



**HAL**  
open science

## Evolution of iron minerals in a 100 years-old Technosol. Consequences on Zn mobility

Samuel Coussy, Sylvain Grangeon, Philippe Bataillard, Hicham Khodja,  
Nicolas Maubec, Pierre Faure, Christophe Schwartz, Robin Dagois

### ► To cite this version:

Samuel Coussy, Sylvain Grangeon, Philippe Bataillard, Hicham Khodja, Nicolas Maubec, et al.. Evolution of iron minerals in a 100 years-old Technosol. Consequences on Zn mobility: Consequences on Zn mobility. *Geoderma*, 2017, 290, pp.19-32. 10.1016/j.geoderma.2016.12.009 . cea-01424855

**HAL Id: cea-01424855**

**<https://cea.hal.science/cea-01424855>**

Submitted on 3 Jan 2017

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - ShareAlike 4.0 International License

1 **Evolution of iron minerals in a 100 years-old Technosol.**  
2 **Consequences on Zn mobility**

3 **Samuel Coussy<sup>a\*</sup>, Sylvain Grangeon<sup>a</sup>, Philippe Bataillard<sup>a</sup>, Hicham Khodja<sup>b</sup>, Nicolas Maubec<sup>a</sup>,**  
4 **Pierre Faure<sup>c,d</sup>, Christophe Schwartz<sup>e,f</sup>, Robin Dagois<sup>a,c,d,e,f,g</sup>**

5 *<sup>a</sup>BRGM, 3 Avenue C. Guillemin BP 36009, 45060 ORLEANS Cedex 2, France*

6 *<sup>b</sup>LEEL, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay 91191 Gif sur Yvette Cedex,*  
7 *France*

8 *<sup>c</sup>Laboratoire Interdisciplinaire des Environnements Continentaux, UMR 7360, CNRS, Vandœuvre-lès-*  
9 *Nancy, France*

10 *<sup>d</sup>Laboratoire Interdisciplinaire des Environnements Continentaux, UMR 7360, Université de*  
11 *Lorraine, Vandœuvre-lès-Nancy, France*

12 *<sup>e</sup>Laboratoire Sols et Environnement, UMR 1120, INRA, Vandœuvre-lès-Nancy, France*

13 *<sup>f</sup>Laboratoire Sols et Environnement, UMR 1120, Université de Lorraine, Vandœuvre-lès-Nancy,*  
14 *France*

15 *<sup>g</sup>ADEME, 20 Avenue du Grésillé, 49000 Angers*

16

17 E-mail adresses : s.coussy@brgm.fr, s.grangeon@brgm.fr, p.bataillard@brgm.fr,  
18 hicham.khodja@cea.fr, n.maubec@brgm.fr, pierre.faure@univ-lorraine.fr, christophe.schwartz@univ-  
19 lorraine.fr, robin.dagois@univ-lorraine.fr

20 \* Corresponding author: Tél: +33 (0)2.38.64.38.43 Fax: +33 (0)2.38.64.37.60

## 21 1. Introduction

22

23 The industrial revolution in Europe that mainly took place in the 19<sup>th</sup> century and the  
24 concomitant growth of urban activities led to major changes in land use. Many new  
25 factories created at that time produced high quantities of wastes (smelter slags, brick  
26 residues, coke or coal) which were extensively used as backfill materials for levelling  
27 purposes (Lehmann and Stahr, 2007; Testiati et al., 2013; Nehls et al., 2013). Since  
28 that time, these wastes – often contaminated with trace metals – became the parental  
29 material of soils which developed thanks to alteration mechanisms due to mechanical,  
30 geochemical and biological processes. The newly formed soils are generally called  
31 Technosols or Anthropic Soils (Rossiter, 2007; WRB, 2006) because they contain at  
32 least 20% of man-made materials within the first 100 cm of the profile. Although  
33 contaminated, these materials present a pedologic interest since they fulfill several  
34 functions such as biomass production, storage-filtration and transformation of  
35 nutriments, trace elements and water, or formation of ecological niches (Morel et al.,  
36 2015). Furthermore, they are now a central compartment for urban re-developers who  
37 try to build the city in the city to preserve agricultural soils (Reeve et al., 2012).  
38 Understanding their fate is then of primary importance.

39 Pedogenesis processes generally take place in a timescale of thousands of years  
40 (Minasny et al., 2008; Salvador-Blanes et al., 2007) and involve structural changes in  
41 the soil profile, including incorporation and transformation of organic matter as well  
42 as mineral dissolution and/or precipitation (Costantini et al., 2006; Duchaufour, 1976;  
43 Néel et al., 2003). Technosols are often contaminated (e.g. Tsoлова et al., 2014; Wanat  
44 et al., 2013) and, by analogy with natural and cultivated soils (Huot et al., 2013),  
45 pedogenetic evolution will certainly influence the speciation, mobility and

46 bioavailability of pollutants they contain. However, the kinetics and mechanisms of  
47 this evolution, as well as the consequences on pollutant speciation and mobility, are  
48 poorly constrained. It is currently admitted that the pedogenic processes occurring in  
49 Technosols are comparable to those occurring in natural soils, but can be accelerated  
50 due to the large thermodynamic disequilibria that can exist between the media of  
51 formation of the initial wastes and their new context of deposition (Séré et al., 2010;  
52 Leguédois et al., 2016). Coherently, several studies showed that early pedological  
53 transformations could be observed in Technosols, including oxidation,  
54 decarbonation, secondary minerals precipitation, roots colonization and even  
55 humification in the first centimeters of the solum (Bataillard et al., 2008; Norra, 2006;  
56 Séré et al., 2010), although the first industrial activities started in Europe at maximum  
57 200 years ago.

58 Investigation of the kinetics and mechanisms of Technosols formation can be  
59 performed by studying soil profiles where the deeper horizons are considered less  
60 evolved than the upper horizons submitted to climatic and biologic alteration (Brahy et  
61 al., 2000; Demattê and da Silva Terra, 2014; Egli et al., 2008). Hence, the deeper  
62 horizons in a selected Technosol profile could be considered as the parent material of  
63 the upper parts of the same profile. In this hypothesis, the characterization of the  
64 surface and deep horizons gives valuable information about the evolution of the parent  
65 material and the rates of alteration. However, because these materials have been  
66 deposited by human activities, it may be pointed out that these horizons may also  
67 differ due to their origin. This complicates the understanding of alteration impact on  
68 the chemistry of Technosols: each observation and analytical result must be  
69 interpreted with care.

70 In this study, the iron (Fe) status evolution is characterized during the early alteration  
71 processes occurring in a 100-year old Technosol, and its consequences in terms of Zn  
72 mobility are assessed. Fe, an ubiquitous element in natural and anthropic materials, is  
73 of special interest because Fe minerals (i) are reported to be reliable and well-accepted  
74 markers of soil evolution in soil sciences and (ii) control to a large extent the  
75 distribution and mobility of trace metals in soils, especially in the absence of Mn  
76 species (Bakker et al., 1996; Buol et al., 1973; Uzarowicz and Skiba, 2011). The slow  
77 transformation of primary Fe-bearing silicates in oxic and well-drained conditions lead  
78 to Fe depletion and precipitation of Fe (hydr)oxides such as goethite, lepidocrocite,  
79 ferrihydrite or magnetite (Bakker et al., 1996; Tawornpruek et al., 2006). Formation of  
80 free Fe (hydr)oxides can lead to the coating of soil particles with a thin film of these  
81 Fe (hydr)oxides (Ben-Dor et al., 2006). These mechanisms can compete with Fe  
82 complexation within the soil organic matter (Tipping et al., 2002).

83 For this study, a ~2m depth profile was sampled in a 100 years-old Technosol  
84 developed on backfills that contain significant concentrations of metals (e.g. Zn).  
85 Samples were characterized at different depths in order to quantify the changes in the  
86 chemical status of Fe, to identify the main mechanisms responsible for the mobility of  
87 trace elements such as Zn and to understand its consequences in terms of long-term  
88 potential emission by the Technosol.

89

## 90 2. Material and Methods

### 91 2.1. Field site description

92 The present study was conducted at the “Union” former industrial site (Tourcoing, France),  
93 located 50° 42’ 35” N, 3° 9’ 52” E. The site was occupied from the 19<sup>th</sup> century by several

94 types of industries, such as textile industries, breweries, smelters, chemical industries,  
95 transport companies, and a gas plant (Figure 1). A rail yard was built at the end of the 19<sup>th</sup>  
96 century at the north-west part of the site. Its reconversion for new activities is currently in  
97 progress.

98 A parcel of about 1,500 m<sup>2</sup> was chosen at the northern part of the former rail yard (Figure 1).  
99 The parcel shows a gentle slope from west to east, so that the railway (SW) is higher than the  
100 road (NE). The parcel is free of any buildings.

101 A total of 5 pits were dug in the parcel and briefly investigated. Only one pit was held up and  
102 kept for further investigation, whereas the remaining pits were filled up. Pit selection was  
103 done according to the following criteria:

- 104 - Absence of material recently backfilled at the surface (e.g. recent natural earthy material was  
105 found in some pits), and presence of aged backfills with evidences of vegetation development;
- 106 - Presence of a similar backfill material in depth which was not submitted to surface  
107 alteration.

108

## 109 2.2 Technosol profile dating

110 Investigations were carried out at the archives of the SNCF (French railways) to assess the  
111 probable date of setting of the backfills in the Technosol profile. A mail dating back October  
112 6<sup>th</sup>, 1884 has indicated the establishment of a rail yard in the sector. Other archive documents  
113 pointed out the construction of a railway in 1889, other earthworks in 1897 and the  
114 construction of a special rail in 1898. Since then, no major works were done in the sector. The  
115 study of aerial photographs taken between 1950 and 2015 proved that the frame of the rail

116 yard always remained similar to the one represented in a map dating back 1898 (see  
117 supplementary material). Those photographs indicate also that the area where the Technosol is  
118 located has never been built since then. Thus, the area of study was not reworked for a  
119 century.

120

## 121 2.3. Technosol sampling and analyses

### 122 2.3.1. Soil profile sampling

123 The whole soil profile was sampled as a function of depth. Two types of samples were  
124 collected: composite samples (~1 kg per sample) for bulk analyses and samples representative  
125 of a given depth in the profile for punctual investigations (hereafter denominated “slices”).

126 Composite samples were taken within the following range of depth: 0-10 cm (samples A), 30-  
127 40 cm (samples C), 110-130 cm (samples E) and 175-185 cm (samples F). At each depth  
128 range, three replicates were taken on a same horizon (Figure 2). The samples were kept as it is  
129 in plastic bags and stored at 4 °C before analyses.

130 Soil slices were taken at 5 cm (LM1), 90 cm (LM2) and 180 cm (LM3) deep. The soil  
131 structure was preserved (non-destructive sampling using cylinders) and 3 thin sections  
132 embedded with epoxy resin were elaborated (final thickness: 30 µm).

133

### 134 2.3.2. Bulk analyses

135 In laboratory, after measuring the water content of the composite samples, the soil pH was  
136 measured in a 1:5 (volume fraction) suspension of soil in deionized water according to NF

137 ISO 10390. The total organic carbon content (TOC) was determined by dry combustion  
138 analysis according to NF ISO 10694. Organic carbon was analyzed after removal of  
139 carbonates by acidification using hydrochloric acid. Grain size distribution and total elemental  
140 concentrations were determined according to standardized methods (AFNOR, 1996, NF X  
141 31–147). Cation exchange capacity (CEC) and exchangeable cations were measured with the  
142 cobaltihexamine chloride method (Orsini and Rémy, 1976), which can safely be used here, as  
143 samples contain little or no Fe(II)-bearing minerals (Hadi et al., 2016).

144

### 145 2.3.3 Leaching tests and selective dissolution

146 The release of trace elements was assessed by leaching of the composite samples. The 3  
147 replicate samples taken at each depth range were tested. The samples were air dried and  
148 sieved (cut-off diameter of 2 mm). Then, the leaching tests were conducted at room  
149 temperature ( $20^{\circ}\text{C}\pm 2^{\circ}\text{C}$ ), in closed PTFE reactors with continuous stirring during 24h. A  
150 liquid/solid ratio of 10 was used with deionized water, corresponding to 10 g of dry sample in  
151 100 mL water. The leachates were then filtrated (cut-off diameter of  $0.45\ \mu\text{m}$ ) and analyzed  
152 by ICP-AES (major and trace elements such as Zn).

153 The Fe status was assessed by selective dissolution, using both Dithionite-Citrate-Bicarbonate  
154 (DCB) and pyrophosphate methods, done in parallel on aliquots. The methods used are  
155 detailed in Table 1. DCB selectively solubilizes pedogenic oxides and hydroxides (Mehra and  
156 Jackson, 1960). This method can solubilize crystalline Fe (hydr)oxides (hematite, goethite),  
157 non-crystalline Fe (hydr)oxides and Fe and Al organic complexes, whereas magnetite is  
158 slightly attacked and clays are unaffected. The pyrophosphate method was used to dissolve  
159 amorphous Fe(III), Fe(II) complexes and/or very poorly crystalline compounds (Pansu and  
160 Gautheyrou, 2006). Well-crystallized Fe (hydr)oxides like goethite and hematite are not



161 attacked and slightly ordered Fe (hydr)oxides are only slightly solubilized. Claff et al. (2010)  
162 tested the effect of these sequential chemical extractions on synthetic Fe minerals  
163 representative of some of those most abundant in the environment (e.g., akaganeite,  
164 ferrihydrite, goethite, hematite, jarosite, magnetite, pyrite and schwertmannite). They  
165 demonstrated that sodium pyrophosphate does not dissolve any of the tested minerals. The  
166 DCB procedure dissolves totally or significantly akaganeite, magnetite, goethite, hematite and  
167 ferrihydrite, and to a minor extent, jarosite.

168

#### 169 2.3.4 Powder X-Ray diffraction analysis (XRD) on composite samples

170 The mineralogical assemblage of each composite sample was assessed by XRD, using a  
171 Siemens D5000 diffractometer with cobalt X-ray tube (CoK $\alpha$  radiation). The powdered  
172 composite samples were scanned with steps of 0.03°2 $\theta$  and a counting time of 10s per step, in  
173 the 4-84°2 $\theta$  angular range. Mineral identification and semi-quantitative determination of  
174 relative abundances of crystalline phases was performed using the software DIFFRAC plus  
175 EVA.

176 XRD patterns of composite samples were subjected to quantitative mineralogical analysis  
177 using the SIROQUANT<sup>TM</sup> software. The quantification is based on the principles of Rietveld  
178 refinement (Rietveld, 1969). In addition to crystalline phases, SIROQUANT<sup>TM</sup> was used to  
179 indirectly determine the amorphous phase content by spiking the samples with corundum  
180 internal standard. A precisely evaluated proportion of corundum by weight (target value of  
181 10%) was added to the samples. The amorphous content was calculated by a routine within  
182 the SIROQUANT<sup>TM</sup> program using a correction based on the weight-in proportion in the  
183 spike added prior to the XRD analysis.

