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Author(s): Kuva, Jukka; Sammaljärvi, J.; Parkkonen, Joni; Siitari-Kauppi, M.; Lehtonen, M.; Turpeinen, T.; Timonen, Jussi; Voutilainen, M.

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1 Imaging connected porosity of crystalline rock by contrast agent-aided X-ray microtomography and
2 scanning electron microscopy

3 J. Kuva^{a,b}, J. Sammaljärvi^{b*}, J. Parkkonen^a, M. Siitari-Kauppi^b, M. Lehtonen^c, T. Turpeinen^d, J.
4 Timonen^a, M. Voutilainen^b

5 *: Corresponding author

6 a: University of Jyväskylä, Department of Physics, P.O. Box 35, 40014 University of Jyväskylä,
7 Finland, , jukka.kuva@iki.fi, joni.parkkonen@jyu.fi, jussi.t.timonen@jyu.fi

8 b: University of Helsinki, Department of Chemistry, P.O. Box 55, 00014 University of Helsinki,
9 Finland, +348504486642, juuso.sammaljarvi@helsinki.fi, marja.siihari-kauppi@helsinki.fi,
10 ma.voutilainen@helsinki.fi

11 c: Geological Survey of Finland, Betonimiehenkuja 4, 02151 Espoo, Finland,
12 marja.lehtonen@gtk.fi

13 d: VTT Technical Research Centre of Finland Ltd, P.O. Box 1603, 40101 Jyväskylä, Finland,
14 tuomas.turpeinen@vtt.fi

15 Keywords: X-ray microtomography, Scanning electron microscopy, Energy dispersive X-ray
16 spectrometry, Connected porosity, Crystalline rock

17 **Abstract**

18 We set out to study connected porosity of crystalline rock using X-ray microtomography and
19 scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) with caesium
20 chloride as a contrast agent. Caesium is an important radionuclide regarding the final deposition of
21 nuclear waste and also forms dense phases that can be readily distinguished by X-ray
22 microtomography and SEM-EDS. Six samples from two sites, Olkiluoto (Finland) and Grimsel
23 (Switzerland), where transport properties of crystalline rock are being studied in-situ, were

24 investigated using X-ray microtomography and SEM-EDS. The samples were imaged with X-ray
25 microtomography, immersed in a saturated caesium chloride (CsCl) solution for 141, 249 and 365
26 days and imaged again with X-ray microtomography. CsCl inside the samples was successfully
27 detected with X-ray microtomography and it had completely penetrated all six samples. SEM-EDS
28 elemental mapping was used to study the location of caesium in the samples in detail with
29 quantitative mineral information. Precipitated CsCl was found in the connected pore space in
30 Olkiluoto veined gneiss and in lesser amounts in Grimsel granodiorite. Only a very small amount of
31 precipitated CsCl was observed in the Grimsel granodiorite samples. In Olkiluoto veined gneiss
32 caesium was found in pinitised areas of cordierite grains. In the pinitised areas caesium was found
33 in notable excess compared to chloride, possibly due to the combination of small pore size and
34 negatively charged surfaces. In addition, elevated concentrations of caesium were found in kaolinite
35 and sphalerite phases. The findings concerning the location of CsCl were congruent with X-ray
36 microtomography.

37

38 **Lay abstract**

39 Crystalline rocks have small amount of empty space, porosity, in them. This porosity has large
40 influence on the properties of the rock and therefore its applications. Different techniques exists to
41 visualize this pore space. In this work we have used X-ray tomography and Scanning Electron
42 Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS). As the pores in crystalline
43 rock usually have diameters of few micrometres or less, it is difficult to see them without something
44 to enhance the contrast and highlight the pore space. Therefore we tested a method to highlight the
45 pore space with a contrast agent introduced via saturated water solution, which forms dense phases
46 that are clearly visible in both X-ray tomography and SEM-EDS. We used CsCl as a contrast agent
47 in two different types of crystalline rock samples. Different immersion times were used to test the
48 speed in which the contrast agent intrudes into the pores of the rock. The samples were dried after

49 the immersion. Thereafter methyl methacrylate was intruded into the sample and polymerised
50 therein to fix the CsCl in place. The results showed that CsCl phases highlighted the connected pore
51 space of the rock in both X-ray tomography and SEM-EDS. Open fissures showed improved
52 contrast and especially noteworthy contrast improvement was noted in cordierite that had
53 undergone alteration to pinitite, a mixture of clay minerals. In pinitite it was also noted that caesium
54 was found often in considerably higher abundance than its counter ion chloride. This was probably
55 because due to chloride's negative charge, it was excluded from the smallest pores with negatively
56 charged surfaces.

57

58 **1. INTRODUCTION**

59 The microstructure of rock has been studied for decades with various methods and motivations
60 (McWilliams 1966; Hoagland, et al. 1973; Vernon 2004; Zabler, et al. 2008; Kuva, et al. 2012).
61 Computed X-ray microtomography (Radon 1917; Cormack 1963; Hounsfield 1973; Kak and
62 Slanley 2001; Stock 2009; Maire and Withers 2014), a method that was first used for medical
63 purposes (Hounsfield 1973), has been widely used to study geological samples (Zabler, et al. 2008;
64 Kuva, et al. 2012; Cnudde & Boone 2013; Wildenschild and Sheppard 2013; Jacques, et al. 2014;
65 Thiemeyer, et al. 2015). It is a powerful method, which can non-invasively obtain three dimensional
66 density maps of rock samples. The method has relatively recently become so accurate, that it has
67 been used to determine material parameters such as porosity (Farber, et al. 2003), grain size
68 distribution (Thovert, et al. 2001), tortuosity (Gommes, et al. 2009) and permeability (Gouze and
69 Luquot 2011). These parameters characterize the structure and transport properties of rock, but
70 unfortunately the resolution of the method is not good enough for a detailed analysis of sub-
71 micrometre features of centimetre scale low porous geological samples. X-ray microtomography
72 can, however, be improved by using a marker fluid with a high X-ray attenuation coefficient
73 (Ketcham and Iturrino 2005; Singh, et al. 2011; Bultreys, et al. 2015) or combining it with

74 complementary methods, such as the ^{14}C -polymethylmethacrylate (C-14-PMMA) autoradiography
75 technique (Hellmuth, et al. 1993; Voutilainen, et al. 2012). Due to recent progress in laboratory
76 equipment and with the use of synchrotron radiation (Fusseis, et al. 2014) computed
77 microtomography has become fast enough to obtain “four dimensional” images, that are able to
78 show temporal changes in three dimensional images (Mokso, et al. 2011; Lowe, et al. 2013;
79 Eastwood, et al. 2014; Bultreys, et al. 2015).

80 SEM (Nixon 1969), combined with EDS (Russ 1971), has also been used for decades to study
81 elemental composition of minerals in geological samples (Krinsley and Margolis 1969; Jones, et al.
82 1981; Watt, et al. 2000; Reed 2005; Robinet, et al. 2015). It is a flexible tool that can be used to
83 obtain detailed two dimensional information on the pore space of a sample with a resolution
84 approaching $0.1\ \mu\text{m}$ (Sardini, et al. 2006) as well as to identify elements and minerals via elemental
85 mapping, but its limited field of view restricts its suitability for large samples (Sardini, et al. 1999).

86 SEM-EDS is most useful when combined with methods more suitable for larger samples, such as
87 X-ray microtomography (Voutilainen, et al. 2013) and the ^{14}C -PMMA autoradiography technique
88 (Cassiaux, et al. 2006; Leskinen, et al. 2007; Sammaljärvi, et al. 2017). SEM-EDS imaging can be
89 enhanced using contrast agents to highlight features. Wood’s metal is an alloy of different metals
90 that has a low melting point ($70\ ^\circ\text{C}$), which is an often used contrast agent to highlight pore space in
91 variety of materials (Abell, et al., 1999; Hildenbrand & Urai, 2003; Kaufmann, 2009; Desbois et al.,
92 2016). Wood’s metal also has good X-ray attenuation coefficient which is why it has also been used
93 as a contrast agent in X-ray tomography (Pyrak-Nolte, et al., 1995; Pyrak-Nolte, et al., 1997).

94 Wood’s metal has been reported to intrude at least $10\ \text{nm}$ size pores (Klaver, et al., 2015) and 4.1
95 nm pore sizes have been reported as well (Desbois, et al., 2016). This however can still leave
96 notable amount of pore space unfilled, if there are mineral phases with very small pore sizes.

97 Wood’s metal intrusion is also a pressure-driven process and this can be a cause of artefacts

98 (Klaver, et al., 2015). Therefore, our first goal was to set out to investigate another type of contrast
99 agent for both X-ray tomography and SEM-EDS without the necessity of pressure-driven intrusion.
100 Diffusion and sorption in crystalline rock are well known in large scales and on a molecular level,
101 but in micrometre scale there are still many uncertainties that have led to conscious underestimation
102 of the retarding capacity of the bedrock in applications such as the safety assessment of a nuclear
103 waste depository (Posiva Oy 2013). It has also been shown that the heterogeneity of the rock
104 structure and mineralogy can have a significant effect on the observed transport properties
105 (Voutilainen, et al. 2013; Muuri, et al. 2016). A second goal of the study was to highlight the
106 migration routes within the crystalline rock using a contrast agent.

107 The samples were chosen with two in-situ transport experiments in mind, Water Phase
108 Diffusion Experiment (WPDE), an advection-matrix diffusion experiment being conducted under
109 the “rock matrix REtention PROPERTIES” (REPRO) project (Aalto, et al. 2009; Voutilainen, et al.
110 2014) in the REPRO-niche (Toropainen 2012) in ONKALO, Olkiluoto, Finland and Long Term
111 Diffusion experiment (LTD) (Soler, et al. 2015), another matrix diffusion experiment, which was
112 conducted at the Grimsel test site, Switzerland. Thus we chose to investigate Olkiluoto veined
113 gneiss and Grimsel granodiorite. The Grimsel in-situ experiment, as well as an in-situ Through
114 Diffusion Experiment (TDE) in Olkiluoto, have used caesium as a tracer in concentrations
115 resembling the repository conditions. Results of caesium from the LTD experiment indicate that the
116 mineral heterogeneity of the rock is important for retention of caesium (Jokelainen, et al. 2013;
117 Voutilainen, et al. 2017). This factor combined with the high X-ray attenuation coefficient of
118 caesium, and the possibility of facile intrusion via water solution, led to the decision to choose CsCl
119 as the potential contrast agent. In order to test the feasibility of detecting caesium phase at all,
120 saturated solution was used. Three samples of each rock type were investigated with computed X-
121 ray microtomography and SEM-EDS.

