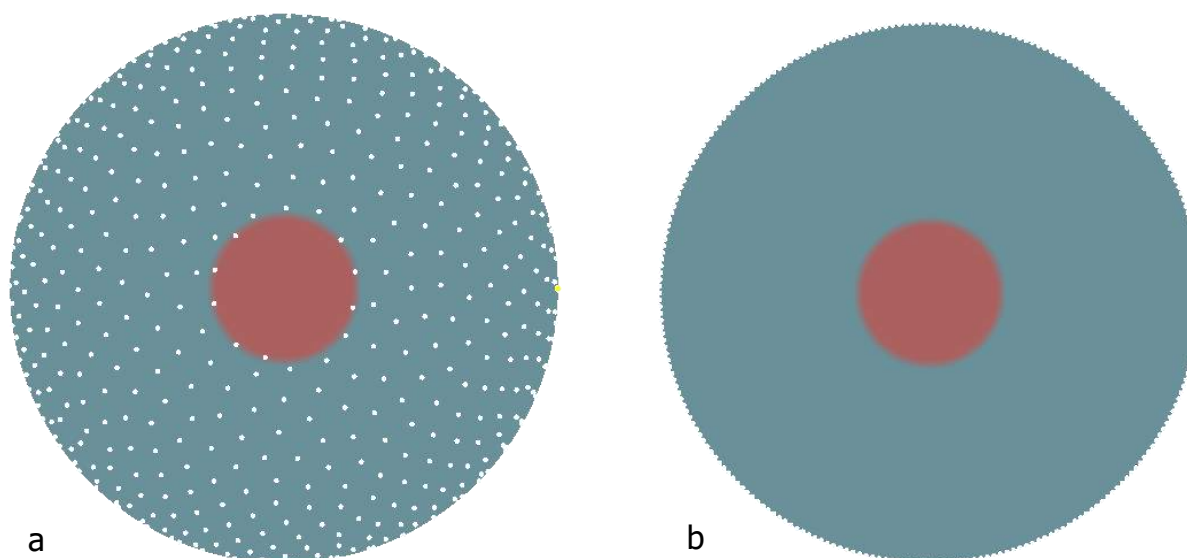


Fig. 2.26: RTI light positions for a) LDR configuration b) HDR configuration

RTI relighting visualizations were generated using LDR acquisitions. RTI maps were generated for a specific region in the centre of every model glass (one or two model glass from each aging period) with both LDR and HDR configurations. Here all the maps corresponded to an area of $\sim 24 \times 21 \text{ mm}^2$ acquired from the model glass (Fig. 2.27a). Figure 2.27b shows an image acquired by light perpendicular to the model glass (parallel to the camera vision) before the start of the RTI acquisition.

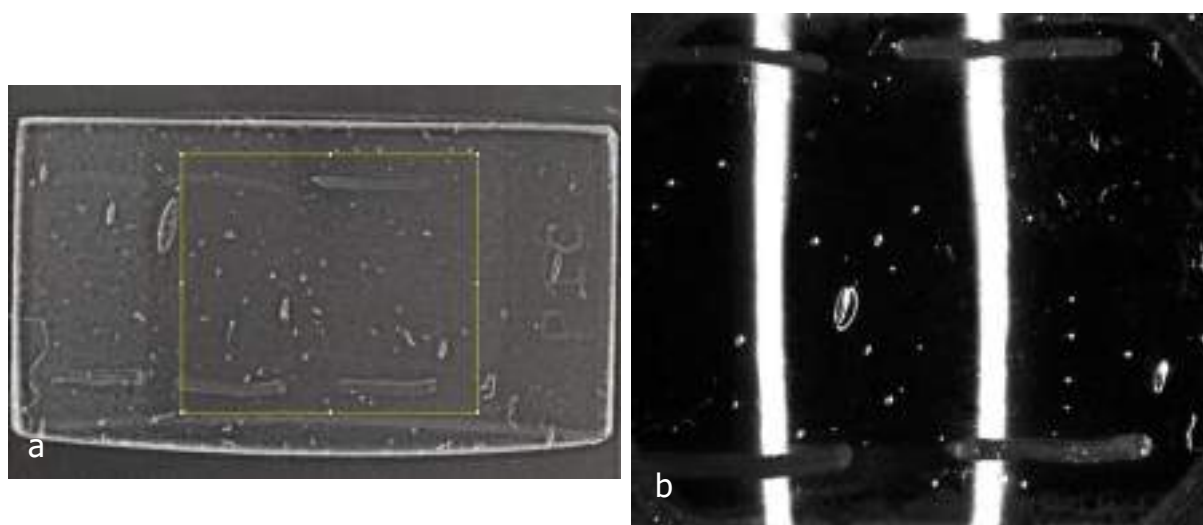


Fig. 2.27: a) TCPL photograph of P model glass aged for 9 months, with a yellow rectangle highlighting the area acquired by RTI ($24 \times 21 \text{ mm}^2$), b) White light image ($24 \times 21 \text{ mm}^2$) from RTI setup

RTI data were processed using MatLab®, to generate maps of statistical descriptors (such as mean, median and kurtosis). Apart from this X-RTI MSA tool was used for producing relighting visualization for the RTI data, which is developed by the manufacturers of the RTI system and ImageJ was used for the analyses of the RTI maps.

The LDR configuration was successful in creating interactive relighting visualizations for the model glass, which clearly show SN (inside blue rectangle), scratches (inside yellow rectangles), fine cracks (inside red rectangle) and bubbles (inside green rectangles), using the interactive MSA tool (Fig. 2.28). LDR images are necessary for the relighting video creation since the algorithm cannot work with HDR images (personal communication from Marvin Nurit).

Besides the relighting, RTI data can be used to produce normal maps using local geometry as well as statistical maps using local reflectance. Both maps were generated using descriptors which can characterise different local reflectance features [136] which were used here to visualize different degradation phenomena on corroded glass surfaces. This is possible because light is reflected differently from isotropic or anisotropic features on the surface. Reflectance response of an isotropic geometry is homogenous and does not vary with the angle of incident light, while for an anisotropic geometry, it varies depending on whether the angle of incident light is parallel (low response) or perpendicular (high response), so the scale of variation is large. RTI data were processed using Matlab®, to generate maps statistical descriptors (Table 2.11) since maps of geometrical descriptors were not found useful for the present research.

These statistical descriptors are based on moments and quantiles or percentiles. First moment or $E(X)$ is the measure of the central location known as mean or average. It is linear, i.e., if we add or multiply all measurements by the same constant, then the average undergoes the same operation. In the case of an RTI acquisition, with a strictly linear camera, changing the exposure time by a coefficient is equivalent to modifying the average by the same coefficient [136]. The average is used to discriminate between points on the surface whose average angular reflectance intensity is different from the rest of the points (Fig. 2.30a and b). The map at HDR has clearly higher average reflectance than LDR map. Both show similar features of bubbles and few cracks.

The fourth moment is known as kurtosis which allows to describe the tails of the reflectance per pixel distribution or 31.8% of the values (Fig. 2.29) and thus to estimate the presence or absence of outliers. The further the value is from the mean or median, the more it contributes to the kurtosis, so a high kurtosis value indicates the presence of outliers in large or small quantities [136].

The kurtosis map for LDR shows a few cracks, SN, bubbles and dust particles on the surface but not on the whole sample as the central part lacked information while in case of HDR acquisition it does not provide any clearly distinguished features other than bubbles and some dust particles and some faintly perceptible cracks (Fig. 2.30c and d).

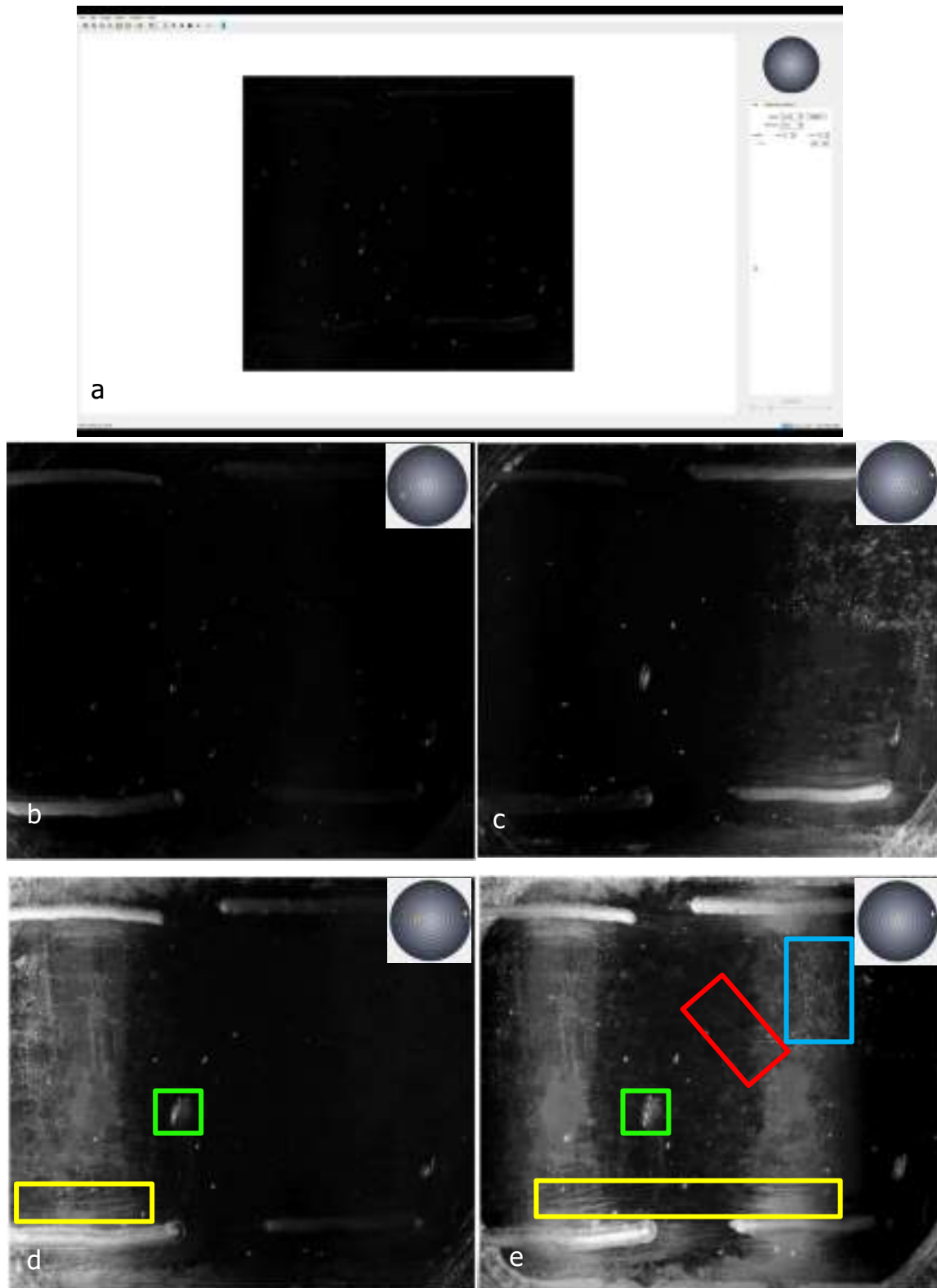


Fig. 2.28: a) MSA tool UI showing relighting visualization of P model glass aged for 9 months built from LDR images along with trajectory of the light path shown on the top right corner (yellow circle showing the light position in the embedded image) b-d) Various screenshots from relighting visualisation at different light positions showing SN (inside blue rectangle), scratches (inside yellow rectangles), fine cracks (inside red rectangle) and bubbles (inside green rectangles) (Field of view: $24 \times 21 \text{ mm}^2$)

Table 2.12: List of RTI-derived statistical and geometric descriptors used in this research.

Name of descriptor	Definition
Reflectance statistical descriptors	
Mean	Corresponds to the sum of the measurements divided by the number of measurements
Median	Divides the pixel distribution into two parts, so that 50% of the distribution is below the median and 50% above
Kurtosis	Describe the tails of the reflectance per pixel distribution or 31.8% of the values
Skewness	Estimates whether distribution of a pixel is normal (zero skewness) or how it deviates from a normal distribution
Standard Deviation	Describes the dispersion of the data, the lower the standard deviation, the closer the data is to the mean and vice versa
Max	Shows maximum reflectance at any point
Min	Shows minimum reflectance at any point
Dynamic Ratio	Ratio between the maximum and minimum
Energy	Energy increases the contrast of the data by summing the values to the power of two
Entropy	Measures the level of ‘uncertainty’ or ‘chaos’ in a distribution
Variation Coefficient	Ratio between the standard deviation and the mean

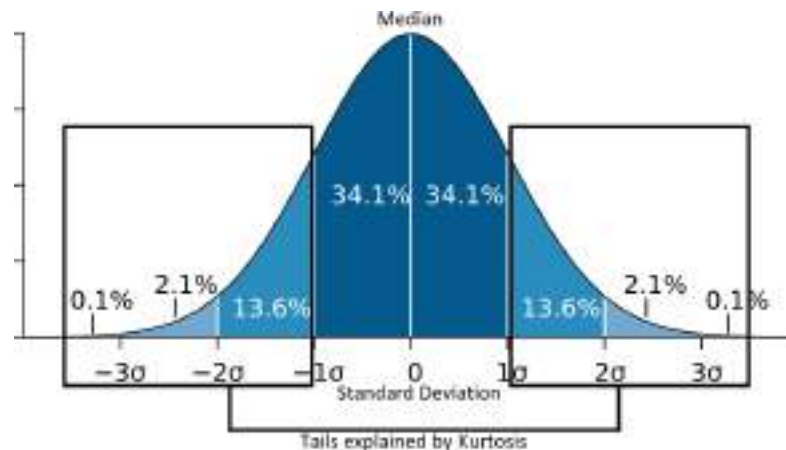


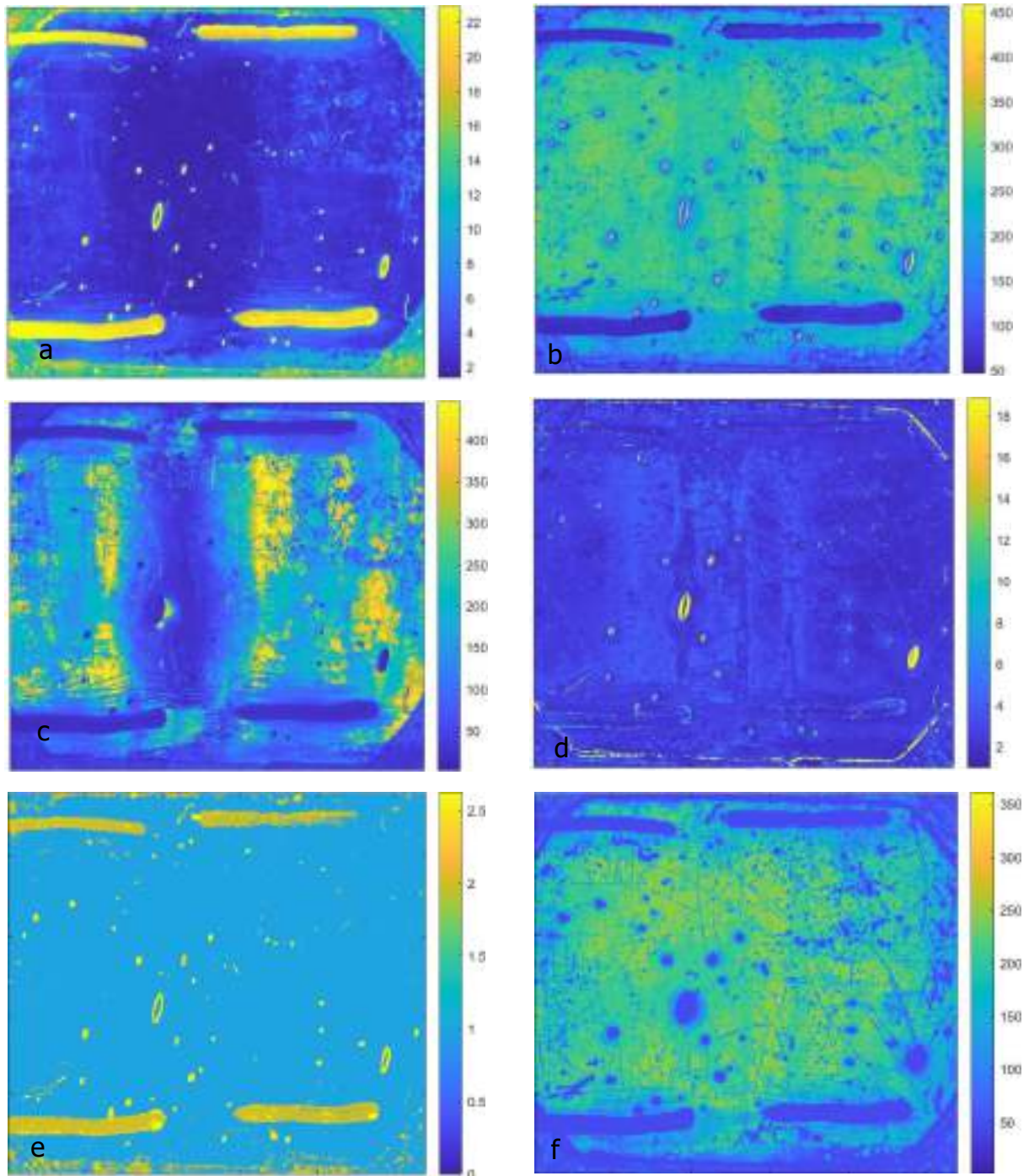
Fig. 2.29. A normal distribution curve explaining median and kurtosis descriptors

The q quantiles describe a distribution by dividing it into q intervals containing the same number of data (9).

$$Q_{(p|q)}[x] \equiv P(x \leq Q_{(p|q)}) = \frac{p}{q} \quad (9)$$

where $Q_{(p|q)}$ is the p -th q quantile to be found, q is the number of quantiles, p is the p -th quantile and $P(Y)$ is the probability of Y . Quantiles are more robust when the distribution has outliers as opposed to the descriptors such as those for moments. The minimum and maximum are $Q(0/q)$ and $Q(q/q)$ respectively. They allow us to know the limits of each point on the surface. One of the uses of quantiles is to understand if a point of the surface has a constant or exceptional behaviour [136]. The minimum map shows only bubbles and engravings clearly for LDR map as they have the highest value of minimum reflectance in comparison to the rest of the surface

(Fig. 2.30e). In other words, these features are the brightest at every light position. Nonetheless, in the case of HDR acquisitions, bubbles, cracks, SN and dust particles have the lowest minimum reflectance values thereby distinctly showing them (Fig. 2.30f).



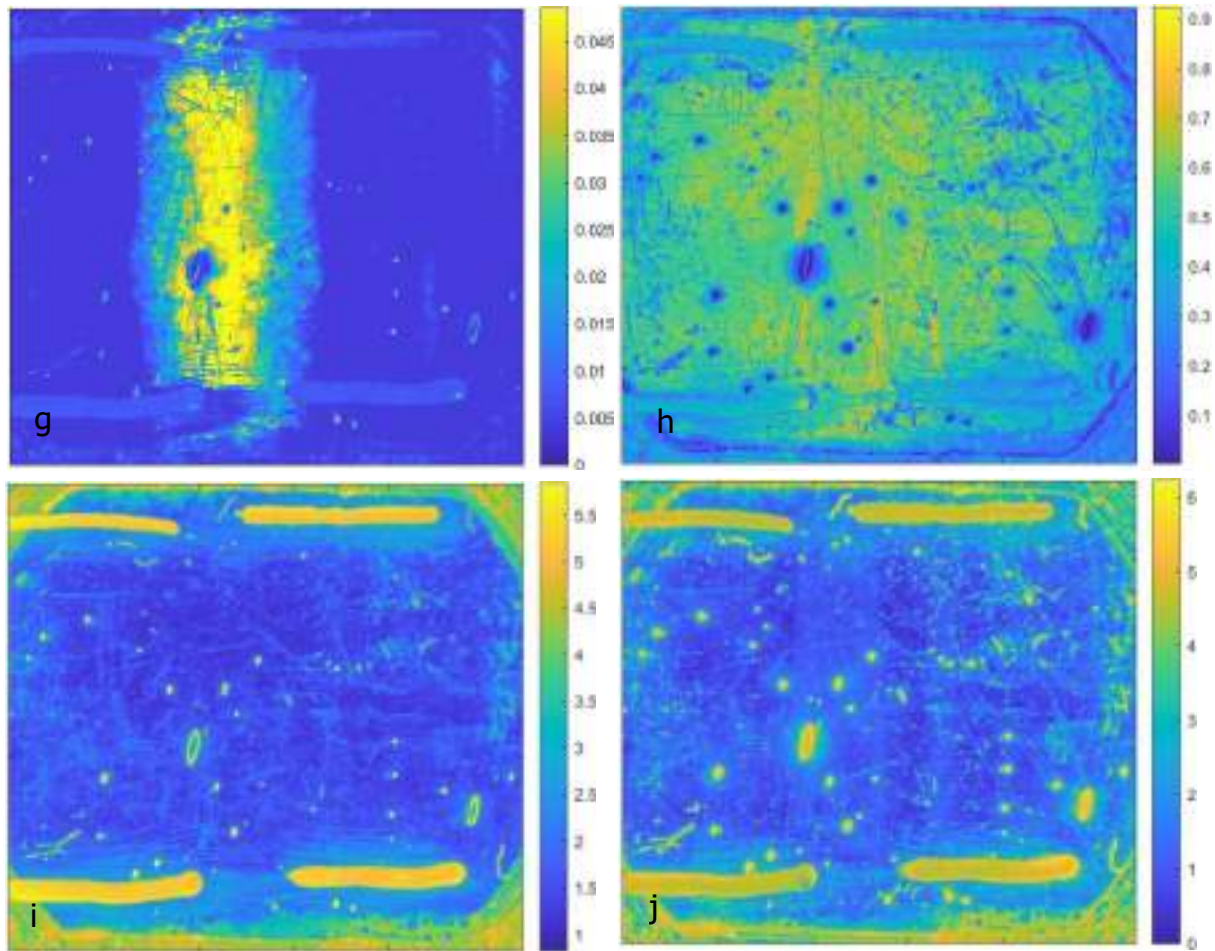


Fig. 2.30: LDR map for a) mean c) kurtosis e) minimum g) dynamic ratio and i) entropy map and HDR map for b) mean d) kurtosis f) minimum h) dynamic ratio and j) entropy map for P model glass aged for 9 months (wiped in the centre) (Field of view: $24 \times 21 \text{ mm}^2$)

The dynamic ratio is the ratio between the maximum and minimum reflectance at a point which allows us to know the amplitude of the angular response of a point on the surface. Thus, two distributions can have a different minimum and maximum but the same dynamic ratio. The larger the dynamic ratio of a surface point, the larger the scale of the values of its angular reflectance [136]. In case of LDR map, only the central featureless shows a high dynamic ratio as compared to the corrosion features and therefore can be identified in the centre (Fig. 2.30g). However, in case of HDR map the whole featureless space of the surface has higher dynamic ratio as compared to the corrosion features and therefore we can distinguish the cracks, SNs, dust particles and bubbles similar to minimum map but with more clarity (Fig. 2.30h).

The (Shannon) entropy measures the level of ‘uncertainty’ or ‘chaos’ in a distribution. If the local angular reflectance of the points on a surface is chaotic, then they are likely to be more difficult to model because they cannot be represented by simple functions without loss of information. The estimation of the entropy is made on the probability of occurrence of each value of the local angular reflectance [136]. It can be seen that the points with the highest entropy are those belonging to surface anomalies such as cracks, SN, dust or bubbles have geometrical properties such that their angular reflectance is chaotic, or difficult to model. Whereas the rest of the surface has a lower entropy and is therefore likely to be simpler to

model. Once again, the HDR maps provides more clarity as compared to the LDR map (Fig. 2.30i and j).

Entropy maps were found to be the best for visualizing cracks in HDR configuration. In case of dried samples with coarse cracking also, the cracks are clearly visible (Fig. 2.31).

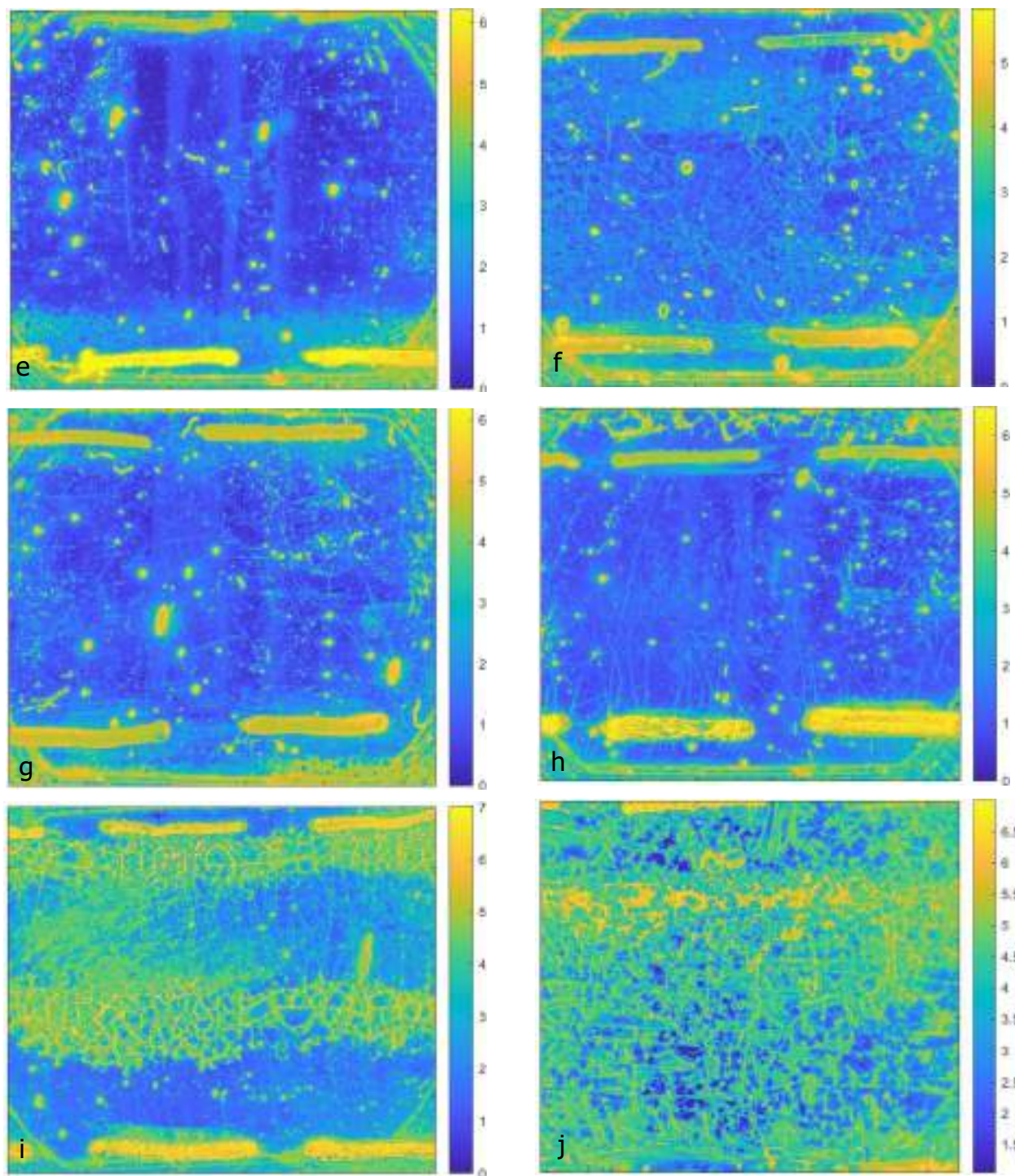


Fig. 2.31: HDR entropy map showing cracks on the surface of corroded model glass aged for a) 3 months b) 6 months c) 9 months d) 12 months e) 17 months f) 17 months and dried for 15 minutes (Field of view: $24 \times 21 \text{ mm}^2$)

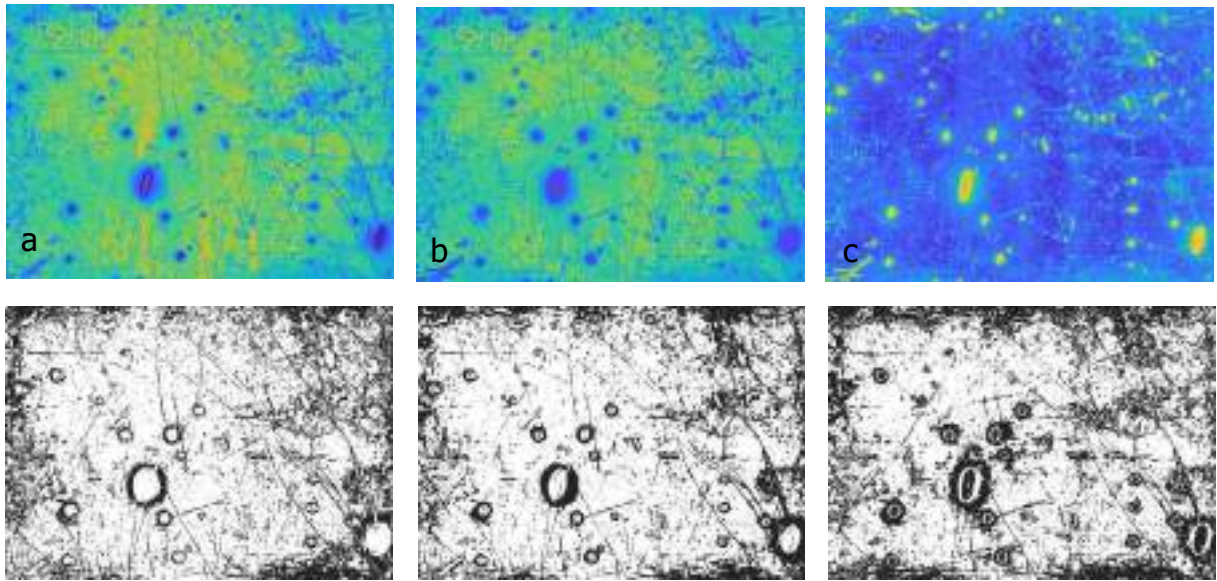
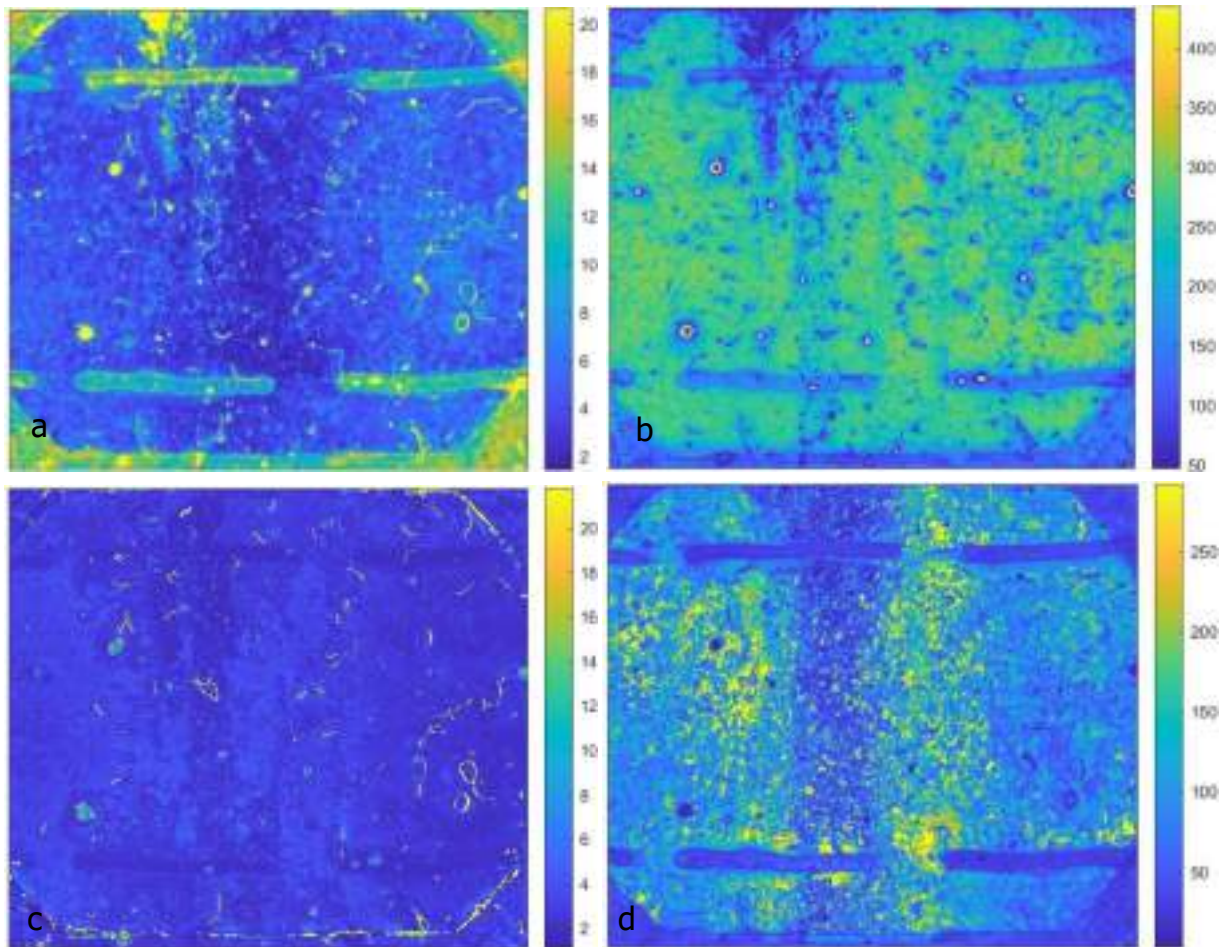


Fig. 2.32: a) Dynamic ratio, b) minimum and c) entropy map thresholded to quantify cracks (Field of view: $24 \times 21 \text{ mm}^2$)

Similarly, the same maps for unwiped P sample were compared to find which ones provide best visualisation of SNs (Fig. 2.33).



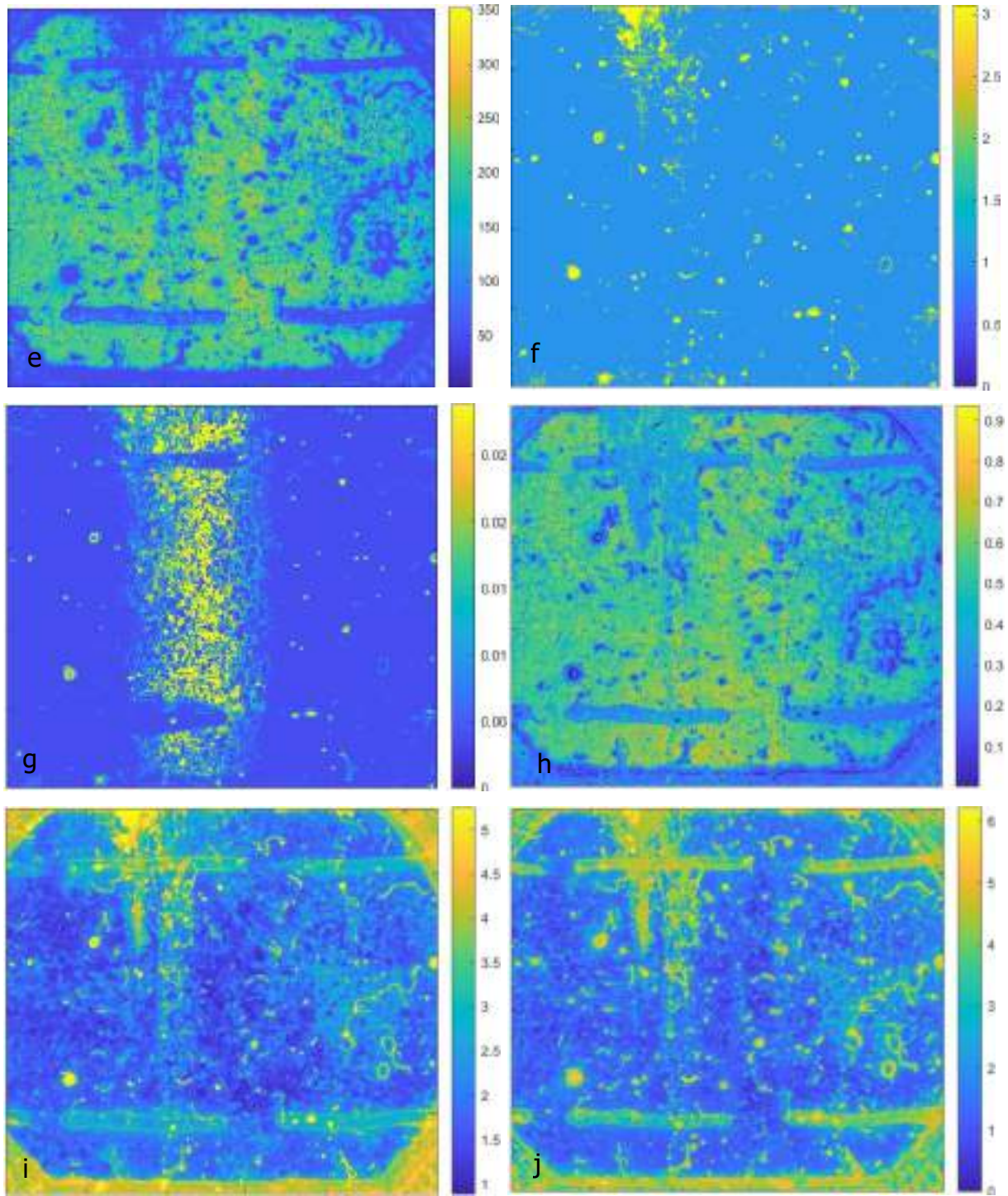


Fig 2.33. LDR map for a) mean c) kurtosis e) minimum g) dynamic ratio and i) entropy map and HDR map for b) mean d) kurtosis f) minimum h) dynamic ratio and j) entropy map for P model glass aged for 9 months (unwiped) (Field of view: $24 \times 21 \text{ mm}^2$)

After evaluating all the above-mentioned maps in LDR and HDR configurations only the minimum, dynamic ratio, and entropy HDR maps were processed to quantify cracks using RTI data. This selection was based on the clarity and quantity of information obtained. Crack quantification was done using colour thresholding in ImageJ. The thresholded images show a lot of noise due to the high reflectance from bubbles and dust particles and the area in their

vicinity which makes quantification unreliable (Fig. 2.32). Therefore, cracks were manually traced over the RTI entropy map and measured using ImageJ.

A novel methodology was devised for combining HDR imaging with RTI. This approach was designed to facilitate the measurement of surfaces exhibiting a wide dynamic range while mitigating the challenges associated with exposure time configuration. This configuration challenge arises when two different light angles can yield greatly distinct angular reflectance responses from the surface. Unlike LDR imaging, which is a conventional acquisition method, High Dynamic Range RTI (HD-RTI) offers enhanced capabilities for surface characterization. The data obtained through HD-RTI acquisitions can be regarded as a comprehensive representation of the surface's response, unhindered by sensor limitations. [139]. Interestingly, the LDR configuration was more useful to visualise SNs especially with the standard deviation map (Fig 2.34a), while with HDR configuration, it was not possible to distinguish SNs in any of the maps (Fig 2.34b). The specific reason of this difference in the behaviour of glass in LDR and HDR can only be understood with further in-depth research. The standard deviation describes the dispersion of the data, the lower the standard deviation, the closer the data is to the mean and vice versa. In the case of RTI, it could be an indicator of the dynamic variation of the surface points. Indeed, a large standard deviation for a surface point indicates that this point has an angular reflectance of which 68.2% of the intensity values vary between two distant values. While a small standard deviation indicates that the point has an angular reflectance intensity that varies between two nearby values. In the case of an anisotropic geometry, such as the engravings or SNs or bubbles, the standard deviation will be larger. The response of an anisotropic geometry varies depending on whether the angle of illumination is parallel (low response) or perpendicular (high response) so the scale of variation is large.

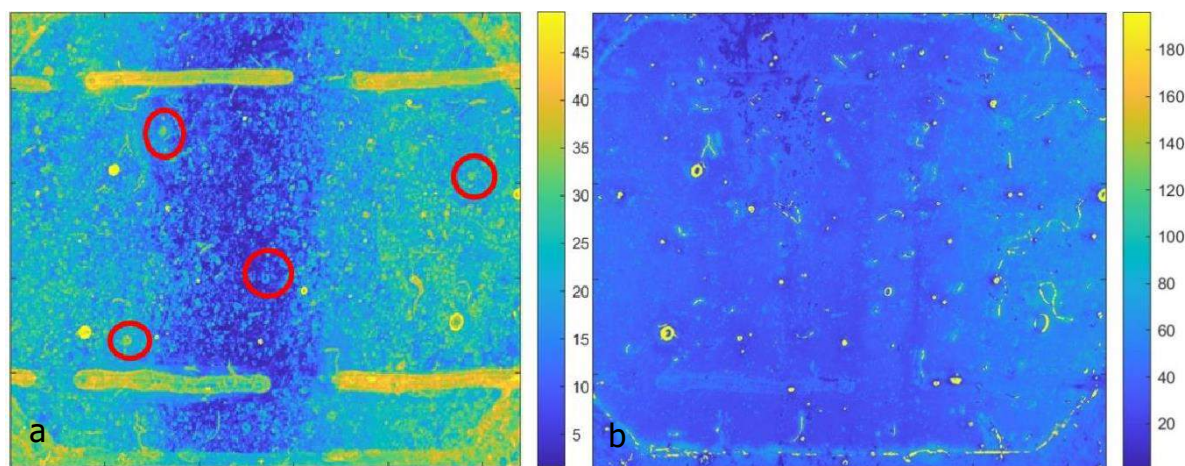


Fig. 2.34: Standard deviation map for P model glass aged for 9 months (unwiped) with the two configurations a) LDR b) HDR (Field of view: $24 \times 21 \text{ mm}^2$)

Conclusions on the imaging techniques:

The most useful analytical protocols were established for the documentation of transparent and colourless model glass. Digital photography of glass using transmitted white LED lights is already well-established practice. Along with this, the use of cross-polarized and transmitted

light was also introduced in this research which surely provides more clarity to the photographs due to a black background. Digital microscopy displayed SN and fine cracks better in reflected light while crack network and delaminations could be visualized better in transmitted light. In the case of HSI, acquisitions in transmitted light using halogen lamps and glass diffusers were found to be optimum. VNIR images could not provide any useful information in the context of glass corrosion. However, SWIR was found to be advantageous and therefore, would be described in the results.

As far as RTI was concerned, both LDR and HDR configurations need to be used to produce re-lighting visualization videos as well as the quantification of SN and cracks using LDR standard deviation maps and HDR entropy maps, respectively. Further research could help to produce even better results with these two techniques for visualizing glass.

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SECTION II

Chapter 3: Results

3.1. Historical glass composition and model glass formulation

For the three glass objects, 10-15 points were measured on both the alteration layer sample as well as the bulk sample. The bulk composition could be easily distinguished from the surface composition and all the three glass objects could be categorized as potash-lime glasses (Table 3.1). The relative standard deviations (RSD) of the measurements fall under acceptable limits (<10%) for all the major oxides (present in concentrations above 2%: SiO₂, CaO and K₂O).

Table 3.1: Average values and relative standard deviation for bulk glass composition for the three glass objects LM12433 (15 points), LM15473 (10 points) and AG1078 (15 points).

Element oxide	LM12433 Bulk			LM15473 Bulk			AG1078 Bulk		
	Avg wt%	St. Dev.	RSD	Avg wt%	St. Dev.	RSD	Avg wt%	St. Dev.	RSD
Na ₂ O	0.62	0.08	12.32	1.72	0.37	21.56	1.57	0.31	19.96
MgO	0.50	0.08	15.75	0.31	0.13	42.71	0.37	0.16	43.24
Al ₂ O ₃	1.24	0.13	10.09	1.48	0.16	10.65	1.27	0.18	14.18
SiO ₂	70.67	0.77	1.096	72.23	1.78	2.47	74.71	1.26	1.69
P ₂ O ₅	1.24	0.20	16.16	0.14	0.12	88.66	0.24	0.22	92.45
SO ₃	0.10	0.13	131.5	0.50	0.17	33.74	0.64	0.21	33.44
Cl ⁻	0.21	0.09	43.9	0.40	0.11	27.58	0.45	0.13	29.42
K ₂ O	20.09	0.62	3.097	18.19	1.42	7.79	17.62	1.37	7.80
CaO	4.35	0.17	3.892	4.40	0.39	8.92	3.22	0.28	8.72
MnO	0.99	0.14	14.19	0.65	0.23	35.50			

For the purpose of formulation of model glass composition, the analyzed glass constituents, determined in mole percent (or converted in this case), were first grouped according to the following system:

- SiO₂ network former, usually SiO₂.
- R₂O network converters, monovalent oxides such as e.g., Na₂O, K₂O, Sn₂O
- RO network converter, divalent oxides such as CaO, MgO, MnO
- R₂O₃ Oxides such as e.g., Al₂O₃, Fe₂O₃

The correspondingly grouped values are prepared for entry in the ternary state diagram (Fig. 3.1). According to table 3.2, the three glass objects fell in the Z category.

Table 3.2: Axis values for entry in the ternary diagram (rounding error compensated, conversion of the values in mol%).

Object	SiO ₂	R ₂ O	RO
LM12433	78	14	8
LM15473	80	14	6
AG1078	83	13	4



Fig. 3.1: Ternary state diagram with processed glass analyses of different glasses. Stable glasses (A, M, R) lie approximately in the middle of the diagram, glasses that are very susceptible to corrosion (H, J, Q) are at the lower right edge. W and Z show damage even in the museum. The remaining glasses show various corrosion phenomena [1]

They replicated the high-potassium alkali lime silicate composition assessed by SEM-EDX on historical microsamples of the three corroded historical glass objects (Table 3.1).

The composition of model glass was the formulated by the Fraunhofer Institute for Silicate Research by excluding trace components and modifying the content of sodium, potassium, and calcium (Table 3.3). This formulation was based on a rough estimate of the durability of alkaline silicate glasses made using an empirical model developed by Iliffe and Newton [2].

3.2. Model glass composition

Table 3.3: Average values and relative standard deviation for bulk glass composition for five model glass samples and comparison with the intended composition

Element	Avg. MG1	Avg. MG2	Avg. MG3	Avg. MG4	Avg. MG5	Avg.	SD	RSD (%)	Fraunhofer composition	Glass blower composition
Na ₂ O	3.93	4.18	3.95	4.69	3.90	4.13	0.33	8.00	3.00	3.07
Al ₂ O ₃	1.11	1.20	1.17	1.18	1.17	1.17	0.03	2.78	-	-
SiO ₂	70.57	69.73	70.86	69.90	71.79	70.57	0.83	1.17	71.00	71.00
K ₂ O	21.43	21.52	21.09	21.38	20.28	21.14	0.51	2.40	23.50	23.67
CaO	2.94	2.90	2.92	2.86	2.87	2.90	0.04	1.23	2.50	2.52

The recipe provided used by the glass blower specified the composition of the model glasses which was verified by analyzing spare pieces (not subjected to aging) using SEM-EDX and EPMA. The compositions of glass before artificial aging could be compared with composition

of the glass after artificial aging in order to understand the corrosion mechanisms and chemical changes in glass due to corrosion.

The RSD of the measurements fell under acceptable limits ($<10\%$) for all the oxides measured (SiO_2 , CaO , NaO and K_2O). However, alumina was also found in the samples at an average composition of $1.17 \pm 0.03\%$, which could be due to impurities in the silica used for the manufacture of model glasses. The RSD was determined to be 8% for NaO and $< 3\%$ for all the other oxides (Table 3.3).

3.3. Aging environment measurements

To ensure alternating RH, the RH was measured with the MSR data logger in the V desiccator for throughout the aging period of 17 months. The RH logger was not exposed to higher concentrations of VOCs in the P or PV desiccator to avoid unreliable readings and damage to the instrument. Given that the data logger was not able to be calibrated precisely, the RH values did not show good correspondence with the intended RH values using preconditioned silica gel. However, an overall ΔRH was calculated from the RH data recorded by the data logger i.e. $37 \pm 2\%$ which was in accordance with the initially intended ΔRH of 40% (75%-30%). The temperature could be seen fluctuating between 19 – 24 °C. An example of a typical data logger RH and temperature graph is given in Fig. 3.2.

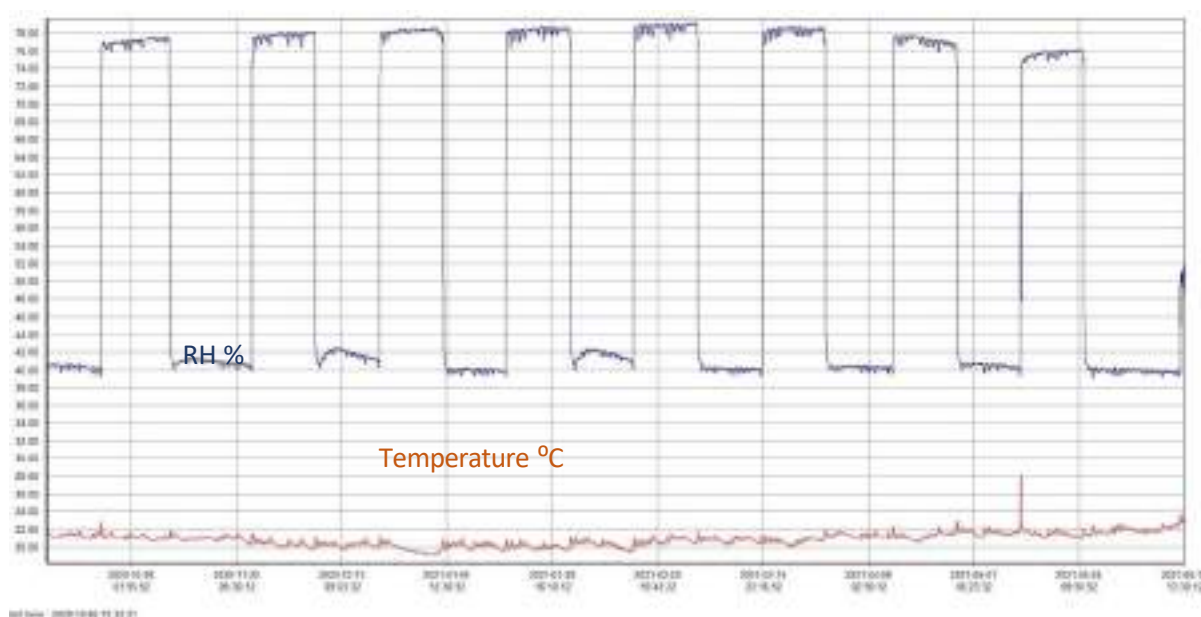


Fig. 3.2: RH and T graph recorded by data logger for V aging cycle 9 to 25

3.4. VOC pollutant concentration in P, PV and V conditions

A typical PID reading curve of acetic acid (AA) concentration for a P and PV aging cycle is given in fig. 3.3 respectively. The readings were high for the initial 2-3 days after which they reach a lower value, which remained more or less constant until the desiccators were opened

for the next cycle. This behaviour could be due to the absorption of VOC pollutants by the preconditioned silica gel in the beginning days of the cycle. In case of P, the curve followed a logarithmic function until the first 10 days after which it became asymptotic showing that the concentration of the acid in gas phase took about 5 to 6 days to reach to attain equilibrium in the closed environment after which it remained more or less static. This curve with a negative slope showed that the gaseous concentration of acetic acid the desiccator reduces with time as the preconditioned silica gel absorbed the VOC until an equilibrium was reached inside the desiccator (Fig. 3.3). However, in case of PV, with 35% RH, it seemed to take longer for the VOCs to be homogeneously dispersed in the desiccator while for 70% RH, the trend was similar to that of P. Excluding the beginning 2/3 points in the PV 35% RH curve, all the VOC concentration curves of P and PV showed a logarithmic fit (Fig. 3). As could be observed, the values were not repeatable given the surface area of preconditioned silica gel available for absorption of VOCs and the unreliability of the PID measurements in extreme RH conditions as mentioned in section 2.5.

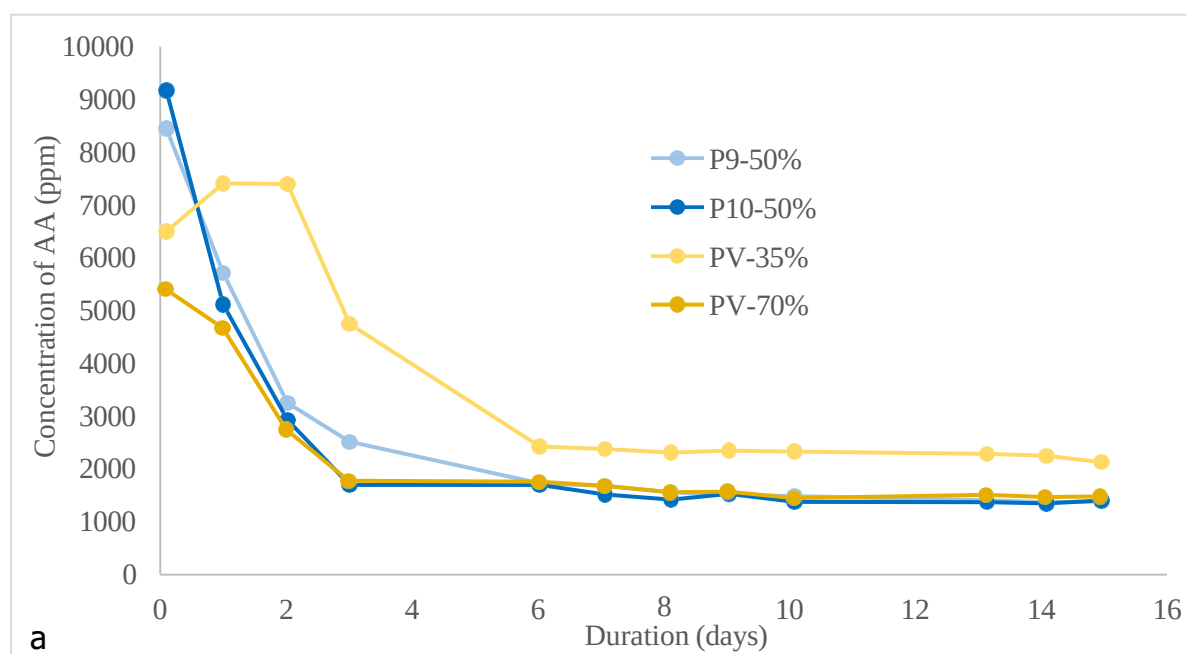


Fig. 3.3: PID readings for acetic acid concentration (ppm) for aging cycle 9 and 10 (6 Oct – 21 Oct; 21 Oct – 5 Nov 2020) for aging condition a) P at 50 % RH and room temperature (blue) and b) PV at 35% RH and room temperature (orange)

An average of the readings was taken for each cycle of parallel running empty desiccators to calculate the VOC concentration generated in the desiccator. The average concentration for all the aging cycles of P and PV with preconditioned silica gel as RH material is shown in figure 3.4. The average VOC concentrations were 4076 ± 776 and 2824 ± 501 ppm respectively for P and PV, indicating that the average VOC concentration was higher in P than in PV.

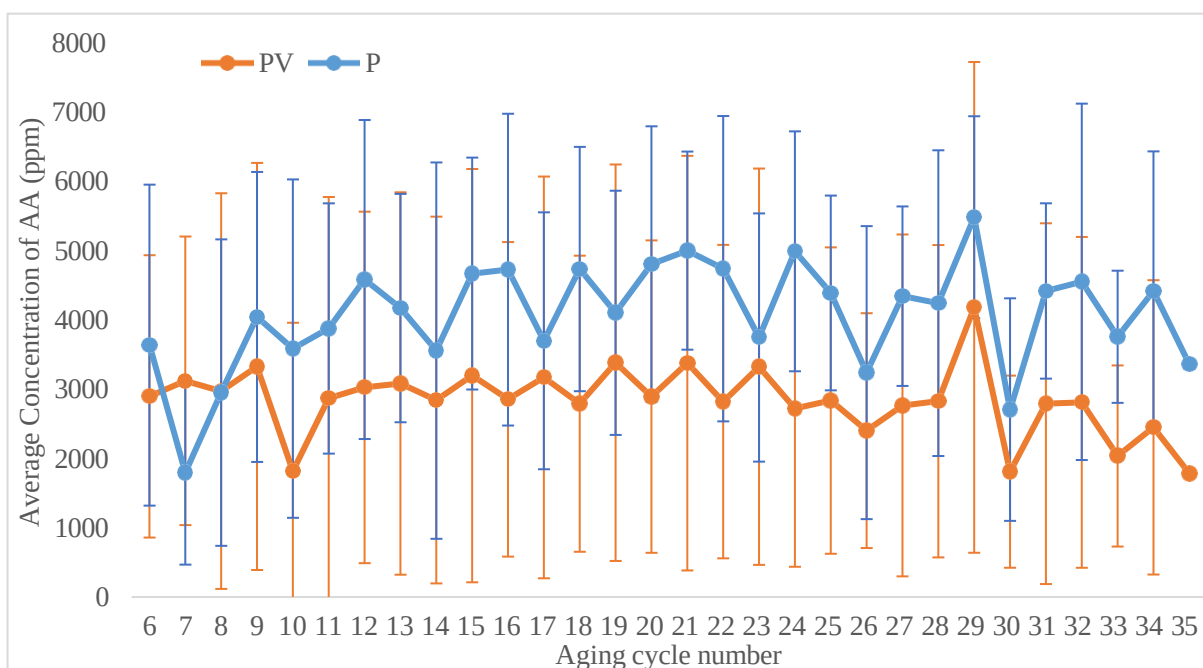


Fig. 3.4: Average VOC concentration in empty desiccator at different running cycles with preconditioned silica gel for P (fixed 50% RH) (blue) and PV (alternating 75%-35% RH) (orange) condition with error bars showing standard deviation.

After the first withdrawal after 3 months, Raman analyses identified acetates and formates on the V model-glass, indicating the presence of pollutants in the aging setup. Thereafter, pollutant concentration inside the V aging desiccator was measured regularly with PID, which recorded a maximum concentration of 15 ppm acetic acid. These pollutants were most probably released from the preconditioned silica gel used for controlling the RH which was later confirmed with further analyses (Annex I).

Towards the end of the aging experiments, passive sampling was performed for 8 hours in an empty desiccator using 50% preconditioned silica gel and 100 times less VOC pollutants as compared to the original aging experiment setup, to keep the concentration measurable within the provided passive sampler which could only measure values between 200 and 20000 $\mu\text{g}/\text{m}^3$. This experiment was also monitored using PID to compare the results for acetic acid (Table 3.4).

Table 3.4: Comparison of VOC (acetic acid) measurement results from PID and passive sampling, as well as formic acid measurements obtained by passive sampling

VOC	Passive sampler ($\mu\text{g}/\text{m}^3$)	PID (average of readings over 8 hours) ($\mu\text{g}/\text{m}^3$)
acetic acid (P)	6600	34800 ± 350
formic acid (P)	3100	-
acetic acid (PV)	<2900	18669 ± 2707
Formic Acid (PV)	4650	-
Acetic Acid (V)	<3050	21420 ± 1006
Formic Acid (V)	<2450	-

As can be seen from the results, no correspondence was found between the PID readings and the passive sampler result. However, given that the PID readings were in a similar range for all the aging cycles, the readings seemed to be consistent among themselves and therefore, if inaccurate, would be caused by a systemic instrument error of the PID. At this point in the research, this could not be verified.

Although not much could be discerned from the passive sampler results, it was evident that VOC and RH measurements in extreme environments created for this research were not easy to obtain reliably. The final verdict on the accuracy of the results obtained from the two methods present a whole new topic of research which could lead to the evaluation of PID as a suitable monitoring device. Such uncertainty in case of aging experiments could only be alleviated by using expensive climate chambers with regulated pollutant flow systems. In the present case, it was conjectured that the concentration of VOCs in the P desiccators was the highest among the three conditions.

3.5. Visual changes in corroded glass

This section describes the visual signs of corrosion present on the aged model glass as seen in visible light with naked eyes and other macro imaging techniques such as RGB photography.

Visual inspection of P and PV corroded glass showed wet salt neocrystallizations (SN) on the surface starting from the first withdrawal after 3 months. These SN had an acidic pH of 2. In many cases, some liquid was collected in the grooves of the glass stands most probably indicating a run-off of the liquid SN from the glass surface. Nonetheless, in the case of V corroded glass, one could see a haziness on the surface making the glass surface look duller than the original and no wetness could be seen with naked eyes. Although the SN hide fine cracks under them, some fine and coarse cracks were visible on P and PV model glass after wiping the surface. Such cracks were not present in any of the V model glass.

In case of the model glass dried after 17 months of aging, only the P and PV model showed coarse cracking network with more intense cracking along two vertical lines while there was no cracking discernible on the V model glass.

Digital photography with transmitted light (TL) passing through a white background didn't provide a very clear image of the model glasses and the exposure time (shutter speed) should be reduced to be able to capture details such as engravings (Annex II). Additionally, the engravings were much less visible on corroded model glass (Fig. 3.5a and b), most probably hidden beneath a liquid film. However coarse cracks could be visualized on model glass aged for 17 months even in TL (Fig. 3.5c).

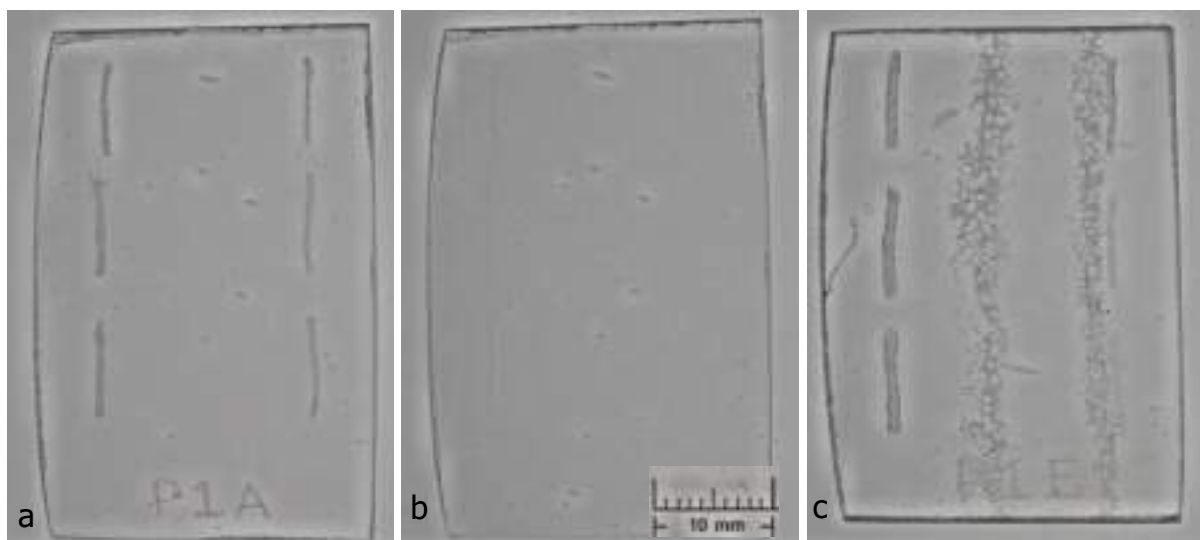


Fig. 3.5: Photographs of P model glasses acquired in transmitted light: a) unaged b) aged for 3 months c) aged for 17 months and dried

Photos acquired in TCPL showed that no global strain had developed until 17 months of aging for any of the model glass P, PV or V (Annex III). Nonetheless, the use of TCPL showed a real improvement compared with TL, as the resulting black background showed clearly discernible dust particles on the glass surface and bubbles (Fig. 3.6). In certain cases, some darker circular features were also visible. In the present example, they can be noticed at the top of the samples inside the yellow rectangle (Fig. 3.6a). TCPL photographs could show both fine and coarse cracks clearly when not covered by liquid SN (Fig 3.6b).

A comparison of P, PV and V photographs after 17 months aging showed circular wet SN on P and PV glass (indicated by white lines in Fig. 3.7) and haziness on V glass. This was the case for model glass from all the withdrawal periods (Fig. 3.9).

The corroded model glass surface was best visualized using RL photography done with intense torch lights rather than diffused light but only in specific areas of the surface at grazing angles. P and PV distinctly showed SN (Fig 3.8a and b) while V surface shows a haziness (Fig 3.8c). RL photography with diffused studio lights on black background could not show any features (Annex IV).

In summary, photography showed whatever was visible to the naked eyes and TCPL photography was found to be the best for transparent colourless glass. The P and PV model glass displayed wet SN on the whole surface due to which any cracks underneath were not visible (Fig. 3.9). Nonetheless, a few coarse cracks with delamination were visible on model glass aged for 17 months intense along one vertical line on the right side (inside yellow rectangle in Fig. 3.9e).

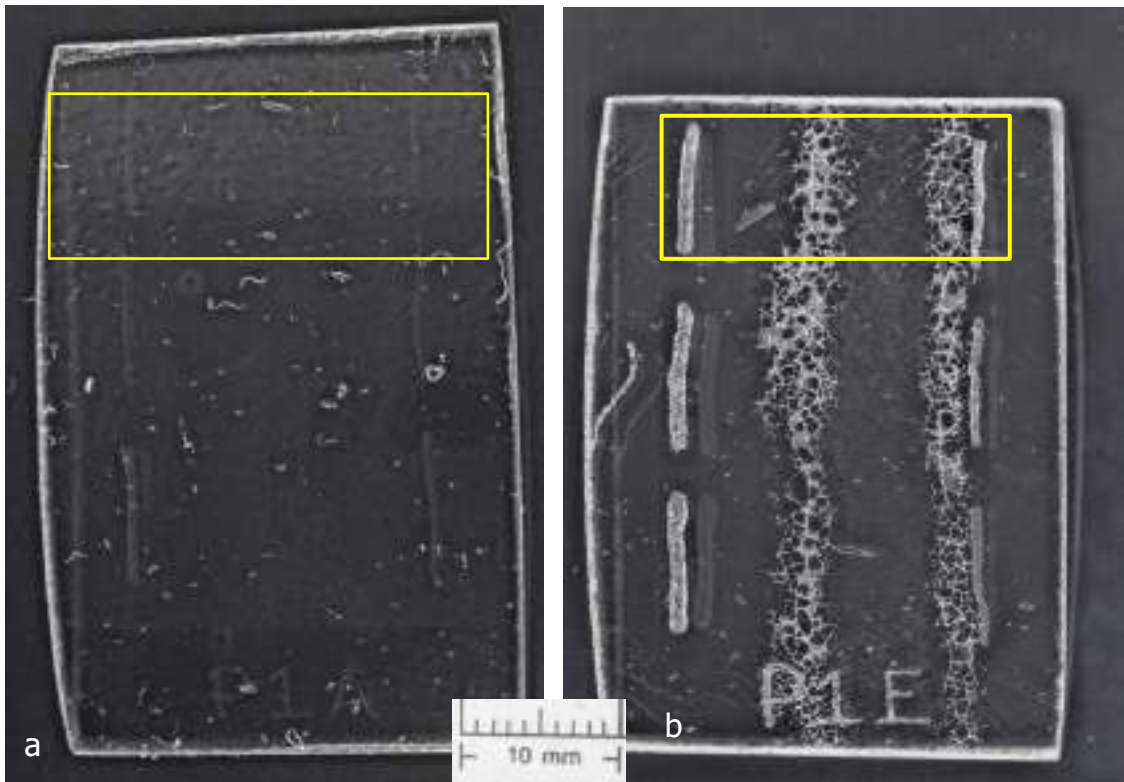


Fig. 3.6: TCPL photographs of P model glass aged for a) 3 months and b) 17 months

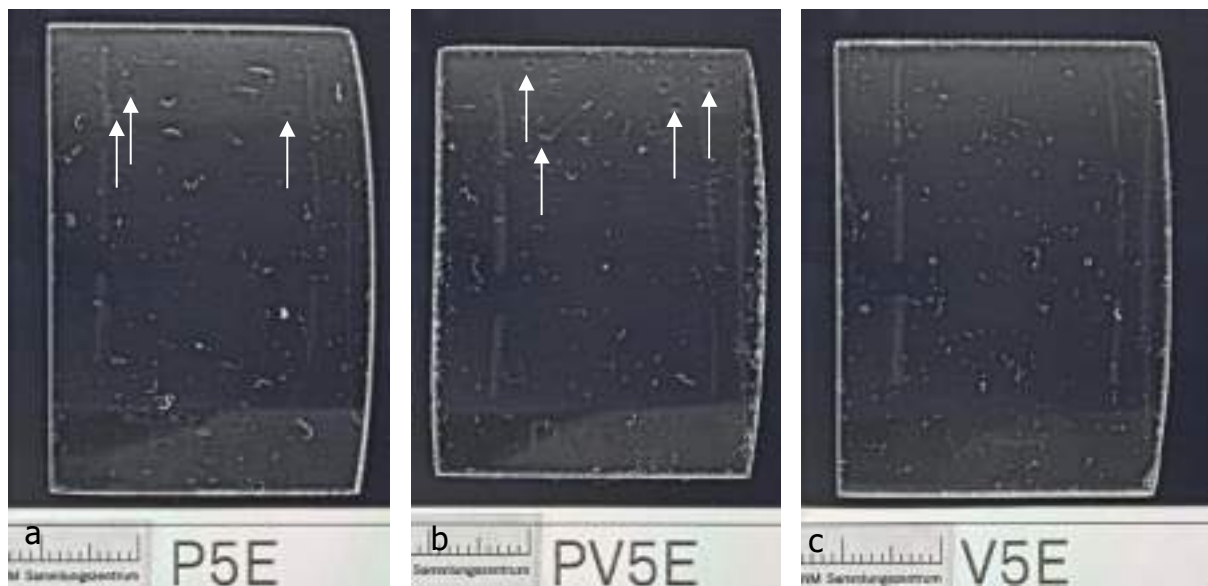


Fig. 3.7: TCPL photographs of model glass aged for 17 months from aging condition a) P b) PV and c) V. Circular wet SN indicated by white arrows

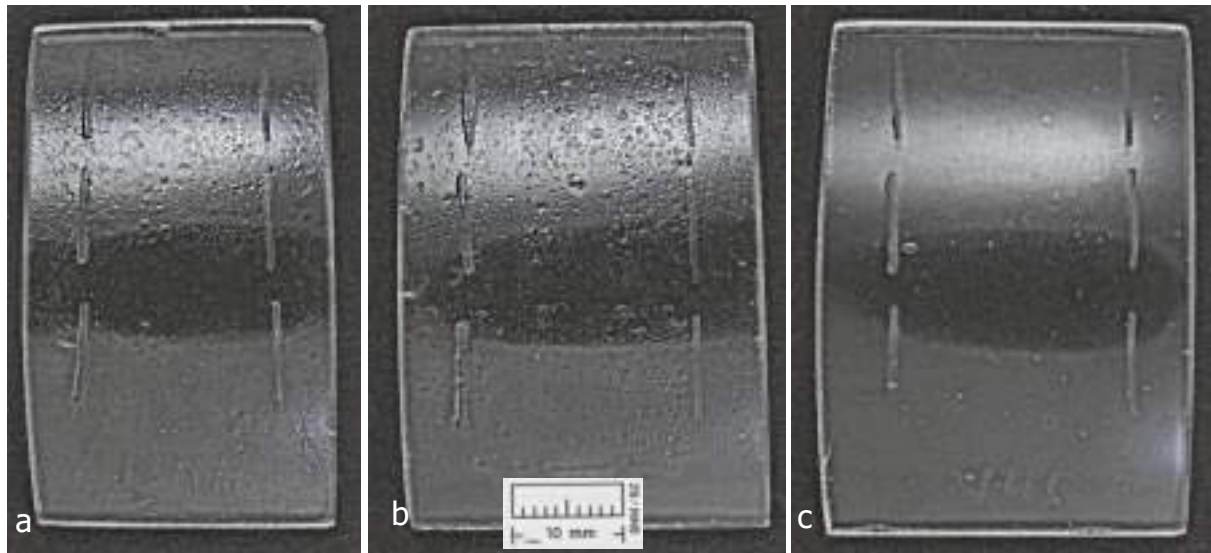


Fig. 3.8: RL photographs of model glass aged for 9 months from aging condition a) P b) PV and c) V



Fig 3.9: TCPL images of P model glass aged for a) 3 b) 6 c) 9 d) 12 and e) 17 months, PV model glass aged for f) 3 g) 6 h) 9 i) 12 and j) 17 months and V model glass aged for k) 3 l) 6 m) 9 n) 12 and o) 17 months

Hyperspectral images acquired at a distance of 30 cm from the camera to the glass also offered a good visualization of the whole sample in both SWIR and VNIR range (Fig. 3.12) showing the visual changes in corroded glass. While the HSI acquired at a closer distance (3 cm) could only document part of the model glass in SWIR ($\approx 5 \times 2$ cm) (Fig. 3.12a) and the whole sample for VNIR (Fig. 3.10). Nonetheless, VNIR images showed features, also visible, with naked eyes such as cracks, engravings, labels, bubbles, and dust particles. The darker areas showing partial delamination with wet SNs trapped under the scales could be seen along two vertical lines in case of the 17 months aged model glass (Fig. 3.10a) while in case of the dried one, a narrow region of more intense coarse cracks could be observed bound by two vertical lines on the right side (Fig. 3.10b). This evidently showed that the corrosion was more severe along these vertical lines running along the sample.

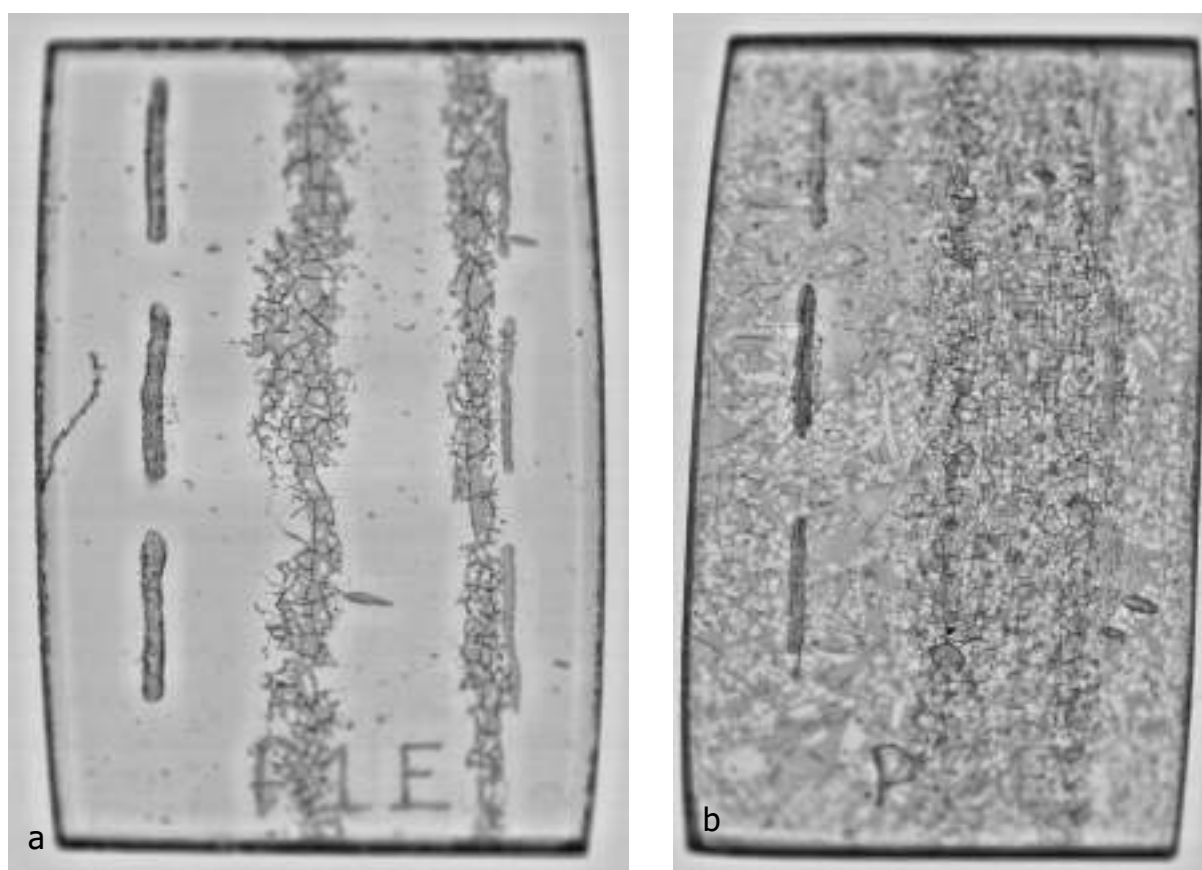


Fig. 3.10 Hyperspectral image of P model glass sample at 700 nm (VNIR) taken using 3 cm lens and aged for a) 17 months and b) 17 months and dried (Field of view: $\approx 5 \text{ cm} \times 3 \text{ cm}$)

HSI data however provided visual and chemical changes for the model glass simultaneously, providing both spatial and spectral data for every acquisition point. Therefore, it will be discussed in further detail under chemical changes.

3.6. Quantification and characterization of visual signs of corrosion

Various features were identified on corroded model glass surface to attempt quantification and subsequent characterization such as SN, microcracks and delamination. In order to facilitate the visualization of fine microcracks which could not be discerned easily under the wet SN, one of the two model glass used for imaging was wiped in the centre using soft tissue and mixture of ethanol and water.

3.6.1. Wet salt neocrystallizations

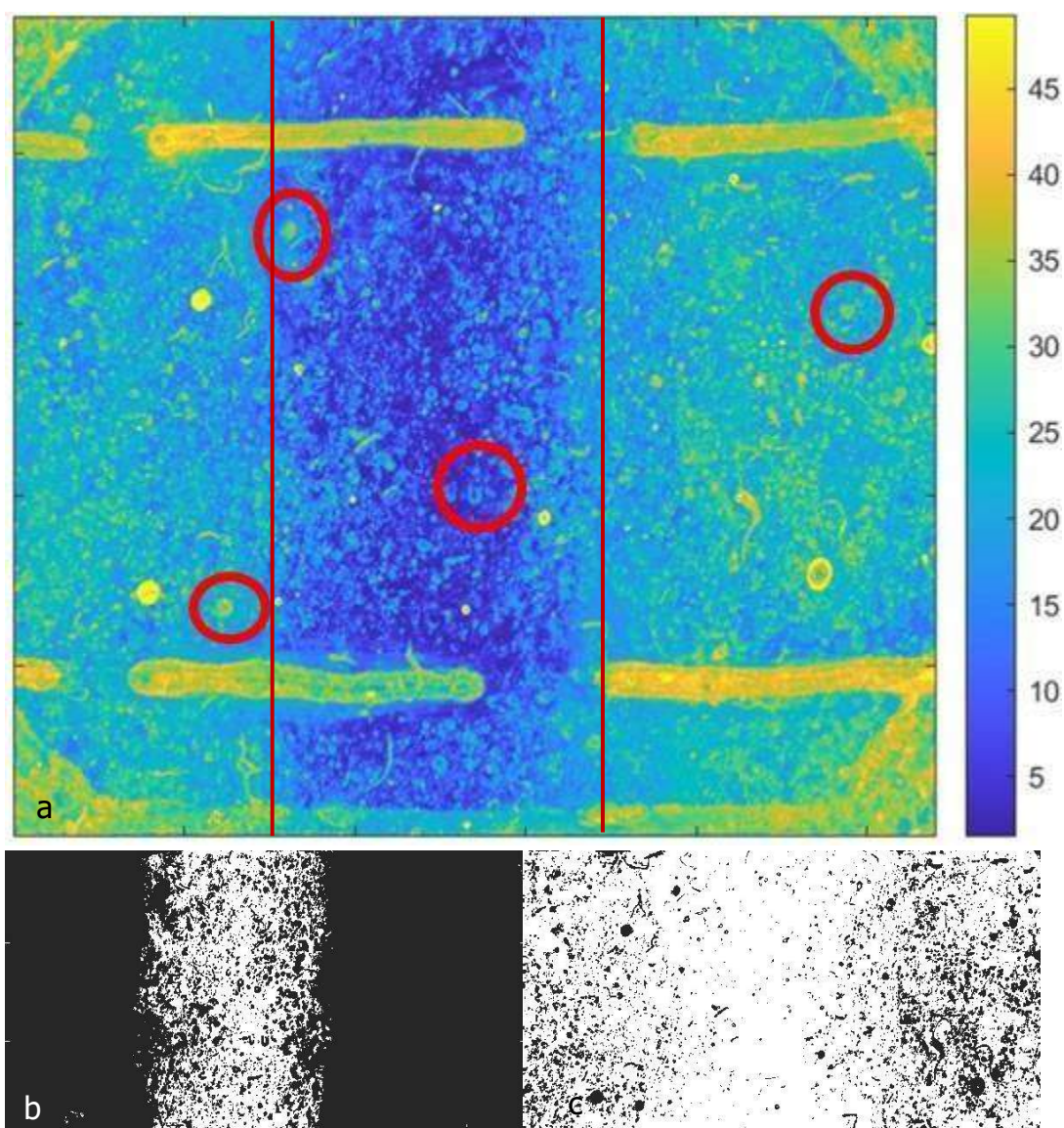


Fig. 3.11: a) RTI standard deviation map in LDR configuration for P model glass aged for 9 months (unwiped) showing wet SN (examples inside red circles); b) central region c) peripheral region of the map after thresholding (Field of view: $24 \times 21 \text{ mm}^2$)

Given that RL photography successfully showed SN and cracks in different types of lights and their positions, further visualization of corrosion features and their quantification was attempted with RTI acquisitions. The statistical descriptor map of standard deviation using LDR

configuration was used for SN quantification (examples seen in blue-green and yellow colour inside red circles in fig 3.11a) (Annex V) by colour thresholding on the maps acquired from 1 unwiped model glass each from every withdrawal of P and PV (unwiped samples). Due to the difference in the background colour of the central part as compared to the rest of the map, the colour thresholding could not be done together for the whole sample for quantification of SN (Fig. 3.11a) but was divided into two regions (Fig. 3.11b and c). Furthermore, the air bubbles in the glass disturbed the results.

The SWIR images from 3 cm lens produced a better-resolved image with more clarity (Fig. 3.12a) in comparison to the more pixelated image from 30 cm lens (Fig. 3.12b), especially for visualizing SN which can be seen as the dark grey circular or elliptical features in the SWIR images at 1910 nm indicating molecular water and OH⁻ species (some examples are shown inside red circles in fig 3.12) (Annex VI). Since the dark features in HSI images indicated not only SN on surface but also molecular water and OH⁻ present in the corroded glass matrix, they could not be used for quantification of SN with greyscale thresholding.

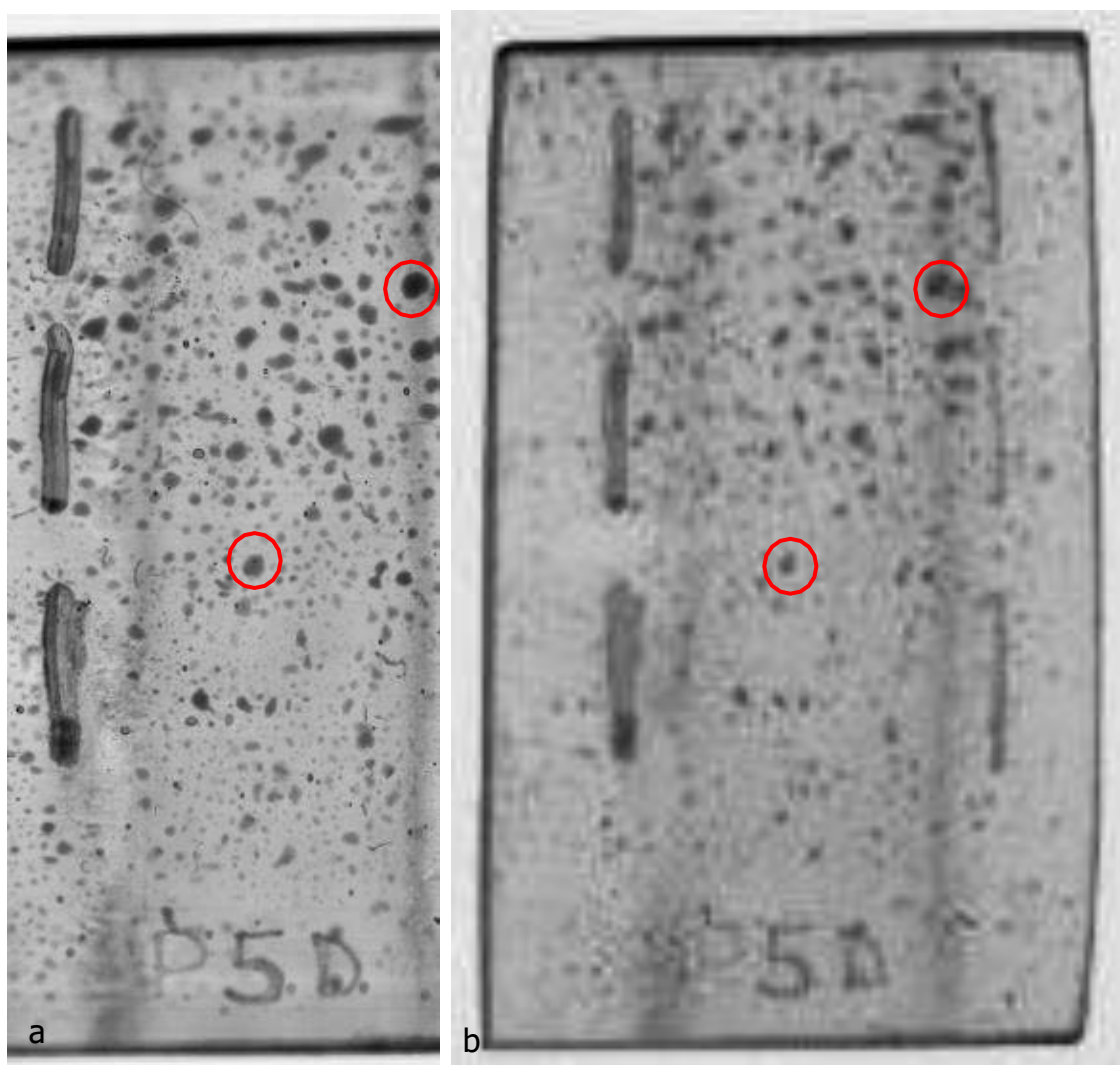


Fig. 3.12 Hyperspectral image of P model glass sample aged for 12 months at 1906 nm (SWIR) with a) 3 cm ($\approx 5 \text{ cm} \times 2 \text{ cm}$) and b) 30 cm lens ($\approx 5 \text{ cm} \times 3 \text{ cm}$)

The most detailed analyses on SN quantification were performed using DM. Five model glass from each withdrawal period and aging condition were imaged with digital microscope using RL and TL. SNs could be clearly seen in the digital microscopy images with RL as shiny circular, elliptical or irregular features (Fig. 3.13) in all the P, PV and V model glasses. While SN on P and PV were large enough to be seen with naked eyes, photography, RTI and HSI, the SN on V seen by DM could not be visualized by these macro imaging techniques. The size of these SN was very small and therefore, only appeared as a haziness on the surface of V model glass. Apart from this, it is evident that the SN sizes and distribution was not homogenous over the entire model glass for P and PV with usually smaller sized SN on the two sides and the larger sized SN in the central part of the model glass for (for example Fig. 3.13a and 3.14a).

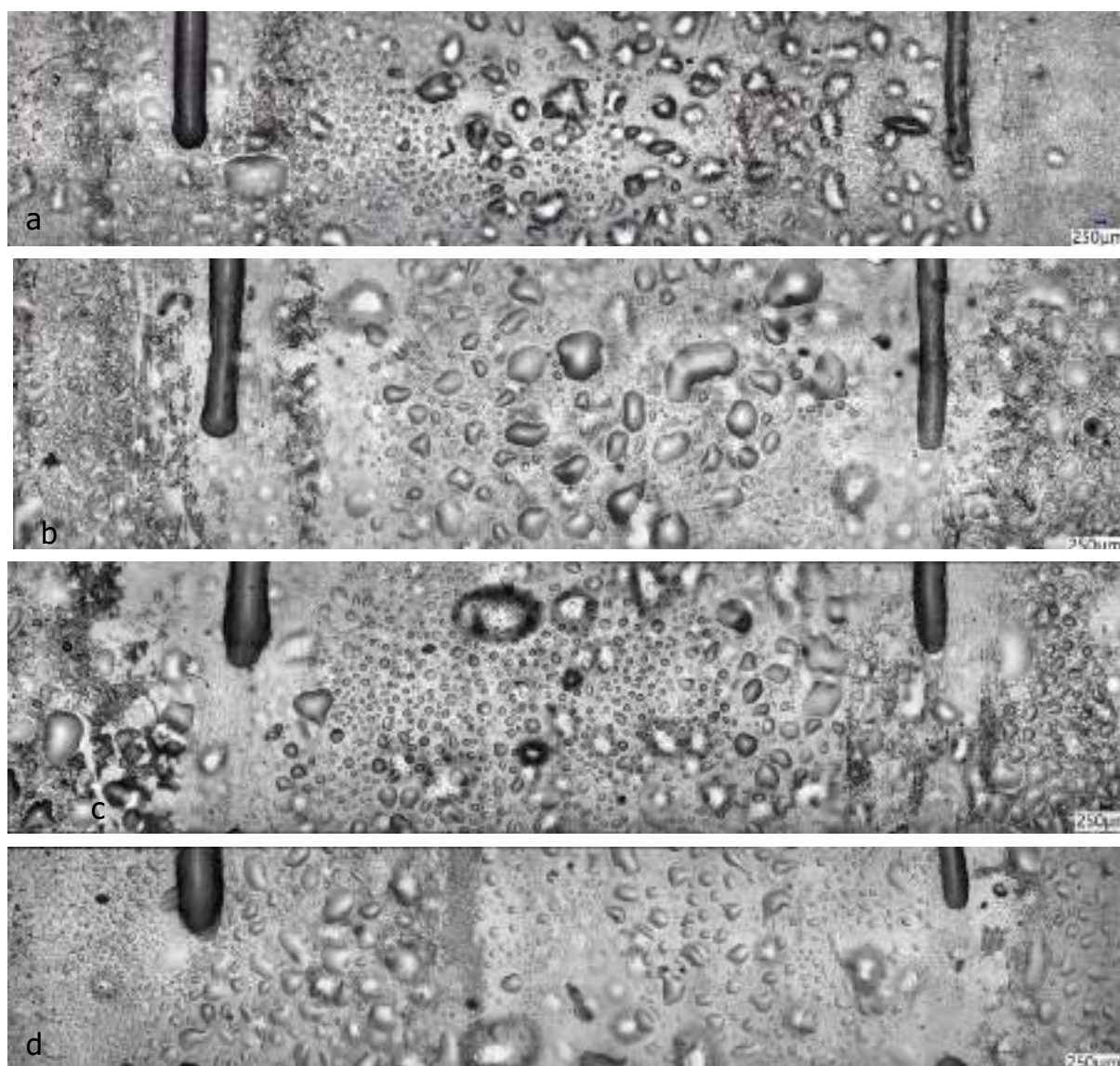


Fig 3.13: DM photomicrographs at original magnification 100× for P model glass aged for a) 3 b) 6 c) 9 and d) 12 months

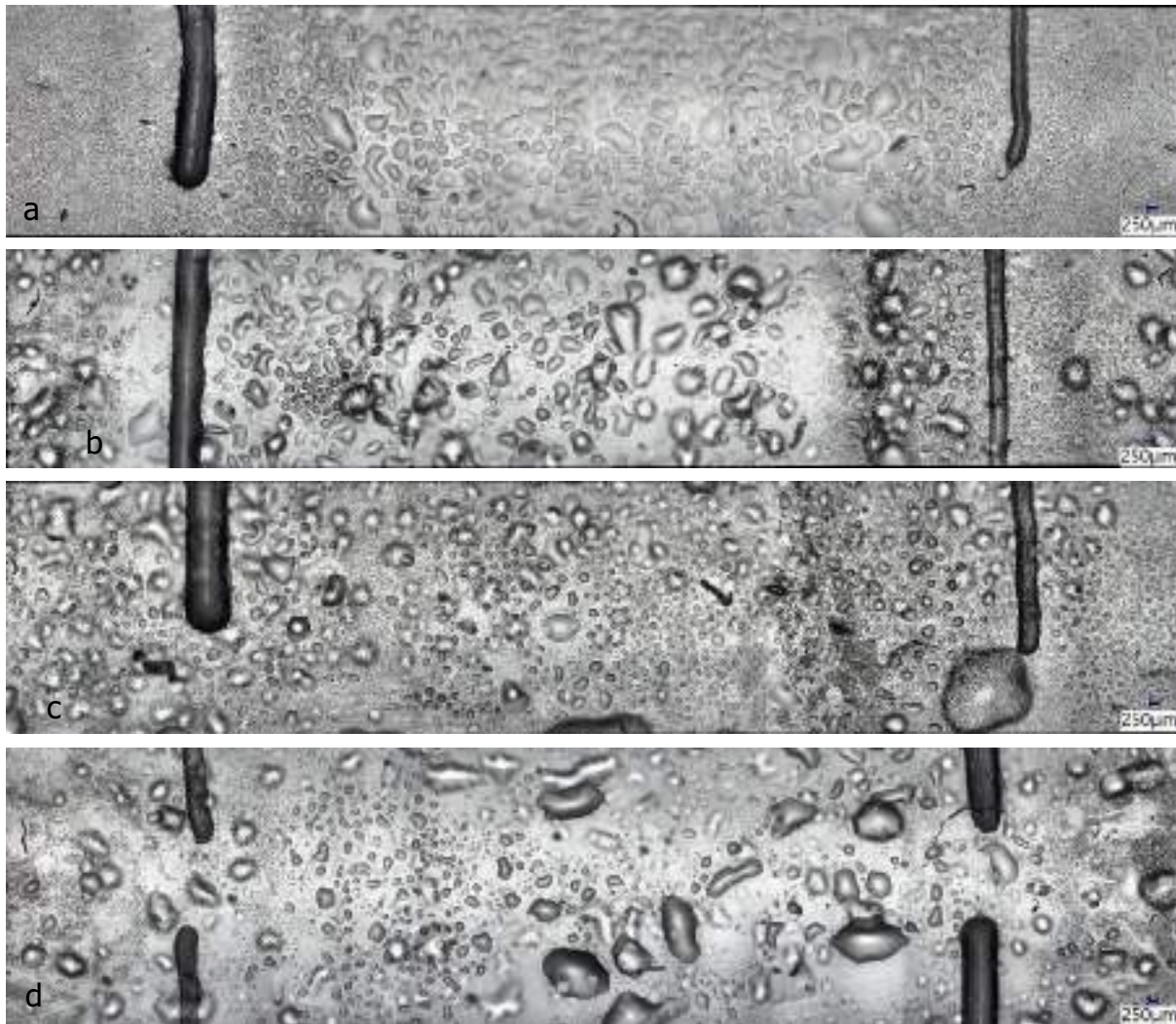


Fig 3.14: DM photomicrographs at original magnification 100× for PV model glass aged for a) 3 b) 6 c) 9 and d) 12 months

However, in case of V model glass, the SN sizes were much smaller but more homogenous over the entire surface showing wet SN (Fig. 3.15). They also seemed to be increasing in size with aging period.

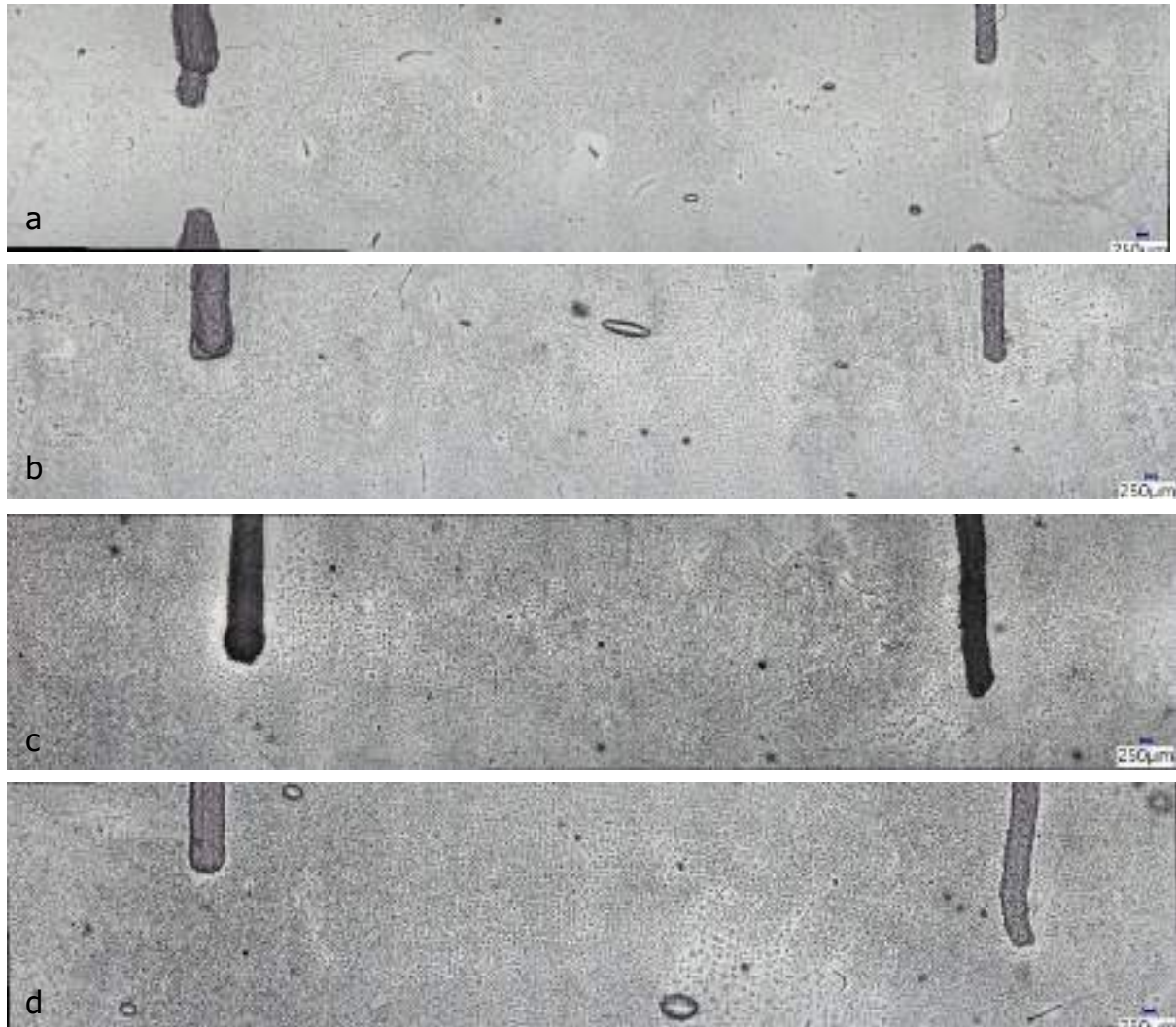


Fig 3.15: DM photomicrographs at original magnification 100× for V model glass aged for a) 3 b) 6 c) 9 and d) 12 months

A typical frequency distribution of the number of SN with a specific range of area in μm^2 is shown for P model glass aged for three months (Table 3.5) showing the heterogeneity in the sizes of SN and the maximum area of SN for each model glass aged for different period.

From the table 3.6, it is evident that the SN sizes in V model glass were much smaller than P and PV. However, there is not much difference in the most commonly occurring SN sizes among the different aging periods in V as well as PV model glass. Nonetheless, the P model glass show an initial increase in SN sizes until 12 months of aging after which there was a significant drop for 17 months aged model glass, indicating the reduction in sizes due to run-off of large enough SN.

Table 3.5: Frequency distribution of SN sizes in μm^2 for P model glass aged for 3 months.

Area (μm^2)	50	100	150	200	250	300	350	400	450	500	550	600	650	700	750	800	850
Frequency	103013	117	65	36	19	20	8	8	9	9	5	1	0	1	1	1	1

Table 3.6: Table showing the SN range of area (in μm^2) with the highest frequency along with approximate largest area for the three different aging conditions and five different aging periods

	3m	6m	9m	12m	17m
P	0-50, 850	0-100, 1400	0-100, 1400	0-150, 1350	0-50, 650
PV	0-100, 1400	0-100, 1000	0-100, 1200	0-100, 1500	0-100, 1400
V	0-20, 280	0-20, 360	0-20, 240	0-20, 150	0-20, 100

DM data was selected for further comparison since stray reflections and shadows due to bubbles could be removed by manual intervention (Annex VII), unlike in the case of RTI (Annex V). Such stray reflections could greatly affect the accuracy of quantification since they produced circular shadows similar to the wet SN.

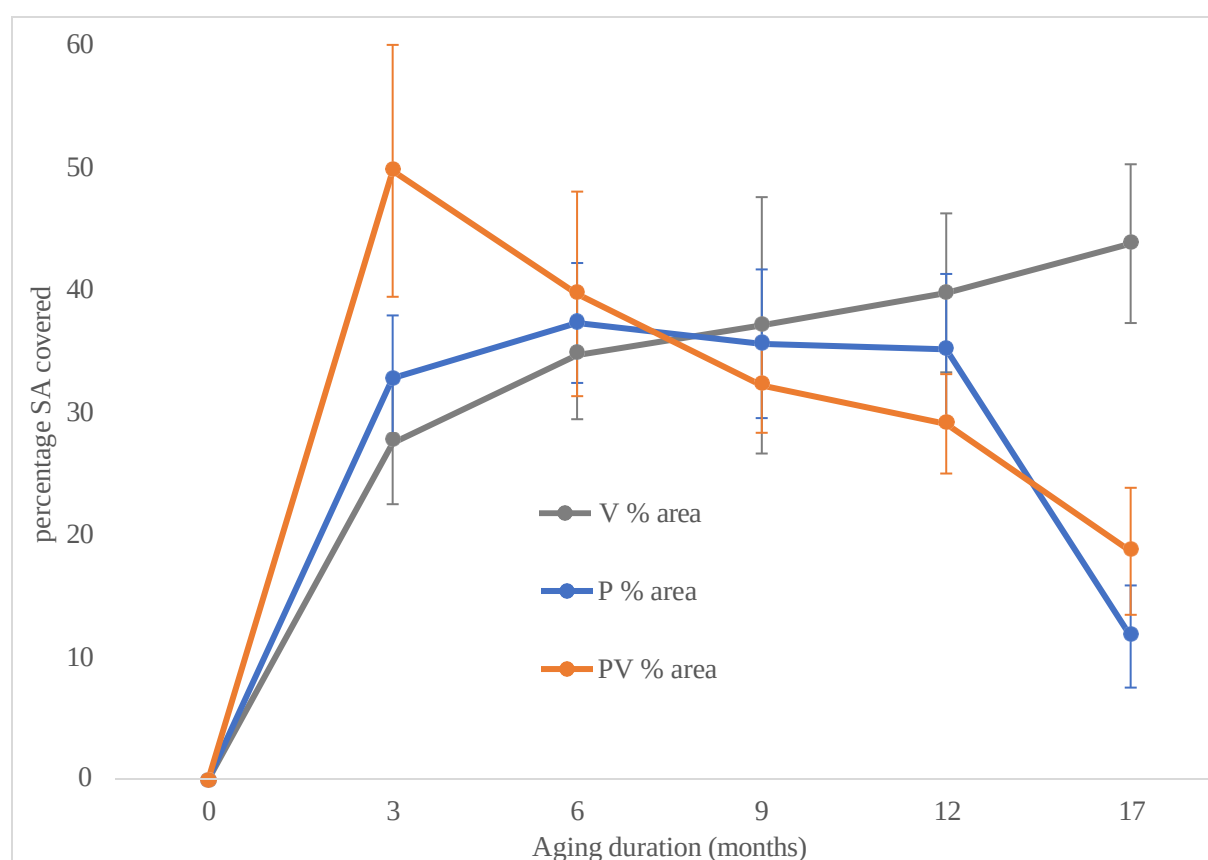


Fig. 3.16: Temporal progression of percentage surface area covered by SN for P (blue), PV (orange) and V (grey) model glass calculated from digital photomicrographs with error bars showing standard deviation

The DM results showed a huge variation in the SN number and percentage surface area covered by SN on every corroded model glass surface. For P model glass, the percentage surface area covered by SN did not show any changes during the first 12 months of aging (Fig. 3.16, blue) while the number of SN reduces after six months of aging (Table 3.7) indicating coalescence of the SNs together forming less but larger droplets. Both values drop greatly

after 17 months of aging showing the possible run off of bigger SN droplets down the model glass samples after reaching a certain dimension starting only after 12 months of aging.

In case of PV model glass, the percentage surface area covered by SN showed a decreasing trend throughout the aging periods possible due to continuous surface run off of bigger SN droplets down the model glass samples after reaching a certain dimension (Fig. 3.16, orange). The number of SN reduced after three months of aging and then showed an increasing trend afterwards, indicating continuous formation of newer SN (Table 3.7).

V model glass showed an increasing trend for percentage surface area covered by SN throughout the aging period (Fig. 3.16, grey) while the number of SN showed a decreasing trend throughout indicating coalescence of the smaller droplets to form bigger ones (Table 3.6). The size of SN on V did not grow to an extent where the surface tension would not be able to hold the SN droplets and therefore did not show any run off from the surface until 17 months of aging. When comparing the values of the three aging conditions, it is clear that the number of SN developed on V were much higher than in P or PV (Table 3.7).

Table 3.7: Temporal progression of number of SN in P, PV and V model glass calculated from digital photomicrographs along with standard deviation for 15 to 30 different areas (5mm x 5mm) from 5 model glass from each aging batch

Aging duration	3 months	6 months	9 months	12 months	17 months
P	2363	2816	1272	1586	1331
σ	1040	1852	287	1823	768
V	37747	17767	17512	14435	12584
σ	13868	4888	5455	3310	4984
PV	2539	1718	3139	3880	5755
σ	1697	1445	1595	2474	2857

3.6.2. Microcracks

Quantification of fine cracks was achieved from RTI (Shannon) entropy maps created using HDR configuration from one wiped sample for each aging batch and DM images from five model glass for each aging batch (no wiping of the sample was required). These were the only two imaging techniques, which allowed the visualization of fine cracks with a good contrast against the background. It was not possible to automatically extract fine cracks using thresholding on the model glass surfaces, which were covered with SN (Fig. 3.17a). Therefore, the cracks were traced manually over every sample's area of 5 mm $\times$ 5 mm for DM (Fig. 3.17b) (Annex VII) and over the map for RTI (Fig. 3.17c and d) (Annex VIII) and finally the total length of all the cracks present in all the sample areas from one aging batch were summed up and divided by the total area of the images analysed to calculate the crack density in mm⁻¹.

Fine cracks were observed on both P and PV model glass starting from 3 months of aging. In case of V model glass, cracks were not observed even after 17 months of aging indicating that the VOC concentration affected the formation of cracks on the corroded glass surface. The comparison of crack density calculated from both the modalities (DM and RTI) showed comparable results and the fine crack density showed a tendency towards increase as the aging period increased. (Fig. 3.17e).

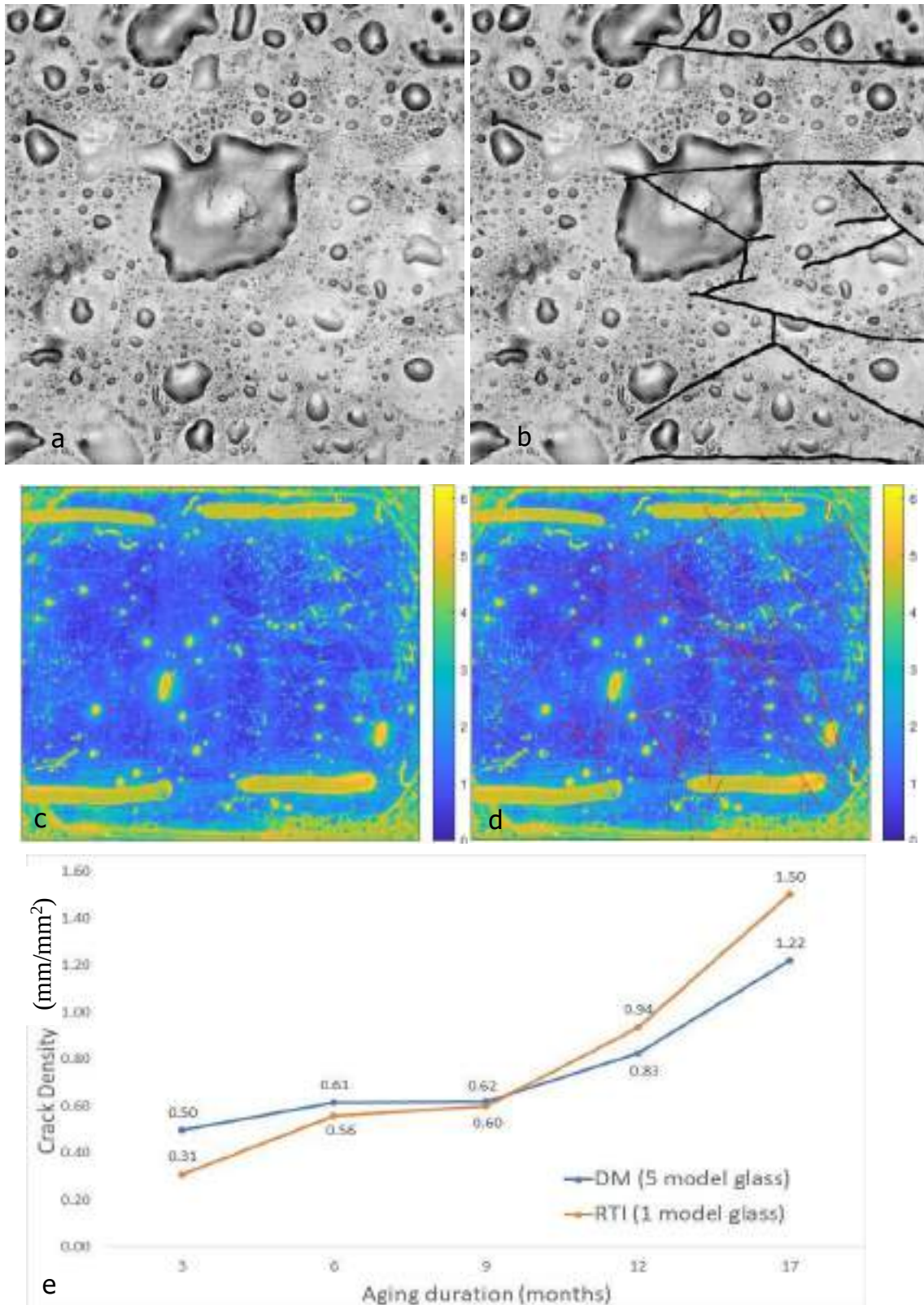


Fig. 3.17 a) Photomicrograph of size extracted from DM image of P model glass aged for 9 months b) photomicrograph after thresholding showing the impossibility to isolate the cracks (Field of view: 5 mm x 5mm) c) Image showing manual tracing of cracks from the photomicrograph d) (Shannon) entropy map of model glass aged for 9 months along with e) the manual tracing of cracks (Field of view: 24 × 21 mm²) f) Graph showing temporal progression of crack density for P model glass calculated from RTI (orange) and DM (blue) data [3]

Fine cracks were only seen on P and PV model glass and not on V model glass. Even though the results from RTI and DM were in accordance with each other, DM data had larger number of samples analysed and therefore was used for comparison of cracking in P and PV model glass. The graph showed that the cracks density was higher for P than PV for every aging period and was increasing with aging period for both the conditions (Fig. 3.18).

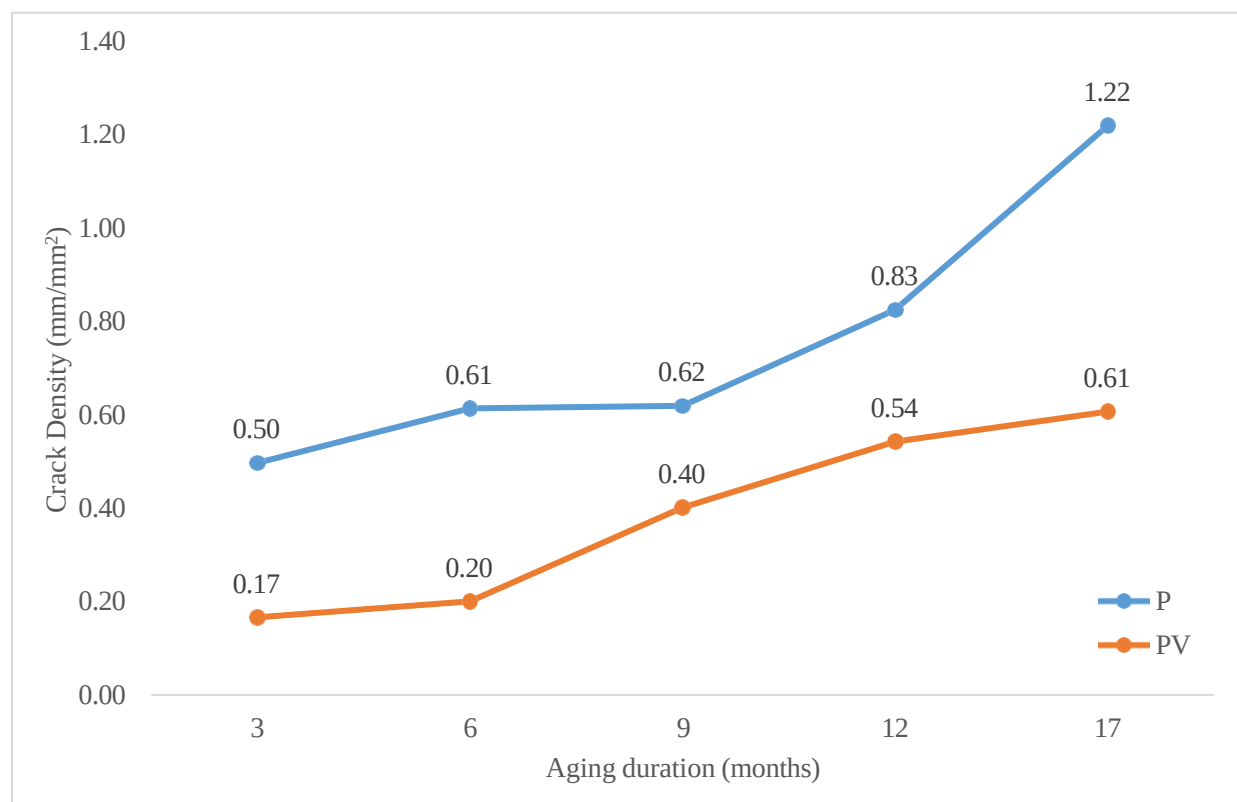


Fig. 3.18 Temporal progression of crack density for P and PV model glass calculated using DM images

3.6.3. Partial delamination

Partial delamination was seen on the P and PV model glass aged for 17 months and dried, which showed a lot of whitish grey partially delaminated flakes on the glass surface (Fig. 3.19). The coarse crack network was widely spread with more intense delamination along two vertical lines (inside yellow rectangles in Fig. 3.19a). The V model glass did not show any cracking.

The delaminated area was compared for both P and PV using greyscale thresholding to find out which aging condition produced more severe delamination after drying. The data was quantified using RL photographs on black background. Three dried model glass from each P and PV were analysed for the delaminated part on the surface using an area of 19 mm × 40 mm in the centre, excluding the engravings (yellow rectangle in fig. 3.20a). The images were thresholded to quantify the delaminated area shown in black colour in figure 3.20c and d. As was already visible from the images, P model glass showed much higher extent of partial delamination than PV model glass (Fig 3.20a and b, Table 3.8).

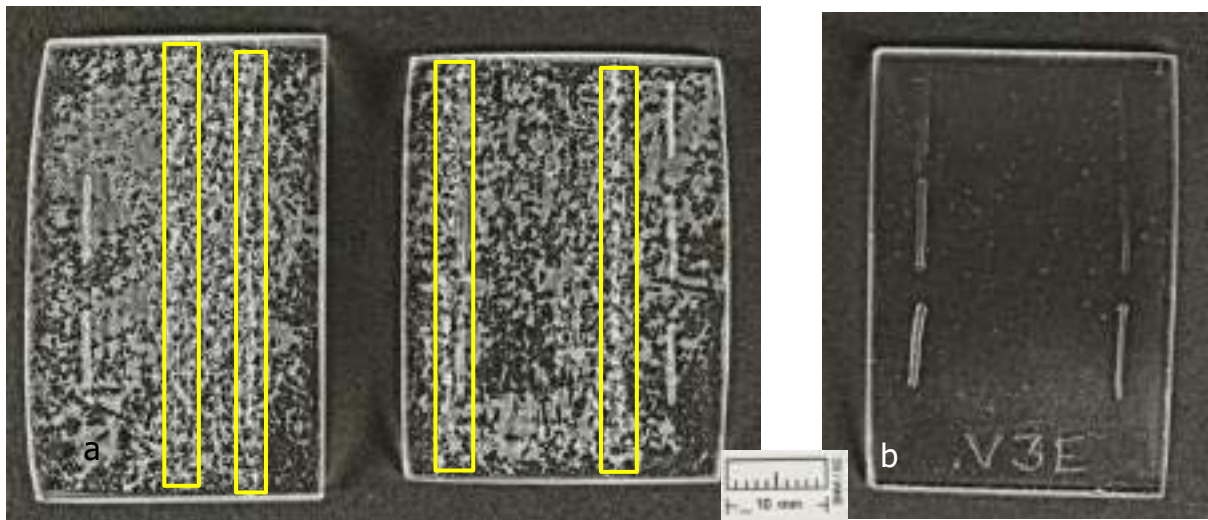


Fig. 3.19: RL image of model glass aged for 17 months and dried for 15 minutes a) P and b) V conditions

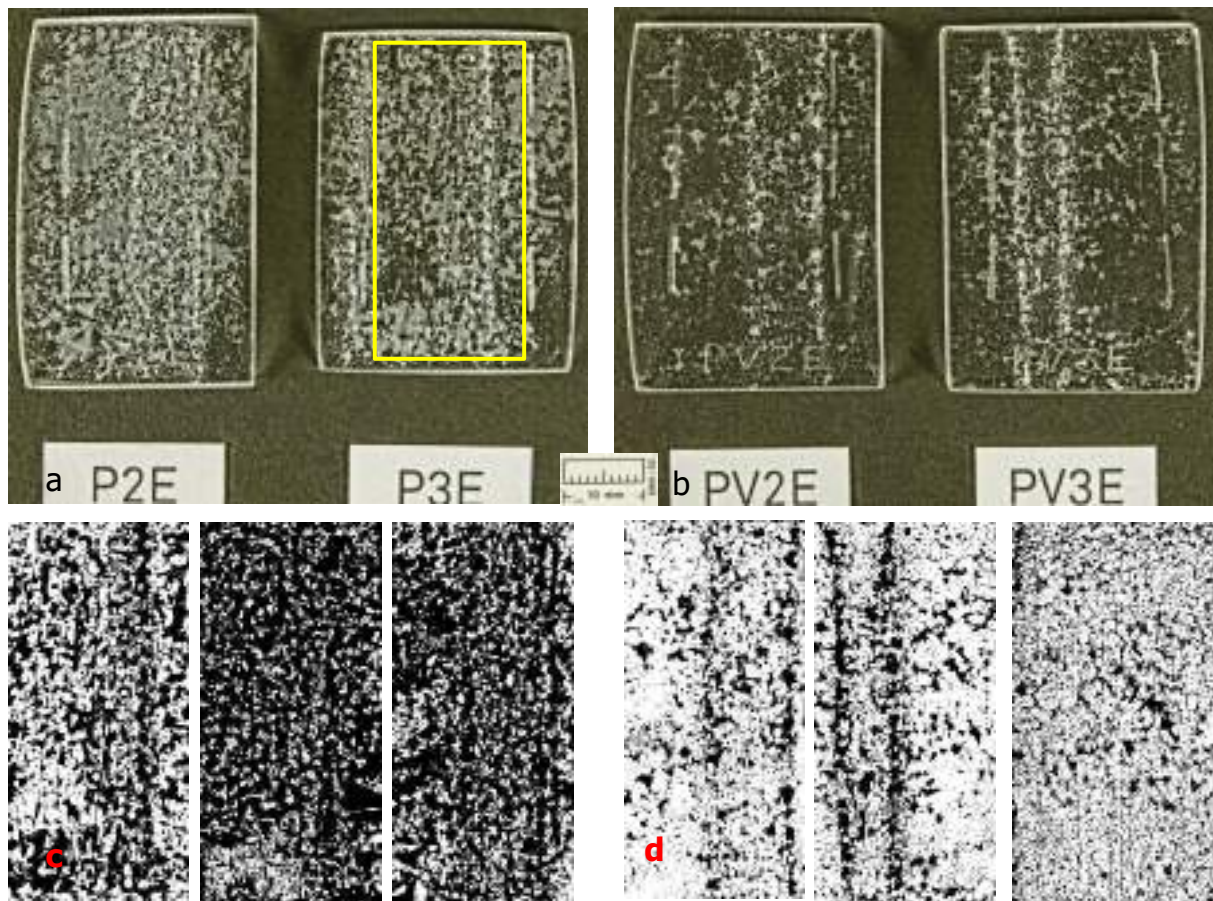


Fig. 3.20: RL light photographs of model glass aged for 17 months and dried for 15 minutes from aging condition a) P b) PV showing thresholded delamination area for three model glasses from c) P and d) PV conditions (Field of view: $\approx 5 \text{ cm} \times 2 \text{ cm}$)

Table 3.8: Quantification for partial delamination using RL images

Sample	P (percentage)	PV (percentage)
area partially delaminated from RL RGB images	64.21 ± 12.49	28.15 ± 2.94

3.7. Chemical changes in corroded glass

3.7.1. Composition of SN

SN compounds were identified using FTIR and Raman spectroscopies. FTIR spectra showed the presence of formate salts in the band around 1600 cm^{-1} along with possibly formic acid at 1340 and 670 cm^{-1} for P, PV and V model glass (Fig. 3.21). However, due to a broad band between 1400 and 1670 cm^{-1} , it was not possible to differentiate between sodium formates (peak at 1632 cm^{-1}) or potassium formates (peak at 1591 cm^{-1}) as well as adsorbed water (peak at 1630 cm^{-1}). The presence of formic acid on the surface indicated that the high concentration of formic acid might have saturated the desiccator environment due to which formic acid had precipitated on the aging glass surface (Fig. 3.21). This also presumably caused the acidic pH of 2 on the surface of P and PV model glass and maintained an acidic pH on their surface throughout the course of aging.

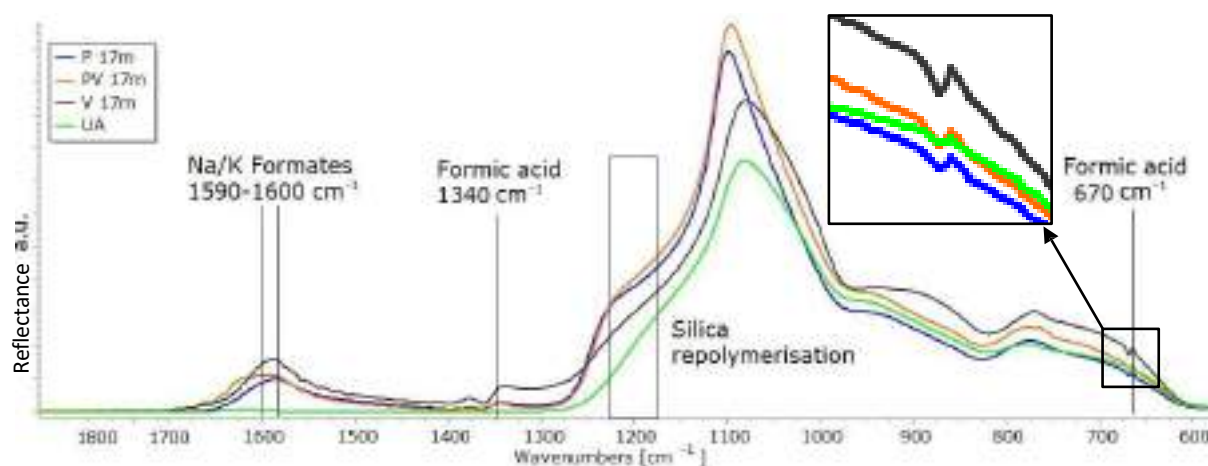


Fig. 3.21: FTIR spectra of P (blue), PV (orange), V (grey) aged for 17 months showing the SN present on the surface. Inset showing formic acid peak at 670 cm^{-1} zoomed in

Raman analyses identified the presence of formate salt neocrystallizations on the surface of all the corroded model glass. The formates present were potassium formate (HCOOK) with major peaks at 764 , 1352 cm^{-1} , and 2814 cm^{-1} [4] and sodium formate (NaHCOO) with major peaks at 1370 cm^{-1} and a band doublet at 2730 cm^{-1} and 2820 cm^{-1} characteristic of NaHCOO (aq) [5] (Fig. 3.22a and b). Apart from this, potassium carbonate (main Raman peak at 1065 cm^{-1}) and potassium/sodium acetate ($\text{CH}_3\text{COOK/Na}$) with major peaks at 926 cm^{-1} , 1412 cm^{-1} , and

2931 cm^{-1} [6] were also identified at fewer points on P and PV model glass (Fig. 3.22b). In case of V, more instances of acetate salts were found than P and PV and no noticeable presence of carbonates (Table 3.9).

Table 3.9: Number of Raman spectra (out of total 60 spectra) from each aging batch showing potassium carbonate and potassium/sodium acetate salts.

	Model Glass P					Model Glass PV					Model Glass V				
Model	3m	6m	9m	12m	17m	3m	6m	9m	12m	17m	3m	6m	9m	12m	17m
K_2CO_3	6	10	5	9	16	10	9	8	11	14	1	-	-	-	-
CH_3COOK	2	3	2	7	-	8	4	3	1	4	16	24	26	17	19

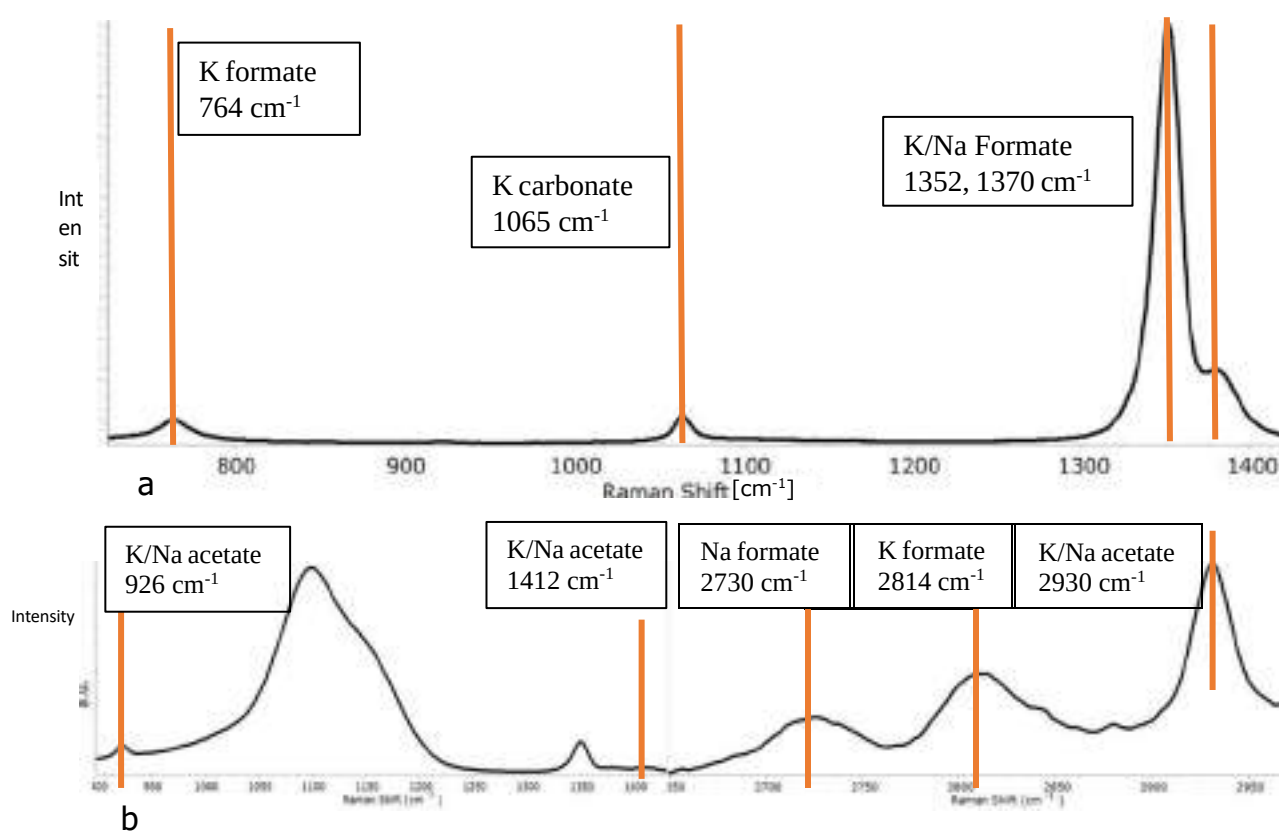


Fig. 3.22: The identification of SN using Raman spectroscopy on P, PV and V model glass showing peaks of a) K/Na Formates and K Carbonate in the 700-1400 cm^{-1} range b) K/Na Formates and acetates in the 900-3000 cm^{-1} range

Apart from this, a single incident of potassium sulphate (981 cm^{-1}) was also found on P model glass.

A single area of 80 μm x 80 μm was mapped on the surface of one model glass from each aging batch for P and PV model glass (yellow rectangle in figure 28a). Raman mapping of the surface (Fig. 3.23b, c and d) showed the spatial distribution of the formates. Potassium formate and sodium formate salts deliquesce at 15% RH and 51% RH, respectively. Since, sodium formate

is present along with potassium formate, their mixture is deliquescent at RH lower than 15% explaining the liquid nature of the SN observed on the corroded model glass surfaces (Fig. 3.23a). Acetate salts were not identified on P and PV model glass, both of which produced similar maps.

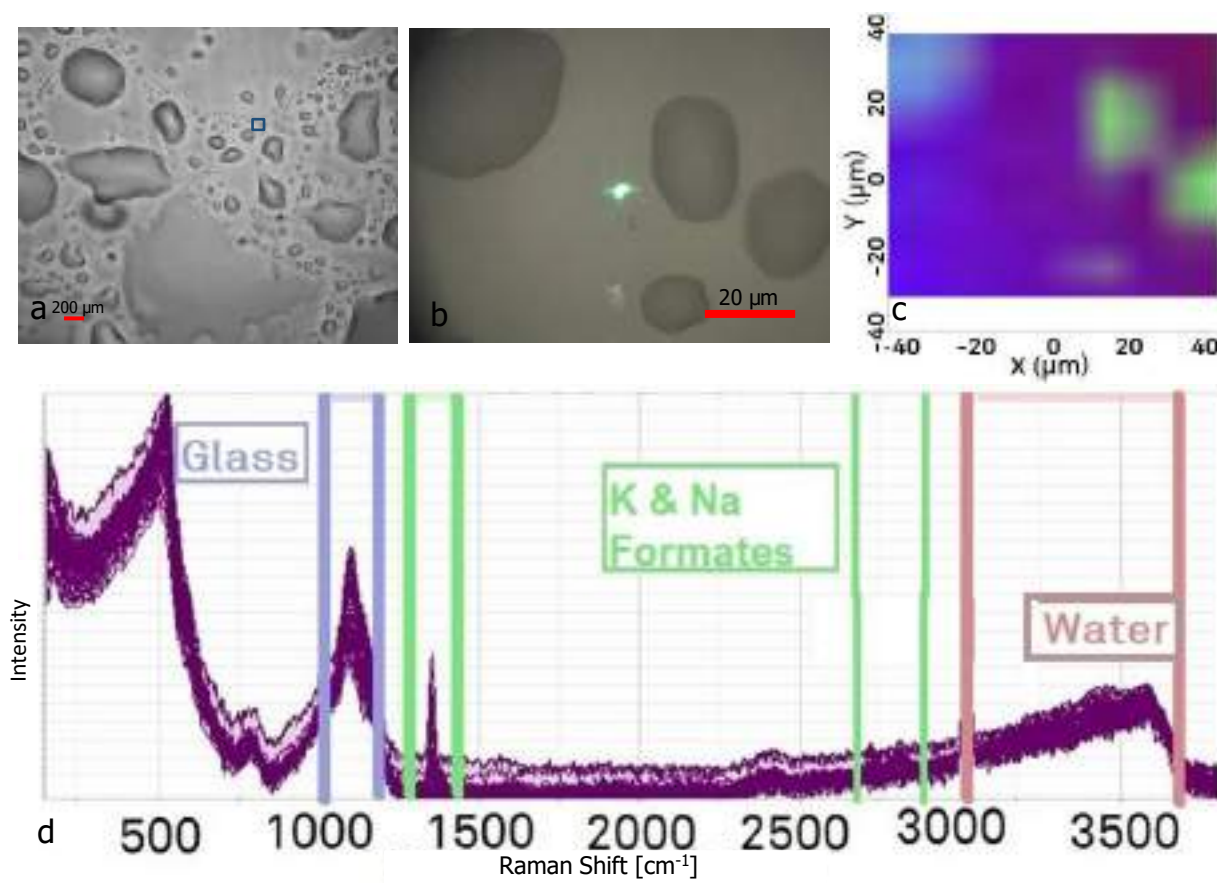


Fig. 3.23: a) Photomicrograph of P model glass aged for 6 months showing area selected for Raman mapping b) Image of the mapped $80 \times 80 \mu\text{m}$ area using Raman microscope at 100x original magnification c) Chemical map of the P model glass showing glass (blue), K/Na formates (green) and water (red) d), and spectra of all the points mapped using Raman microscope with spectral regions selected for mapping: glass (band at 1100 cm^{-1}), K/Na formates (at $1350\text{-}1380 \text{ cm}^{-1}$) and water (band between 2800 and 3800 cm^{-1})

The V Raman map of $400 \mu\text{m} \times 400 \mu\text{m}$ (Fig. 29a) show the spatial distribution of the formates (Fig. 3.24b, green) and acetate (Fig. 29c, pink), established using the strong peaks at 1352 cm^{-1} and 926 cm^{-1} , respectively. Formate salts cover a larger area than that covered by acetate salts. Potassium formate and acetate deliquescing at 15% RH and 23% RH at 20°C , respectively, absorb water at ambient conditions, explaining the liquid SNs observed on the model glass surfaces.

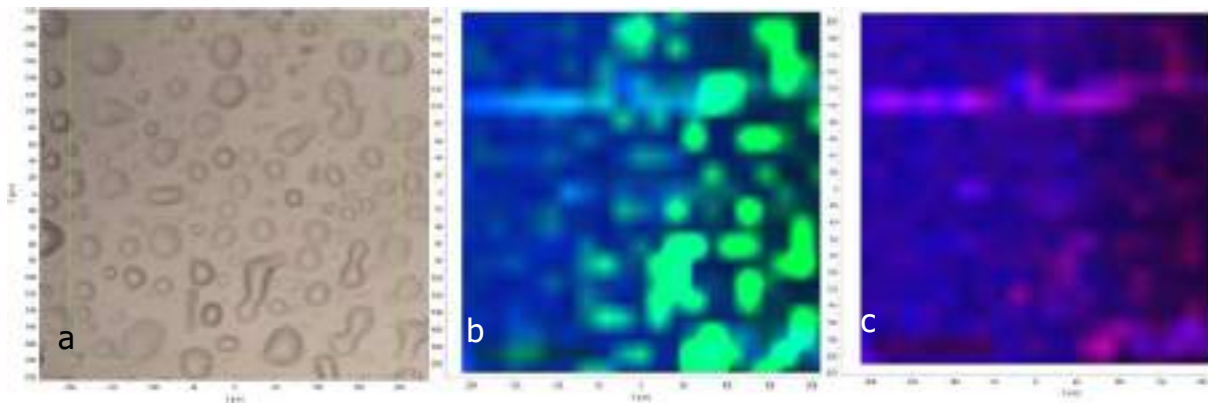


Fig. 3.24 a) Photomicrograph of V model glass aged for 6 months showing area selected for Raman mapping b) Image of the mapped $400\ \mu\text{m} \times 400\ \mu\text{m}$ area using Raman microscope at 100x original magnification c) Chemical map of the V model glass ($1100\ \text{cm}^{-1}$, blue), K formate ($1352\ \text{cm}^{-1}$, green) and K acetate ($926\ \text{cm}^{-1}$, red) [7]

3.7.2. Weight Changes

As can be seen from the figure 30, weight change was positive until 12 months, higher change after 3 and 6 months but lower after 9 and 12 months of aging for both P and PV. This occurred as a result of the difference in the weight loss due to leaching of the alkali cations out of the glass matrix and the weight gain due to the formation of the hygroscopic SNs on the surface of the glass surface when the leached-out cations reacted with the atmospheric anions (mostly formates in the present case). Until 12 months of aging, weight gain due to SNs was more than the weight loss due to leaching. Weight loss was ultimately evident for the samples aged for 17 months owing to the leaching of alkali from the glass matrix forming deliquescent SNs on the model glass surface, which had run off from the surface by this time.

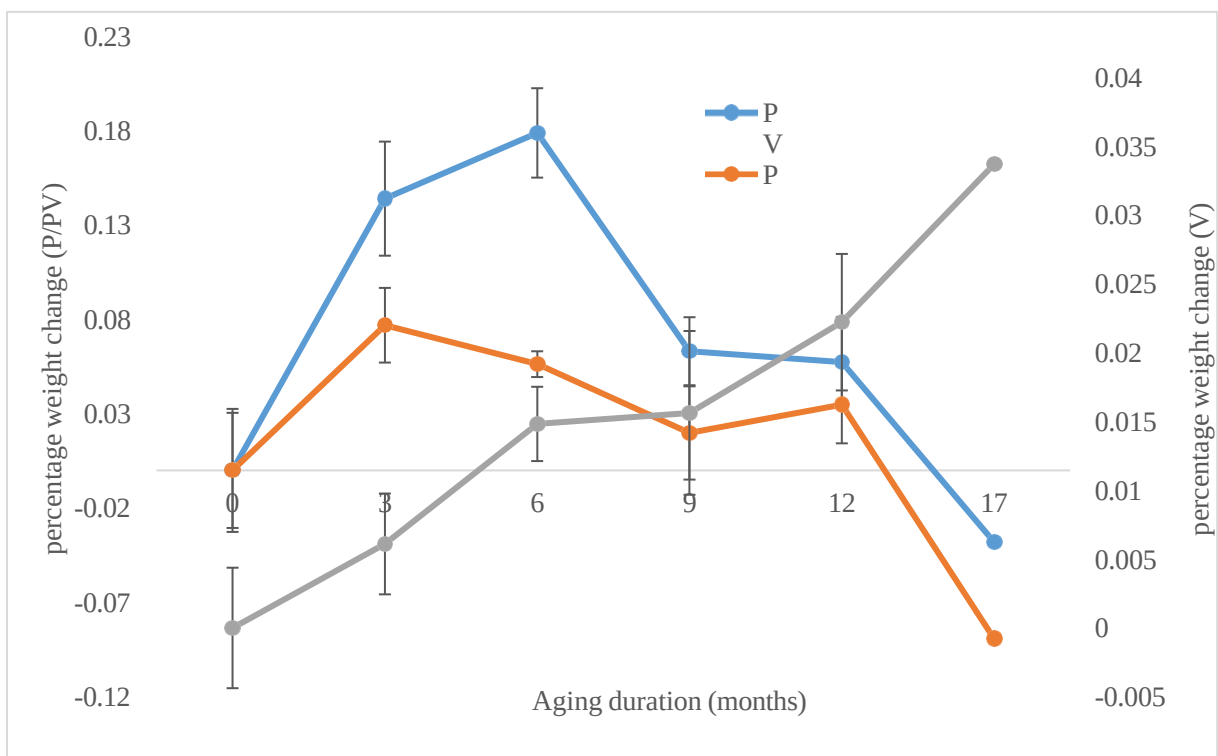


Fig. 3.25: Temporal progression of average weight change percentage for P (blue), PV (orange) and V (grey) model glass

In case of the V model glass, the weight of the model glass samples increased slightly following aging, with increases in percentage weight gain after 3, 6, 12 and 17 months of aging (Fig. 3.25), indicating water uptake by the glass matrix and formation of SNs on the model glass surface which did not reach a size large enough to run off the surface and make the weight loss due to leaching evident.

3.7.3. Changes in silicate species

Ten points each on 3 model glass were analysed before and after aging with FTIR spectroscopy in reflection mode. An average of 30 spectra for each aging batch was calculated. The FTIR spectra showed changes in silicate species due to corrosion (Fig. 3.26).

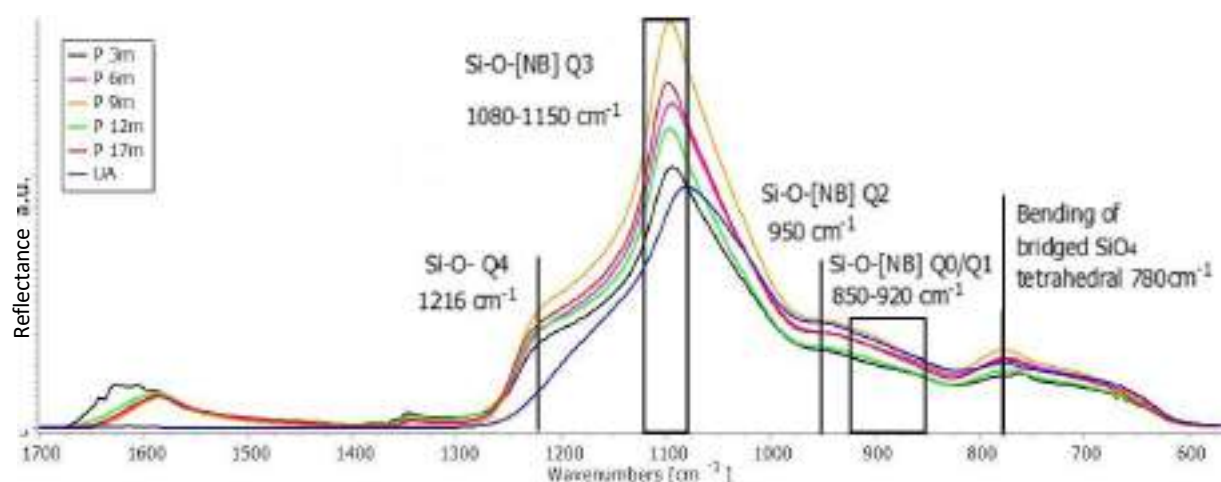


Fig. 3.26: Average FTIR spectra for corroded P model glass compared with unaged (UA) glass average spectrum for withdrawal periods of 3m (black), 6m (pink), 9m (orange), 12m (green), 17m (red) and unaged glass (blue)

All the spectra showed changes in the glass band in reference to unaged glass specifically with the shifting of the peak at 1080 cm^{-1} towards higher wavenumber indicating reduction in Q3 silica species (Fig. 3.26) and reaching close to 1100 cm^{-1} for the model glass aged for 17 months. With a 4 cm^{-1} spectral resolution of the FTIR acquisition, the shift between unaged and P and PV (Annex IX) corroded model glass is significant while V model glass did not show any shift with respect to unaged glass (Table 3.10) (Annex IX). The formation of a shoulder at 1216 cm^{-1} indicated formation of new Q4 rings [8]. The Q2 position at 950 cm^{-1} , Q0/Q1 position at 950 cm^{-1} and SiO_4 tetrahedral bending at 780 cm^{-1} did not show any temporal trend.

In case of Raman spectra of unaged and aged P and PV samples, peak shifts were observed in the glass structure starting from the first 3 months onwards showing a progressive shift in the stretching (ν) Q3 band at 1100 cm^{-1} towards lower wavenumbers indicating depolymerisation of the original glass matrix, formation of a shoulder in the stretching Si-O Q2 + Si-OH between 990 cm^{-1} and 1040 cm^{-1} and shifting of the bending (δ) Q3 peak at 530 cm^{-1} towards 490 cm^{-1} indicating the formation of new Si-O-Si and Q4 rings on the surface (Fig. 3.27a and b). V model glass showed no modifications until 17 months of aging (Fig. 3.27c).

