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1     **Composition and molecular scale structure of nanophases formed by**  
2                     **precipitation of biotite weathering products**

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11    **Abstract**

12  
13    Because of their large surface area and reactivity, nanometric-size soil mineral phases  
14    have a high potential for soil organic matter stabilization, contaminant sorption or soil  
15    aggregation. In the literature, Fe and Al phases have been the main targets of batch-  
16    synthesized nanomineral studies while nano-aluminosilicates (Al and Si phases) have  
17    been mainly studied in Andic soils. In the present work, we synthesized secondary  
18    nanophases of Fe, Al and Si. To simulate a system as close as possible to soil conditions,  
19    we conducted laboratory simulations of the processes of (1) biotite alteration in acidic  
20    conditions producing a Al Si Fe Mg K leachate solution and (2) the following  
21    neoformation of secondary nanophases by titrating the leachate solution to pH 4.2, 5  
22    and 7. The morphology of the nanophases, their size, crystallinity and chemistry were  
23    characterized by TEM-EDX on single particles and their local atomic structure by EXAFS  
24    (Extended X-ray Absorption Fine Structure) at the Fe absorption K-edge. The main  
25    nanophases formed were amorphous particles 10 to 60 nm in size whose composition  
26    (dominated by Fe and Si) was strongly controlled by the pH conditions at the end of the  
27    titration. At pH 4.2 and pH 7, the structure of the nanophases was dominated by the  
28    polymerization of Fe, which was hindered by Al, Si, Mg and K. Conversely, at pH 5, the  
29    polymerization of Fe was counteracted by precipitation of high amounts of Si. The  
30    synthesized nanophases were estimated to be rather analogous to nanophases formed in  
31    natural biotite-bearing soils. Because of their small size and potential high surface

32 reactivity, the adsorption capacities of these nanophases with respect to the OM should  
33 be revisited in the framework of soil C storage.

## 34 **1 Introduction**

35 Because of their large surface area, large percentage of surface atoms with  
36 unbalanced charge and large number of surface functional groups per unit of mass,  
37 nanometric-size mineral phases have a high potential for soil organic matter  
38 stabilization (Levard et al., 2012; Qafoku, 2010), contaminant adsorption, (Levard et al.,  
39 2009) or soil aggregation (Asano and Wagai, 2014) . These natural nanoparticles (NPs)  
40 may occur either as « mineral NPs » (defined as minerals that can also exist in larger  
41 sizes) or as « nanominerals » (defined as minerals that only exist at the nanometric  
42 scale) (Hochella et al., 2008).

43 In surface environments, Fe and Al systems have been the main subjects of previous  
44 studies due to soil observations (Kaiser and Guggenberger, 2000) as well as due to the  
45 poor solubility of Fe and Al species in most soil pH and redox conditions (pH above  $\approx 2$   
46 for Fe in oxidative conditions and pH above  $\approx 5$  for Al). However nanominerals other  
47 than Al and Fe oxy-hydroxides are known to form in surface systems, one of the best  
48 known examples being the Al and Si imogolite/allophane phases (Basile-Doelsch et al.,  
49 2007; Basile-Doelsch et al., 2005; Basile-Doelsch et al., 2015; de Junet et al., 2013; Torn  
50 et al., 1997).

51 Released by the continuous alteration of the primary minerals, Al, Si, Fe, etc. can form  
52 nanominerals at the surface of the primary mineral or at a distance from the initial  
53 altered surfaces. Direct formation of nanophases by the weathering of rock material has  
54 been described in oxic waters (Faimon, 2003; Zänker et al., 2006). In presence of organic  
55 matter, these newly formed nanophases can complex the organic compounds and  
56 stabilize them for extended periods of time. The conceptual model proposed by Basile-  
57 Doelsch et al. (2015) represents this mechanism. To validate the model, it is necessary to  
58 show that (1) the products of the alteration of primary minerals are likely to form  
59 nanophases and (2) these nanophases complex the OM. In this paper, we focus on step  
60 (1). We characterized the chemical nature and the structure of the nanophases formed  
61 from the elements resulting from the alteration of a primary mineral in the absence of  
62 OM. For this purpose, we considered biotite as a common soil primary mineral able to

63 provide a complex combination of elements (Fe, Al, Si, Mg and K) via weathering.

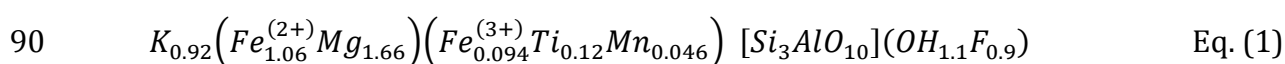
64 The formation of nanophases from a solution requires a polymerizing step by  
65 hydrolysis of metallic cations like Fe or Al (Doelsch et al., 2000; Manceau and Drits,  
66 1993; Rose et al., 1997). In oxic conditions and at pH higher than 3-4, Fe<sup>3+</sup> for instance, is  
67 known to be insoluble and reactive. (Byrne et al., 2000; Dousma and Debruyne, 1976;  
68 Rose and Waite, 2003). Polymerization steps start from elementary monomeric building  
69 blocks such as [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> octahedron and are accomplished via intramolecular  
70 condensation that initially involves deprotonation (Combes et al., 1989; Rose et al.,  
71 1997). Formation of small clusters via edge and double corner sharing between Fe  
72 octahedra is all included in the initial stage of “nucleation” which is followed by later  
73 stages of growth and aggregation (Rose et al., 1997; Wells, 1984). Polymerization routes  
74 have also been found for Al, with the formation of a transient Al<sub>13</sub> polymer (Bottero et  
75 al., 1980). It has been shown that Si can strongly impair the polymerization stages in  
76 both elements (Doelsch et al., 2000; Lartiges et al., 1997).

77 Our experimental protocol combined a weathering step that provided a complex  
78 solution of Fe, Si, Al, K and Mg cations, followed by the polymerization of nanophases in  
79 a range of pH corresponding to soil conditions (pH 4.2, 5 and 7). The atomic structures  
80 of the nanophases were determined by Fe k-edge EXAFS (Extended X-ray Absorption  
81 Fine Structure) spectroscopy and size, shape, crystallinity and chemical composition by  
82 TEM-EDX. Three main questions are raised in this paper: (1) Does the proposed  
83 experimental protocol make it possible to obtain nanophases? (2) Are the polymerized  
84 nanophases homogeneous or of variable chemical composition? (3) Are the nanophases  
85 obtained representative of phases that can form in soils?

## 86 **2 Materials and Methods**

### 87 **2.1 Experimental protocol**

88 The biotite studied comes from Bancroft, Ontario Canada (Ward Science) (Turpault  
89 and Trotignon (1994)):



91 Biotite was mechanically ground (< 50 μm) in a zirconium oxide ‘ball mill’ setup,  
92 washed, sieved with ultra pure water and dried at 40°C.



93 *Dissolution step:* 33 g of < 50  $\mu\text{m}$  biotite particles were placed in 1L of pH=2  $\text{HNO}_3$   
94 solution (solid:liquid ratio of 1:30). After 29 days, the dissolved species were separated  
95 from non-weathered biotite particles using Tangential Filtration flow (TFF) (Spectrum  
96 Labs) at a cut-off size of 10 kD (pore size of  $\sim 2$  nm). The filtered solution is hereafter  
97 referred to as 'leachate solution'. Concentrations of dissolved species in the leachate  
98 solution were monitored with an inductively coupled plasma atomic emission  
99 spectrophotometer (ICP-AES, Horiba Jobin-Yvon "Ultima C", Longjumeau, France). The  
100 measurement uncertainty was < 10%. The preliminary experimental setup that  
101 contributed to the design of the above dissolution protocol is detailed in supplementary  
102 information (Figure A1 and Table A1).