122 2. MATERIALS AND EXPERIMENTAL METHODS

123 2.1. Samples

124 Olkiluoto bedrock was formed 1.80-1.91 billion years ago by the deformation and metamorphosis
125 of supracrustal, metasedimentary and metavolcanic rocks (Kärki & Paulamäki 2006). On the other
126 hand the Grimsel bedrock is only about 0.03-0.30 billion years old and has undergone
127 transformations after that as well (Kralik, et al. 1992). Thus there is a sharp contrast in the ages of
128 the bedrock in the two sites.

129 Veined gneiss is one of the main rock types in Olkiluoto bedrock around the ONKALO site.
130 The samples for this study are taken from about 400 m deep within the bedrock (Toropainen 2012).
131 The Olkiluoto veined gneiss contains migmatites with vein-like, elongated leucosomes (Kärki &
132 Paulamäki 2006). A typical porosity value for Olkiluoto veined gneiss from experimental site of
133 REPRO project is around 0.73 % (Ikonen, et al., 2015). SEM imaging revealed open unfilled pores
134 mostly in the range of a few micrometres in the Olkiluoto veined gneiss (Sammaljärvi, et al., 2017).
135 Recent studies applying C-14-PMMA autoradiography have shown that there are considerable
136 amount of nanometre scale pores and their contribution to transport by diffusion can be considered
137 remarkable (Sammaljärvi, et al., 2017; Kuva, et al., 2016). The main minerals of Olkiluoto veined
138 gneiss are biotite (~30 %), quartz (~30 %), potassium feldspar (~15 %) and plagioclase (~15 %).
139 Common accessory minerals are muscovite, chlorite, cordierite (often pinitised), sillimanite,
140 epidote, garnet and opaque minerals (~10 % total). Interlamellar space of biotite is often filled with
141 kaolinite, chlorite and illite, and clay minerals are found in pinitised cordierites as well
142 (Sammaljärvi, et al. 2017). This, along with the random nature of the leucosome veins, means that
143 the rock is very heterogeneous and anisotropic from microscopic to decametre scales (Aaltonen, et
144 al. 2016; Ikonen, et al. 2015).

145 Grimsel Test Site on the other hand is located in the Swiss Alps and lies at a depth of about
146 450 m below the ground surface. Grimsel bedrock around the Grimsel Test Site consists of Grimsel

147 granodiorite and Aare granite. A typical porosity value for Grimsel granodiorite is around 0.5-1.0 %
148 (Ikonen et al., 2016, Möri et al., 2003). Various analyses done previously on Grimsel granodiorite
149 by SEM found grain boundaries and pores also in the range of a few micrometres (Möri, et al.,
150 2003; Kelokaski, et al., 2006) but the mean pore diameter as measured by Hg-porosimetry was
151 found to be in the nanometre range (Kelokaski, et al., 2006). Furthermore, recent studies applying
152 C-14-PMMA autoradiography have shown that mineral grains with intra granular nanometre scale
153 pores (e.g. biotite) affect considerably the transport of radionuclides (Voutilainen, et al., 2017). The
154 main minerals of Grimsel granodiorite, which was used in this work, are quartz (~35 %),
155 plagioclase (~30 %), potassium feldspar (~30 %) and biotite (~5 %). Minor constituents include
156 muscovite, chlorite, epidote, allanite, zircon and apatite (Alexander, et al. 1990; Frick, et al. 1992).
157 The biotite and clay mineral content is an important quality, as the sorption of cations is known to
158 be significantly higher in biotite and clays than in other non-altered main minerals of crystalline
159 rock (Ittner, et al. 1990; Tsukamoto and Ohe 1993; Jokelainen, et al. 2013). Caesium sorption has
160 been studied in both rock types using lower caesium concentration than here and these studies have
161 shown high sorption on biotite, although clay minerals also contributed to the sorption (Muuri, et al.
162 2016; 2017).

163 From both rock types described above three cubic samples ($1 \cdot 1 \cdot 1 \text{ cm}^3$), six in total, were
164 sawn (see Fig. 1). The samples were taken close to each other to ensure they had roughly similar
165 composition and structure. Olkiluoto veined gneiss samples were taken from drill core ONK-PP323
166 in REPRO niche (Ikonen, et al. 2015) and Grimsel granodiorite samples from LTD monopole 1 drill
167 hole in AU gallery at Grimsel test site (Ikonen, et al. 2016). Five of the six faces of the samples
168 were sealed with an epoxy resin to allow CsCl to intrude the sample from only one side. For each
169 sample the face opposite to the open one was attached to a sample holder for microtomographic
170 imaging.

171

172 Figure 1. One sample from both rock types, Olkiluoto veined gneiss on the left and Grimsel
173 granodiorite on the right, prepared for X-ray microtomography. Sample size is 1·1·1 cm³.

174 **2.2. X-ray microtomography**

175 Computed X-ray microtomography is a method where, by detecting the difference in X-ray
176 attenuation between different parts of a sample, three dimensional images of a sample are produced
177 non-invasively. The sample is rotated with small increments and a two dimensional projection is
178 taken at each step. The projections, of which a few hundred to a few thousand are usually taken, can
179 then be computationally reconstructed into a three dimensional X-ray attenuation map. As the X-ray
180 attenuation coefficient of a material is generally proportional to the elemental composition and
181 density of the sample, this can also be interpreted as a three dimensional density map.

182 The microtomographic images used in this work were obtained with a SkyScan 1172
183 (Bruker microCT, Kontich, Belgium) table top scanner, which has a tungsten anode X-ray tube with
184 polychromatic spectra and conical X-ray beam. They were imaged with a 6.1 µm voxel size using a
185 source voltage of 100 kV and a source current of 80 µA. In order to reduce beam hardening, X-rays
186 with low energy were filtered out from X-ray spectra using aluminium and copper filters. After this
187 treatment the maximum intensity of spectra is at 59 keV (K α energy of tungsten) and the theoretical
188 maximum energy is 100 keV. The samples were scanned over a 203.8 degree rotation with a 0.2
189 degree rotation step, resulting in a total of 1020 projections. Each projection was averaged over 10
190 exposures of 6479 ms and the total scanning time was roughly 20 hours. The images were
191 reconstructed with the SkyScan NRecon software using a ring artefact correction setting of 6-12 and
192 beam hardening correction of 45-50 %. NRecon software applies Feldkamp algorithm (Feldkamp et
193 al., 1984) for reconstruction and has an in-built alignment tool that is based on comparison of two
194 projections taken from opposite directions.

195 The resolution of X-ray microtomography is 6.1 μm , and the majority of the pores in
196 Grimsel granodiorite and Olkiluoto veined gneiss remain undetected. It is however expected that
197 caesium chloride increases a local X-ray attenuation which is a parameter that is averaged over the
198 volume of each voxel. On the other hand, pores within the mineral grain decrease the local X-ray
199 attenuation, but often in natural materials the decrease is lost due to noise of signal and thus
200 comparison of images taken before and after intrusion experiment is needed.

201 **2.3. Scanning electron microscopy**

202 The samples were carbon coated for the analyses and the analyses were performed using a field
203 emission scanning electron microscope (FE-SEM) JEOL JSM 7100F Schottky (JEOL, Tokyo,
204 Japan), attached to an Oxford Instruments energy dispersive spectrometer (EDS) X-max 80 mm^2
205 and Hitachi S-4800 (Hitachi, Tokyo, Japan) model with Oxford instruments X-sight X-ray
206 diffractometer. The energy resolution of the EDS detectors used is about 130 eV for Mn Ka with
207 processing capabilities multichannel analyser with 2048 channels at 10 eV/ch The FE-SEM-EDS
208 systems were operated by Oxford Instruments INCA and AZtec softwares. The analytical data
209 obtained was semiquantitative and the sum of the components was normalized to 100 %. Typical
210 detection limits in point analysis for different elements range between 0.3-0.5 wt%. For caesium the
211 detection limit is 0.4 wt%. The FE-SEM-EDS was used in high vacuum mode with COMPO back
212 scattered signal, 20 kV accelerating voltage and 1 nA probe current. . Elemental distribution maps
213 were generated over the sections with Aztec with a montage technique that combines several
214 individual high-resolution elemental maps and back scattered electron (BSE) images together.

215 **2.4. CsCl intrusion experiments**

216 All six samples were first imaged with X-ray microtomography and then submerged in a saturated
217 CsCl solution. It was assumed that CsCl or caesium, if concentrated enough, could be detected
218 using X-ray microtomography due to its high density (high X-ray attenuation) in the connected pore
219 space of the rock samples. The precipitate might alter the transport pathways and even block some

220 pores but the result would probably only be reduced connectivity and increased tortuosity (Noiriel,
221 et al., 2016). All samples remained submerged in saturated CsCl solution for 141 days, after which
222 one sample of each type was imaged again with X-ray microtomography. The next two samples
223 were imaged after 249 days of immersion and the final two samples after 365 days of immersion.

224 For image analysis the microtomographic three dimensional images taken before and
225 after immersion in saturated CsCl solution, had to be perfectly aligned. This was done with an in-
226 house program that required the user to identify three features from the first image and the same
227 three features from the second image. These features were mainly small grains of high density
228 minerals, roughly 5·5·5 voxels in size, of which the middle voxel was identified as the feature. The
229 program then defined the Euclidean transform that matches the features optimally and used this
230 transform to align the images.

231 The samples that had been submerged for 141 days were dried and then impregnated
232 with methyl methacrylate (MMA) which was subsequently polymerized to polymethylmethacrylate
233 (PMMA) to fix the caesium phases into the pore space. This step is necessary as CsCl is a water-
234 soluble compound which could be washed away during the sample handling. MMA is expected to
235 fill any space left vacant by the contrast agent and also intrude into the pores within the CsCl
236 precipitate itself. As MMA is a hydrophobic compound, it is not expected to dissolve the CsCl
237 precipitate. There is however possibility that the polymerization heat and the contraction of MMA
238 as it polymerizes could affect the CsCl precipitate. The MMA is however diluted by the rock matrix
239 and there is only small volume of MMA in any given volume, dampening the possible effects of the
240 polymerisation process. This process has also been found to work for celestite precipitated into
241 compacted illite (Chagneau, et al., 2015). After the polymerization, these two samples were then
242 sawn in half, polished, carbon coated and investigated with SEM-EDS. An illustration of the
243 different steps in the transport experiment is shown in Fig. 2.

244

245 Figure 2. Illustration of the different steps of the experiment. Samples were first imaged with
246 microtomography, then immersed in a saturated CsCl solution for 141, 249 and 365 days, then
247 imaged with microtomography and SEM-EDS.