Table 3.10: Shift in the position of the Q3 peak for different aging condition and periods (resolution 4 cm^{-1})

	Unaged	3 months	6 months	9 months	12 months	17 months
P	1080	1095	1095	1097	1097	1099
PV	1080	1095	1095	1093	1095	1095
V	1080	1080	1080	1080	1080	1080

Principle component analyses (PCA) was also performed on the Raman data to cluster the samples based on the different Raman spectral components thereby showing the differences among P, PV and V conditions. The scree plot showed that up to 8 components could explain about 95% of the variance and therefore, the other 10 components were not analysed (Fig. 3.28a). Finally, only component 1 and 2 showed four identifiable clusters in the score plot (Fig. 3.28b and c). The biggest cluster was of V model glass aged for different periods (inside purple circle) characterized by the area of $\nu \text{Q3}' + \text{Q4}$, νQ3 and 588 cm^{-1} band along with the positions of νQ3 and δQ3 bands which did not show any major shifts for the V model glass. The P model glass aged for 12 and 17 months were characterised by the higher area of the $\nu \text{Si-OH}$ shoulder at 1023 cm^{-1} , δQ4 around $\approx 500 \text{ cm}^{-1}$ and Q3/Q4 around $\approx 1040 \text{ cm}^{-1}$ (inside black circle). The PV model glass aged for 17 months were clustered by the position of the δQ0 which shifted to higher frequency than in the non-corroded model glass (inside orange circle). A smaller cluster of few spectra of the P model glass aged for 17 months were clustered based on the area of the νQ2 and δQ3 bands (Fig 3.28d). No clear clusters were identified which could be utilized for characterizing Raman data on the corroded glass.

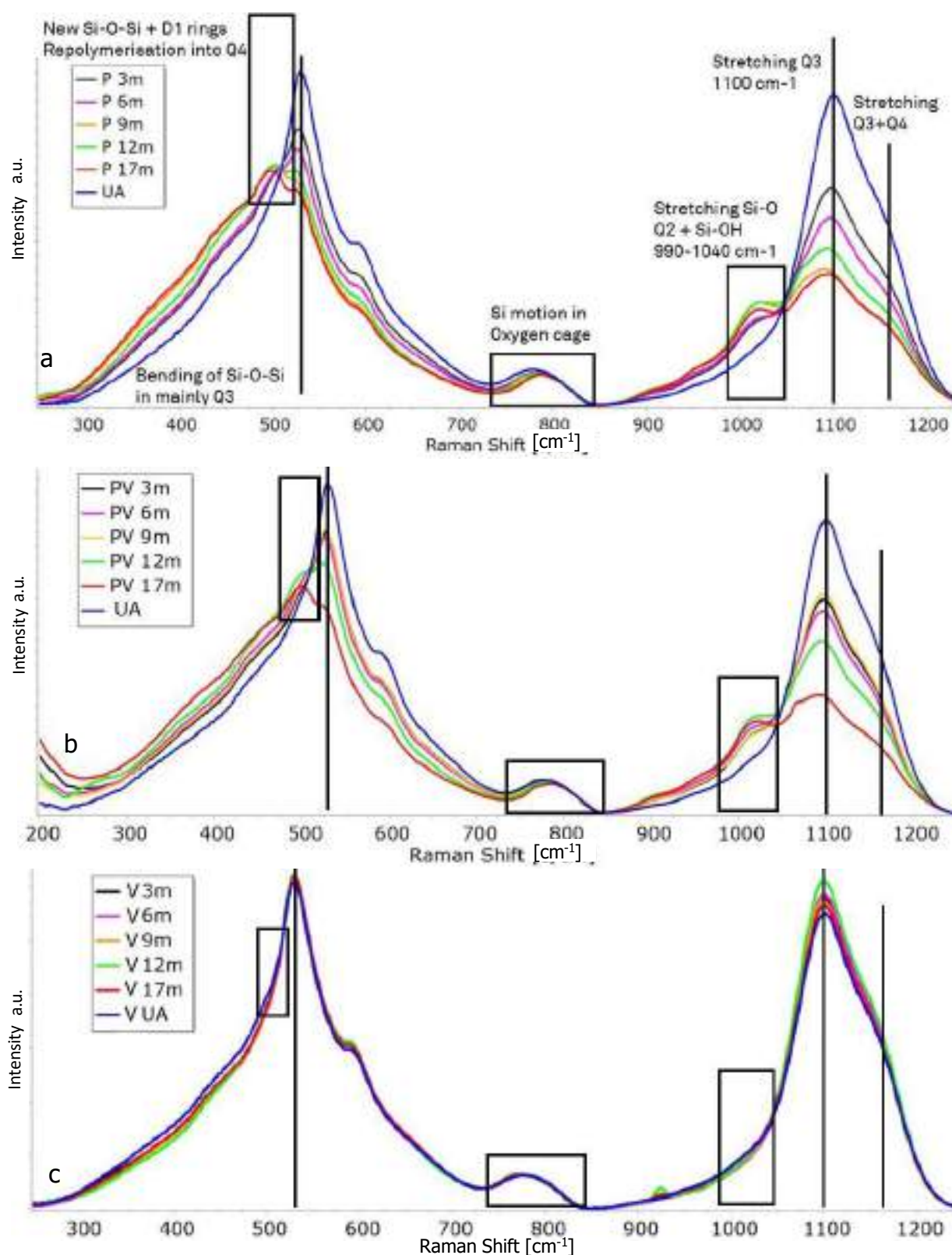


Fig 3.27: Temporal progression of the average Raman spectra for corroded model glass in the glass band region for aging condition a) P, b) PV and c) V for withdrawal periods of 3m (black), 6m (pink), 9m (orange), 12m (green), 17m (red) and unaged glass (blue)

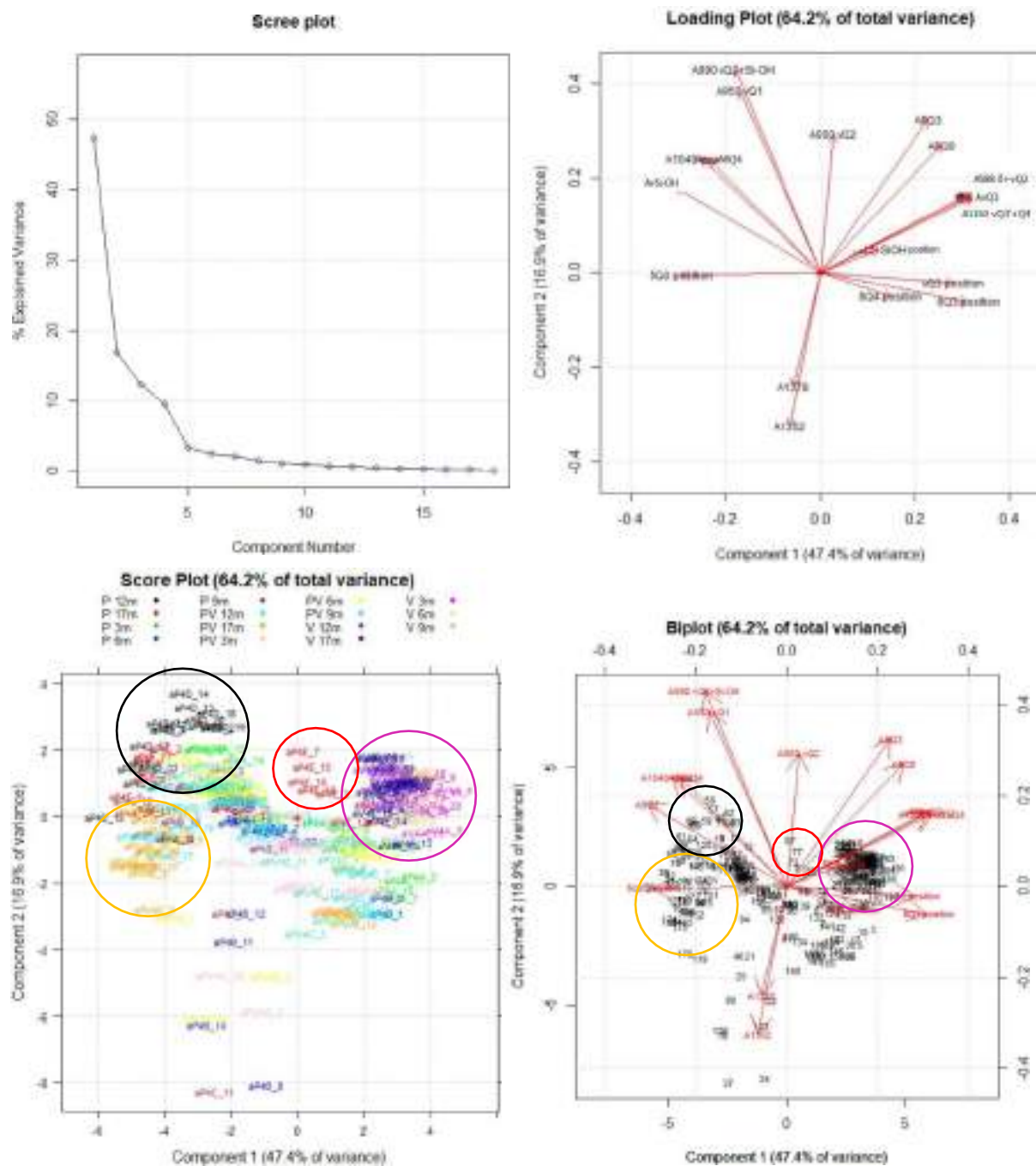


Fig 3.28: a) Scree plot showing the percentage of variance explained by the 18 components b) Loading plot showing the loadings on the major components 1 and 2 c) Score plot showing the scores of each individual spectra for component 1 and 2 along with identifiable clusters. Colours are based on the aging batches P 3m (green), P 6m (violet), P 9m (brown), P 12m (black), P 17m (red), PV 3m (pink), PV 6m (yellow), PV 9m (light blue), PV 12m (cyan), PV 17m (orange), V 3m (magenta), V 6m (dull yellow), V 9m (grey), V 12m (purple), PV 17m (dark blue) d) Biplot showing the scores along with the loadings

Q4/Q3 FTIR ratio

Raman and FTIR spectra include a comprehensive information of the silicate species in the glass. However, being a very localized analyses, the spectra vary greatly due to the heterogeneity of the glass corrosion on the surface as well as in depth. The average FTIR spectra

for each aging batch were deconvoluted using gaussian curves for peak fitting from the Q3 peak at approx. 1100 cm^{-1} and the shoulder pertaining to Q4 at 1200 cm^{-1} to calculate Q4/Q3 ratio which showed the corrosion extent. The value of the ratio after salt aging (0 month aged) for P and PV model glass were similar to each other and much higher than V, to begin with. The temporal trend in case of P showed an increasing trend since Q4 might increase slightly due to repolymerization of silicate network during network rearrangement while Q3 will reduce greatly with increasing corrosion due to leaching out of the alkali ions. However, in case of PV the trend was opposite as the ratio decreased with time maybe indicating that the reduction in Q3 was not as drastic as in case of P (Fig. 3.29). Presently, this trend was not in accordance with the rest of the data and could not be interpreted satisfactorily. The V model glass also showed an increasing trend for the ratio in which case a polynomial fitting showed that the rate of change of the ratio was directly proportional to time. Therefore, in case of P and V model glass a progressive increase in corrosion can be observed with time especially in terms of leaching mechanism. No other correlations were found among any other deconvoluted bands for FTIR spectra.

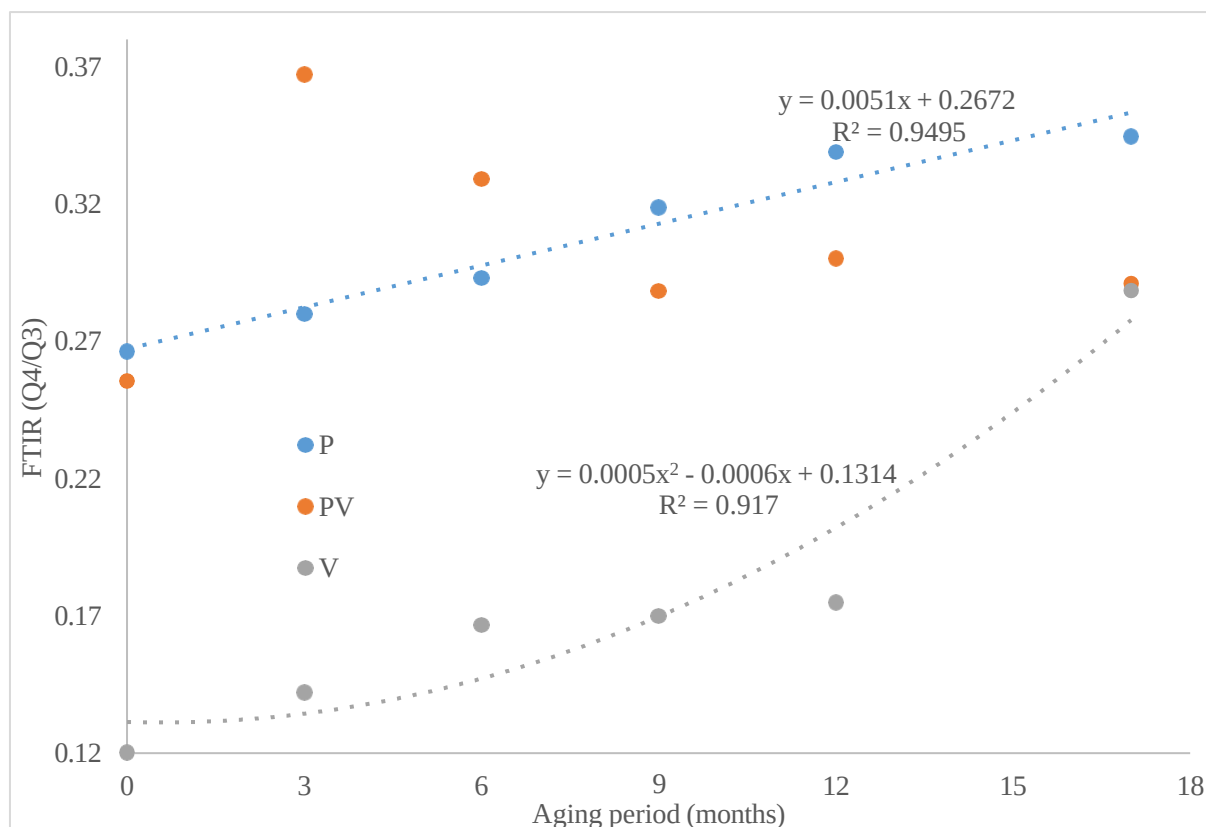


Fig. 3.29: Temporal progression of Q4/Q3 ratio from averaged FTIR spectra for P (blue), PV (orange) and V (grey) model glass. Average spectra calculated using Spectragryph

Raman Q3/Q2 ratio

Raman Q3/Q2 ratio was calculated by dividing the peak found for Q3 stretching in the region of 1100 cm^{-1} by the peak forming the shoulder at 1023 cm^{-1} pertaining to Q2 stretching. The

value of the ratio after salt aging (0 month aged) for P and PV model glass were similar to each other and lower than V, to begin with. As can be seen, the value of the ratio for V model glass was different from that of P and PV after 3 months of aging in saturated salt solutions.

In case of P and PV, the Q3/Q2 ratio decreased with time since the change in Q2 would be much lesser as compared to decrease in Q3 due to the preferential leaching of monovalent ions (K^+/Na^+). This trend was therefore typical of the leaching observed in monovalent element rich glass. However, in the case of V, there was no proper trend which could be observed other than a second-degree polynomial fitting (Fig. 3.30).

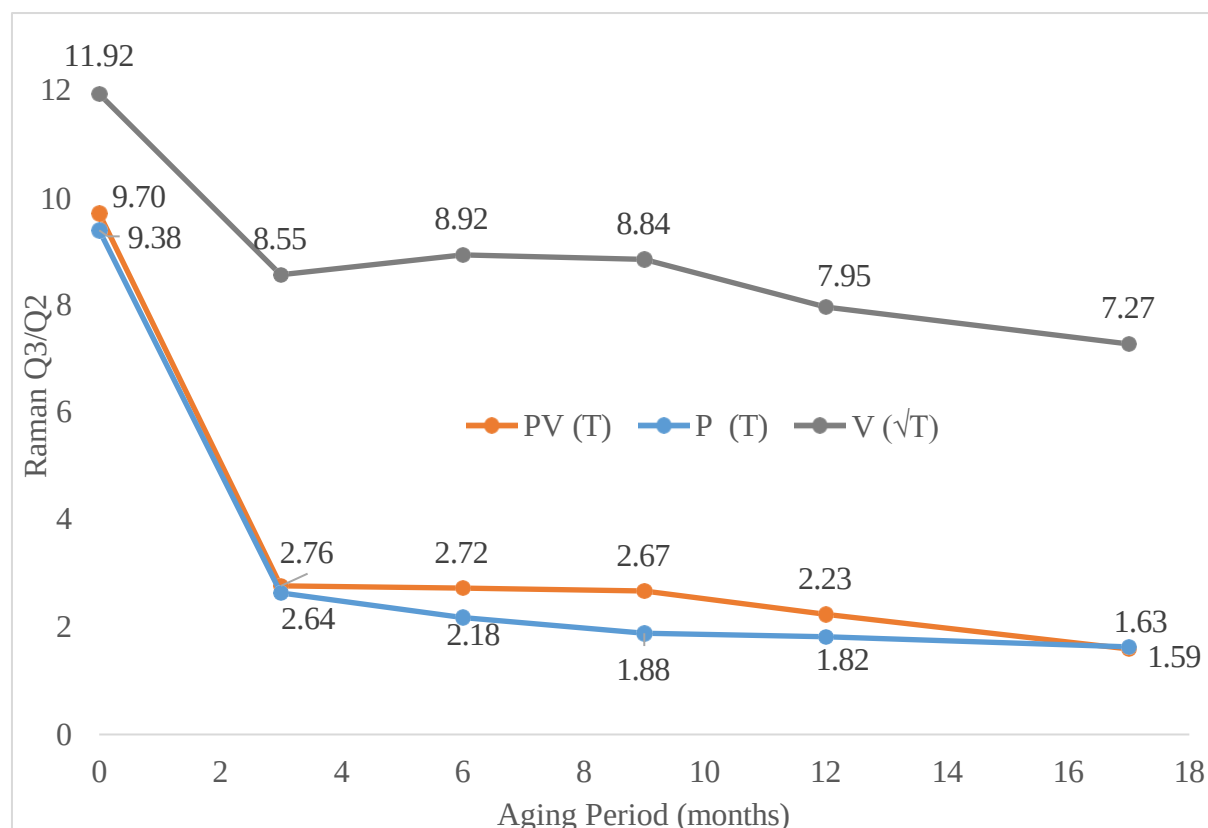


Fig. 3.30: Temporal progression of the ratio of Q3/Q2 peaks for P (blue), PV (orange) and V (grey) model glass. Average spectra calculated using Spectragryph

Polymerisation index

The polymerization index (I_p) indicates the silica content and polymerization degree by measuring the ratio between the areas of the Si-O bending modes ($\approx 500\text{ cm}^{-1}$) and the Si-O stretching modes ($\approx 1000\text{ cm}^{-1}$) and could be a reliable indicator of the degree of polymerization in glassy systems [9]. The level of therefore, the temporal change in I_p for average spectra of P, PV and V were plotted (Fig. 3.31). The value of the index after salt aging (0 month aged) for P, PV and V model glass were similar to each other to begin with. In case of P and PV, a linear temporal relationship could be observed change which reduces with time while the V model glass could not show any trendline for I_p . The trend shows a progressive increase in polymerization of P and PV model glass linear with time unlike for V model glass.

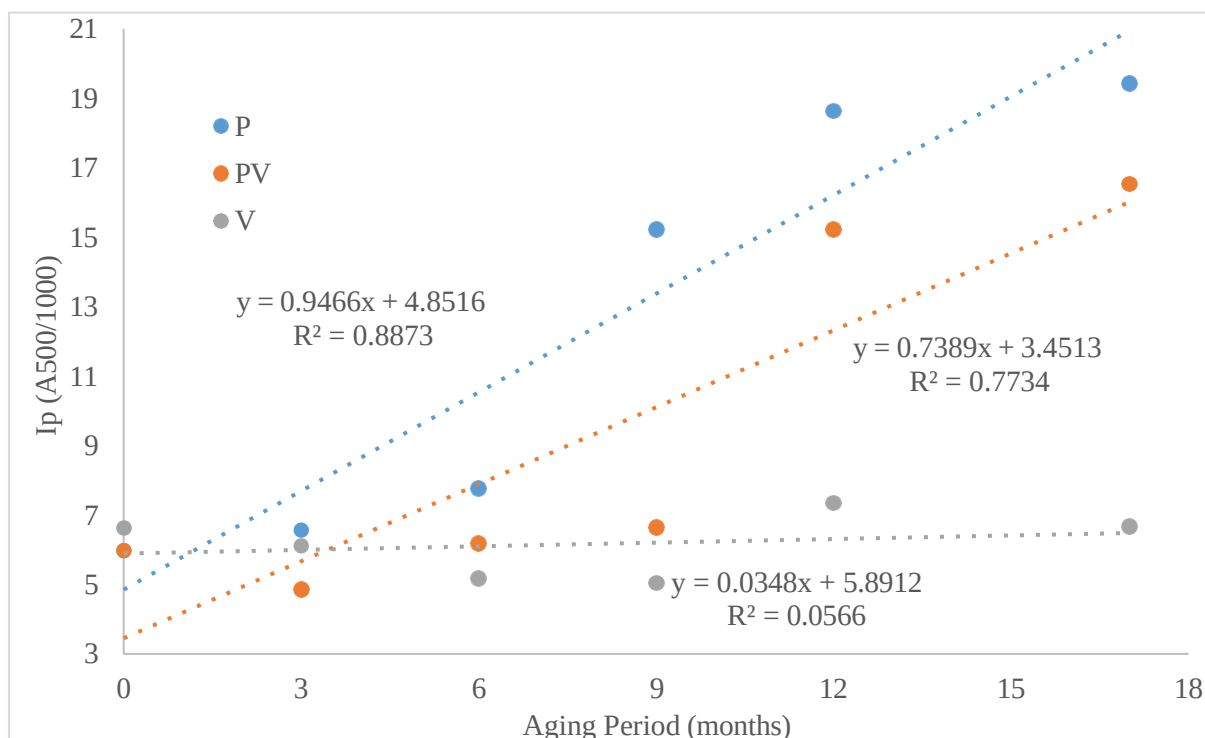


Fig. 3.31: Temporal progression of polymerisation index (I_p) from averaged Raman spectra for P (blue), PV (orange) and V (grey) model glass. Average spectra calculated using Spectragryph

3.7.4. Hydration of the glass matrix

The extent of hydration of the glass matrix was analysed using FTIR, Raman and HSI spectra and was quantified using the peak areas related to water as proxy to characterize the extent of corrosion.

FTIR spectra of glass could also give information about the OH^- and H_2O vibrations in the higher wavenumber region between 3000 to 3600 cm^{-1} . Broad bands of irregular shapes were evident in this region (Fig 3.32a, b and c). However, the area under this band could not be correlated with the aging period for P, PV and P model glass using FTIR spectra in reflection mode, since this band usually requires analyses in transmission mode for quantification. Studies with transmission mode FTIR on glass could be performed with thinner samples of standardized thickness. Water band could also be observed in Raman spectra between 2800 cm^{-1} and 3800 cm^{-1} for showing the hydration of the silicate matrix (Fig. 3.32d, e and f). However, the extent of dissolution of water in the glass matrix was not homogenous over the entire surface, and, therefore, the results can vary depending on the location of analysis. This might also explain the lack of any temporal trends as well. The Raman water band was also deconvoluted for further normalized water and OH^- speciation.

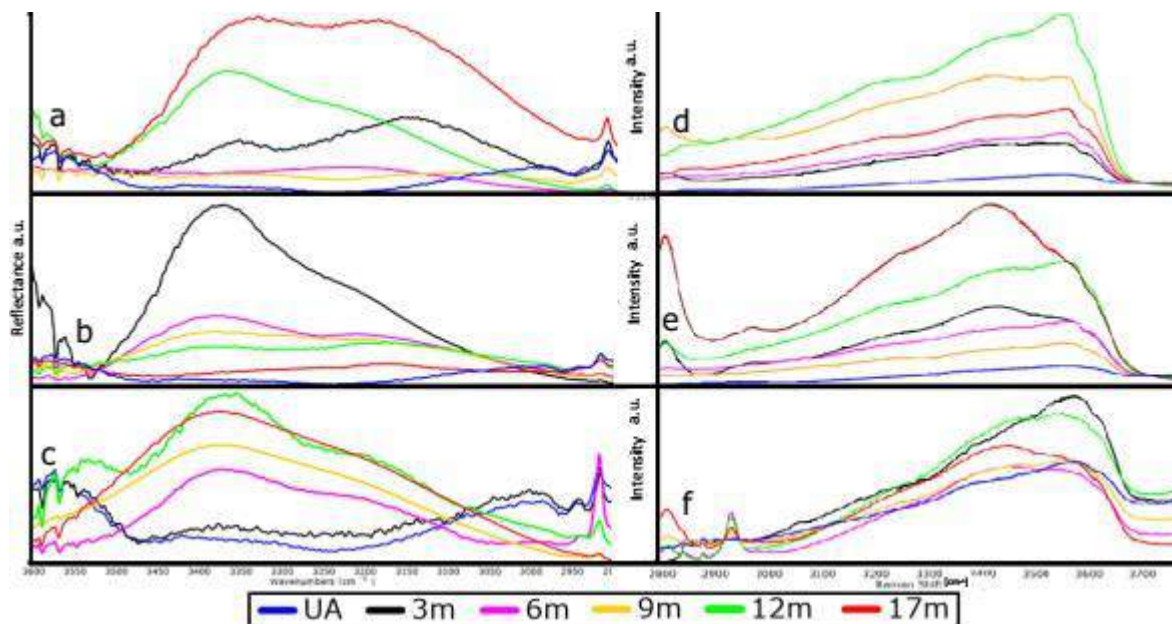


Fig 3.32: Temporal progression of the average for model glass in the water band region extracted from FTIR between 2900 and 3600 cm^{-1} from aging condition a) P b) PV and c) V; extracted from Raman spectra between 2800 cm^{-1} and 3800 cm^{-1} from aging condition d) P e) PV and f) V for withdrawal periods of 3m (black), 6m (pink), 9m (orange), 12m (green), 17m (red) and unaged glass (blue)

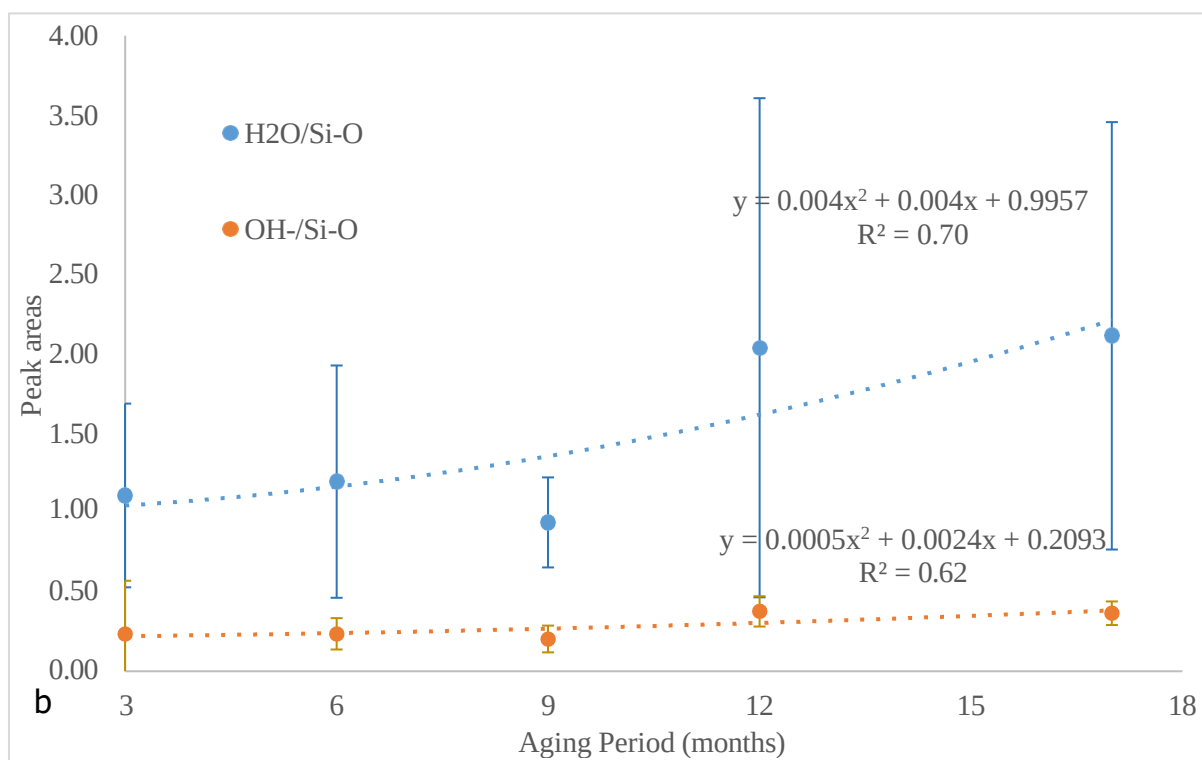
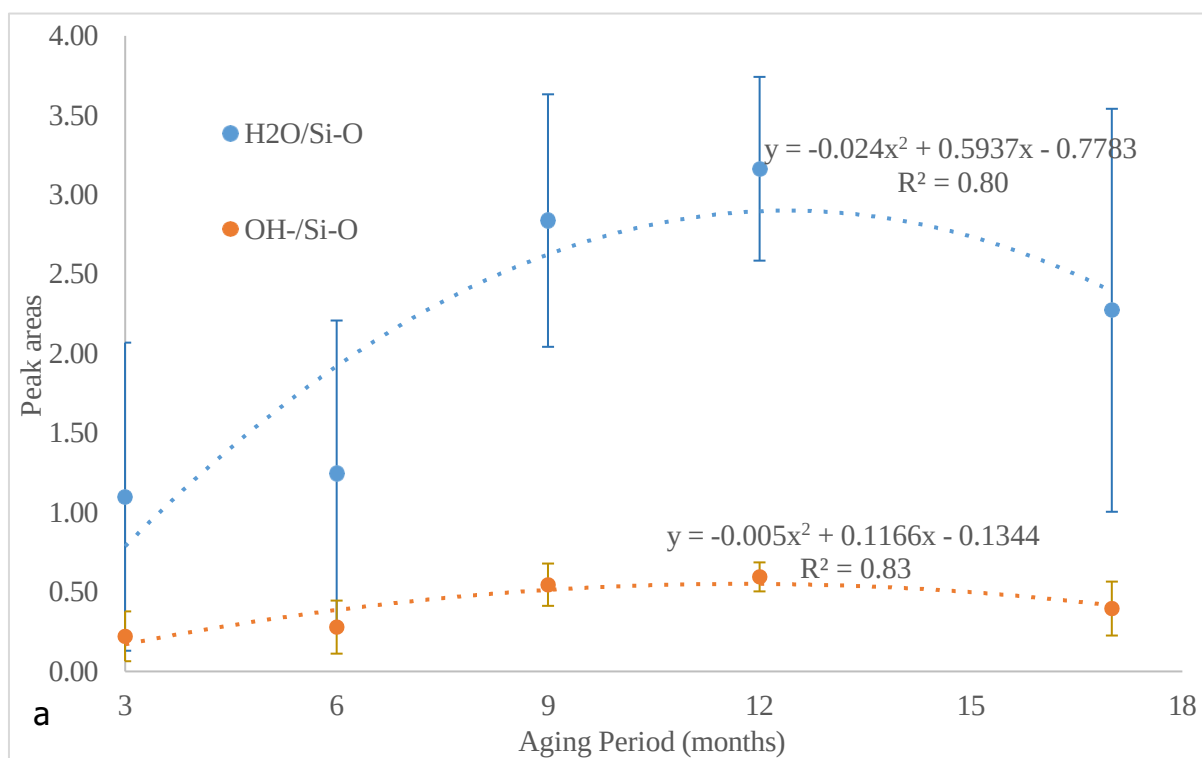
The change in the Raman water band area calculated from the same points before and after aging, showed similar trend of increasing extent of hydration with aging period for both P and PV, especially in the case of PV but the data was not statistically significant due to a very large variability in the results. In case of V model glass, no clear trend was visible (Table 3.11).

Table 3.11: Temporal progression of the average percentage change in water band area between 2800 cm^{-1} and 3800 cm^{-1} of P, PV and V model glass along with standard deviation (σ)

Aging period	3 months	6 months	9 months	12 months	17 months
P	204.39	174.76	269.52	646.27	536.41
σ	192.37	131.04	200.80	176.73	426.46
PV	139.40	156.53	258.18	739.50	809.38
σ	169.60	140.95	143.38	142.70	940.94
V	427.86	351.77	129.44	275.44	208.14
σ	131.04	89.27	117.53	185.99	201.96

Amount of water and OH^- present in the alteration layer

The normalized molecular water and OH^- speciation calculated from the deconvoluted water band each compared for P, PV and V model glass. The amount of OH^- was much lower than the amount of molecular water for both P (Fig 3.33a) and PV (Fig 3.33b) indicating that the rate of leaching must be higher than the network dissolution process in both cases. However, this is not the case for V model glass wherein there is no significant difference in the amount of water and OH^- species (Fig 3.33c).



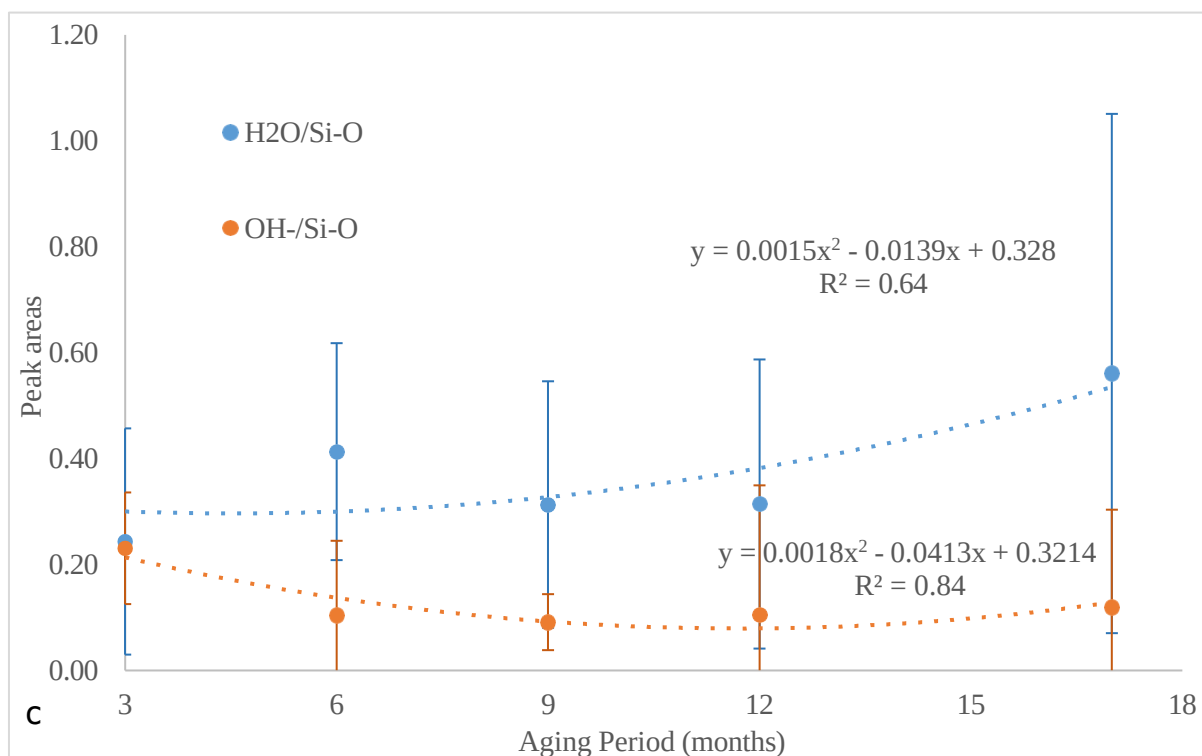


Fig. 3.33: Temporal progression of normalized molecular water and OH- species calculated from Raman water band for a) P (blue) b) PV (orange) and c) V (grey) model glass with error bars showing standard deviation

While Raman spectroscopy showed a great variation depending on the point chosen due to the heterogeneity of glass corrosion, the HSI SWIR curves were obtained by taking into account a very large area of the sample giving a global idea of the extent of hydration for the whole glass, and therefore could provide more statistically representative data. Consequently, clear temporal trends in increasing of water and OH⁻ uptake could be observed.

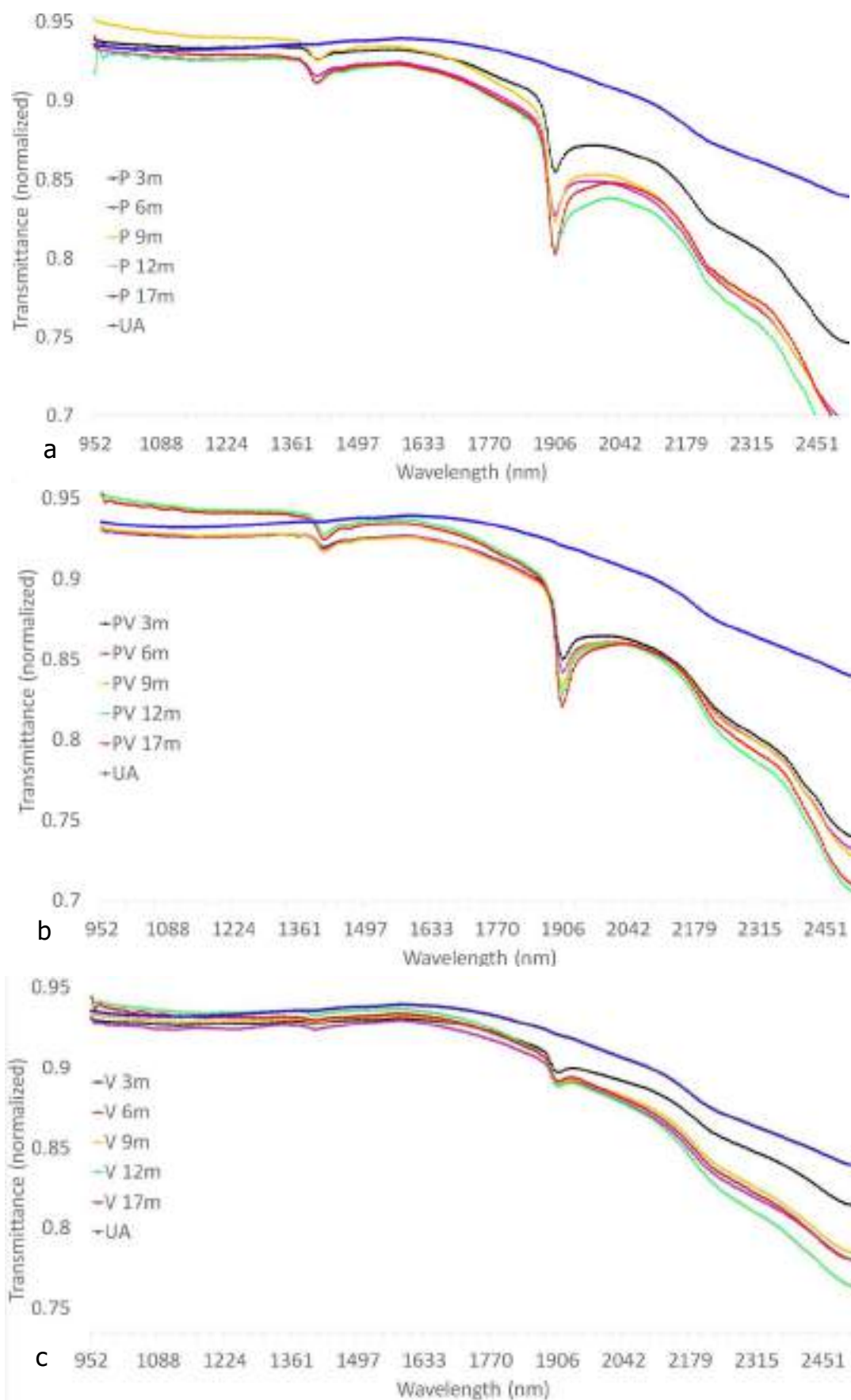


Fig. 3.34: SWIR average spectra of model glass aged for 3 months (black), 6 months (pink), 9 months (orange), 12 months (green) and 17 months (red) along with unaged reference glass (UA) (blue) model glass acquired by 30 cm focal length lens for aging condition a) P b) PV c) V

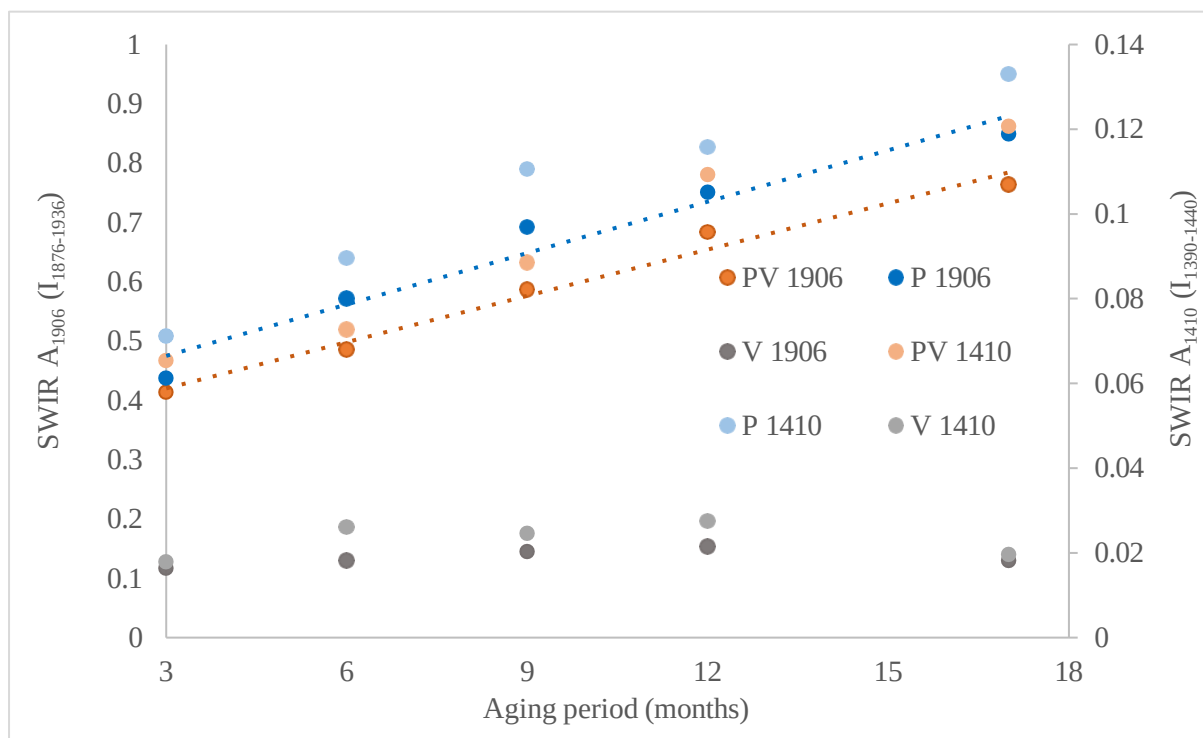


Fig. 3.35: Graph showing the progression of SWIR A₁₄₁₀ (I₁₃₉₀₋₁₄₄₀) and SWIR A₁₉₀₆ (I₁₈₇₆₋₁₉₃₆) for P (light and dark blue), PV (light and dark orange) and V (light and dark grey) model glass. Average spectra calculated using ImageJ

The SWIR average spectra (acquired with 30 cm lens) of two P model glass aged for 3, 6, 9, 12 and 17 months each, showed two prominent peaks ≈ 1410 nm and ≈ 1906 nm, which did not occur in the unaged reference glass. These indicated the presence of OH⁻ species and molecular water absorbed in the corroded model glass matrix. There was a progressive increase in the peak intensity at ≈ 1410 nm and to greater extent at ≈ 1906 nm (Fig. 3.34a and c) which could be also quantified using the integral of the area between 1390-1440, centred at 1410 nm SWIR A₁₄₁₀ (I₁₃₉₀₋₁₄₄₀) and between 1876-1936 nm, centred at 1906 nm SWIR A₁₉₀₆ (I₁₈₇₆₋₁₉₃₆) in reference to their individual baseline. Both I₁₃₉₀₋₁₄₄₀ and I₁₈₇₆₋₁₉₃₆ progressively increase with aging period for both P and PV model glass, therefore show a linearly increasing temporal trend with all the values of $R^2 > 0.90$. Both the curves are in positive correlation with each other showing that the increase in the two peaks is in the same direction and by similar percentages, even if not visible just by looking at the spectra (Fig 3.34b and d). Nonetheless, in case of V model glass, no such trend was observed which was similar to the results from Raman water band (Fig 3.35).

Transmittance spectroscopy was conducted at random locations on glass samples from the PV model. The findings revealed distinct peaks at approximately 1410 nm and roughly 1906 nm in the PV-aged glass specimens. Notably, these peaks were absent in the reference glass sample (Fig. 3.36), affirming the successful validation of the HSI. Notably, the signal to noise ratio is much higher in the TS spectra. The noise increased greatly from 2000 nm onwards.

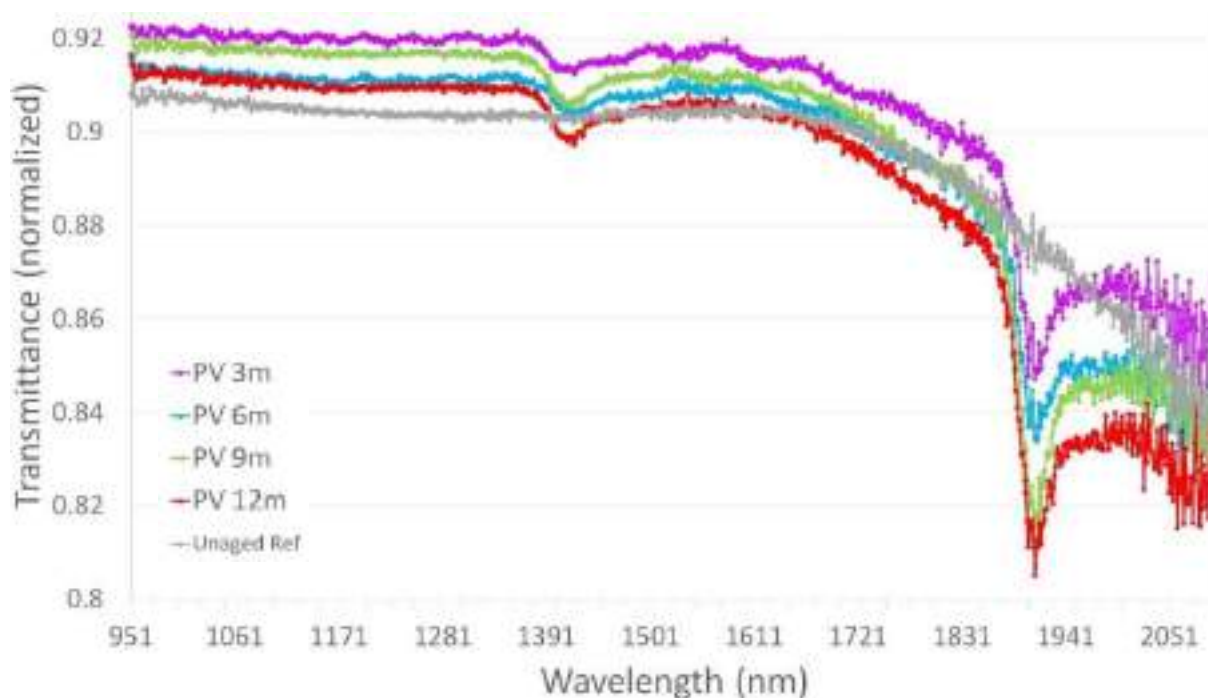


Fig. 3.36: TS spectra of PV model glass aged for 3 months (pink), 6 months (blue), 9 months (green) and 12 months (blue along with the Unaged reference (grey) [10]

3.8. Heterogeneity of glass corrosion

Visualizations of the corroded model glass samples at ≈ 1410 nm and ≈ 1906 nm obtained by SWIR HSI were compared. Figure 38 report the example of P model glass aged to 17 months. Given the low intensity of the OH^- peak at ≈ 1410 nm, only a light grey line was visible in the centre of the sample bound by two darker regions (Fig. 3.37a), while at ≈ 1906 nm different features and regions can be seen (Fig. 3.37b). The different grey levels in this image, allowed the identification of different regions. The same information could be visualised using the grey value distribution across a transversal area of the sample (in this case, the white rectangular area taken at the bottom in Fig 3.37b (Fig. 3.37c). To be noticed that the grey values became lower as the pixel became darker. It was then possible to visualize 5 main regions and for each of these obtain a typical spectrum, which was extracted at points 1-5 (Fig. 3.37d):

1. Light grey region vertically on left and right side of the sample centre (demarcated by blue lines in figure 3.37c). The spectrum showed peaks at ≈ 1410 nm and ≈ 1906 nm, indicating the presence of molecular water and OH^- species.
2. A darker grey region mostly in the sample centre (demarcated by yellow lines in figure 3.37c). A representative spectrum of this area (taken at point 2) showed peaks at ≈ 1410 nm and at ≈ 1906 nm; the intensity of the latter peak is higher than at point 1.
3. A pair of dark grey lines running vertically on left and right side of the sample (demarcated by green lines in figure 3.37c). The spectrum showed peak at ≈ 1410 nm and ≈ 1906 nm. The intensity at ≈ 1906 nm was higher than at point 1 and 2. This indicated a higher extent of

molecular water absorption. All these features were not visible with naked eyes or RGB photography in transmitted light (Fig. 3.5 and 3.7) or reflected light (Fig. 3.8).

4. Dark black circular or oval spots (demarcated by red lines in figure 3.37c) were characterised by very broad and intense bands between ≈ 1410 – 1470 nm (arising from OH^- and H_2O overtones) and ≈ 1906 – 1960 nm (indicating the presence of water molecules inside silica cages and as films on the surface). Indeed, these were wet SN of deliquescent formate salts (chemically assessed by Raman spectroscopy). These were also visible with naked eyes but could not be seen with RGB photography in TL (Fig. 3.5 and 3.7) or RL (Fig. 3.8).

5. Lighter grey narrow band in the centre of the model glass which was visible at 1410 as well as 1906 nm. This region shows higher water uptake than region 1 but less than region 2 and 3.

Thus, the visualization as well as the spectra clearly showed variable water uptake by the glass matrix due to the non-homogeneous nature of the model glass surface.

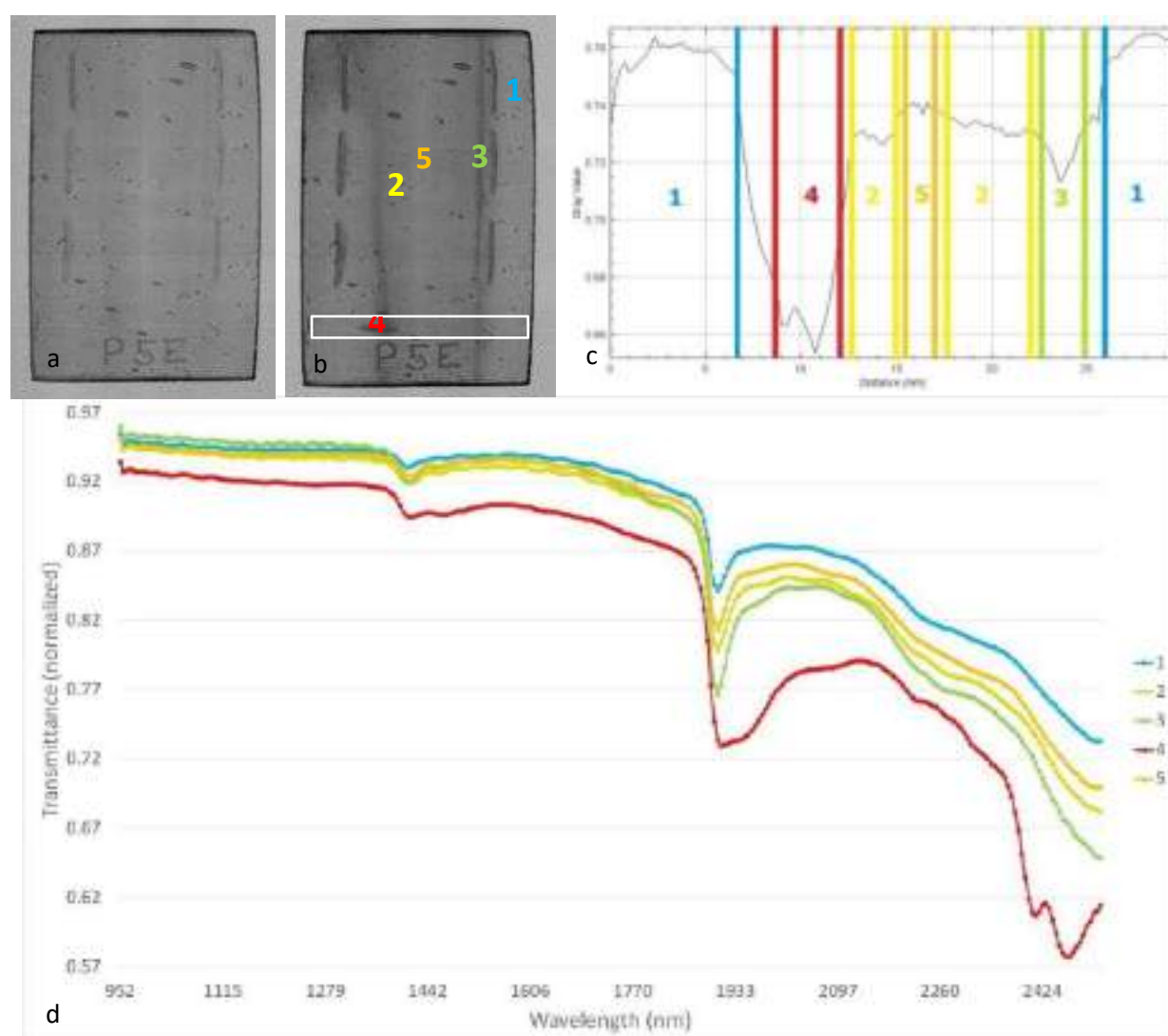


Fig. 3.37: P model glass sample aged to 17 months: SWIR image at a) 1410 nm b) 1906 nm (Field of view: ≈ 5 cm $\times$ 3 cm) representing five visually distinct regions c) Grey values of area in white rectangle (in image b) demarcating five visually distinct regions d) SWIR spectra corresponding to point 1 (blue), 2 (yellow), 3 (green), 4 (red) and 5 (orange)

Similarly heterogenous regions were detected in PV model glass as well. In case of the example of PV model glass aged for 12 months, four main regions were identified:

1. Light grey region vertically on left and right side of the sample centre (demarcated by blue lines in figure 3.38c). The spectrum shows peaks at ≈ 1410 nm and ≈ 1906 nm, indicating the presence of molecular water and OH⁻ species.
2. A darker grey region mostly in the sample centre (demarcated by yellow lines in figure 3.38c). A representative spectrum of this area (taken at point 2) shows peaks at ≈ 1410 nm and at ≈ 1906 nm; the intensity of the latter peak is higher than at point 1.
3. A pair of dark grey lines running vertically on left and right side of the sample (demarcated by green lines in figure 3.38c). The spectrum shows peak at ≈ 1410 nm and ≈ 1906 nm. The intensity at ≈ 1906 nm is higher than at point 1 and 2. This indicates a higher extent of molecular water absorption. All these features are not visible with naked eyes or RGB photography in transmitted light (Fig. 3.5 and 3.7) or reflected light (Fig. 3.8).

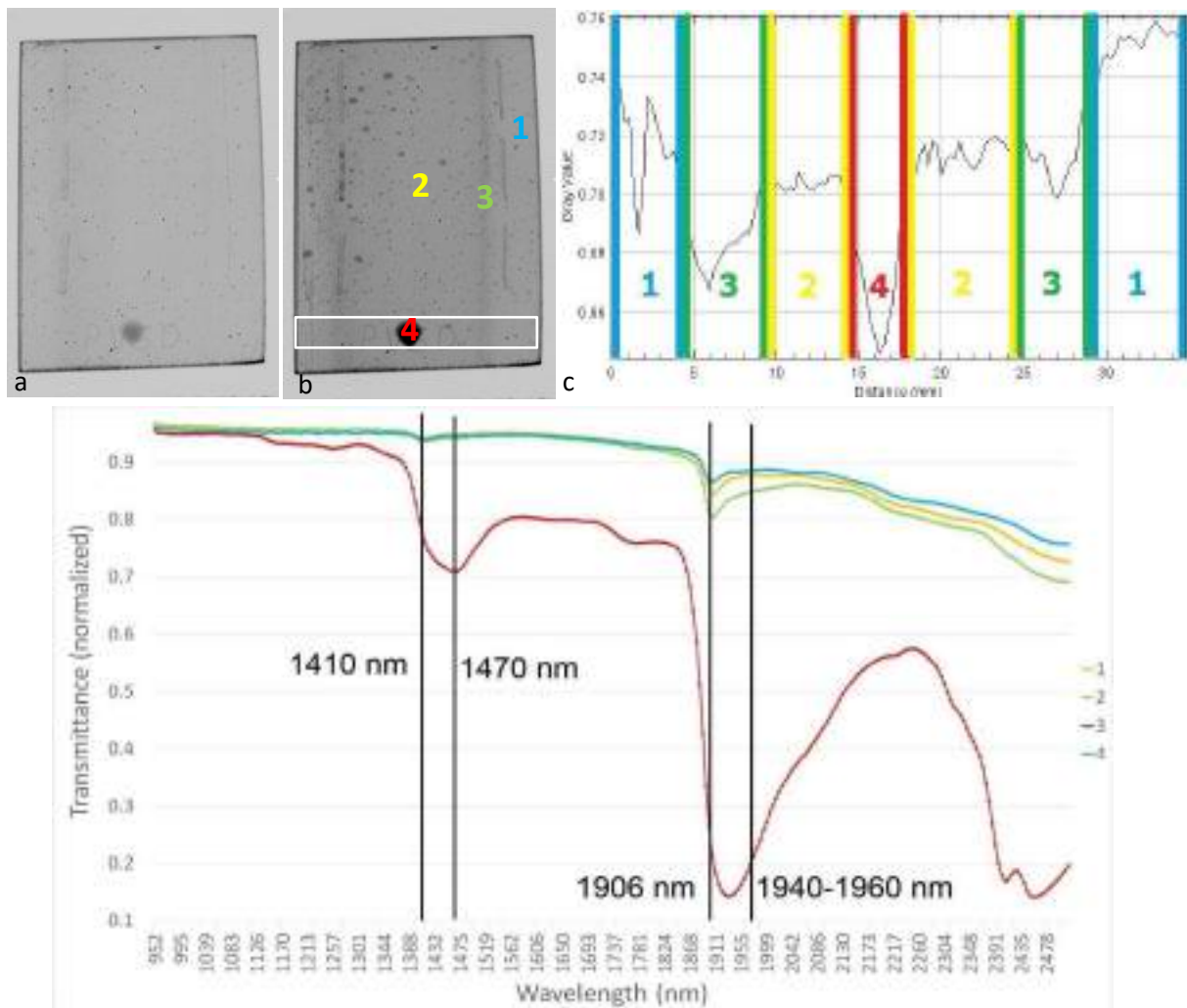


Fig. 3.38: PV model glass sample aged to 12 months: SWIR image at a) 1410 nm b) 1906 nm (Field of view: ≈ 5 cm $\times$ 3 cm) representing four visually distinct regions c) Grey values of area in white rectangle demarcating the four visually distinct regions d) SWIR spectra corresponding to point 1 (blue), 2 (yellow), 3 (green), and 4 (red) [10]

4. Dark black circular spots (demarcated by red lines in figure 3.38c) corresponding to SNs are characterised by very broad and intense bands between $\approx 1410\text{--}1470$ nm (OH- and H₂O overtones) and $\approx 1906\text{--}1960$ nm (water molecules inside silica cages and as films on the surface). These are also visible with naked eye but cannot be seen with RGB photography in transmitted light (Fig. 3.5 and 3.7) or reflected light (Fig. 3.8).

This heterogeneous corrosion and its temporal progression in P, PV and V model glass could therefore be also visualized spatially with the SWIR images (Fig. 3.39). For the P and PV model glass, the multiple distinct regions previously described could be seen starting from 3 months of aging. After three months of aging, a single darker line running vertically across the sample at the left side of the sample dividing the sample into two different regions of darker and lighter shades could be observed (Fig. 3.39a and f). After six months of aging, two lines are visible across the sample length on both the right and left sides with a darker region between them (Fig. 3.39b and g). The sample withdrawn after nine months showed not only two dark lines running across the centre but also a broad darker region between them, which was distinct from the rest of the sample (Fig. 3.39c and h). Sample aged for 12 months showed two dark lines running across the sample with the right-side line darker than the left one (Fig. 3.39d and i). Once again, P and PV sample aged to 17 months showed visible cracking preferentially along two lines running across the length of the sample (Fig. 3.39e and j). The number, locations, and extent of corrosion of such distinct heterogenous regions varied among the different model glass. These dark lines might be a result of surface discontinuities developed on the glass surface during manufacturing which later due to run-off of SN, displayed higher extent of corrosion than the rest of the glass. The larger wet SN, formed due to coalescence of smaller SN, ran down across the length of the model glass due to gravity, since the samples were kept in vertical position inside the desiccators during the aging. To the contrary, V samples did not distinctly show regions until 12 months of aging (Fig. 3.39k-o) as they didn't experience run-off. At 17 months, a pair of faintly dark lines at the centre of the sample (Fig. 3.39o) could be seen where later intense cracking developed.

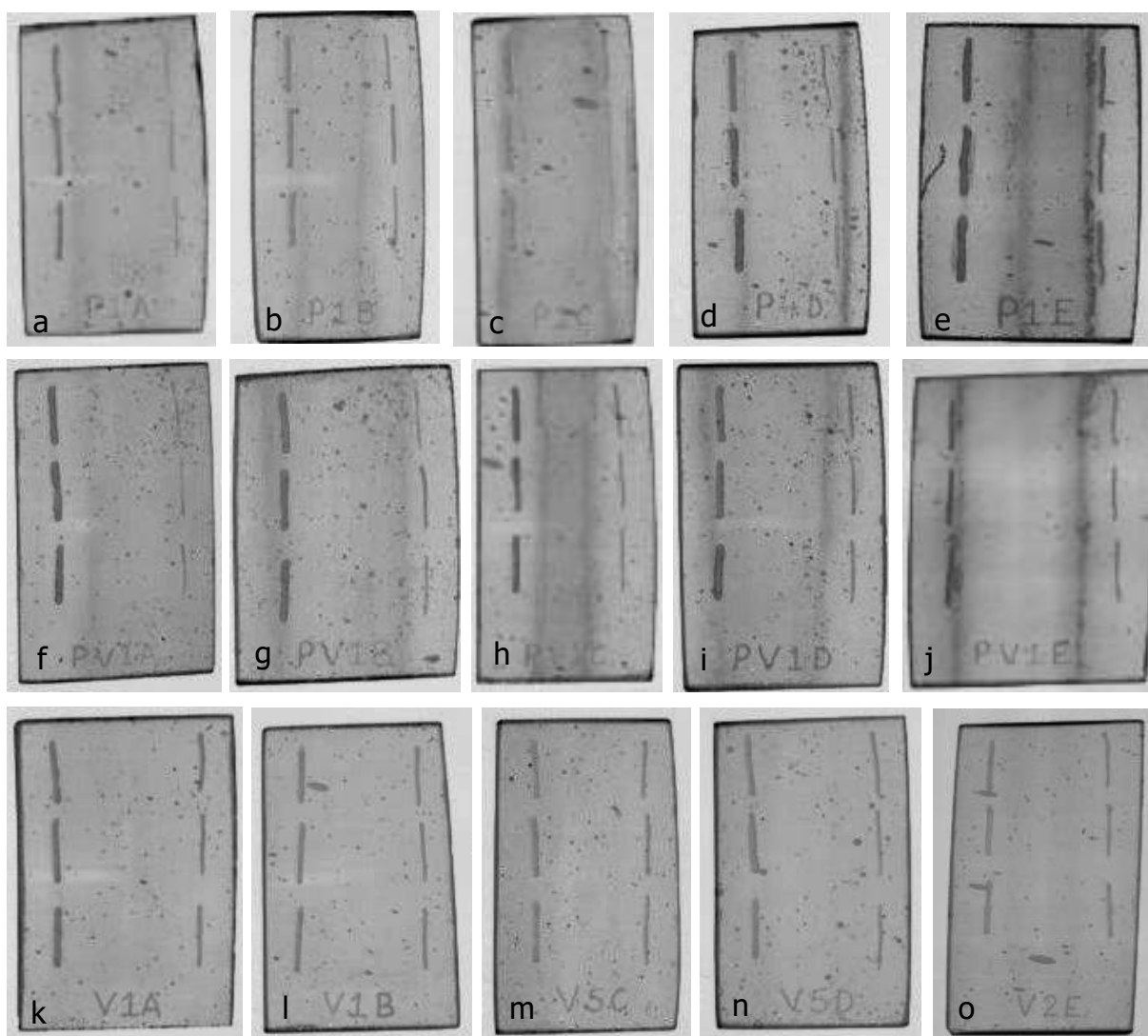


Fig 3.39: SWIR images recorded with 30 cm lens (1906 nm) of P model glass sample (Field of view: $\approx 5\text{ cm} \times 3\text{ cm}$) aged for a) 3 b) 6 c) 9 d) 12 and e) 17 months; PV model glass sample aged for f) 3 g) 6 h) 9 i) 12 and j) 17 months, V model glass sample aged for k) 3 l) 6 m) 9 n) 12 and o) 17 months

This heterogeneity was confirmed by Raman point analyses as well. The Raman spectra of P and PV corroded glass varied greatly from one point to another owing to the heterogeneous nature of glass corrosion which is evident by comparing spectra of different points from the same model glass (Fig. 3.40).

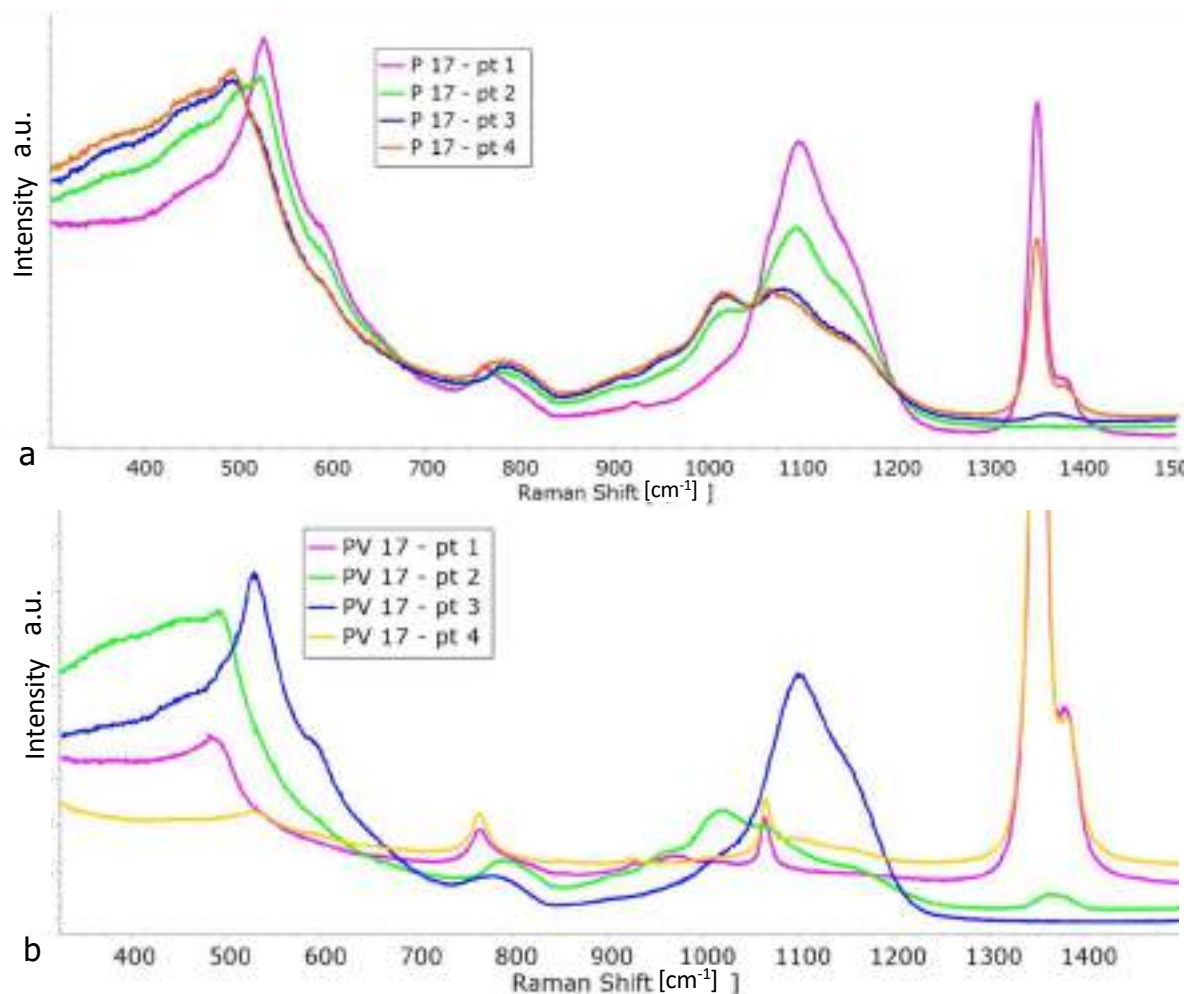


Fig. 3.40: Spectra of four distinct points on the surface of model glass aged for 17 months from aging condition a) P and b) PV (different colours denote spectra from different points)

The heterogeneity of the corroded layer (or alteration layer) on P and PV model glass was also observed using SEM imaging (Annex X). Each model glass sample exhibited an alteration layer on its outer surface. When viewed with backscattering, this layer appears darker than the main body of the glass, indicating a potential enrichment in hydrogenated compounds and implying a leaching mechanism. This layer varies greatly in thickness containing highly degraded areas along with less corroded or unaffected regions, as shown in Fig. 3.41, which depict some of the images from P sample aged for 17 months.

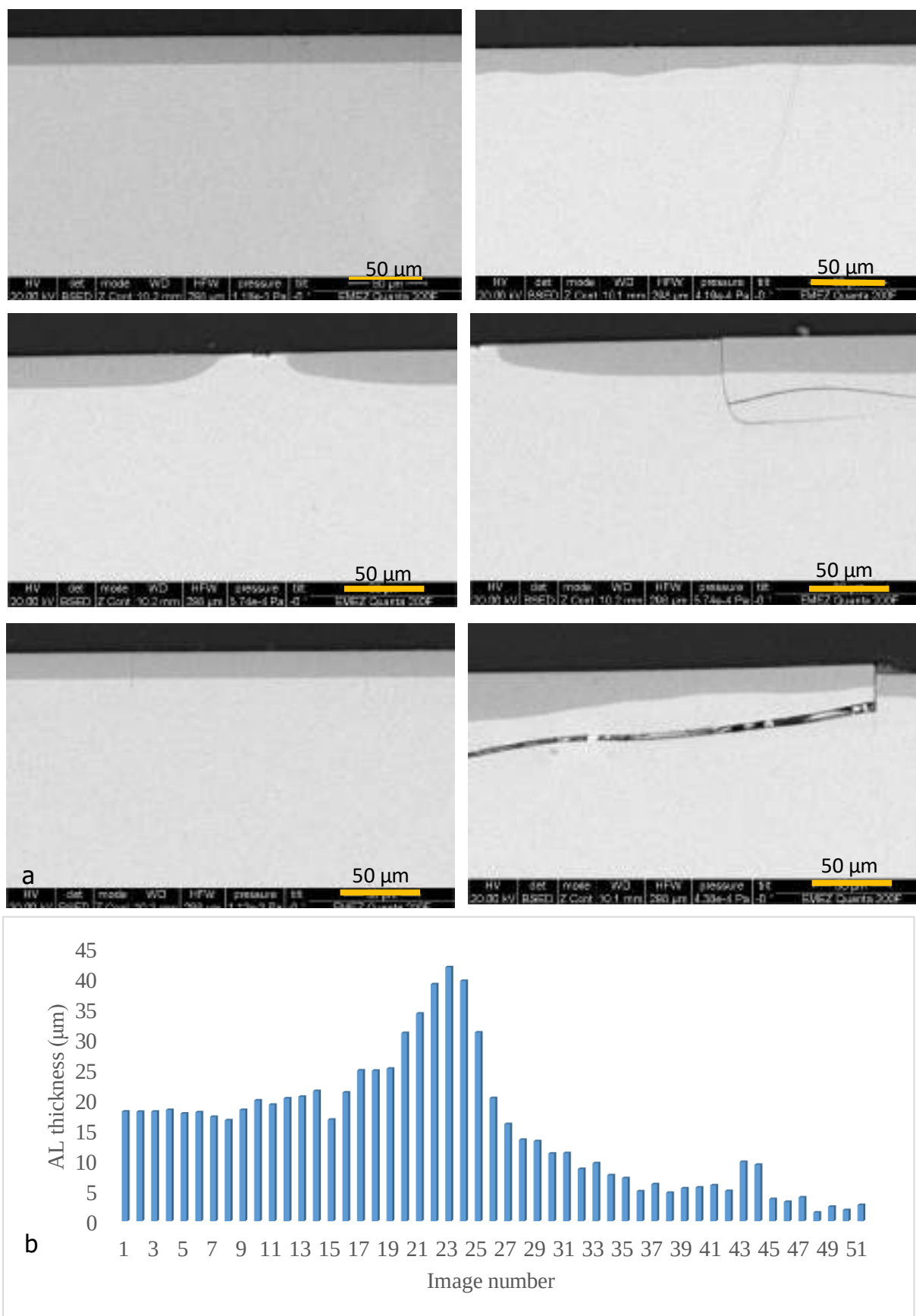


Fig. 3.41: a) 6 SEM images from P model glass aged for 17 months showing the heterogeneity of the alteration layer taken at 1000 $\times$ original magnification b) Histogram showing the alteration layer thickness (in μm) from the total investigated 51 areas (see Annex X)

3.9. In-depth analysis of the alteration layer

SEM-EDX provided an in-depth analysis of the alteration layer (AL) and its morphology (Fig. 3.42). The AL (darker in colour in figure 3.42) was observed to be heterogenous and displayed no cracks until 3 months of aging (Fig. 3.42b). From 6 months onwards, vertical cracks could be seen going into the bulk glass (Fig. 3.42b) while horizontal cracks could be seen only in model glass aged for 17 months (Fig. 3.42c) in both P and PV model glass dried and non-dried, indicating delamination on the glass surface at the interface of the AL and the bulk glass (lighter in colour in figure 3.42).

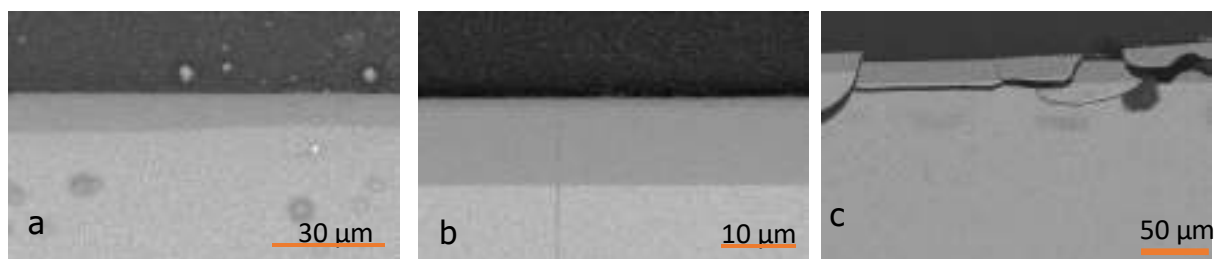


Fig 3.42: SEM images of model glass sample cross-sections a) P 3 months aged b) P 6 months aged c) PV 17 months aged

Taking the model glass aged for three months in the presence of saturated salt solutions as the initial thickness of AL, the change in its thickness was computed from each SEM image and then averaged for each model glass sample (Table 3.12). The value of the AL thickness after salt aging (0 month aged) for P and V model glass were similar to each other at above 3 μm and lower than PV, to begin with. In case of P model glass, the AL thickness was 5.24 μm after 3 months of aging (in addition to 3 months of aging with salt solutions) which increased up to 13 μm by 6 months and further does not show increase until after 17 months of aging. Similarly in case of PV model glass, the AL thickness was 9.08 μm after 3 months of aging increasing up to 12 μm after 9 months of aging which increased to 17 μm after 17 months of aging. As expected, there was a large variation in the thickness across the samples given the highly heterogenous nature of glass corrosion, while in case of V model glass, only 9 and 17 month aged samples were analysed showing similar alteration layer thickness. The mean thickness of the alteration layer for each sample is given in table 3.12 along with the maximum, minimum and standard deviation.

Table 3.12: Mean thickness of the leached layer in μm along with the maximum, minimum and standard deviation for each analysed aged sample along with samples after 3 months of salt aging (0m)

Sample (no. of images)	Mean	Maximum	Minimum	St. Dev
P 0m (17)	3.19	3.65	2.76	0.26
P 3m (27)	5.24	6.50	1.50	2.30
P 6m (32)	13.28	10.30	9.70	0.20
P 9m (36)	12.81	22.70	1.20	6.40
P 12m (20)	13.01	10.30	9.30	0.30
P 17m (57)	16.24	38.60	1.40	10.30
PV 0m (6)	6.45	6.69	6.25	0.18
PV 3m (45)	9.08	4.70	6.30	0.90
PV 6m (13)	10.29	4.00	3.40	0.20
PV 9m (49)	12.30	9.50	1.40	2.10
PV 12m (41)	12.29	11.60	2.50	2.60
PV 17m (40)	17.28	21.90	3.90	5.00
V 0m (24)	3.50	4.17	2.31	0.63
V 9m (21)	3.10	3.50	1.70	0.50
V 17m (42)	3.20	5.20	2.30	0.60

All the SEM profiles such as shown in figure 3.43 show the evidence of leaching out of K^+ and Na^+ . As mentioned earlier, SEM cross-section analyses did not give evidence of Ca^{++} leaching. The change in the K^+ (Fig. 3.44a) and Na^+ (Fig. 3.44b) oxide percentage in the alteration layer as compared to an average composition of the bulk glass was plotted against time to determine the rate of leaching for P, PV and V model glass. Data from V was obtained for only two aging periods of 9 and 17 months since SEM imaging did not show any considerable increase in alteration layer thickness until 17 months of aging. Therefore, due to time restraints, profiling from only two withdrawals periods for V were taken to compare the values with P and PV. There was not much difference for leaching of both K^+ and Na^+ .

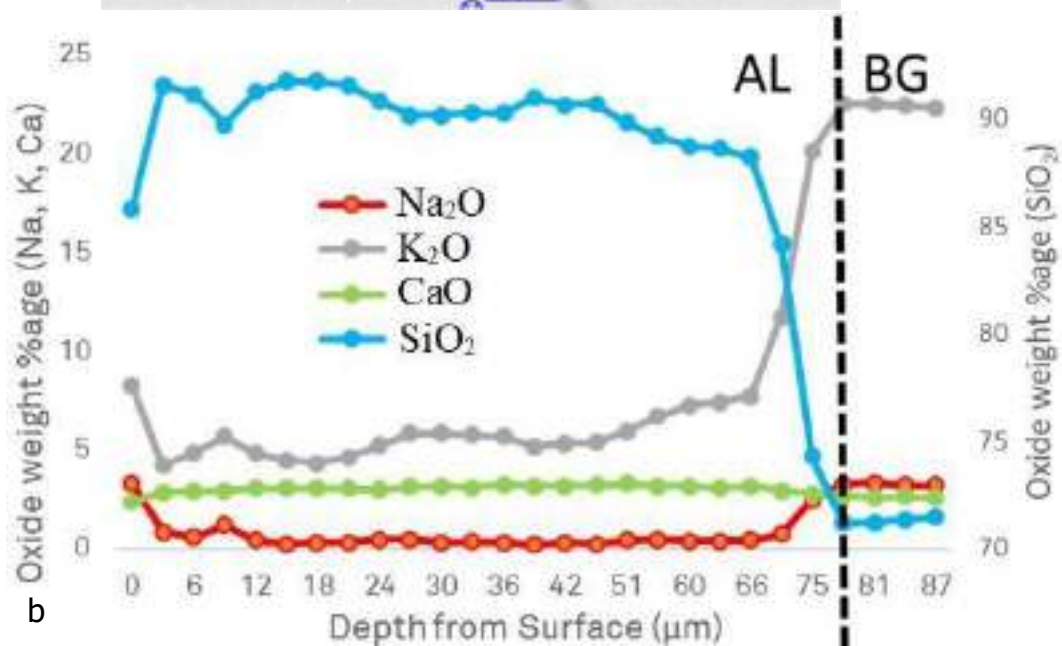
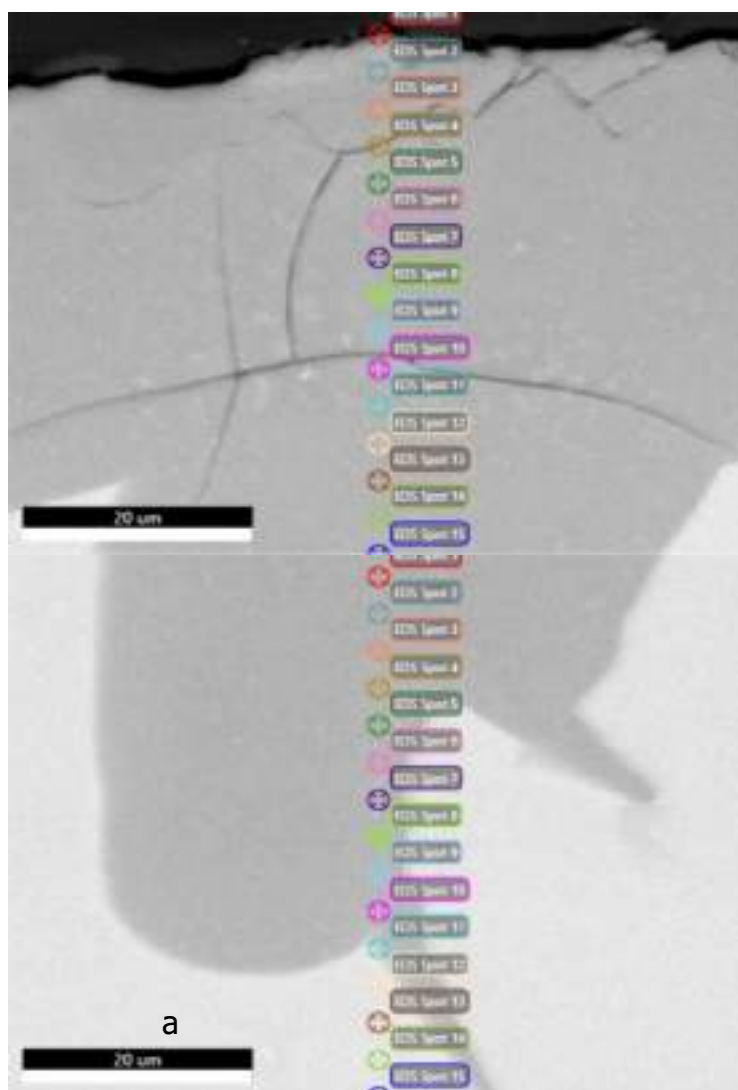


Fig 3.43: a) Overlying SEM images of cross-section used for line profile quantification from P model glass aged for 17 months. b) percentage oxide weight of the four major components of the model glass across the line profile sodium (red), potassium (grey), calcium (green) and silicon (blue)

The modification of chemical composition in a glass was accessed by SEM-EDX profile, an example is given in figure 3.43 for P model glass aged for 17 months, showing the four major components of the model glass. The sodium and potassium percentage were respectively 3.3 and 8.3 % on the top surface owing to the presence of SN; concentrations drop to 0.85 and 4.2% moving into the alteration layer, while the silicon percentage was much higher than the bulk glass. The percentage of the potassium increased gradually from 4 to 7 percent until 66 μm (spot 8 in lower image) after which there was an increase to 12 percent and further increase to 23 % as it reaches 78 μm (spot 12 in lower image). The point number 4 between 6 and 12 microns showed increase in both potassium and sodium and corresponds with a crack. This indicated that the sodium and potassium species were probably concentrated in the crack in the form of SNs. Spot number 12 demarcated the boundary of the alteration layer at approx. 78 μm which was clearly leached of the alkali metals sodium and potassium and the rest of the points after this were present in the bulk glass as understood from the composition as well. Sodium showed a similar trend as potassium. Meanwhile silica percentage was inversely correlated to the alkali metals and showed a gradual decrease in percentage until it reaches the original bulk glass composition. Calcium did not show any significant changes in its percentage showing that it is not or only slightly leached out of the glass matrix.

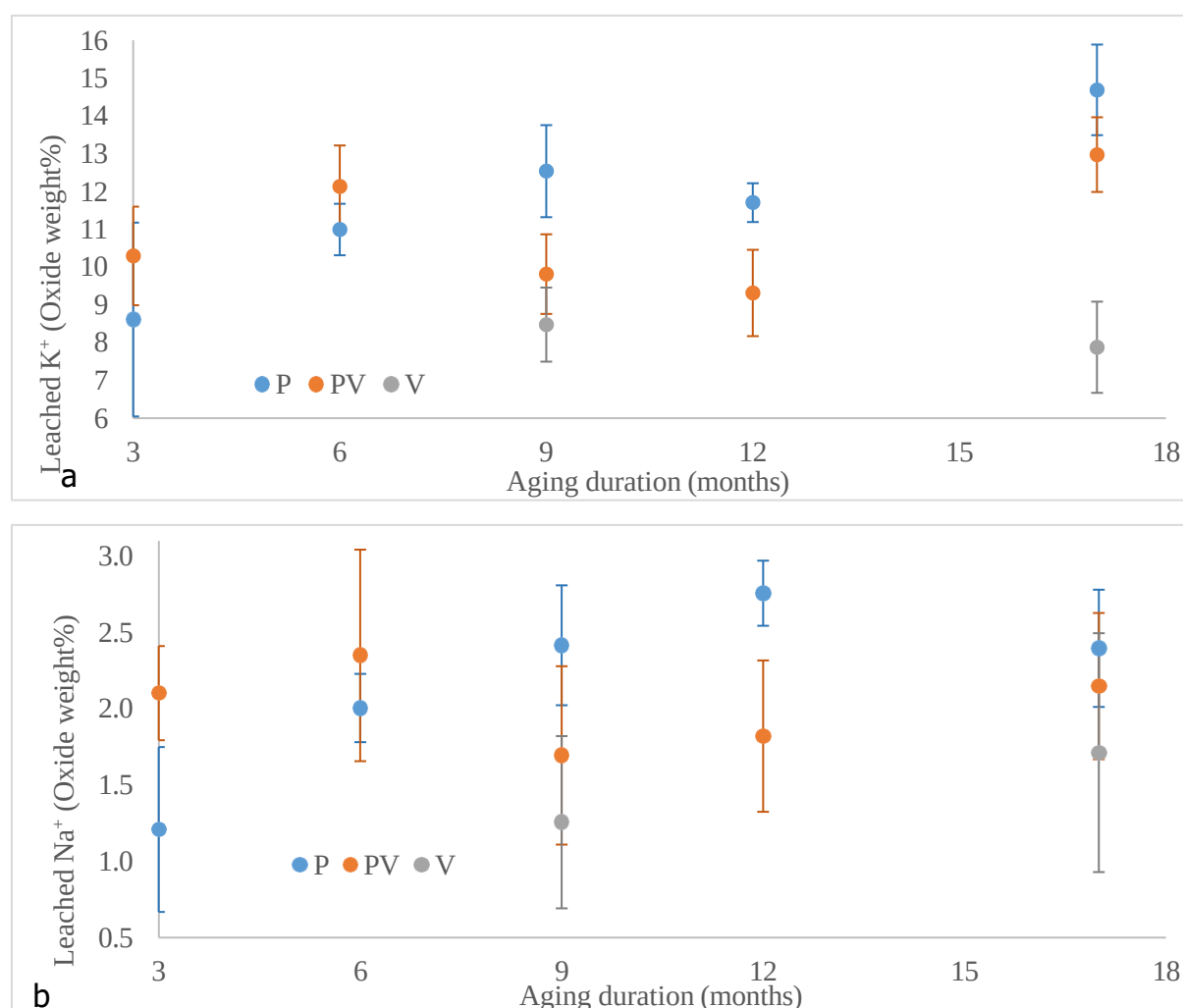


Fig. 3.44: Temporal evolution of the amount of leached out a) K⁺ b) Na⁺ P (blue), PV (orange) and V (grey) model glass calculated from SEM cross sectional analyses. Error bars showing standard deviation

3.10. Analyses of model glass dried to induce cracks

To achieve advanced stages of glass corrosion for understanding the mechanisms better, as well as to develop an adequate documentation protocol, samples aged for 17 months were dried for some time. Coarse cracks were developed on the model glass, these SWIR images showed that the cracks were usually intense in region bounded by the two vertical lines which represent zones of preferential corrosion (see section 3.8). This region appears darker in the image, therefore showing higher water uptake than the rest of the sample. There were either no cracks or fine cracks on the rest of the top surface (Fig. 3.45a-c). Interestingly, the spectra of the dried model

glass did not show any significant difference as compared to the model glass aged to 17 months which were not dried (Fig. 3.45d) for all the P, PV and V model glass indicating that drying for 15 minutes did not dehydrate the corroded glass matrix. Additionally, there was no change in the weight of the model glass before and after drying.

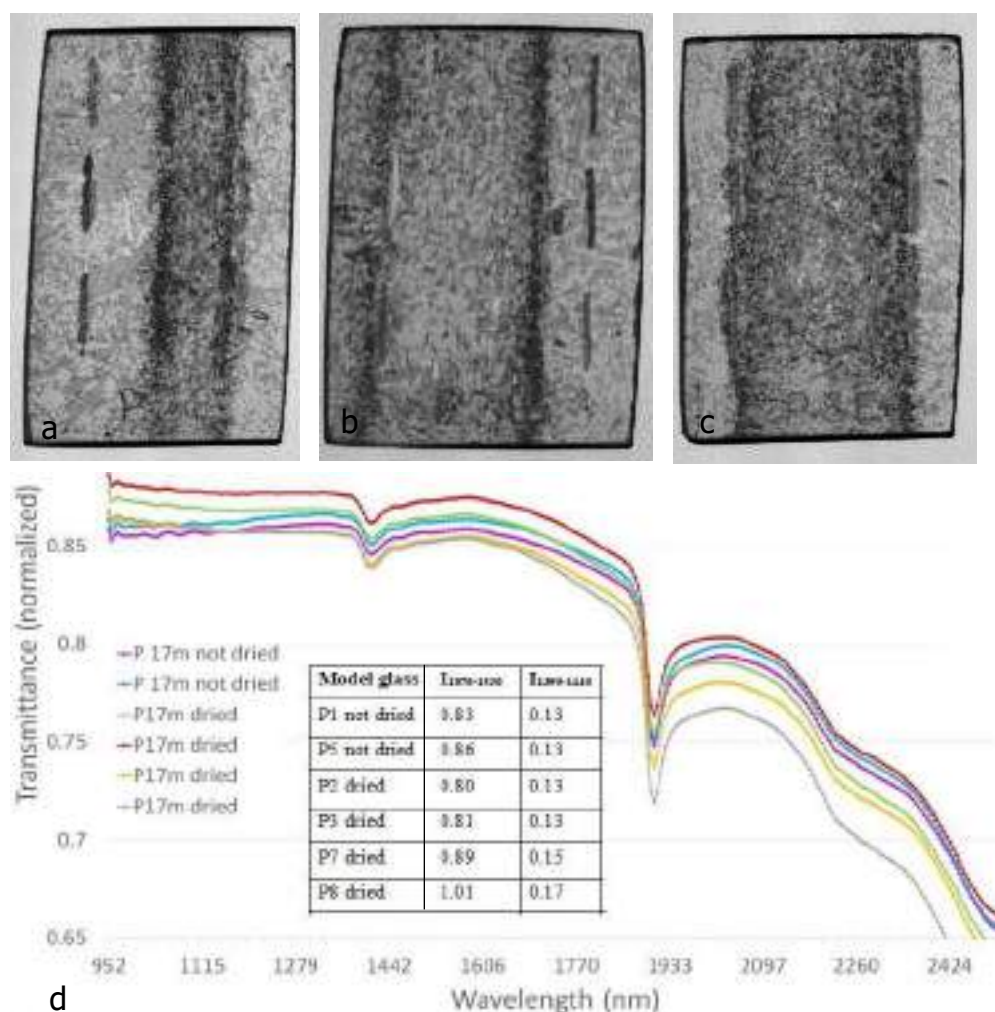


Fig. 3.45: a-c) SWIR images recorded with 30 cm lens (1906 nm) of P model glass sample aged for 17 months and dried (Field of view: $\approx 5 \text{ cm} \times 3 \text{ cm}$); d) Average spectra of P model glass aged for 17 months compared to those aged for 17 months and table showing the values of the integral for the bands $I_{1390-1440}$ and $I_{1876-1936}$

3.11. Conclusions

The various analytical and imaging techniques were successful in categorizing corrosion in the different model glass aged for different periods in three different conditions i.e., P, PV and P. The VOC concentration was not able to be measured but P might have had higher amount of VOCs than PV and therefore, showed higher extent of corrosion in almost all the parameters. Both PV and P corroded in higher concentrations of VOCs showed a much higher extent of corrosion than V model glass corroded at much lower concentrations. The wet SN and cracks were quantified successfully using DM while Raman and FTIR spectroscopy helped to understand the structural changes in silicate species. As far as RTI was concerned, the range of changes that the RTI system could detect went from microscopic fine cracks to coarse cracks which could only be quantified on RTI maps by manual tracing. Automatic detection and quantification of SN was successful in case of larger sized SN for P and PV but not in case of smaller SN such as on V model glass. HSI in the SWIR range was successful in providing global scale information about corrosion via water and hydroxyl absorbed by the glass matrix. The SWIR images of the model glass showed a lot of heterogeneity in corrosion, specifically due to the presence of surface discontinuities presumably developed during manufacturing. The SWIR spectra was helpful in quantifying the extent of corrosion by using water and hydroxyl peaks. The heterogeneity was also observed with SEM images of the alteration layer along with elemental profiles which showed that majorly the monovalent alkalis were leached out of the alteration layer and calcium did not show much changes. Finally, delaminations were also developed by drying the corroded model glass for 15 minutes at 100°C which however did not result in any extraction of the absorbed water.

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SECTION III

Chapter 4: Mechanisms of corrosion

4.1. Correlation between different characterization parameters

A correlation matrix was calculated for the various characterization results gathered in chapter 3, to compare the physical signs of corrosion namely crack density (section 3.7.2) (CD), percentage area covered by SN (section 3.7.1) (% SN) and percentage change in weight (section 3.8.2) (ΔW) with chemical changes in the corroded glass such as FTIR Q4/Q3 ratio (section 3.8.3) (Q4/Q3), Alteration Layer thickness (section 3.10) (AL), SWIR A_{1906} (section 3.8.4) (A_{1906}), Raman Q3/Q2 ratio (section 3.8.3) (Q3/Q2), Raman $H_2O+OH/Si-O$ ratio (section 3.8.4) (H_2O), leached K^+ (K^+) (section 3.10) and Na^+ (Na^+) (section 3.10) and polymerisation index (I_p) (section 3.8.3) from P, PV and V model glass. Many correlations were found (considering $\chi^2 \geq 0.70$ as significant).

In order to understand the influence of different aging environment, correlation matrixes were calculated separately for P, PV and V model glass.

In case of P model glass (Table 4.1), the number of “relevant” correlations were much higher than for PV (Table 4.2) and V (Table 4.3). Moreover, it was found that the crack density was in negative correlation with both percentage area covered by SN as well with percentage change in weight. This showed that cracks develop more only when the percentage area covered by SN is reduced, indicating that the absence of the wet hygroscopic SN on the surface might induce drying up of the local surface leading to development of cracks (Table 4.1). However, it cannot be excluded that, the detection of cracks might also be lower due to the SN covering a larger surface area. Such wet SN might obscure the cracks under them which can be detected better after the SN have run off from the surface.

The percentage of weight change is highly correlated with the percentage of area covered by SN which led to an increase in the weight in the early stages since all the extracted cations stayed at the surface to create wet SN along with the atmospheric anions and moisture, and it was only after the SN started to run off that weight loss became visible. Apart from this, the weight change percentage showed negative correlation with the FTIR Q4/Q3 ratio, since the values of the ratio increase with increasing corrosion as the peak area for Q4 species remain more or less unchanged while the peak area for Q3 species constantly decrease. Therefore, as weight decreases due to corrosion, FTIR Q4/Q3 ratio increases. Similarly, the AL thickness and SWIR A_{1906} were also negatively correlated to changes in weight because the AL depleted in alkali is less dense than bulk glass and therefore, as its thickness increases, the weight of the glass decreases. Similarly, SWIR A_{1906} increases with increased absorption of H_2O and OH^- in the glass leading to decrease in the weight of the corroded glass. Understandably this is why weight change was also negatively correlated with leached out K^+ , the more the amount of K^+ leached out of glass, the lower will be the weight. Additionally, the weight of the model glass reduces as the degree of polymerisation increases. The Raman Q3/Q2 ratio was in positive correlation with the weight change because with advanced leaching this ratio decreases with time while weight of the model glass also reduces.

Table 4.1: Correlation matrix for various characterisation parameters: crack density (CD), percentage area covered by SN (% SN) and percentage change in weight (ΔW), FTIR Q4/Q3 ratio (Q4/Q3), Alteration Layer thickness (AL), SWIR A_{1906} (A_{1906}), Raman Q3/Q2 ratio (Q3/Q2), Raman $H_2O+OH/Si-O$ ratio (H_2O), leached K^+ (K^+) and Na^+ (Na^+) and polymerisation index (I_p) for P model glass (Bold numbers indicate significant correlations with $\chi^2 > 0.70$)

<i>P</i>	<i>CD</i>	<i>% SN</i>	ΔW	<i>Q4/Q3</i>	<i>AL</i>	A_{1906}	<i>Q3/Q2</i>	H_2O	K^+	Na^+	<i>I_p</i>
CD	1										
% SN	-0.88	1									
ΔW	-0.94	0.91	1.00								
Q4/Q3	0.84	-0.55	-0.78	1.00							
AL	0.75	-0.45	-0.74	0.78	1.00						
A1906	0.87	-0.60	-0.85	0.98	0.88	1.00					
Q3/Q2	-0.80	0.49	0.79	-0.95	-0.93	-0.99	1.00				
H₂O	0.38	-0.03	-0.35	0.81	0.52	0.74	-0.76	1.00			
K⁺	0.86	-0.68	-0.92	0.86	0.92	0.95	-0.95	0.57	1.00		
Na⁺	0.57	-0.14	-0.50	0.88	0.83	0.88	-0.92	0.88	0.75	1.00	
I_p	0.80	-0.52	-0.75	0.99	0.72	0.96	-0.93	0.86	0.83	0.87	1

In case of PV model glass (Table 4.2), it was found that the crack density was in negative correlation with Q4/Q3 FTIR ratio indicating that the increase in the ratio due to increasing corrosion would lead to decrease in the crack density, which is anomalous to the rest of the results. This is the case for all the correlations of FTIR Q4/Q3 ratio which are exactly opposite of the expected trends. Therefore, it could be surmised that the ratio does not give correct values in case of PV and was considered as an outlier. Crack density showed similar correlations like P model glass, in case of AL thickness, SWIR A_{1906} , Raman Q3/Q2 ratio and I_p . The interesting point is that crack density shows no correlation with leached out K^+/Na^+ but a positive correlation with normalized Raman water band and very strong correlation with SWIR A_{1906} . This might indicate that probably leaching was not the predominant factor for the development of cracks in PV model glass. Moreover, it is interesting to note that the leached K^+ and Na^+ were also not correlated to any of the other parameters in contrast to P model glass. The reason for the PV model glass having a higher pH than P model glass could not be interpreted with these results.

This means that the pH of PV surface might be raised resulting in lower concentration of acidic ions specifically formates promoting network dissolution over leaching. In contrast to P model glass therefore, the percentage area covered by SN for PV glass displayed significant and negative correlations with AL thickness, SWIR A_{1906} , Raman normalized water band and I_p . The Raman Q3/Q2 ratio reduces with increasing corrosion which was why it showed positive correlation with the percentage area covered by SN.

Table 4.2: Correlation matrix for various characterisation parameters: crack density (CD), percentage area covered by SN (% SN) and percentage change in weight (ΔW), FTIR Q4/Q3 ratio (Q4/Q3), Alteration Layer thickness (AL), SWIR A_{1906} (A_{1906}), Raman Q3/Q2 ratio (Q3/Q2), Raman $H_2O+OH/Si-O$ ratio (H_2O), leached K^+ (K^+) and Na^+ (Na^+) and polymerisation index (I_p) for PV model glass (Bold numbers indicate significant correlations with $\chi^2 > 0.70$).

PV	CD	% SN	ΔW	Q4/Q3	AL	A_{1906}	Q3/Q2	H_2O	K^+	Na^+	I_p
CD	1.00										
% SN	-0.95	1.00									
ΔW	-0.93	0.89	1.00								
Q4/Q3	-0.84	0.90	0.74	1.00							
AL	0.88	-0.95	-0.94	-0.76	1.00						
A_{1906}	0.99	-0.98	-0.92	-0.85	0.92	1.00					
Q3/Q2	-0.86	0.88	0.89	0.58	-0.94	-0.90	1.00				
H_2O	0.80	-0.73	-0.68	-0.43	0.69	0.82	-0.88	1.00			
K^+	0.08	-0.34	-0.20	-0.05	0.50	0.22	-0.49	0.24	1.00		
Na^+	-0.42	0.23	0.37	0.50	-0.09	-0.30	-0.04	0.04	0.78	1.00	
I_p	0.93	-0.86	-0.82	-0.63	0.82	0.93	-0.92	0.97	0.21	-0.14	1

In case of V model glass (Table 4.3), fewer correlations were established. The change in weight was in positive correlation with alteration thickness, owing to the fact that the weight of V model glass increased due to formation of wet SN on the surface which did not run off from the surface. Therefore, even though the alkali leached out of the bulk glass, they still remained on the surface of the glass thereby increasing the weight with time. Similarly, weight change was correlated to other parameters such as Raman Q3/Q2 ratio and normalized Raman water band negatively and positively, respectively in contrast with P and PV model glass. This also owes to the fact that the continual increase of weight of V model glass does not reflect the material loss due to leaching out of alkali from the model glass as a result of corrosion. AL thickness was positively correlated with FTIR Q4/Q3 ratio since they both increase with increasing corrosion. The SWIR A_{1906} did not show any correlations. The most interesting part was that the leached-out K^+ was not correlated with any of the parameters other than leached out Na^+ . However, the leached out Na^+ was positively correlated to the FTIR Q4/Q3 ratio and Raman normalized water band as well as negatively correlated with Raman Q3/Q2 ratio and leached out K^+ . This might indicate that Na^+ might be the alkali which leaches out at early stages of corrosion later followed by K^+ . According to previous literature [1][2], Na^+ ions are known to be more mobile than K^+ ions. Accordingly, it is possible that Na^+ ions may leach out before K^+ ions from corroded glass. However, it is important to consider that the leaching behaviour of ions is a complex process influenced by various factors, including the specific conditions of the corrosion environment. Further research specifically focused on the leaching behaviour of Na^+ and K^+ ions in mixed-alkali silicate glasses is needed to provide a more definitive answer regarding their leaching sequence.

Table 4.3: Correlation matrix for various characterisation parameters: crack density (CD), percentage area covered by SN (% SN) and percentage change in weight (ΔW), FTIR Q4/Q3 ratio (Q4/Q3), Alteration Layer thickness (AL), SWIR A₁₉₀₆ (A₁₉₀₆), Raman Q3/Q2 ratio (Q3/Q2), Raman H₂O+OH/Si-O ratio (H₂O), leached K⁺ (K⁺) and Na⁺ (Na⁺) and polymerisation index (I_p) for V model glass (Bold numbers indicate significant correlations with $\chi^2 > 0.70$).

V	% SN	ΔW	Q4/Q3	AL	A1906	Q3/Q2	H ₂ O	K ⁺	Na ⁺	I _p
% SN	1.00									
ΔW	0.96	1.00								
Q4/Q3	0.81	0.93	1.00							
AL	0.69	0.76	0.90	1.00						
A1906	0.58	0.36	0.01	-0.01	1.00					
Q3/Q2	-0.69	-0.84	-0.84	-0.65	-0.09	1.00				
H ₂ O	0.62	0.77	0.91	0.76	-0.26	-0.66	1.00			
K ⁺	-0.11	-0.34	-0.39	-0.02	0.40	0.59	-0.55	1.00		
Na ⁺	0.36	0.59	0.70	0.38	-0.38	-0.78	0.78	-0.93	1.00	
I _p	0.38	0.49	0.35	0.08	0.25	-0.79	0.15	-0.61	0.59	1

From the three different aging conditions, the parameters which produced the maximum correlations for P and PV model glass were fitted to find the temporal kinetics of corrosion namely crack density, AL thickness, SWIR A₁₉₀₆ and Raman Q3/Q2 ratio.

In case of V model glass, FTIR Q4/Q3 ratio, Raman Q3/Q2 ratio and normalized Raman water band produced most correlations and were therefore fitted to find the temporal trends. These curves will be discussed in the context of the two main mechanisms of corrosion namely leaching (interdiffusion) or network dissolution (congruent dissolution) in sections 4.2 and 4.3, respectively.

4.2. Leaching

5 to 10 line profiles for each sample were analysed using EDX and quantified using bulk glass composition of the model glass obtained by EPMA as standard, results are summarised in Table 4. This gave detailed data for the changes in the elemental composition in the leached layer as compared to the glass bulk for each analysed aged sample. The Δ_{bulk} values for sodium and potassium were negative proving that they were leached out of the alteration layer. At the same time, the alteration layer was more enriched in aluminium, silicon and calcium.

In case of P, the Δ_{bulk} values for potassium and sodium could not show any clear temporal trend. However higher values for potassium indicate that it was preferentially leached during aging. This is not the case with PV model glass, where sodium was preferentially leached after 17 months as compared to potassium. However, there was no temporal trend visible for the potassium values of PV model glass. For V model glass, the sodium values showed an increase but potassium values did not seem changing, which were still lower even after 17 months of aging than values for P and PV after 3 months of aging. No significant leaching out for calcium was detected whichever the aging condition.

Table 4.4: SEM–EDX Elemental composition (mean and standard deviation, σ) of bulk glass, of Alteration Layer (AL) and $\Delta\text{bulk}([\text{AL}]-[\text{Bulk}])/[\text{Bulk}]$ (in weight percentage of oxides) of P, PV and V model glass aged for 3, 6, 9, 1, and 17 months (only 9 and 17 months for V condition)

			Na ₂ O	Al ₂ O ₃	SiO ₂	K ₂ O	CaO
P3m	Bulk	Mean $\pm\sigma$	3.89 $\pm$ 1.48	0.47 $\pm$ 0.19	63.75 $\pm$ 23.91	18.69 $\pm$ 7.02	2.09 $\pm$ 0.79
	AL	Mean $\pm\sigma$	2.81 $\pm$ 1.17	0.64 $\pm$ 0.27	72.07 $\pm$ 27.12	11.04 $\pm$ 4.69	2.32 $\pm$ 0.90
		Δ Bulk	-0.28	0.38	0.13	-0.41	0.11
P6m	Bulk	Mean $\pm\sigma$	3.96 $\pm$ 0.20	0.52 $\pm$ 0.04	71.16 $\pm$ 0.28	21.87 $\pm$ 0.17	2.50 $\pm$ 0.06
	AL	Mean $\pm\sigma$	1.96 $\pm$ 0.12	0.67 $\pm$ 0.02	83.59 $\pm$ 0.68	10.87 $\pm$ 0.63	2.91 $\pm$ 0.04
		Δ Bulk	-0.51	0.30	0.17	-0.50	0.17
P9m	Bulk	Mean $\pm\sigma$	3.89 $\pm$ 0.34	0.51 $\pm$ 0.06	71.50 $\pm$ 0.35	21.51 $\pm$ 0.40	2.55 $\pm$ 0.04
	AL	Mean $\pm\sigma$	1.90 $\pm$ 1.16	0.70 $\pm$ 0.14	85.51 $\pm$ 2.26	8.97 $\pm$ 1.45	2.88 $\pm$ 0.17
		Δ Bulk	-0.51	0.37	0.20	-0.58	0.13
P12m	Bulk	Mean $\pm\sigma$	4.15 $\pm$ 0.21	0.47 $\pm$ 0.06	71.96 $\pm$ 0.06	20.98 $\pm$ 0.16	2.45 $\pm$ 0.05
	AL	Mean $\pm\sigma$	1.39 $\pm$ 0.28	0.59 $\pm$ 0.10	85.85 $\pm$ 0.34	9.27 $\pm$ 0.47	2.89 $\pm$ 0.07
		Δ Bulk	-0.66	0.27	0.19	-0.56	0.18
P17m	Bulk	Mean $\pm\sigma$	3.75 $\pm$ 0.34	0.50 $\pm$ 0.06	70.90 $\pm$ 0.82	22.09 $\pm$ 0.46	2.71 $\pm$ 0.43
	AL	Mean $\pm\sigma$	2.31 $\pm$ 2.40	0.71 $\pm$ 0.22	85.35 $\pm$ 6.26	8.58 $\pm$ 3.13	3.04 $\pm$ 0.61
		Δ Bulk	-0.38	0.43	0.20	-0.61	0.12
PV3m	Bulk	Mean $\pm\sigma$	4.04 $\pm$ 0.23	0.50 $\pm$ 0.02	71.80 $\pm$ 0.27	21.23 $\pm$ 0.18	2.42 $\pm$ 0.04
	AL	Mean $\pm\sigma$	1.94 $\pm$ 0.32	0.66 $\pm$ 0.10	83.68 $\pm$ 1.32	10.94 $\pm$ 1.37	2.74 $\pm$ 0.11
		Δ Bulk	-0.52	0.32	0.17	-0.48	0.13
PV6m	Bulk	Mean $\pm\sigma$	4.34 $\pm$ 0.16	0.53 $\pm$ 0.04	71.66 $\pm$ 0.15	21.02 $\pm$ 0.10	2.45 $\pm$ 0.04
	AL	Mean $\pm\sigma$	1.99 $\pm$ 0.63	0.72 $\pm$ 0.07	85.56 $\pm$ 1.55	8.89 $\pm$ 1.08	2.84 $\pm$ 0.11
		Δ Bulk	-0.54	0.35	0.19	-0.58	0.16
PV9m	Bulk	Mean $\pm\sigma$	3.31 $\pm$ 0.36	0.45 $\pm$ 0.09	72.89 $\pm$ 0.59	20.73 $\pm$ 0.38	2.63 $\pm$ 0.08
	AL	Mean $\pm\sigma$	1.61 $\pm$ 0.56	0.52 $\pm$ 0.18	84.08 $\pm$ 1.24	10.91 $\pm$ 0.87	2.87 $\pm$ 0.09
		Δ Bulk	-0.51	0.15	0.15	-0.47	0.09
PV12m	Bulk	Mean $\pm\sigma$	3.35 $\pm$ 0.48	0.46 $\pm$ 0.09	73.19 $\pm$ 1.17	20.38 $\pm$ 0.84	2.62 $\pm$ 0.05
	AL	Mean $\pm\sigma$	1.53 $\pm$ 0.19	0.57 $\pm$ 0.09	83.86 $\pm$ 1.55	11.07 $\pm$ 1.53	2.97 $\pm$ 0.06
		Δ Bulk	-0.54	0.23	0.15	-0.46	0.13
PV17m	Bulk	Mean $\pm\sigma$	2.85 $\pm$ 0.41	0.46 $\pm$ 0.02	73.46 $\pm$ 0.95	20.65 $\pm$ 0.68	2.58 $\pm$ 0.09
	AL	Mean $\pm\sigma$	0.70 $\pm$ 0.16	0.50 $\pm$ 0.03	88.28 $\pm$ 0.89	7.68 $\pm$ 0.68	2.84 $\pm$ 0.16
		Δ Bulk	-0.75	0.09	0.20	-0.63	0.10
V9m	Bulk	Mean $\pm\sigma$	3.86 $\pm$ 0.48	0.47 $\pm$ 0.11	71.59 $\pm$ 0.63	21.59 $\pm$ 0.15	2.50 $\pm$ 0.06
	AL	Mean $\pm\sigma$	2.88 $\pm$ 0.64	0.74 $\pm$ 0.08	80.60 $\pm$ 1.43	13.12 $\pm$ 0.90	2.67 $\pm$ 0.08
		Δ Bulk	-0.25	0.59	0.13	-0.39	0.07
V17m	Bulk	Mean $\pm\sigma$	4.19 $\pm$ 0.82	0.54 $\pm$ 0.04	71.76 $\pm$ 1.99	21.04 $\pm$ 1.28	2.47 $\pm$ 0.13
	AL	Mean $\pm\sigma$	2.48 $\pm$ 0.20	0.67 $\pm$ 0.07	81.09 $\pm$ 0.71	13.16 $\pm$ 0.81	2.60 $\pm$ 0.02
		Δ Bulk	-0.41	0.25	0.13	-0.37	0.05

The two selected parameters for P and PV which could be attributed to leaching were AL thickness and Raman Q3/Q2 ratio and for V only Raman Q3/Q2 ratio was selected. For glass corrosion in unsaturated media, most of the literature has suggested a square-root temporal kinetics for leaching or interdiffusion [3][4][5] while few studies have shown an exponential increase in hydration thickness with time.

Therefore, regression curves were also fitted to both AL thickness (Fig. 4.1) and Raman Q3/Q2 ratio (Fig. 4.2) and showed a good linear fit for P and PV with the square root of time in hours in accordance with previous literature mentioned above. In case of V, leaching does not seem

to follow the linear dependence on square root of time but showed a polynomial fit of degree 2 showing that the rate of corrosion increases with time.

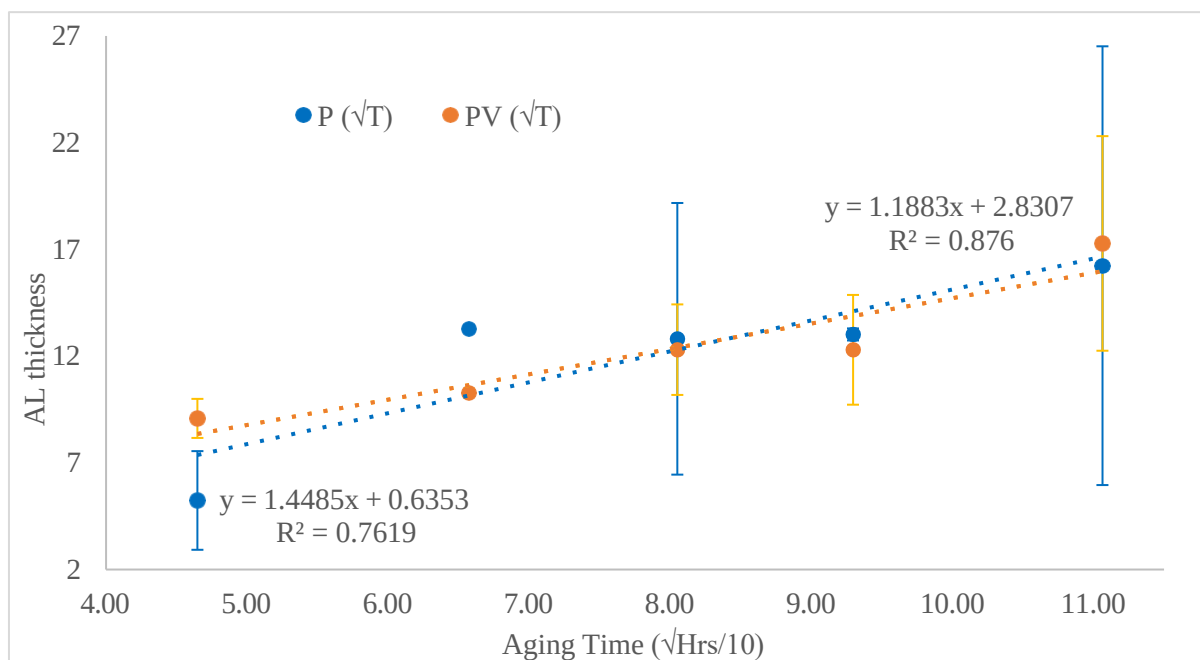


Fig. 4.1: Temporal progression of average thickness of the alteration layer developed on P (blue) and PV (orange) model glass measured by SEM with error bars showing standard deviation

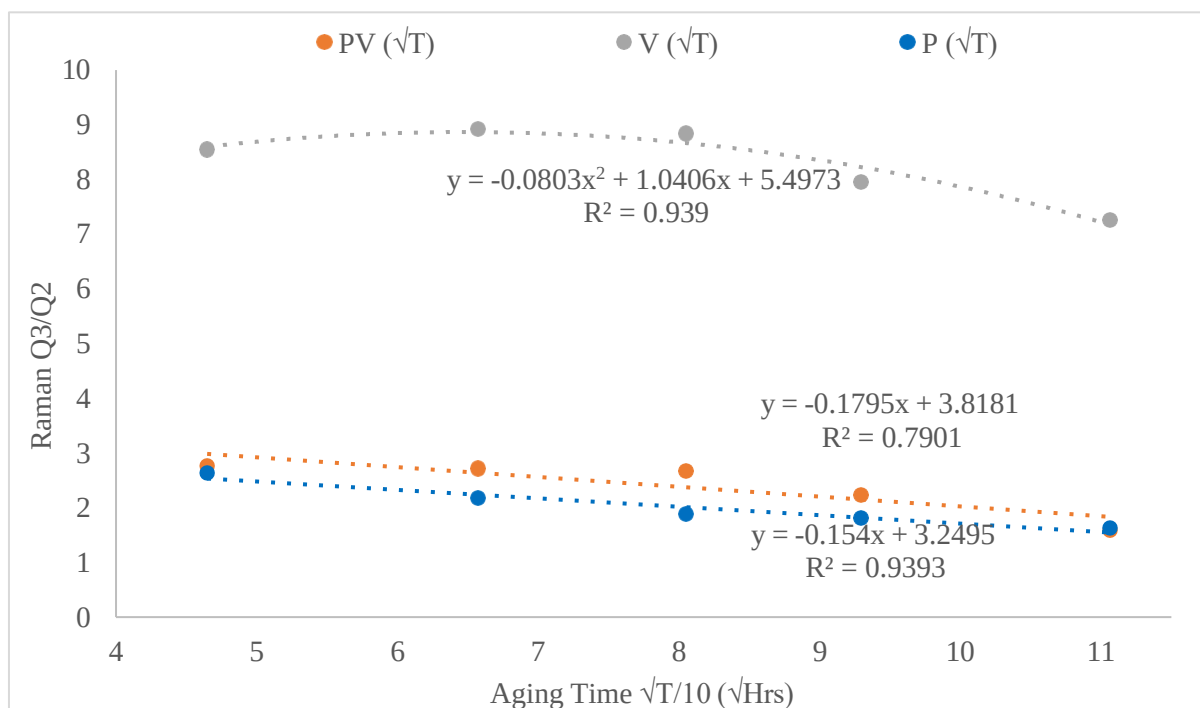


Fig. 4.2: Temporal progression of Raman Q3/Q2 developed on P (blue), PV (orange) and V (grey) model glass. Average spectra calculated using Spectragryph

4.3. Leaching + network dissolution

The other two selected parameters of P and PV namely crack density and SWIR A_{1906} could be attributed to leaching along with network dissolution. Previous literature suggests a linear dependence with time for congruent dissolution after the initial faster rate of interdiffusion or leaching [4][8].

Many different curves were fitted out of which linear fitting was found to be with the highest regression coefficient for all the data series. This was in accordance with the literature as well. Both P and PV showed a linear increase in SWIR A_{1906} indicating an overall increase in water and OH^- absorption by the corroded model glass overtime (Fig 4.3), indicating that there is constant rate of corrosion for the P and PV model glass.

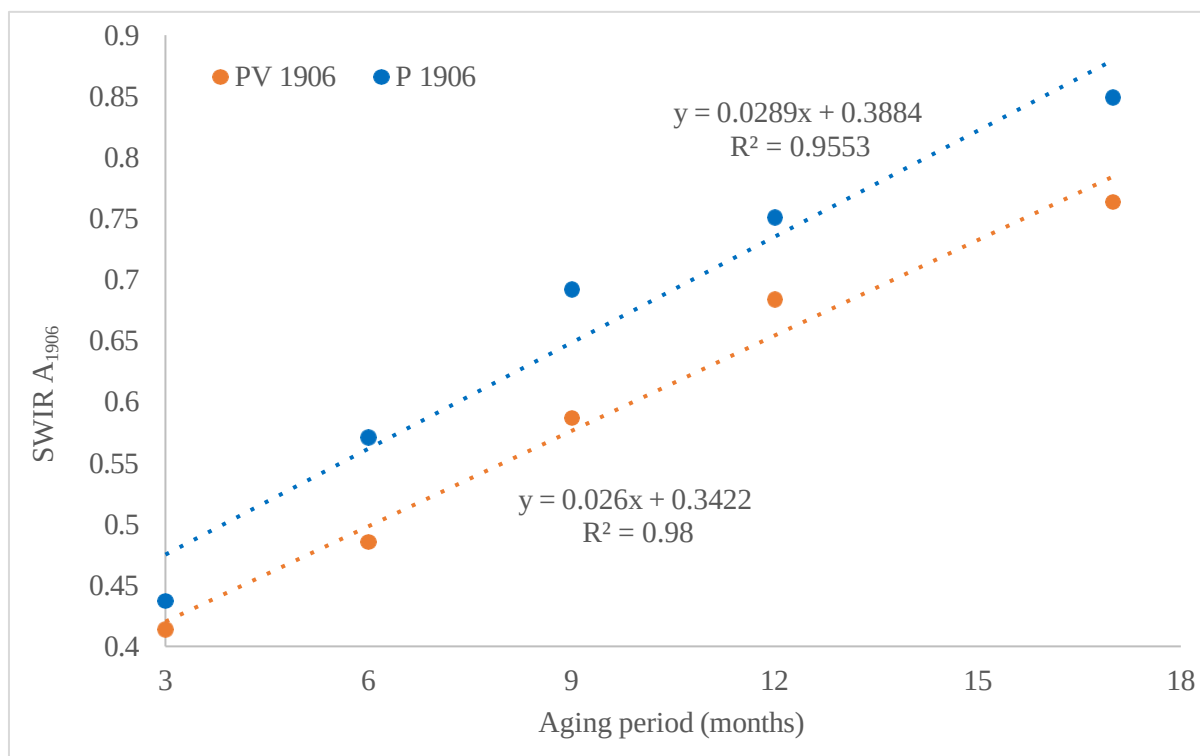


Fig. 4.3: Temporal progression of the SWIR A_{1906} for P (blue) and PV (orange) conditions. Average spectra calculated using ImageJ

As mentioned in 3.4, cracking was found only in P and PV model glass and not in V model glass. Therefore, there must be a certain prerequisite of the extent of leaching and network dissolution which was not attained by V model glass until 17 months of aging including all the parameters which were correlated to crack density such as AL thickness, water and OH^- content, leached out K^+ and the polymerization index. The data shows that all of these parameters displayed much lower values for V model glass than that in P and PV for every aging period and therefore can be considered as the limiting factor for the development of cracks.

The crack density for PV and P displayed a linear tendency of increasing with aging period with constant rate of increase for both. Interestingly, both the values and the rate of increase is higher for P model glass than PV model glass (Fig 4.4).

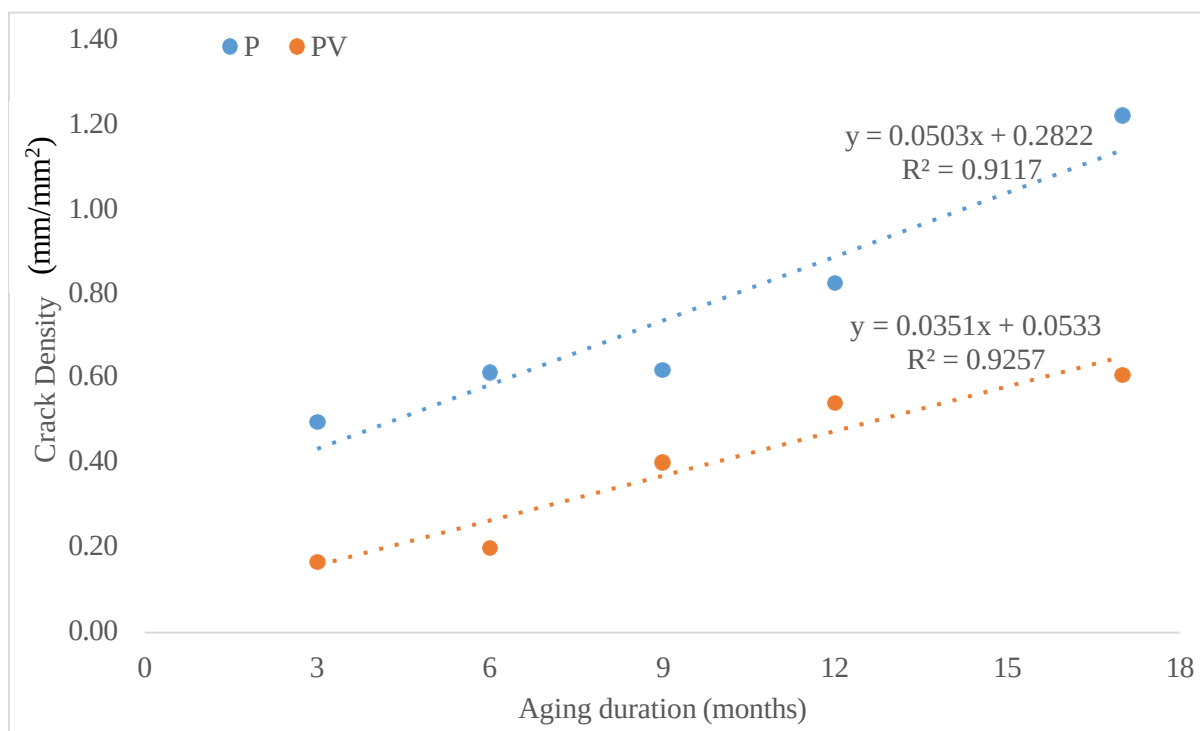


Fig. 4.4: Temporal progression of total crack density for P (blue) and PV (orange) model glass calculated using DM images

The curve fitting in case of V model glass for normalized water band and FTIR Q4/Q3 ratio produced only polynomial fit of degree 2 with time showing that the rate of leaching and network dissolution increases with time at low VOC concentration, unlike a constant rate of increase for P and PV model glass at much higher VOC concentration (Fig. 4.5 and 4.6). Although both the rate of leaching and dissolution were increasing with time for V model glass, the absolute value of the rate at 17 months was still much lower than that for P and PV. Nonetheless, the possibility cannot be denied that as the rate increases with time, at some point in future it might still attain a value at which irreversible damage due to corrosion could occur on the glass object.

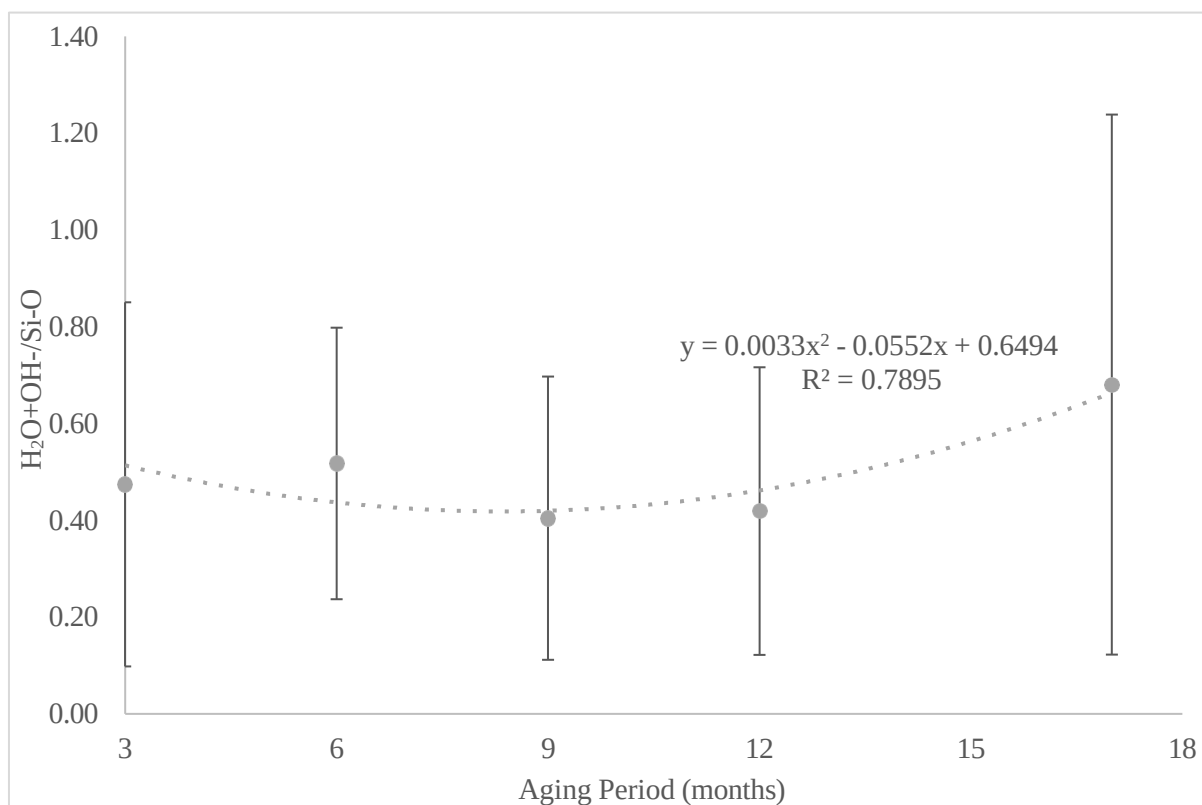


Fig. 4.5. Temporal progression of Raman normalized water band for V model glass (grey) calculated using Raman deconvolution with error bars showing standard deviation

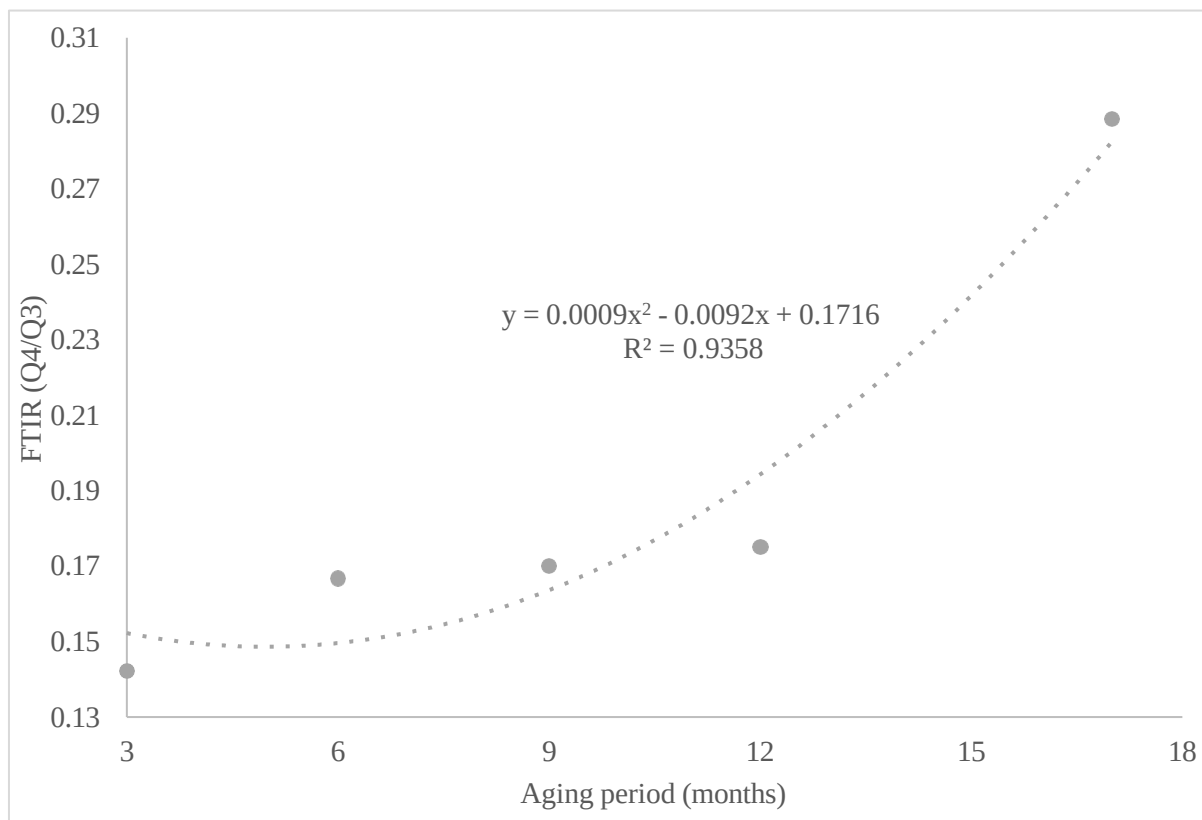


Fig. 4.6. Temporal progression of Q4/Q3 ratio for V model glass (grey) calculated using FTIR spectra. Average spectra calculated using Spectragryph

4.4. Chemical characterisation of salt neocrystallizations

In mixed pollutant environment, different pollutants compete with one another, which may be due to differences in their acid-ionization constants. For P and PV model glass, formates dominated the salt neocrystallizations even though the amount of liquid formic acid used in the aging setup was 2.5 times less than the amount of liquid acetic acid. The higher volatility of formic acid means that it evaporates more readily at lower temperatures than acetic acid, making it more likely to be encountered as a vapor or gas in the environment and therefore dominating the desiccator environment.

Formic acid was also observed on the surface of the model glass with FTIR measurements (section 3.7.5) indicating that the atmosphere inside the desiccator was saturated with so much formic acid that it precipitated on the surface of the aging model glass due to which the pH on the surface didn't rise to more than 2 (as tested by the pH strips). Therefore, water and formic acid were the two main factors controlling glass degradation in P and PV conditions. Further research would be needed to understand the quantity of formic acid present on the model glass surface in the different conditions which might affect the corrosion mechanisms greatly. Potassium (DRH=19% RH) and sodium formate (DRH=51%) [11] do not crystallise since their mixture is usually deliquescent at a RH value lower than normal ambient RH.

In case of V model glass, where formic acid and acetic acid gaseous concentration was much lower and comparable with each other. Formates were found at almost all the points of analyses along with more instances of acetates as compared to P and PV.

Apart from these, fewer unexpected instances of sulphates and carbonates were also observed on the model glass as discussed in section 3.8.1 showing the reaction of the alkali present in the glass with other atmospheric pollutants like SO₂ and CO₂ already present in the ambient environment.

4.5. Understanding of the delamination

In certain instances, the corroded layer may detach partially or completely from the bulk glass, leading to partial or complete delamination. Such detachment happened in case of P and PV model glass aged for 17 months (Annex IV), only in very dry conditions after the RH went below 45% in laboratories outside Switzerland in winter¹, where the model glass were taken for HSI. This delamination occurred mostly along the lines of higher corrosion developed on the model glass due to already present surface discontinuities (section 3.9). More severe network of cracking was developed in P and PV model glass aged for 17 months and dried for 15 minutes at 100 ± 2°C. This indicated that a certain threshold of relative humidity or in other words dry surface conditions initiate the development of delamination. The microscopic analyses of the delaminated P and PV model glass surface aged for 17 months and dried for 15 minutes in transmitted light at 100 times original magnification showed the presence of a coarse

¹ The model glass were taken to Norway for Hyperspectral Imaging.

cracking network wherein some areas appear darker than the others (Fig. 4.7a). These were the delaminated regions with a liquid underneath them. This liquid can be seen as entering some of the newly detached scales via capillary suction. While in the non-dried model glass, the deliquescent salt neocrystallizations were present in higher quantity on the surface as long as no dense crack network or delamination were present but as soon as a crack network developed in the dried model glass, the solution was “sucked” into the cracks. Giving rise to the hypothesis that the salt solution tries first to enter the vertical cracks and went under the partially detached flake as soon as they appeared.

Such liquid pockets trapped under the scales were also found by Robinet [9]. The liquid was not analysed but according to this reference, probably contained concentrated KOH solution as potassium carbonates and sulphates crystallised under the glass on contact with CO₂ and SO₂ in the air. Although the liquid under the scales was not analysed in this research as well, it is speculated that the liquid is nothing other than the liquid SN (majorly formates) which entered under the delaminated scales and thus also makes the cleaning of the corroded glass difficult.

The microphotographs using reflected light showed the presence of the few remaining wet formate salt neocrystallizations present on the surface (Fig. 4.7b). In addition, they gave even more details on the topology of the delamination. The specular reflection coming off the delaminated scales show a radial conchoidal fracture pattern which is the result of stress on the glass and its breakage due to contraction. Such fractures extend outward in a line from the point on the glass where the stress originated. The point of the origin of the stress was found to be at the inside of the flakes extending outwards towards the edges of the cracks. This stress was generated by the contraction of glass in dry conditions, which draws moisture out of the cracks in the glass, causing the glass to contract. The delamination possibly originated at the interface of the alteration layer and bulk glass due to their differential contraction. Such delamination might not only happen at the interface of the AL and bulk glass, but also within the AL where interfaces might be created due to different extent of corrosion.

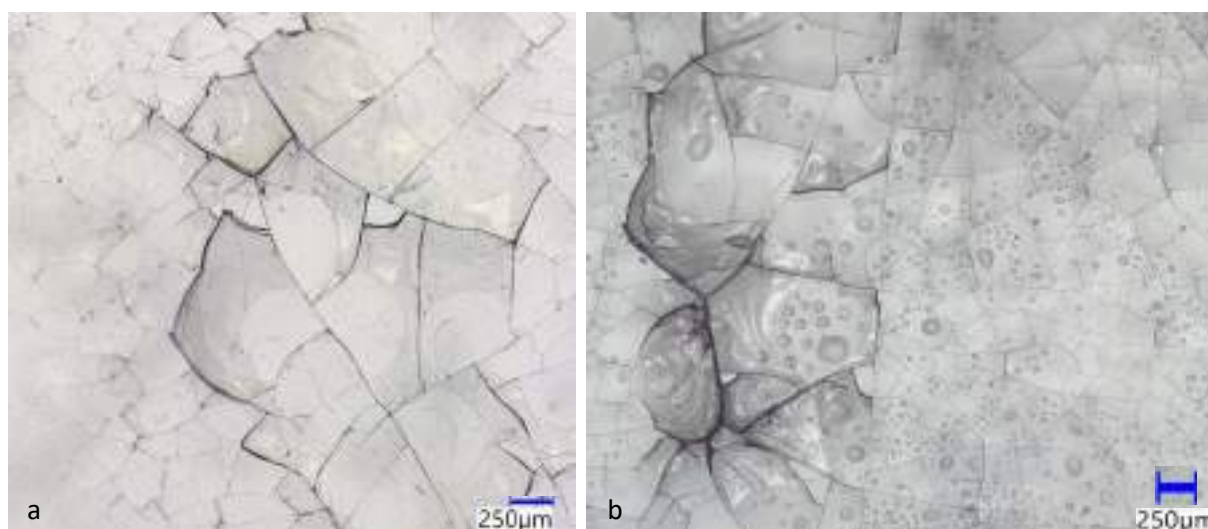


Fig. 4.7: Photomicrographs of two areas of PV model glass aged for 17 months and dried at 100× original magnification in a) transmitted light and b) reflected light

The delaminated surface was further documented with optical shadow effect mode (OEM) in reflected light at 200×original magnification (Fig 4.8). The topology of the surface along with the delaminated regions can be seen more clearly at different light directions. Numerous tiny bubbles were also seen in the liquid which do not seem to be moving suggesting a thick and viscous liquid under the delamination (shown by orange arrows).

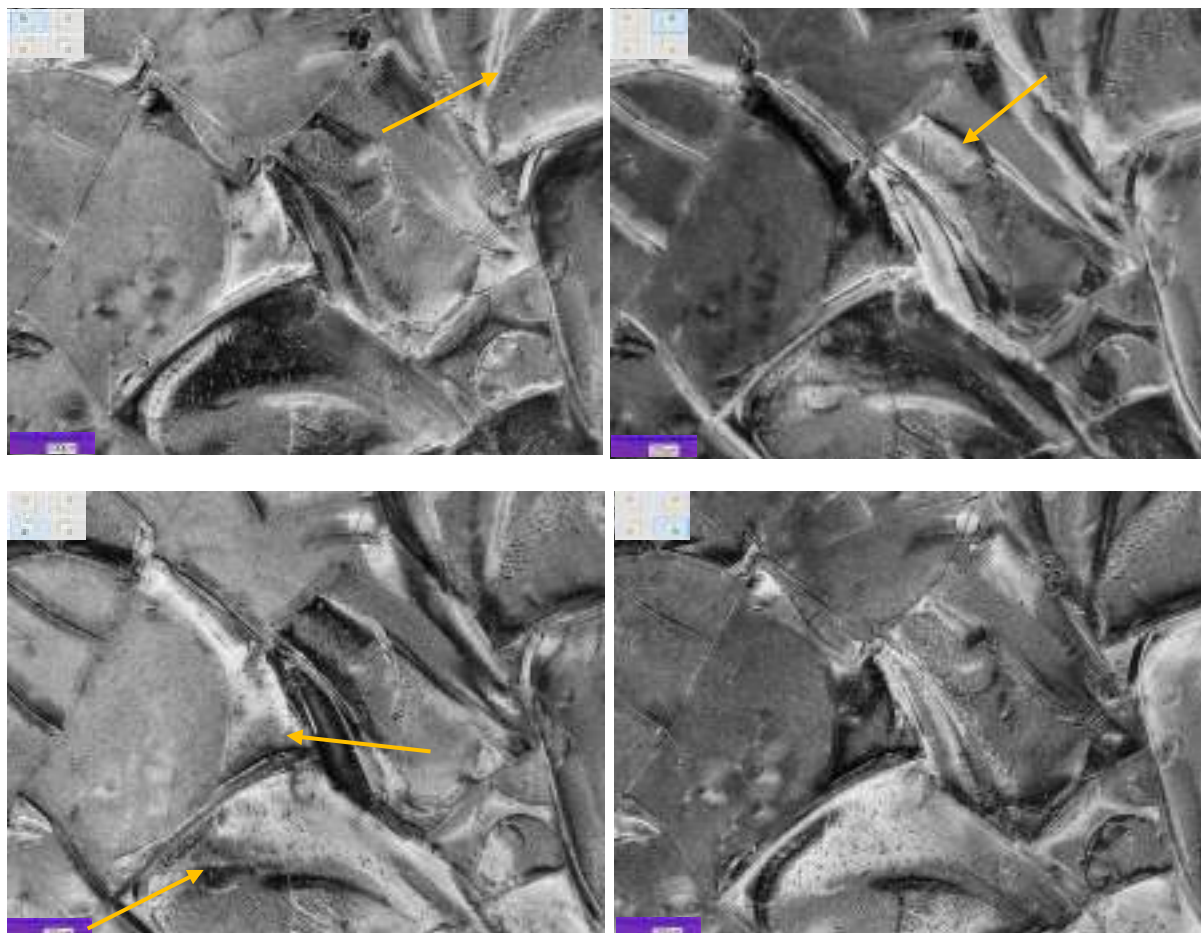


Fig 4.8: Photomicrograph of PV model glass aged for 17 months and dried at 200× original magnification in reflected light and optical shadow effect mode simulating four different angles of lighting

4.6. Summary of the corrosion mechanisms

A final attempt at summarising the corrosion mechanisms understanding from this study is proposed in this section along with schematic diagram showing the corrosion of the model glass in the three different aging environments studied wherein the corrosion in higher concentration of VOCs i.e., in P and PV conditions was found very different from corrosion in V condition at much lower VOC concentration and are described thus (Fig 4.9). The 3 months of aging in salt solution has been shown as the starting point for the aging (mentioned as month 0) which showed the formation of alteration layer on the surface of the glass along with surface discontinuities on the surface most probably produced during the manufacturing process (Fig. 4.9a and g).

Corrosion on glass starts with the interaction of atmospheric humidity with glass. It is assumed that a single monolayer of water molecules is adsorbed on the material at RH values below

35%, while at higher RH values, the amount of water molecule layers increases with RH [12][13].

Si-OH groups are created when unsatisfied Si-O- and Si- links on the surface of glass, as a result of glass creation, quickly react with ambient water. The composition of the glass, its heating and cooling cycles, the surface polish, and the relative humidity of the environment all have an impact on the thickness of the water molecule layer and its rate of formation. The surface structure of the glass determines the type of physical and chemical adsorption, and the hydroxyl sites serve as adsorption and reaction sites [14].

