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# Corrosion at the carbon steel- clay compact interface at 90°C: insight into short- and long-term corrosion aspects

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## Abstract

Rods of low alloy carbon steel were corroded under anoxic conditions in compact clay at 90°C. Gravimetrically-assessed corrosion damage equalled 8.5 μm at 7 months, then slowly increased to 29.5 μm at 76 months. The corrosion damage was heterogeneous at 7 months, and two distinct aspects coexisted: steel was replaced by (Fe,Si,O) corrosion products in some areas, and by Si-poor hydroxide and covered by akaganeite (FeO(OH,Cl)) in others, indicating corrosion in suboxic conditions. A magnetite fringe contacted the steel surface. For greater reaction times, akaganeite disappeared, and only (Fe,Si,O) corrosion products containing Fe sulfide and chukanovite were detected.

## Keywords

Carbon steel (A) ; Clay (A) ; SEM (B) ; XRD (B) ; Raman spectroscopy (B)

## 26 **1 Introduction**

27 Due to its low cost, durability, and advantageous mechanical properties, low-alloy carbon steel (C-  
28 steel) has been widely used in the oil, gas, geothermal and drinking water industries. Based on the extensive  
29 knowledge gained from these applications, it has also been investigated as a material for the production of  
30 long-term barriers surrounding High-Level nuclear Waste (HLW) in deep geologic repositories. For  
31 example, the French design relies on confining HLW glass and its stainless steel containers within C-steel  
32 overpacks inserted in C-steel cased tunnels drilled within the host rock [1, 2]. The potential host rock,  
33 Callovo-Oxfordian (COx) claystone, has been selected because of its good confinement properties and low  
34 permeability. The overpacks should protect the stainless steel containers, and *de facto* the nuclear glass,  
35 during the thermal phase ( $T \geq 50^\circ\text{C}$ ). The casing (also made of C-steel) should guarantee the reversibility  
36 of the waste disposal over the operation period of the repository (more than one century). In early designs,  
37 contact between clay and casing C-steel was expected, resulting in corrosion in a compact C-steel-clay  
38 interface and ultimately degradation of the casing mechanical properties. After sealing of the repository,  
39 corrosion is first expected to occur in the presence of oxygen. Next, rapid consumption of  $\text{O}_2$  by corrosion  
40 and biogenic processes will lead to anoxic conditions [3], and radioactive decay will increase the  
41 temperature up to  $90^\circ\text{C}$  at the overpack outer surface. Under this combination of contact geometry and  
42 physico-chemical conditions, general corrosion was expected to predominate for C-steel [4, 5]. However,  
43 recent work has demonstrated that pitting corrosion also could occur, though with limited effect as pits  
44 would remain metastable and tend to close up [5]. Hence, a better understanding of C-steel corrosion in  
45 contact with clay was deemed necessary to predict the long-term behaviour of C-steel envelopes in the  
46 repository.

47 Insight into the interaction of C-steel with complex environmental materials can be obtained from a  
48 variety of integrated experiments and *in situ* observations. For example, the study of steel archaeological  
49 artefacts embedded in water-saturated anoxic soils provided a unique insight into corrosion processes  
50 operating at ambient temperature [6-12]. Microstructural characterisation of the corrosion interfaces  
51 revealed their structural layering and the prevalence of Fe oxide and (hydroxy)carbonate. Yet,  
52 investigation of these corrosion systems operating at (near)-ambient temperature provides only limited  
53 insight into the effect of temperature on e.g. corrosion rate (CR), precipitation rates of solids, and the nature

54 of corrosion products (CP) under repository representative conditions. Integrated experiments with pure  
55 ferrite in contact with clay at temperatures about 90 °C were designed to address these issues [13-21].  
56 These investigations were performed for up to two years and revealed the formation of distinct corrosion  
57 layers essentially made of magnetite ( $\text{Fe}_3\text{O}_4$ ) close to the metal, Fe silicate, and siderite ( $\text{FeCO}_3$ ) [18, 19,  
58 22]. However, results obtained on pure ferrite cannot be readily applied to cementite-containing C-steel.  
59 Actually, for pure ferrite, both cathodic and anodic reactions occur at the same interfacial location (though  
60 not necessarily at the same time), resulting in the formation of a protective barrier layer made of Fe oxide  
61 [23-26]. In contrast, for C-steel, the presence of cementite, which exhibits a lower overpotential, will  
62 favour localized galvanic coupling, leading somehow to substantially greater corrosion kinetics [27, 28].  
63 In fact, these differences are readily observed in several experiments comparing the behaviour of pure iron  
64 and C-steel under similar solution conditions [29]. Thus, a thorough investigation of CR and CP at the C-  
65 steel-clay interface, possibly over periods of several years, is warranted.

66 The present study investigates the damage rates and interface evolution resulting from over six years of  
67 C-steel corrosion in clay rock at 90°C under anoxic, water-saturated conditions. These experiments  
68 extend and complete previous observations made on shorter time scales [30]. Corrosion damage was  
69 quantified by gravimetric analysis, or by direct estimates on sample sections; both methods suggested a  
70 short-to-long term transition in CR. The nature and distribution of CP were identified, their evolution  
71 with time confirming a change in corrosion control from suboxic to anoxic carbonated clay conditions.

## 72 **2 Materials and methods**

### 73 **2.1 Starting materials**

74 All steel samples were made of A37 C-steel, with a composition (wt %) of 0.12C–0.62Mn–0.22Si–  
75 0.12P–0.12S–0.008Al–0.03Cr–0.04Cu–0.02Ni – balance Fe. The C-steel, taken from a cold-rolled bar, is  
76 essentially ferritic, with about 8% of pearlite textured in bands aligned along the rolling direction. Clay  
77 was cored from the CO<sub>x</sub> formation in the Meuse-Haute Marne Underground Laboratory (Bure, France).  
78 It essentially contains calcite ( $\text{CaCO}_3$ ; 30 wt.%), quartz ( $\text{SiO}_2$ ; 30 wt.%), interstratified illite-smectite (~35  
79 wt. %), and minor amounts of pyrite ( $\text{FeS}_2$ ), siderite, and feldspars ( $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-(Na,K)AlSi}_3\text{O}_8$ ) [31, 32].

80 Synthetic clay porewater was prepared fresh by dissolving salts in high-purity water. The porewater  
81 composition (Table 1) is representative of the CO<sub>x</sub> formation [33, 34]

## 82 **2.2 Experimental setup**

83 Three steel sample geometries were implemented (Figure 1a). Type 1 was a massive C-steel rod  
84 (diameter 10 mm, length 30 mm) and was devoted to the study of the massive C- steel-clay interfaces.  
85 Type 2 was made using two short rods of 14 and 15 mm length, respectively, separated by a PTFE disk (9  
86 mm diameter, 1 mm thickness), to investigate corrosion in a pseudo-crack. Type 3 was made using an A37  
87 tube sealed with two disks (total length 30 mm, outer diameter 16 mm), pierced with six holes and  
88 containing a small A37 rod (diameter 8 mm, length 20 mm) insulated from the external tube by  
89 polytetrafluoroethylene (PTFE) rings to avoid galvanic coupling. These specimens, thereafter referred to  
90 as ‘microcontainers’, were designed to investigate entry of clay porewater into the space between the  
91 liner/casing and the overpack. Samples were inserted in clay cylinders with clay lids, both machined from  
92 CO<sub>x</sub> clay and with the cylindrical axis oriented perpendicular to the clay sedimentary plane (Figure 1b,c).  
93 These setups were then inserted into high-pressure cells with welded lids, and saturated with synthetic clay  
94 porewater. The high-pressure cells were immersed in an oil bath heated at 90 °C, with the axes of the clay  
95 cylinders (and of the specimens) oriented horizontally (Figure 1d). The synthetic clay porewater was  
96 pushed from a reservoir through the clay cylinders by applying an upstream overpressure ranging from 12  
97 to 27 bars (He). This overpressure generated a slow but steady renewal of the porewater around the  
98 specimens. The pressure cells were fed in parallel from the reservoir to guarantee identical input  
99 conditions. Vessels with a low internal pressure (initially ~1 bar) were placed downstream to collect the  
100 flux water and possible reaction gases (e.g. hydrogen). At given times, one cell from each of the three  
101 types of samples was removed and dismantled. Upon dismantling the first samples, a weak odour of rotten  
102 eggs was noted, suggesting the presence of a limited amount of hydrogen sulfide. One sample of each type  
103 was transferred into a glove box for structural characterisation, and the others were used for gravimetric  
104 measurement of the corrosion damage, after treatment in an acid bath (to remove oxides and residual clay  
105 parts) containing corrosion inhibitors (to minimize metal dissolution). The overall uncertainty for the

106 damage values averages  $\pm 0.6 \mu\text{m}$ . In this contribution, only the massive rods were investigated (Table 2).  
107 Results for the specimens with pseudo-cracks and the microcontainers will be given in a sequel.

### 108 **2.3 Sample preparation for microcharacterisation**

109 For microstructural characterisation, C-steel samples and adhering clay were embedded with epoxy  
110 resin. The massive rods (Type 1) were cut perpendicular to the rod axis, fitted into 25 mm moulds, and  
111 then impregnated with epoxy resin (Epofix, Struers). Impregnated sections were polished using silicon  
112 carbide (SiC) papers, and diamond pastes in ethanol, down to a final roughness of  $1 \mu\text{m}$ . Preparation was  
113 performed in a glove box under a  $\text{N}_2$  atmosphere to minimize sample oxidation.

114 For micro X-Ray Diffraction ( $\mu\text{XRD}$ ), the polished surfaces were thinned to  $100 \mu\text{m}$  and mounted on  
115 a sample holder under anoxic conditions, as described elsewhere [35, 36].

### 116 **2.4 Microcharacterisation techniques**

117 For optical imaging and micro Raman spectroscopy ( $\mu\text{RS}$ ), sample sections were kept in airtight boxes  
118 with a 1 mm thick glass window. An Olympus BX51M microscope equipped with a CCD camera (Sony  
119 Exwave HAD) was used to image the corrosion interface, and the images were stitched using the analySIS  
120 software. Micro Raman spectra were recorded on microspectrometers (Renishaw Invia for the first  
121 samples, and later LabRam HR800) with  $50\times$  long-range objectives, laser beams with wavelengths of 532  
122 or 785 nm and power outputs of  $\sim 500 \mu\text{W}$ . Spectra were accumulated to obtain a correct signal-to-noise  
123 ratio.