248 **3. RESULTS**

249 **3.1. X-ray microtomographic imaging**

250 All six samples were imaged with X-ray microtomography before and after immersion to a
251 saturated CsCl solution. Cross-sections of the three dimensional microtomographic images (one
252 representative slice was chosen for each sample), as well as the images showing the difference
253 between the pre- and post-immersion images, are shown in Figs. 3-4. The main minerals are the
254 same in both rock types. In pre-immersion images the main minerals are seen as light grey (biotite),
255 intermediate grey (potassium feldspar and plagioclase) and dark grey (quartz). Some accessory
256 minerals are seen as white spots and other might overlap with the grey values of the main minerals.
257 In post-immersion images the new areas with increased grey value show location of CsCl as it is
258 heavier than the main elements in the minerals. In the images showing the difference between pre-
259 and post-immersion images the change in attenuation of X-rays and location of caesium is even
260 more pronounced. It is clearly visible that Olkiluoto veined gneiss contains more biotite which is an
261 iron rich mineral and denser than feldspars and quartz. In both sample types the foliation is shown
262 in the images. It is more pronounced in veined gneiss in this scale, which has smaller grain size than
263 Grimsel granodiorite. It can also be seen that the orientation of the minerals varies from sample to
264 sample. It is parallel to CsCl intrusion in most samples, but perpendicular to it in one sample from
265 both sites.

266

267 Figure 3. Microtomographic cross-sections of the Olkiluoto veined gneiss samples immersed in the
268 saturated CsCl solution for 141 days (top row), 249 days (middle row) and 365 days (bottom row)
269 taken before (left column) and after (middle column) the saturated CsCl solution immersion, along
270 with a difference of the two (right column). A lighter grayscale value indicates a denser mineral.
271 The CsCl solution intrusion surface is the upper edge. Sample width is 1 cm.

272

273 Figure 4. Microtomographic cross-sections of the Grimsel granodiorite samples immersed in the
274 saturated CsCl solution for 141 days (top row), 249 days (middle row) and 365 days (bottom row)
275 taken before (left column) and after (middle column) saturated CsCl solution immersion, along with
276 a difference of the two (right column). A lighter grayscale value indicates a denser mineral. The
277 CsCl solution intrusion surface is the upper edge. Sample width is 1 cm.

278 It is evident that there is very little CsCl intrusion in Grimsel granodiorite, as the quantities
279 observed are small (see Fig. 4.). According to qualitative inspection of cross-sections show that
280 increase in attenuation of X-rays due to accumulation of caesium are mainly located in biotite areas.
281 In Grimsel granodiorite a slightly higher porosity has been observed for biotite than the rest of the
282 minerals.

283 In Olkiluoto veined gneiss there is intrusion of CsCl throughout the samples in large
284 quantities (see Fig. 3.). Qualitative inspection showed that the highest changes in attenuation of the
285 X-rays are located at intermediate grey areas. These areas should not have high porosities or large
286 pore apertures since they should be represent the potassium feldspar and plagioclase. However,
287 Olkiluoto veined gneiss contains cordierite grains (6.6 vol-%) which are known to have relatively
288 high porosities if they have experienced alteration to pinite (Ikonen, et al., 2015; Sammaljärvi, et
289 al., 2017). In order to resolve the mineral phase of the areas with large changes in attenuation of X-
290 rays SEM-EDS –analyses were performed. It is noteworthy that almost no pores or fissures can be

291 seen in the images, as the apertures are mostly below the 6.1 μm resolution used. The CsCl does,
292 however, reveal many pores and areas of high local porosity which was the main aim of this study.

293 **3.2. Analysis of the microtomographic images**

294 In an attempt to quantify the amount of CsCl and pure caesium in the samples and the intrusion
295 profiles, Z-profiles of the difference images in Figs. 3-4 were determined. This was done by taking
296 an average grayscale value for each horizontal voxel plane from the intrusion surface to the bottom
297 of the sample in the three dimensional image. Thus we could obtain a dimensionless estimate for
298 the amount of caesium in the samples as a function of distance from the intrusion face, which is
299 shown in Fig. 5. This makes the difference in caesium infiltration between the two rock types even
300 clearer. There is much more caesium in the Olkiluoto veined gneiss samples. In fact, the Olkiluoto
301 veined gneiss samples are completely saturated with all diffusion times, even when the foliation has
302 been perpendicular to the intrusion (365 days). This can be seen by the overlapping of the curves
303 and a lack of slope inside the sample. The variation seen in the Z-profiles is due to the varying
304 contents of minerals, as a function of distance from the intrusion face. The high values at the
305 intrusion surface are due to caesium precipitated on the sample surface. The Grimsel granodiorite
306 samples seem to be saturated too, but they lack the high porosity mineral clusters that act as CsCl
307 sinks in Olkiluoto veined gneiss. The difference in pore structures can already be seen by
308 comparing previous C-14-PMMA autoradiography studies of the two rock types (Kelokaski, et al.
309 2006; Ikonen, et al. 2015). As there is no change as a function of time, no information on intrusion
310 rate could be obtained. The differences in the profiles of the Olkiluoto veined gneiss samples can be
311 attributed to the differences between the samples themselves.

312

313 Figure 5. Z-profiles of microtomographic images depicting the change in the Olkiluoto veined
314 gneiss (left panel) and the Grimsel granodiorite (right panel) samples caused by immersion into the

315 saturated CsCl solution. Much more significant caesium intrusion can be seen in the Olkiluoto
316 veined gneiss samples than the Grimsel granodiorite samples. The profiles peak at ~5000 for
317 Grimsel granodiorite and ~3000 for Olkiluoto veined gneiss.

318 The grayscale changes were also investigated from each sample by comparing the grayscale values
319 of single voxels from pre-immersion images to the grayscale values of corresponding voxels in the
320 post-immersion images. The images were converted from 16 bits to 8 bits with a linear conversion
321 for this analysis. The loss of grayscale data resolution was deemed acceptable as the comparison
322 was mainly qualitative in nature. The contour plots obtained this way can be seen in Figs. 6-7. In an
323 ideal case with no caesium intrusion these plots would just have a sharp ridge at the $x=y$ line. Any
324 caesium intrusion increases the grayscale value of a voxel and is then seen as a shift towards the
325 positive y -axis. In the Olkiluoto veined gneiss samples (Fig. 6) there is a clear shift of the first
326 grayscale peak, located between grayscale values 50-100. This peak contains mainly quartz and
327 feldspars, which can be visually separated from a microtomographic image but are too similar to be
328 quantitatively distinguished (which has already been shown by Boone, et al. 2011 and Kuva, et al.
329 2012), and the other less pronounced peak located between grayscale values 125-150 contains
330 biotite. In the Grimsel granodiorite samples (Fig. 7) the intruded caesium can be seen as a slight
331 shift of the profile towards the positive y -axis for all the minerals which is in line with the previous
332 finding that the porosity of different minerals in Grimsel granodiorite are fairly close to each other.

333

334 Figure 6. Comparisons of grayscale values (8 bit) of voxels before the immersion into the saturated
335 CsCl solution and the grayscale values of the corresponding voxels after the immersion into the
336 saturated CsCl solution for Olkiluoto veined gneiss samples immersed for 141 days (left panel), 249
337 days (middle panel) and 365 days (right panel). The colours describes the amount of voxels. A clear
338 shift in the peak located between values 50-100 can be seen on each image. A smaller shift is also
339 seen in the peak located between values 125-150, indicating some retention of caesium.

340

341 Figure 7. Comparisons of grayscale values (8 bit) of voxels before the immersion into the saturated
342 CsCl solution and the grayscale values of the corresponding voxels after the immersion into the
343 saturated CsCl solution for Grimsel granodiorite samples immersed for 141 days (left panel), 249
344 days (middle panel) and 365 days (right panel). The colours describes the amount of voxels. A
345 small shift towards the positive y-axis is seen for all minerals.

346 **3.3. SEM-EDS Analysis**

347 The PMMA impregnated samples were analysed with SEM-EDS to see the location and content of
348 CsCl in respect to different minerals. Only very little caesium was found in the Grimsel granodiorite
349 sample and all of the caesium was as pure precipitated CsCl in micrometre scale pores. These pores
350 with pure precipitate were, however, found throughout the whole sample which proves that the
351 precipitate has not blocked up the migration routes in the Grimsel granodiorite. Furthermore, it can
352 be assumed according to the data shown in Figs. 5 and 7 that there might be elevated concentration
353 of caesium in some minerals having the pores below micrometre scale but the amount is below the
354 detection limit of the SEM-EDS (<0.4 wt%).

355 In the Olkiluoto veined gneiss sample, a significant amount of caesium was found using
356 SEM-EDS. Examples of caesium findings by SEM-EDS are shown in Fig. 8. In some cases
357 intragranular pores and fissures contained precipitated CsCl. The CsCl precipitates were found in
358 different shapes and sizes as can be seen in the Fig. 8. In Olkiluoto veined gneiss the largest
359 quantities of caesium were found in pinitised areas of cordierite grains. Pinite is an alteration
360 product of cordierite with a varying composition which can include muscovite, chlorite, berthierine,
361 illite and smectite in various ratios and interlayers (Ogiermann, 2002). In Fig. 8. an example of such
362 a location is shown with a pinitised cordierite grain, sphalerite, zircon inclusions, a biotite grain and
363 a fractured quartz grain. Here caesium was also found in sphalerite, wherein no chloride was

364 detected. Another example of pinitised cordierite containing caesium and chloride, together with
365 biotite and muscovite, is also shown. In the pinitised grains caesium was found in considerable
366 excess compared to chloride. In some areas of particularly high caesium abundance no chloride
367 could be reliably detected. All in all, both caesium and chloride were found in pinitised cordierite in
368 differing abundances and ratios. In CsCl itself the atomic ratio of caesium to chloride is 1.
369 However, in pinite this ratio ranged from 2.0 to 6.2 (see Table 1.). Chloride was not always detected
370 together with caesium in the point analyses. In addition, a biotite grain with a kaolinite-filled
371 interlamellar space near the edge of the sample is shown in Fig. 8. Caesium was found in parity
372 ratio with chloride in the kaolinite-filled interlamellar space. Furthermore, in this case caesium
373 chloride was also found in a 10 µm wide band in biotite starting from the edge of the original CsCl
374 intrusion, along with chloride.

375

376 Figure 8. SEM BSE images. Upper left: Quartz (Q) grains with CsCl precipitate in its intragranular
377 fissure. Upper right: Fractured quartz grain, intact biotite (BT) lamellae and partially pinitised
378 cordierite (CRD) grain. Small grains of sphalerite (SP) and Zircon (ZRN). Caesium and chloride
379 found in pinite (PI) and high content of caesium found in sphalerite. Lower left: Biotite lamellae
380 from the edge of the sample and interlamellar pores filled with kaolinite (KLN). Caesium and
381 chloride found in parity abundance in kaolinite. Caesium, along with chloride, found in large
382 abundance in a 10 µm deep area in the disturbed biotite. Lower right: Highly pinitised cordierite
383 grain adjacent to biotite and muscovite (MU). Large abundances of caesium and some chloride
384 were found in the pinite with their abundance correlating directly with the level of pinitisation.

