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Wuhib Zewde Tamrat, Jérôme Rose, O. Grauby, Emmanuel Doelsch, Clément Levard, et al.. Soil organo-mineral associations formed by co-precipitation of Fe, Si and Al in presence of organic ligands. *Geochimica et Cosmochimica Acta*, 2019, 260, pp.15-28. 10.1016/j.gca.2019.05.043 . hal-02272705

HAL Id: hal-02272705

<https://amu.hal.science/hal-02272705v1>

Submitted on 29 Aug 2019

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1 **Soil organo-mineral associations formed by co-precipitation of Fe, Si and Al in presence of**
2 **organic ligands**

3
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12

13

14 **Abstract**

15 Weathering of silicates supplies a range of cations (mainly Si, Al, Fe, but also Ca, Mg, Na, K,
16 Mn) to the soil solution. There, cations can interact with charged functional groups of
17 dissolved soil organic matter (OM). Unlike Al and Fe, Si does not directly bind to natural OM.
18 However, the role of Si in the mechanisms of OM stabilization by coprecipitation with short
19 range order mineral phases (SRO) may have been underestimated. The formation of
20 coprecipitates was tested by titrating a biotite-weathering solution up to pH 5 in presence of
21 3,4-Dihydroxy-L-phenylalanine (DOPA) with initial (Fe+Al):C ratio ranging from 3 to 0.003. Size,
22 crystallinity, chemical composition and the local structure of the coprecipitates were analyzed
23 by TEM-EDX and Fe K-edge EXAFS. Coprecipitates are amorphous particles whatever the
24 (Fe+Al):C ratio, but their size, composition and local structure were nevertheless seen to
25 progressively vary with increasing C content. In low C samples (high (Fe+Al):C), coprecipitates
26 were 2-40 nm in size and were dominated by Si (30 to 70%). Fe represented only 20-50% of
27 the mineral phase and was structured in small oligomers of Fe octahedra. Around 20% of the
28 Fe of the coprecipitates were bound to C. Conversely, in high C samples (low (Fe+Al):C),
29 coprecipitates were 10-90 nm in size and Fe was the main component (45-70%). Fe was almost
30 exclusively linked to OM by monomeric Fe-O-C bonds. Si (5-40%) and Al (15-35%) were able
31 to form oligomers occluded in the Fe-OM network. In samples with intermediate C content
32 ((Fe+Al):C=0.3), the coprecipitates had 5-200 nm size particles. We suggest these
33 coprecipitates are structured in a loose irregular 3D network of amorphous small oligomers of
34 Fe (25-75%), Si (15-50%), and Al (10-35%), forming an amorphous and open-structured
35 mineral skeleton. Within this mineral network, we suggest the organic compounds are linked
36 either by bonds with Fe and Al to the skeleton, by monomeric Fe-O-C in the porosity of the
37 network, or by weak bonds with other OM. This conceptual model provides an alternative to
38 the standard view that SRO-OM is formed by ferrihydrite and amorphous Al(OH)₃. We suggest
39 naming the structure “Nanosized Coprecipitates of inorganic oligomers with organics” with

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40 “nanoCLICs” as acronym. The presence of Si in the inorganic structures may have an impact
41 not only on the amount of OM stabilized by the nanoCLICs, but in the longer term, on the
42 persistence of the OM stabilization potential by metallic oligomers.

43

44

45 1 Introduction

46 Organo-mineral interactions are known to play a key role in stabilizing organic matter (OM) in
47 soils (Baldock and Skjemstad, 2000; Kleber et al., 2015; Kögel-Knabner et al., 2008; Schmidt et
48 al., 2011), because bonds between organic compounds and mineral surfaces minimize
49 microbial degradation of organic compounds (Eusterhues et al., 2014; Jones and Edwards,
50 1998; Porras et al., 2018; Saidy et al., 2015; Scheel et al., 2007b). Understanding the
51 mechanisms governing the formation of organo-mineral associations is therefore a major
52 challenge in view of increasing soil C stocks (Minasny et al., 2017; Paustian et al., 2016).
53 Colloidal and short-range-order (SRO) minerals are increasingly considered as important
54 mineral phases in the control of OM dynamics (Basile-Doelsch et al., 2005; Basile-Doelsch et
55 al., 2007; Basile-Doelsch et al., 2015; Bonnard et al., 2012; Finley et al., 2018; Keiluweit et al.,
56 2015; Kramer and Chadwick, 2018; Levard et al., 2012; Rasmussen et al., 2018). Indeed, their
57 very small size (ranging from a few nanometers to a few tens of nanometers) and their poorly
58 crystallized structure provide them with both large surface reactivity and large specific
59 surfaces. These properties mean SRO is highly capable of binding with some functional groups
60 of soil OM.