184

### 185 2.3.5 Fe and Zn X ray absorption spectroscopy (XAS) analysis on composite samples

186 To complement selective dissolution for the study of Fe status, XAS analyses were carried out  
187 on composite samples. Moreover, the status of Zn, a recurrent trace element occurring in this  
188 Technosol, was also studied by XAS. The experiments were carried out at the Pacific  
189 Northwest Consortium Synchrotron Radiation Facility (PNCSTRF) bending magnet beamline  
190 of the Advanced Photon Source (Argonne, IL, USA). The XAS spectra of composite samples  
191 were recorded, as well as those of reference minerals: natural hematite, natural 6L  
192 ferrihydrite, synthetic goethite and synthetic 2L and 6L ferrihydrite. Experiences of Zn co-  
193 precipitation and sorption onto ferrihydrite and goethite were also carried out. All ferrihydrite  
194 and goethite syntheses were performed using previously developed protocols (Schulze, 1984;  
195 Waychunas et al., 1993). X-ray absorption near-edge spectroscopy (XANES) spectra were  
196 systematically recorded. In addition, if the concentration of the element targeted (Fe or Zn) in  
197 the sample was sufficient, X-ray absorption fine structure spectroscopy (EXAFS) spectra  
198 were also collected. Fe XANES and EXAFS spectra were recorded in the range 6962-7912  
199 eV, in transmission mode. The monochromator used was a double Si(111)–Si(220) crystal. A  
200 Fe foil was placed between the second and third ionization chamber for energy calibration.  
201 Each sample was scanned between 6 and 10 times, to increase the signal-to-noise ratio in the  
202 EXAFS region. All absorption spectra were calibrated according to the Fe K-edge position at  
203 7128 eV corresponding to the maximum of the first derivative. EXAFS spectra were extracted  
204 using a spline function adjusted by minimizing the Fourier transform magnitude at radial  
205 distances  $<1 \text{ \AA}$ . EXAFS spectra were deglitched if necessary. Radial structure functions were  
206 obtained by Fourier transform of the EXAFS spectra, using a Kaiser-Bessel apodization  
207 function with a smoothing parameter of 3.0. Data reduction was done using the Iffefit  
208 software package (Ravel and Newville, 2005).

209 The Fe-bearing minerals building up the composite samples were determined by linear  
210 combination fit of the EXAFS spectra. The minimum number of components needed to  
211 reproduce the EXAFS spectra was determined by principal components analysis (Manceau et  
212 al., 2002) using the entire set of composite samples spectra. The minimum of the indicator  
213 function (0.017) shows that two components are needed to reproduce the whole set of spectra  
214 (Table 2).

215 Linear combinations were done between 3 and 11 Å<sup>-1</sup> in the EXAFS region. During the  
216 simulation, the following commonly used parameter was minimized:

$$R = \frac{\sum_{i=0}^n (data_i - fit_i)^2}{data^2} \times 100$$

217 Where  $n$  is the number of data point,  $data_i$  is the data point number  $i$ , and  $fit_i$  is the fit value at  
218 point  $i$ .

219 The sum of the wt.% of each compound obtained after least square fitting calculations was  
220 also used as a goodness-of-fit parameter, since it should reach values close to 100 wt.% in a  
221 reliable reconstitution.

222 For Zn, XANES spectra were recorded in fluorescence mode (multi-element Canberra Ge  
223 detector), in the range 9511-10361 eV. Each sample was scanned 12 times and resulting  
224 spectra were averaged.

225

### 226 2.3.6 Nuclear microprobe investigations

227 Textural information was provided by nuclear microprobe analyses on thin sections made  
228 from samples collected at a precise depth. These experiments were performed using the

229 Laboratoire d'Etude des Eléments Légers nuclear microprobe in Saclay, France (Khodja et al.,  
230 2001).  $\mu$ -PIXE and  $\mu$ -RBS analyses were carried out on Fe-bearing phases pre-selected by  
231 SEM-EDS mapping. PIXE and RBS were used simultaneously to check the consistency of the  
232 results. Analyses were performed with 3.07 MeV  $4\text{He}^+$  (Isaure et al., 2001) and oxygen  
233 quantified through resonant scattering. The size of the incident  $4\text{He}^+$  beam was approximately  
234  $4 \times 4 \mu\text{m}^2$ . Prior analyses, both PIXE and RBS detection setups were calibrated with suitable  
235 standards.

236 All measurements were performed by electrostatically scanning the beam on pre-selected  
237 areas, and elemental contents from regions of interest were obtained by combining SIMNRA  
238 software (Mayer, 1997) for RBS and GUPIXWIN software (Campbell et al., 2010) for PIXE.

239 Major and trace elements were quantified by  $\mu$ -PIXE and oxygen by  $\mu$ -RBS. H and C cannot  
240 be quantified (only semi-quantification).

241

## 242 3. Results

### 243 3.1 Soil characteristics

244 The Technosol profile is made of several horizons of anthropogenic backfills from the surface  
245 to ~190 cm (Figure 2). These backfills consist in successions of homogeneous yellow-white  
246 pebbles horizons with heterogeneous backfills composed of a sandy brownish/darkish  
247 material mixed with bricks and concrete fragments. Coal and slag fragments are also found in  
248 these materials. Roots are present from the surface to ~170 cm depth. Below the backfill  
249 materials, quaternary yellow silts are observed. Brick fragments were found at the transition  
250 of the backfills and the quaternary silts (~200 cm). Below, the silts seem un-impacted by  
251 human activities.

252 The Technosol investigated here belongs either to the sandy loam class or to the silt loam  
253 class according to the FAO guideline for soil description (2006) because it contains 41-61%  
254 sand, 30-50% silt and only 8% clay at maximum (Table 3). Total organic carbon is abundant  
255 ( $> 20 \text{ g } 100\text{g}^{-1}$ ) over the whole profile, probably due to the coal fragments found in the  
256 backfills. No particular biological investigation was performed, but it is noteworthy that no  
257 earthworm activity was observed in the profile.

258 pH and CEC are similar for the three replicate samples located on a same horizon, indicating  
259 that soil properties are homogeneous for a given depth. pH steadily increases with depth from  
260 7.5 in surface sample to 8.5 in the deepest horizon. Oppositely, CEC decreases from  $\sim 23 \text{ meq}$   
261  $100 \text{ g}^{-1}$  to 8-9  $\text{meq } 100 \text{ g}^{-1}$ . Fe concentrations vary from 6 to 2 wt. % in the profile, with no  
262 specific trend with depth. Such generally high Fe concentration cannot be quantitatively  
263 accounted for by the presence of crystalline Fe phases because hematite, the main Fe-bearing  
264 mineral detected by XRD, accounts for 0-3 wt. % of the mineral assemblage (Table 4). Thus,  
265 amorphous phases certainly contain Fe. Indeed, the mineralogical assemblage (Table 4) of the  
266 Technosol is mainly composed of an amorphous phase which can be formed by organic  
267 matter (Table 3) and contributes to 45-68 wt.% of the sample. Major minerals such as quartz  
268 and calcite are also present. In addition to hematite, accessory phases are constituted of  
269 phyllosilicates (illite, kaolinite) and sulphates (natrojarosite, syngenite). Such assemblage is  
270 typical of oxidized slags (Navarro and Martínez, 2010). Note that this Technosol contains  
271 significant amounts of trace metals such as Zn (Table 3), but also As and Pb (see total  
272 concentrations in supplementary material).

273

274

275

### 276 3.2 Evolution of the Fe status along the profile

277 Fe status was first assessed by selective dissolution, using DCB and pyrophosphate methods  
278 (Figure 3). The fraction of total Fe complexed to surfaces (including organic matter) is  
279 negligible, as only 0.5-2 % of total Fe content is extracted by pyrophosphate, with no  
280 dependence on depth in the profile. Contrastingly, 30-60 wt % of total Fe content is extracted  
281 by DCB, indicating the presence of “free” Fe (“free” Fe covers different status: Fe oxides and  
282 hydroxides as well as exchangeable Fe).

283 DCB results show that 20-30 % more of the total Fe is present as “free” Fe at the surface as  
284 compared to the bottom of the profile. Such higher Fe extraction near surface could be due to  
285 a depth-dependent mechanism of oxidation of primary Fe-bearing species. However, the  
286 studied materials already contain oxides inherited from the past industrial activities, either  
287 under crystallized (hematite) or glassy (amorphous phase) states, the latter having a typical  
288 structure of melting-quenching, coming from slags (Figure 4). To distinguish between Fe  
289 (hydr)oxides inherited from the past and (hydr)oxides newly precipitated since the deposit of  
290 the backfills, XAS was employed.

291 A first analysis of all XANES spectra, collected on samples originating from various depths,  
292 shows a high degree of similarity between them, witnessing generally similar Fe-bearing  
293 phases and Fe oxidation state over the whole profile (Figure 5a). In particular, the pre-edge  
294 features located at ~10–20 eV before the edge jump and which are particularly sensitive to  
295 the Fe oxidation state are similar for all samples, with a maximum located at ~7114.3 eV,  
296 indicative of the predominance of Fe(III) species throughout the profile (Sundman et al.,  
297 2014). Upon closer examination, however, the first derivatives shows a change with depth in  
298 the respective contributions of two inflexion points at 7124 eV and 7128 eV. As the 7124 eV  
299 and 7128 eV contributions are respectively attributable to Fe(II) and Fe(III) (Sundman et al.,

2014), such variations are attributed to a slightly higher contribution of Fe(II) in the lower part of the profile and not to statistical fluctuations because the first derivative of XANES spectra of two samples from a same horizon showed similar contributions of each inflexion point (Figure 5b and c). SEM-EDS observation of a sample taken at 175-185 cm depth (sample F1) evidenced the regular presence of particles of ~10  $\mu\text{m}$  in width and containing solely Fe and S (Figure 6). These Fe sulphides could be at the origin of the slightly higher Fe(II) signal observed in depth by XANES. They were not detected by XAS and XRD (see Table 4, Figure 5 and Figure 7) because of their minor abundance as compared to the other Fe-bearing phases.

The mineralogy of the Fe-bearing phases was further assessed by least-square fitting of EXAFS spectra. Assuming that the evolution as a function of depth is due to weathering, and assuming that the sample collected in the bottom is representative of the lowest degree of weathering, samples from the bottom to the top can be described as a mixture of the sample from the bottom, plus additional component(s) that were formed during weathering. From PCA analysis (see above), only two components are required to describe the whole system. Following this approach, simulation of the spectra from samples collected in the surface horizon (A1) and at intermediate depth (E1) was performed, assuming that they could be described as a weighted sum of sample from the bottom (F1), plus an additional mineral that results from weathering. For the surface sample, the best fit (Figure 7) was obtained with 77% of sample from the bottom plus 25% of ferrihydrite. This is consistent with the DCB extraction results, as the increase in the DCB-extractable fraction between depth (sample F) and surface (sample A) was equal to 20-30%. Note that the sum of the weighted fraction of the two components is close to 1, thus reinforcing the confidence in simulation results. For the intermediate sample, the best fit (Figure 7) was obtained with 85% of sample from the bottom plus 15% of ferrihydrite, confirming that ferrihydrite proportion decreases with depth.

325 These results indicate a change in the status of Fe along depth. An assumption is that this  
326 change could influence the speciation of trace elements. The specific case of Zn is addressed  
327 in this paper since it is present in significant concentrations (up to 4,000  $\mu\text{g g}^{-1}$ ) in the profile.  
328 The status of Zn was investigated in relation with Fe but also with Mn status since Mn-  
329 bearing phases can also be major scavengers of trace metals (Grangeon et al., 2012;  
330 Koschinsky and Hein, 2003; Manceau et al., 2000; Peacock and Sherman, 2007).

331

### 332 3.3 Evolution of the Zn status along the Technosol profile and assessment of Zn mobility

333 The evolution of Zn speciation was first assessed using Zn-K edge XANES analysis of  
334 composite samples, as it provides an integrating view. Data are presented as a function of  
335 depth for two sets of replicate samples (Figure 8).

336 The XANES spectra are similar for each replicate samples, indicating that Zn speciation is  
337 similar at any location at the same depth. Contrastingly, changes with depth are observed. The  
338 contribution at 9668.5 eV is higher in the deepest samples (F1 and F3) whereas the peak at  
339 9665.5 eV is more pronounced in the surface samples (A, C and E). In Zn-ferrihydrite  
340 reference sample, the main contribution is located at 9665.5 eV. According to Cismasu et al.  
341 (2013) and Waychunas et al. (2003), the position of the edge is indicative of Zn coordination.  
342 When coordination is octahedral, the XANES spectrum only has one well defined edge,  
343 whereas when coordination is tetrahedral, the XANES presents several maxima, as it is the  
344 case here. Indeed, all XANES spectra have two maxima at  $\sim 9665.5$  eV and  $\sim 9668.5$  eV. Thus,  
345 in presently studied samples, Zn coordination is tetrahedral. With increasing depth, the  
346 intensity of the maximum at  $\sim 9665.5$  eV relative to that at  $\sim 9668.5$  eV evolves, and is lowest  
347 at the maximum depth. As discussed by Waychunas et al., 2003, this is indicative of an  
348 increasing number of heavy (*e.g.* Fe) scattering atoms around Zn, and thus of sorption to



349 better-crystallized phases. Consequently, in the deeper horizons, Zn is associated to phases  
350 having a higher degree of crystallinity than in the surface horizons. This demonstrates that the  
351 weathering processes during soil evolution influence Zn speciation, but do not necessarily  
352 relate to Zn mobility as, for example, it gives no information on the solubility of the sorbing  
353 phases. To study Zn mobility, and to compare this element to other major elements, leaching  
354 of the composite samples was performed. The results indicate that Fe, Mn and Zn are all very  
355 little labile throughout the whole profile (Figure 9). Thus, all these elements probably are  
356 under the form of mineral phases (Fe, Mn) or strongly bound to mineral phases (Zn), which  
357 are determined in the following.

358 Zn content was investigated first using pyrophosphate extraction, which showed that the  
359 fraction of total complexed Zn, partly borne by organic matter is, within uncertainties,  
360 constant and equal on average to 18% (Figure 10a). Thus, although organic matter is a  
361 significant Zn reservoir, it does not represent the only Zn bearing-phase. The Zn content of  
362 the DCB-soluble fraction was investigated next. Fe extraction yields are presented here above  
363 (Figure 4b), and those from Mn and Zn are shown in Figure 10b. Both Zn and Mn are  
364 significantly affected by DCB extraction. Zn extraction yield (35% on average) is, within  
365 uncertainties, constant over the whole profile, while Mn has a slightly different behavior,  $69 \pm$   
366  $4 \%$  being extracted in the first 40 cm depth,  $51 \pm 6 \%$  at 120 cm depth and  $62 \pm 4 \%$  at 180  
367 cm depth (Figure 10b). As DCB solubilizes Mn (hydr)oxides (Mehra and Jackson, 1960), it  
368 can be concluded that Mn is mainly present in the profile as discrete Mn (hydr)oxide(s). Here  
369 above, it was shown that Fe is also mainly present as (hydr)oxides. These two (hydr)oxides  
370 can potentially bear Zn, which is confirmed by the tetrahedral coordination of Zn assessed by  
371 EXAFS. Note that, although within uncertainties, the fraction of Zn extracted by DCB might  
372 increase with depth. However, as Zn concentration in the deepest sampling point (175-185 cm  
373 depth) is 10 times lower than in the surface horizon (0-10 cm depth), and even 26 times lower

374 than in the sampling point just above (110-130 cm depth), a small quantity of Fe and Mn  
375 (hydr)oxides that would have migrated from the upper horizons (or a limited contamination,  
376 for example during sampling) may have led to such apparent slight change extraction yield.  
377 According to this assumption, Zn is probably associated in depth with the Fe (hydr)oxides  
378 originally present in the backfills, but also with the newly formed Fe (hydr)oxides at the  
379 surface of the profile that would have migrated.

380 To summarize, in this profile and on average, less than 0.1 % of total Zn is H<sub>2</sub>O-extractable,  
381 up to 18 % of total Zn would be bound to organic matter, 35 % of total Zn would be adsorbed  
382 onto Fe/Mn (hydr)oxides, and about 47 % of total Zn is present under a residual form (that  
383 cannot be accessed with any of the extractant used here). To better constrain this distribution,  
384  $\mu$ -PIXE and  $\mu$ -RBS are now used with a twofold aim: first, cross-check results from chemical  
385 extraction and in particular the association between Zn and Fe/Mn pedogenic (hydr)oxides,  
386 second, determine the nature of the residual form. These analyses were performed on sample  
387 LM2 sample (90 cm depth).