385 Summary of caesium and chloride abundances and their ratios are shown in Table 1. A large range
386 of values were found in pinite. There was a direct correlation of retention of caesium with the level
387 of pinitisation. In kaolinite the retention was lower but still notable and the range of values was
388 narrower. Retention of caesium on sphalerite grains was considerable, while chloride retention was

389 not observed. Sphalerite is not, however, a common mineral in Olkiluoto veined gneiss and
390 therefore a range could not be established.

391

392 Table 1. Caesium and chloride abundances in atomic% and their ratios sorted by the minerals where
393 they were found in notable amounts. The values given are averages with the ranges given in
394 brackets. In few areas of pinitite that had the highest caesium abundances, the chloride abundance
395 could not be determined.

396

397 Elemental maps of caesium and chloride with corresponding BSE SEM image from a larger area of
398 the Olkiluoto veined gneiss sample are shown in Fig. 9. It can be seen that caesium is found in high
399 abundance with roughly similar amount chloride and in notable excess compared to chloride. In
400 both cases caesium appears to reside in the porous spaces of the rock sample which, in the case of
401 excessive abundance of caesium, were identified to be congruent with pinitised cordierite. There is
402 background noise in the elemental maps due to the long measurement times involved. In the case of
403 caesium, the titanium found in biotite can also interfere due to X-ray emissions with energies very
404 similar to those of caesium.

405

406 Figure 9. BSE SEM image of a larger part of the Olkiluoto veined gneiss sample (left panel) along
407 with an elemental map of caesium (middle panel) and chloride (right panel) from the same area,
408 showing that some caesium patches are precipitated with roughly similar amount of chloride
409 (examples marked with A) and other with less chloride (examples marked with B).

410 Finally, the Olkiluoto veined gneiss sample imaged with SEM-EDS was imaged again
411 with X-ray microtomography. This was done to find the surface corresponding to the SEM images

412 from the microtomographic image significantly easier and to make sure that if the MMA-
413 impregnation caused any changes in the caesium inside the sample, the same changes would be
414 present in the microtomographic image. The surface corresponding to the SEM images was then
415 located from the microtomographic image. This surface, shown along with a difference image
416 compared to the original microtomographic image of the same sample in Fig. 10, shows that CsCl
417 could be detected with X-ray microtomography as well in corresponding locations and concentrated
418 caesium was observed in pinitised cordierites. According to SEM-EDS analyses these locations
419 contained from 1.1 to 8.0 atomic% of caesium which leads to a finding that such abundances can be
420 easily detected with X-ray microtomography when using the different methods.

421

422 Figure 10. X-ray microtomographic cross-section of a Olkiluoto veined gneiss sample with an area
423 corresponding with that of Fig. 9 (left panel) and a corresponding difference image with the first
424 microtomographic imaging of the same sample, showing CsCl in connected pore space and
425 concentrated caesium in pinitised cordierite grains. A and B areas correspond to the marked areas in
426 Fig.9.

427 **4. DISCUSSION and CONCLUSIONS**

428 The primary objective of this work was to test if connected porosity within crystalline rock could be
429 seen using CsCl as a contrast agent. This objective was achieved as it was found that CsCl enhanced
430 the local X-ray attenuation so that connected porosity Olkiluoto veined gneiss and Grimsel
431 granodiorite, to a lesser extent, could be imaged.

432 The two rock types are different in their mineralogy and the structure of the pore network,
433 which was seen in the results. Much more significant caesium intrusion was seen in Olkiluoto
434 veined gneiss than Grimsel granodiorite, despite earlier studies showing Grimsel granodiorite to be
435 more conductive than Olkiluoto veined gneiss (Kelokaski, et al. 2006; Kuva, et al. 2015). In

436 Olkiluoto veined gneiss there are more areas of high local porosity congruent with cordierites and
437 its alteration product pinitite where CsCl was accumulated. These highly porous areas were more
438 easily distinguished with the improved contrast using the SEM-EDS and X-ray microtomography.
439 No clear time dependence on the intrusion depth was detected, which likely means that all samples
440 were already saturated after 141 days of immersion and thus no information on intrusion rate was
441 obtained. Complete infiltration of the CsCl into the Olkiluoto veined gneiss samples showed that
442 connected transport pathways remained open despite the CsCl precipitation in the pore openings.
443 Presence of micrometre scale pores may have caused the complete infiltration of CsCl in relatively
444 short time. However, previous studies have shown that porosity of these samples has considerable
445 contribution from nanometre scale pores and thus their contribution cannot be neglected.

446 Closer investigation of the microtomographic images showed that in Olkiluoto veined gneiss
447 the CsCl precipitates were found most extensively in cordierite grains and in some extent in
448 pinitised cordierite grains. This is expected as the most pronounced effect is coming from the
449 caesium that is accumulated in the pore space of the rock, since the cation exchange capacity of
450 biotite and studied rock samples is relatively low considering the effect it can have on the local
451 attenuation coefficient (Olin, et al. 2006; Muuri, et al. 2016; 2017). In Grimsel granodiorite the
452 density change was smaller and took place relatively evenly in all minerals. The results by X-ray
453 microtomography were supplemented and verified using SEM-EDS analyses which showed that
454 both sample types had precipitated CsCl in the micrometre scale pores throughout the sample. The
455 CsCl precipitates came in a variety of shapes and sizes. This is probably due to the sample drying
456 before the impregnation and the PMMA impregnation procedure itself, which could disrupt the
457 precipitate structure. However without the PMMA impregnation procedure, the precipitate would
458 likely be washed off during the SEM-EDS sample preparation. Not all fissures were found to be
459 filled with CsCl. Some of the fissures however can have come about after the immersion with the
460 CsCl solution as the result of the sample preparation (Schild, et al., 2001). Similar procedure has

461 been done on compacted illite wherein celestite was precipitated into the pores structure and
462 similar-looking structures were obtained (Chagneau, et al., 2015). In the Olkiluoto veined gneiss the
463 highest abundances of CsCl were found in pinitised cordierite, with other notable locations of high
464 caesium abundance being the kaolinite-filled interlamellar space of biotite and on sphalerite. In
465 biotite itself caesium was found in notable amounts in the disturbed edge zone. In the elemental
466 mapping of Fig 9. In pinite caesium was found in notable excess compared to chloride. The excess
467 of caesium compared to chloride in pinite indicates that caesium experiences more retention in
468 pinite than chloride. In some points, no chloride could be detected at all. These points corresponded
469 mostly with areas of pinite where highest amounts of caesium where found. It is likely that these
470 points corresponded to fine-grained clay minerals where chloride is not able to enter in detectable
471 amounts due to possible anion exclusion. This causes the effective porosity for cations to be
472 significantly higher than the effective porosity for anions (Smith, et al., 2004). Anion exclusion has
473 been shown to be comparatively high in smectite and illite, but less so in kaolinite (Glaus, et al.,
474 2010). This could explain why caesium was found in excess compared to chloride only in pinite but
475 not in the interlamellar kaolinite. Anion exclusion is usually not complete, unless special measures,
476 such as clogging pores with celestite beforehand are used (Chagneau, et al., 2015). As no such
477 treatment preceded the CsCl-immersion, chloride was usually found also in pinite, in small, sub
478 parity quantities. Caesium is, however, also a strong sorber on edge sites of illite, which may also
479 contribute to its strong retention in pinite, even though saturation concentration used in this work is
480 not ideal for sorption (Wahlberg & Fishman, 1962). Future experiment with water and anionic
481 tracers will be done to clarify the mechanisms behind the observed results. Comparison to
482 microtomographic images of the same sample confirmed that the same areas could be distinguished
483 with microtomography. In the Grimsel granodiorite samples the caesium was found only as
484 precipitated CsCl in a few connected pore apertures. This effect certainly arose from the differences
485 in mineral and pore structures.

486 Based on the results obtained it can be said that X-ray microtomography is a capable
487 tool in investigating transport pathways in tight crystalline rock when combined with a suitable
488 contrast agent. The results can be enhanced and complemented with SEM-EDS. Looking beyond
489 the results obtained in this study, the methods applied here could be: (1) used in an experiment with
490 shorter immersion times to obtain information on intrusion speed, (2) further developed by applying
491 autoradiography to provide complementary imaging for spatial activity distribution with a
492 radioactive contrast agent, and (3) applied to provide spatial distribution of the elements used in in
493 situ-diffusion experiments such as LTD and TDE.

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688

689 **7. FIGURE & TABLE CAPTIONS**

690 Figure 1. One sample from both rock types, Olkiluoto veined gneiss on the left and Grimsel
691 granodiorite on the right, prepared for X-ray microtomography. Sample size is 1·1·1 cm³.

692

693 Figure 2. Illustration of the different steps of the experiment. Samples were first imaged with
694 microtomography, then immersed in a saturated CsCl solution for 141, 249 and 365 days, then
695 imaged with microtomography and SEM-EDS.

696

697 Figure 3. Microtomographic cross-sections of the Olkiluoto veined gneiss samples immersed in the
698 saturated CsCl solution for 141 days (top row), 249 days (middle row) and 365 days (bottom row)
699 taken before (left column) and after (middle column) the saturated CsCl solution immersion, along
700 with a difference of the two (right column). A lighter grayscale value indicates a denser mineral.
701 The CsCl solution intrusion surface is the upper edge. Sample width is 1 cm.

702

703 Figure 4. Microtomographic cross-sections of the Grimsel granodiorite samples immersed in the
704 saturated CsCl solution for 141 days (top row), 249 days (middle row) and 365 days (bottom row)
705 taken before (left column) and after (middle column) saturated CsCl solution immersion, along with
706 a difference of the two (right column). A lighter grayscale value indicates a denser mineral. The
707 CsCl solution intrusion surface is the upper edge. Sample width is 1 cm.

708

709 Figure 5. Z-profiles of microtomographic images depicting the change in the Olkiluoto veined
710 gneiss (left panel) and the Grimsel granodiorite (right panel) samples caused by immersion into the
711 saturated CsCl solution. Much more significant caesium intrusion can be seen in the Olkiluoto

712 veined gneiss samples than the Grimsel granodiorite samples. The profiles peak at ~5000 for
713 Grimsel granodiorite and ~3000 for Olkiluoto veined gneiss.

714

715 Figure 6. Comparisons of grayscale values (8 bit) of voxels before the immersion into the saturated
716 CsCl solution and the grayscale values of the corresponding voxels after the immersion into the
717 saturated CsCl solution for Olkiluoto veined gneiss samples immersed for 141 days (left panel), 249
718 days (middle panel) and 365 days (right panel). The colours describes the amount of voxels. A clear
719 shift in the peak located between values 50-100 can be seen on each image. A smaller shift is also
720 seen in the peak located between values 125-150, indicating some retention of caesium.