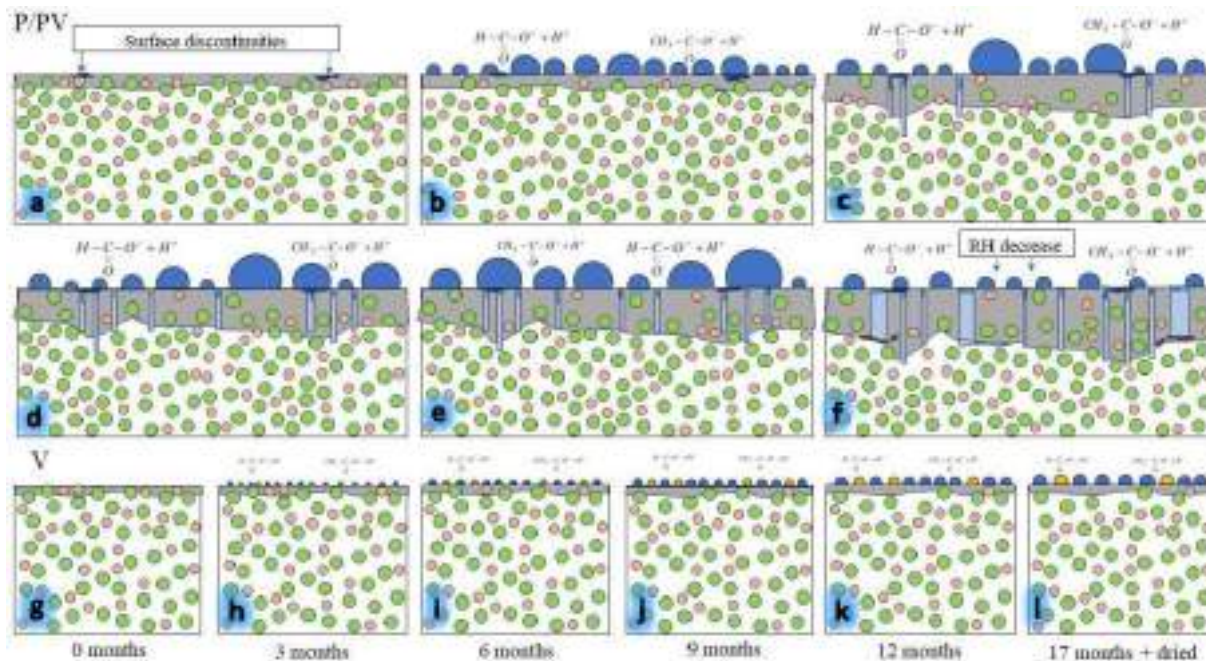


Fig. 4.9: Schematic diagram of glass aged for different durations in the condition P/PV for a) 0 months (3 months in presence of saturated salt solutions) b) 3 months c) 6 months d) 9 months e) 12 months f) 17 months and dried; in condition V for different durations g) 0 months h) 3 months i) 6 months j) 9 months k) 12 months l) 17 months and dried

Due to ion exchange and hydrolysis reactions which impact mobile glass components i.e. alkali metals, certain constituents of the glass precipitate as salt neocrystallizations on the surface (Na^+ and K^+ in this case), which can accelerate the glass alteration rate. In the case of high VOC concentrations (P and PV model glass), potassium and sodium leached from the glass to interact with formate ions, which dominated the ambient atmosphere, to form hygroscopic formates on the corroded surface (Fig. 4.9b). Subsequently, hydrolysis, particularly of silicon, leads to the initial glass dissolution. The difference between these two kinetics results in the formation of a heterogeneous alteration layer on the surface of glass. The deliquescent nature of these salt neocrystallizations and their increase in size due to further water and pollutant adsorption, induce coalescence as more and more such salts are formed. Once the liquid salt droplet is big enough so that the effect of gravity is more than its surface tension, the drop will run down the vertically standing model glass. As a result of the surface discontinuities already present on the glass, the corrosion was much higher in regions with discontinuities leading to the formation of bands visible in SWIR HSI having higher amount of water and hydroxyl absorbed in the glass

matrix (Fig. 4.9c). In the case of the P and PV model glass standing vertically in the aging environment, this is validated by the formation of the bands (1 or mostly 2) of higher water content as seen in section 3.8. Surface runoff could induce further mass loss in the form of cations and anions.

It was found that the presence of high concentration of VOC pollutants exacerbate the corrosion due to extensive leaching in acidic atmospheres (glass surface pH = 2 measured on the surface of model glass right after withdrawal with pH paper). The presence or absence of SN on the surface influenced also the alteration thickness greatly, as freshly exposed areas would lead to further corrosion. Therefore, corrosion in the presence of VOC especially formic acid (since potassium formate salts are deliquescent) would lead to aggravation of heterogeneous regions of different extent of glass corrosion within the same model glass (or museum objects). In case of corrosion in the presence of VOCs, acid pollutants increase and maintain the surface water film's acidity, further speeding up the selective leaching of alkali ions. As a result, in acidic atmospheres, the leaching reaction always predominates, with a ten-fold increase in kinetics compared to non-polluted atmospheres [10].

On the sub-surface of the glass, an alkaline solution develops, helping to break down the silicate matrix by hydrolysis and network dissolution. The silicate network rearranges to create a repolymerised layer which is even more depleted in alkalis and mostly composed of Q4 species (section 3.4). Due to the weakening of the glass structure, vertical cracks going into the glass develop (section 3.8) which were found to be more concentrated in the zones of surface discontinuities (Fig 4.9d).

The vertical cracks could act as additional pathways for the water and the pollutants to enter further into the glass including the bulk since new formate salt neocrystallizations form continuously and coalesce keeping the surface covered by wet SN (Fig. 4.9e). On a drastic reduction of the atmospheric RH (such as on drying after 17 months of aging), more intense cracks and delamination were developed along the bands formed due to the discontinuities. These radial conchoidal partial delaminations develop on the horizontal plane between the silica rich hydrated layer and the leached layer leading to delamination. This delamination typically indicates high stresses at a central point from which the fractures extend outward towards the vertical cracks. Due to capillary action, water along with the ionic species might seep into some of the cracks while dissolving the chemical bonds holding the glass network together and degrading the strength of the structure. Consequently, the percentage of area covered by the salt neocrystallizations also drastically reduced for P and PV after 17 months of aging (Fig 4.9f). The corrosion extent of P model glass seemed to be slightly higher than PV until 17 months of aging but this difference was not significant and could be a result of higher concentration of VOCs in the P condition. Apart from that, PV showed a prevalence of dissolution in comparison to P which showed prevalence of leaching. Thus, the integrity of the glass matrix in case of PV will be affected more than P and could lead to higher extent of network rearrangement in case of PV.

In the case of low VOC concentrations (condition V) model glass only showed presence of microscopic salt neocrystallizations from the first three months of aging (Fig. 4.9h). For the V condition, the amount of formic acid and acetic acid in the ambient atmosphere was comparable

(section 3.4). Therefore, both formates and acetates were found on the surface as salt neocrystallizations. Important to note is that while in P and PV, potassium ions leached to the greater extent, at low concentration in V, sodium ions leached out first probably due to their higher mobility (Fig. 4.9i). As the corrosion progresses, the size of the salt neocrystallizations continuously increased due to coalescence (Fig. 4.9j). The percentage of area covered by salt neocrystallizations also continuously increased indicating continuous formation of new salt neocrystallizations (Fig. 4.9k). the size of the SN never reached to a point where it might run off the surface. Since the parameters such as alteration layer thickness, water and OH⁻ absorbed in the glass matrix, K⁺ leaching and polymerisation index did not reach a specific threshold for V model glass, they didn't develop cracks until 17 months of aging even after a drastic reduction of the RH (Fig. 4.9l).

In the present research, leaching and dissolution both were observed in case of PV and P, while V model glass displayed only slight leaching. This indicates that the progression of corrosion in the presence of high concentrations of VOC is much faster than in low VOC concentrations. In case of the V model glass corroded at 1000 times less VOC concentration than those in P and PV. Therefore, while the rate of corrosion increased continuously with time at low concentration V, for P and PV model glass it was much higher and constant.

As a result, V model glass were nowhere close to the corrosion extent of the P and PV model glass. In case of V model glass, only the leaching phase was achieved but no Raman shift in the silicate species was seen indicating that network dissolution and rearrangement phase was not reached (section 3.4). Nonetheless, with a rate of corrosion constantly increasing with time, it could be imagined that the rate could reach as high as P and PV but it would take much longer.

Chapter 5: Application on real historical objects and proposed monitoring protocol

Out of the documentation and analytical methodology developed using model glass, some of the techniques were applied on the three selected museum objects as well as on aged 3D model cups aged along with the model glass. Some techniques applied on the model glass were also required adjustments for the historical glass. The results are discussed in this chapter along with the proposed protocol for the monitoring and documentation of VOC induced corrosion on museum glass objects.

5.1. Macro-documentation of the glass objects

Photography in transmitted light led to visualization of the historical glass objects showing coarse cracks as well as discolouration. The photography set up described for the model glass (section 2.14) could not be directly applied for the 3D historical glass objects and needed some modifications. The setup used for the photography included placing the glass object upright on a solid plexiglass inside white photo studio tent made of translucent white fabric. Such a tent helps to diffuse the light transmitting through the object. A hard studio white light was placed at the back of the object so that the light transmitted through the object could be captured by the Digital Single-Lens Reflect (DSLR) camera placed on a stationary stand in front of the object kept in many different orientations (Fig. 5.1). Such a setup greatly reduces stray specular reflections.



Fig. 5.1: Schematic diagram of the photography setup for the 3D glass objects

Apertures play a crucial role in photography when capturing transparent 3D objects. A small aperture results in a greater depth of field, making more of the 3D object appear in focus from the foreground to the background. This is beneficial to capture the entire object to be sharp and clear. However, using extremely small apertures can lead to diffraction, which causes a decrease in image sharpness. This is more noticeable in transparent 3D objects because diffraction can obscure fine details, reduce contrast, and result in a less crisp image. Therefore, for better resolution and clarity mid-range apertures often result in the best compromise between depth

of field and image sharpness as very wide apertures may also lead to softness in areas of the object that are not in focus.

The images were successful in showing microcracks on the surface of the glass objects especially coarse cracks (Fig. 5.2) even though the whole object was not in focus in a single image. Apart from this, LM12433 showed also complete discolouration with a pinkish hue on the glass possibly owing to the oxidation of manganese present in the glass (Fig. 2c and d). Therefore, an overall documentation of glass objects could be undertaken using transmitted white light.





Fig. 5.2: Transmitted light photographs of a) AG1078 b) LM12433 c) LM15473 in different orientations of front, back and curved side (©SNM)

5.2. Micro-documentation of the glass objects

The central parts of the glass objects could be accessed and imaged using the movable stage of the digital microscope in transmitted as well as reflected light. The digital microscopy images showed different extent of corrosion for all the three objects. Additionally, the regions of the objects which were not accessible on the movable stage such as the neck, handle and curved side were imaged using the flexible arm and transmitted light. Corrosion was found to be highly heterogenous within the same object as well.



Fig. 5.3: Keyence digital microscopy setup along with flexible arm being used for imaging the neck region of LM15473 in transmitted light (©SNM)

The AG1078 flask displayed coarse cracking network with polygonal cracks on the rounded body on both the sides (Fig 5.4a). The curved outer side of the flask displayed arced cracks along with T-junction cracks (Fig 5.4d) while the neck showed fine parallel cracks on the inner side (Fig 5.4e) and a denser polygonal crack network indicating higher corrosion on the outside than on the inside of the neck of the flask (Fig 5.4f). Such arced cracks are typically found on curved surfaces such as those found on glass flutes in Brostoff et al. [15].

The flask also displayed very few instances of partial delamination showing the presence of liquid entering under the scales. This can be seen in the darker areas of the image especially around the edges of the crack network (examples inside yellow rectangles in figure 5.4a and b). This is similar to what was developed in the case of model glass aged for 17 months and dried for 15 minutes mentioned in paragraph 4.5 (Fig. 4.7). However, some of the delaminated regions also showed that the liquid seeped under the scales had dried up already leaving perhaps dried salts (Fig. 5.4c).

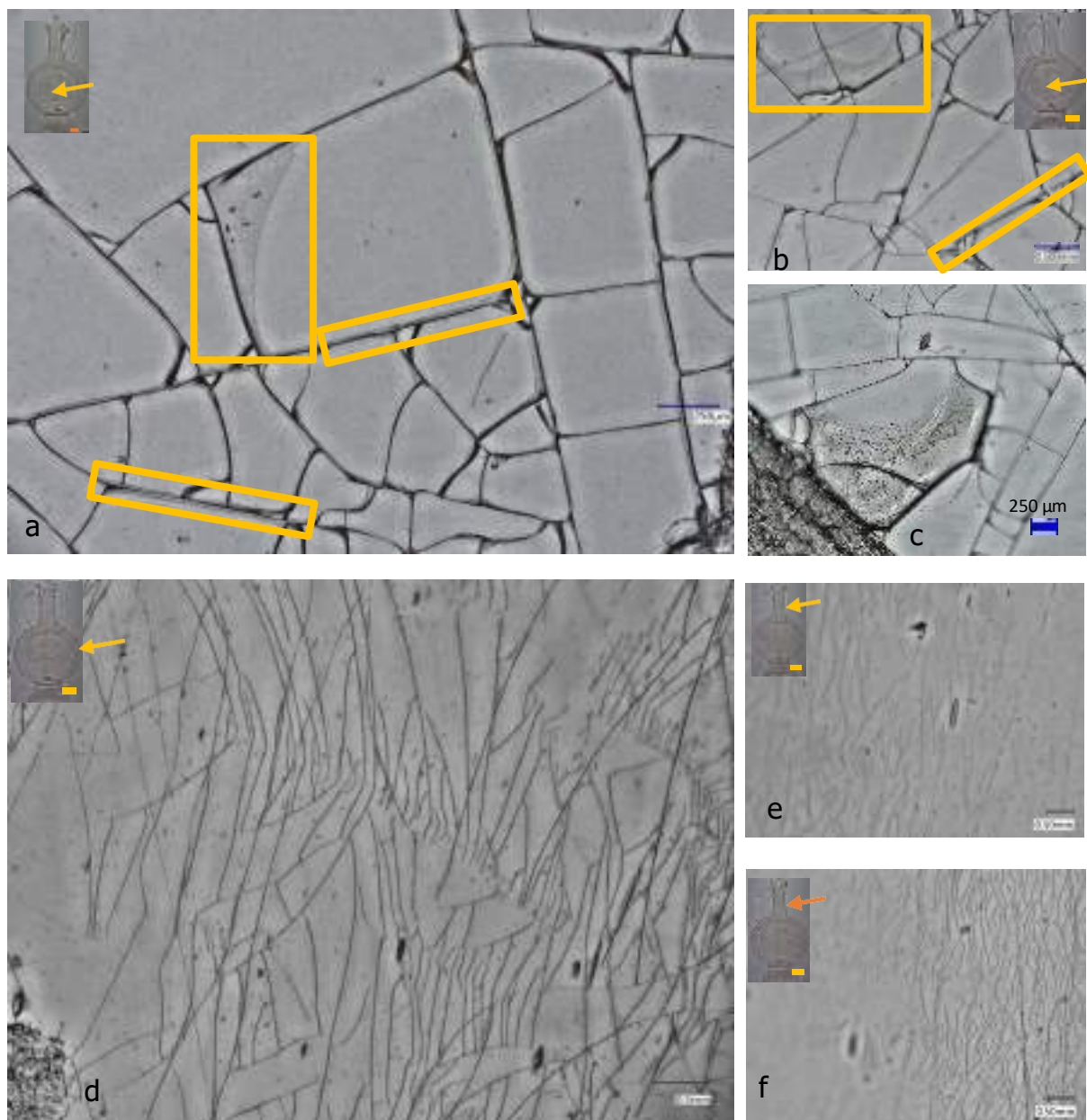


Fig. 5.4: Digital microphotographs of AG1078 in transmitted light showing a) front wall (yellow rectangles showing liquid seeped under partially delaminated scales) at 100× original magnification b) back side (yellow rectangles showing liquid seeped under partially delaminated scales) at 50× original magnification c) back wall showing dried up liquid under a partially delaminated scale at 100× original magnification; d) curved side of the object at 50× original magnification e) inner wall of the neck at 50× original magnification f) outer wall of the neck at 50× original magnification (yellow arrow indicate the outside of the wall, orange arrow indicate inside of the wall) (©SNM)

The glass tumbler LM12433 displayed coarse crack network on both inner and outer sides of the walls (Fig. 5.5). However, partial delamination with trapped liquid under the scales was only found on the inner side of the object. Once again, the liquid had already dried up leaving only precipitates in some of the delaminations (Fig. 5.5c) while in others the liquid could still be seen. Therefore, it can be surmised that the inner side of the glass was more corroded than the outer side. This might be due to the usage of the object in the past. The body of this object was seemingly much more thoroughly cracked than all the other objects.

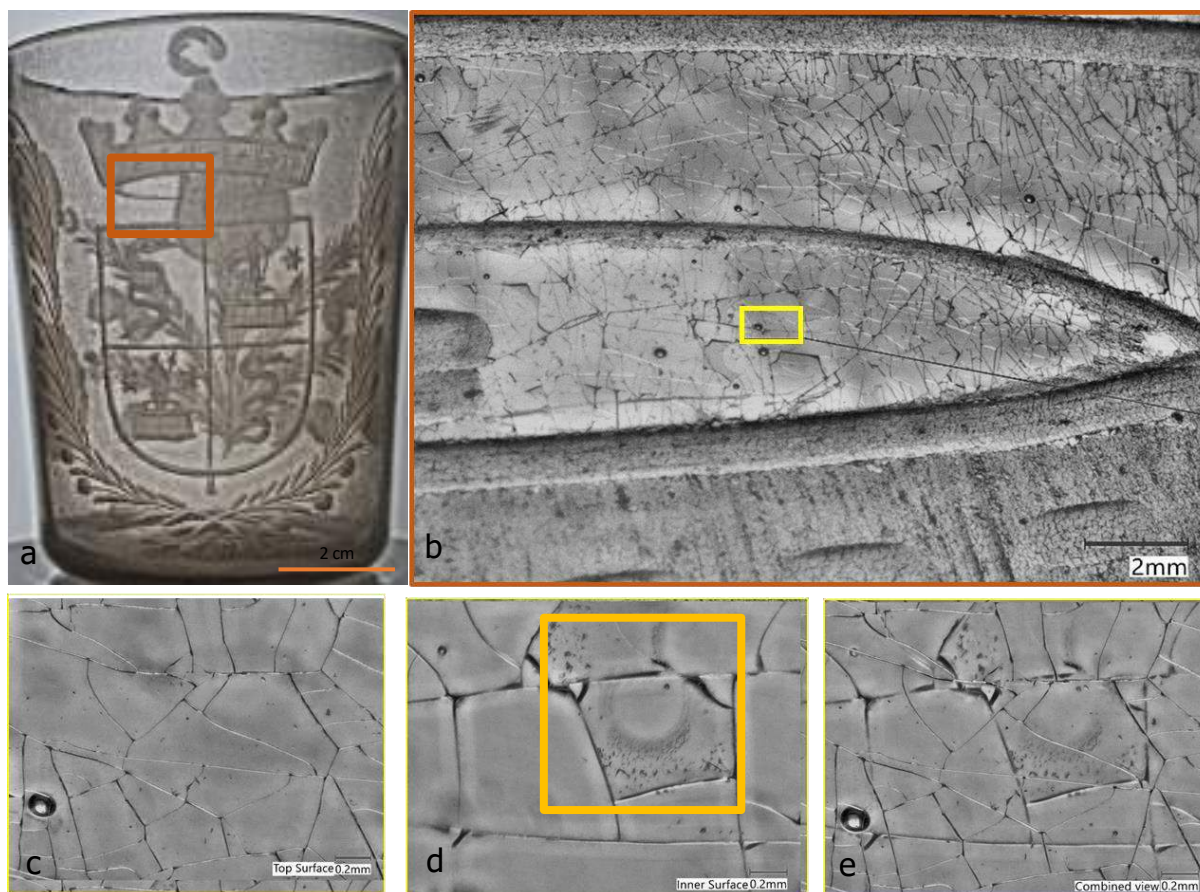


Fig. 5.5: a) Photograph of LM12433 showing localization of the region imaged using DM; Digital microphotographs in reflected light showing b) the coarse cracking network at 20× original magnification c) outer surface at 120× original magnification d) inner surface showing partial delamination side (yellow rectangle showing liquid seeped under partially delaminated scales and dried, leaving precipitates) at 120× original magnification e) combined view of both outer and inner surface at 120× original magnification (©SNM)

The LM15473 flask had one side showing only few fine cracks indicating the lowest extent of corrosion among all the three objects (Fig. 5.6a). Nonetheless, the other side presumably in contact with chipwood was found to be extremely corroded with a dense crack network and large extent of partially delaminated scales filled with the liquid (which had mostly dried up leaving the precipitates) as well as fully delaminated regions showing the characteristic conchoidal fractures. In case of the figure 5.6b, a small central part with fine cracks can be seen surrounded by partially delaminations with the dried-up liquid under them (indicated by red arrow in figure 5.6d). These partial delaminations were finally surrounded by complete delaminations (indicated by blue arrow in figure 5d) which were present all over the outer part of the figure 5.6c. Even within the heavily corroded area, much less corroded regions could be identified probably due to difference in local composition or environment (Fig. 5.6b).

The region where the neck starts above the body displayed parallel cracks on the outside along with partial delamination filled with the liquids on the inside once again indicating more corroded inner side which might be due to the use of the flasks in the past (Fig. 5.6c).

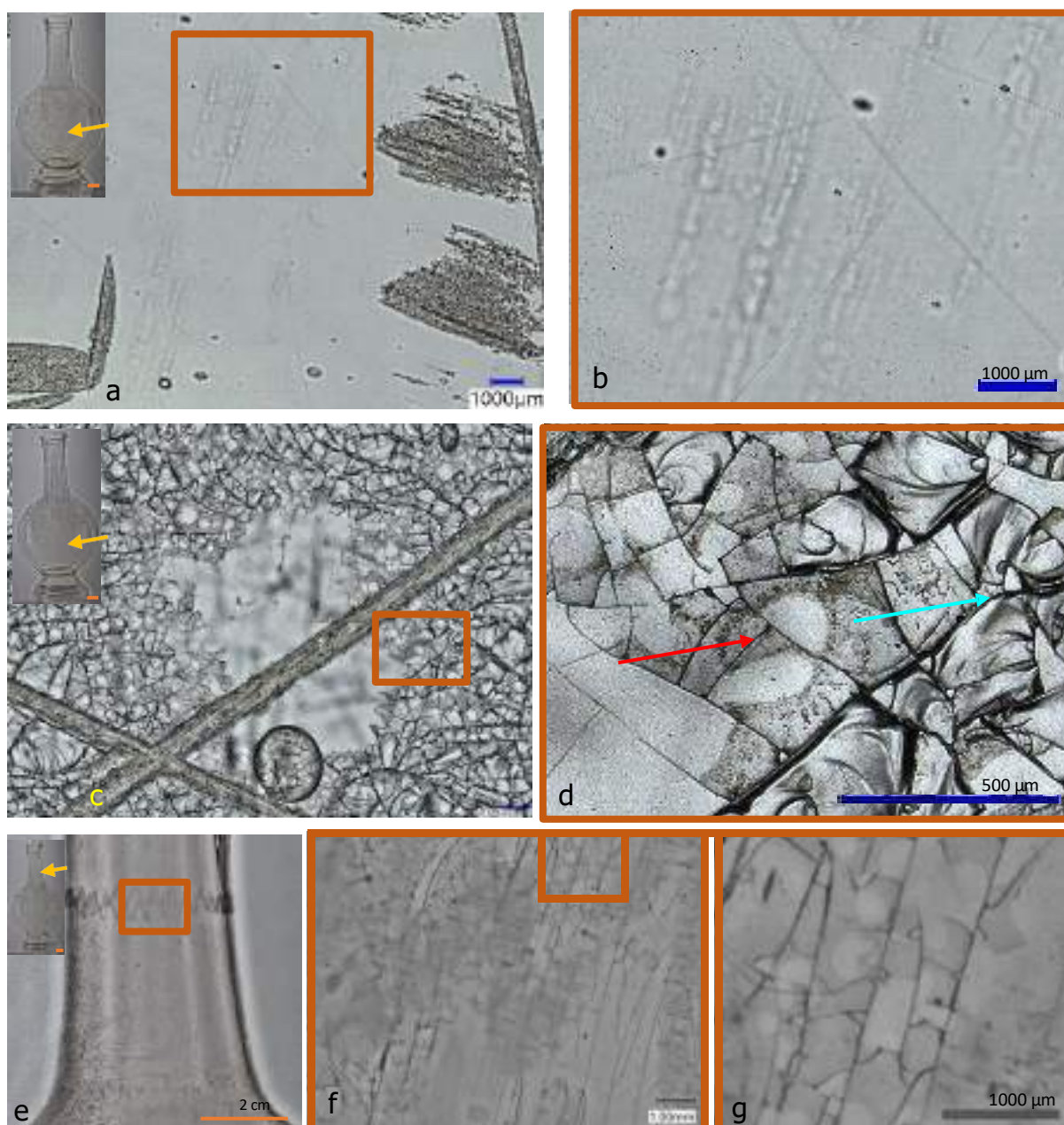


Fig. 5.6: Digital microphotographs of LM15473 a) in transmitted light showing fine cracks on the less corroded side at 40x original magnification b) zoom of a selected area showing very few fine cracks c) showing a central region without any cracking surrounded by coarse cracking network with many partial and complete delaminations on the severely corroded side at 50× original magnification d) zoom of a region showing partial delaminations next to the area without cracks (red arrow) and complete delaminations on the outer part of the image (blue arrow) e) digital photograph zoomed in to show the neck region with engraving imaged by DM f) digital micrograph of selected region in transmitted light showing neck with parallel cracks and delamination at 40× original magnification g) zoom of selected area showing blurred delaminations on the inner side of the neck (©SNM)

5.3. Identification of the salt neocrystallizations

As mentioned in section 1.2, FTIR was performed on these glass objects showing the presence of formates and acetates both before and after the cleaning of the objects with water and ethanol mixture. Similar to the corroded model glass, more instances of formates than acetates were found (Fig. 5.7). Moreover, in some cases, the spectrum showed changes before and after cleaning (Fig. 5.7b) probably indicating some structural changes in the glass matrix, which might be due to cleaning. However, this cannot be said with certainty since the two points might not be exactly located at the same place thus leading to the spectra which did not overlap over each other.

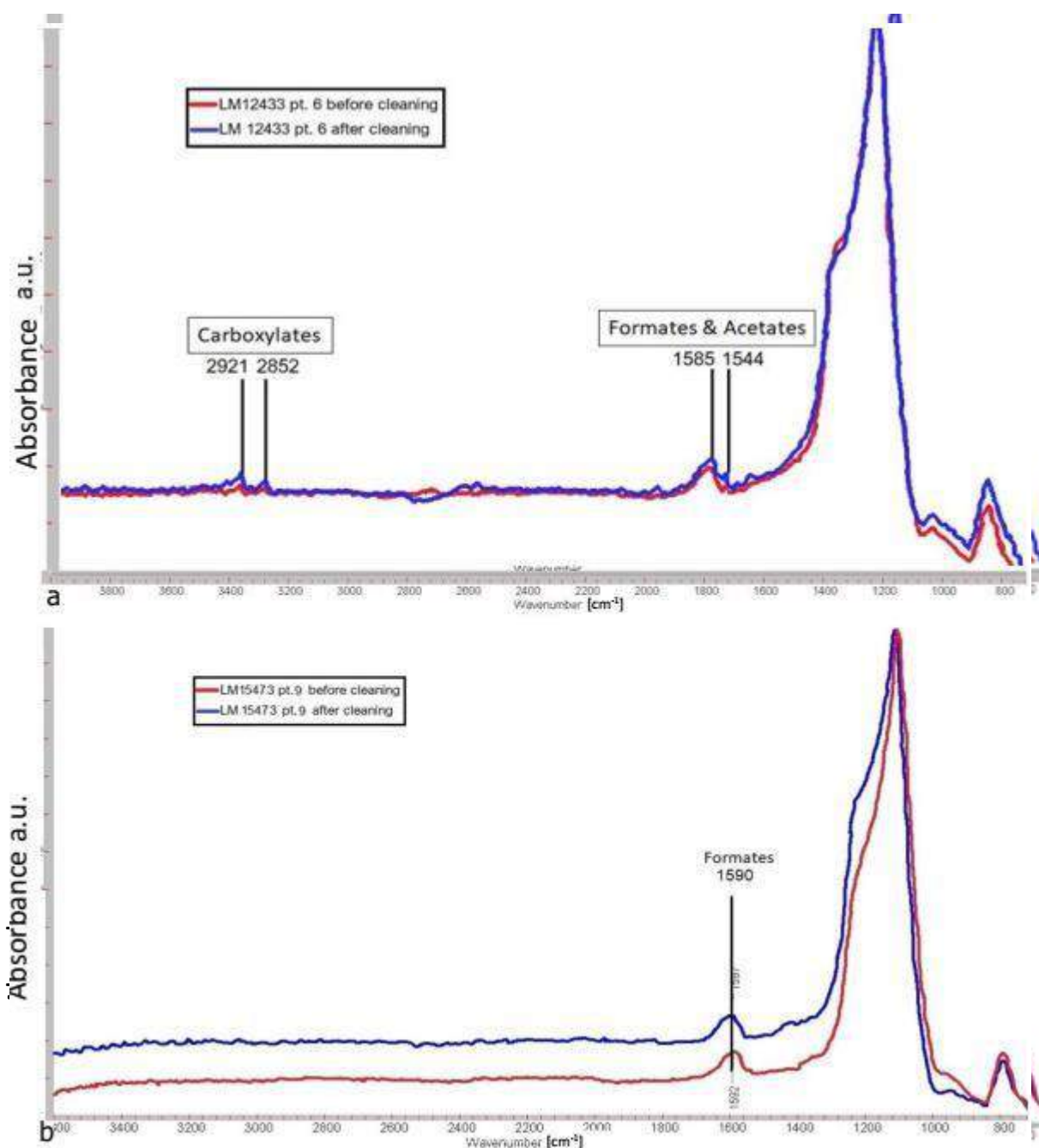


Fig. 5.7 FTIR spectra in reflection mode from a) LM12433 showing presence of formates and acetates b) LM15473 showing presence of formates before and after cleaning with water and ethanol (© SNM)

5.4. Thickness of the alteration layer

The determination of the thickness of the alteration layer had to be accessed non-destructively. Several attempts were made through Raman profiling, due to high corrosion, most of the spectra were dominated by the fluorescence, therefore no profiles were collected for object LM12433, while few of them were collected for AG1078 and LM15473. The AL thickness was found to be between 30-45 μm for AG1078 (1 point) and $<15\text{ }\mu\text{m}$ (3 points) and 30-45 μm (1 point) for LM15473. This could be measured by finding the depth until which the Raman spectra showed a shift in the Q3 stretching (blue line) and Q4 bending (yellow line) peak positions from the bulk spectra as shown in figure 5.8. Taking into account the heterogeneity of the corrosion these values cannot be taken into account as fully representative of the object corrosion state.

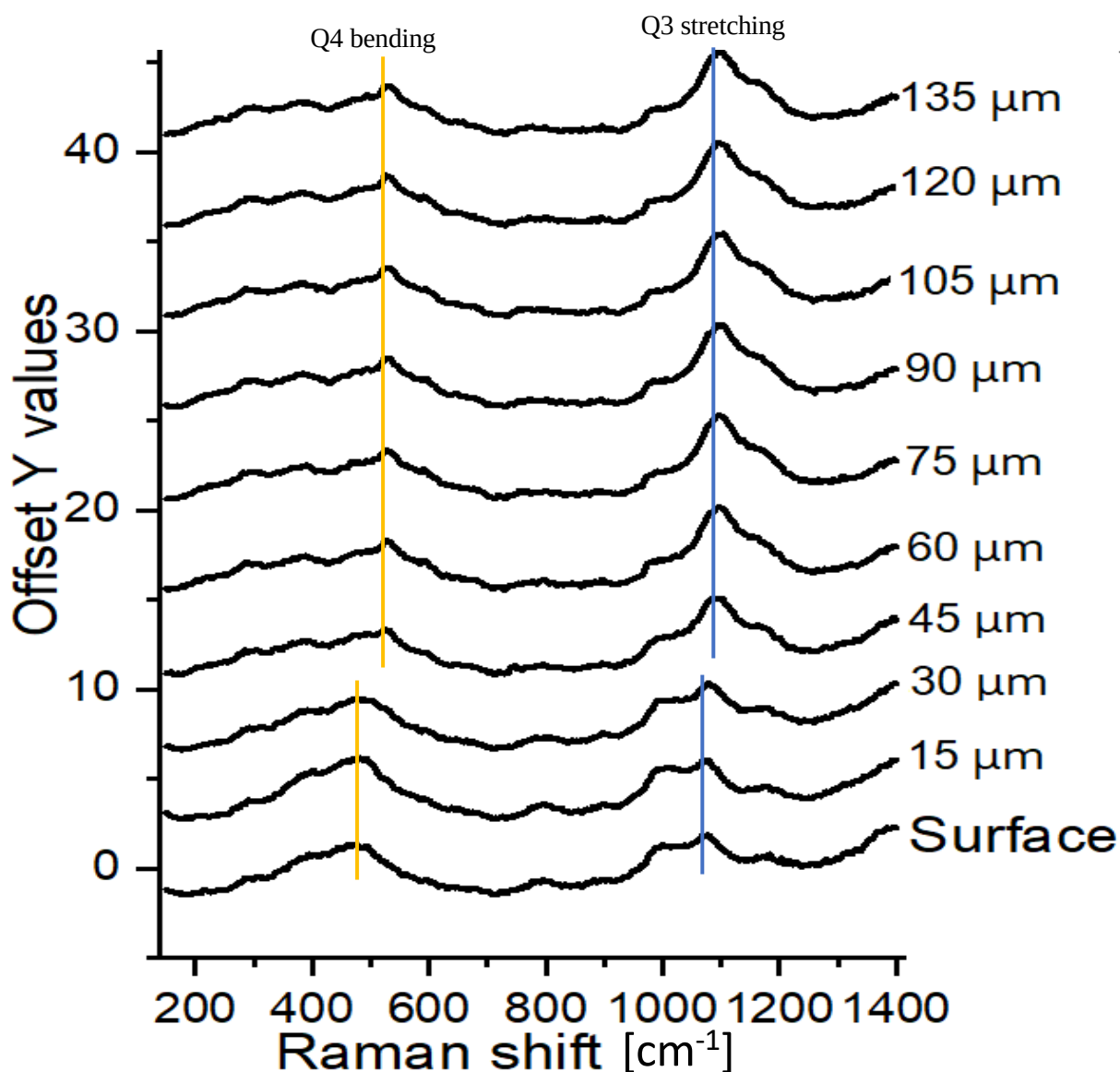


Fig. 5.8: Example of a depth profile from AG1078 indicating the alteration layer thickness between 30-45 μm with yellow lines indicating Q4 bending peaks and blue lines indicating Q3 bending peaks

5.5. Elemental changes in the glass objects

The SEM-EDX results from microsamples of altered layer and bulk glass showed the differences in major constituents viz. sodium, silicon, potassium and calcium. The dealkalization of the bulk glass could be observed for potassium and sodium leached out of the altered layer. The maximum change was found in LM12433 in case of potassium leached out while LM15473 didn't show a big difference. The altered layer was more enriched in silica than the bulk and AG1078 showed the highest value of Δ Bulk and LM 15473 showed the lowest values for both sodium and silicon. The amount of calcium was slightly higher in the altered layer than in the bulk for all the glass objects. LM12433 also showed higher amount of manganese in the alteration layer than bulk glass since manganese present in the original glass had oxidized leading to the complete discolouration of the object due to which it had a pinkish hue (Table 5.1).

It is interesting to notice that the values of Δ Bulk in case of LM12433 and AG1078 for potassium and sodium dioxide were found to be closer to the values obtained for P and PV model glass while those of LM15473 were found to be closer to those obtained from V model glass (section 4.2).

Table 5.1: SEM–EDX Elemental composition (mean and standard deviation, σ) of bulk glass, of Alteration Layer (AL) and Δ bulk([AL]-[Bulk])/[Bulk]) (in weight percentage of oxides) for the three glass objects LM12433 (15 points), LM15473 (10 points) and AG1078 (10 points).

			Na ₂ O	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	MnO
AG1078	Bulk	Mean	1.46	1.24	74.61	17.67	3.30	
		σ	0.31	0.20	1.56	1.70	0.30	
	AL	Mean	0.49	1.33	84.59	8.04	3.98	
		σ	0.30	0.14	3.93	3.81	0.45	
		Δ Bulk	-0.67	0.07	0.13	-0.55	0.20	
LM12433	Bulk	Mean	0.54	1.42	74.20	16.24	4.47	0.97
		σ	0.18	0.50	5.82	6.30	0.30	0.14
	AL	Mean	0.46	1.86	82.30	6.22	4.96	1.16
		σ	0.17	1.46	2.10	1.67	1.10	0.31
		Δ Bulk	-0.13	0.31	0.11	-0.62	0.11	0.19
LM15473	Bulk	Mean	1.72	1.48	72.23	18.19	4.40	
		σ	0.37	0.16	1.78	1.42	0.39	
	AL	Mean	1.31	1.35	74.99	15.48	5.16	
		σ	0.51	0.20	3.69	3.63	0.43	
		Δ Bulk	-0.24	-0.09	0.04	-0.15	0.17	

5.6. Changes in the glass matrix

To understand the changes in silicate species and water and OH⁻ absorption, FTIR (in transmission mode) and Raman spectroscopy were also performed on microsamples taken for

SEM-EDX from the bottom of the object. Samples from the alteration layer and bulk of each of the three selected objects were analysed out of which the alteration layer samples collected from LM12433 could not generate any useful FTIR spectra and those from alteration layer of LM15473 could not generate any Raman spectra. To partially remediate this inconvenience the spectra of the Raman profiling were used instead.

The area of water band from each of the FTIR spectra from the glass objects' microsamples again showed the heterogeneity of the corrosion. While the area was comparable for AG1078 alteration layer and bulk, the alteration layer in LM15473 showed much higher water and OH⁻ content as compared to the bulk glass (Fig 5.9).

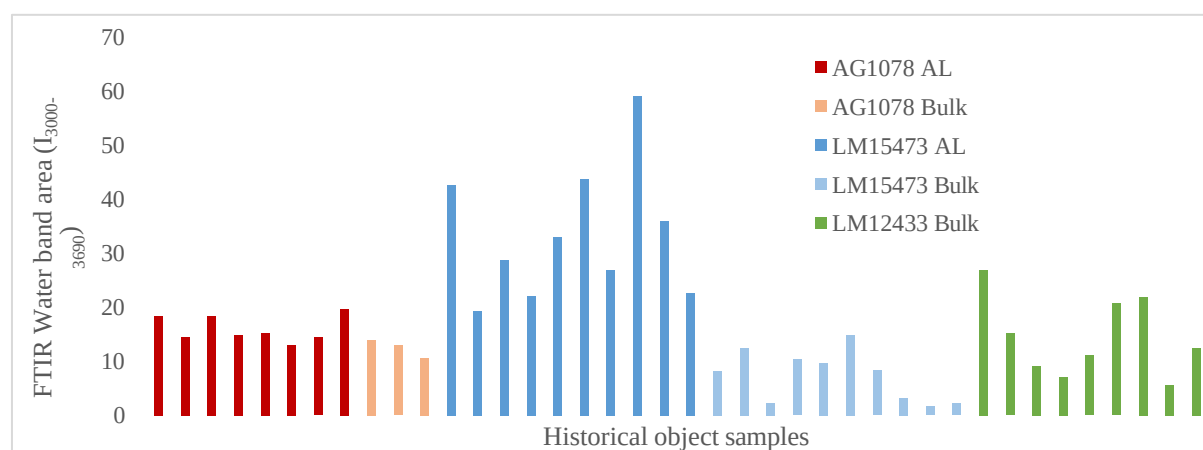


Fig. 5.9: The area of the water band between 2800-3600 cm⁻¹ from FTIR spectra of historical objects using microsamples

The same spectra were then used to calculate FTIR Q4/Q3 ratio for both AG1078 and LM15473 showing that the values of the ratio increased in the alteration layer as compared to the bulk glass which was expected (Table 5.2). The percentage change between the value in alteration layer and bulk glass spectra was higher for AG1078 indicating higher corrosion extent as also understood by the appearance of the objects.

The Raman spectra comparison between the bulk and altered region of the historical objects (Fig. 5.10, 5.11 and 5.12) revealed substantial changes in the structure, suggesting an increase in polymerization upon alteration. Nonetheless, it is important to note that the all the bulk glass and altered layer spectra exhibited a sharp band around the ≈ 980 cm⁻¹ region, similar to sulphate (SO₄⁻) stretching peak signature, as reported by Lenoir et al. [16] and Konijnendijk and Buster in [17]. This characteristic is indicative of a glass melt that has not undergone sufficient annealing [18].

Table 5.2: Q4/Q3 ratio calculated from FTIR spectra for bulk glass and alteration layer of AG1078 and LM15473, together with percentage of change

	Bulk	AL	% change
AG1078	0.34±0.00	0.48±0.04	41.2
LM15473	0.13±0.03	0.15±0.02	15.4

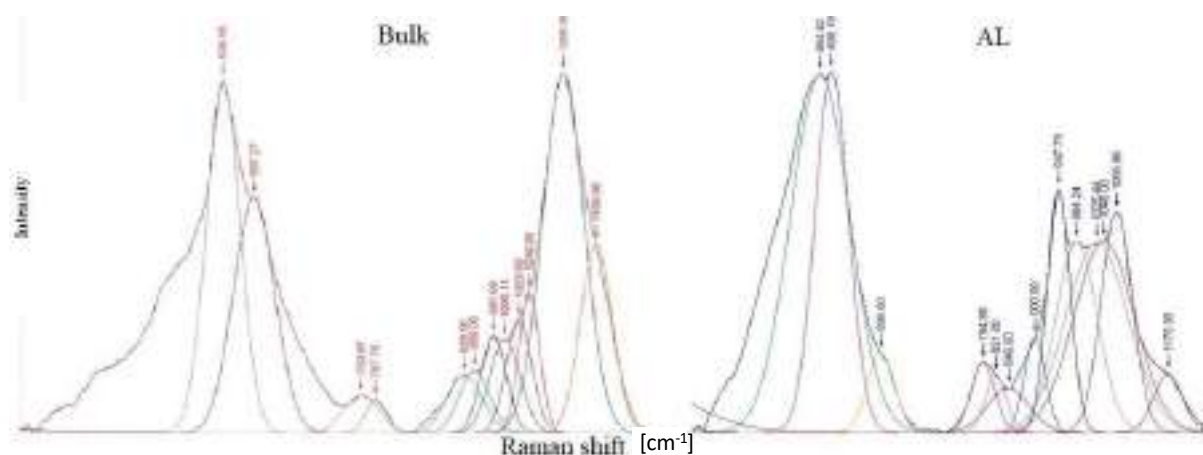


Fig. 5.10: Raman spectra showing curve fitting for LM12433

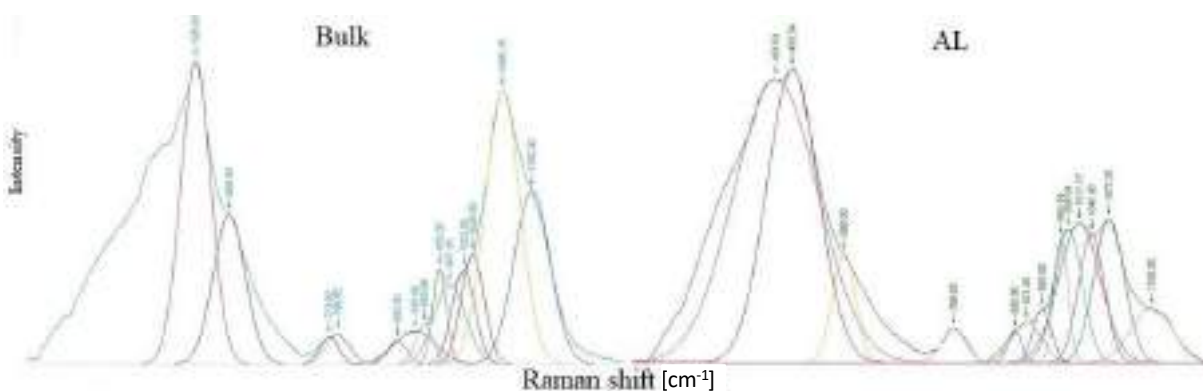


Fig. 5.11: Raman spectra showing curve fitting for AG1078

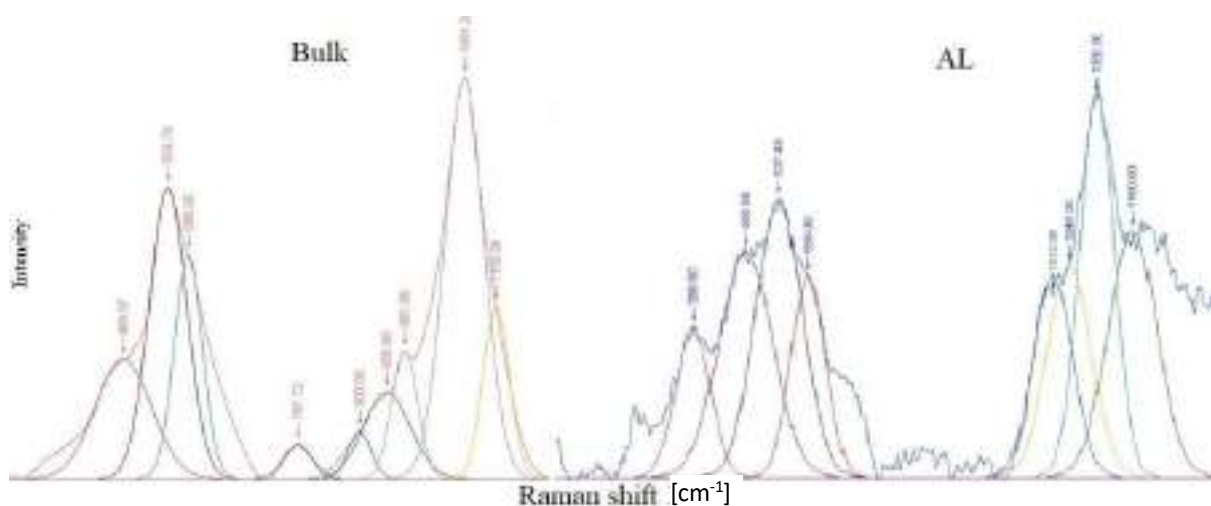


Fig. 5.12: Raman spectra showing curve fitting for LM15473²

² Note that the resolution of the AL spectrum is lower because of being taken from Raman profiling with a lower S/N ratio

Table 5.3: Table showing the peaks found in bulk glass and alteration layer Raman spectra for LM12433, AG1078 and LM15473

S. No.	Assignment	LM 12433		AG 1078		LM15473	
		Bulk	AL	Bulk	AL	Bulk	AL
1	fully polymerized Q4 units		464.42		463.54		388
2	fully polymerized Q4 units		488.19		493.54	469.97	480
3	δ Si-O-Si in Q3 units	536.55		525.91		550.79	537.43
4	Mixed ν - δ vibration in Q2 structural units	587.27	588	588	588	588	588
5	Q0	763.97		773.82		787.72	
6	Q0	787.75		787.75	788.03		
7	cage-like vibrations of Si in Q4 tetrahedra		794.85		797.05		
8	cage-like vibrations of Si in Q4 tetrahedra		821				
9	Q1		846	900	900	900	
10	Q1	900	900	933.55	921	950	
11	Q1	933.55					
12	ν Q2	950	947.79	949.88	950		
13	Similar to sulphate (SO ₄ ²⁻) stretching	981.09	984.24	978.3	984.24	981.86	
14	ν Q2+Si-OH	1000.1		997.25	998.04	997.25	998.04
15	ν Q2+Si-OH	1023	1025.4	1023	1017.77		1012
16	ν Si-O vibrations in specific Q3 or Q4 units	1040	1040	1040	1040	1040	1040
17	ν Si-O mode of Q3 species	1096	1065.9	1095.2	1072.25	1091.24	1088
18	ν Q3' (different from Q3) + Q4	1150	1170	1150	1150	1150	1150

The analysis of vibrational components in the altered and bulk glass spectra (Table 5.3), carried out using curve-fitting techniques, revealed significant changes. Specifically, the components for AG1078 and LM12433 at 526-536, 763-773, and 1091-1095 cm⁻¹ almost entirely disappeared (Table 5.3), while the component at 1150 cm⁻¹ exhibited a considerable decrease (Fig. 5.10, 5.11 and 5.12). The component at $\approx$ 1095 cm⁻¹ is known to be associated with the Si-O stretching vibration of Q3 species, which is prominent in the alkali glasses studied. Moreover, the bands at 536 cm⁻¹ and 550 cm⁻¹ were attributed to the Si-O-Si bending vibrations in depolymerized species, mainly Q3. In case of LM15473, the 550 cm⁻¹ and 1096 cm⁻¹ showed a shift towards lower wavelength i.e. 537 and 1088 cm⁻¹, respectively. This indicated a decrease in the Q3 species. The change in 1150 cm⁻¹ was not discernible due to lower resolution of the AL spectrum. As previously discussed in the initial stages of this investigation, the positions of these bands are influenced by the Si-O-Si average angle and the cation content of the glass. The reduction or disappearance of depolymerized species, especially Q3 species, was directly linked to the leaching of alkali ions from the glass structure. The assignment of the peaks in altered layer and bulk spectra for each glass object can be understood in more detail by referring to table 1.3 in paragraph 1.4.

Using Raman deconvolution, Q3/Q2 ratio and polymerization index were calculated for the bulk glass and alteration layer spectra for all the three objects. As expected, the value of Q3/Q2 was much lower for alteration layer than bulk and the polymerization index (Ip) had an opposite trend (Table 5.4). According to the percentage of change between bulk glass and alteration layer

values, it was found that LM12433 was the most corroded followed by AG1078 and LM15473. This is also in accordance with the results from elemental changes discussed in section 5.5.

Table 5.4: Q3/Q2 ratio and polymerization index (Ip) calculated for bulk glass and alteration layer of all the glass objects from Raman spectra acquired on the microsamples, together with percentage of change.

	Q3/Q2			Ip		
	Bulk	AL	% change	Bulk	AL	% change
AG1078	4.42	0.74	83.22	2.79	4.04	44.70
LM15473	5.34	1.66	68.97	0.86	1.16	35.64
LM12433	5.07	0.58	88.55	1.51	2.22	46.40

5.7 Validation of the aging

The model glass corroded using artificial aging protocol in this research were successful in replicating corrosion similar to what was observed on the actual historical objects. It was observed that the corrosion products found on the historical glass were formats in most cases which was same as observed for P and PV model glass wherein, only formate SN were found on the corroded samples. V model glass showed evidence of acetate SN as well, which were also found in lesser extent on historical glass. Corrosion in the presence of VOCs on both the model glass and historical glass was also found to be highly heterogenous, especially by observing the water bands of the FTIR spectra as well as the SEM-EDX elemental results from the historical objects (Annex XI).

The most interesting part was the similarity in the delaminations produced on both of these due to drastic reduction in RH, showing trapped liquid under the scales which was seemingly dried up in case of the corroded historical glass objects in contrast to the model glass.

Raman spectroscopy also showed the shifting towards lower wavenumber or complete disappearance of the Q3 bending ($526\text{--}550\text{ cm}^{-1}$) and stretching ($1091\text{--}1095\text{ cm}^{-1}$). The values for the historical glass objects of FTIR Q4/Q3 and Ip showed an increase for the alteration layer in relation to the bulk and vice versa for Raman Q3/Q2 in agreement with the trends found for the corroded model glass. Therefore, the aging experiment protocol was validated by all these similarities.

5.8. Early identification of corrosion in 3D objects using HSI

The model cups aged for 17 months in P and PV condition showed visible wet salt neocrystallizations all over the cup while the V model cup did not show any salt neocrystallizations with naked eyes but a haziness and loss of transparency.

The methodology of water and OH^- detection in corroded glass developed on model glass could not be applied to the real historical objects due to logistical reasons and therefore were applied on the model cups corroded for 17 months in the 3 different conditions compared with an unaged reference model cup (Fig. 5.13). In addition, some preliminary investigations were made using couple of model glass in different arrangements to mimic 3D objects.



Fig. 5.13: RGB photographs of model cups in a) PV b) V c) P aging conditions and d) Unaged Reference (Ref)

5.9. Visualisation using model samples to simulate 3D objects

Aged and unaged model glass were placed in front of each other to simulate 3D and how factors such as the distance between the walls i.e. bigger or smaller objects as well as the heterogeneity of corrosion such as different extent of corrosion on different sides of the object would influence the acquired SWIR spectra. For this reason, three different combinations of the aged and reference model glass were kept at distances of 1, 2, 3 and 4 cm apart from each other

1. a PV model glass aged for 12 months (A, unwiped in the centre) kept in front of unaged reference glass (UA), hereby referred to as A-UA (Fig 5.14)
2. an unaged reference glass kept in front of PV model glass aged for 12 months (unwiped in the centre), hereby referred to as UA-A (Fig 5.14)
3. a PV model glass aged for 12 months (wiped in the centre) kept in front of PV model glass aged for 12 months (unwiped in the centre), hereby referred to as A-A (Fig 5.14)

It was found for all the three combinations that the distance between the two model glass did not affect the spectra at all. Hence, no restriction on the size of the 3D object would be applicable in case of SWIR HSI with transmitted light up to a distance of 4 cm between the two walls (Fig 5.15). The spectra were only affected by the combined effect of the corroded model glass whether one or two in the combination as well as their position.

All the three curves present the same bands, but with different peak areas even though the peak areas for A-UA and UA-A are very similar. The shape of the curve is different for UA-A and A-UA in the 1940-1960 region (Fig. 5.16, inside black rectangle) pertaining to the Hydrogen-bonded H_2O molecules in voids or films on silica surfaces leading to slight shoulder in this region for A-UA in contrast to UA-A. Although, the areas of both 1410 and 1906 peaks were similar for both the cases, this shoulder region could be useful for detecting if a water film or wet SN are present on the front surface. As expected, the peak areas in A-A were much higher (almost double) than both A-UA and UA-A combinations since it has contribution from two corroded model glass instead of one (Fig. 5.16).

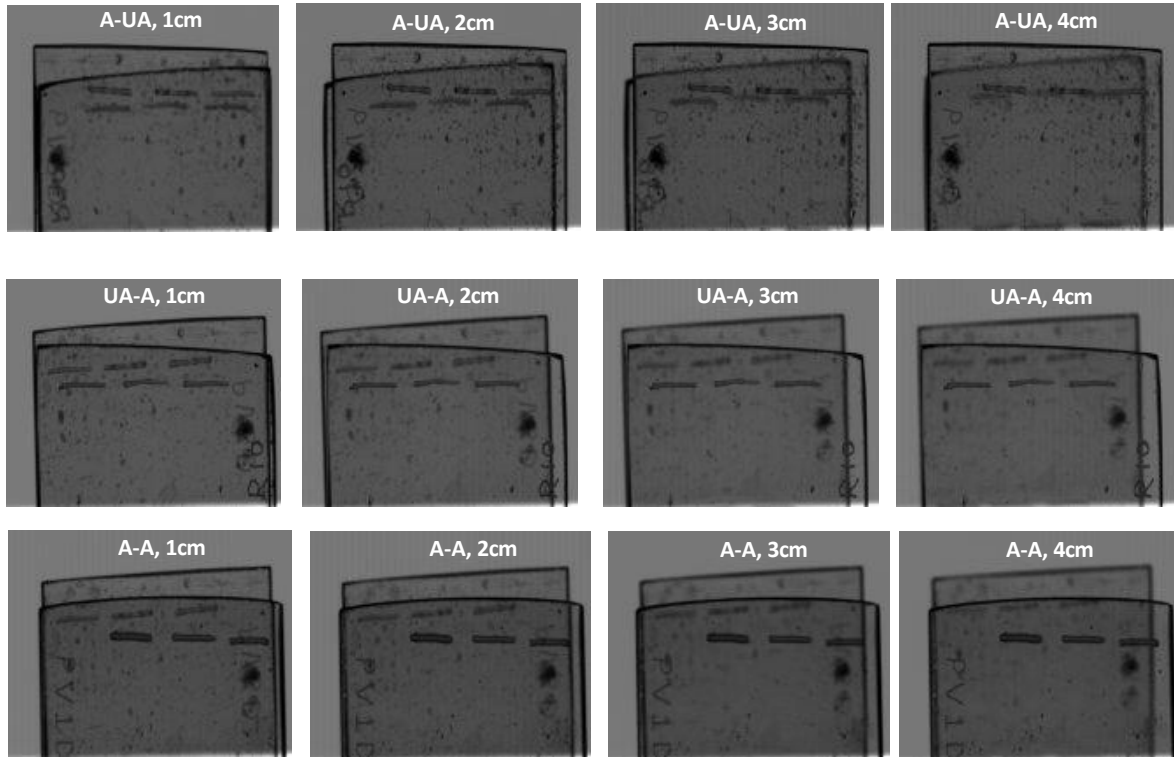


Fig. 5.14: SWIR images at 1906 nm for three different configurations of PV aged (A) and unaged (UA) model glass kept at different distances (1, 2, 3 and 4 cm) one to each other. From top to bottom row, A in front of UA model glass (A-UA), UA in front of A (UA-A) and two superimposed A model glasses (A-A) (Field of view: $\approx 4\text{ cm} \times 5.5\text{ cm}$)

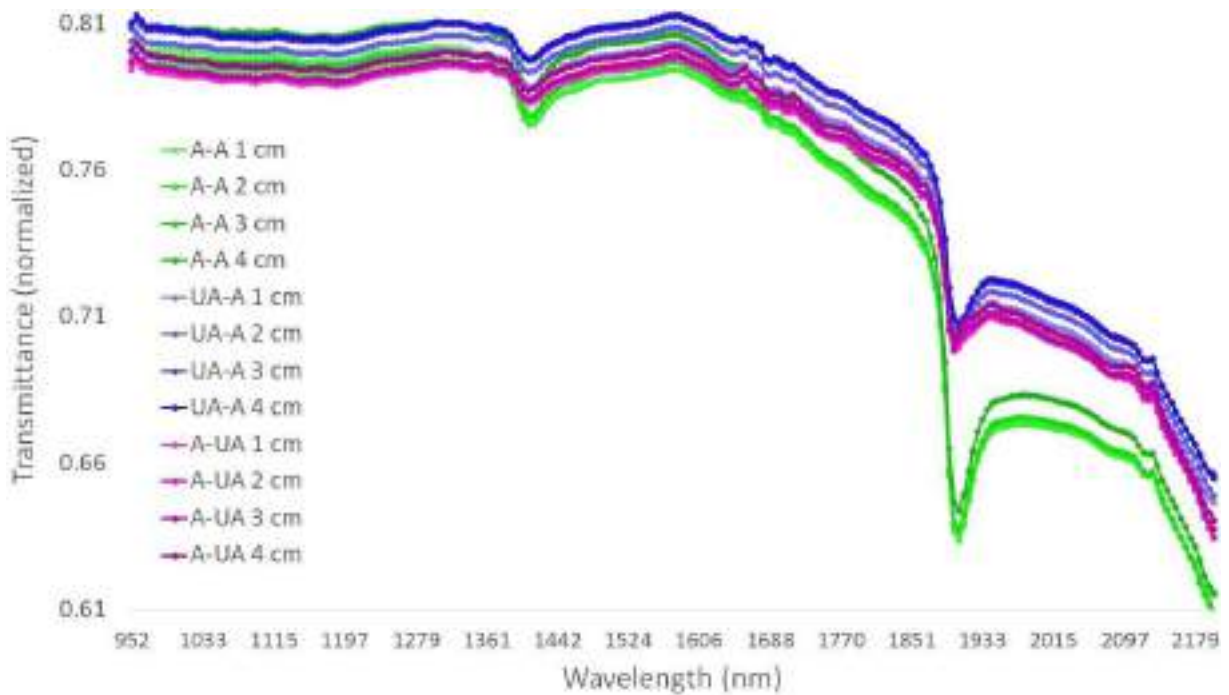


Fig. 5.15: SWIR spectra of the three different configurations (A-A, UA-A and A-UA) of model glasses kept at different distances (1, 2, 3 and 4 cm). From top to bottom row, two superimposed A model glasses (A-A, green lines), UA in front of A (UA-A, blue lines), A in front of UA model glass (A-UA, magenta lines)

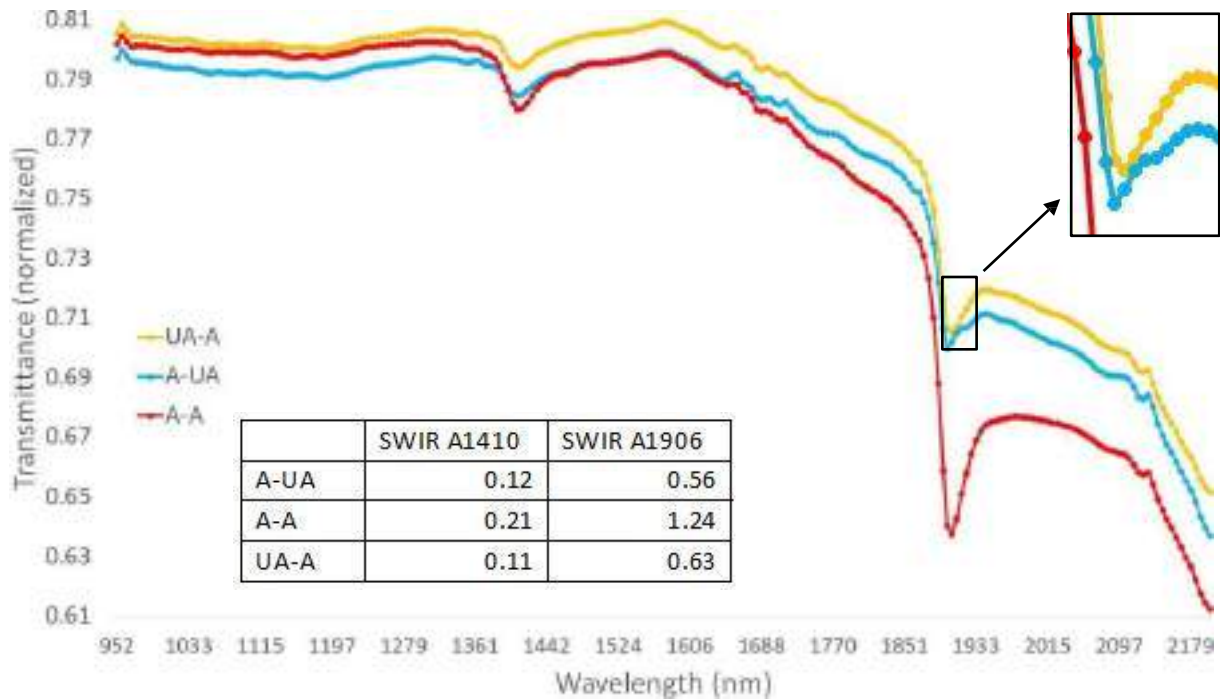


Fig. 5.16: Comparison of the SWIR spectra of the three different configurations A-UA, UA-A and A-A along with inset of zoom of the shoulder in A-UA spectrum in the 1940-1960 region

It could be concluded that SWIR HSI was able to detect the presence of corrosion even in the case of 3D objects however it also presented the limitation that it would need an additional visual inspection for an object to understand which wall is more corroded since the spectra produce peaks based on both the walls of an object. Additionally, it would be difficult to conclude if the object has one wall highly corroded or two walls corroded enough given that both the spectra could produce the same area of peaks. Therefore, the interpretation of the curves must be carefully and thoughtfully done.

5.10. Visualization of model cups

In case of 3D model cup, light was captured by the camera through the two walls (i.e., four interfaces) of the model cup standing upright. Preliminary trials showed that focusing on the front or the back wall of the cup and the distance between the two walls does not really affect the spectra of the double walls. Some areas appear too dark as intensity of the transmitted light was too low such as the left and right side and the bottom. Six different positions were recorded for each model cup to capture the whole of the 3D objects rotating the cup each time by 60° angle (Fig. 5.17a).

The different orientations of the same model cup produced spectra with the same peaks and their areas, as can be seen from the graph comparing six spectra from the same model cup, the example of PV cup is presented in figure 5.17b.

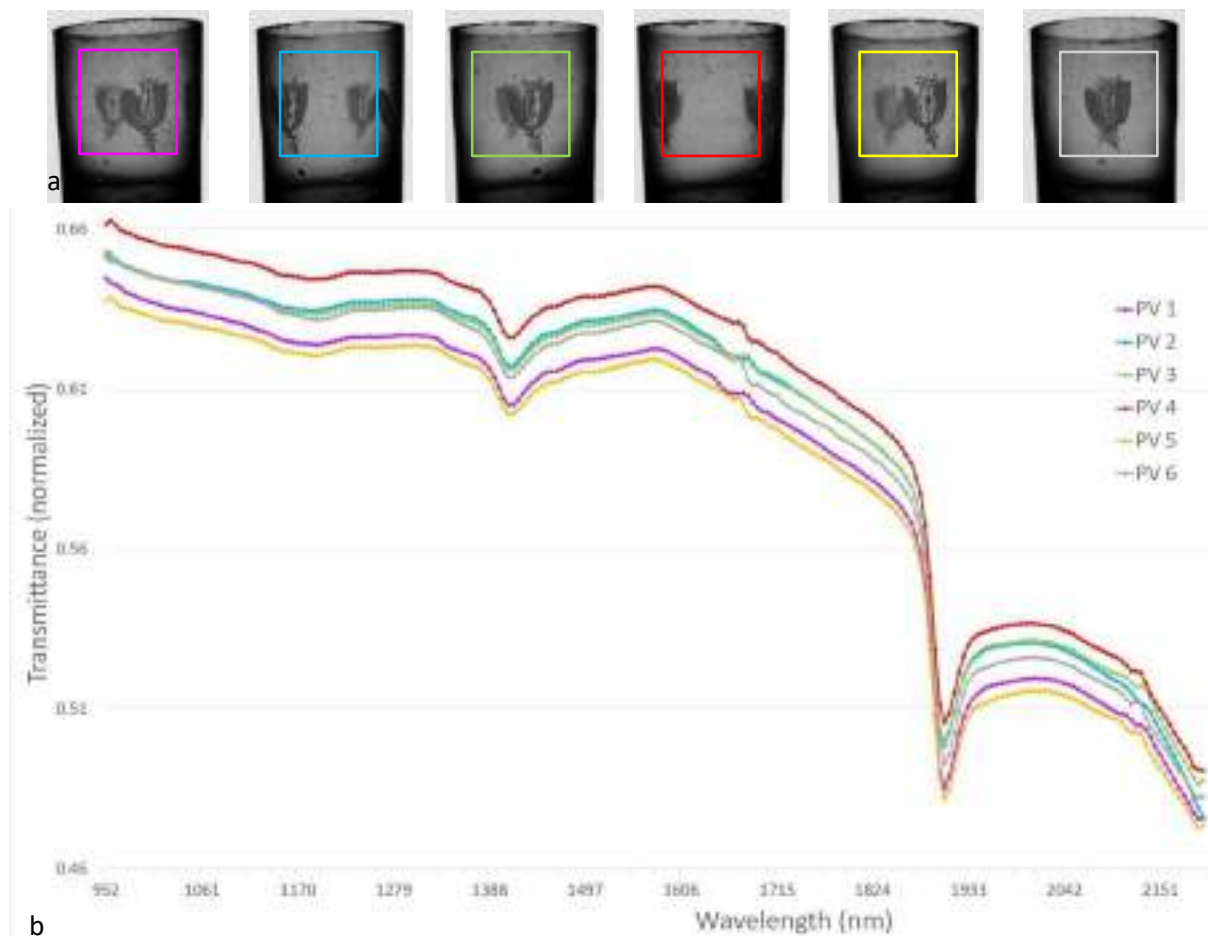


Fig. 5.17: a) SWIR images at 1906 nm for PV model cup aged for 17 months in six different orientations changing by 60° angle (Field of view: 7 cm × 6 cm) b) SWIR spectra taken in different position (taken in the areas represented inside the coloured rectangles) Spectra for model cups were cut off above 2200 nm to remove a noisy region

The exploratory research on imaging 3D transparent glass objects was successful in documenting salt neocrystallizations as well as heterogeneities on both P and PV model cups using SWIR camera. The P and PV model cups displayed bands running around the curve of the cups which appear darker than the rest of the cup (some of them indicated by orange arrows in figure 5.18). These bands were interpreted as zones with higher corrosion, and were found to be similar to the darker bands observed on the model glass as well again running along the curve of the glass (section 3.9). These could be surface discontinuities produced due to the manufacturing process by the use of a tool, thereby creating zones where corrosion was exacerbated by the run off of the wet SN. These bands were not observed in case of V model glass since they did not show any run-off of the wet SN.

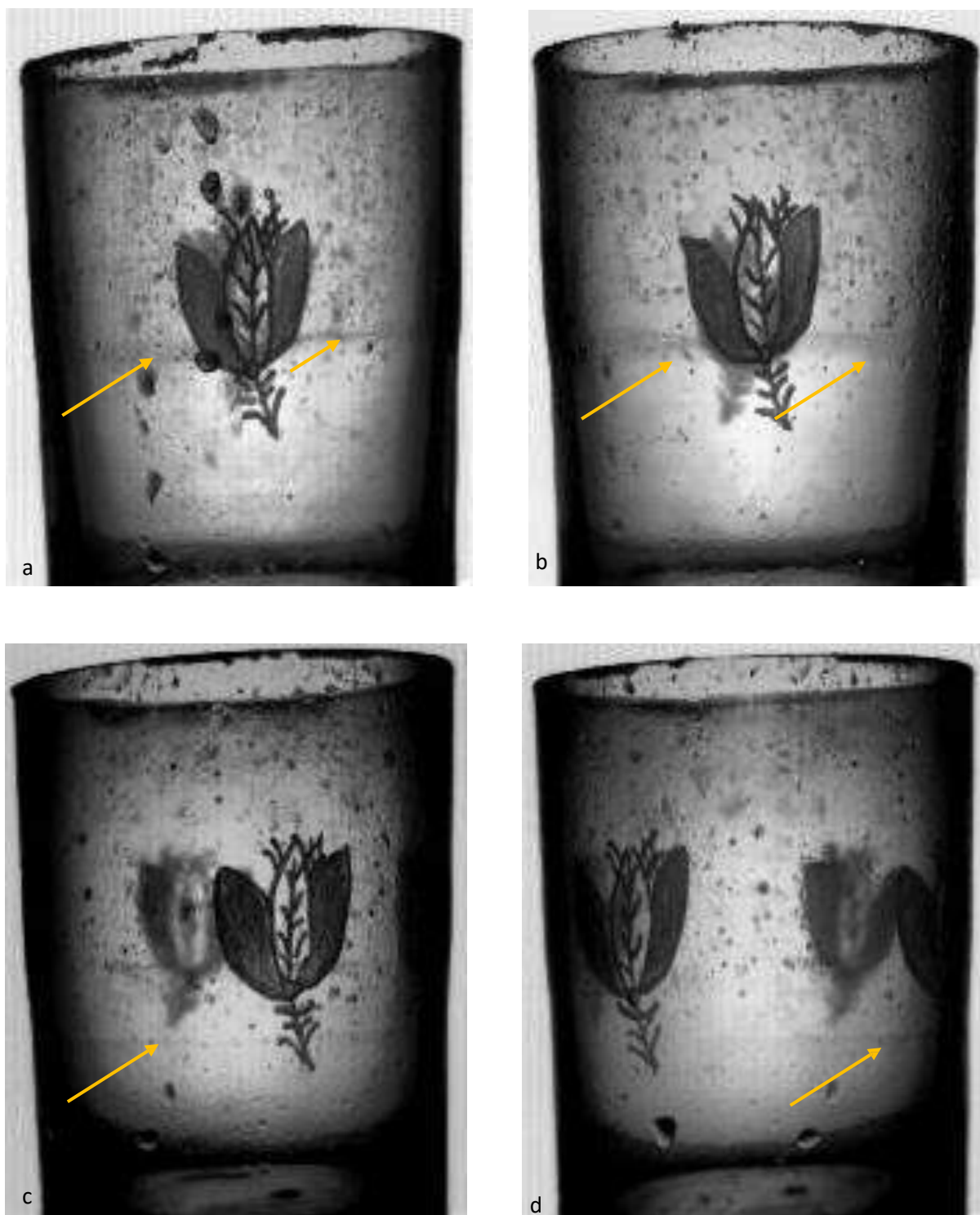


Fig. 5.18: SWIR images for model cups aged for 17 months at 1906 nm for conditions a) and b) P, c) and d) PV (Field of view: 7 cm $\times$ 6 cm)

A comparison of the images at ≈ 1410 nm and ≈ 1906 nm clearly helped in distinguishing between wet salt neocrystallizations and dry salt neocrystallizations (Fig. 5.19a-b). It could be observed that dry salts were opaque in both the images (Fig.5.19, within the yellow rectangles) while the wet salt neocrystallizations were transparent at ≈ 1410 nm but opaque at ≈ 1906 nm (Fig.5.19, within the blue rectangles). Moreover, it was interesting to note that the wet salt

neocrystallizations present on the back wall (opposite to the camera focus) could be also observed although blurred and a lighter grey at 1906 nm (Fig 5.19, within the orange rectangles) (Fig. 5.19a and b).

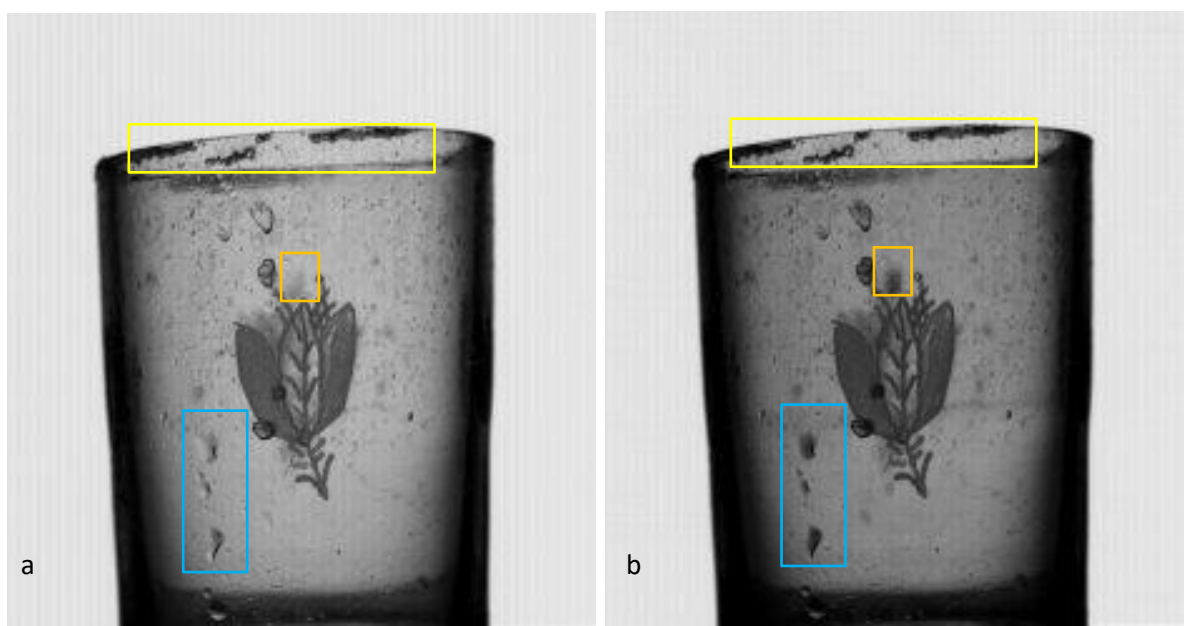


Fig. 5.19 SWIR images for PV model cup aged for 17 months at a) 1410 nm b) 1906 nm (Field of view: 9 cm $\times$ 8 cm)

In the case of V cups, there were no clear visual signs of corrosion other than some haziness and loss of transparency (Fig. 5.20). Therefore, SWIR can document presence of corrosion even at very early stages.



Fig. 5.20: SWIR images at 1906 nm for V model cup aged for 17 months in three different orientations (Field of view: 9 cm $\times$ 8 cm)

An average of six spectra was calculated for each model cup (extracted from area within the coloured rectangles as shown in Fig. 5.17a). When comparing these spectra from different conditions, it could be seen that P and PV model cups had much higher extent of corrosion as compared to V model cup based on the 1410 and 1906 nm peaks (Fig. 5.21, Table 5.5). The area under both the peaks were slightly higher in P than PV (Table 5.5). It is worth noting that the SWIR A_{1906} value of the model cups correspond with those of the model glass (section 3.7.4)

which are roughly double of them (since two walls of the cups contribute to the spectra). Both the peak areas for the V model cups were much lower than P or PV model cups. The A_{1906} value for V model cup was much higher than the reference cup.

Table 5.5: Average values of the integral of $I_{1390-1440}$ and $I_{1876-1936}$ calculated from SWIR spectra for the different model cups aged in P, PV and V conditions along with unaged reference

Aging condition	$I_{1390-1440}$	Standard Deviation	$I_{1876-1936}$	Standard Deviation
Ref	0.02	0.01	0.04	0.05
P	0.22	0.00	1.35	0.03
PV	0.21	0.00	1.26	0.03
V	0.05	0.00	0.2	0.01

The integral of the spectral band centred at 1410 nm ($I_{1390-1440}$) and 1906 nm ($I_{1876-1936}$) could be used to obtain an estimation and therefore compare the extent of hydration and dissolution between different aging environments and periods. The ≈ 1410 nm peak seemed to correspond to advanced stages of corrosion since it indicated changes in the quantity of OH^- species indicating possible network dissolution due to hydrolysis while leaching indicated by ≈ 1906 nm peak was much higher in extent. While to the naked eyes only a “haziness” or loss of transparency was visible for V model glass, a small peak could be seen at 1906 nm indicating that HSI can detect even early stages of corrosion not discernible by visual inspection.

For 3D model cups, HSI offered visualisation of SN, heterogeneities presumably due to manufacturing, identification of corrosion and comparison of the corrosion extent in different conditions and at different stages. The results on model cups were found to be very similar to model glass.

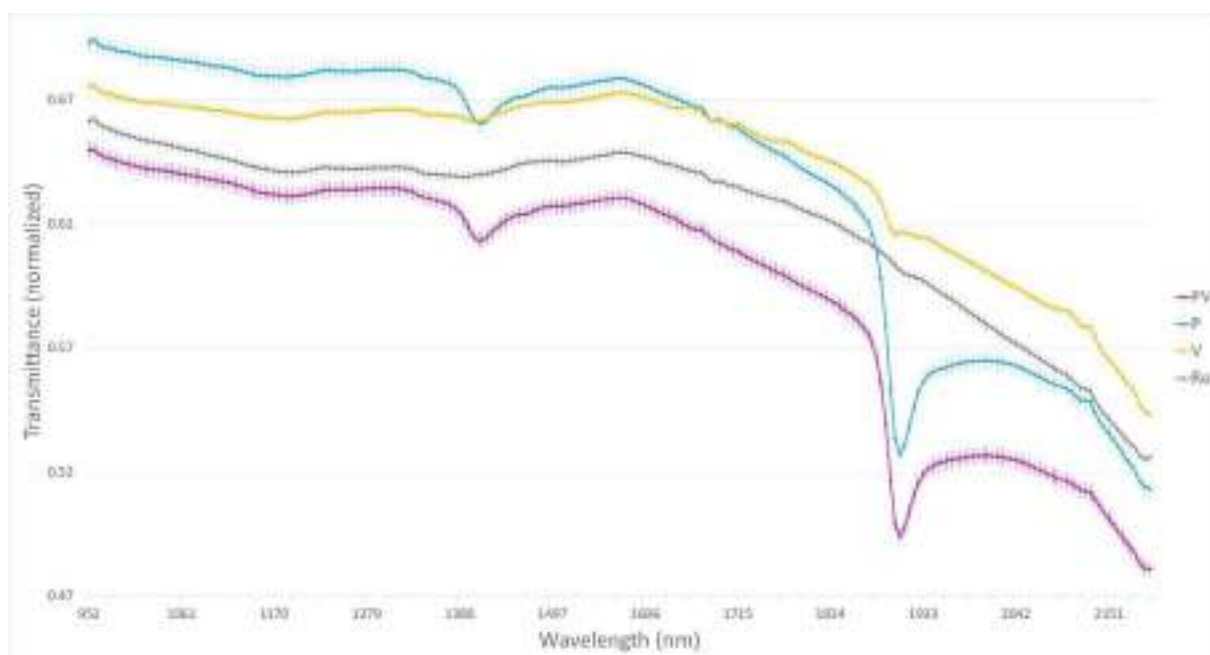


Fig. 5.21: SWIR average spectra for all the model cups aged in different conditions P (blue), PV (magenta) and V (yellow) and unaged reference (ref, black) (error bars showing standard deviation)

5.11. General conclusions and proposed identification and documentation protocol for actual historical objects

The aging of the model glass and model cups in the presence of VOC was successful since it produced corrosion similar to that found in the actual historical objects of the museum. The aging in P and PV conditions with higher concentrations of VOC produced high extent of leaching and network dissolution in the model glass leading to the formation of formate salt neocrystallizations, cracks and a silica rich alkali depleted alteration layer on the surface. Further drying was able to produce delaminations with liquid trapped under them similar to those found on the glass objects. In case of V condition with much lower concentration of VOCs, the alteration layer did reach the critical thickness necessary to favour the formation of cracks. The rate of leaching followed a linear trend with square root of time while rate of network dissolution followed the linear temporal trend for both P and PV. The V model glass displayed much lower rate but increasing with time. As the VOC concentrations used in V aging environment are comparable to values found in museums, this result proves that the corrosion of glass object in museum is inevitable in the presence of VOC.

After working with all the results in this research, a documentation and identification protocol is suggested in this section. Such a methodology will help in detecting early corrosion signs and in monitoring changes due to corrosion over time in case of transparent colourless glass objects corroded in the presence of VOCs.

Early identification of corrosion, documentation, and regular monitoring: This could be achieved using SWIR HSI which was found to be able to identify corrosion even when not visible with naked eyes. A regular monitoring using this technique would be able to find out whether the corrosion is progressing or not. However, it presents some limitations in case of 3D objects as two separate walls of an object cannot be separately analysed by HSI. Apart from this, HSI was not able to document fine cracks therefore it cannot distinguish between two objects with and without cracks if they have the same water content. Therefore, visual inspection would be recommended along with HSI to interpret the results reliably.

HSI can also be considered as a technique for documenting glass corrosion on transparent objects at a global level. The images extracted at specific wavelength, namely 1410 and 1906 have proved to be a valuable for showing and documenting the heterogeneity of VOC-induced corrosion. In addition, as HSI allowed the investigation of much larger areas of the object than the other chemical analyses technique (such as Raman and FTIR), by selecting pertinent parameters such as SWIR A_{1906} (see below), HSI could be used to assess and categorize the extent of corrosion on glass objects. This research shows that the minimum threshold of change which could be measured using SWIR is very low as corrosion on model glass aged in very low VOC could be detected right from the first withdrawal of three months.

For laboratories where SWIR HSI is not readily available, FTIR and Raman spectroscopy could be used for initial identification. FTIR was able to quantify even smaller changes in the silicate species due to corrosion especially in case of V model glass as shown in section 4.3 after deconvolution. Both of these techniques present difficulty to analyse the alteration layer and bulk glass of highly corroded historical objects using z-axis profiling. Better quality data could be acquired from microsamples if allowed to take. Apart from that, there are many limitations

of such approaches. Firstly, due to heterogeneity, a lot of points would need to be analysed to make the data statistically representative since the severe heterogeneity of corrosion in presence of VOC is well-established, which could be very time consuming. Moreover, the interpretation and deconvolution of spectra requires high-level expertise, might be also time consuming. Deconvolution would be required especially if the corrosion extent is to be quantified.

A mere look at the collected spectra might not be able to show any signs of corrosion at early stages as already understood by looking at V model glass spectra. However, for P and PV model glass, changes in the spectra could be observed easily.

Documentation of cracks and SN: While coarse cracks and large sized SN could be documented using RGB photography or SWIR imaging, it was found that digital microscopy was the best option for proper quantification of these features even in incipient stages for 3D objects. DM equipped with automatic auto-focus stitching also allowed for the global documentation of 3d objects especially using the flexible arm. Additionally, the hardware and software user interface were easy to use and did not require long training hours to learn. Further research is required to develop the application of RTI for such documentation of 3D objects using robotic arm which is an ongoing research project in ImVia lab, UBFC, Dijon. This could make the documentation repeatable, quantifiable as well as much faster generating both descriptor maps as well as interactive re-lighting videos.

Even though visual inspection can already give information about the species of large-sized salt neocrytallizations present on the corroded surface, Raman spectroscopy characterization is required for a precise identification of the SN because knowing the species can also give information about their corrosivity as well as about the potential sources of pollutants.

Categorization of corrosion extent: Global scale parameters such as SWIR A_{1906} and SWIR A_{1410} could be employed along with visual inspection to categorize the extent of corrosion on different glass objects. Below is shown an attempt at categorizing the corrosion extent on the model glass and model cups corroded in the three different P, PV (higher VOC concentrations and V (lower VOC concentration) aging conditions for different aging periods (Table 5.6). In the present case four categories of corrosion were created:

- A) Not Corroded: SWIR $A_{1906} < 0.10$, SWIR $A_{1410} < 0.02$; No opacification or SN or cracks visible on the object
- B) Initial stage corrosion: $0.10 < \text{SWIR } A_{1906} < 0.30$, $0.02 < \text{SWIR } A_{1410} < 0.05$; No cracks or SN can be observed with naked eyes, slight loss of transparency and glossiness of the glass surface
- C) Intermediate stage corrosion: $0.30 < \text{SWIR } A_{1906} < 0.60$, $0.05 < \text{SWIR } A_{1410} < 0.10$: SN and fine cracks could be observed on the surface
- D) Advanced stage corrosion: $0.60 < \text{SWIR } A_{1906}$, $0.10 < \text{SWIR } A_{1410}$: SN and fine cracks could be observed on the surface. Coarse crack network and delamination could also be observed.

Table 5.6: Categorization of the corrosion extent of model glass and model cups based on SWIR A₁₉₀₆ and SWIR A₁₄₁₀ values

Name	A1906	A1410	Category
P (3m)	0.44	0.07	Intermediate stage
P (6m)	0.57	0.09	Intermediate stage
P (9m)	0.70	0.11	Severely Corroded
P (12m)	0.75	0.12	Severely Corroded
P (17m)	0.85	0.13	Severely Corroded
PV (3m)	0.44	0.06	Intermediate stage
PV (6m)	0.48	0.07	Intermediate stage
PV (9m)	0.59	0.09	Intermediate stage
PV (12m)	0.68	0.11	Severely Corroded
PV (17m)	0.76	0.12	Severely Corroded
V (3m)	0.12	0.02	Initial stage
V (6m)	0.13	0.03	Initial stage
V (9m)	0.15	0.02	Initial stage
V (12m)	0.15	0.03	Initial stage
V (17m)	0.13	0.02	Initial stage
P cup	1.35 (0.68/wall)	0.22 (0.11/wall)	Severely Corroded
PV cup	1.26 (0.63/wall)	0.21 (0.11/wall)	Severely Corroded
V cup	0.20 (0.10/wall)	0.05(0.02/wall)	Initial stage
Ref cup	0.04 (0.02/wall)	0.02(0.01/wall)	Not corroded

This categorization could be applied for museum glass objects as well. Since actual museum objects were not tested for this research, further research is needed to see if comparable values could be found in 3D objects. With the current information, it could be assumed that the values from a full corroded 3D object would be double the values of the model glass.

5.12. Final Remarks

The study was successful in answering most of the research questions leading to a better understanding of the corrosion mechanisms in presence of VOC pollutants especially for potash-lime silicate glass. The kinetics of corrosion were understood for corrosion at higher VOC concentration as well as lower VOC concentration (closer to real museum conditions). The role of RH was not established due to problems encountered with the VOC concentrations. The VOC concentrations therefore dominated the artificial aging. It was found that while the rate of corrosion was much higher at higher concentrations of VOCs, even at lower concentrations the corrosion rate increased with time and therefore presented danger for any historical glass object kept in such conditions. The temporal trends discussed here are surely limited to the duration of the experiment i.e. of 17 months of aging and therefore do not necessarily reflect the “long term” trends experienced by the actual objects over a much longer period of time.

The study was also successful in establishing a precise and reliable documentation methodology indicating the most useful imaging techniques for identifying global level corrosion changes in

glass objects. The SWIR HSI turned out to be useful for both visualization as well as characterization of glass corrosion and presents good preliminary results to suggest that it can be used for regular monitoring of glass objects.

Ultimately, some of these techniques were also applied on actual glass objects from the museum as well as on 3D model objects. It would be safe to say that techniques such as digital microscopy and SWIR HSI could be potentially employed by museums which wish to regularly monitor their glass collections after proper tests and trials. The acquisition for 3D objects should be optimized regarding the acquisition parameters and setup and data interpretation should be supported with visual observations as well to come to reliable conclusions.

5.12. Limitations of the research

The major limitations of this study occurred in the experimental design of the artificial aging due to various reasons. In the absence of standard laboratory infrastructure such as climate chambers and environmental test chambers with proper VOC injection system and flow meters, the experiments were run inside glass desiccators to be handled manually.

Moreover, three important corrosion factors namely temperature, relative humidity and VOC pollutants needed to be assessed to understand corrosion in the museum old storage. Out of these relative humidity and VOC pollutants were selected to be studied. Both of these parameters presented problems as mentioned.

Instead of separately exploring the effects of acetic acid and formic acid at relevant concentrations, both compounds were applied together, which makes it impossible to attribute any of the observed effects to one or the other component but might give an idea of the global effect of storing glass objects in chipwood, as was the case in the old depot.

The monitoring and measurement of the gaseous concentration was also found to be unreliable with both PID and passive samplers due to multiple factors such as high relative humidity and poor absorption on Tenax. Thus, a realistic assessment of their concentration was not possible.

Additionally, the relative humidity control material absorbed gaseous VOC pollutants resulting in changes in experimental design and making it difficult to assess the amount of VOC to be applied in the aging setup. It turned out that the applied concentrations of three orders of magnitude higher than relevant concentrations observed under real conditions, resulted in condensation of liquid acid films on the glass items especially of formic acid, as demonstrated by the acidic pH values measured and confirmed by the detection of formic acid by FTIR on corroded model glass.

5.13. Perspectives

The present study leaves a lot of further scope for research since many new questions arose during the course of this work which have not yet been fully resolved.

The effect of acetic acid, formic acid and formaldehyde could be studied separately in the case of glass corrosion using appropriate experimental systems. Such data on the temporal

progression of glass corrosion could be recorded for a much longer period of time using model glass or actual historical objects which could help to model the glass corrosion kinetics and therefore can be used for further simulations of the extent of glass corrosion present on a glass object and could even predict its future course depending on its condition and storage.

Some of the novel techniques applied in this research work need more data to be acquired in order to test their reproducibility and reliability. This is definitely true in case of HSI and RTI, wherein more samples should be analysed to be able to develop model based on the quantifiable variables extracted from these techniques will could allow to monitor the evolution of glass object with time. Even simulations could be produced for visualizing the foreseen future condition of any glass object.

Multispectral imaging could be explored instead of HSI focusing on the most important bands in the SWIR range which were found to be most useful for characterizing corrosion in this study. This could reduce the cost and time for the analyses and can provide a more efficient imaging and monitoring technique.

The quantification of cracks was done via manual tracing on DM and RTI images. This is something which could be further automated using artificial intelligence and is a big topic of research in itself.

Research could be done on understanding what produced the discontinuities during manufacturing process on the model glass and cups leading to zones of exacerbated corrosion. It would be interesting to understand how these discontinuities arise and how they affect the corrosion process. This topic has not been discussed in literature yet probably because only a global scale technique such as HSI could document them.

Apart from this, the composition of the liquid trapped under the delaminated scales was not found. Previous literature also did not provide any certain answers. A study into this phenomenon would lead to a better understanding of the corrosion mechanisms.

Ultimately, cleaning tests need to be performed to find out the best methods of removing the corrosion products from glass objects corroded in the presence of VOCs. This problem would be exacerbated by the presence of delaminations with liquid trapped under them. Research needs to be done on how to clean such objects and how to store them so that further corrosion could be slowed.

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List of presentations and publications

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- Presentation of research for the NO CHANGE Workshop Trondheim, Norway at the NTNU University Museum on 05 October 21.
- “Analysis and monitoring of degradation of historical glasses” at the Colour lunch at NTNU on 01 March 2022
- “Application of Hyperspectral Imaging for characterizing historical glass corrosion” at InArt22, in Paris, from 28 June 2022 - 6 July 2022
- “Application of non-destructive techniques to understand VOC-induced corrosion mechanisms” at Chemistry for Cultural Heritage (CHEMCH22), in Ravenna, from 4 July 2022 – 8 July 2022
- “Non-destructive analyses of VOC-induced corrosion of historical glass objects in museum environment” at International Congress on Glass (ICG22), in Berlin, on 8 July 2022

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- ‘Application of Reflectance Transformation Imaging for visualizing early signs of corrosion in historical glass corrosion’ at the Archiving 2023 conference, organized by the Society for Imaging Sciences and Technology in Oslo from 19 June 2023 - 23 June 2023
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ANNEXES

Annex I¹

The presence of formate and acetate salts on V model glass prompted further experiments to identify the source of the pollutants in the desiccator, all of which were performed using unaged model-glass samples. The first experiment was performed in a desiccator that had not been recently used. However, since acetate and formate neocrystallizations were found on the model-glass samples from this experiment, newly purchased desiccators or tightly clipped RP ESCAL Neo bags were used for further experiments. To eliminate any other possible contamination, accessories including ceramic bowls, glass stands, and metal plates were not used for these experiments. Moreover, model-glass samples aged for six months were cleaned with a solution of ethanol and water after withdrawal and were stored with and without activated charcoal for one month (Table I.1).

Table I.1. Various experiments investigating contamination source

Experiment number	Model glass	Container	Additional material	Salt neocrystallizations
1	Unaged	Used desiccator	35% RH or 70% RH preconditioned silica gel	Yes
2		New desiccator		
3		RP ESCAL Neo bag		
4	Aged six months, cleaned	New desiccator	Activated charcoal	No
5		New desiccator	None	

From these experiments, it was concluded that the preconditioned silica gel had released VOC pollutants and must be the source of contamination. To verify this hypothesis, Oddy tests were performed twice, clearly showing major modifications of the lead coupons (Figure I.1a) and slight changes to the copper coupons (Figure I.1b) exposed to all three types of preconditioned silica gel. No changes to the silver coupons were visually observed (data not shown). Accordingly, the 35%, 50%, and 70% RH preconditioned silica gels were all graded unsuitable for permanent exhibitions.

¹ Source: Sharma, D., Rothenhaeusler, U., Schmidt-Ott, K., Joseph, E., George, S., Lombardo, T.: Multi-modal analysis of transparent glass to detect early signs of volatile organic compounds-induced corrosion due to contaminated silica gel. In: Roemich, H., Fair, L. (eds.) Recent Advances in Glass and Ceramics Conservation 2022: the 6th Interim Meeting of the ICOM-CC Glass and Ceramics Working Group, Lisbon: Portugal (2022).

LEAD					COPPER			
Sample	Test 1		Test 2		Test 1		Test 2	
Reference								
Preconditioned silica gel 35%								
Preconditioned silica gel 50%								
Preconditioned silica gel 70%								

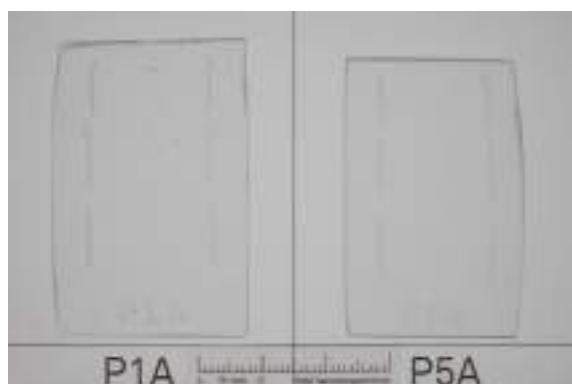
Fig. I.1: Oddy test results on a) lead and b) copper coupons

Annex II

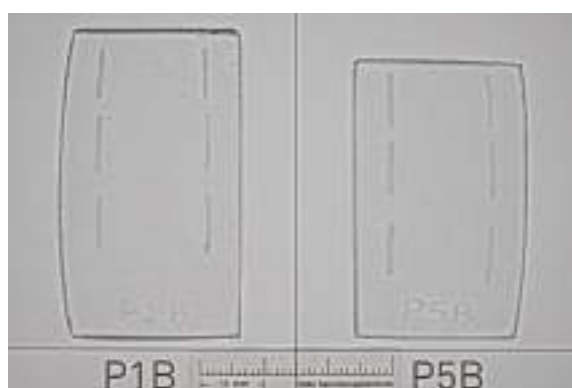
RGB transmitted light photographs of model glass before and after aging

Before

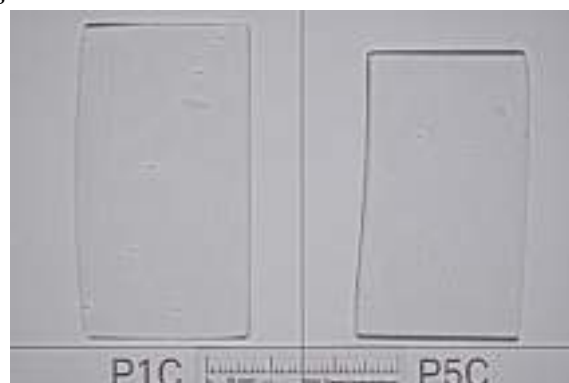
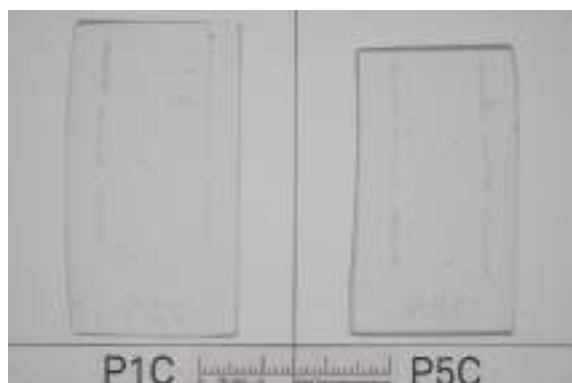
After



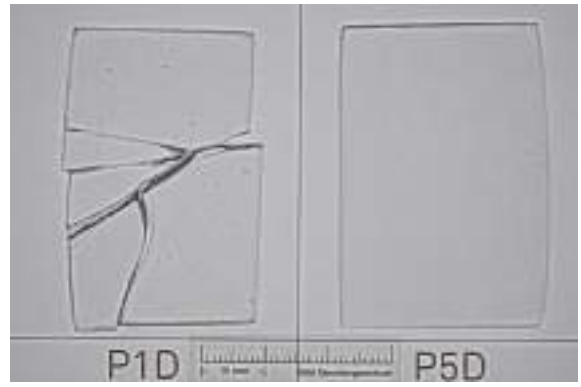
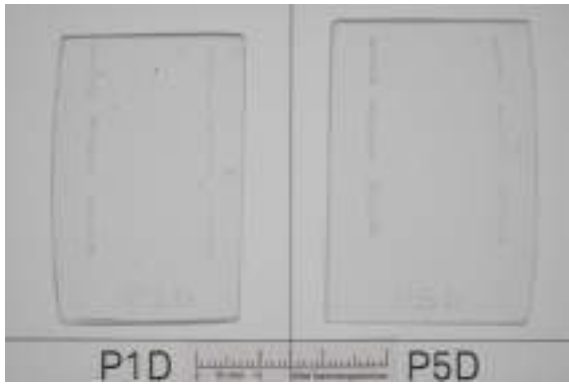
P 3 months



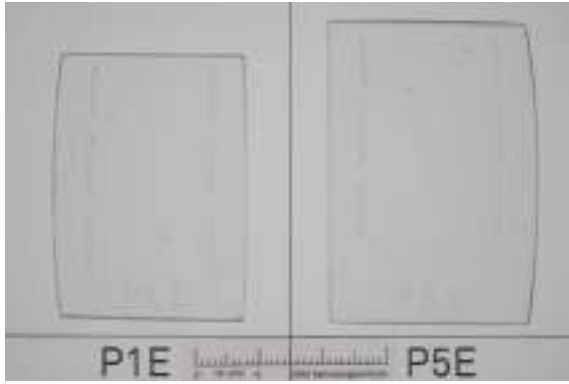
P 6 months



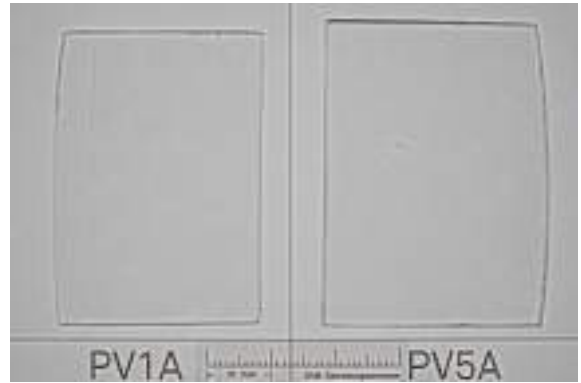
P 9 months



P 12 months



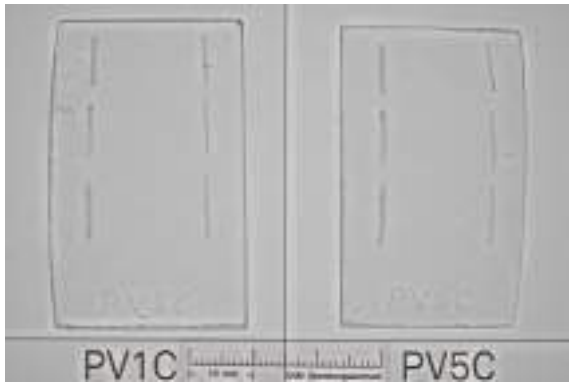
P 17 months



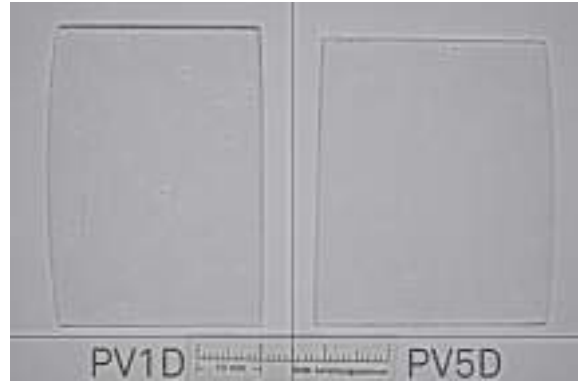
PV 3 months



PV 6 months



PV 9 months



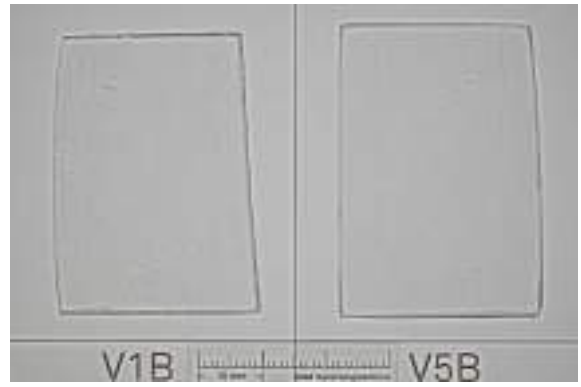
PV 12 months



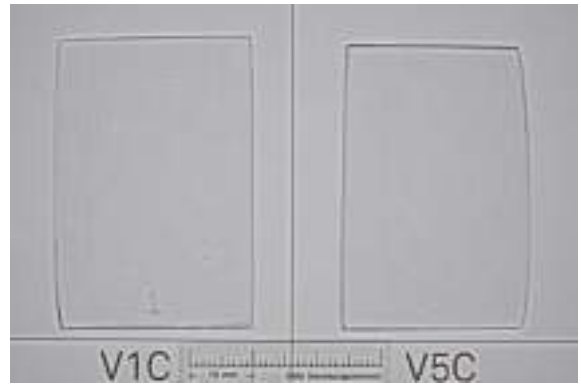
PV 17 months



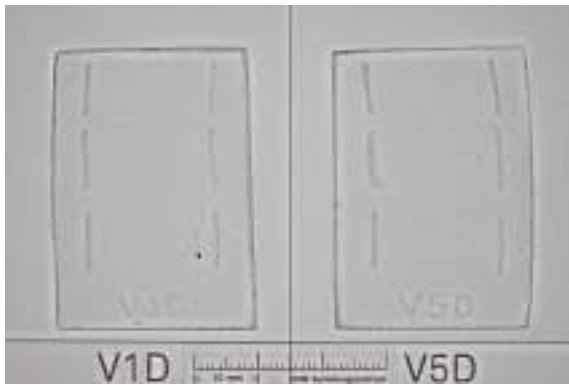
V 3 months



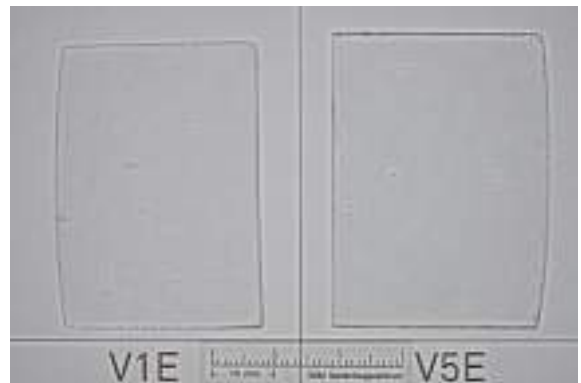
V 6 months



V 9 months



V 12 months



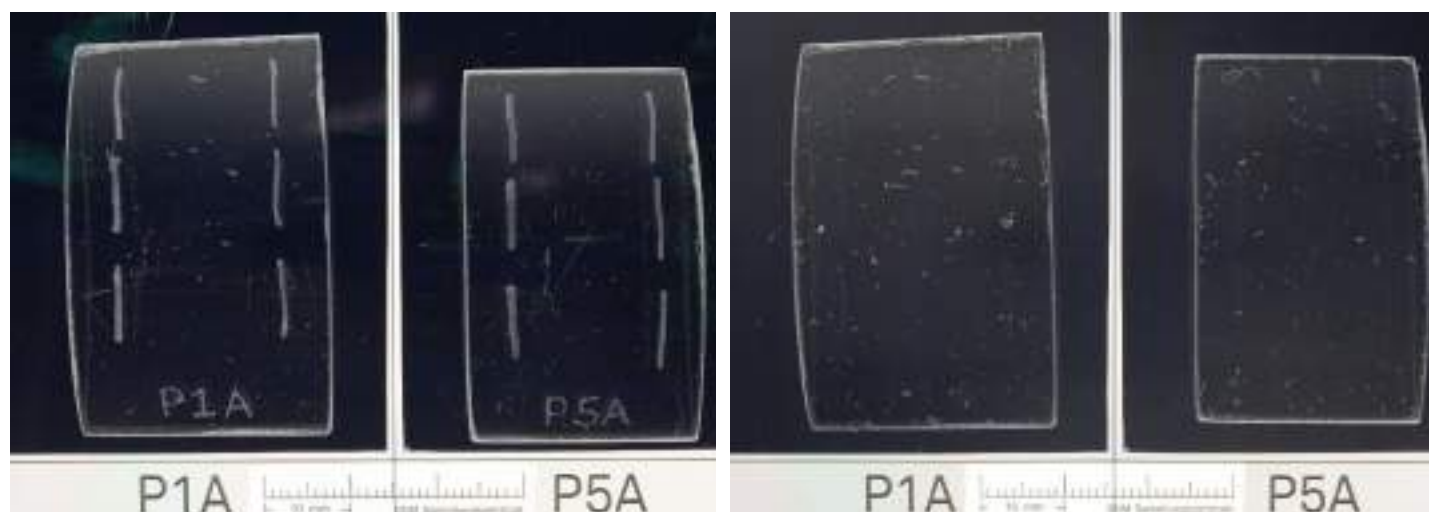
V 17 months

Annex III

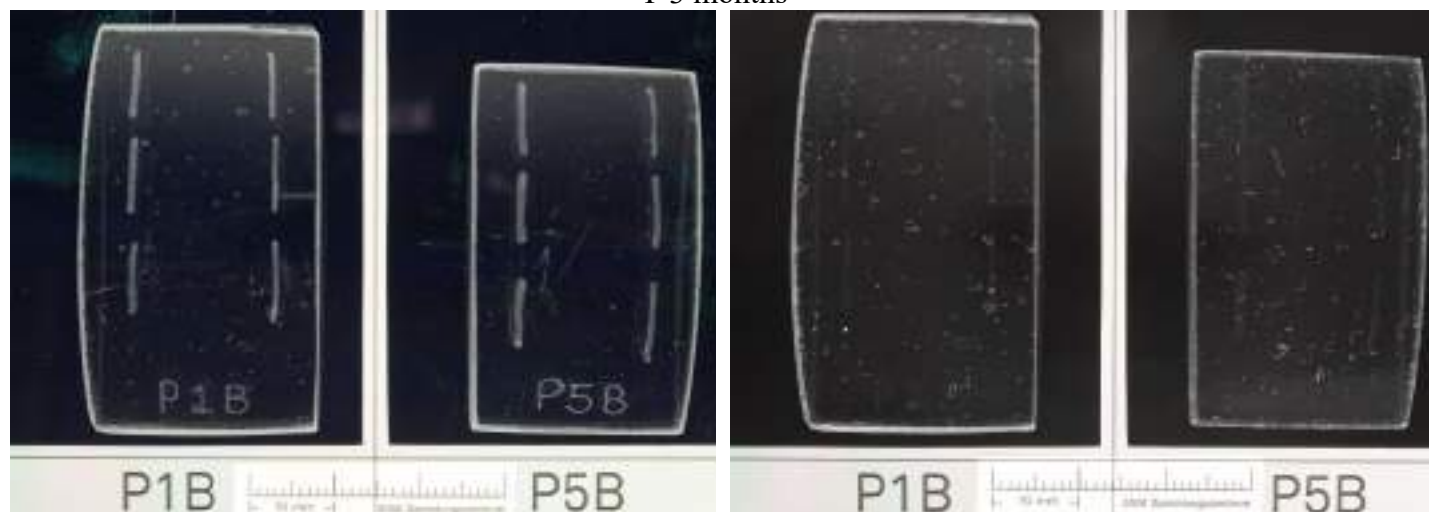
RGB transmitted and cross-polarised light photographs of model glass before and after aging

Before

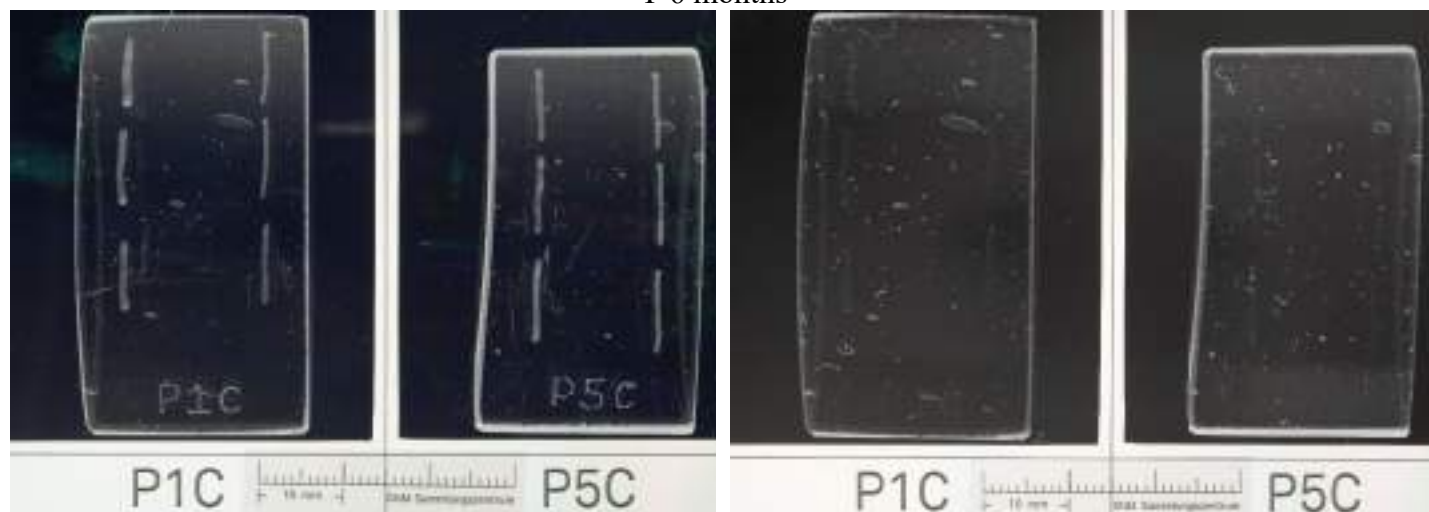
After



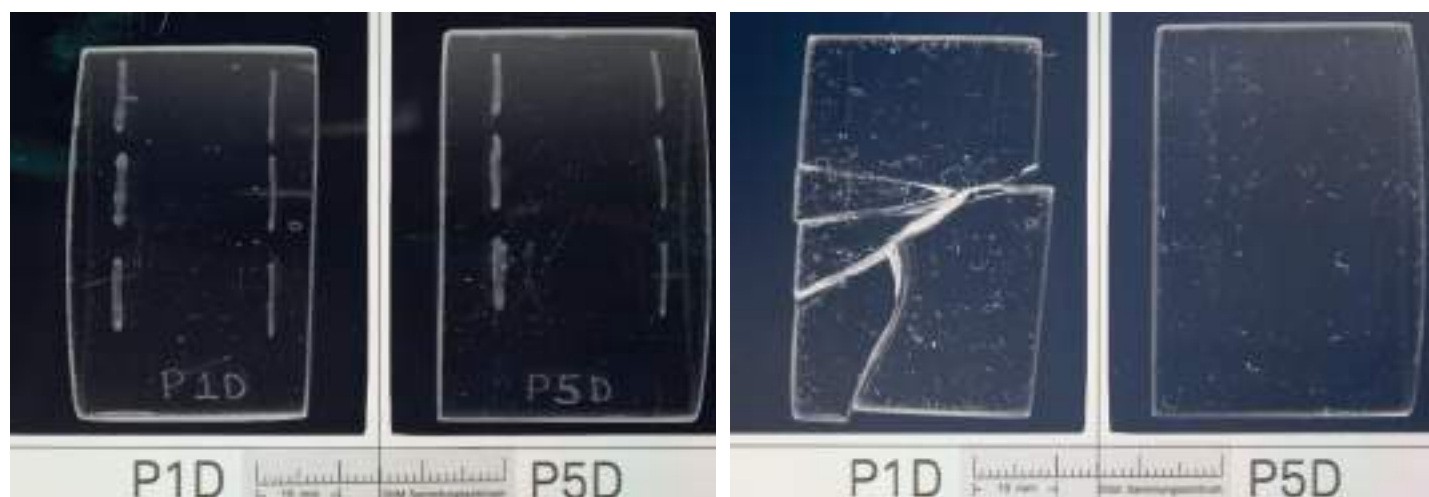
P 3 months



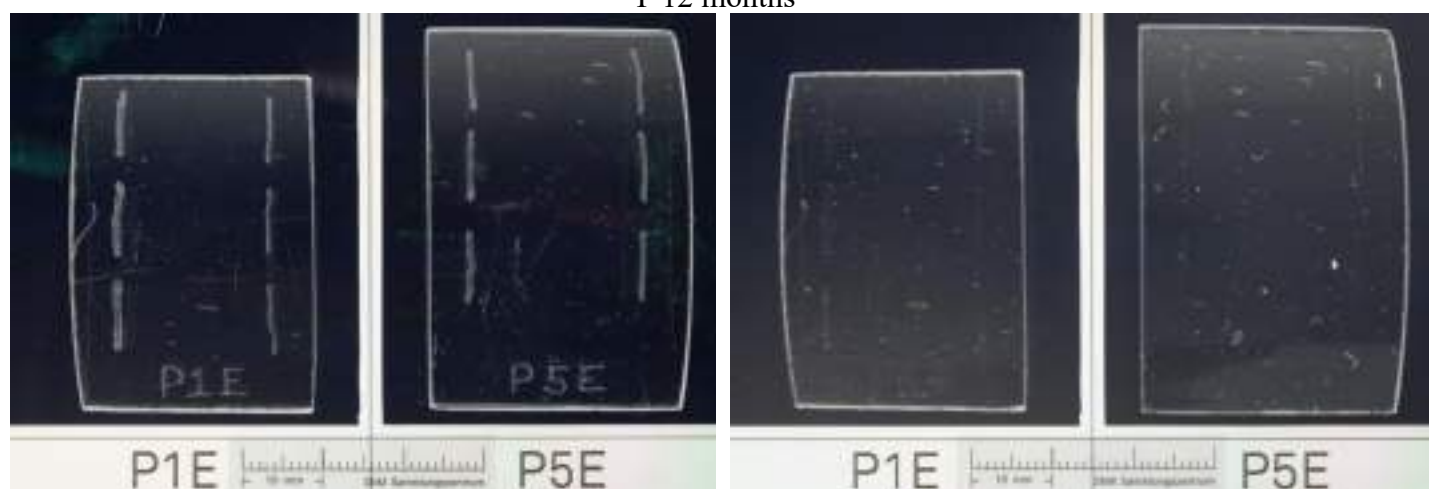
P 6 months



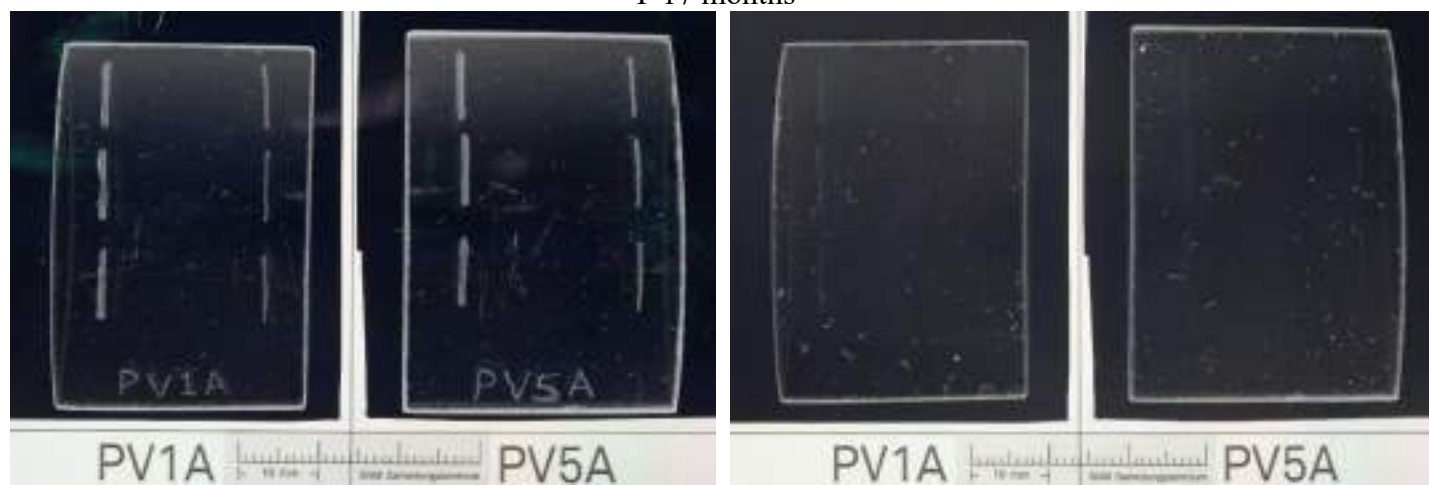
P 9 months



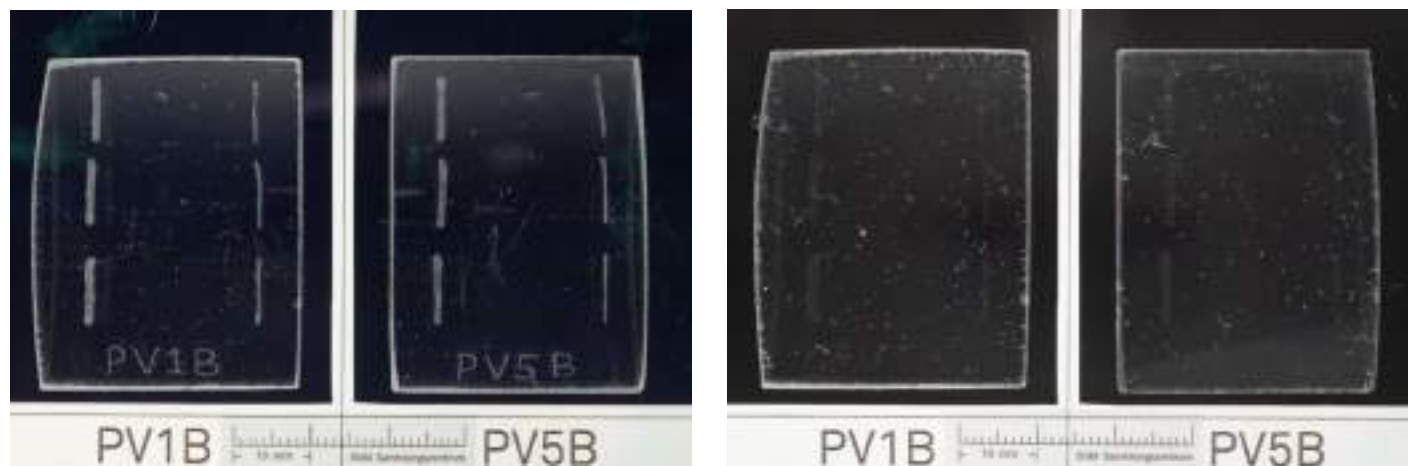
P 12 months



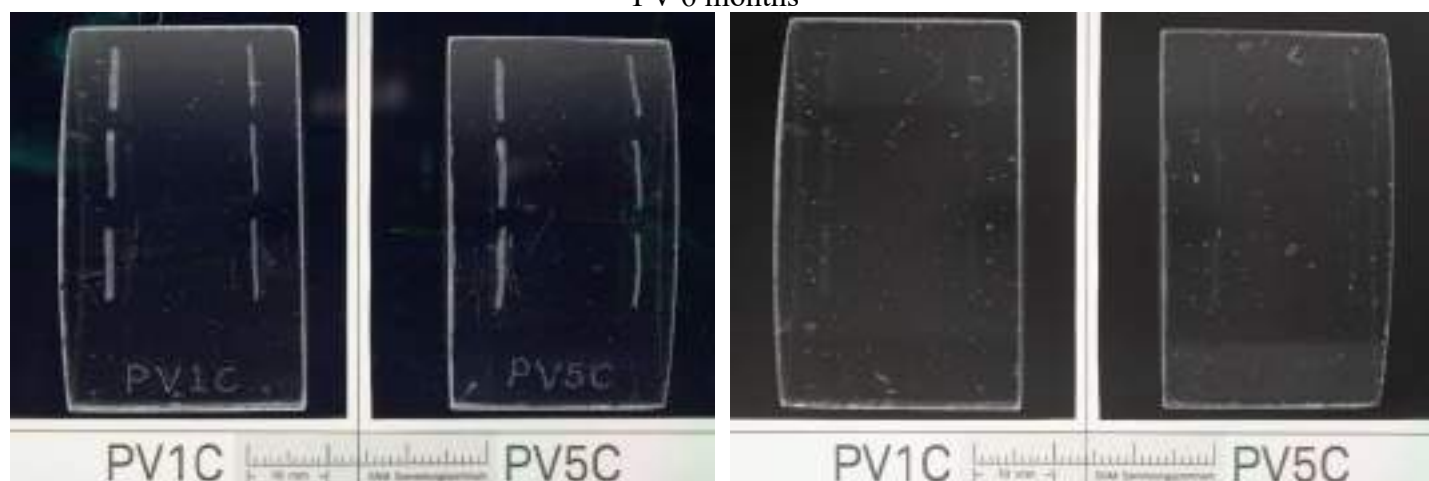
P 17 months



PV 3 months



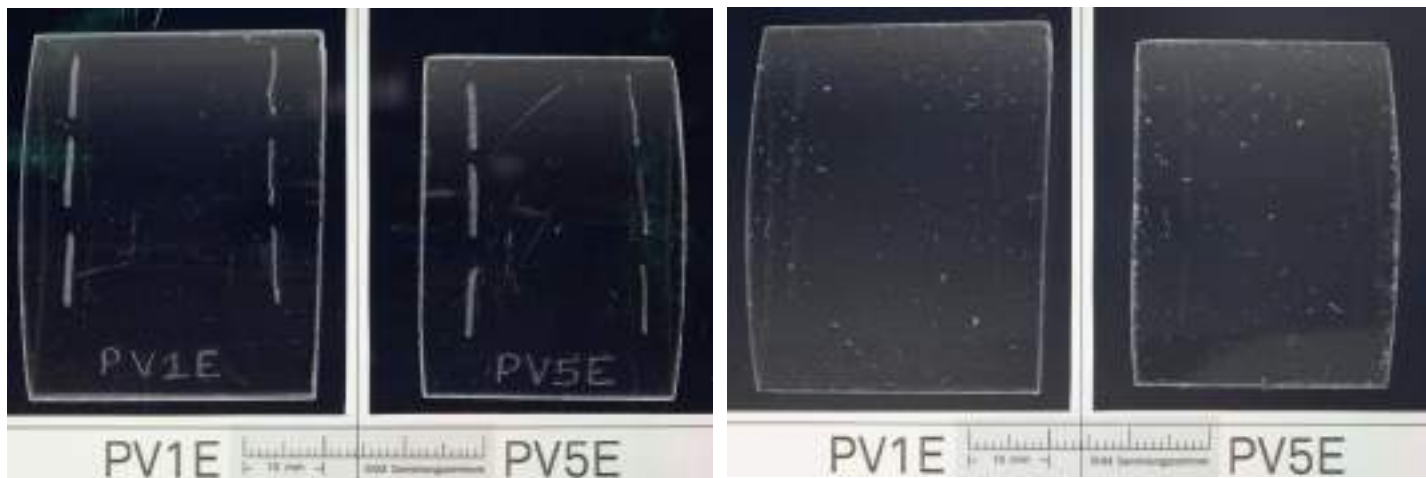
PV 6 months



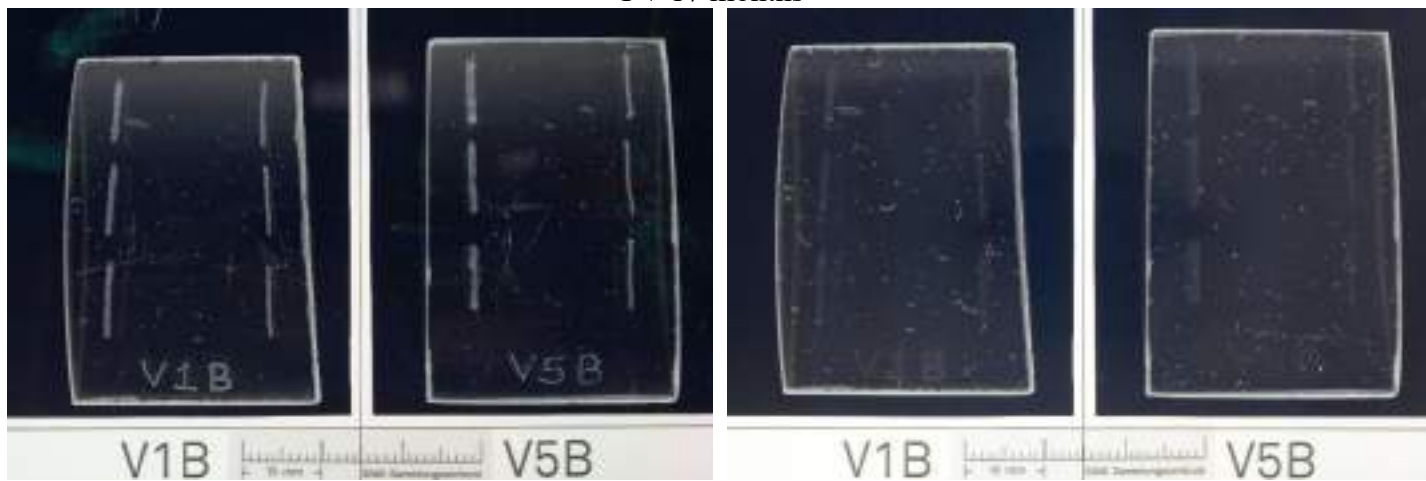
PV 9 months



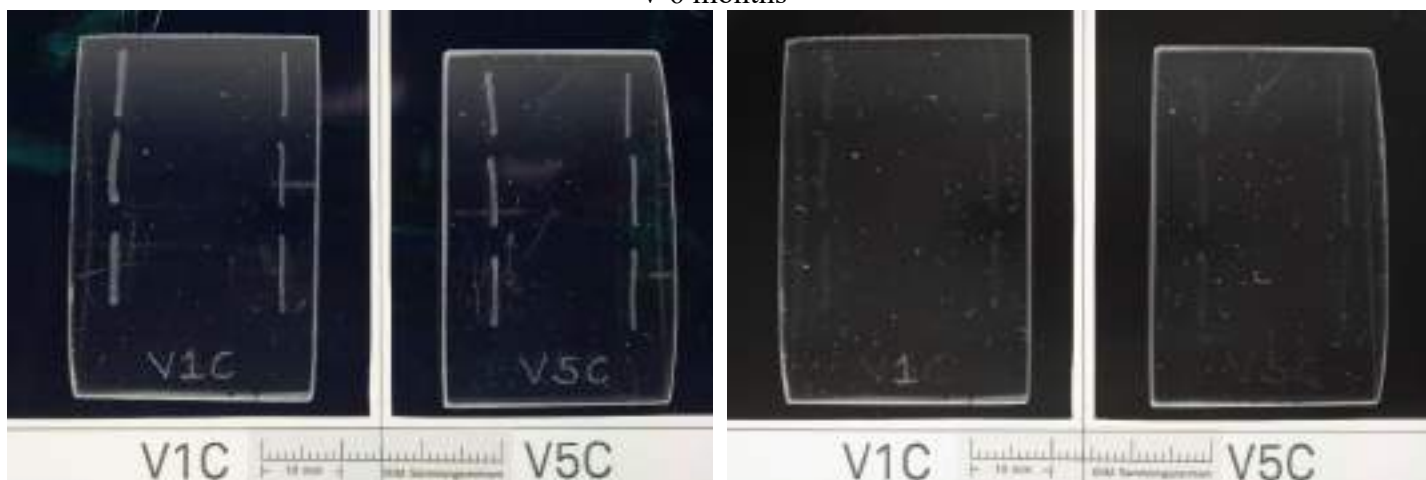
PV 12 months



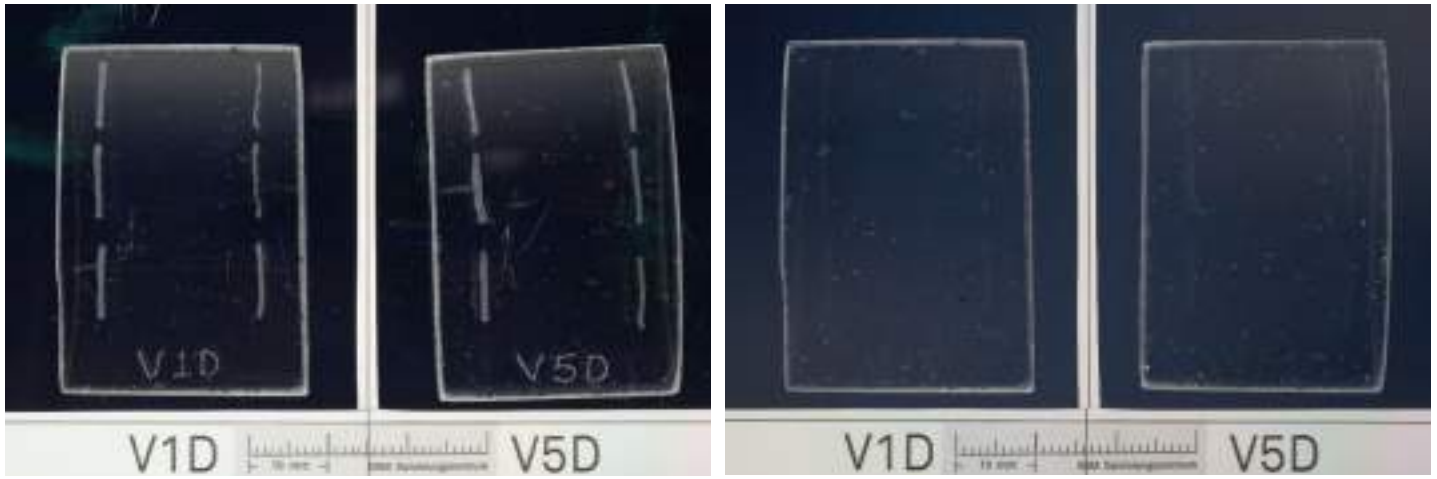
PV 17 months



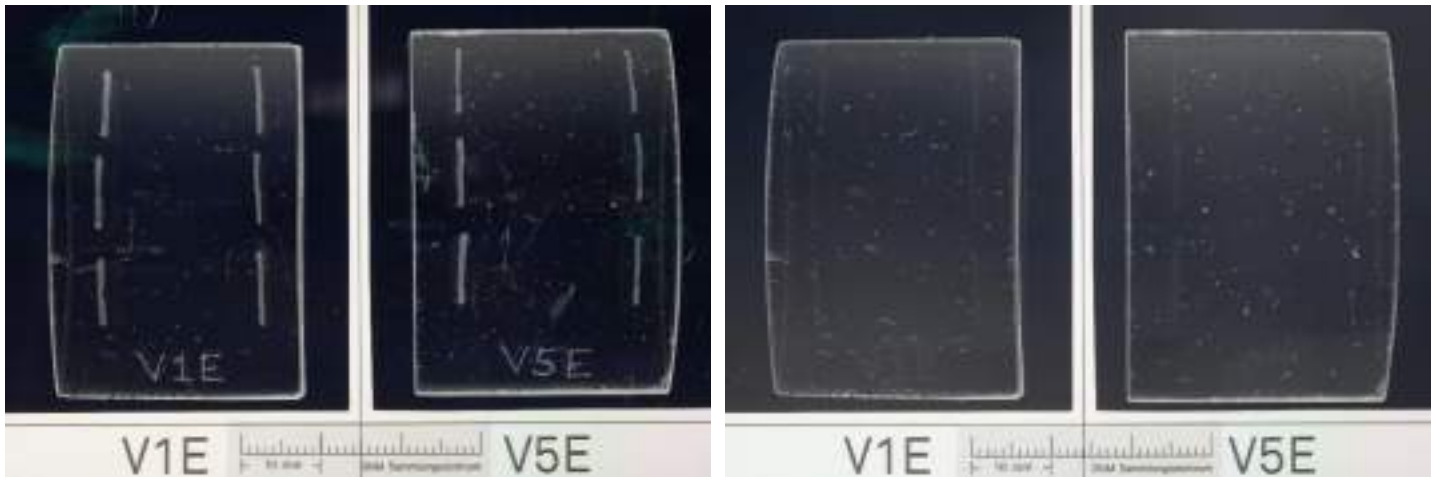
V 6 months



V 9 months



V 12 months



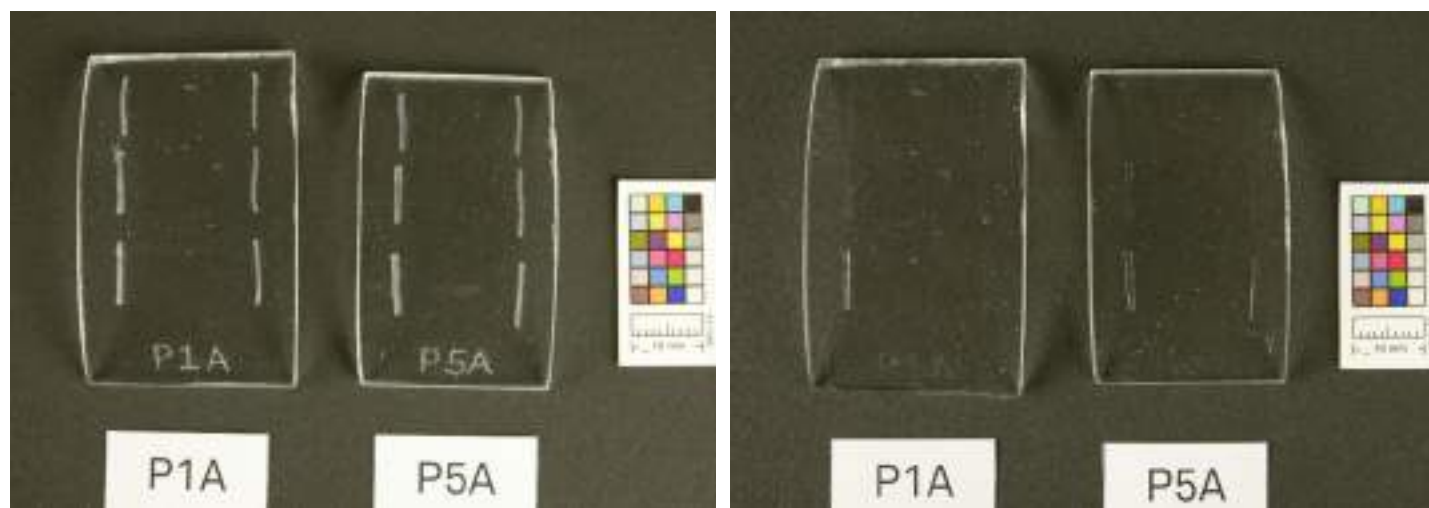
V 17 months

Annex IV

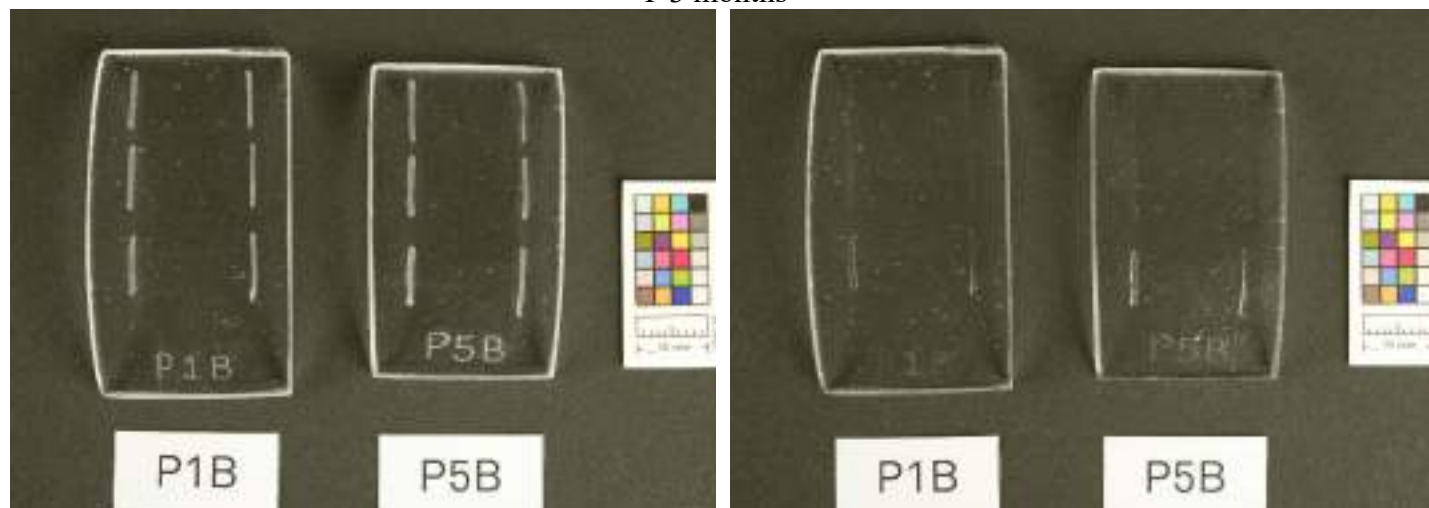
RGB reflected light photographs of model glass before and after aging in diffused lighting

Before

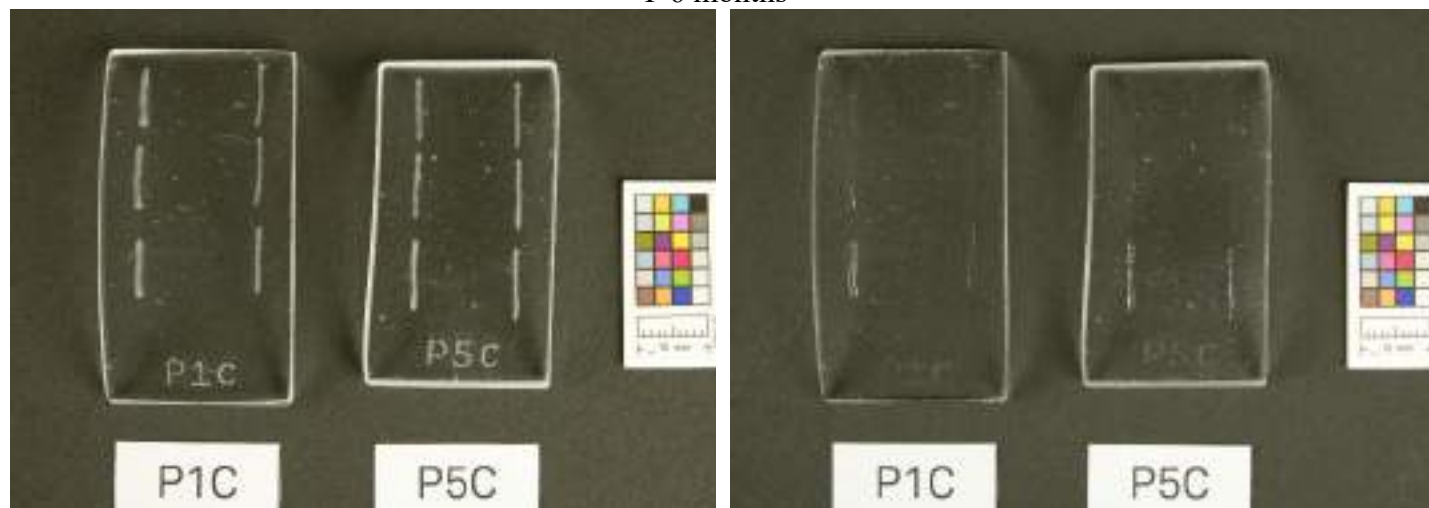
After



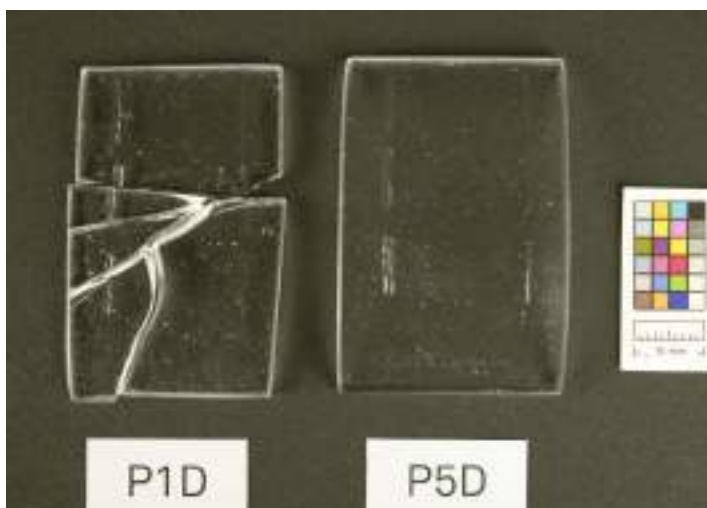
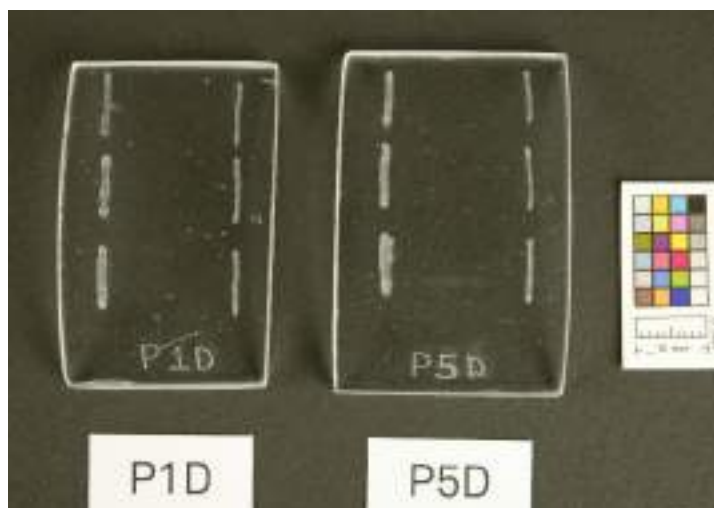
P 3 months