103 *Polymerization step:* Nanophases were precipitated by increasing the pH of the  
104 leachate solution. The initial pH (2) was raised by adding 0.2N NaOH (Sigma Aldrich) at  
105 a constant rate of 70  $\mu\text{L}/\text{min}$  (785 DMP Titrino). Pyrex beakers and stir bars were used.  
106 Three final pH values were targeted: 4.2, 5 and 7. To determine the target pH values, a  
107 preliminary titration curve of the leachate solution was performed (Figure A2). The  
108 slope of this curve changed at pH 4.2 and 5. The variations in slope pointed to changes in  
109 the nature of the hydrolyzing system, inferring correlative changes in the nature and/or  
110 structure of the polymerized phases. At pH 7, the addition of NaOH no longer had an  
111 effect on polymerisation. The durations of titration were 1.4, 1.5 and 1.67 hours at pH  
112 4.2, 5 and 7 respectively. When the target pH was reached, a 1 ml aliquot of sample was  
113 collected for TEM-EDX analyses and the remaining solution was ultra-centrifuged at 80  
114 000 rpm for 2 h to separate precipitated nanophases from the dissolved species. The  
115 settled particles were freeze-dried for EXAFS analyses. The whole experimental protocol  
116 is summarized in Figure A3.

## 117 **2.2 TEM images and analyses**

118 Images were obtained and chemical analyses of nanophases were performed using a  
119 transmission electron microscope coupled with an EDX analyzer (JEOL JEM 2011 TEM).  
120 For each sample, EDX analyses were performed on a set of around 40 nanophases of  
121 different sizes. The parameters were 50 000X magnification, an angular tilt of  $20^\circ$   
122 toward the detector, energy range of 40 keV, and corrected counting time of 30 s. A  
123 constant beam density was set at  $\sim 63.5$  pA.cm<sup>-2</sup>. Fe, Si, Al, K, and Mg were quantified

124 using the Bruker AXS MET line mark data quantification procedure (Berthonneau et al.,  
125 2014). The size of each EDX-analyzed nanoparticle was subsequently measured on the  
126 corresponding micrograph.

### 127 2.3 EXAFS at the Fe K edge

128 Extended X-ray absorption fine structure (EXAFS) spectroscopy at the Fe K-edge data  
129 was performed at the ESRF synchrotron source on the FAME beam line (Grenoble,  
130 France) and on beam line 11.1 at the ELETTRA synchrotron (Trieste, Italy). Spectra  
131 were acquired using Si(220) and Si(111) double crystal monochromators at the ESRF  
132 and ELETTRA for the samples and the references respectively. Spectra were acquired at  
133 ambient conditions in both transmission and fluorescence modes (30-element solid-  
134 state Ge detector (Canberra, France)). All the samples were pressed into 5 mm diameter  
135 pellets mixed with boron nitride as a dilution agent. Each spectrum comprised an  
136 average of 3 to 5 individual spectra taken 107 eV below and 849 eV ( $14.75 \text{ \AA}^{-1}$ ) above  
137 the absorption edge of Fe (7112 eV) at a counting rate of 2-9 seconds until  $14.75 \text{ \AA}^{-1}$ . To  
138 get representative spectra and minimize the risk of beam damage, each spectrum was  
139 collected at a different pellet location. Data were treated using Athena software (Ravel  
140 and Newville, 2005). All radial distances in the RDF (Radial Distribution Function) were  
141 not corrected for phase shift (Figure 3b). According to the relation  $\Delta R = \pi/2k$ , the  
142 minimum distance resolution of  $0.11 \text{ \AA}$  was achieved.

143 A two-stage approach was used for the quantitative analysis of EXAFS data. The first  
144 stage consisted of using linear combination fitting (LCF) based on EXAFS spectral library  
145 of reference compounds. The second stage consisted of shell by shell fitting (SSF) to  
146 investigate the atomic environment of Fe. The two quantitative methods were  
147 performed at all three pH. The results of the two methods were in agreement. Only the  
148 SSF method is described in the paper because this method provided additional  
149 information on the local structure. Details of the LCF are presented in supplementary  
150 information.

151 Goethite, Ferrihydrite, Fe short range order (Fe-SRO) phase and Fe dimers were used  
152 as references. Goethite provides the highest Fe polymerization level of all reference  
153 compounds with 4 Fe-Fe octahedra edge-sharing and 4 double corner-sharing  
154 interactions. Ferrihydrite is characterized by fewer edge interactions (2 to 2.5) and  
155 double corner interactions ( $\sim 3-5$ ) than goethite (Maillot et al., 2011; Michel et al., 2007).

156 Fe-SRO is composed of Fe polymers formed in Si rich solutions. Fe polymers are  
157 characterized by 2 edge-sharing but only a 0.6 double corner interaction. Fe polymers  
158 were synthesized at pH 5 in presence of Si (Si/Fe=4), conditions in which there are no  
159 Si-O-Fe interactions (Doelsch et al., 2000; Doelsch et al., 2001). For Fe dimers only 1  
160 edge-sharing coordination has been described (Rose et al., 1996)). (See Supplementary  
161 Information for details on reference samples).

162 Shell by shell fitting (SSF) was used to extract structural information such as the  
163 coordination number ( $N_j$ ) and interatomic distances ( $R_j$ ) relative to the absorber atom  
164 using the software code Artemis (Ravel and Newville, 2005). The contributions of the  
165 different atomic shells were assessed using back-Fourier transform of the pseudo-radial  
166 distribution function. These partial EXAFS functions were then least-squares fitted by a  
167 theoretical function (in the single-scattering approximation) in order to determine the  
168 structural and chemical parameters of the atomic neighbors in the atomic shells around  
169 Fe. Uncertainties for radial distances remained within a conservative  $\pm 0.02$  Å range  
170 typical in the determination of this parameter (Pokrovski et al., 2002). Varying the k  
171 weight magnified or eliminated different sections of the EXAFS signal. A k weight of 3  
172 was used for SSF techniques. To determine an appropriate value for  $E_0$  and amplitude  
173 reduction factor ( $S_0^2$ ), the lepidocrocite spectrum with pre-confirmed structural  
174 information was used to set those values to 2eV ( $\pm 2$ eV) and 0.75 respectively. It is worth  
175 noting that in complex media, various fits of similar quality can be obtained. It is  
176 therefore important to recall that structural results are not necessarily univocal.

## 177 **3 Results**

### 178 **3.1 Chemical composition of the leachate solution and conditions for the** 179 **formation of nanophases**

180 The chemical composition of the leachate solution is presented in Table 1. Fe, Mg and  
181 Si were the main contributors to the leachate solution, while Al and K contributed to a  
182 lesser extent. Mn and Ti concentrations were negligible (Figure A1) and were not  
183 included in the atomic proportions.

184 The preliminary titration experiment of the leachate solution (Figure A2) showed  
185 that pH 4.2, pH 5 and pH 7 were the values at which changes in the polymerization

186 regime could be expected. Theoretically, nanophases formed at these three different pH  
187 should thus reveal differences in chemical composition and/or atomic structure.