124 For scanning electron microscopy (SEM), samples were coated with a thin carbon layer, and then  
125 transferred quickly into the microscope. The microscope (JEOL JSM7000-F with a field emission gun)  
126 was operated at 10 kV and 1.6-2 nA. Images were obtained in Backscattered Electron (BSE) mode, and  
127 Energy-Dispersive X-ray (EDX) spectra were recorded on Points of Interest (PI) using a silicon-drift  
128 detector (Bruker XFlash 5010) and processed with the Esprit system (Bruker). A top hat background  
129 removal and a  $\phi\rho z$  algorithm were sequentially used to correct the EDX spectra for absorption and  
130 secondary fluorescence. Quantifications are given in atomic percent (at.%), and are rounded to two  
131 significant digits in the text. Maps of raw counts for selected chemical elements were recorded by sample

132 continuous scanning and adding the EDX signal on each pixel. The dwell time per pixel per frame was  
133 ~256  $\mu\text{s}$ , and total counting times were 2 to 16 h. One map was collected at a higher probe current (10 nA)  
134 and subject to extensive quantitative analysis, as detailed in a companion paper (Prêt *et al.*, in preparation).

135 The  $\mu\text{XRD}$  data were recorded in transmission mode, with the polished surface oriented vertically and  
136 perpendicularly to the incident X-ray beam. X-rays from a rotating anode source (Mo  $\text{K}\alpha$  radiation) were  
137 focused to  $30\times 50\ \mu\text{m}^2$  (vertical $\times$ horizontal). Diffraction patterns were collected with a 2D Image plate  
138 detector (GE Healthcare) and integrated with the FIT2D software [37].

139 Micro X-Ray Fluorescence ( $\mu\text{XRF}$ ) and micro X-ray Absorption Fine Structure ( $\mu\text{XAFS}$ ) spectra were  
140 recorded on the LUCIA beamline [38] of the SOLEIL synchrotron (Saint Aubin, France). The synchrotron  
141 ring was operated at 2.75 GeV and 400 mA. X-rays were obtained from an undulator source, and X-ray  
142 energies at the Si and S K-edges were selected using an InSb(111) double crystal monochromator. The  
143 beam was focused down to  $3\times 4\ \mu\text{m}^2$  and  $10\times 10\ \mu\text{m}^2$  (vertical $\times$ horizontal) at the S and Si K-edges,  
144 respectively, by a Kirkpatrick-Baez setup. The samples were glued on a copper sample holder in the glove  
145 box, kept in an anoxic container, and rapidly transferred ( $< 5\ \text{min}$ ) from the container to the beamline  
146 experimental chamber. The chamber atmosphere was then pumped to  $< 1\ \text{mbar}$ , and the sample cooled to  
147 150 K by a cooling thread bound to the cold head of a He cryostat. The normal to the sample plane was  
148 tilted horizontally by  $10^\circ$  off the X-ray beam, and X-ray fluorescence was recorded using a single-element  
149 silicon drift detector at  $90^\circ$  with respect to the incident X-ray beam. Elemental maps were collected by  
150 sample scanning with a dwell time of 1 s per pixel.  $\mu\text{XAFS}$  spectra were collected on PI and corrected for  
151 self-absorption [39, 40]. Minerals references were pressed into pellets for  $\mu\text{XAFS}$  measurements. Data  
152 reduction and analysis was performed using standard procedures and the Athena-Iffefit software [41-44].

## 153 **3 Results**

### 154 **3.1 Gravimetric analysis**

155 Gravimetric assessments for simultaneously sampled specimens showed some scatter (Figure 2), part  
156 of which can be attributed to the intrinsic heterogeneity in C-steel microstructure and clay. Sample damage  
157 after 7 months of reaction is significant, averaging  $8.5 \pm 3\ \mu\text{m}$ . With increasing reaction time, the damage

158 increased at a slower rate, and after 76 months, it amounts to  $29.5 \pm 3 \mu\text{m}$ . It thus appears that damage of  
159 the massive rods in contact with clay was quite limited, even after 76 months.

160 Evaluation of the corrosion kinetics (or damage evolution with exposure time) throughout the 76  
161 months was assessed by fitting logarithmic, power or linear laws according to different prevailing  
162 mechanisms. The logarithmic law did not fit the data well, and was discarded. In contrast, the power law  
163 (PL) provides a reasonably good fit for damage values below 40 months, even if some discrepancy appears  
164 for longer exposure times (Figure 2). The best fit was obtained using the equation:

$$Damage_{PL}(t) = 10.6 \times t^{0.49} \quad (1)$$

165 where  $Damage_{PL}(t)$  (in  $\mu\text{m}$ ) is the modeled damaged thickness (in  $\mu\text{m}$ ) using the PL and  $t$  is the time (in  
166 years). The exponent value of 0.49 suggests that the damage evolution with time is parabolic. The liner  
167 law (LL) fits very well all data points, but fails to meet the origin coordinates. The best-fit is given by

$$Damage_{LL}(t) = 6.7 + 3.54 \times t \quad (2)$$

168 The LL also provides greater values for long-term damage. It may thus be used for conservative  
169 extrapolations beyond the experiment duration, assuming the corrosion mechanism does not change.

### 170 **3.2 Interfacial characterisation**

171 Heterogeneous generalized corrosion was observed for all cross-sections, with hardly corroded areas  
172 coexisting with local depressions (Figure 3). For the 7-months specimens, the depressions had depths of  
173 usually  $\sim 10 \mu\text{m}$ , with a few values down to  $\sim 30 \mu\text{m}$  (Figure 3a-c). The maximum depth of these  
174 depressions increased to  $90 \mu\text{m}$  after 76 months of reaction time. These depressions were filled with CP,  
175 sometimes mixed with cementite *lamellae*, confirming the CP replaced C-steel by inward growth (Figure  
176 3d). Hence they correspond to a Dense Products Layer (DPL). For corrosion times over 40 months, the  
177 DPL seemed to differentiate into two distinct sublayers of slightly contrasted electron density (Figure 3e,f).  
178 The DPL was overlaid with an irregular and relatively thin layer (about  $5 \mu\text{m}$  thick; Figure 3c,d,f), hereafter  
179 referred to as Median Corrosion Layer (MCL). This MCL also contained cementite *lamellae*; the top of  
180 the MCL coincided with the end of cementite *lamellae*, highlighting the Trace of the Original Steel Surface



181 (TOSS). Finally, particles with greater electron density (visible as brighter areas on BSE images) could be  
182 observed locally inside the clay rock close to the TOSS, forming a Transformed Matrix Layer (TML).

183 From the CP analysis, two distinct types of corrosion interfaces could be discriminated for the 7-months  
184 specimen. Most of the 7-months DPL was essentially made of a (Fe, Si) (hydr)oxide (Figure 4a) containing  
185 substantial amounts of Na (Table 3, PI 2-3). In some areas, this layer seemed to directly contact the C-steel,  
186 but in other areas it was separated from metal by a fringe of iron oxide (Table 3, PI 1, Figure 4b). The  
187 MCL composition is notably distinct from the DPL. In most areas, the MCL has a fair amount of Fe and  
188 Ca and is enriched in O with respect to the DPL (Table 3, PI 4-5), suggesting the formation of a Ca-rich  
189 siderite (ankerite;  $(\text{Fe,Ca})\text{CO}_3$ ). This composition could vary locally, as shown by the observation of some  
190 O-depleted, S-enriched areas. Although not quantified in these early characterisations, coupled (Cu,S)  
191 contributions could also be observed by EDX analysis, suggesting the formation of Cu sulfide. Finally, the  
192 clay rock close to the TOSS was somewhat mixed with (Fe, Ca)-containing material, suggesting the  
193 precipitation of ankerite (Table 3, PI 6).

194 In some limited areas of the interface for the 7-months specimen, a notably distinct interfacial  
195 arrangement could be observed (Figure 5a). The Si content of the DPL was notably low (1.3-1.4 at.%),  
196 and this depletion is balanced by Fe enrichment (Table 4, PI 1-2). The  $\mu\text{RS}$  signal of the DPL corresponds  
197 to poorly ordered  $\text{Fe}^{\text{III}}$  (hydr)oxide (Figure 5b). The MCL was still present with an ankerite-type  
198 composition (Table 4, PI 3). In contrast, most of the clay was replaced by a massive Fe (hydr)oxide  
199 significantly enriched in Cl (up to 0.9 at.%, Table 4, PI 4-5), and identified by  $\mu\text{RS}$  as akaganeite  
200 ( $\text{FeO}(\text{OH,Cl})$ ) (Figure 5c). The presence of  $\text{Fe}^{\text{III}}$  (hydr)oxides indicates that some initial stages of C-steel  
201 corrosion occurred under (sub)oxic conditions, probably due to residual oxygen in the setup. Even at trace  
202 levels, oxygen can induce the formation of pit-like corrosion areas, thus explaining the heterogeneity in  
203 surface damage [45, 46].

204 Compared to these 7-months sample, the corrosion interfaces from 15 to 76 months of reaction showed  
205 remarkable consistency in terms of the nature and distribution of CP (Figure 6). Firstly, akaganeite or any  
206 other Cl-containing solid were no longer observed. Next, most of the DPL appeared enriched in O (56-70  
207 at.%) and Si (from 5 to 21 at.%) (Table 5, PI 1, 2, 5-7, 9, and 10). A magnetite fringe between the C-steel

208 and CP was observed only on a thin fraction of the interface (for example less than 0.2 % of the entire C18  
209 interfacial cross-section). In addition, the DPL layer contains around 1-2 at.% of S, with end values around  
210 0.7 and 2.5 at.%. Some Al enrichment was detected in the C09 DPL, reaching about 1 at.% (Table 5, PI 1-  
211 2), and Na was significantly present in the C12 DPL (1.2 to 1.6 at.%; Table 5, PI 5-7). The wide  
212 fluctuations in Fe/Si ratios (from 1 to 4) may be attributed to the coexistence of several Fe silicates in  
213 varying amounts, possibly also intermixed with Fe (hydroxy)carbonate (Prêt *et al.*, in preparation).  
214 Additional proof for the coexistence of two Fe-rich solid phases was provided by  $\mu$ RS data displaying a  
215 peak near  $1070\text{ cm}^{-1}$ , which diagnostic of chukanovite ( $\text{Fe}_2(\text{OH})_2\text{CO}_3$ ), and bands near 258-260, 285, 314,  
216 and  $358\text{ cm}^{-1}$  assigned to Fe sulfide (Figure 7). Interestingly, Fe silicate, although being the major  
217 component of the layer, had no conspicuous  $\mu$ RS contribution.

