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Phosphate dental cements aged in vivo up to 25 years

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Phosphate dental cements aged *in vivo* up to 25 years

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Abstract

Phosphates particularly zinc phosphates is a family of conventional dental cements that was developed a century ago and has been in use until today despite the fact that a number of new resin composite cements have been introduced in the market through the years. A close inspection of the *in vivo* aged samples provides insights to the margins and to the micro-leakage thus would sharpen the understanding and inspire the future development of the cements and cementation interfaces between the dental restorations and the natural tooth or implant abutment. This study highlights the cementation interface and its structural change during *in vivo* aging. Besides the focused studies on phosphate cements, limited investigation has also been performed on resin composite cements as references.

Keywords: dental cements, phosphates, chemically bonded ceramics, resin composites, aging

1. Introduction

Dental restorations are luted on the natural teeth or implant abutments to ensure decent retention and to seal the margin from infiltration of saliva and intraoral fluids. Many types of luting cement materials have been used by the date with different properties that include zinc phosphate, zinc polycarboxylate, glass ionomer, resin ionomer, composites and adhesive resin¹. The newly developed resin composite cements have usually better adhesion behaviors than the classical phosphate cements. They are less soluble and are faster to harden, thus decreases the treatment time. One drawback of strong concern on resin composite cements is the fact that the excess cement squeezed inside the gingiva gap is more difficult to remove and may cause pulp irritation^{1,2}.

Even though the adhesion provided by calcium or zinc phosphate cements are known to be lower than that provided by the newer resin-based cements, there are evidence indicating that the phosphate cement luted restorations stayed in use without obvious problem. Zinc phosphate cement anchors the restorations purely mechanically. In general, it has good compressive strength whereas low tensile strength. It underwent dissolution/chemical changes in oral environment³. However, despite or owing to these problems zinc phosphate appeared a reliable cement with success rate of incredible 74% after 15years with conventional fixed partial dentures⁴ and restorations with over 20 and even up to 45 years working time^{2,5}

In practice, a cementation gap is always present between the restorations and tooth/implant abutment and its width is determined by the design and the type of cement used, as well the preparation method and the skills of the dentist. This cementation gap close to margin end, known as marginal gap, effects the bonding strength, the dissolution of the cement and the marginal leakage⁶. Different luting cements affects the sealing ability and the possible obstructions of dental fluid penetration into the marginal leakage as well the resistance to bite stresses^{7,8}.

McLean and von Fraunhofer suggested that the maximum tolerable cementation gap should be 120 μm but this figure was questioned by Kydd et al. who showed that even the marginal gaps up to a width of 244 μm in gold crown zinc phosphate lasted longer than 20 years^{5,9}. The width of the cementation gap will affect the micro-leakage that is depending on the cementation layer thickness. When the thickness of the cementation layer was 25-75 μm there was not seen any changes in the micro-leakage whereas when this thickness was greater than 150 μm the micro-leakage became significantly higher^{5,10}.

Even though the zinc phosphate cement luted restorations have shown to last long time, it has been reported that the marginal leakage in restorations may be responsible for different failures of the restorations. One of such failures is the bacterial colonization that in minor case can result in marginal discoloration and in severe cases may lead to pulpal pathosis, periodontal disease, and microbiological ingress and secondary caries¹¹⁻¹⁴.

Not only has the marginal gap caused problem to the restorations but also the bacterial adhesion on the excess cement. The excess cement squeezed out from the marginal end generates a rough surface in the gingiva gap that favors the bacterial adhesion and can behavior as the origin to peri-implant mucosities and peri-implantitis^{15,16}. It has been shown that surface finish and proper removal of the excess cement will minimize the bacterial adhesion positively¹⁷.

A close inspection of the *in vivo* aged samples would provide insides to the margins and to the micro-leakage thus sharpen the understanding and inspire the future development of the cements and cementation interface. The aim of this work was to study the cementation interfaces and the structural change of the cement during *in vivo* aging. All the samples were extracted teeth and implants with cemented restorations remaining on them. Although the designed focus was on phosphate cements, limited amount of samples with resin composite cements collected were also investigated and discussed as the references.

2. Materials and methods

2.1 Collection of the samples

Dental restorations after a varying time of *in vivo* service were removed from the patients and collected. The detailed list of the collected samples is presented in the Table 1. It is noted that the restoration *b* and *f* were fractured during removal and *e* was removed because of infections. The restoration *a*, *c*, and *d* were in good conditions but no patient's situation and other information were recorded. However, it is noted that the loss of coherence between the restoration and natural tooth or implant abutment was not the reason.

The collected restorations were in use for different *in vivo* times, varying from 6 to 25 years. The materials used for making restorations and abutments changed between the samples and also the type of phosphate cements and the way of using the phosphate cements. Both calcium and zinc phosphates and resin composite cements containing alumina and silica as fillers are included in the samples. The phosphate cements were used both in luting and in cavity lining.

Table 1. The list of collected samples of *in vivo* aged restorations

Sample	Restoration material	Type of cement	Abutment	Age (years)	Luting/lining	Notes
a	Co-Cr alloy	Zinc phosphate	Ti	6	Luting	
b	Al-Si-O	Calcium phosphate	Tooth	25	Luting	Fractured
c	Au-Pd alloy	Zinc phosphate	Tooth	9	Luting	
d	Au-Pd alloy	Calcium phosphate	Tooth	21	Luting, cavity lining	Fractured
e	Ni-Cr-Mo alloy	Zinc phosphate	Tooth	6	Cavity lining	Resin based cement for luting

f	Co-Cr alloy	Calcium phosphate	Au-Pd alloy	20	Cavity lining	Resin based cement for luting
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The collected restorations were first inspected with a light microscope (S8APO, Leica Microsystems, Germany) followed by the characterization using scanning electron microscopes (SEM). The as received restorations were washed with ethanol in ultra-sonic bath prior SEM where the outside surface and interfaces between the restoration/cement/abutment were investigated. After the characterization of the outside surface the restorations were cut horizontally or/and vertically with low speed saw and investigated with SEM without polishing and after polishing to 1 μm surface finish. More detailed investigation of the interfaces was conducted after the cross sections polishing by an Argon-ion beam polisher (CP-09010, JEOL, Japan) with the acceleration voltage of 5 kV for 15 hours. An field emission scanning electron microscope (SEM) (JSM-7000F, Jeol, Japan) equipped with an energy dispersive spectroscopy (EDS) detector (INCAx-sight, Oxford Instruments, UK) and a tabletop scanning electron microscope (TM3000, JEOL) were used for SEM investigations of the clean surfaces without any additional coating.

XRD and Raman spectra were used for analyzing the phase assembly in *in vivo* aged cements that was compared to freshly made zinc phosphate cement prepared according the instruction from the producer (Harward cement, Hoppegarten, Germany). After the microstructure characterization the cements were carefully removed and analyzed using XRD with $\text{Cu}\alpha 1$ radiation (X'Pert Pro, PANalytical, Netherlands) and Raman spectra normalized to the peak at 110 cm^{-1} (785 nm red laser, LabRAM HR, HORIBA, United States of America).

3. Results

3.1 Pores and porosity

Pores or voids with different size generated during the mixing and setting of the cement, as shown in Figure 1 and 2, were observed both in freshly made and aged cements. They can be classified to two types, of which one is spherical-shaped with the formation of faceted crystals inside whereas the other with irregular shapes having smooth inner surfaces without crystals inside. The formation of these pores can be originate to the inclusion of the air bubbles during the mixing or evaporation of the water during the setting. The latter most likely leads to the formation of micro-pores up to 10 μm in diameter while the former produces pores up to 172 μm . The spherical pores shows crystal formation independent to the size. It is noted that the pores on the surface of phosphate cements exposed to gingiva or oral liquids are covered with body tissue, indicating a good biocompatibility of the cements.

3.2 Crystallization and growth of hopeite

The uneven reaction during setting gives possibility for crystal growth in the pores as seen in Figure 1 for freshly made zinc phosphate cement as an example. Similar crystals are seen in the *in vivo* aged zinc phosphate samples, as seen in Figure 2a and b, and it is obvious that the crystals have grown in size during the aging. The XRD analysis confirms that the crystals can be attributed to the crystalline form of zinc phosphate $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ("hopeite")^{18,19} together with the typically unreacted ZnO and MgO in an amorphous matrix, Fig 3a. The XRD on the freshly made zinc phosphate cement did not show peaks for hopeite even though the visual investigation reveals the crystals indicating a larger formation and growth of the hopeite during the aging.

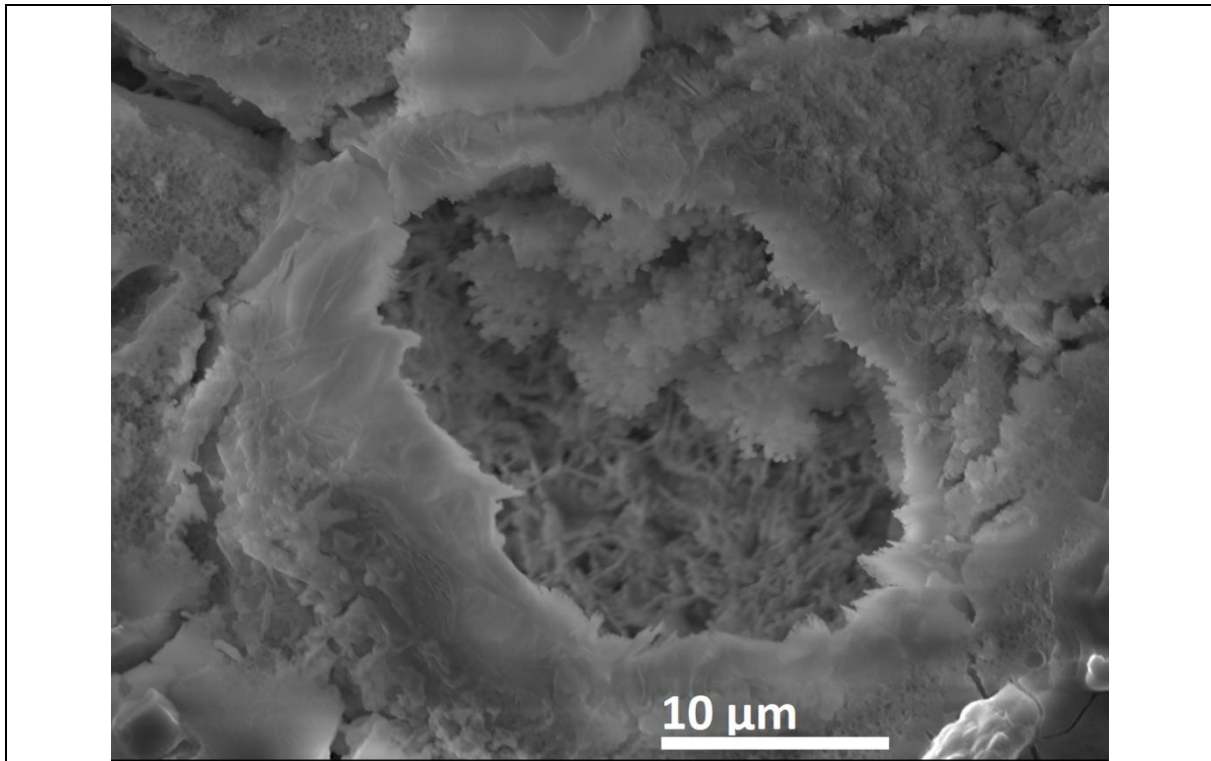


Figure 1. SEM image revealing the formation of crystals inside a pore observed in freshly made zinc phosphate cement.

The crystals are also observed in the calcium phosphate cement in contact with gingiva as shown in the Figure 2c, the composition of these crystals could not be confirmed due the difficulties to take the XRD but they are presumably hydroxyapatite. However, similar cement in the oral environment did not show such crystals in SEM but the XRD in Figure 3b shows increased intensity of the peaks for hydroxyapatite in an otherwise amorphous cement, confirming the good biocompatibility as already seen in the SEM. It is worth to note that no significant crystalline peaks attributed to solid filler particles (alumina, silica, fluorine) were detected after *in vivo* aging indicating the retention of the calcium phosphate cement in the oral environment.

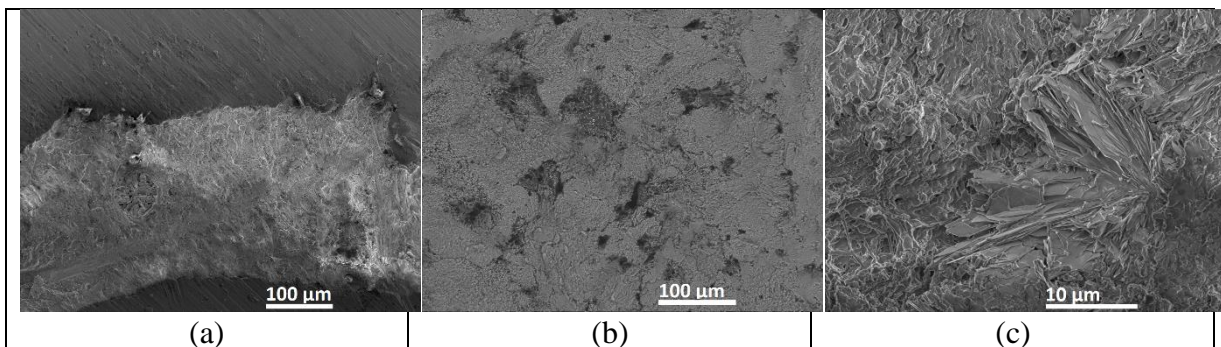


Figure 2. SEM images revealing the formation of large crystals inside the pores in a zinc phosphate cement after 6 years *in vivo* aging, sample a (a), the pores on the surface of the cement after 25 years *in vivo* aging, sample b, exposed to oral environment that are covered

with body tissues appeared dark color in BS mode (b), and the crystal growth in a calcium phosphate cement after 25 years *in vivo* aging in contacting with gingiva, sample b (d).