388 The association between Zn and Fe (hydr)oxides could be straightforwardly and regularly  
389 observed, as exemplified in Figure 11. The grain showed in this image is made of coal, with a  
390 Fe coating having a size of about 50  $\mu$ m on the edge. The morphology suggests that the Fe  
391 (hydr)oxide is a secondary phase and was formed during soil evolution. Using quantitative  
392 analyses performed two regions of interest (ROI – Table 5), this Fe (hydr)oxide is probably  
393 the ferrihydrite identified using EXAFS spectroscopy, since Fe/O atomic ratios in the two  
394 ROIs (respectively 0.42 and 0.51) are lower than the theoretical Fe/O ratio of hematite (0.66),  
395 but are consistent with Fe/O ratio of ferrihydrite (theoretical value from 0.42 to 0.57  
396 depending on the hydration state). Table 5 indicates also that Zn/Fe atomic ratio could reach  
397 up to 17%, which further confirms that ferrihydrite is a very efficient sink for metallic trace  
398 elements.

399 The nature of the Zn-bearing phase forming the residual phase was found to be complex, as  
400 demonstrated in Figure 12 and Table 6, where complex associations between Zn, Mn, Fe, S  
401 and O could be quantified. The quantitative analysis carried out in some regions of interest  
402 (ROI) show various elemental proportions (Table 6). The grain is composed of different Fe-  
403 compounds: Fe (hydr)oxides (ROI 3,4,6) and Mn, Zn, Fe-bearing sulphates (ROI 1 and 5).  
404 Interestingly, these latter are likely a mix of sulphides undergoing oxidation and forming  
405 sulphates (see the white arrow in Figure 12 b and c), since the S/O ratio of 0.42 (ROI 1 and 5),  
406 are higher than the expected ratio in a sulphate (0.25). It is interesting to note that the external  
407 part of the grain (ROI 3 and 4) do not contain sulphur. It is only composed of Fe (hydr)oxides,  
408 and contain less than 0.2 atomic percent of Zn. Fe/O atomic ratio calculated for all the Fe  
409 (hydr)oxides (see Table 6) range from 0.45 to 0.48. These values are lower than Fe/O ratio of  
410 hematite (0.66) and goethite (0.5), but are consistent with Fe/O ratio of ferrihydrite (0.42-0.57  
411 depending on the hydration state).

412

#### 413 4. Discussion

414 The study of the Fe status by several methods of investigation throughout the Technosol  
415 profile indicates that (i) Fe is mainly under Fe(III) form, with a contribution of Fe(II) in the  
416 deeper samples, (ii) some Fe species inherited from the past have been oxidized and  
417 secondary minerals are constituted of Fe-bearing sulphates (jarosite) and Fe (hydr)oxides, (iii)  
418 Fe(III) is mainly under the form of ferrihydrite, as evidenced by XAS,  $\mu$ -PIXE and  $\mu$ -RBS  
419 (iv) 20 to 30% more Fe (hydr)oxides are present in the surface than in depth. Ferrihydrite  
420 forms coatings surrounding different grains of the Technosol, in consistence with a  
421 neoformation induced by weathering processes. Previous studies have shown that in slags,  
422 secondary minerals formed by oxidation can be present as coatings on surfaces and as

423 precipitates of various phases such as amorphous Fe, Al (hydr)oxides, chalcantite, siderotil,  
424 jarosite, brochantite or gypsum (Navarro and Martínez, 2010; Piatak et al., 2004). Fe sulphate  
425 and Fe (hydr)oxides are both secondary minerals formed by oxidation of Fe-bearing sulphides  
426 (Blowes et al., 2005). Such reaction typical of acid mine drainage can be encountered in all  
427 kind of wastes containing sulphides. In the present study, this assumption is consistent with  
428 the sulphates found by XRD and  $\mu$ -PIXE, as well as the Fe sulphides encountered in depth  
429 (see Figure 6 above). However, the pH remains near-neutral to slightly basic since the net-  
430 acid-generating potential was probably exceeded by the net-neutralizing potential due to a low  
431 sulphide/neutralizing minerals ratio (e.g. Plante et al., 2011). Thus, the main evolution driver  
432 of this 100 years-old Technosol is oxidation, which affects the Fe status, the CEC and the  
433 related trace elements mobility. The presence of free Fe at the surface of this Technosol is of  
434 interest since it provides the soil with an efficient trace metals sink and since such Fe is easily  
435 accessible to plants (Pansu and Gautheyrou, 2006). According to Navarro and Martínez  
436 (2010), the formation of secondary phases (e.g. jarosite, gypsum, goethite, ferrihydrite) may  
437 control the distribution of trace elements in the pore water and the degree to which they are  
438 mobilized into the environment. Dissolution of primary minerals leads to trace elements  
439 release in pore water solution. These trace elements can precipitate to form secondary  
440 minerals, or can be sorbed onto these secondary minerals.

441 In the studied Technosol, XANES revealed that Zn has tetrahedral coordination and is sorbed  
442 to phases of increasing crystallinity when depth increases. This could indicate that the  
443 amorphous Fe (hydr)oxides inherited from the past are slightly more crystalline than the  
444 newly formed Fe (hydr)oxides at the surface. Soil formation on such material does not induce  
445 a dramatic increase of Zn solubility since efficient scavengers are concomitantly formed in the  
446 system. Zn-bearing phases identified in the present study are: complex Fe, Mn, Zn sulphides,  
447 which may be the primary Zn-bearing phase, sulphates which may be the oxidation product of

448 the sulphides, organic matter, and ferrihydrite. On the contrary, no Zn-bearing Mn  
449 (hydr)oxides were found, even if there are known to be important sinks of trace elements such  
450 as Zn.

451 The assumption that the deeper horizons are the parent material in this Technosol profile is  
452 difficult to prove since the characteristics of the original material at the time of backfill  
453 deposit are unknown. However, the observed evolution of Fe mineralogy with depth, as well  
454 as Zn speciation change and CEC decrease with depth, is a clue for the validity of this  
455 assumption.

456 This study also highlights that DCB selective extraction method is relevant to investigate Fe  
457 status in a Technosol, since the relative proportion of “free” Fe - mainly Fe (hydr)oxides -  
458 quantified by DCB (20-30% in surface) is similar to the ones estimated by EXAFS linear  
459 combination fitting (25% in surface). DCB is also interesting to assess the relations between  
460 all the “free” Fe species and trace elements such as Zn, even if the concentrations of Zn bound  
461 to Fe (hydr)oxides are probably underestimated by this extraction. Indeed, dithionites are  
462 labile compounds which undergo rapid disproportionation in aqueous solution due to their  
463 sensitivity to oxygen. This decomposition is rapid at  $\text{pH} < 5.5$  but also occur at neutral and  
464 basic pH (de Carvalho and Schwedt, 2001). It produces mainly thiosulphate and bisulphite  
465 which will be the final product of the disproportionation. But intermediate sulphide and  
466 elemental sulfur, playing a catalytic role, are also encountered in solution as minor  
467 decomposition products (de Carvalho and Schwedt, 2001; Wayman and Lem, 1970).  
468 Dissolved sulphide can react with Zn to precipitate ZnS during DCB extraction (Rao et al.,  
469 2008). This would explain the gap between DCB results which show that only 35% of total  
470 Zn is dissolved whereas XANES and nuclear microprobe indicate a major contribution of Zn  
471 associated with ferrihydrite.

472 In the future, this Technosol will potentially evolve again because some phases are not  
473 thermodynamically stable in conditions of pH observed here. For instance, jarosite is known  
474 to be stable at  $\text{pH} < 3$  (Blowes et al., 2005), whereas the pH in the Technosol is near-neutral to  
475 slightly basic. Moreover, the input of organic matter at the surface based on organic C  
476 determination, is slightly visible after 100 years of evolution. Pyrophosphate extractions have  
477 shown that Fe and Zn are variably complexed to surfaces (including organic matter).  
478 However, the pyrophosphate extract does not only determine organic forms but also dissolves  
479 poorly crystalline mineral phases (e.g. Kaiser and Zech, 1996). Mineralogical investigations  
480 confirmed that Fe and Zn are not complexed on coal which is the most abundant carbon phase  
481 of the Technosol. Indeed, Fe and Zn were not observed at the surface of the coal grains (see  
482 Figure 11). Though, other clues of evolution are visible in the studied Technosol. CEC is  
483 higher near surface and could indicate that the soil surface reached a higher evolution stage  
484 than the deeper horizons, either due to weathering or to bioturbation. Organic matter will  
485 probably play an important role in the future on major and trace element speciation.

486

## 487 5. Conclusions and environmental implications

488 Technosols are highly heterogenous and widely differ from one place to another because of  
489 the variety of their constitutive man-made materials. In this study, a Technosol made of  
490 smelter slags, i.e. containing high amounts of coal and Fe (hydr)oxides was characterized. The  
491 results indicate that 100 years of soil evolution has led to the precipitation of secondary  
492 minerals (including Fe (hydr)oxides and Fe sulphates) at the surface of the profile. This  
493 behavior is similar to pedogenic processes occurring in natural soils, but other specific  
494 evolutions due to large thermodynamic disequilibrium can be highlighted, in particular  
495 sulphide oxidation and sulphate precipitation. This specific behavior of Technosols over time

496 can be generalized to all kinds of Technosols, even if the final reaction products are not  
497 similar. Such evolution influences pollutants mobility including trace elements release. In this  
498 specific study, Technosol evolution does not induce a dramatic increase of Zn solubility since  
499 efficient scavengers are concomitantly formed in the system. However, this behavior is not  
500 generic and will depend on the type of Technosol and on the secondary minerals formed as  
501 well as on the nature and amount of organic matter. If the trace metals sinks are not abundant  
502 and/or efficient, this could potentially represent a risk of mobilization of trace metals. This  
503 must be carefully examined through case studies.

504

## 505 Acknowledgments

506 The authors would like to acknowledge the French Environmental Agency (Ademe; H  l  ne  
507 Roussel) for their financial support (REITERRE research program) and advices through this  
508 work. S.G. acknowledges partial funding by the ANR (NACRE—ANR-14-CE01-0006). The  
509 XAFS experiments were performed at the Advanced Photon Source (sector 20). Sector 20  
510 facilities at the Advanced Photon Source, and research at these facilities, are supported by the  
511 US Department of Energy - Basic Energy Sciences, the Canadian Light Source and its  
512 funding partners, the University of Washington, and the Advanced Photon Source. Use of the  
513 Advanced Photon Source, an Office of Science User Facility operated for the U.S.  
514 Department of Energy (DOE) Office of Science by Argonne National Laboratory, was  
515 supported by the U.S. DOE under Contract No. DE-AC02-06CH11357. Special thanks to  
516 Robert Gordon and Michael Pape, who helped with the experiments at the beamline.

517

## 518 References

519 Bakker, L., Lowe, D.J., Jongmans, A.G., 1996. A micromorphological study of pedogenic  
520 processes in an evolutionary soil sequence formed on Late Quaternary rhyolitic tephra  
521 deposits, North Island, New Zealand. *Quaternary International* 34–36(0), 249-261.

522 Bataillard, P., Grangeon, S., Quinn, P., Mosselmans, F., Lahfid, A., Wille, G., Joulain, C.,  
523 Battaglia-Brunet, F., 2014. Iron and arsenic speciation in marine sediments undergoing a  
524 resuspension event: the impact of biotic activity. *Journal of Soils and Sediments* 14(3), 615-  
525 629.

526 Bataillard, P., Guérin, V., Lions, J., Girondelot, B., Laboudigue, A., van der Lee, J., Raepsaet,  
527 C., Gallien, J., 2008. Mobilité des éléments traces dans un Anthropeol développé sur des  
528 sédiments de curage fortement contaminés - 1 - Migration à l'échelle du profil. *Étude et*  
529 *Gestion des Sols*, pp. 7-18.

530 Ben-Dor, E., Levin, N., Singer, A., Karnieli, A., Braun, O., Kidron, G.J., 2006. Quantitative  
531 mapping of the soil rubification process on sand dunes using an airborne hyperspectral sensor.  
532 *Geoderma* 131(1–2), 1-21.

533 Blowes, D.W., Ptacek, C.J., Jambor, J.L., Weisener, C.G., 2005. The geochemistry of acid  
534 mine drainage. *Treatise on Geochemistry, Vol 9: Environmental Geochemistry*, 149-204.

535 Brahy, V., Deckers, J., Delvaux, B., 2000. Estimation of soil weathering stage and acid  
536 neutralizing capacity in a toposequence Luvisol–Cambisol on loess under deciduous forest in  
537 Belgium. *European Journal of Soil Science* 51(1), 1-13.

538 Buol, S., Hole, F., McCracken, R., 1973. Soil genesis and classification. The Iowa State  
539 University Press, Ames, pp. 360.



540 Campbell, J.L., Boyd, N.I., Grassi, N., Bonnicksen, P., Maxwell, J.A., 2010. The Guelph PIXE  
541 software package IV. Nuclear Instruments and Methods in Physics Research Section B: Beam  
542 Interactions with Materials and Atoms 268(20), 3356-3363.

543 Cismasu, A.C., Levard, C., Michel, F.M., Brown Jr, G.E., 2013. Properties of impurity-  
544 bearing ferrihydrite II: Insights into the surface structure and composition of pure, Al- and Si-  
545 bearing ferrihydrite from Zn(II) sorption experiments and Zn K-edge X-ray absorption  
546 spectroscopy. *Geochimica et Cosmochimica Acta* 119, 46-60.

547 Claff, S.R., Sullivan, L.A., Burton, E.D., Bush, R.T., 2010. A sequential extraction procedure  
548 for acid sulphate soils: partitioning of iron. *Geoderma* 155, 224–230.

549 Costantini, E.A.C., Lessovaia, S., Vodyanitskii, Y., 2006. Using the analysis of iron and iron  
550 oxides in paleosols (TEM, geochemistry and iron forms) for the assessment of present and  
551 past pedogenesis. *Quaternary International* 156–157, 200-211.

552 de Carvalho, L.M., Schwedt, G., 2001. Polarographic determination of dithionite and its  
553 decomposition products: kinetic aspects, stabilizers, and analytical application. *Analytica  
554 Chimica Acta* 436(2), 293-300.

555 Demattê, J.A.M., da Silva Terra, F., 2014. Spectral pedology: A new perspective on  
556 evaluation of soils along pedogenetic alterations. *Geoderma* 217–218, 190-200.

557 Duchaufour, P., 1976. Dynamics of organic matter in soils of temperate regions: Its action on  
558 pedogenesis. *Geoderma* 15(1), 31-40.

559 Egli, M., Merkli, C., Sartori, G., Mirabella, A., Plötze, M., 2008. Weathering, mineralogical  
560 evolution and soil organic matter along a Holocene soil toposequence developed on  
561 carbonate-rich materials. *Geomorphology* 97(3–4), 675-696.

562 FAO, 2006. Guidelines for soil description. Food and Agriculture Organization of the United  
563 Nations, Rome.

564 Grangeon, S., Manceau, A., Guilhermet, J., Gaillot, A.-C., Lanson, M., Lanson, B., 2012. Zn  
565 sorption modifies dynamically the layer and interlayer structure of vernadite. *Geochimica Et*  
566 *Cosmochimica Acta* 85, 302-313.

567 Hadi, J., Tournassat, C., Lerouge, C., 2016. Pitfalls in using the hexaamminecobalt method  
568 for cation exchange capacity measurements on clay minerals and clay-rocks: Redox  
569 interferences between the cationic dye and the sample. *Applied Clay Science* 119, Part 2, 393-  
570 400.

571 Huot, H., Simonnot, M.-O., Marion, P., Yvon, J., De Donato, P., Morel, J.-L., 2013.  
572 Characteristics and potential pedogenetic processes of a Technosol developing on iron  
573 industry deposits. *Journal of Soils and Sediments* 13(3), 555-568.

574 Ingerslev, M., 1997. Effects of liming and fertilization on growth, soil chemistry and soil  
575 water chemistry in a Norway spruce plantation on a nutrient-poor soil in Denmark. *Forest*  
576 *Ecology and Management* 92(1-3), 55-66.