218 In an attempt to characterize the nature of the Fe silicate phase,  $\mu$ XAFS spectroscopy was performed  
219 on the CP within a corrosion depression of the C15 sample (Figure 8). As a preliminary step, the location  
220 of the corrosion layers was determined using  $\mu$ XRF spectroscopy (Figure 8a,b). Several  $\mu$ XAFS spectra  
221 were collected in the DPL layer (PI X1-X4) or in the nearby clay (PI X5, X6). All spectra display the main  
222 absorption “white line” (peak A) at 1847 eV typical of Si in a silicate group [47] (Figure 8c). Additional  
223 examination showed that all spectra except X5 were dissimilar to the amorphous silica or quartz references,  
224 but were rather similar to the clay references (Figure 8c). Specifically, sample spectra displayed a weak  
225 shoulder (labelled B) near 1851 eV and broad absorption bands near 1856.9-1857.2 (peak C) and 1862.8-  
226 1863.1 eV (peak D). The peak positions and amplitudes were similar to those observed for nontronite  
227 (nominally  $\text{Na}_{0.3}\text{Fe}_2(\text{Al}_{0.3}\text{Si}_{3.7})\text{O}_{10}(\text{OH})_2$ ) (features B, C, D at 1850.2, 1856.8 and 1863.2 eV, respectively)  
228 or montmorillonite (nominally  $\text{Na}_{0.3}\text{Al}_{1.7}\text{Mg}_{0.3}(\text{Si}_4)\text{O}_{10}(\text{OH})_2$ ) (1850.8, 1857.2 and 18652.9 eV,  
229 respectively) suggesting a phyllosilicate tetrahedral-octahedral-tetrahedral (TOT)-like structure. Feature B  
230 in the sample is also close to the positions observed for greenalite (nominally  $\text{Fe}_3(\text{Si}_2)\text{O}_5(\text{OH})_4$ ) (1850.9  
231 eV) or chamosite (nominally  $(\text{Fe},\text{Mg},\text{Al})_6(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_8$ ) (1850.8 eV), but peak C for these references  
232 (1856.2 and 1856.4 eV, respectively) are shifted to lower values compared to the samples. Finally, the  
233 montmorillonite spectrum displays an additional shoulder near 1866.5 eV (D') which is absent in sample

234 spectra. Overall, this comparison suggests that Si environment in the DPL compares with Si in nontronite,  
235 yet additional contributions from minor environments are not excluded.

236 In addition to Si, the chemical nature of S, a DPL trace compound, was investigated by S K-edge  
237  $\mu$ XAFS spectroscopy. Areas of significant S content and PI candidates were first located by  $\mu$ XRF  
238 mapping (Figure 9a-c). Spectra collected at these PI all display a first peak at 2470 eV, followed by a broad  
239 band near 2476 eV (Figure 9d). The first peak is intermediate in position between the peaks for S at an  
240 oxidation state of  $-II$ , as in chalcopyrite, and  $-I$ , as in pyrite ( $FeS_2$ ) [48]. This suggests that the oxidation  
241 state of S for this contribution is intermediate between  $-II$  and  $-I$ . The broad band is similar in position to  
242 the band observed for chalcopyrite, suggesting that the S chemical environment would be somewhat  
243 similar to that observed in a sulfide compound. This clearly points to  $S^{(-II)}$ , perhaps partially oxidized. This  
244 inference was confirmed by comparison with the spectrum of S in pyrrhotite ( $Fe_7S_8$ ) [49], meaning that S  
245 is present as an Fe sulfide. This result corroborates  $\mu$ RS observations of oxidized mackinawite in the DPL  
246 (Figure 7). A second, narrow peak could sometimes be observed near 2482 eV, but the intensity of this  
247 band quickly decreased upon X-ray irradiation. This narrow band was attributed to  $S^{(VI)}$  in sulphate groups  
248 (Figure 9) [48], and its decrease in amplitude indicated that photoreduction issues were not completely  
249 resolved by the cryogenic setup. Interestingly, though, quantitative analysis performed in the companion  
250 paper hinted at the possible presence of a sulphate solid (i.e. gypsum,  $CaSO_4$ ) in the DPL for the 76-months  
251 sample (Prêt *et al.*, in preparation).

252 The MCL between the DPL and clay is somewhat discontinuous, yet it can be found indifferently over  
253 areas of extended or limited corrosion. It contains Fe ( $\sim 12$  at.%), Ca, ( $\sim 6$  at.%) and Mg (up to 2.5 at.%).  
254 The O content is about 78 at.%, resulting in  $O/(Mg + Fe + Ca)$  ratio around 3-4, which is typical of  
255 (hydrated) carbonate minerals (Table 5, PI 8). This composition corresponds to ankerite, the presence of  
256 which was confirmed by  $\mu$ RS data showing the typical bands at 185, 286, and 1090  $cm^{-1}$  (Figure 10).  
257 Ankerite formation in clay near the TOSS was often observed in setups operated under comparable  
258 conditions [18, 19, 21, 22]. Laterally, ankerite can be replaced by Fe sulfide or Cu sulfide (Cu maps of C6  
259 and C15, Figure 6). The Cu/S ratio for these solids is close to 2, suggesting the formation of  $Cu_2S$  (Table  
260 5, PI 3).

261 Finally, the clay in contact with the corrosion surface contains significant amounts of Si, Al, K, and Ca,  
262 as expected. Close to the interface, the clay matrix also contains Fe-rich minerals with a chemical  
263 composition corresponding to ankerite (Table 5, PI 4). In a few instances, grains of chalcopyrite were  
264 observed and identified by  $\mu$ RS.

265 In conclusion, corrosion at the C-steel-clay interfaces shows some consistent trends over the reaction  
266 time from 7 to 76 months, with the formation of a Si-rich DPL, of a MCL essentially made of ankerite and  
267 Fe or Cu sulfide, and of a TML containing ankerite and, locally, chalcopyrite. A unique feature of the  
268 samples with the shortest reaction time (7 months) is the presence of Cl-containing Fe<sup>(III)</sup> oxyhydroxyde  
269 (akaganeite), indicating initial suboxic corrosion. With increasing corrosion time, akaganeite disappears,  
270 the Na content in the DPL generally decreases, and the corrosion interface becomes remarkably steady in  
271 terms of structure and composition. Note that corrosion may occur next to pearlite particles, leaving  
272 cementite *lamellae* mixed with CP (e.g. Figure 6, BSE image of C12). Overall, however, the location of  
273 the areas with the greatest damage seems to be independent of the proximity of cementite *lamellae*, and is  
274 probably rather driven by the presence of C-steel defects or clay heterogeneities nucleating corrosion  
275 depressions.

### 276 **3.3 Estimation of corrosion damage at the C-steel-clay interface from** 277 **sample sections**

278 Estimation of the corroded thickness of metal can be made by measuring the distance between the  
279 TOSS and the current C-steel-CP interface. Since the rod cross-section is circular, the TOSS was estimated  
280 by a circle touching the metal surface in areas of almost nonexistent corrosion. Damaged thicknesses were  
281 measured on the SEM images along *radii* oriented every 1° from the circle center (up 360 measures). The  
282 estimated thicknesses (Table 6) are generally consistent with values obtained from gravimetric analysis.  
283 The calculated large standard deviations do not result from uncertainty in thickness measurements (very  
284 liberally estimated to be  $\pm 5 \mu\text{m}$ ), but rather reflect the heterogeneity of the corrosion around the sample,  
285 as usually observed in contact with clay or soil [50].

## 286 **4 Discussion**

### 287 **4.1 Mechanisms of corrosion at the C-steel-clay interface**

288 The systematic investigation of the C-steel-clay interface corroded at 90°C for increasing times  
289 provides a unique insight into the evolution of the interfacial morphology and mineralogy. For the whole  
290 series of samples, corrosion is isovolumic and heterogeneous, with shallow depressions and large, hardly  
291 damaged areas. Over time, the relative proportion of significantly damaged areas increases, a clear  
292 indication of generalized corrosion. For a reaction time of seven months, corrosion results in the formation  
293 of Fe (hydr)oxide (magnetite detected by  $\mu$ XRD), of a (Fe,Si) (hydr)oxide phase containing significant  
294 amounts of Na, and of a median fringe (the MCL) of ankerite and (Cu,Fe) sulfide. The TML is present  
295 over the entire surface, and contains either ankerite dispersed in the clay matrix, or Cl-containing  
296 akaganeite indicating (sub)oxic conditions during the initial period of time. Akaganeite preferential  
297 formation over Cl-free phases may result from the moderate concentration of Cl<sup>-</sup> (about 0.035 mol/kg) in  
298 the synthetic porewater (Table 1). This initial stage coincides with a significant increase in steel damage  
299 ( $8.5 \pm 3 \mu\text{m}$ ).

300 The three structural units (DPL, MCL, and TML) persist throughout the corrosion period, yet after 15  
301 months, the extent and nature of DPL and TML are modified. For the DPL, magnetite is detected only at  
302 a few areas at the C-steel interface, in relative amounts decreasing with reaction time. Nanoscale  
303 characterisations have shown that a nanometric layer of a few tens of nm present at the interface can still  
304 be present and act as a barrier layer controlling the corrosion of C-steel [24-26]. Chukanovite, a Fe  
305 hydroxycarbonate, is present as well, but only after 15 months of reaction. This late formation compares  
306 with chukanovite absence for reaction times  $\leq 8$  months for ferrite corroding under free (non-polarized)  
307 conditions [18, 19]. In contrast, chukanovite was detected after extensive corrosion, either for  
308 archeological samples [10], for corrosion enhanced by anodic polarization [19], or for two years of free  
309 corrosion [22]. This observation hints at the possible role of chukanovite as a medium term, possibly long-  
310 term corrosion phase in nuclear waste repository. However, it also appears that chukanovite did not form  
311 a distinct structural unit, but rather was dispersed in the Fe silicate phase. At the temperature of the

312 experiment, it is unlikely that chukanovite formation could be explained by kinetics constraints alone.  
313 Clearly, this phase is (meta)stable over long periods.

314 The TML evolution is marked by the disappearance of akaganeite and other Cl-rich phases after 7  
315 months of reaction. Akaganeite clearly is a transient phase, and its destabilization probably corresponds to  
316 slightly varying chemical conditions from the initial (sub)oxic phase (from 0 to 7 months), to reductive,  
317 fully saturated conditions (>7 months). The initial suboxic conditions can explain the heterogeneity in  
318 C-steel damage, as heterogeneities in oxygen concentrations could lead to galvanic decoupling [45, 46].