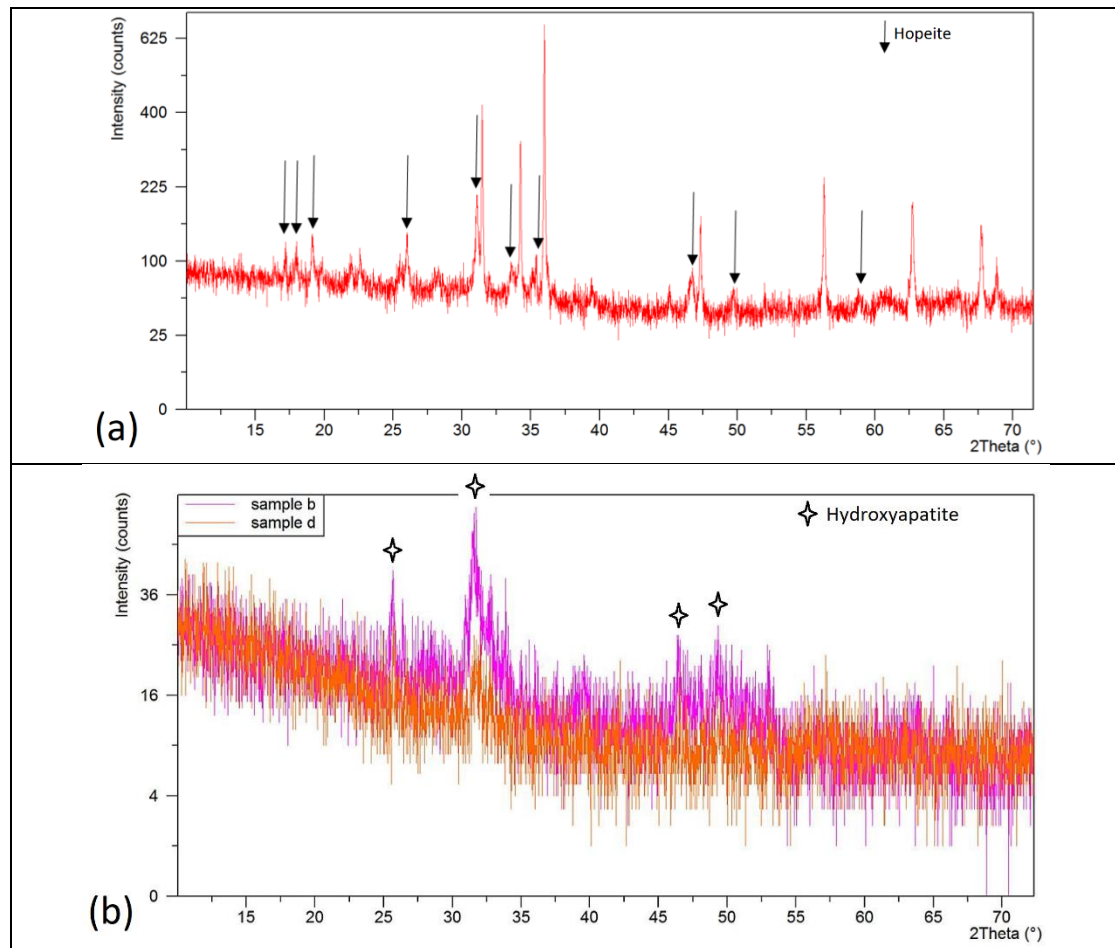


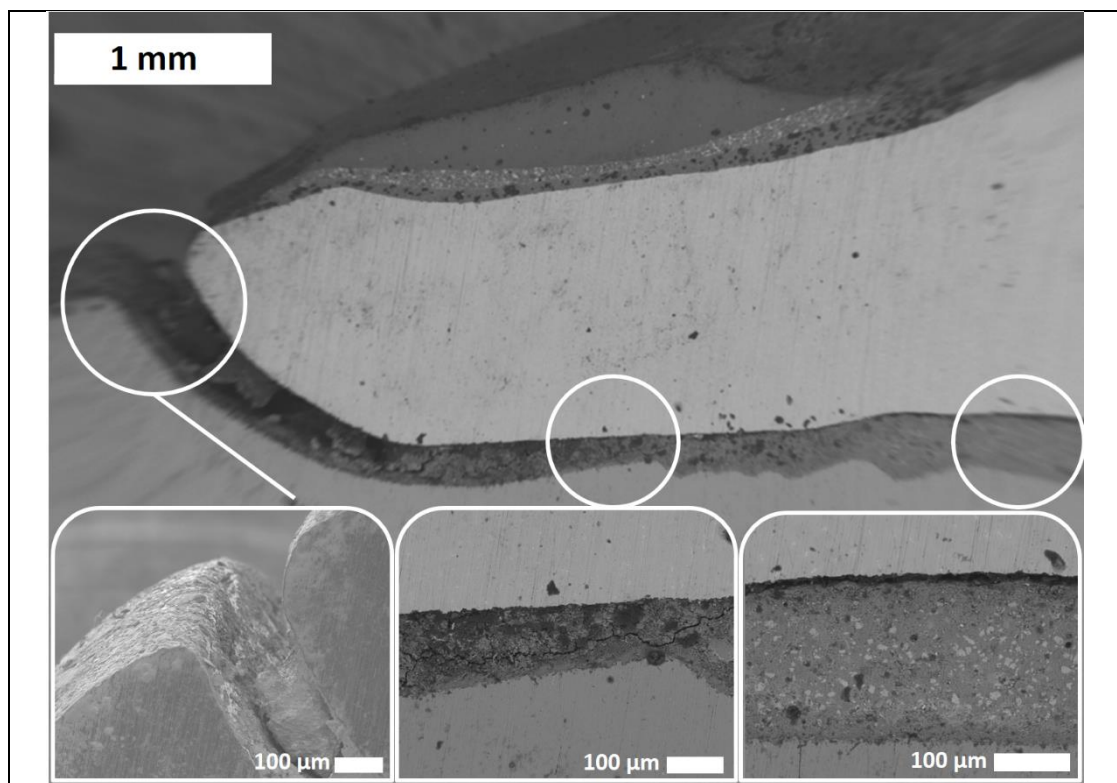
Figure 3. XRD patterns taken on the horizontally cut surface of a zinc phosphate cement *in vivo* aged for 6 years (sample *a*) (a), and on two calcium phosphate cement samples *in vivo* aged for 25 years (sample *b*) and 21 years (sample *d*), respectively (b).

3.3 Cracks and changes in ZnO₂ content

Cracks were observed in all *in vivo* aged phosphate cements samples in the cement matrix along the interfaces either between cement and tooth/abutment or between cement and restoration. The location of the detached interface (gap) depended on the cement material used. The most severe cracking in the cement is located at the margin end, as demonstrated in the Figure 4, where the SEM image taken on a vertically cross-sectioned sample *a* is presented. Close to the margin the cement is severely cracked and even lost. The cracks formed in the cement expose the cement to the oral environment thus affect the chemical composition of the cement. The zinc phosphate cement is known to decompose/dissolve^{10,20,21} in oral environment and this is also the case here. The EDS analysis confirms the chemical changes of the cement. The EDS results for the sample with 9 years *in vivo* close to the margin end of the restoration

1 is shown in Figure 5. The change of composition is confirmed also with Raman, shown in
2 Figure 6 after 25 years *in vivo* aging in comparison with the freshly made cement. The Raman
3 shift connected to ZnO (101, 388 and 437 cm⁻¹) are decreased during aging when compared to
4 a freshly made cement. The typical microstructure of zinc phosphate remains deeper in the
5 marginal gap, as see in the insets in the Figure 4. The microstructure after the ZnO₂ dissolution
6 becomes more porous and fragile deteriorating the mechanical properties of the cement It is
7 noted that the chemical composition of the phosphate cement remains intact and only zinc oxide
8 particles are disappeared. The dissolution starts where there is an access to the oral environment.
9 So, the cement starts to dissolve in the interfacial gaps between the cement and restoration or
10 between the cement and tooth/abutment as well close to the cracks. The dissolution process
11 **ought to be** time depended^{20,21}; the longer time the restoration is in use the larger dissolution of
12 zinc oxide and deterioration of the mechanical properties of the cement **but it is not seen clearly**
13 **because there are even other factors affecting the reliability of the restoration such as**
14 **mechanical erosion and the gap width.**
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17 The calcium phosphate cement shows similar retention behavior close to the marginal
18 end of the restoration with cracks inside the cement. EDS analysis revealed also a chemical
19 change where the filler particles made of alumina, fluoride and silica are hard to detect close to
20 the margin end. They can be detected again at similar distances from the margin as Zn for zinc
21 phosphate cement shown in Figure 5.
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54 Figure 4. SEM images taken on a vertically cross-sectioned zinc phosphate cement sample *in vivo*
55 aged for 6 years (sample a) revealing cracking and loss of cement at the margin end. Insets
56 are images taken with higher magnification at the spots indicated by the circles.
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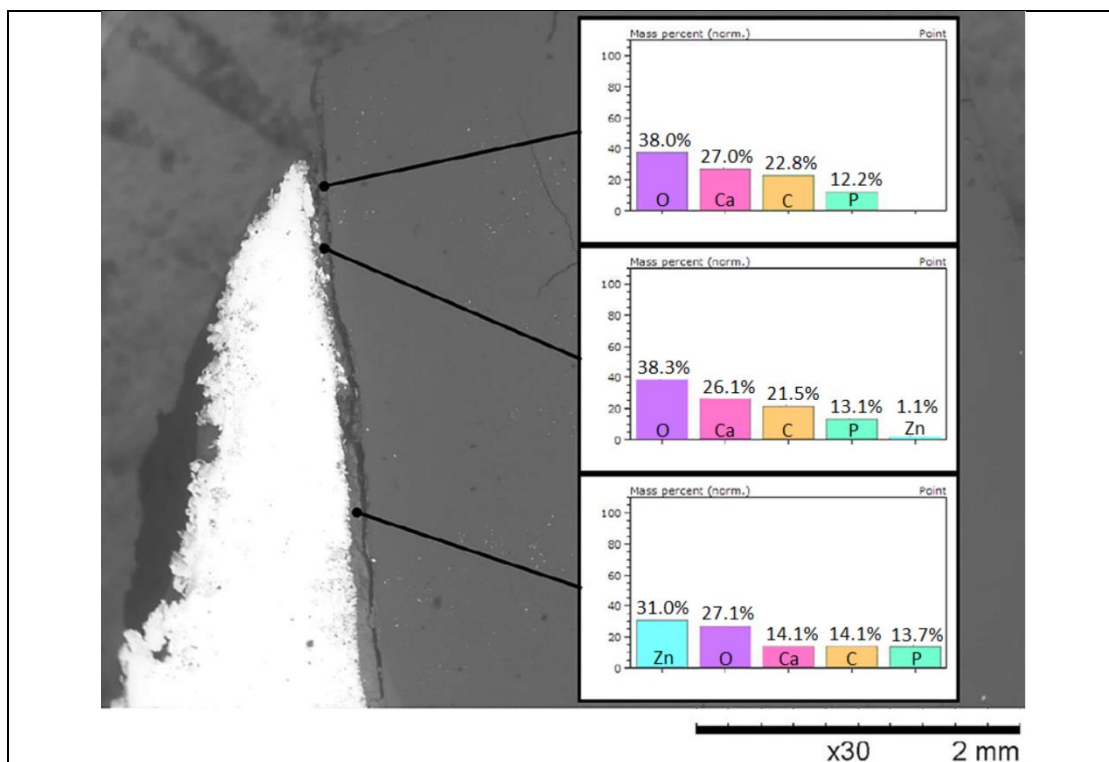


Figure 5. EDS analysis at the margin end of a zinc phosphate cement samples in vivo aged for 9 years (sample *c*), indicating the change of zinc and carbon content. The inserts show the EDX results for indicated area on the cement.