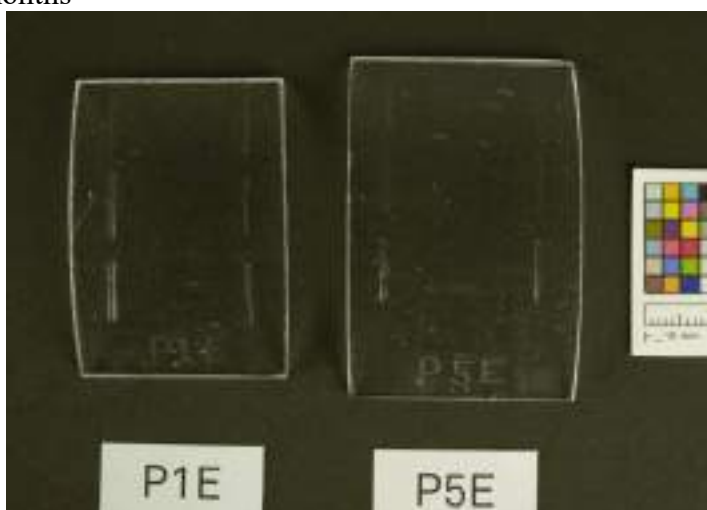
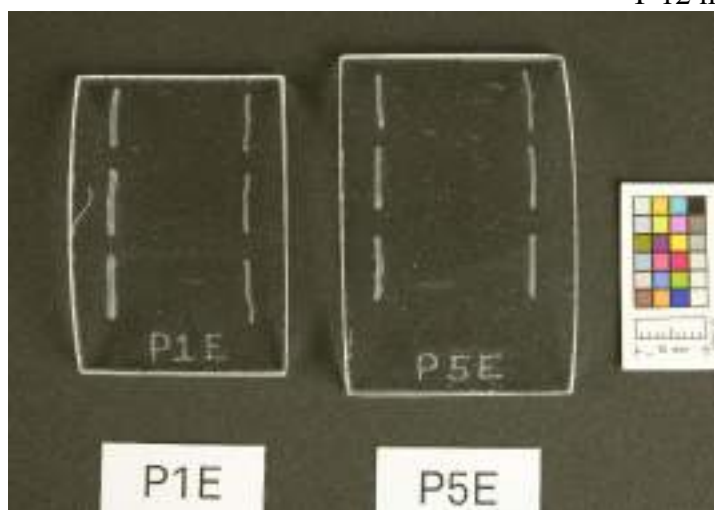
P 6 months



P 9 months



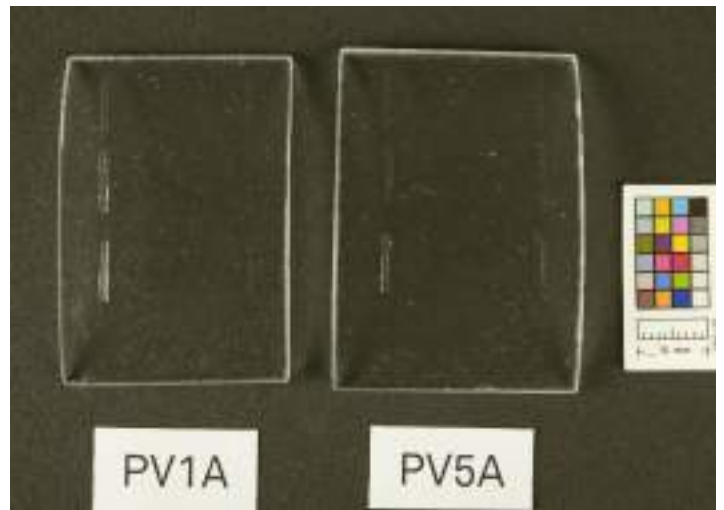
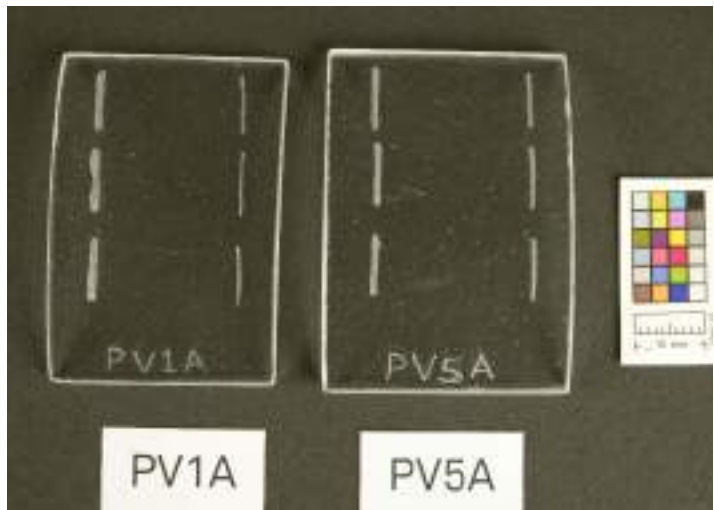
P 12 months



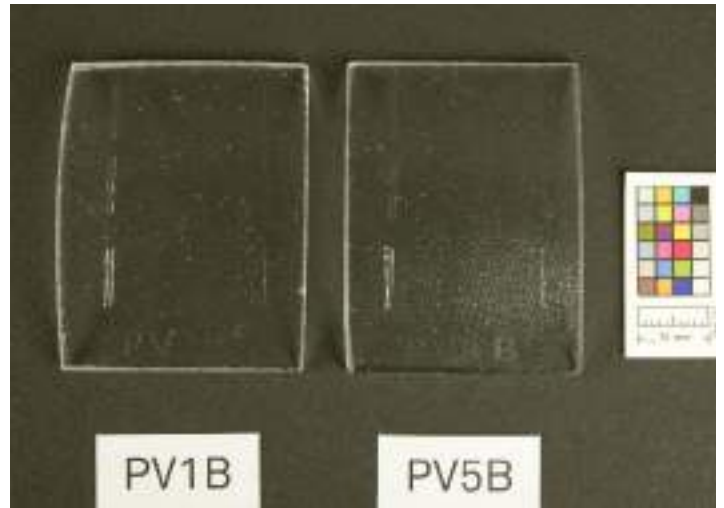
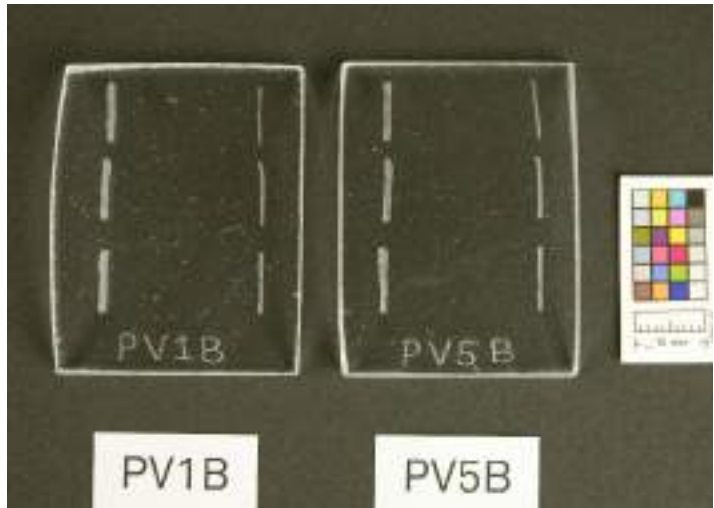
P 17 months



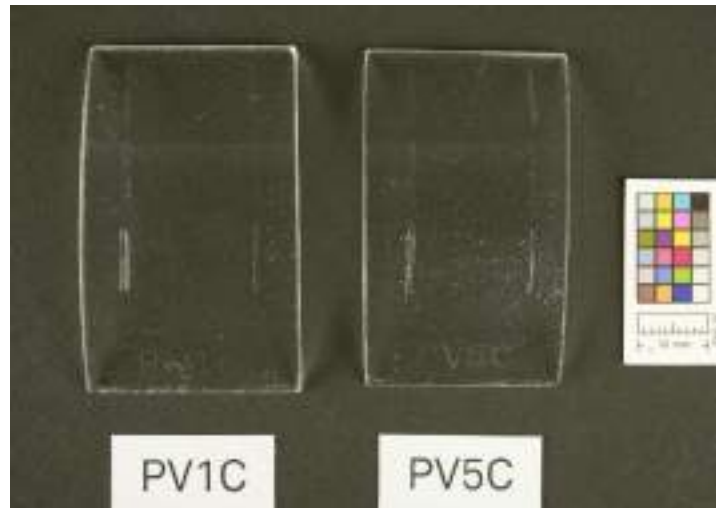
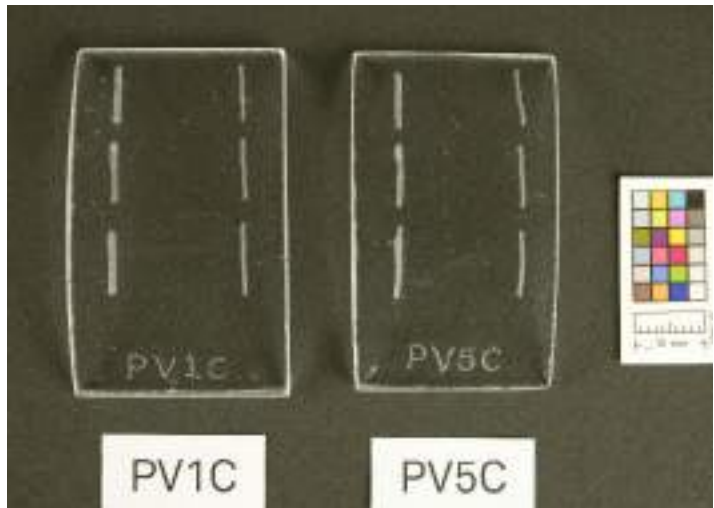
P 17 months



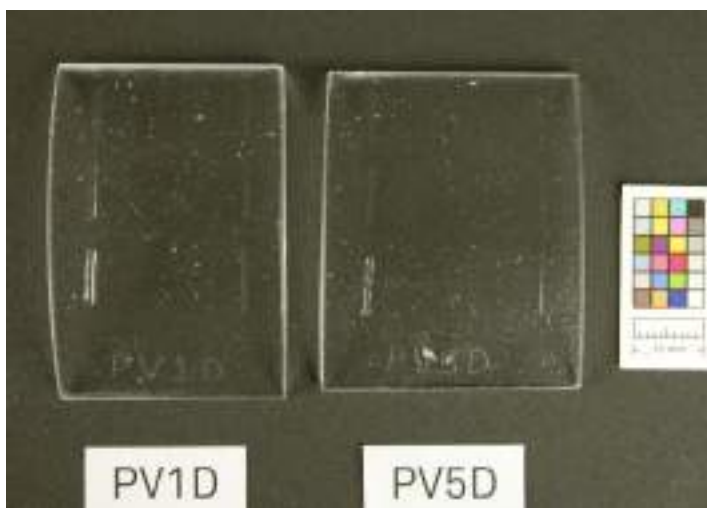
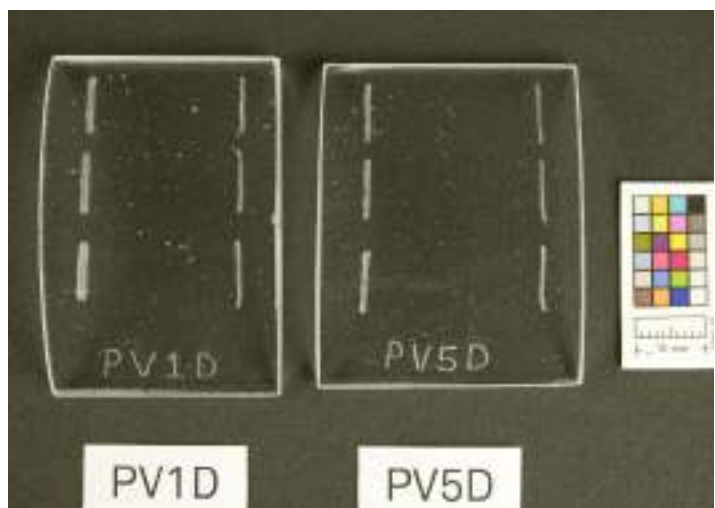
PV 3 months



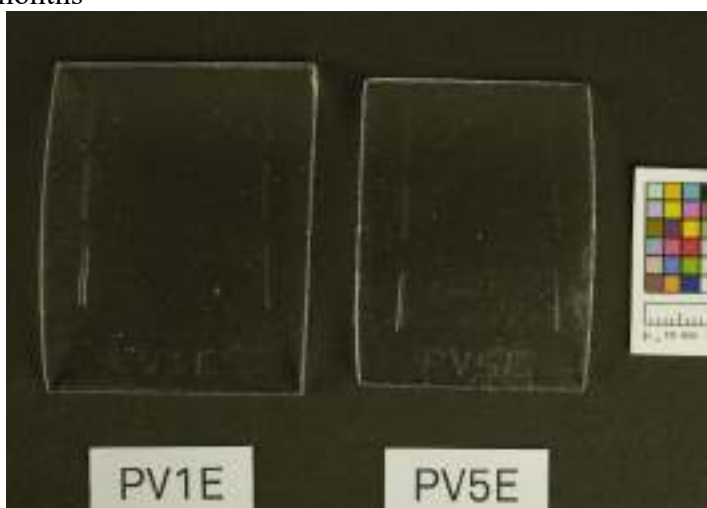
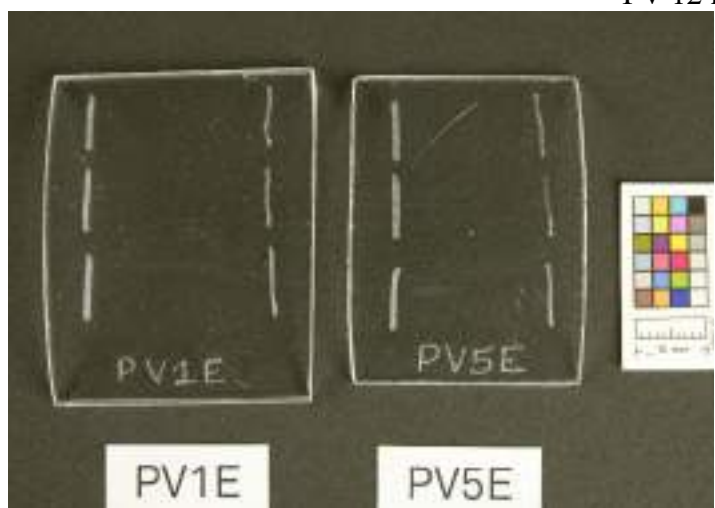
PV 6 months



PV 9 months



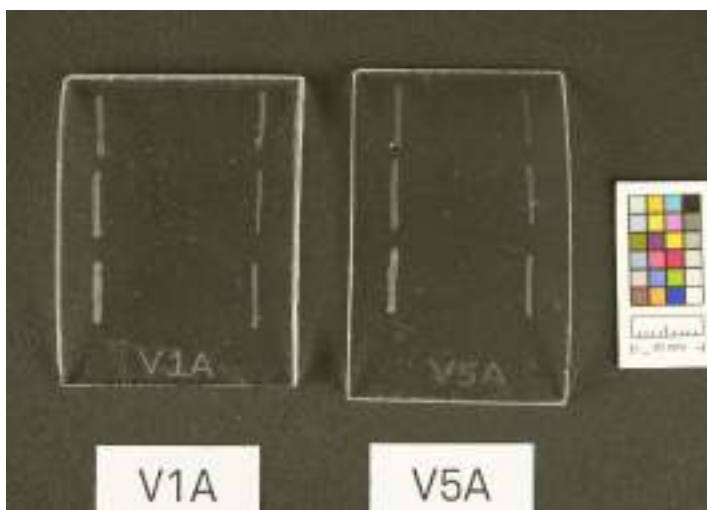
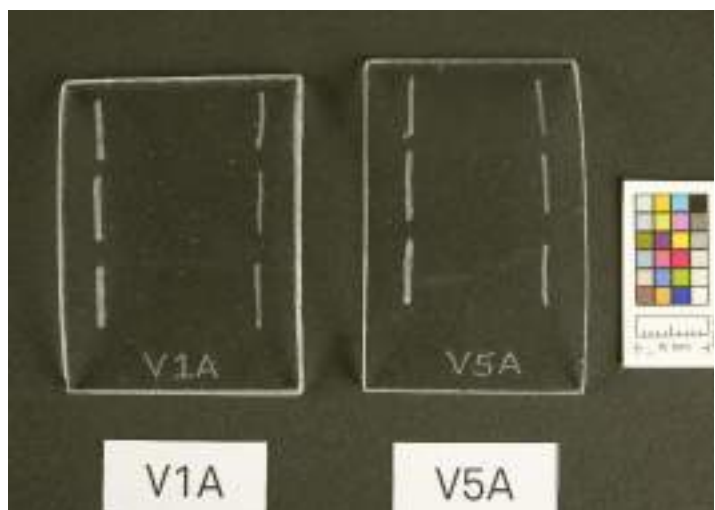
PV 12 months



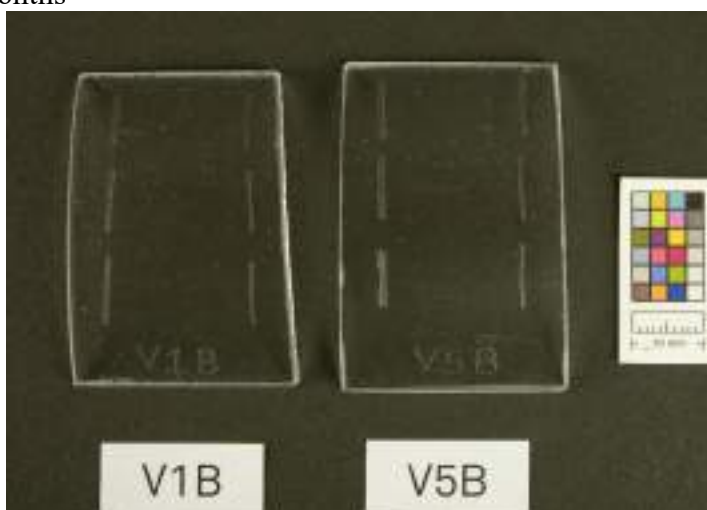
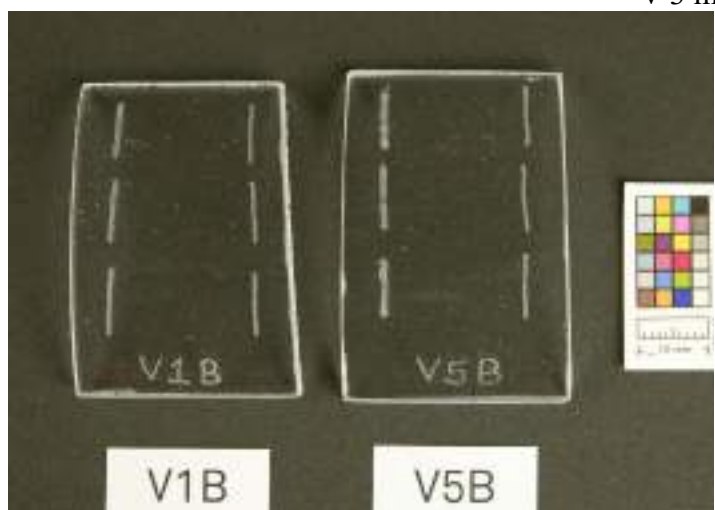
PV 17 months



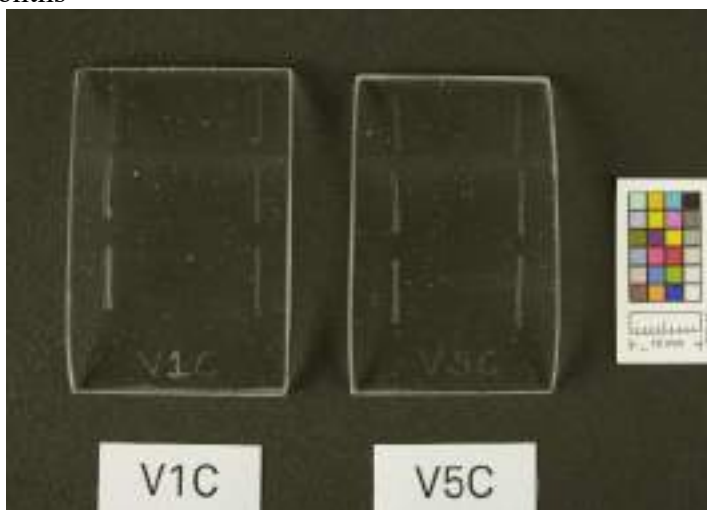
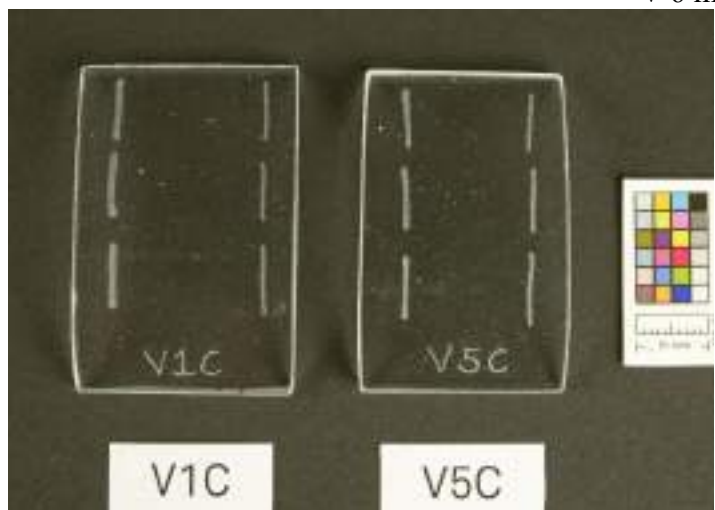
PV 17 months



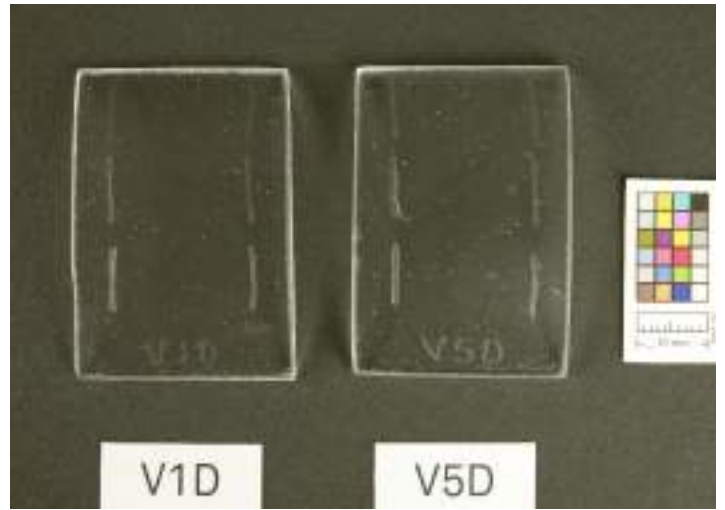
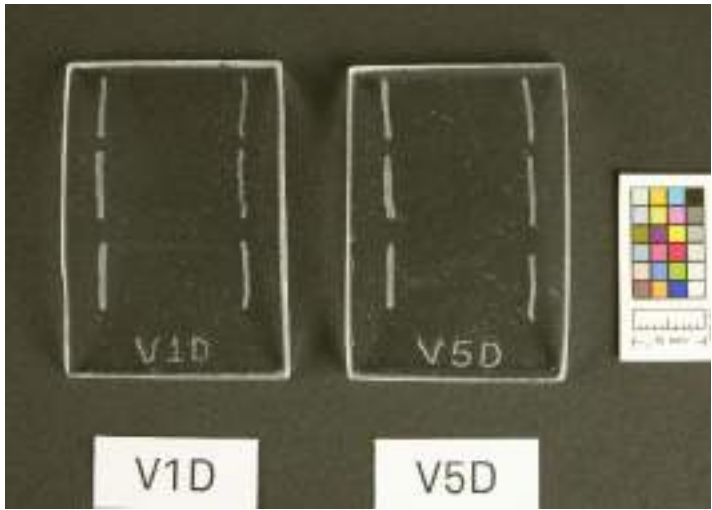
V 3 months



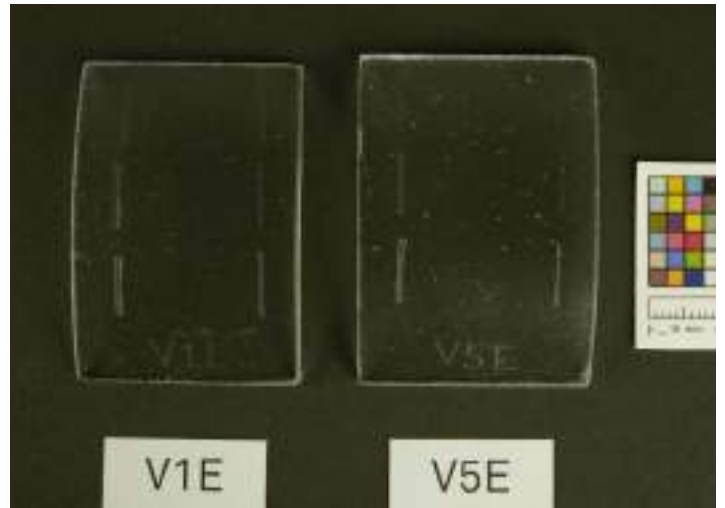
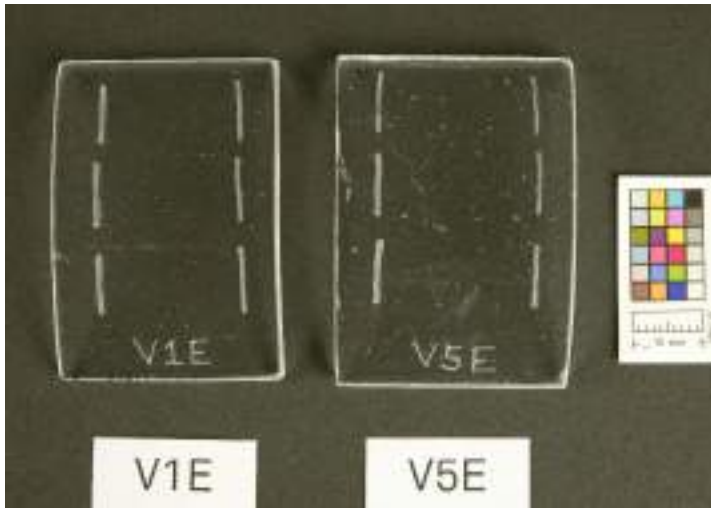
V 6 months



V 9 months



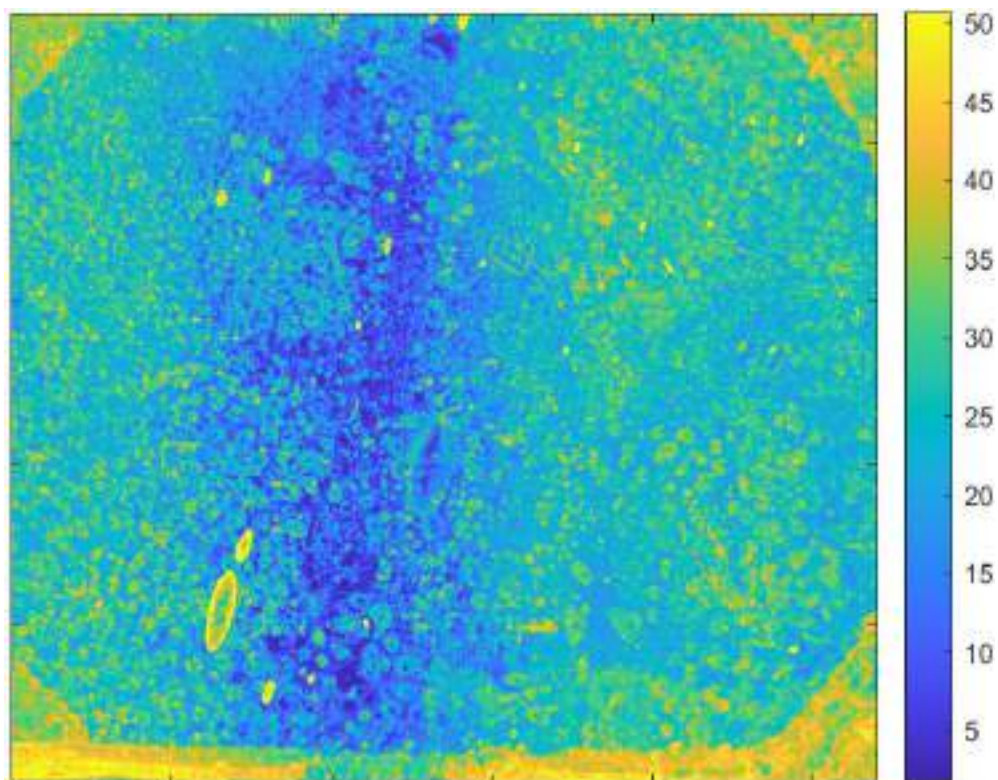
V 12 months



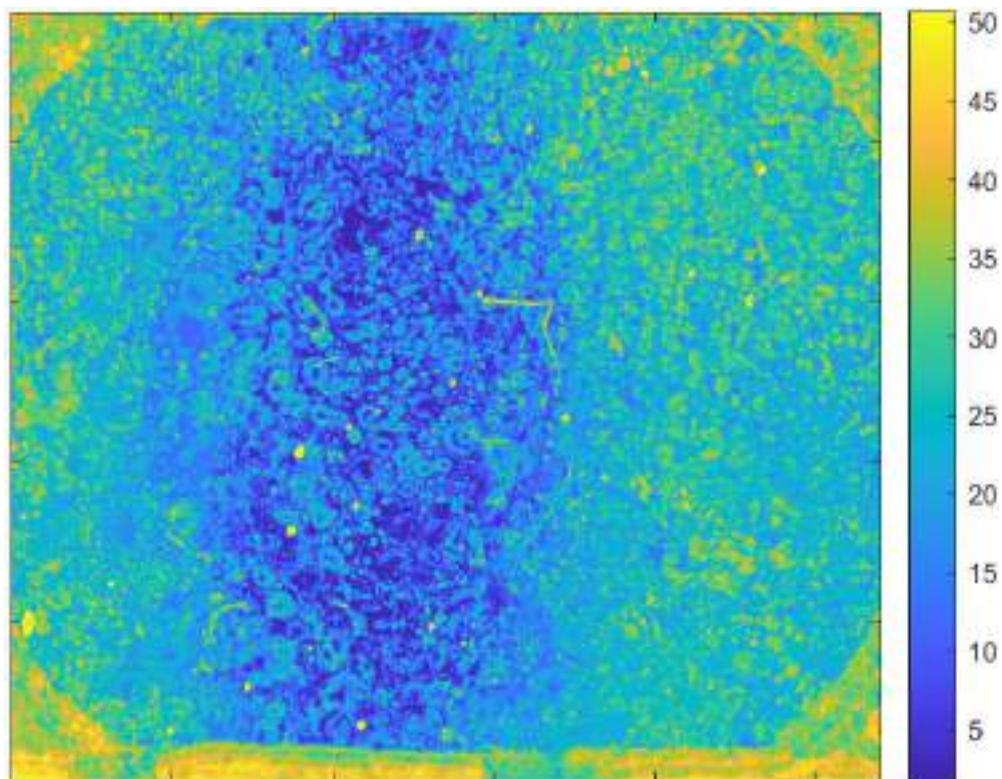
V 17 months

Annex V

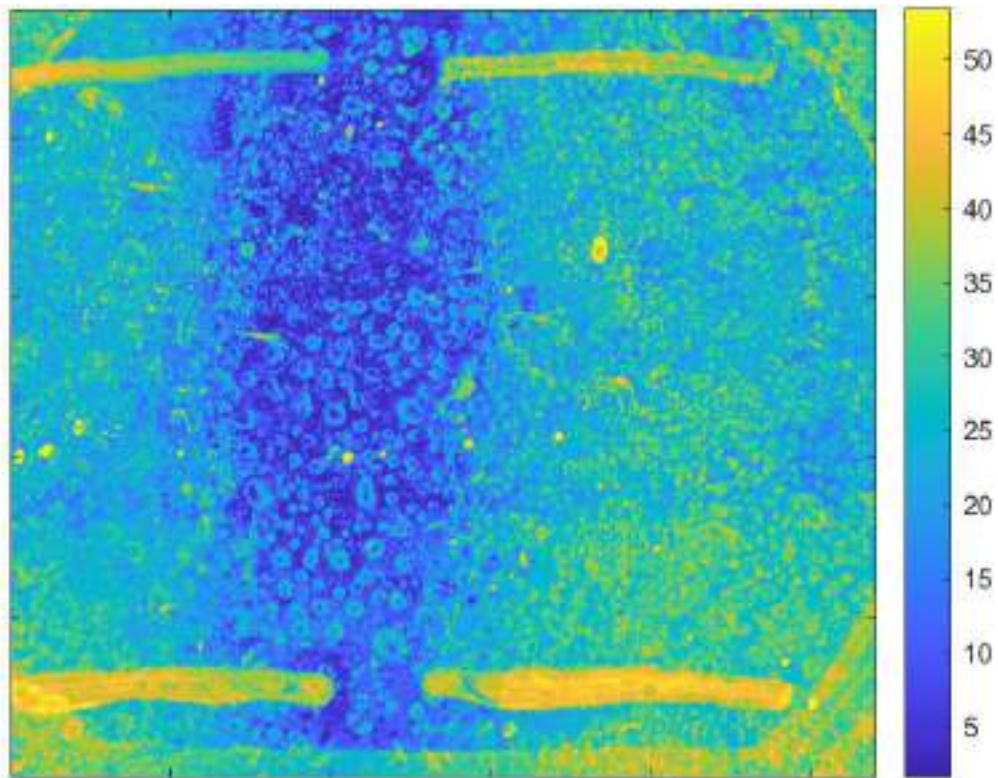
LDR Standard deviation RTI maps for visualizing wet SN on PV model glass (Image size: ($\approx 24 \times 21$ mm²))



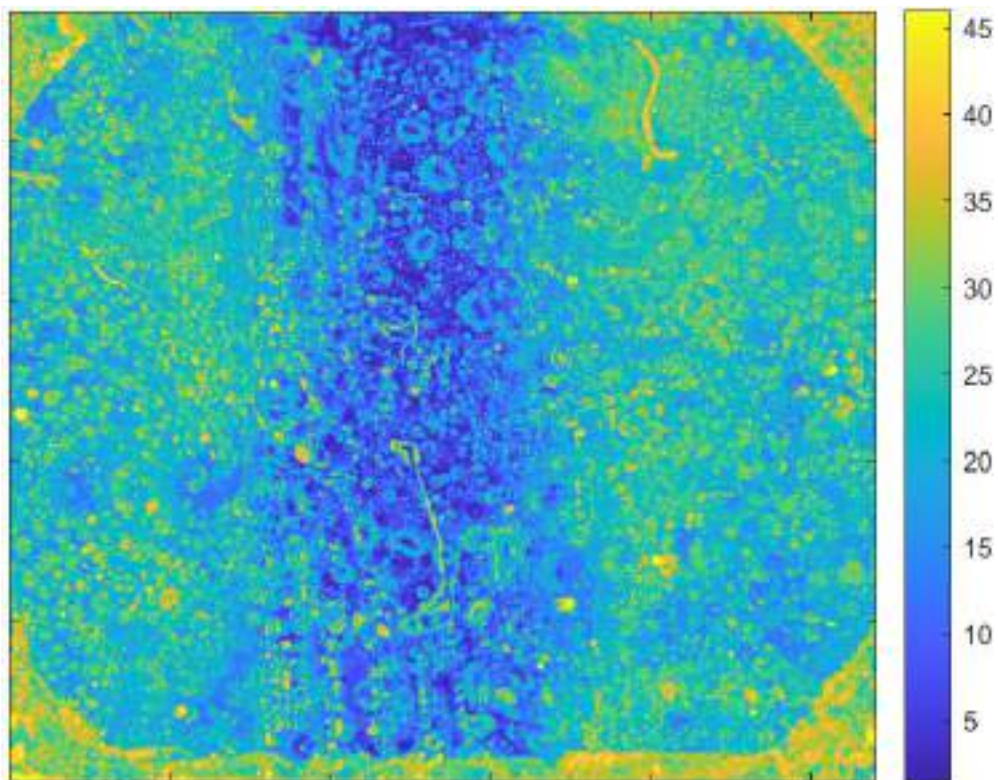
PV 3 months



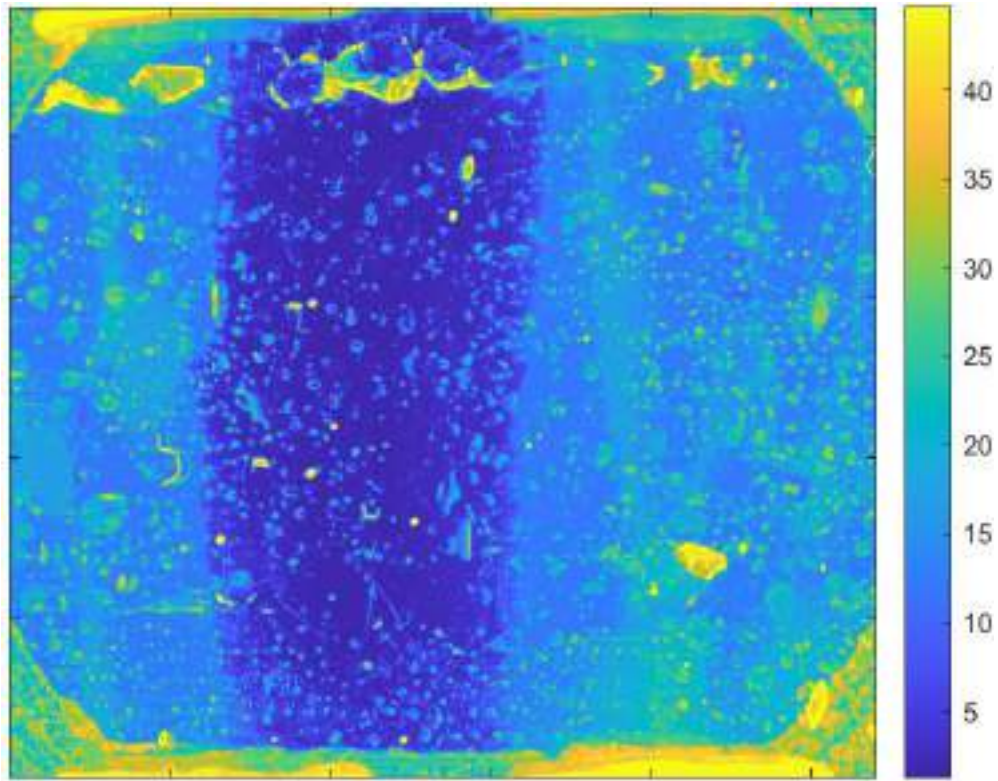
PV 6 months



PV 9 months



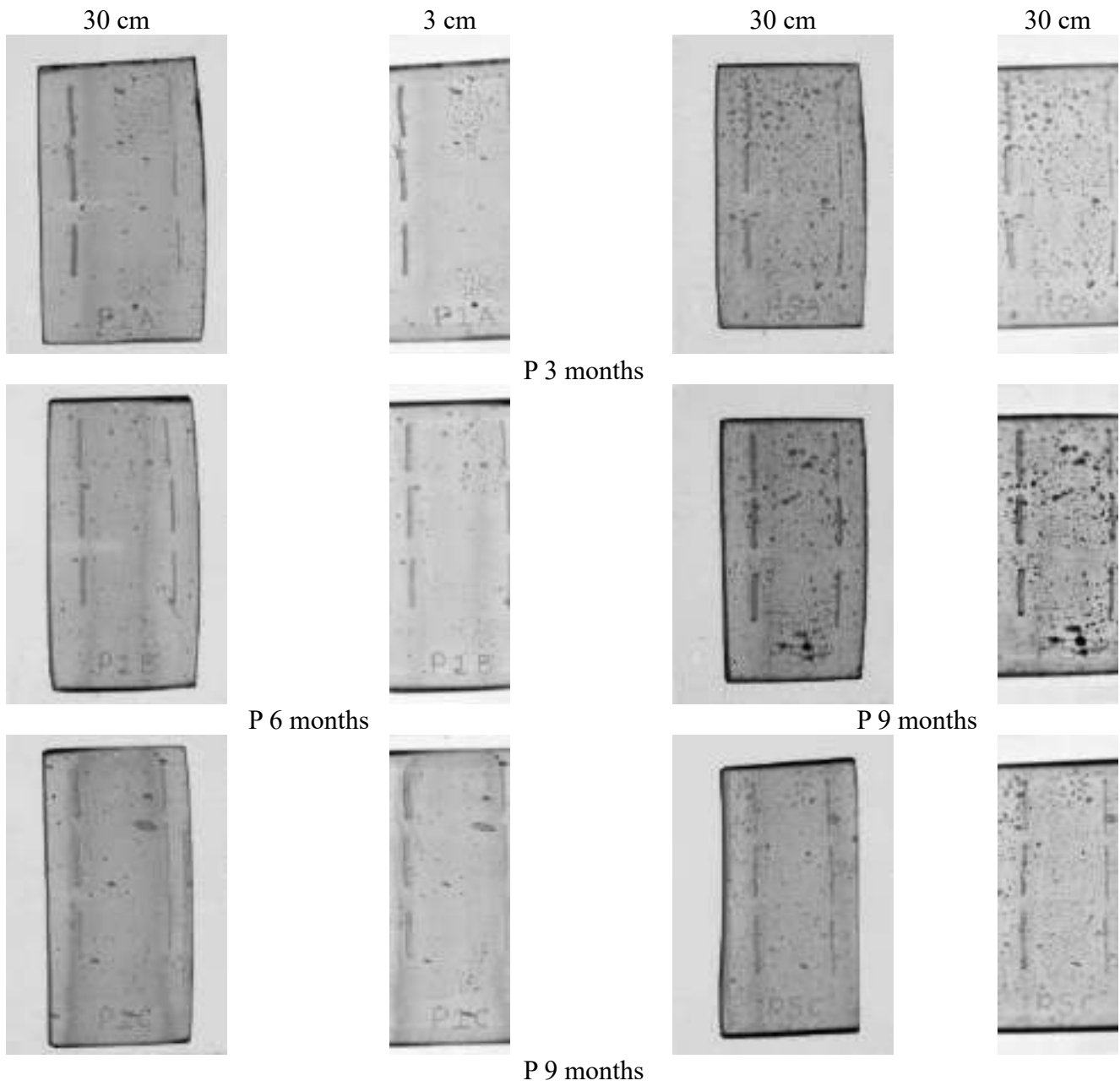
PV 12 months

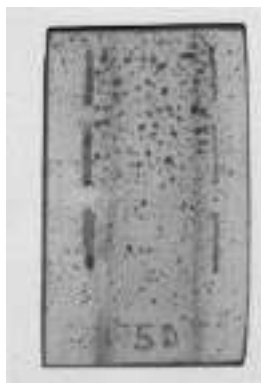
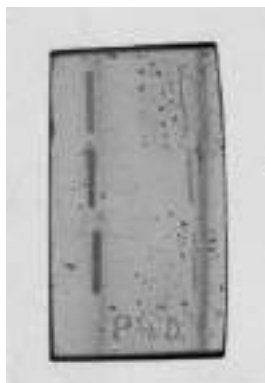


PV 17 months

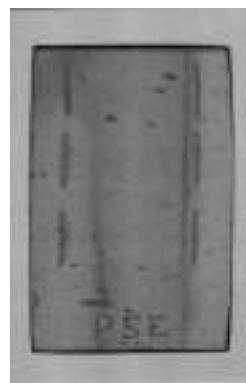
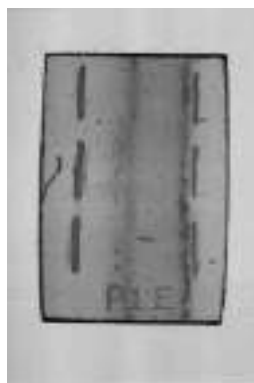
Annex VI

SWIR HSI images at 1906 nm from 30 cm (Image size: $\approx 6\text{cm} \times 4\text{cm}$) and 3 cm lens (Image size: $\approx 6\text{cm} \times 2\text{cm}$)

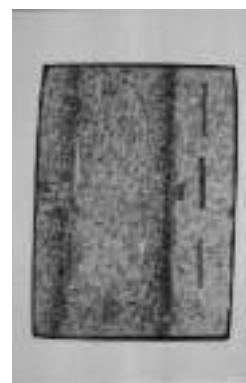
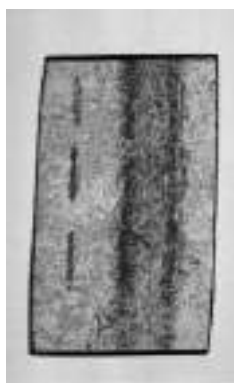




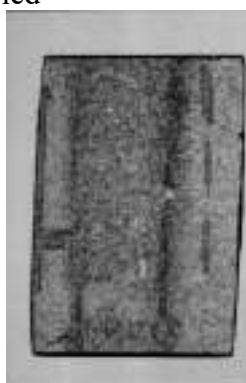
P 12 months



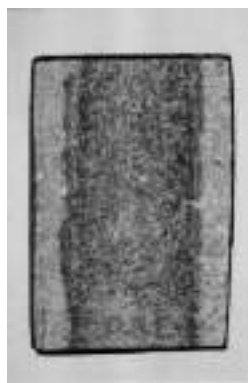
P 17 months



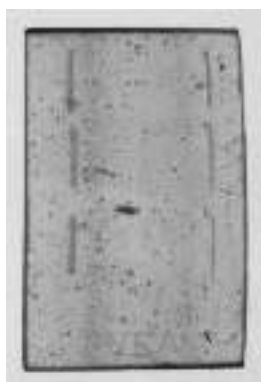
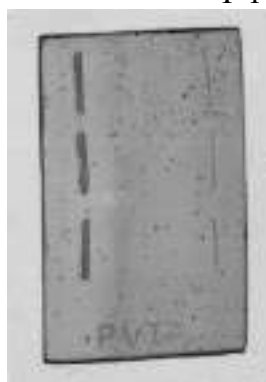
P 17 months and dried



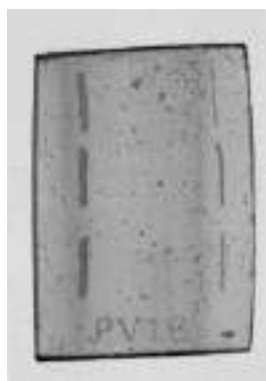
P 17 months and dried



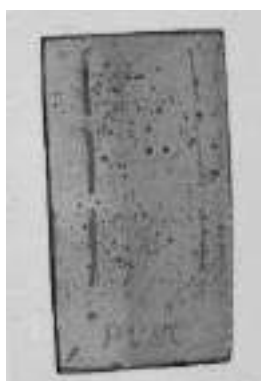
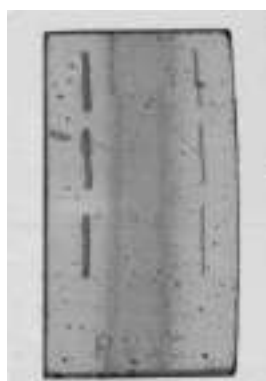
P 17 months and dried



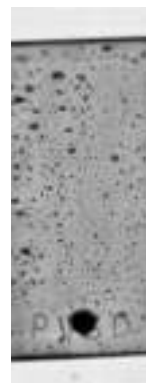
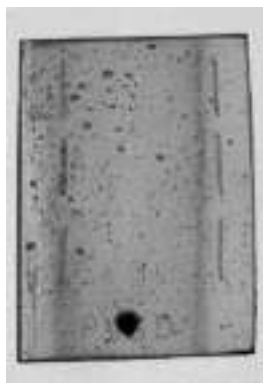
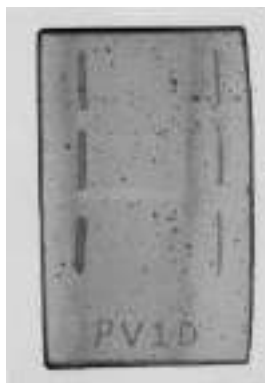
PV 3 months



PV 6 months



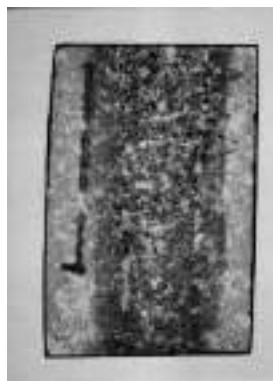
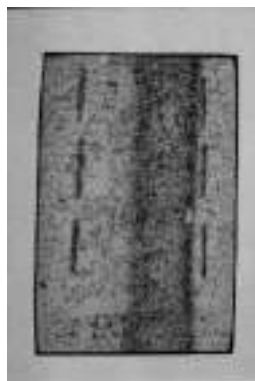
PV 9 months



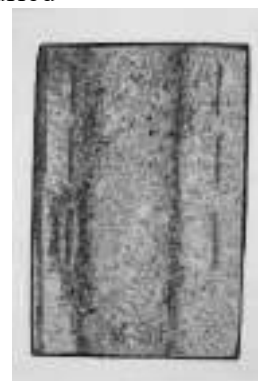
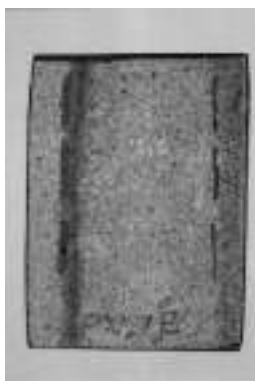
PV 12 months



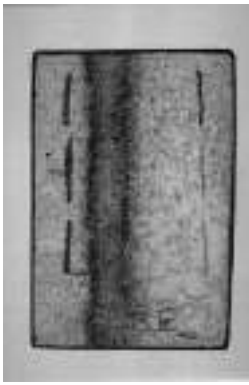
PV 17 months



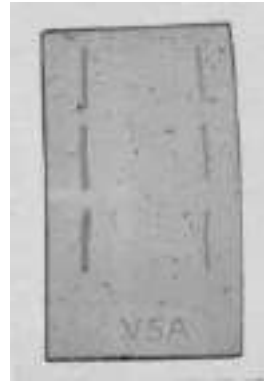
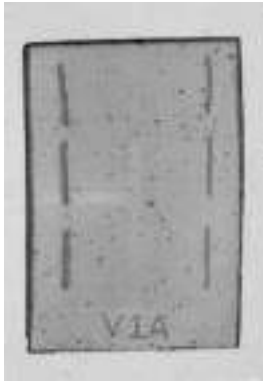
PV 17 months and dried



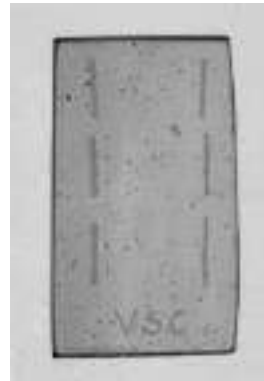
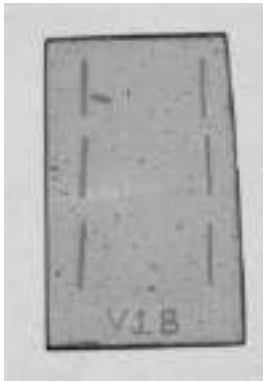
PV 17 months and dried



PV 17 months and dried

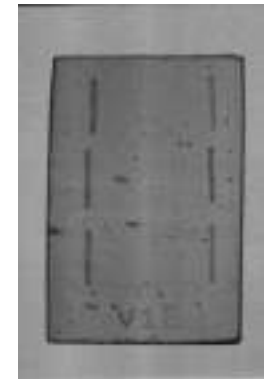
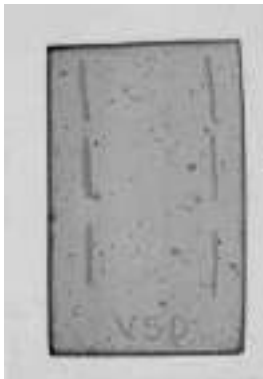


V 3 months



V 6 months

V 9 months



V 12 months

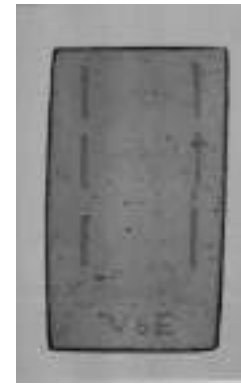
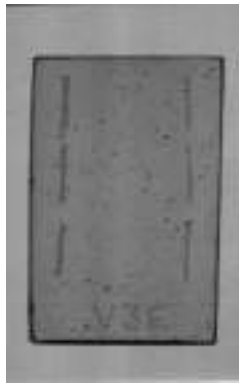
V 17 months



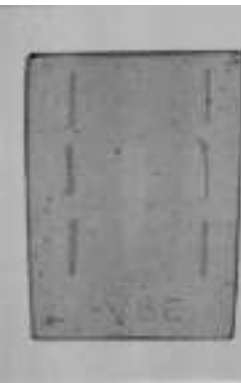
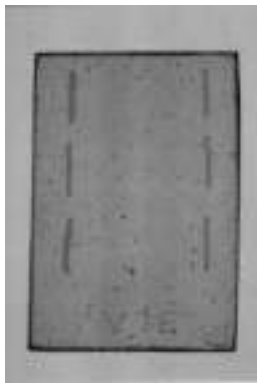
V 17 months



V 17 months and dried



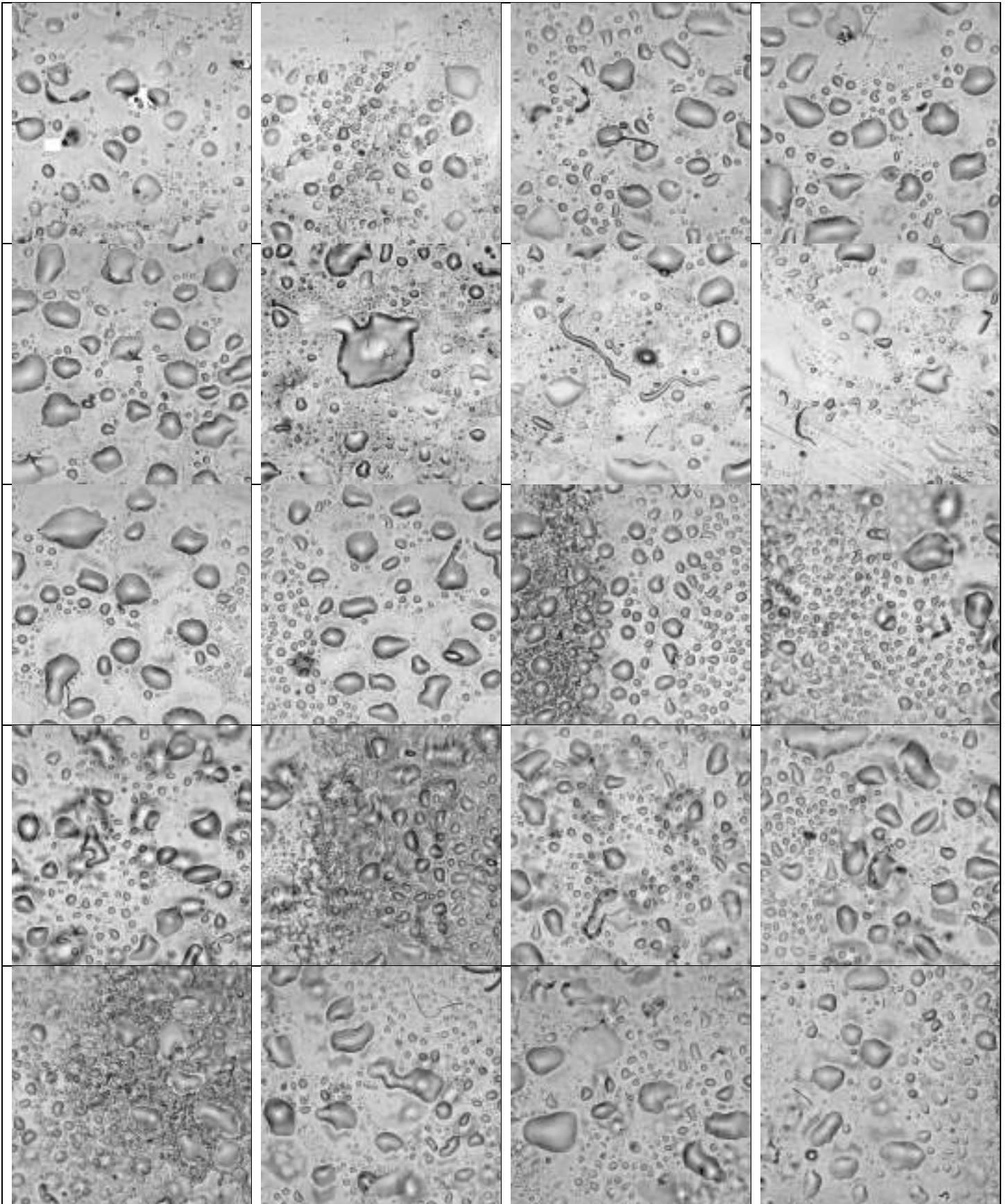
V 17 months and dried

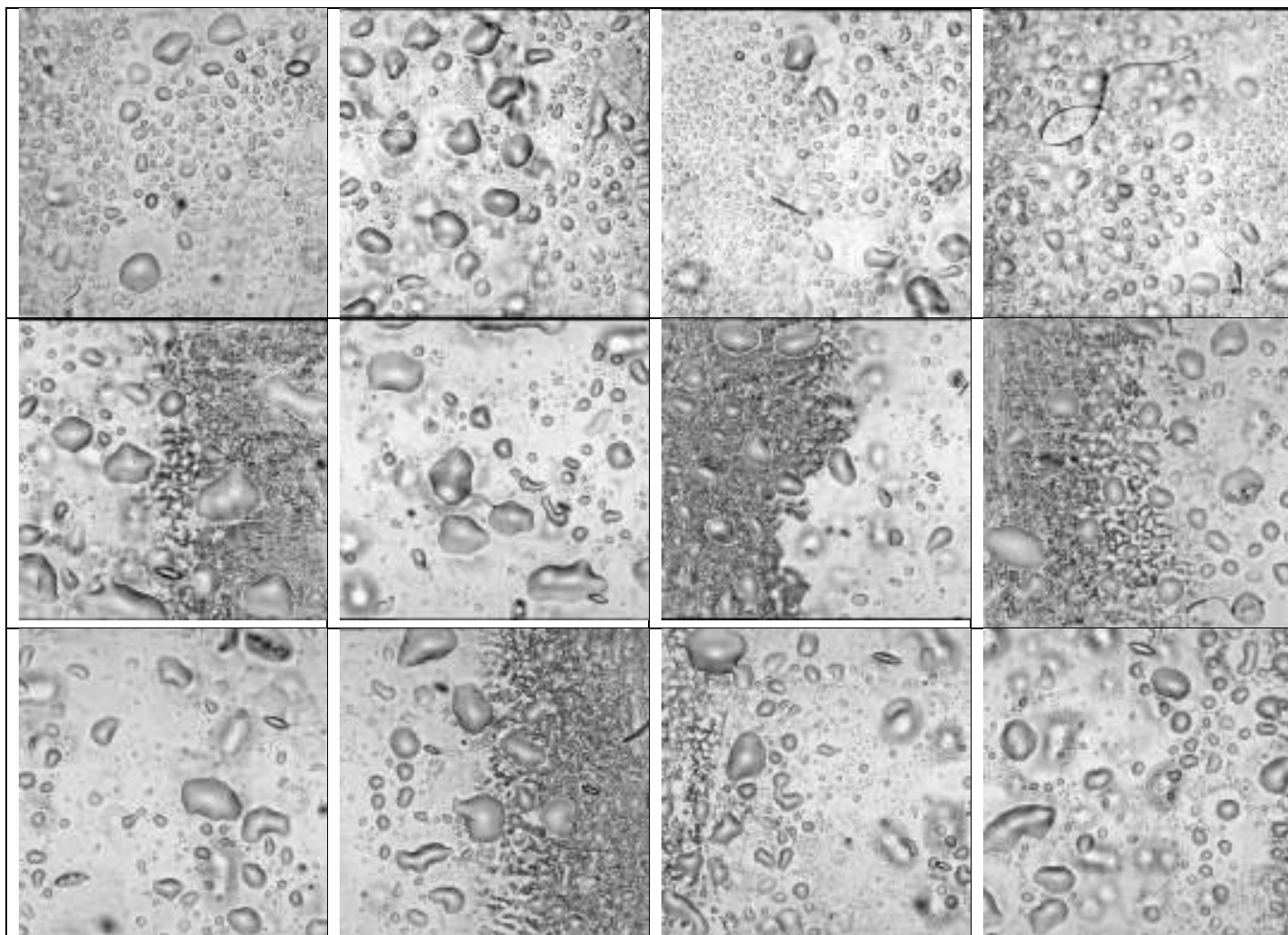


V 17 months and dried

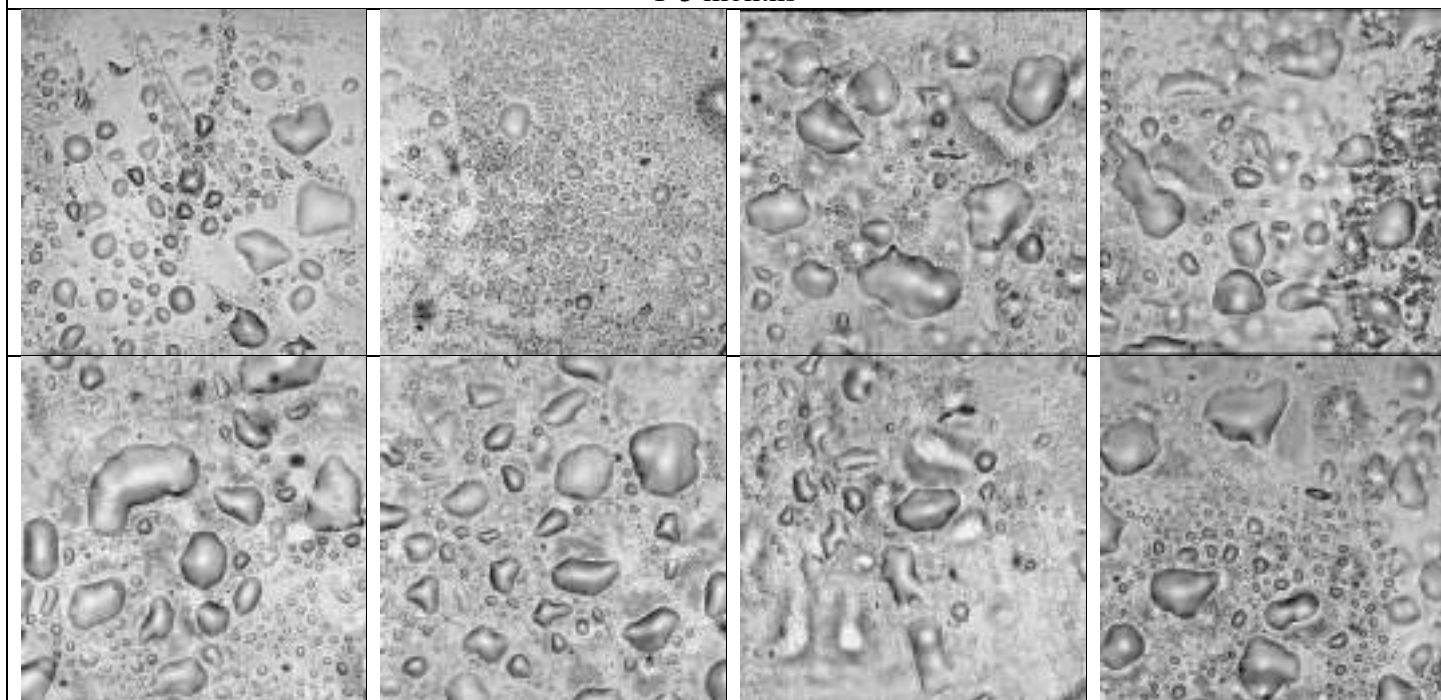
Annex VII

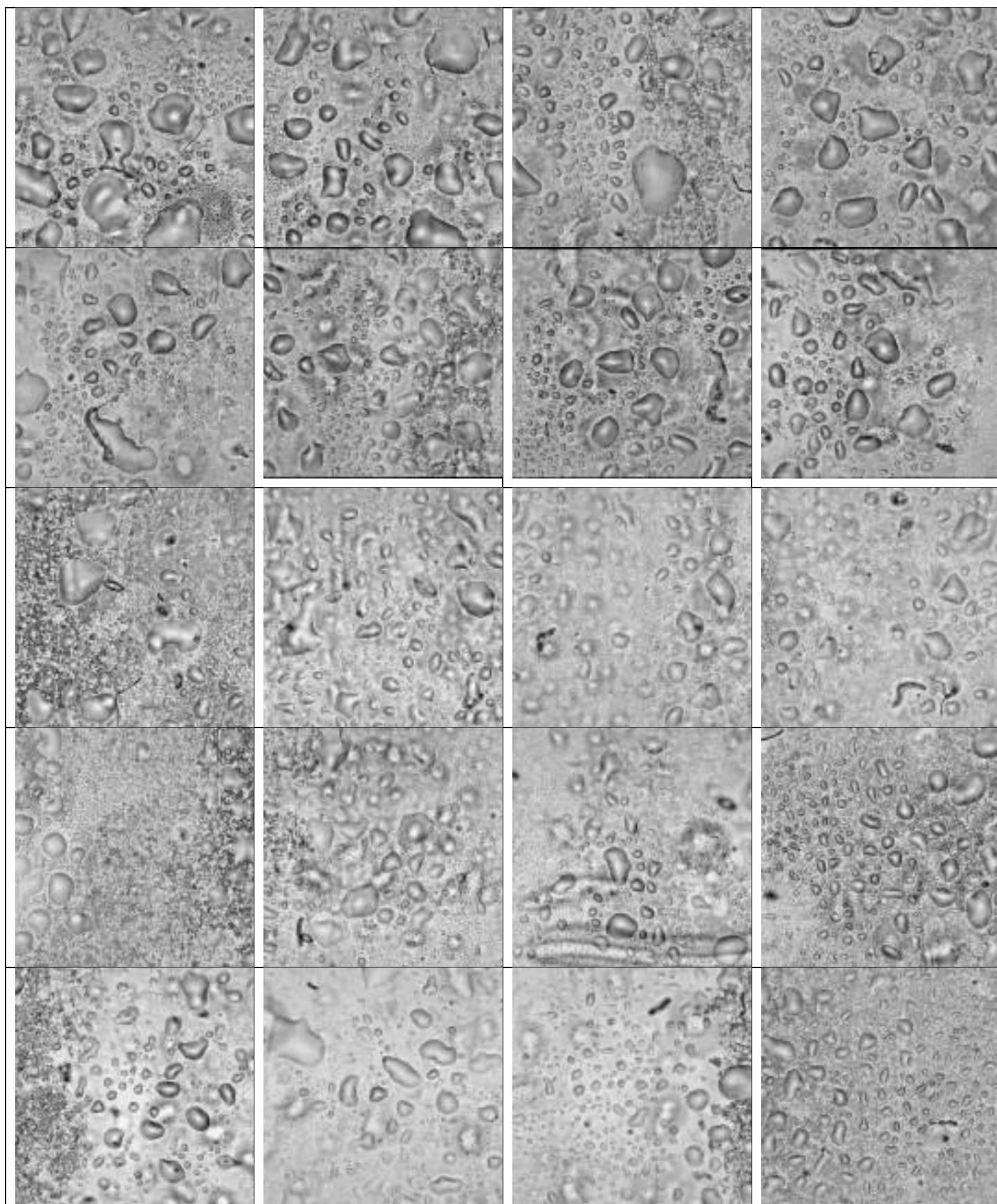
5mm x 5mm extracted areas from digital micrographs to quantify wet SN and cracks

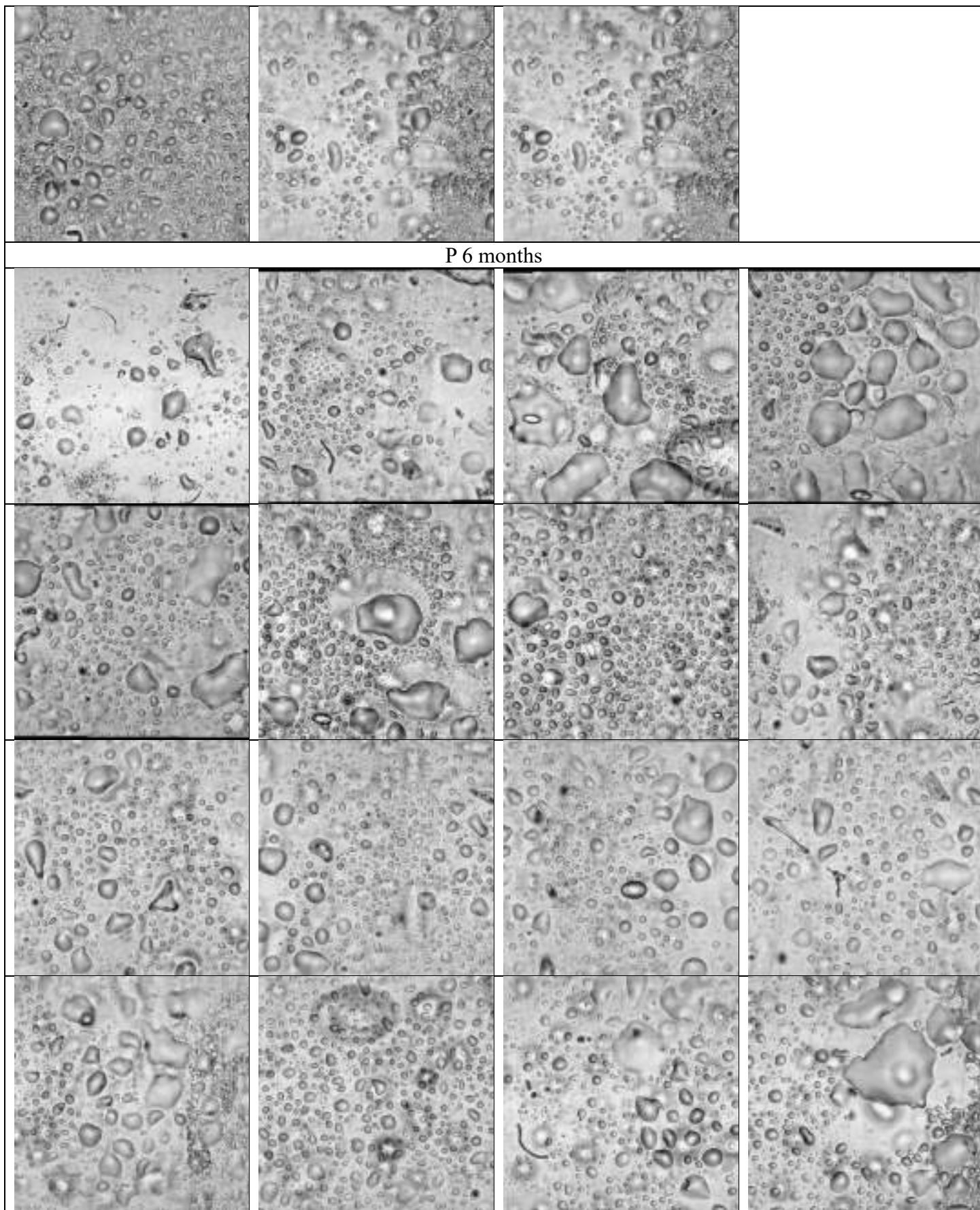


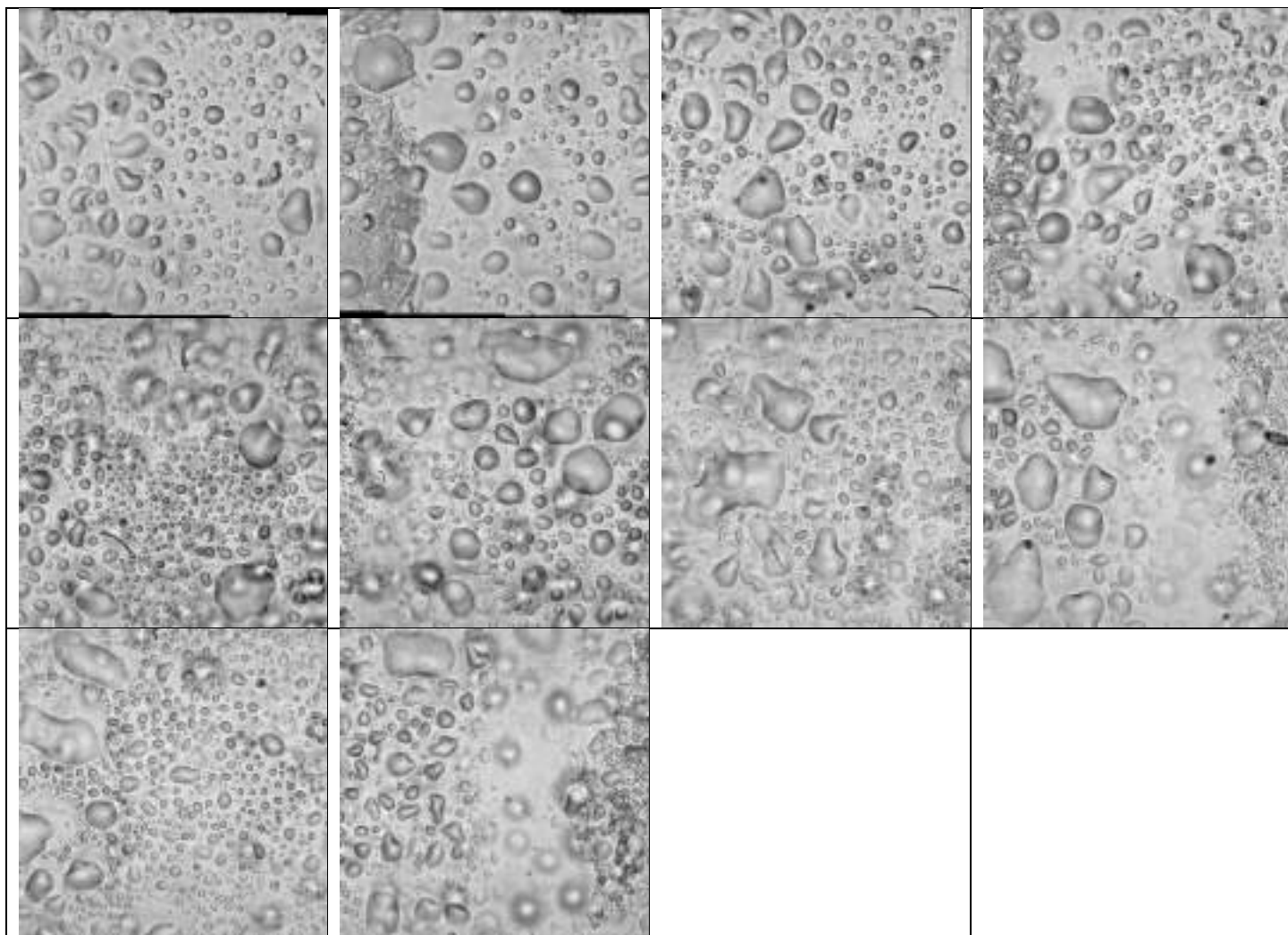


P 3 months

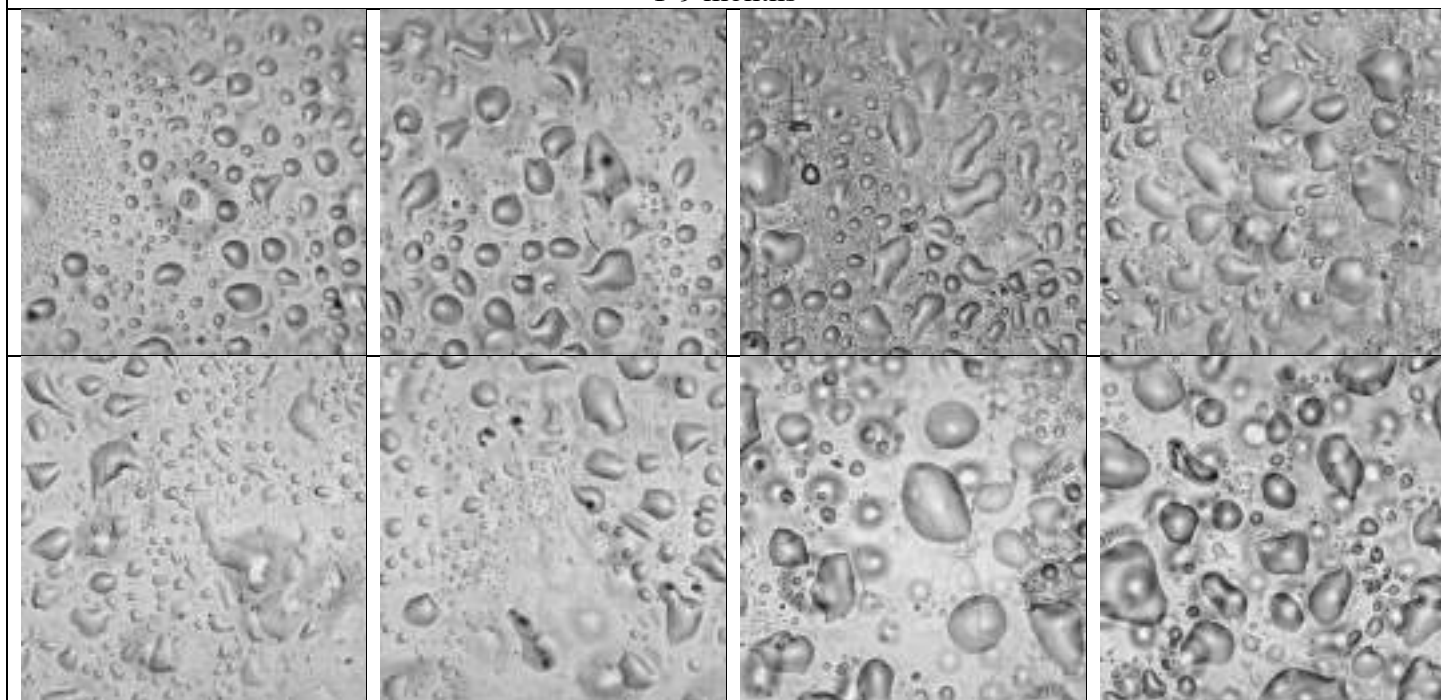


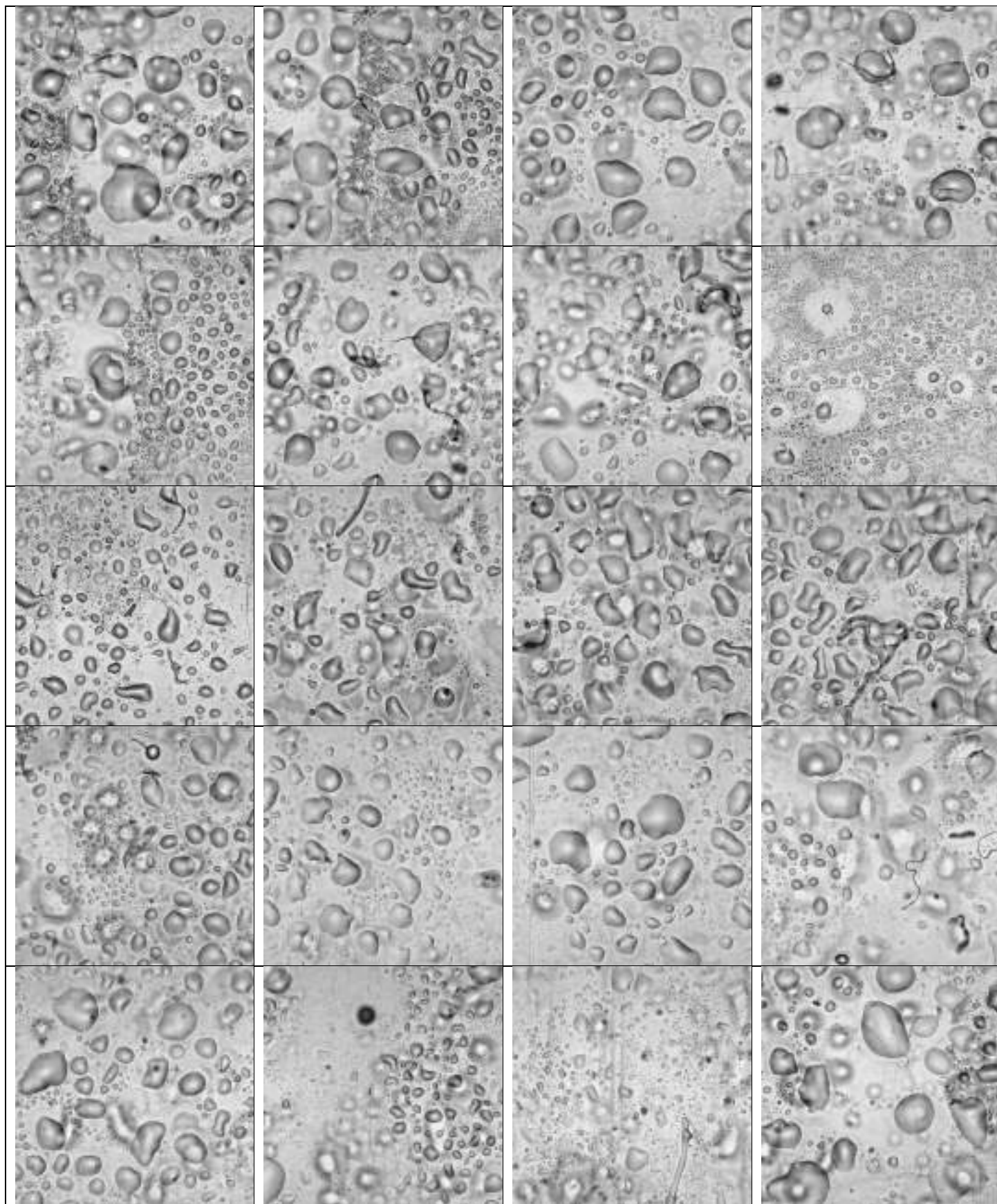


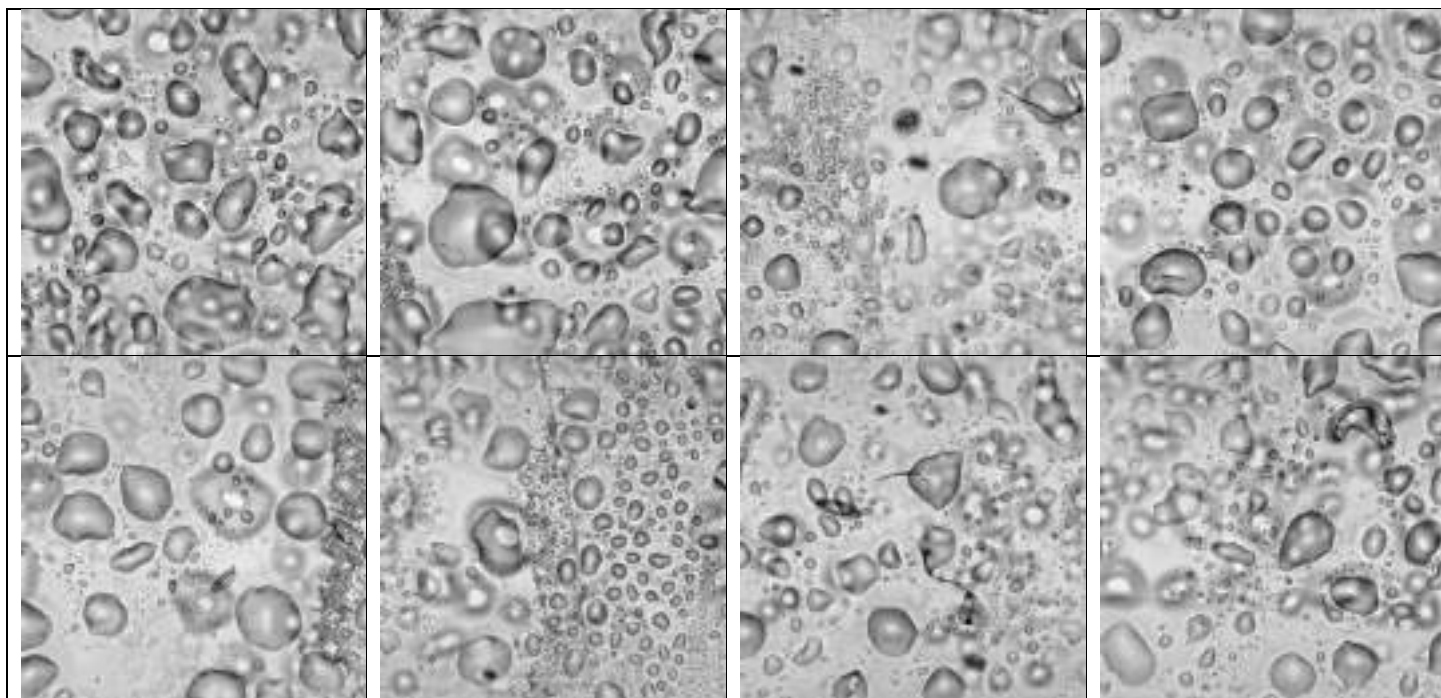




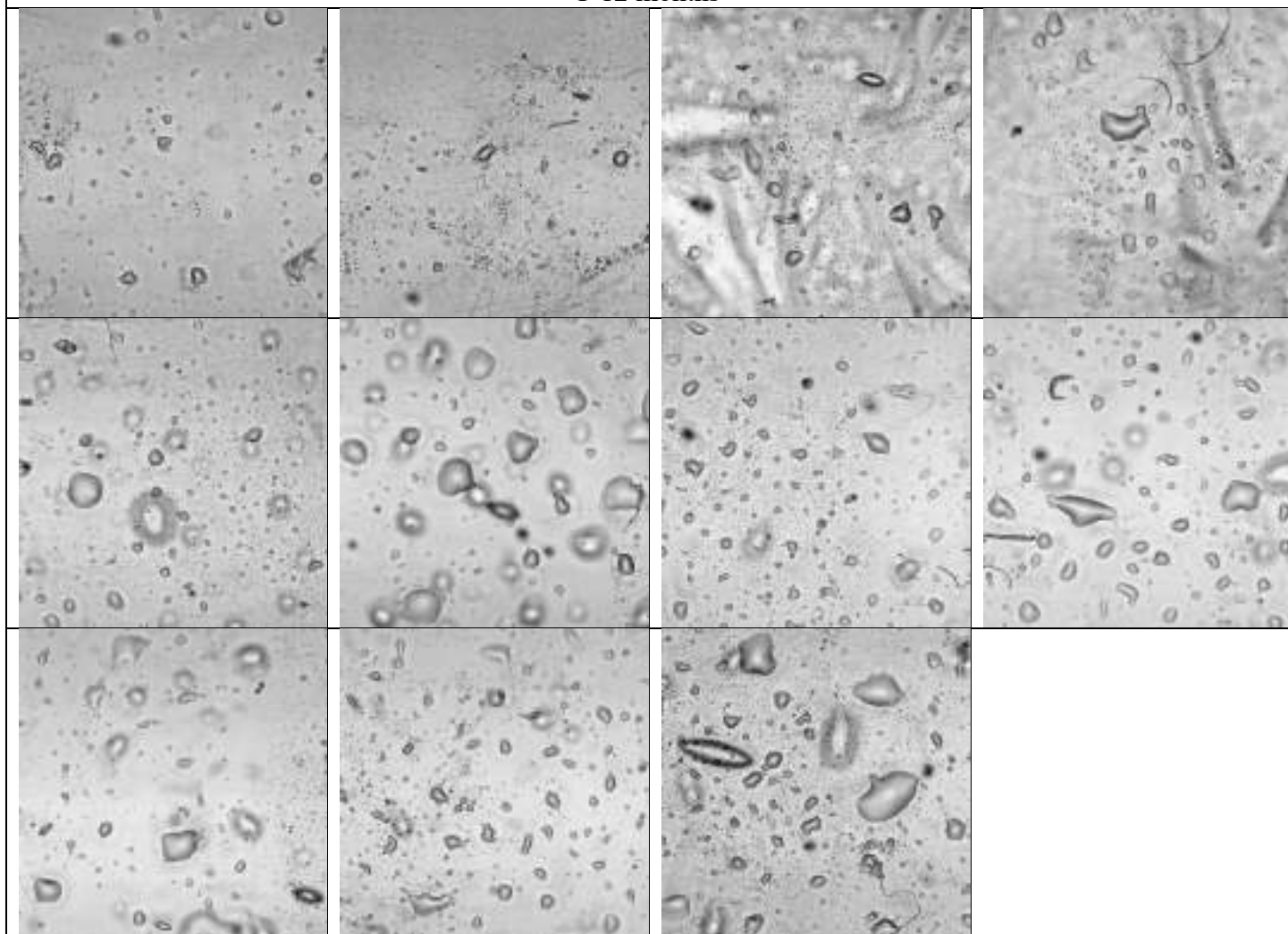
P 9 months



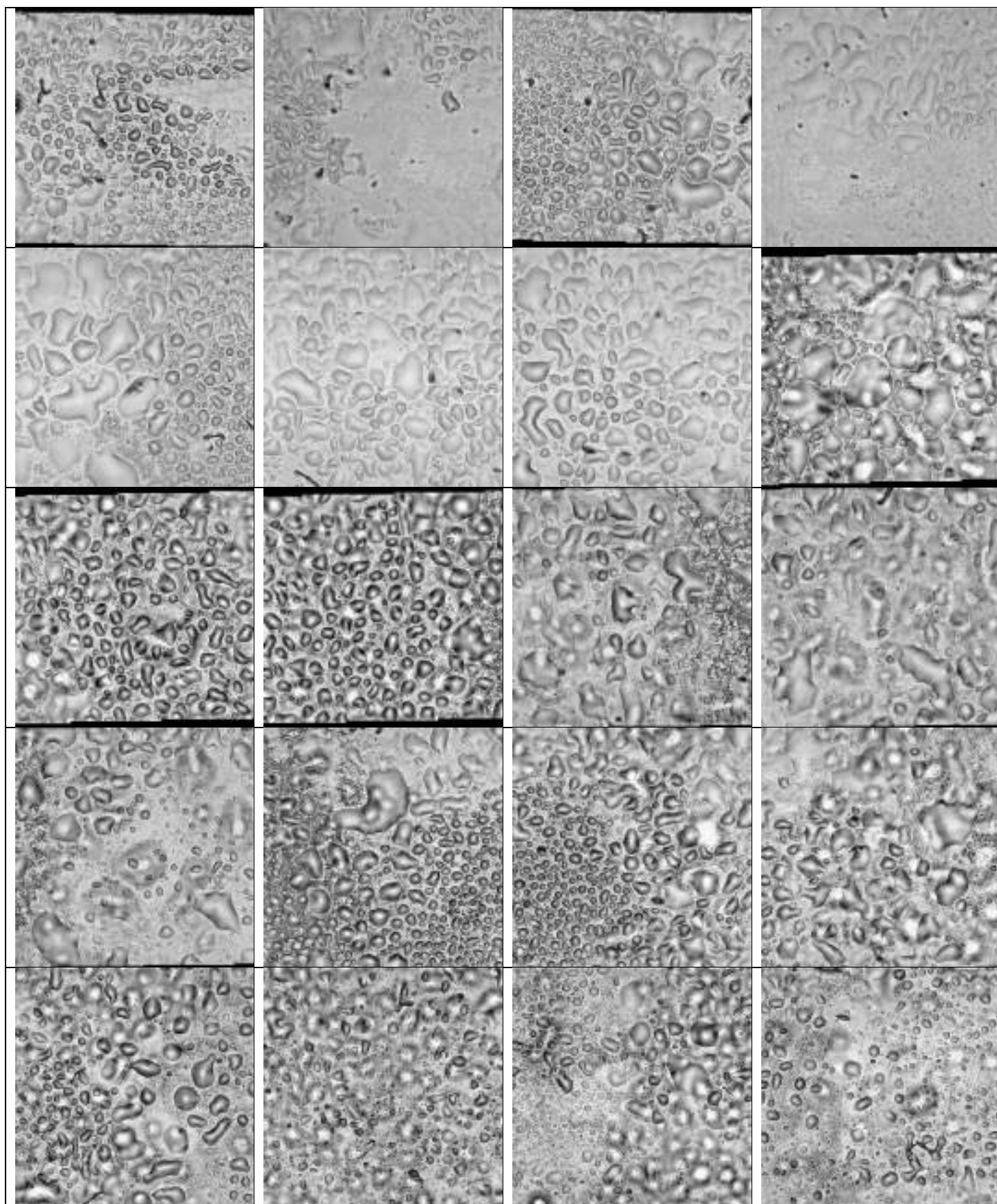


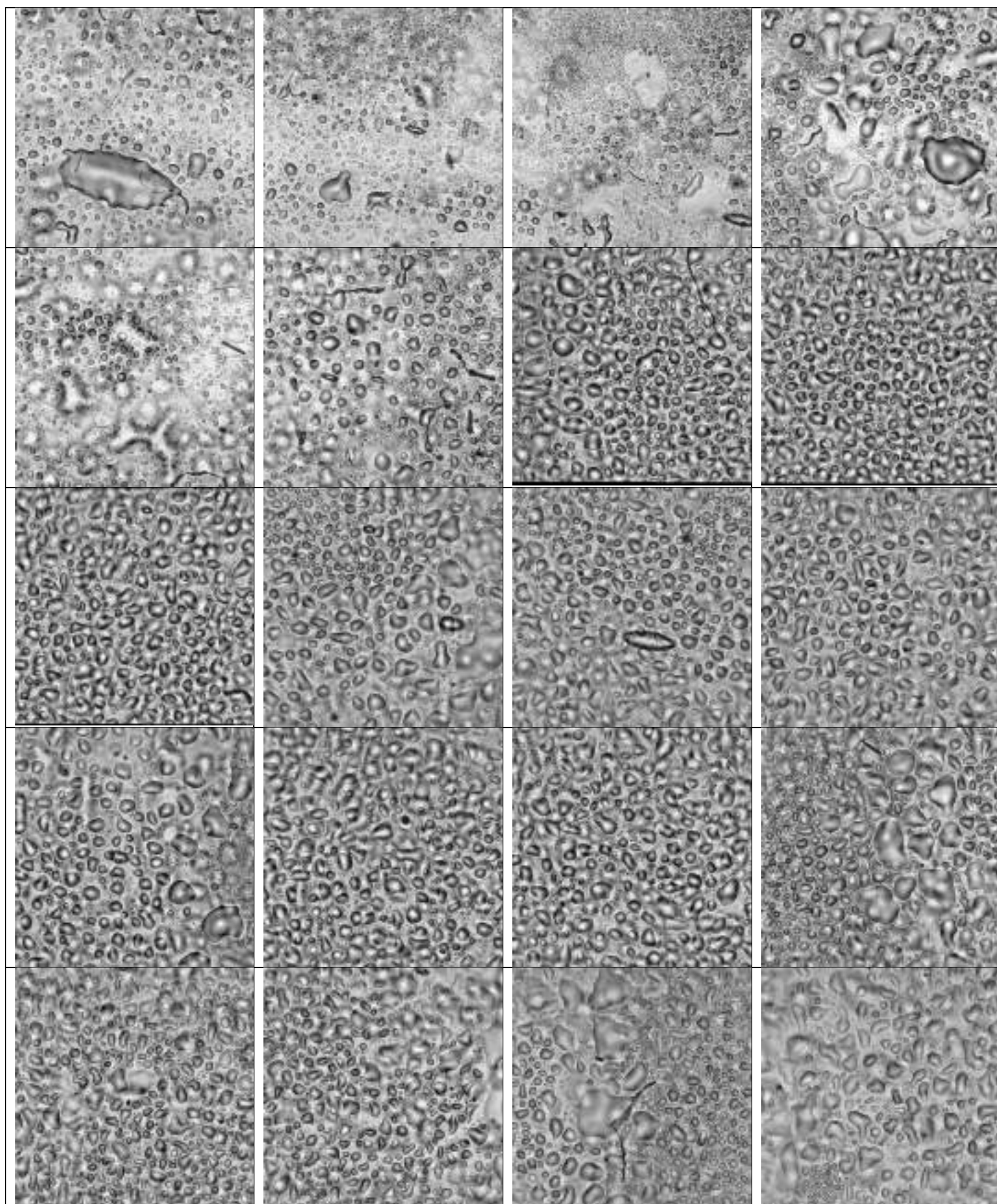


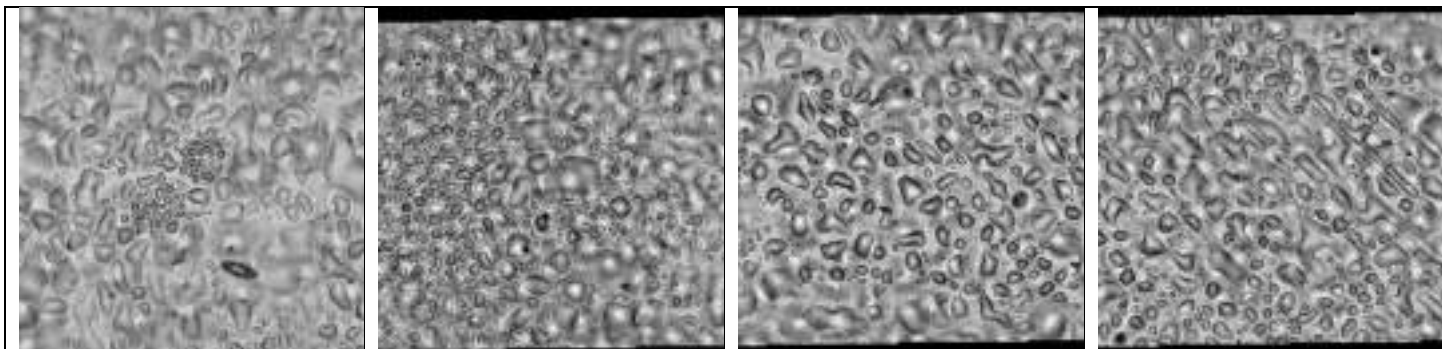
P 12 months



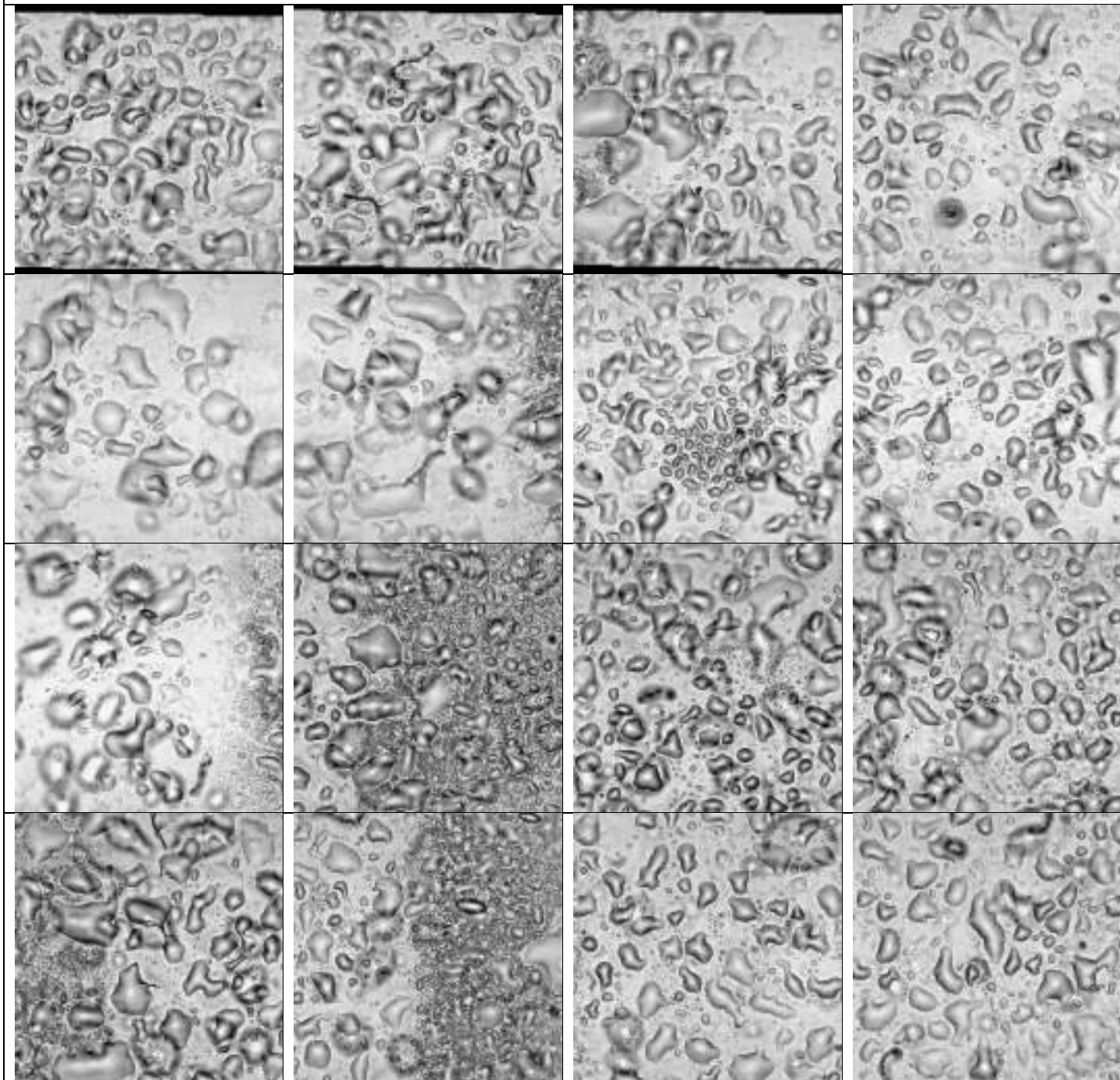
P 17 months

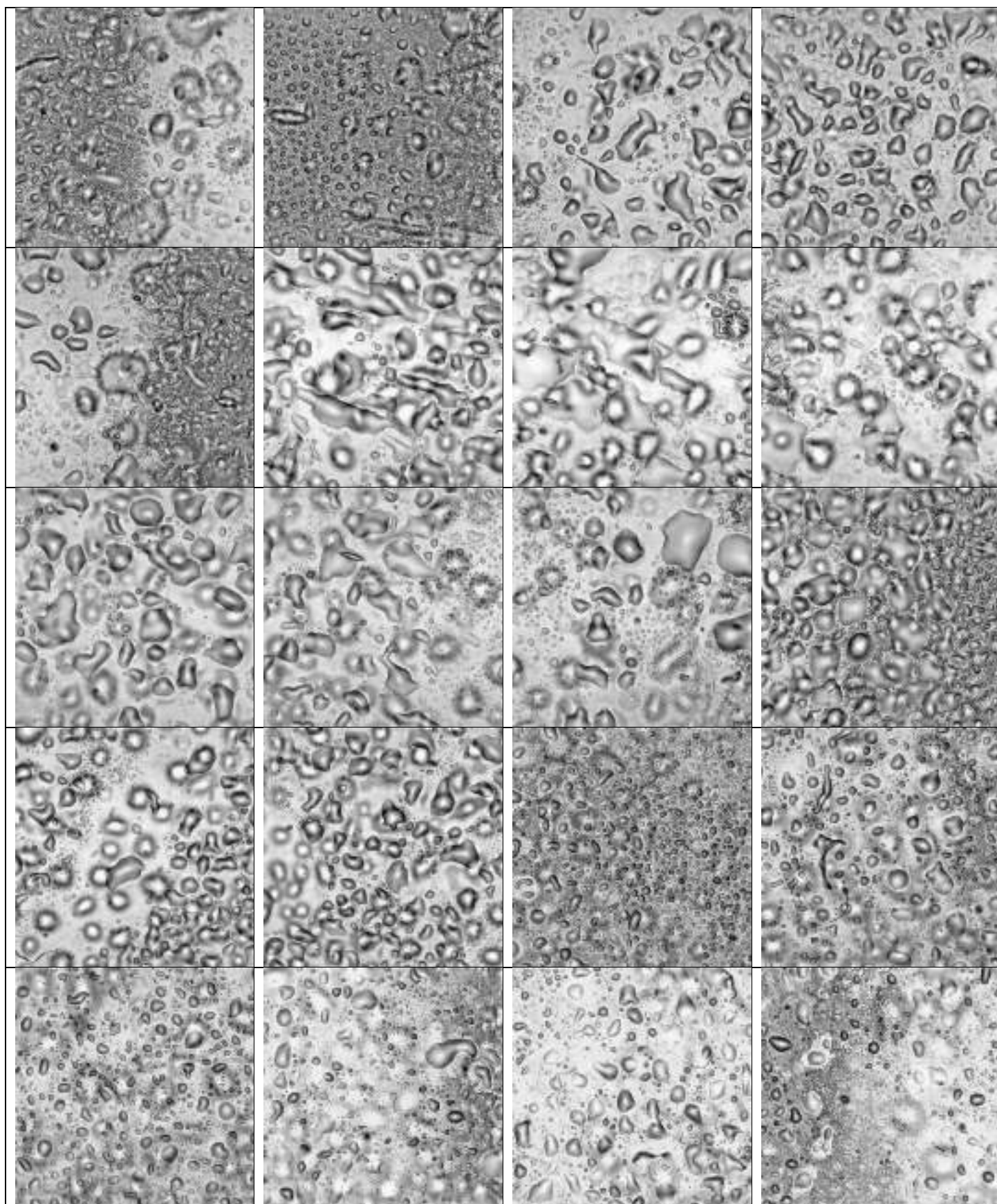


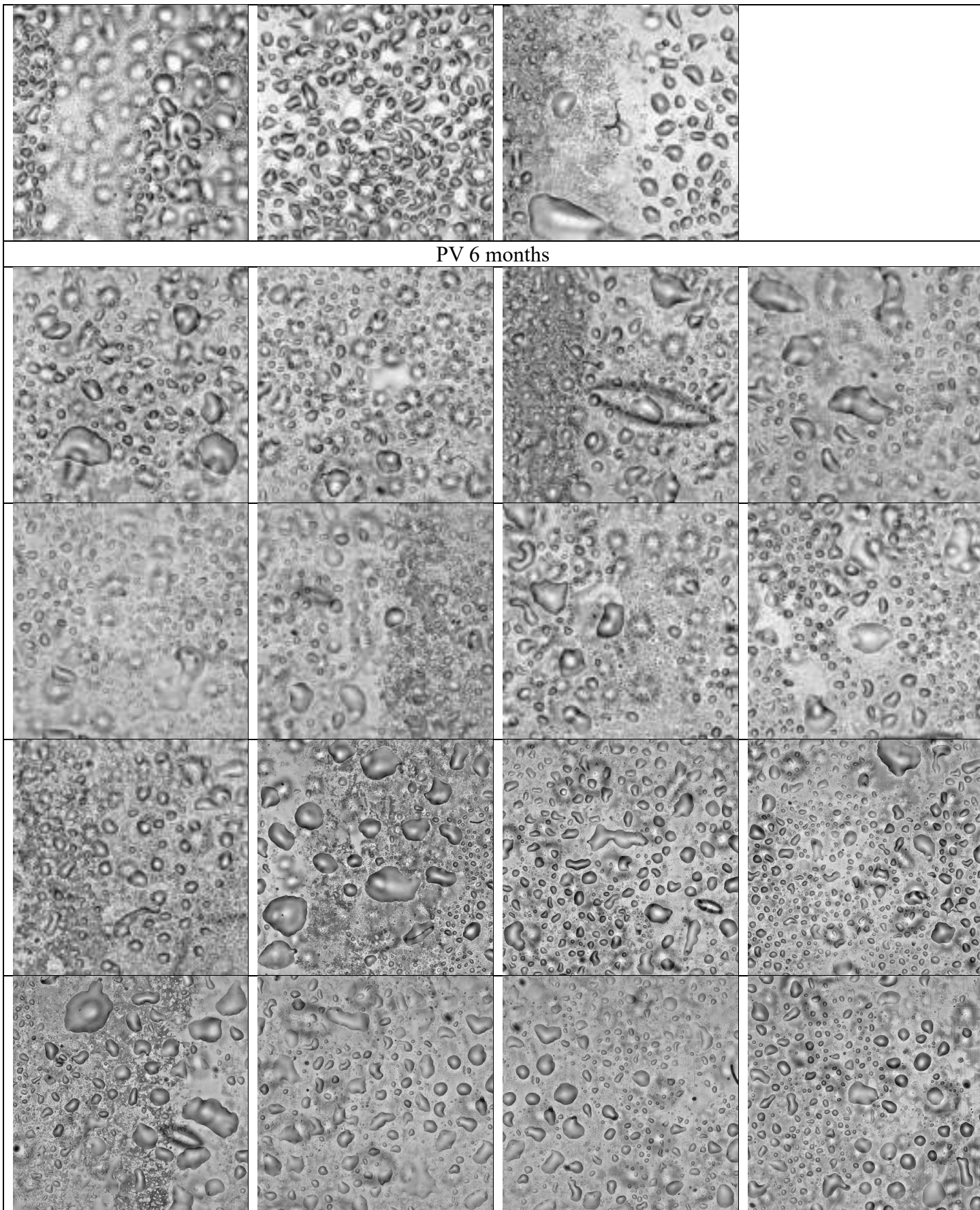


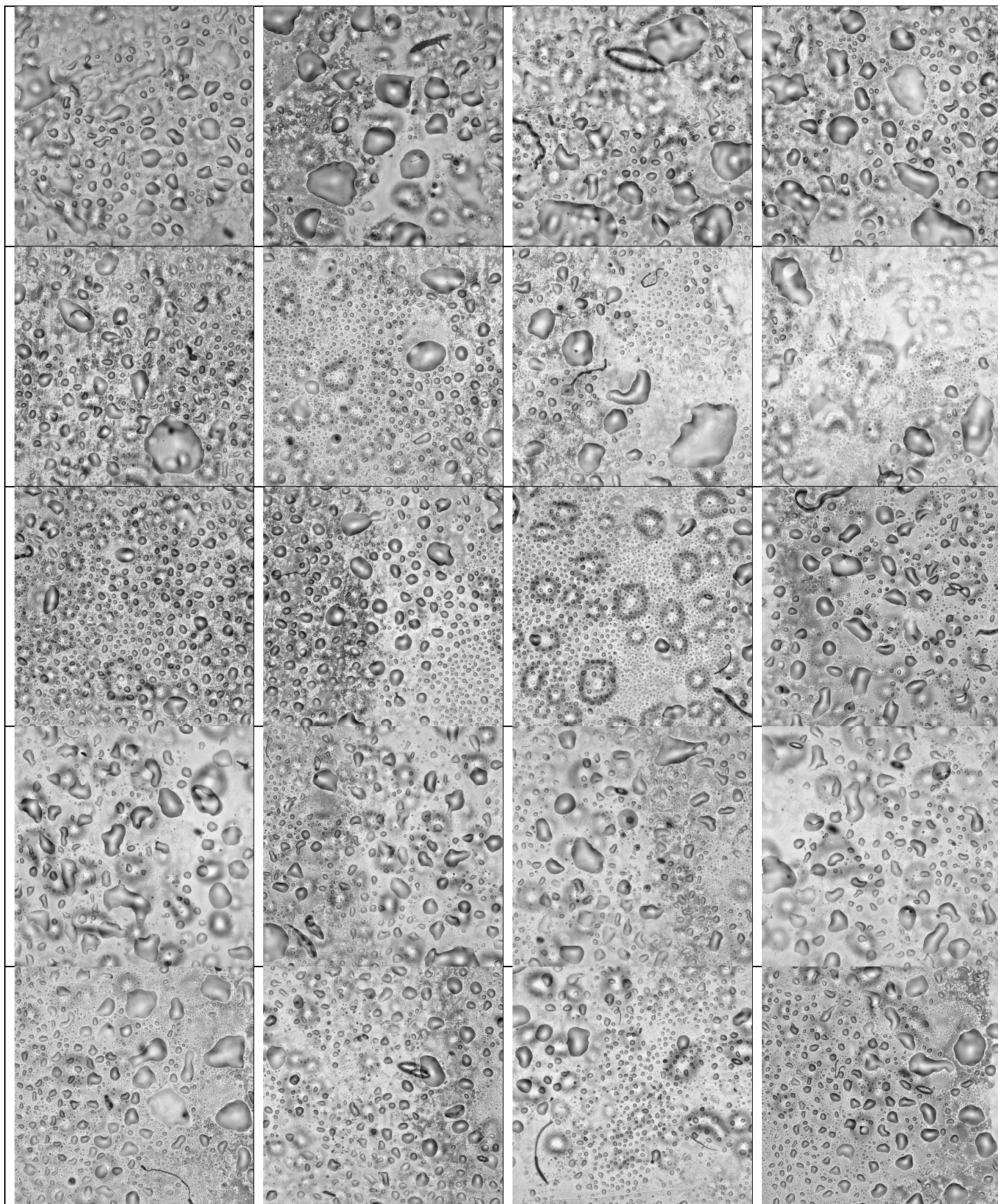


PV 3 months

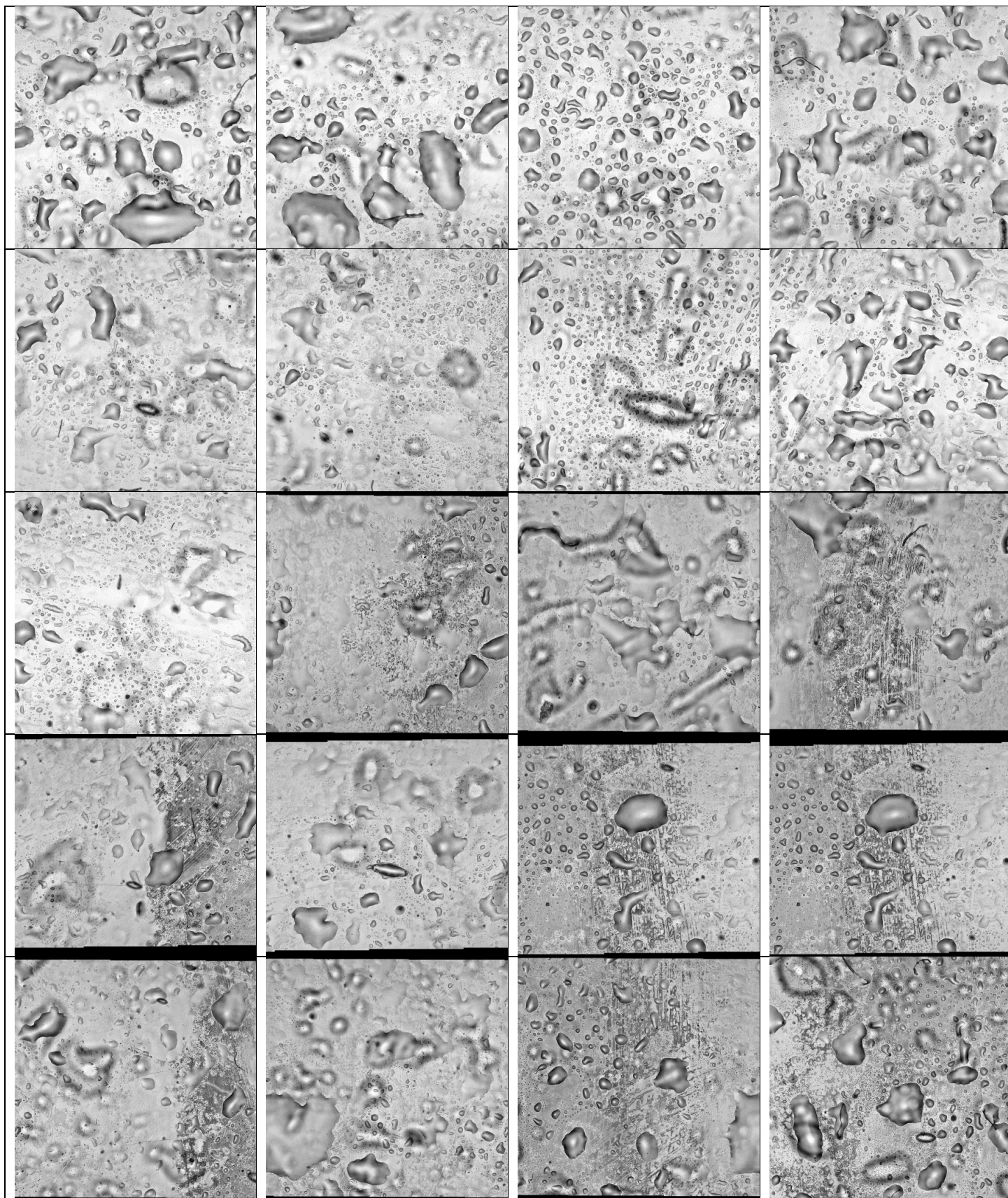


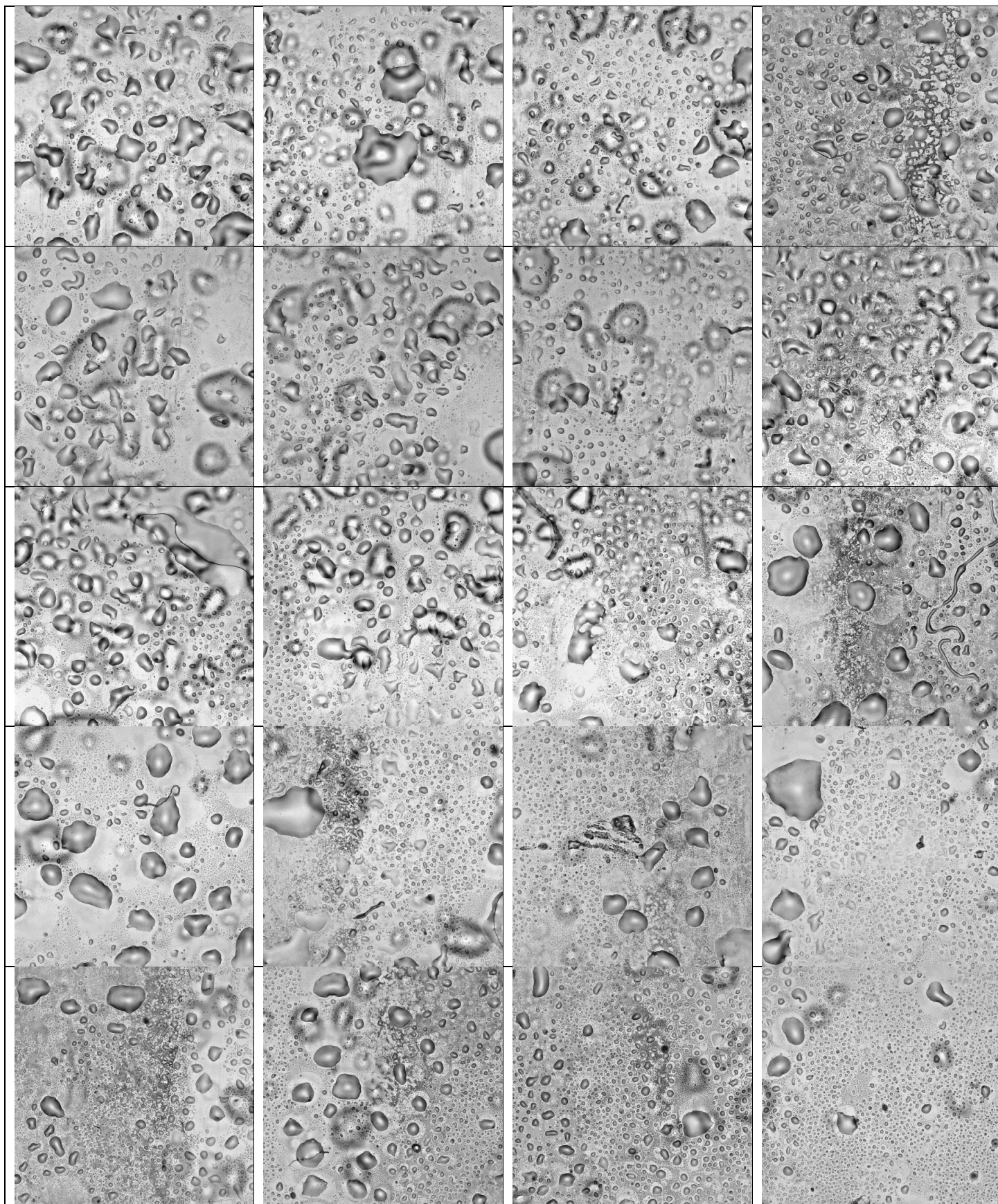




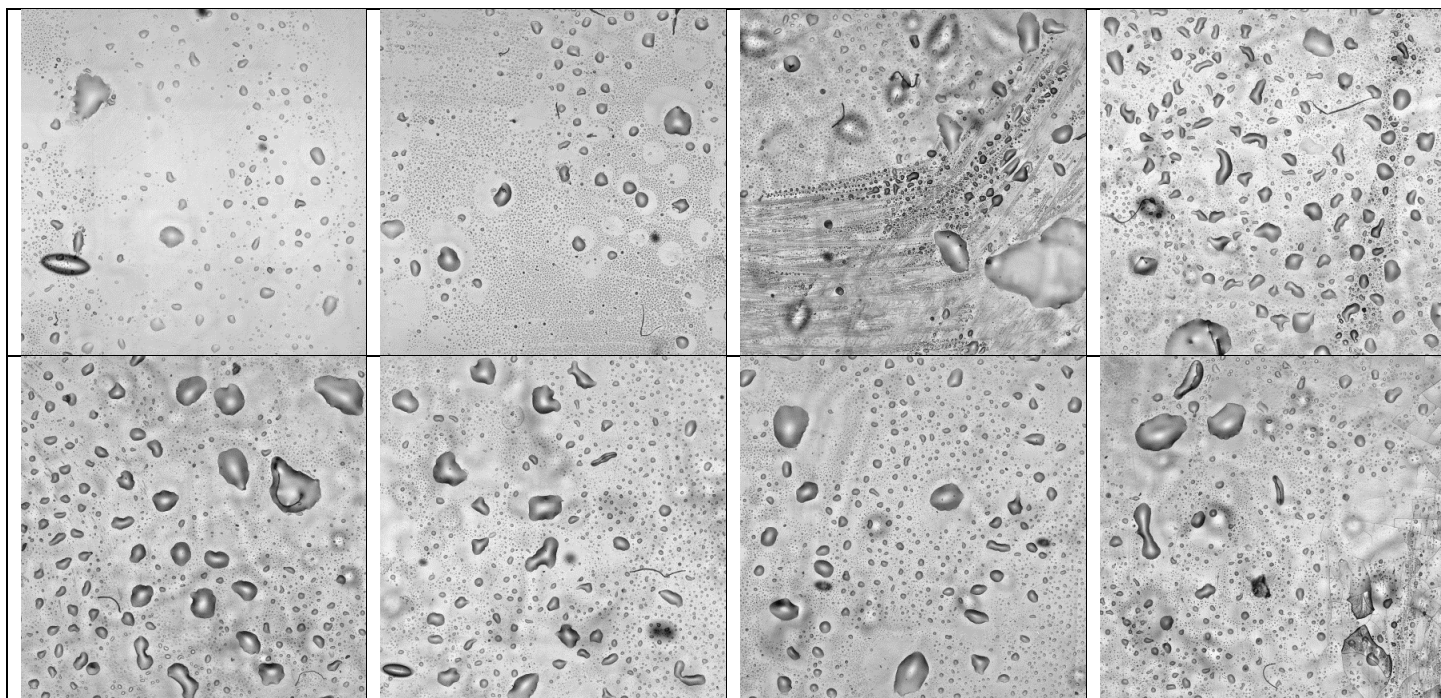


PV 9 months

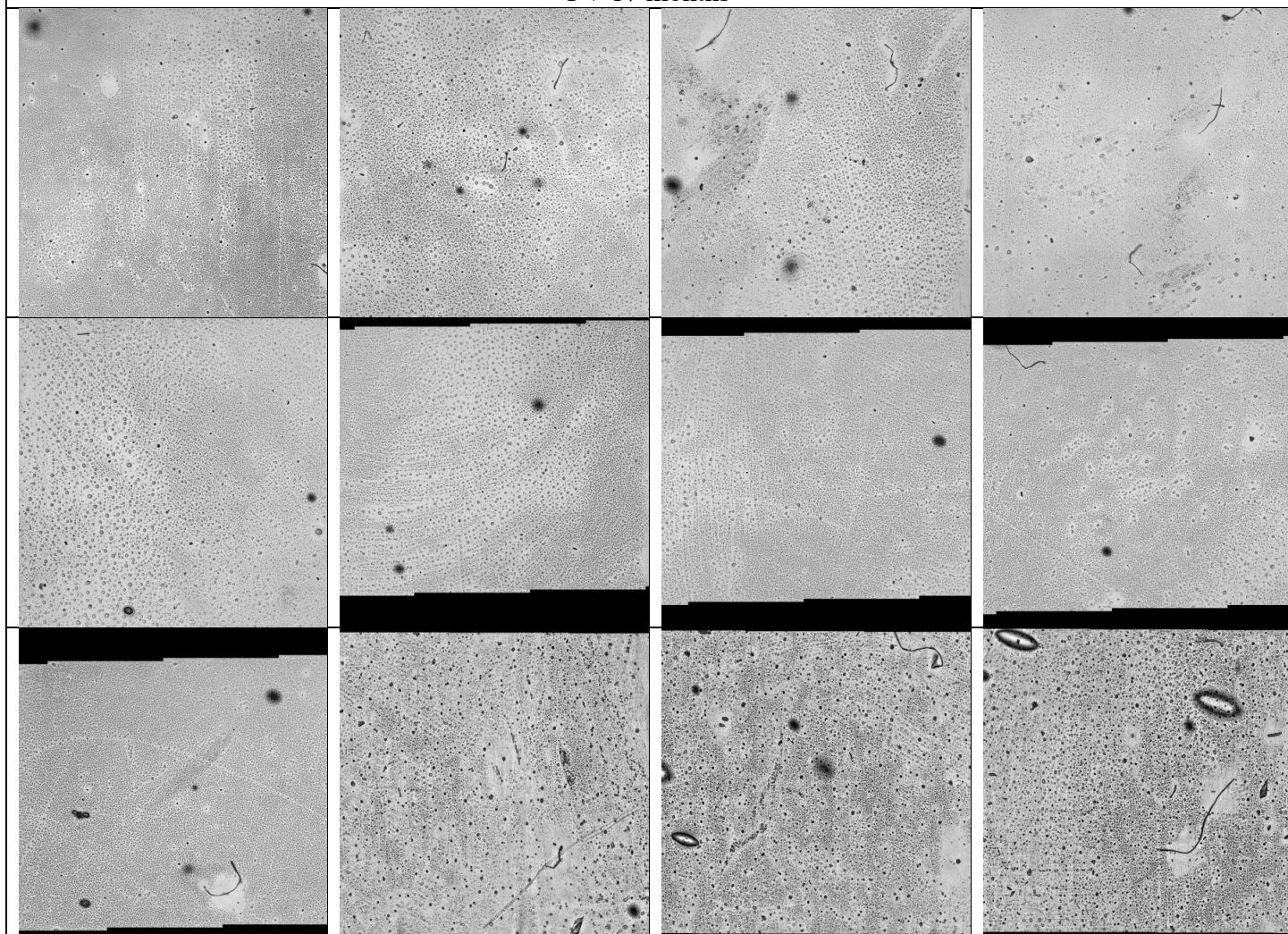


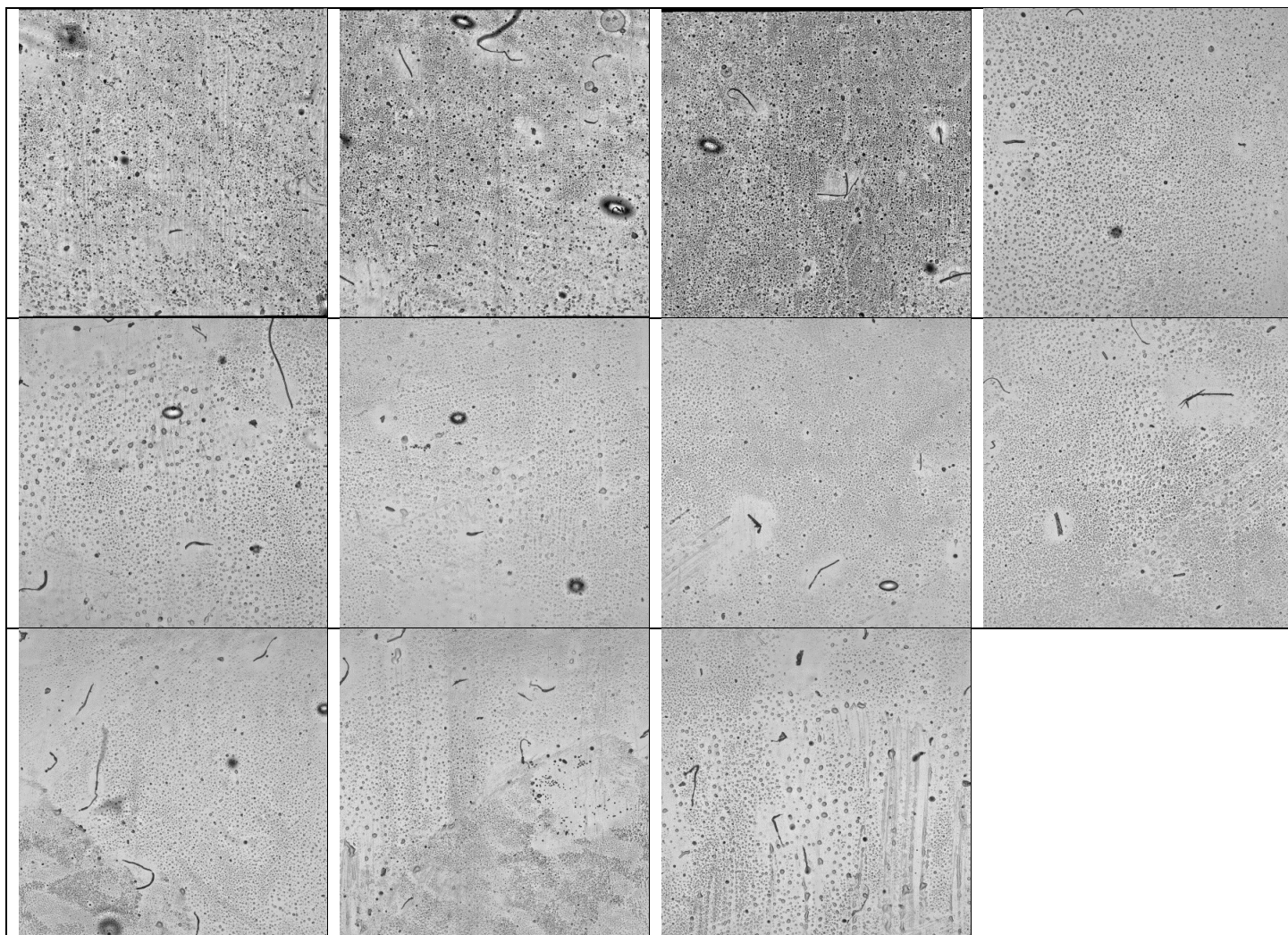


PV 12 months

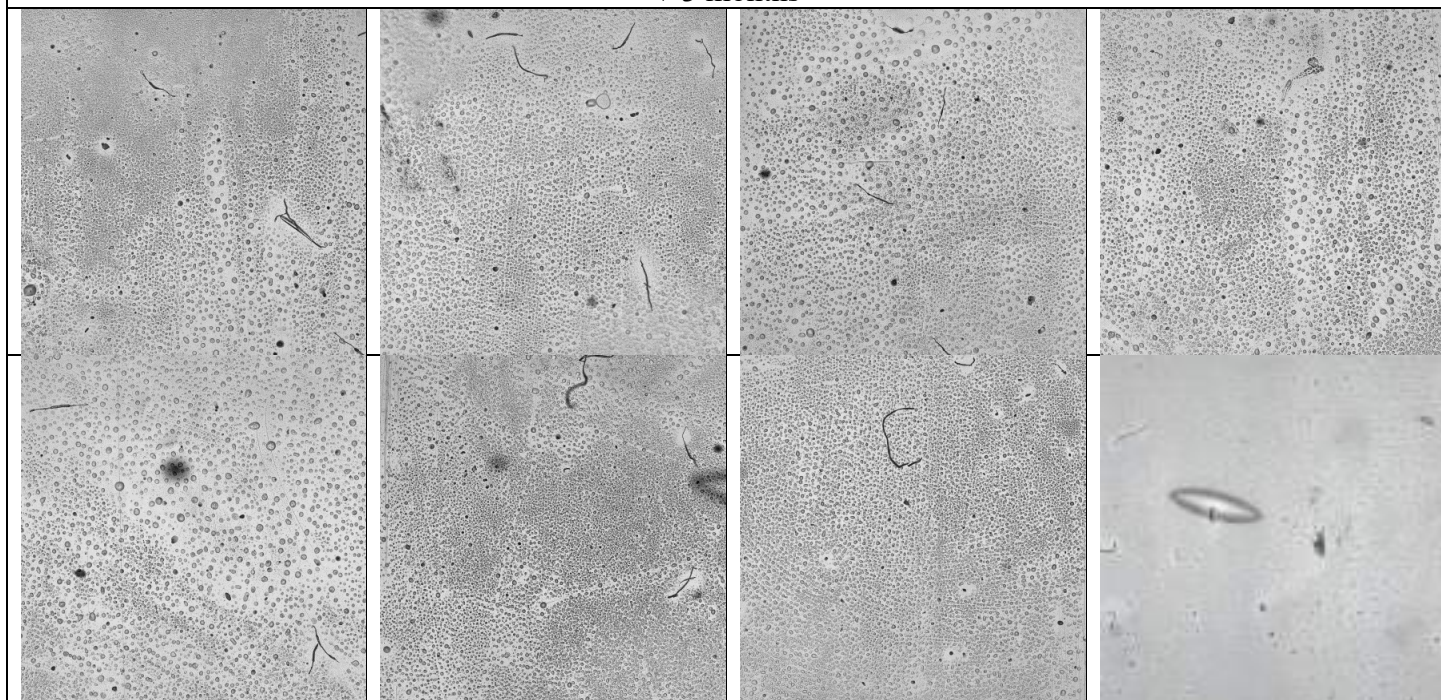


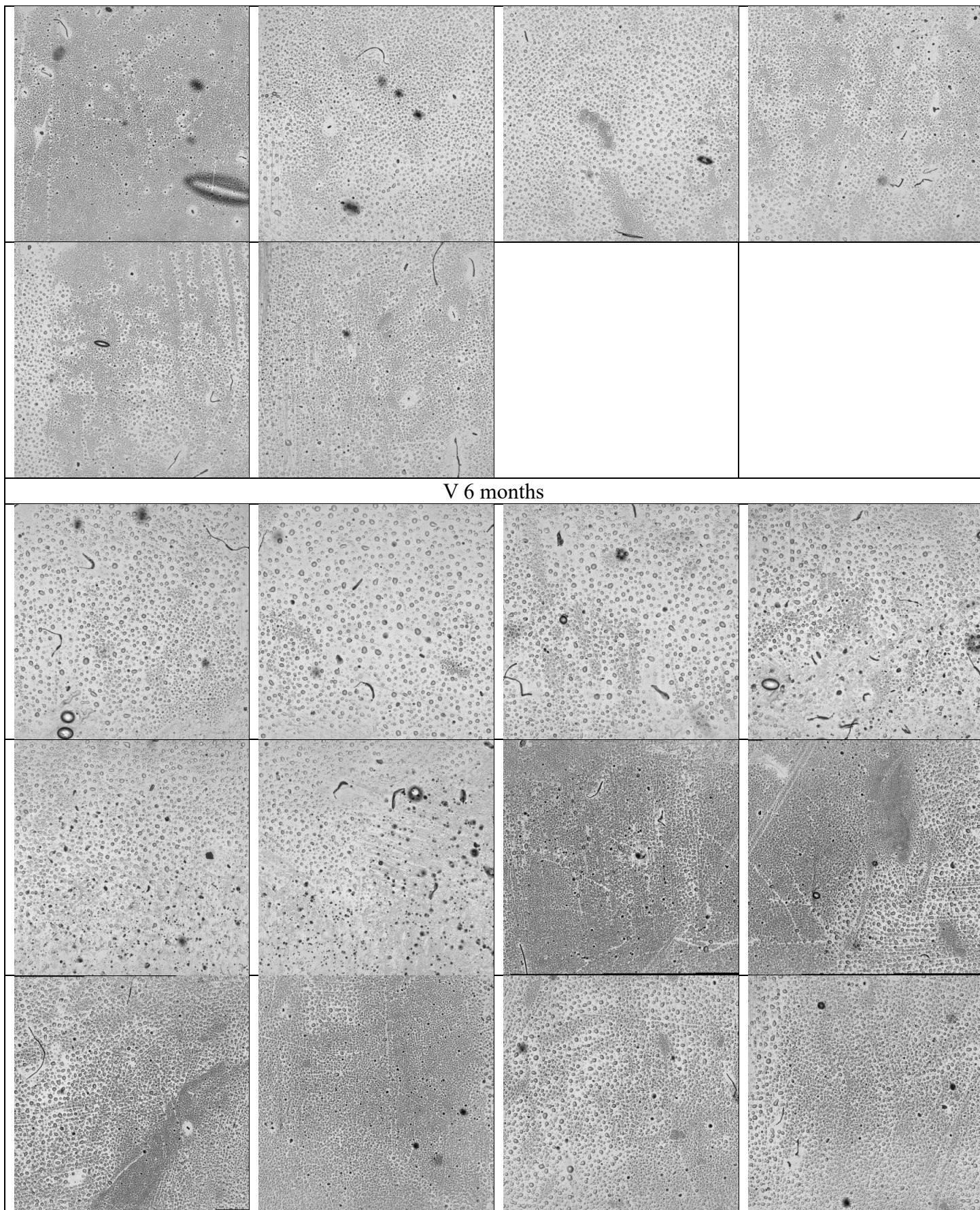
PV 17 months

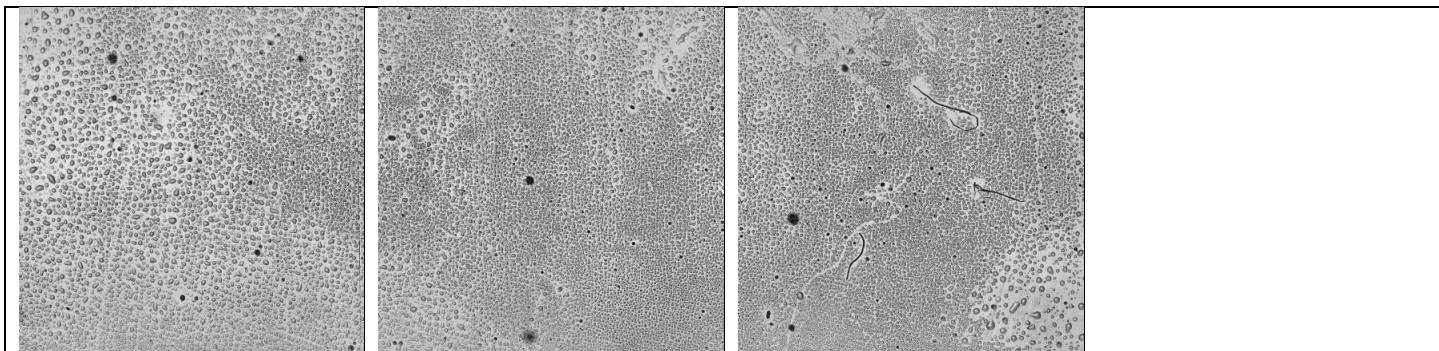




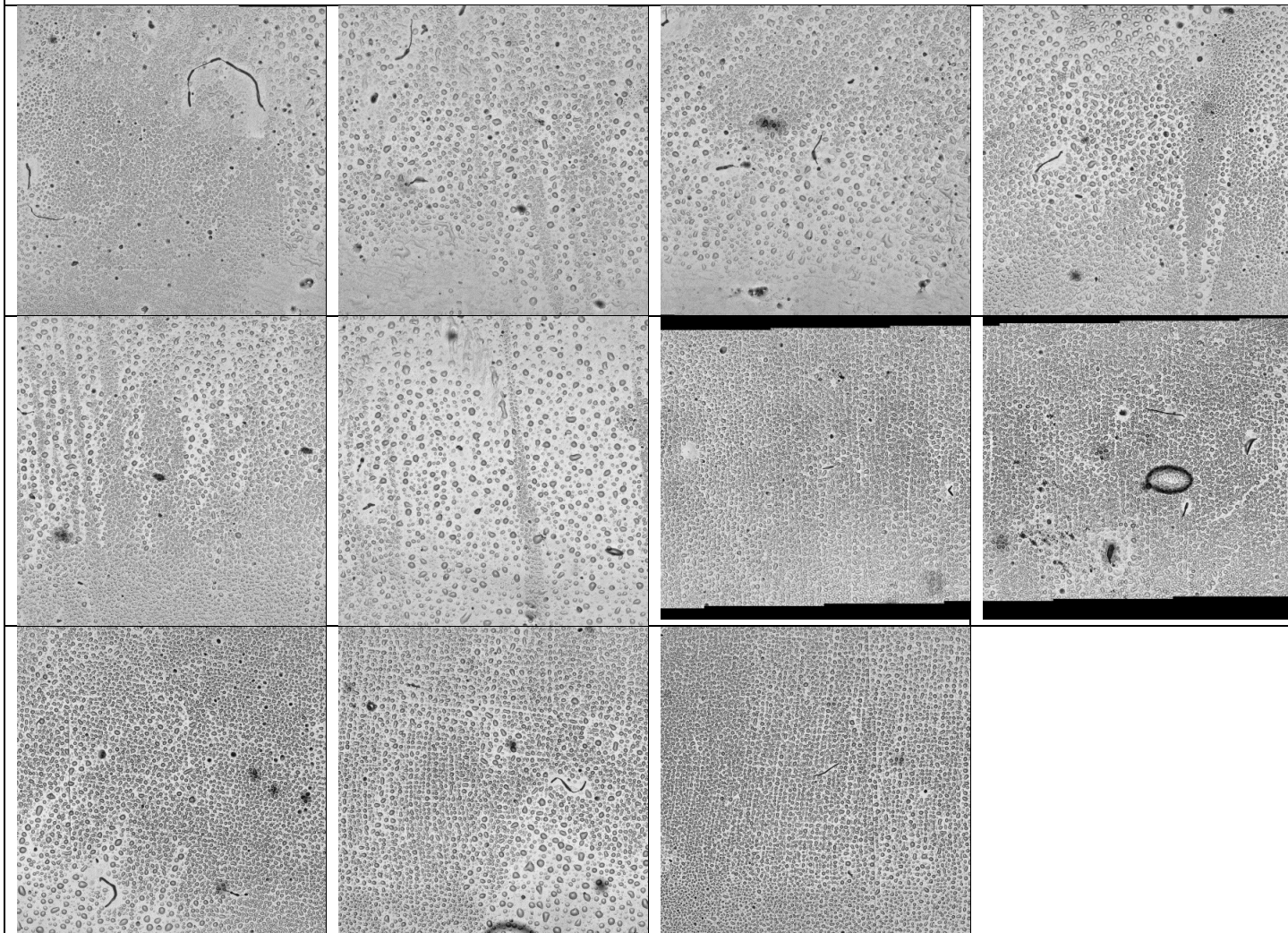
V 3 months



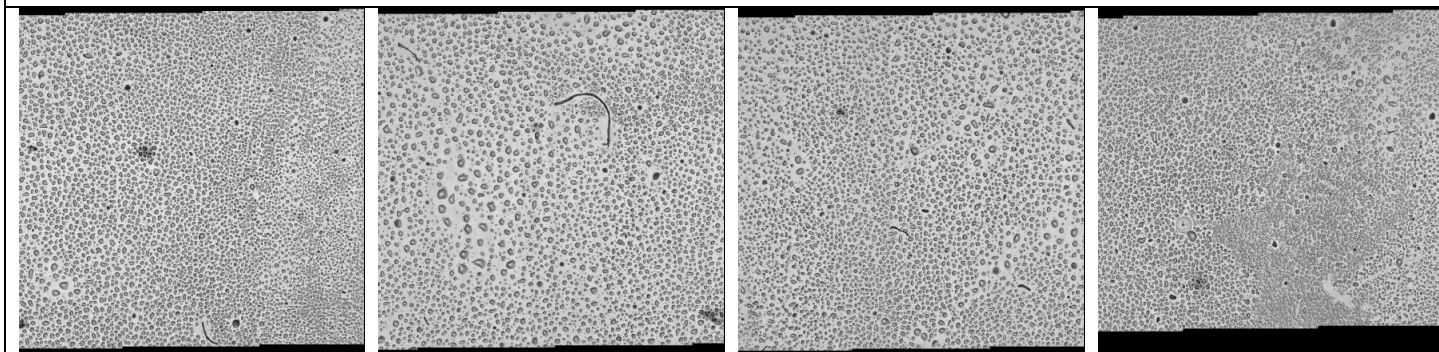


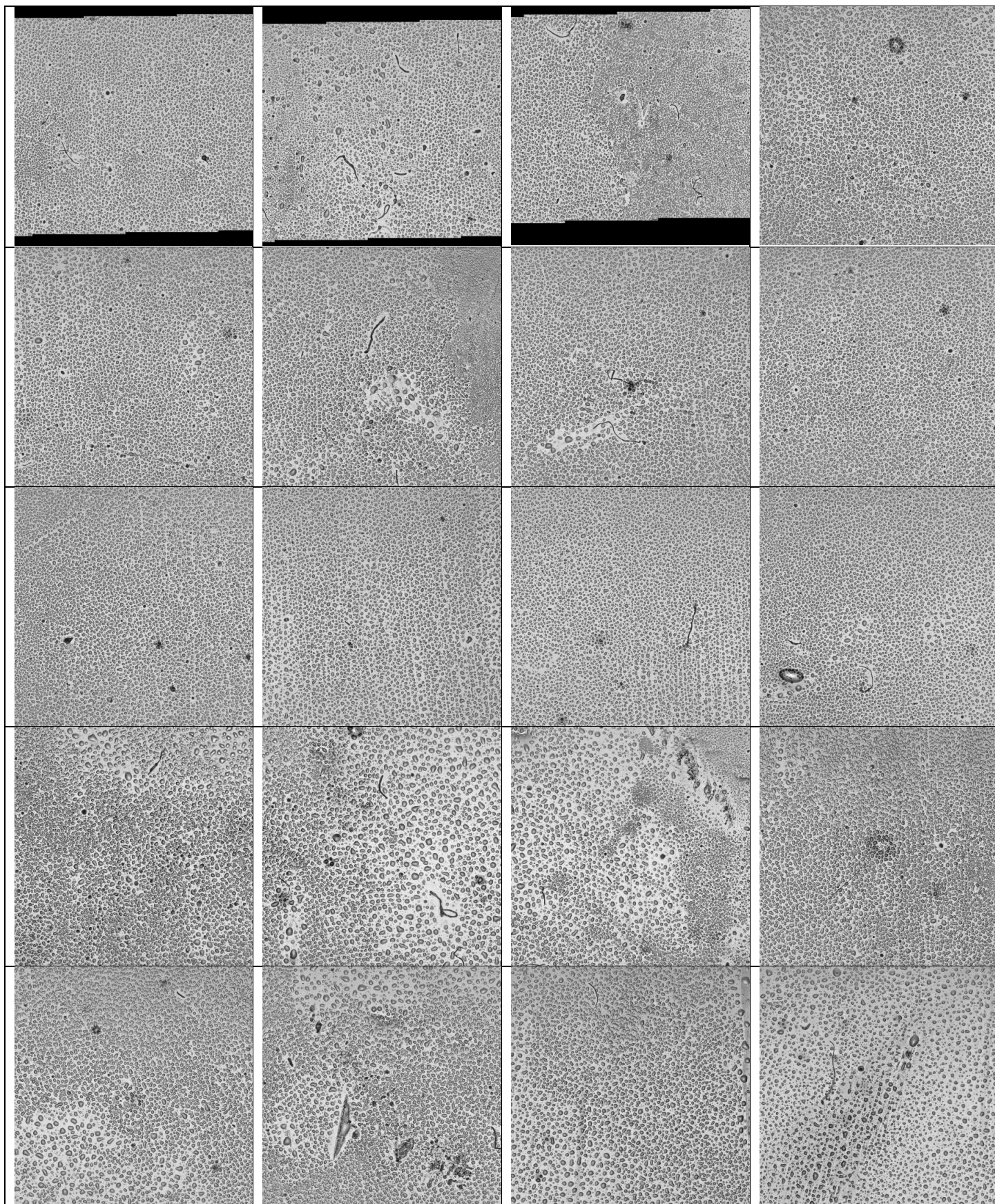


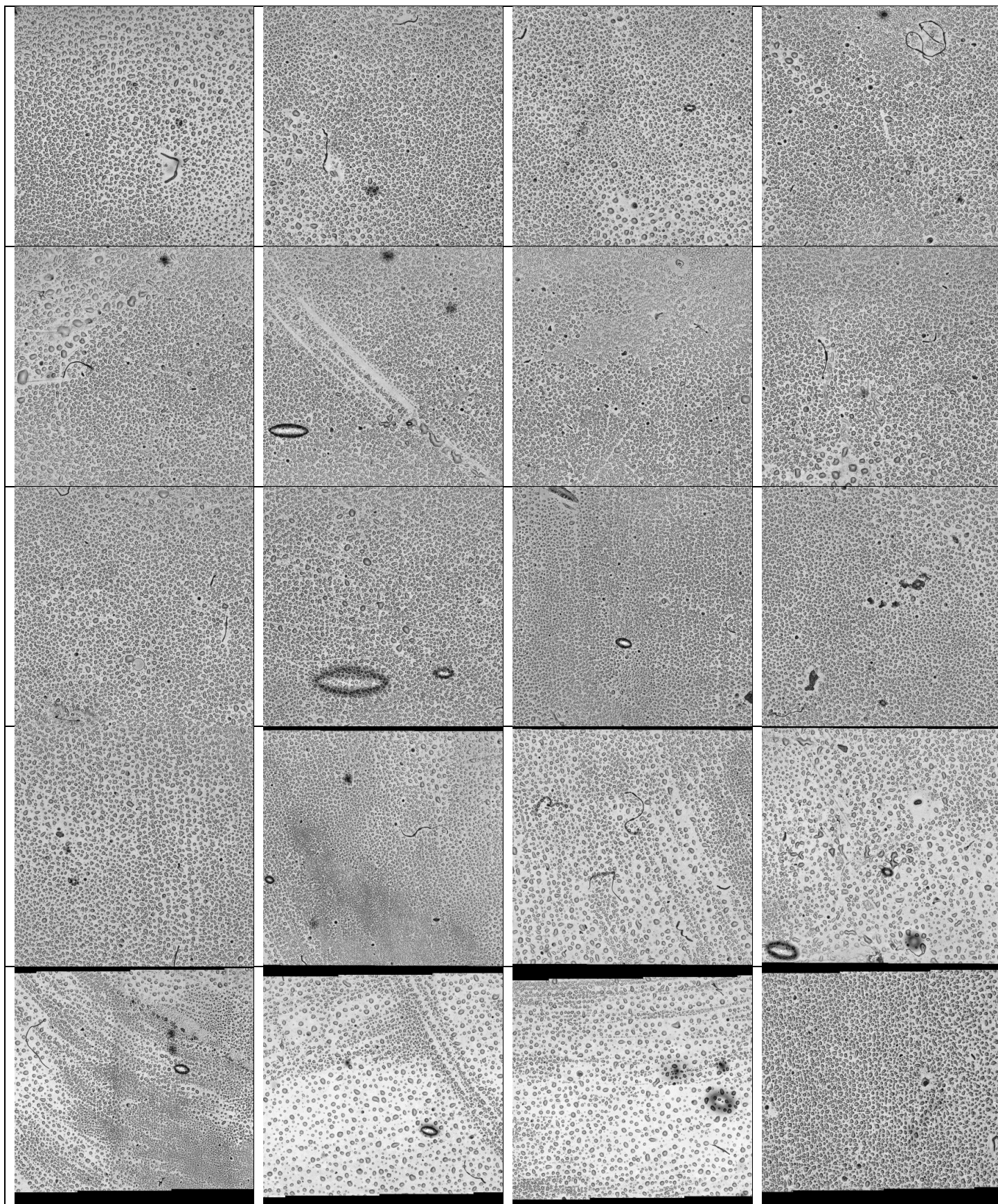
V 9 months

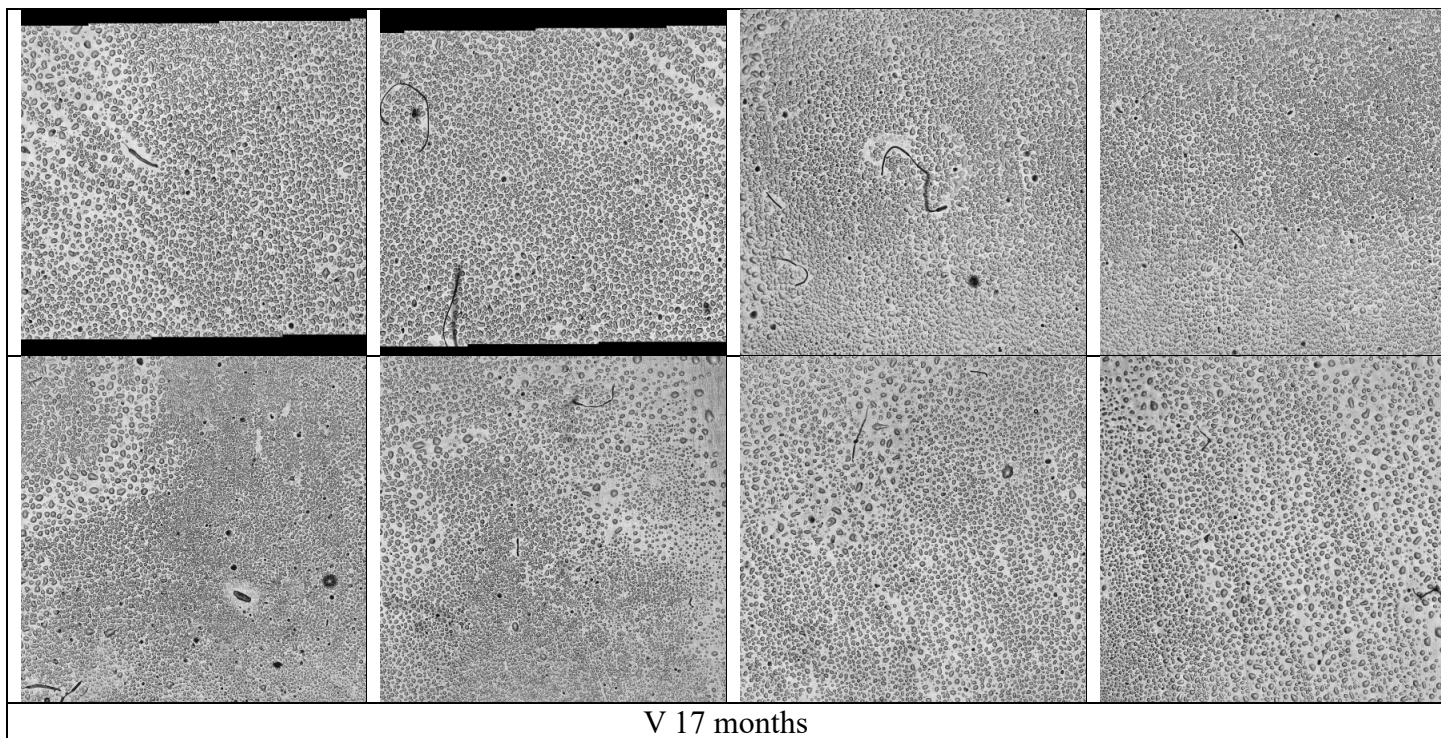


V 12 months



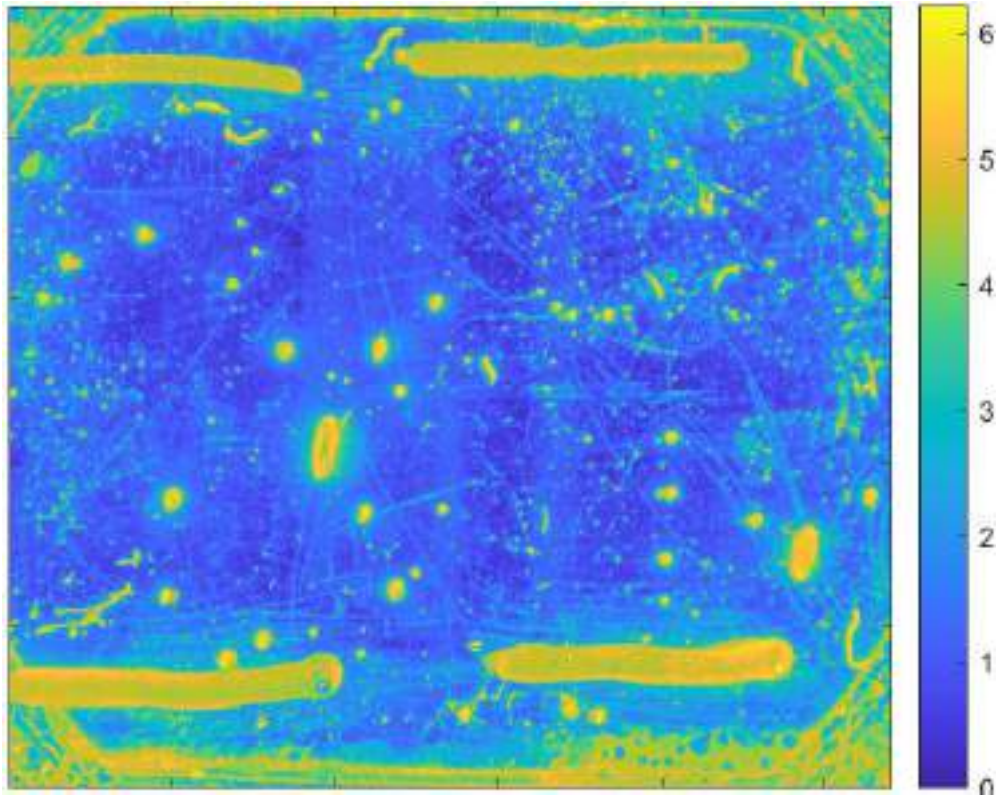




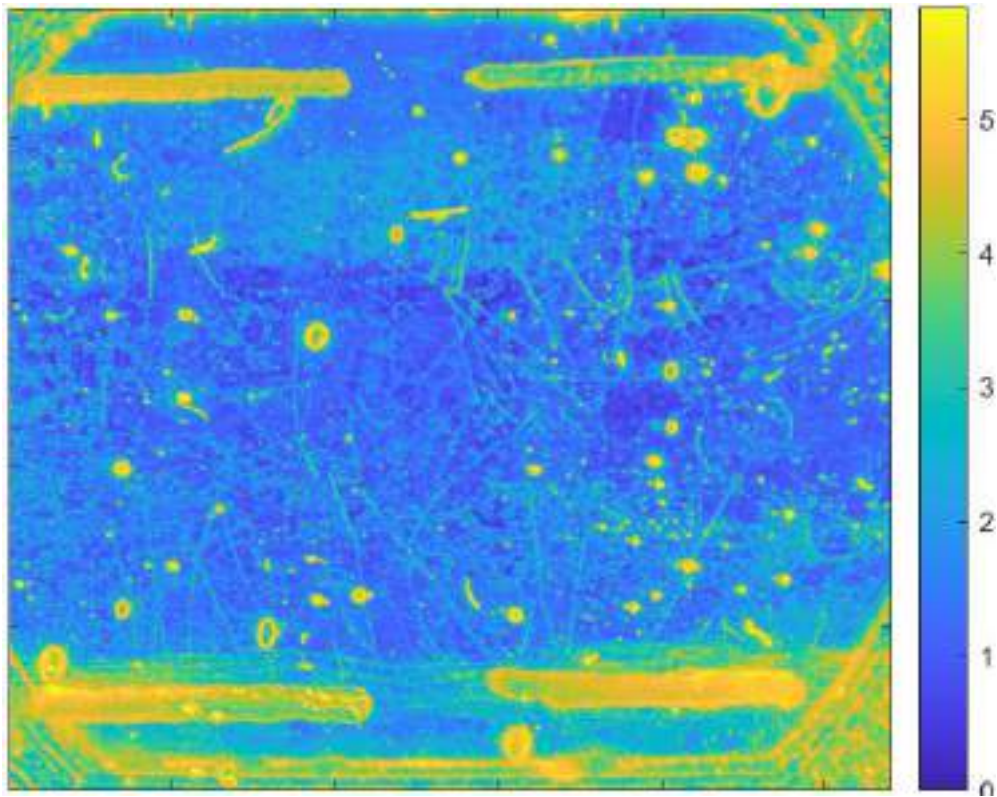


Annex VIII

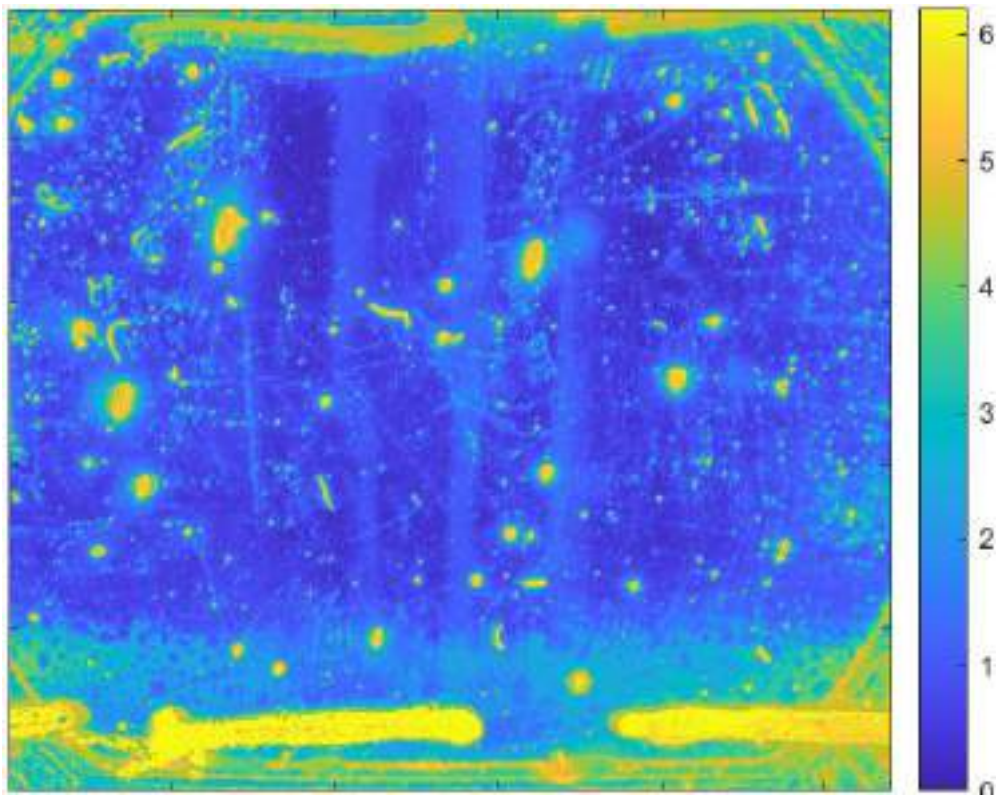
LDR (Shannon) Entropy RTI maps for visualizing fine cracks on P model glass (Image size: $\approx 24 \times 21 \text{ mm}^2$)