577 Isaure, M.P., Laboudigue, A., Manceau, A., Sarret, G., Tiffreau, C., Trocellier, P., 2001.  
578 Characterisation of zinc in slags originated from a contaminated sediment by coupling  $\mu$ -  
579 PIXE,  $\mu$ -RBS,  $\mu$ -EXAFS and powder EXAFS spectroscopy. *Nuclear Instruments and*  
580 *Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 181(1-  
581 4), 598-602.

582 Kaiser, K., Zech, W., 1996. Defects in estimation of aluminium in humus complexes of  
583 podzolic soils by pyrophosphate extraction. *Soil Science* 161, 452-458.

584 Khodja, H., Berthoumieux, E., Daudin, L., Gallien, J.-P., 2001. The Pierre Süe Laboratory  
585 nuclear microprobe as a multi-disciplinary analysis tool. *Nuclear Instruments and Methods in*  
586 *Physics Research Section B: Beam Interactions with Materials and Atoms* 181(1–4), 83-86.

587 Koschinsky, A., Hein, J.R., 2003. Uptake of elements from seawater by ferromanganese  
588 crusts: solid-phase associations and seawater speciation. *Marine Geology* 198(3-4), 331-351.

589 Leguédois, S., Séré, G., Auclerc, A., Cortet, J., Huot, H., Ouvrard, S., Watteau, F., Schwartz,  
590 C., Morel, J.L. 2016. Modelling pedogenesis of Technosols. *Geoderma*, 262, 199-212.

591 Lehmann, A., Stahr, K., 2007. Nature and significance of anthropogenic urban soils. *Journal*  
592 *of Soils and Sediments* 7(4), 247-260.

593 Manceau, A., Lanson, B., Schlegel, M.L., Harge, J.C., Musso, M., Eybert-Berard, L.,  
594 Hazemann, J.L., Chateigner, D., Lambelle, G.M., 2000. Quantitative Zn speciation in smelter-  
595 contaminated soils by EXAFS spectroscopy. *American Journal of Science* 300(4), 289-343.

596 Manceau, A., Marcus, M.A., Tamura, N., 2002. Quantitative Speciation of Heavy Metals in  
597 Soils and Sediments by Synchrotron X-ray Techniques. *Reviews in Mineralogy and*  
598 *Geochemistry* 49(1), 341-428.

599 Mayer, M., 1997. SIMNRA User's Guide. Report IPP 9/113, Max-Planck-Institute für  
600 Plasmaphysik, Garching, Germany.

601 Mehra, O.P., Jackson, M.L., 1960. Iron oxide removal from soils and clays by a dithionite-  
602 citrate system buffered with sodium bicarbonate. *Clays and Clay Minerals*, pp. 317-327.

603 Minasny, B., McBratney, A.B., Salvador-Blanes, S., 2008. Quantitative models for  
604 pedogenesis — A review. *Geoderma* 144(1–2), 140-157.

605 Morel, J., Chenu, C., Lorenz, K., 2015. Ecosystem services provided by soils of urban,  
606 industrial, traffic, mining, and military areas (SUITMAs). *Journal of Soils and Sediments*  
607 15(8), 1659-1666.

608 Navarro, A., Martínez, F., 2010. The use of soil-flushing to remediate metal contamination in  
609 a smelting slag dumping area: Column and pilot-scale experiments. *Engineering Geology*  
610 115(1–2), 16-27.

611 Néel, C., Bril, H., Courtin-Nomade, A., Dutreuil, J.-P., 2003. Factors affecting natural  
612 development of soil on 35-year-old sulphide-rich mine tailings. *Geoderma* 111(1–2), 1-20.

613 Nehls, T., Rokia, S., Mekiffer, B., Schwartz, C., Wessolek, G., 2013. Contribution of bricks  
614 to urban soil properties. *Journal of Soils and Sediments* 13(3), 575-584.

615 Norra, S., 2006. Urban Soil Science on the 18th WCSS. *Journal of Soils and Sediments* 6(3),  
616 189-189.

617 Orsini, L., Rémy, J.C., 1976. The use of the chloride of cobaltihexamine for the simultaneous  
618 determination of the exchange capacity and exchangeable bases in soils. *Sci. Sol*, pp. 269-  
619 275.

620 Pansu, M., Gautheyrou, J., 2006. Mineralogical Separation by Selective Dissolution. In:  
621 Springer (Ed.), *Handbook of soil analysis. Mineralogical, Organic and Inorganic Methods.*,  
622 pp. 167-219.

623 Peacock, C.L., Sherman, D.M., 2007. Crystal-chemistry of Ni in marine ferromanganese  
624 crusts and nodules. *American Mineralogist* 92(7), 1087-1092.

625 Piatak, N.M., Seal Ii, R.R., Hammarstrom, J.M., 2004. Mineralogical and geochemical  
626 controls on the release of trace elements from slag produced by base- and precious-metal  
627 smelting at abandoned mine sites. *Applied Geochemistry* 19(7), 1039-1064.

628 Plante, B., Benzaazoua, M., Bussière, B., 2001. Predicting Geochemical Behaviour of Waste  
629 Rock with Low Acid Generating Potential Using Laboratory Kinetic Tests. *Mine Water and*  
630 *the Environment* 30, 2–21.

631 Rao, C.R.M., Sahuquillo, A., Sanchez, J.F.L., 2008. A review of the different methods applied  
632 in environmental geochemistry for single and sequential extraction of trace elements in soils  
633 and related materials. *Water Air and Soil Pollution* 189(1-4), 291-333.

634 Ravel, B., Newville, M., 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-  
635 ray absorption spectroscopy using IFEFFIT. *Journal of Synchrotron Radiation* 12(4), 537-  
636 541.

637 Reeve, A., Desha, C., Hargroves, C., Newman, P., Hargreaves, D., 2012. A basis for a  
638 pragmatic inquiry into the policy considerations related to the increased application of  
639 Biophilic Urbanism, 11th Urban Environment Symposium, pp. 16-19.

640 Rietveld, H., 1969. A profile refinement method for nuclear and magnetic structures. *Journal*  
641 *of Applied Crystallography* 2(2), 65-71.

642 Rossiter, D.G., 2007. Classification of urban and industrial soils in the world reference base  
643 for soil resources. *Journal of Soils and Sediments* 7(2), 96-100.

644 Salvador-Blanes, S., Minasny, B., McBratney, A.B., 2007. Modelling long-term in situ soil  
645 profile evolution: application to the genesis of soil profiles containing stone layers. *European*  
646 *Journal of Soil Science* 58(6), 1535-1548.

647 Schulze, D., 1984. The influence of aluminum on iron oxides. VIII. Unit-cell dimensions of  
648 Al-substituted goethites and estimation of Al from them. *Clays Clay Miner* 32, 27-39.

649 Séré, G., Schwartz, C., Ouvrard, S., Renat, J.C., Watteau, F., Villemin, G., Morel, J.L., 2010.  
650 Early pedogenic evolution of constructed Technosols. *Journal of Soils and Sediments* 10(7),  
651 1246-1254.

652 Sundman, A., Karlsson, T., Laudon, H., Persson, P., 2014. XAS study of iron speciation in  
653 soils and waters from a boreal catchment. *Chemical Geology* 364, 93-102.

654 Tawornpruek, S., Kheoruenromne, I., Suddhiprakarn, A., Gilkes, R.J., 2006. Properties of red  
655 Oxisols on calcareous sedimentary rocks in Thailand. *Geoderma* 136(3-4), 477-493.

656 Testiati, E., Parinet, J., Massiani, C., Laffont-Schwob, I., Rabier, J., Pfeifer, H.-R., Lenoble,  
657 V., Masotti, V., Prudent, P., 2013. Trace metal and metalloid contamination levels in soils and  
658 in two native plant species of a former industrial site: Evaluation of the phytostabilization  
659 potential. *Journal of Hazardous Materials* 248-249, 131-141.

660 Tipping, E., Rey-Castro, C., Bryan, S.E., Hamilton-Taylor, J., 2002. Al(III) and Fe(III)  
661 binding by humic substances in freshwaters, and implications for trace metal speciation.  
662 *Geochimica et Cosmochimica Acta* 66(18), 3211-3224.

663 Tsoлова, V.T., Hristova, M.B., Borrás, J.B., Pascual, N.R., Banov, M.D., 2014. Pb, Cu and Zn  
664 geochemistry in reclaimed soils (Technosols) of Bulgaria. *Journal of Geochemical*  
665 *Exploration* 144, 337-344. Uzarowicz, Ł., Skiba, S., 2011. Technogenic soils developed on  
666 mine spoils containing iron sulphides: Mineral transformations as an indicator of pedogenesis.  
667 *Geoderma* 163(1-2), 95-108.

668 Wanat, N., Austruy, A., Joussein, E., Soubrand, M., Hitmi, A., Gauthier-Moussard, C.,  
669 Lenain, J.F., Vernay, P., Munch, J.C., Pichon, M., 2013. Potentials of *Miscanthus x giganteus*  
670 grown on highly contaminated Technosols. *Journal of Geochemical Exploration* 126, 78-  
671 84. Waychunas, G.A., Fuller, C.C., Davis, J.A., Rehr, J.J., 2003. Surface complexation and  
672 precipitate geometry for aqueous Zn(II) sorption on ferrihydrite: II. XANES analysis and  
673 simulation. *Geochimica et Cosmochimica Acta* 67(5), 1031-1043.

674 Waychunas, G.A., Rea, B.A., Fuller, C.C., Davis, J.A., 1993. Surface chemistry of  
675 ferrihydrite: Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate.  
676 *Geochimica et Cosmochimica Acta* 57(10), 2251-2269.

677 Wayman, M., Lem, W.J., 1970. Decomposition of aqueous dithionite. Part II. A reaction  
678 mechanism for the decomposition of aqueous sodium dithionite. *Canadian Journal of*  
679 *Chemistry* 48(5), 782-787.

680 WRB, 2006. World Reference Base for Soil Resource 2006, 2nd ed. World Resources Report,  
681 103. FAO, Rome.

682

683

684

685

Table 1 Summary of selective dissolution procedures (from Bataillard et al., 2014)

Fraction	Reagent	Shaking time and temperature
Citrate-bicarbonate-dithionite (CBD)	0.3 M Na Citrate pH 7.3+Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> +NaCl saturated solution	1 g DM moist sediment/10 ml 0.3 M NaCitrate pH 7.3+0.4 g Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> +2 mL NaCl saturated solution Heat 15 min 80 °C Centrifugation 5 min at about 3,000 g Repeated twice
Sodium pyrophosphate	0.05 M Na <sub>4</sub> O <sub>7</sub> P <sub>2</sub>	2 g DM moist sediment/200 ml Na <sub>4</sub> O <sub>7</sub> P <sub>2</sub> Agitation 16 H, 20 °C±5 °C. Centrifugation 20 min 18,000 rpm



Table 2: Results of the principal component analysis on the 8 composite sample spectra. The minimum of the indicator (IND) function shows that two components are needed to reproduce the whole set of spectra.

<b>Component</b>	<b>Eigenvalue</b>	<b>IND<sup>a</sup></b>
1	13.7	0.018
2	1.7	0.017
3	0.9	0.022
4	0.8	0.028
5	0.6	0.040
6	0.4	0.085
7	0.4	0.32

<sup>a</sup>Indicator function

Table 3. Technosol characteristics and properties (ND: not determined)

Soil sample	Depth (cm)	Texture (%)			pH	Total organic carbon (g 100g <sup>-1</sup> )	CEC (meq 100g <sup>-1</sup> )	Total Fe (wt. %)	Total Mn (wt. %)	Total Zn (mg kg <sup>-1</sup> )
		Clay	Silt	Sand						
<b>A1</b>	0-10	8	50	42	7.5	25	22.8	4.5	0.06	1817
<b>A2</b>			ND		7.6	26.3	21.3	4.8	0.06	1245
<b>A3</b>			ND		7.7	24.9	20.1	4.2	0.06	1365
<b>C1</b>	30-40	8	31	61	7.8	35.3	15.6	5.3	0.06	656
<b>C2</b>			ND		8.2	38.0	14.8	5.3	0.06	552
<b>C3</b>			ND		8.2	28.8	14.3	3.9	0.06	928
<b>E1</b>	110-130	8	39	53	8.3	38.9	10.1	4.2	0.06	4021
<b>E2</b>			ND		8.3	27.4	10.7	4.5	0.09	3677
<b>E3</b>			ND		8.4	25.3	10.9	5.3	0.12	4740
<b>F1</b>	175-185	5	30	65	8.4	31.8	9.5	2.2	0.03	760
<b>F2</b>			ND		8.5	48.7	8.1	2.0	0.03	180
<b>F3</b>			ND		8.5	46.8	9.2	2.0	0.03	312

Table 4. Relative proportion of crystalline minerals in the bulk composite samples of the Technosol profil estimated by Rietveld analysis (ND: not detected)

<b>Mineral proportion (wt.%)<sup>a</sup></b>	<b>A1</b>	<b>C1</b>	<b>E1</b>	<b>F1</b>
<b>Quartz</b>	31	14	15	23
<b>Calcite</b>	4	2	1	5
<b>Albite</b>	2	1	<1	1
<b>Microcline</b>	1	<1	<1	1
<b>Dolomite</b>	4	1	1	ND
<b>Natrojarosite</b>	<1	<1	ND	1
<b>Hematite</b>	2	3	<1	1
<b>Mullite</b>	3	3	2	1
<b>Syngenite</b>	1	<1	<1	<1
<b>Illite/mica</b>	4	4	10	6
<b>Kaolinite</b>	3	4	4	1
<b>Amorphous phase</b>	45	68	67	60

<sup>a</sup>Error on these results: +/- 5 wt%

Table 5. Quantitative elementary results obtained by  $\mu$ -PIXE and  $\mu$ -RBS on two regions of interests (ROI) of the grain in the isolated sample LM2 as shown in Figure 11.

<b>Atomic fraction (%)</b>	<b>ROI 1</b>	<b>ROI 2</b>
<b>O<sup>a</sup></b>	36.6	30.4
<b>Si<sup>b</sup></b>	2.4	6.3
<b>P<sup>b</sup></b>	0.3	0.7
<b>S<sup>b</sup></b>	0.8	0.9
<b>Cl<sup>b</sup></b>	0	0
<b>K<sup>b</sup></b>	0	0.1
<b>Ca<sup>b</sup></b>	0.1	0.6
<b>Ti<sup>b</sup></b>	0	0
<b>Mn<sup>b</sup></b>	0	0
<b>Fe<sup>b</sup></b>	18.8	12.6
<b>Zn<sup>b</sup></b>	0.7	2.1
<b>As<sup>b</sup></b>	0	0
<b>Pb<sup>b</sup></b>	0.2	0.2
<b>Fe/O atomic ratio</b>	0.51	0.42

<sup>a</sup> Error on O is  $\pm 5\%$

<sup>b</sup> Error on these elements is comprised between 1 and 5% when the atomic fraction is lower than 1%, elsewhere the error is lower than 1%.

Table 6. Quantitative elementary results obtained by  $\mu$ -PIXE and  $\mu$ -RBS on five regions of interests (ROI) of the grain in the isolated sample LM2 as shown in Figure 12.