## 188 **3.2 TEM-EDX characterization of nanophases**

189 Polymerization experiments resulted in nanophases obtained at three final pH 4.2, 5  
190 and 7. Collected masses of nanophases ranged between 11 to 15 mg. Regardless of the  
191 pH, particles were aggregated, forming distinct clusters of small and large particles  
192 (Figure 1). The size distribution showed a bimodal Gaussian fit with maxima at 6 ( $\pm 3.7$ )  
193 nm and 30 ( $\pm 15$ ) nm.  $\sim 15$  nm was the cut-off size between smaller and larger particles.  
194 Volume estimates showed that the volume of larger particles was 50 times larger than  
195 the volume of smaller particles. Electron diffraction analyses revealed a diffuse pattern  
196 across all pH and particle sizes (Figure 1).

197 Fe and Si mainly composed the nanophases regardless of the pH and size range  
198 (Figure 2 A and B). The proportions of Fe and Si were higher than in the leachate  
199 solution, indicating preferential polymerization of Fe and Si compared with the other  
200 elements. The proportions of Al in the nanophases were close to those in the leachate  
201 solution. The contribution of Al was limited, even at  $\text{pH} \geq 5$  when polymerization of Al  
202 was theoretically expected. The proportions of K and Mg in the nanophases were in the  
203 same range as that of Al. However, they were significantly depleted in the nanophases  
204 compared to in the leachate solution. Finally, in terms of general trends as a function of  
205 pH, pH 5 represented a singular case in which the large particles were extremely Si  
206 enriched and Fe and Al depleted.

## 207 **3.3 EXAFS at the Fe K-edge: iron atomic range structure**

### 208 **3.3.1 Comparison of raw data**

209 The structural interactions between Fe octahedra are represented as signals at  $\sim 5.2$   
210  $\text{\AA}^{-1}$  and  $\sim 7.5 \text{\AA}^{-1}$  on the EXAFS spectra (Figure 3a and Figure B1) (Mikutta, 2011; Mikutta  
211 et al., 2010; Pokrovski et al., 2003). These interactions were also observed as peaks in R-  
212 space at radial distances of  $\sim 2.7 \text{\AA}$  and  $\sim 3.2 \text{\AA}$  corresponding to edge and double corner  
213 sharing interactions respectively (Figure 3b) (Rose et al., 1997). In transiting from the  
214 'goethite and 2L ferrihydrite' to 'Fe-SRO and Fe dimers' references, i.e. with decreasing  
215 Fe octahedra polymerization, the weak intensity in k-space at  $\sim 5.2 \text{\AA}^{-1}$  converted into a

216 faint shoulder and the intensity of the  $\sim 7.5 \text{ \AA}^{-1}$  feature decreased. The above change in  
217 crystalline order was also seen in R-space with the double corner peak at  $\sim 3.2 \text{ \AA}$   
218 disappearing and peak at  $\sim 2.7 \text{ \AA}$  decreasing in intensity. In the reference standards, the  
219 locations of these Fe-Fe markers changes from a shoulder to a fully formed peak as the  
220 Fe polymerization increases from Fe dimers to Goethite. This increase in Fe  
221 polymerization is accompanied by shift in location of the signals from lower to higher  
222 wavenumber values.

223 Features at  $\sim 5.2 \text{ \AA}^{-1}$  and  $\sim 7.5 \text{ \AA}^{-1}$  on the experimental EXAFS spectra showed that iron  
224 polymers larger than dimers were formed during the precipitation steps at each pH  
225 (Figure 3). Phases formed at the pH 4.2 produced a spectrum for the above-mentioned  
226 Fe-Fe markers whose intensity was between that for goethite and 2L ferrihydrite. These  
227 phases produced distinct structural signals with the highest intensity of all the samples  
228 (Figure 3). For pH 5 and 7 phases, collective comparison of k and R-space spectra gave  
229 an average between 2L ferrihydrite and Fe-SRO references. The intensities of these two  
230 samples were weaker than that of the pH 4.2 sample.

### 231 3.3.2 Quantitative analysis of EXAFS data using shell by shell fitting

232 In all samples, the first coordination sphere around iron was composed of oxygen  
233 atoms at a distance of  $1.96 \pm 0.02 \text{ \AA}$  (Table 2). The coordination number varied from 6.3-  
234  $6.5 \pm 1.3$  for pH 4.2 and pH 7. This result showed the formation of iron octahedra as the  
235 main iron species. However, at pH 5, the coordination number was significantly lower  
236 ( $4.9 \pm 1.0$ ). This number was either related to iron octahedra considering the 15-25%  
237 range error (2000; O'Day et al., 1994) or to the presence of a proportion of tetrahedral  
238 coordinated iron like in ferrihydrite due to a Keggin-like motif (Maillot et al., 2011;  
239 Michel et al., 2007).

240 The SSF of the second and third coordination spheres of all samples was performed  
241 by successively testing Fe-Fe, Fe-Si and Fe-Al atomic pairs. R-factors of all three atomic  
242 shell fits were systematically better than two atomic shell fits. Only three shell fits were  
243 selected (Figure 4). Detailed steps in the SSF for all three phases are given in Figures C2.  
244 For the pH 4.2 sample, the best solution was obtained with Fe in the 2<sup>nd</sup> atomic shell  
245 with  $N_{\text{Fe}2} = 1.5 \pm 0.3$  at  $R_{\text{Fe-Fe}2} = 3.01 \pm 0.02 \text{ \AA}$  and Fe in the 3<sup>rd</sup> atomic shell with  $N_{\text{Fe}3} = 1.9 \pm 0.4$   
246 at a distance of  $R_{\text{Fe-Fe}3} = 3.38 \pm 0.02 \text{ \AA}$ . The interatomic distances were in agreement with  
247 Fe-Fe octahedra edge and double corners sharing. The total Fe-Fe coordination number

248 (N=3.4±20%) indicates a low level of polymerization (Table B1 and B2). For the pH 5  
249 sample, two solutions had almost equal quality of fit (only differing in the path used for  
250 the 3<sup>rd</sup> atomic shell). The first solution used Fe-Fe<sub>2</sub> edge sharing interaction at  
251 R=3.01±0.02 Å with N<sub>Fe2</sub>=1.1±0.2 and Fe-Si (or Al) path at R=3.18±0.02 Å with  
252 N<sub>Si</sub>=3.9±0.8. The Fe-Si (Al) distance corresponded to a single corner sharing between the  
253 Fe octahedron and the Si (or Al) tetrahedron. The second solution only used Fe-Fe  
254 octahedra edge sharing with Fe-Fe<sub>2</sub> at R=2.99±0.02 Å with N<sub>Fe2</sub>=1.2±0.2 and Fe-Fe<sub>3</sub> path  
255 at R=3.13±0.02 Å with N<sub>Fe3</sub>=0.6±0.1. However, in both cases, the Fe-Fe coordination  
256 number (1.1-1.8±20%) was much smaller than for the pH 4.2 sample. For the pH 7  
257 sample, the best fits showed 3 solutions. The fit with the Fe-Fe<sub>2</sub> edge sharing path at  
258 R=3.07±0.02 Å with N<sub>Fe2</sub>=3.4±0.7 and the Fe-Fe<sub>3</sub> double corner sharing path at  
259 R=3.36±0.02 Å with N<sub>Fe3</sub>=0.5±0.1 could be the most reliable solution, according to the Fe  
260 dominant composition of the nanophases. Whatever the solution, at pH 7, the total Fe-Fe  
261 coordination number (2.5-3±20%) was higher than at pH 5 but lower than at pH 4.2.