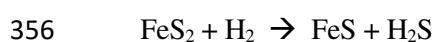
319 At this point, it seems that the transformation of the clay matrix in contact with C-steel is essentially  
320 limited to precipitation of ankerite in clay porosity. Little to no formation of Fe-rich clay minerals has been  
321 observed, contrary to mixed iron-clay slurries reacted under anoxic conditions [51-59]. The near-absence  
322 of clay transformation was also observed in previous experiments using massive iron samples in bentonite  
323 at 80 °C [60]. In fact, the formation of Fe silicate in clay-iron powder mixtures may relate to the high  
324 surface area of powdered iron, with corrosion resulting in an important supply in dissolved Fe and OH.  
325 The increase in pH then promotes the dissolution of silicate species and stabilizes carbonate solids, thereby  
326 increasing the silicate/carbonate ratio in solution and favoring precipitation of Fe silicate. In the compact  
327 massive system investigated here, precipitation of Fe silicate occurs too, but in the DPL. This leads to a  
328 decrease in the pH gradient within the DPL, so that precipitation of Fe silicate in the TML is unfavourable,  
329 at least over the timescale of the experiment.

330 Taken together, these results suggest that the corrosion mechanism operating at the microscopic scale  
331 is gradually modified from 0 to 15 months, and then does not change significantly from 15 to 76 months.  
332 This general observation is consistent with interpolations of gravimetric results. Indeed, gravimetric  
333 measures fit well with an almost parabolic law for the first 15 months, consistent with a diffusion-  
334 controlled corrosion regime. The diffusion-controlling medium must still be identified, and could be clay  
335 or the DPL. However, this stage of CR controlled by diffusion appears to be short term. Data for the long  
336 term exposure fit better with a linear law, which is consistent with a CR driven by a steady-state reaction.  
337 This suggests that diffusion within clay and / or DPL has reached a steady state, which seems at odd with  
338 the increasing thickness of DPL due to ongoing corrosion. A somewhat distinct behaviour was observed

339 for pure ferrite (Armco iron) in compact clay, i.e. a continuous decrease in CR (down to < 1 µm/year after  
340 2 years; [22]). This discrepancy may be related to the significant impact of the metal microstructure and  
341 composition [29]. Unlike Armco iron, A-57 steel contains pearlite grains made by stacking of cementite  
342 and ferrite *lamellae*. Oxidation of the ferrite leaves cementite *lamellae*, which can act as cathodic sites,  
343 thus enhancing the cathodic reaction compared to pure ferrite [27, 28, 61]. Because these *lamellae* remain  
344 at the same positions in the DPL, the diffusion distance toward cementite does not change, explaining  
345 steady-state. Note however that there is no mineralogical evidence for the location of cathodic reaction on  
346 cementite. Another surface reaction possibly controlling the CR is the formation of a thin protective layer  
347 at the steel-CP interface [23]. This layer would form by solid-state oxidation of steel, and dissolve to form  
348 other CP at the DPL contact. Indeed magnetite is still found at the interface with steel even after 76 months  
349 exposure, possibly revealing the presence of a thinner (a few nm thick) barrier layer.

#### 350 **4.2 On the presence of sulfur compounds**

351 Sulfur-containing solids were detected essentially as sulphate and Fe sulfide in the DPL, as (Fe,Cu)  
352 sulfide in the MCL, or as chalcopyrite in clay. The supply of sulphate can easily be traced to porewater.  
353 Sulfide may form by reduction of porewater sulphate, possibly by CP [62], which would result in the  
354 accumulation of this element in the DPL. Sulfide can also be supplied by pyrite reduction by H<sub>2</sub> released  
355 by corrosion [63], according to



357 This reaction would result in the formation of FeS and the release of sulfide. To assess the possibility of  
358 this reduction reaction, pyrite grains near the corrosion interface were examined for alteration and  
359 dissolution features. Most grains appeared to be intact, but severely altered pyrite was observed at least in  
360 one location within 100 µm of the TOSS (Figure 11). Interestingly, though, pyrite appeared to be dissolved,  
361 not replaced by Fe sulfide, suggesting a full dissolution, i.e.



363 Finally, sulfide can also be supplied by sulphate reduction via the activity of sulphate-reducing  
364 prokaryotes (SRP). Indeed, the smell of hydrogen sulfide for the first series of samples suggested some

365 limited bioactivity, possibly occurring in the initial space between C-steel surfaces and holes walls. With  
366 reaction time, clay swelling, and PC precipitation, however, this space collapse precluded any further  
367 significant bioactivity. In fact, the location of the sulfide phase in the DPL compares with recent results on  
368 the sulfidation of corrosion layers in the presence of bacteria [64]. The preferential location of Fe sulfide  
369 phases in the DPL may be related to a greatest Fe<sup>(III)</sup> concentration in this unit coupled with a greater pH.  
370 Another possibility is that sulfide preferentially precipitates within the DPL due to the interaction with  
371 Fe<sup>(III)</sup>-containing phases. Indeed, sulfide immobilization can occur via reaction with Fe<sup>(III)</sup>-containing  
372 (hydr)oxides, a reaction which takes places within weeks [65-68]. Such a reaction would be possible with  
373 any residual magnetite present in the DPL.

374 Another interesting observation is the presence of Cu sulfide phase in the MCL. Copper is a trace  
375 element in COX clay, with a content of 6 to 19 mg/kg, and has been observed in bulk clay as chalcopyrite.  
376 Whether this Cu can be readily available for diffusion toward the C-steel surface is not clear. It can be  
377 surmised however that Cu predominantly binds to organic matter [69, 70] and clay minerals [71], as in  
378 soils, and so it should be fairly labile.

379 Next, Cu sulfide is much more stable than Fe sulfide such as FeS. This is illustrated by comparing the  
380 dissolution reactions and constants [72] for FeS



381 and CuS



382 The much smaller  $K_{\text{CuS}}$  clearly demonstrates that this phase is very stable. Combining (3) and (4) shows  
383 that FeS and CuS are at equilibrium for a concentration ratio of

$$[\text{Fe}^{2+}]/[\text{Cu}^{2+}] = K_{\text{FeS}} / K_{\text{CuS}} = 10^{18} \quad (5)$$

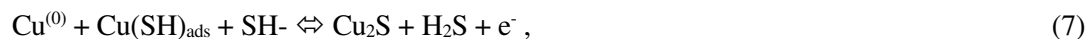
384 where  $[\text{Fe}^{2+}]$  and  $[\text{Cu}^{2+}]$  are dissolved concentrations of Fe<sup>2+</sup> and Cu<sup>2+</sup>, respectively. In other words, the  
385 formation of CuS is extremely favored with respect to FeS, even at trace amounts of Cu [73]. Yet, it is



386 surprising that Cu solid would precipitate only near the TOSS, and not in the clay. Therefore, a mechanism  
387 responsible for the preconcentration of Cu near the steel surface has to be invoked. One possible such  
388 mechanism is the reduction of Cu at cathodic sites under reducing anoxic conditions [74]. This is due to  
389 the higher electrochemical potential of the Cu<sup>(II)</sup>/Cu<sup>(0)</sup> couple ( $E^0_{\text{Cu(II)/Cu(0)}} = 0.33 \text{ V/SHE}$  at 25°C) compared  
390 to the Fe<sup>(II)</sup>/Fe<sup>(0)</sup> couple ( $-0.44 \text{ V/SHE}$  at 25°C). The location of Cu reduction is then governed both by the  
391 availability of electrons, and by transport considerations dictating that Cu primarily reduces on the first  
392 encountered cathodic sites during migration. For Cu migrating from clay, these sites are located on the  
393 external parts of the C-steel sample. After DPL formation, Cu<sup>(0)</sup> would be insulated from steel. In principle,  
394 Cu<sup>(0)</sup> is stable under anoxic conditions, but it can oxidize in presence of dissolved sulfide. The oxidation  
395 mechanism would involve a first step of SH<sup>-</sup> sorption according to [75, 76]



396 where Cu(SH)<sub>ads</sub> is the chemisorbed species. The Cu surface then further reacts with SH<sup>-</sup> leading to the  
397 formation of Cu<sub>2</sub>S according to



398 These two anodic reactions are coupled with the cathodic reaction of proton reduction from water or H<sub>2</sub>S.  
399 The expected formation of Cu<sub>2</sub>S is in agreement with the chemical composition of Cu sulfide observed in  
400 the MCL (Table 5, PI 3).

401 The Cu sulfide fringes were also located next to the TOSS for samples with longer reacting times. No  
402 Cu is detected within the DPL, either because Cu remains located on the outer fringes, or because the  
403 concentrations are too low in this inner layer. This scarcity of Cu within the layer can have several  
404 explanations. First, this absence could simply result from an exhaustion of Cu supply from clay, so that no  
405 additional precipitate forms. Second, it may result from electron transport in the DPL to the TOSS. The  
406 nature of electron-conducting solids is not clear, but recent investigations on C-steel corroded in clay water  
407 suggest that Fe silicate can display some substantial electron-conducting properties [36].

### 408 **4.3 Implications for the design of nuclear waste repository systems**

409 Our results confirm that the limited CR observed for ferrite in contact with clay for two years also  
410 applies for C-steel in such a compact setting over six years. These rates are almost one order of magnitude  
411 lower than observed for C-steel in porewater or clay slurry [24, 77]. The discrepancy between these  
412 experiments and our compact system probably results from the much smaller diffusivity in clay, restricting  
413 the transport of reactants. Thus the CR is controlled not only by surface electrochemical reactions, but also  
414 by the diffusive transport of chemical species in the matrix and eventually by formation-dissolution of  
415 metal-CP interfacial magnetite. The net effect of this transport limitation would be to maintain a dense  
416 protective layer near the C-steel interface, limiting diffusion of Fe and oxygen. The thin layer of magnetite  
417 would be this barrier layer.

418 Our discussion suggests that the mechanism controlling the rate of C-steel corrosion should operate over  
419 timescales longer than our current experiments. This permits extrapolations over long periods of time of  
420 Equation 2 (LL), which can be considered conservative. After 10 and 100 years the uniform damage values  
421 of 42  $\mu\text{m}$  and 320  $\mu\text{m}$  (LL) are found, respectively. Calculated damage over 1000 years equal 3500  $\mu\text{m}$   
422 (LL).