721

722 Figure 7. Comparisons of grayscale values (8 bit) of voxels before the immersion into the saturated
723 CsCl solution and the grayscale values of the corresponding voxels after the immersion into the
724 saturated CsCl solution for Grimsel granodiorite samples immersed for 141 days (left panel), 249
725 days (middle panel) and 365 days (right panel). The colours describes the amount of voxels. A
726 small shift towards the positive y-axis is seen for all minerals.

727

728 Figure 8. SEM BSE images. Upper left: Quartz (Q) grains with CsCl precipitate in its intragranular
729 fissure. Upper right: Fractured quartz grain, intact biotite (BT) lamellae and partially pinitised
730 cordierite (CRD) grain. Small grains of sphalerite (SP) and Zircon (ZRN). Caesium and chloride
731 found in pinite (PI) and high content of caesium found in sphalerite. Lower left: Biotite lamellae
732 from the edge of the sample and interlamellar pores filled with kaolinite (KLN). Caesium and
733 chloride found in parity abundance in kaolinite. Caesium, along with chloride, found in large
734 abundance in a 10 µm deep area in the disturbed biotite. Lower right: Highly pinitised cordierite

735 grain adjacent to biotite and muscovite (MU). Large abundances of caesium and some chloride
736 were found in the pinitite with their abundance correlating directly with the level of pinitisation.

737

738 Figure 9. BSE SEM image of a larger part of the Olkiluoto veined gneiss sample (left panel) along
739 with an elemental map of caesium (middle panel) and chloride (right panel) from the same area,
740 showing that some caesium patches are precipitated with roughly similar amount of chloride
741 (examples marked with A) and other with less chloride (examples marked with B).

742

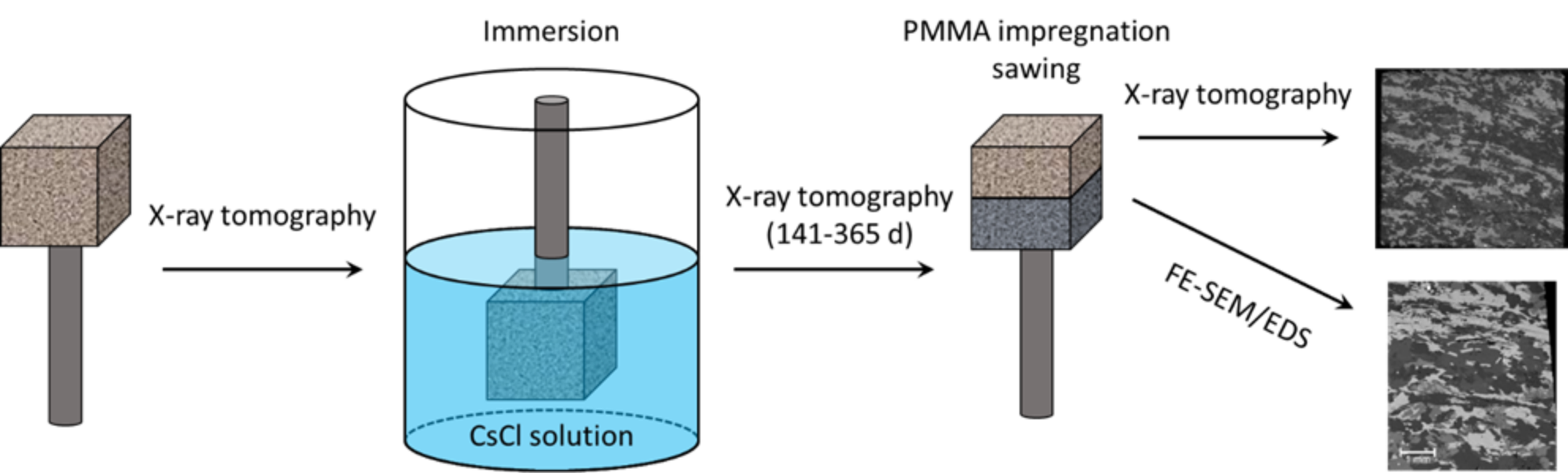
743 Figure 10. X-ray microtomographic cross-section of a Olkiluoto veined gneiss sample with an area
744 corresponding with that of Fig. 9 (left panel) and a corresponding difference image (right panel)
745 with the first microtomographic imaging of the same sample, showing CsCl in connected pore
746 space and concentrated caesium in pinitised cordierite grains. A and B areas correspond to the
747 marked areas in Fig.9.

748

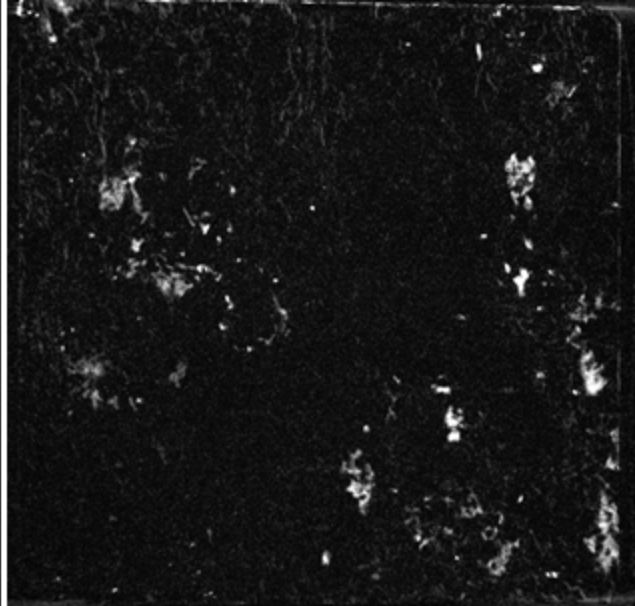
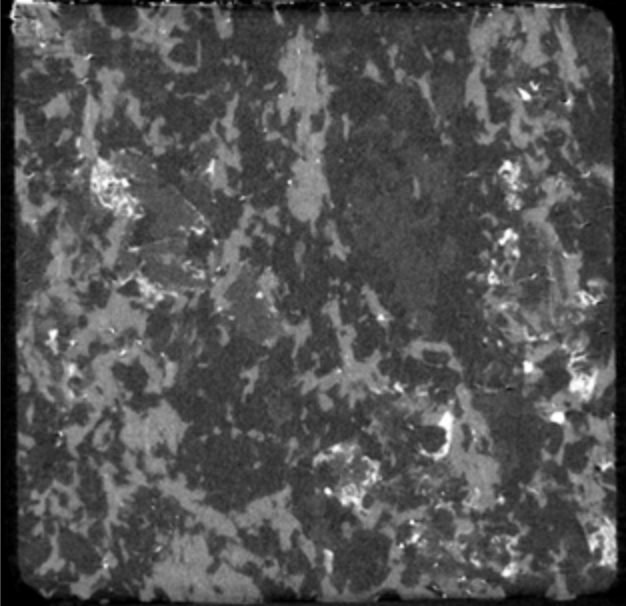
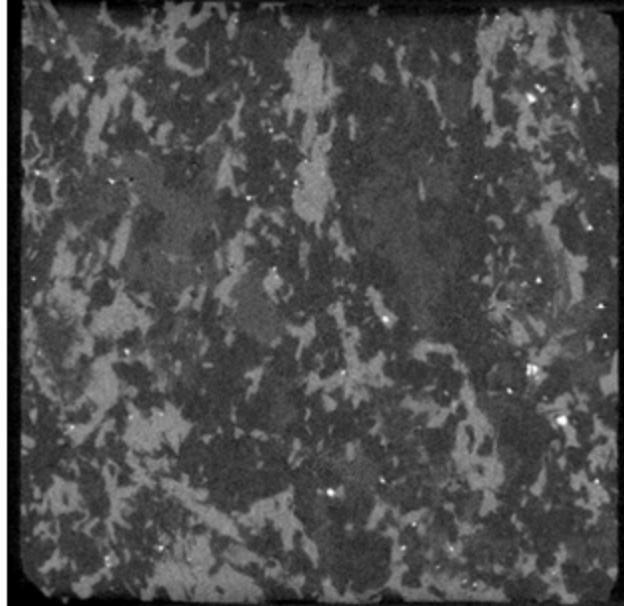
749 Table 1. Caesium and chloride abundances in atomic% and their ratios sorted by the minerals where
750 they were found in notable amounts. The values given are averages with the ranges given in
751 brackets. In few areas of pinitite that had the highest caesium abundances, the chloride abundance
752 could not be determined.

753

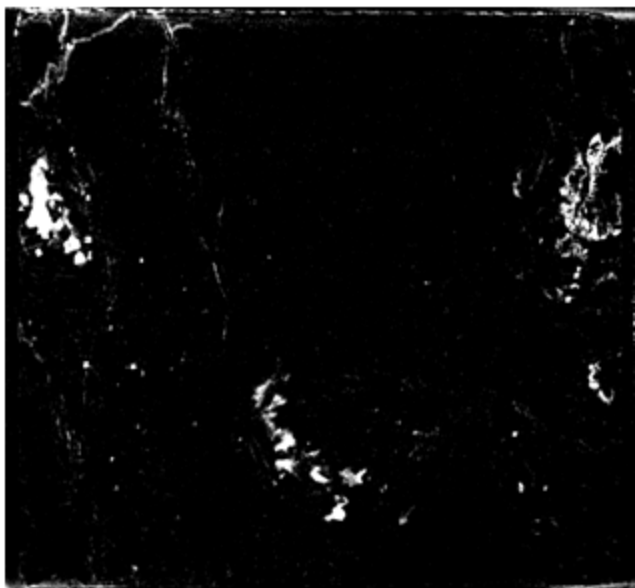
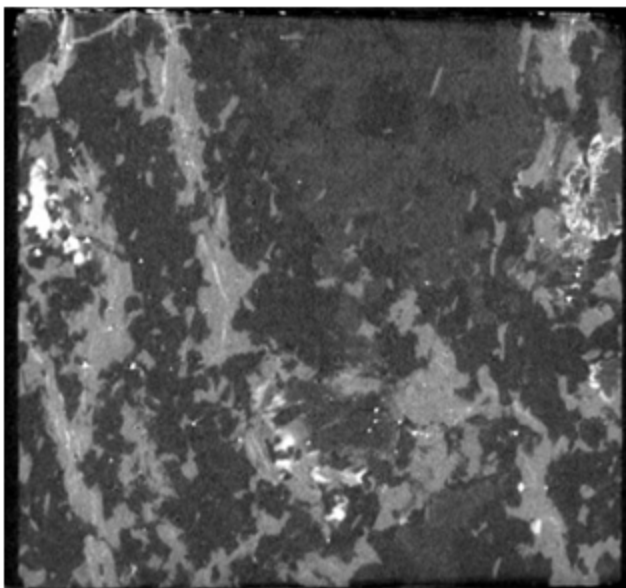
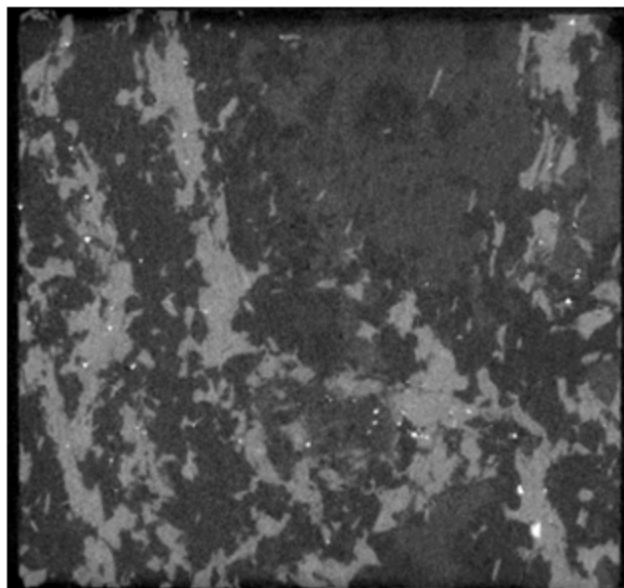