<b>Atomic fraction (%)</b>	<b>ROI 1</b>	<b>ROI 2</b>	<b>ROI 3</b>	<b>ROI 4</b>	<b>ROI 5</b>
<b>O<sup>a</sup></b>	36.2	40.2	40	34.2	37.8
<b>Si<sup>b</sup></b>	13.8	0.5	0.2	13.4	0.6
<b>P<sup>b</sup></b>	0	0.5	0.1	0.2	0.1
<b>S<sup>b</sup></b>	15.3	0.2	0.1	14.0	0.9
<b>Cl<sup>b</sup></b>	0.2	0	0	0	0.1
<b>K<sup>b</sup></b>	0.3	0	0	0.2	0
<b>Ca<sup>b</sup></b>	2.2	0.3	0.2	1.7	0.1
<b>Ti<sup>b</sup></b>	0.2	0	0	0.1	0
<b>Mn<sup>b</sup></b>	3.0	0	0	2.0	0
<b>Fe<sup>b</sup></b>	3.8	18.1	19.0	4.6	17.2
<b>Zn<sup>b</sup></b>	7.5	0.2	0.1	6.5	0.1
<b>As<sup>b</sup></b>	0	0.1	0	0	0
<b>Pb<sup>b</sup></b>	0.8	0	0	0	0
<b>Fe/O atomic ratio</b>	-	0.45	0.48	-	0.46

<sup>a</sup> Error on O is  $\pm 5\%$

<sup>b</sup> Error on these elements is comprised between 1 and 13% when the atomic fraction is lower than 1%, elsewhere the error is lower than 1%.

Figure 1

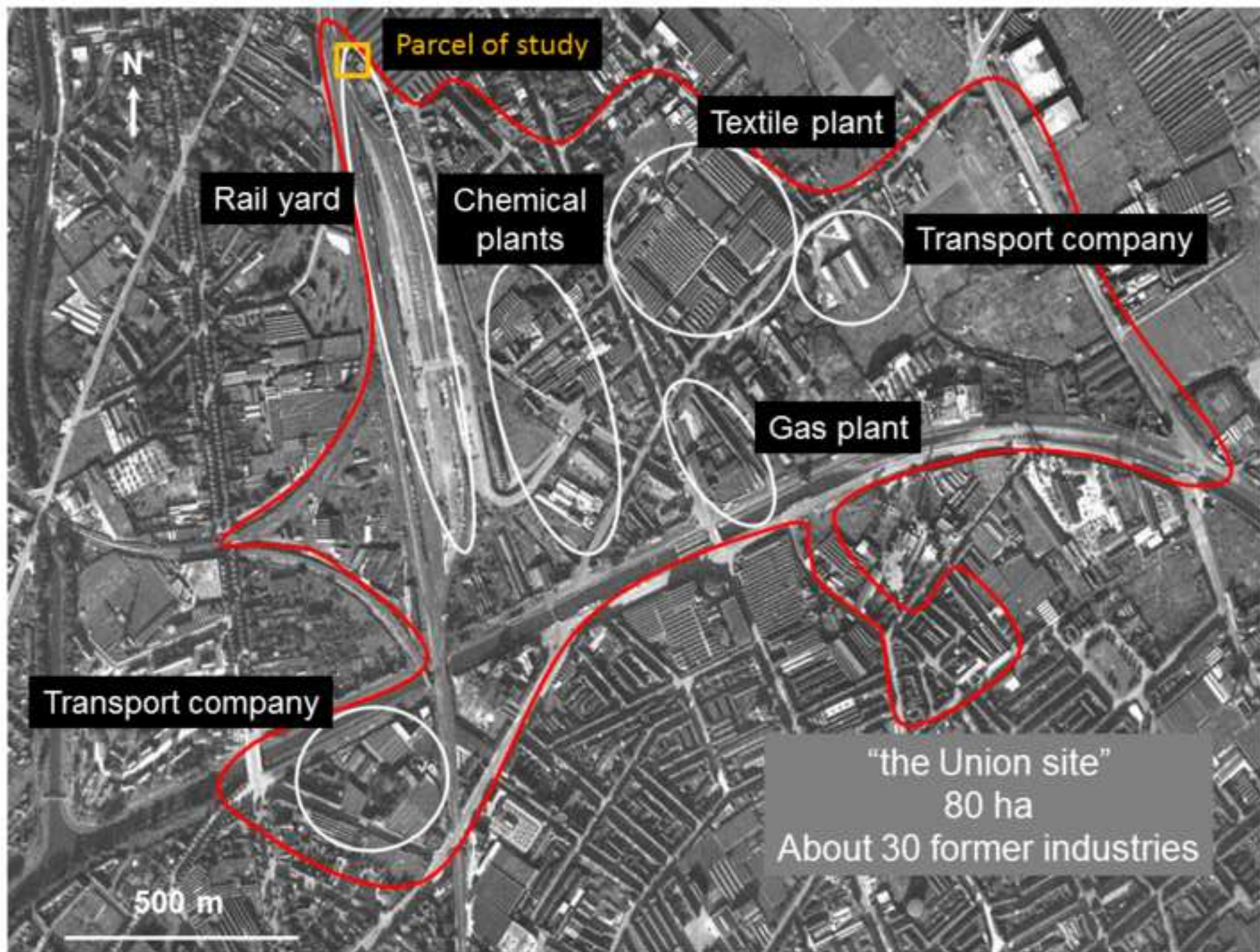


Figure 2

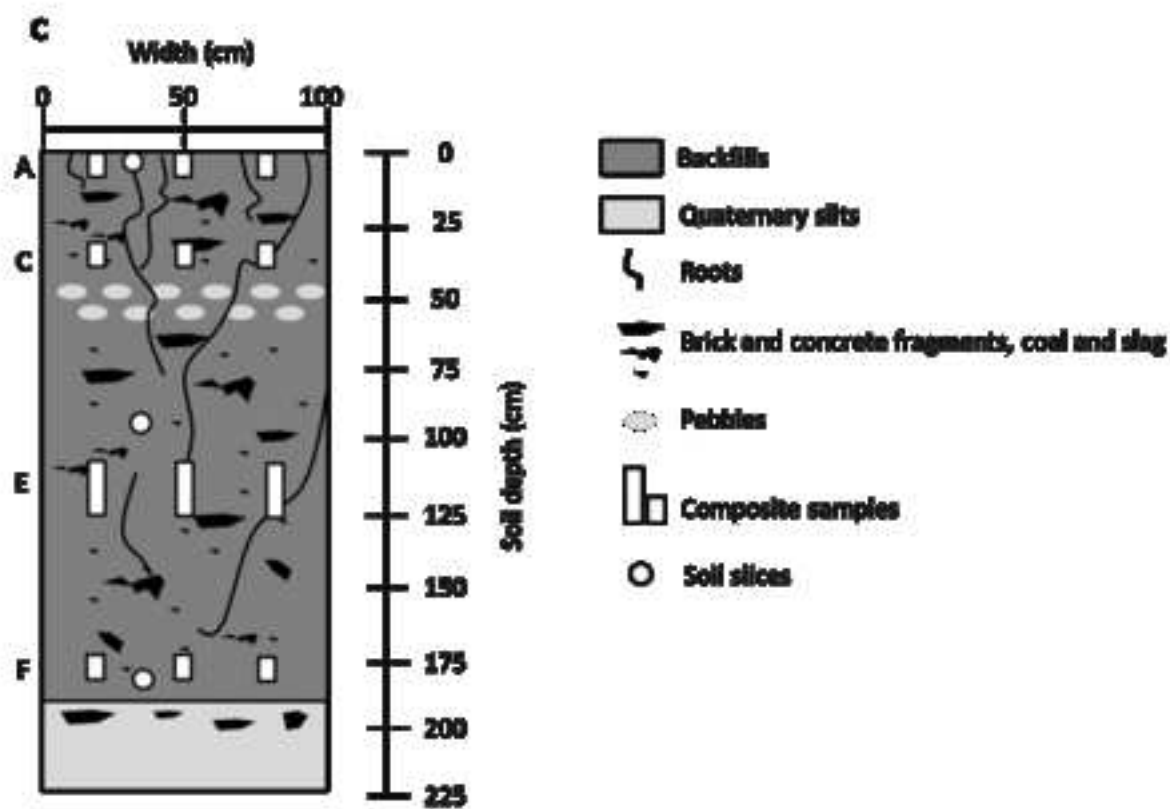
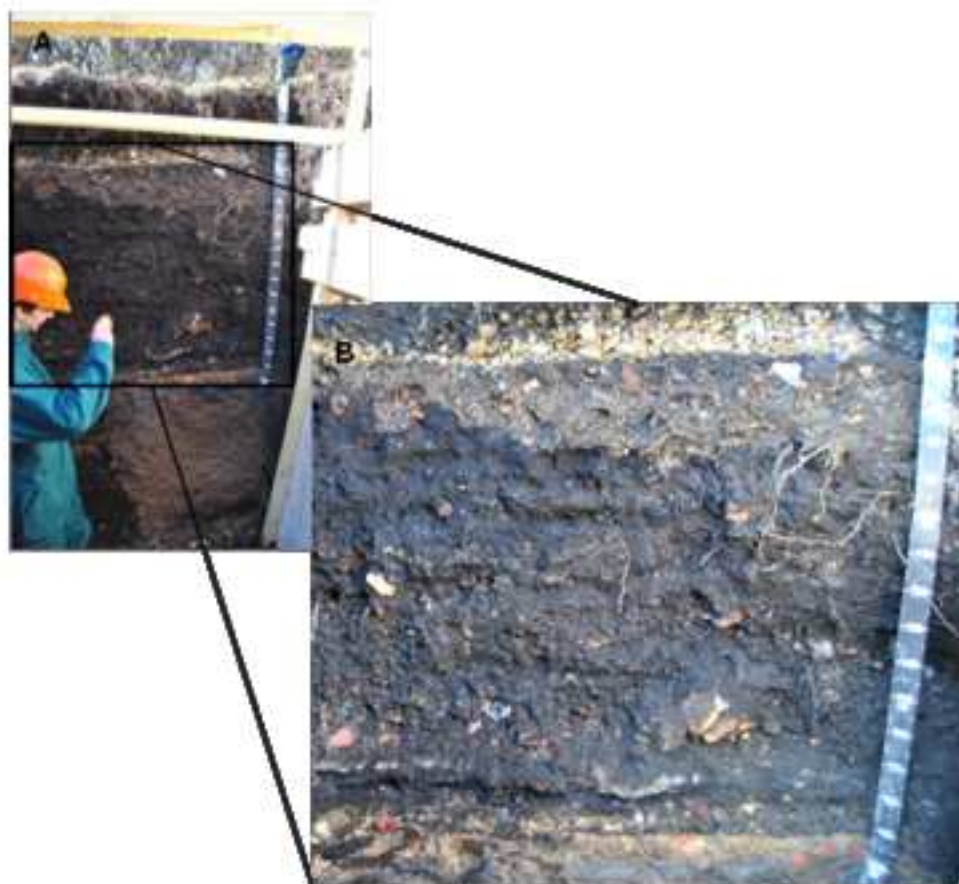


Figure 3

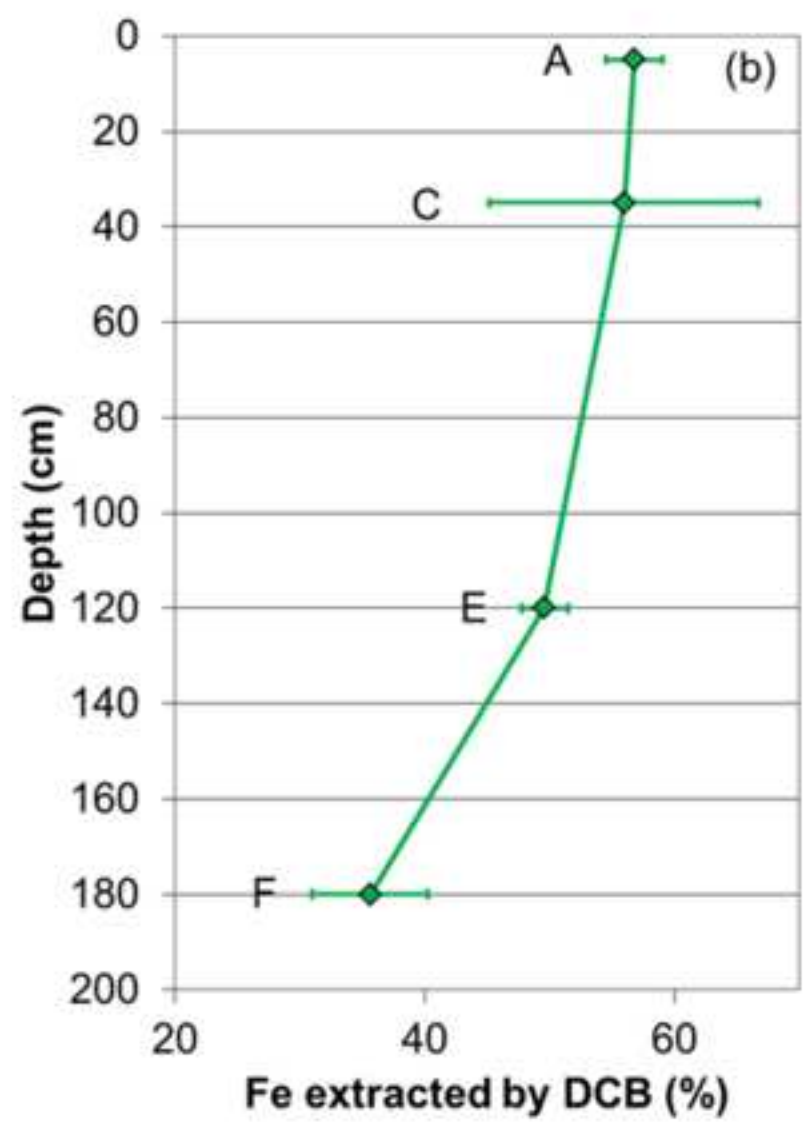
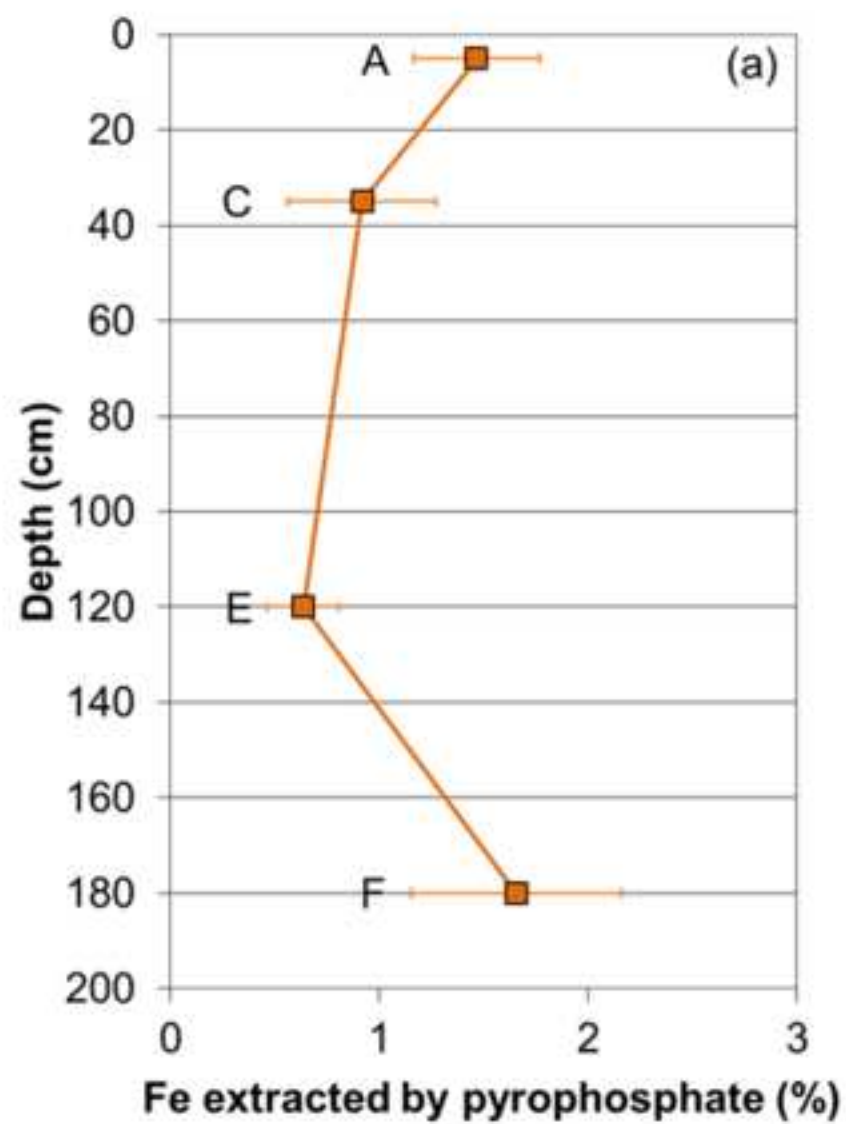