## 423 **5 Concluding remarks**

424 The present study provides a unique insight into the long-term evolution of CR and the nature of CP in  
425 a compact C-steel-clay system. One salient point is the short-term coexistence of hardly corroded areas  
426 with areas of significant damage. This variability can be understood in the light of heterogeneities in clay,  
427 C-steel composition and defect distribution, and differential exposure to oxygen, leading to galvanic  
428 coupling between distinct areas. A second point of interest is the change in interfacial CP during the initial  
429 period of 13 months, meaning that corrosion processes observed prior to this time may not be relevant for  
430 long-term behavior. The implication is that investigations on the C-steel surfaces (including  
431 electrochemical ones) have to be performed on over rather long timescales to yield meaningful insight into  
432 long-term corrosion processes. Third, the CR remains constant, or even steadily decreases with increasing  
433 reaction time, and yet the proportion of C-steel surface showing significant damage increases with time.  
434 This suggests that the DPL can be somewhat protective with respect to corrosion, possibly by limiting

435 diffusion of dissolved species to and away from the C-steel surface and from cathodic sites. Interestingly,  
436 the CR remained near-constant although the distance between the metal-CP and the TOSS increases with  
437 time, suggesting that corrosion is not controlled by transport of reactants and products in the bulk DPL.  
438 This conclusion is in line with the presence of a nanoscale barrier of Fe oxide controlling the diffusion of  
439 atoms between C-steel and CP [23]. There is no evidence suggesting the possible onset of any new  
440 mechanism for longer reaction times.

441 Overall, extrapolation from damage values points to a steady to slightly decreasing rate of CR after one  
442 year. A change in corrosion regime is suggested to explain both modifications of interfaces in CP, and  
443 damage evolution within the first two years exposure, moving to a magnetite dissolution-driven regime.  
444 The rates are notably greater than those observed for pure ferrite, in agreement with some previous studies  
445 of C-steel corrosion [29]. Yet, assuming the corrosion mechanism observed after six years persists over  
446 long-term periods, a cumulated average damage of about four mm over 1000 years is calculated. This  
447 reasonable value guarantees HLW confinement over an extended time span well after the thermal peak. In  
448 principle, allowance should be made for the heterogeneous depths of corrosion depressions, for which a  
449 full mechanistic modelling is yet desirable. However, our observations suggest that generalized corrosion  
450 over the entire C-steel interface should prevail over long timescales.

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## 457 **Data availability**

458 The raw/processed data required to reproduce these findings cannot be shared at this time due to legal  
459 reasons.

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## 670 **7 Figure captions**

671 Figure 1. (a) Schematic illustration of the three types of sample geometry used in the Corrida setup.  
672 (b) Schematic illustration and (c) image of the geometry containment for three massive probes in  
673 a clay cylinder (upper argillite lid removed in the image). (d) Schematic illustration of the Corrida  
674 setup.

675 Figure 2. Sample damage as a function of reaction time for the massive rods (■). Also illustrated are  
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677 Figure 3. Scanning electron image in Backscattered Electron (BSE) mode of the steel-clay corrosion  
678 interface as a function of reaction time. DPL: dense product layer. MCL: median corrosion layer;  
679 TML: transformed matrix layer. (a-c) C06, 7 months of reaction. (d) C12, 27 months of reaction. (e)  
680 C15, 40 months of reaction. (f) C18, 76 months of reaction.

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686 Points of Interest analyzed by EDX spectrometry are indicated on the BSE images.

687 Figure 7. Optical image and  $\mu$ RS data for the steel-clay corrosion interface (27 months of reaction).

688 Figure 8. (a) BSE image of the DPL layer at the carbon-steel corrosion interface of the C15 sample (40  
689 months of reaction), with location of the area probed by  $\mu$ XRF (square). (b)  $\mu$ XRF image of Si  
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691 lowest – red: highest). Also indicated are the PI probed by  $\mu$ XAFS spectroscopy. (c) Si K-edge spectra  
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693 Figure 9. (a) BSE image of the DPL layer at the steel-clay corrosion interface (C15 sample, 40 months  
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696  $\mu$ XAFS spectroscopy. The local S concentration is in “temperature” scale (violet: lowest – red:  
697 highest). (d) Sulfur K-edge spectra of PI in the DPL layer.

698 Figure 10. (a) SEM-BSE image of the carbon-steel Median Corrosion Layer (MCL) (C12 sample, 27  
699 months of reaction), with location of the PI probed by  $\mu$ RS. (b,c) micro-Raman spectra at the PI of  
700 the MCL.

701 Figure 11. BSE image of a pyrite grain near the steel-clay interface, with clear evidence of alteration  
702 features.

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705 **8 Tables**

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Table 1. Composition of the synthetic porewater used in this study.

Species	Concentration (mmol/kg)
Na <sup>+</sup>	7.3
K <sup>+</sup>	2.5
Mg <sup>2+</sup>	6.5
Ca <sup>2+</sup>	8.6
Si(OH) <sub>4</sub>	0.1
HCO <sub>3</sub> <sup>-</sup>	1.6
Cl <sup>-</sup>	35
SO <sub>4</sub> <sup>2-</sup>	1.7

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Table 2. Samples investigated in this study.

Name	Reaction time
<b>C06</b>	7 month
<b>C09</b>	13 months
<b>C12</b>	27 months
<b>C15</b>	40 months
<b>C18</b>	76 months

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Table 3. Quantification of SEM-EDX analyses of CP present at the “Cl-poor” steel-clay interface of the C06 sample (7 months). The corresponding points of Interest (PI) are illustrated in Figure 4.

PI	Composition (at.%)									
	O	Na	Mg	Al	Si	S	Cl	K	Ca	Fe
1	73.5	0.8	0.1	0.1	0.9	0.6	0	0	1.3	22.6
2	76.4	1.6	0.1	0.1	8.1	0.6	0	0.1	0.5	12.6
3	77	1.4	0	0.1	7.3	0.5	0	0.1	0.5	13.1
4	78.8	0.8	0.1	0.1	3.3	0.7	0	0	3.5	12.7
5	77.2	0.8	0.1	0.2	1.2	0.6	0	0.1	2.4	17.5
6	77.3	0.2	0.5	1.6	3.2	0.2	0.1	0.4	6.2	9.7

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Table 4. Quantification of SEM-EDX analyses of CP present at the “Cl-rich” steel-clay interface of the C06 sample (7 months). The corresponding PI are illustrated in Figure 5.

PI	Composition (at.%)									
	O	Na	Mg	Al	Si	S	Cl	K	Ca	Fe
1	75.2	1.6	0	0.1	1.4	0.3	0	0	0.9	20.5
2	73.6	1.1	0	0.1	1.3	0.3	0	0.1	0.8	22.7
3	76.2	0.6	0.4	0.6	2.7	0.2	0	0.1	5.2	14
4	78.4	0.2	0	0.1	0.2	0.5	0.7	0	0.3	19.5
5	76.2	0.2	0	0.2	0.5	0.4	0.9	0.1	0.2	21.4

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Table 5. Quantification of SEM-EDX analyses of CP present at the steel-clay interface of the samples reacted from 15 to 76 months. The corresponding PI are illustrated in Figure 6.

Sample Name	PI	Composition (at.%)										
		O	Na	Mg	Al	Si	S	Cl	K	Ca	Fe	Cu
C09	1	69.9	0.1	0.1	0.9	4.9	0.7	0	0	0.3	22.7	n.m. <sup>a</sup>
	2	64.1	0.6	0.3	1.1	9.1	2.5	0.1	0.2	0.2	20.9	0
	3	3.8	0.	0.1	3.3	0.7	28.2	0.1	0	0.2	14.6	49.0
	4	75.1	0.3	0.6	2.0	2.0	0.2	0.2	0.2	4.6	14.9	0.2
C12	5	68.7	1.2	0.5	0.1	7.2	0.8	0	0	0.2	21.2	n.m.
	6	63.1	1.5	0.8	0.1	10.7	1.7	0.1	0.1	0.5	21.4	n.m.
	7	60.1	1.6	1.0	0	18.1	1.3	0	0.1	0.2	17.6	n.m.
	8	78.4	0.6	2.5	0	0.2	0.2	0	0	5.8	12.0	n.m.
C18	9	67.6	0.6	0.3	0.4	13.4	1.1	0.1	0	0.2	15.8	0.4
	10	56.2	0.6	0.9	1.1	20.9	1.6	0.6	0	1.2	16.4	0.4
	11	72.3	0.1	1.6	0	0.1	0.1	0	0	5.2	20.6	0.1

720 <sup>a</sup>: n.m.: not measured

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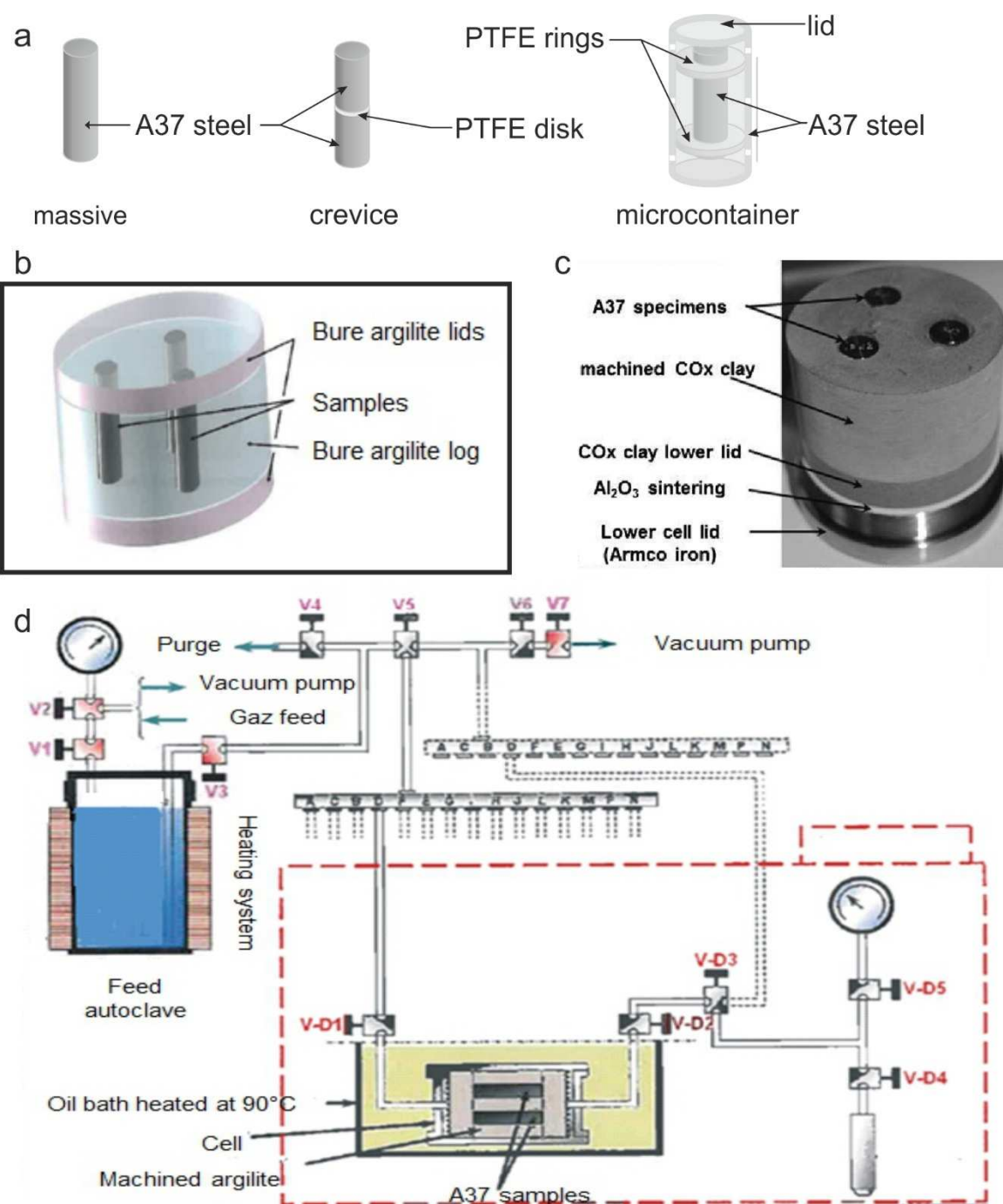
Table 6. Comparison of the average corrosion damage at the steel-clay interface from systematic measurements of damage thickness and from gravimetric measurements.