61
62 The Fe and Al oxy-hydroxides interacting with OM have been mainly studied using
63 experimental batch approaches with either natural OM extracts or low molecular weight
64 organic compounds (for a review, see Kleber et al. (2015)). Two formation processes have
65 been investigated: adsorption (reaction of OM to post-synthesis SRO) and co-precipitation
66 (formation of SRO in the presence of OM). Studies that compared the two processes showed
67 that coprecipitation resulted in much higher maximum C contents than adsorption (Chen et
68 al., 2014; Mikutta et al., 2014; Mikutta et al., 2011). According to Mikutta et al. (2011),
69 coprecipitation is a process wherein monomeric or polymeric aqueous metal species (Al or Fe)
70 form a mixed metal–organic solid from the solution after reacting with organic compounds.
71 To experimentally address the question of how Fe and Al interact with OM at the molecular
72 level in the coprecipitates, spectroscopic and scattering probes are required (Chen et al.,
73 2016), and extended X-ray absorption fine structure (EXAFS) spectroscopy is one of the most
74 useful methods to study local Fe coordination environments at molecular scale (Chen et al.,
75 2014; Karlsson and Persson, 2010; Karlsson et al., 2008; Mikutta, 2011; Rose et al., 1998; Vilg e
76 et al., 1999b). EXAFS makes it possible to refine the speciation of Fe by distinguishing (1) SROs
77 (polymers made of a few dozen atoms organized at the scale of a few nanometers), (2)
78 oligomers (i.e. dimers of 2 atoms, trimers of 3 atoms or a slightly larger number of non-
79 ordered atoms), and (3) monomers (a single atom). Soil scientists often use SRO to refer to
80 these different forms of Fe, as opposed to the Fe of well-crystallized oxides. To be more
81 rigorous, we use the terms Fe-nanophase (without OM) and Fe-coprecipitate (with OM) when
82 the speciation of Fe is not given. By extension, we use Al-nanophase and Al-coprecipitate in
83 the same way.

84
85 In the case of Fe-coprecipitates, SRO_{Fe}-OM are often described as spherical 2-5 nm ferrihydrite
86 crystallites aggregated in an OM matrix (Chen et al., 2016; Eusterhues et al., 2008; Mikutta et
87 al., 2008; Mikutta et al., 2014; Schwertmann et al., 2005). This model of Fe oxy-hydroxide
88 occlusion in OM is well illustrated in several studies (Du et al., 2018; Eusterhues et al., 2014;
89 Kleber et al., 2015). The density of SRO_{Fe}-OM aggregates (Eusterhues et al., 2008; Guenet et
90 al., 2017; Mikutta, 2011; Mikutta et al., 2008) together with the size of the ferrihydrite
91 crystallites and their crystallinity (Eusterhues et al., 2008; Mikutta, 2011; Mikutta et al., 2010;

92 Schwertmann et al., 2005) has been shown to vary with the experimental conditions. In a
93 limited number of studies, Fe-coprecipitates were reported to be formed by Fe-oligomers,
94 without reaching the polymerization level of ferrihydrite (Angelico et al., 2014; Mikutta, 2011;
95 Vilg e et al., 1999b). Other authors frequently reported that a variable proportion of
96 mononuclear Fe formed Fe-OM complexes (Chen et al., 2016; Eusterhues et al., 2008; Karlsson
97 and Persson, 2010, 2012; Karlsson et al., 2008; Mikutta et al., 2010; Schwertmann et al., 2005).
98 Thus, as a function of the Fe:C ratio (from 100 down to 0.01, Kleber et al. (2015)), OM
99 composition and pH, several Fe phases may coexist: (1) polymerized nano-oxy-hydroxides
100 (dominant at high Fe:C ratios); (2) oligomeric clusters (dominant at intermediate Fe:C ratios);
101 and (3) mononuclear complexes (dominant at low Fe:C ratios) (Chen et al., 2016; Mikutta,
102 2011). These co-existing phases led Guenet et al. (2017) to propose a model of fractal
103 organization of Fe-coprecipitates. Aside from the differences in the structure of Fe-
104 coprecipitates described in the studies cited above, all the authors acknowledge that the
105 strong complexation between Fe and OM hinders the polymerization of Fe by occupying the
106 crystal growth sites. Using low molecular weight organic compounds made it possible to focus
107 on the main organic ligands involved in the Fe-O-C bindings. For example, Mikutta (2011)
108 showed that catecholate bonds are more efficient in complexing Fe than carboxylate and
109 salicylate bonds, and also that the position of the phenol group on an aromatic ring rather
110 than the number of phenol groups controls the ligand's interaction with Fe.

111
112 Concerning Al, despite the fact that aqueous cationic Al concentration in oxic soil pore water
113 may exceed that of Fe (because Al is more soluble than Fe hydroxides (Scheel et al., 2007b)),
114 Al-coprecipitates have received less attention than Fe-coprecipitates with respect to the
115 problem of OM in the soil. This may be because X ray spectroscopic techniques are much more
116 difficult to implement for Al than for Fe. Nevertheless, like Fe, the Al phases in coprecipitates
117 are described as solid amorphous phases (often noted $Al(OH)_3$) as well as monomeric Al, both
118 interacting with OM in proportions that vary with the experimental conditions (Mikutta et al.,
119 2011; Scheel et al., 2007b; Schneider et al., 2010). The local structure of the polymerized Al
120 phases has rarely been described, except when nuclear magnetic resonance approaches were
121 used, when it was shown that OM may hinder the polymerization of tridecamer (Al_{13}), limiting
122 the speciation of Al to small oligomers (dimers and trimers) and monomers (Masion and
123 Bertsch, 1997; Masion et al., 2000). Thus, like for Fe, the extent of polymerization of Al in Al-
124 coprecipitates varies with Al:C ratio, pH and nature of OM.

125
126 However, soil solutions are not pure Al or Fe solutions. A limited number of studies focused
127 on the formation of multi-cation coprecipitates. By testing mixtures of Al and Fe, Mikutta et
128 al. (2014) observed low amounts of Al in the Fe-Al-coprecipitates, and that the presence of Al
129 did not affect ferrihydrite crystallinity. Nierop et al. (2002) also concluded that Fe binds more
130 readily to OM than does Al, but noted that the initial metal/carbon ratio (M:C, M being Fe+Al)
131 also controlled the Fe:Al ratio in the Fe-Al-coprecipitates (Vilg e et al., 1999a).