Figure 4

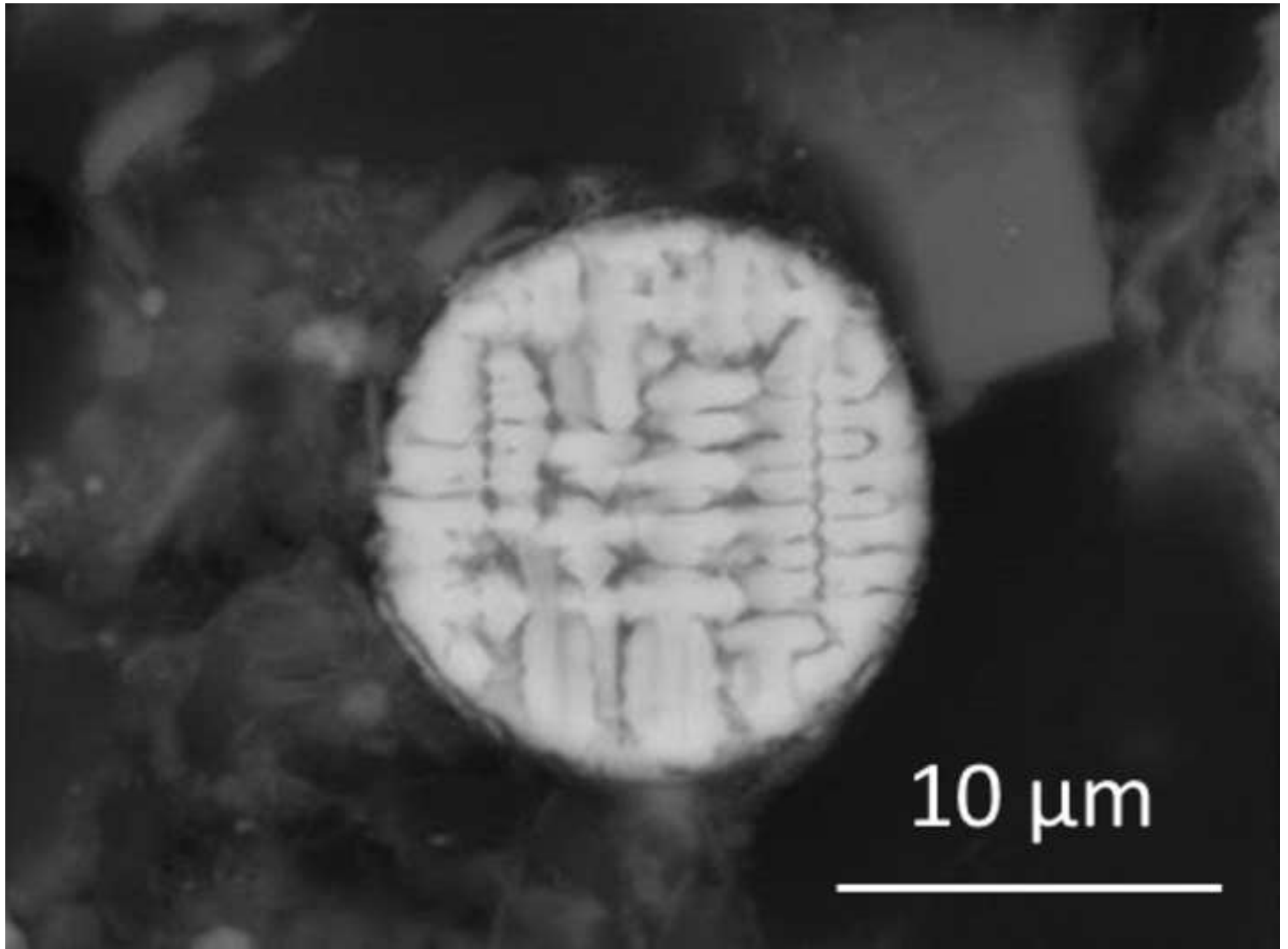


Figure 5

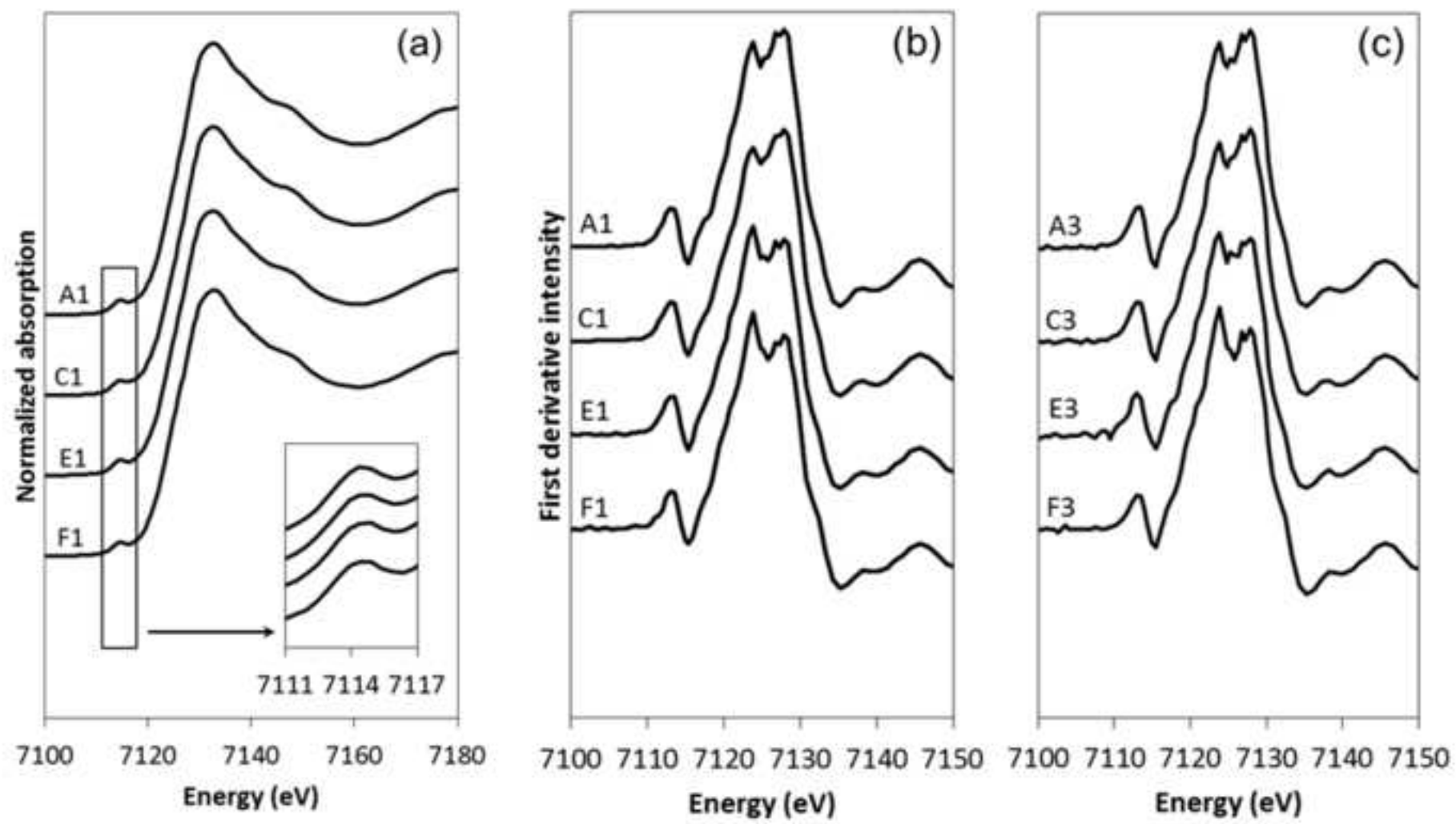


Figure 6

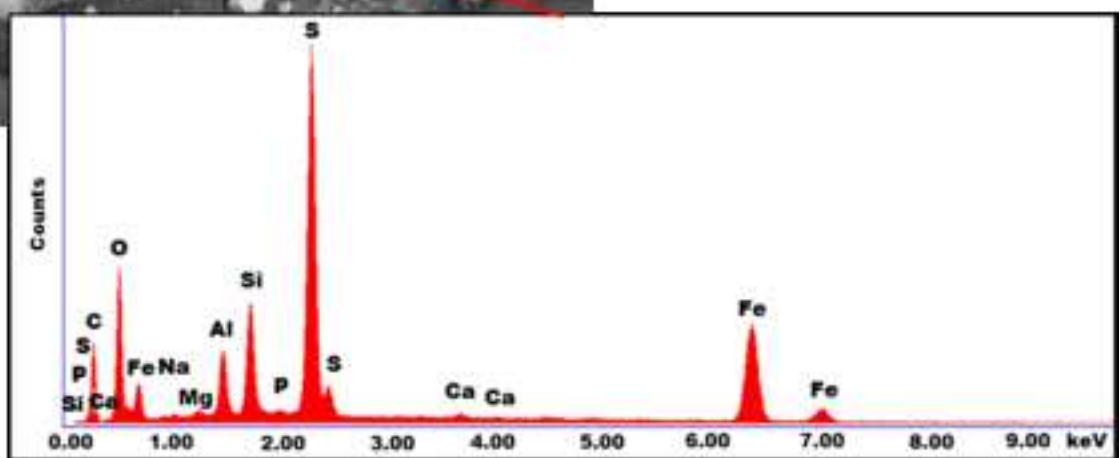
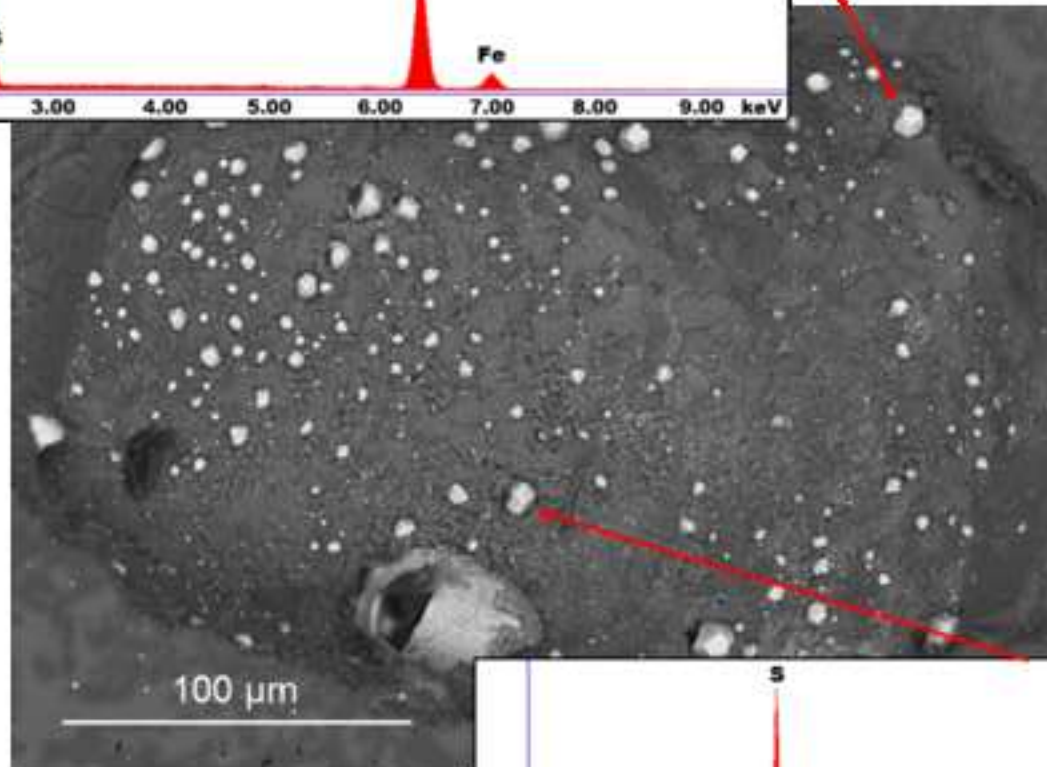
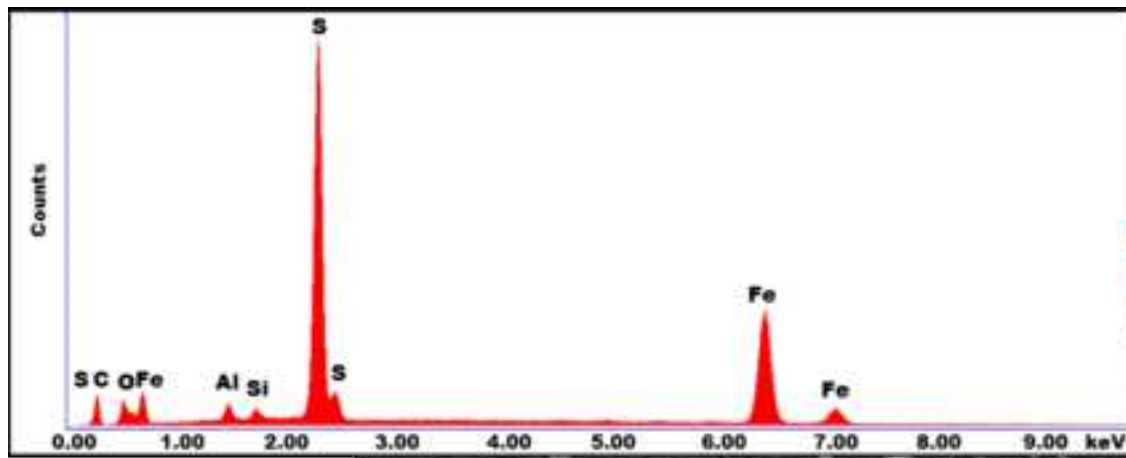