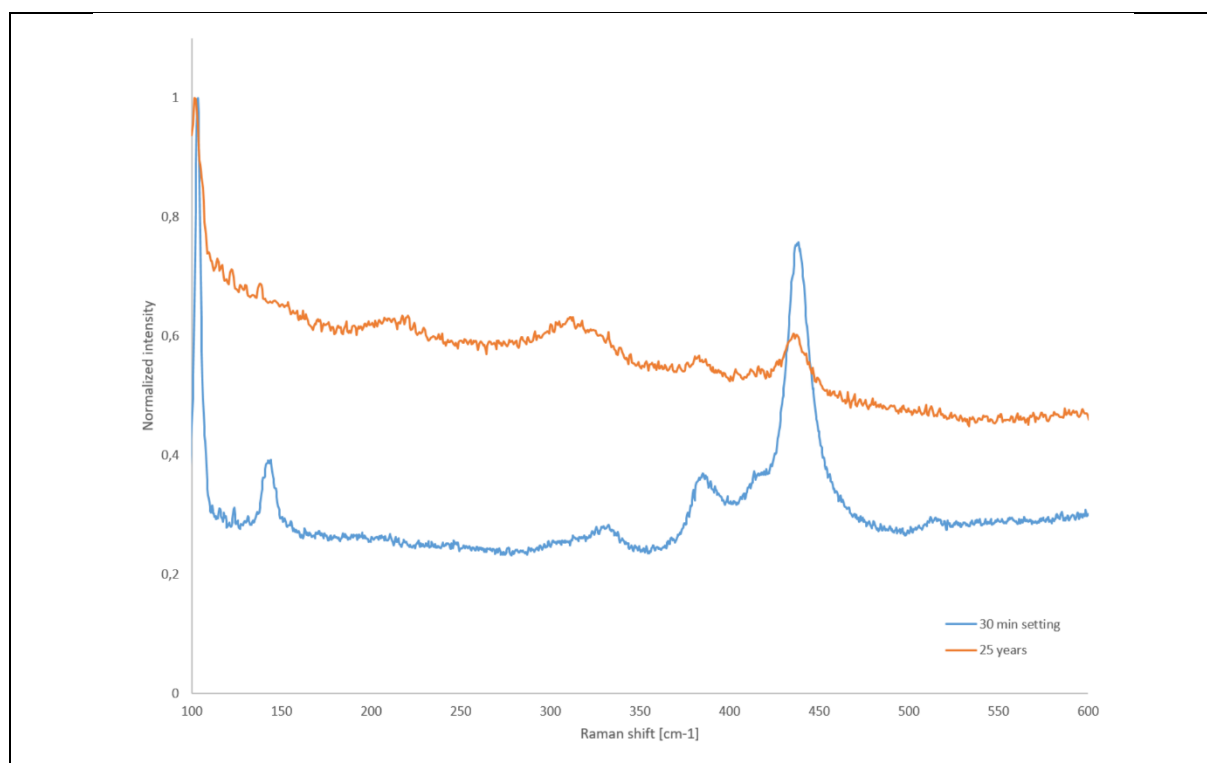
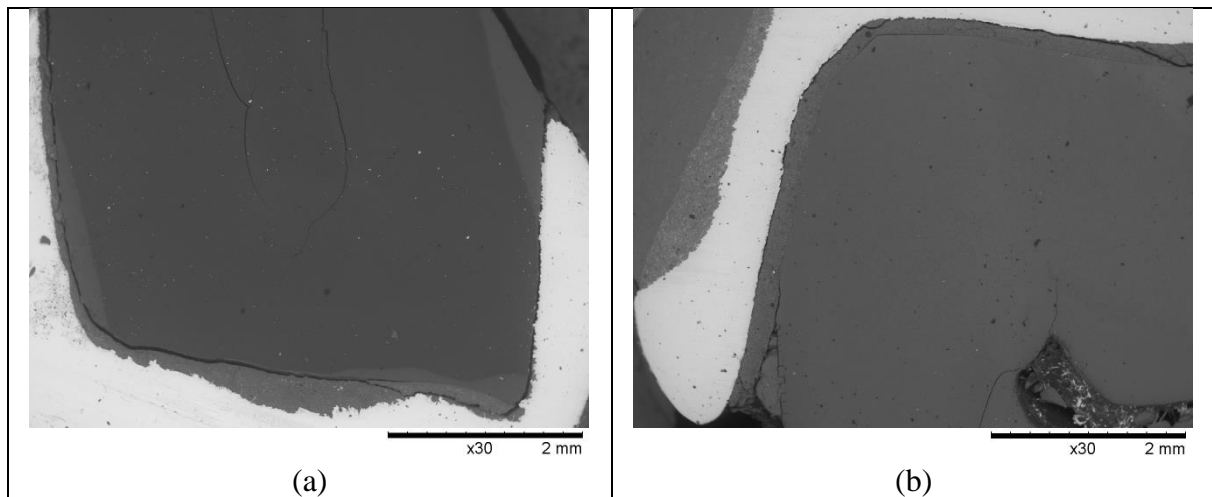


Figure 6. Normalized Raman shifts recorded in freshly made zinc phosphate cement and the one after 25 years in vivo aging, sample *b*.

3.4 Debonding and the formation of interfacial gaps

1 The observed crack formation along the interfaces either between cement and
2 tooth/abutment or between cement and restoration in all *in vivo* aged restorations led to the
3 interfacial detachment, *i.e.* the formation of interfacial gaps. The location of the interfacial gap
4 varies depending on the cement used. The zinc phosphate cement is detached often inside the
5 cement or on the interface between cement and tooth, see Figure 7a, while the interface between
6 cement and metal restoration remained intact. It must be noted that the interfaces between metal
7 and zinc phosphate are generally good and the cracking of the cement occurs mainly inside the
8 cement matrix, not on the interfaces as shown in the Figure 4 where the Titanium was used as
9 abutment and CoCr as restoration.

10 Calcium phosphate cement detached on the interface between cement and tooth and also
11 in some cases on the interface between cement and restoration. Sample *e* is a single crown luted
12 by resin composite cement with alumina and silica as fillers and zinc phosphate cement was
13 used at the top of the tooth for lining. The resin composite cement detached on the interface
14 between cement and crown. When the interfacial gap got closer to zinc phosphate lining it
15 moved to the interface between cement and tooth as seen in Figure 7b. It is also noted that the
16 interface debonding is a common feature that is observed in all the samples investigated in the
17 current study.



38 Figure 7. SEM images taken on the vertically cross-sectioned samples revealing the interfacial
39 debonding taking place on the interface between the zinc phosphate and tooth observed in
40 sample *c* (a), respectively, on the interface between the resin cement and crown that is turn to
41 the interface between zinc phosphate cement and tooth when zinc phosphate cement is used for
42 lining (upper right corner), sample *e* (b).

45 3.5 Carbon contamination

46 The SEM image shown in Figure 8 revealed that the marginal gap was filled by
47 biological masses in sample *a* after 6 years *in vivo* aging. As the cementation gap of the
48 restoration at the margin end was exposed to oral environment once cracked, the infiltration of
49 saliva/oral fluid may not only affect the overall chemical composition and mechanical
50 properties of the cements but also enable the deposition/accumulation of infiltrated biological
51 matter **that can be recognized as carbon contamination**. This is seen in all the samples as
52 demonstrated in the Figures 2, 5 and 8, where the backscatter SEM images reveals carbon
53 contamination existing even inside the pores besides along the interfacial gaps of the cement at
54 the margin end of the restorations. The carbon contamination was not only observed in the
55 marginal end of the restorations but also on the top of the tooth, as is seen in Figure 9 where the
56 zinc phosphate lining at the very top of the tooth is contaminated with carbon. The detected
57 carbon signalizes the infiltration of carbon-containing biological masses to the top through the
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interfacial gaps formed between resin composite cement and the restoration. Furthermore, it must be mentioned that the zinc phosphate lining appeared very brittle, inside which many cracks formed during cutting of the sample if not already formed during the *in vivo* service.

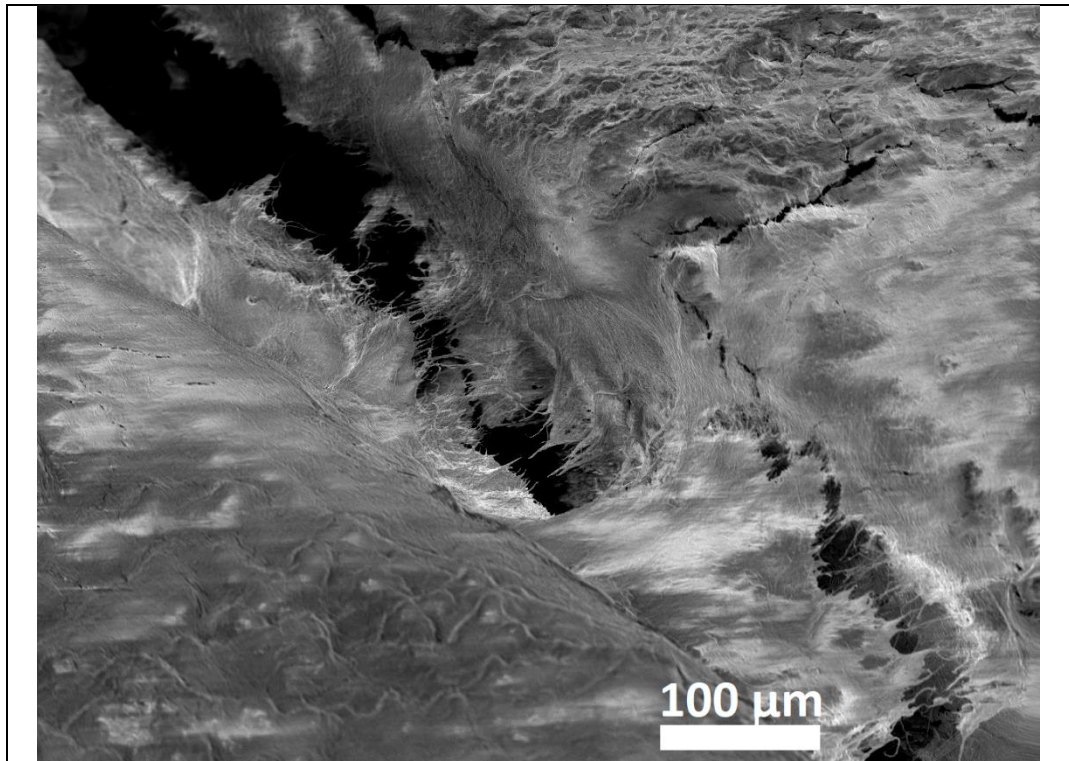
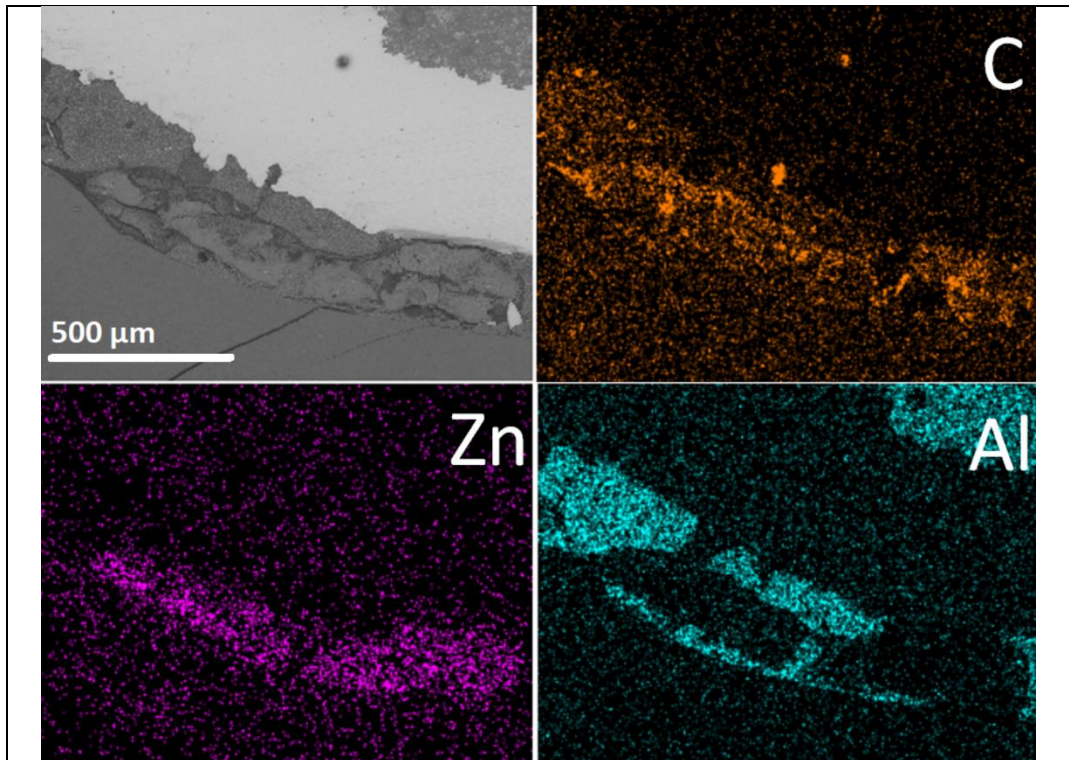


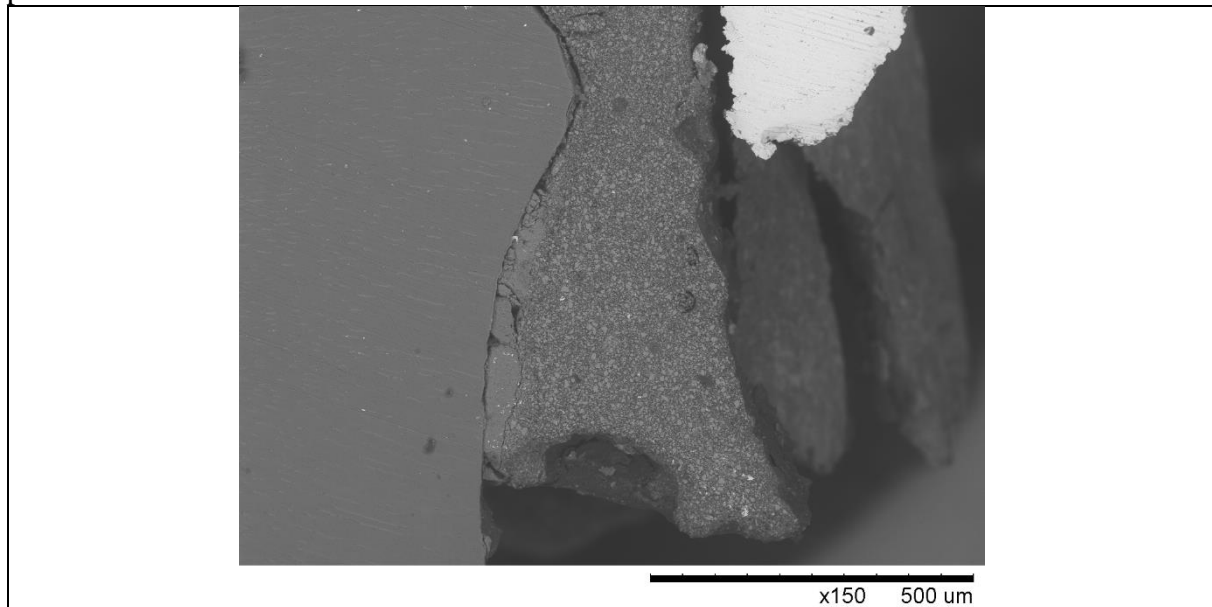
Figure 8. An SEM image revealing the filling of the marginal gap by biological masses in sample *a* after 6 years *in vivo* aging when a zinc phosphate cement was used.