132
133 Although silicon is one of the main elements in soils, it has rarely been considered as an
134 element of interest in batch synthesis of coprecipitates. This is due to the non-charged form
135 of Si (neutral $Si(OH)_4$ at the pH of soil solutions), which shows that Si does not spontaneously
136 link with natural OM (Pokrovski and Schott, 1998). However, the presence of Si may modify
137 the structures of the Fe-coprecipitates and Al-coprecipitates. In natural systems, imogolite
138 type materials are also examples of Si bearing $SRO_{Al,Si}$ known to stabilize large amounts of OM

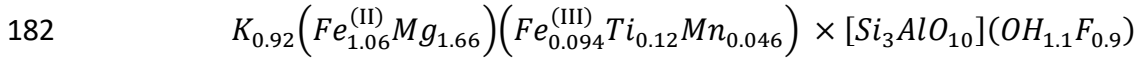
139 in andosols (Basile-Doelsch et al., 2005; Basile-Doelsch et al., 2007; Levard et al., 2012). Finally,
140 in systems containing no OM, it has been shown that Si inhibits Fe polymerization, the local
141 structure of Fe-Si-nanophases varying with the Si:Fe ratio, pH, and redox state (Doelsch et al.,
142 2000, 2002; Doelsch et al., 2001). Recently, the formation of SRO was also tested in a more
143 complex solution including Fe, Al, Si, Mg, K obtained through experimental biotite weathering
144 (Tamrat et al., 2018). These authors showed that the nanophases were amorphous particles
145 10–60 nm in size, whose composition (dominated by Fe and Si) was strongly controlled by pH.
146 At pH 4.2 and pH 7, the structure of the nanophases was dominated by Fe oligomers. Its
147 polymerization was hindered by Al, Si, Mg and K. At pH 5, the Fe-Fe coordination number was
148 even lower, polymerization being counteracted by the precipitation of high amounts of Si.

149
150 The present work is based on three hypotheses: (1) Fe-coprecipitate and Al-coprecipitate
151 systems are not the only coprecipitates to take into account in OM stabilization issues; (2) In
152 soils in which silicate minerals are present and provide a range of cations upon weathering,
153 not only $\text{Fe}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})^{2+}$ but also $\text{Si}(\text{OH})_4$, Mg^{2+} , Ca^{2+} , K^{2+} , etc. contribute to the
154 structures of the coprecipitates; (3) Si, which does not directly interact with OM, also
155 contributes to the formation of metal-OM-coprecipitates in soils. To verify these hypothesis,
156 we tested the capacity of dissolved Fe Al and Si to form Fe-Al-Si-coprecipitates in presence of
157 an organic ligand. Coprecipitates were formed in batch experiments by titrating a biotite-
158 weathered solution up to pH 5 (Tamrat et al., 2018) in presence of OM. 3,4-Dihydroxy-L-
159 phenylalanine (DOPA) was selected as a model of OM for three reasons: (1) it is a low
160 molecular weight organic compound and low molecular weight organic compounds are known
161 to be the main OM compounds stabilized (Lehmann and Kleber, 2015; Sutton and Sposito,
162 2005), (2) using a single molecule avoids uncertainties linked to fractionation of natural OM
163 during coprecipitation (Eusterhues et al., 2011; Mikutta et al., 2007; Scheel et al., 2007b;
164 Schneider et al., 2010) and (3) functional groups of DOPA (amine, carboxyl, aromatic ring and
165 hydroxyl groups) represent main functional groups known in organo-mineral stabilization
166 processes (Mikutta, 2011; Zimmerman et al., 2004). Coprecipitation at pH 5 was preferred to
167 emphasize the effects of Si (Tamrat et al., 2018) while the molar M:C ratios ranged between
168 3 and 0.003. Together with the Fe-Al-Si-nanophases synthesized without OM (Tamrat et al.,
169 2018), this series covers the range of experimental M:C conditions used in previous Fe- and
170 Al-coprecipitate studies (Kleber et al., 2015). The present work focused on the
171 characterization of size, crystallinity and chemical composition of Fe-Al-Si-coprecipitates by
172 TEM-EDX and of their local structure using Fe k-edge EXAFS (extended X-ray absorption fine
173 structure) spectroscopy. The main objectives of the paper are (1) to describe the structure of
174 Fe-Al-Si-coprecipitates at the local scale as a function of the M:C ratio; (2) to propose a
175 conceptual model of the coprecipitates' structure in a Fe, Al, Si and OM system; (3) to evaluate
176 the potential implications of the presence of such Fe-Al-Si-coprecipitates in soils with respect
177 to the concepts of organomineral interactions.

178 2 Materials and Methods

179 2.1 Materials

180 The weathered biotite came from Bancroft, Ontario Canada (Ward Science) and had the
181 following chemical composition:



183 3,4-Dihydroxy-L-phenylalanine [(HO)₂C₆H₃CH₂CH(NH₂)CO₂H] (Sigma Aldrich) was used (Figure
 184 A1) as a model of a soil organic compound. It presents the following functional groups: amine,
 185 carboxyl and an aromatic ring with double hydroxyl groups. At pH5, the amine group exists in
 186 NH³⁺ state, carboxyl group in COO⁻ and phenol groups in OH state. The main expected
 187 interactions with cations are carboxylate binding (Chen et al., 2016), phenol binding (Chen et
 188 al., 2016) and catecholate binding, through both OH carried by adjacent C in the aromatic ring
 189 (Mikutta, 2011). The nine C in this compound accounted for nine C atoms in subsequent molar
 190 metal to carbon ratios (M:C).