Reaction time (months)	Direct measurements			Gravimetric measurements	
	Number of measurments	Damage thickness (μm)	Dispersion (μm)	Damage thickness (μm)	Standard deviation (μm)
7	325	12	9	8.5	0.8
13	360	19	12	12.7	2.6
27	360	25	18	13.5	2.4
40	360	16	13	18.2	3.7
76	360	43	21	29.5	1.0

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## Figures



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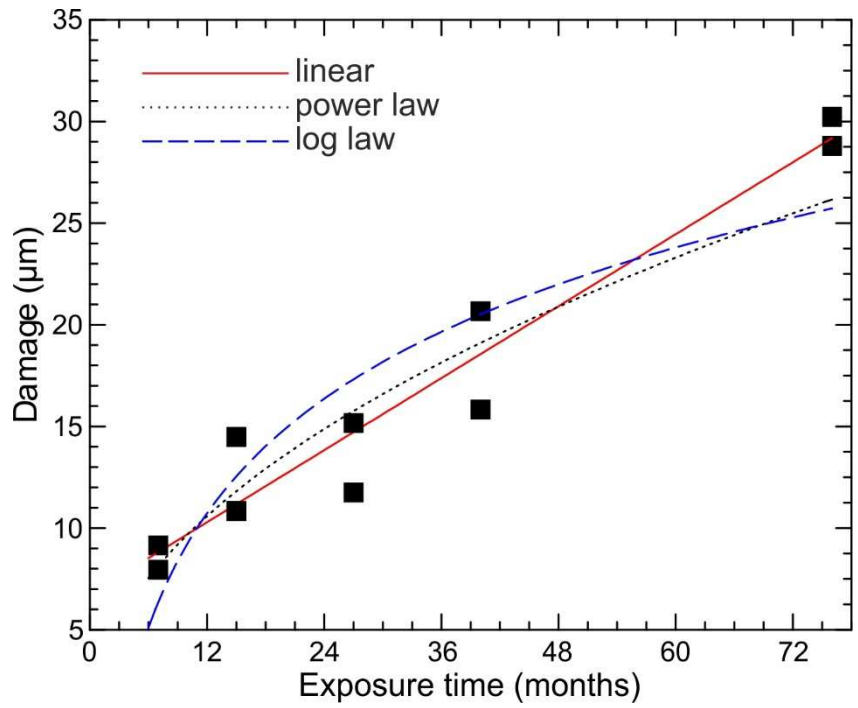
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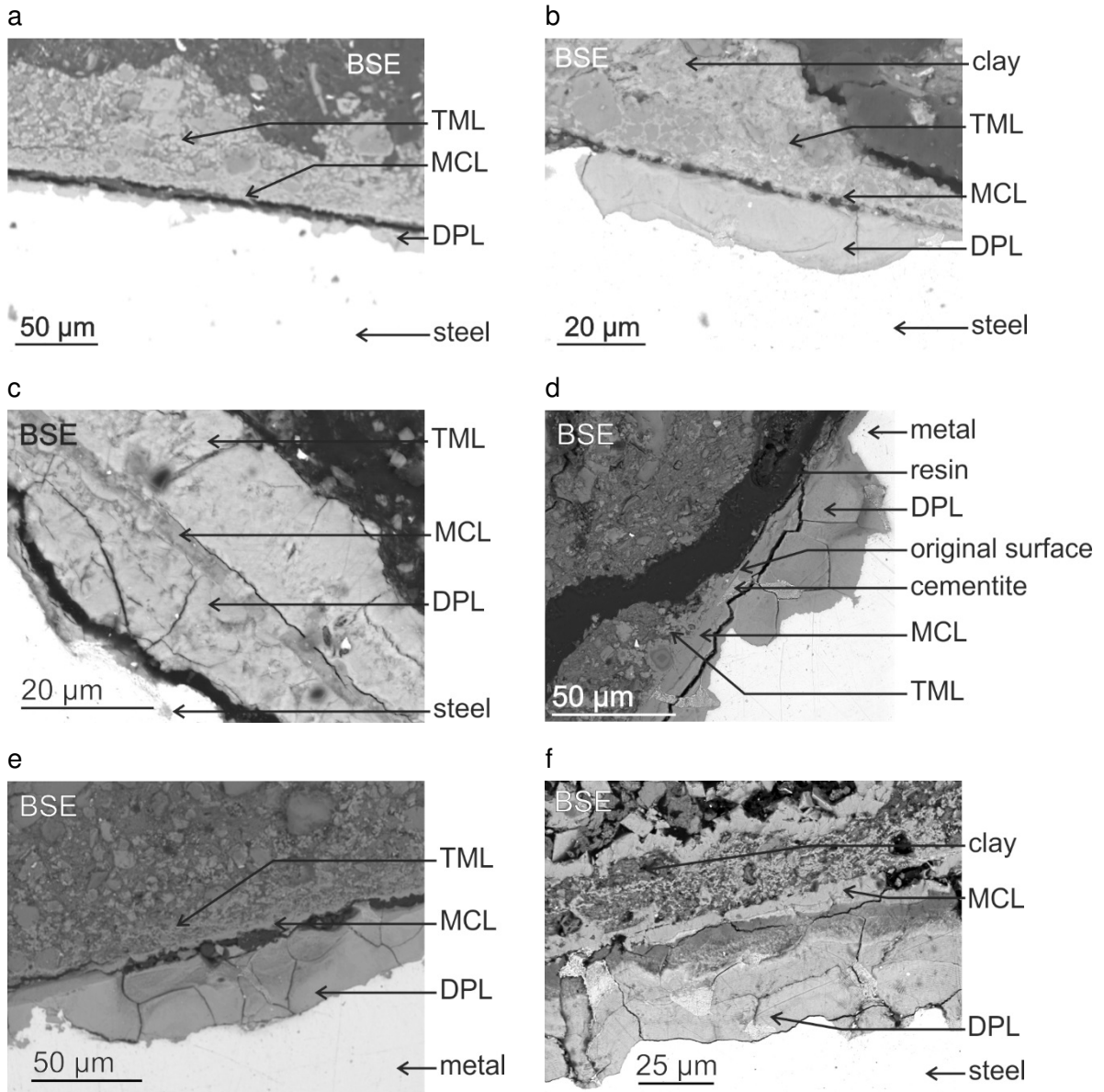
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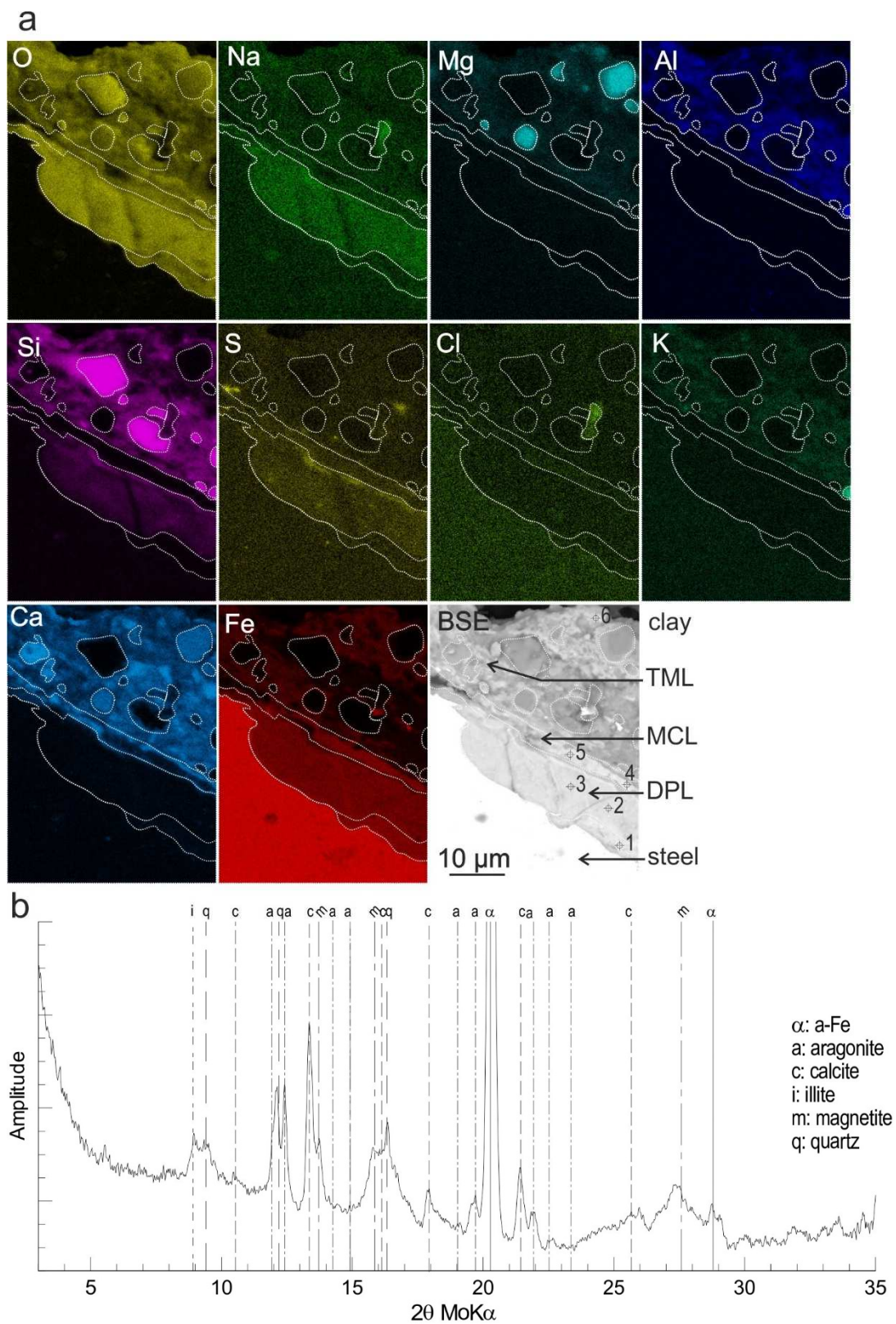
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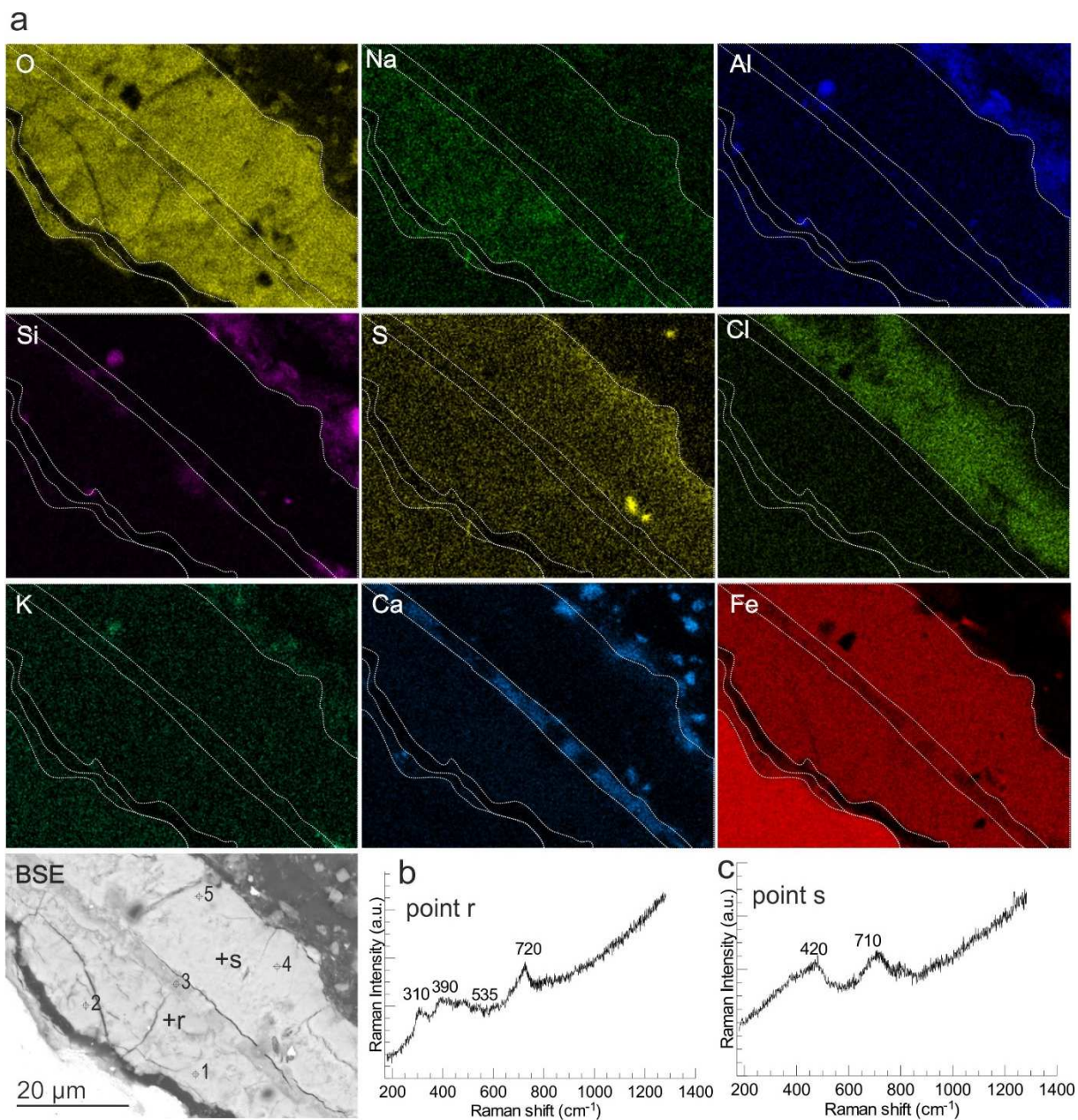