Figure 7

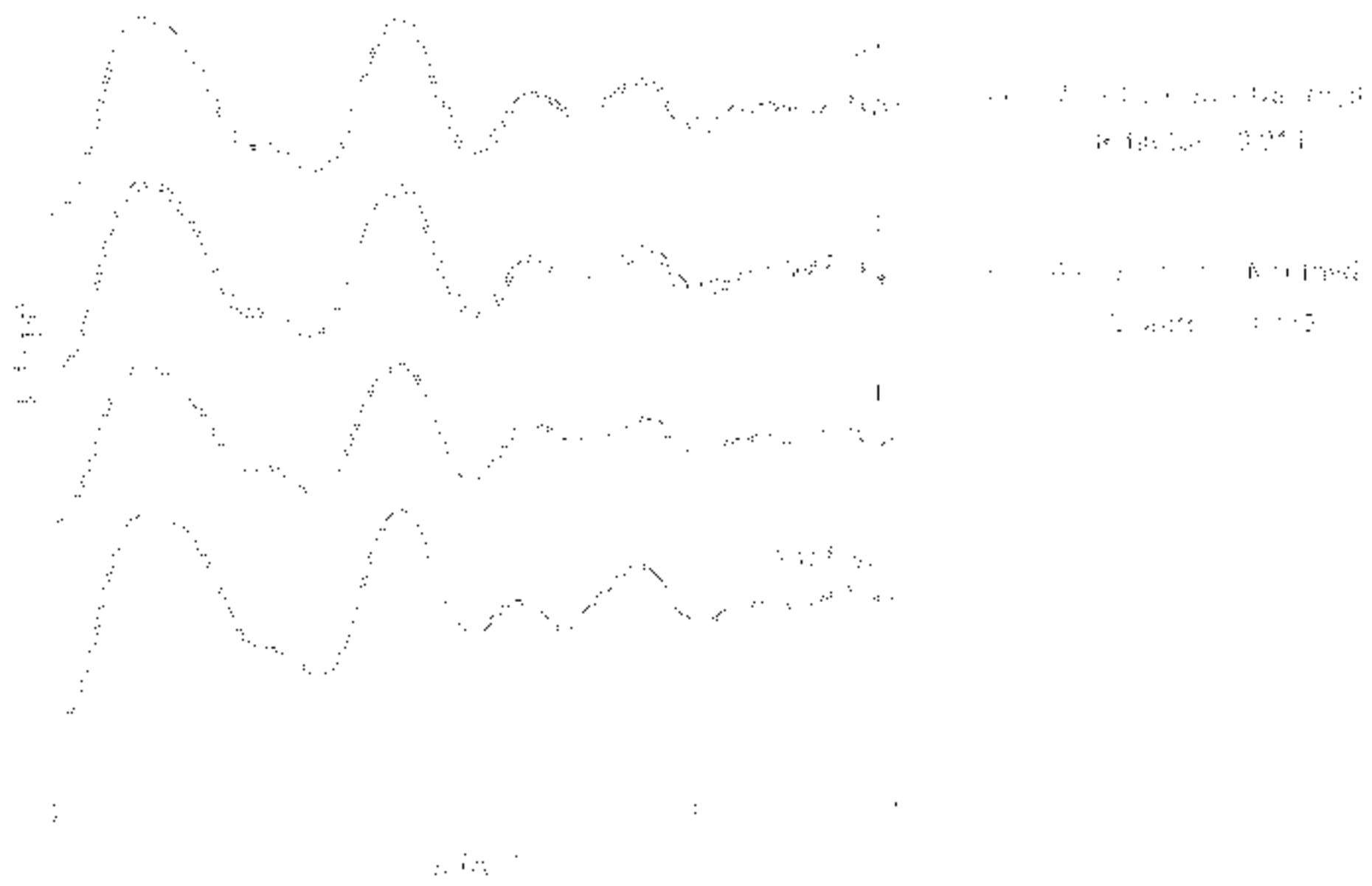


Figure 8

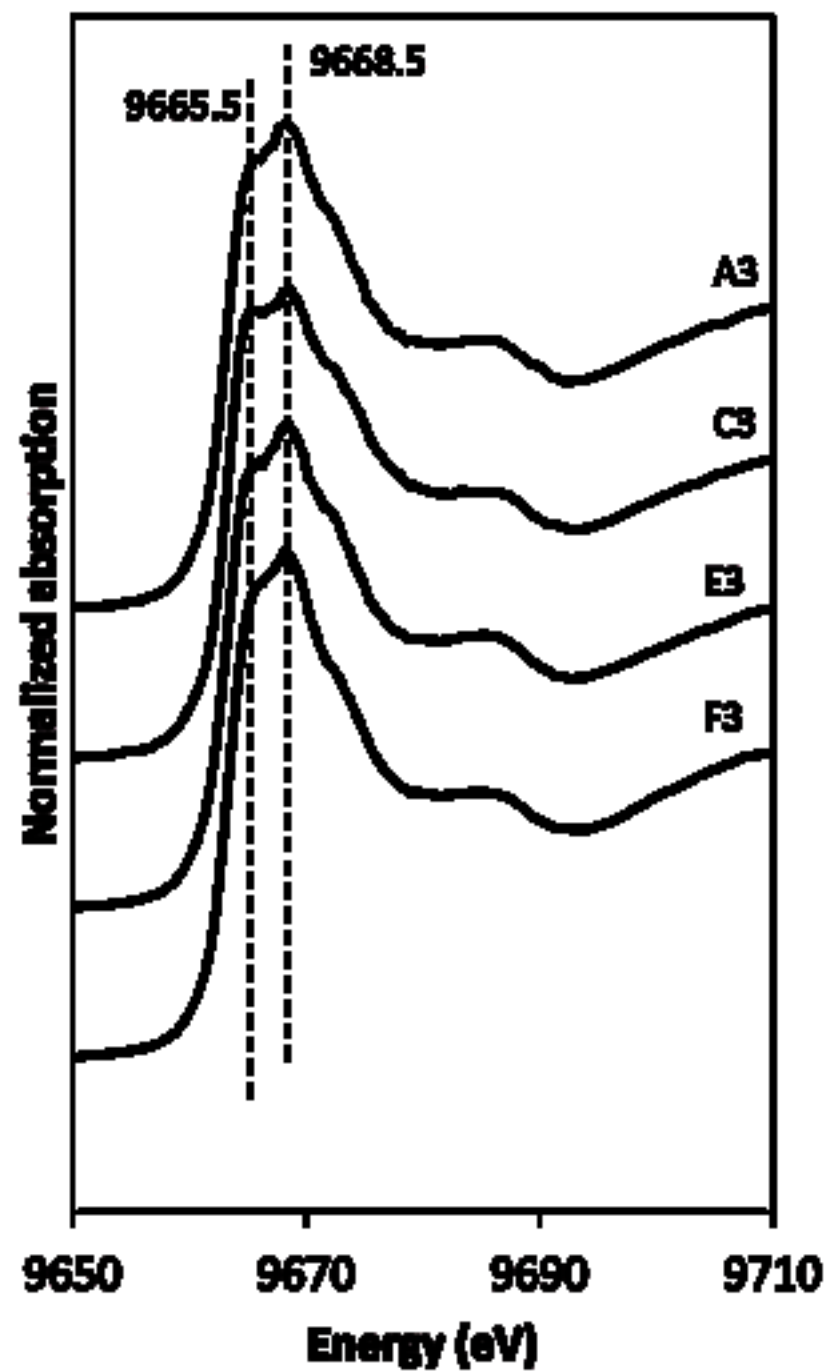
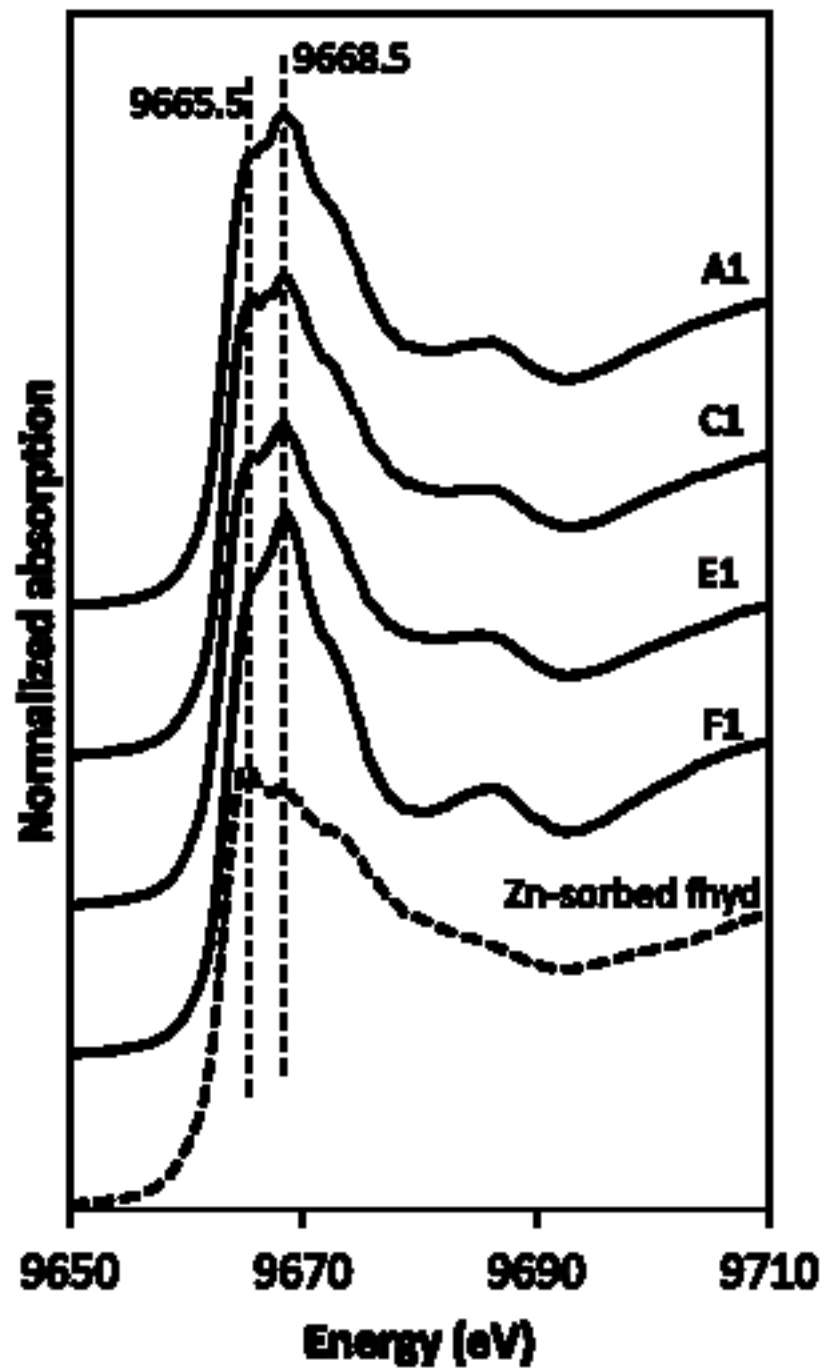


Figure 9

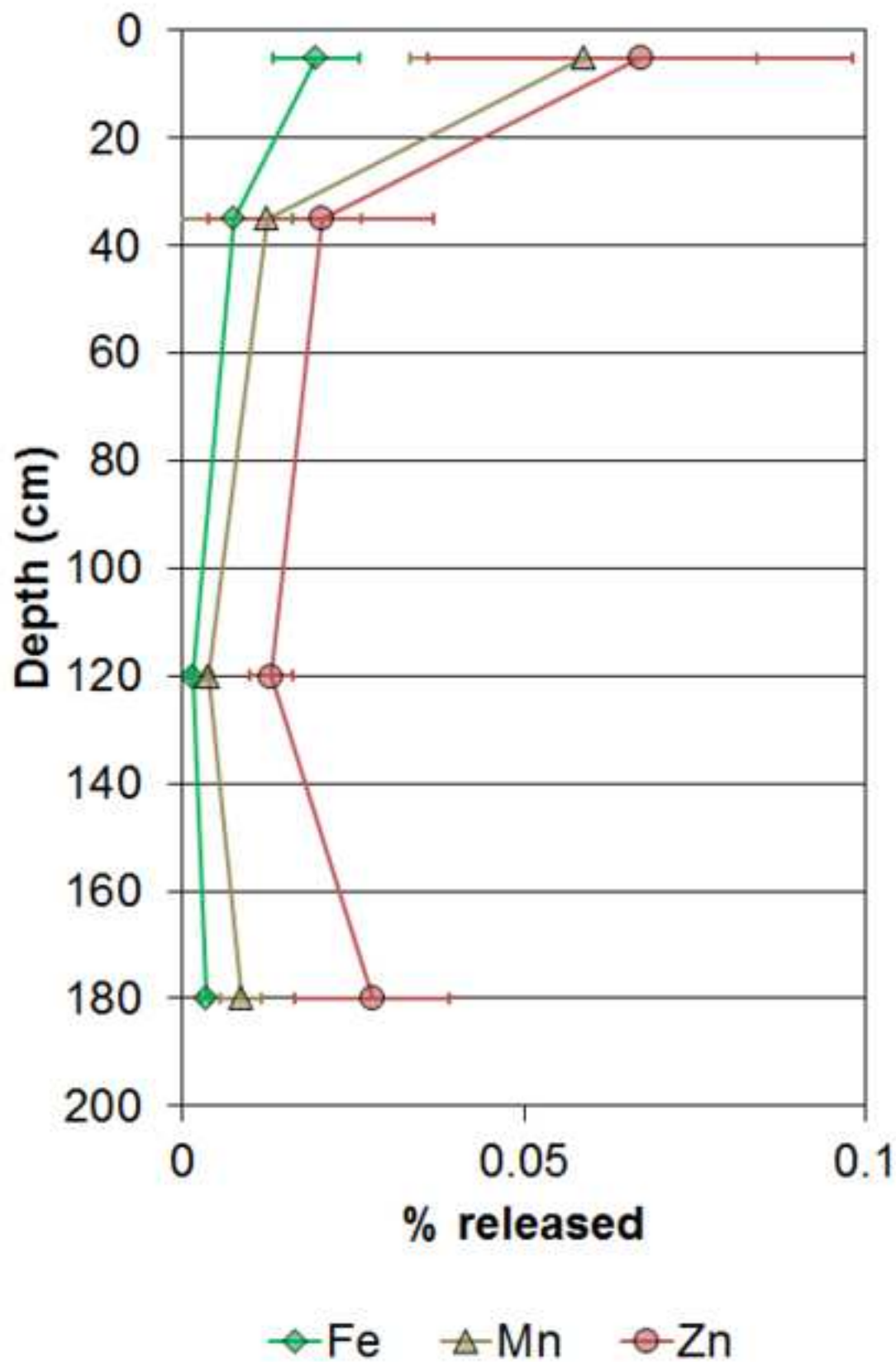


Figure 10

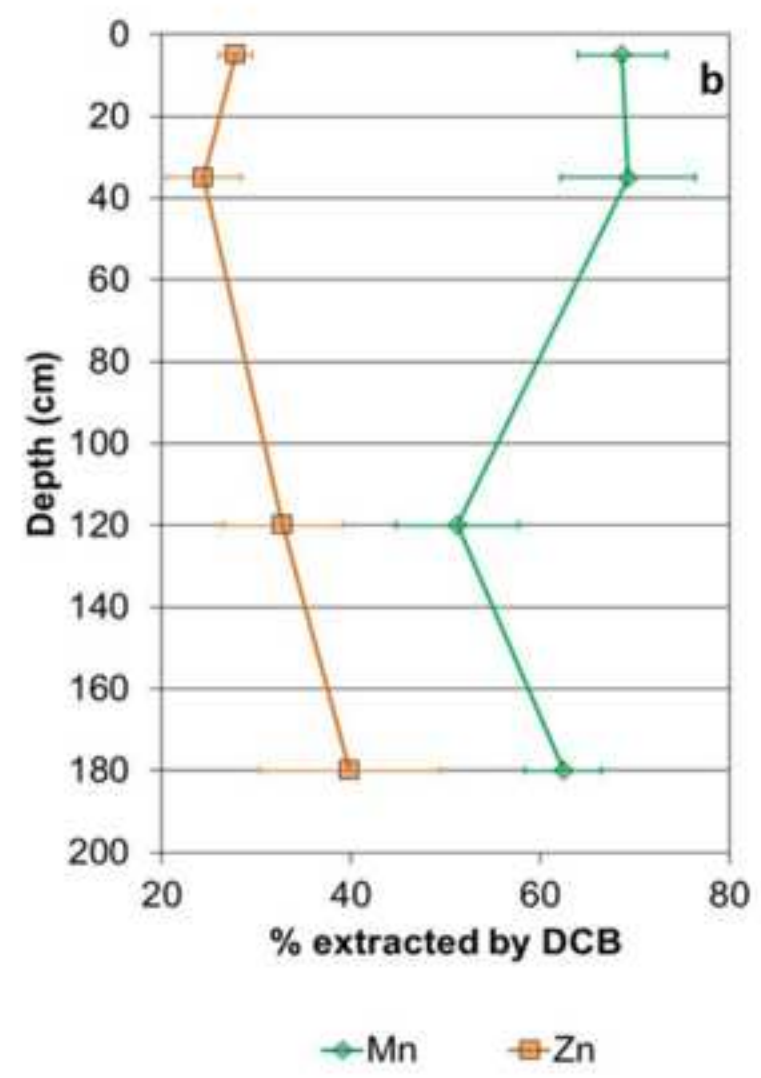
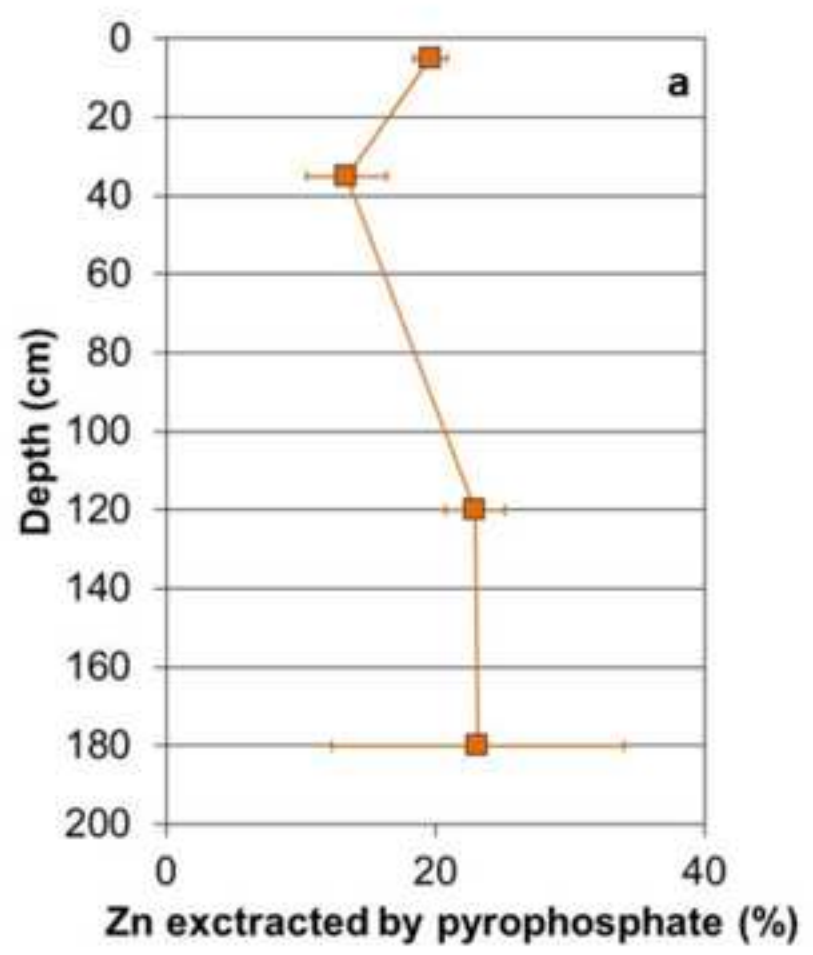