191

192 2.2 Synthesis of the coprecipitates

193 The coprecipitates were synthesized in two steps. The first step consisted of leaching in an
 194 acidic batch solution to collect the leachate solution containing dissolved species induced by
 195 biotite weathering. The second step consisted in increasing the pH of leachate solution (from
 196 2 to 5) in the presence of DOPA to form the coprecipitates.

197 *Biotite weathering:* The steps involved in the dissolution of biotite are detailed in Tamrat et
 198 al. (2018). Briefly, 33 g of ground biotite (< 50 μm) was leached for 29 days in 1 L batches of
 199 constant pH 2 HNO₃ solution (solid:liquid ratio 1:30). Dissolved species (leachate solution)
 200 were collected by Tangential Flow Filtration (TFF) (Spectrum Labs) with a cutoff size of 10 kD.
 201 The final concentrations of the leachate solution (ICP-AES, Horiba Jobin-Yvon "Ultima C",
 202 Longjumeau, France) were Fe 937 μM, Si 1006 μM, Al 614 μM, K 883 μM and Mg 1247 μM.

203 *Synthesis of coprecipitates:* 1.25, 12.57, 125.68 and 1256.7 mg of DOPA were added to 100 ml
 204 of leachate solution at pH 2. This gave initial molar M:C ratios of 2.72, 0.27, 0.027 and 0.0027,
 205 ratios that were then rounded up to 3, 0.3, 0.03 and 0.003 for the purpose of naming the
 206 samples in the following. 'Molar metal concentration' stands for combined concentrations of
 207 the main complexing metals Fe and Al. Coprecipitates were formed by increasing the pH to 5
 208 by adding 0.2M NaOH (Sigma Aldrich) at a constant rate of 70 μL/min (Figure A2). When pH 5
 209 was reached, a 1 ml aliquot of sample was collected for TEM-EDX analyses and the remaining
 210 solution was ultra-centrifuged at 400,000g for 2 h to separate coprecipitates from the
 211 remaining dissolved species. The settled particles (less than 10 mg) were freeze-dried for
 212 EXAFS analyses. The nanophase formed without OM is called No C sample. It is identical to the
 213 pH 5 sample described in Tamrat et al. (2018) and is used here for the purpose of comparison.
 214

215 2.3 Characterization of coprecipitates by TEM-EDX: morphology, size, 216 chemical composition and state of crystallinity

217 The coprecipitates were characterized using a JEOL JEM 2011 Transmission Electron
 218 Microscope (TEM) working at 200 kV at CINaM/ Aix-Marseille University, France. The
 219 parameters were 50 000X magnification, 20° tilt angle toward the EDX detector, energy range
 220 of 40 keV, corrected counting time of 30 s, constant beam density ~63.5 pA.cm⁻². Fe, Si, Al, K,
 221 and Mg were quantified using the Bruker AXS TEM line mark data semi-quantification
 222 procedure (Berthonneau et al., 2014). C was detected in all analyzed particles but C
 223 quantification is not reliable using this method (note that the low mass of collected

224 coprecipitates did not allow us to measure C content using an alternative method). The atomic
225 proportions of analyzed elements thus do not include either C or O in the calculation. EDX
226 chemical analyses were performed on individual particles (30 to 60 per sample). The size of
227 the particles analyzed by EDX was manually measured on micrographs.
228

229 2.4 Characterization of coprecipitates at the local scale: EXAFS at the Fe K- 230 edge (acquisition, reference compounds, data treatment)

231 Extended X-ray absorption fine structure (EXAFS) data were collected at the Fe K-edge (7112
232 eV) at ESRF synchrotron source on the FAME beam line (Grenoble, France) and at ELETTRA
233 synchrotron, beam line 11.1 (Trieste, Italy). Spectra were collected using Si(220) at the ESRF
234 and Si(111) double crystal monochromators at ELETTRA. Data were collected in ambient
235 conditions in both transmission and fluorescence modes (30-element solid-state Ge detector
236 (Canberra, France)).

237 All the samples were mixed with boron nitride as a diluting agent and pressed into 5 mm
238 diameter pellets. An average of 3 to 5 individual spectra comprised each spectrum taken 107
239 eV below and 849 eV above the absorption edge of Fe (7112 eV) at a counting rate of 2-9
240 seconds up to 14.75 \AA^{-1} . To minimize the risk of beam damage and to obtain representative
241 spectra, each spectrum was collected at different pellet locations. Using $\Delta R = \pi/2k$, the
242 minimum distance resolution was determined to be 0.11 \AA . All radial distances referring to
243 Fourier transform functions (FTF) given in the Results section are uncorrected for phase shift.