## 262 4 Discussion

### 263 4.1 Biotite dissolution rate and physical-chemical conditions of polymerization in 264 batches

265 The proportions of Fe, Si, Al, K and Mg in the leachate solution (Table 1) differed from  
266 those in stoichiometry in biotite (Figure A1b). These proportions showed, as expected,  
267 that the dissolution of biotite is incongruent (Kalinowski and Schweda (1996); Turpault  
268 and Trotignon (1994); Bonneville, et al., 2009; Bonneville et al. (2011)). However, the  
269 calculated dissolution rates (Table A1) were slower than the values reported in the  
270 literature (see Bonneville et al. (2011) for a review). A 10 kD filtration was applied in  
271 our protocol. This ~2 nm cutoff allowed the truly dissolved components to be retrieved  
272 separately from the undissolved colloidal particules (Buffle and van Leeuwen, 1992;  
273 McCarthy and Zachara, 1989). By comparison, the most frequently used filtration  
274 protocols in other studies utilized filters with a cutoff size of 200 nm (Bonneville et al.,  
275 2011; Bray et al., 2015) to define the threshold for dissolved species. This difference  
276 may explain the observed slower dissolution rates in our experiments. We thus obtained  
277 a solution with elemental proportions that are representative of the weathering of a

278 mineral (Table 1). This composition is therefore more representative of soil solutions  
279 than solutions produced by commercial metal salts as well as solutions that consider  
280 only Fe and Al ions in the formation of nanophases (Kleber et al. (2015) and references  
281 therein).

282 As revealed by TEM, the polymerization step enabled the formation of nanophases at  
283 pH 4.2, 5 and 7. These values correspond to realistic pH values in soils (Schwertmann  
284 and Murad, 1983; Yong and Phadungchewit, 1993). Moreover, experimental  
285 polymerization involves rapid changes in pH. Such abrupt variations have also been  
286 observed at very small spatial scales (Bonneville et al., 2011) on biotite surfaces.  
287 Consequently, the batch approach used in our protocol, although greatly simplified  
288 compared to a soil system, made it possible to reproduce physical-chemical conditions  
289 that realistically mimic soil processes.

## 290 **4.2 Local structure of nanophases**

### 291 **4.2.1 The presence of Al, Si, Mg and K in the system limits Fe polymerization**

292 The coordination number ( $N_{tot}$ ) is a direct proxy for the degree of polymerization.  
293 The levels of polymerization of the nanophases synthesized in our experiments were  
294 less than 3.4 whatever the pH (Figure 5). This value is lower than the number of Fe-Fe  
295 bonds in polymers synthesized in pure Fe systems (Combes et al., 1990; Combes et al.,  
296 1989; Doelsch et al., 2000). The same difference in values was also observed in systems  
297 in which Fe is hydrolyzed in presence of Si (Doelsch et al., 2003; Doelsch et al., 2000;  
298 Doelsch et al., 2002; Doelsch et al., 2001; Pokrovski et al., 2003). In our case, the  
299 presence of Al, Si, Mg and K in the solution clearly hinders the polymerization of Fe  
300 regardless of pH.

### 301 **4.2.2 The pH controls the local structure of nanophases**

302 At pH 4.2, the level of polymerization of the nanophases was the highest of our  
303 experiments (Figure 5) and Fe was the main element in the nanophases (Figure 2). Fe-  
304 Fe bonds with double corner interactions dominated the local structure. The number of  
305 edge interactions was lower than double corners interactions (Figure 5). These  
306 polymers are therefore structured in three dimensions, resembling the local structure of  
307 the polymers described in systems where Fe polymerizes in the presence of Si at a pH  
308 close to 3 (Doelsch et al., 2000; Pokrovski et al., 2003). The occurrence of Fe-O-Si bonds



309 between Fe octahedra and Si-tetrahedra was not observed (Table 2), which is consistent  
310 with the Fourier transformed infrared (FTIR) results obtained in conditions similar to  
311 our systems (Si/Fe = 1, pH 3) (Doelsch et al., 2001).

312 At pH 7, Fe was still the main element (Figure 2) but its degree of polymerization was  
313 slightly lower than that at pH 4.2. However, unlike pH 4.2, the octahedra were mostly  
314 bounded by their edges (Figure 5), forming rather planar local structures. Again, the  
315 system we studied behaved in a quite similar way to the Fe polymerization systems in  
316 the presence of Si (Doelsch et al., 2000; Doelsch et al., 2001). Moreover, these authors  
317 showed by FTIR the existence of Fe-O-Si bonds at pH 7, in agreement with the third  
318 layer of our quantification by SSF (Table 2).

319 At pH 5, the level of polymerization of Fe was significantly lower than that of the  
320 structures observed at pH 4.2 and 7 (Figure 5). The number of edge interactions was  
321 slightly greater than the number of double corners. This local structure is therefore  
322 quite close to a mixture of dimers and trimers. Quantification by SSF suggests the  
323 potential presence of Fe in tetrahedral form in the local structure as observed by  
324 (Pokrovski et al., 2003), but without clearly demonstrating it. On the other hand, like at  
325 pH 7, SSF analysis (Table 2) suggests the existence of Si-O-Fe bonds that correspond to  
326 the FTIR results obtained at pH 5 for Si/Fe = 1 (Doelsch et al., 2001). Thus, unlike the  
327 nanophases formed at pH 4.2 and 7, the composition of the nanophases formed at pH 5  
328 is largely dominated by Si (Figure 2). Fe is present only as dimers and trimers, probably  
329 isolated in an amorphous silica matrix. The polymerization of Fe at pH 5 was thus  
330 counteracted by the polymerization of high amounts of amorphous Si. Thermodynamic  
331 and/or kinetic mechanisms that control the variations in the proportions of Fe and Si in  
332 the nanophases as a function of pH remain to be explained.

### 333 **4.3 Two stages of precipitation: growth and maturation**

334 The individual nanophases had two particle size ranges (Figure 1) regardless of the  
335 pH considered. The differences in chemical composition as a function of size are better  
336 illustrated in the Fe, Si and Al ternary diagram in Figure 6. Regardless of pH, the  
337 chemical composition of the smaller particles was close to that of the initial leachate  
338 solution, with a slight enrichment in Fe. Two hypotheses can be proposed to highlight  
339 the chemical heterogeneity as function of the particle size. First, since no time series  
340 experiments were conducted the two particle types could have been formed from



341 different precursors or second, the difference may be due to a maturation/aging  
342 mechanisms. In the case of the second hypothesis, the smallest particles could be the  
343 first nanometric phases that polymerize during titration. They could derive from the  
344 rapid growth of the initial nuclei. The chemical compositions of the larger particles  
345 differed from those of the smaller particles at the same pH. They were enriched in Fe at  
346 pH 4.2 and pH 7, and enriched in Si at pH 5. The difference in the composition of the  
347 larger and smaller particles means that simple aggregation of the smaller particles  
348 cannot explain the formation of the larger particles. Instead, we propose that these  
349 particles could be formed after the titration step, when the pH is stable, by a stage of  
350 maturation. Maturation (e.g. Ostwald ripening (Voorhees, 1985)) is a stage of  
351 dissolution/precipitation: the most unstable small particles as a result of the large  
352 surface area can be dissolved and re-precipitation occurs on the surface of other  
353 growing particles. The composition and structure of the nanophases formed during the  
354 hypothesized stage of maturation appeared to be strongly controlled by the pH  
355 conditions.