Figure 11

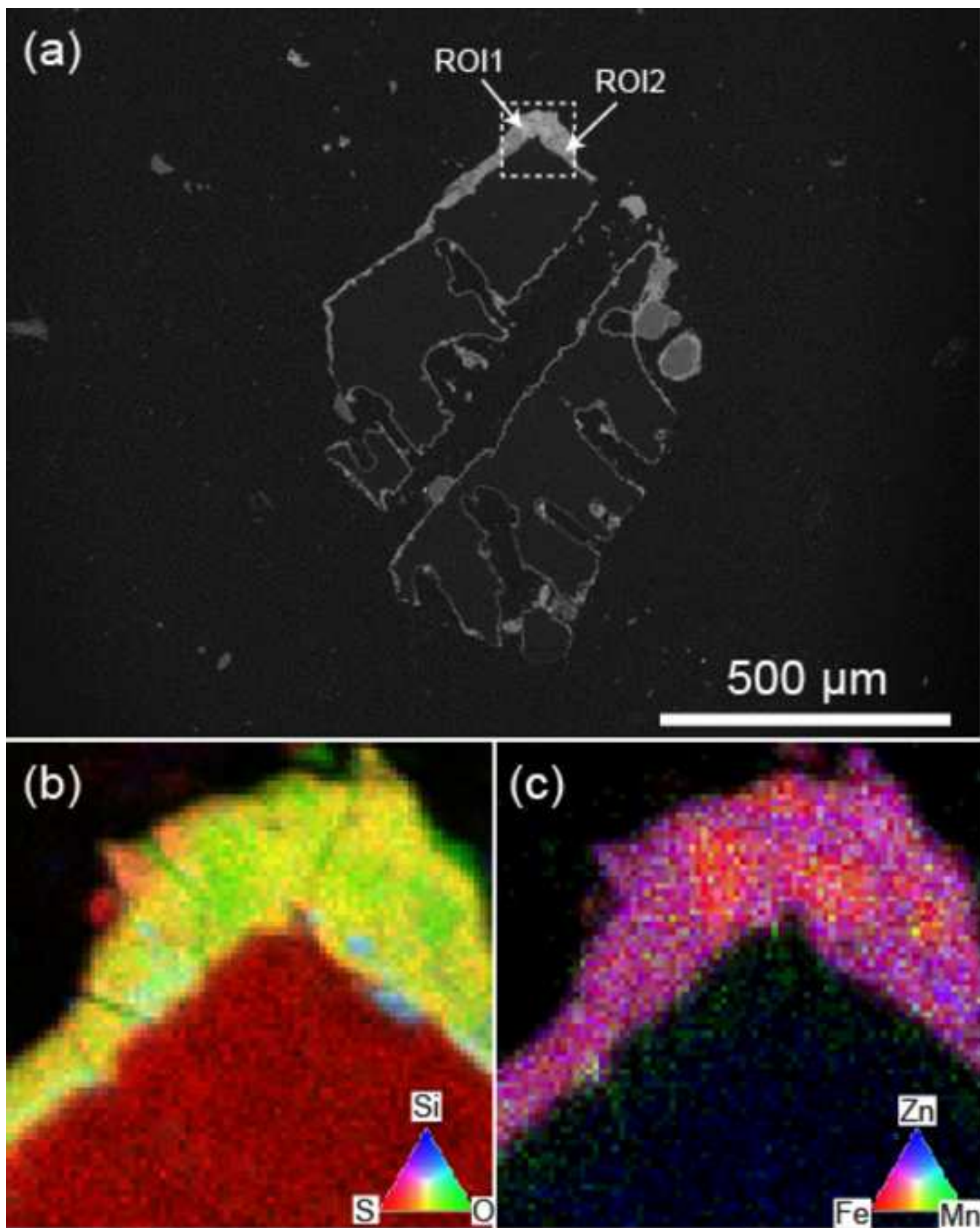




Figure 12

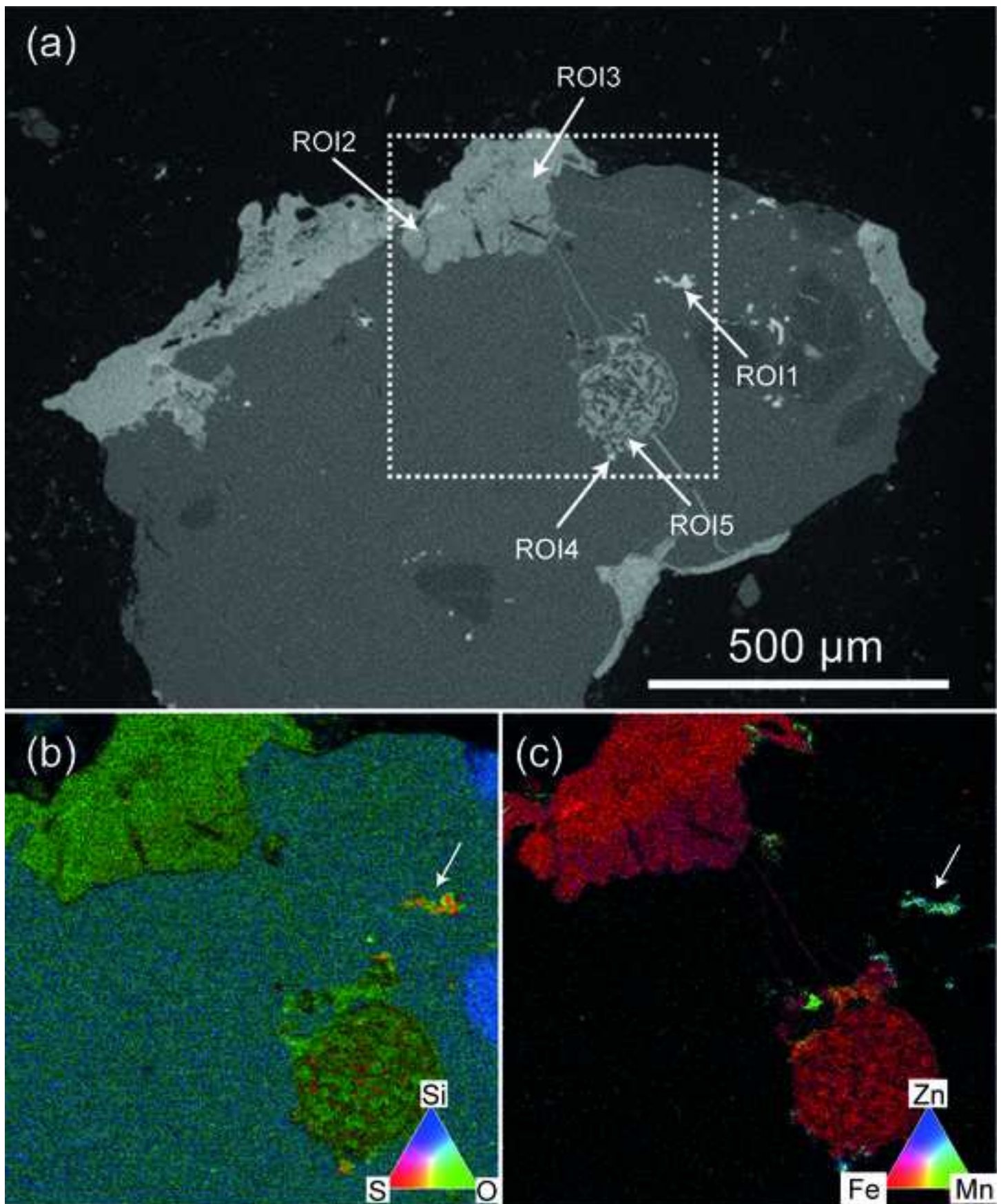


Figure 1. Aerial photograph (1951) of the Union site (red) and location of the main industries (white). The parcel of study is located in the orange square.

Figure 2. Soil profile. A General overview. B. Details of the central zone of the profile. C. Schematic representation of the soil profile.

Figure 3. Fe extracted by pyrophosphate (a) and DCB (b) throughout the soil profile (normalized by the total amounts in Fe of each sample).

Figure 4. Iron (hydr)oxide showing a texture of melting-quenching (in sample A1).

Figure 5. Fe-K edge XANES spectra (a) and corresponding first derivatives (b) and (c) of the composite samples from the Technosol profile located at the following range of depth: 0-10 cm (replicates A1 and A3), 30-40 cm (replicates C1 and C3), 110-130 cm (replicates E1 and E3) and 175-185 cm (replicates F1 and F3). For the replicate samples A3, C3, E3 and F3, only the first derivatives are given.

Figure 6. Fe-S bearing phases dispersed in a silicate mineral in the composite sample F1 (175-185 cm).

Figure 7. Least squares fit of EXAFS spectrum for A1 (0-10 cm, replicate N°1) and E1 (110-130 cm, replicate N°1) composite sample with a combination of ferrihydrite reference (Nat fhyd) and F1 composite sample (175-185 cm, replicate N°1).

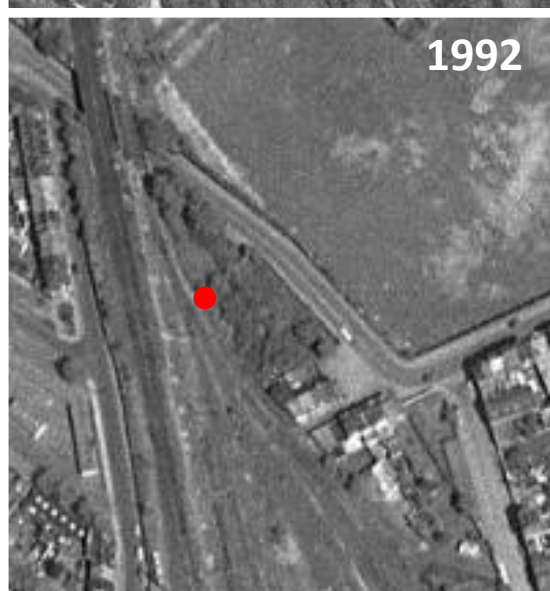
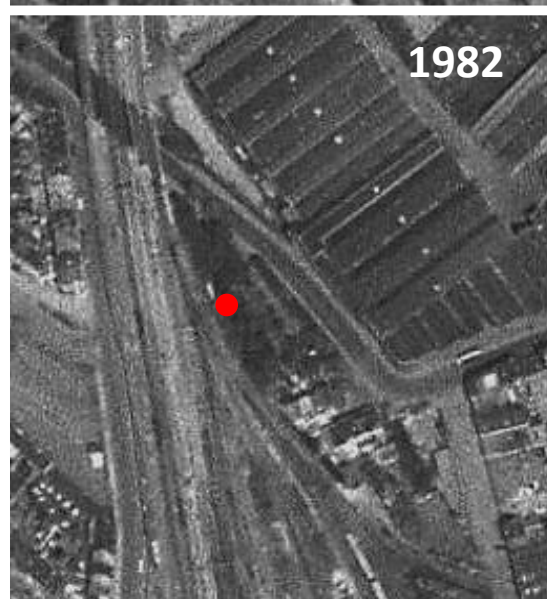
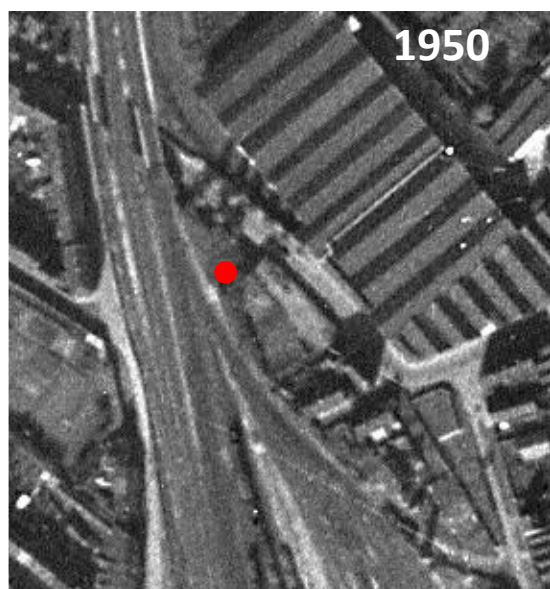
Figure 8. Zn-K edge XANES spectra of the composite samples from the Technosol profile for two sets of replicate samples located at the following range of depth: 0-10 cm (replicates A1 and A3), 30-40 cm (replicates C1 and C3), 110-130 cm (replicates E1 and E3) and 175-185 cm (replicates F1 and F3)., and Zn-K edge XANES spectra of Zn-sorbed ferrihydrite reference sample.

Figure 9. Fe, Mn and Zn released by leaching (% extracted from the total Fe, Mn and Zn content).

Figure 10. a. Zn extracted by pyrophosphate throughout the soil profile (normalized by the total amounts in Zn of each sample). b. Mn and Zn extracted by DCB throughout the soil profile (normalized by the total amounts in Mn and Zn of each sample).

Figure 11. Quantitative elemental mapping showing distribution of Si, S and O (map b) and Fe, Zn and Mn (map c) of a selected grain in LM2.

Figure 12 Quantitative elemental mapping showing distribution of Si, S and O (map b) and Fe, Zn and Mn (map c) of a selected grain in LM2. The white arrow in maps b and c indicate a specific Zn, Fe, Mn and S bearing phase.



Study of aerial photographs between 1950 and 2016. The red dot indicates the location of the chosen pit.