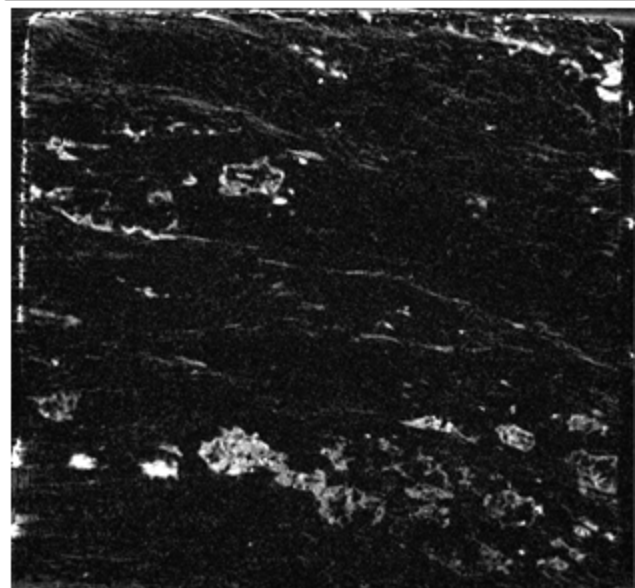
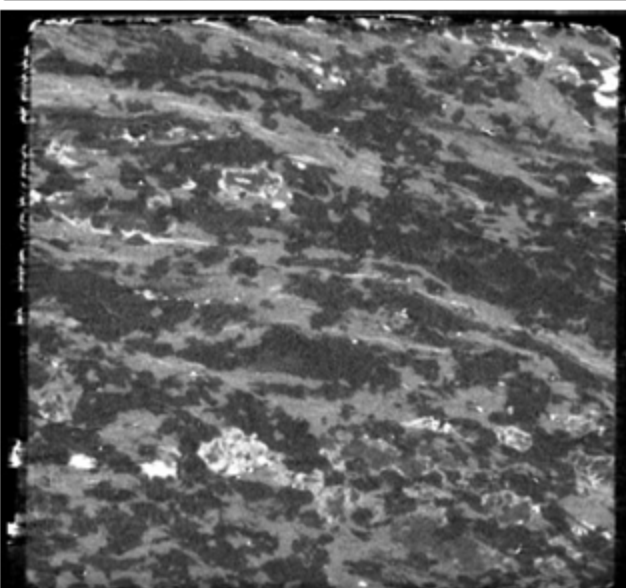
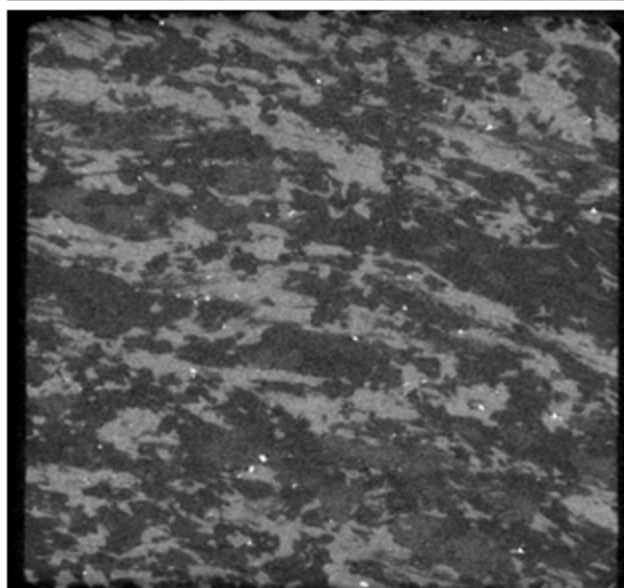
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249 d



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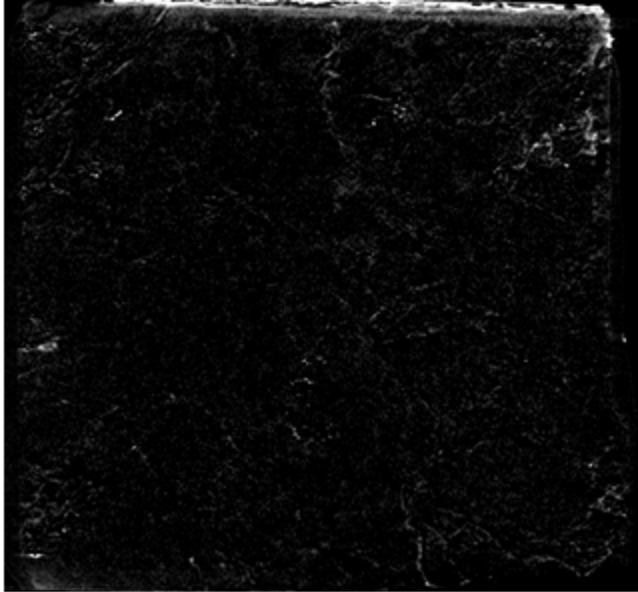
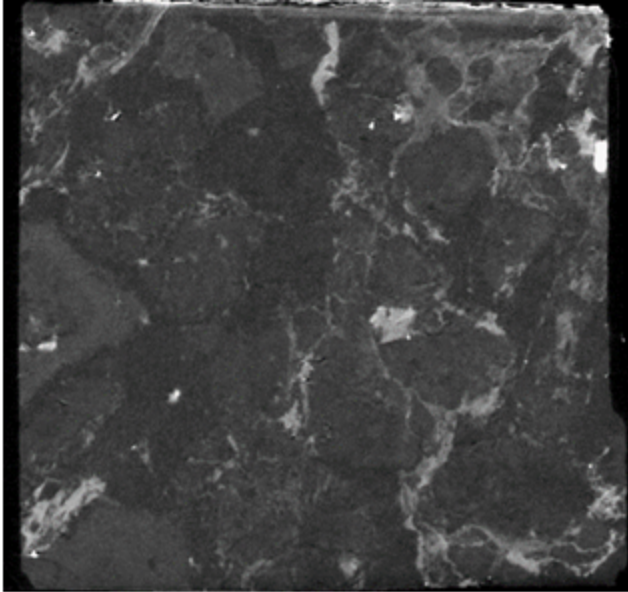
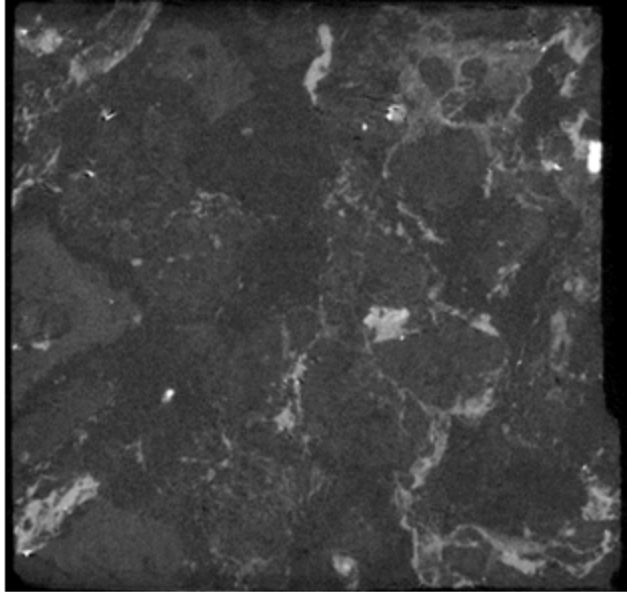