356 The TEM results thus tend to indicate two polymerization steps in the formation of  
357 nanophases: we propose a first initial growth, and second maturation. It is important to  
358 note that data from EXAFS were unable to distinguish between the two stages of  
359 polymerization. EXAFS information is still an average signal over all particle size ranges  
360 within a given sample. However, the observed structural differences, in particular the  
361 contribution of Si to the structure of the particles at pH 5 (Table 2 and Figure 5) tends to  
362 show that the EXAFS signal of the polymerized phases was rather dominated by the  
363 structure of the larger particles.

#### 364 **4.4 Synthetized nanophases are representative of nanophases formed in surface** 365 **environments**

366 In order to test the representativeness of the products formed in our experiment as  
367 analogues to nanophases formed in surface environments, we compared the particles  
368 synthesized with two types of nanophases naturally formed: the altered layer formed at  
369 the surface of biotite and the nanophases formed at a distance from the initial altered  
370 surfaces.

371 The study of Bonneville et al. (2011) is particularly relevant to compare our results  
372 with a layer of biotite alteration, since these authors reproduced the chemical alteration

373 processes at mineral-mycorrhiza interface, representing the hotspot of the weathering  
374 engine at work in soils. The composition of the nanophases formed in our pH 5  
375 experiments are reported in Figure 7 together with their results averaged over the 20  
376 nm thick altered-biotite zone. The comparison shows very similar compositions  
377 between nanophases formed in batch at pH 5 and the products of the surface layer  
378 altered biotite. Moreover, these authors also measured pHs at the mineral-mycorrhiza  
379 interfaces, varying from values below 4.6 up to 5.8. The nanophases formed in our pH 5  
380 experiments can therefore be considered to be formed under rather similar conditions.

381 Even though the chemical compositions of nanophases pH 5 and biotite-altered layer  
382 seemed similar, comparison of local atomic structures was more complex. In an earlier  
383 study, Bonneville et al. (2009) identified the presence of vermiculite and ferrihydrite in  
384 the altered biotite layer. These observations were consistent with those of Murakami et  
385 al. (2003) who, using high resolution TEM, observed these gradual mineralogical  
386 transformations in addition to the presence of chlorite. On the other hand, other studies  
387 tended to show that the alteration layer formed on the mineral surface is amorphous.  
388 The mechanism proposed is no longer a gradual transformation associated with the  
389 preferential diffusion of selected ions, but a process of interfacial dissolution-  
390 reprecipitation (Hellmann et al., 2015; Hellmann et al., 2003; Hellmann et al., 2012). The  
391 results obtained by Kawano and Tomita (2001) on an altered natural bytownite, which  
392 showed alteration of the amorphous layer, also support the latter process. In the case of  
393 an amorphous surface alteration layer, the nanophases synthesized by our protocol  
394 could be good analogs of the surface processes of the minerals.

395 Concerning the second type of nanophases (neofomed nanophases in soils at a  
396 distance from the altered mineral surface), the nanophases in our study may also be  
397 analogs of natural secondary nanomineral phases. Only a few authors have studied the  
398 composition and local atomic structure of such nanophases. Dai et al. (2014) observed  
399 the formation of nanoparticle aggregates after experimental alteration of bentonite by  
400 bacteria. SEM-EDX analyses showed that the nanoparticle aggregates were composed of  
401 Si, Na, Ca, Mg, Al, Fe, K. Wen et al. (2014) also extracted nanophases in a <450 nm  
402 fraction that exhibited Al, Si and Fe compositions and amorphous structures. These two  
403 studies demonstrate that not only Al and Fe, as classically described in literature, but  
404 also other elements such as Si, Na, K, Mg, and Ca may be involved in the formation  
405 secondary nanophases in surface environments. It is therefore probable that the

406 nanophases that were synthesized in the present work are, at least in the case of the  
407 larger particles, representative of some nanophases formed in soils, sediments or other  
408 surface environments.

## 409 **5 Conclusion**

410 This laboratory work simulated the successive processes of biotite alteration and the  
411 following neoformation of secondary phases from ions in solution. The nanophases  
412 formed were amorphous phases that polymerized in two steps: (1) the initial growth  
413 phase formed 2 to 15 nm particles whose chemical composition closely resembled that  
414 of the alteration solution; (2) the maturation phase then resulted in 15 to 60 nm  
415 particles whose compositions are strongly controlled by the pH conditions. At pH 4.2  
416 and pH 7, the structure of the nanophases was dominated by Fe but its polymerization  
417 was hindered by the presence of Al, Si, Mg and K. Conversely, at pH 5, the polymerization  
418 of Fe was counteracted by the polymerization of high amounts of amorphous Si.  
419 Surprisingly, Al appeared to play a minor role in polymerization, regardless of the pH.  
420 However, thermodynamic and/or kinetic mechanisms that control the variations in the  
421 proportions of Fe and Si in the nanophases as a function of pH remain to be explained. In  
422 comparison with previous alteration studies, the laboratory-synthesized phases of our  
423 study were estimated to be analogs of the nanophases formed in natural biotite-bearing  
424 soils at varying distances from biotite surfaces.

425 These nanophases have a high potential for contaminant sorption, aggregation  
426 processes as well as for organic matter stabilization in soils. In the framework of the C  
427 budget issues and the 4 per 1000 initiative, it would be interesting to examine the role  
428 and the mechanisms of the interactions between these Fe, Si, Al, Mg, K nanophases and  
429 soil organic matter. Like for the Fe or Al phases reported in the literature, one could  
430 expect coprecipitation processes leading to-medium to long term stabilization of C in  
431 soils.

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631  
632



633 **Figure caption**

634 **Figure 1: TEM micrographs of nanophases. For each pH, magnification increases from left to right. On 50**  
635 **nm scale images, electronic diffraction is superimposed, revealing the amorphous structure of the**  
636 **nanophases. SP: smaller particles; LP: larger particles.**

637 **Figure 2: TEM-EDX chemical analysis of polymerized particles at three pH expressed in stoichiometric**  
638 **atomic %. The box-and-whisker plots represent the median value, the upper and lower quartiles, as well as**  
639 **the min and max of the data. The chemical composition of the leachate solution (Leachate S.) is also shown for**  
640 **the sake of comparison (bold dashed line, with their respective element specific error values). A: chemical**  
641 **composition of the smaller nanophases; B: chemical composition of the larger nanophases. n: number of**  
642 **particles analyzed.**

643 **Figure 3: EXAFS (a) and RDF (b) plots. Arrows indicate locations of confirmed Fe-Fe signals. Spectra in**  
644 **black represent references. E and DC stand for edge-sharing and double corner sharing interactions**  
645 **respectively. Distances on the RDF are not corrected for phase shifts.**

646 **Figure 4: Shell-by-Shell fitting for samples pH=4.2, pH=5 and pH=7. Fit numbers refer to Table 2.**