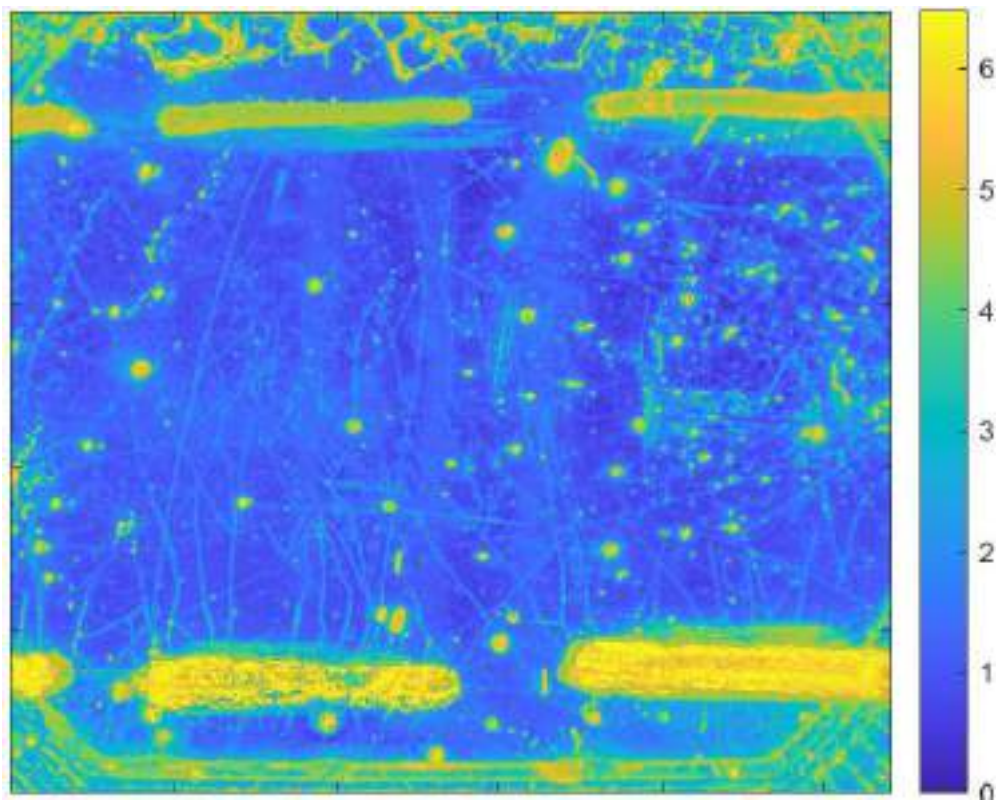
P 3 months



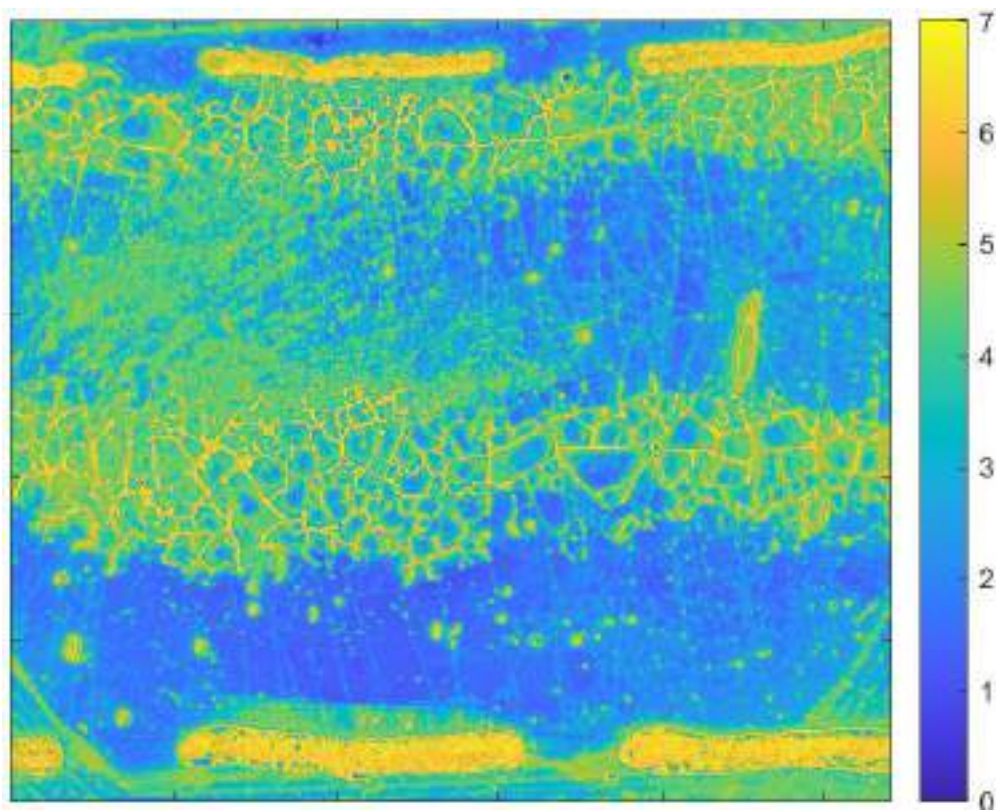
P 6 months



P 9 months

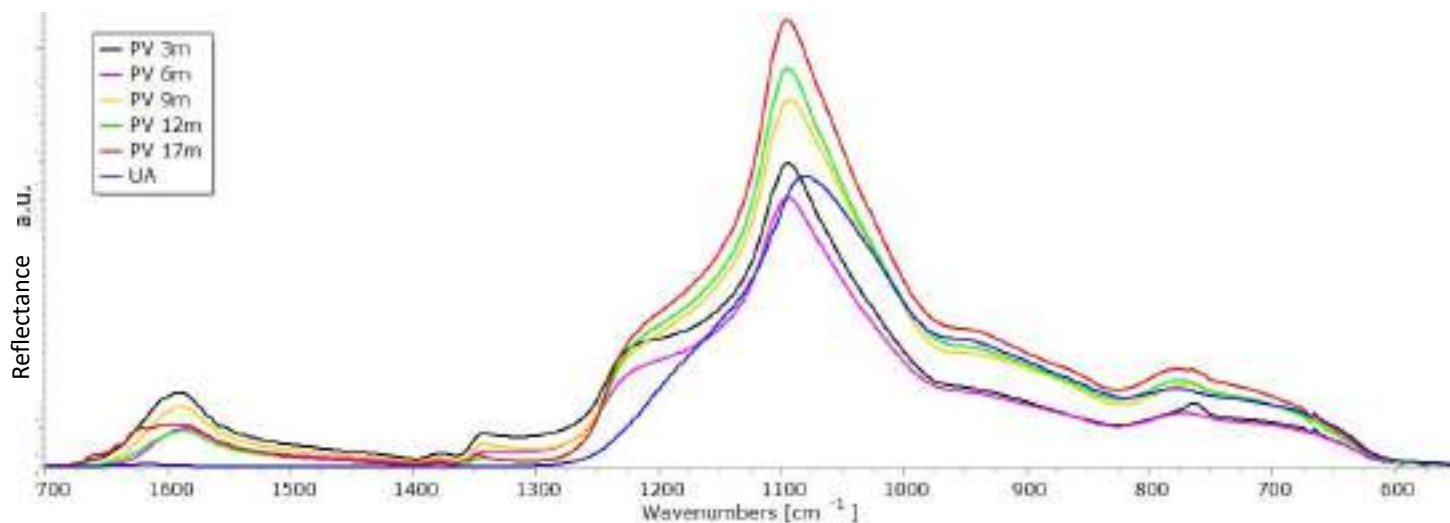


P 12 months

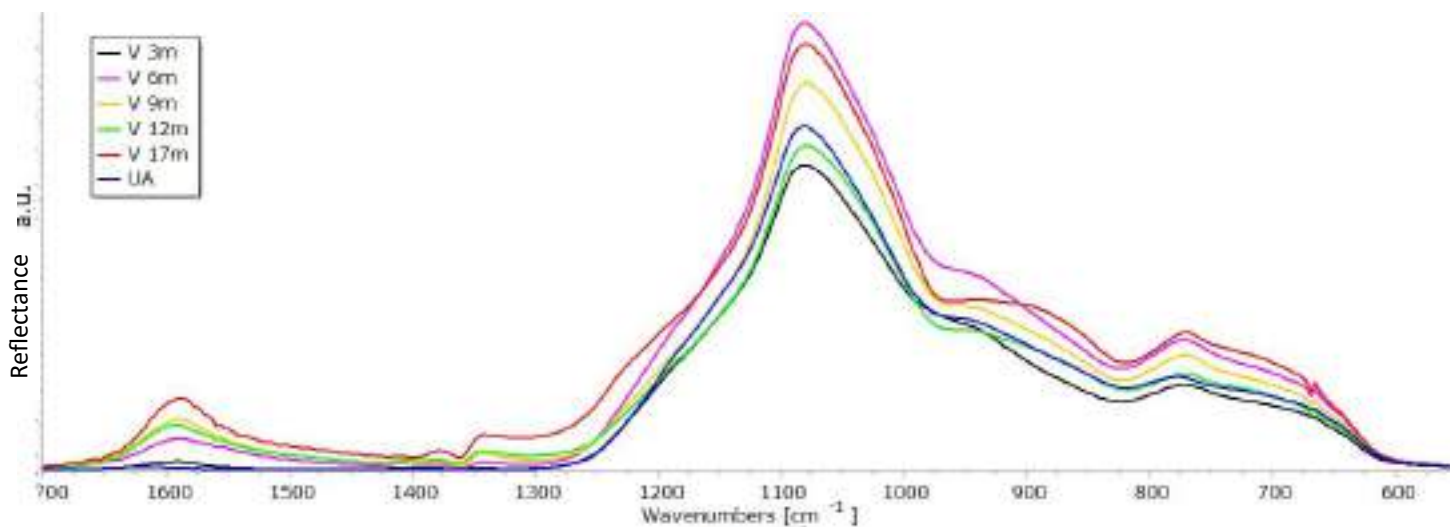


P 17 months (dried)

Annex IX



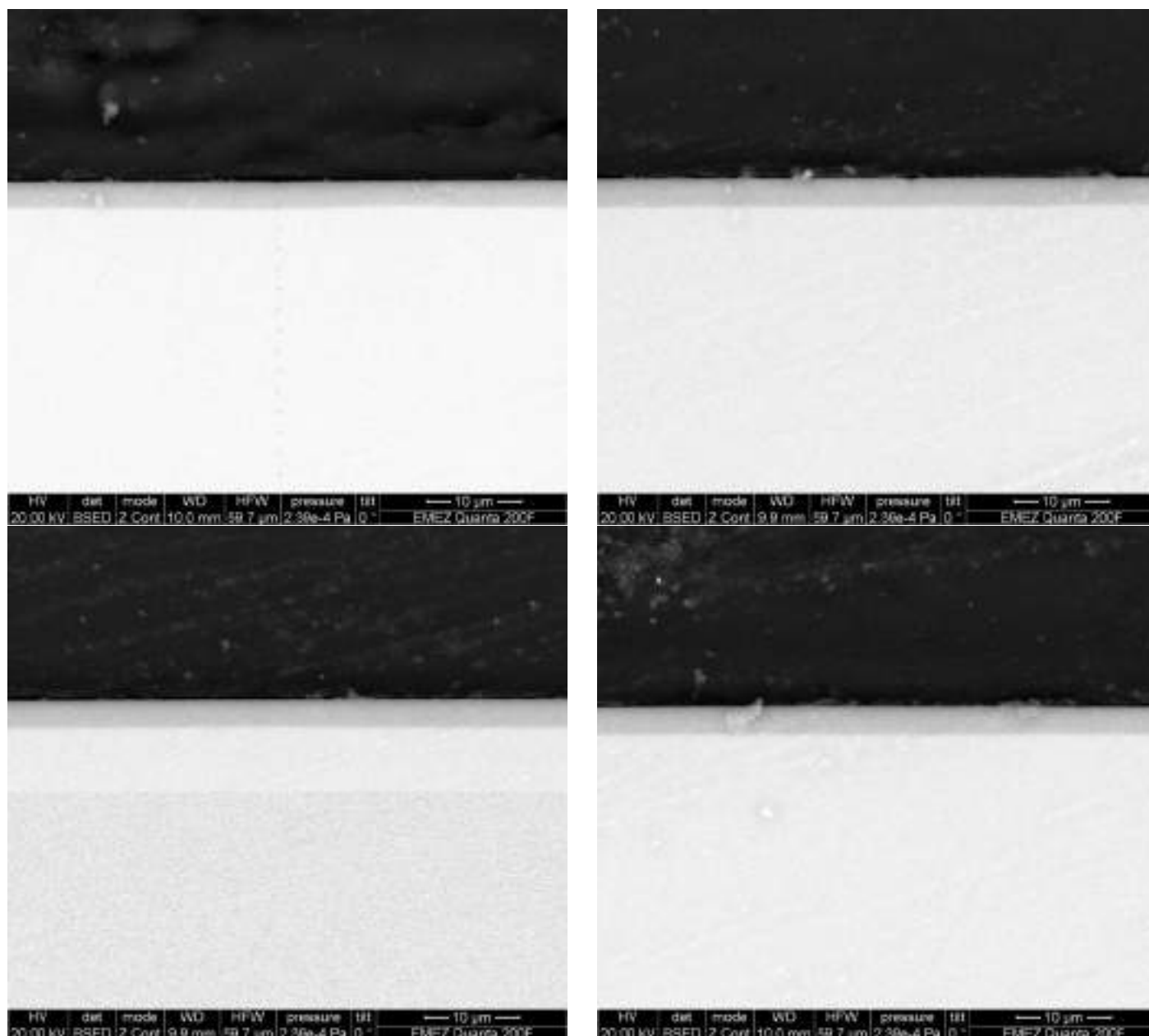
Average FTIR spectra for corroded PV model glass compared with unaged (UA) glass average spectrum for withdrawal periods of 3m (black), 6m (pink), 9m (orange), 12m (green), 17m (red) and unaged glass (blue)

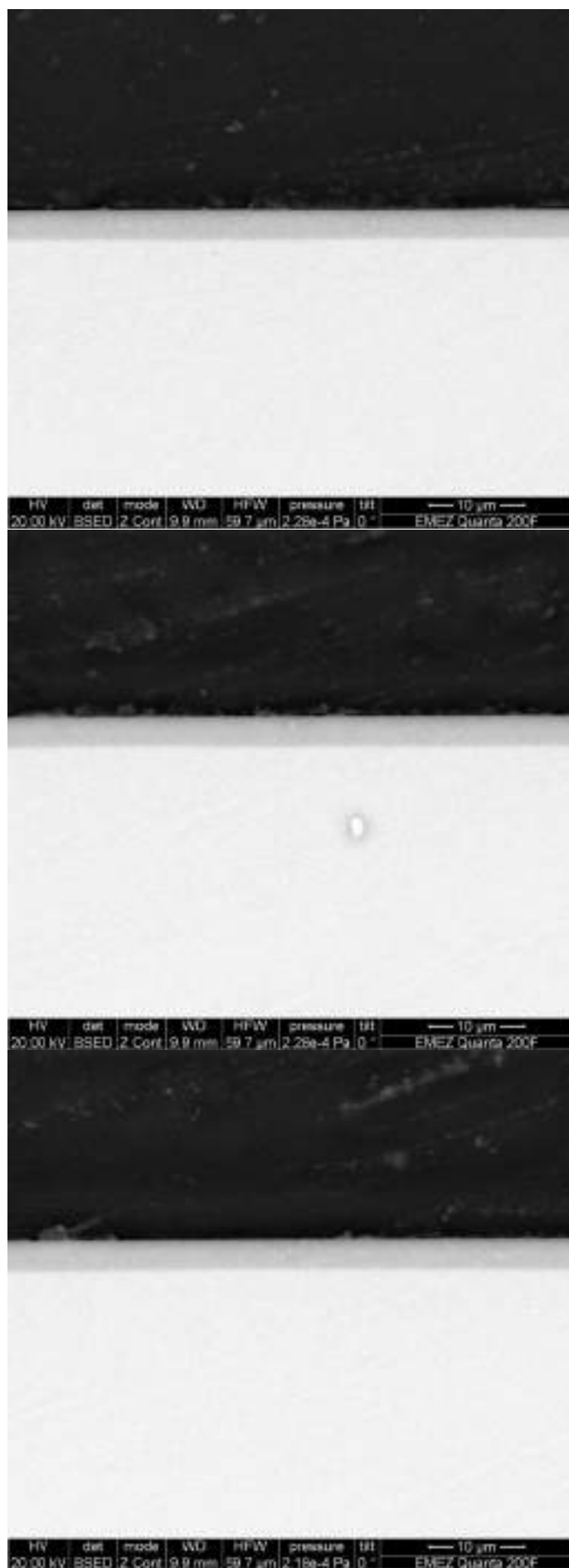
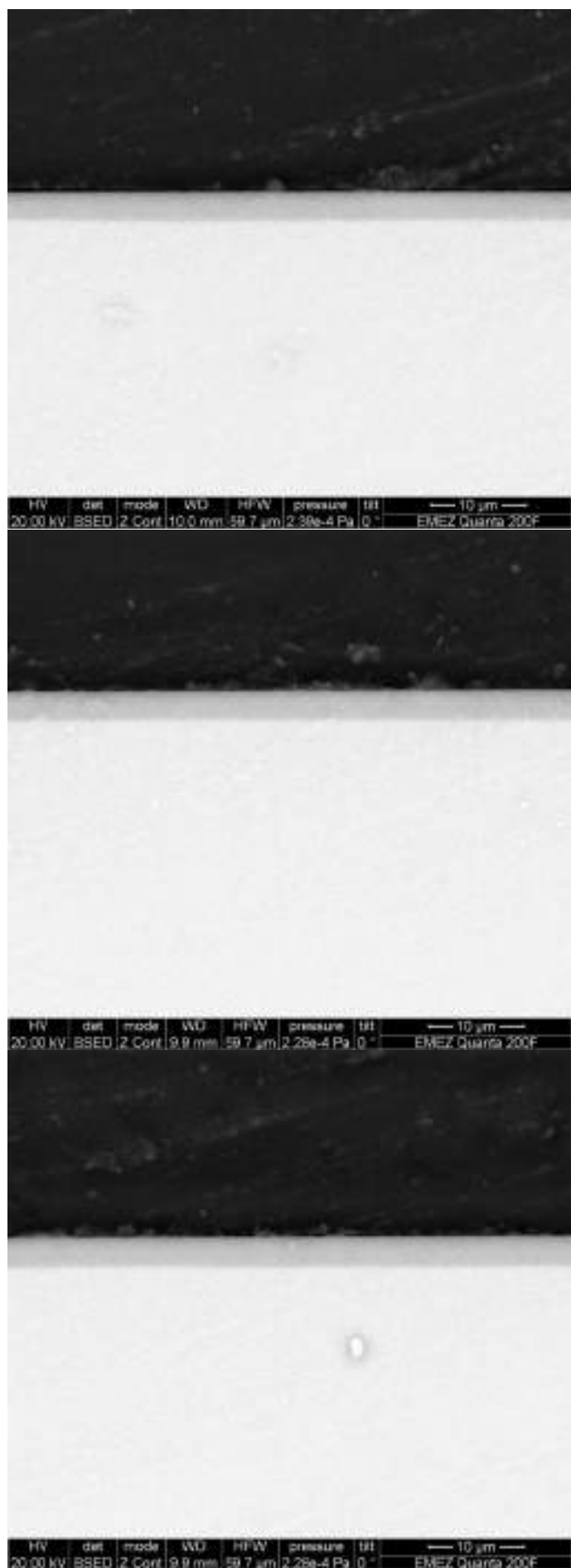


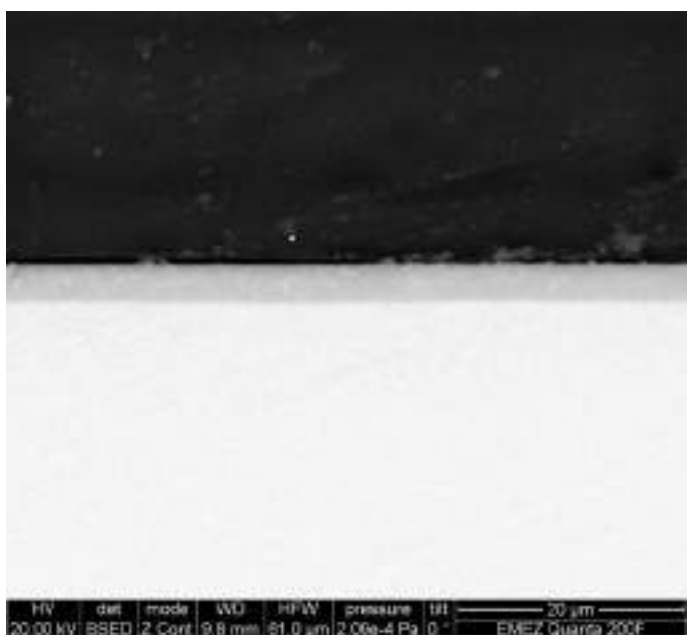
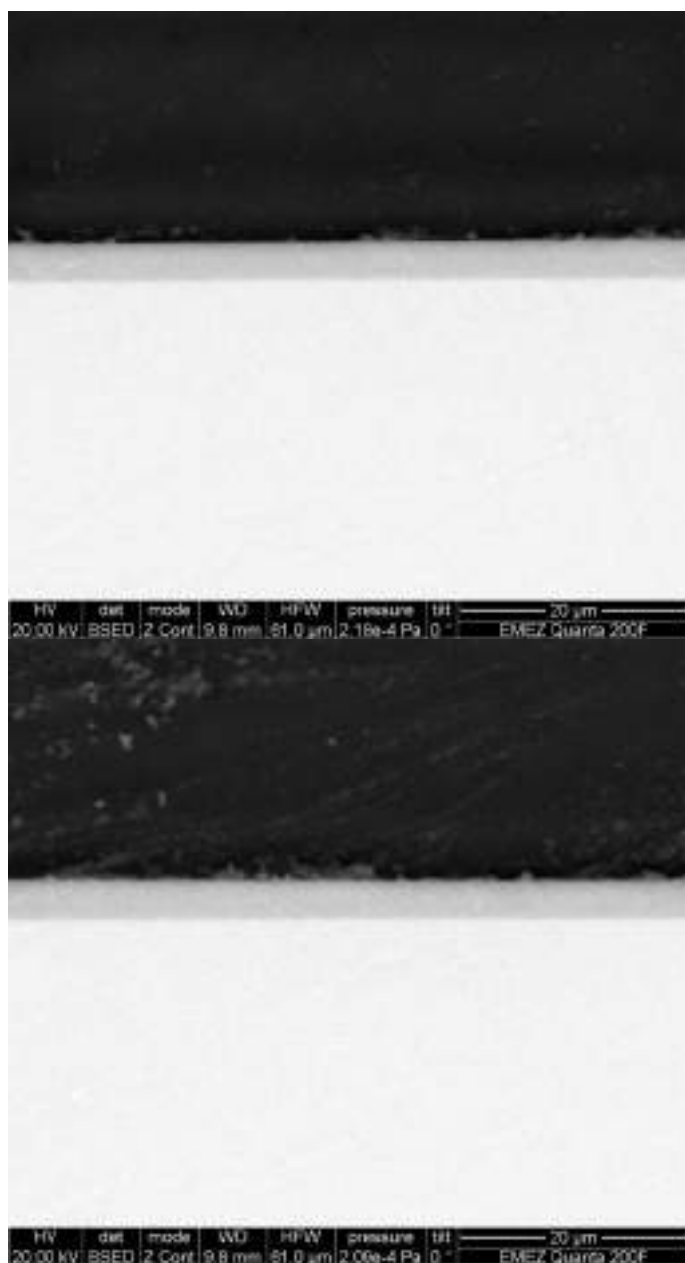
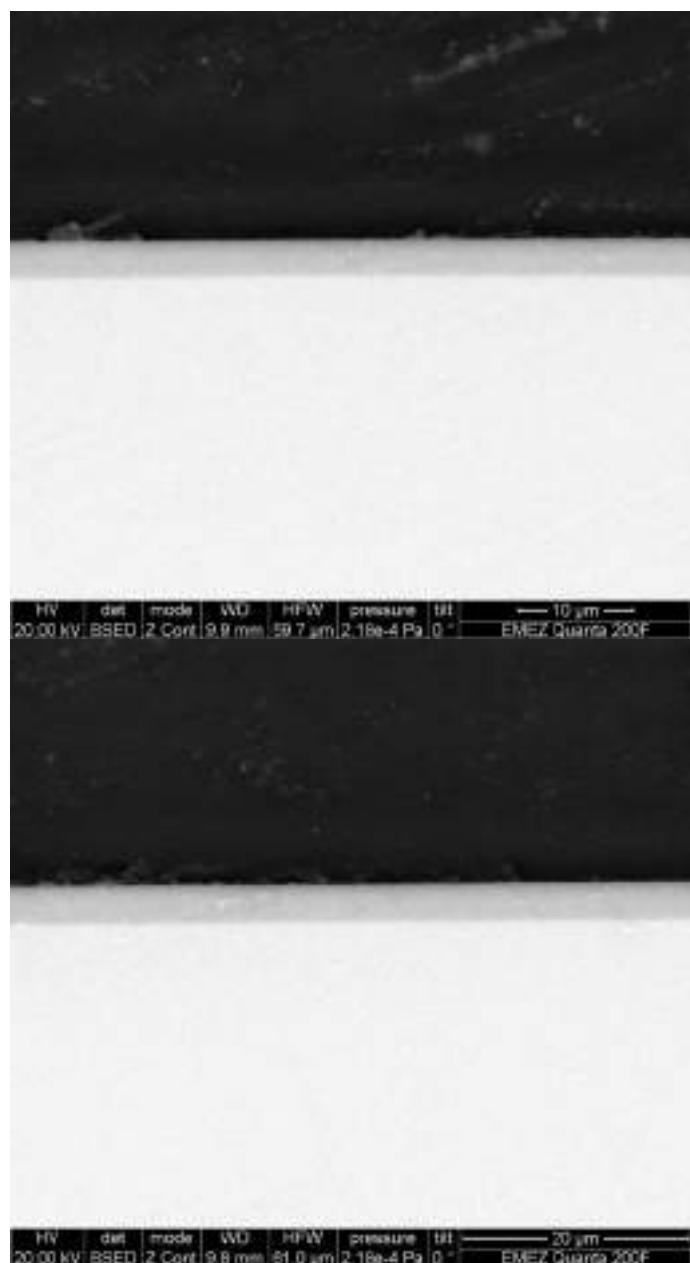
Average FTIR spectra for corroded PV model glass compared with unaged (UA) glass average spectrum for withdrawal periods of 3m (black), 6m (pink), 9m (orange), 12m (green), 17m (red) and unaged glass (blue)

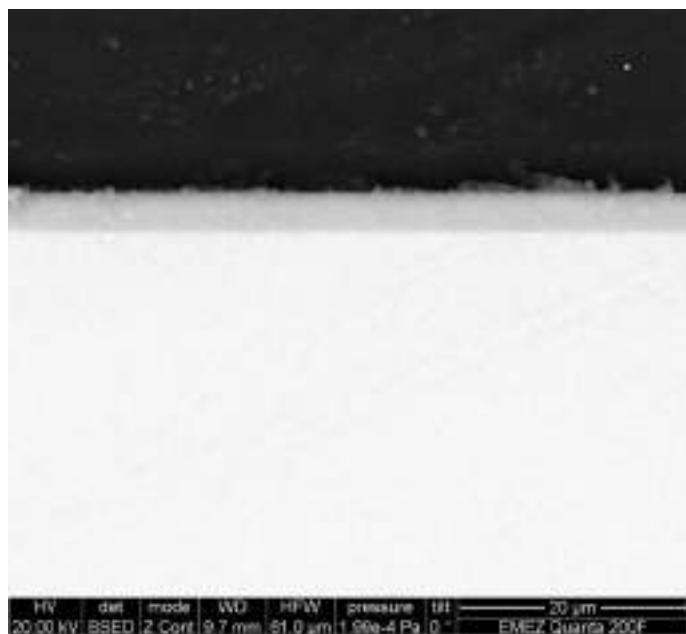
Annex X

SEM images from cross-section samples taken from corroded model glass

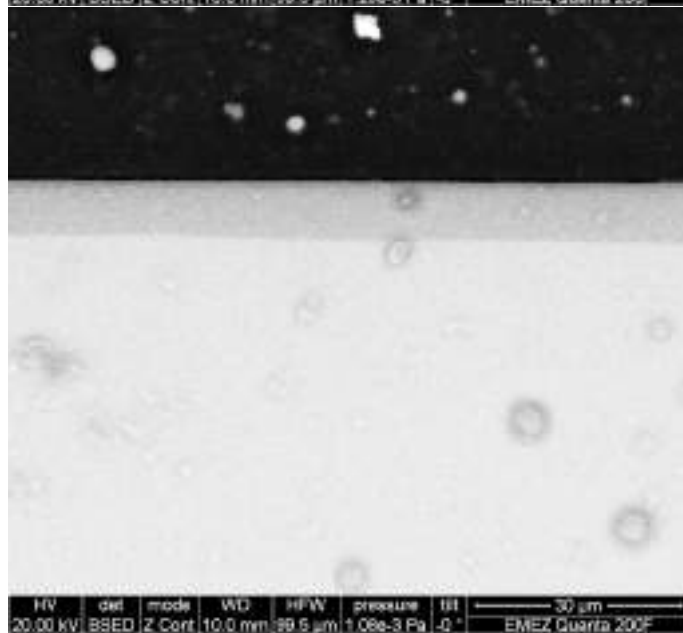
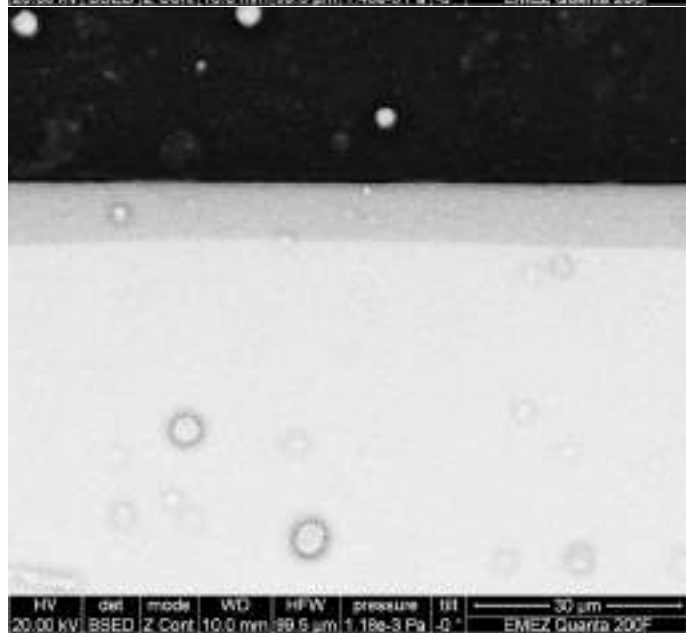
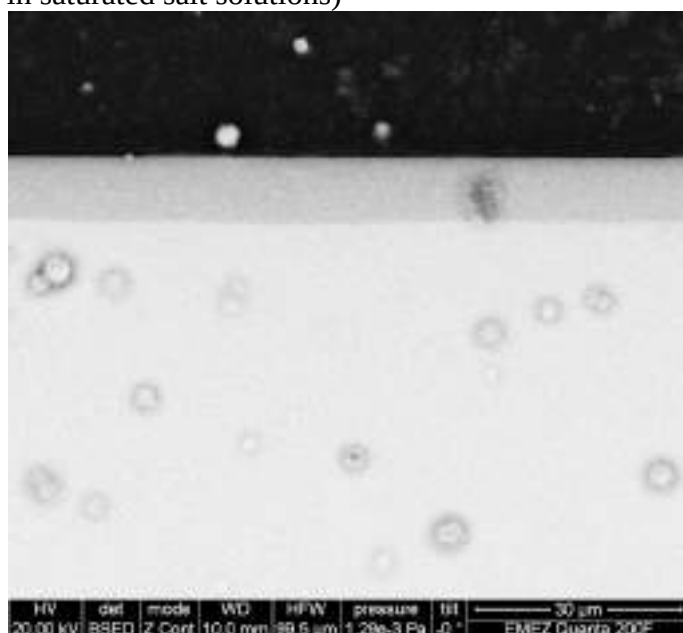
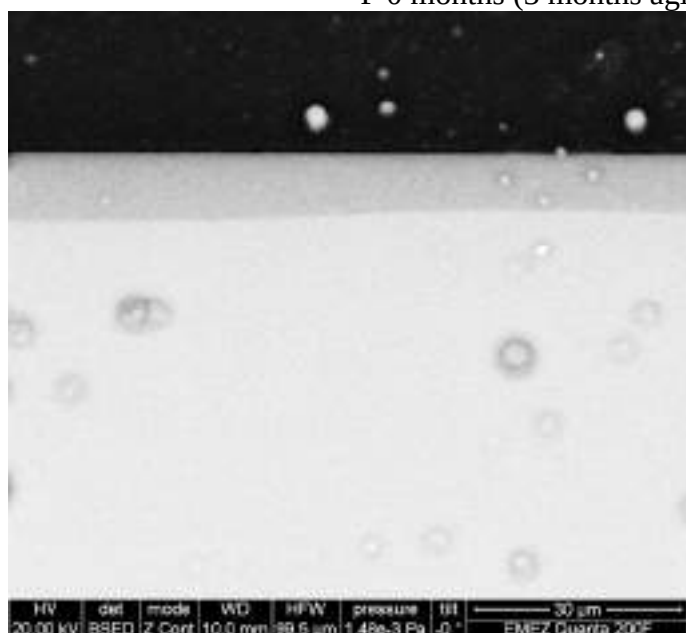


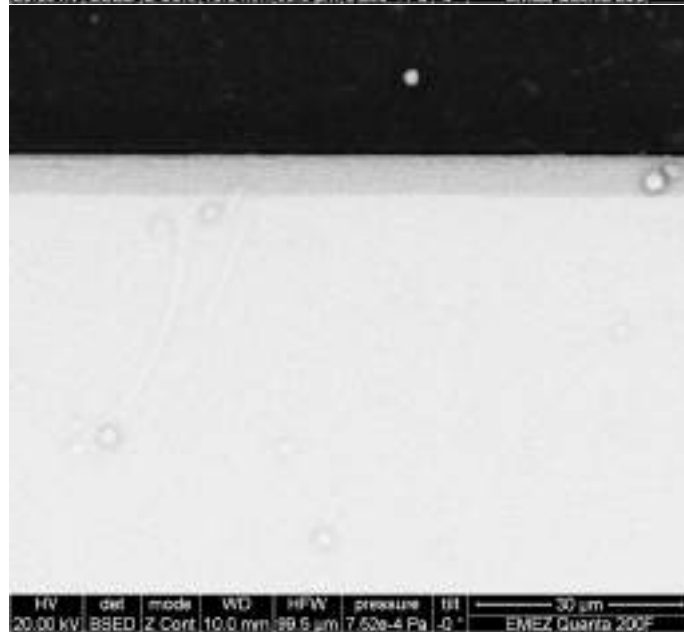
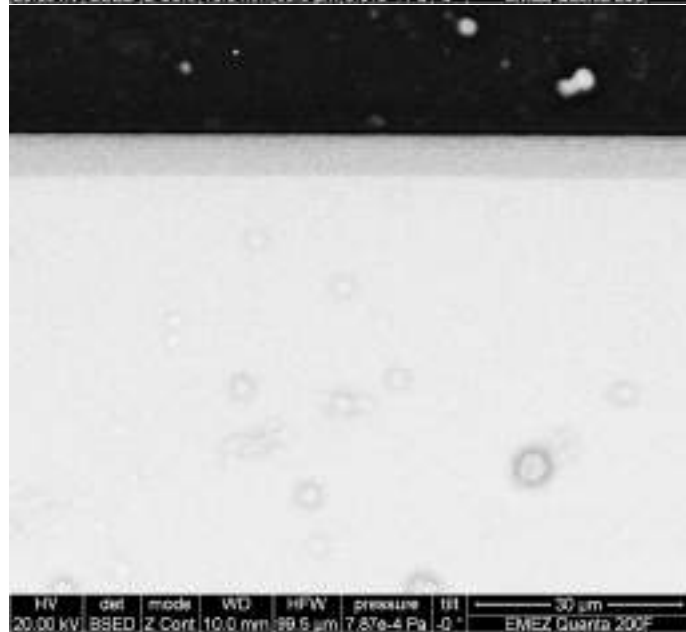
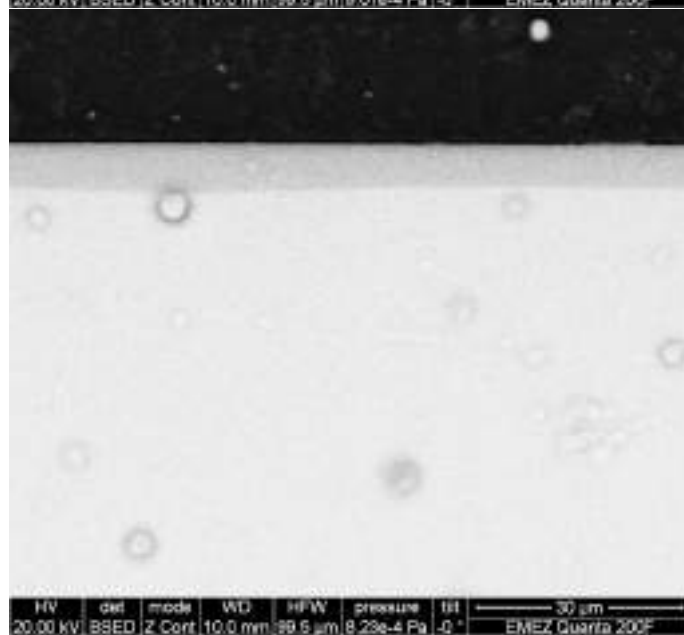
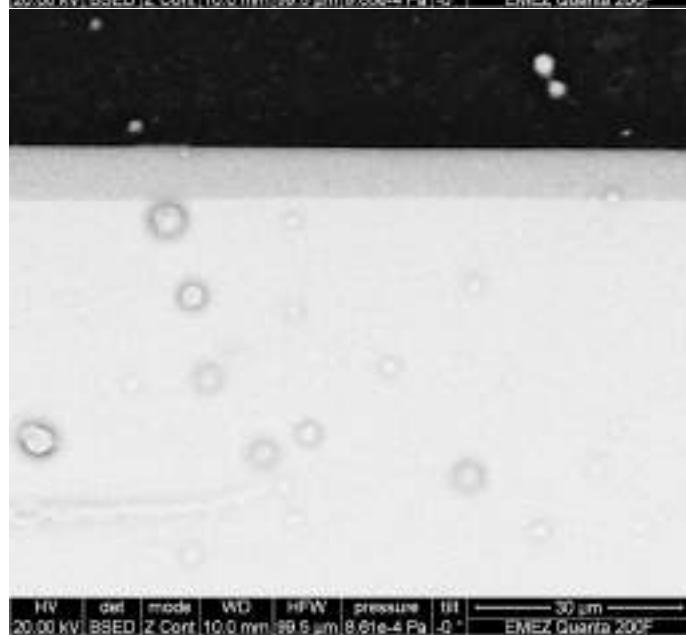
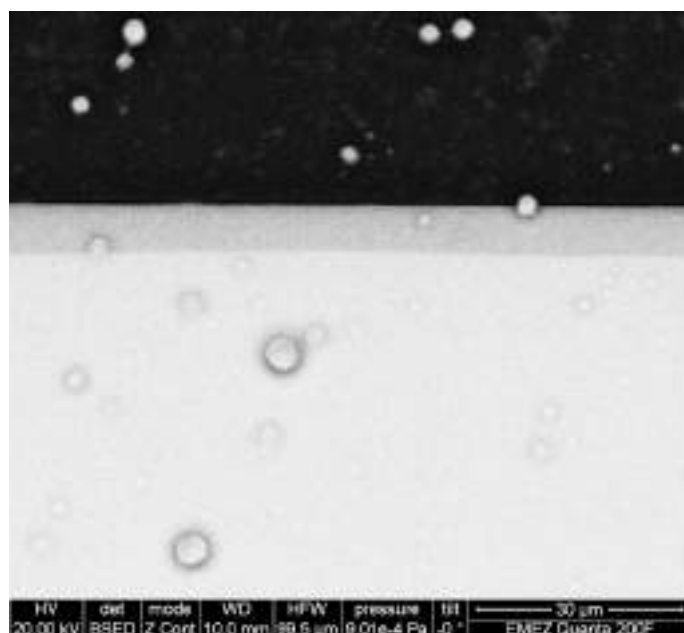
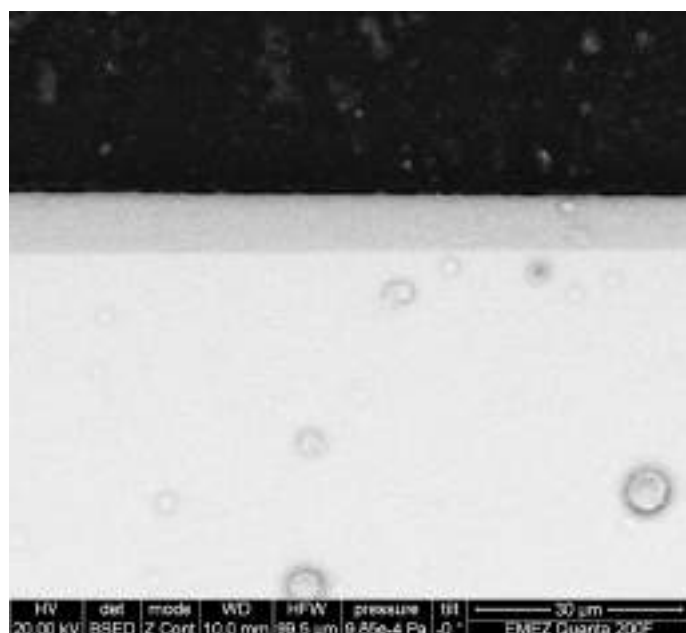


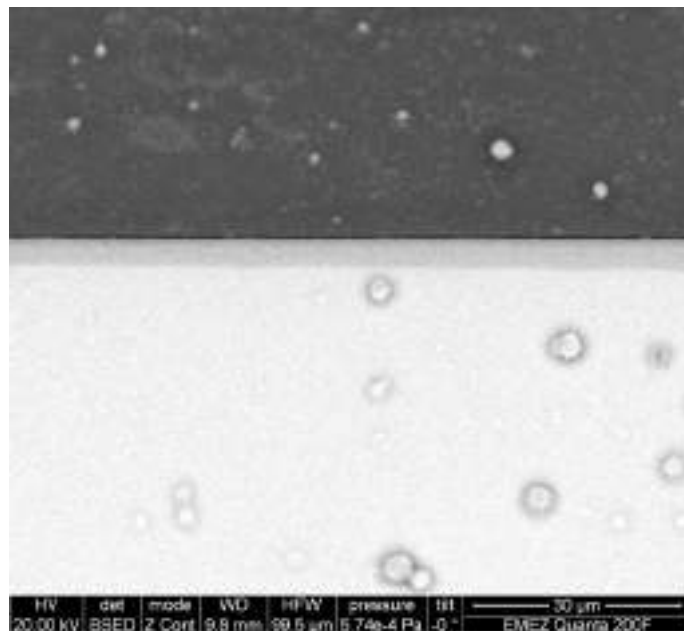
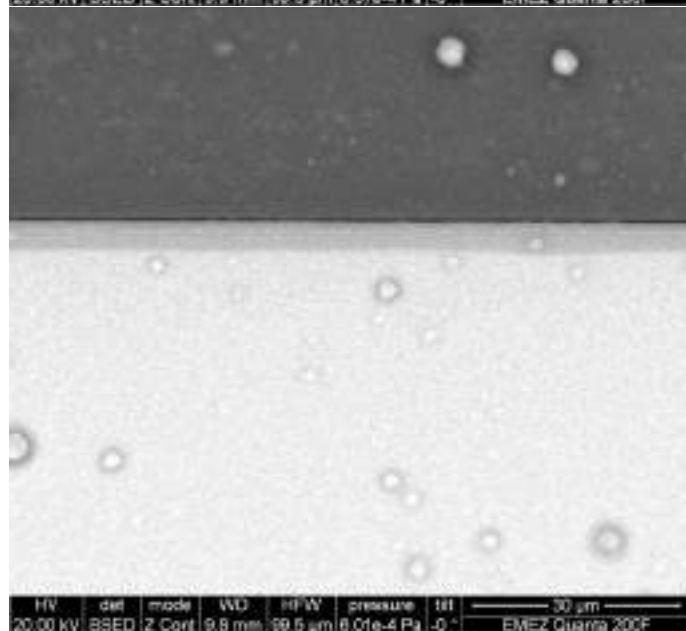
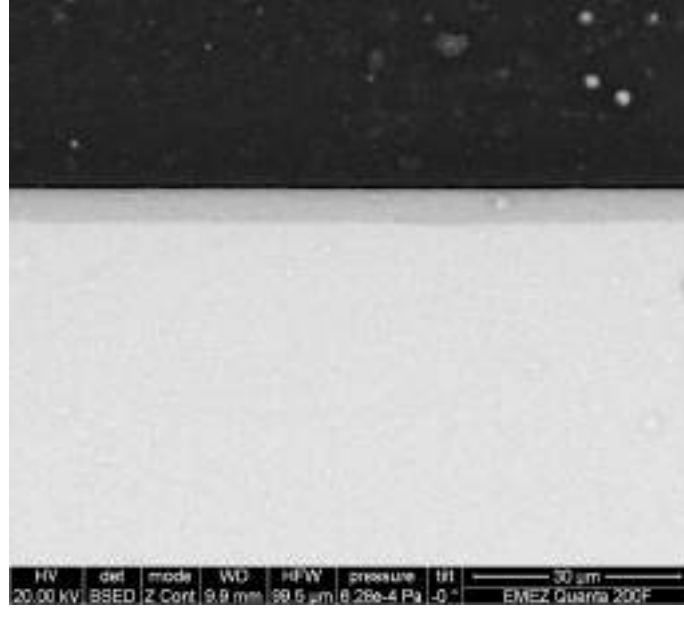
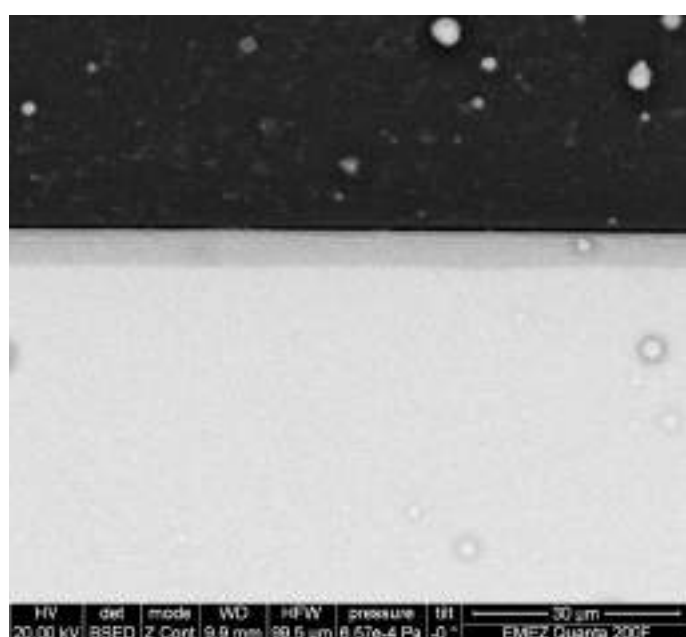
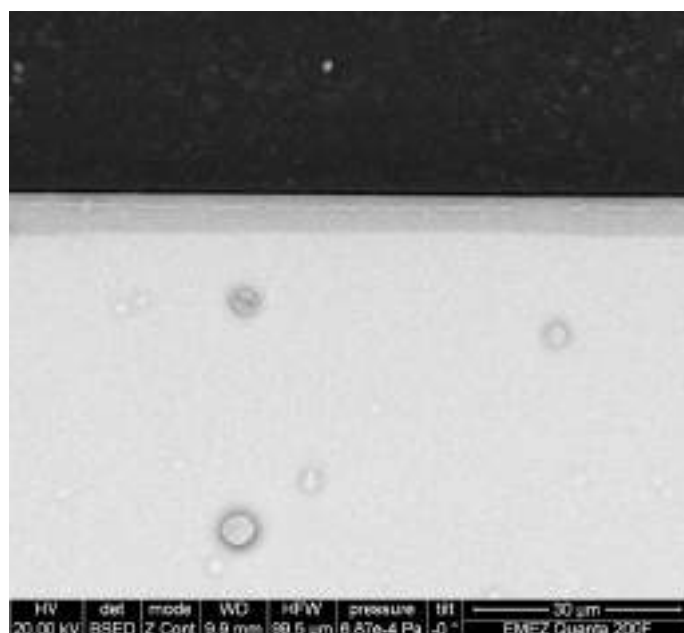
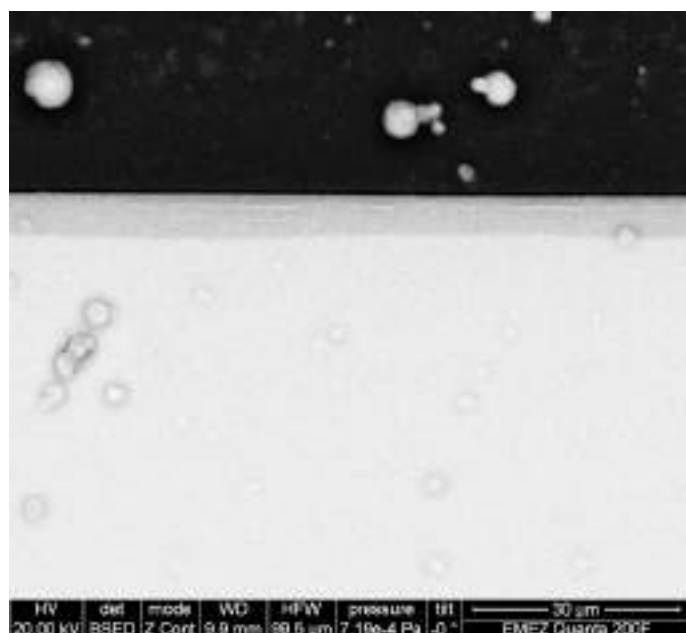


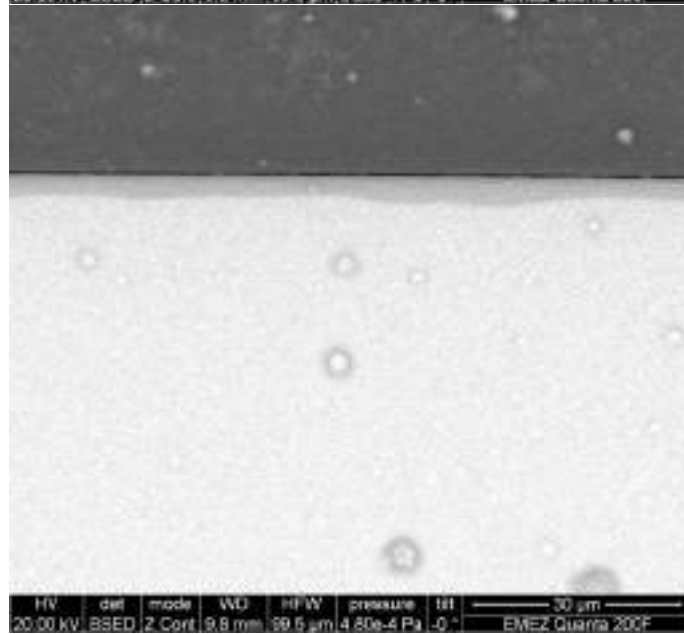
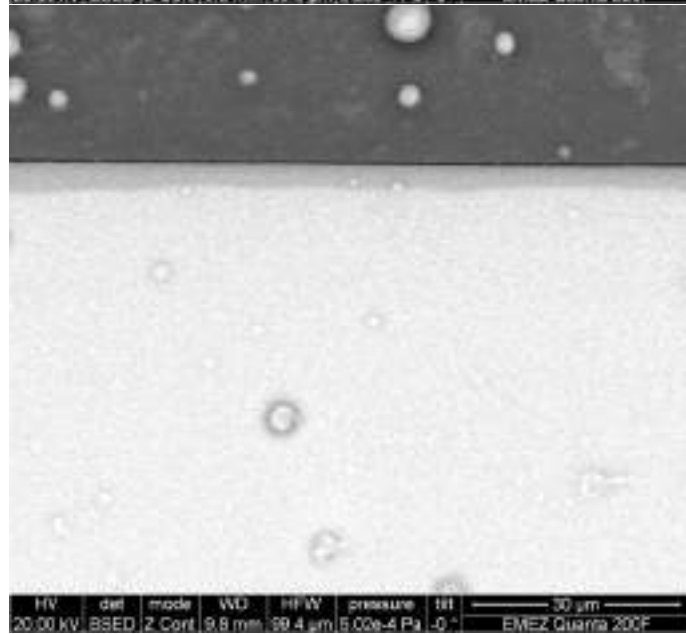
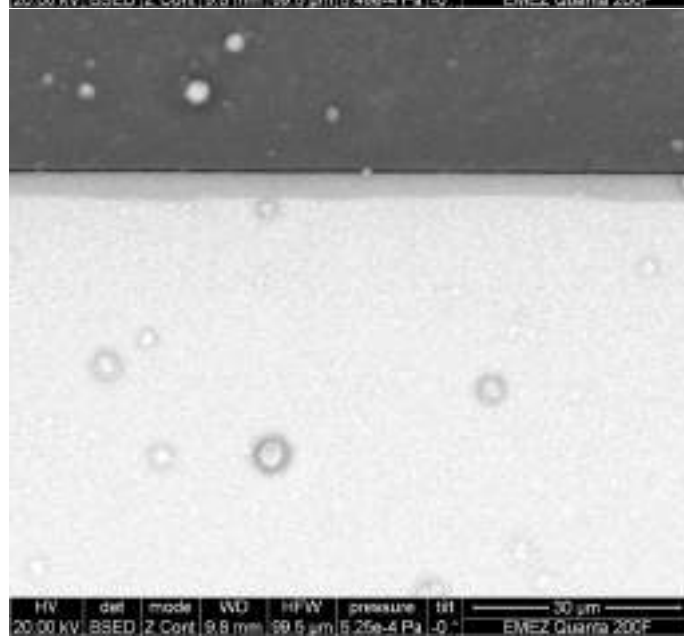
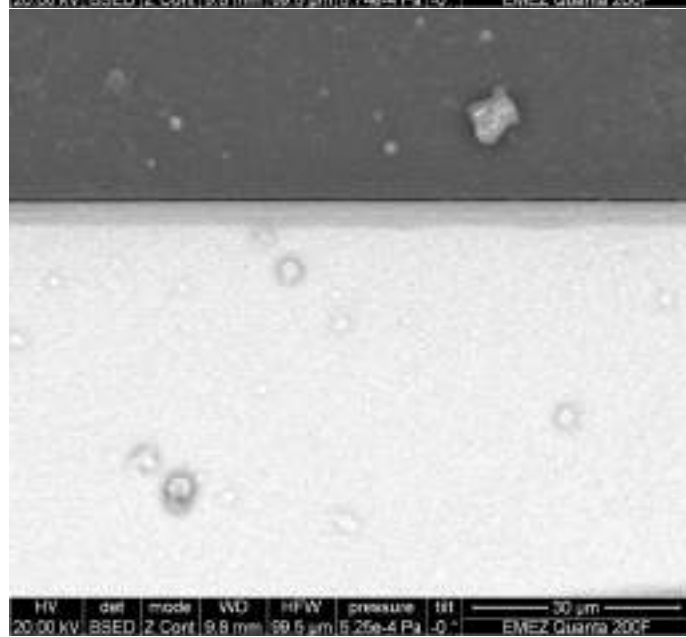
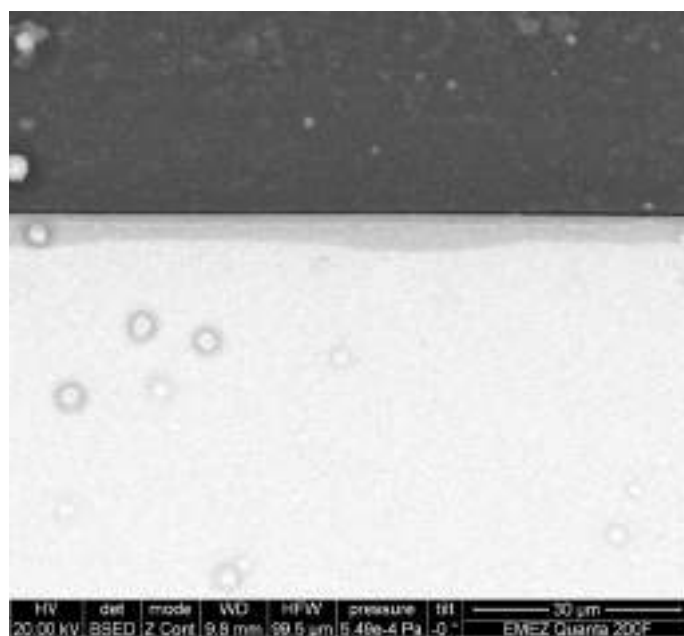
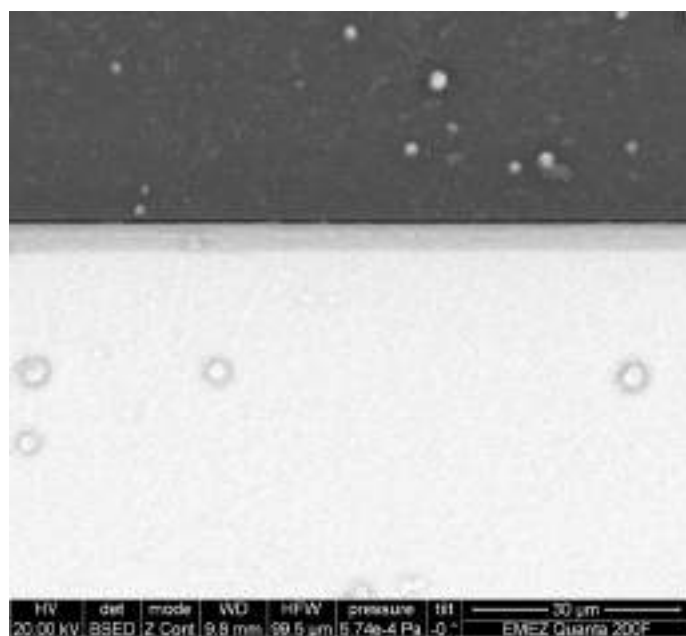


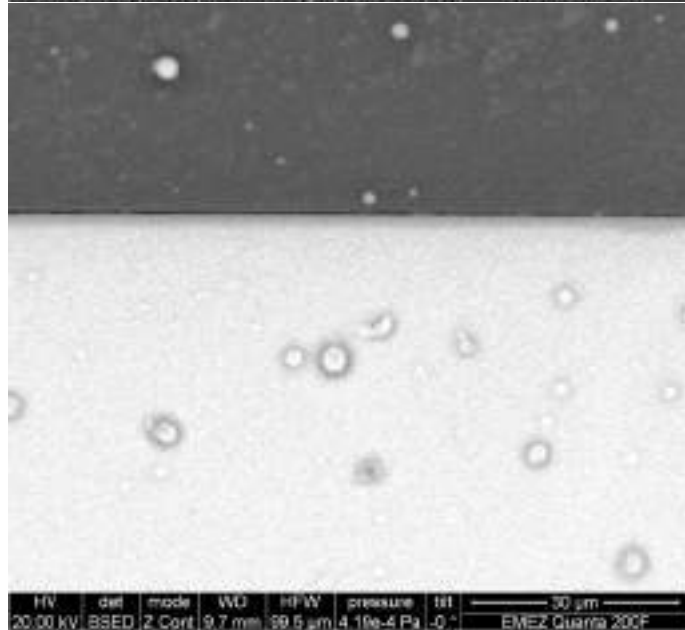
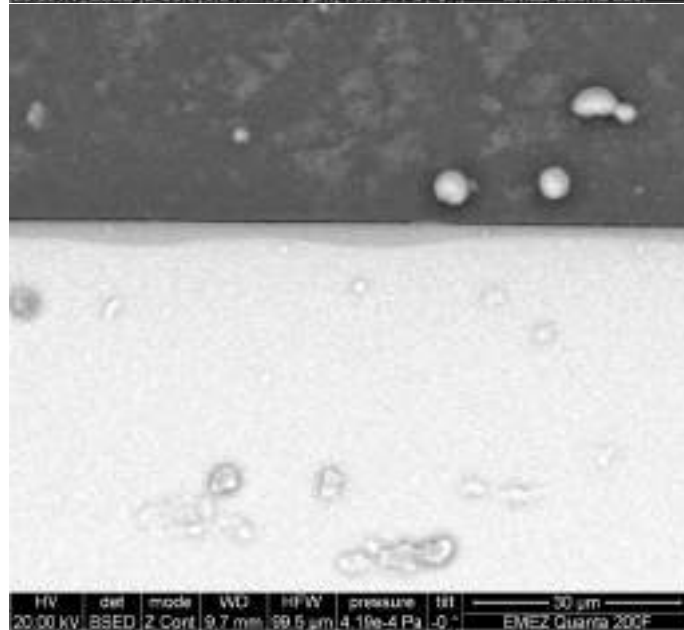
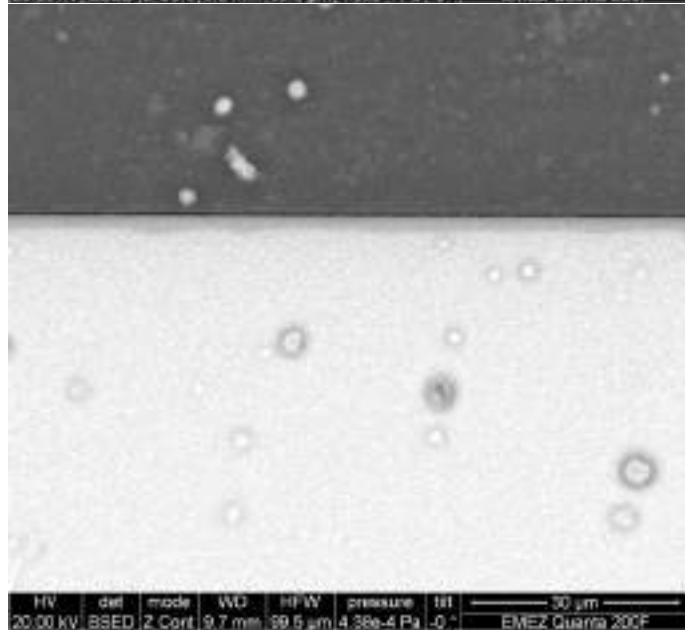
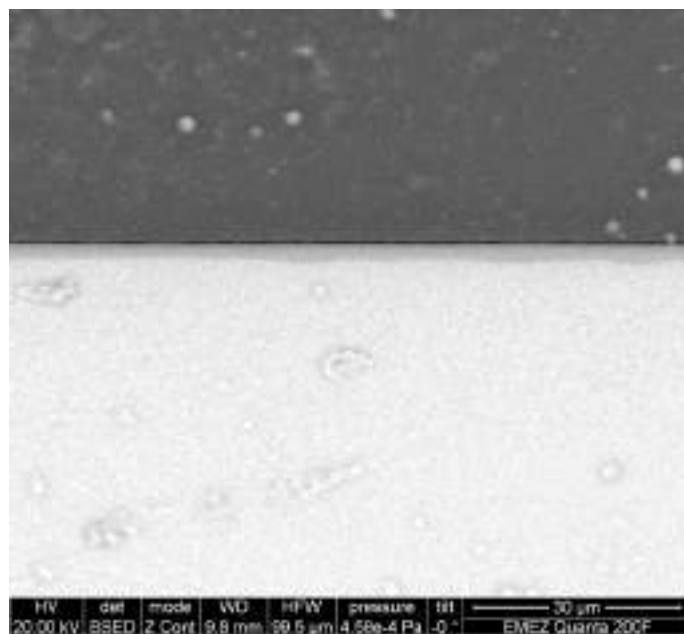
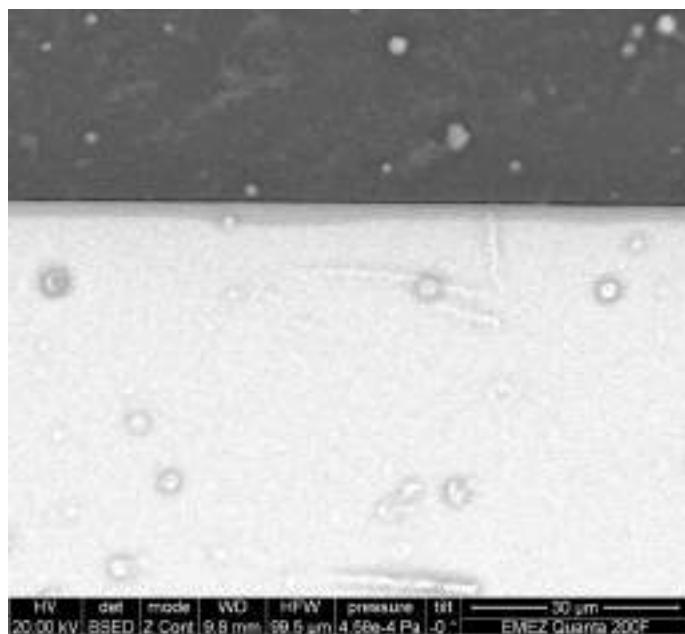
P 0 months (3 months aging in saturated salt solutions)



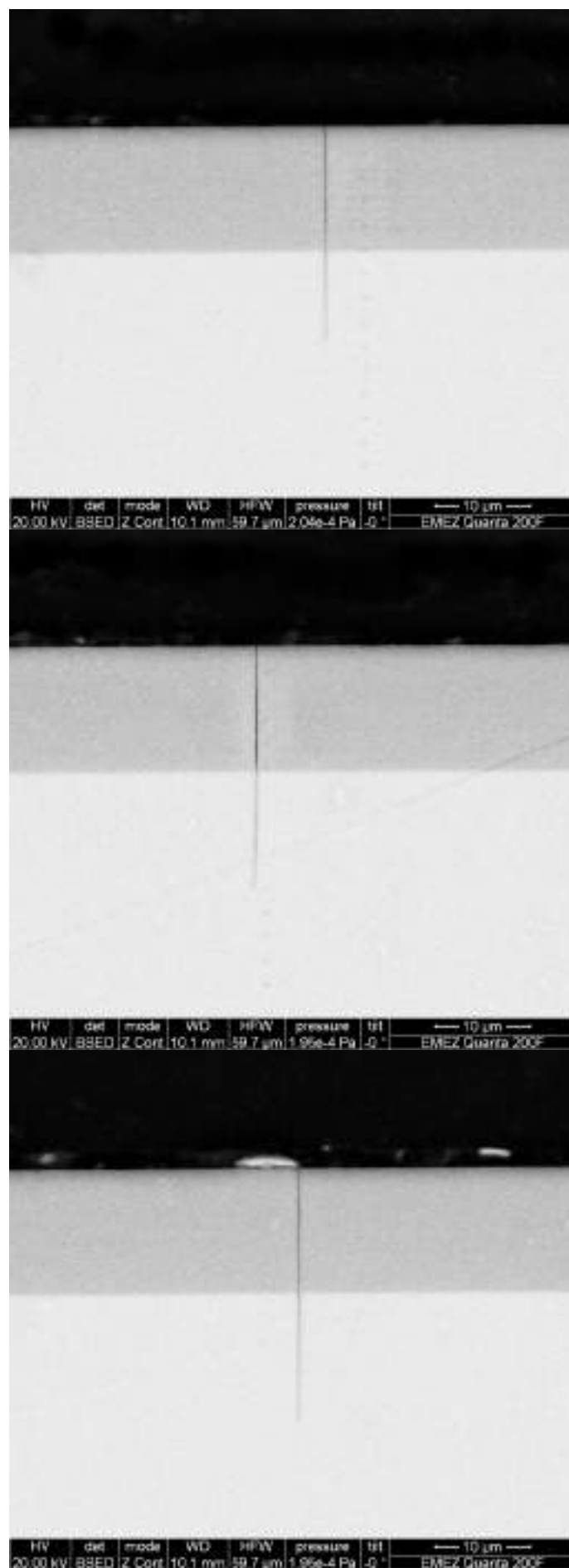
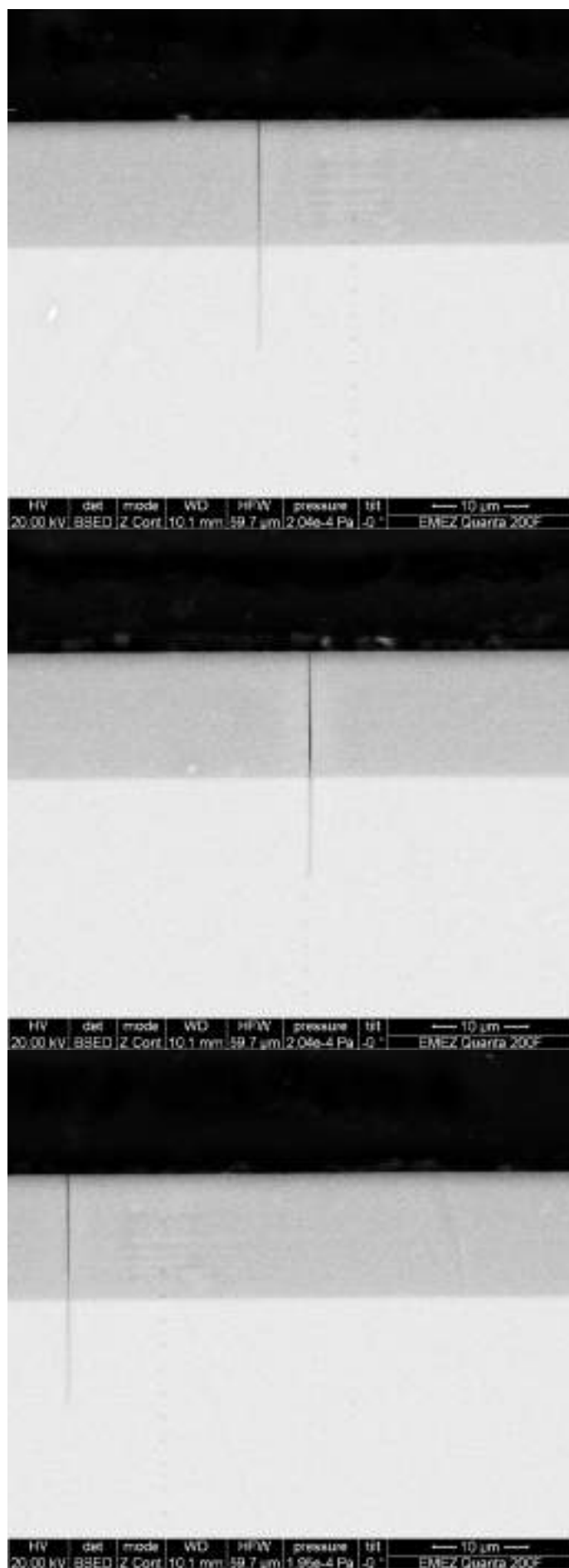


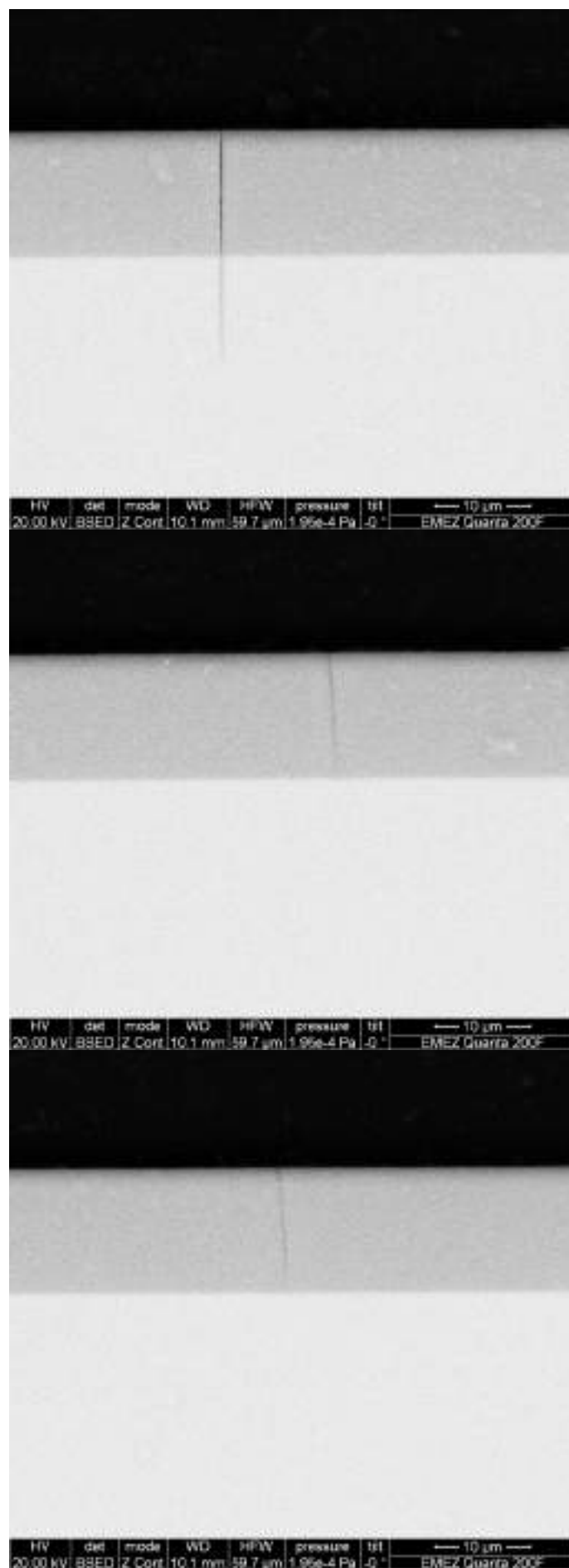
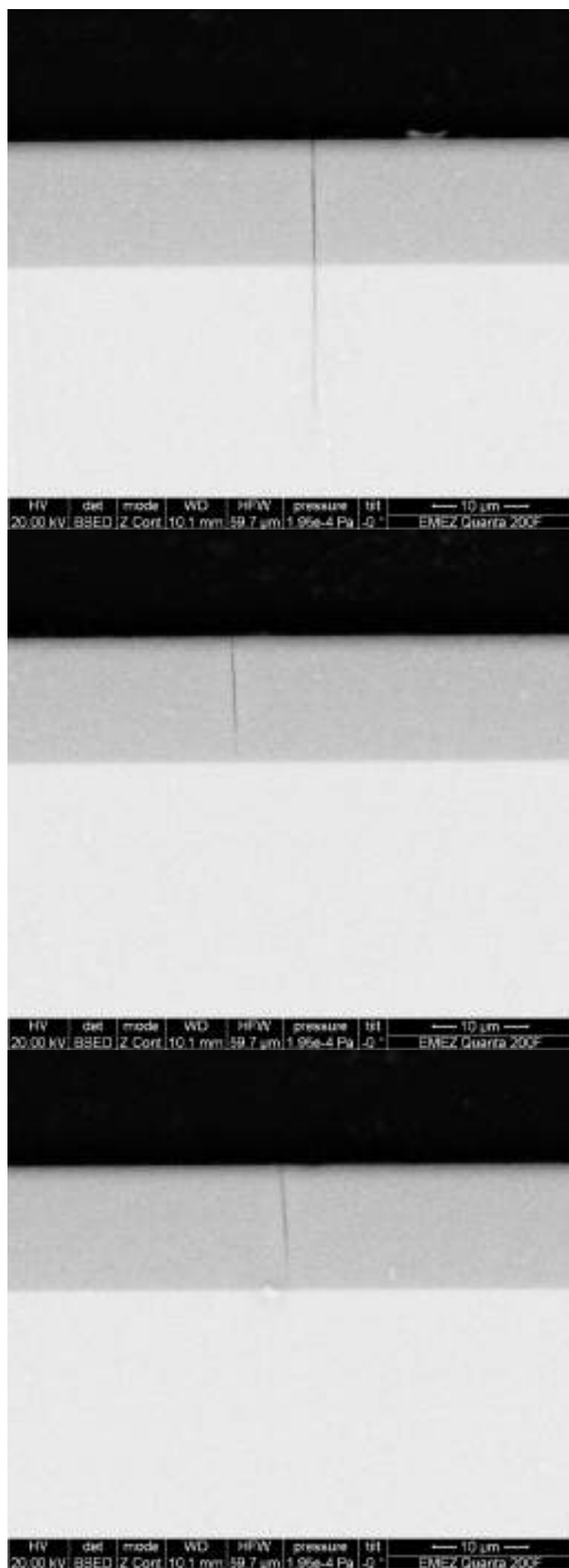


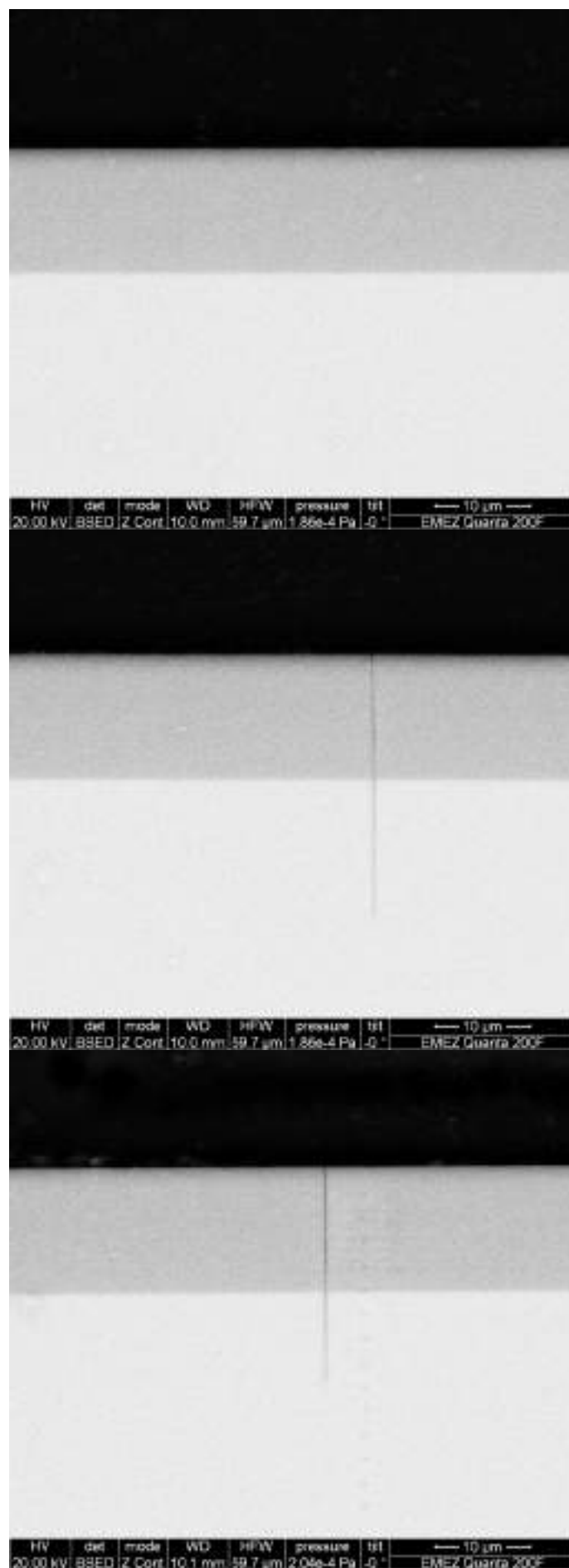
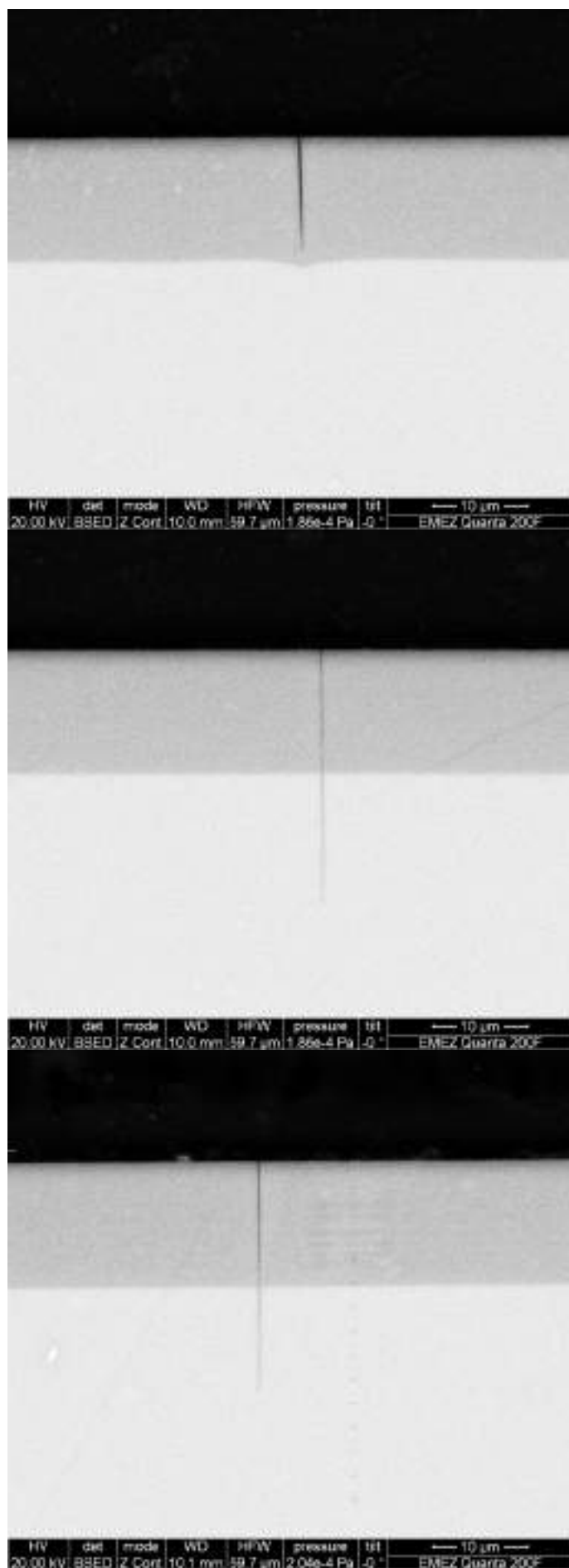


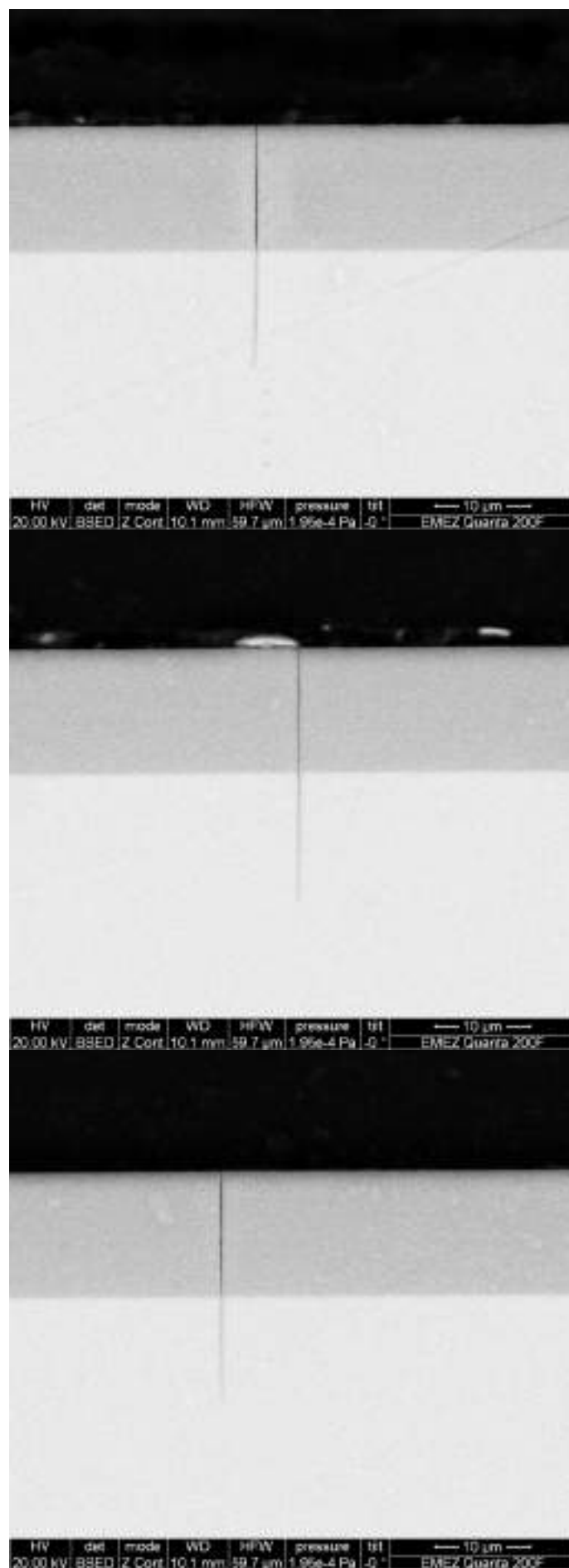
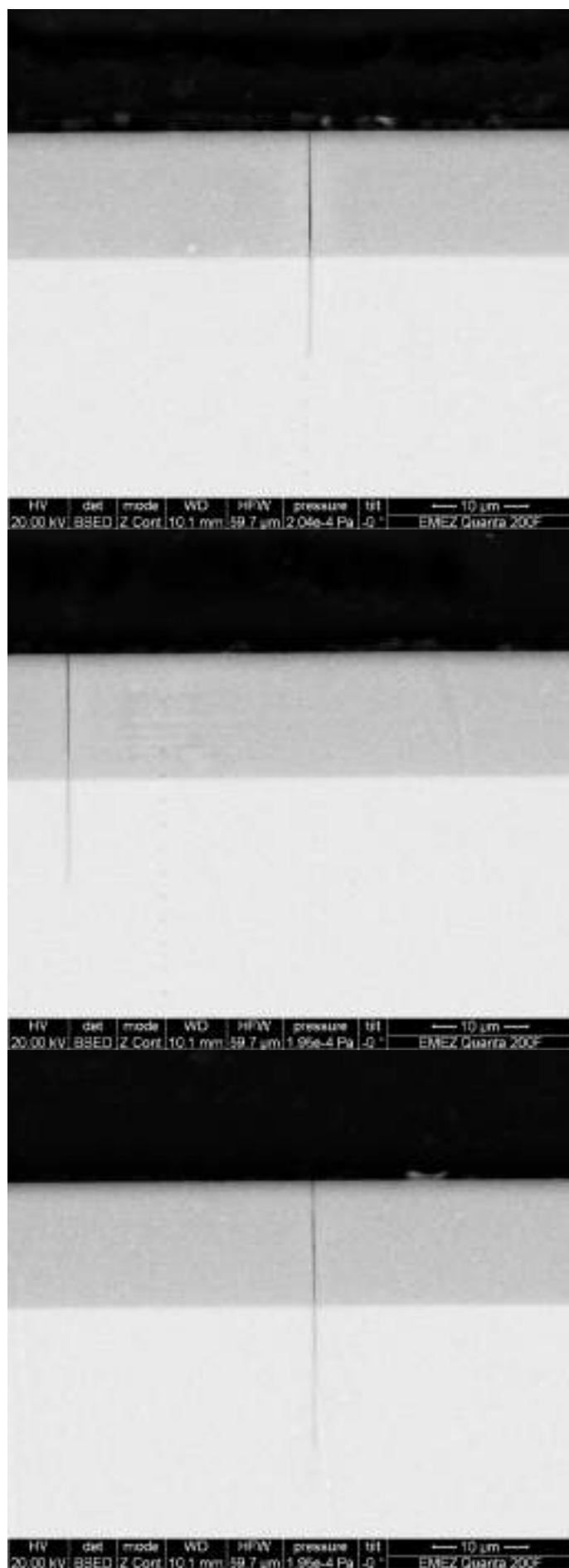


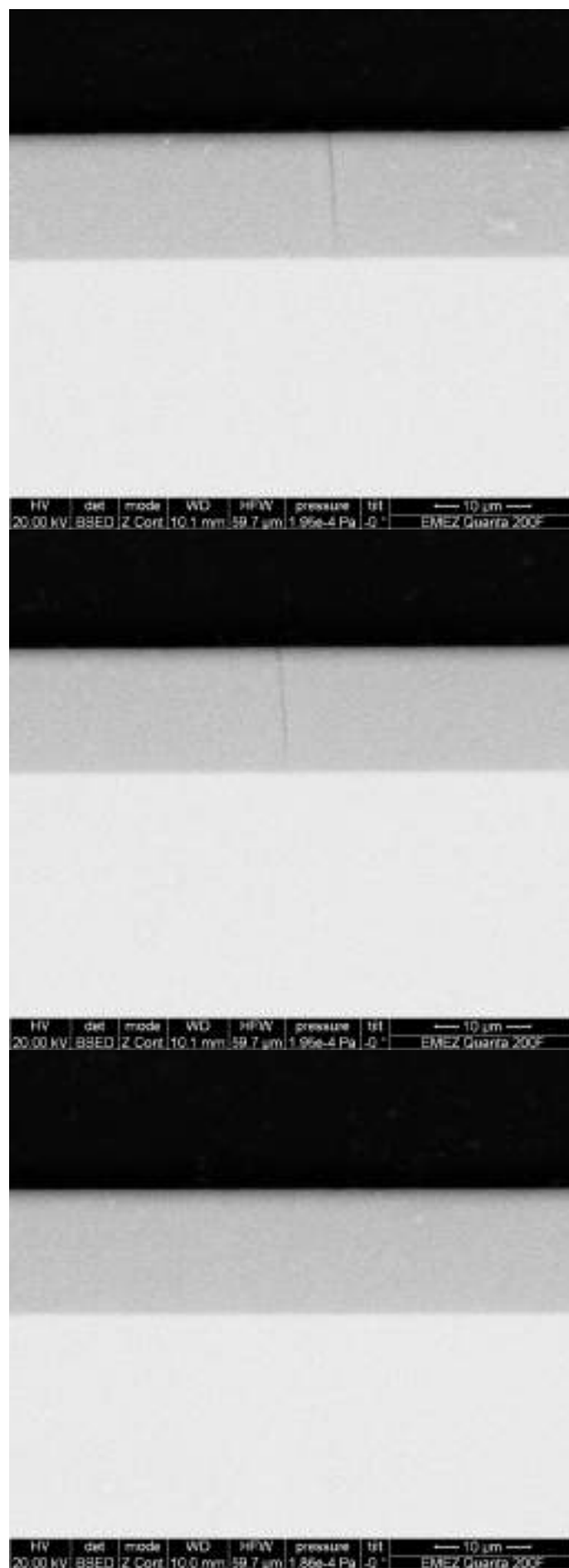
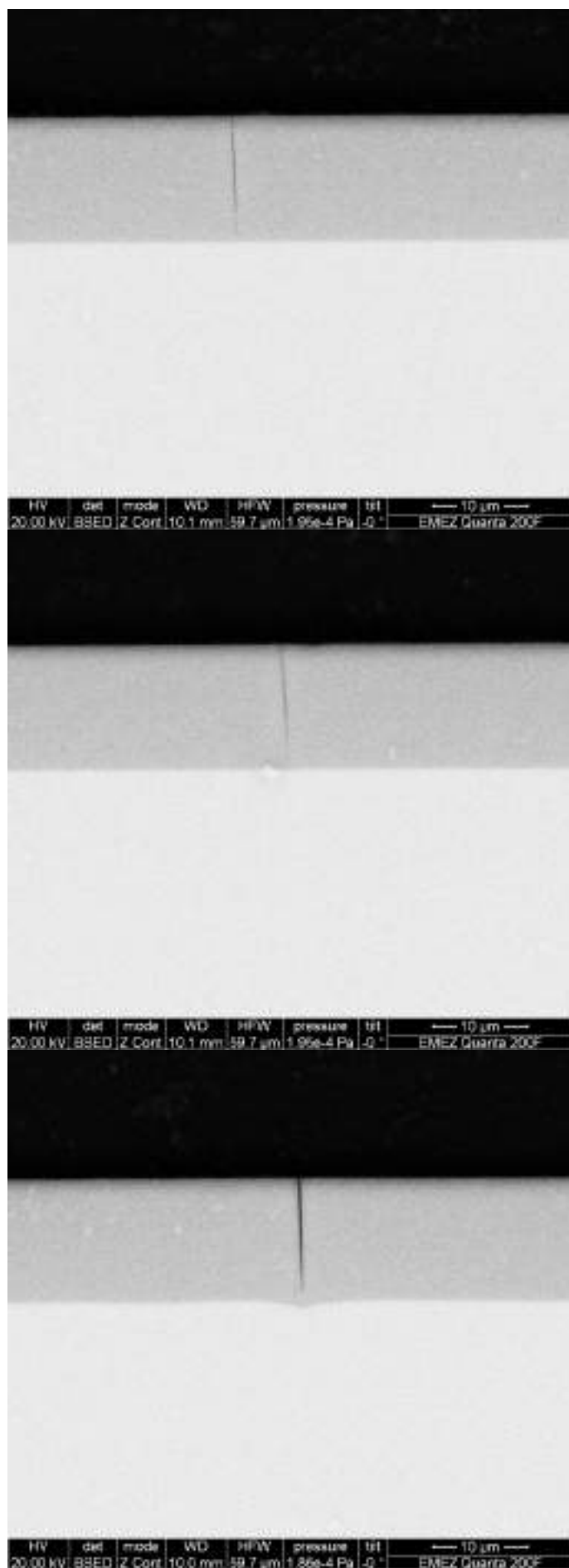
P 3 months

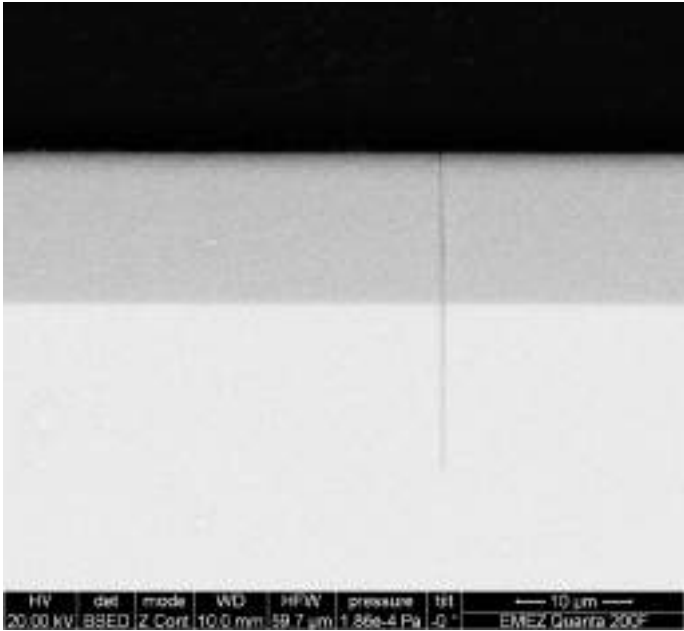
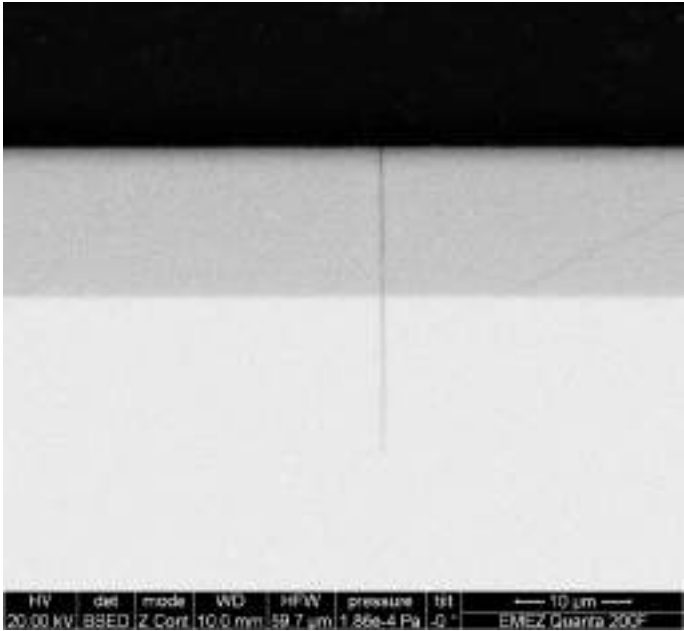




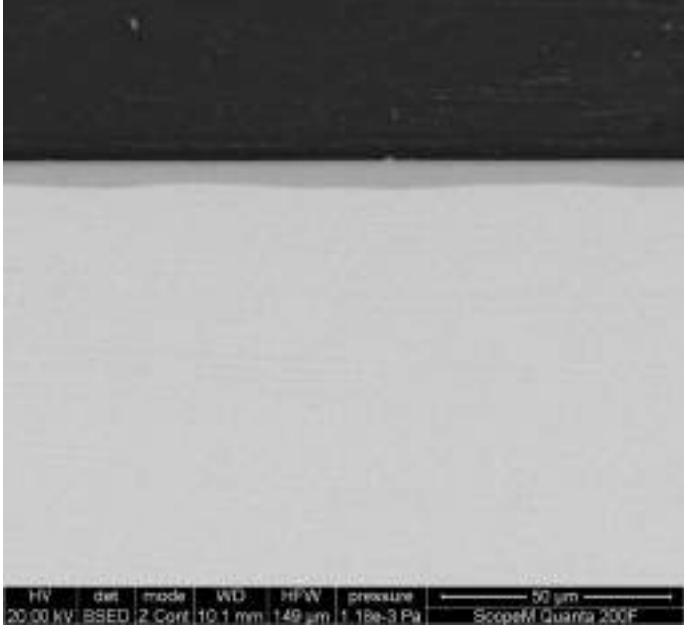
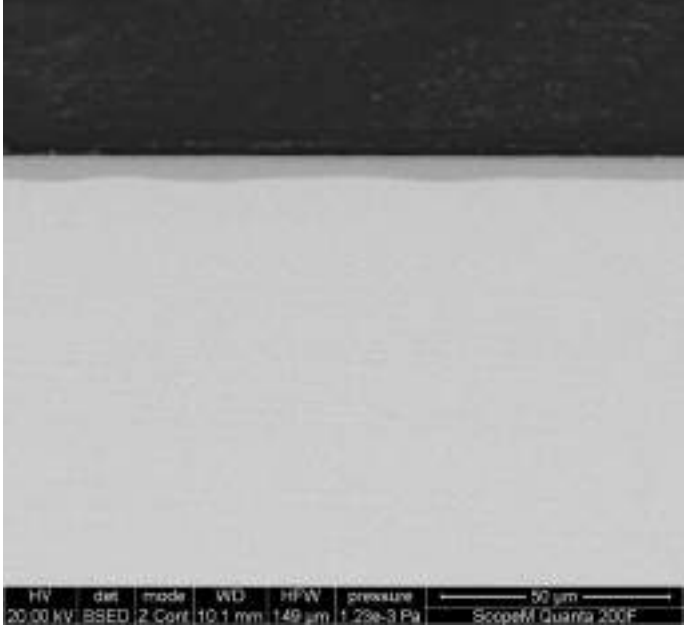
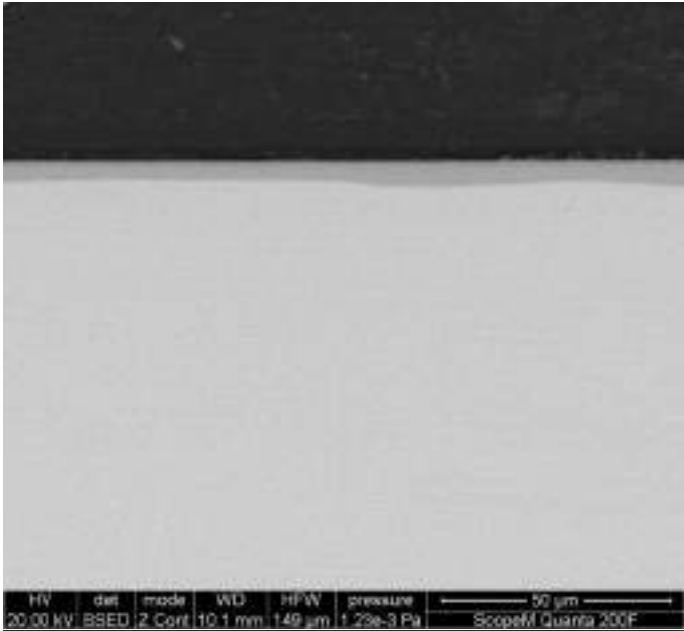
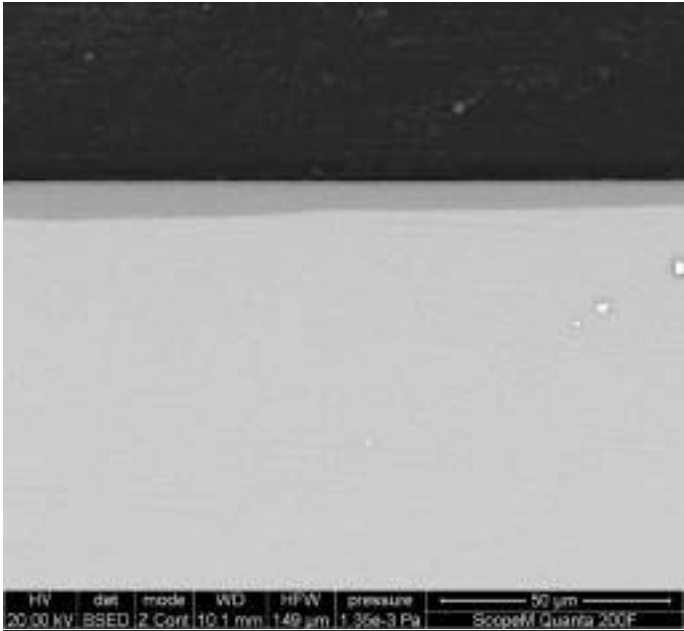


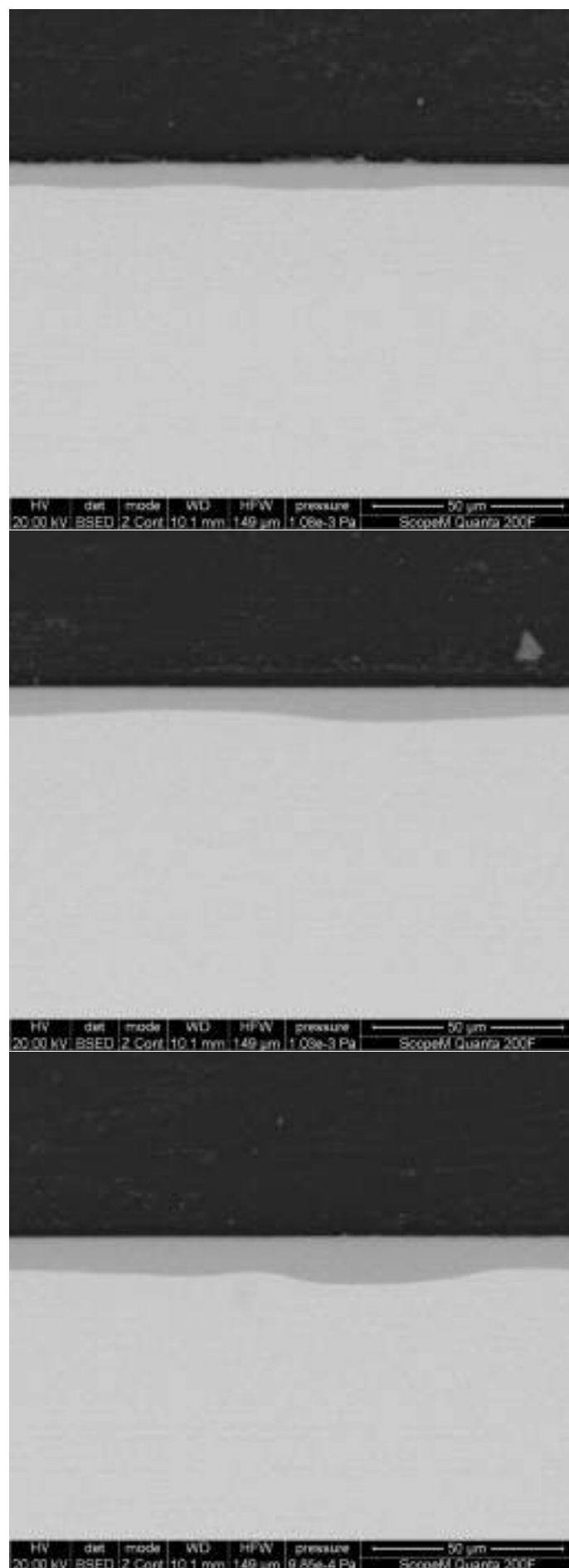
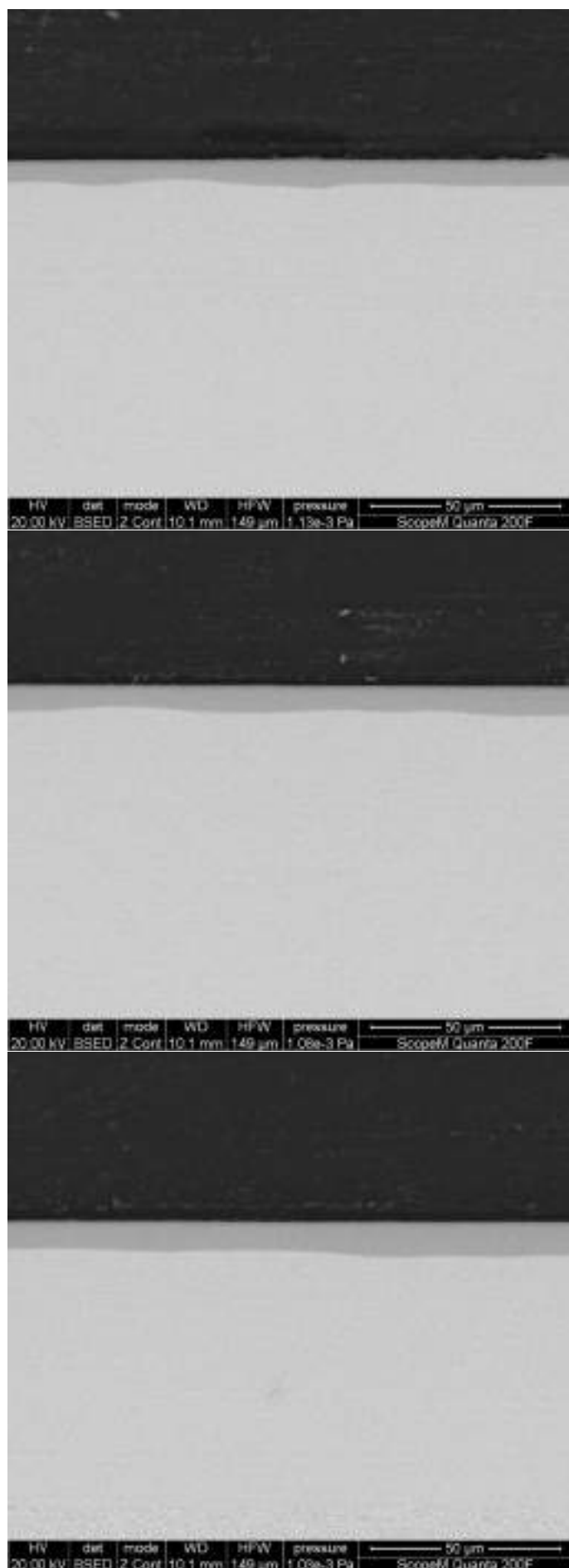


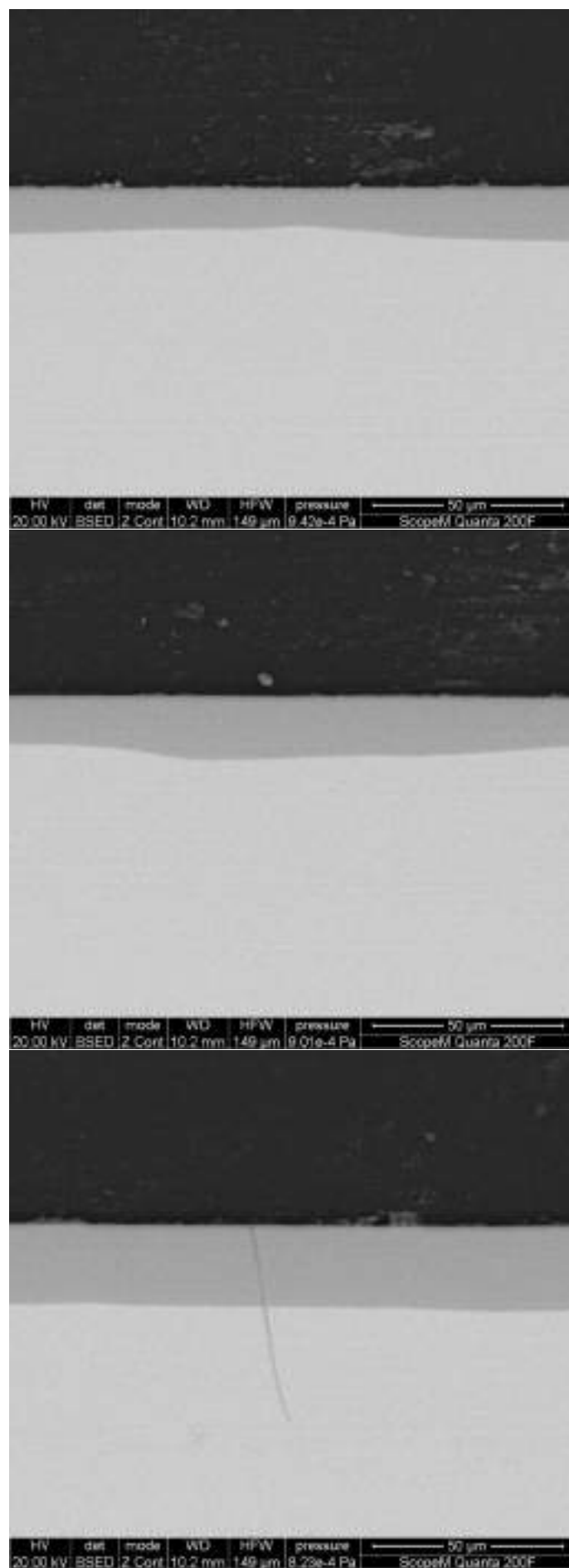
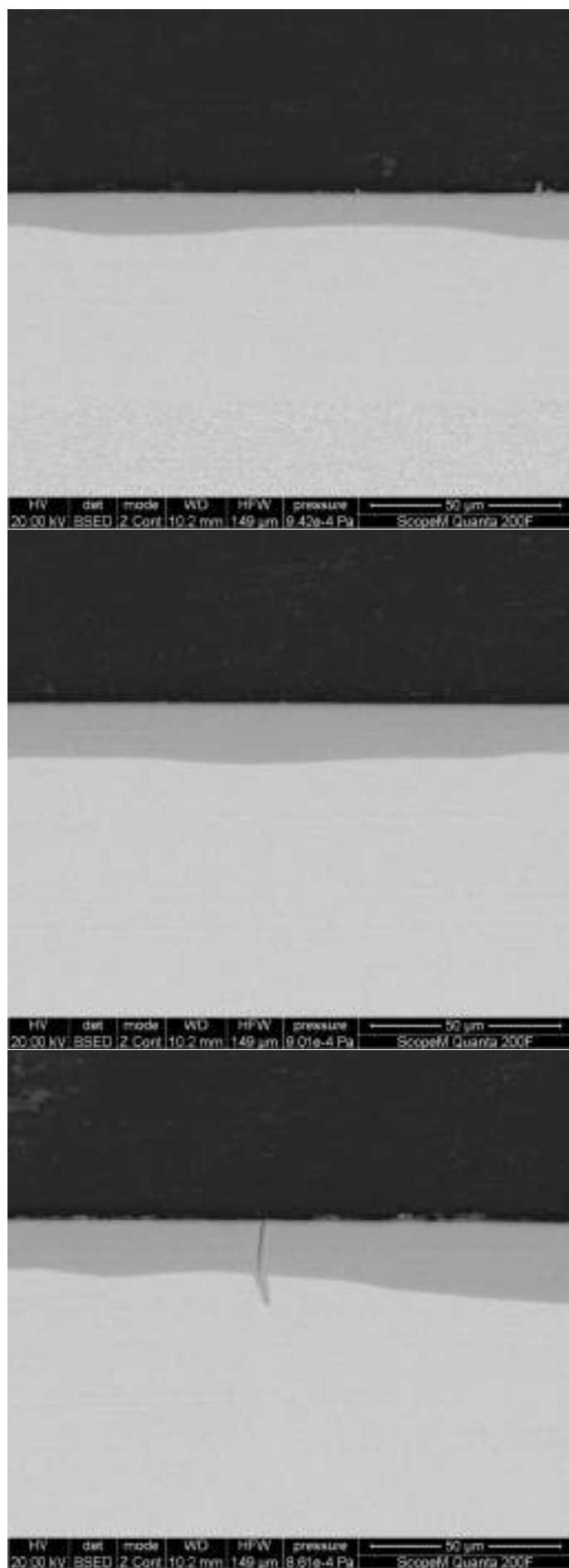


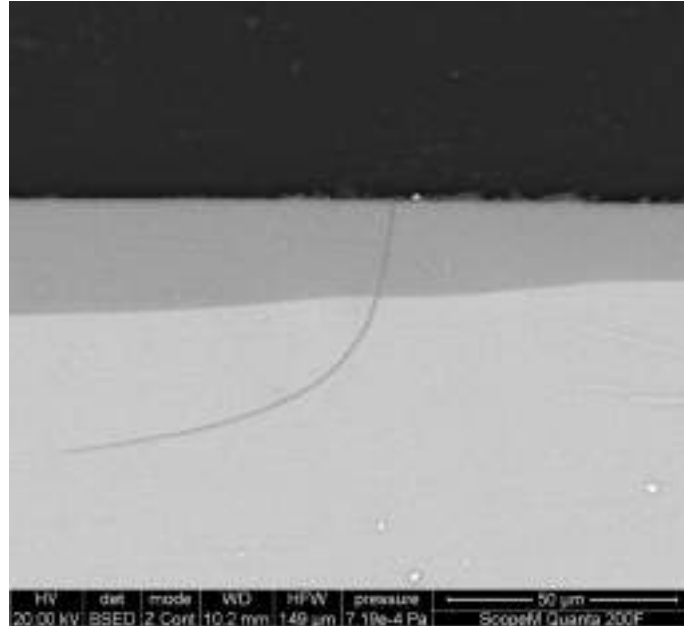
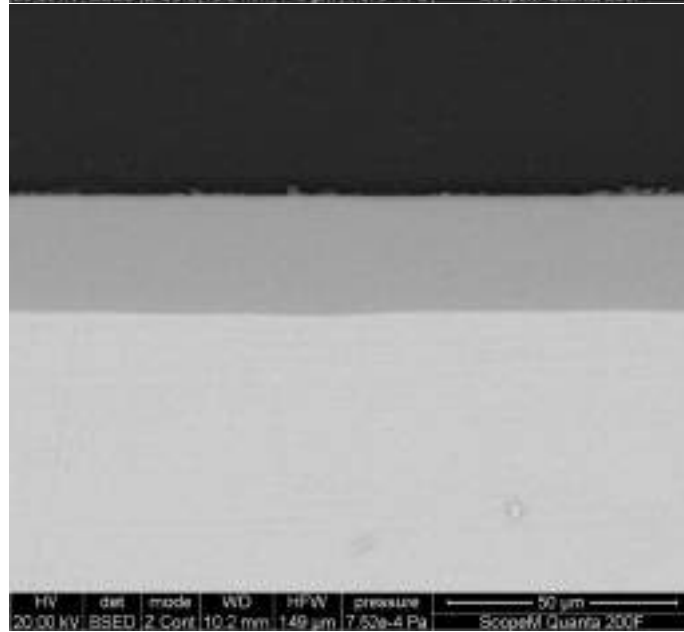
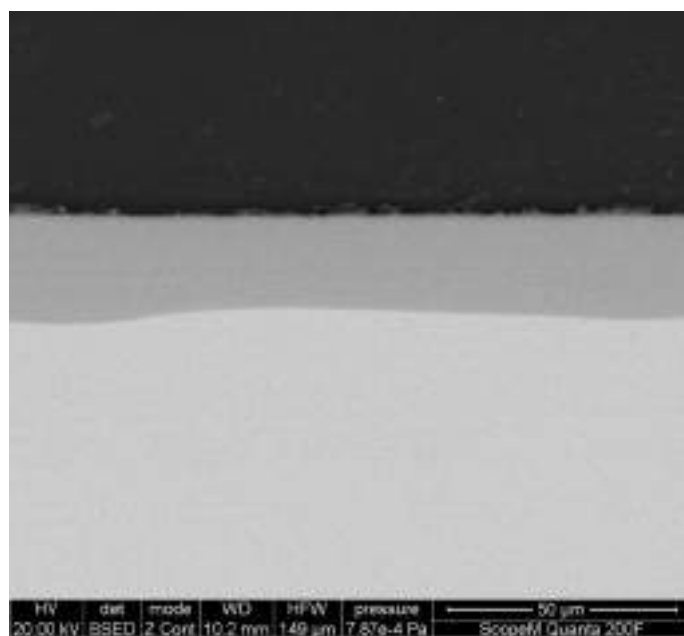
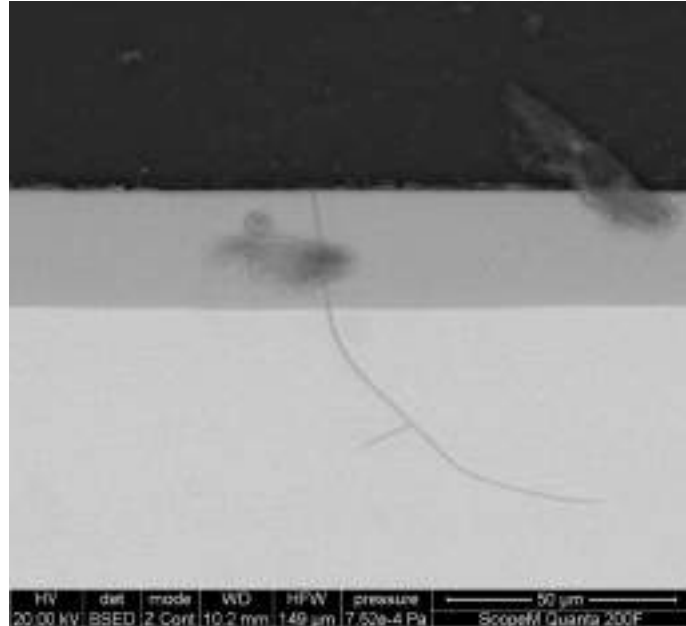
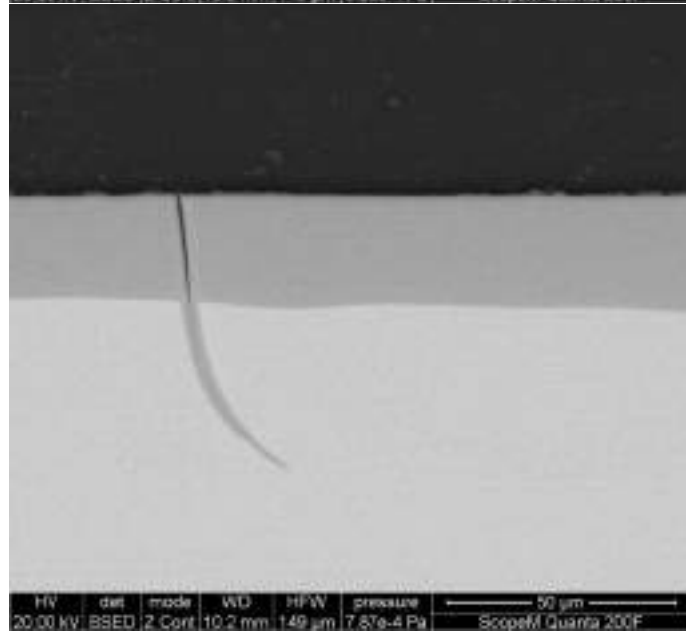
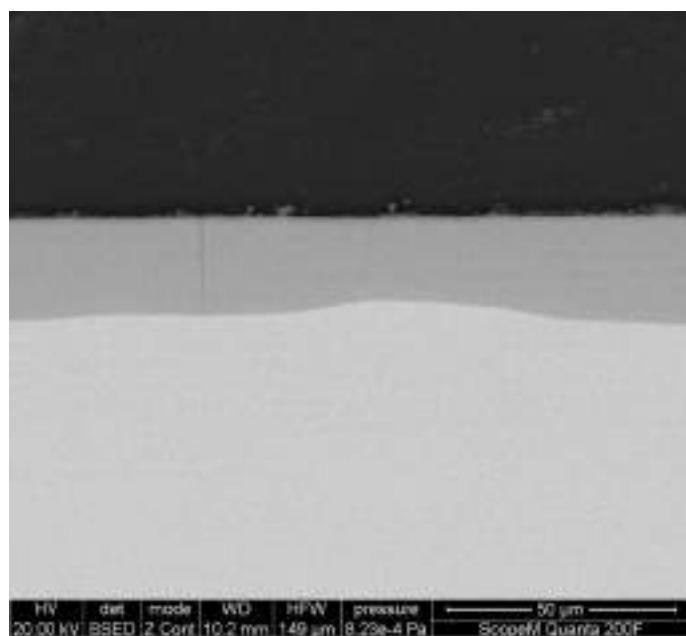


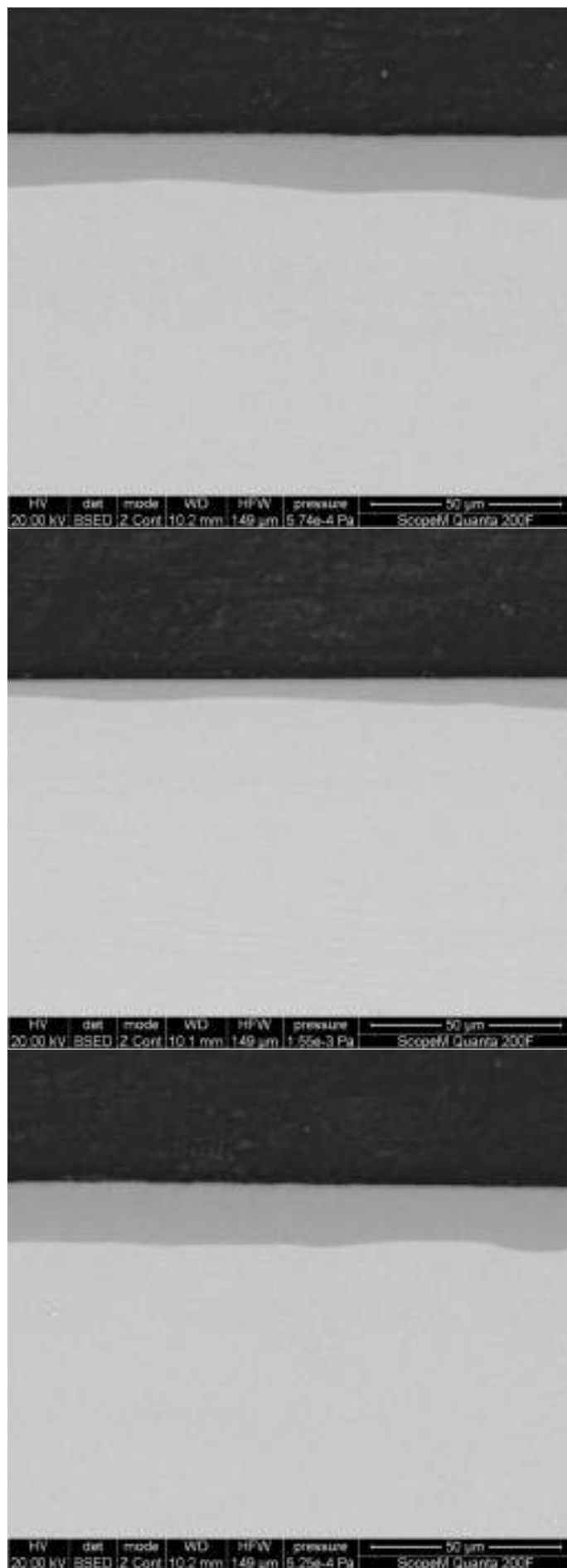
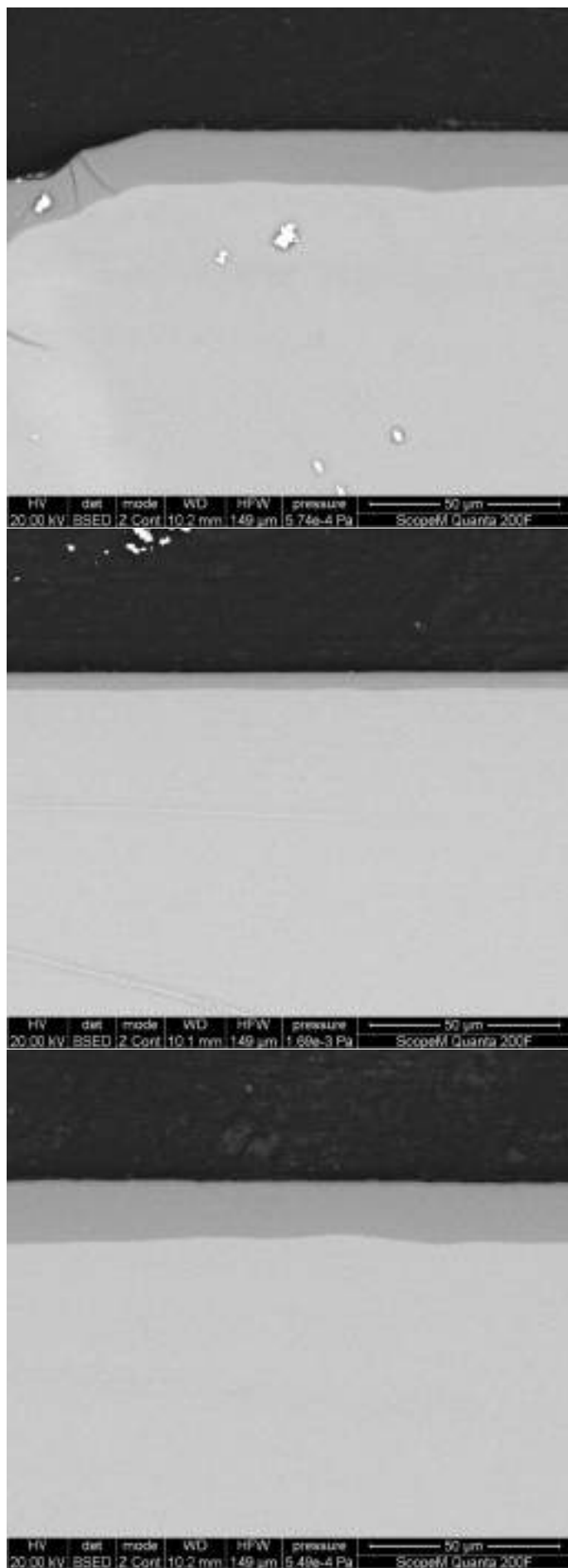
P 6 months