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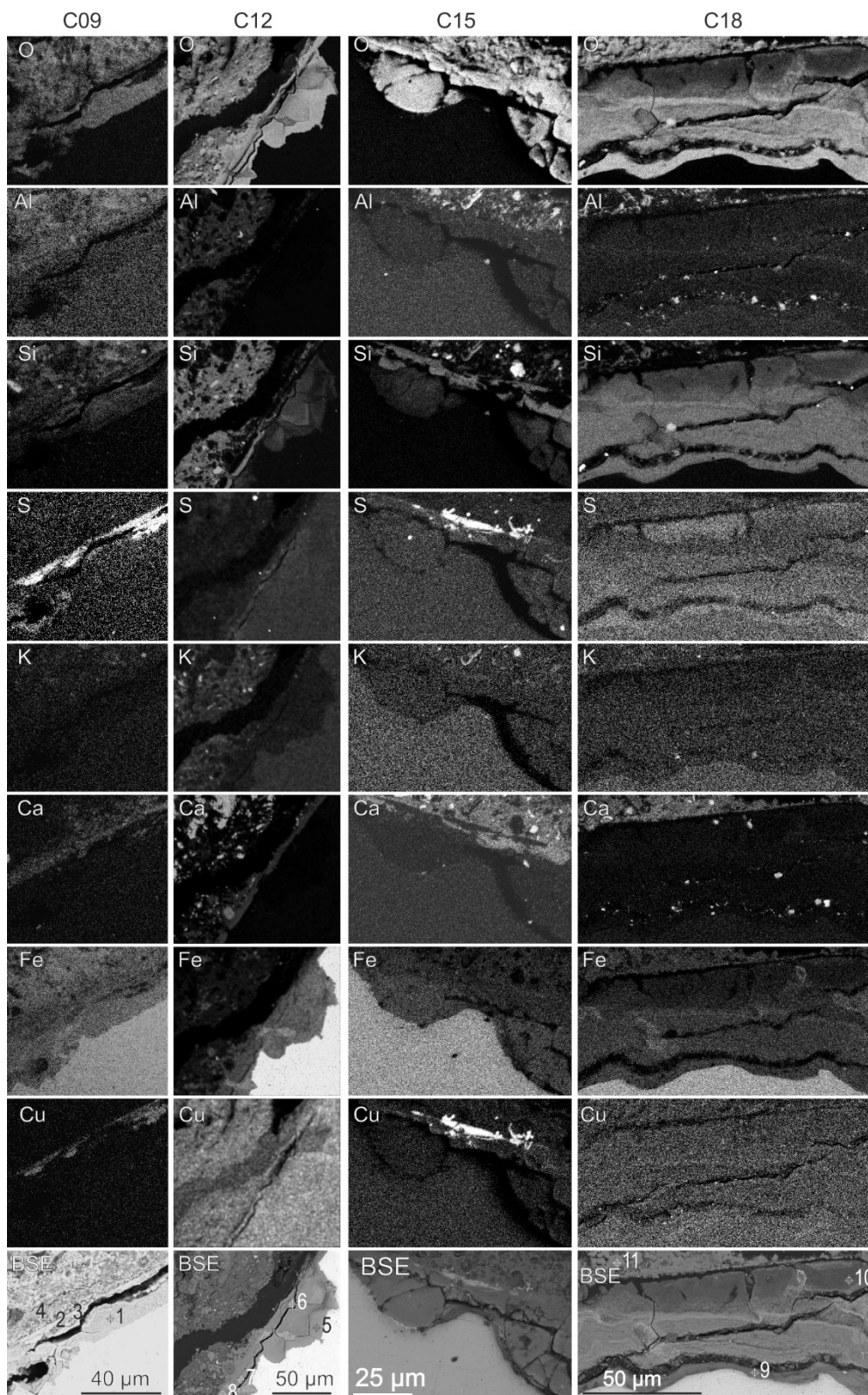