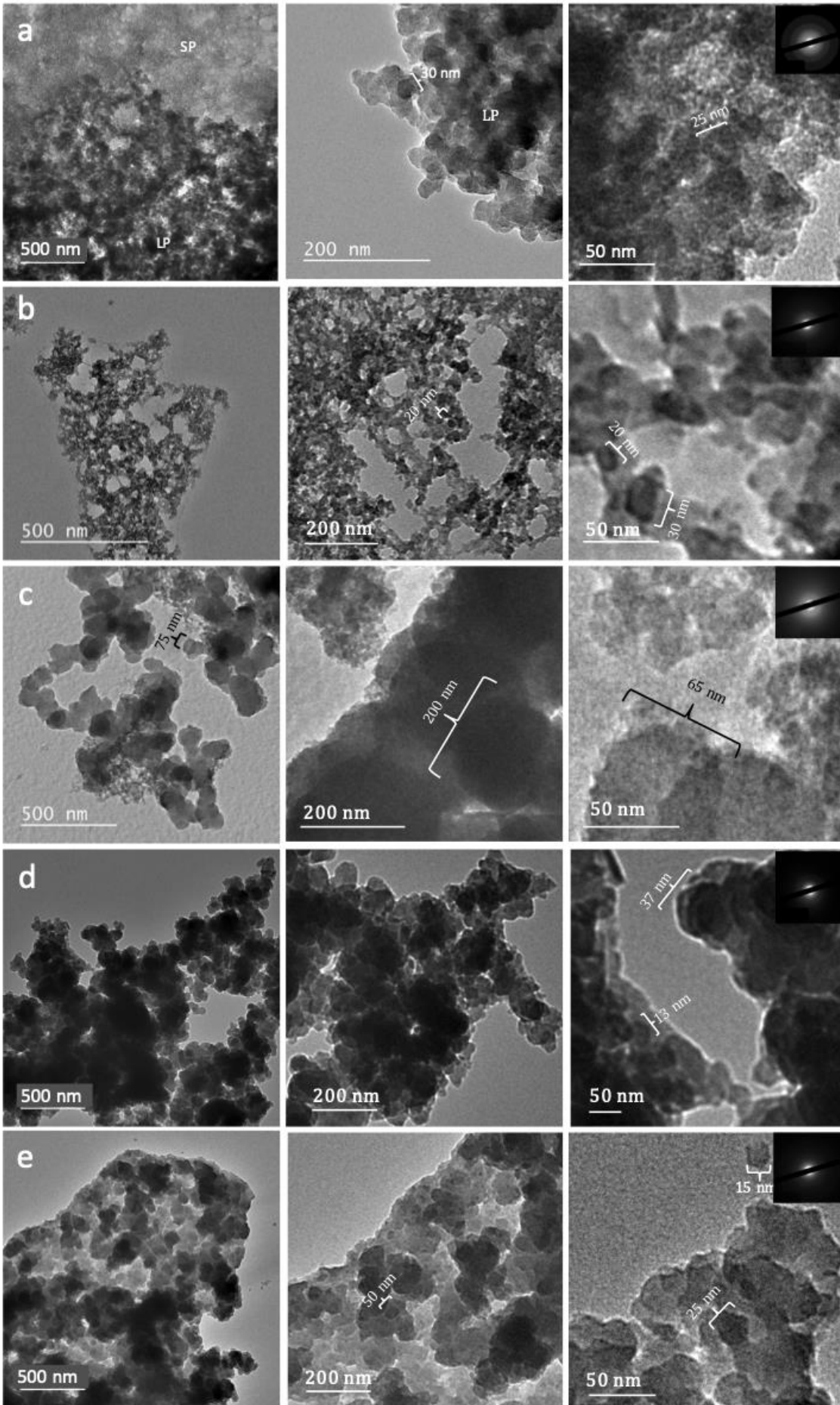
244 Fe speciation in the coprecipitates was assessed by linear combination fitting (LCF) using
245 Athena software (Ravel and Newville, 2005) following the data reduction steps of Michalowicz
246 et al. (1979). LCF is meant to quantitatively reproduce EXAFS spectral features by using the
247 smallest number of reference components. The sensitivity of LCF is within the 10-20% range
248 (O'Day et al., 2004), and no more than three reference components were used. During fitting,
249 all weights were restricted to remain between 0 and 1 without forcing their sum to equal 1
250 (or 100%). The relative goodness-of-fit between the data and the model is described by the
251 residual factor (R-factor, the lower R, the better the fit). The reference standards (Tables B1,
252 B2 and Figure 3) were selected to represent increasing levels of Fe polymerization with iron
253 citrate, Fe-C colloids, Fe dimers, $\text{SRO}_{\text{Fe,Si}}$ and 2L ferrihydrite. Note that descriptions such as Fe-
254 Fe are short for two Fe octahedra interacting, thus making Fe-O-Fe bonds. The designations
255 Fe-Si, Fe-Al and Fe-C are used hereafter to describe Fe interacting with Si tetrahedron, Al
256 octa/tetrahedron and C based molecules, respectively. 2L Ferrihydrite provides the highest Fe
257 polymerization level of all reference compounds with 2.1 edge interactions and 5 double
258 corner interactions (Maillot et al., 2011; Michel et al., 2007). $\text{SRO}_{\text{Fe,Si}}$ is composed of Fe
259 oligomers synthesized at pH 5 in Si rich solutions (Si/Fe=4). These Fe oligomers are
260 characterized by 2.6 edge-sharing and only a 0.6 double corner Fe-Fe interaction but no Fe-O-
261 Si interactions at pH 5 with this Si/Fe ratio (Doelsch et al., 2000; Doelsch et al., 2001). For Fe
262 dimers, only one edge-sharing coordination has been described (Rose et al., 1996). Fe-C
263 colloids have a minimum 0.4 double and 0.7 single corner Fe-Fe interaction with an additional
264 reference to OM complexing Fe with 1.9 C_1 atoms at 2.82 \AA (monodentate) and 1.5 C_2 atoms
265 at 2.98 \AA (bidentate) (Rose et al., 1998). Iron citrate is the chelation of three carboxylic
266 functional groups of a citrate anion with a central Fe atom producing a tridentate
267 mononuclear complex (IUPAC, 2005). Details of the stages of the linear combination fitting

268 (LCF) process are given in Table B3 and Figure B1. Modeling of spectra by shell by shell fitting
269 was attempted but did not succeed, probably because of the complexity and heterogeneity of
270 the samples.