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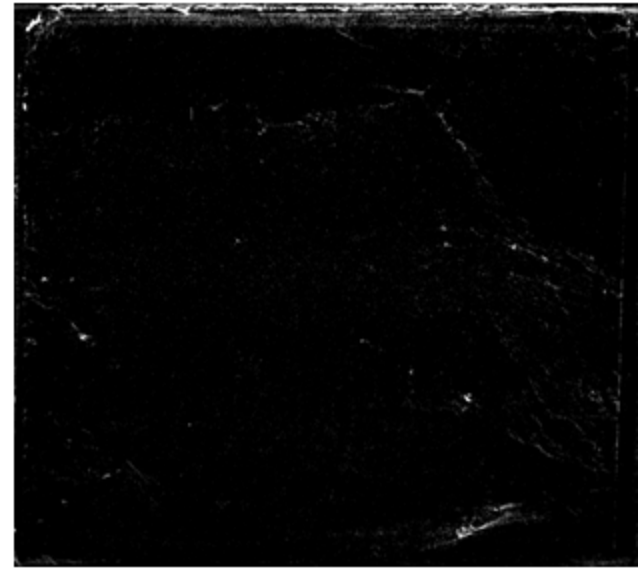
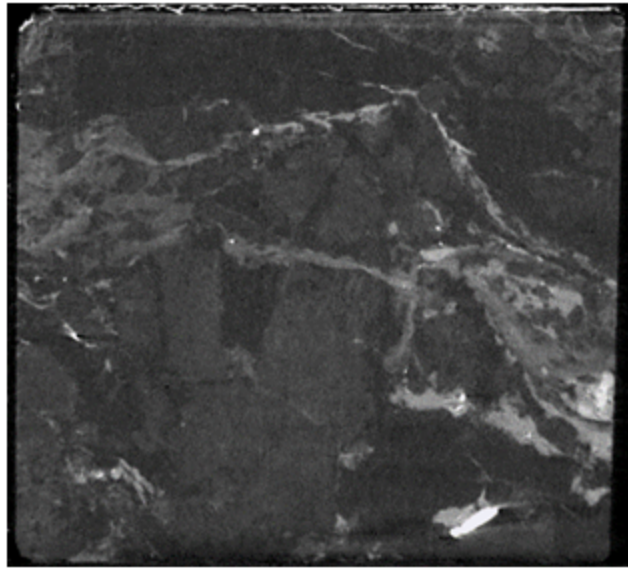
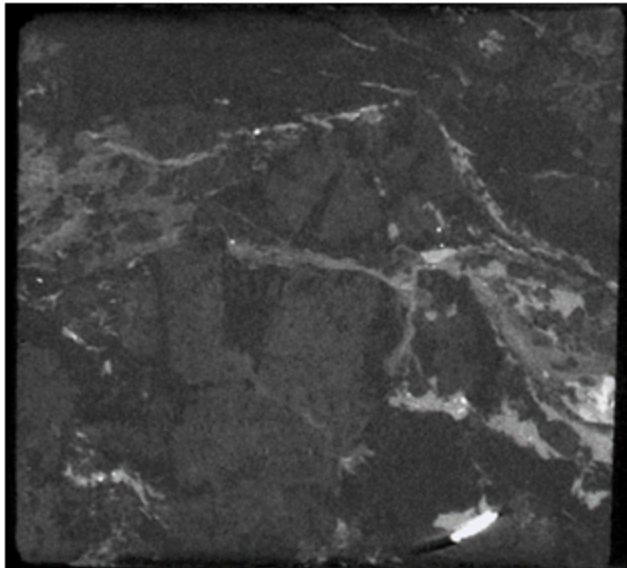
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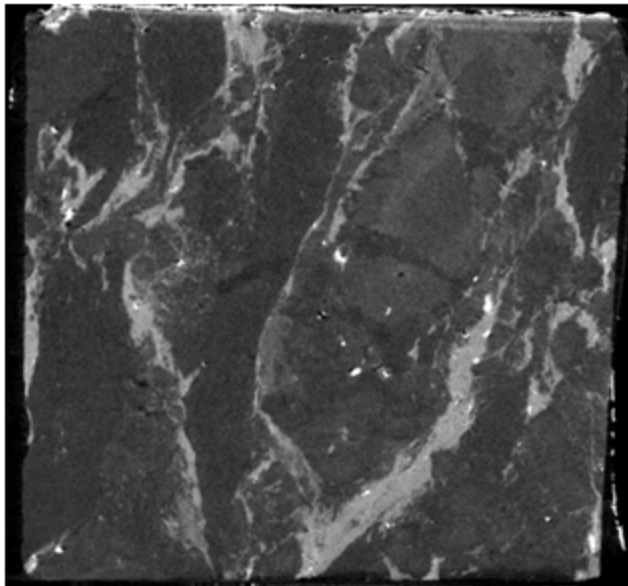
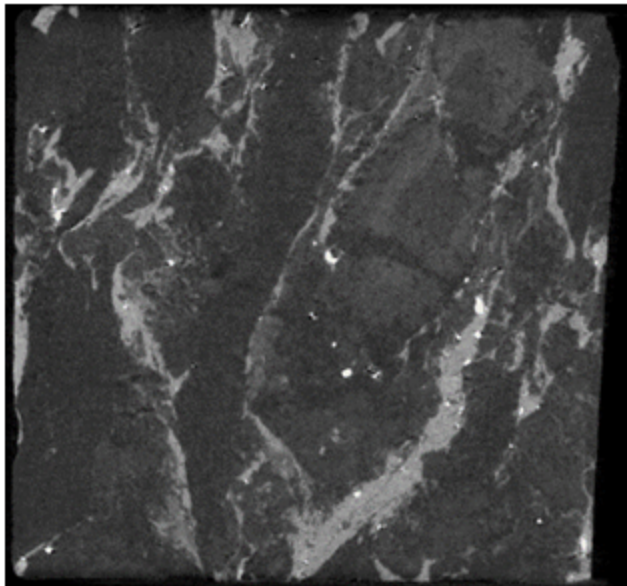
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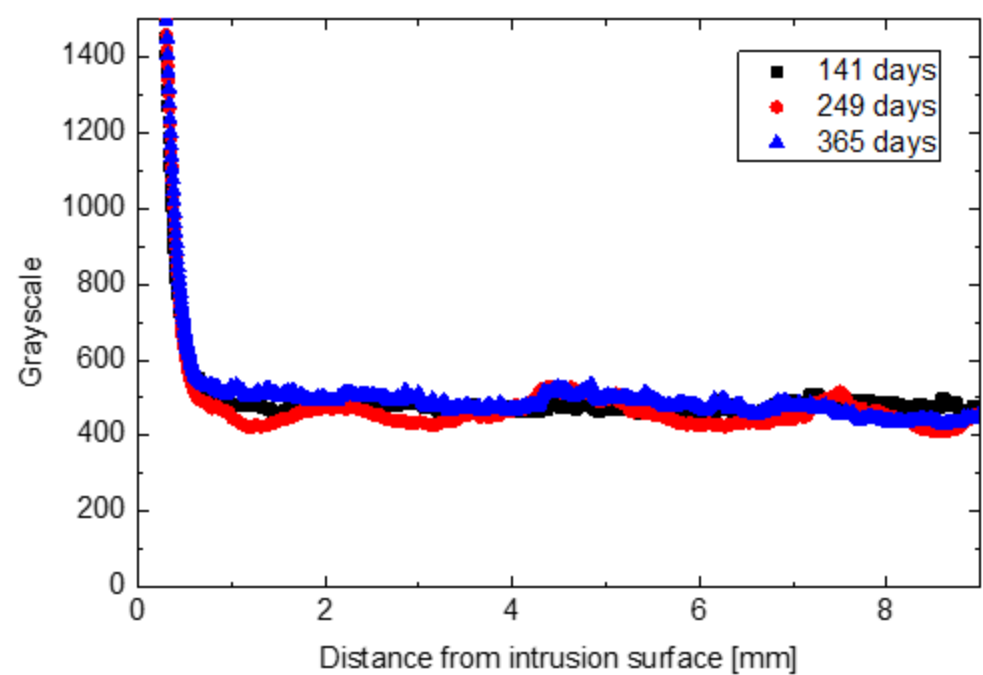
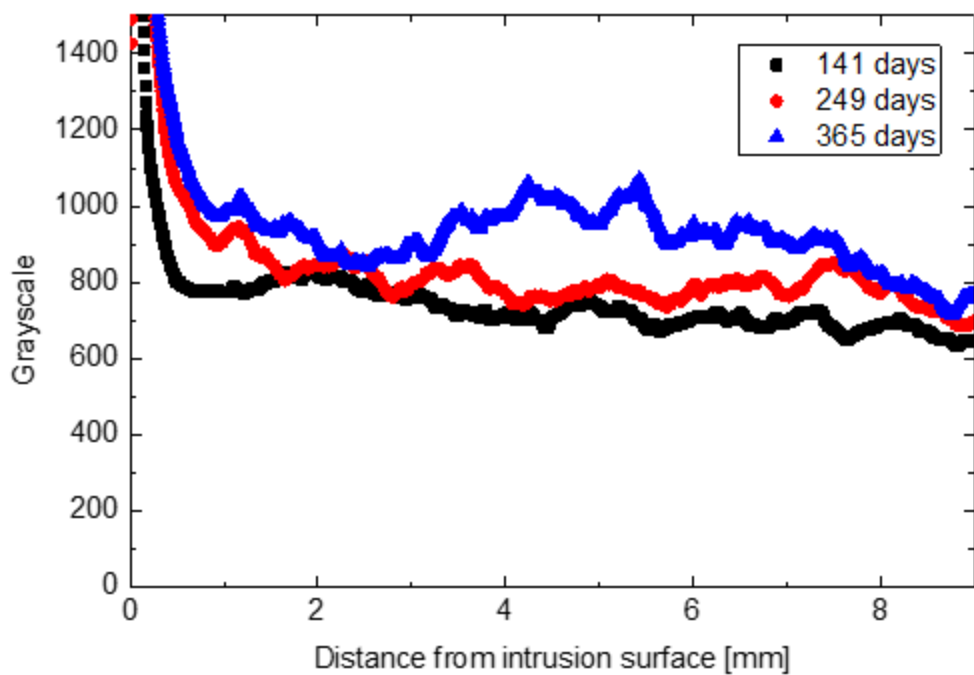
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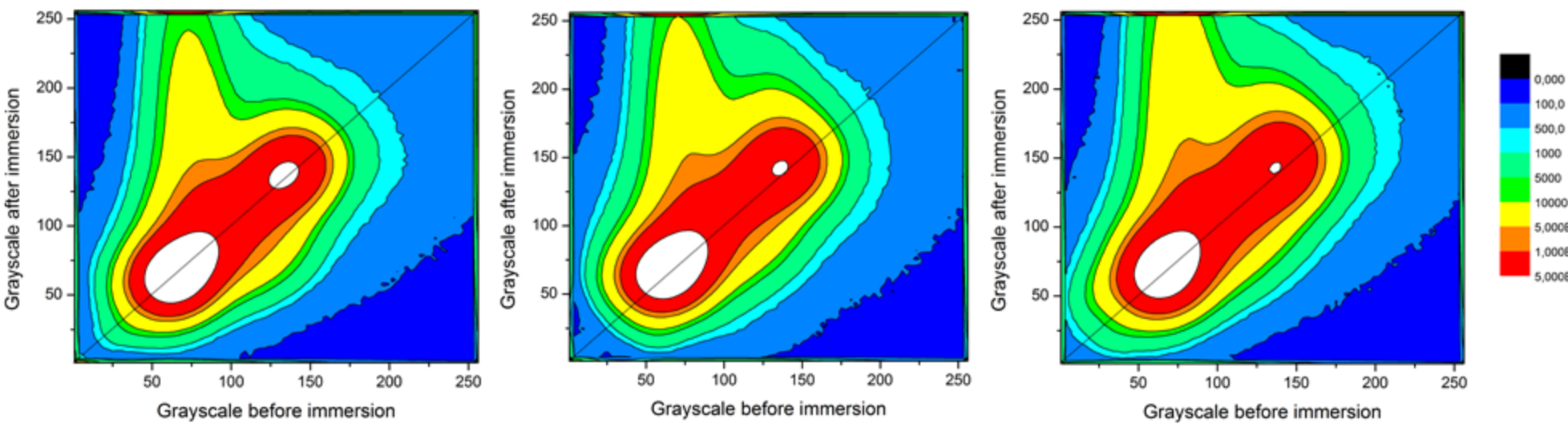