647 **Figure 5: Changes in the coordination numbers for all Fe-Fe atomic pairs in the SSF analysis (Table 2) with**  
648 **the lowest R factors, leading to minimum (min) and maximum values (max) for each type of interaction and**  
649 **for each pH. Total represents the addition of coordination numbers by edge and double corner interactions.**  
650 **Total coordination numbers from pure Fe system from the literature are also shown for the sake of**  
651 **comparison.**

652 **Figure 6: Ternary diagrams of Fe, Si and Al atomic proportions in the nanophases formed at pH 4.2, 5 and**  
653 **7. The white star represents the initial composition of the leachate solution, the small black dots represent**  
654 **the composition of smaller nanophases and the larger grey dots the composition of larger nanophases.**

655 **Figure 7: Chemical compositions expressed as K:Si, Mg:Si, Fe:Si and Al:Si ratios measured by TEM-EDX.**  
656 **Empty circles represent the chemical composition of the surface layer of an altered biotite (Bonneville et al.,**  
657 **2011) averaged over its 20 nm thickness. Black circles represent the mean composition of the larger particles**  
658 **formed in our pH 5 experiment. Error bars are standard deviations.**

659 **Table Caption**

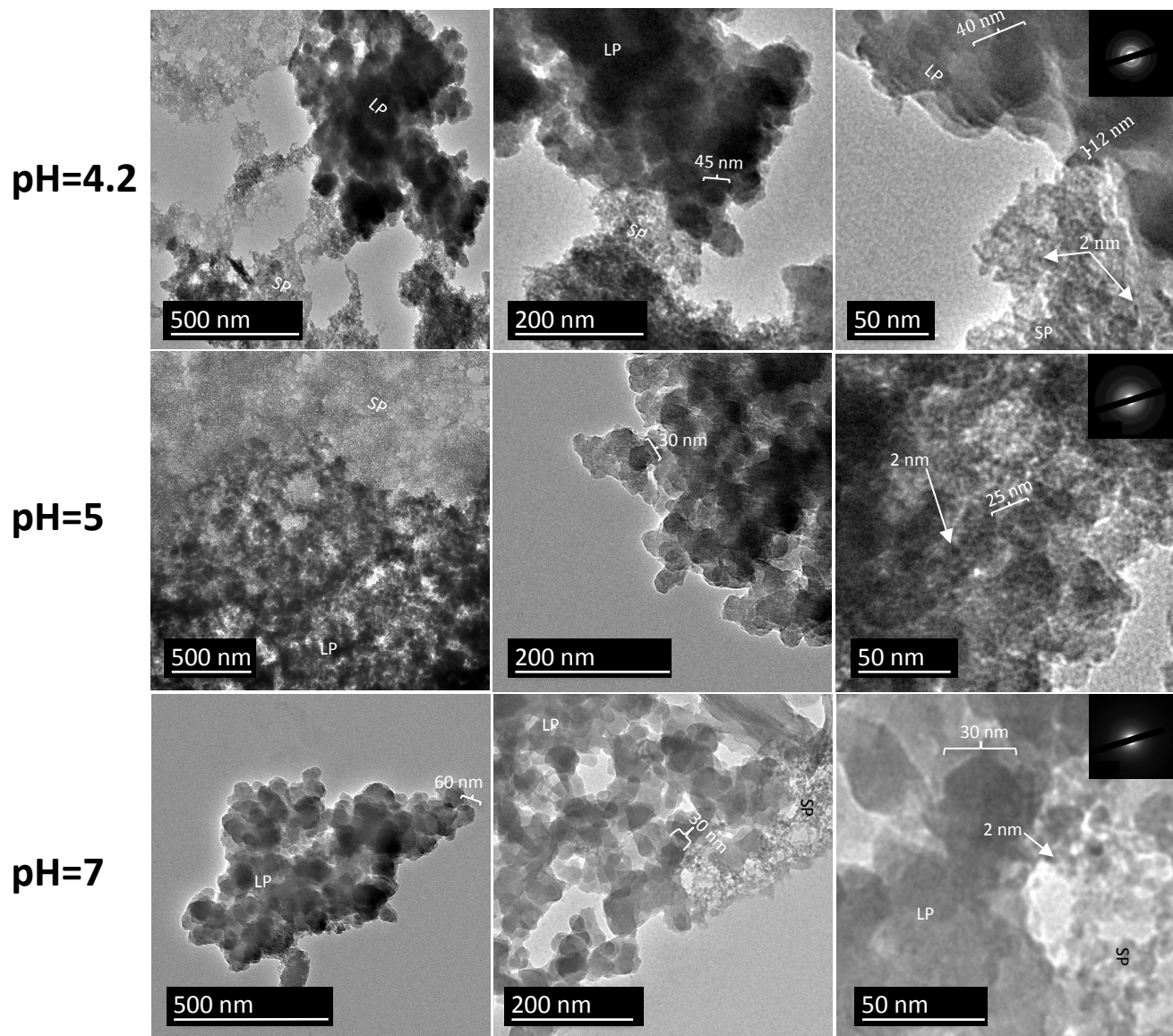
660 **Table 1: Chemical composition of the leachate solution provided by the dissolution experiment.**

661 **Table 2: SSF analysis of pH 4.2, 5 and 7 phases. The R window is the radial distance range over which the**  
662 **fit is carried out. N, R and  $\sigma$  represent the coordination number, radial distance and disorder, respectively.  $E_0$**   
663 **is the starting energy value for the fit and R-factor is a parameter for fit quality. Fe-Fe<sub>2</sub> corresponds to edge**  
664 **sharing, Fe-Fe<sub>3</sub> corresponds to double corner sharing. Fit numbers refer to the graph presented in Figure 4**  
665 **and Figure C1.**