271 3 Results

272 3.1 TEM-EDX results

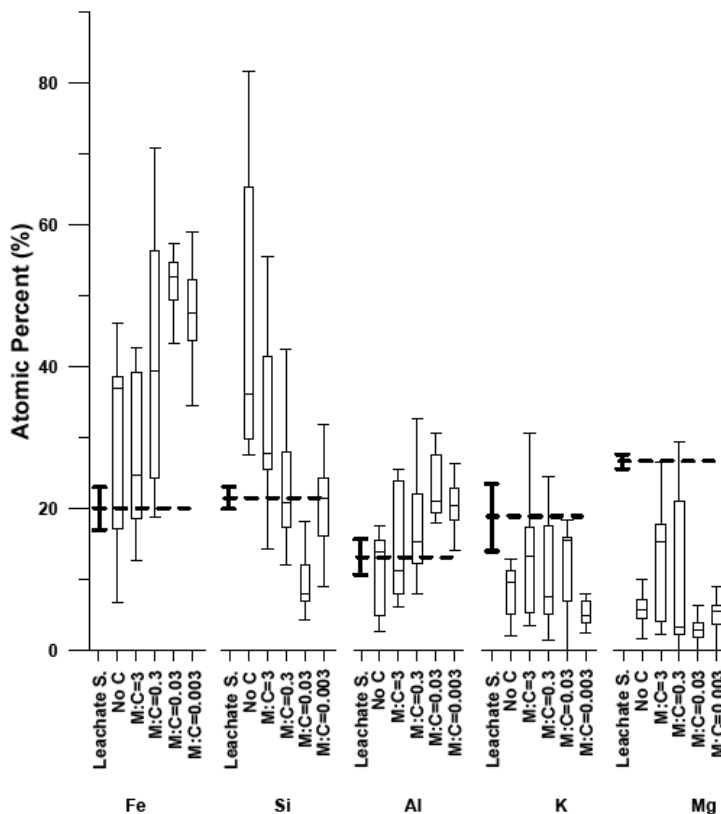
273 TEM micrographs of the coprecipitates are shown in Figure 1. Whatever the M:C ratio,
274 rounded globular particles were formed and aggregated in clusters on the TEM grid. The
275 diameter of the individual spherical particles ranged from 2 to 50 nm for the 'No C', 2 to 40
276 nm for M:C=3, 5 to 200 nm for M:C=0.3, 10 to 90 nm for M:C=0.03 and 15 to 70 nm for
277 M:C=0.003. In the No C sample, the clusters of rather small particles on the one hand, and
278 clusters of large particles on the other hand are described in Tamrat et al. (2018). In M:C=3
279 and M:C=0.3, some clusters of smaller particles were also occasionally observed, but in
280 contrast to the No C sample, their occurrence was rare and differentiating smaller and larger
281 particles was more delicate. Regardless of the size of the particles, electron diffraction
282 analyses (Figure 1) revealed a diffused pattern for all the samples. This pattern is characteristic
283 of amorphous structures.



285 Figure 1: TEM electron micrographs of coprecipitate series at pH=5: (a) 'No C', (b) M:C=3, (c) M:C=0.3, (d) M:C=0.03 and (e)
 286 M:C=0.003. Electron diffraction patterns are shown in the upper right of the 50 nm scale pictures. In the No C sample (a),
 287 LP stands for areas of larger particles and and SP for smaller particles.

288

289 The TEM-EDX analyses showed that Fe and Si were the main metals of the coprecipitates. The
 290 chemical composition patterns were dependent on C content for all elements except K and
 291 Mg (Figure 2). The contribution of Fe and Al increased from No C to M:C=0.03, whereas the
 292 contribution of Si decreased. However, this trend was slightly reversed for M:C=0.003. Mg and
 293 K contributed to the composition of the coprecipitates in rather constant proportions. This
 294 proportion was below the concentration of the leachate solution, whatever the M:C. The
 295 chemical composition of the samples also varied considerably from one particle to another.
 296 Fe and Si showed the highest variability (i.e., the biggest differences between the highest and
 297 lowest concentrations). In the case of Si, variability tended to decrease with decreasing M:C.