1 Figure 9. The SEM/EDS mapping images taken on the sample *e* after 6 years *in vivo* aging
2 when resin composite cement and zinc phosphate cement were used for lining and for luting,
3 respectively. The strong element contrast of aluminum and zinc detected in different regions
4 confirmed the use of a zinc phosphate cement and a resin composite cement containing alumina
5 and silica fillers. The detected carbon content inside the zinc phosphate cement indicated the
6 contamination of the zinc phosphate cement by saliva/ oral fluid via the formed interfacial gap.
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9 3.7 Excess cements

10 At the margin end of the restorations luted by phosphate cements cracks were observed
11 but no excess cement outside the marginal end in any investigated samples. This was not the
12 case when resin composite was used as luting cement. Even though the resin composite
13 containing alumina and silica fillers did not show any chemical change during *in vivo* aging,
14 excess of resin composite cement squeezed outside the marginal end was observed, as seen in
15 the Figure 10. It is clear that this excess resin composite cement in contact with gingiva will
16 give rise to a bacterial growth near the margin and may cause severe problems to patient in the
17 form of infections and indeed this was the case with the samples *e* that was extracted from the
18 patient because of infections.
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42 Figure 10. SEM image of the cross section of sample *e*, revealing the restoration (bright)-
43 cement-tooth (dark) interfaces and the presence of excess cement on the tooth surface outside
44 the marginal end.
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46 4. Discussions

47 Phosphate cements are defined as chemically bonded ceramics that are a family of materials
48 formed and consolidated by chemical reaction instead of thermal diffusion. As these room-
49 temperature-setting materials are easy to produce, they were developed over a century ago.
50 From the results presented above it is clear that the phosphate cements appear brittle thus are
51 sensitive to cracking unlike resin composite cement that does not show major cracking. The
52 problems encountered at the marginal end are related to the cementation material used and the
53 mechanical stresses applied. Øilo et al.²² showed that the chewing causes tensile hoop stresses
54 on the tip of the crowns that would affect the cracking and the debonding of the cement.
55 Interfacial debonding as a common feature was observed in all three types of cements.
56 According to the literature the zinc phosphate debonds mainly on the interface between cement
57 and tooth^{5,23}. This early finding was confirmed in current study, which revealed that the zinc
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1 phosphate preferred the bonding with metallic restorations beyond the bonding to the natural
2 teeth. The different metals used for abutments and crowns made it difficult to draw final
3 conclusions on the calcium phosphate and resin composite cements. There is a small uncertainty
4 in the investigation concerning the interface debonding caused by the drying of the natural teeth
5 during the preparation work. The drying might increase the stresses in the interface and increase
6 the cracking/debonding probability. **After the removal from the oral environment there is no
7 longer a carbon source present and thus** the infiltration of the carbon to the top of the tooth is a
8 distinct evidence proving that the cracking and the debonding is an existing problem existing
9 before sample preparation. The cracking and debonding generate problems that causes the
10 micro-leakage of intraoral fluids into the marginal gaps and the possible infiltration/deposition
11 of biological masses and even bacterial colonization on the surface close to the margin end.
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13 No restorations luted by zinc phosphate were extracted due to the infections in this study.
14 It indicates that the observed micro-leakage is not harmful to the reliability of the phosphate
15 cement luting as it has been already stated in several earlier studies ^{5,11,24-26}. But if the interfacial
16 gaps are broad enough ($>50\ \mu\text{m}$ ²⁷) caution should be taken that such broader gaps might make
17 possible a bacterial ingress and secondary caries not only close to gingiva but even inside the
18 restorations. The major cracking in phosphate cements luted restorations occurs at the margin
19 end where the cement is exposed to oral fluids and often withstands micro-movements under
20 the biting stresses. Both mechanisms will increase the cracking/dissolution of the cement and
21 in that way increase the micro-leakage. The micro-leakage is also depended on the thickness of
22 the cementation layer. According to the literature the layer thickness above $150\ \mu\text{m}$ will
23 increase the dissolution speed of the zinc oxide and thus micro-leakage ¹⁰. It is worth to
24 emphasize that in this study the thickness of cementation layer larger than $150\ \mu\text{m}$ was
25 observed, but the possible formation of secondary caries was not the reason for the removal of
26 the restorations luted by zinc phosphate cement.
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28 The micro-leakage changes the chemical composition of the zinc phosphate cement.
29 Nevertheless, the dissolution did not prohibited that the zinc phosphate luted restorations were
30 used over 20 years without bacterial colonization and obvious increased inflammatory failures
31 in comparison to the resin composite cement luted restorations ^{5,28}. Another issue is the
32 observed missing of alumina and silica fillers at the margin end in calcium phosphate cement.
33 It is hardly possible for alumina and silica particles to dissolve in oral environment, so, the
34 observed missing of alumina and silica fillers most likely ought to be connected to either the
35 harsh sample preparation with the low speed saw causing pullout during the process or to the
36 poorer mechanical properties of the calcium phosphate cement. The reduction of the chemical
37 retention of the phosphate cements by *in vivo* aging and the physical movement of the cement
38 during biting could be other possible reasons responsible for the pullout of the filler particles.
39

40 The long lasting time of restorations luted by zinc phosphate cement should also be
41 connected to the easier removal of the excess cement squeezed out the marginal end. The
42 cleaner surface towards gingiva reduces the possibility to bacterial adhesion at the marginal end
43 opposite to the resin composite cement luted restorations. The removal of the excess resin
44 composite cement is difficult because it is not brittle and very hard to detect with radiographic
45 method ²⁸⁻³⁰. In this study, excess cement facing gingiva or close to gingiva was observed in
46 two resin composite cement luted restoration samples. The excess cement outside the marginal
47 end will give a growing platform for bacterial adhesion that may be quoted as the origin of the
48 secondary caries that would increase the risk of infections. This is evidenced by the fact that
49 one of the restorations luted by resin composite cement in this study was removed because of
50 the inflammation. The excess cement may also cause the peri-implant disease as discussed in
51 review of Valente et al ³¹. Linkevicius et al. showed that 85% of 72 implants developed peri-
52 implant disease when there was found excess cement and that all the patients with excess
53 cement and with earlier problems with peridontitis developed peri-implantitis ³².
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1 With proper phosphate cement preparation the content of pores with hopeite caused by air
2 or water evaporation during the mixing will decrease, thus, the mechanical strength of the
3 cement will increase^{33–35}. This will inhibit the cracking of the cement. In order to decrease the
4 risks caused by excess cement, marginal leakage and debonding on the margins a better
5 marginal fit should be achieved together with the better mixing and working habits with all type
6 of cements.

7 8 **5. Conclusions**

9 Within the limitation of this study it was revealed that pores presented in all samples, with
10 apparently higher concentration in zinc phosphate cement. The formation of platelet tertiary
11 zinc phosphate (“hopeite”) crystals was found confined inside these pores, in which the growth
12 of the crystals continued during *in vivo* aging. The crack formation as a common feature was
13 observed in all phosphate cements, but not in resin composite cements. Severe cracking and
14 loss of cement was observed at the marginal end of the cementation gap of all the samples,
15 which may indicate the risk of marginal leakage after long-term aging. The unreacted zinc oxide
16 particles initially imbedded in the zinc phosphate cement matrix dissolved on the surface of the
17 interfacial debonding gaps close to the margin end. Interfacial debonding was observed at one
18 of the two interfaces between crown and cement respectively between cement and
19 tooth/abutment, *i.e.* at the cement-tooth interface when zinc phosphate cement was used, and at
20 both the cement-crown and cement abutment interface when calcium phosphate and resin
21 composite cements were used. The detected carbon infiltrated along the interfacial debonding
22 gaps and cracks from the marginal surface up to the restorations top may indicate the penetration
23 of protein-containing saliva or possibly even bacteria. The excess calcium phosphate cement
24 piece stuck on the outside of porcelain surface of the crown sample *b* was stable and showed
25 significant retention after a 25 years period in the oral cavity. When resin composite cements
26 were used, excess cement were observed in gingiva gap outside the marginal end of the
27 cementation gap, which rationalized the difficulty commonly faced in daily practice in cleaning
28 up the resin composite cement leaked into the gingiva gap. Comparably, the brittleness of zinc
29 phosphate cement appears an advantage as it enables the easy cleaning of the excess cements
30 squeezed out the marginal end thus reduces the risk of bacterial colonization and the formation
31 of secondary caries.

32 33 **Acknowledgements**

34 We thank Dr. Per Tidehag for valuable discussions.

35 36 **References**

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Ref.: AAC2859

Dear Editor and Reviewer,

Thank you for the valuable comments on our paper. We have carefully read the comments and revised the paper accordingly. The response for each comment by the reviewer is described in more details below. The reviewer comments are indicated by cursive/blue text and our response is written un-cursive and black/red below. The changes made in the manuscript are highlighted with red color in the text.

Reviewer #1:

1, on page 4, in sample preparation for EDX, please provide details for conductive layer coating. Were samples coated by carbon or gold? This is related to the carbon contamination in section 3.5.

The sample preparation for EDX and SEM did not include any coating and the EDX was done on the clean surfaces. The description of the sample preparation for EDX was corrected as followed in the section 2:

“An field emission scanning electron microscope (SEM) (JSM-7000F, Jeol, Japan) equipped with an energy dispersive spectroscopy (EDS) detector (INCAx-sight, Oxford Instruments, UK) and a tabletop scanning electron microscope (TM3000, JEOL) were used for SEM investigations of the clean surfaces without any additional coating.”

2, page 5 line 35-39, '...hydroxyapatite (~ 26° and 32°) and α-tricalcium phosphate (~ 47°) in an otherwise amorphous cement...' please mark diffraction peaks belong to the two phase specifically in Fig.3. By the way, please provide related discussions for the phase marked by arrows in Fig.3.

We are very grateful for this comment because we noticed that the interpretation of the peaks was misleading in Figure 3b and we have now modified the text and the hydroxyapatite peaks are marked in the Figure 3b. The corrected text is as follows:

”However, similar cement in the oral environment did not show such crystals in SEM but the XRD in Figure 3b shows increased intensity of the peaks for hydroxyapatite in an otherwise amorphous cement...”

The discussion about the marked phase of hopeite in Figure 3a is in the section 3.2.

3, page 6 line 60, change 'raman' to 'Raman'.

This change is done

4, page 7 line 10, '...The dissolution process seems to be time depended; the longer time the restoration is in use the larger dissolution of zinc oxide and deterioration of the mechanical properties of the ...' please provide evidence or refs to support your discussion.

Thank you for the comment. This was overstated in the manuscript. The sentence is now changed so that it only speculates and appropriate references are added as no clear evidence is seen for the time dependence. There are other factors such as mechanical erosion and the size of the gap that can have an effect how the restoration will be affected. These effects are difficult to separate from the dissolution in this study. The sentence was changed as follows:

” The dissolution process ought to be time depended^{20,21}; the longer time the restoration is in use the larger dissolution of zinc oxide and deterioration of the mechanical properties of the

cement but it is not seen clearly because there are even other factors affecting the reliability of the restoration such as mechanical erosion and the gap width.”

5, in Fig.4 please enlarge the magnification number to be visible.

This is done

6, in Fig.5, please provide details to explain the insert, at least in Figure 5 caption.

Thank you for the comment the caption for Figure 5 is more precise now. Following sentence was added.

” The inserts show the EDX results for indicated area on the cement.”

7, in section 3.5, explain the basic reason for carbon contamination.