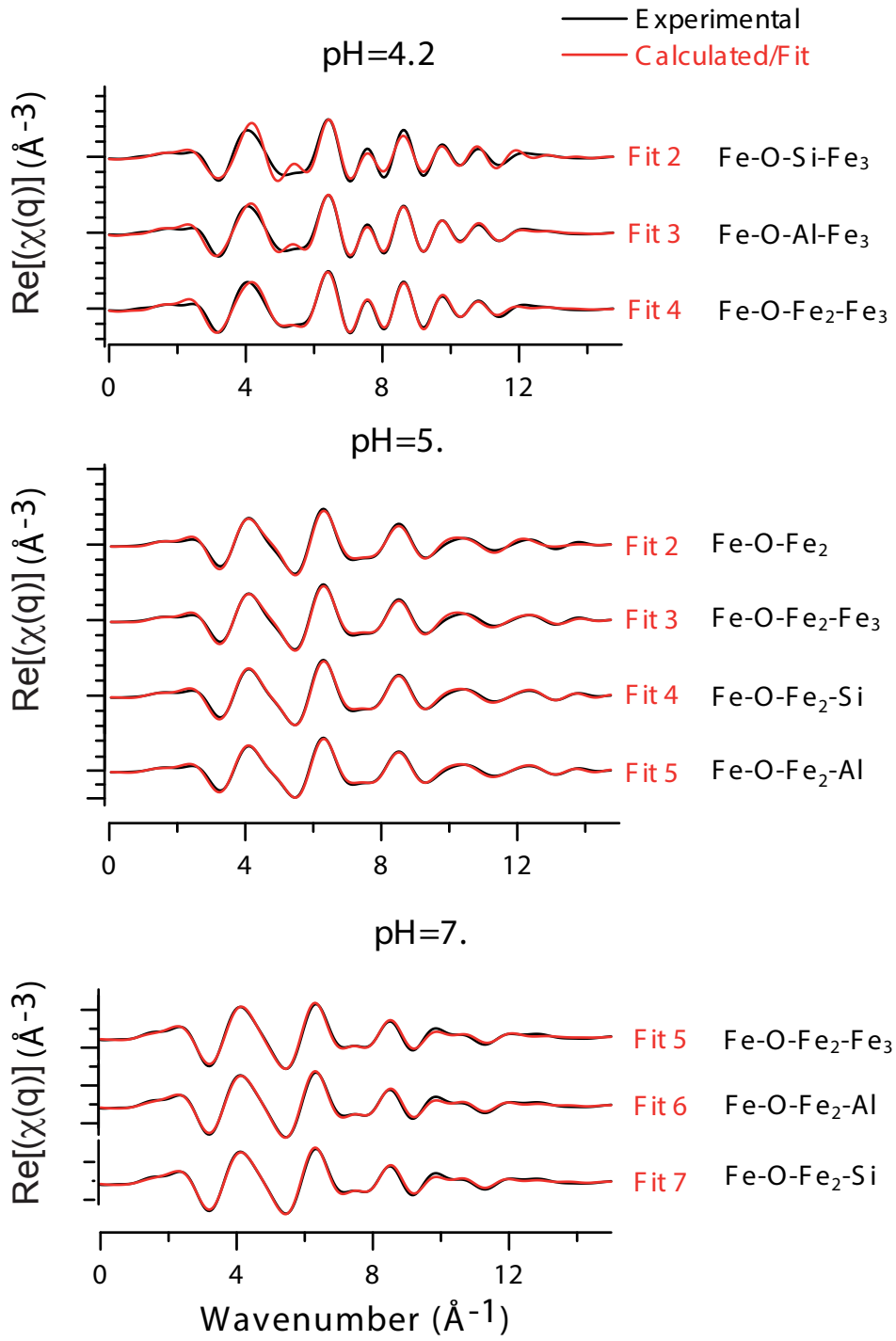
Table

	R window Å	N ±20%	R (Å) ±0.02	$\sigma$ (Å)	N ±20%	R (Å) ±0.02	$\sigma$ (Å)	N ±20%	R (Å) ±0.02	$\sigma$ (Å)	$E_o$ (eV)	R- factor	Fit No	
pH 4.2	1.00-3.63		Fe-O			Fe-Si			Fe-Fe <sub>3</sub>		0,0	0,128	2	
		6.8	1.95	0.12	3.5	3.25	0.05	2.2	3.42	0.06				
			Fe-O			Fe-Al		Fe-Fe <sub>3</sub>				0.0	0.040	3
		6.6	1.94	0.12	3.5	3.02	0.04	1.6	3.40	0.03				
		<b>6.3</b>	<b>1.97</b>	<b>0.12</b>	<b>1.5</b>	<b>3.01</b>	<b>0.08</b>	<b>1.9</b>	<b>3.38</b>	<b>0.08</b>	<b>4.0</b>	<b>0.023</b>	4	
pH 5	1.00-3.09		Fe-O			Fe-Fe <sub>2</sub>			Fe-Fe <sub>3</sub>		3.0	0.010	3	
		4.7	1.96	0.09	1.2	2.99	0.07	0.6	3.13	0.05				
			<b>Fe-O</b>			<b>Fe-Fe<sub>2</sub></b>		<b>Fe-Si</b>				<b>3.0</b>	<b>0.006</b>	<b>4</b>
		<b>4.9</b>	<b>1.96</b>	<b>0.09</b>	<b>1.1</b>	<b>3.01</b>	<b>0.09</b>	<b>3.9</b>	<b>3.18</b>	<b>0.09</b>				
		4.9	1.96	0.09	1.0	3.00	0.08	4.9	3.21	0.08	3.0	0.006	5	
pH 7	1.00-3.24		<b>Fe-O</b>			<b>Fe-Fe<sub>2</sub></b>			<b>Fe-Fe<sub>3</sub></b>		<b>4.0</b>	<b>0.011</b>	<b>5</b>	
		<b>6.5</b>	<b>1.98</b>	<b>0.11</b>	<b>2.5</b>	<b>3.06</b>	<b>0.11</b>	<b>0.5</b>	<b>3.35</b>	<b>0.11</b>				
			Fe-O			Fe-Fe <sub>2</sub>		Fe-Al				4.0	0.011	6
		6.5	1.98	0.11	2.5	3.06	0.11	2.1	3.45	0.08				
		6.5	1.98	0.11	2.6	3.06	0.11	1.6	3.42	0.08	4.0	0.011	7	