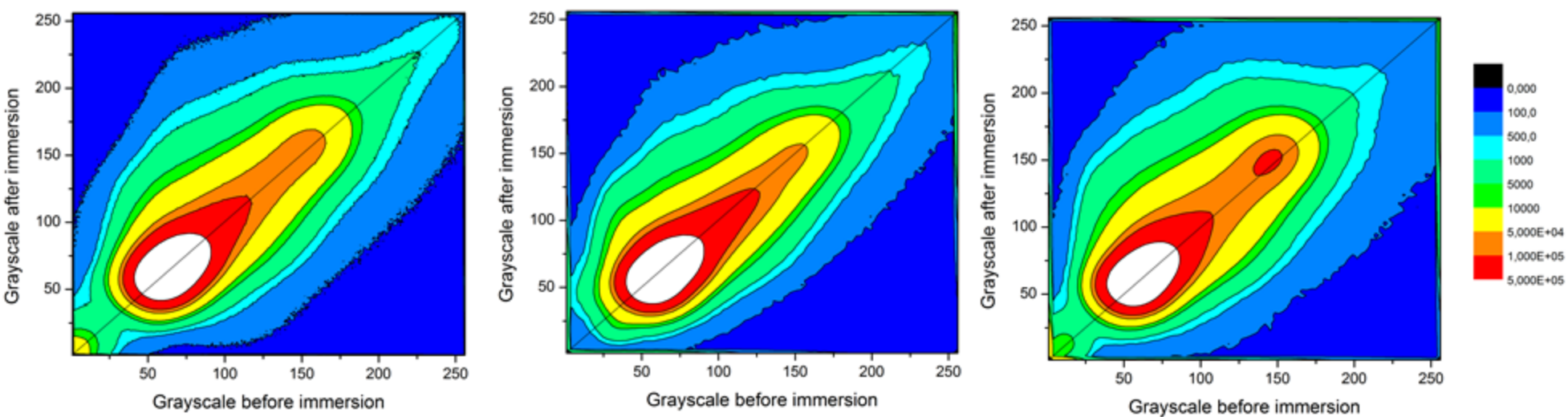
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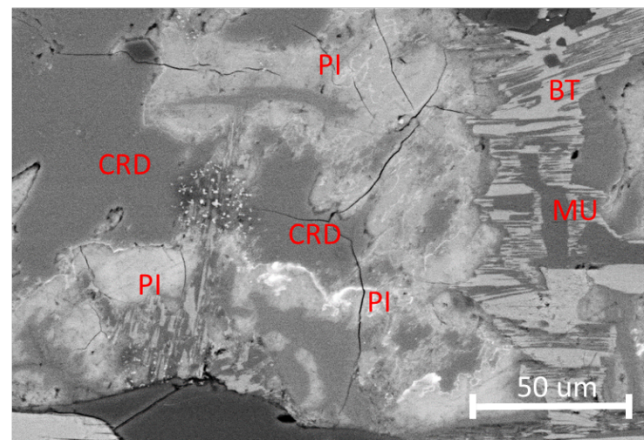
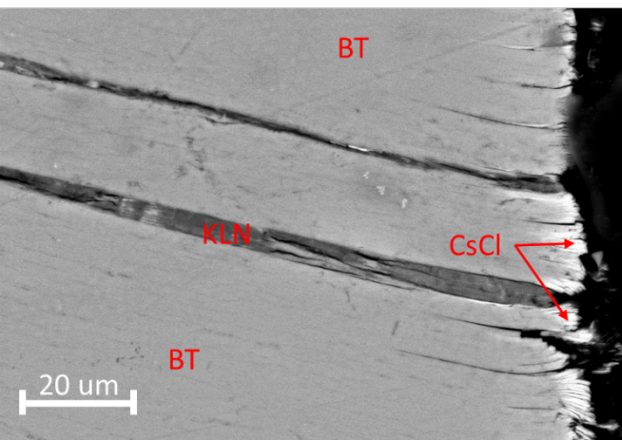
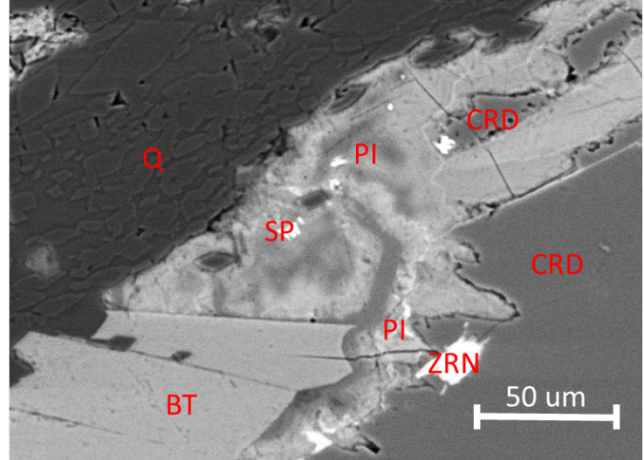
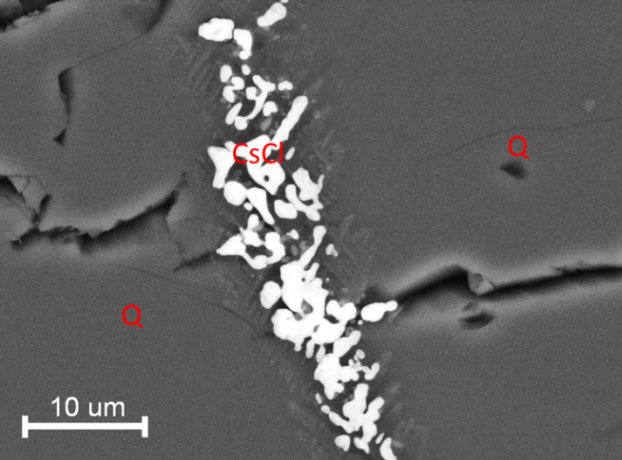
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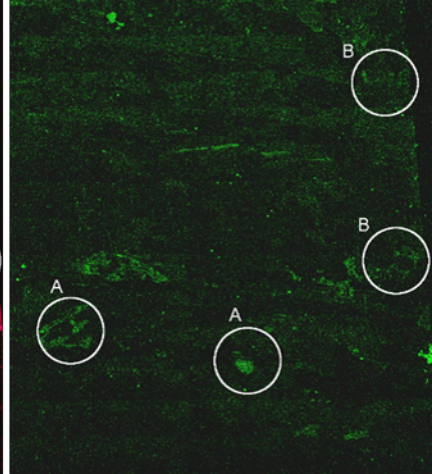
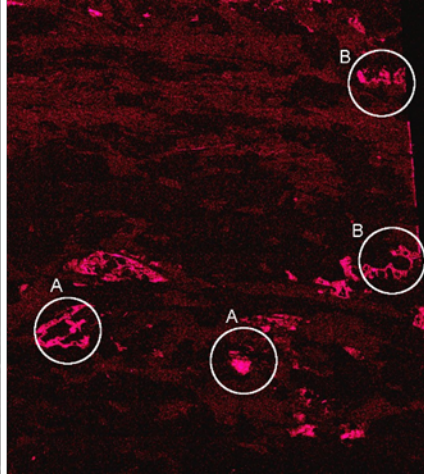
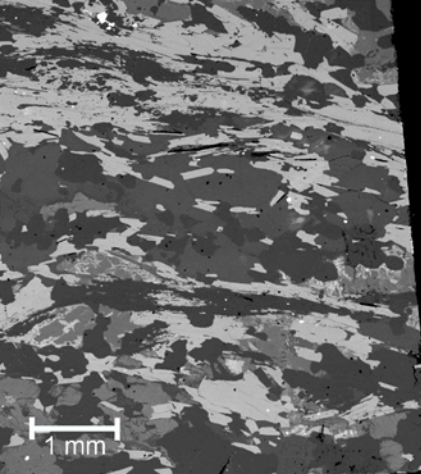
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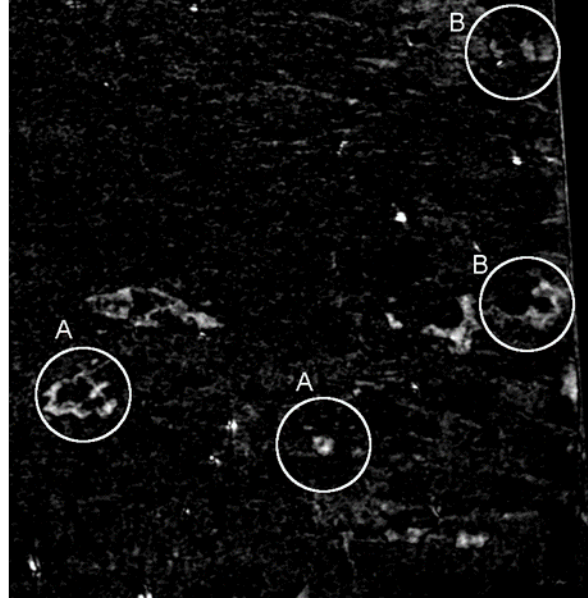
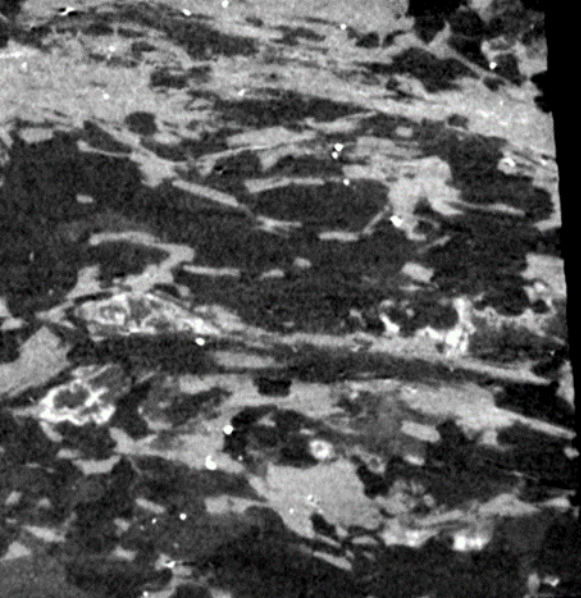


Table 1. Caesium and chloride abundances in atomic% and their ratios sorted by the minerals where they were found in notable amounts. The values given are averages with the ranges given in brackets. In few areas of pinite that had the highest caesium abundances, the chloride abundance could not be determined.

Mineral	Cs atomic %	Cl atomic %	Cs-Cl-ratio
Pinite	1.9 (1.3-2.8)	0.6 (0.4-1.1)	3.5 (2.0-6.3)
	5.4 (2.1-8.0)	No Cl detected	-
Kaolinite	0.9 (0.4-1.2)	0.9 (0.4-1.2)	1.0 (0.9-1.1)
Sphalerite	1.2	No Cl detected	-