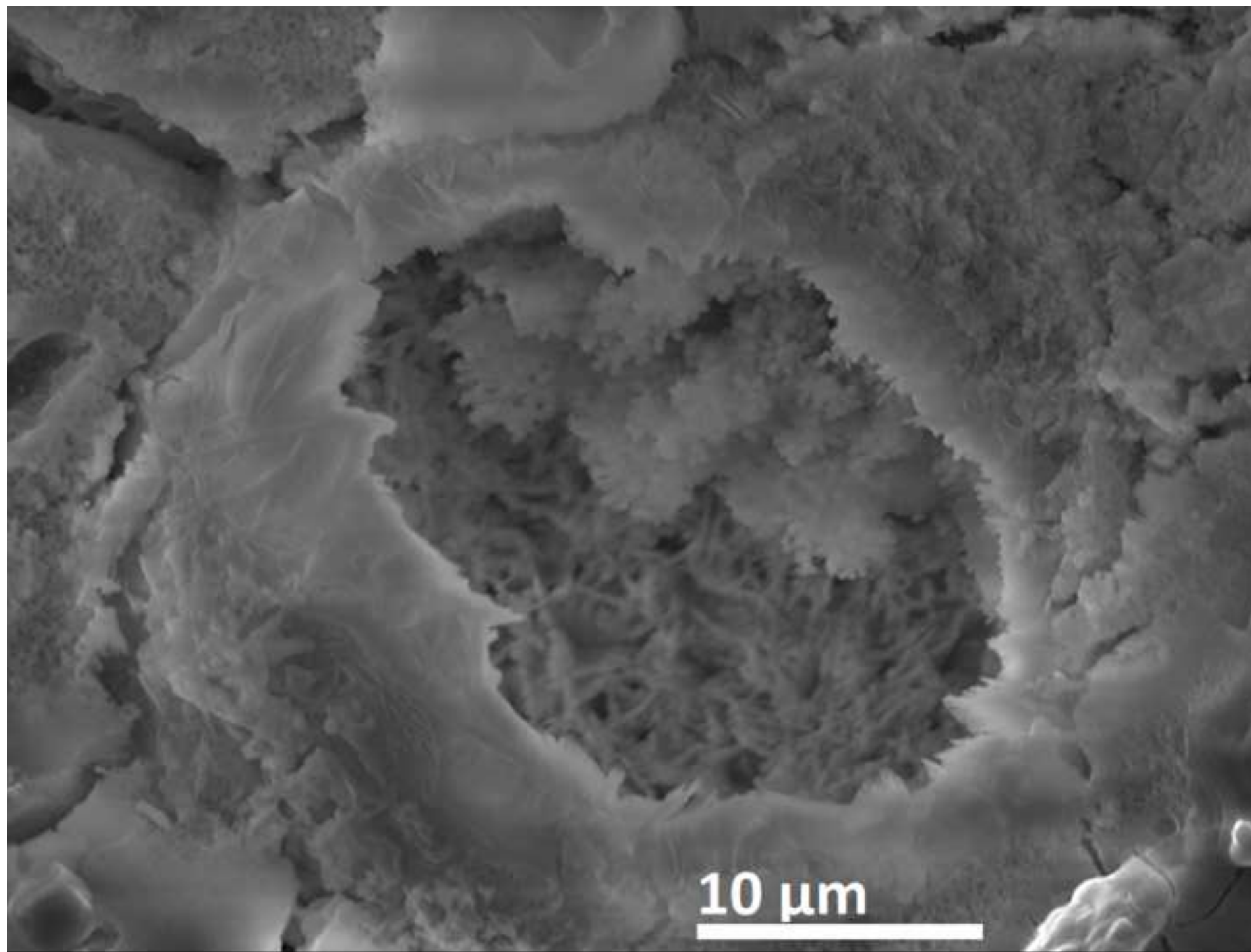
The section 3.5 was clarified in order to explain the source of the carbon contamination. Following modification was added into the text:

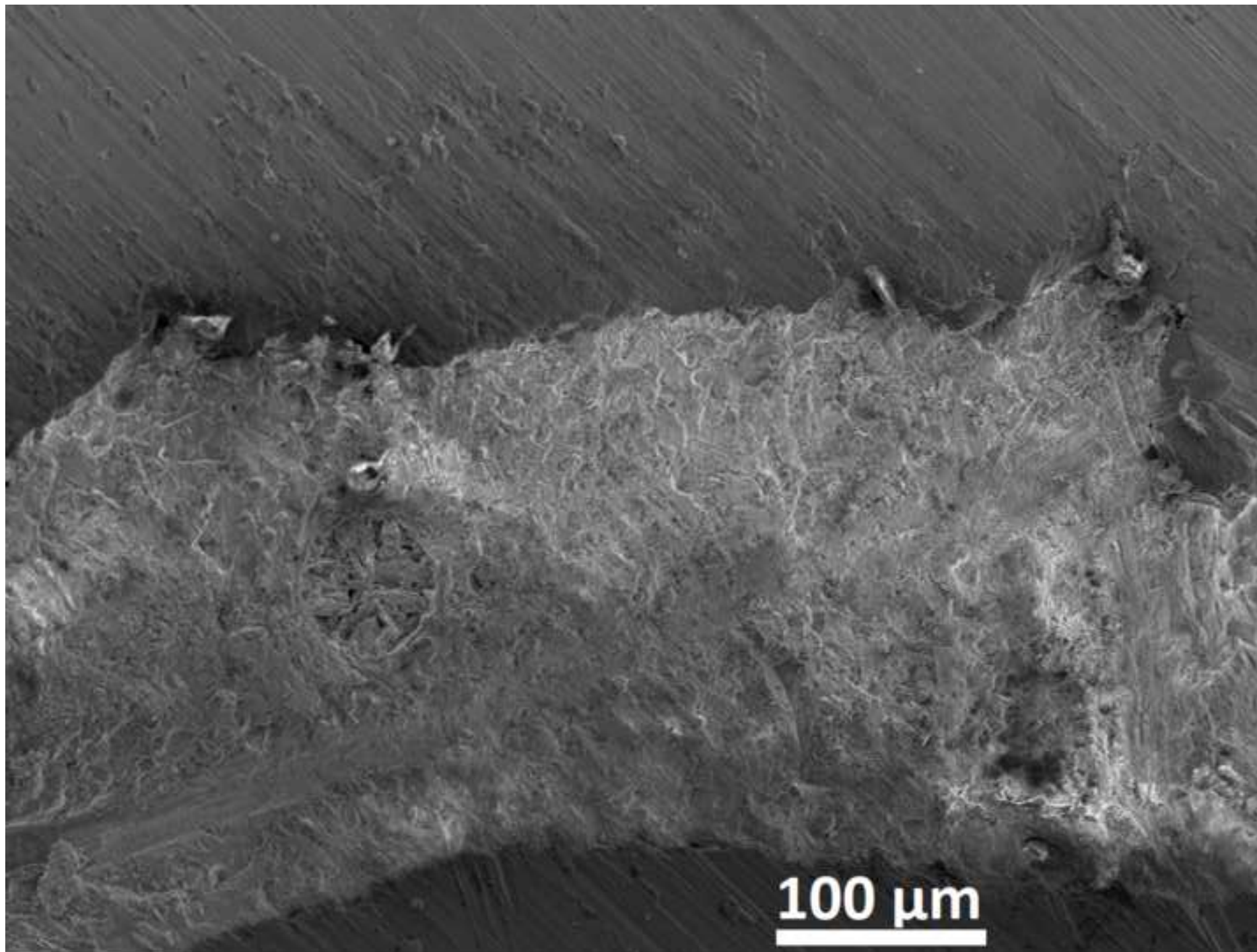
”...infiltrated biological matter **that can even be recognized as carbon contamination**. This is seen in all the samples as demonstrated in the Figures 2, 5 and 8...”

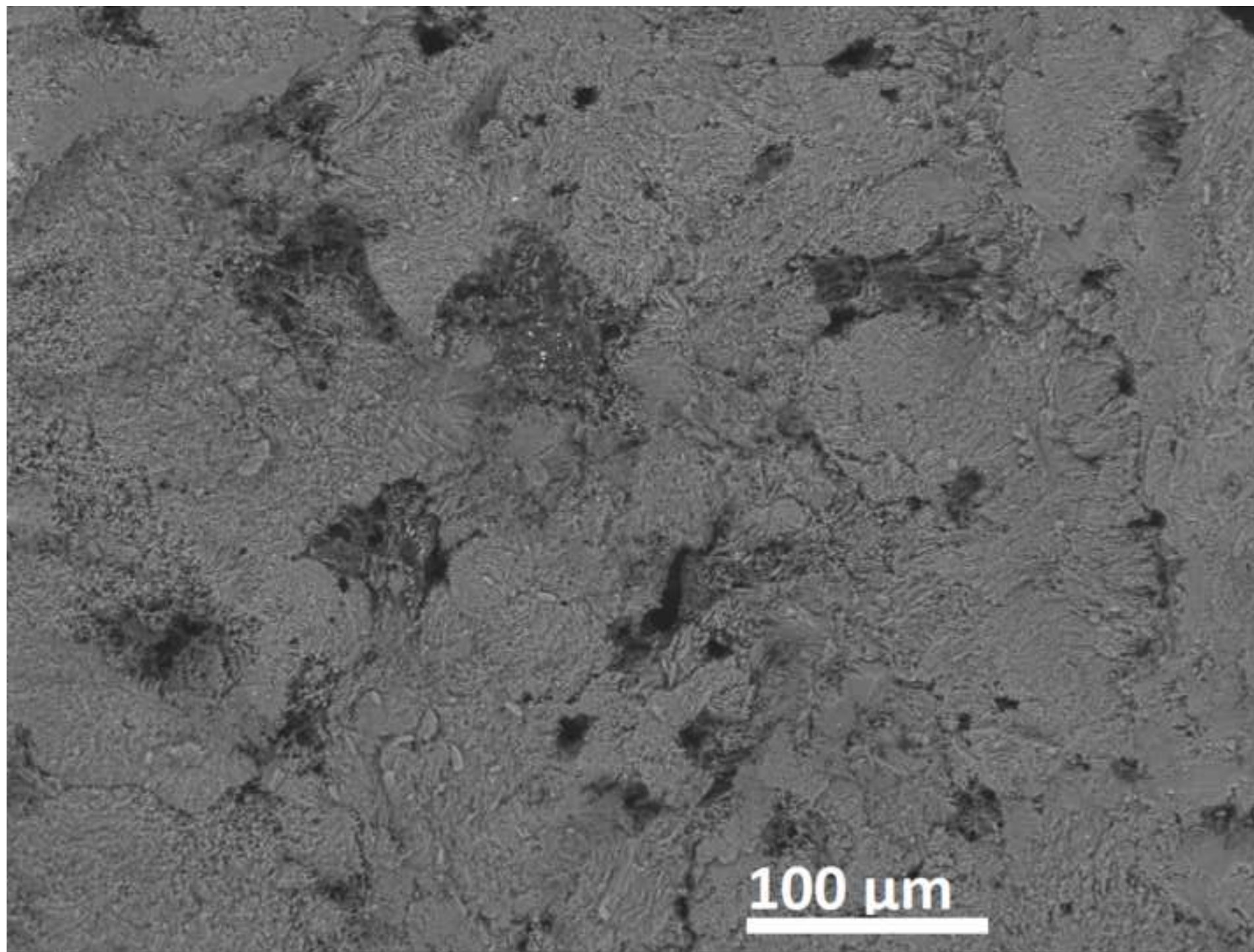
8, page 12, line 2-line 6, 'The drying might increase the stresses in the interface and increase the cracking/debonding probability. But the infiltration of the carbon to the top of the tooth is a distinct evidence proving that the cracking and the debonding is an existing problem existing before sample preparation.' Please explain why.

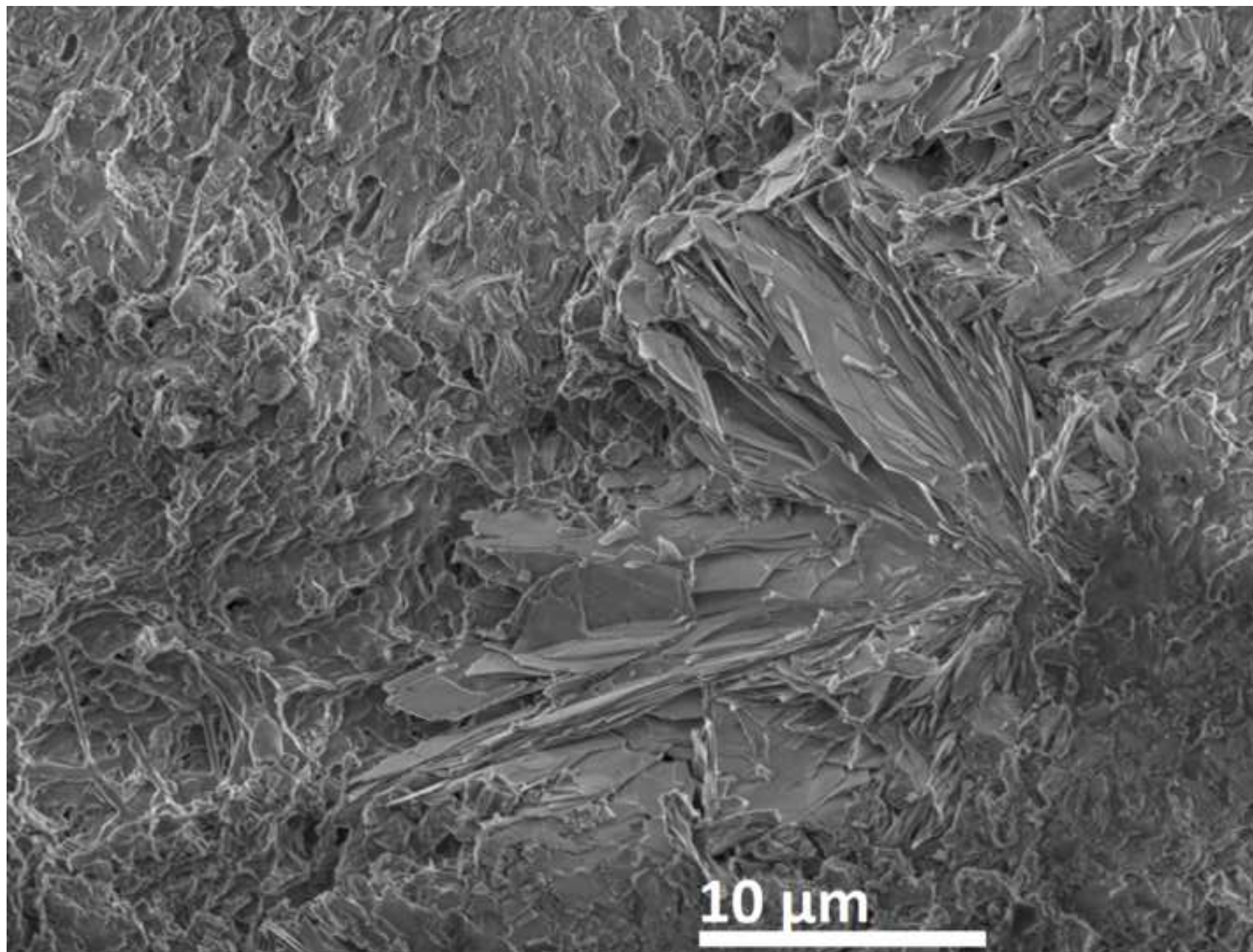
Thank you for this comment. The cracks that are formed during the use of the prosthesis are surrounded and penetrated by intraoral fluids in vivo. After the removal from the mouth there is no longer a source for carbon contamination and thus even though the interface might crack due the drying or handling (cutting, polishing) there is no source for carbon to penetrate into the top. The text was clarified with the following:

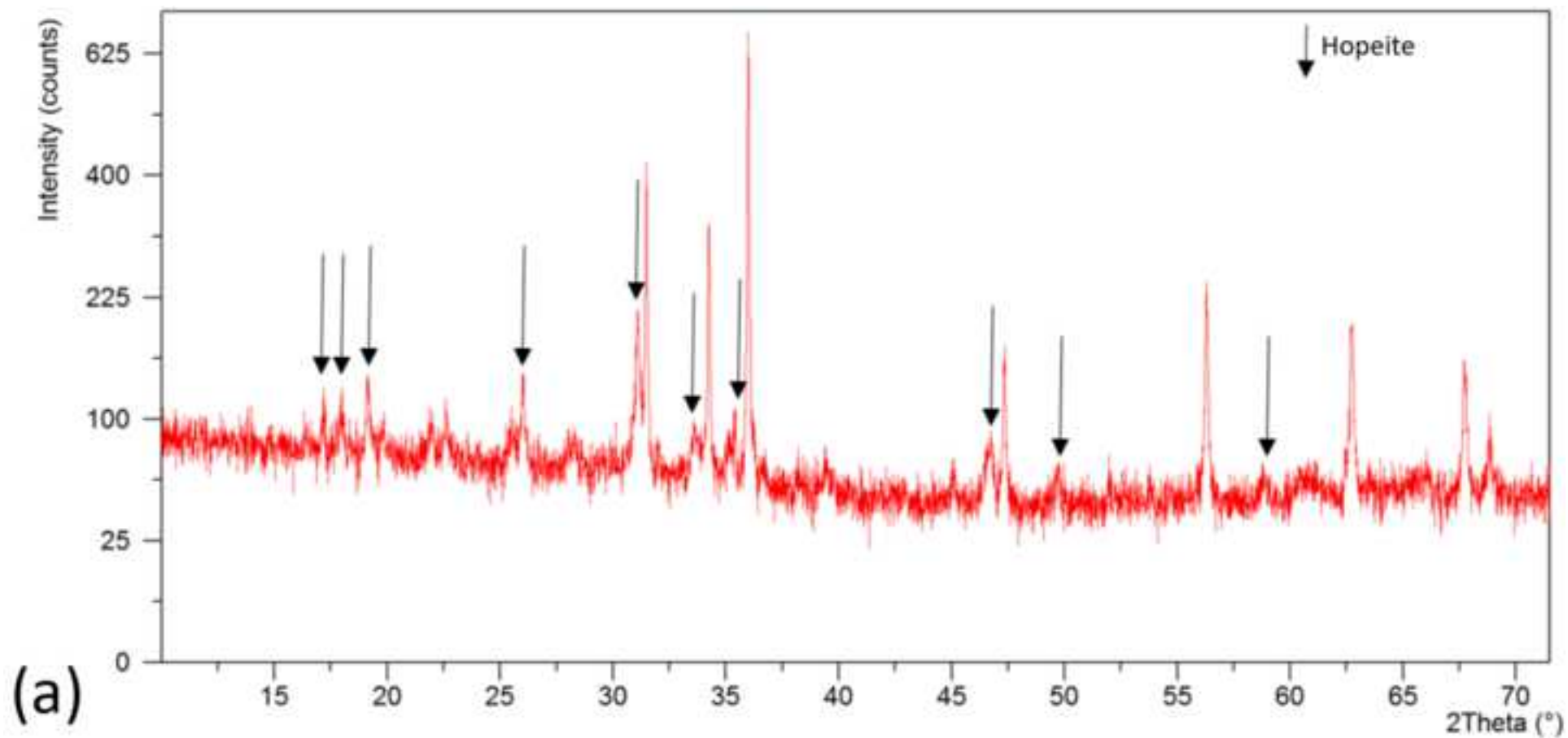
” The drying might increase the stresses in the interface and increase the cracking/debonding probability. **After the prosthesis removal from the oral environment there is no longer a carbon source present and thus** the infiltration of the carbon to the top of the tooth is a distinct evidence proving that the cracking and the debonding is an existing problem existing before sample preparation.”