298

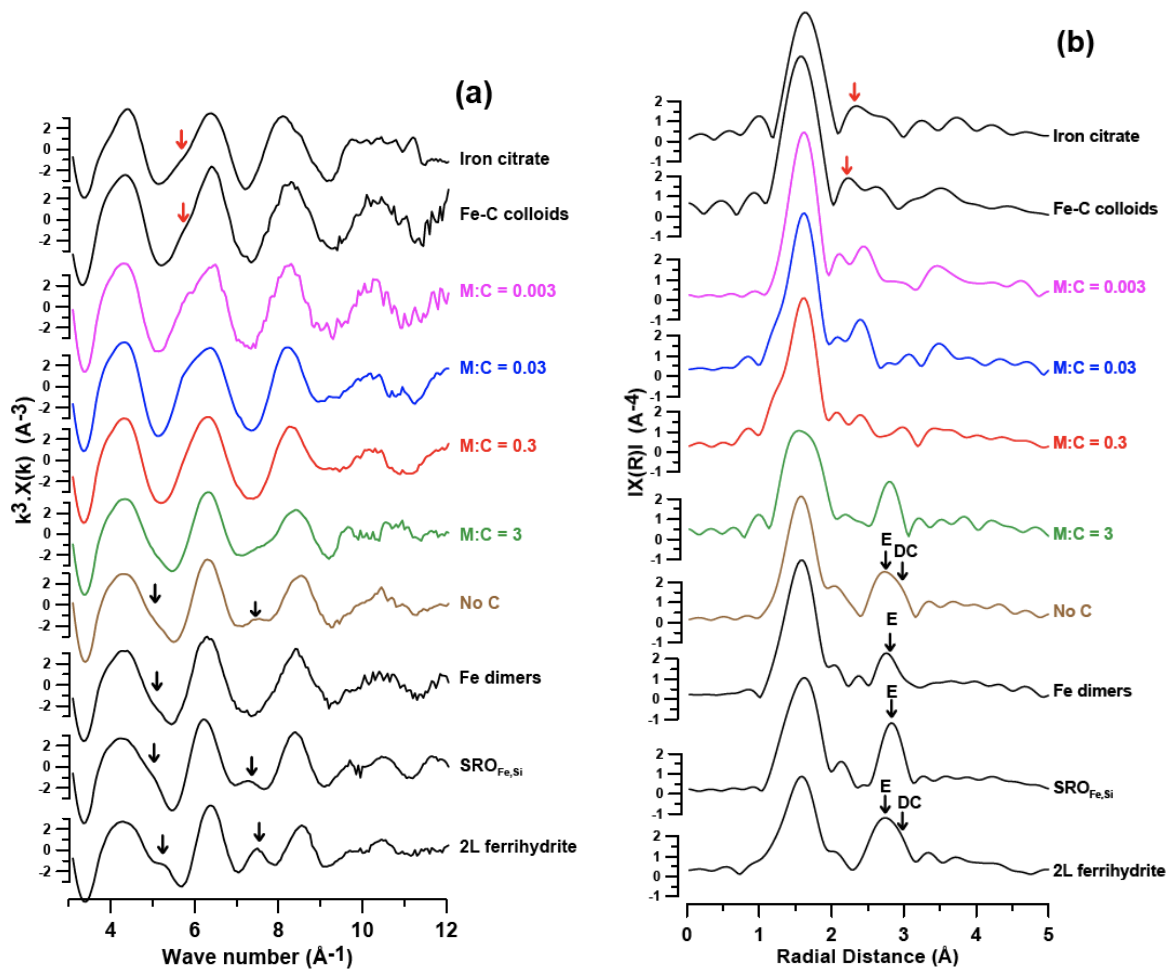
299 Figure 2: TEM-EDX chemical analysis of nanophases (No C) and coprecipitates at the four M:C ratios expressed in
 300 stoichiometric atomic % (excluding C and O). The "box-and-whisker" plots represent median values, the upper and lower
 301 quartiles, as well as the min and max of the data. Number of analyzed particles: No C n=33; M:C=3 n= 42; M:C=0.3 n=30;
 302 M:C=0.03 n=40; M:C=0.003 n=60. For the purpose of comparison, the chemical composition of the leachate solution
 303 (Leachate S.) is also shown as dashed lines with their respective error values.

304 3.2 Fe atomic range order – EXAFS at the Fe k-edge

305 3.2.1 Raw data analysis

306 EXAFS spectra and Fourier transform functions (FTF) are shown in Figure 3. For the reference
 307 samples, in transitioning from the '2L Ferrihydrite, SRO_{Fe,Si} and Fe Dimers' to 'Fe-C Colloids and
 308 Iron citrate' standards, the positive oscillations at $\sim 5.2 \text{ \AA}^{-1}$ and $\sim 7.5 \text{ \AA}^{-1}$ on the EXAFS curves,
 309 which are characteristic signals of Fe-Fe interactions, lost intensity. Instead, a shoulder

310 emerged at $\sim 5.7 \text{ \AA}^{-1}$, which is characteristic of Fe-O-C bonds. For the No C sample, in k-space,
 311 a low intensity positive oscillation was recorded at $\sim 7.5 \text{ \AA}^{-1}$. The signal at $\sim 5.2 \text{ \AA}^{-1}$ was low
 312 intensity and appeared as a shoulder. In R-space, a strong signal of a broad peak with a
 313 shoulder was observed in the range 2.4-3.2 \AA due to Fe-Fe octahedra edge and double corner
 314 interactions respectively (distances are uncorrected for phase shift and have to be shifted by
 315 0.3-0.4 \AA from crystallographic positions toward long distances) (Bottero et al., 1994; Maillot
 316 et al., 2011; Manceau and Gates, 1997; Manceau et al., 2000). M:C=3 showed similar signals
 317 appearing in k-space but at reduced intensities. In R-space, the signal around 2.9 \AA narrowed
 318 to a single peak in the range 2.55-3.05 \AA (with no shoulder). M:C=0.3, in both k and R-spaces,
 319 spectra did not exhibit clear markers of Fe-Fe octahedra interactions, but an R-space peak was
 320 detected at $\sim 2.4 \text{ \AA}$, a signal of Fe-C interactions. M:C=0.03 and M:C=0.003 samples showed
 321 similar EXAFS signals. In both cases, an EXAFS shoulder was detected at $\sim 5.7 \text{ \AA}^{-1}$ and a second
 322 shell R-space peak at $\sim 2.4 \text{ \AA}$. This peak (uncorrected for phase shift) was at a radial distance
 323 shorter than the shortest possible Fe-Fe interaction (Rose et al., 1998). The shortest Fe-Fe
 324 interaction is related to octahedra face sharing with a Fe-Fe distance of 2.9 \AA as in hematite.



325
 326 Figure 3: (a) EXAFS/k-space plots and (b) FTF/R-space plots. FTF peaks between 1.2-2 \AA correspond to the first
 327 coordination sphere of oxygen atoms. On references, markers of Fe-C interactions (red arrows) occur between ~ 2.2
 328 and $\sim 2.5 \text{ \AA}$ and Fe-Fe octahedra (black arrows) at ~ 2.7 and $\sim 3.0 \text{ \AA}$ (for edge (E) and double corner (DC)
 329 interactions respectively). Radial distances are not corrected for phase shift.