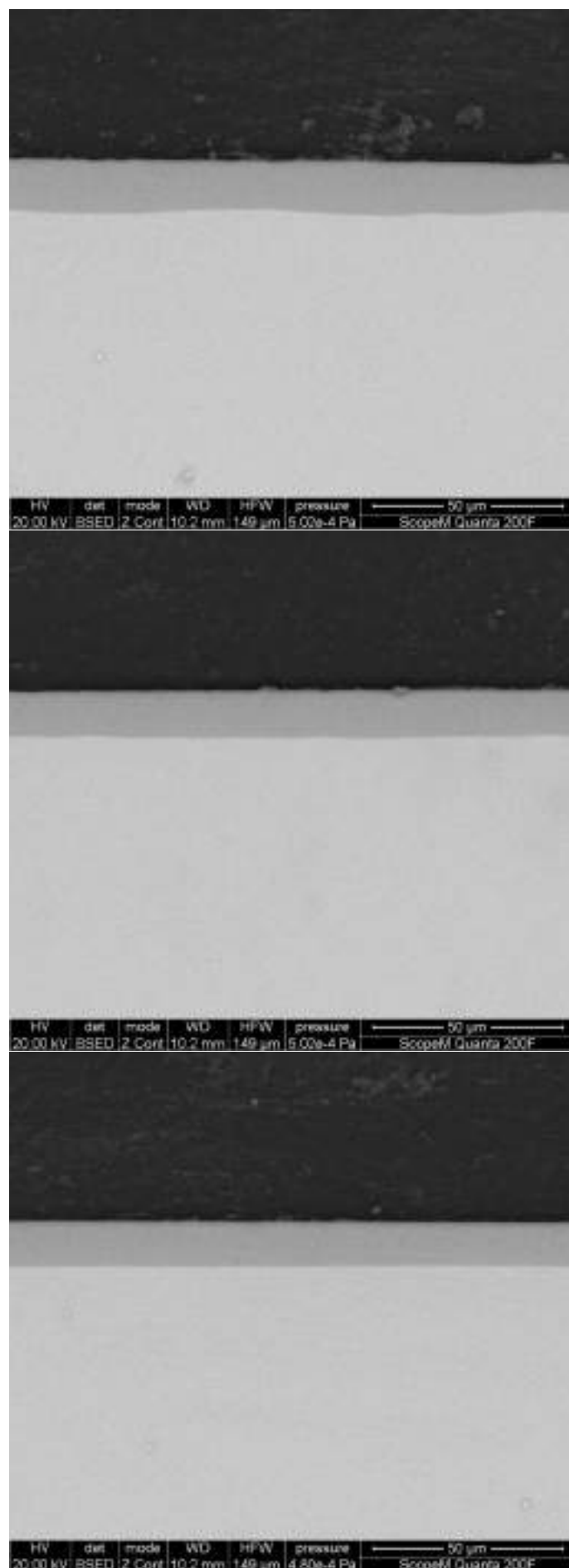
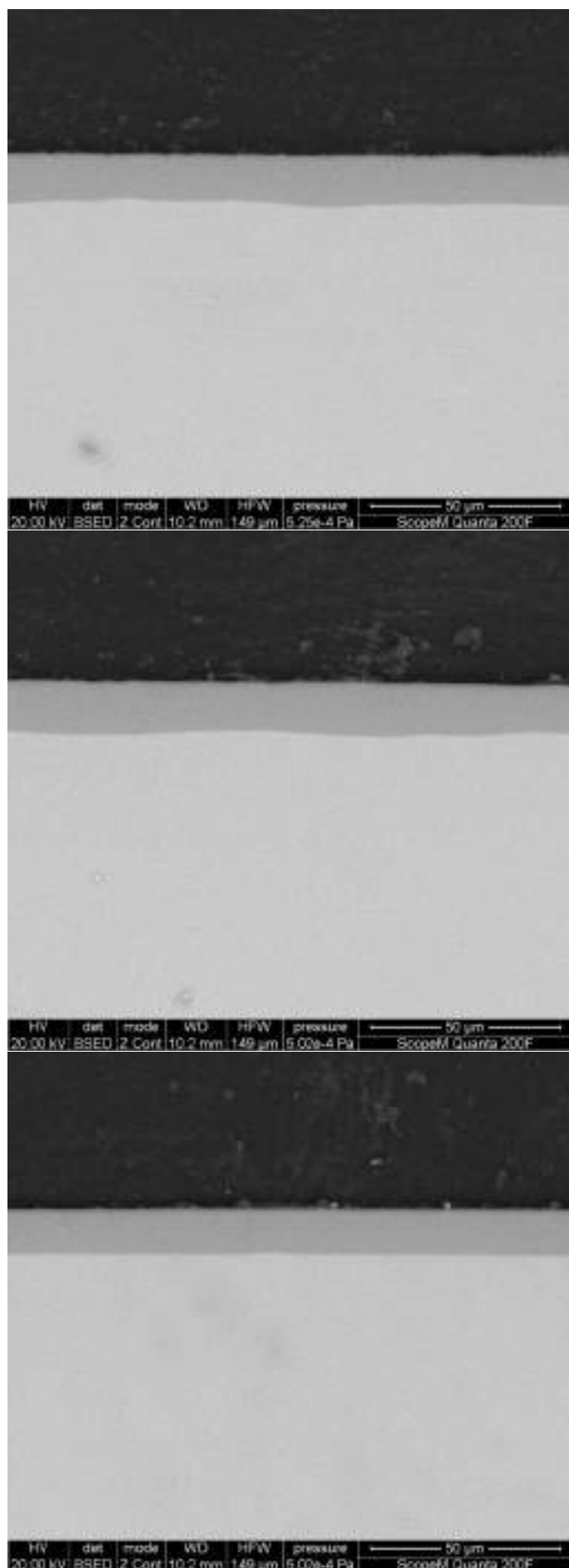


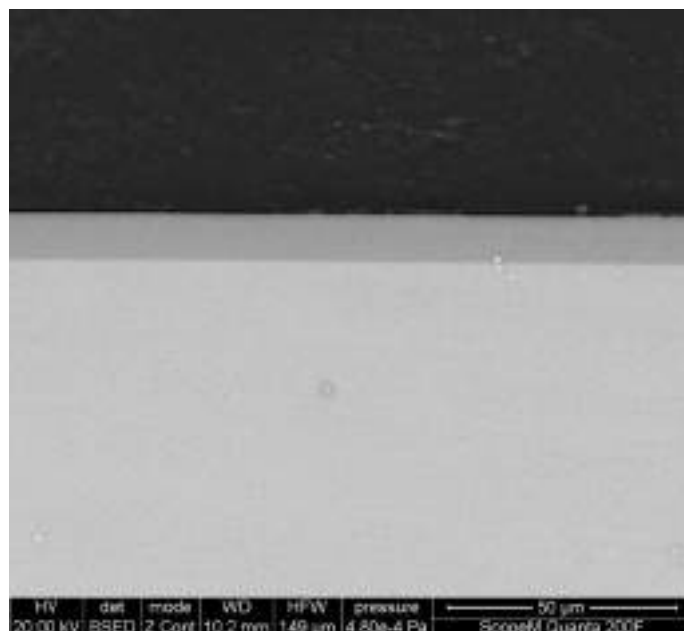
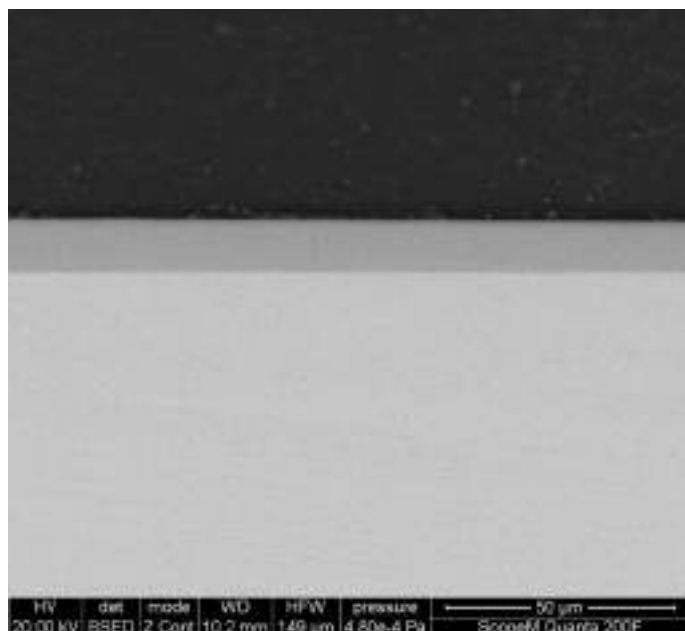




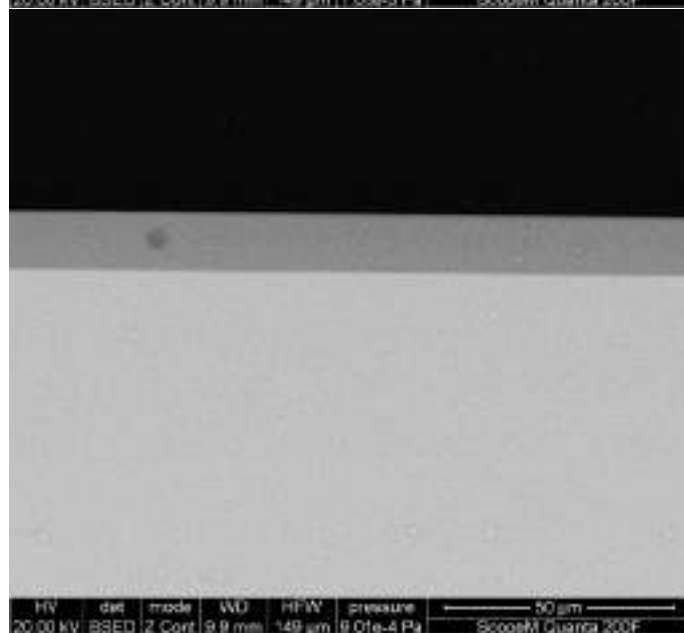
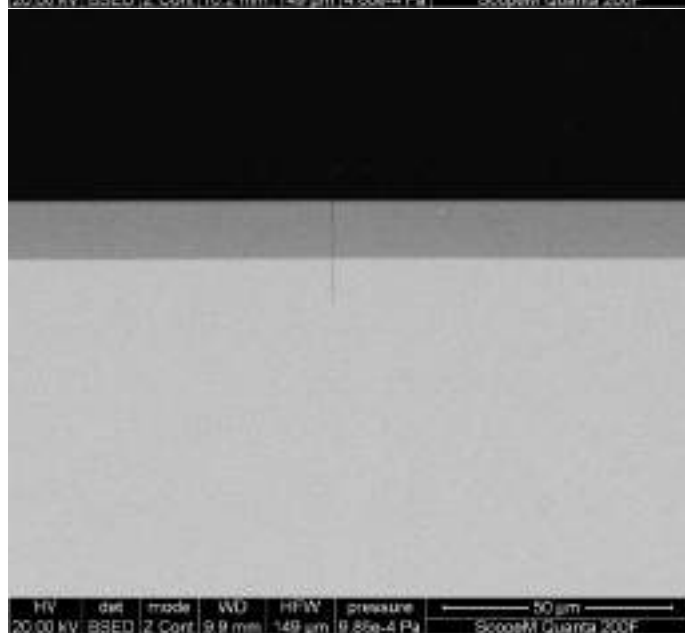
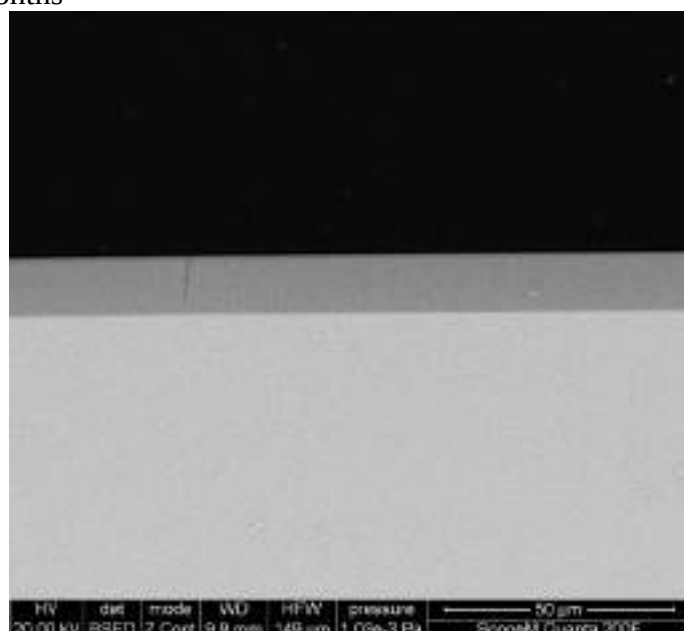
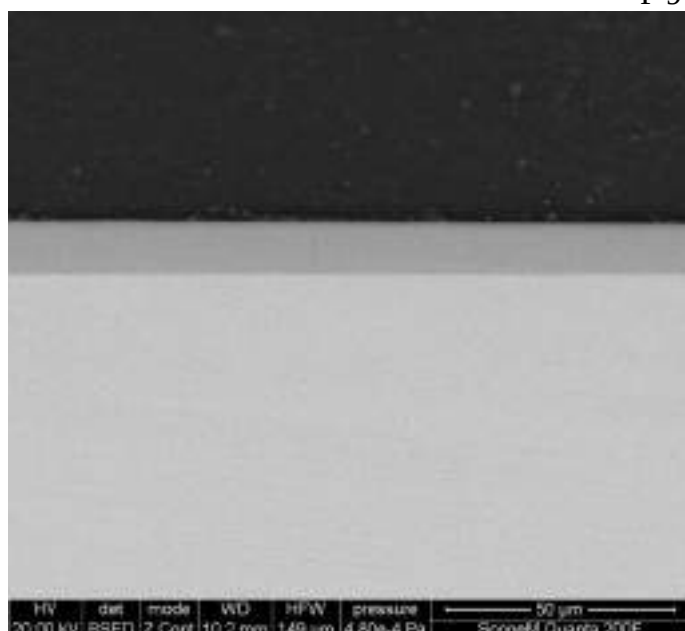


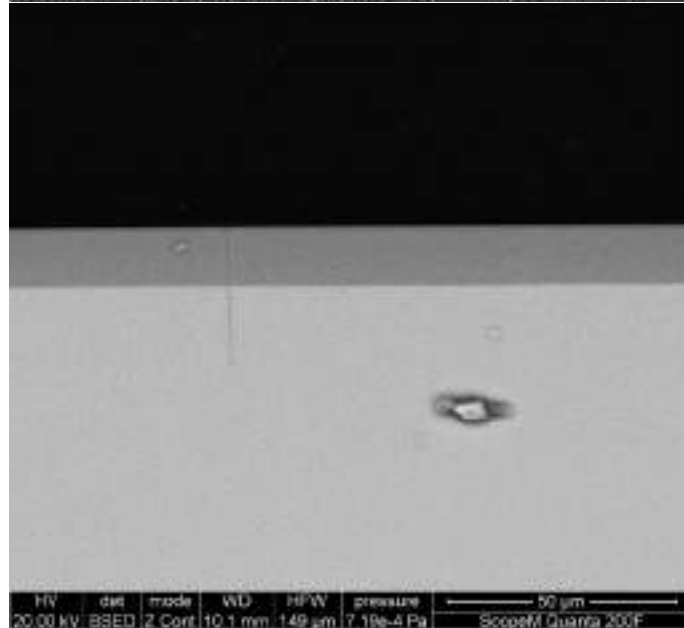
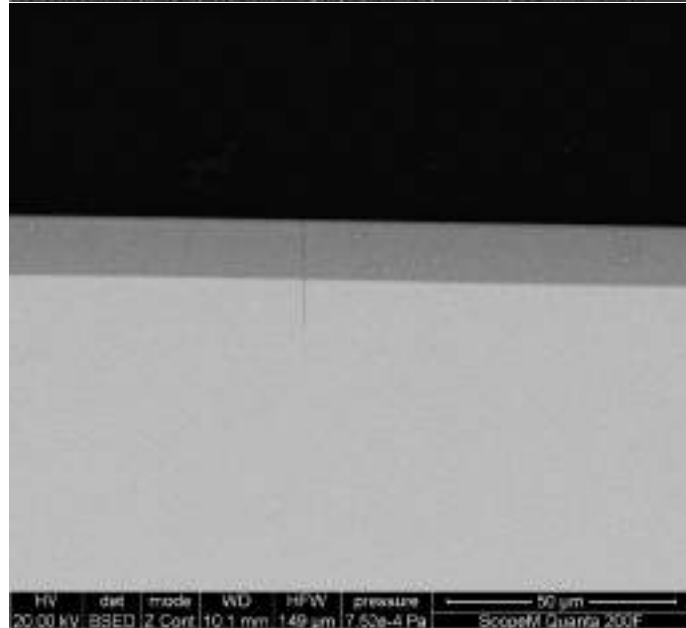
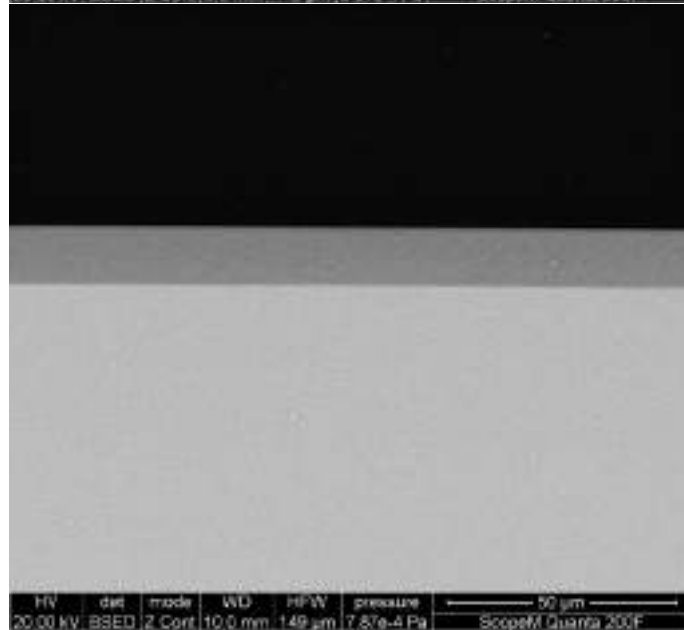
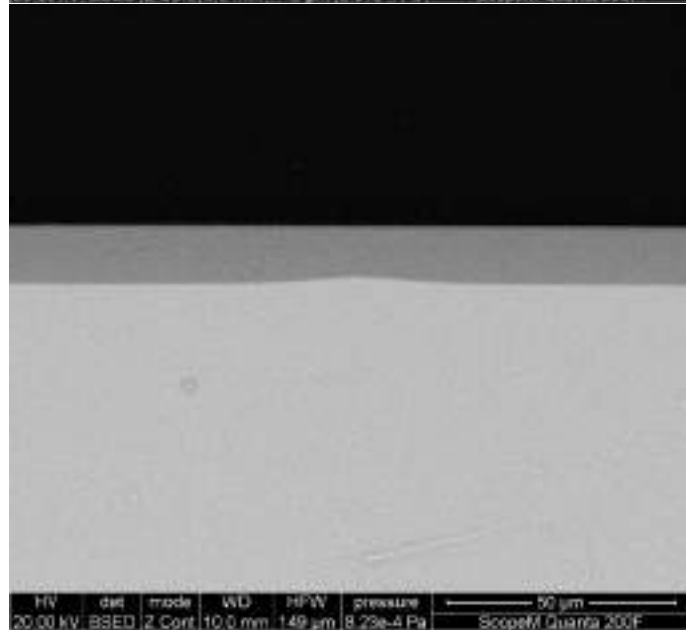
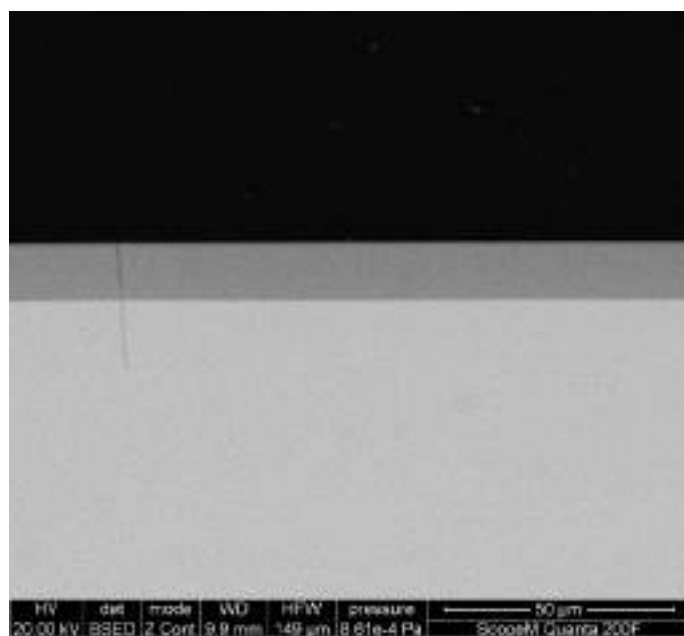
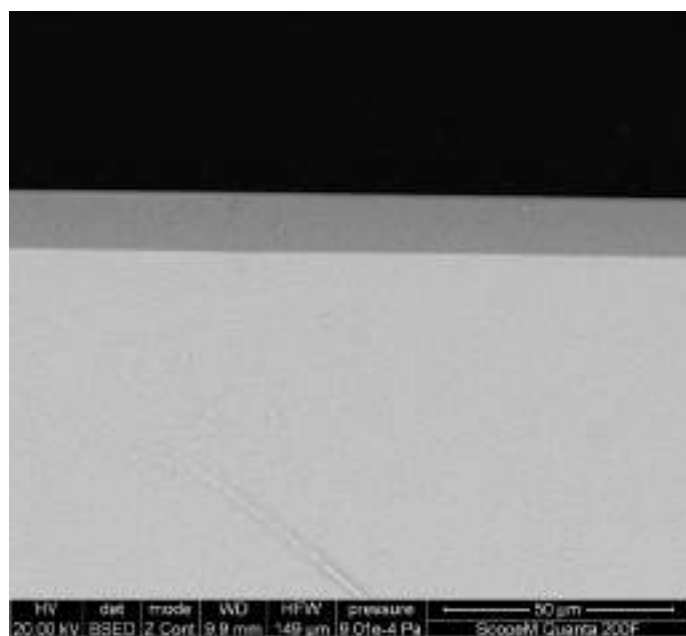


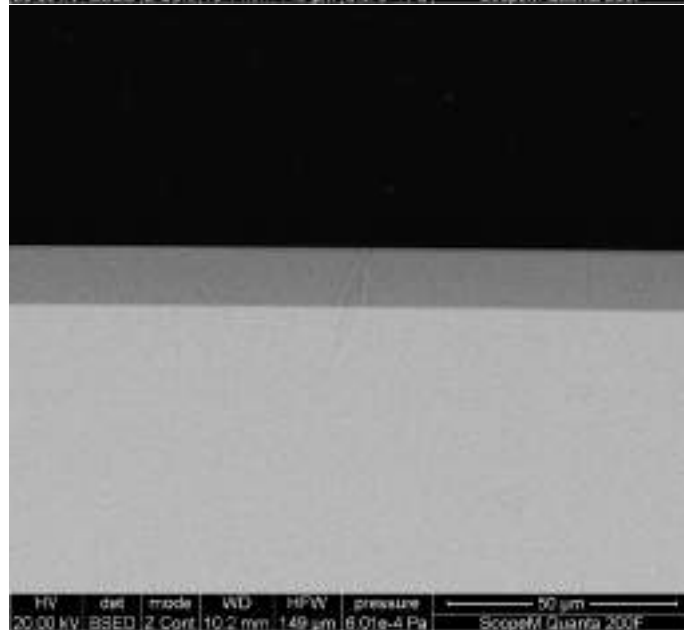
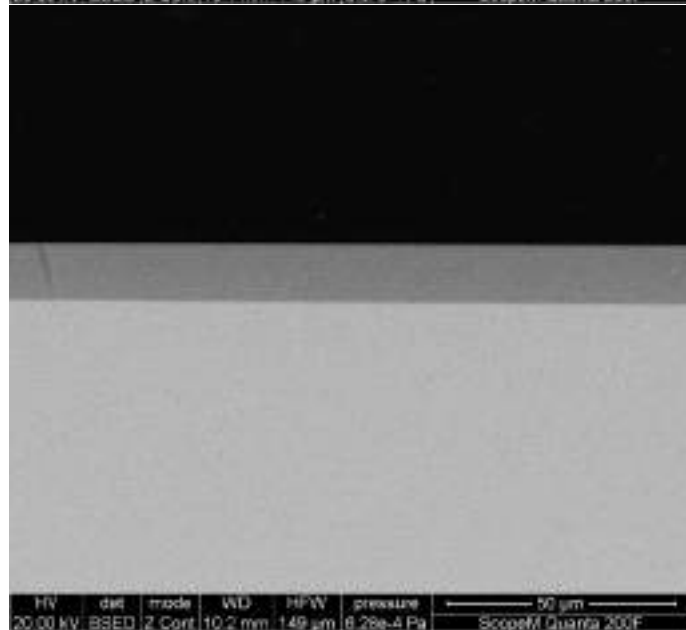
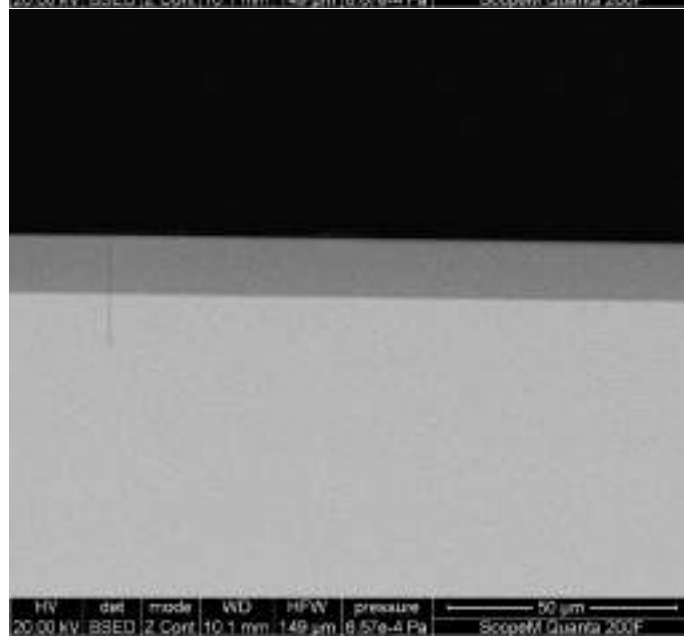
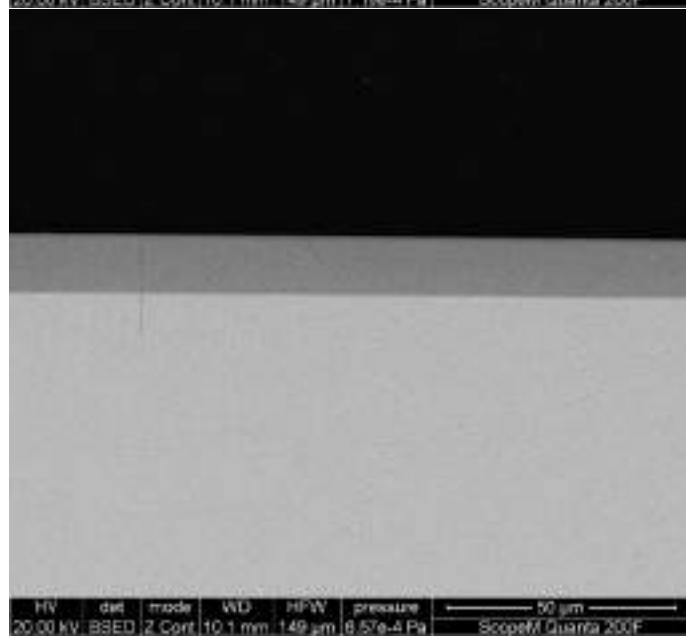
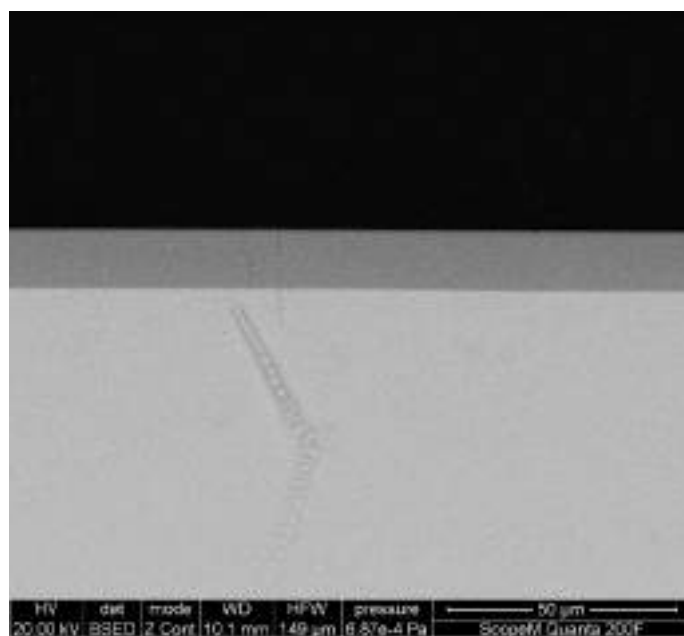
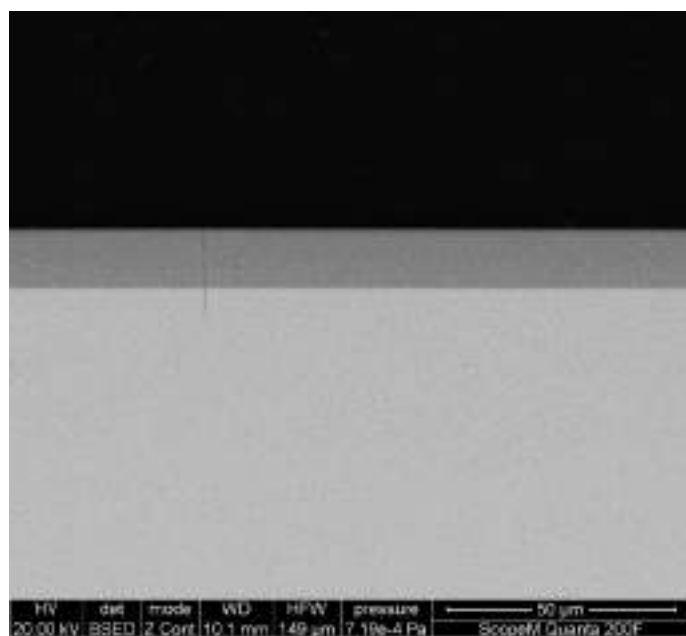


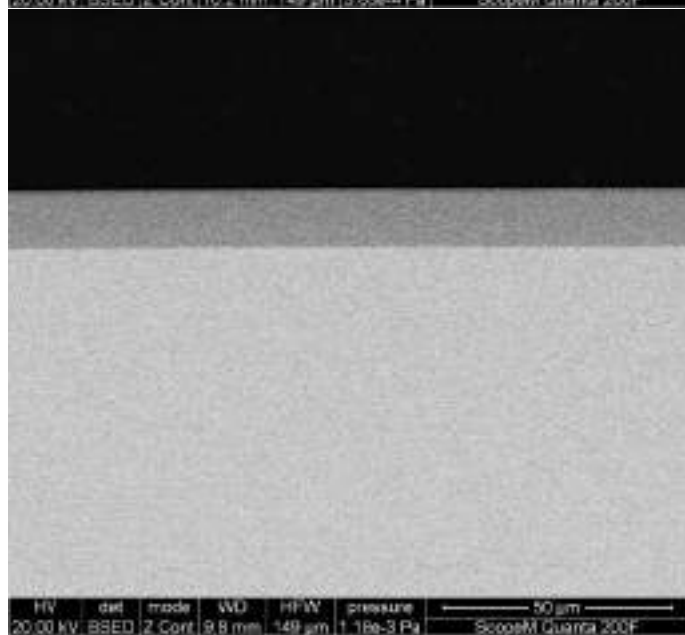
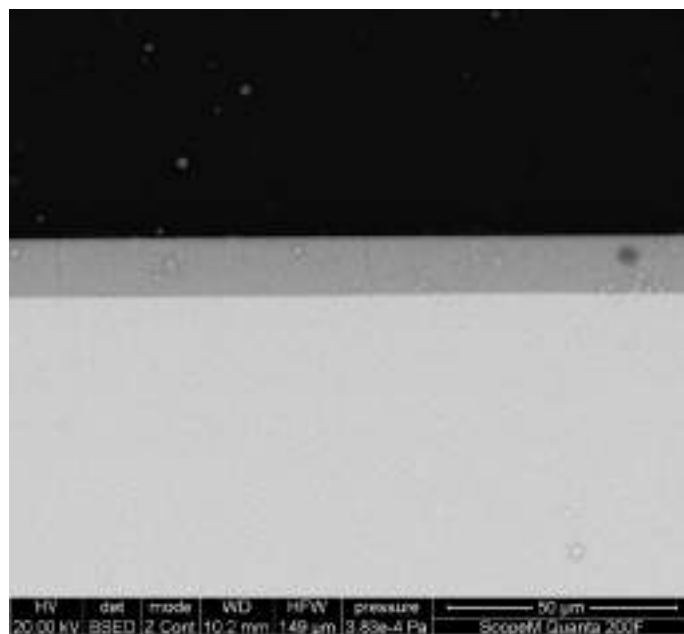
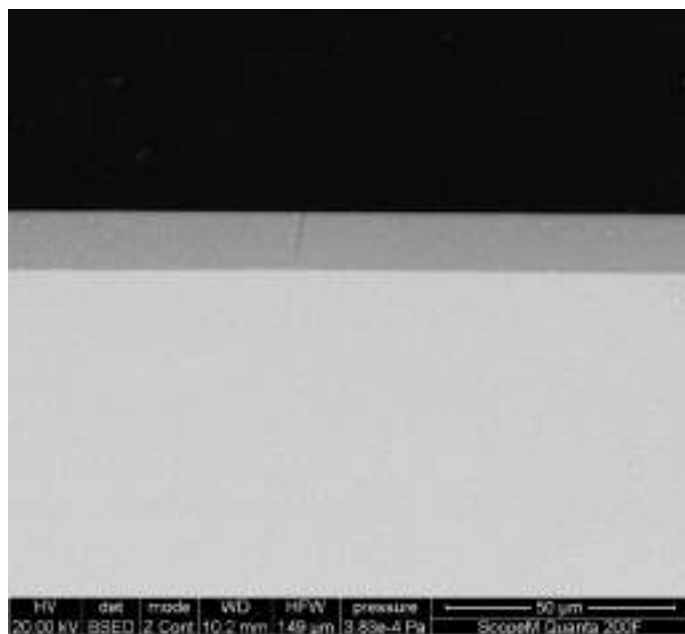


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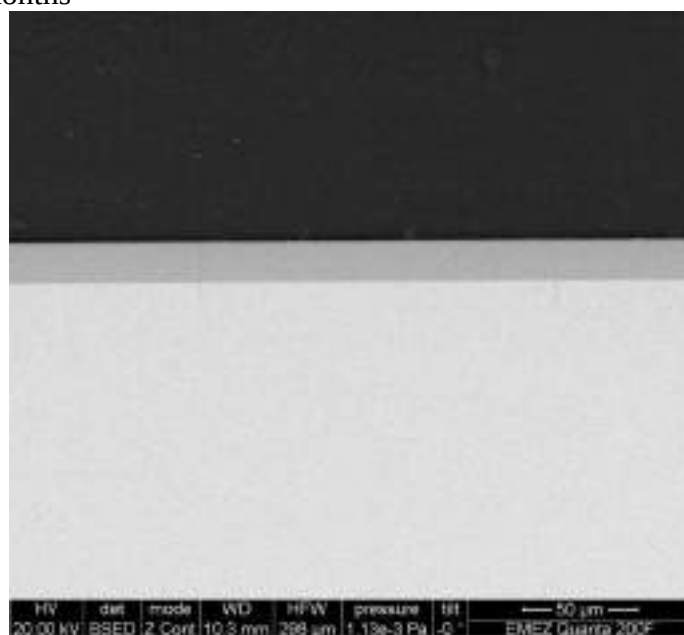
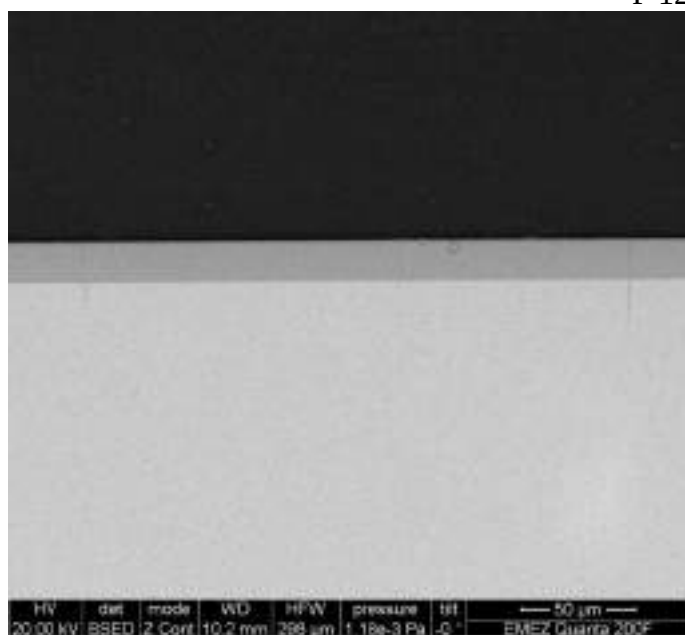


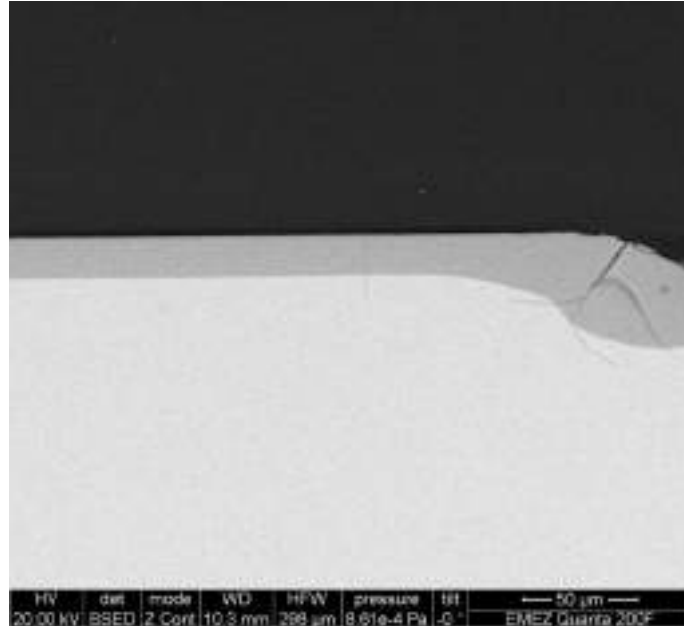
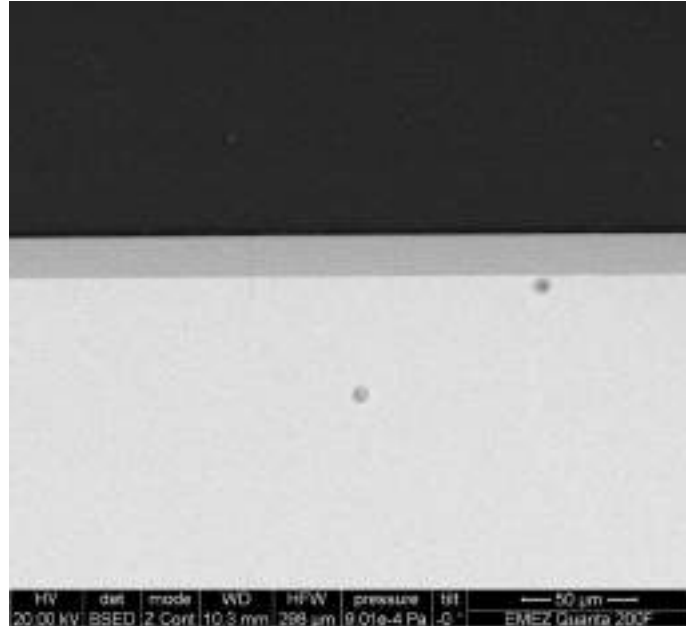
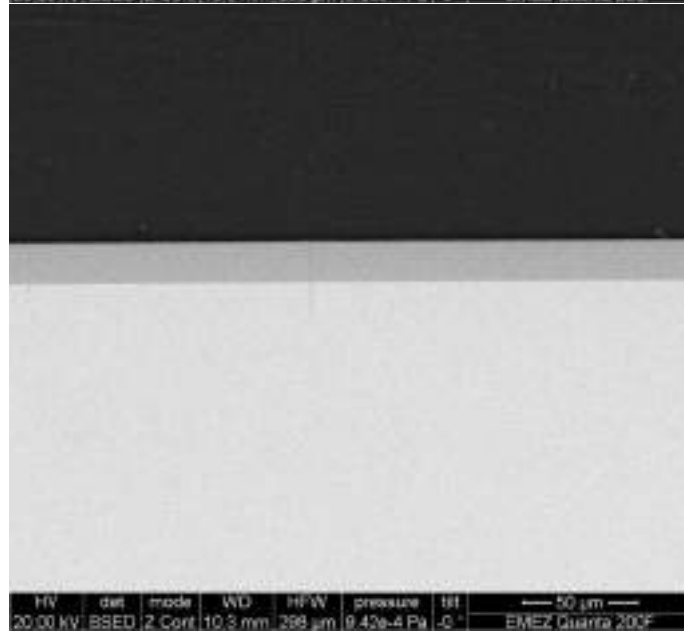
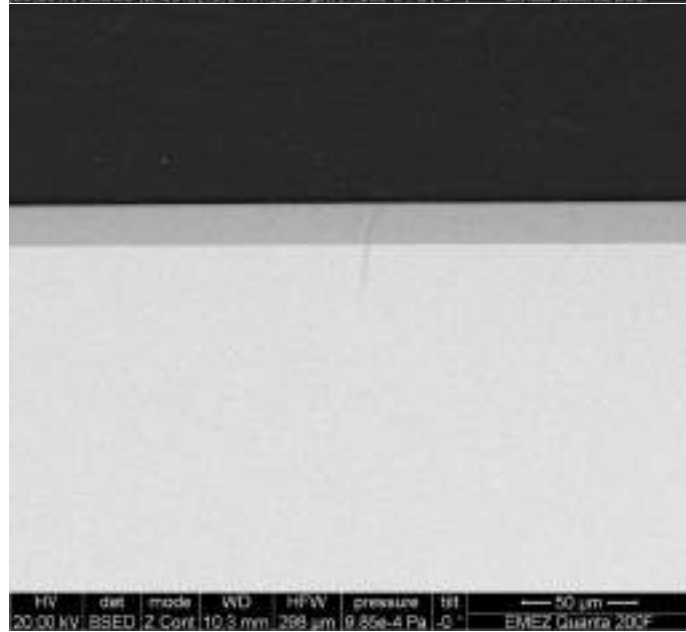
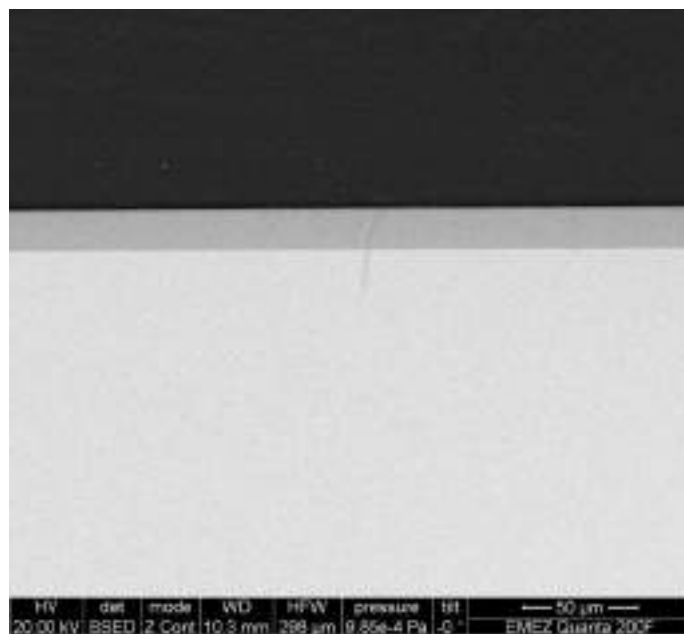
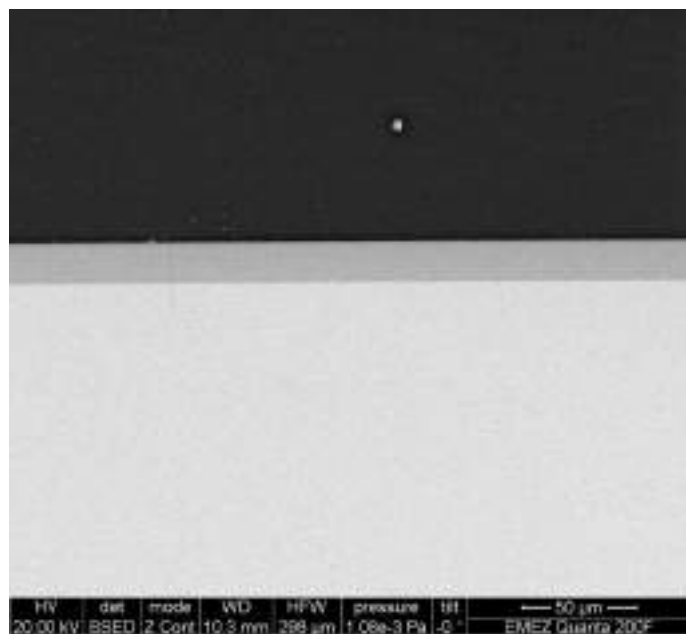


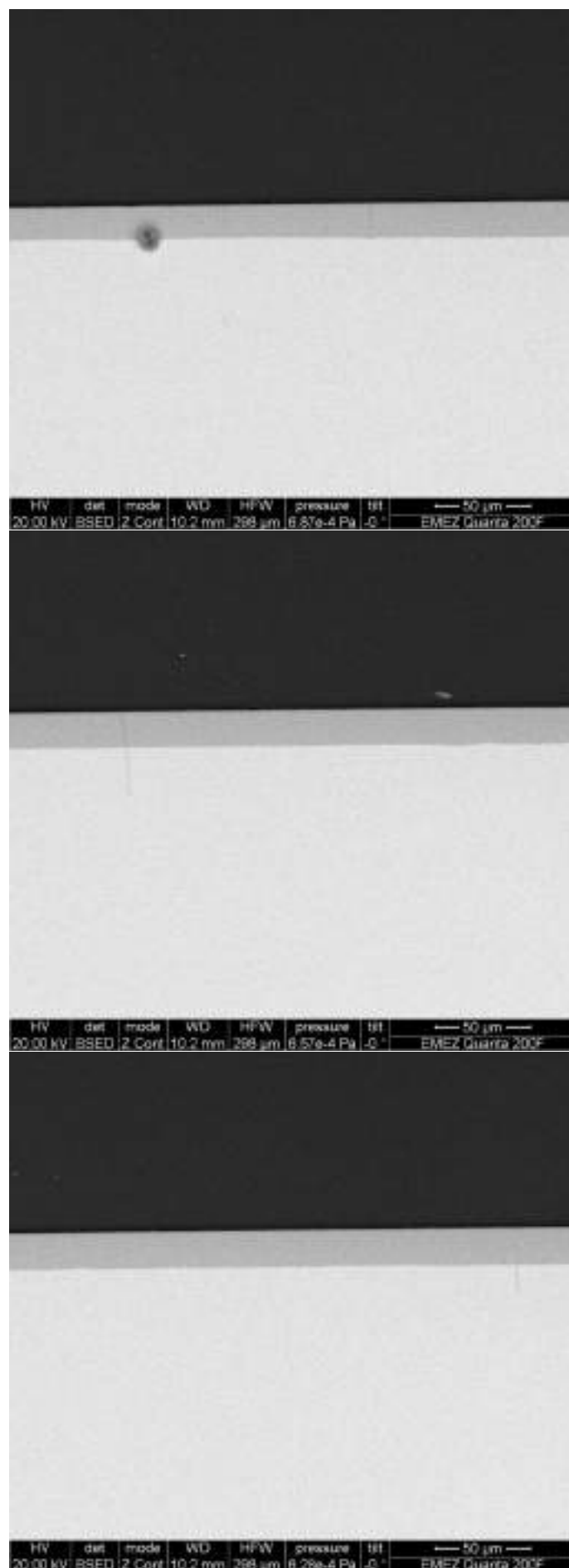
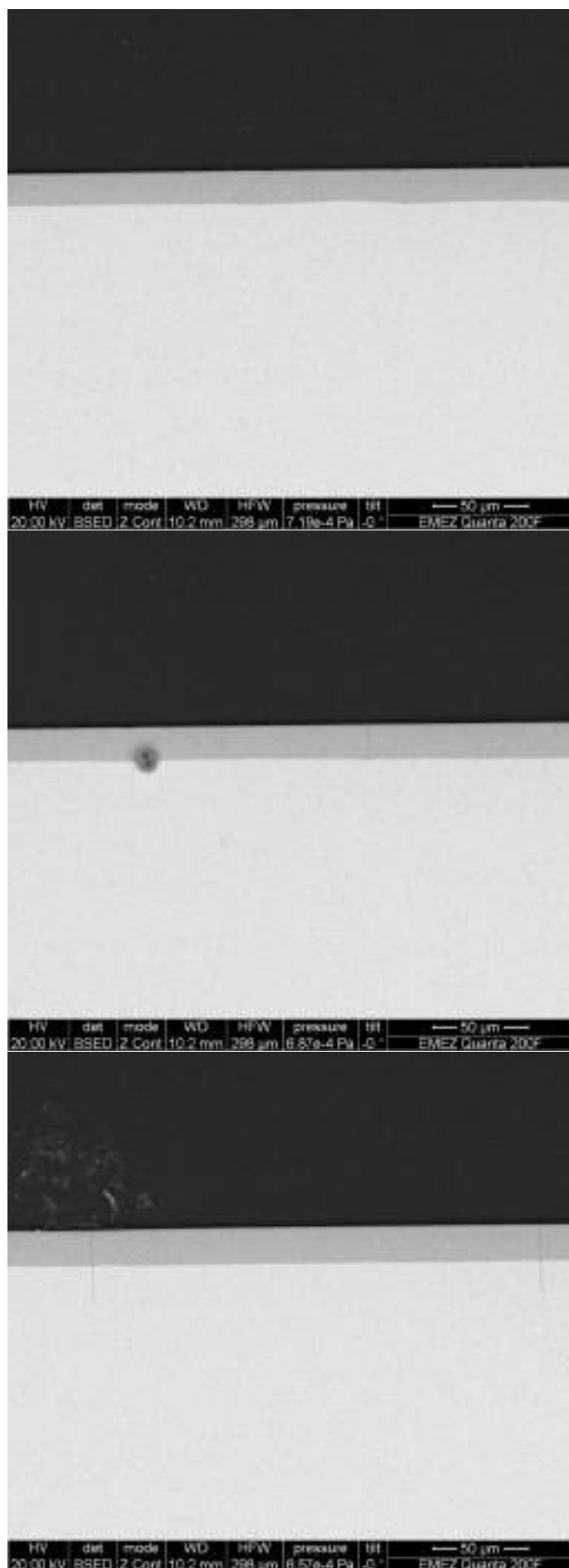


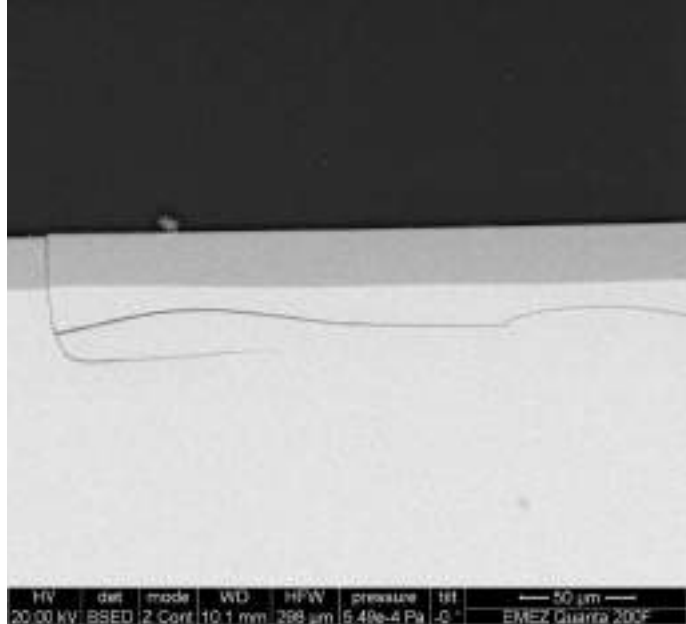
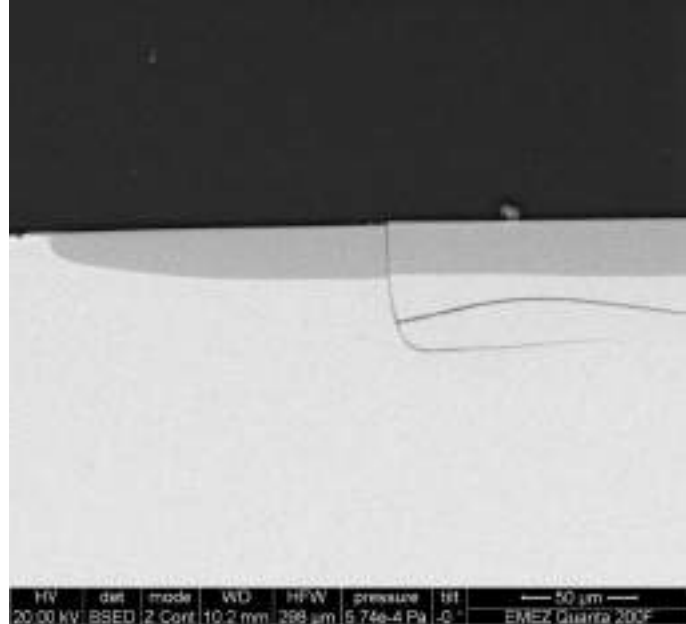
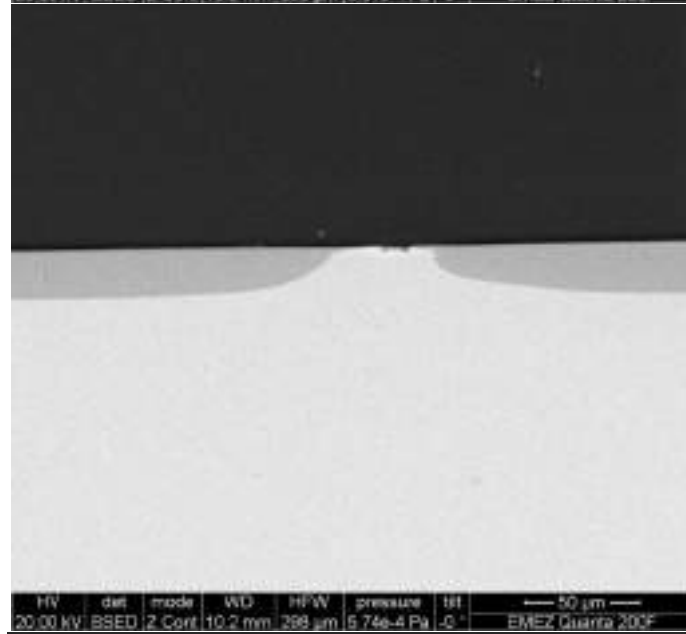
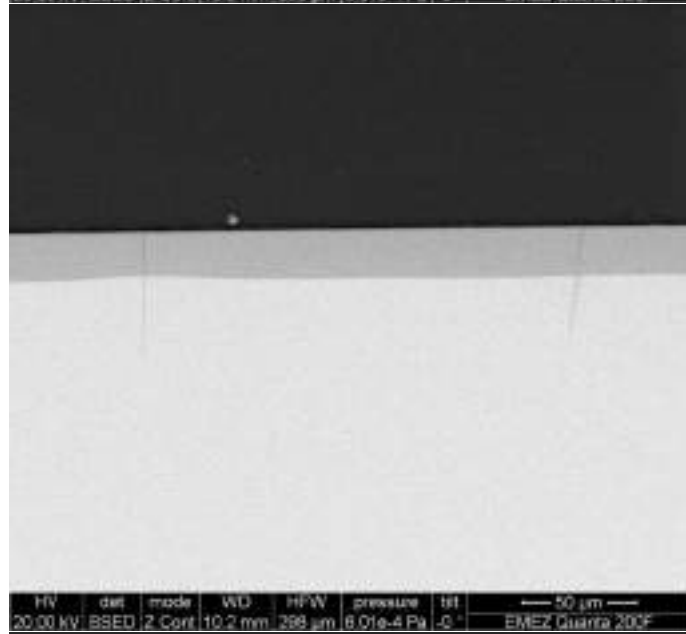
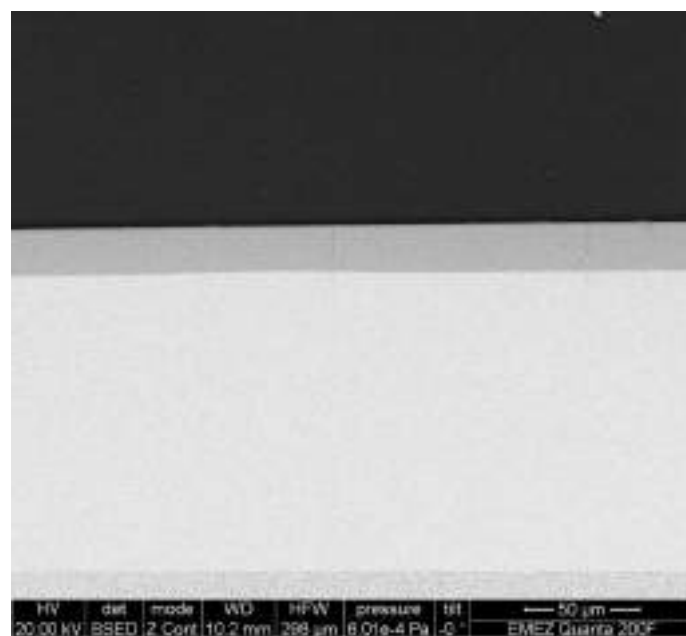
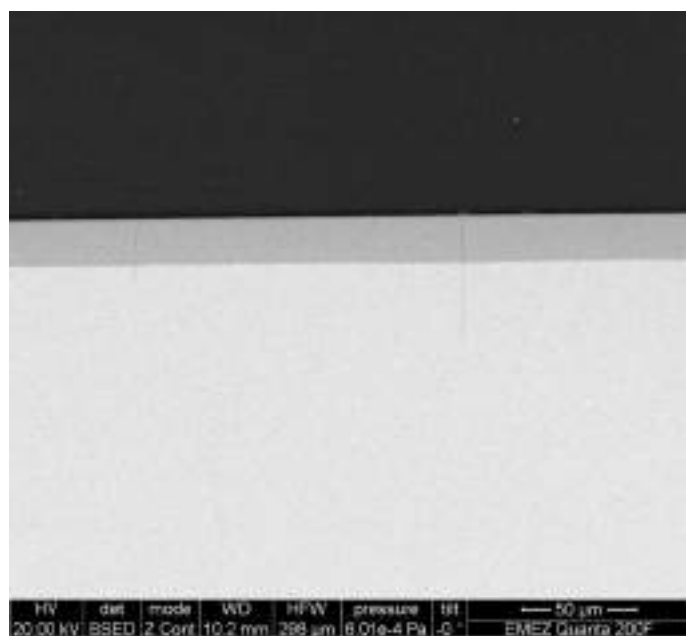


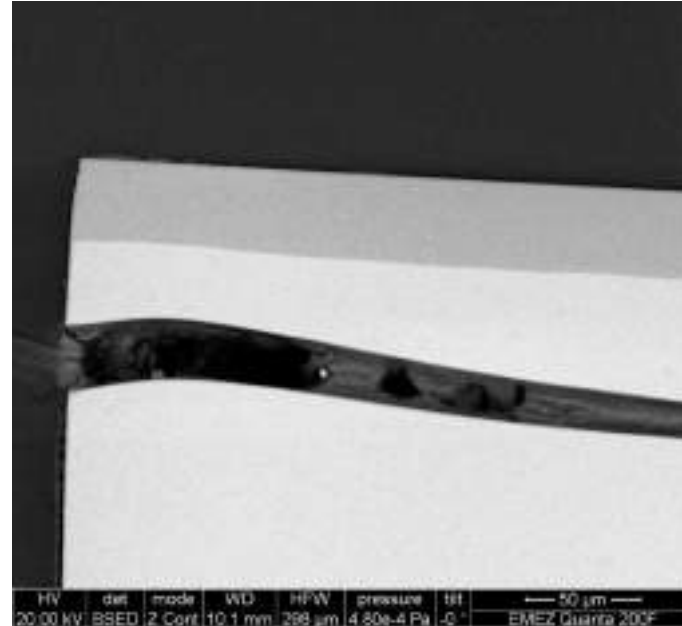
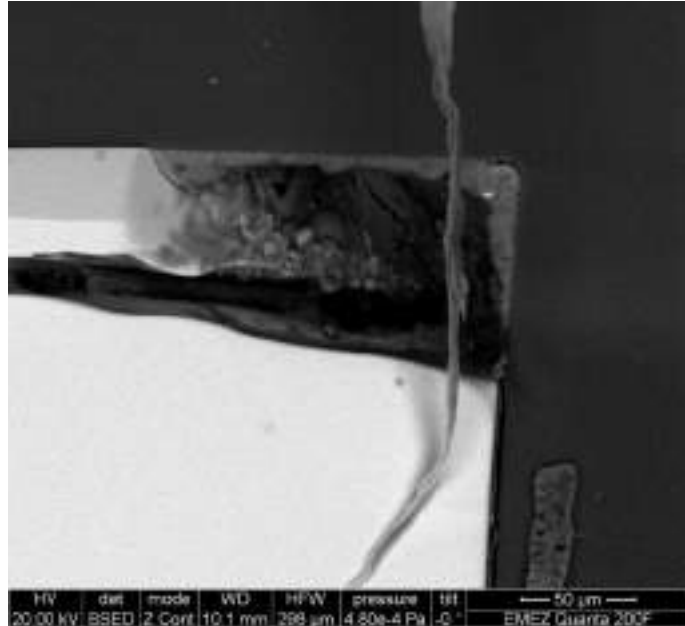
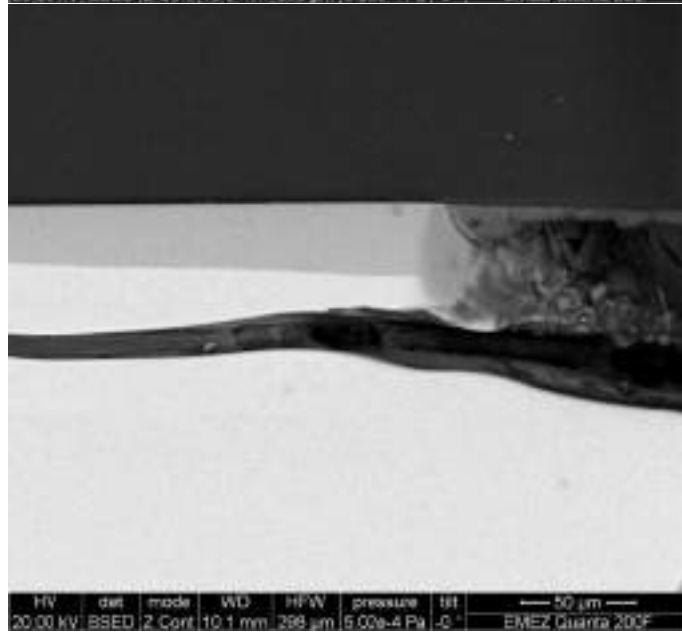
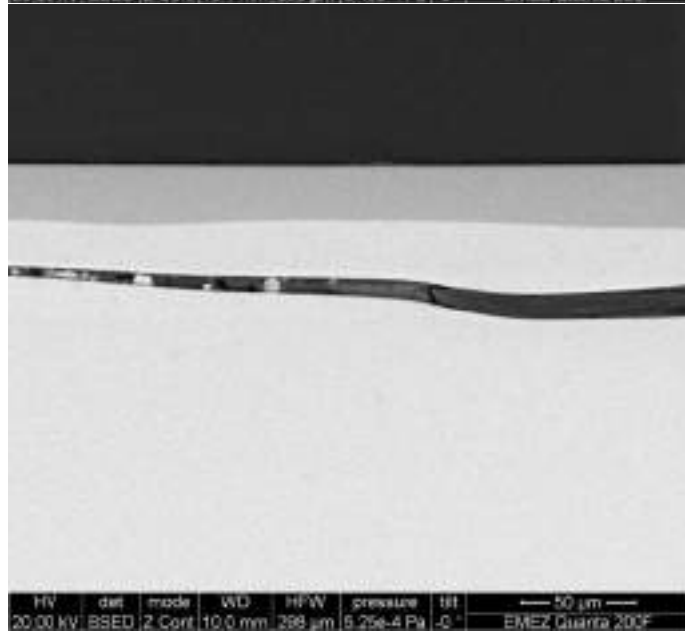
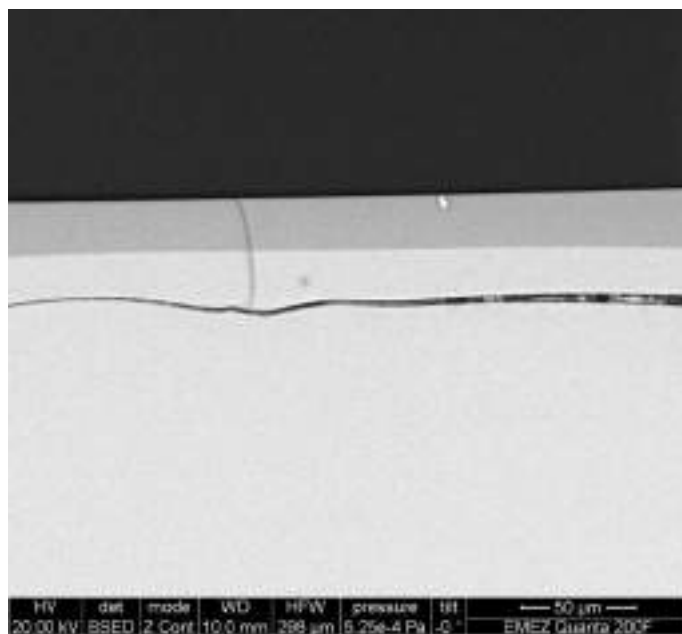
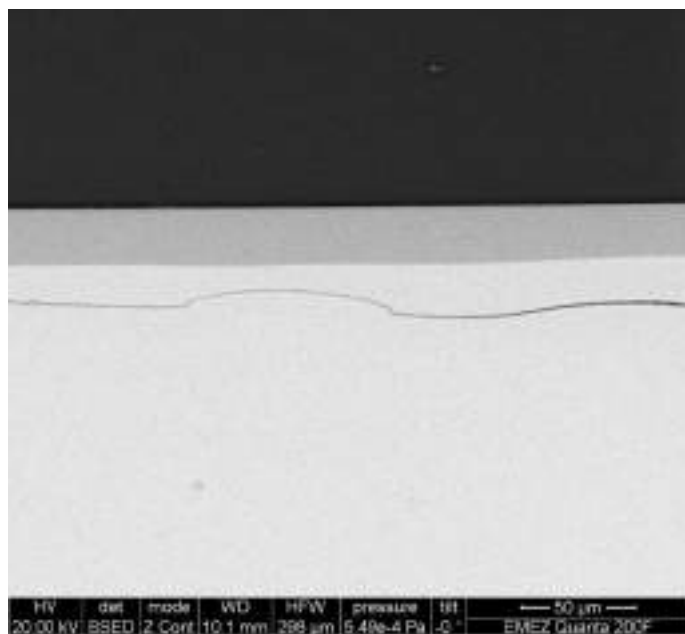
P 12 months

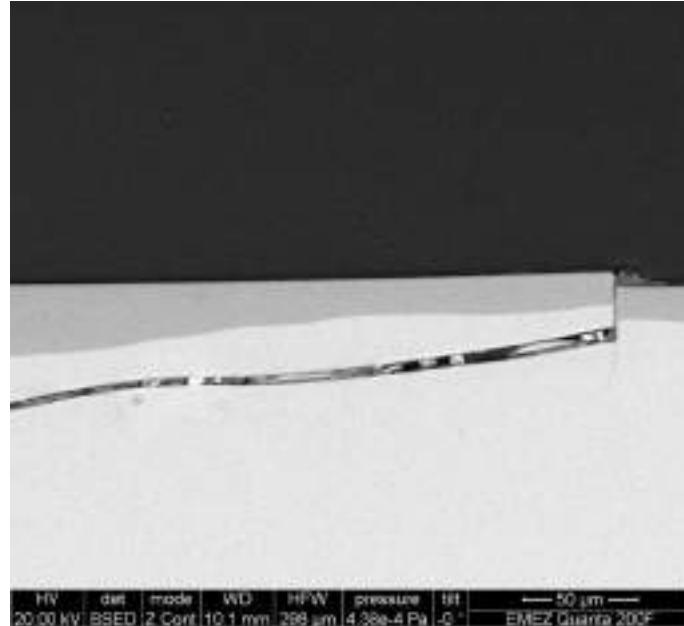
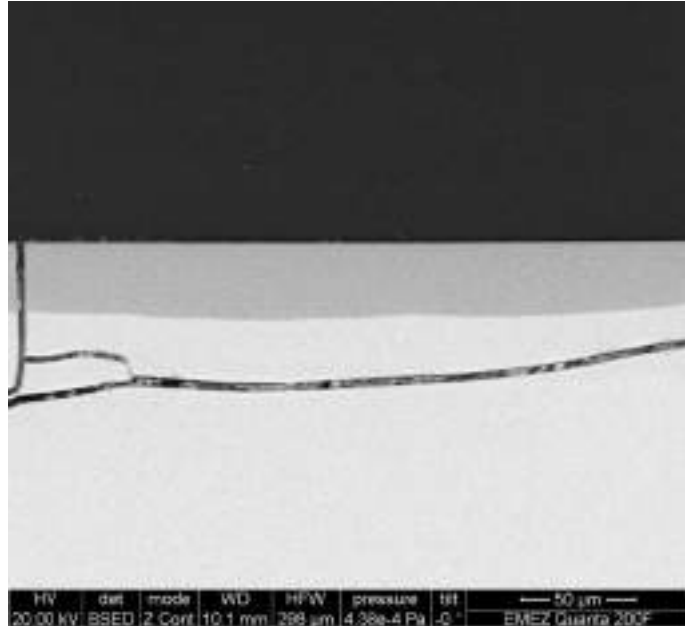
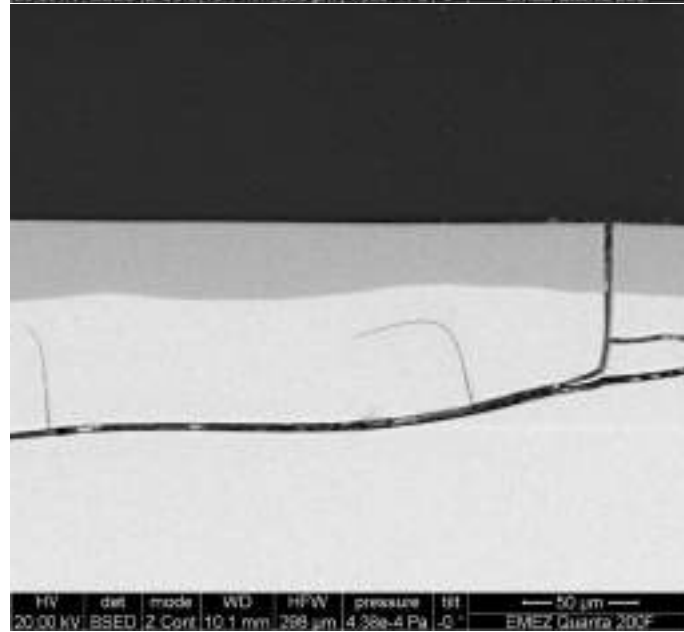
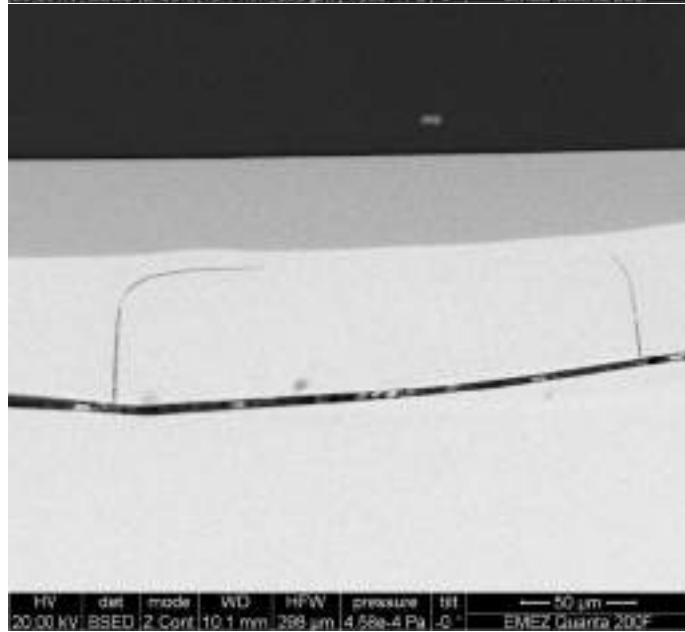
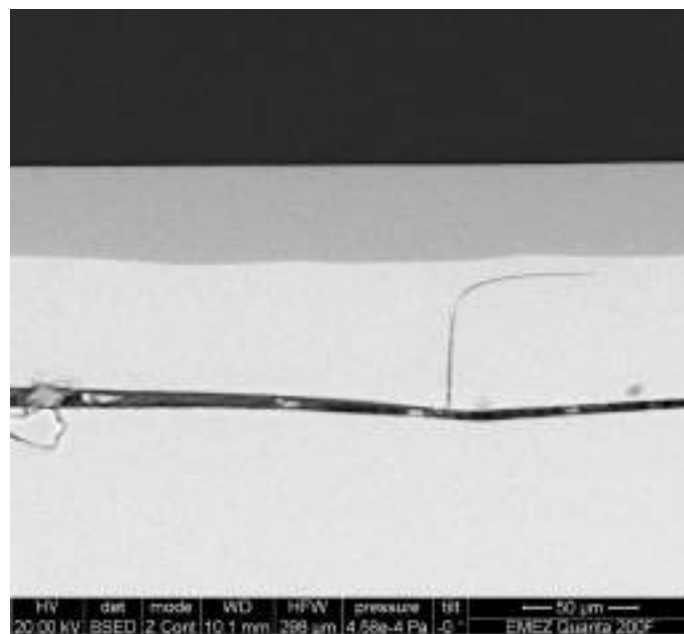
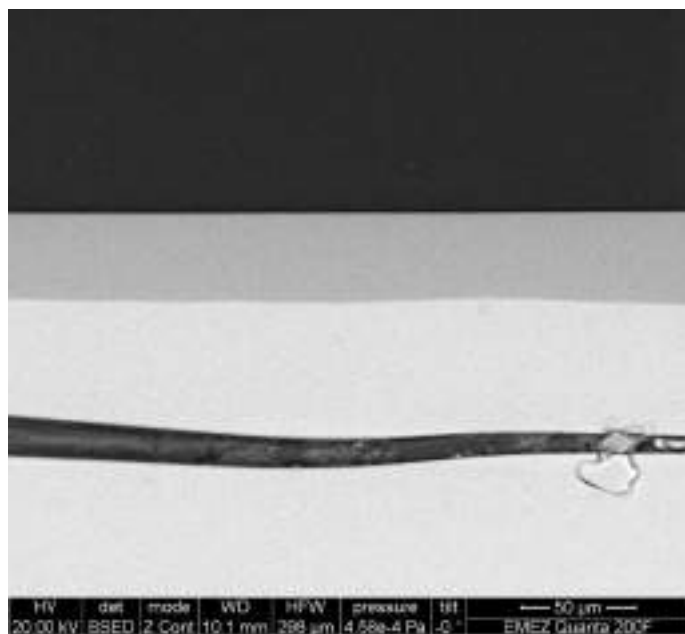


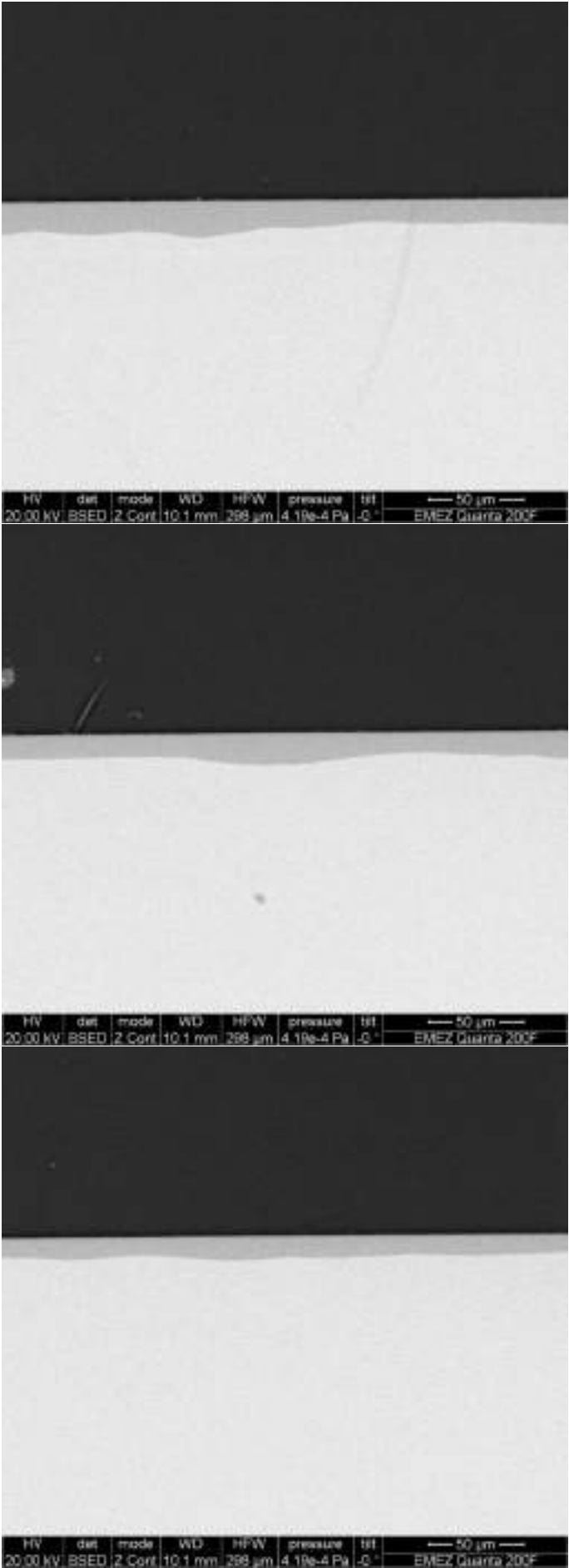
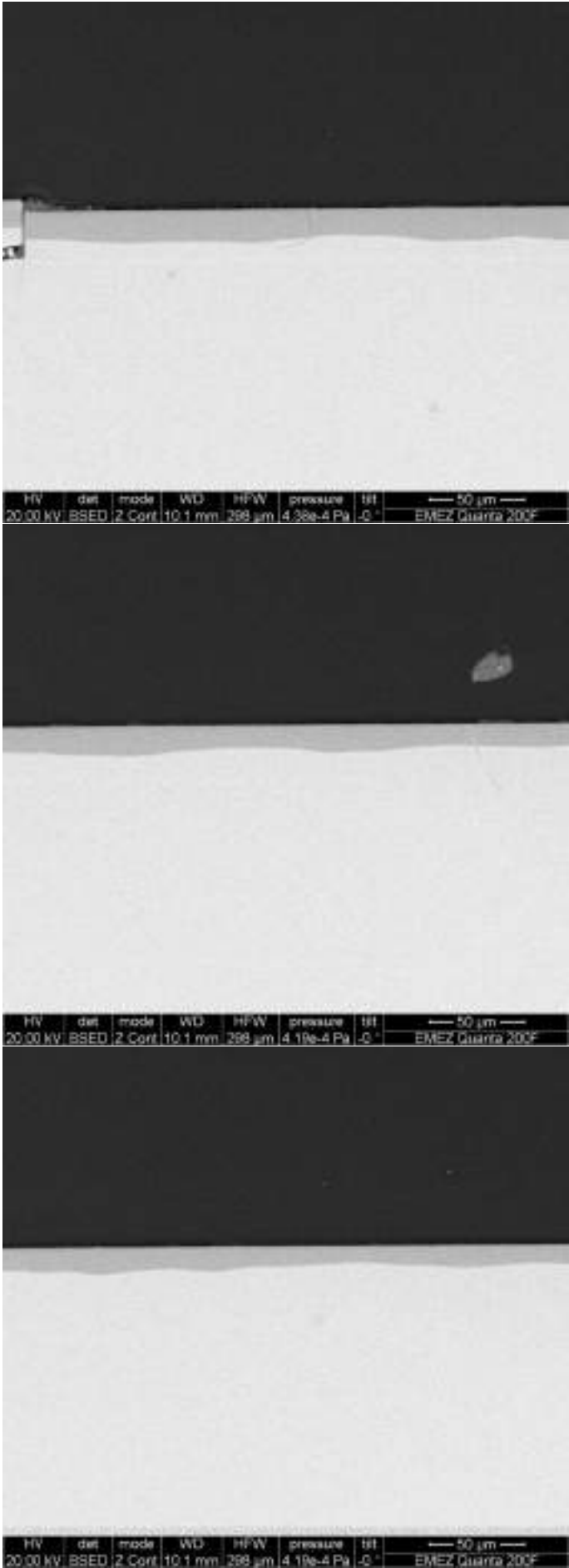


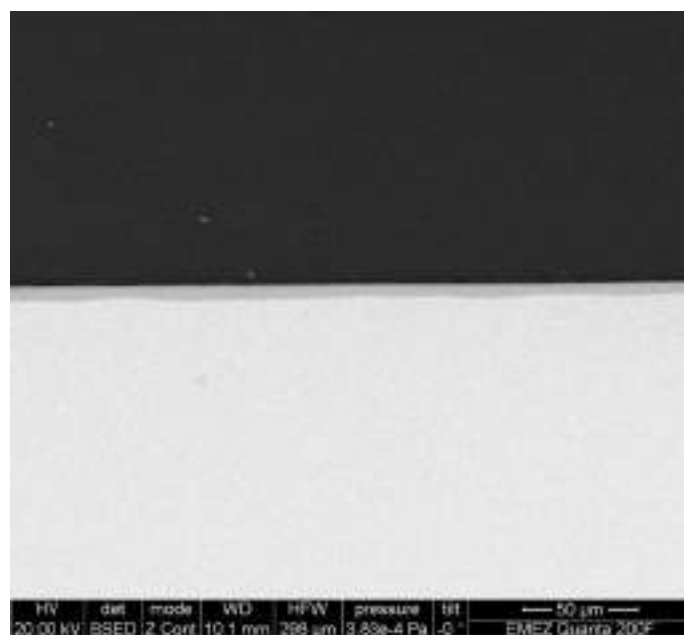
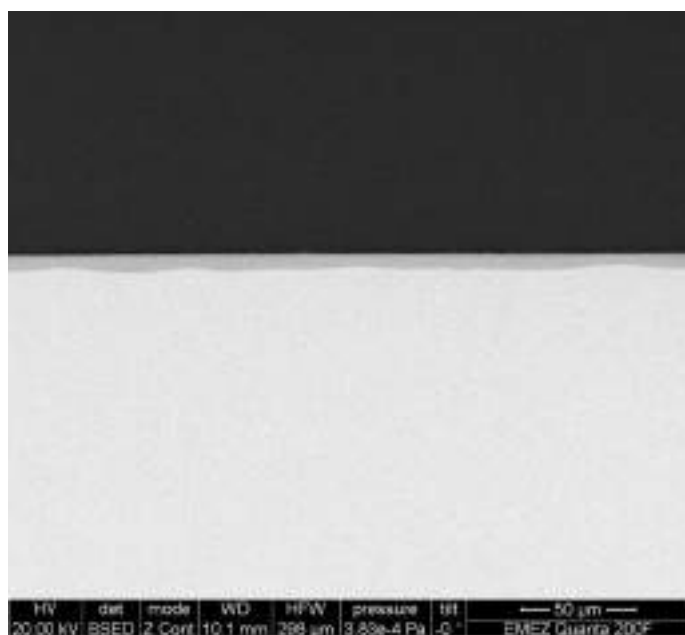
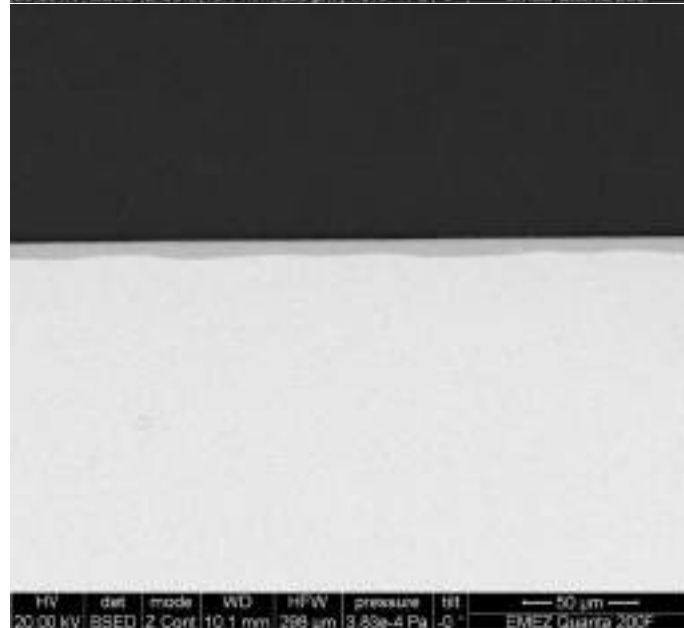
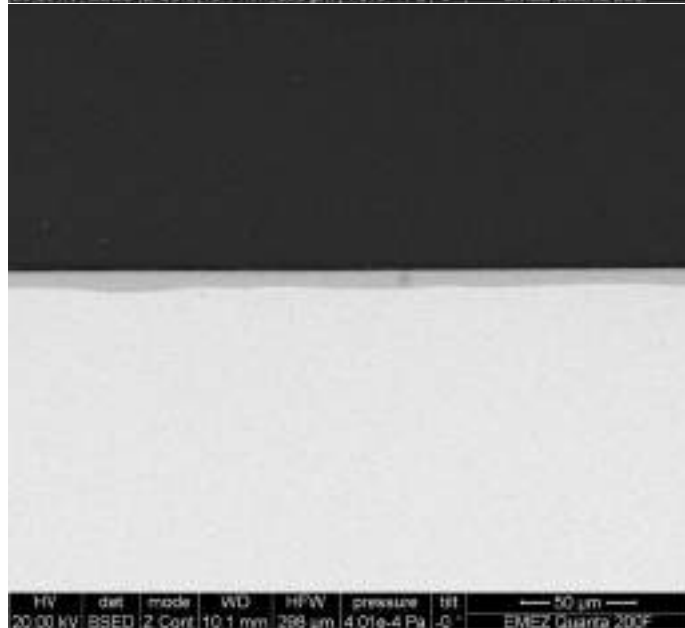
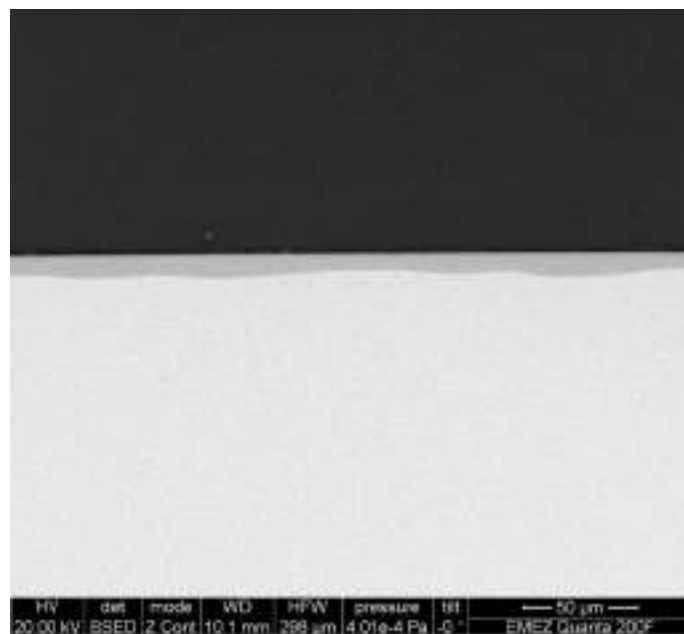
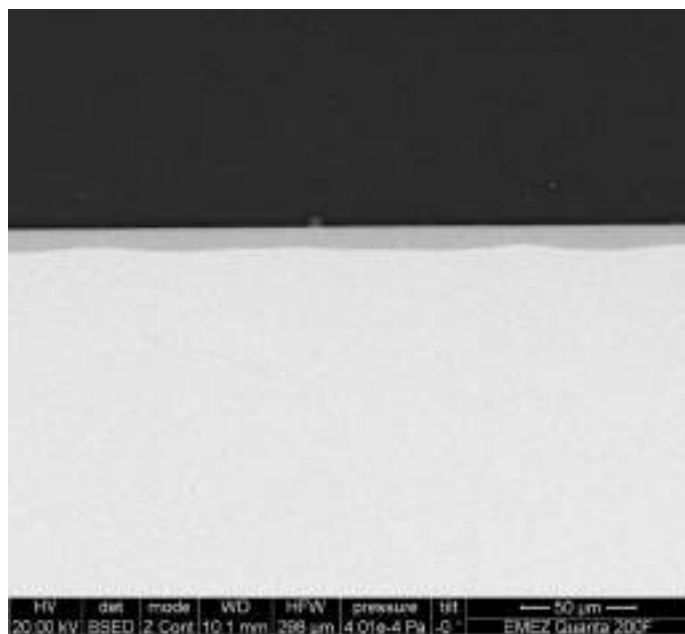


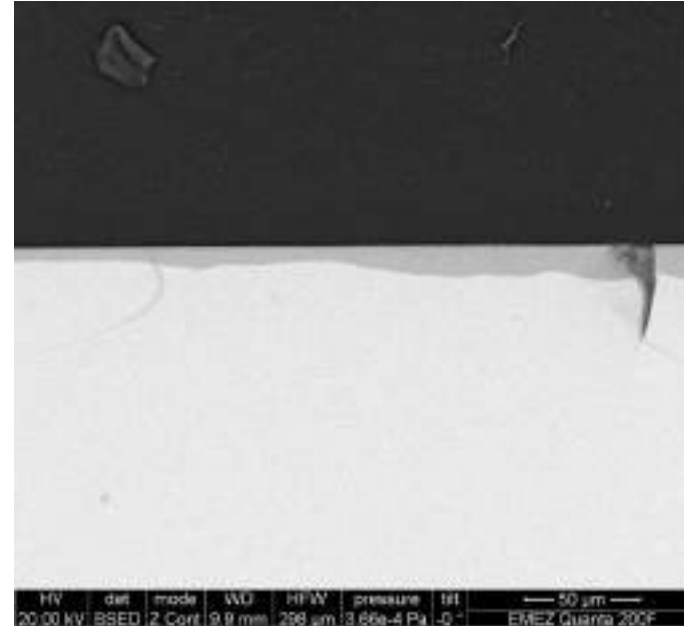
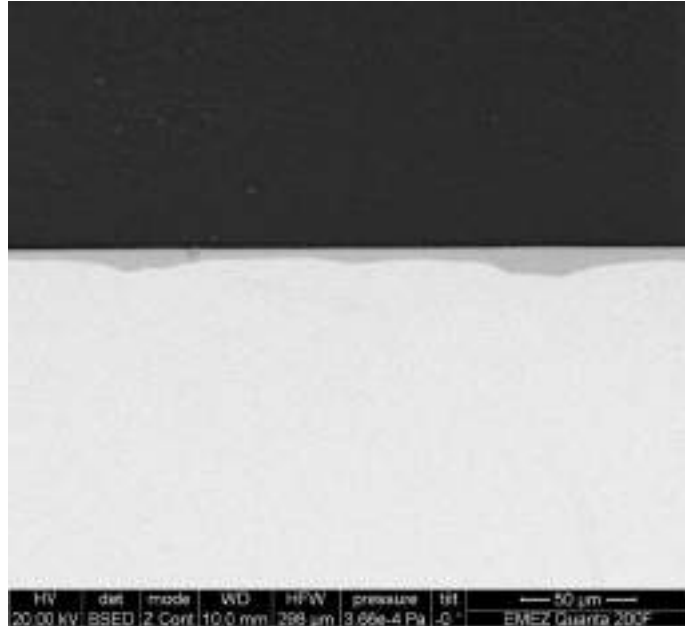
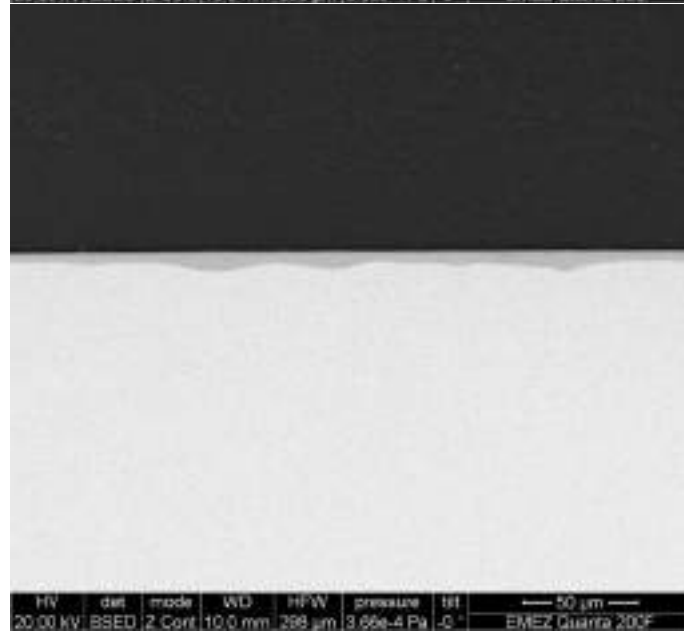
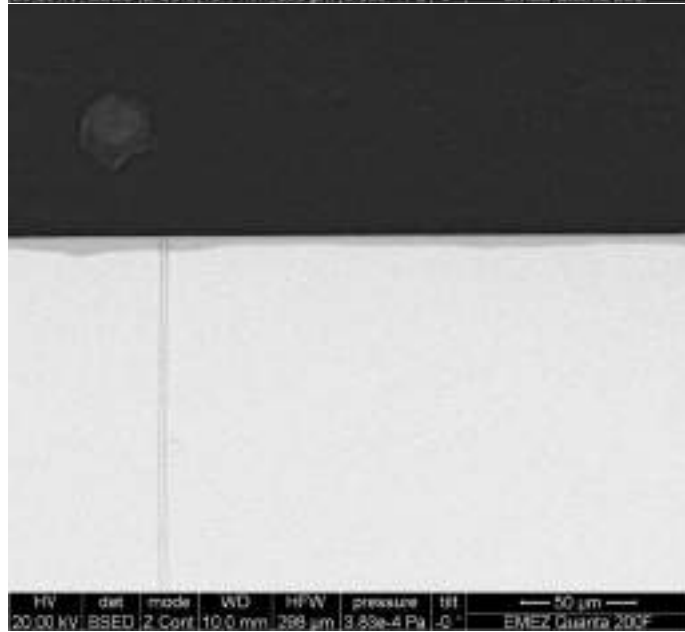
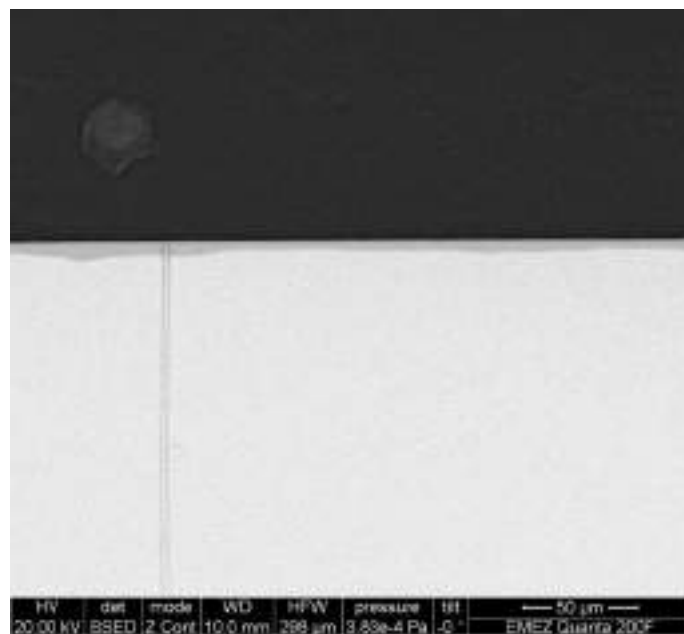
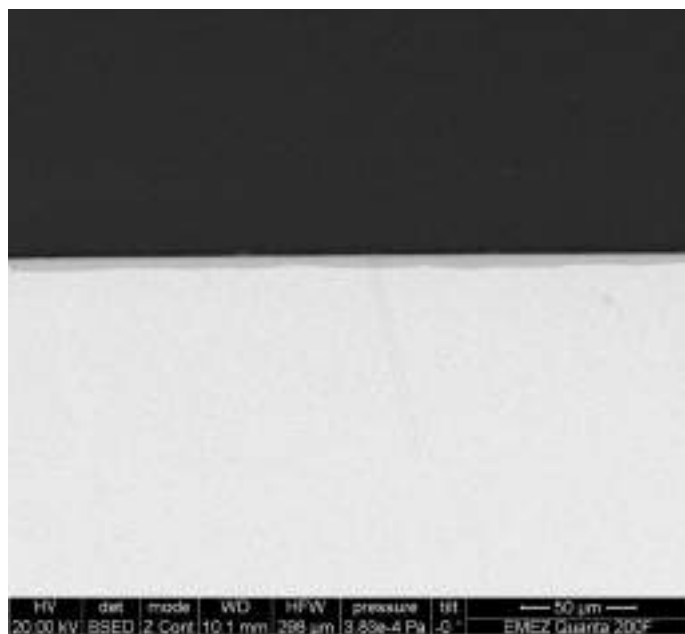


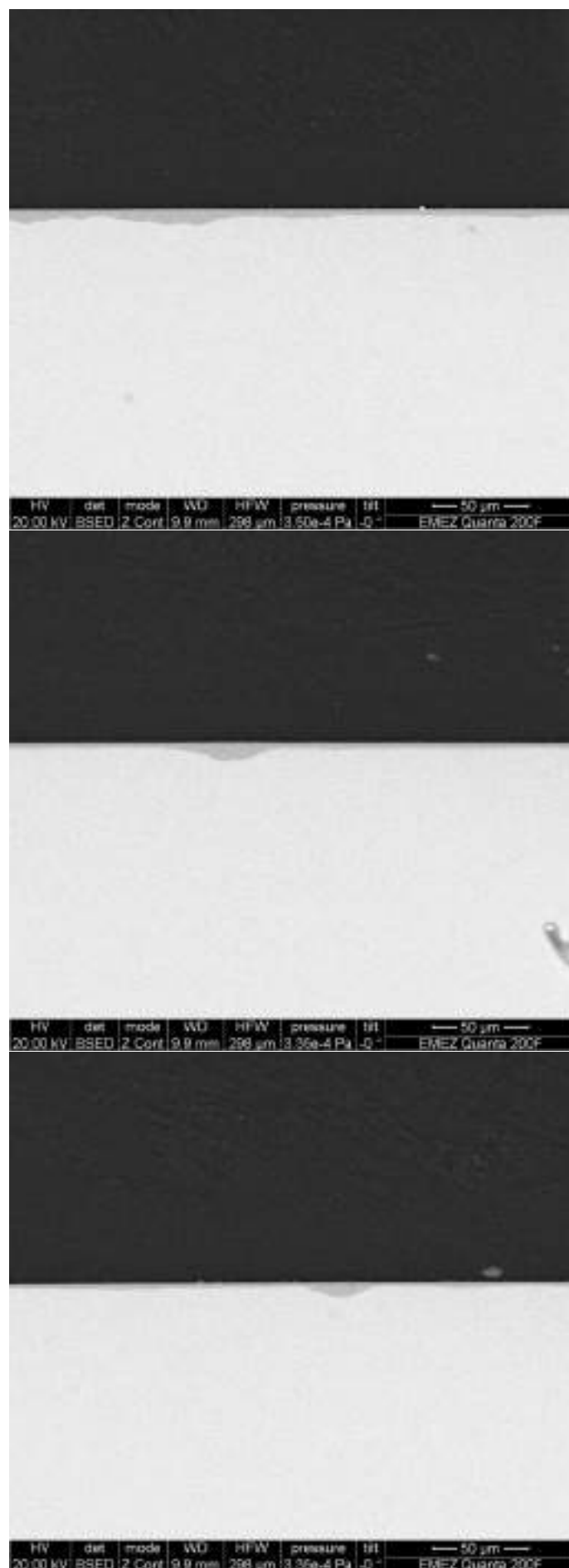
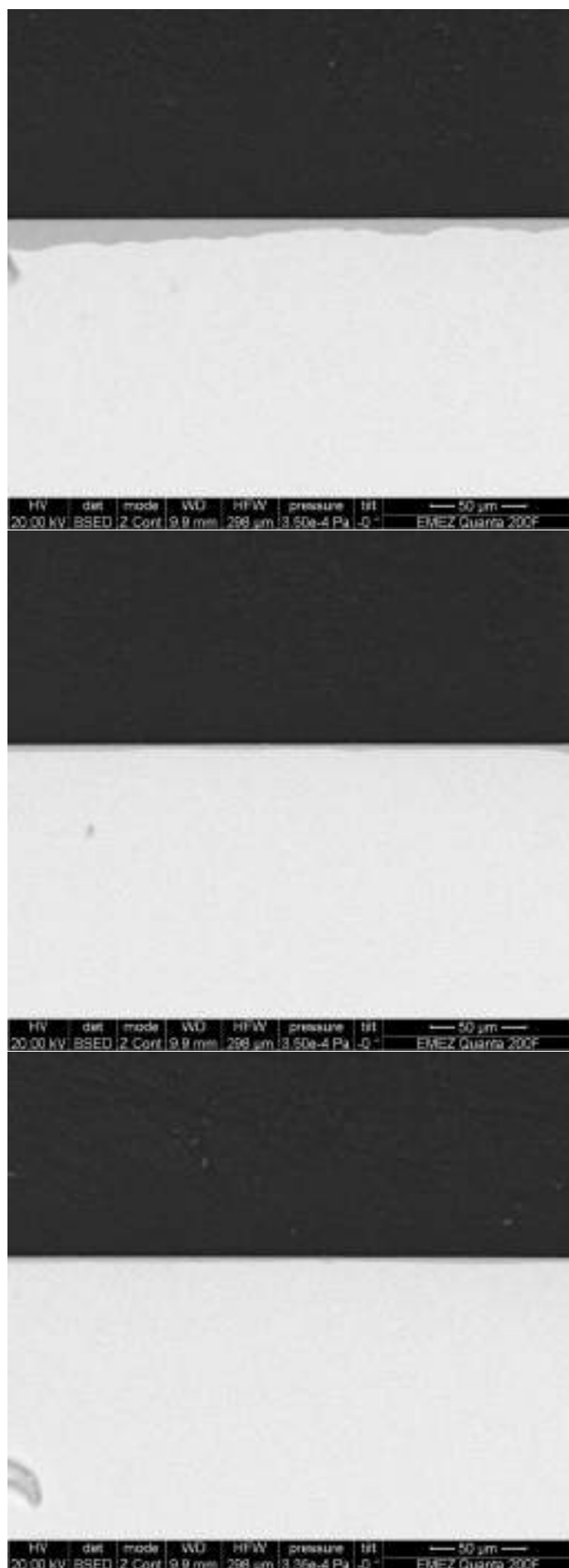


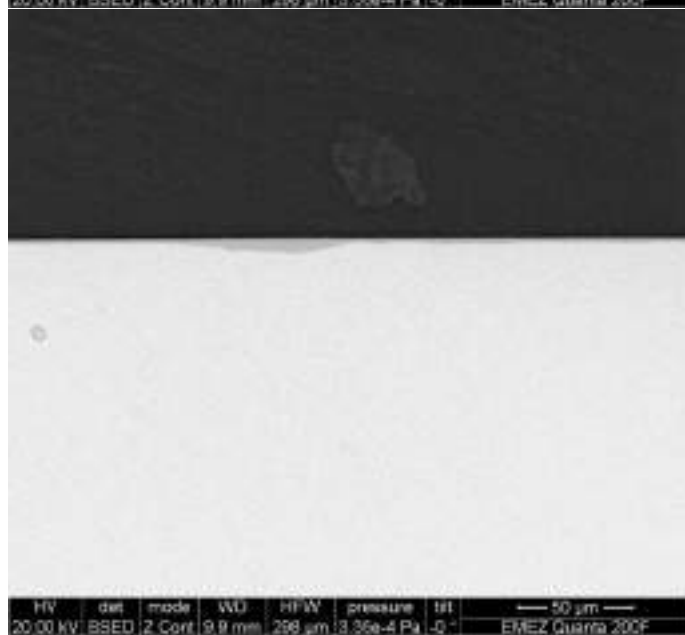
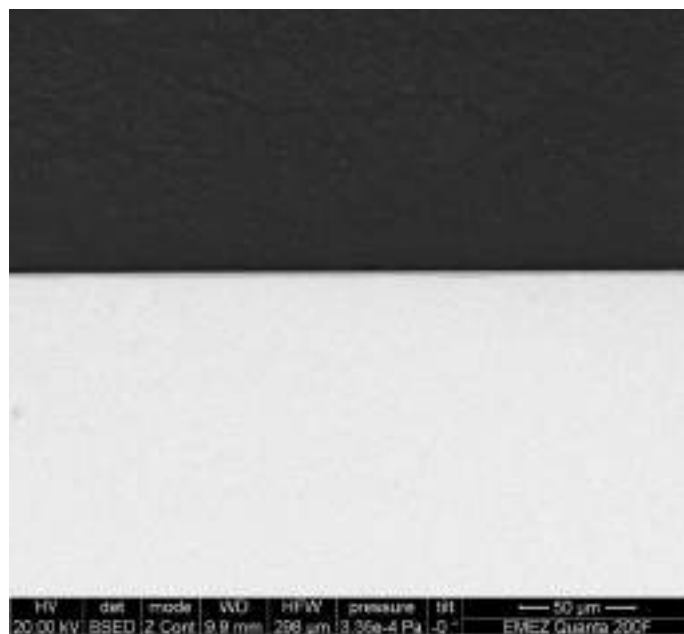
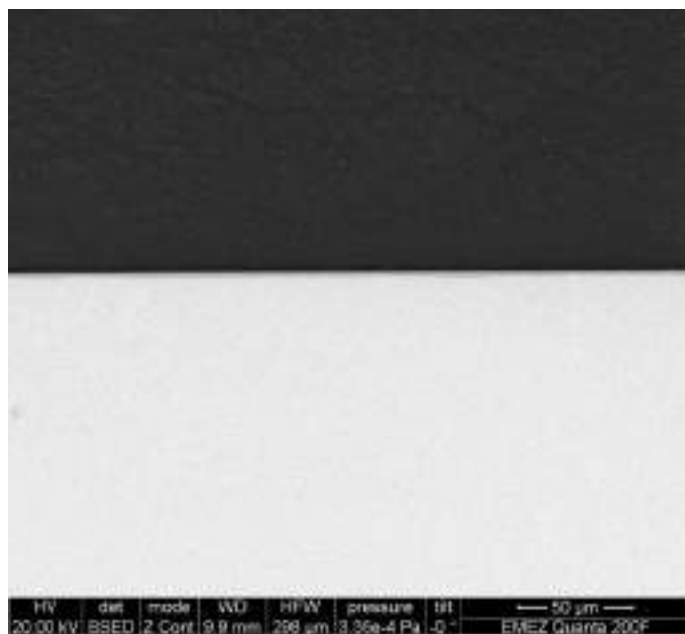




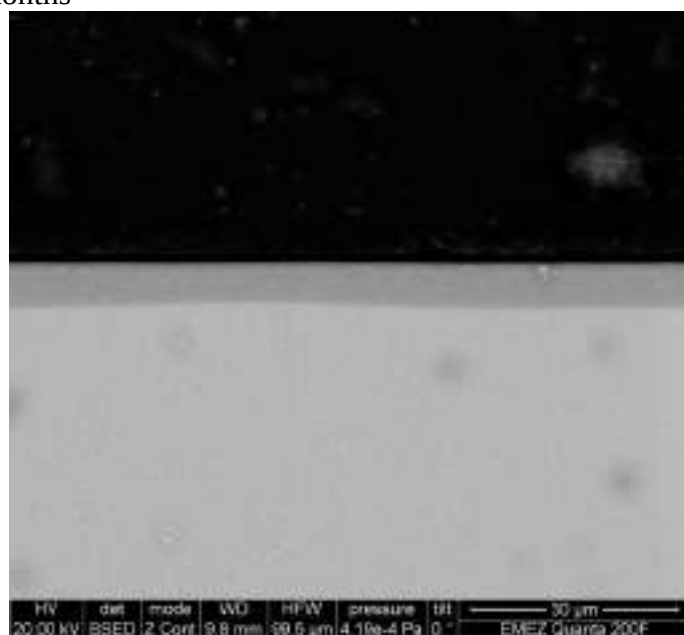
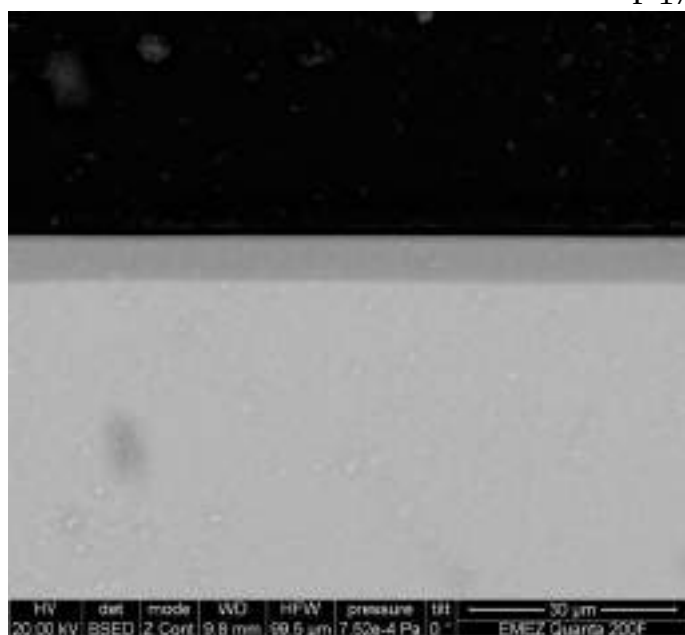


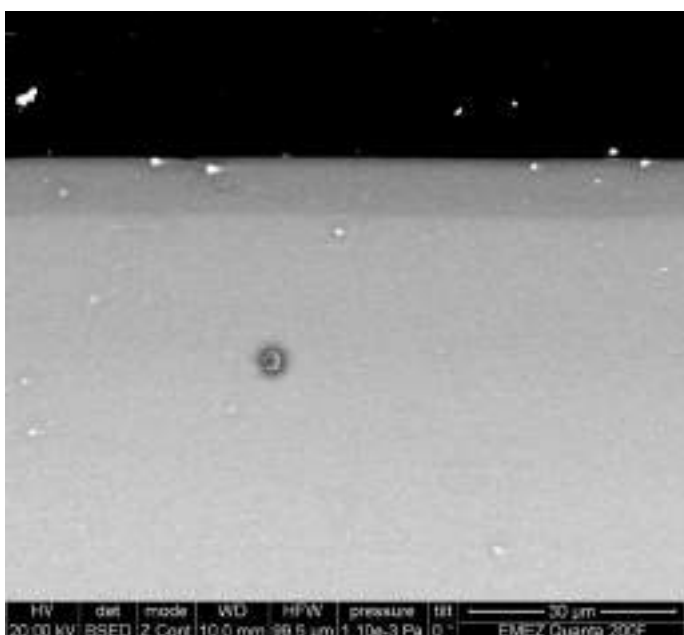
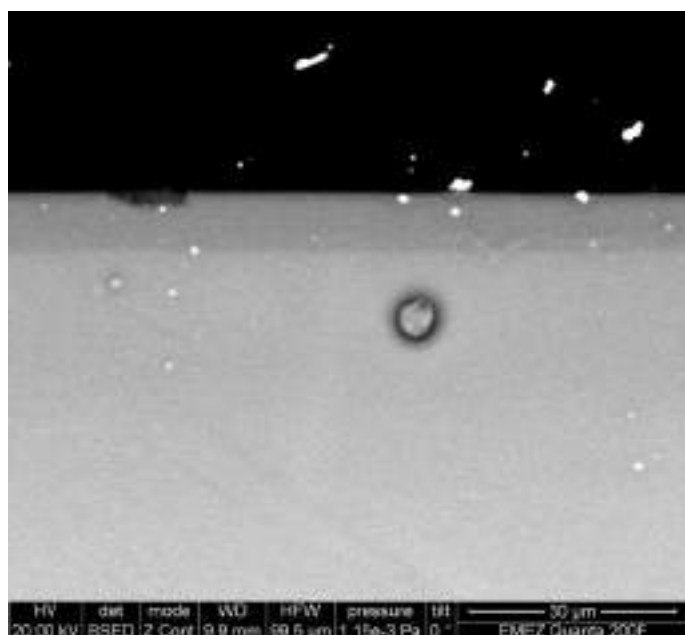
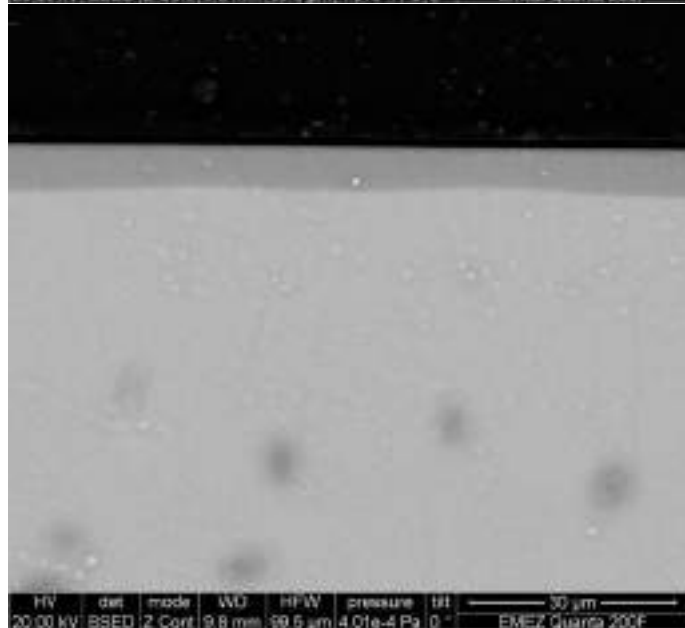
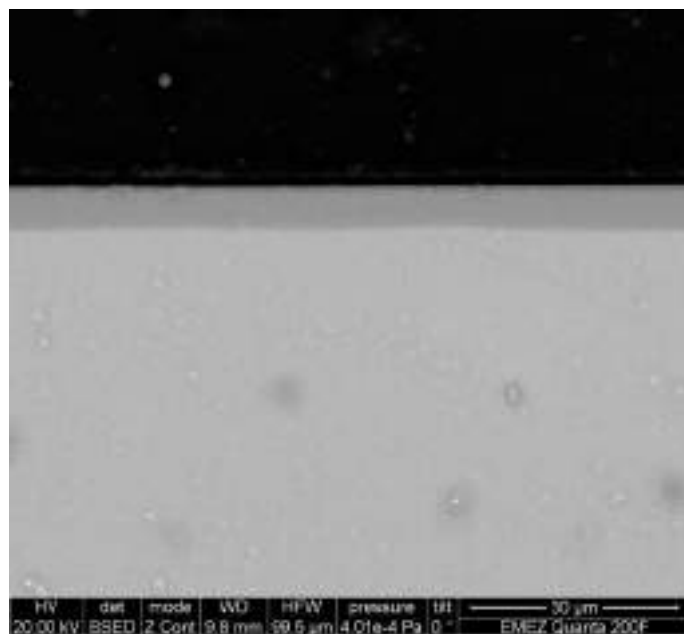
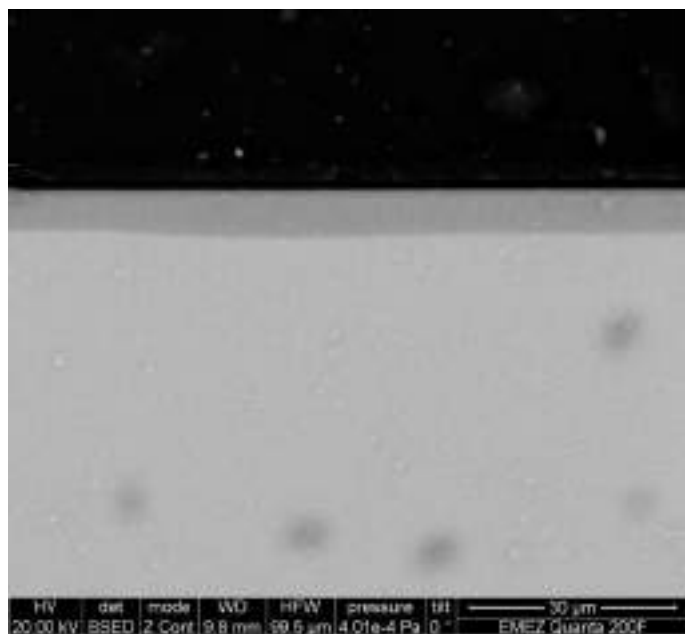


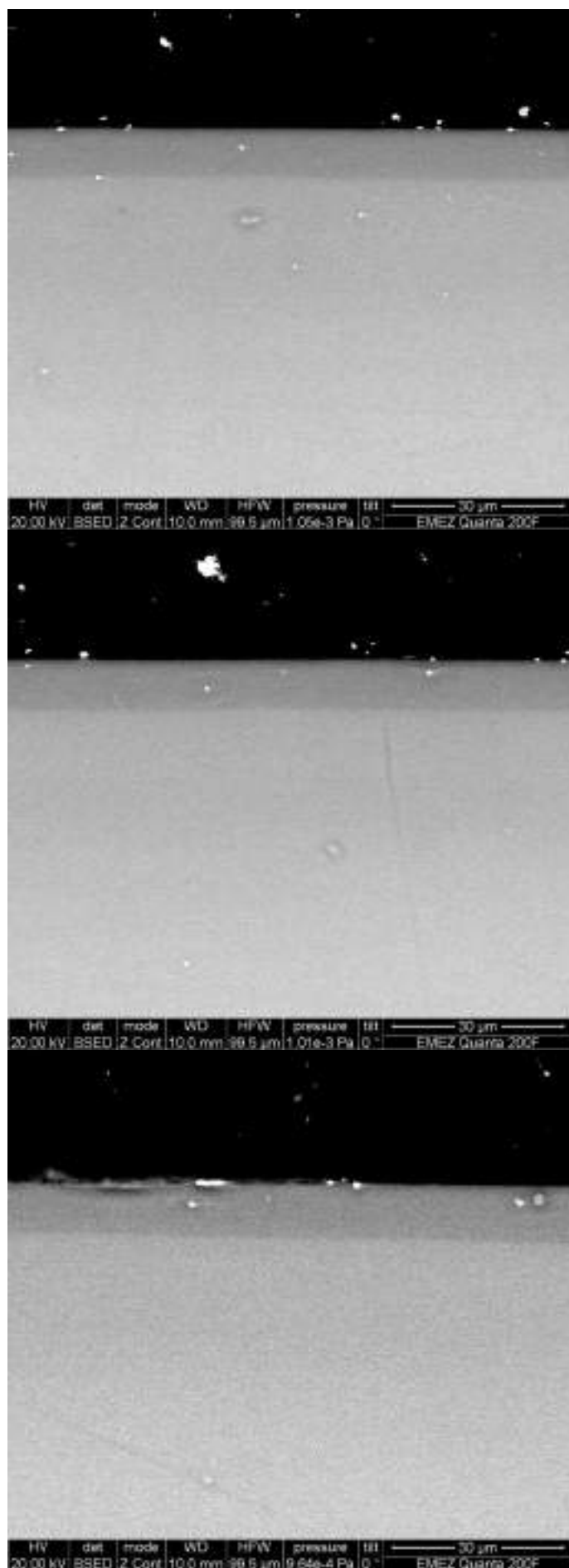


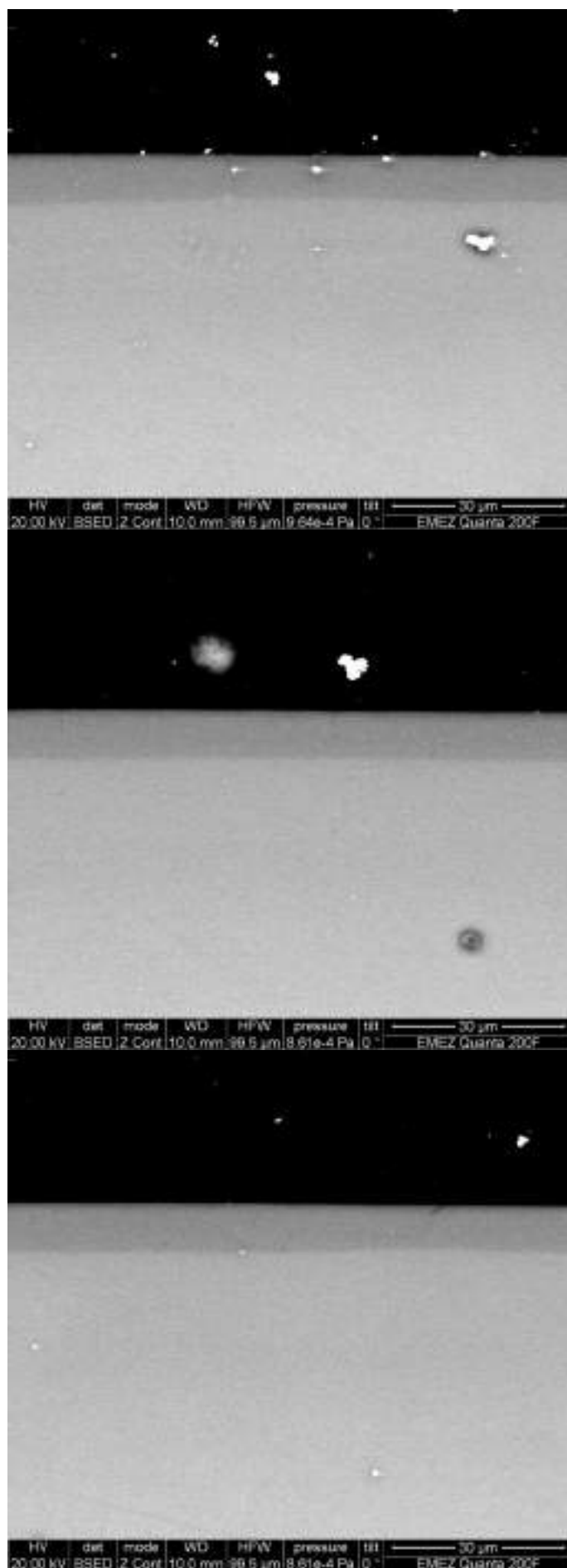
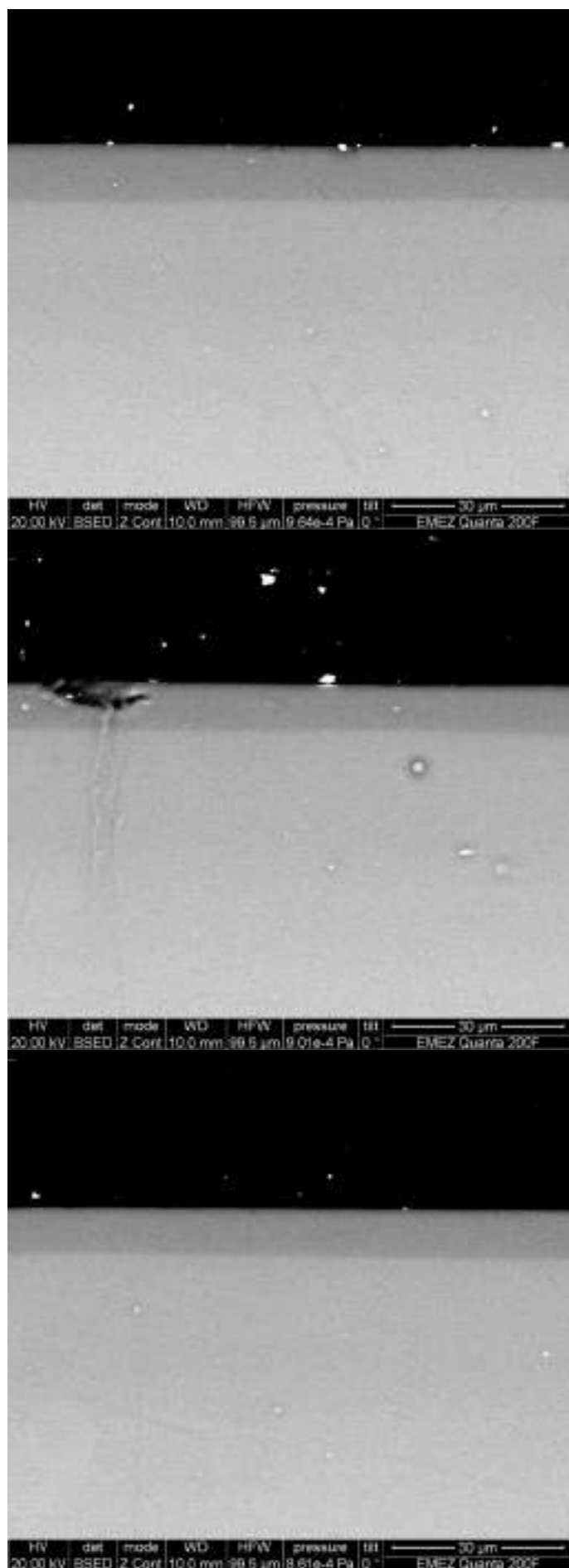


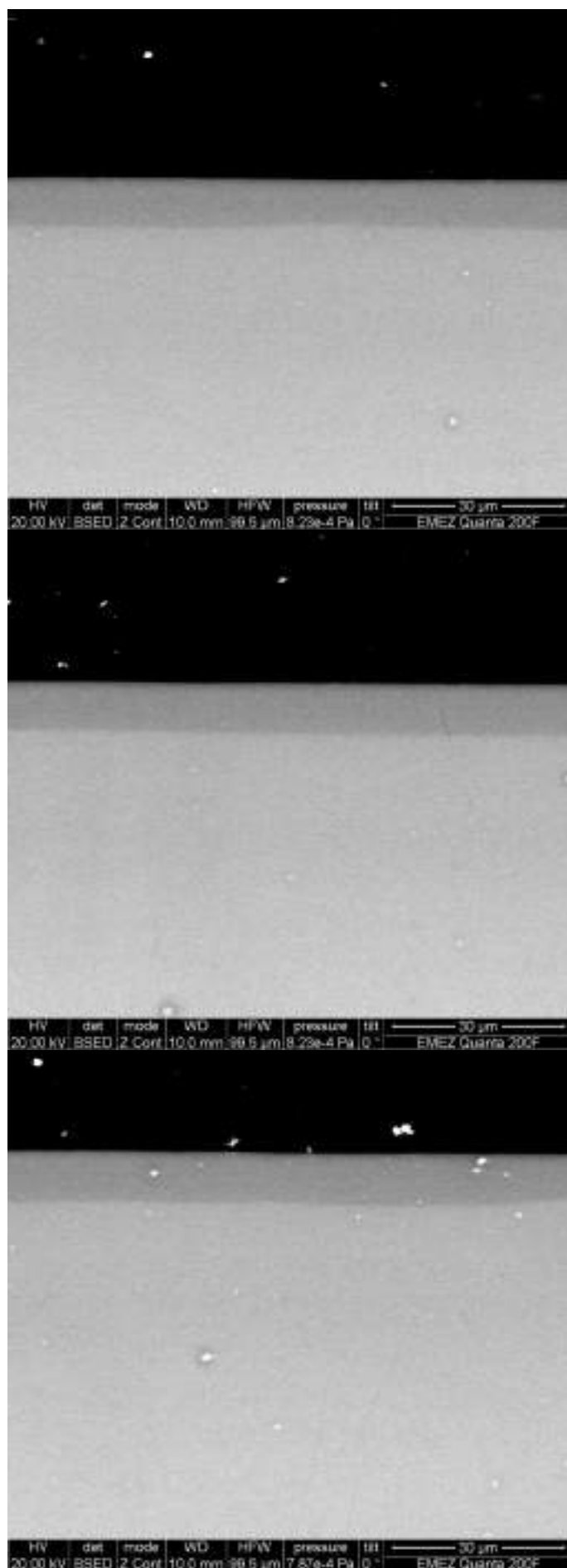
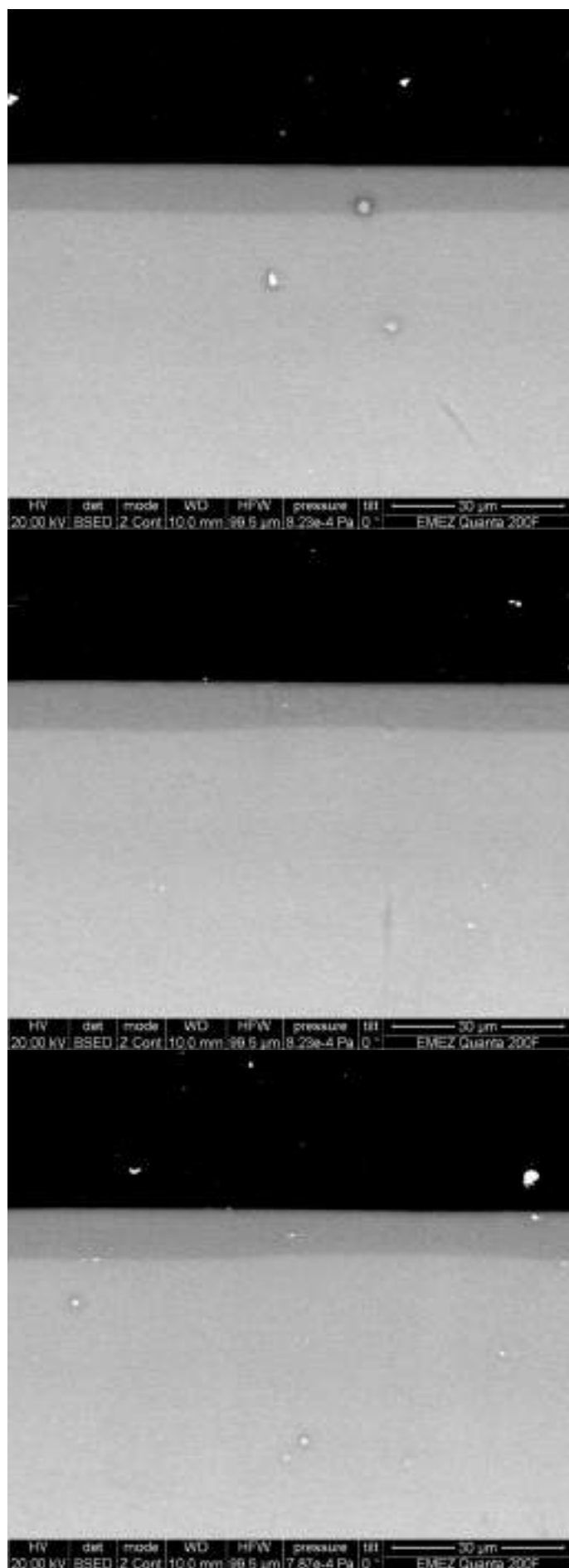
P 17 months

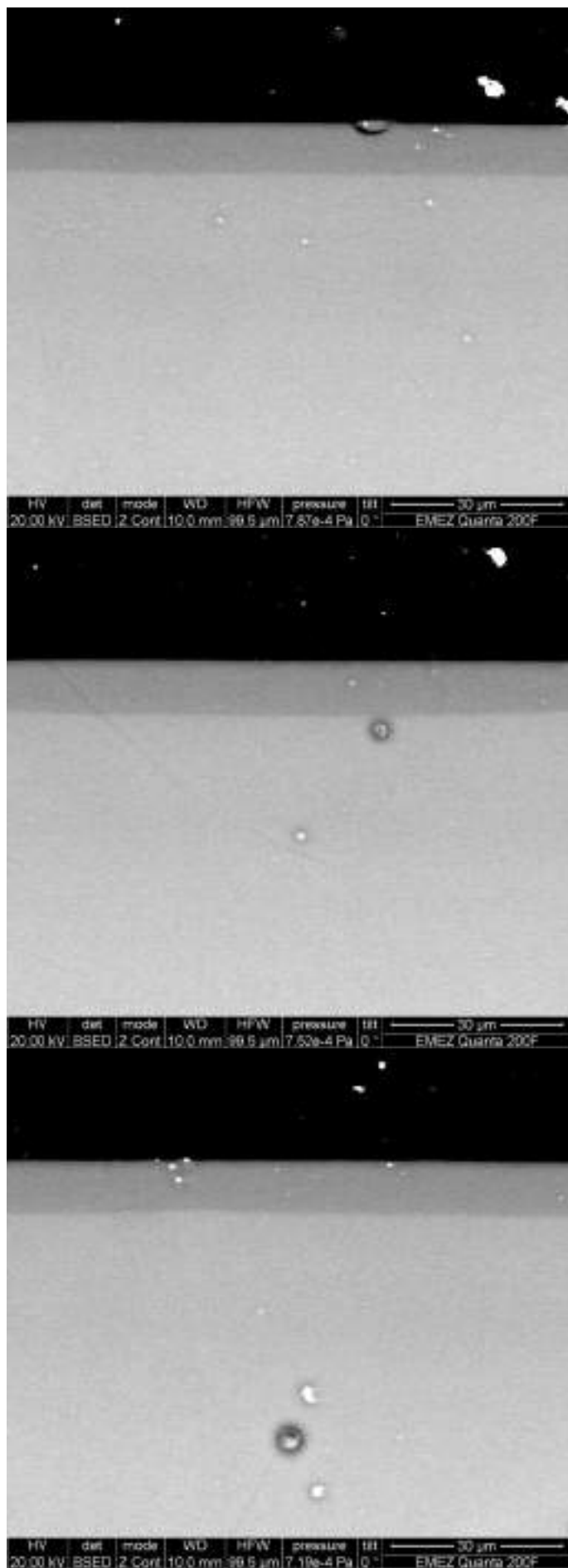


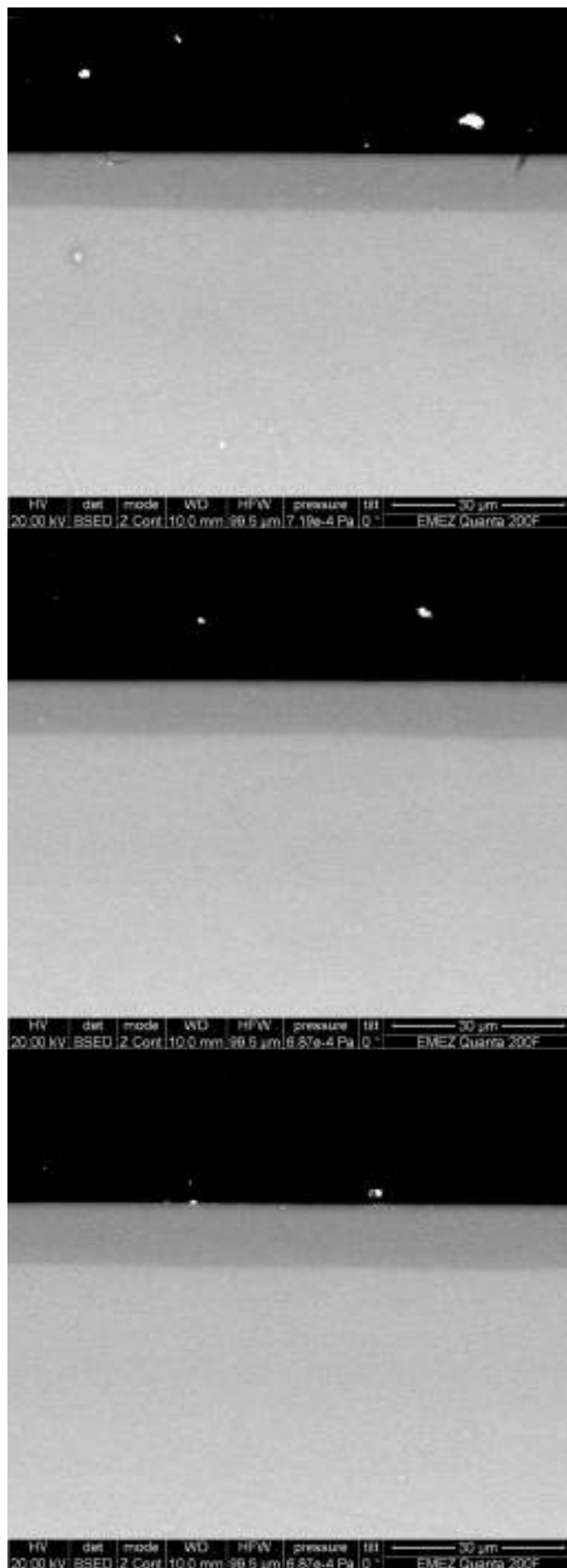
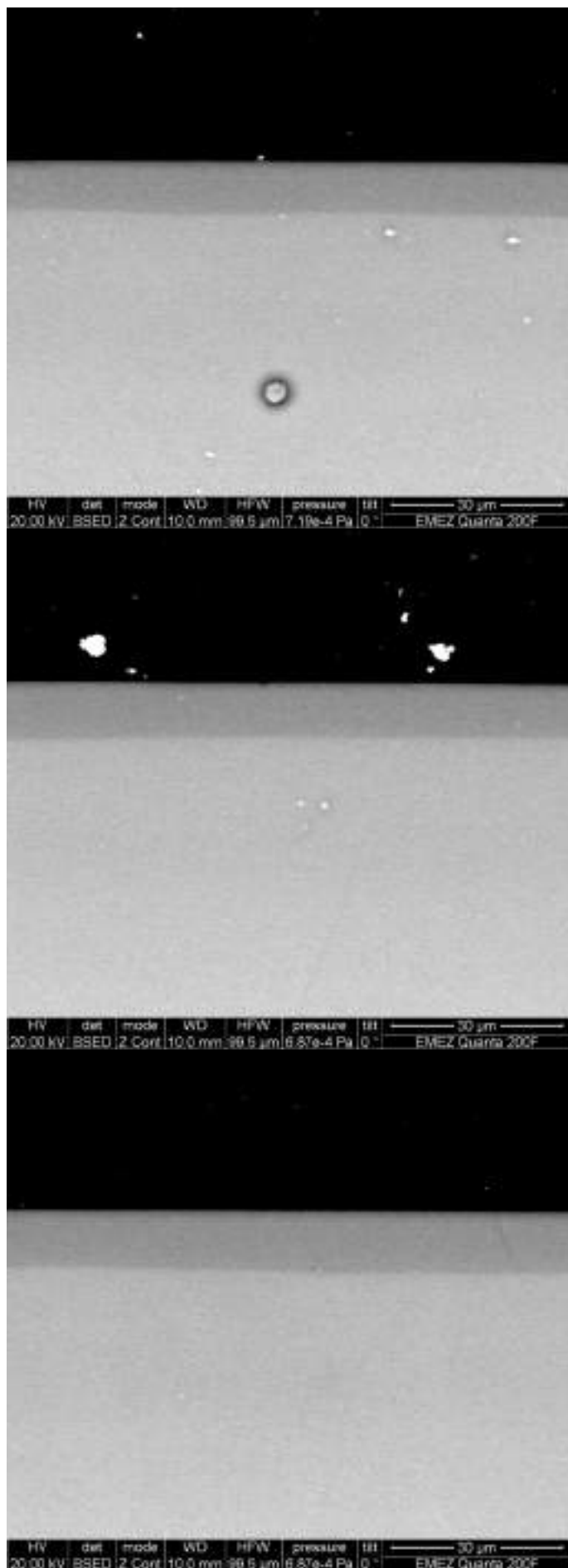