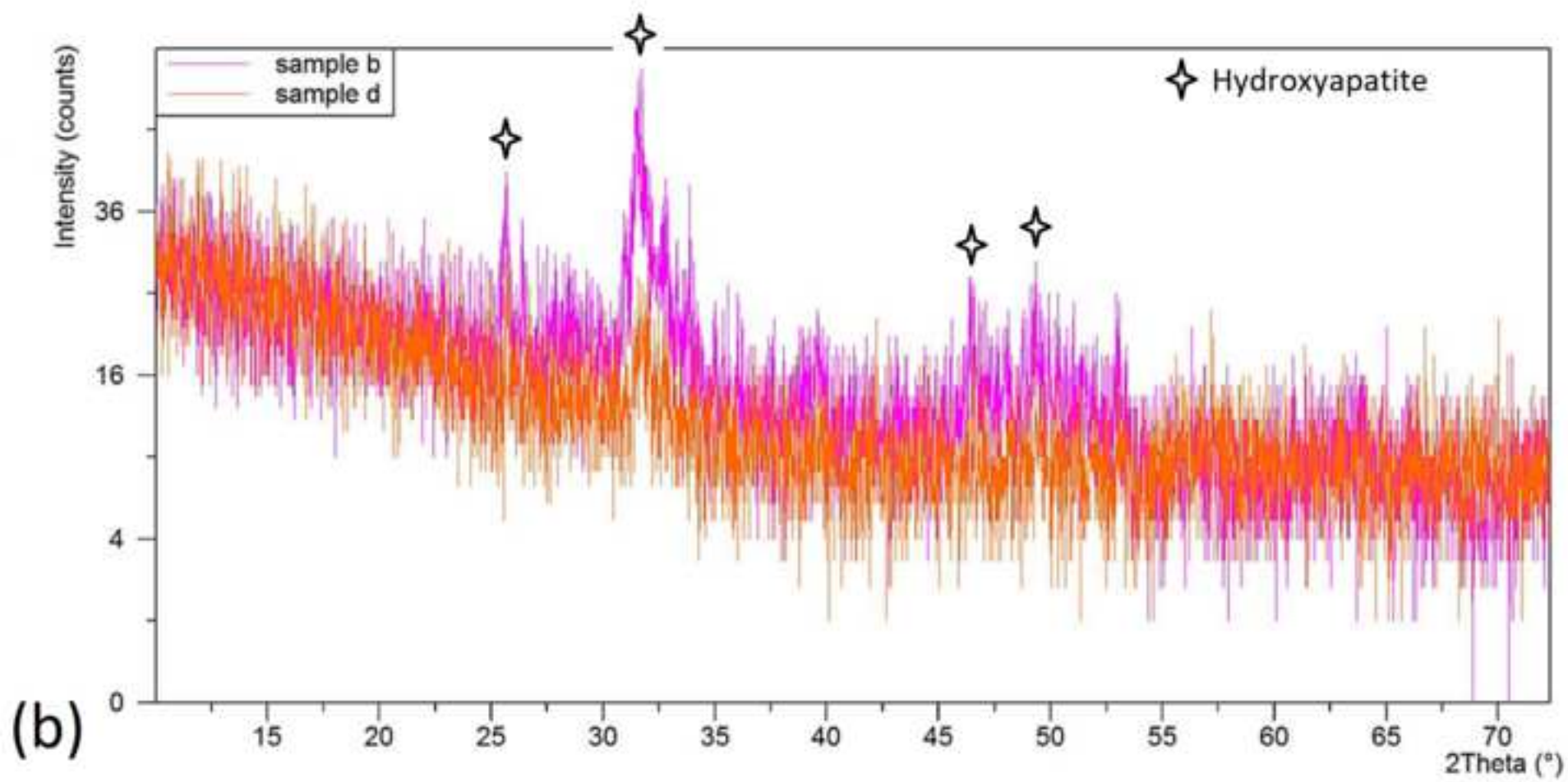


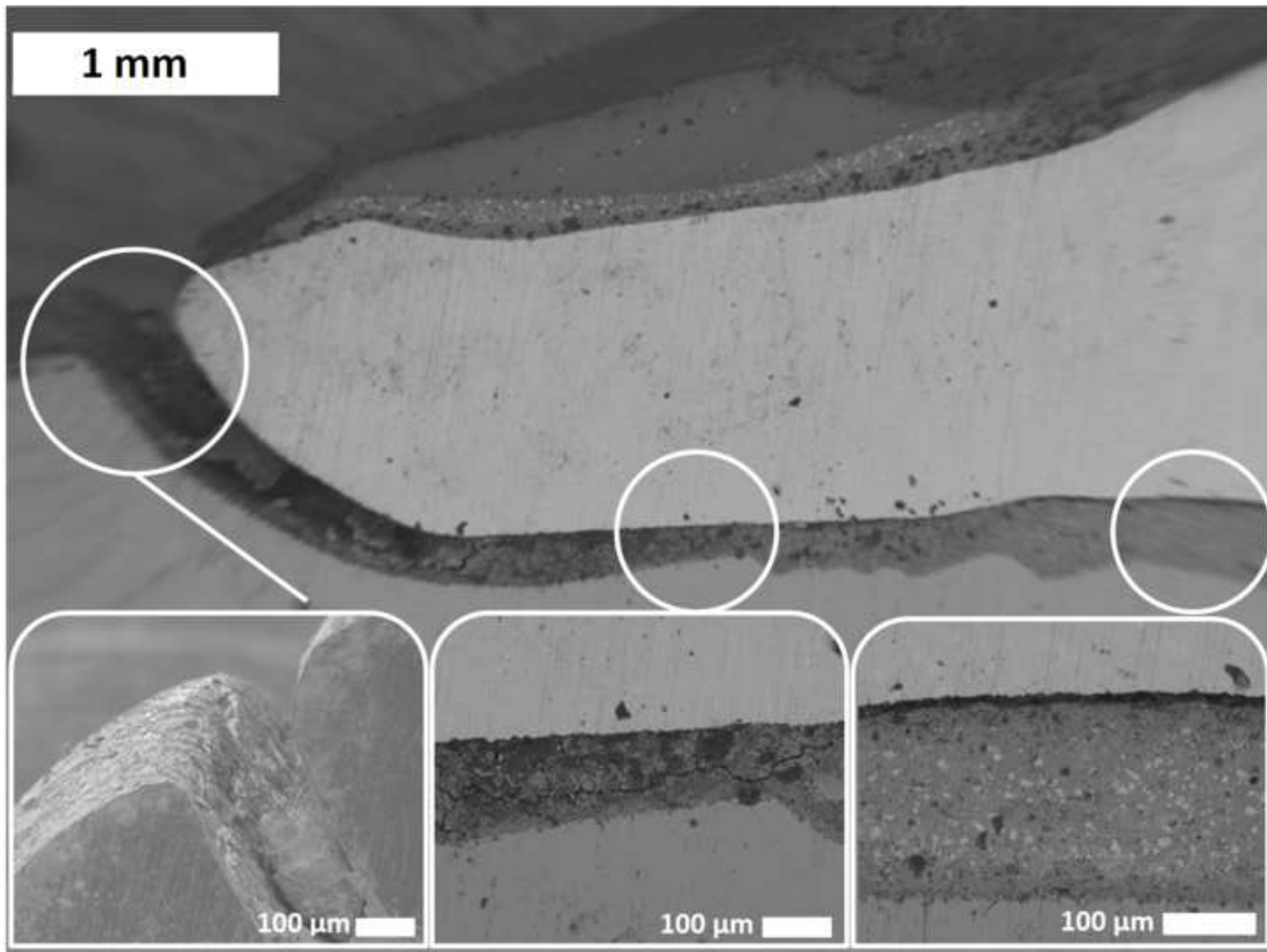


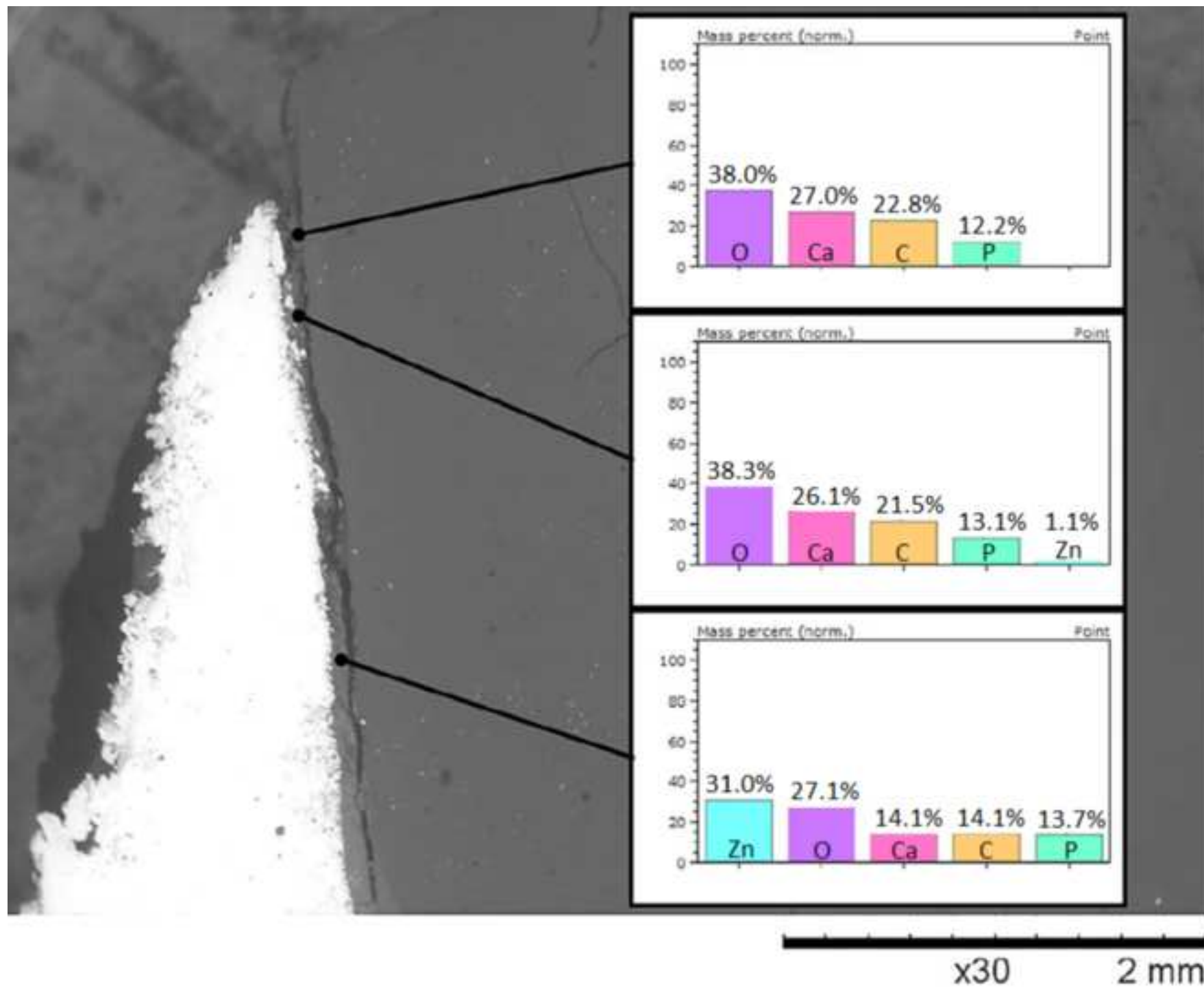


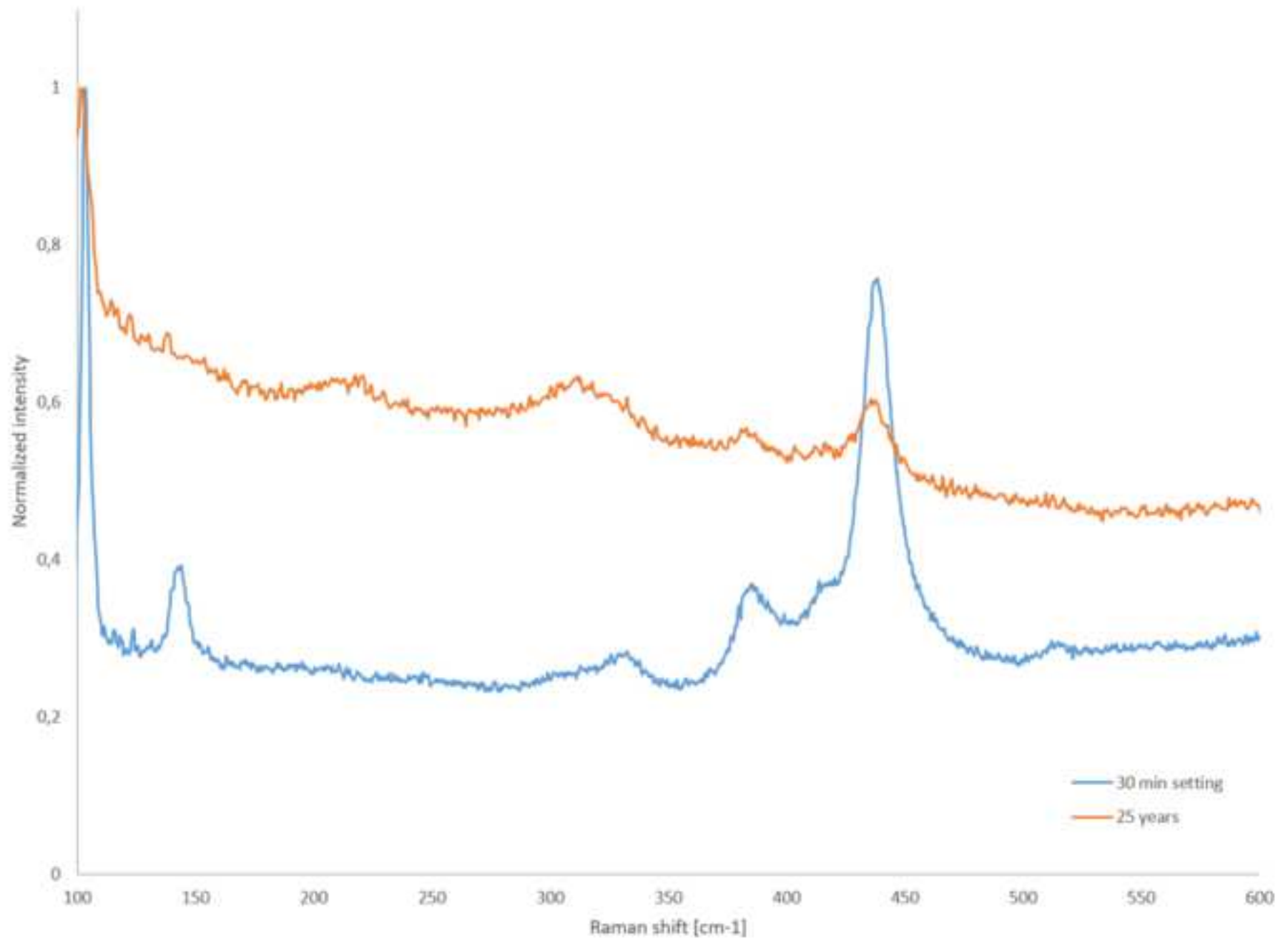


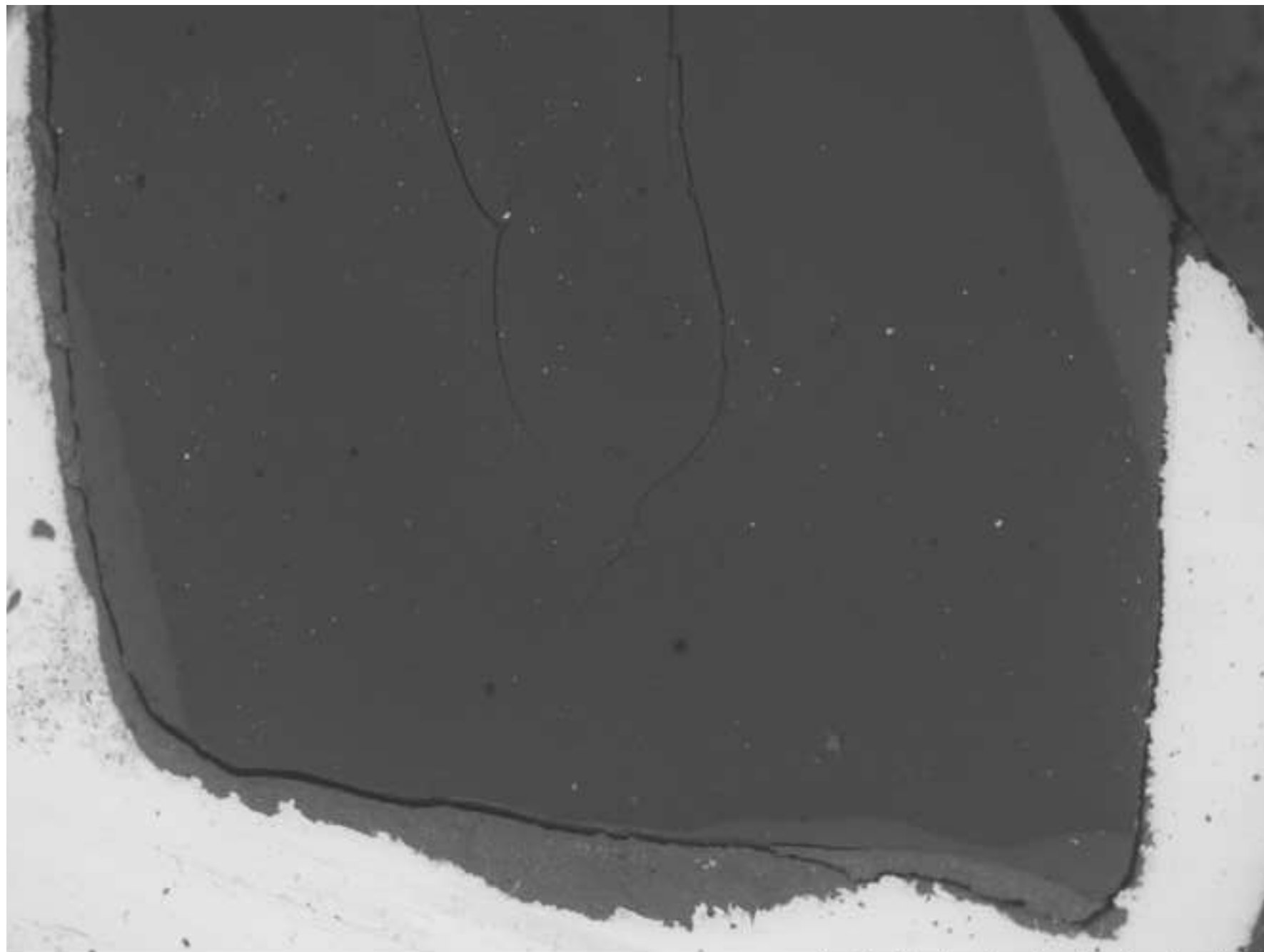