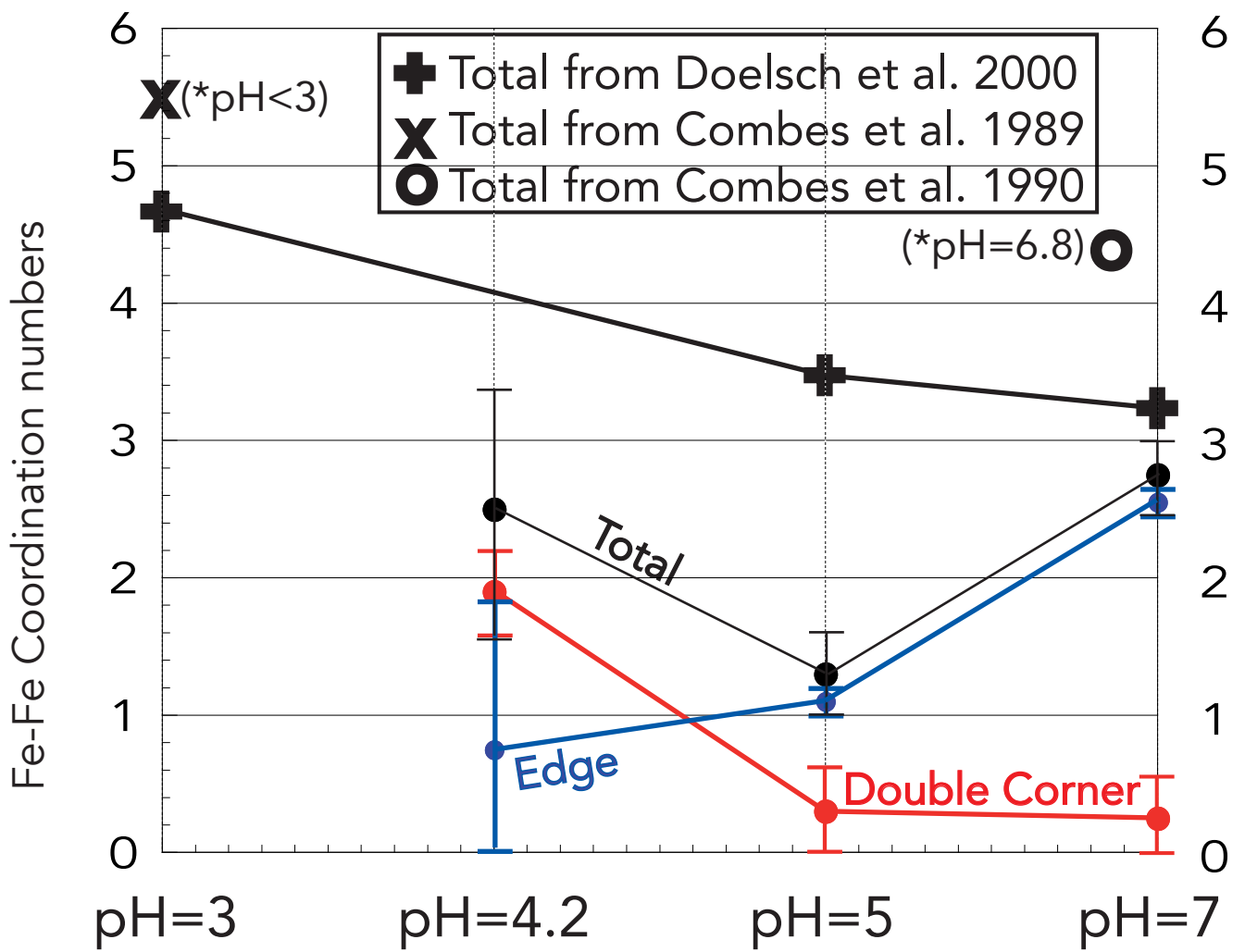
Figure



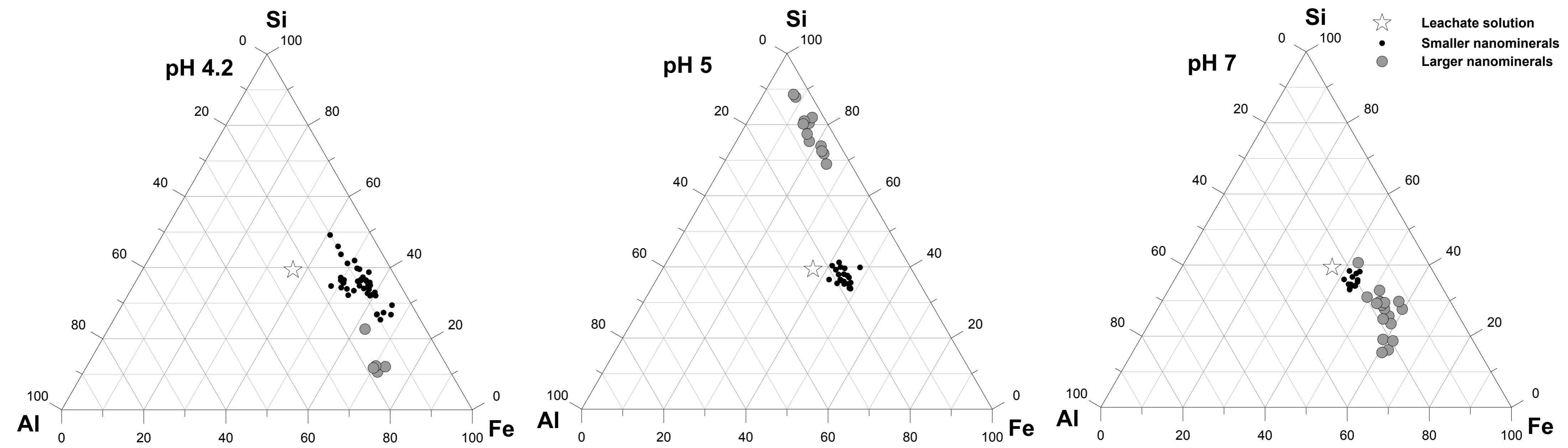
Figure



Figure

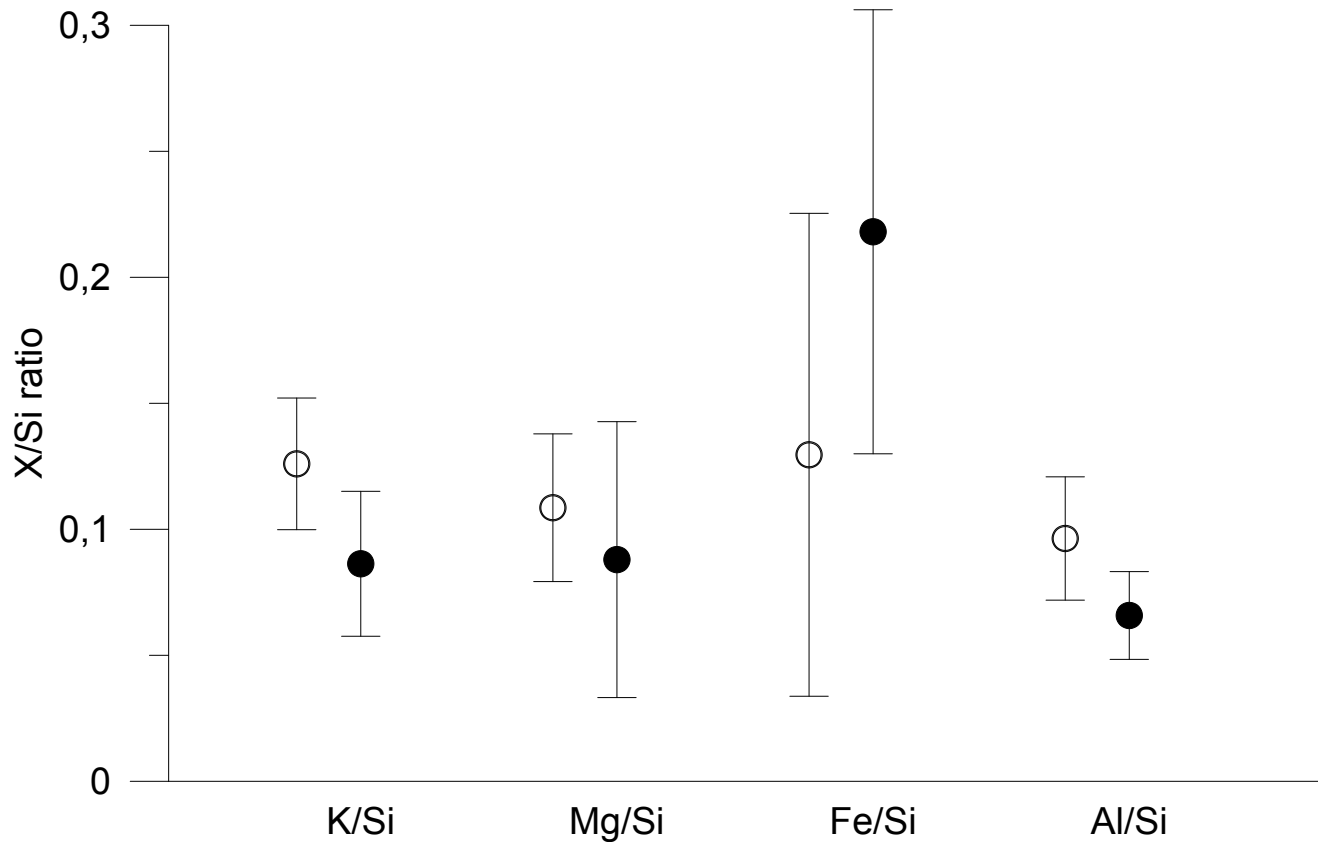


Figure



Figure

- 20 nm layer of altered biotite (Bonneville et al., 2011)
- Larger nanominerals pH 5 (this study)



## Appendix

[Click here to download Appendix: TamratGCA\\_revised\\_4 with corrections.docx](#)



**Electronic Annex**

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