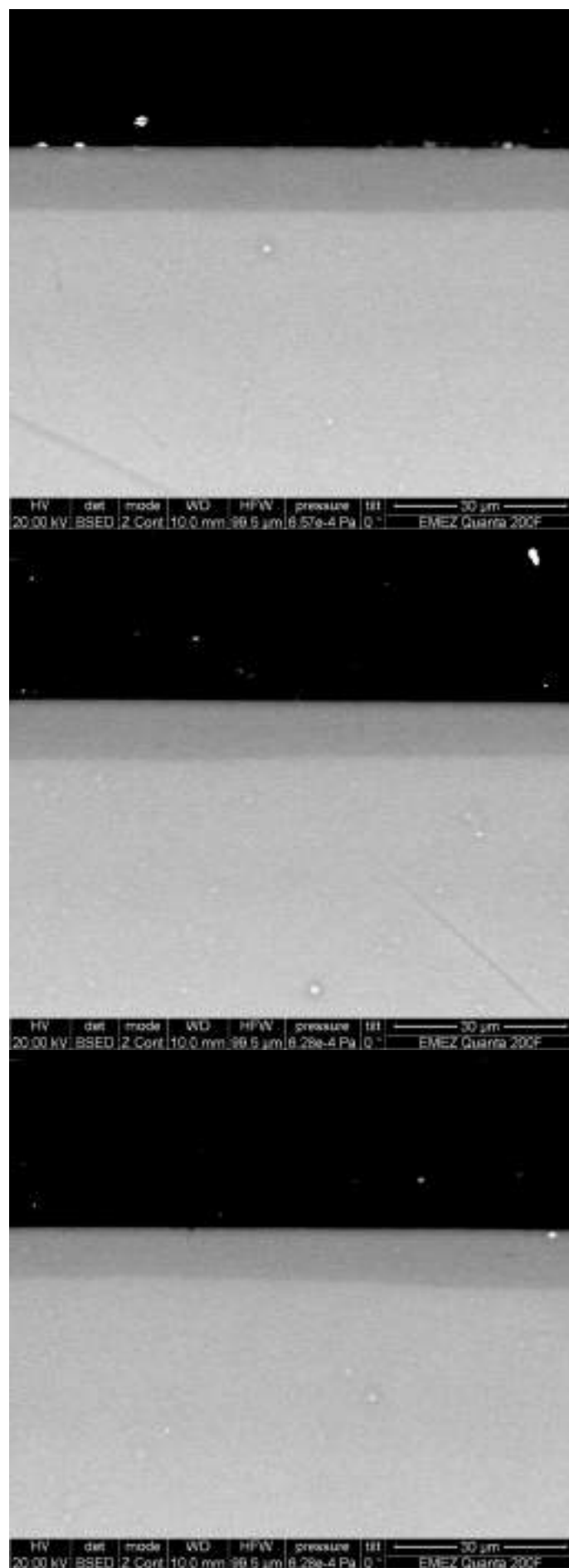
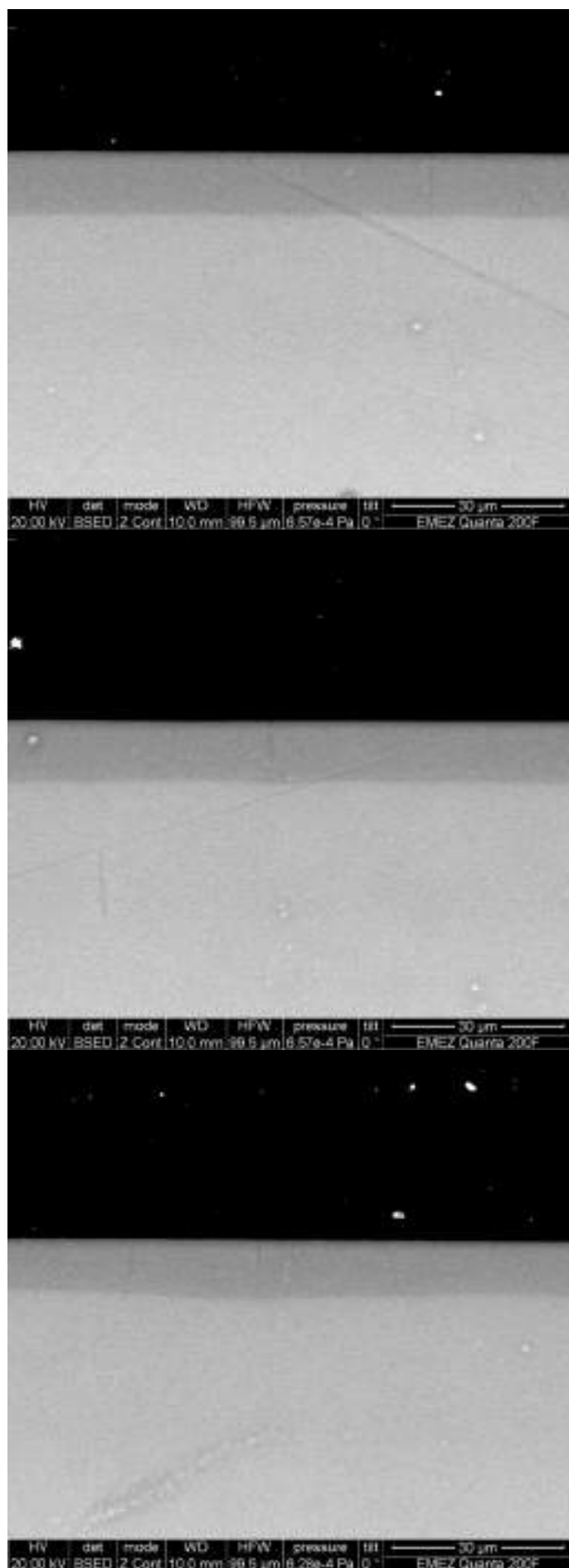


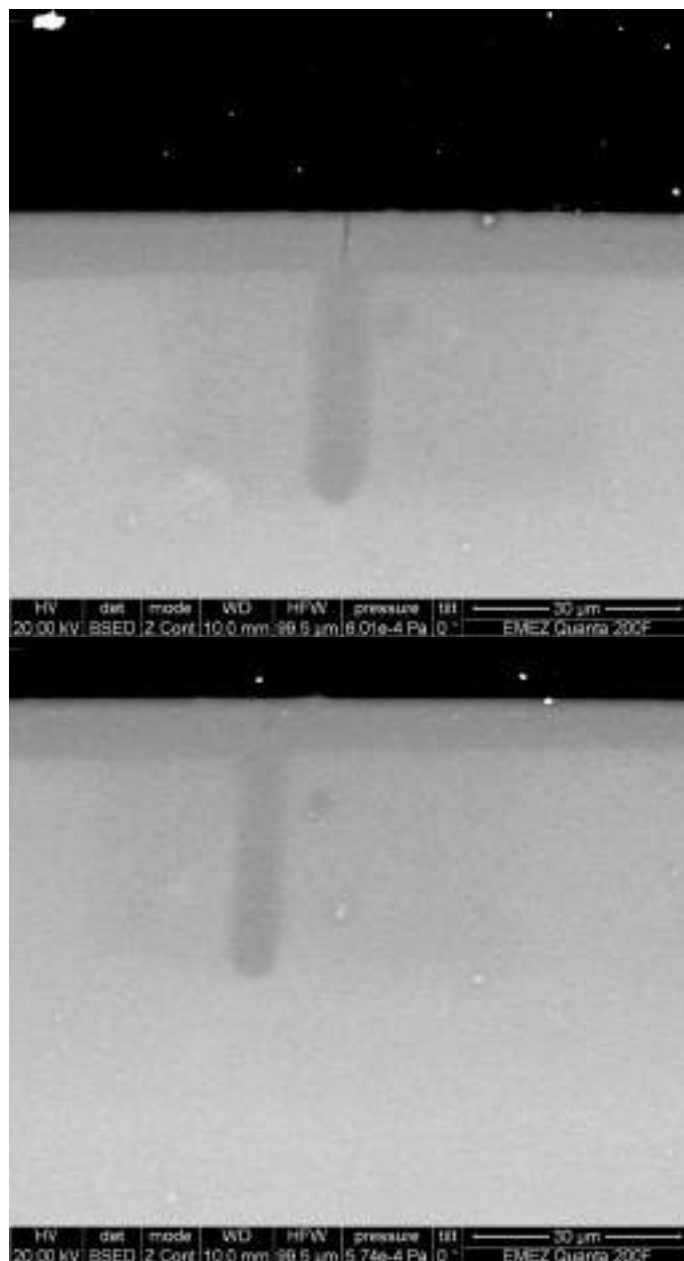
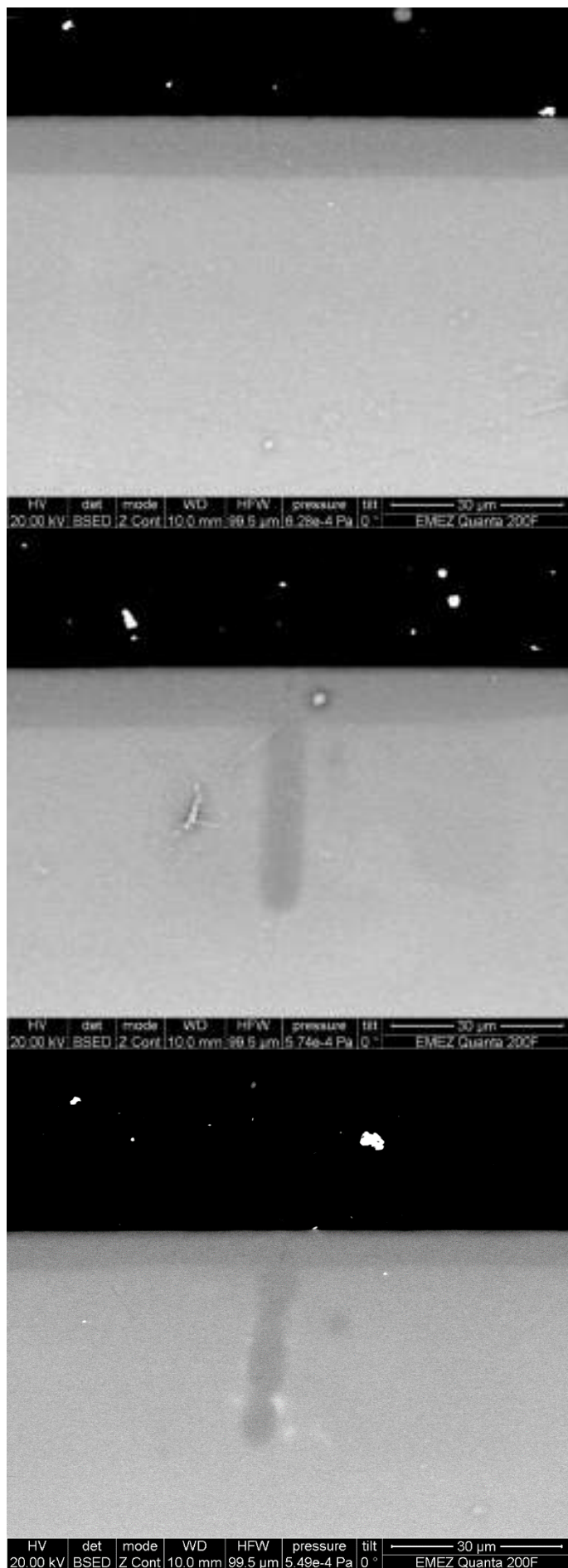




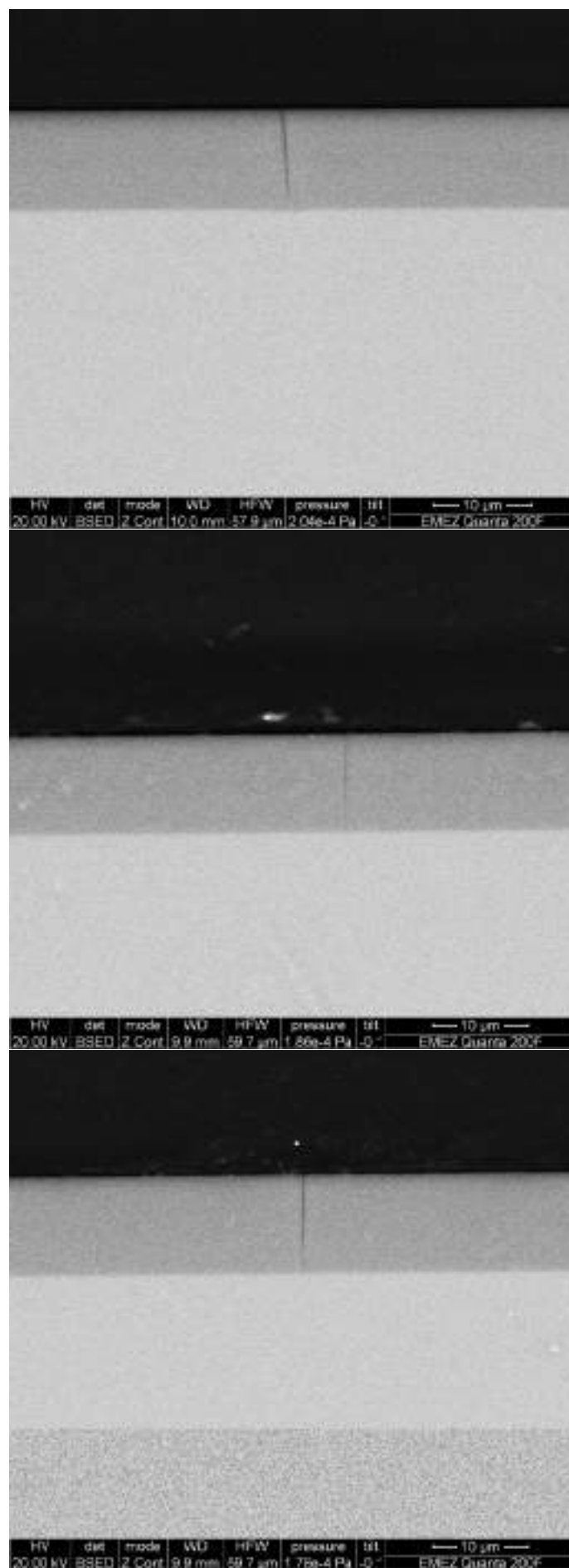
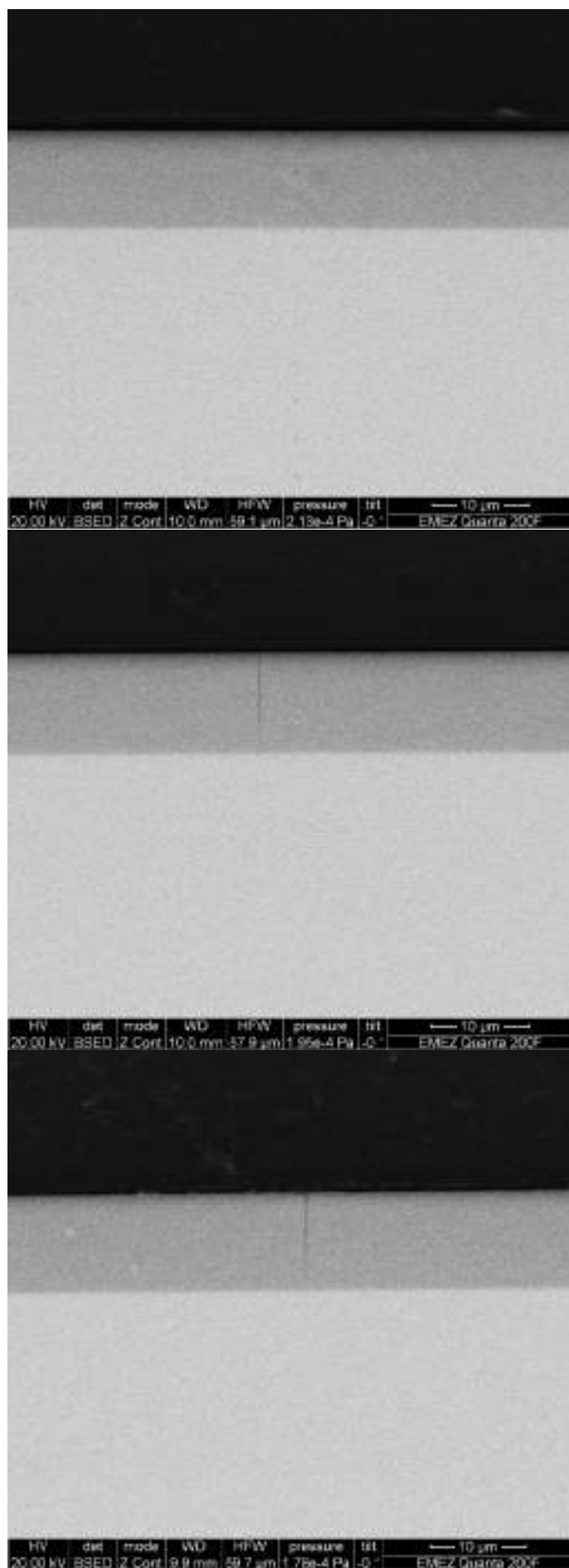


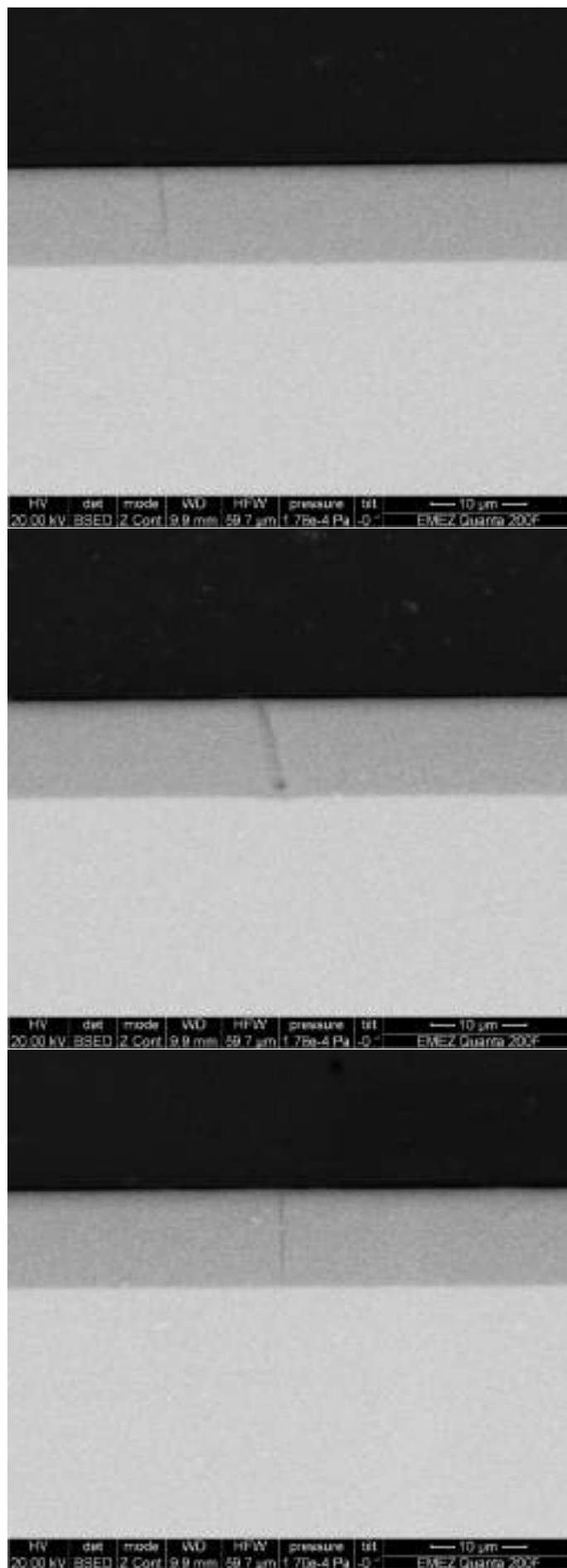
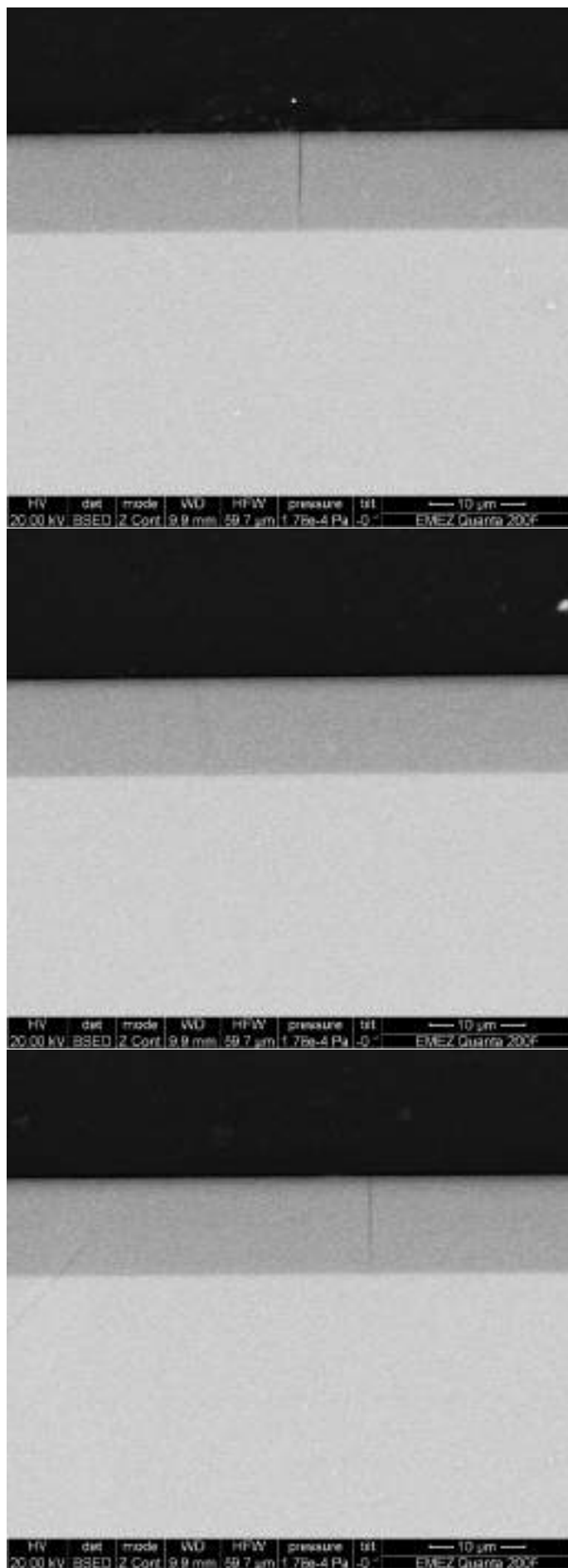


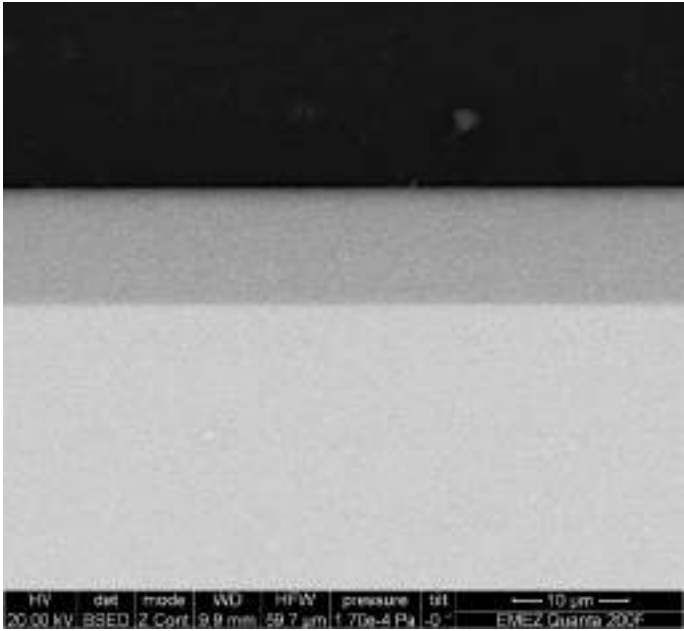




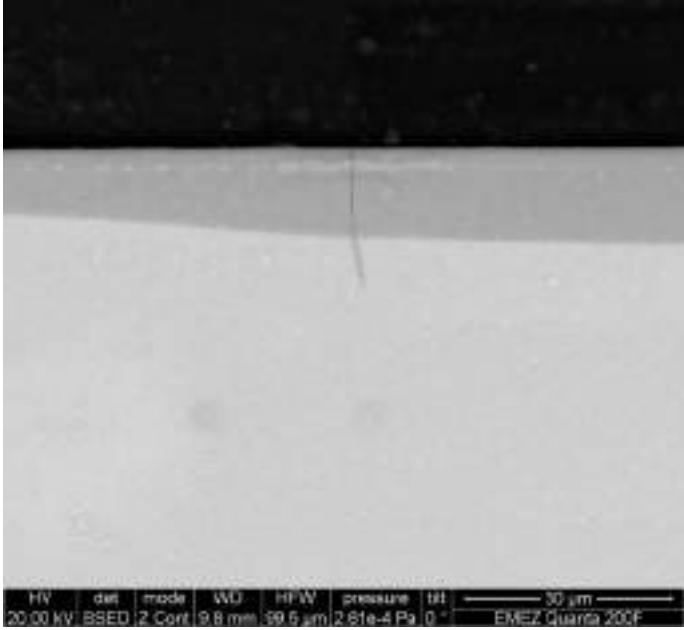
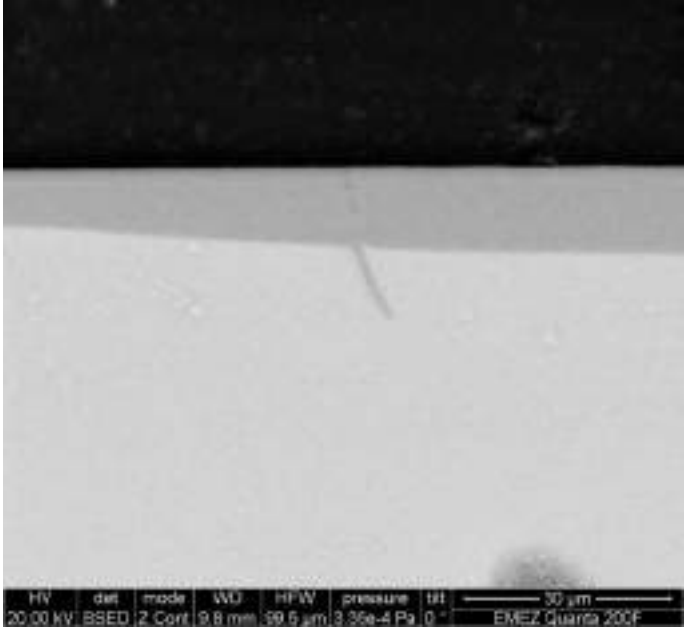
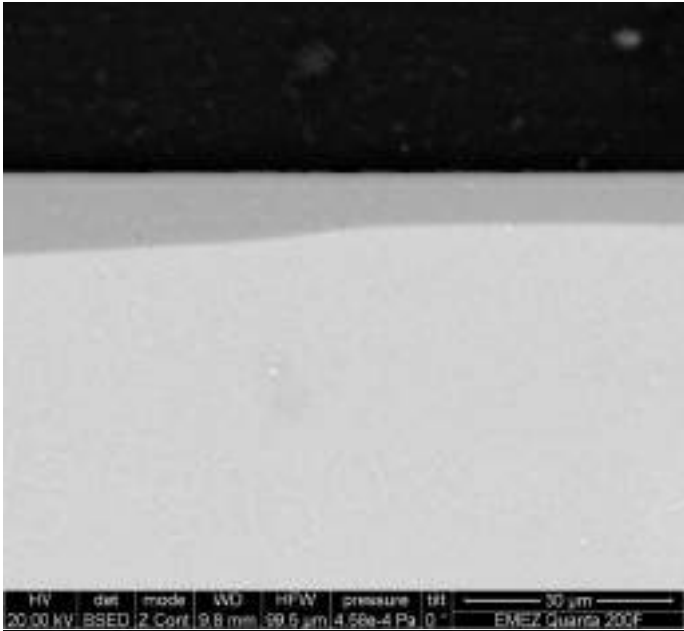
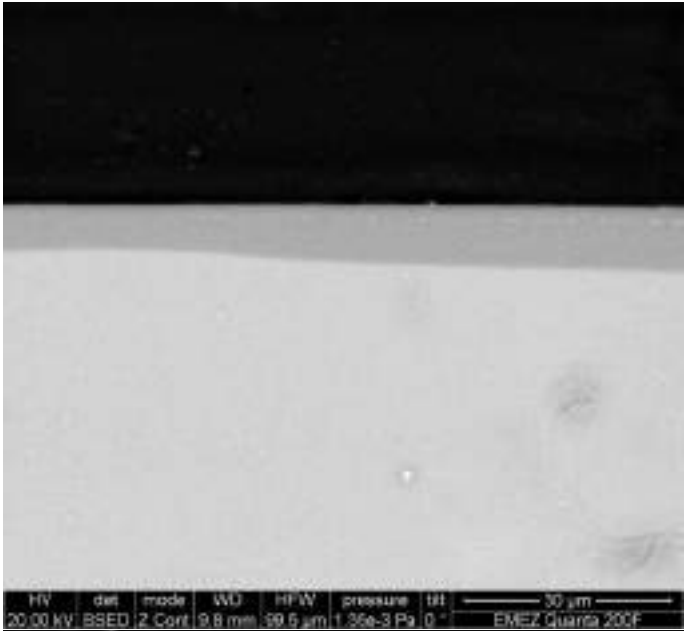
PV 0 months (3 months aging in saturated salt solutions)

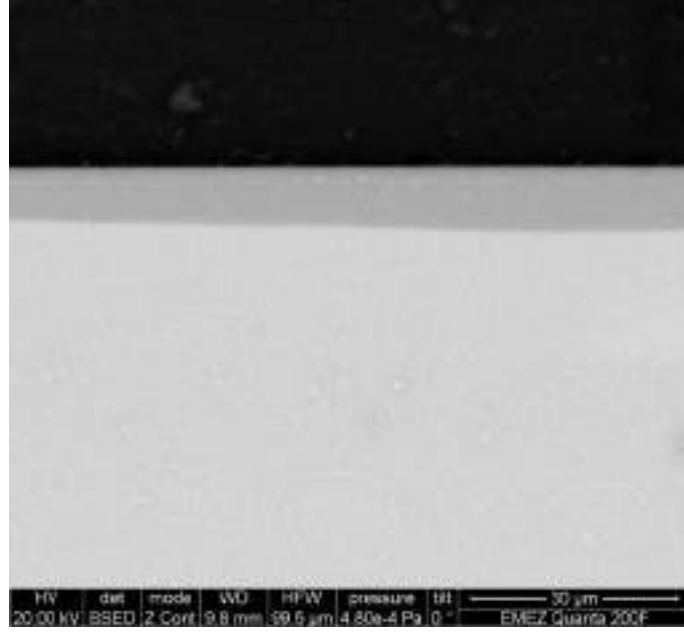
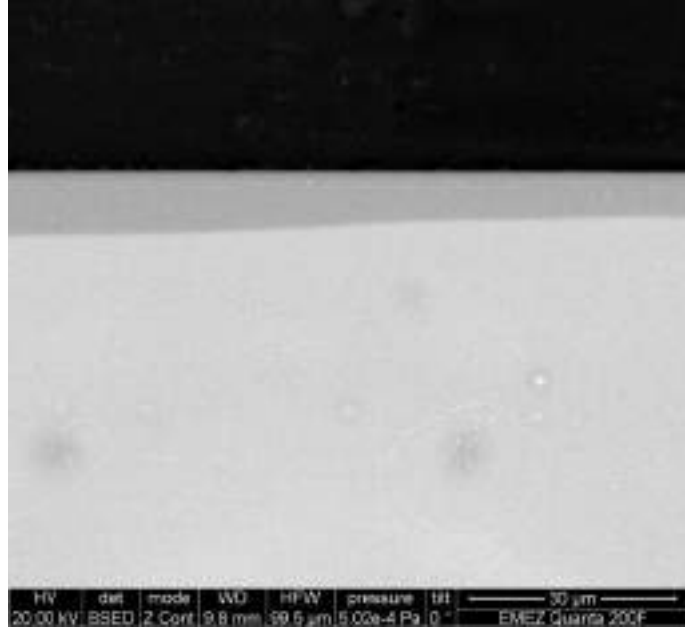
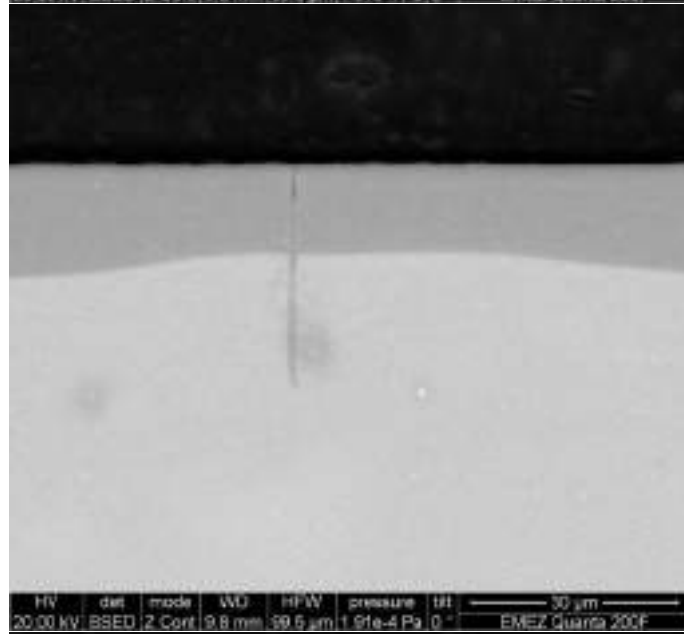
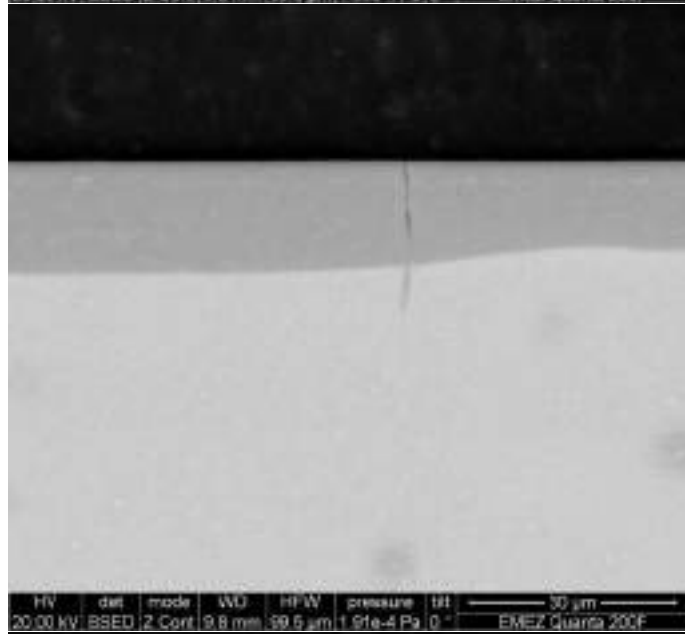
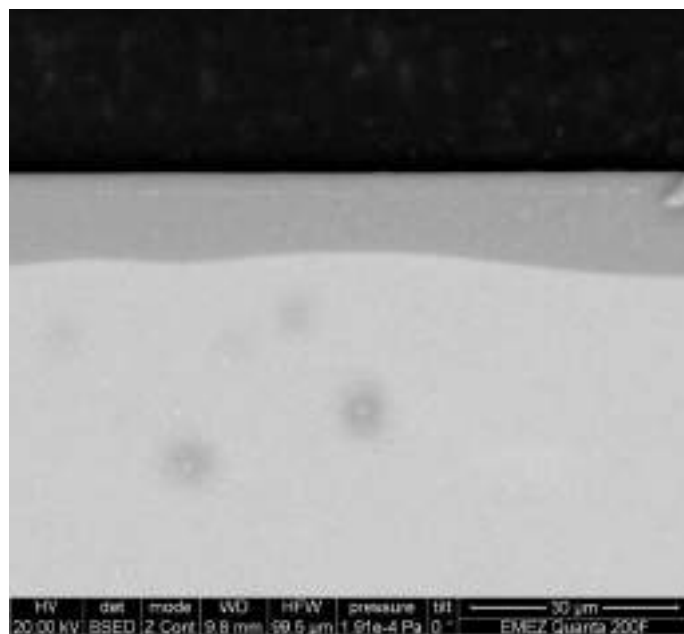
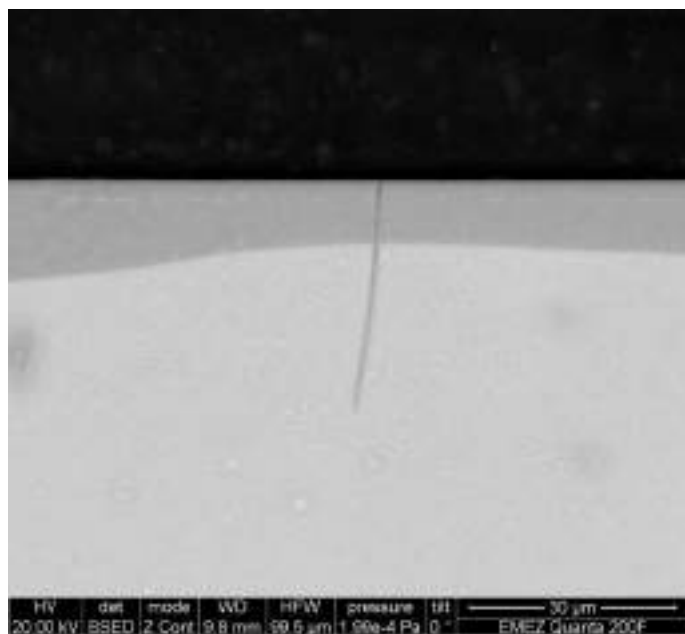


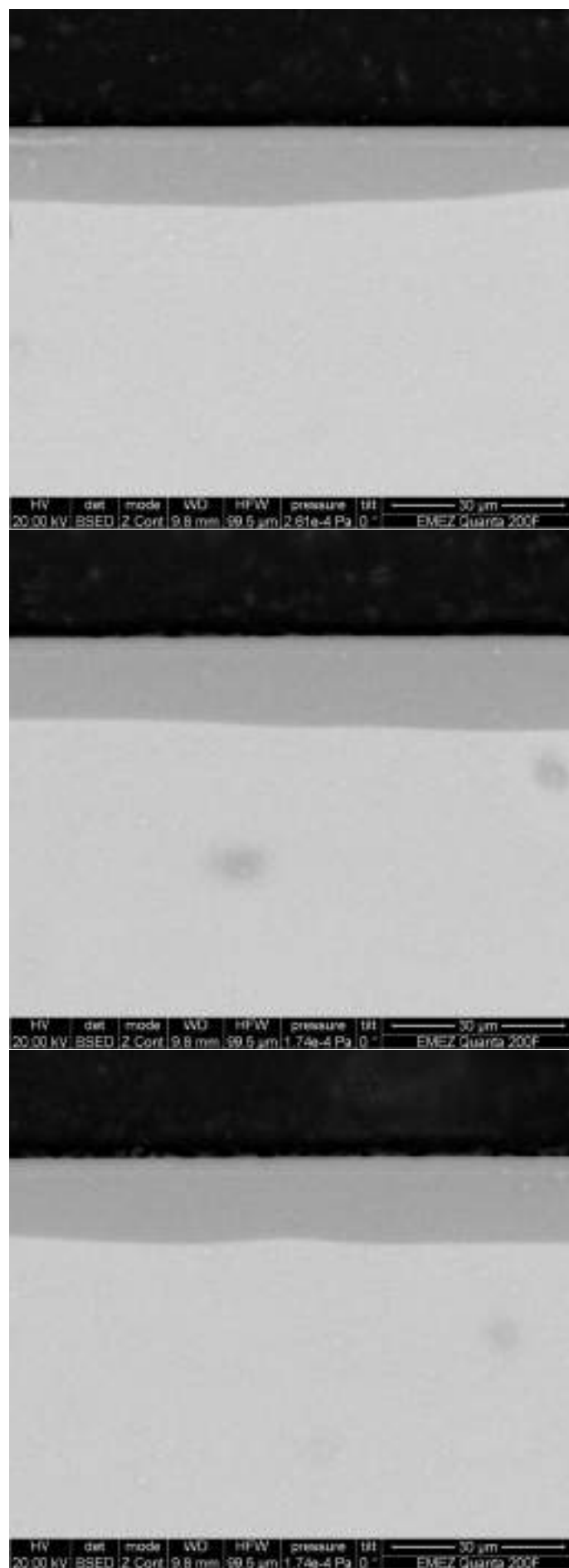
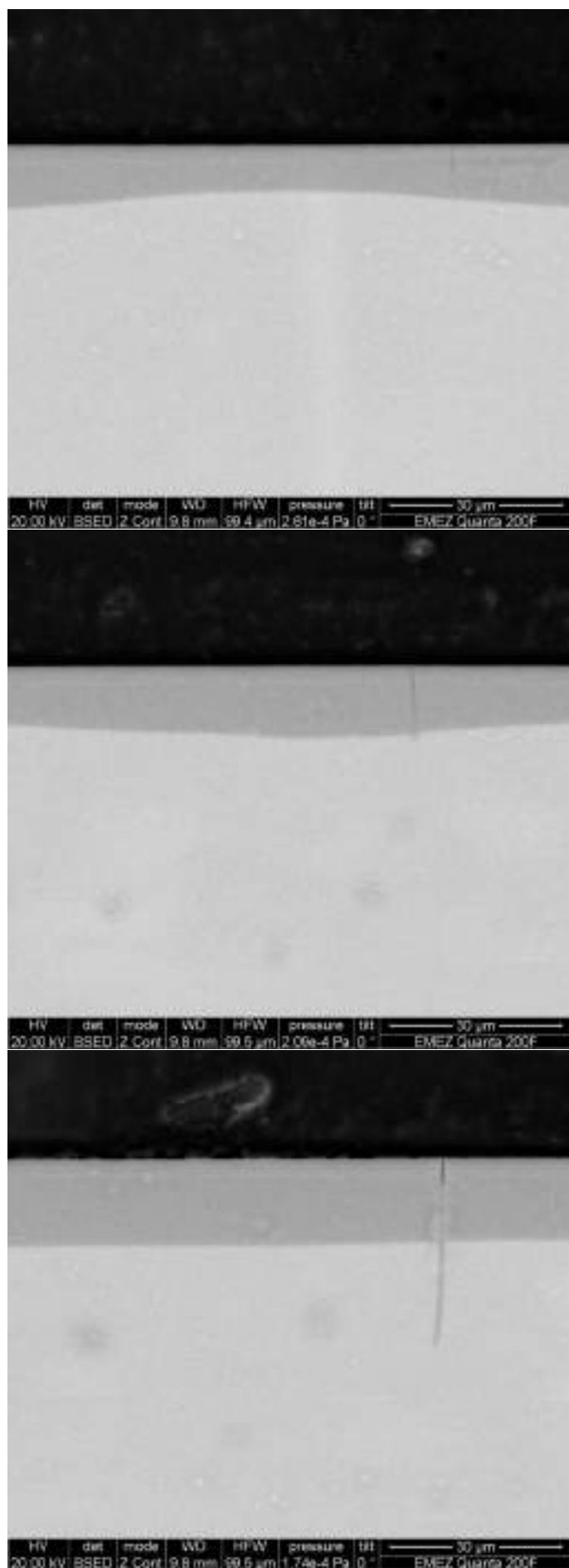


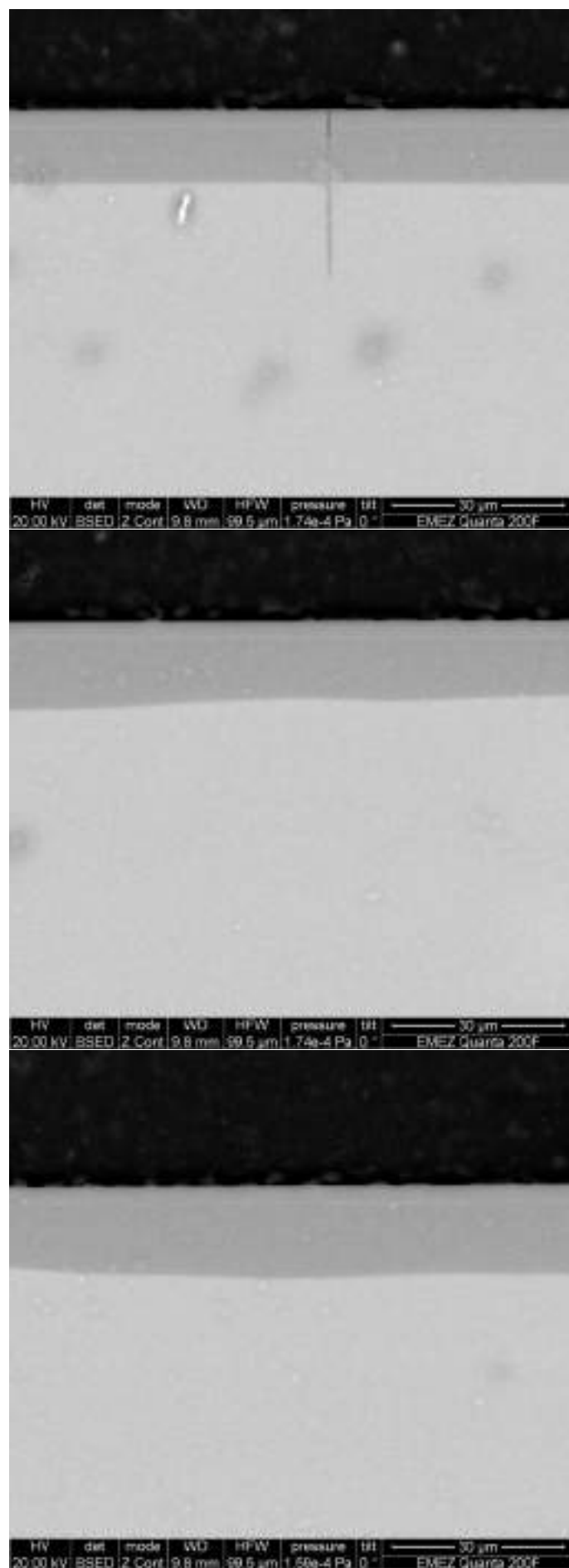
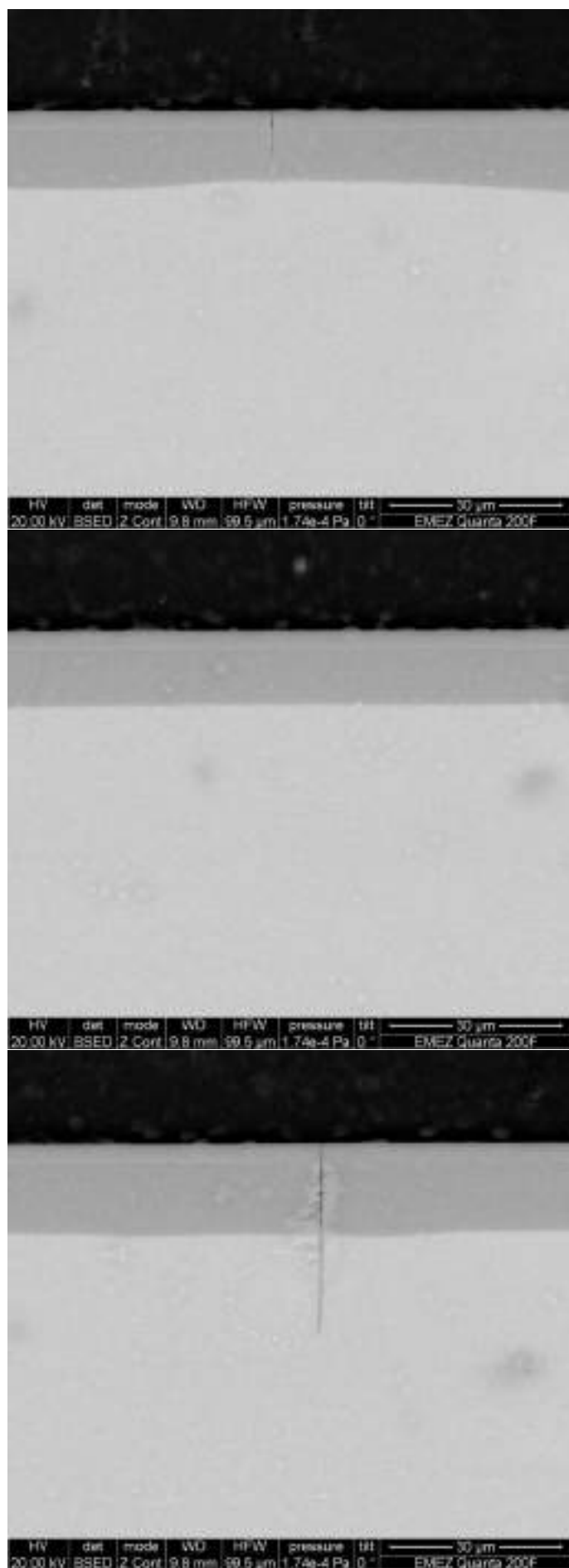


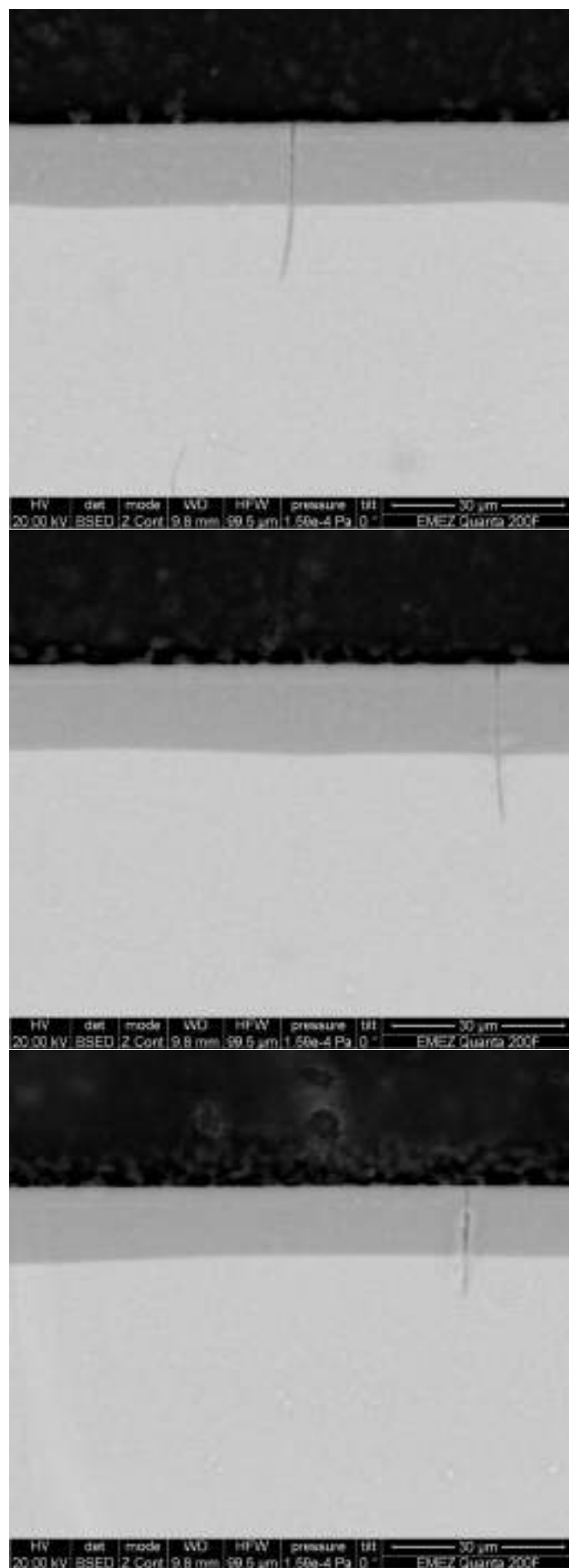
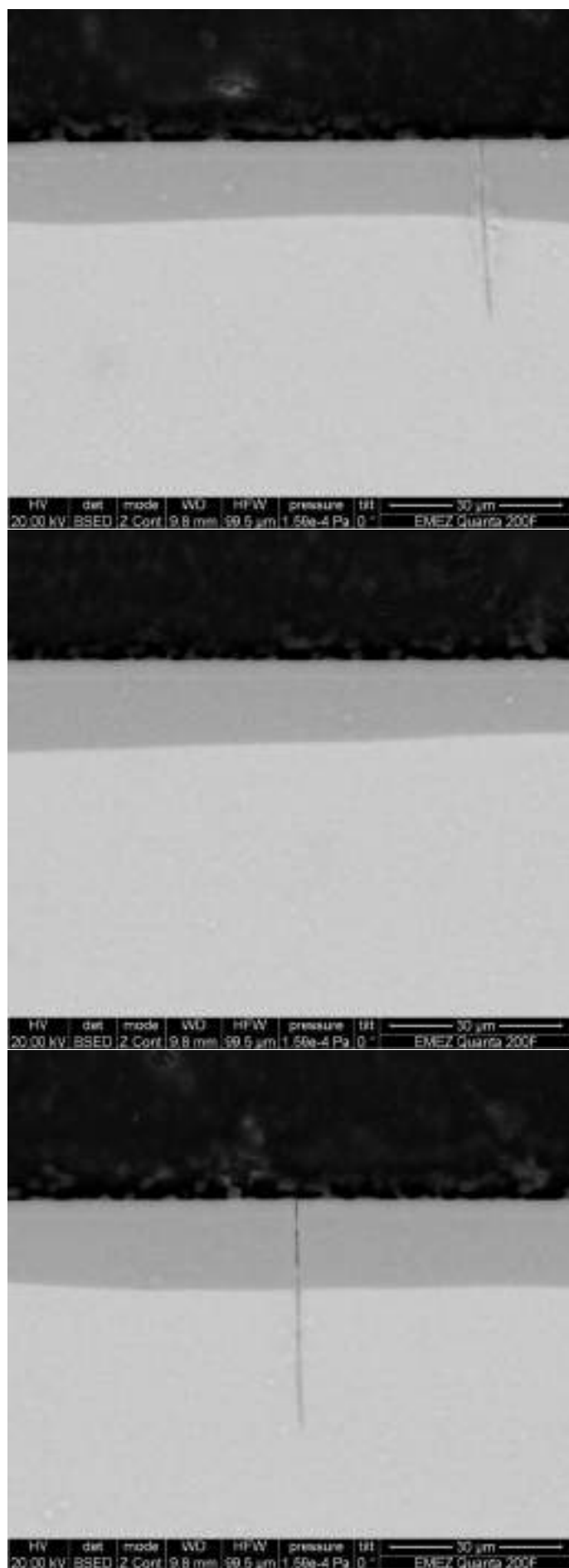
PV 3 months

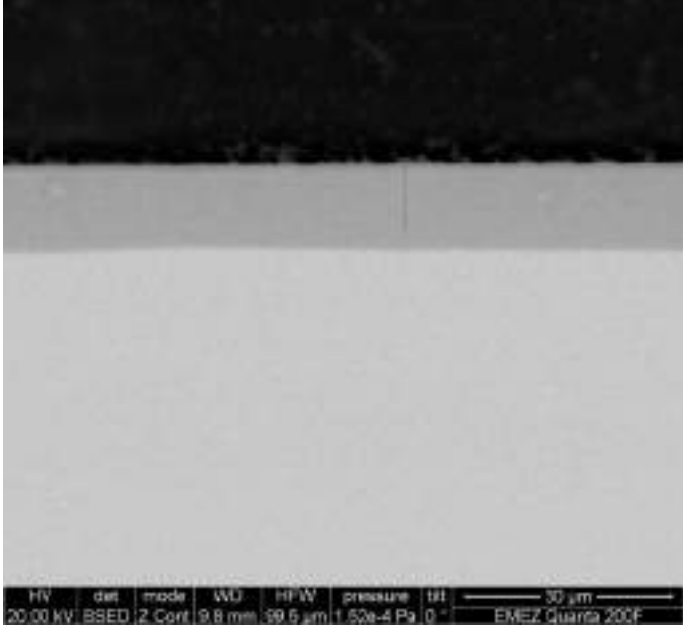
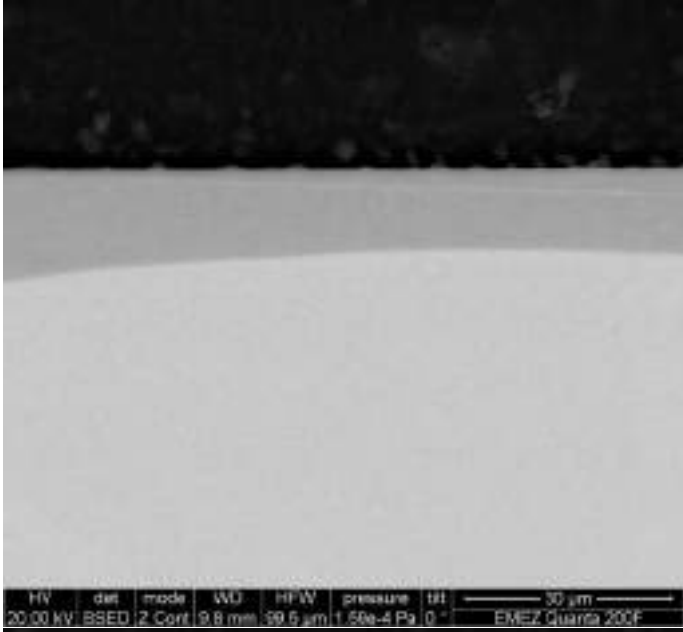
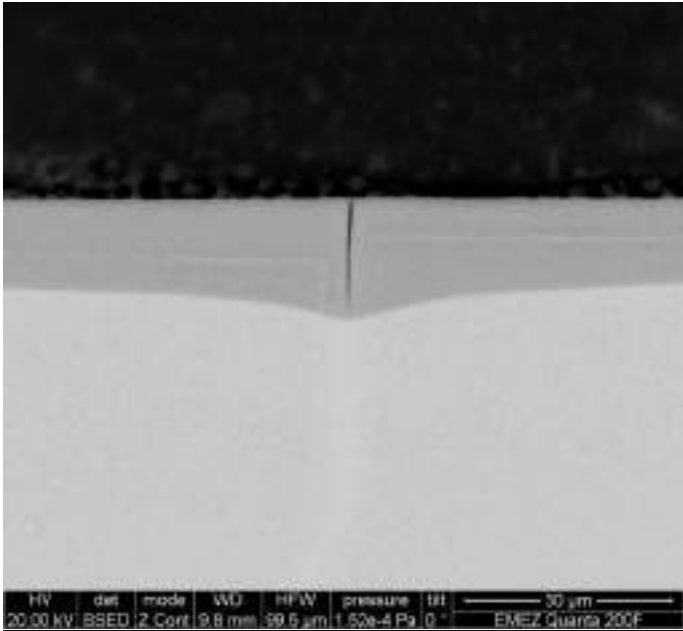
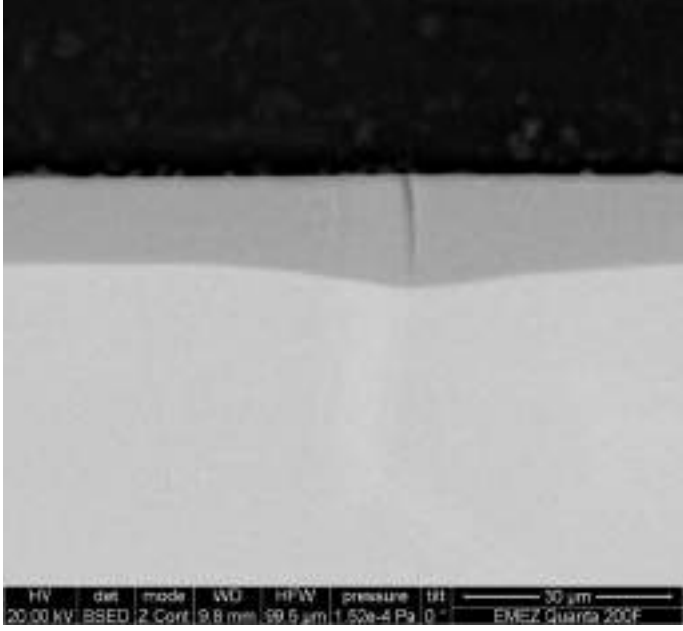
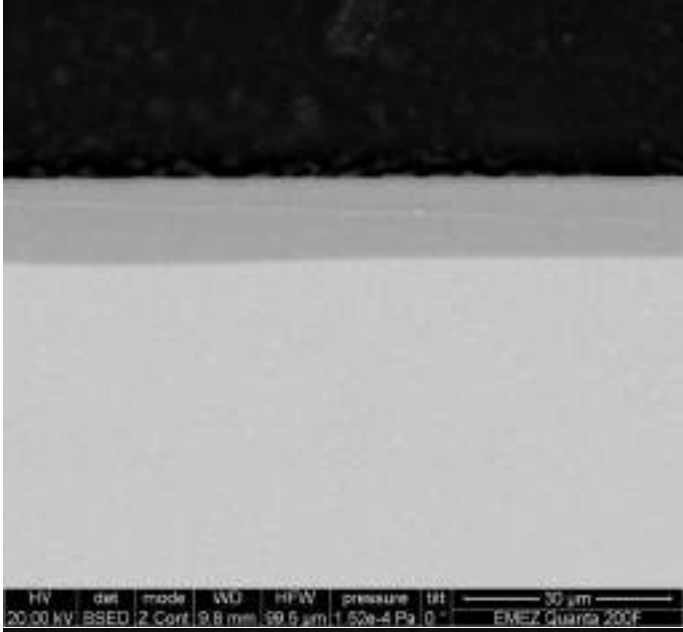
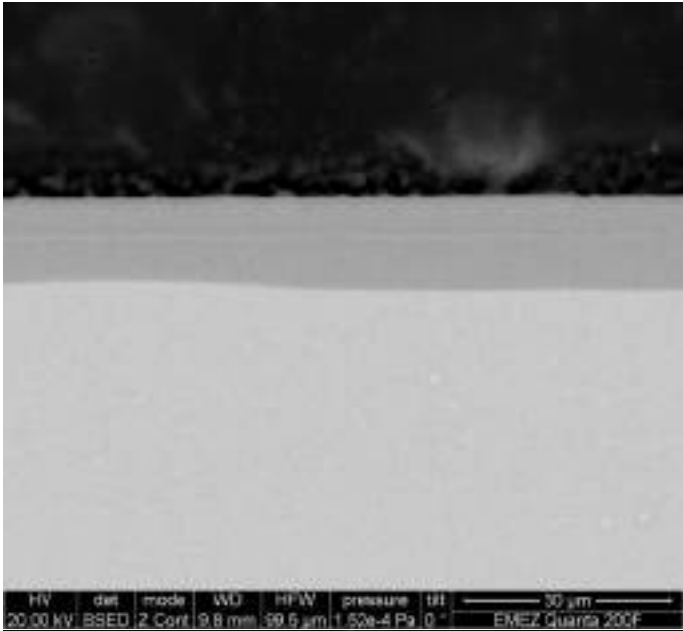


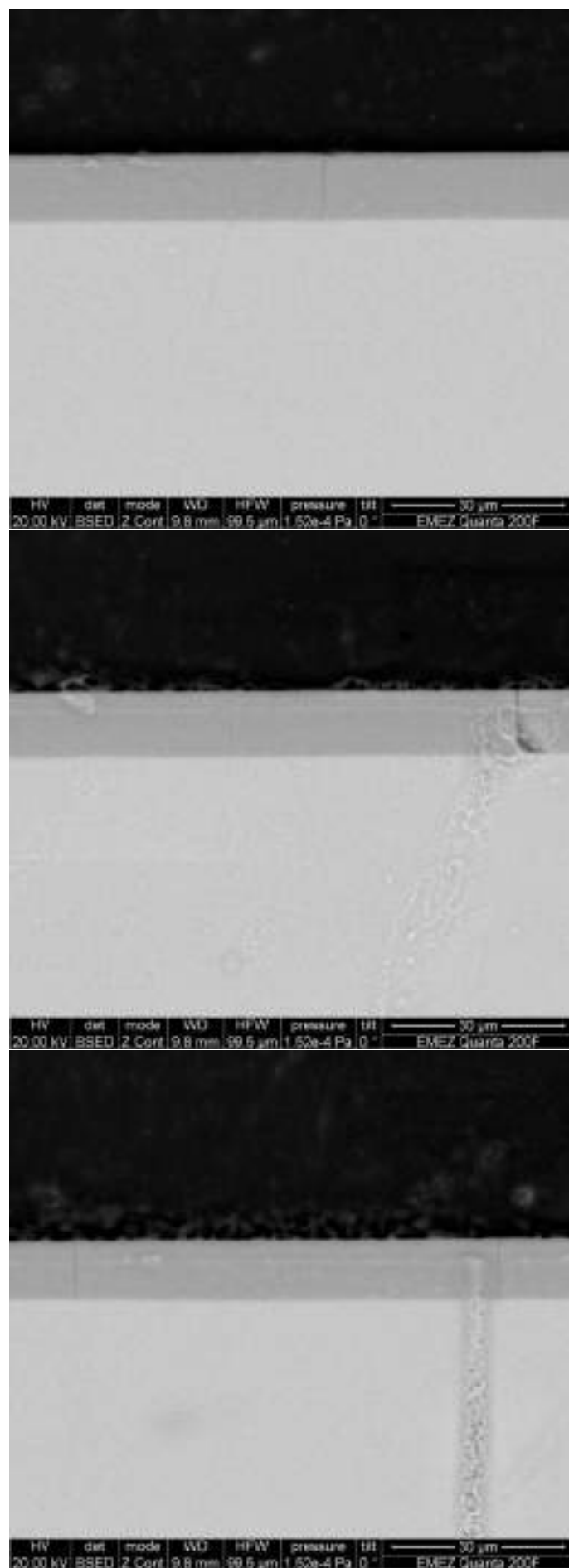
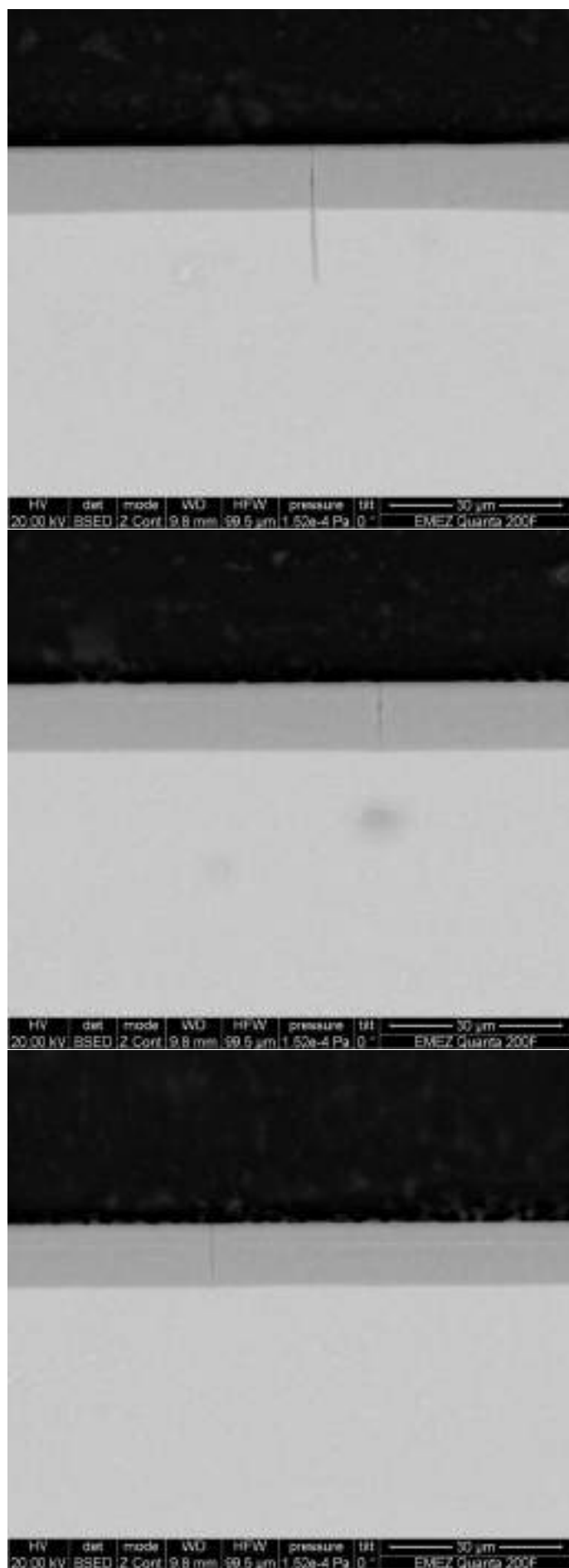


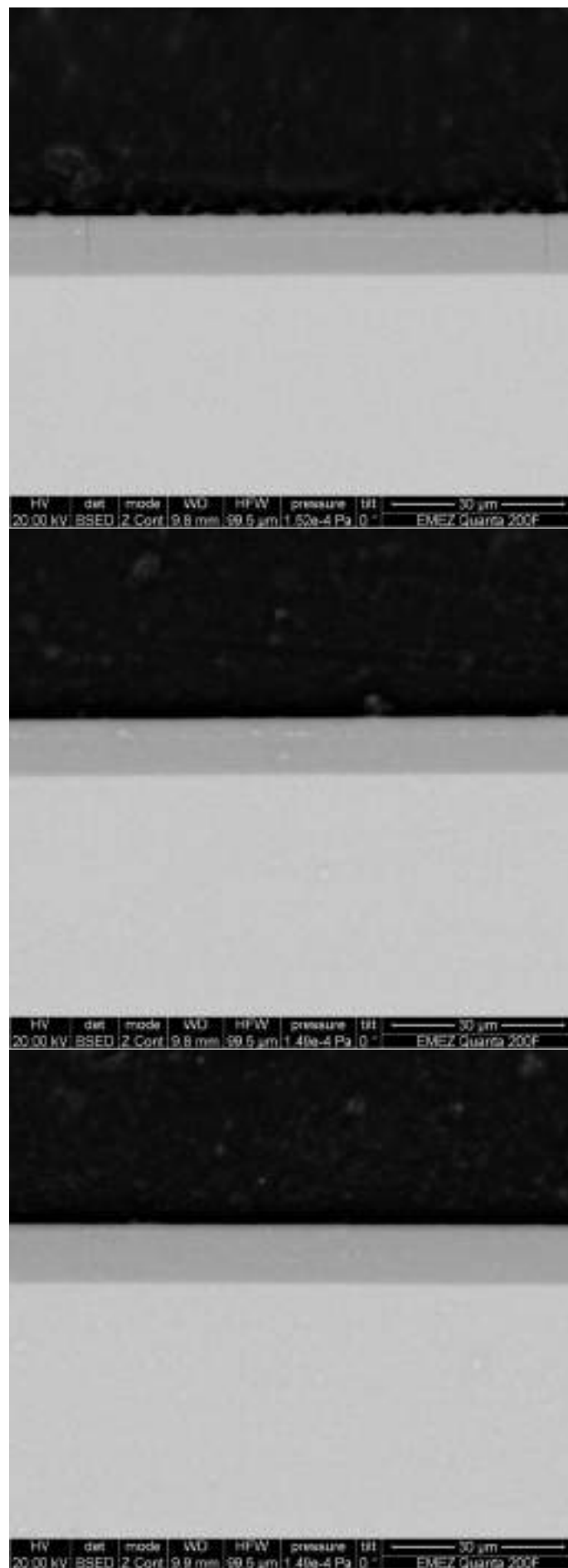


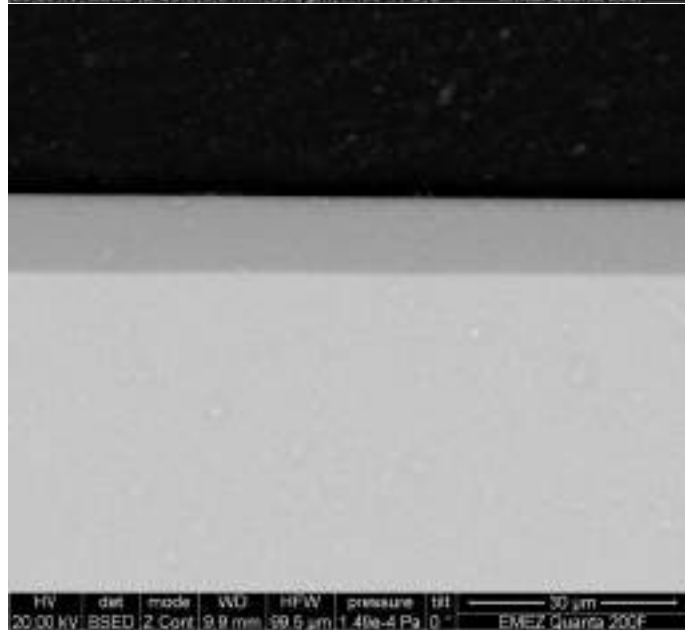
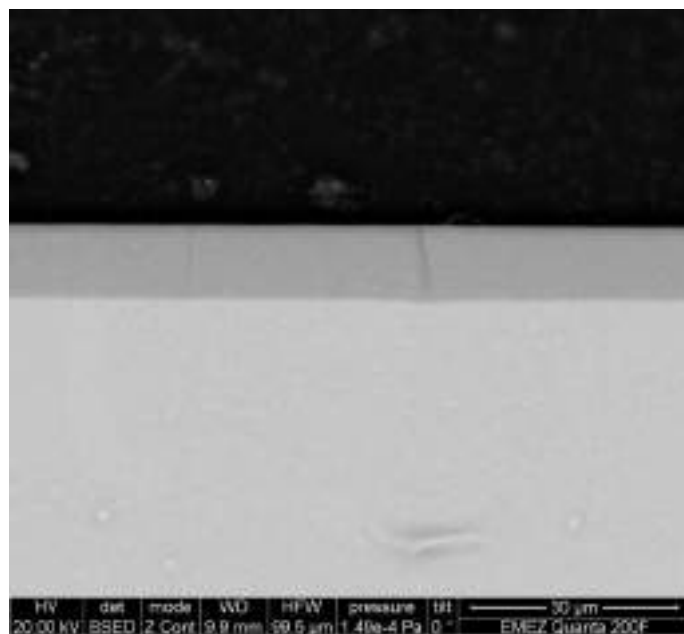
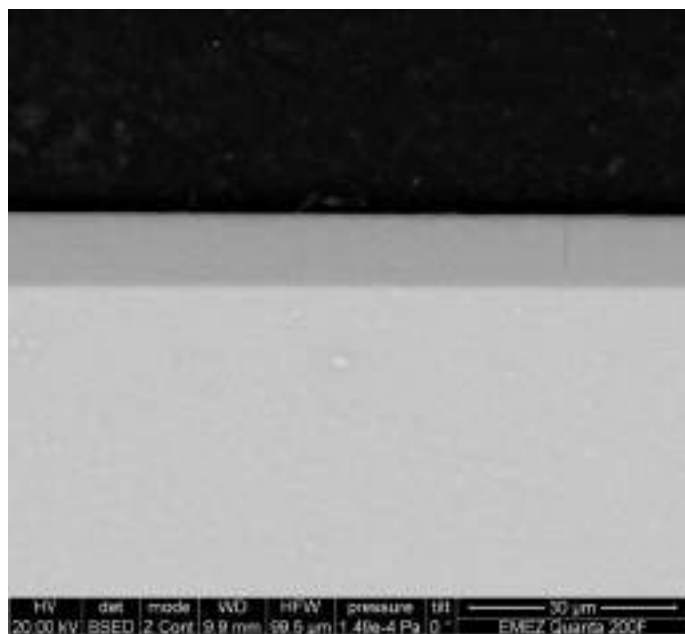




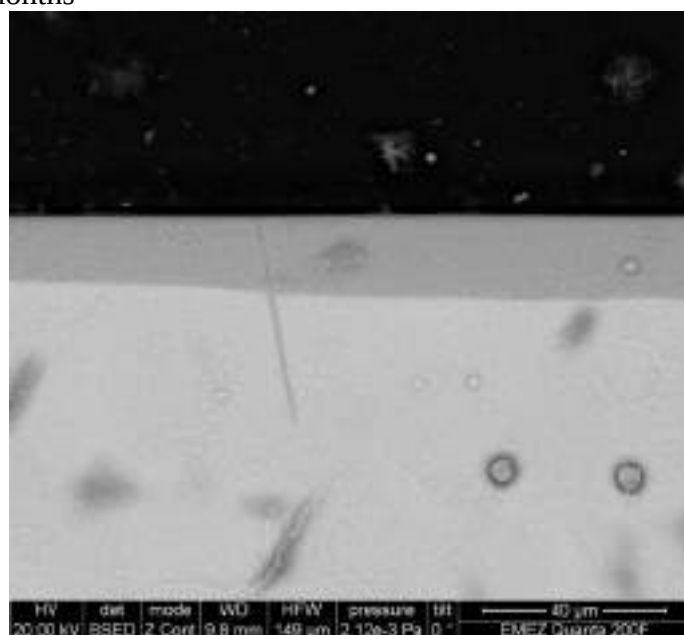
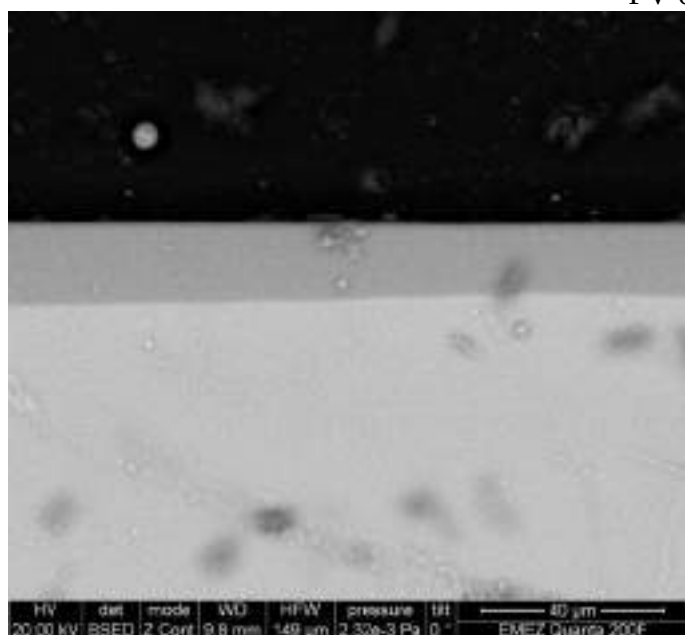


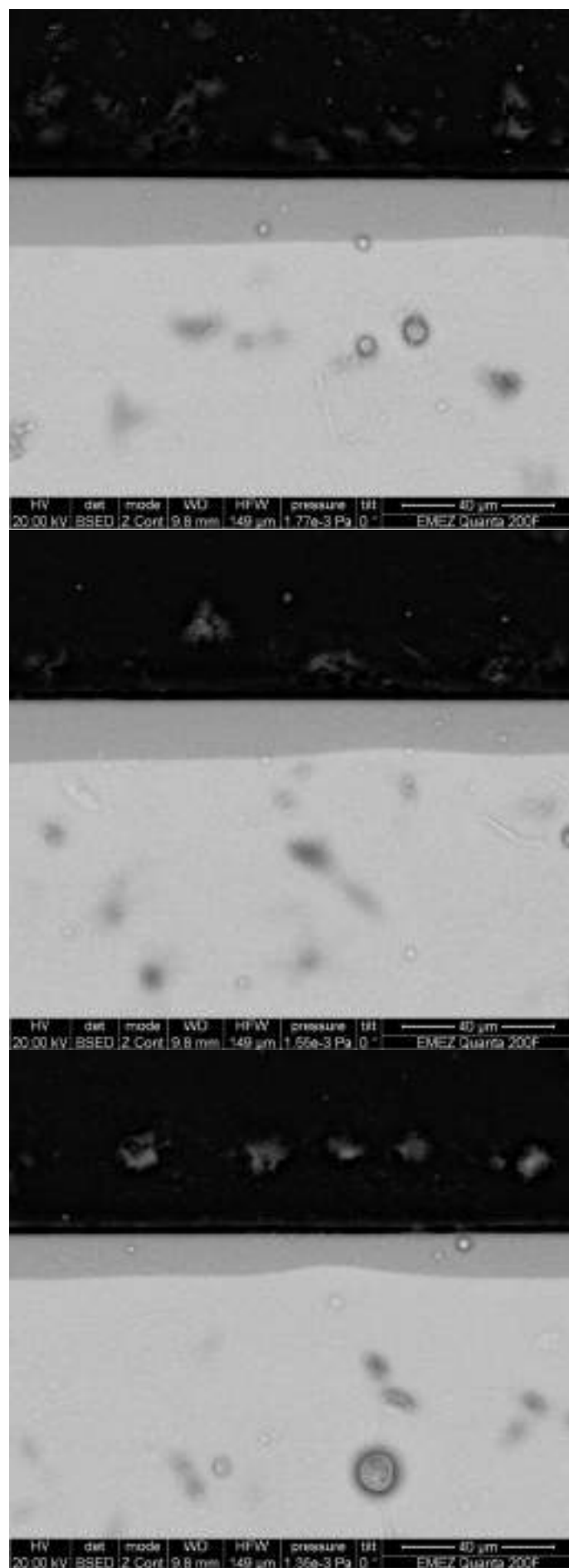
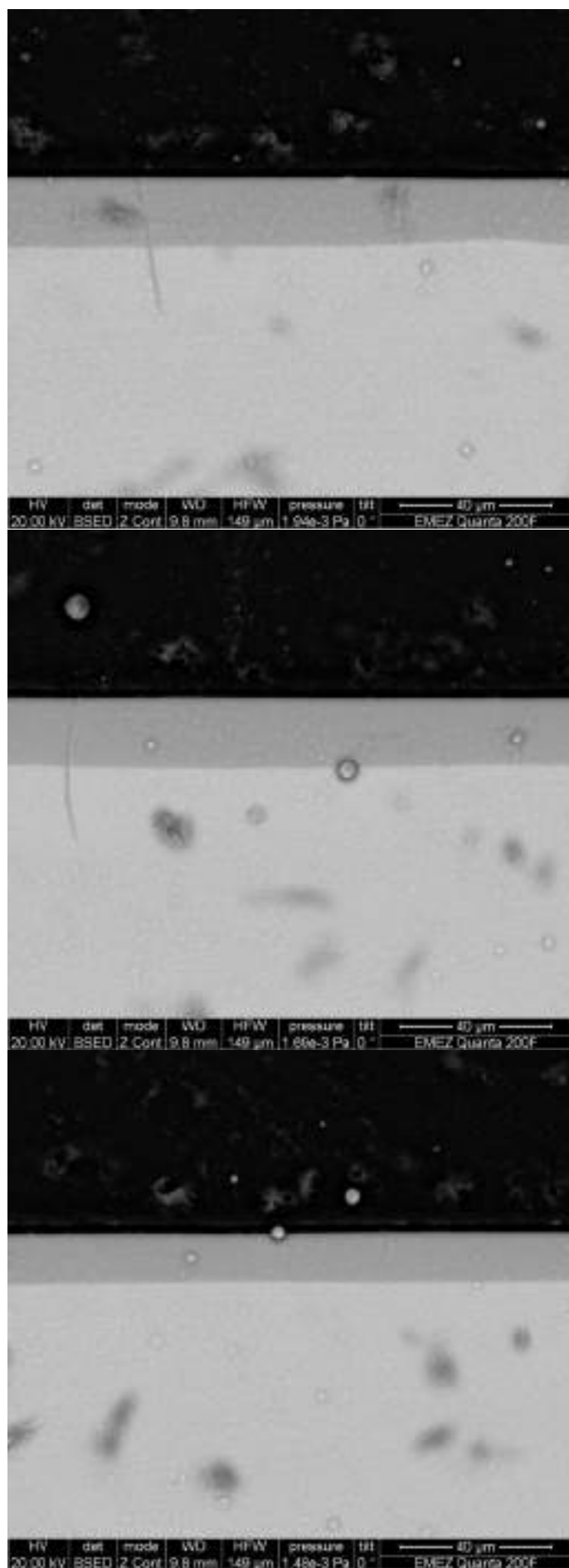


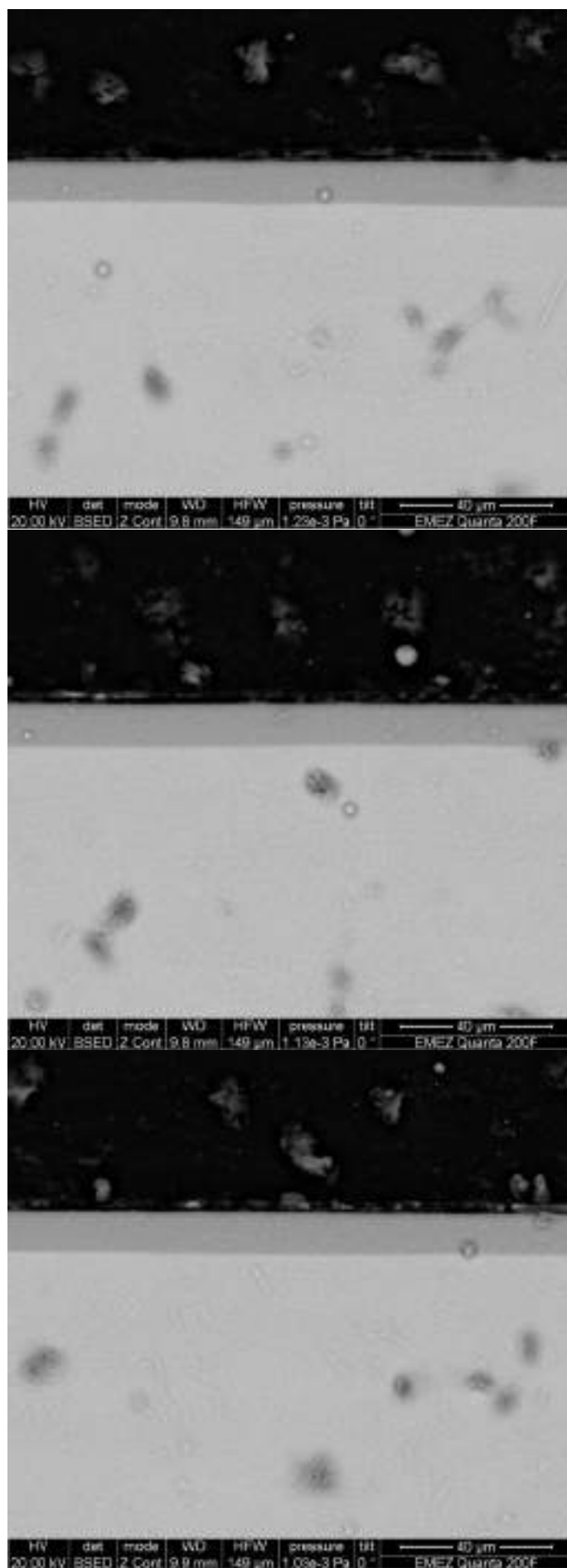
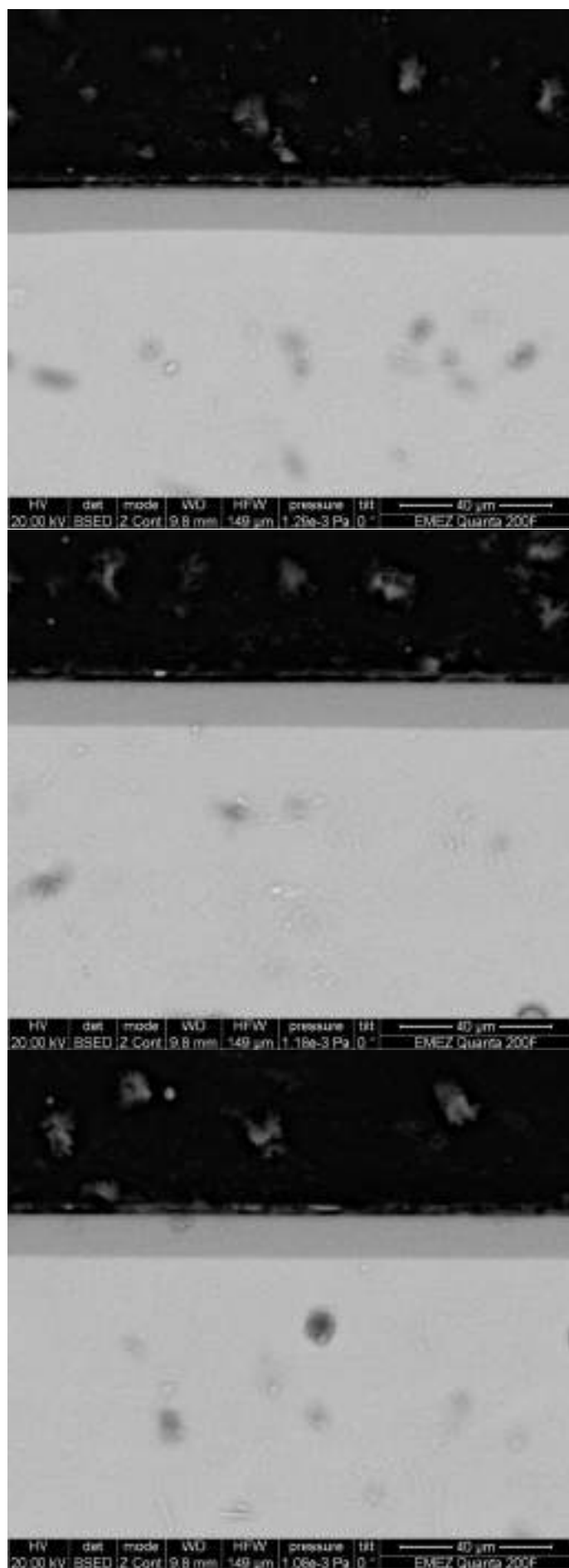


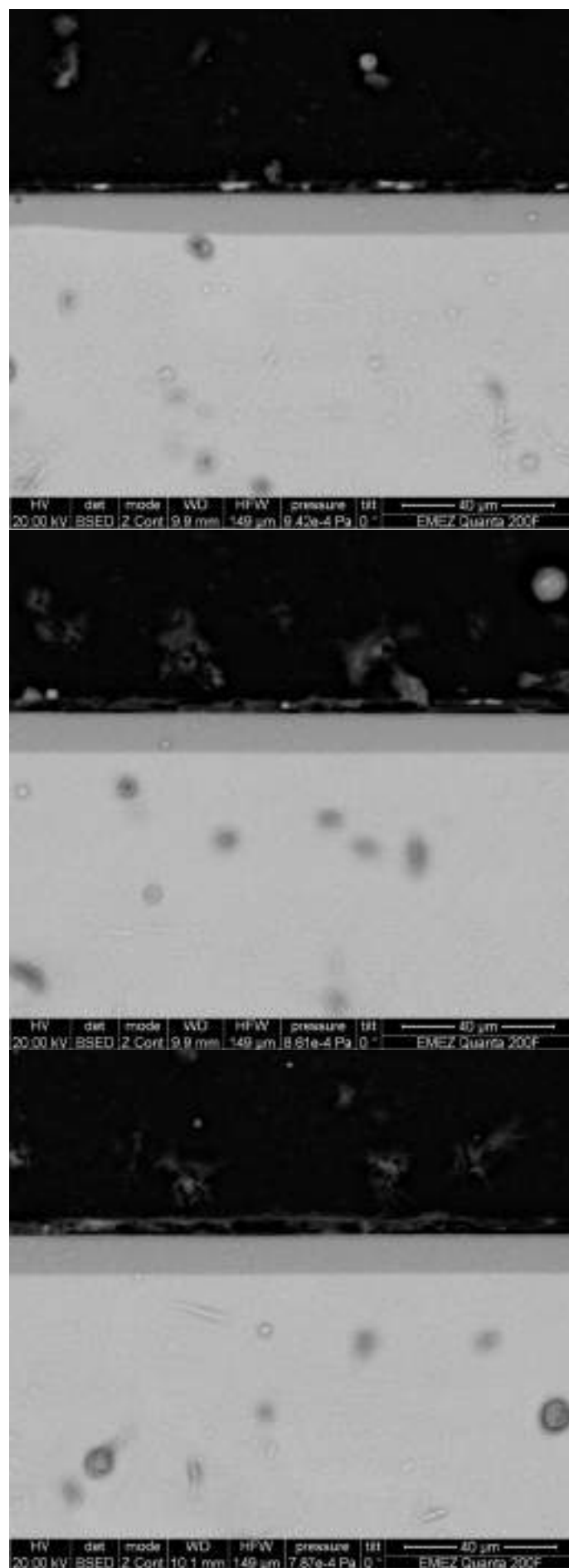
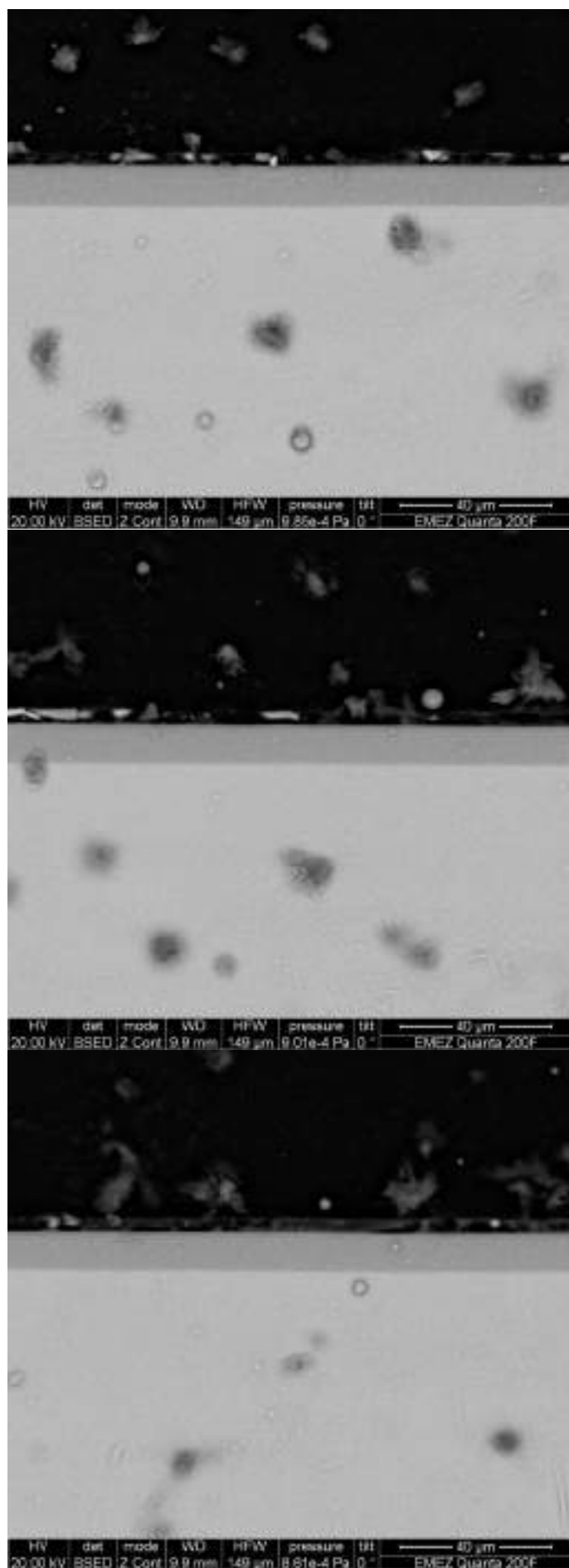


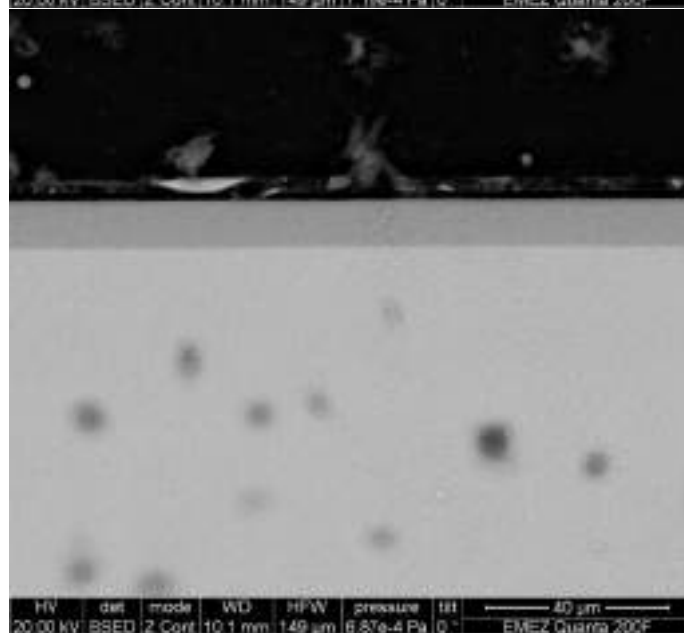
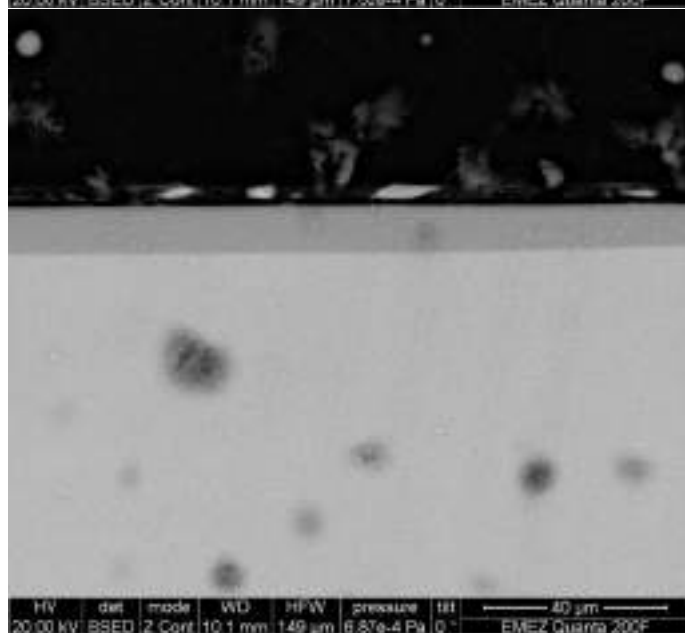
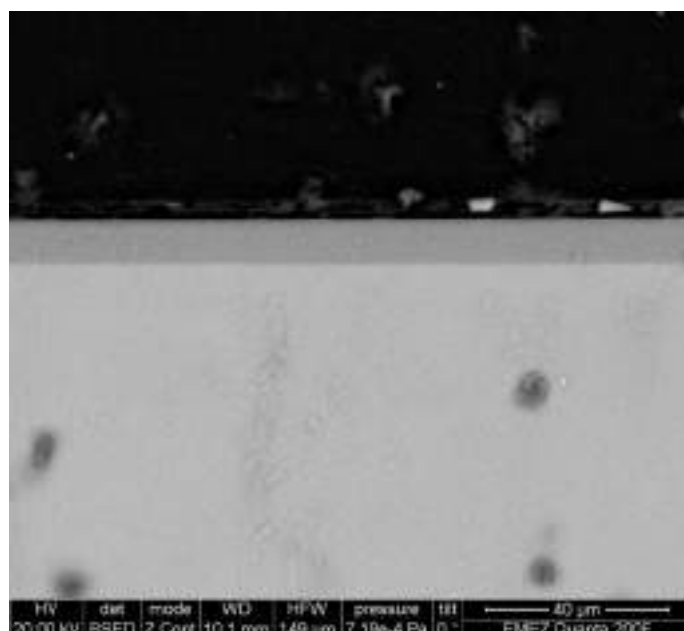
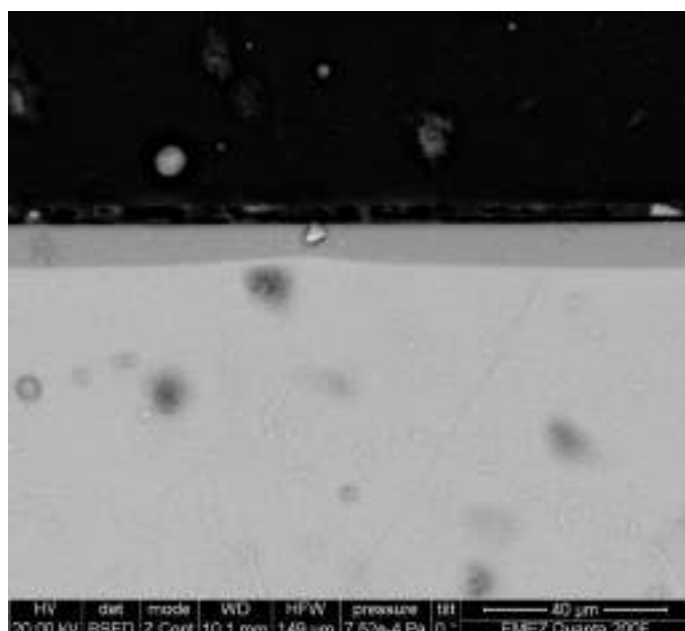
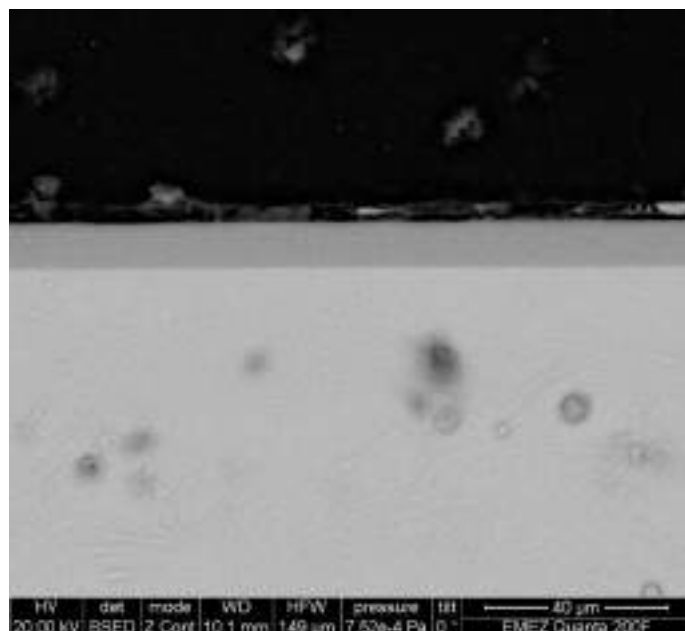
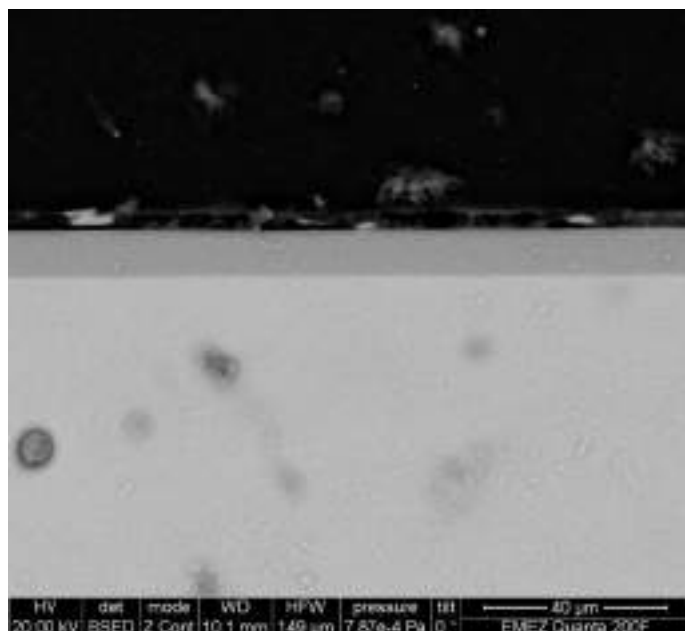
PV 6 months

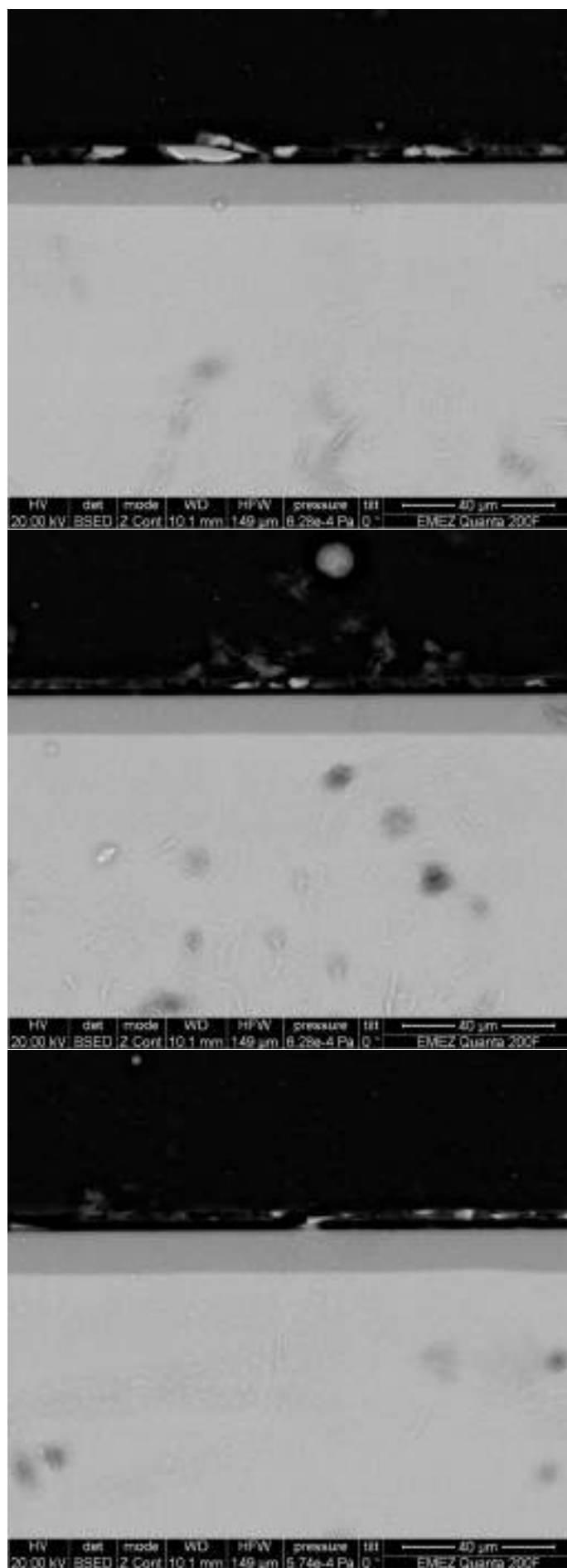
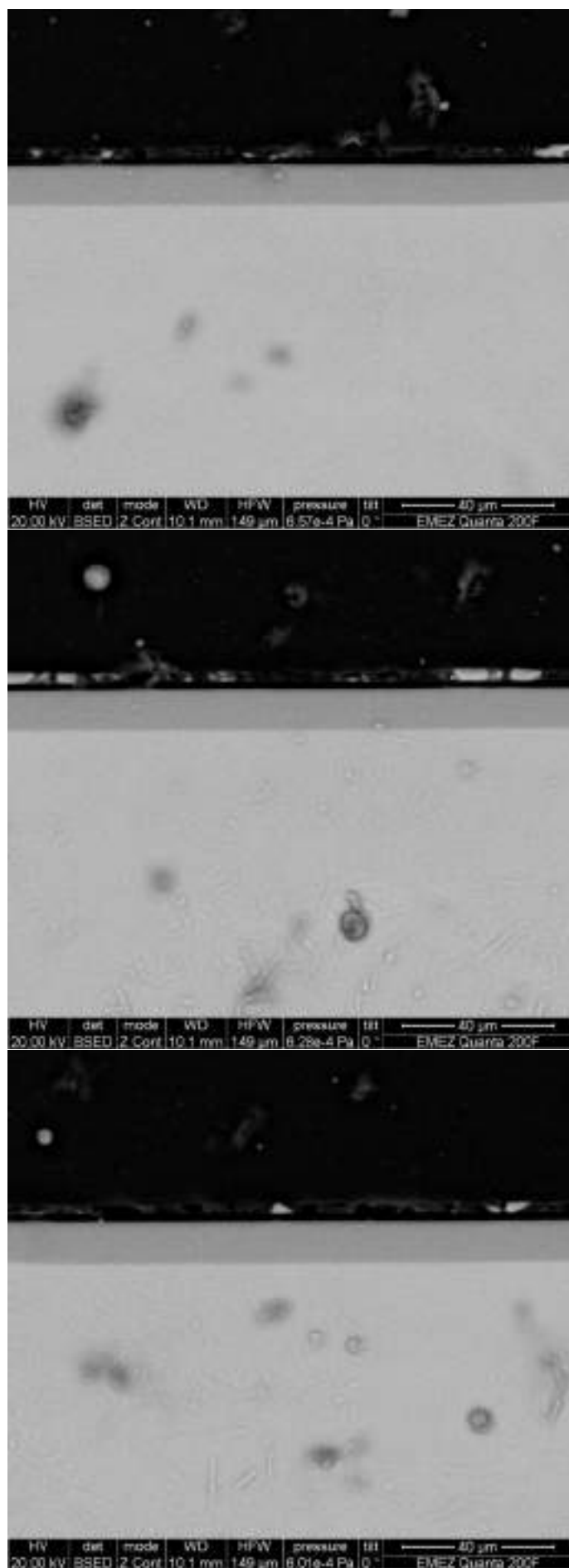


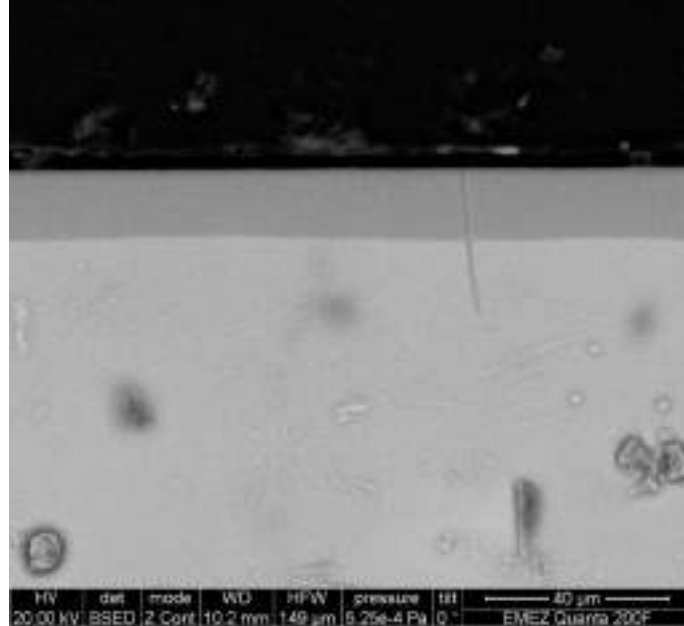
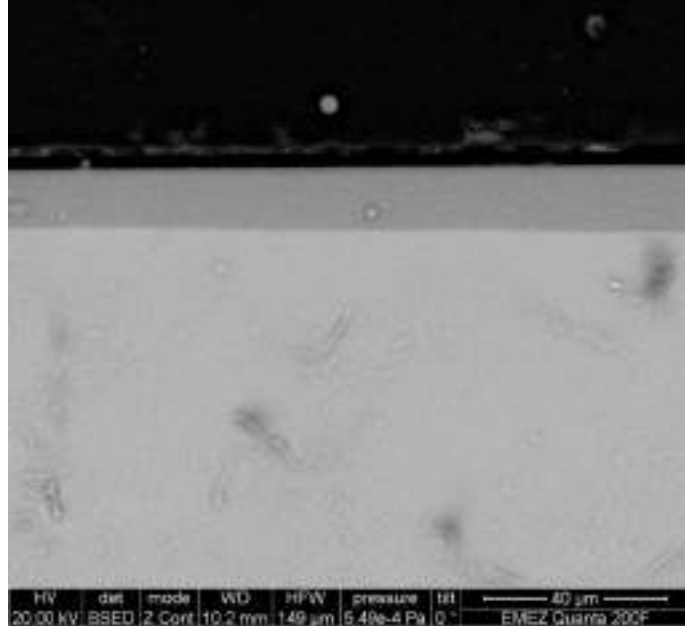
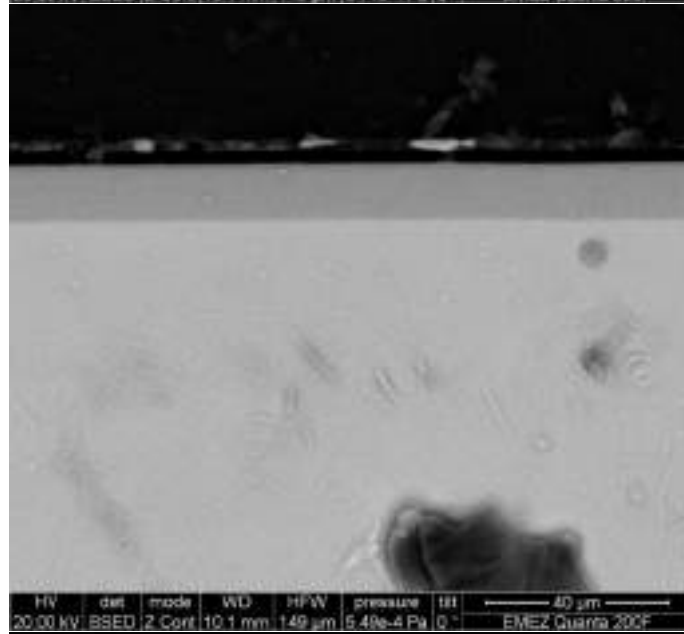
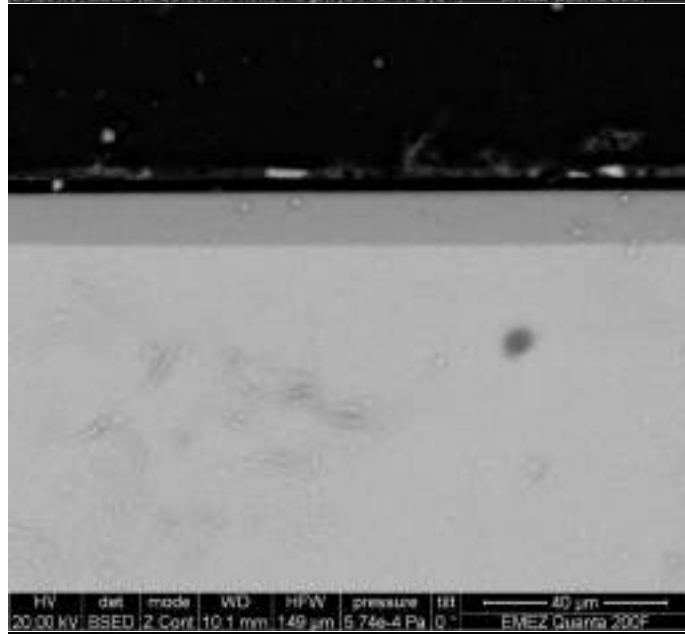
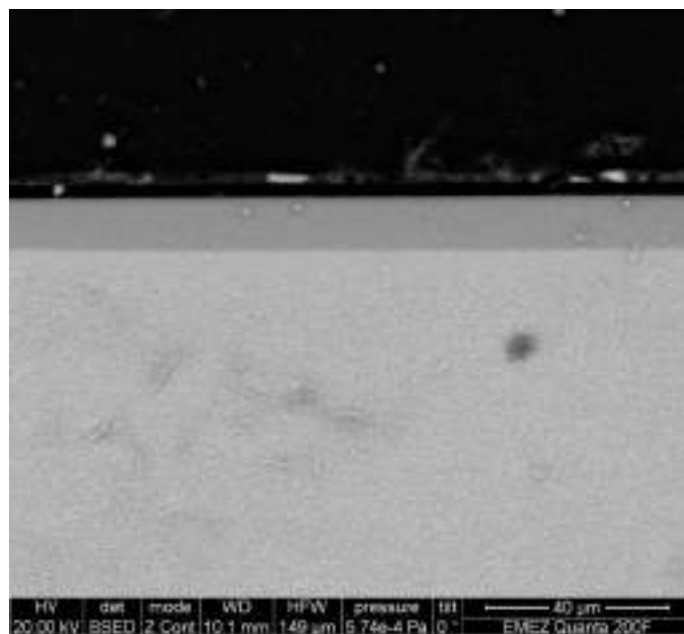
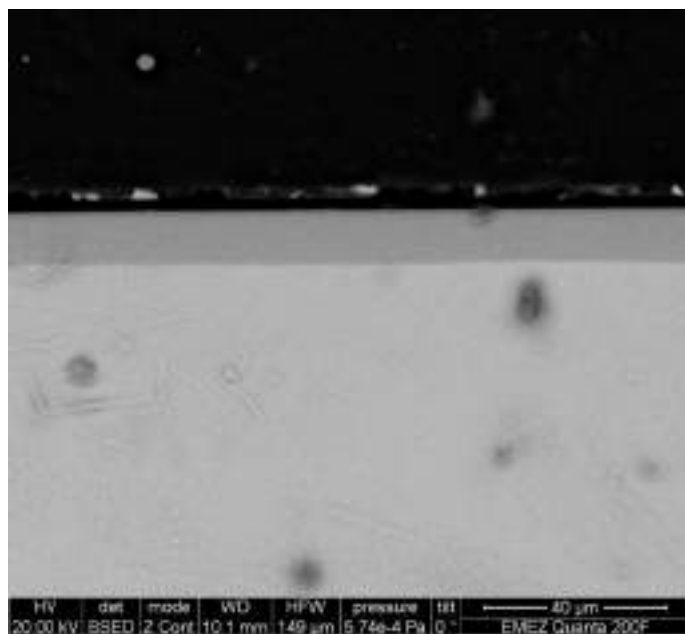


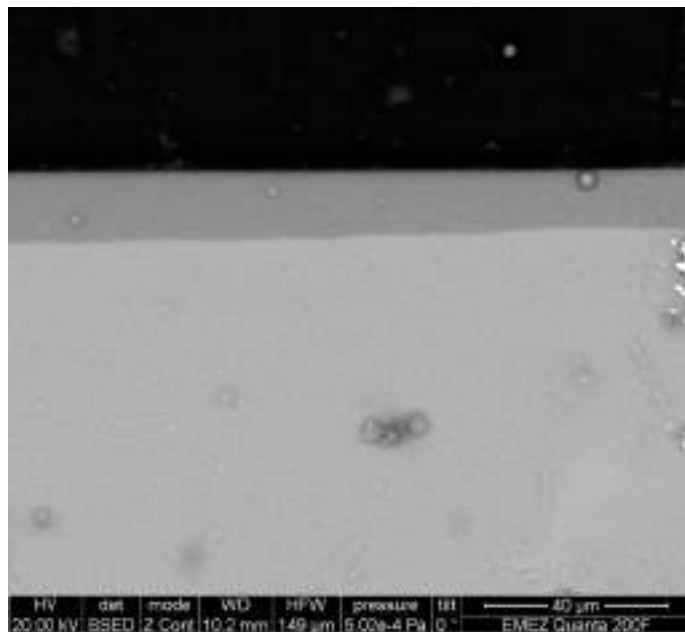
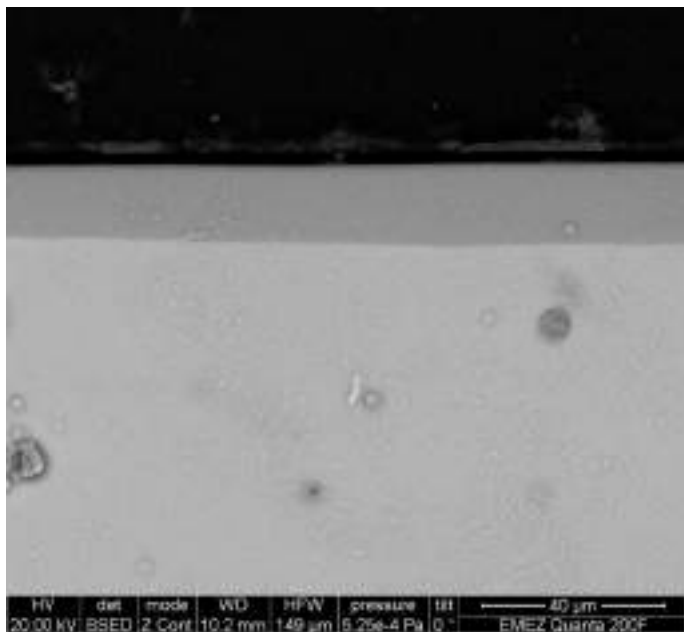




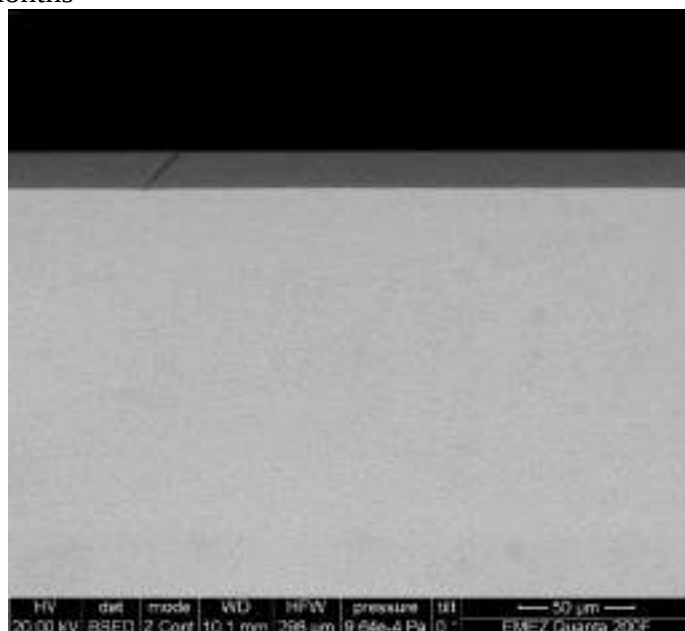
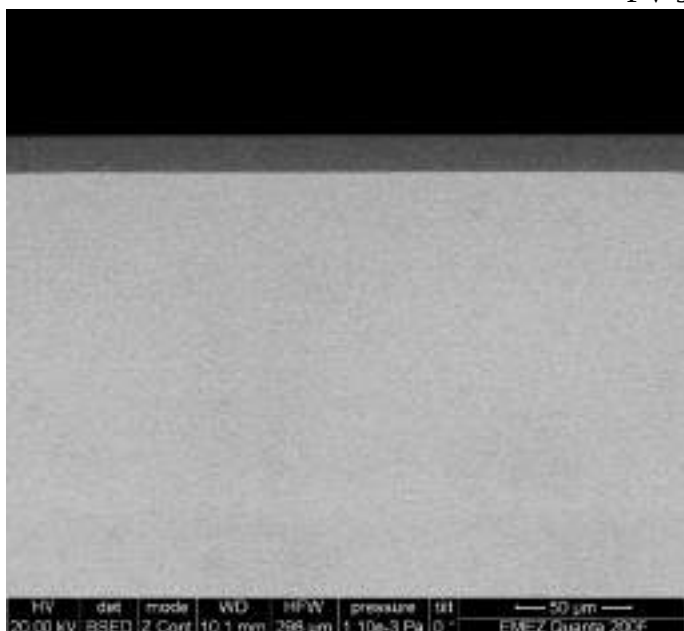




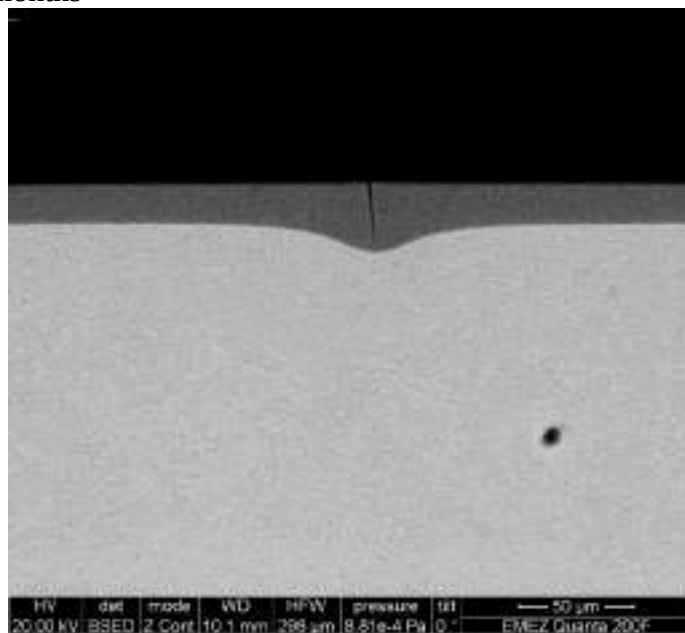
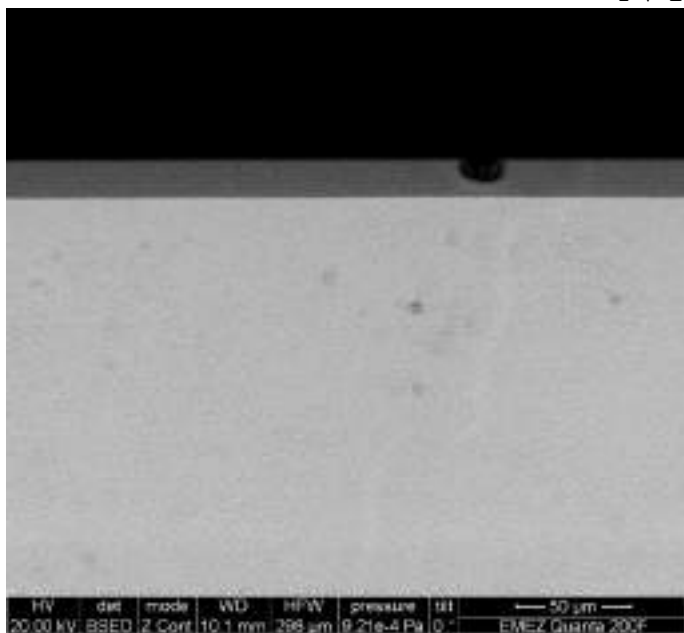


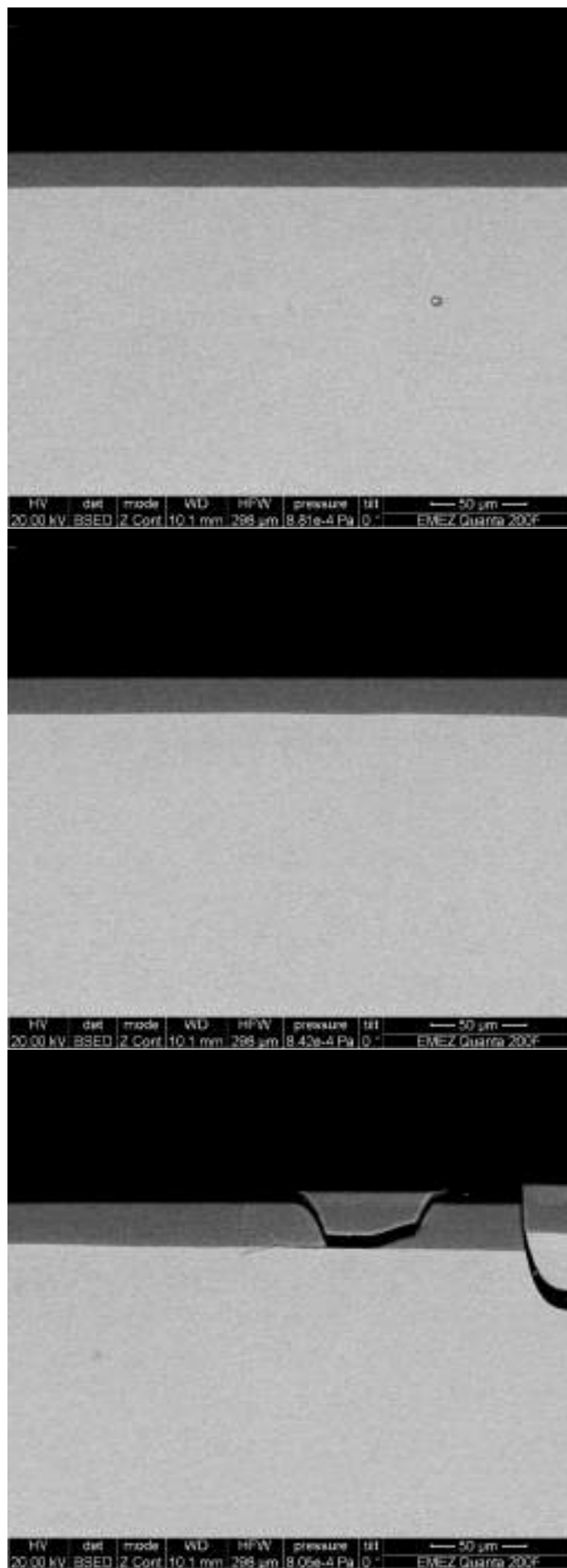
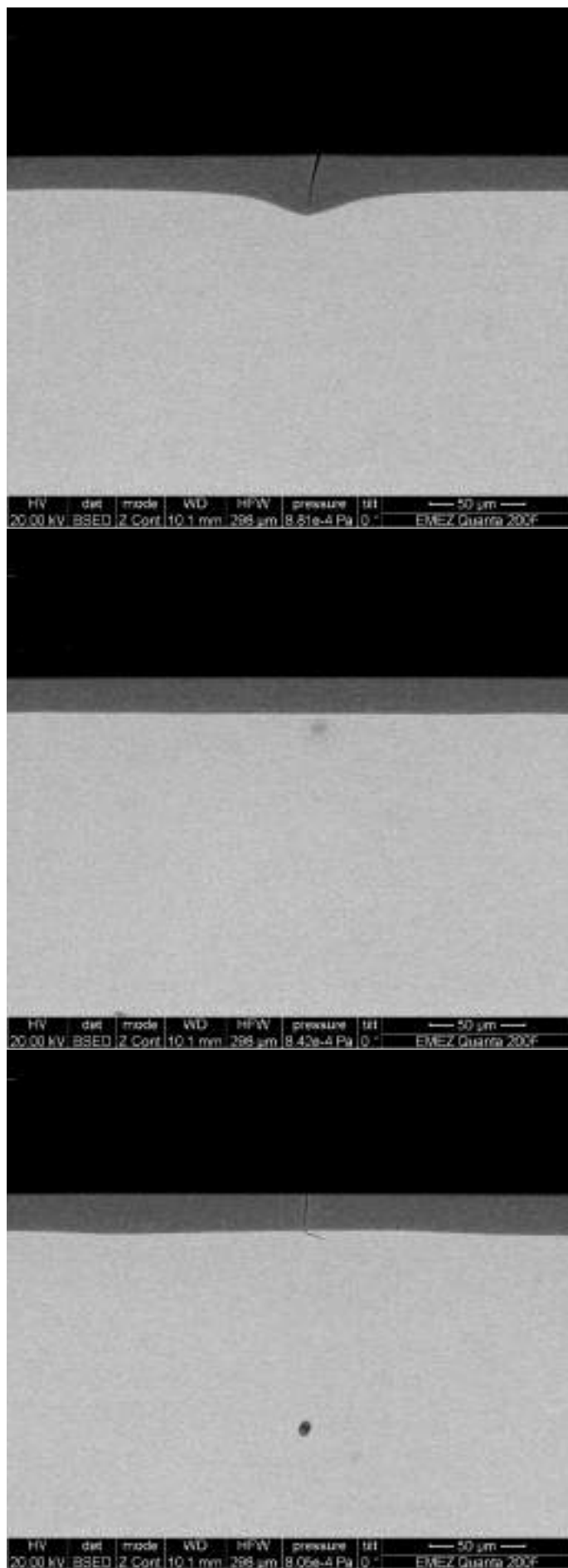


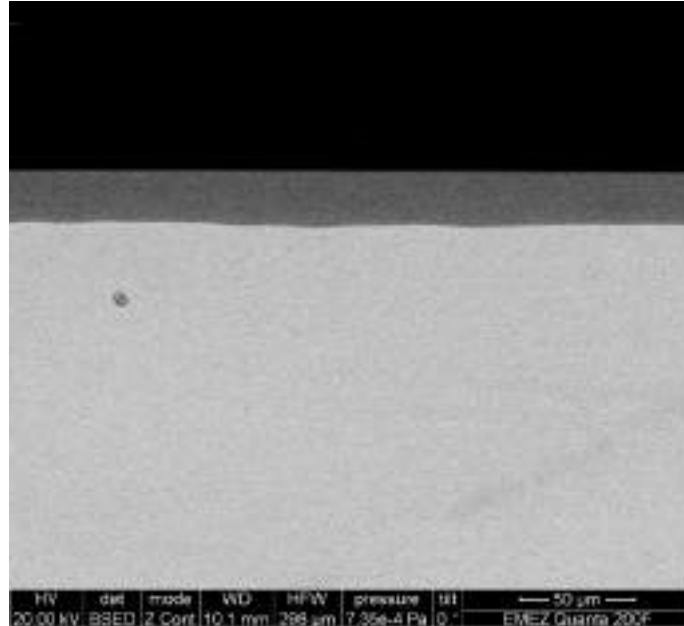
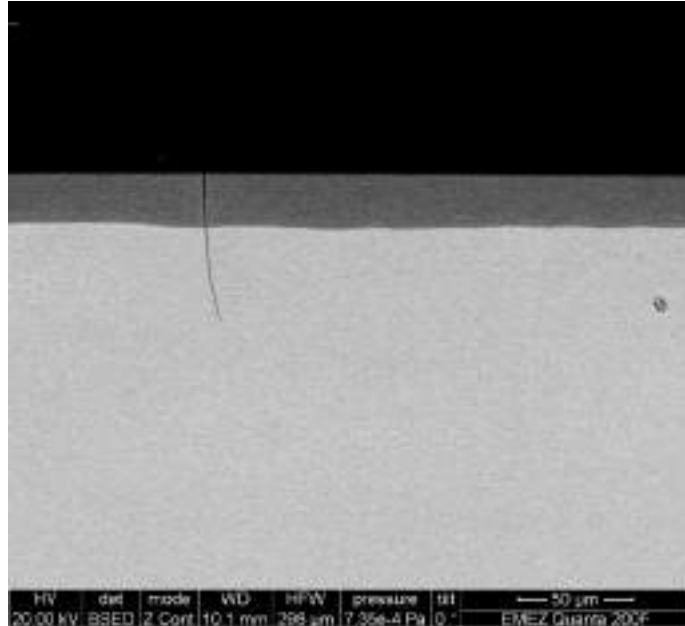
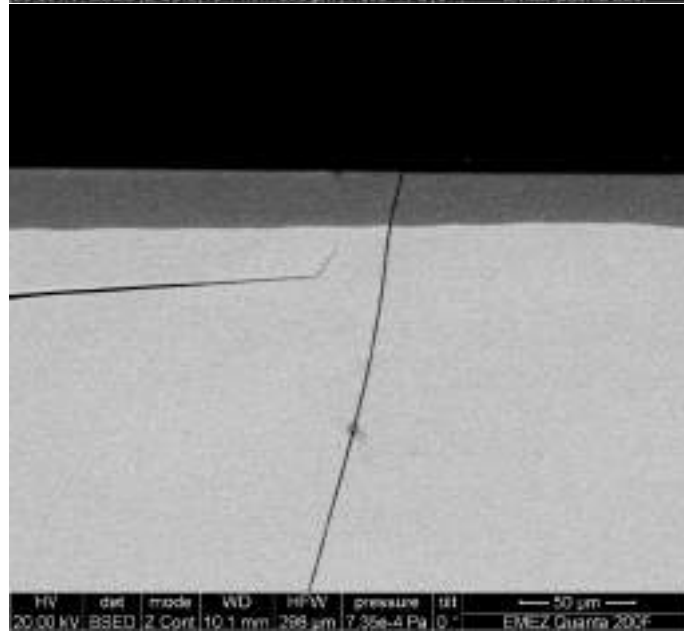
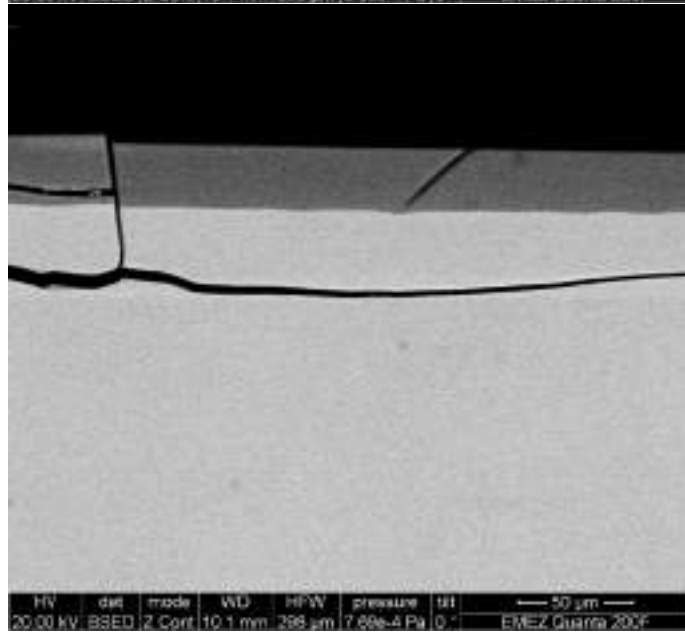
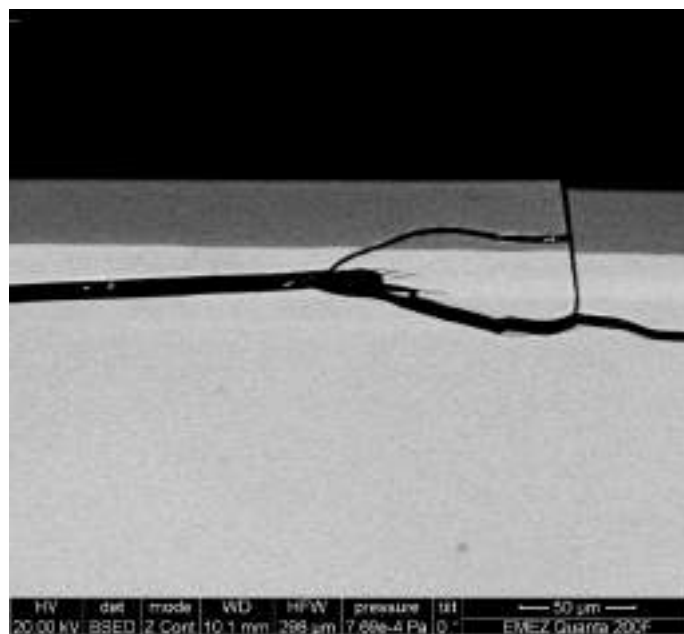
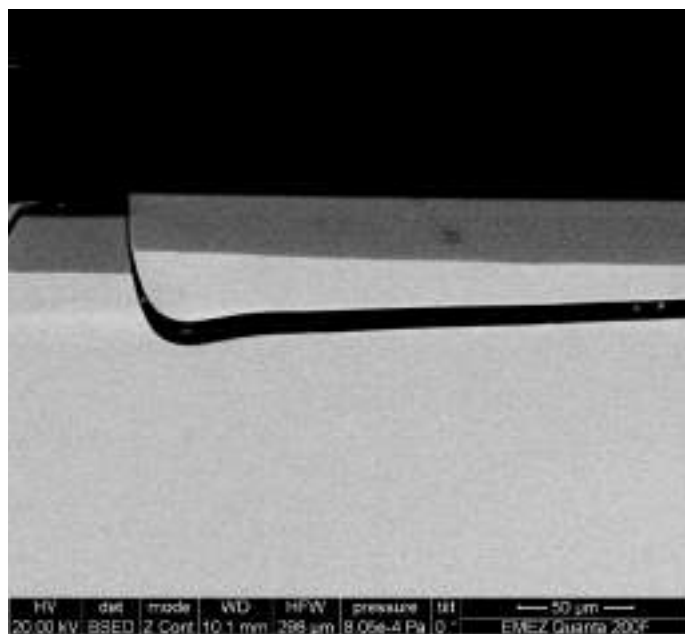
PV 9 months

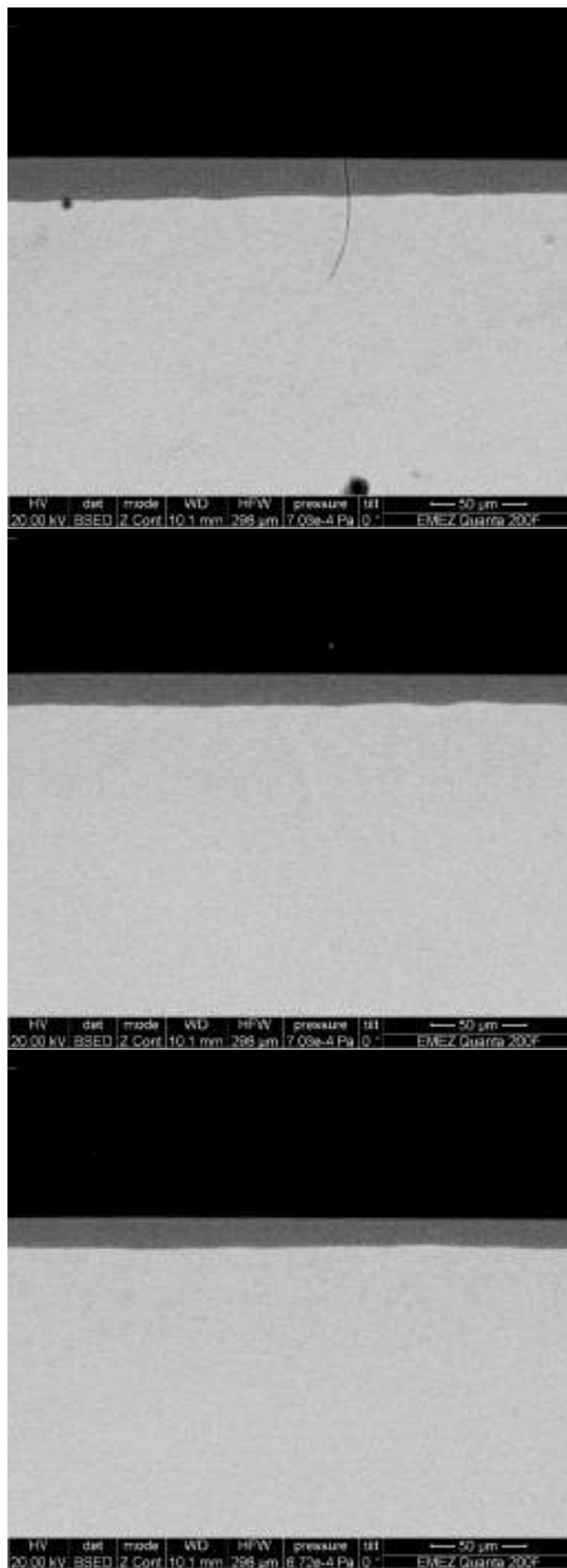
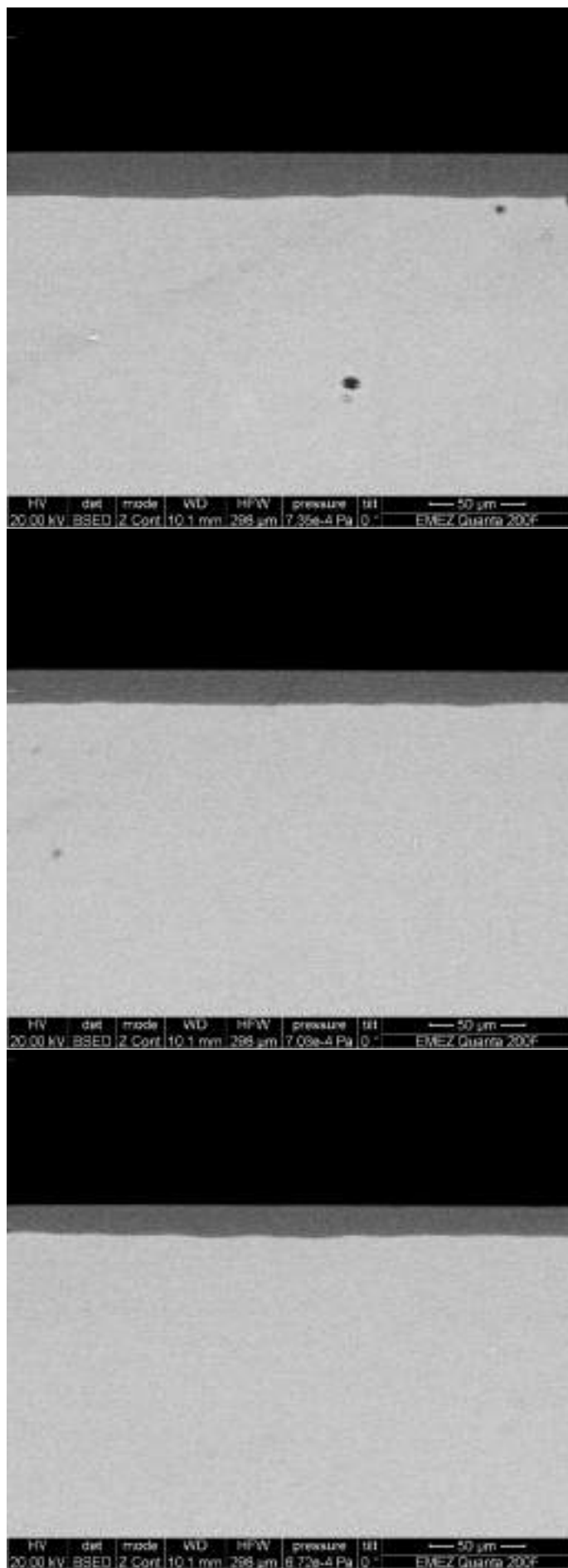