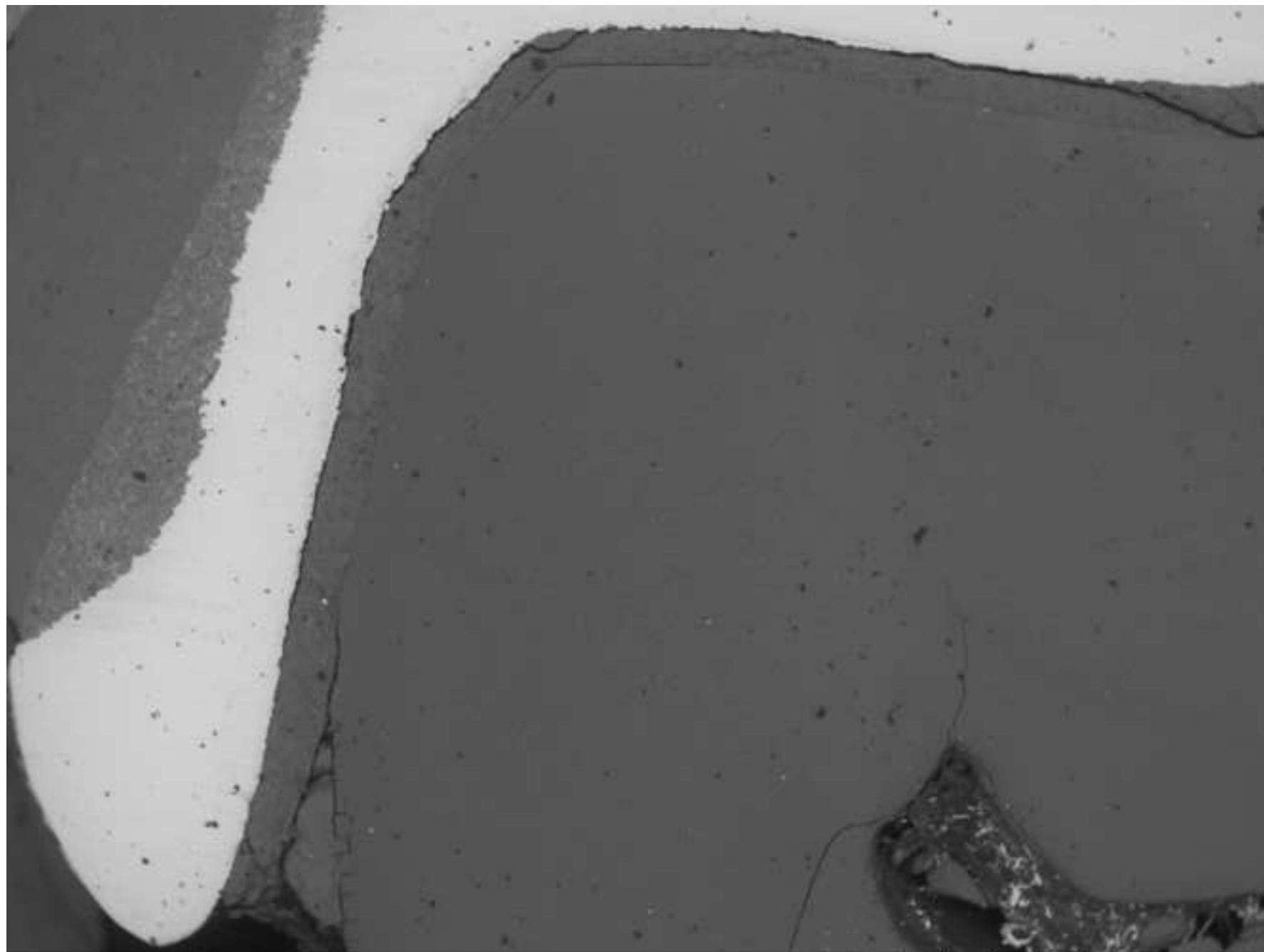






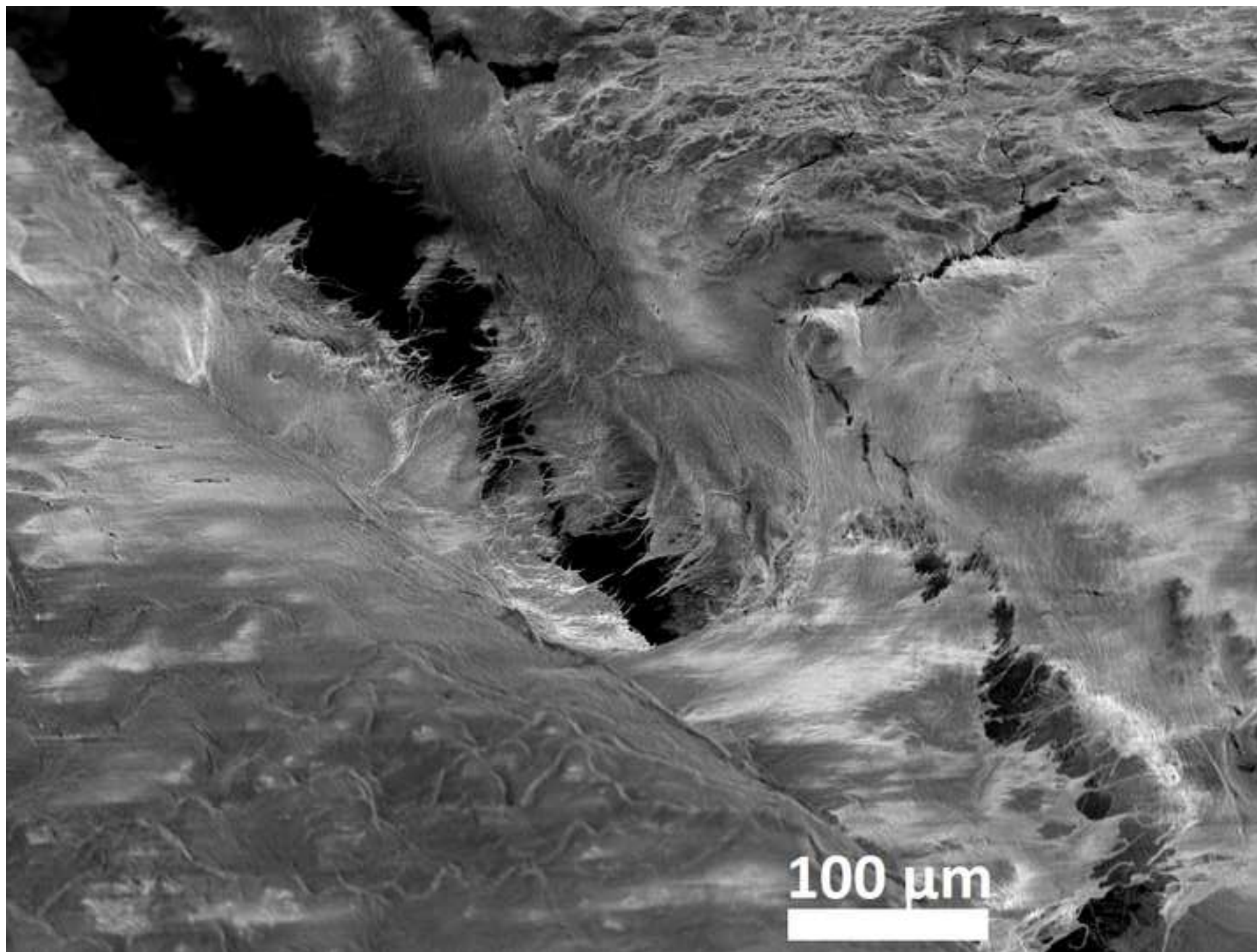


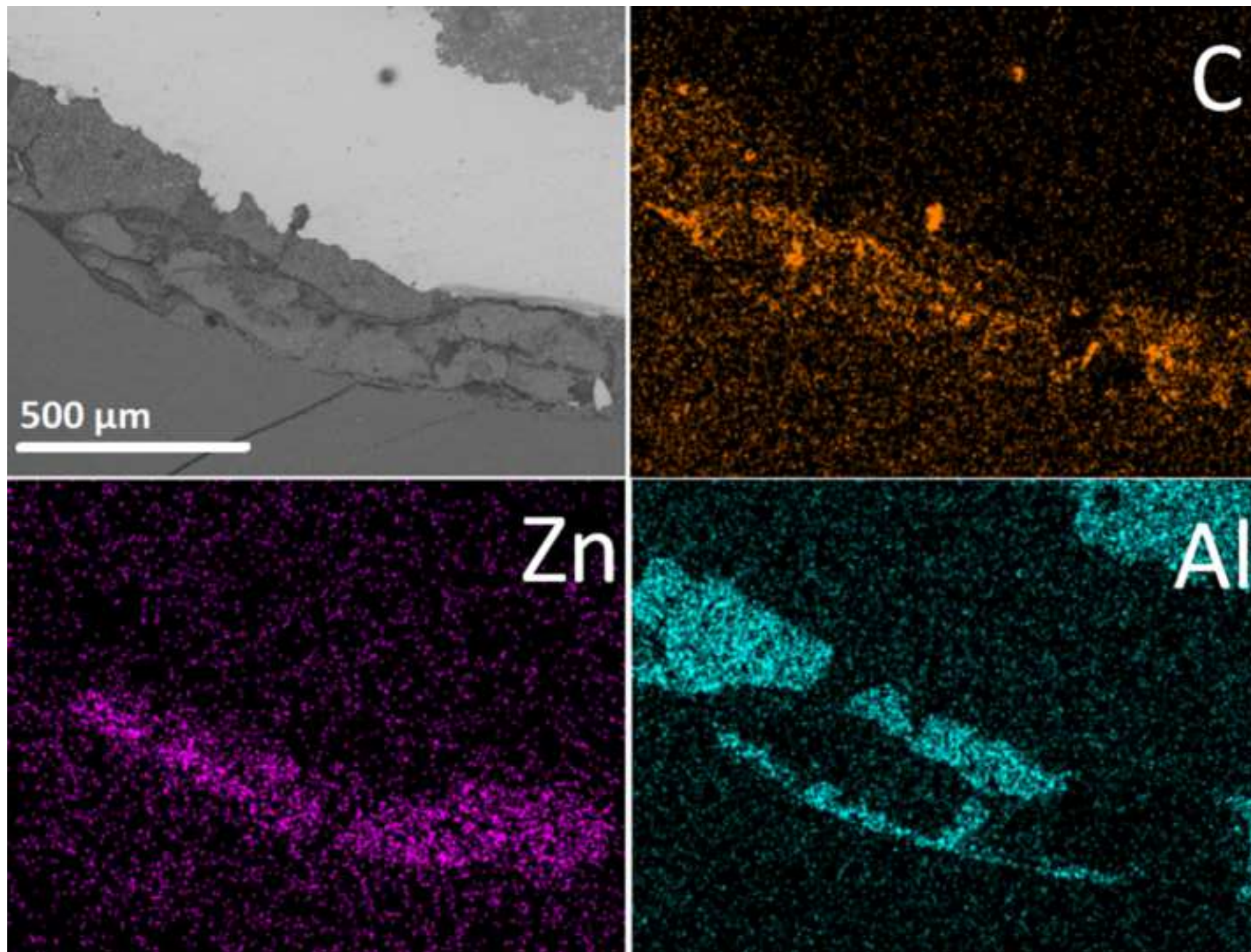
x30 2 mm

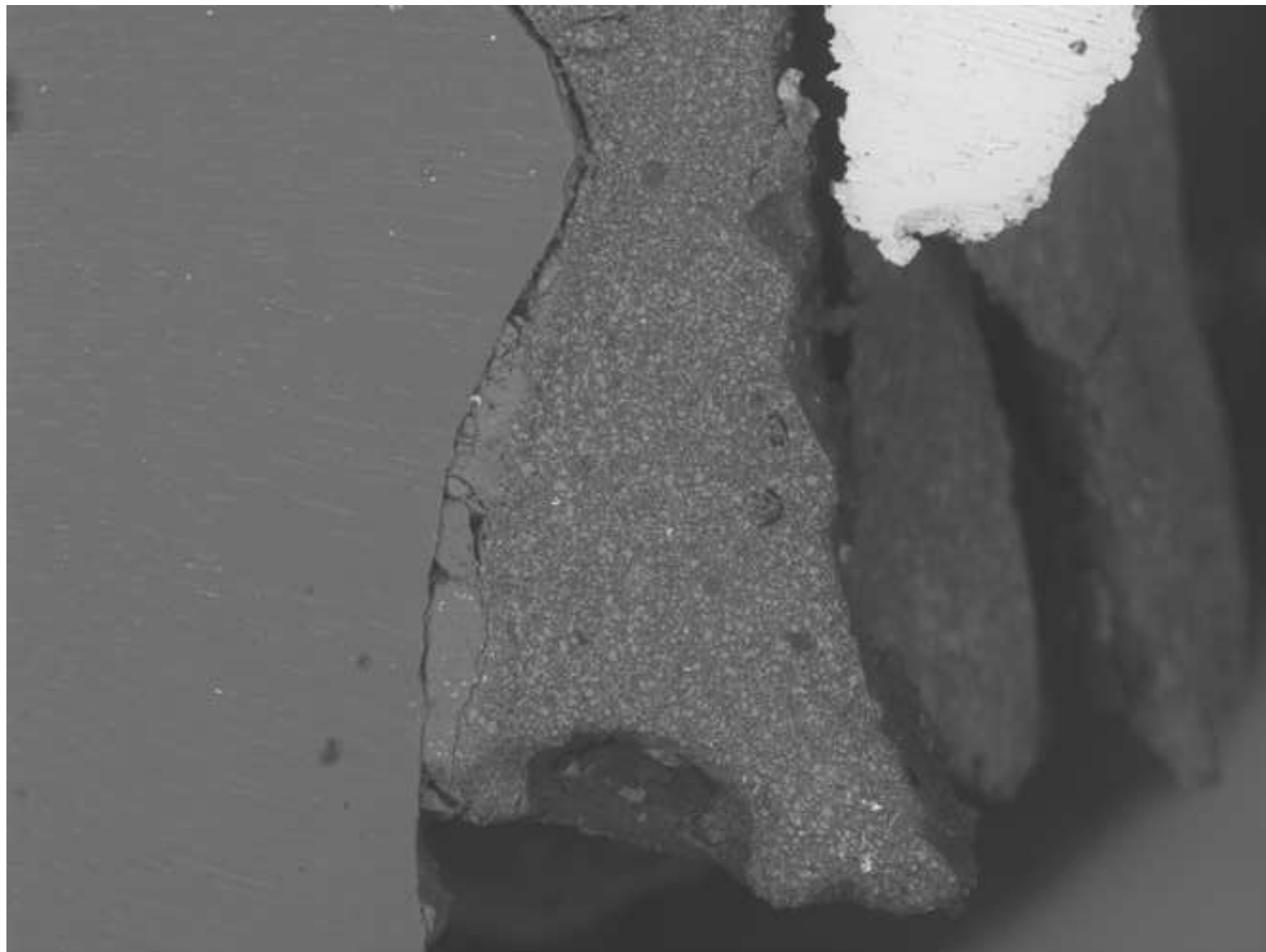


x30

2 mm







x150 500 um