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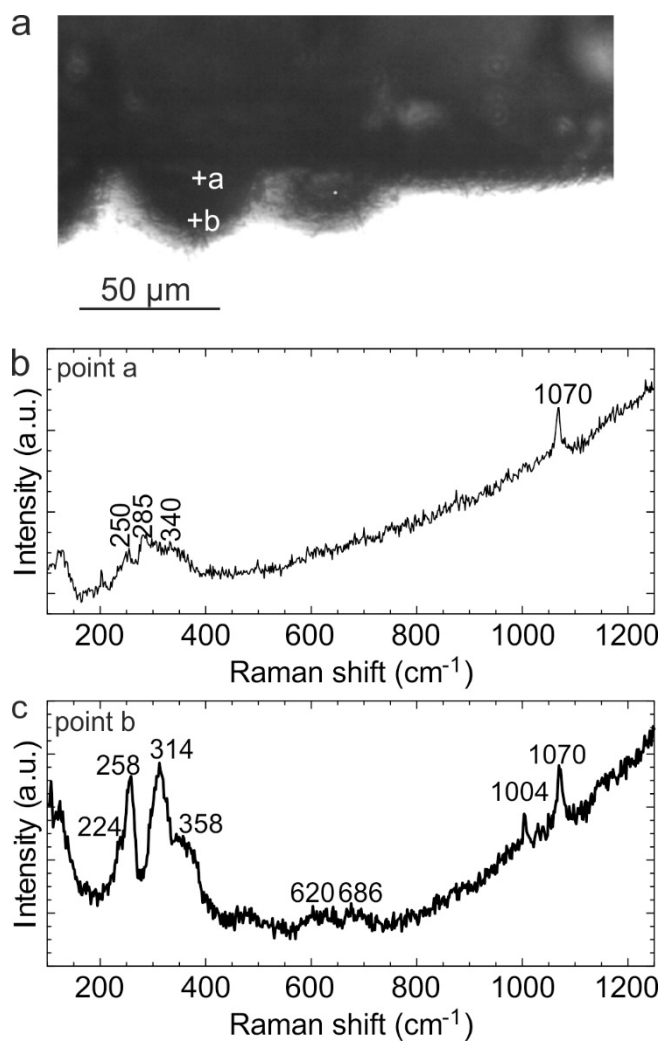
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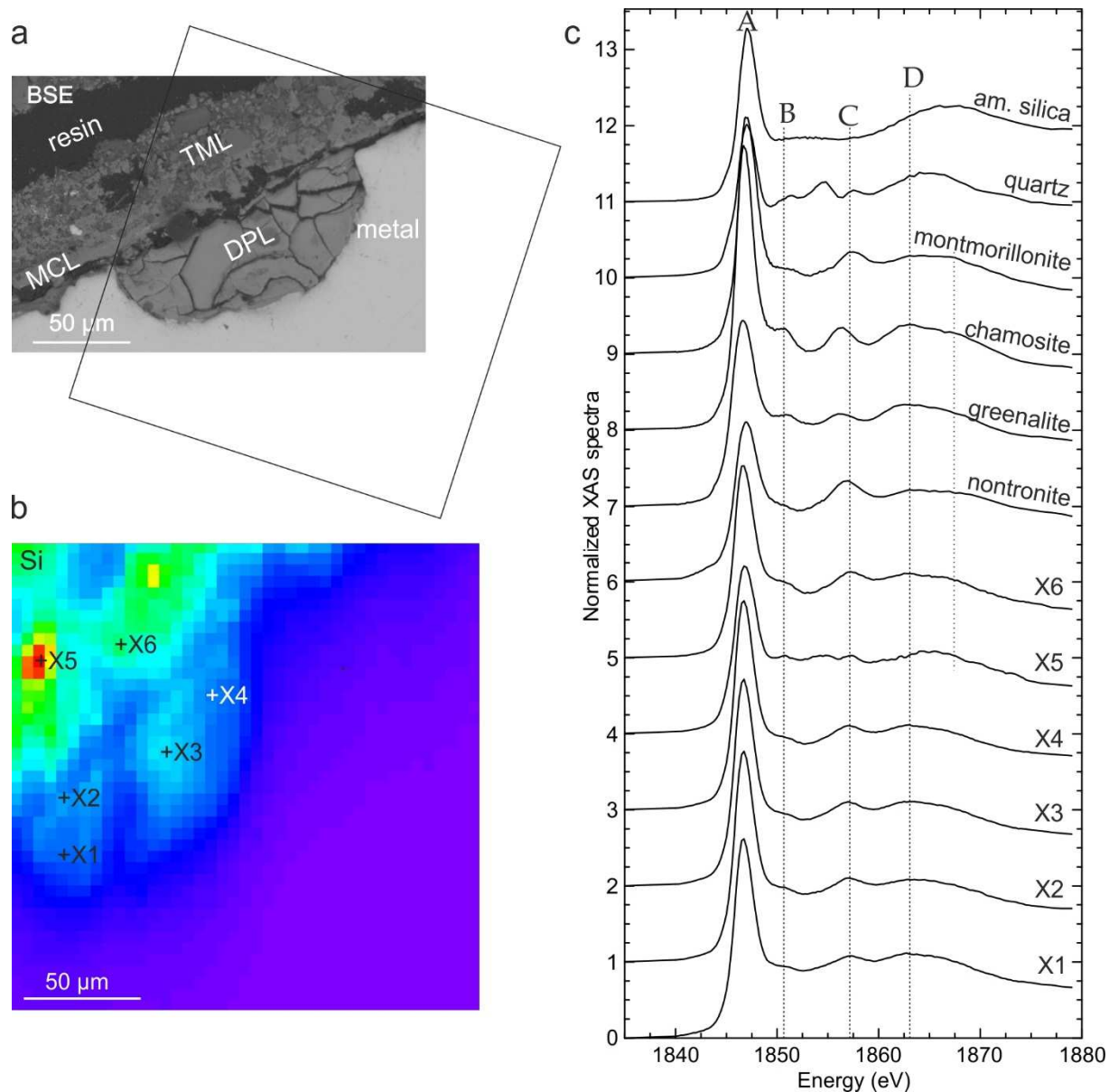
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761 Figure 7. Optical image and  $\mu$ RS data for the steel-clay corrosion interface (27 months of reaction).

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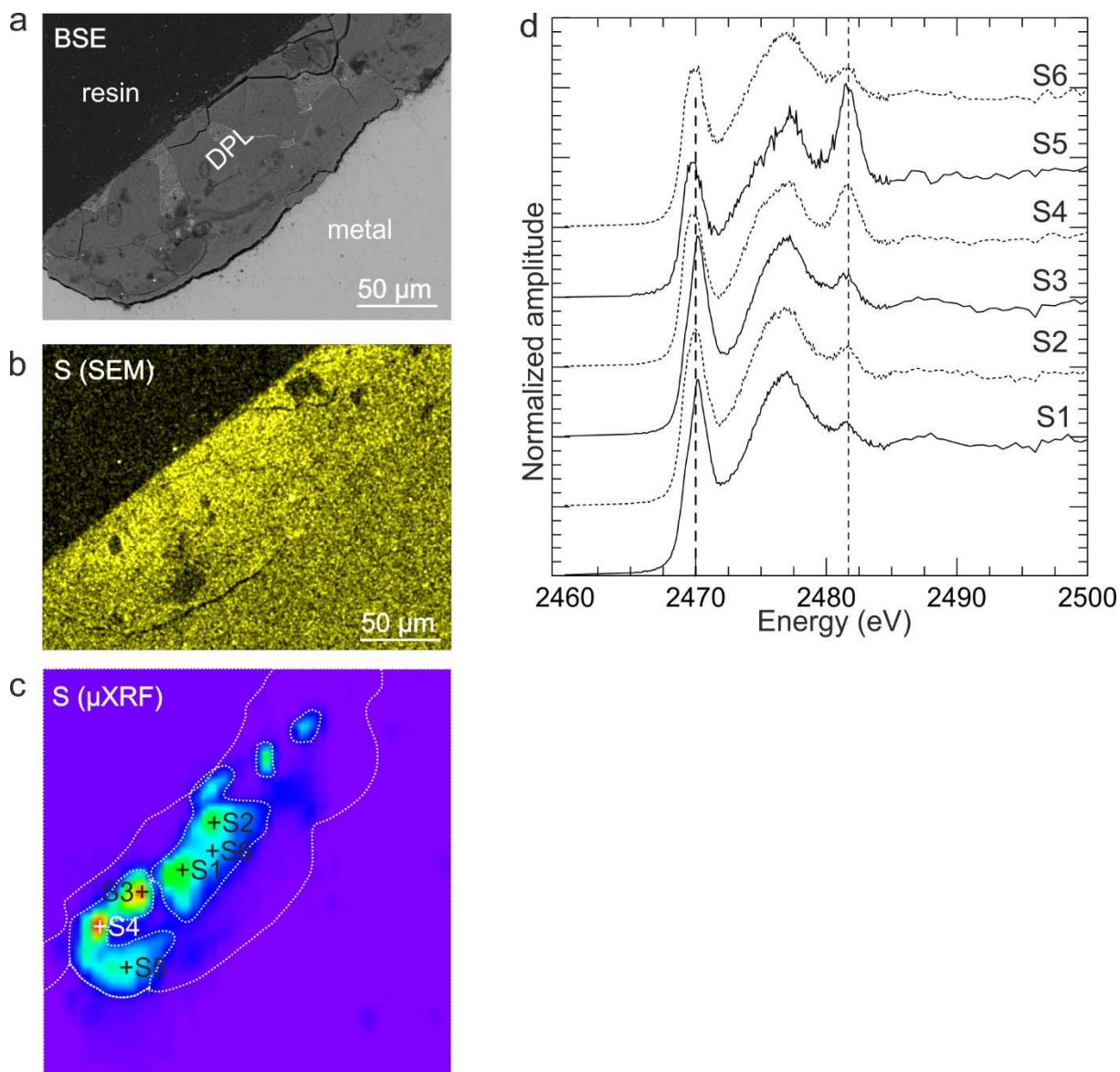
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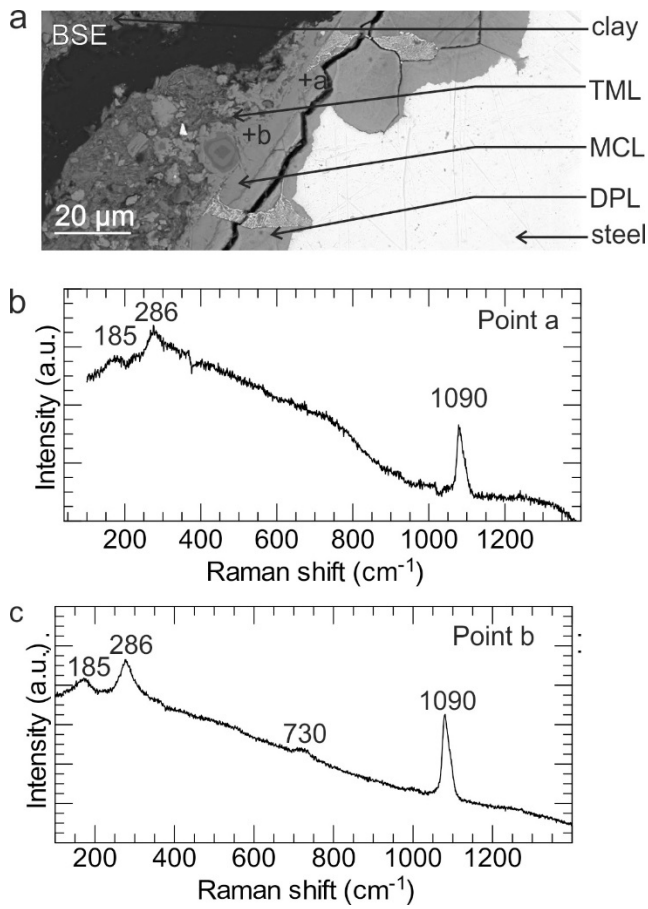
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 777  $\mu$ XAFS spectroscopy. The local S concentration is in “temperature” scale (violet: lowest – red:  
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785 the MCL.

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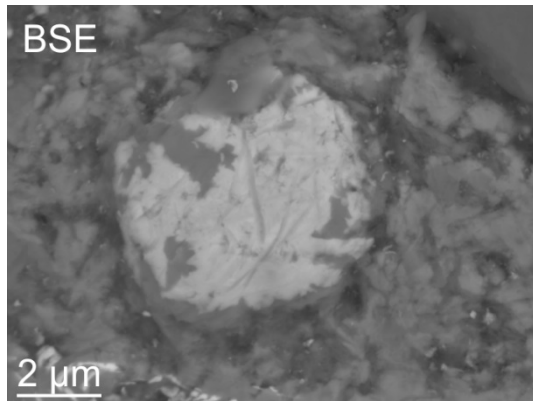
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