PV 12 months

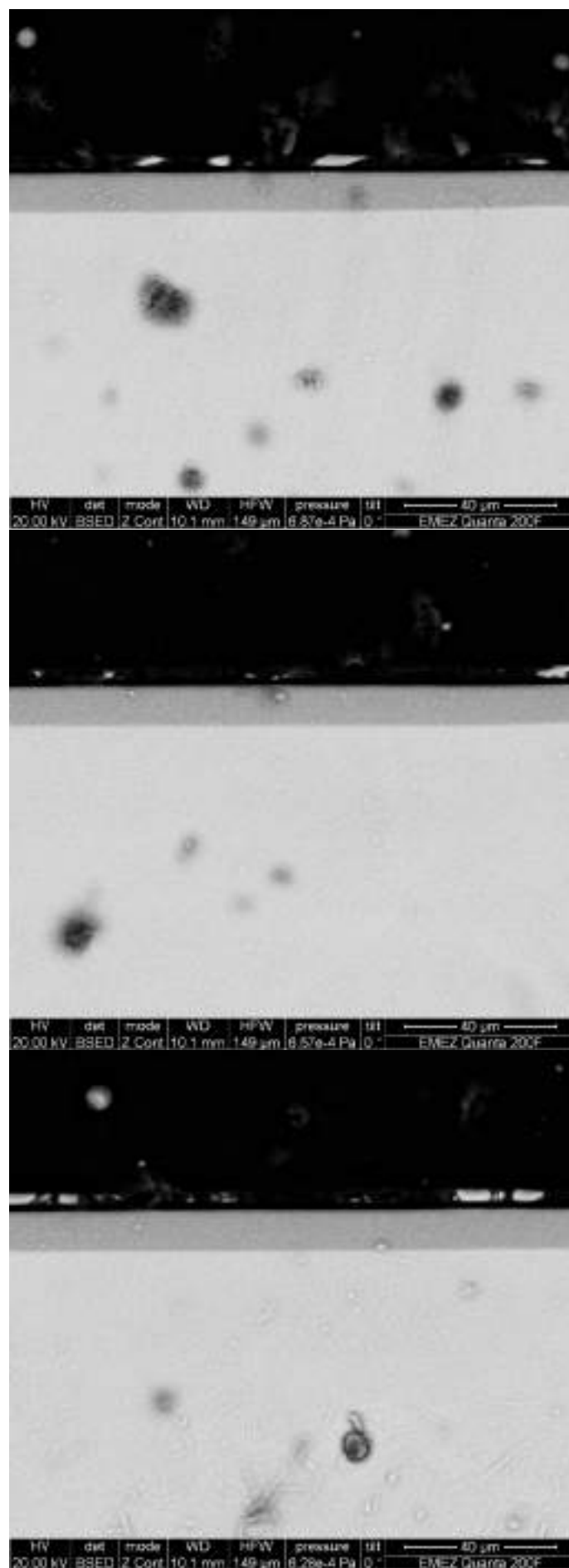
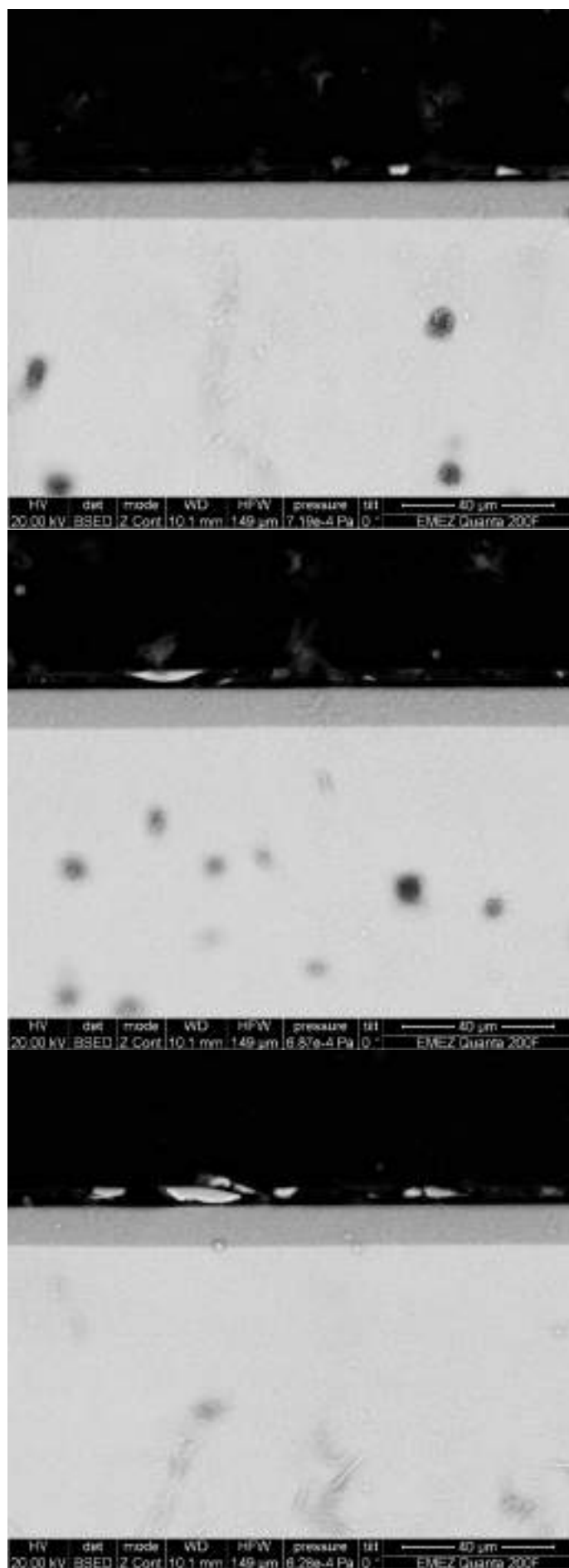


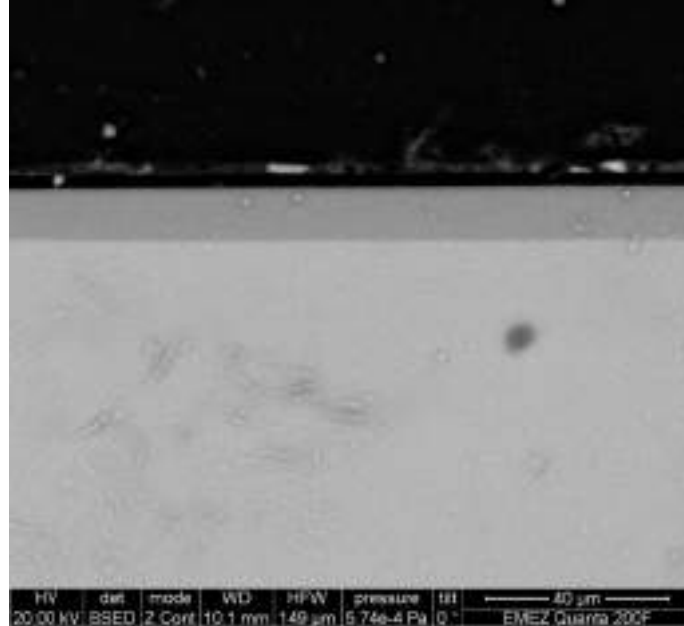
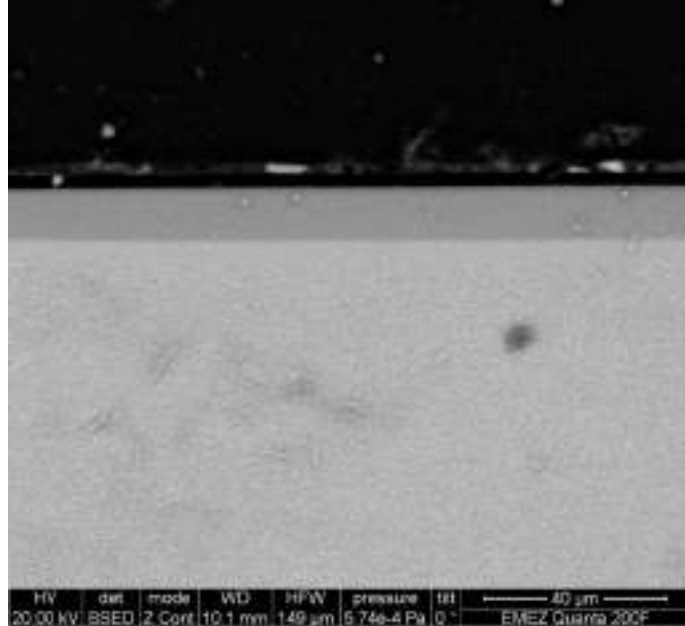
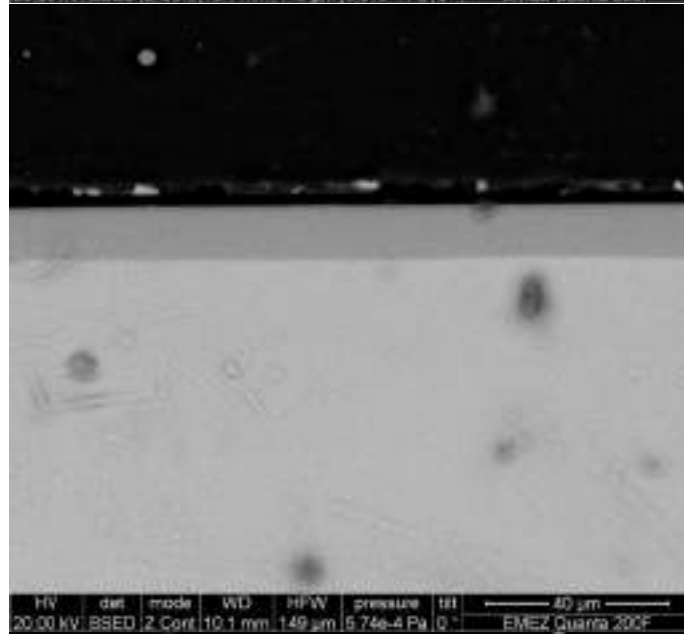
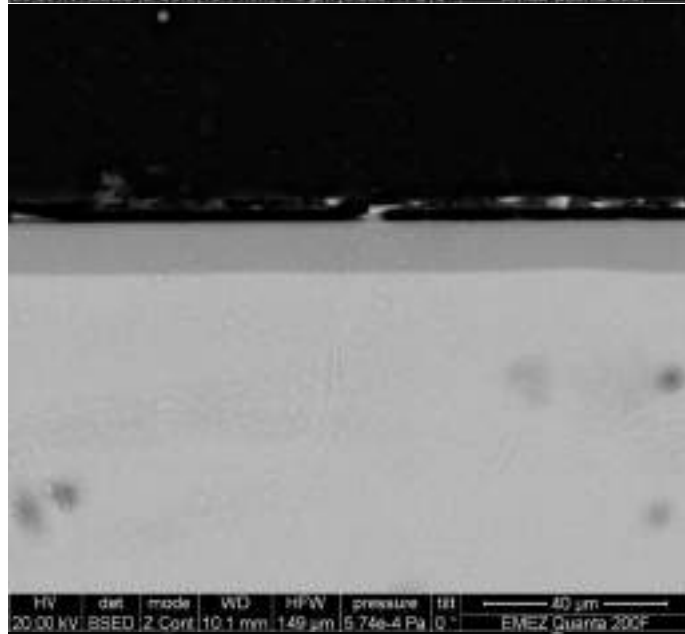
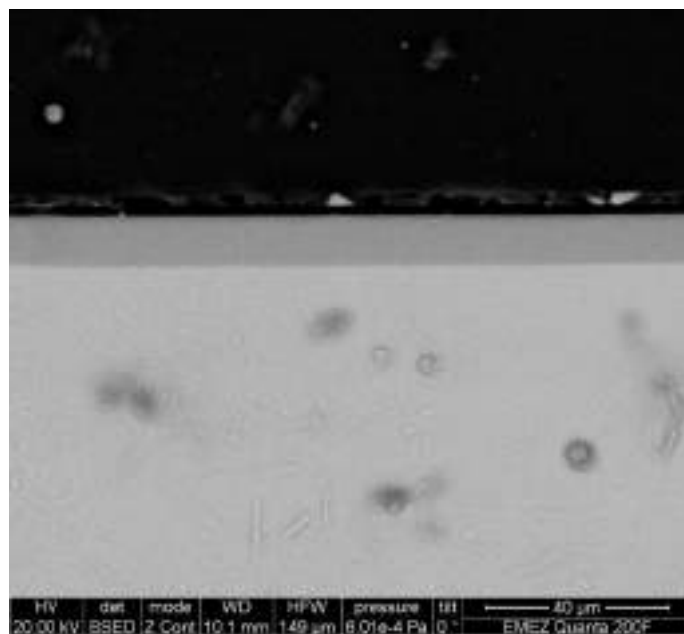
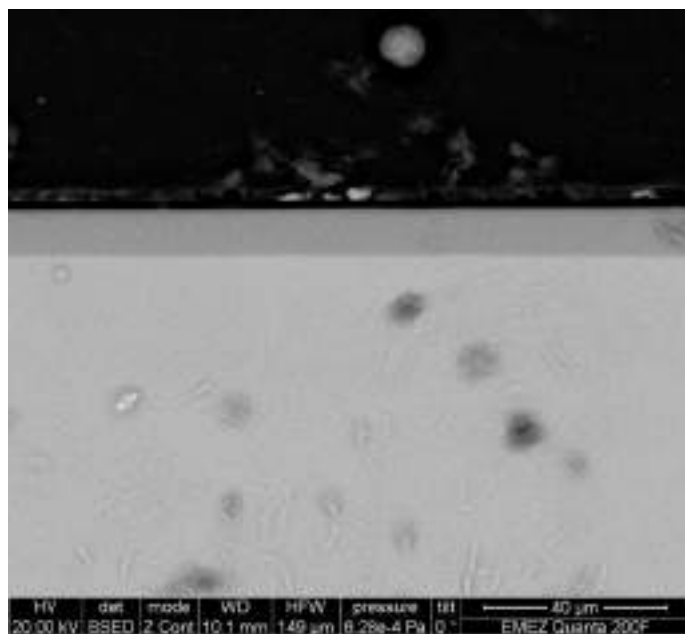


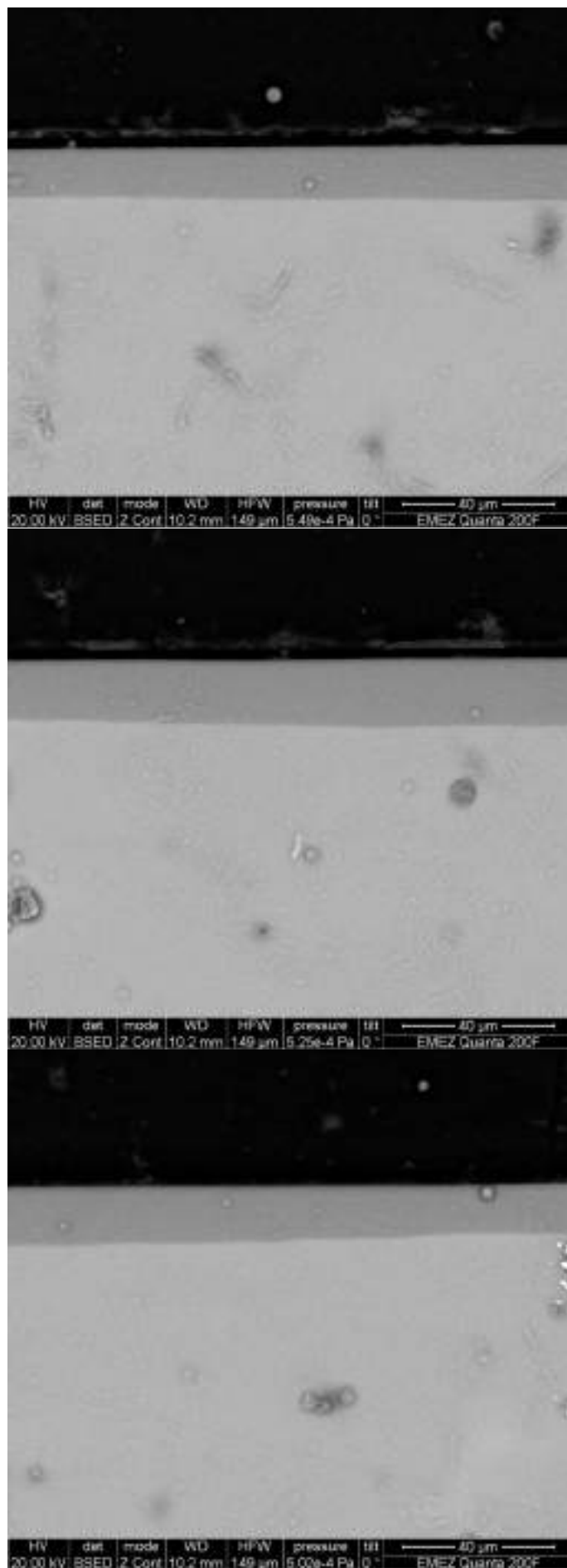
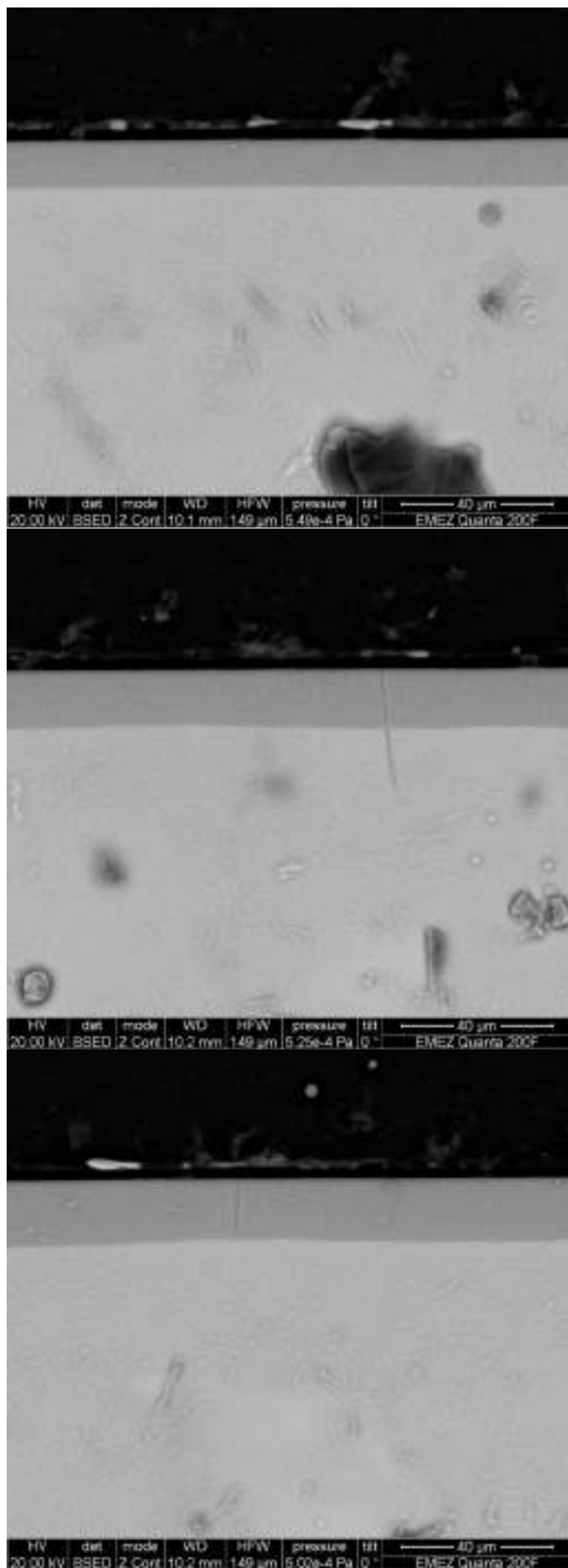




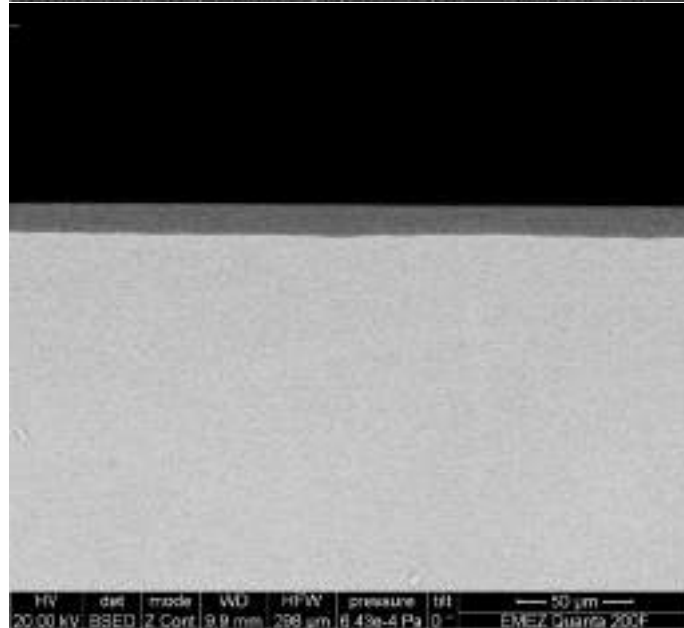
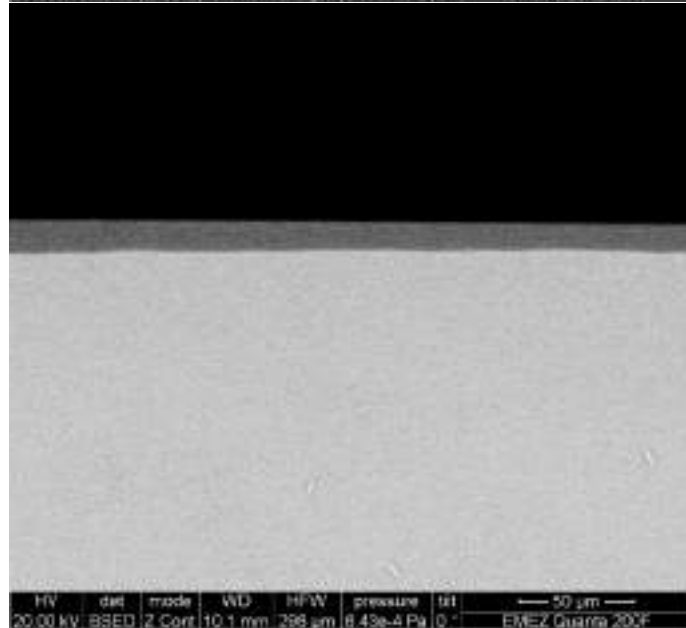
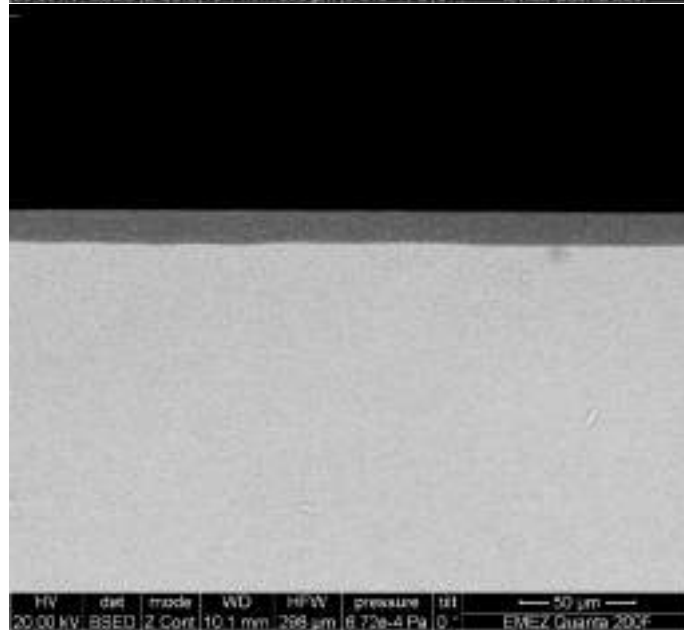
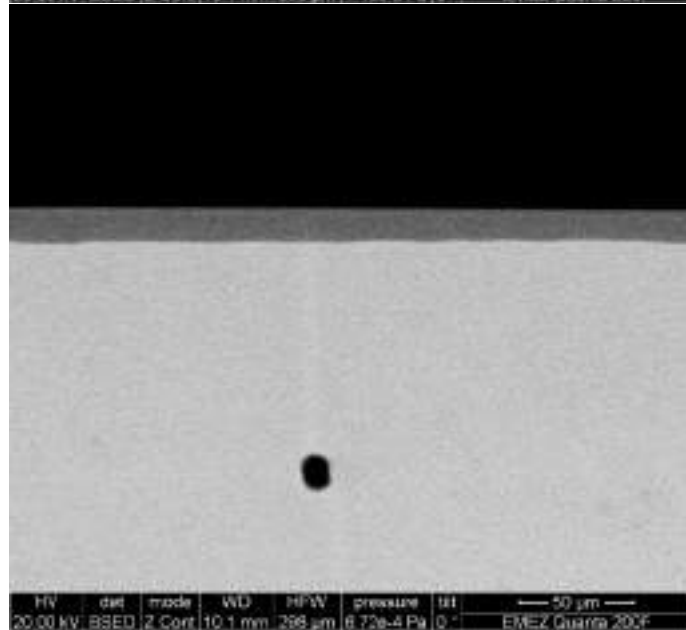
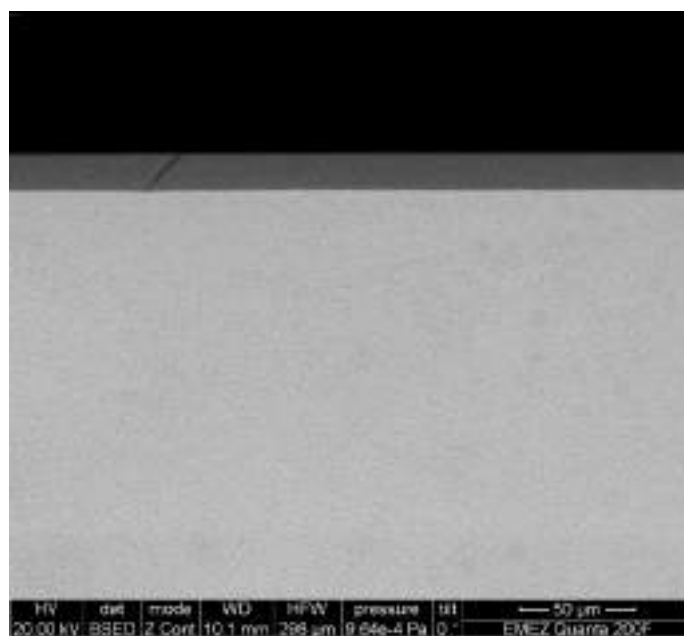
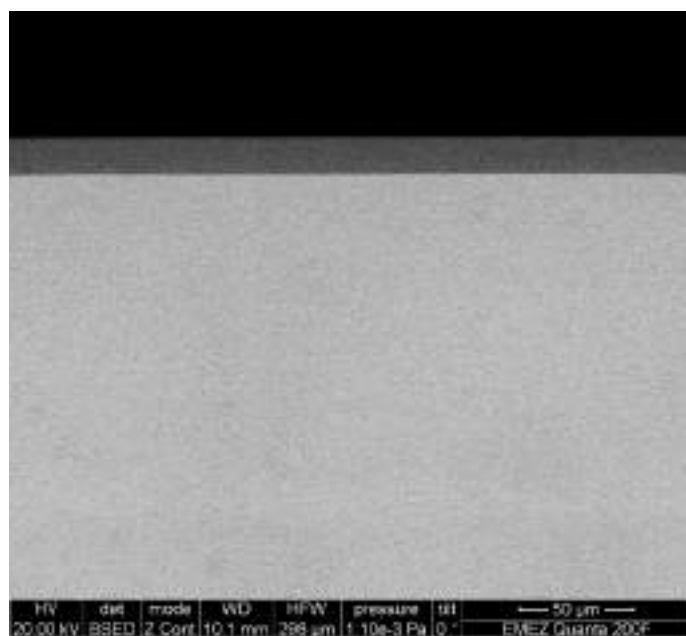
PV 17 months

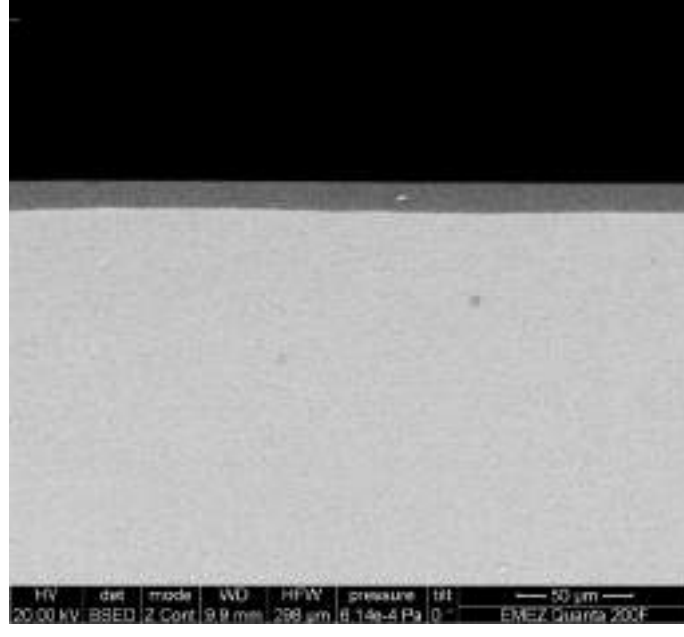
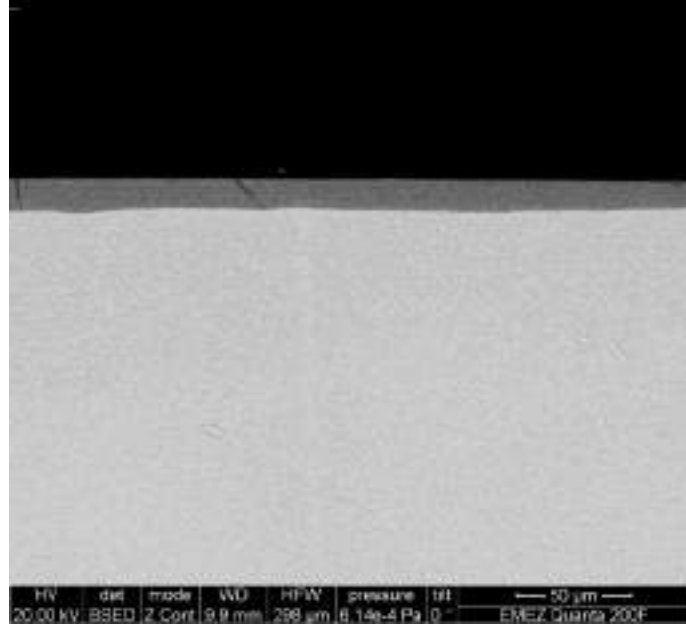
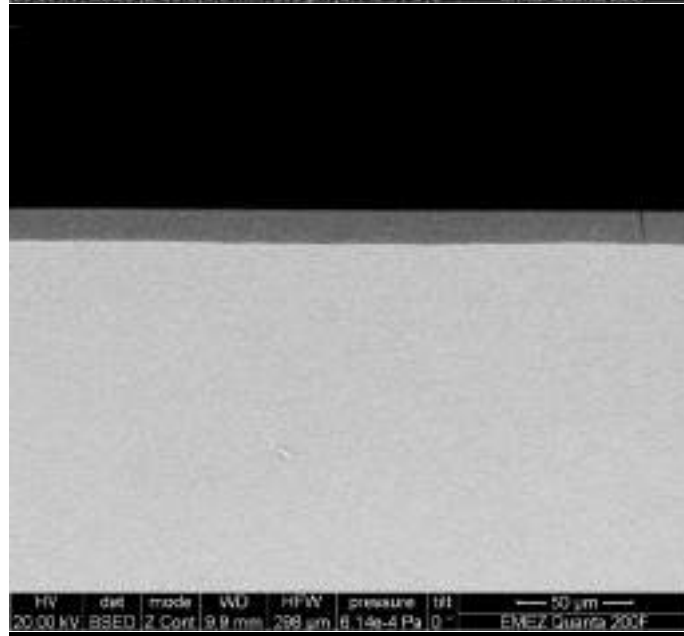
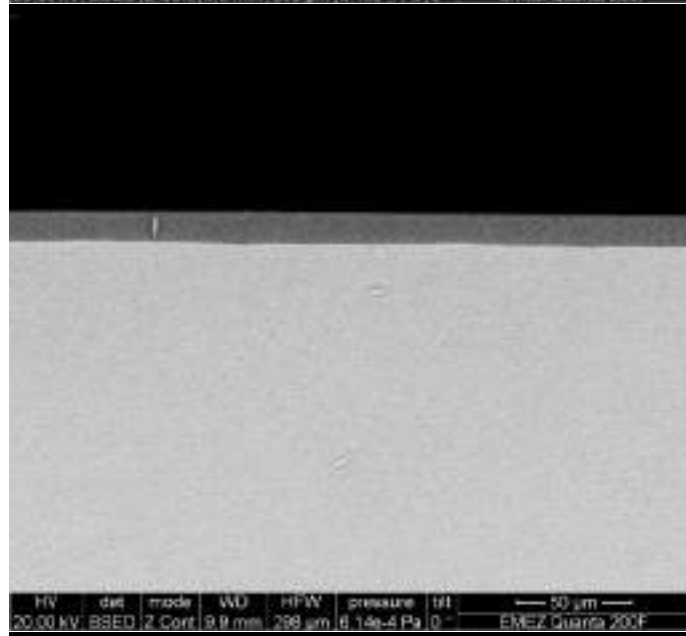
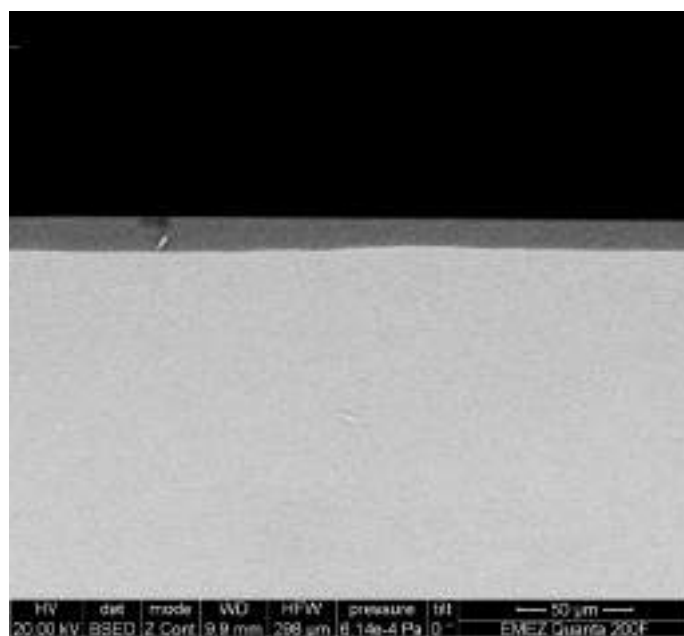
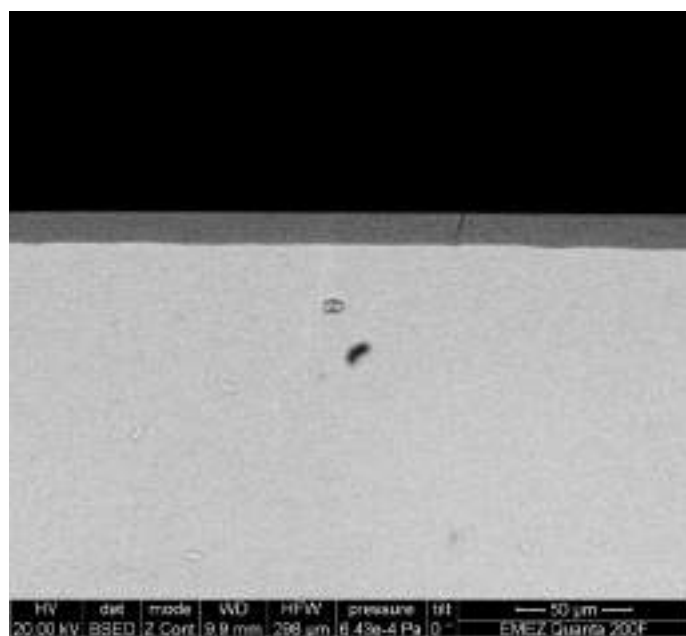


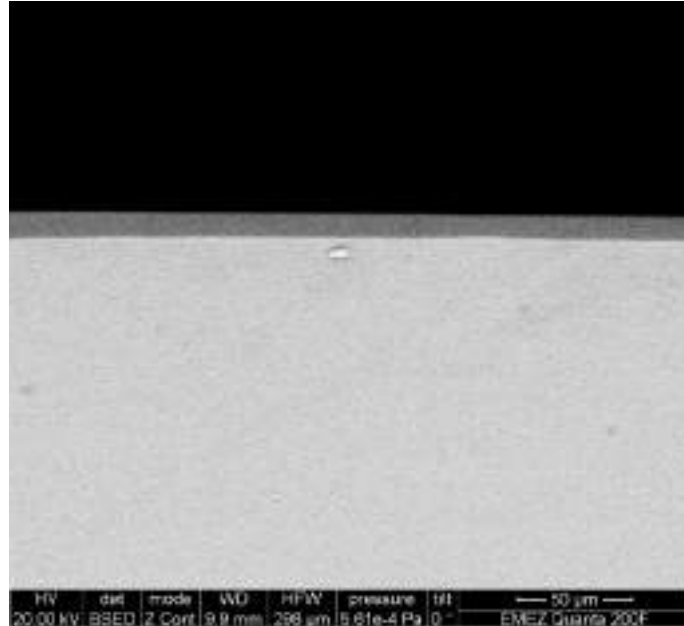
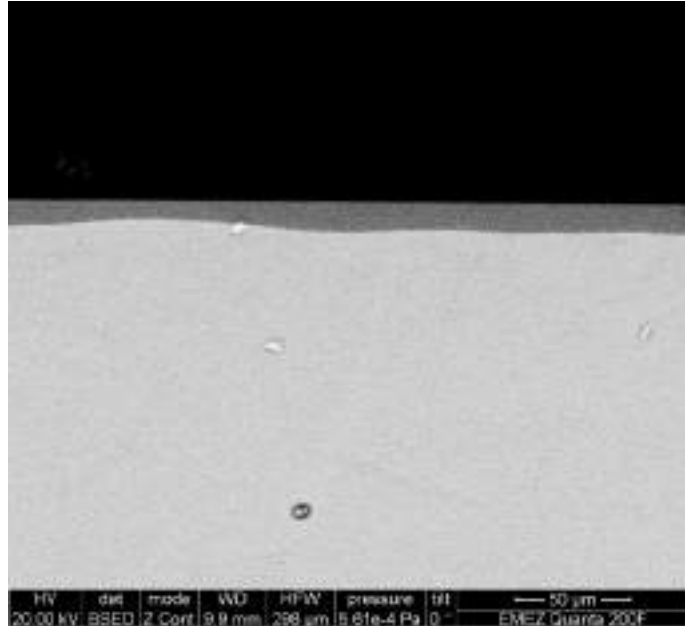
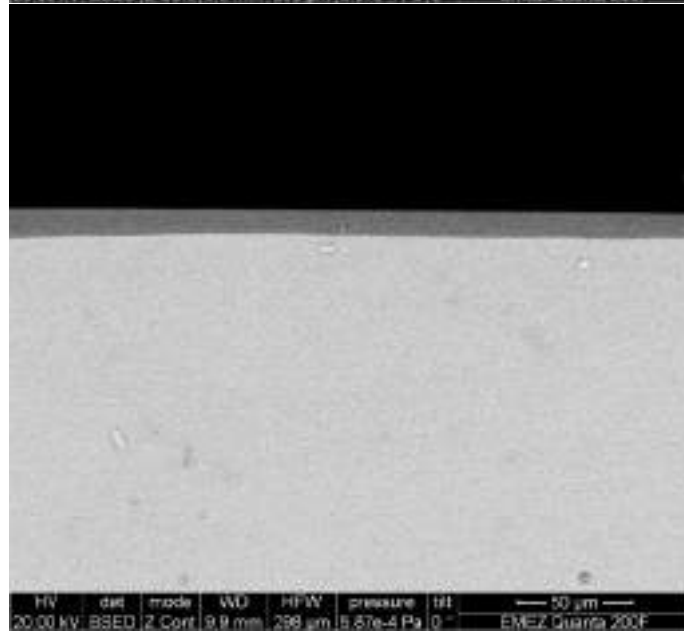
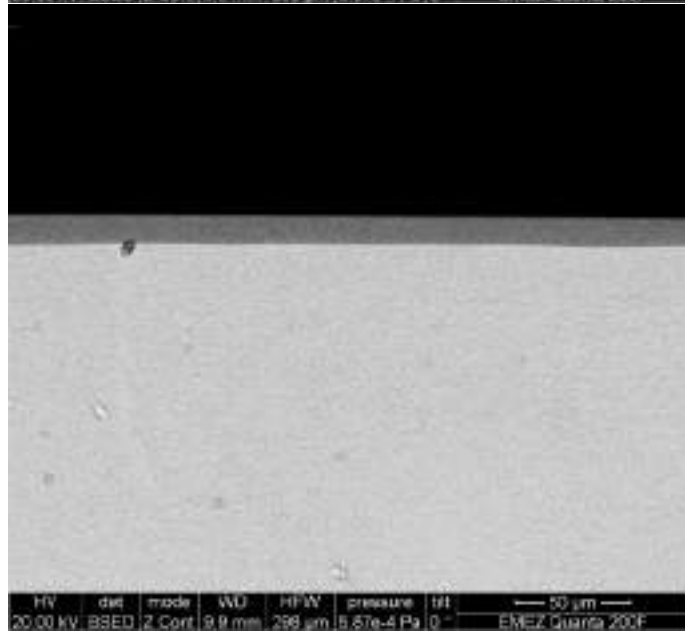
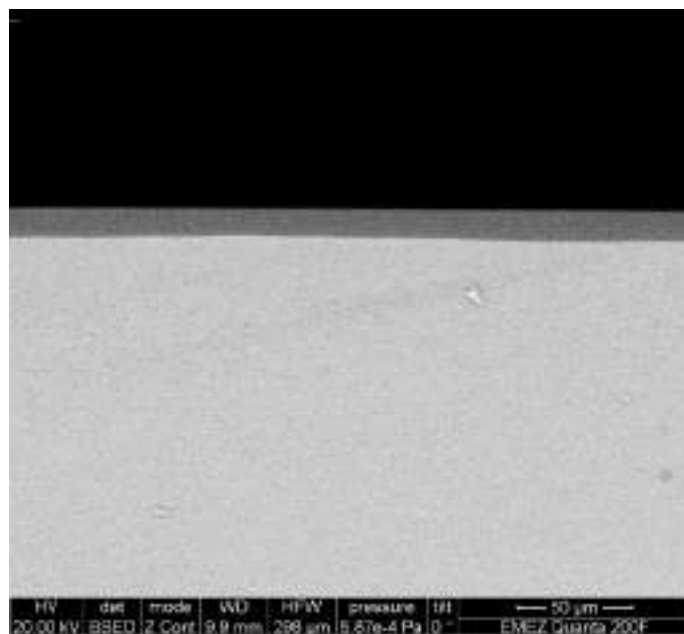
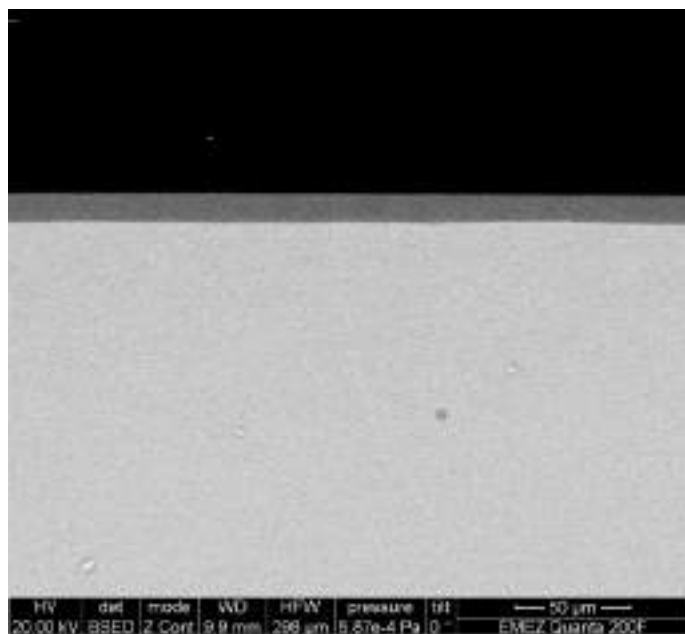


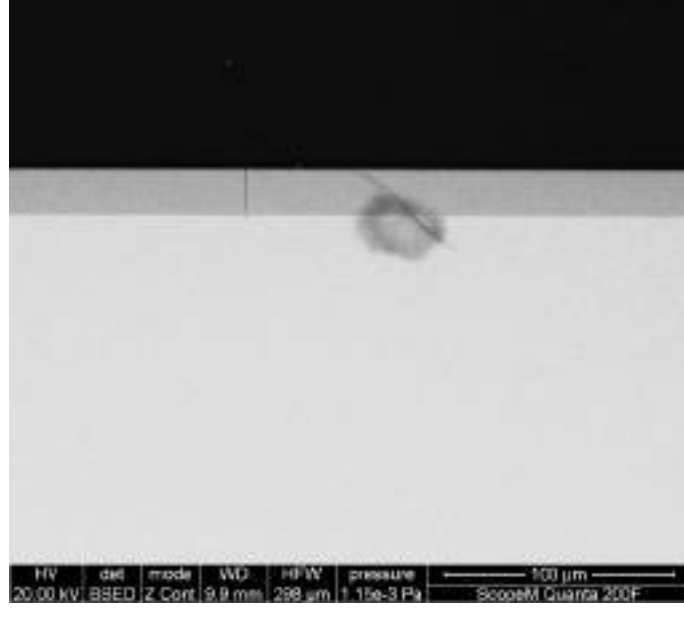
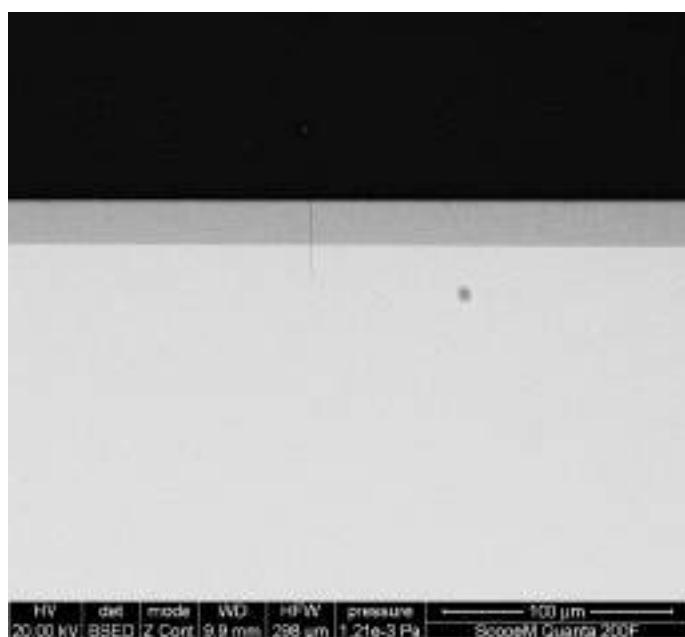
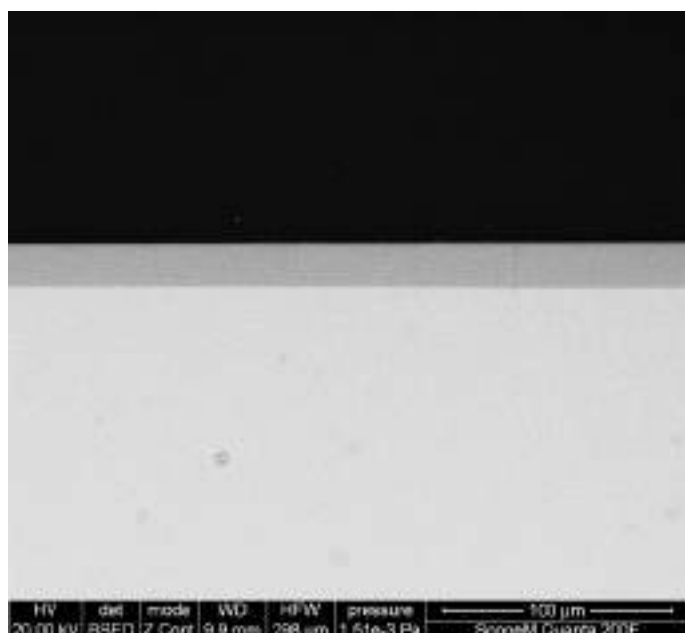
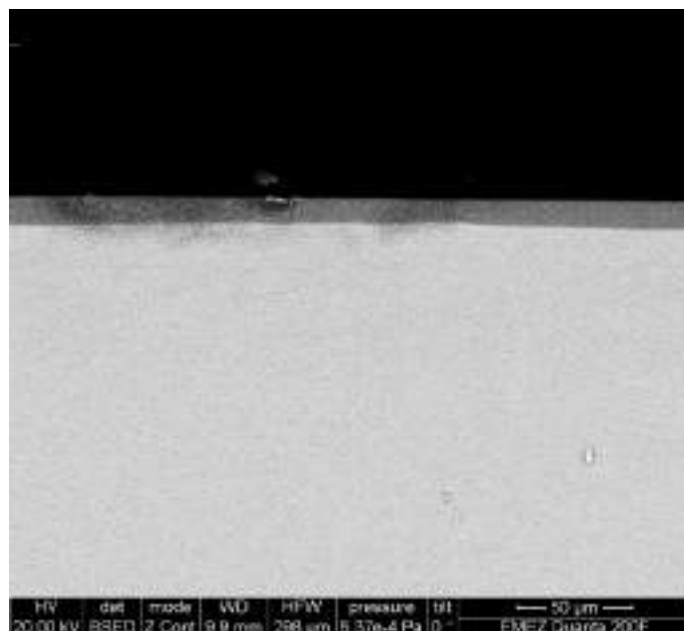
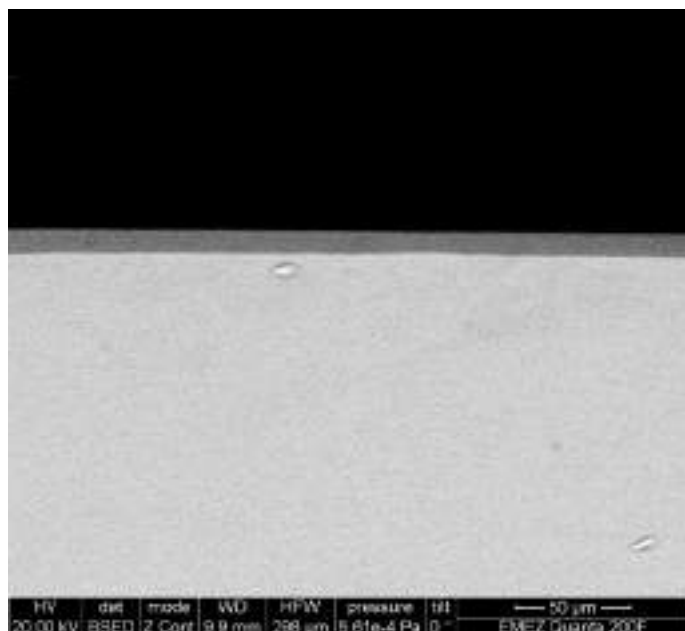


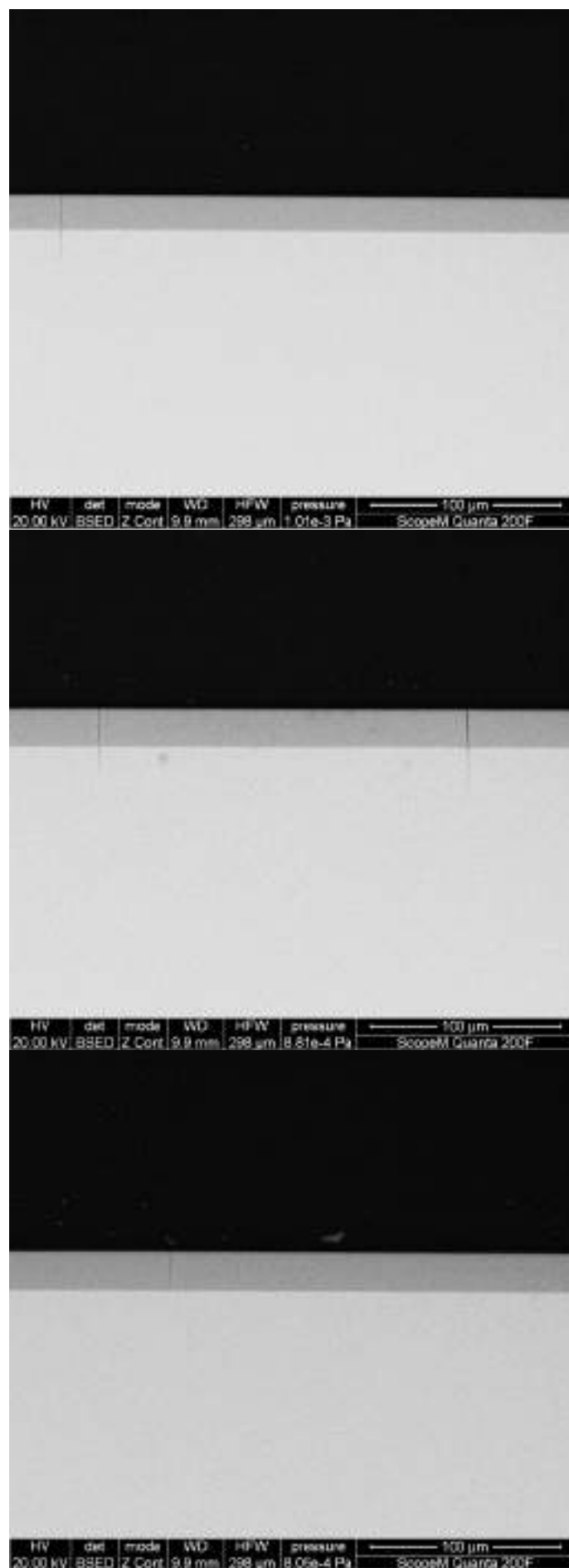
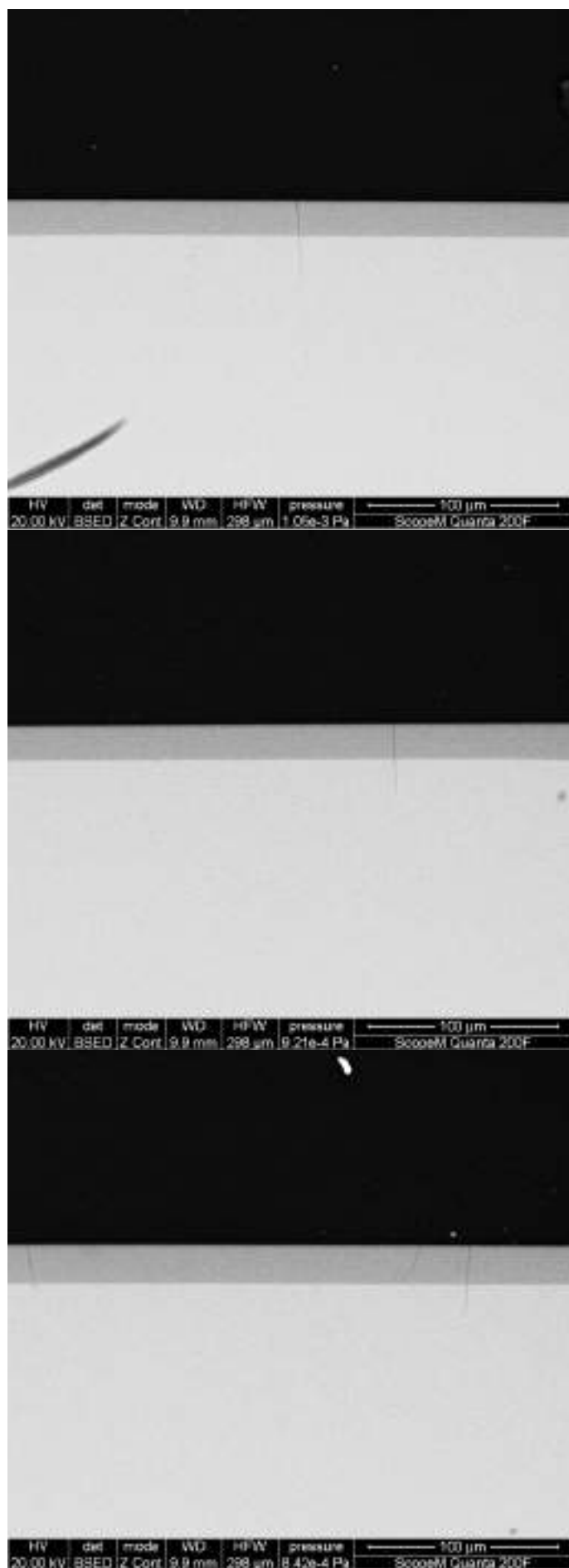
V 0 months (3 months aging in saturated salt solutions)

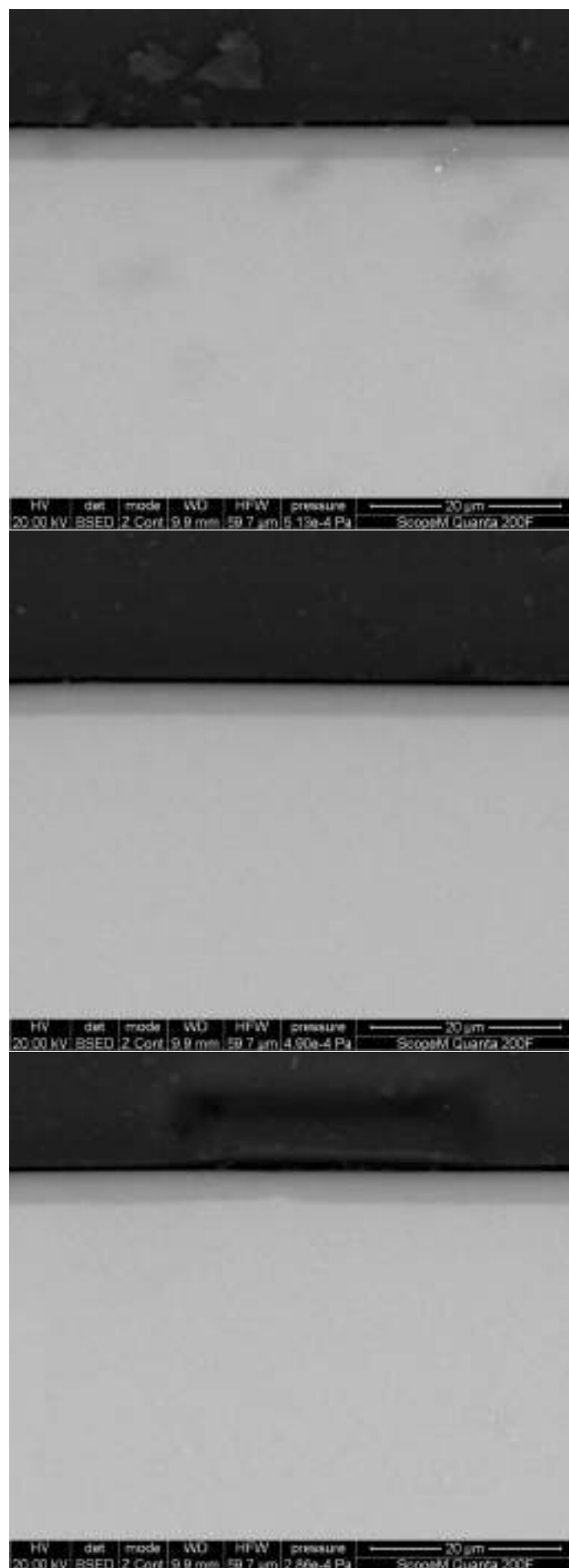
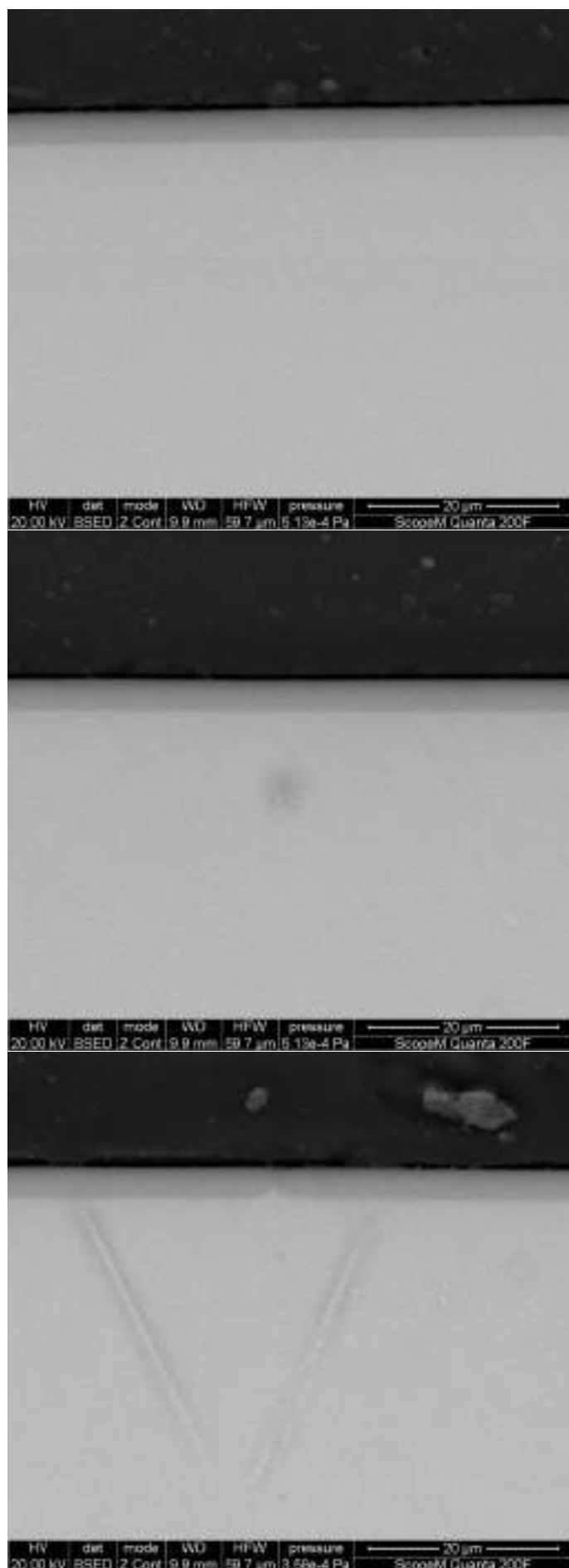


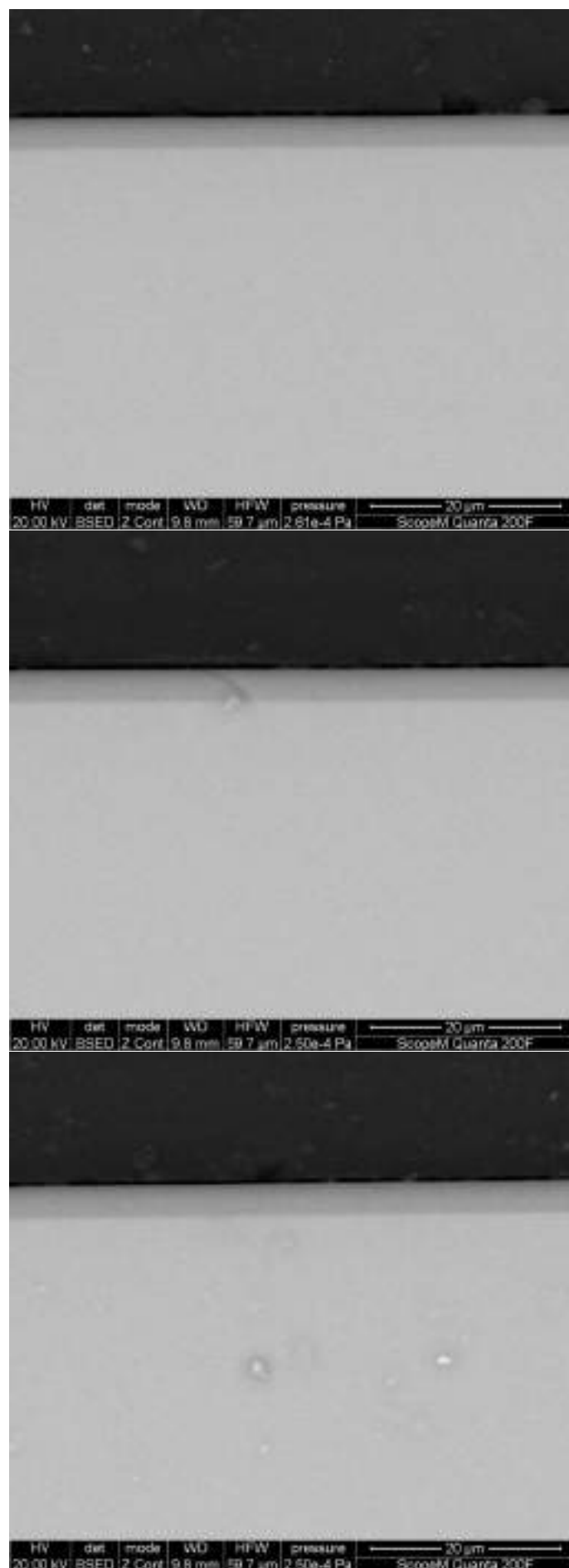
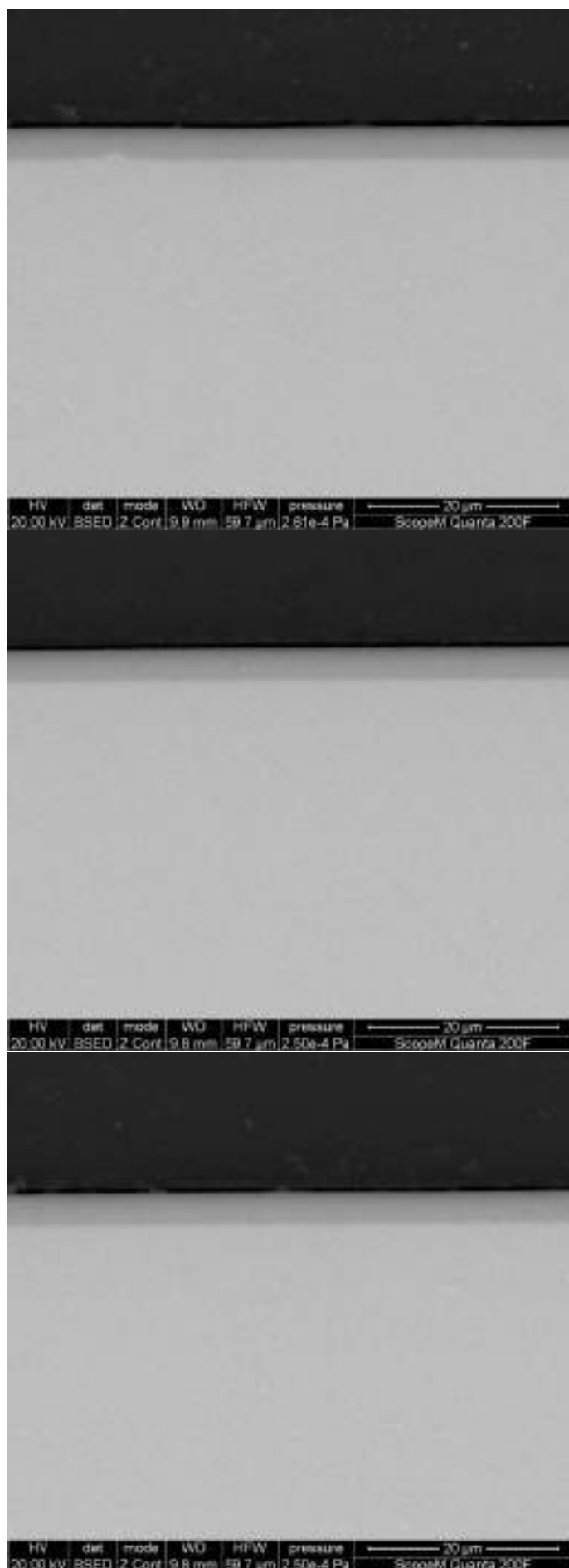


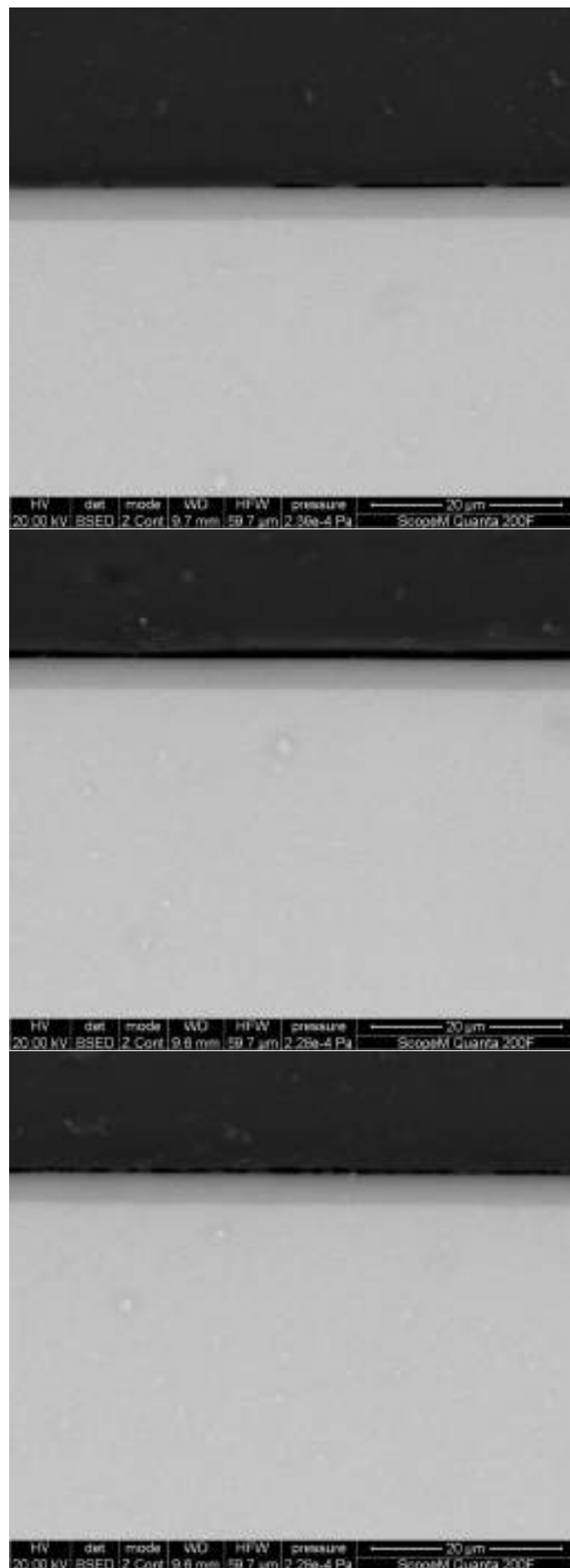
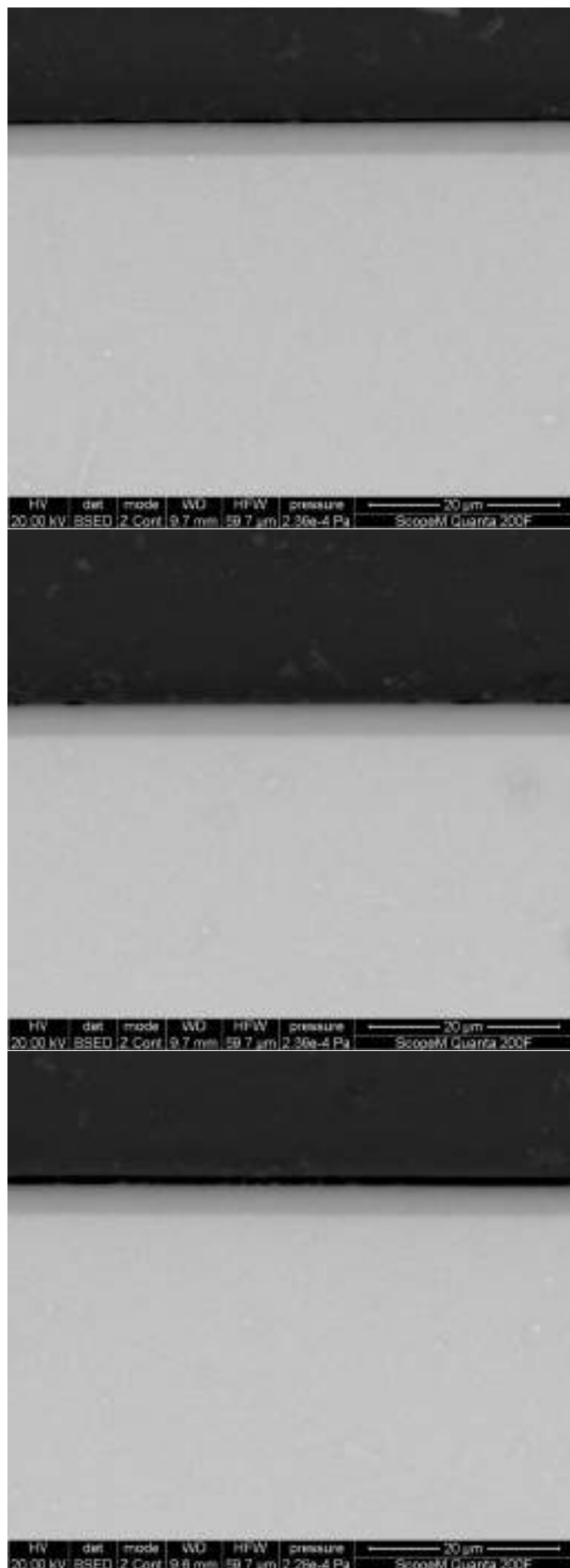


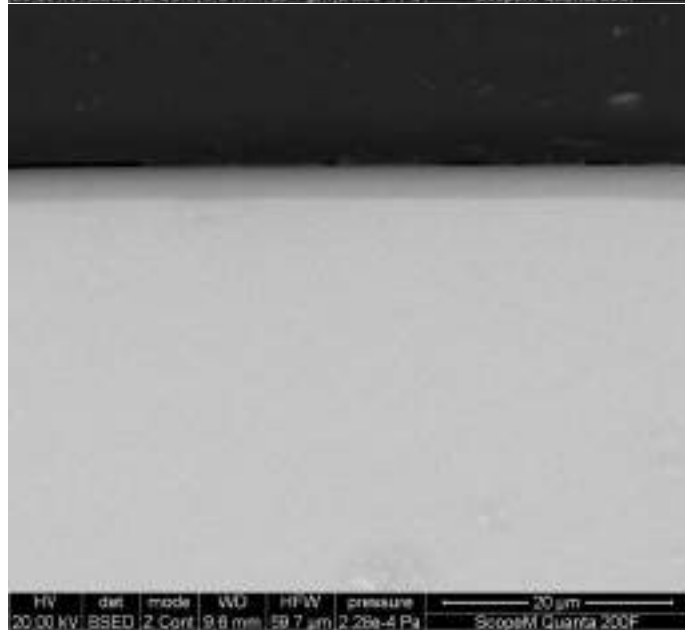
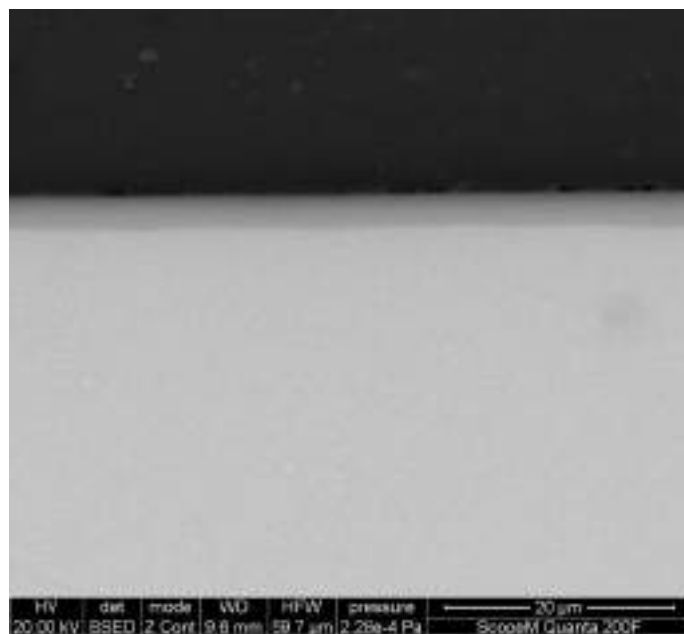
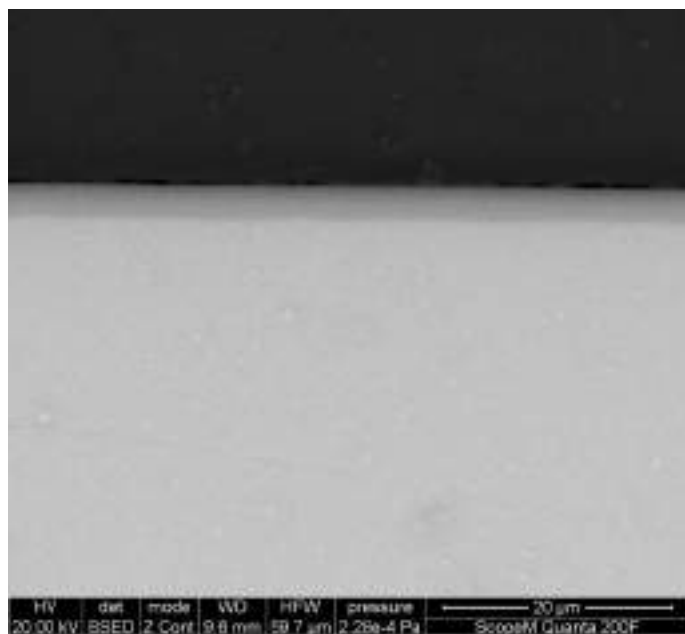




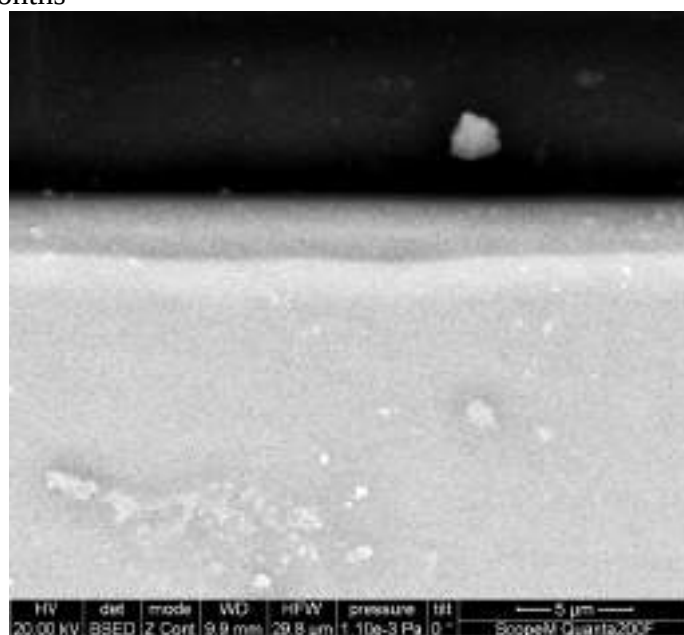
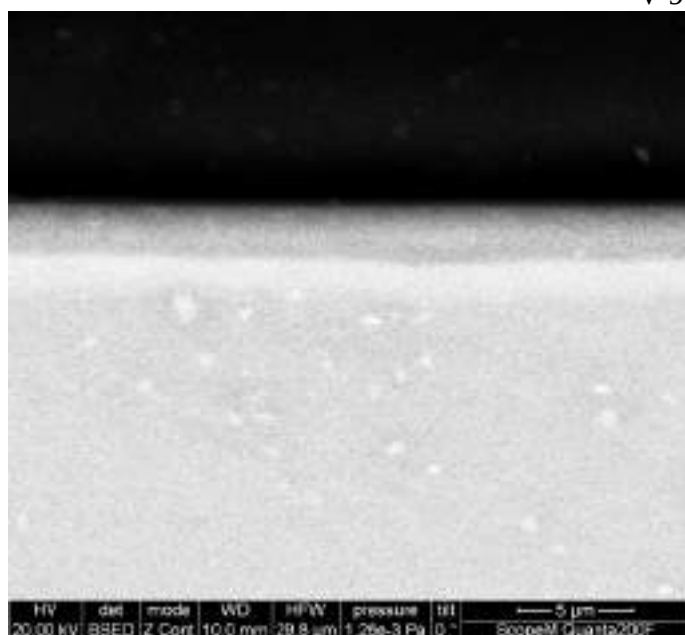


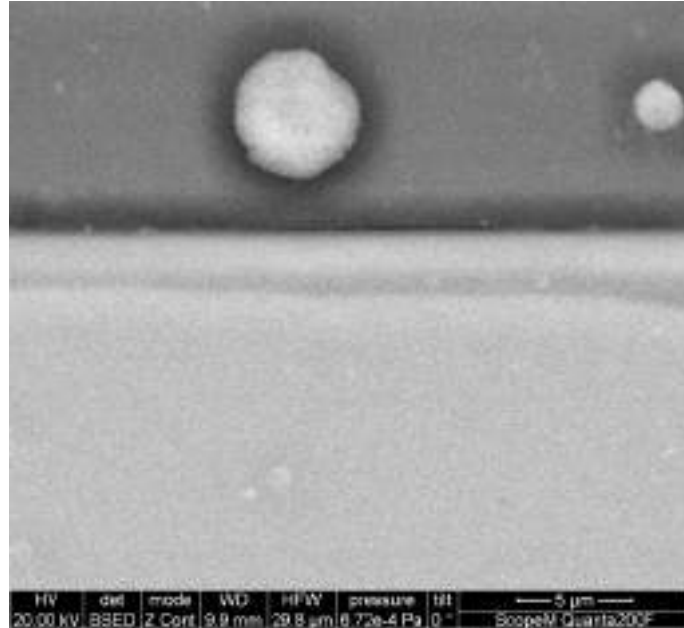
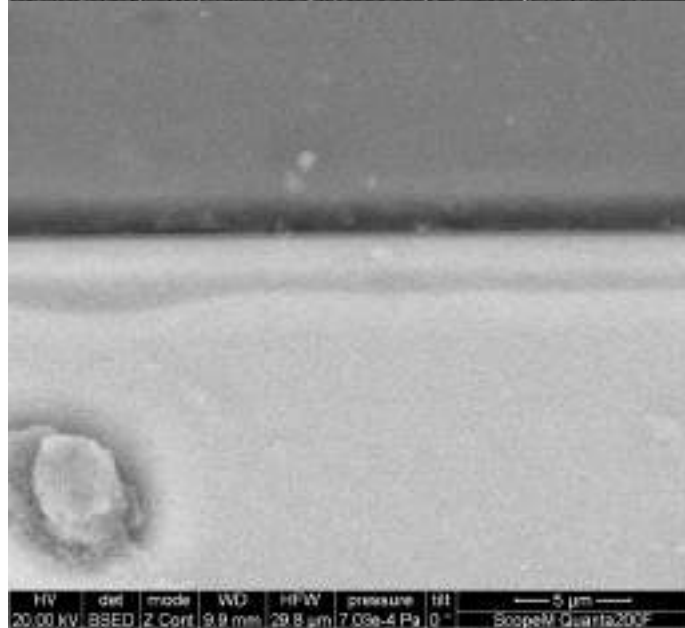
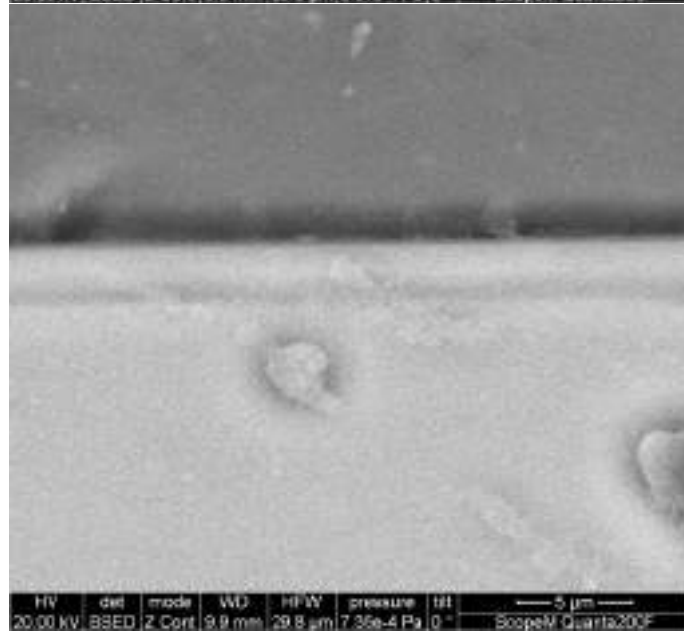
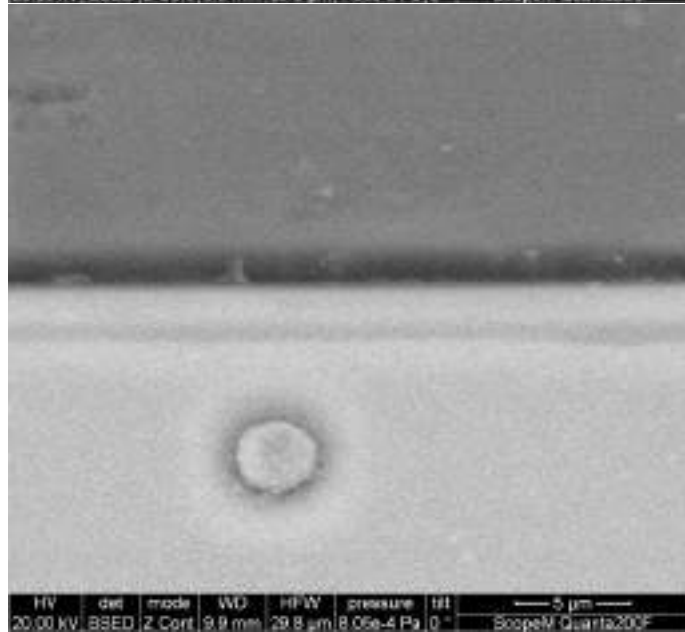
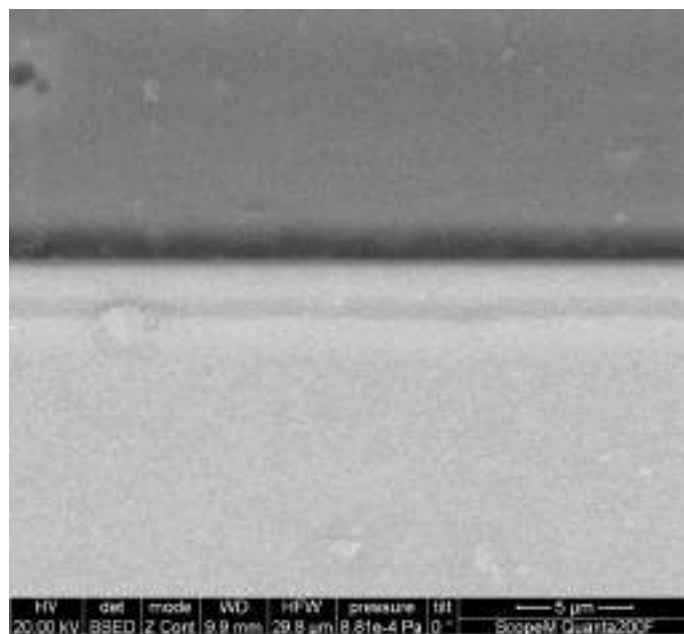
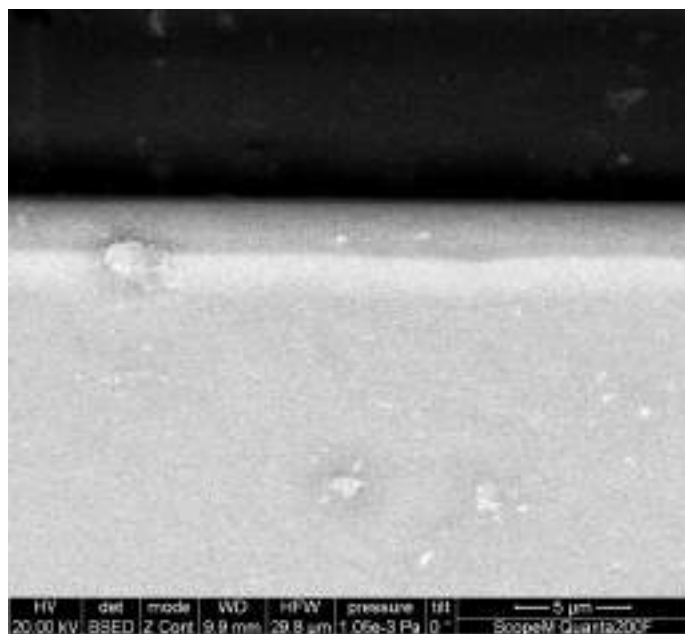


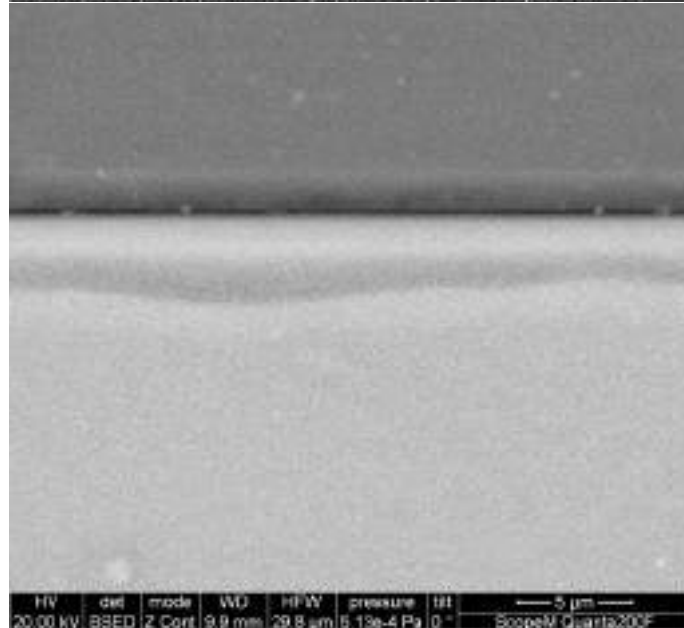
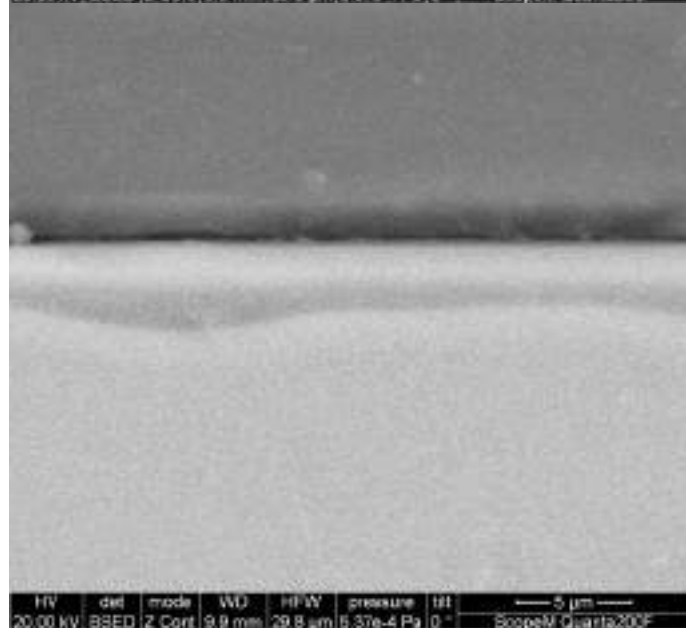
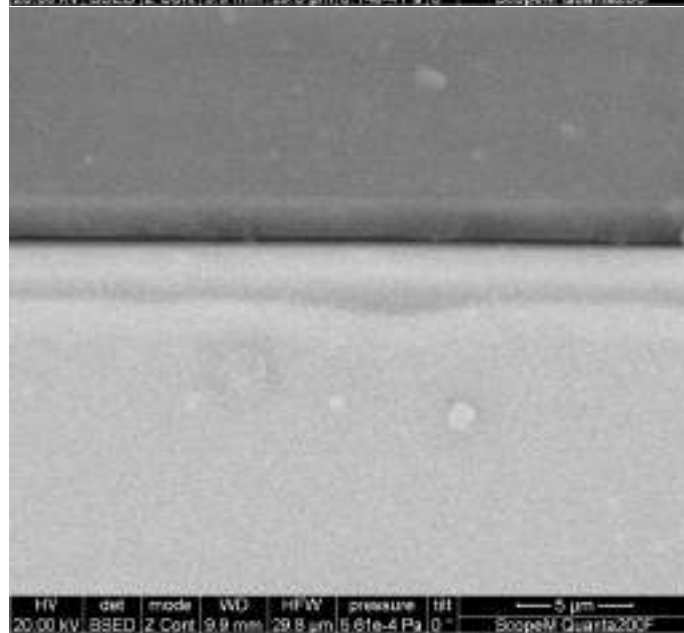
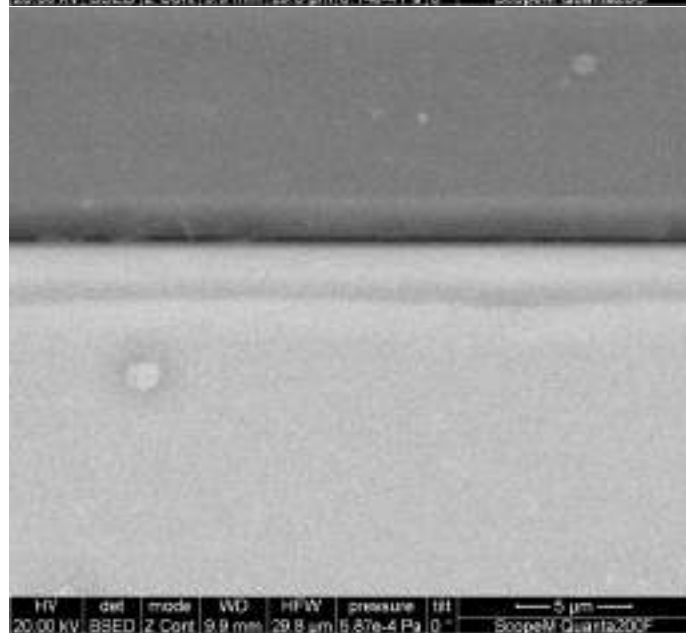
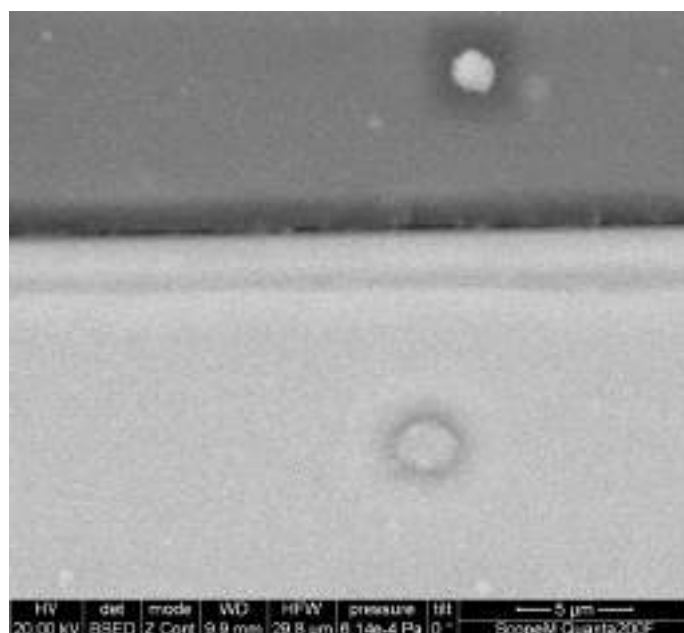
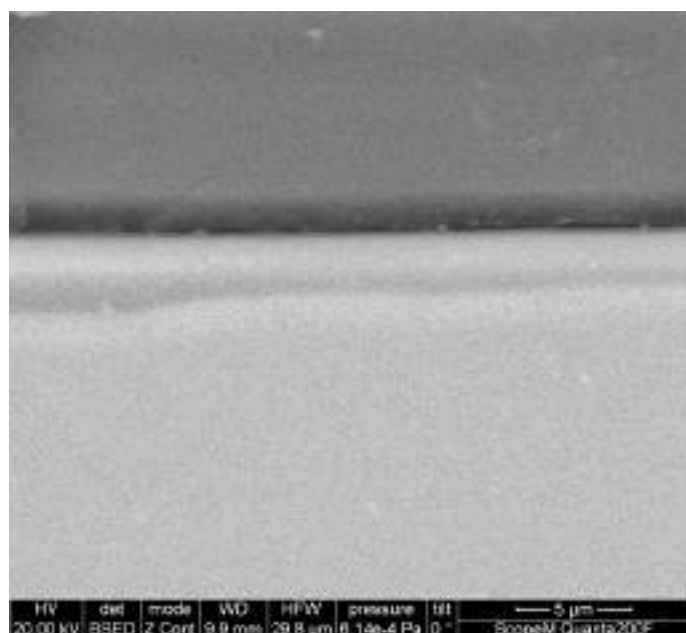


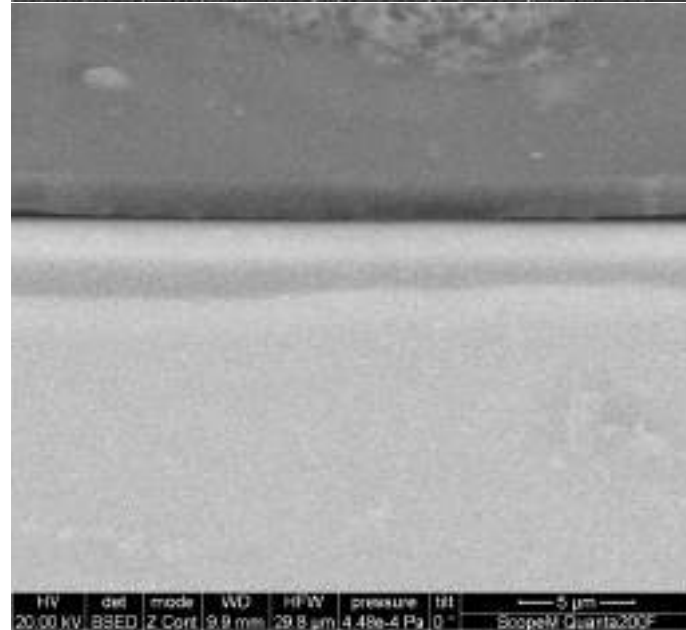
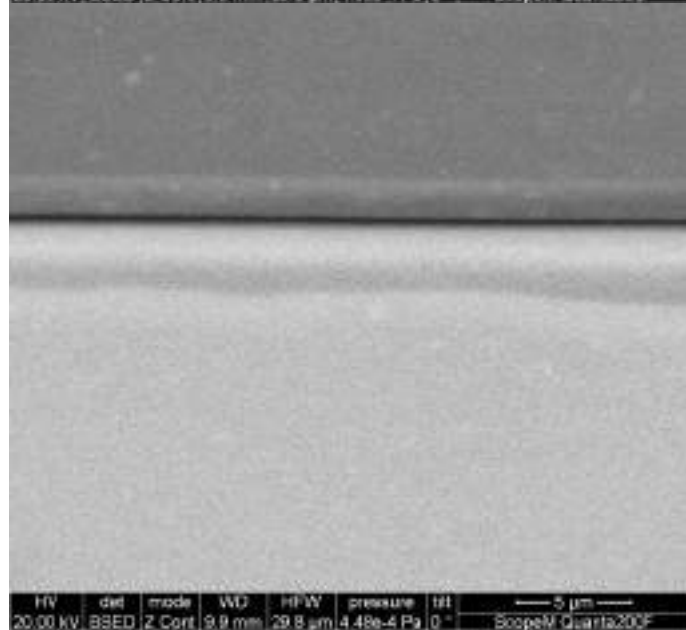
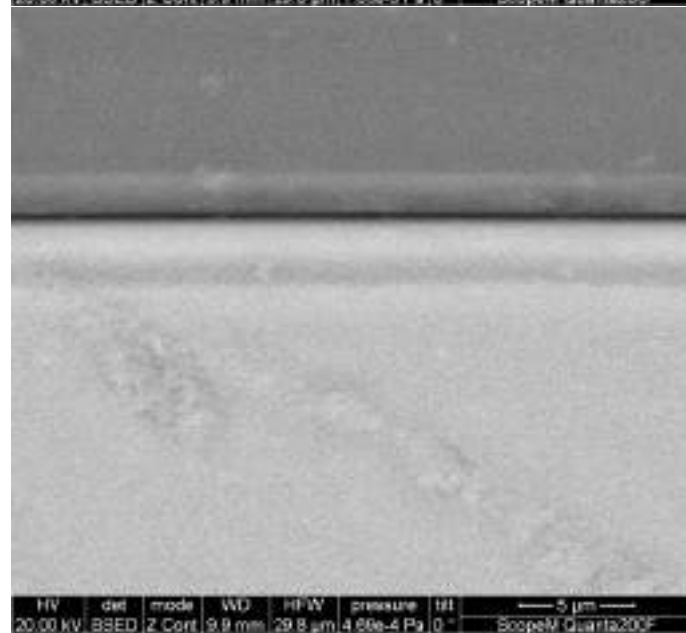
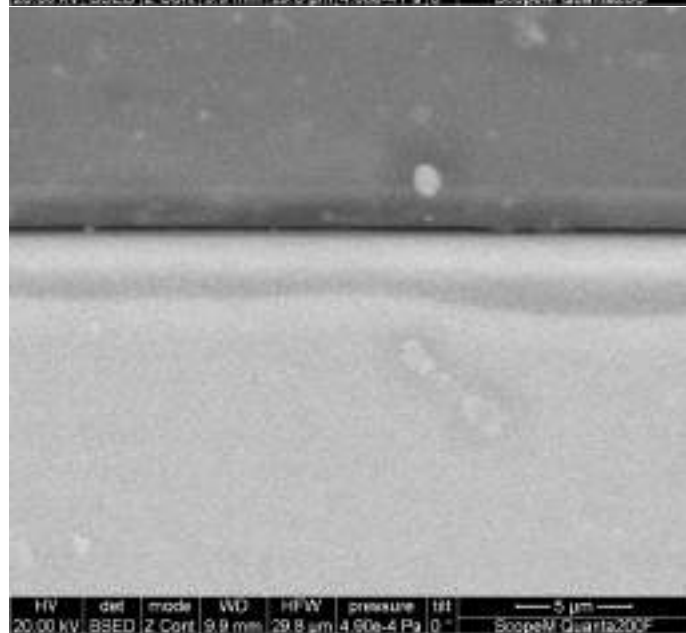
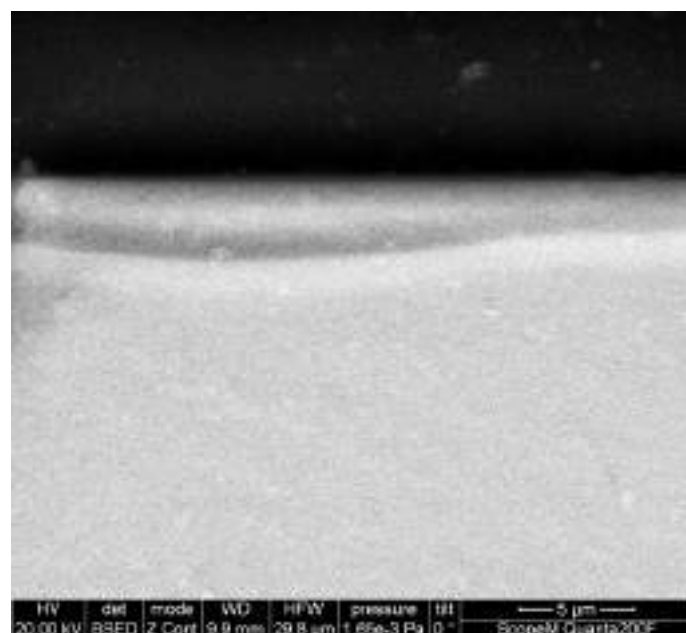
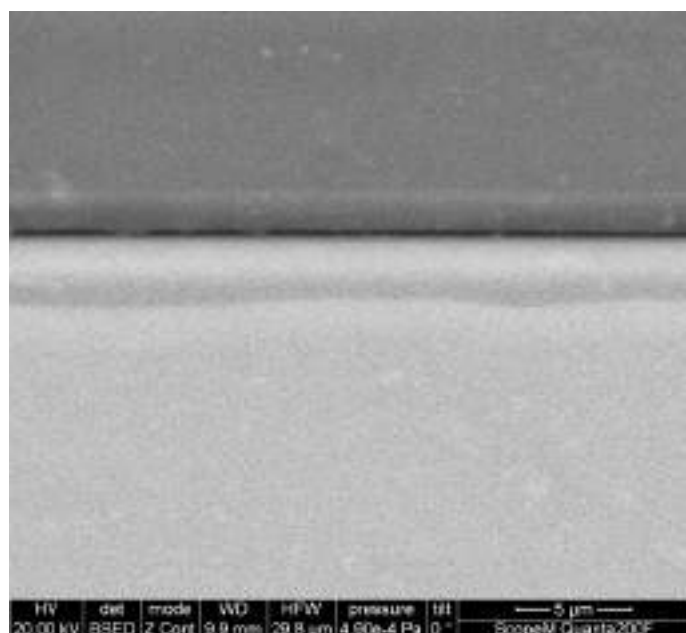


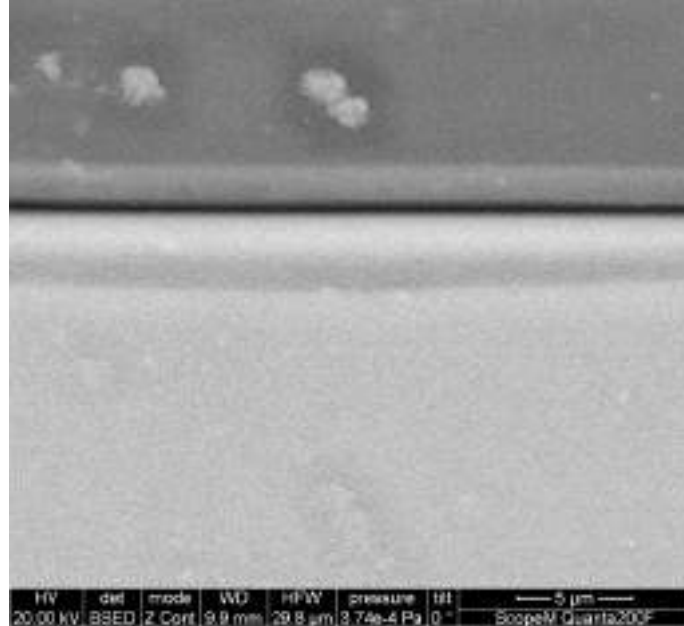
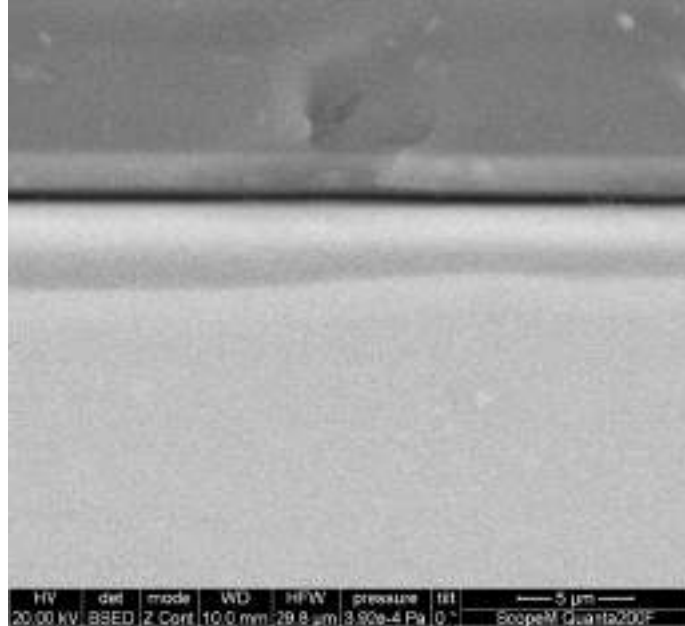
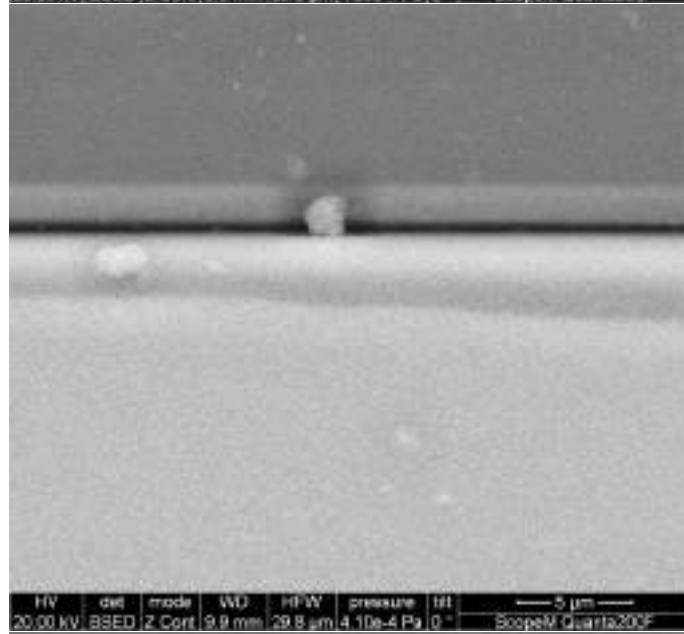
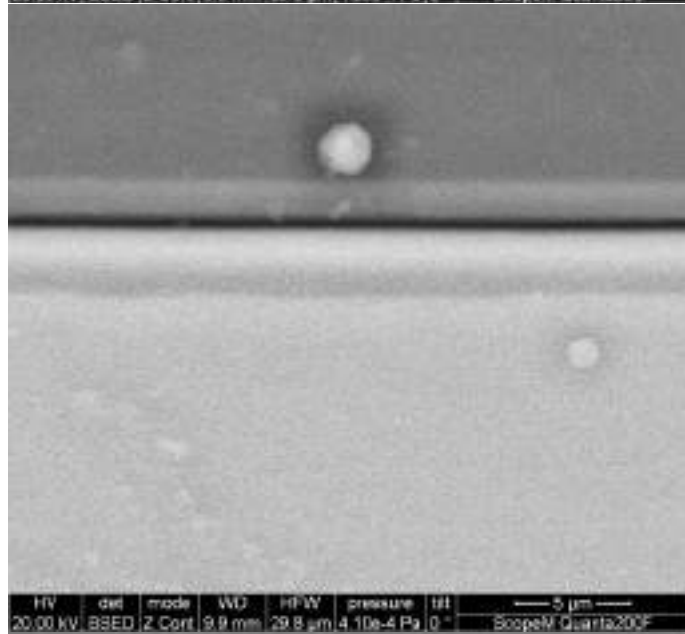
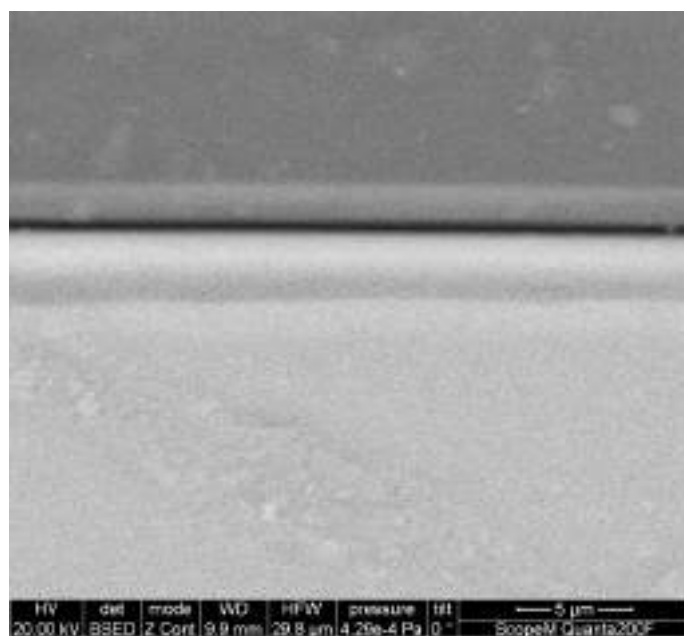
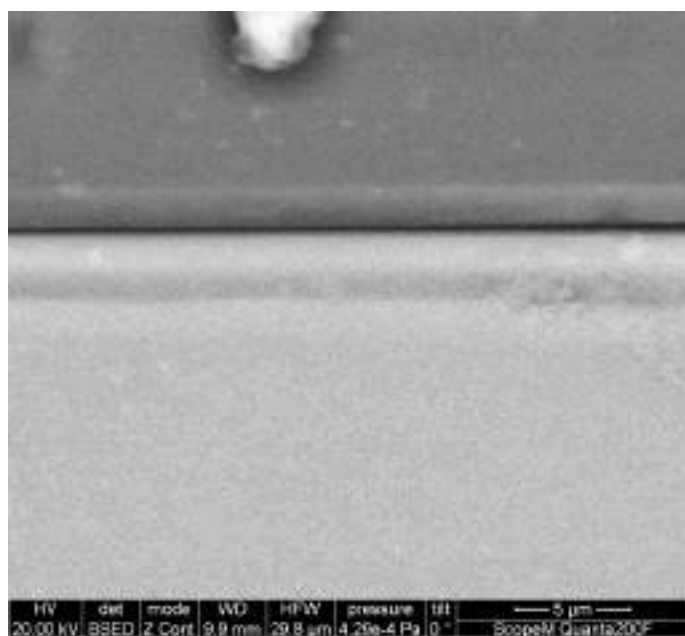
V 9 months

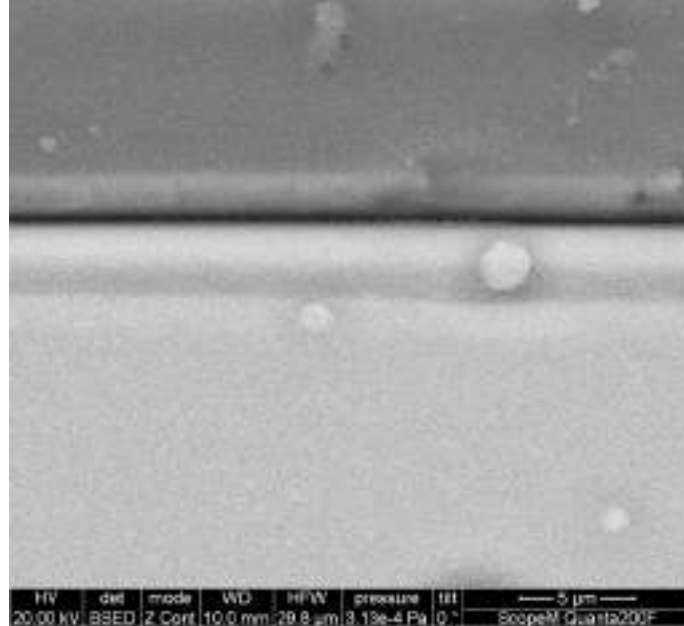
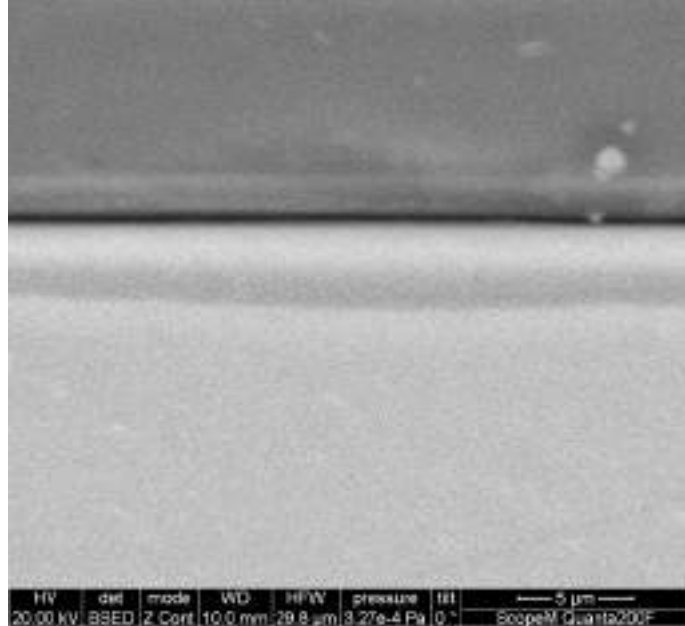
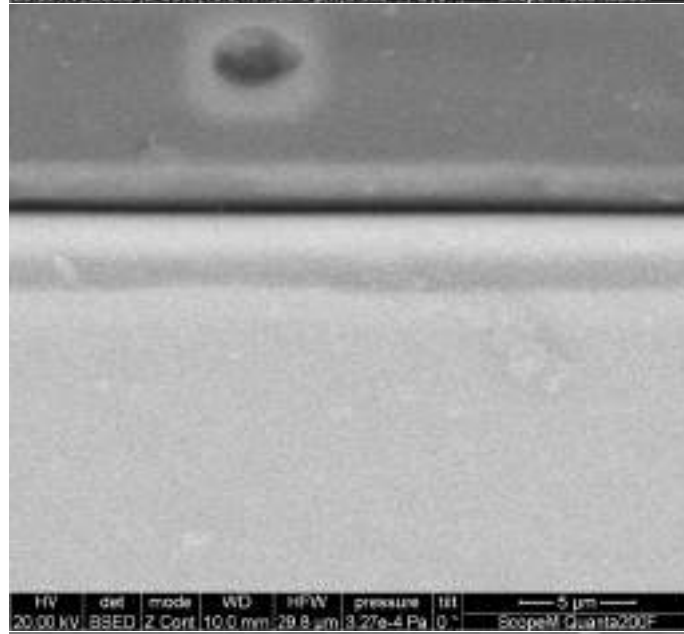
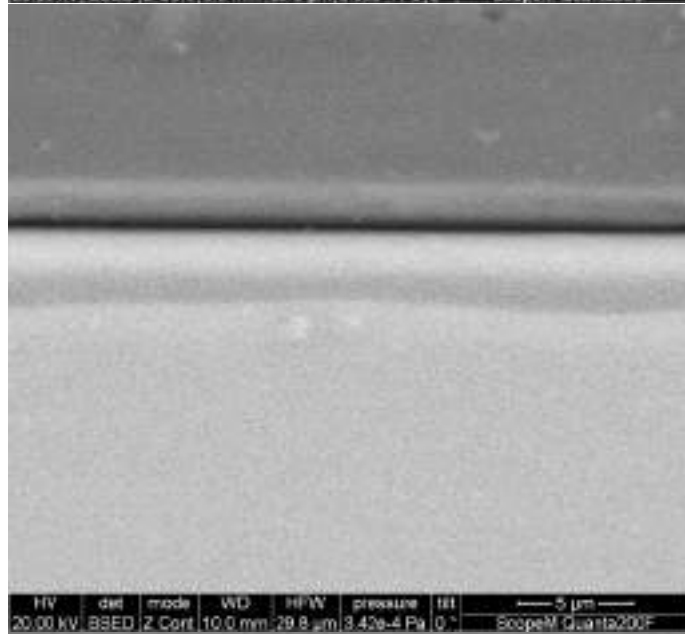
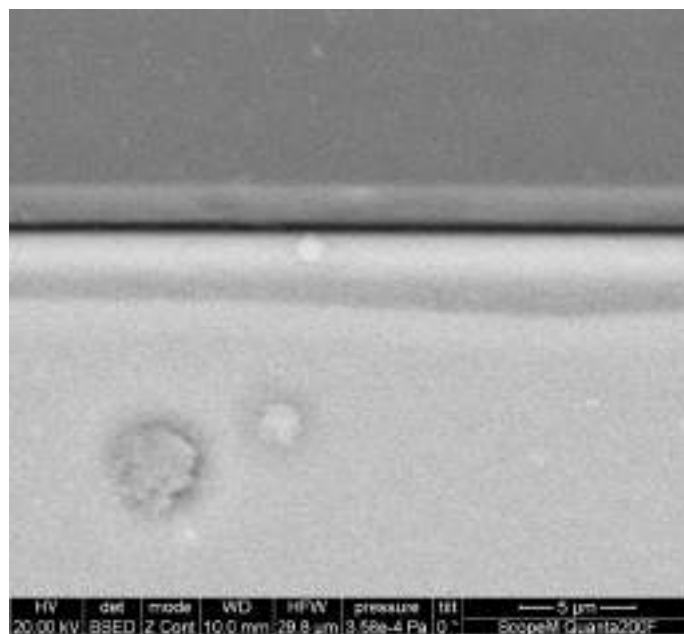
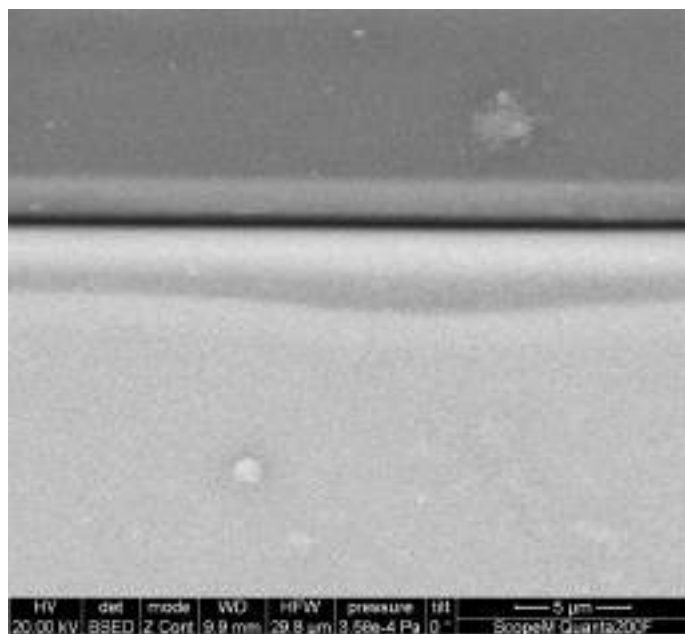


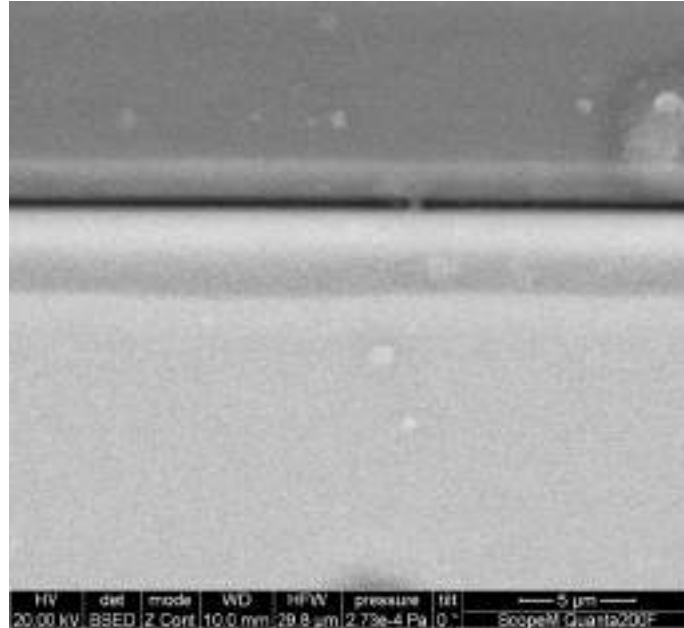
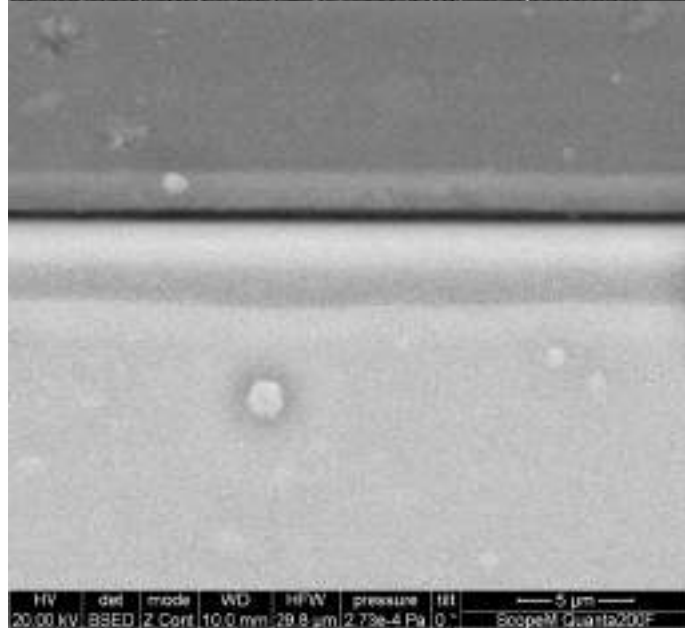
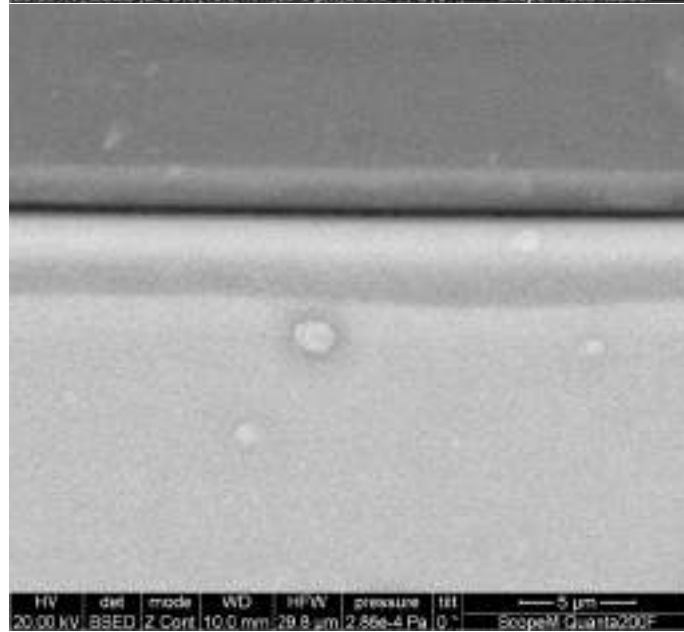
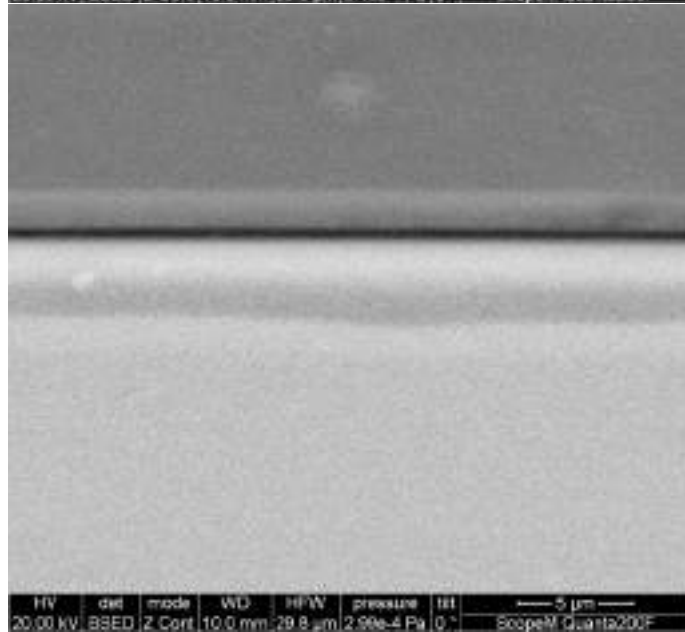
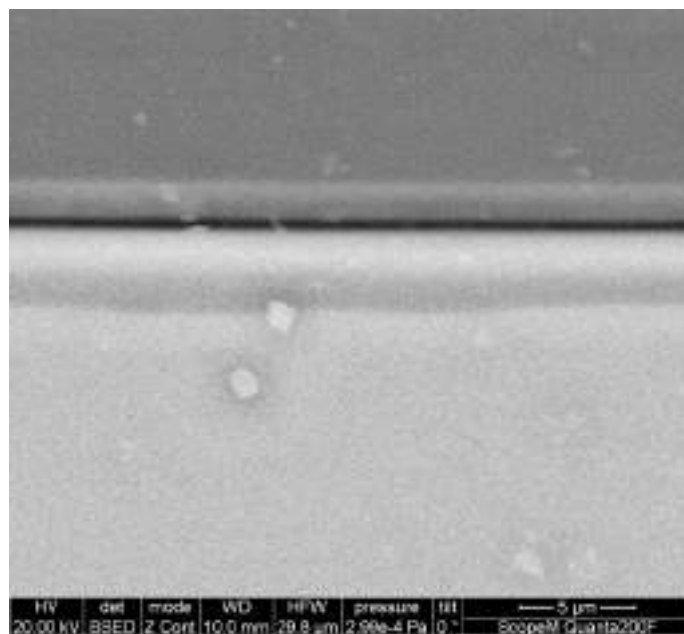
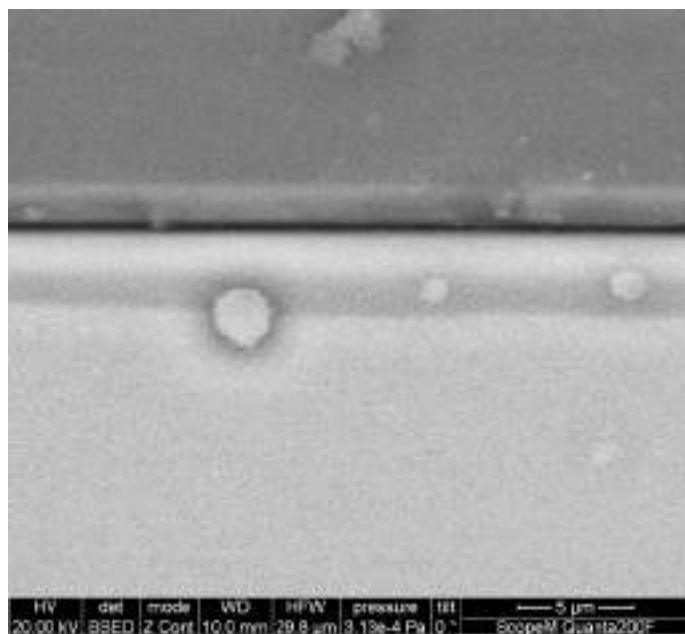


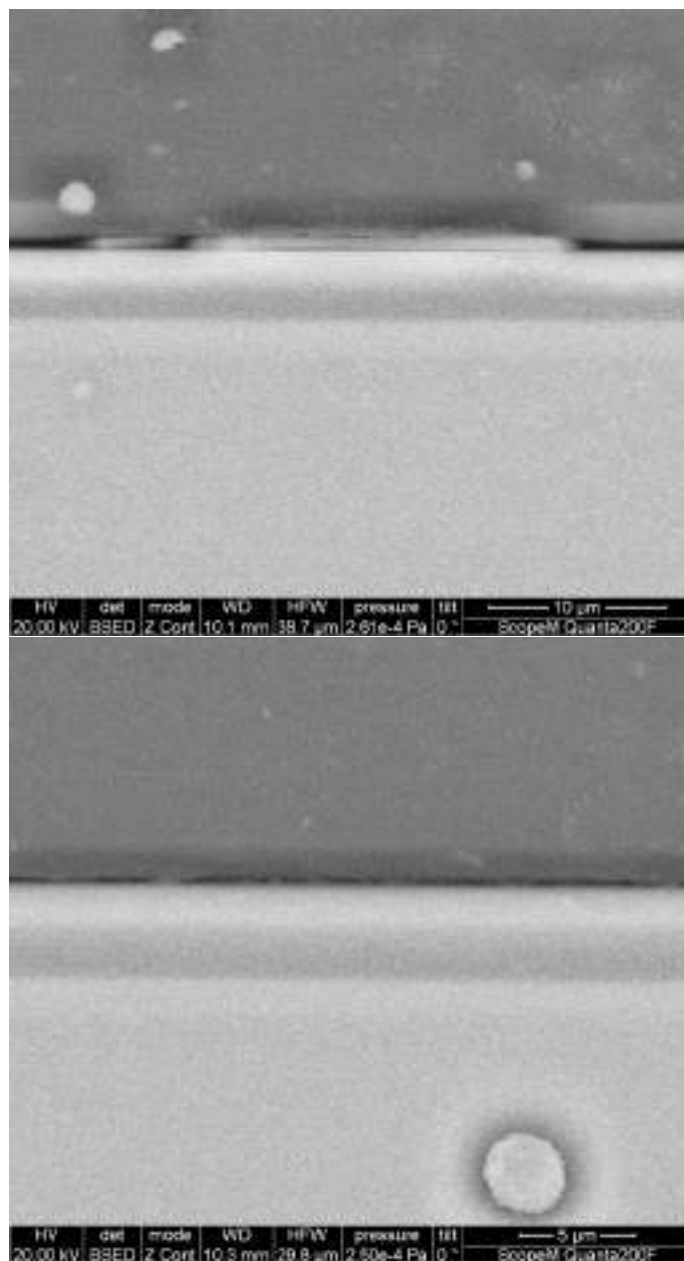
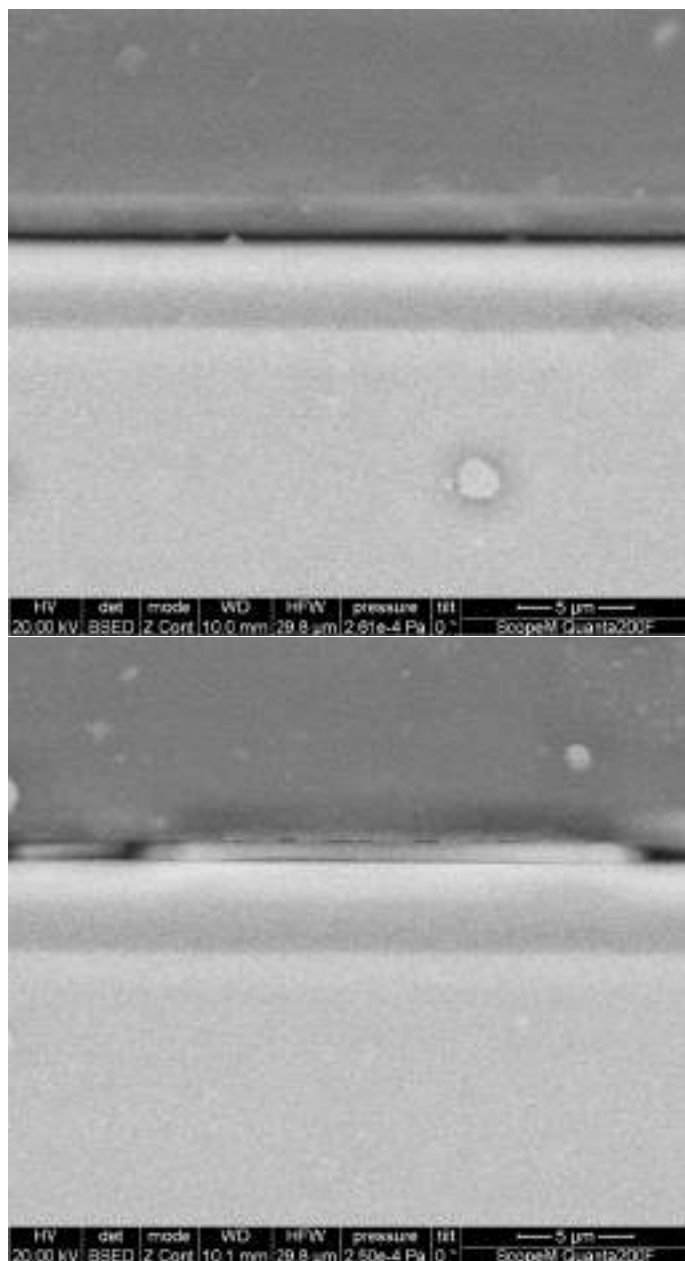












V 17 months

Annex XI

Table XII.1: SEM-EDX results from AG1078 alteration layer analyses on microsamples

AG1078	Pt 1	Pt 2	Pt 3	Pt 4	Pt 5	Pt 6	Pt 7	Pt 8	Pt 9	Pt 10	Pt 11	Avg	St. dev.
Na ₂ O	0.09	0.49	0.44	1.19	0.15	0.42	0.29	0.61	0.47	0.47	0.74	0.49	0.30
MgO	0.16	0.35	0.34	0.46	0.3	0.23	0.32	0.21	0.74	0.18	0.46	0.34	0.17
Al ₂ O ₃	1.22	1.45	1.4	1.12	1.45	1.51	1.25	1.11	1.35	1.44	1.32	1.33	0.14
SiO ₂	86.61	86.44	83.92	73.42	85.83	86.8	87.05	83.82	83.6	85.94	87.06	84.59	3.93
P ₂ O ₅	0	0.2	0.34	0	0.37	0	0.27	0.45	0.12	0	0	0.16	0.17
SO ₃	0.8	0.65	0.81	0.38	1	0.87	0.77	0.82	0.67	0.83	0.2	0.71	0.23
Cl ₂ O	0.32	0.29	0.35	0.46	0.45	0.4	0.45	0.44	0.33	0.22	0.29	0.36	0.08
K ₂ O	6.65	6.27	7.75	19.33	6.62	6.25	6.19	8.09	8.02	7.05	6.23	8.04	3.81
CaO	4.14	3.86	4.64	3.64	3.83	3.53	3.4	4.45	4.7	3.88	3.7	3.98	0.45

Table XII.2: SEM-EDX results from LM12433 alteration layer analyses on microsamples

LM12433	Pt 1	Pt 2	Pt 3	Pt 4	Pt 5	Pt 6	Pt 7	Pt 8	Pt 9	Pt 10	Pt 11	Pt 12	Pt 13	Pt 14	Pt 15	Avg	St. dev.
Na ₂ O	0.6	0.43	0.6	0.27	0.42	0.28	0.53	0.17	0.48	0.5	0.51	0.44	0.88	0.32	0.52	0.46	0.17
MgO	0.68	0.63	0.57	0.36	0.85	0.57	0.7	0.83	0.55	0.61	0.63	0.9	0.7	0.82	0.56	0.66	0.14
Al ₂ O ₃	1.67	1.4	1.58	1.46	1.63	1.41	1.36	1.68	1.11	1.24	1.42	7.1	1.7	1.65	1.45	1.86	1.46
SiO ₂	83.23	84.84	84.49	84.55	83.38	81.32	78.1	84.22	82.48	81.82	82.58	77.95	81.55	82.65	81.36	82.30	2.10
P ₂ O ₅	1.69	1.66	1.66	1.48	1.15	1.61	1.62	1.54	1.98	2.14	1.65	1.34	1.63	1.82	2.14	1.67	0.27
SO ₃	0.2	0	0.58	0	0	0.6	0.2	0	0.44	0.72	0	0	0.58	0	0.33	0.24	0.27
Cl ₂ O	0.26	0.17	0	0.11	0.13	0.25	0	0.18	0.36	0.38	0	0.18	0	0.26	0.34	0.17	0.13
K ₂ O	5.69	4.81	4.79	5.31	6	6.3	11.58	4.89	5.61	6.34	7.61	5.52	6.45	5.68	6.73	6.22	1.67
CaO	4.69	5.09	4.98	5.47	5.21	5.9	4.93	5.45	5.45	5.09	5.1	5.17	1.14	5.48	5.31	4.96	1.10
MnO	1.29	0.97	0.75	0.99	1.25	1.76	0.98	1.05	1.54	1.16	0.5	1.39	1.14	1.32	1.27	1.16	0.31

Table XII.3: SEM-EDX results from LM15473 alteration layer analyses on microsamples

LM15473	Pt 1	Pt 2	Pt 3	Pt 4	Pt 5	Pt 6	Pt 7	Pt 8	Pt 9	Pt 10	Average	St. dev.
Na ₂ O	1.68	1.62	0.84	0.85	2.29	0.79	0.9	1.68	1.44	1.01	1.31	0.51
MgO	0	0.53	0.33	0	0.83	0.65	0.28	0.5	0.4	0.44	0.40	0.26
Al ₂ O ₃	0.97	1.17	1.53	1.18	1.44	1.46	1.34	1.64	1.38	1.39	1.35	0.20
SiO ₂	73.41	72.88	79.57	73.14	72.61	83.16	76.71	72.56	73.63	72.19	74.99	3.69
P ₂ O ₅	0	0	0.32	0.29	0.21	0	0.59	0.26	0	0.12	0.18	0.19
SO ₃	0.26	1.01	0.32	0.75	0.61	0.78	1	1.74	0.34	0.7	0.75	0.44
Cl ₂ O	0.34	0.29	0.34	0.53	0.31	0.38	0.61	0.54	0.32	0.38	0.40	0.11
K ₂ O	18.73	17.39	11.42	17.29	16.71	7.36	13.68	16.14	17.83	18.26	15.48	3.63
CaO	4.62	5.11	5.48	5.98	4.99	5.42	4.9	4.93	4.66	5.51	5.16	0.43

Annex XII

S.No.	RH material	Quantity	Pollutants	Quantity	PID reading AA (ppm)	Purpose	Duration
1	Saturated salt solutions		-	-	-	To check the RH consistency using RH data-logger	15 days
	MgCl ₂	150 mL					
	Mg(NO ₃) ₂	150 mL					
	NaCl	150 mL					
2	Saturated salt solutions					To find out amount of AA for aging	11 days
	MgCl ₂	150 mL	AA	57 µL	38		
	Mg(NO ₃) ₂	150 mL	AA	57 µL	17.4		
	NaCl	150 mL	AA	57 µL	37		
3	Saturated salt solutions					To find out the influence of height in introducing AA into the desiccator for aging	2 days
	NaCl	150 mL	AA (2.5 cm)	57 µL	26		
	NaCl	150 mL	AA (7.5 cm)	57 µL	10.5		
	NaCl	150 mL	AA (12.5 cm)	57 µL	27		
4	Saturated salt solutions					To find out amount of AA for aging	1 day
	NaCl	150 mL	AA	57 µL	34		
	NaCl	150 mL	AA	57 µL	35		
	NaCl	150 mL	AA	57 µL	32.5		
5	-	-	AA	57 µL	1240	To find out AA concentration without RH material	19 days
			AA	57 µL	1280		
			AA	57 µL	1880		
6	Saturated salt solutions					To find out amount of RH material to be used for aging	6 days
	MgCl ₂	45 mL	AA	57 µL	49		
	MgCl ₂	65 mL	AA	57 µL	40		
	Mg(NO ₃) ₂	65 mL	AA	57 µL	21.7		
	Mg(NO ₃) ₂	70 mL	AA	57 µL	17.5		
7	Saturated salt solutions					To find out amount of RH material to be used for aging	5 days
	NaCl	68 mL	AA	5.7 mL	1980		

	NaCl	78 mL	AA	5.7 mL	1640		
8	Saturated salt solutions					To find out amount of AA and RH material to be used for aging	10 days
	MgCl ₂	50 mL	AA	57 µL	18.6		
	MgCl ₂	50 mL	AA	57 µL	24.4		
	Mg(NO ₃) ₂	50 mL	AA	57 µL	10.6		
	Mg(NO ₃) ₂	50 mL	AA	57 µL	10.7		
9	Saturated salt solutions					To find out amount of AA and RH material to be used for aging	10 days
	NaCl	50 mL	AA	5.7 mL	3570		
	NaCl	50 mL	AA	5.7 mL	3560		
10	Saturated salt solutions					To find out amount of AA and RH material to be used for aging	
	MgCl ₂	50 mL	AA	5.7 mL	13000		3 days
	MgCl ₂	100 mL	AA	5.7 mL	11000		
	Mg(NO ₃) ₂	50 mL	AA	5.7 mL	5200		
	Mg(NO ₃) ₂	100 mL	AA	5.7 mL	3150		
11	Saturated salt solutions					To find out amount of AA and RH material to be used for aging	3 days
	NaCl	80 mL	AA	5.7 mL	3100		
	NaCl	100 mL	AA	5.7 mL	2800		
12	Saturated salt solutions					To find out amount of AA and RH material to be used for aging	4 days
	MgCl ₂	50 mL	AA	1.9 mL	3210		
	MgCl ₂	50 mL	AA	1.9 mL	3210		
	MgCl ₂	50 mL	AA	2.3 mL	4030		
	Mg(NO ₃) ₂	50 mL	AA	3.8 mL	2570		
	Mg(NO ₃) ₂	50 mL	AA	3.8 mL	2240		
	Mg(NO ₃) ₂	50 mL	AA	3.8 mL	2480		
13	Preconditioned silica gel					To find out amount of RH material to be used and check any unwanted salt neocrystallizations on glass samples	13 days
	50% RH	175 g	AA	4.2 mL	60.8		
	50% RH	175 g	AA+FA	4.2 mL+1.47 mL	80.8		

14	Preconditioned silica gel					To find out amount of AA+FA and RH material to be used for aging	4 days
	50% RH	60 g	AA+FA	42 mL+14.7 mL	16440		
	36% RH	60 g	AA+FA	42 mL+14.7 mL	15600		
	50% RH	60 g	AA+FA	4.2 mL+1.47 mL	1002		
15	Preconditioned silica gel					To find out amount of AA+FA and RH material to be used for aging	12 days
	35% RH	60 g	AA+FA	8.4 mL+2.94 mL	1520		
	50% RH	60 g	AA+FA	6.3 mL+2.21 mL	7190		
	70% RH	60 g	AA+FA	4.2 mL+1.47 mL	6365		
16	Preconditioned silica gel					To find out amount of AA+FA and RH material to be used for aging	8 days
	35% RH	55.07 g	AA+FA	8.4 mL+2.94 mL	2060		
	50% RH	60 g	AA+FA	5.1 mL+1.79 mL	2110		
	60% RH	65.07 g	AA+FA	4.2 mL+1.47 mL	1910		

AA = Acetic acid, FA = Formic Acid