330

331 **3.2.2 Quantitative analysis of EXAFS data using linear combination fitting (LCF)**

332 LCF fits are presented in supplementary information (Figure B1) and summarized in Table
 333 1. The local structure of phases formed with No C were fitted by a combination of 44% of
 334 2L Ferrihydrite, with 33% of Fe Dimers and 25% of SRO_{Fe,Si}. In the case of M:C=3 samples
 335 (compared to No C samples) the collective contribution of purely Fe containing standards
 336 decreased from 102% to 82% (2L Ferrihydrite at 37% and SRO_{Fe,Si} at 45%). Additionally,
 337 significant contributions to the fit were achieved with iron citrate standard at 30%. At a
 338 10-fold increase in C (M:C=0.3), the dominating contributions to fit shifted from Fe-Fe to
 339 Fe-C containing reference standards, i.e., the fit from C containing standards (iron citrate
 340 + Fe-C colloids) increased from 30% to 72%. And from purely Fe containing standards,
 341 contributions to fit decreased from 82% to a sole contribution of 35% from SRO_{Fe,Si}. A
 342 further 10-fold increase in C concentration (M:C=0.03) resulted in a decrease in the Fe-Fe
 343 contribution from 35% to 14%, whereas Fe-C contributions (iron citrate and Fe-C colloids)
 344 collectively increased from 72% to 94%. With a maximum C content of M:C=0.003, the
 345 differences with the M:C 0.03 were not significant and the Fe speciation was considered
 346 to be equivalent in the two samples.

347

348 **Table 1: Proportions of Fe-O-C and Fe-O-Fe bounds estimated by linear combination fitting. Proportions under the**
 349 **three reference standards designated “Fe-O-Fe” show contributions to fit from pure Fe to Fe interactions. Fe-C colloids**
 350 **represent higher Fe to C interaction with a low but significant Fe to Fe interaction. Fe citrate represents pure Fe to C**
 351 **interactions. The error in the proportions was estimated at around 15%. R-factor indicates the relative goodness-of-**
 352 **fit between the data and the model (values close to 0 represent the best fits, see supplementary information for**
 353 **details).**

354

	Iron Citrate	Fe-C Colloids	Fe Dimers	SRO _{Fe,Si}	2L Ferrihydrite	Sum	R-factor
	Fe-O-C		Fe-O-Fe				
	Fe-O-C	+ Fe-O-Fe					
No C			0.33	0.25	0.44	1.02	0.015
M:C=3	0.30			0.45	0.37	1.12	0.010
M:C=0.3	0.27	0.45		0.35		1.06	0.038
M:C=0.03	0.41	0.53		0.14		1.08	0.059
M:C=0.003	0.59	0.47				1.07	0.055

355

356

357 4 Discussion

358 4.1 Three types of structures of Fe-Al-Si-coprecipitates as a function of the 359 M:C ratio

360 The contribution of Si, Fe and Al shown in the ternary diagrams of Figure 4, as well as the
361 speciation of Fe and the size range of particles summarized in Figure 5, highlighted three main
362 types of coprecipitate structures:

363 - *Type I: high M:C ratio (M:C=3)*. Coprecipitates are mainly represented by amorphous
364 spherical Si, Fe, Al particles 2-40 nm in size (Figure 5). When only Fe, Al and Si are considered,
365 Si is the main component (30% to 70%, Figure 4). Fe is only present at 20-50% and Al at 10-
366 30%. The local structure of Fe is dominated by small oligomers of Fe octahedra. This local
367 structure is close to the "No C" nanophase structure described in Tamrat et al. (2018) for
368 samples with a pH of 5 precipitated without OM. Ferrihydrite is not formed in the Type I
369 coprecipitates, likely due to the dominating presence of Si oligomers (Doelsch et al., 2000;
370 Doelsch et al., 2001; Tamrat et al., 2018). However, the presence of Si does not prevent the
371 formation of Fe-O-C binding, since 20% to 30% of the Fe present in the coprecipitates is linked
372 to OM.

373 - *Type II: intermediate M:C ratio (M:C=0.3)*. Coprecipitates are mainly represented by Fe, Si, Al
374 particles 5-200 nm in size, i.e. by far the largest coprecipitates in the present study. In contrast
375 to Type I, Fe is the main component (25-75%) of most of the particles. Si (15-50%) no longer
376 dominates the composition of the coprecipitates but remains present in significant
377 proportions in the structure. Al (10-35%), is anti-correlated with Fe. The local structure of Fe
378 is dominated by bonds with OM (70%) but 30% of Fe remains linked to Fe. Small oligomers of
379 a few Fe octahedra are thus preserved in Type II coprecipitates. Al may also bind OM, but the
380 methods used here were unable to probe Al speciation to confirm it. Thus, the Type II
381 structure, which combines the network of small oligomers of Si, Fe, and Al associated with OM
382 and monomeric Fe-OM, forms the largest coprecipitates.

383 - *Type III: low M:C ratio (M:C=0.03 and M:C=0.003)*. Coprecipitates of Type III are mainly
384 represented by Fe, Si, Al particles 10-90 nm in size. Fe is the main component (45-70%), but is
385 slightly depleted compared to Type II Fe content. Conversely, Si (5-40%) and Al (15-35%) are
386 slightly enriched compared to Type II. Fe is almost exclusively bound to C (Figure 5) showing
387 that the monomeric Fe-OM complexation is likely the main interaction in the formation of
388 coprecipitates when large quantities of OM are present. However, a few Fe-Fe dimers, trimers
389 or small oligomers may remain, since LCF showed Fe-Fe interactions for M:C=0.03, but within
390 the uncertainty of the method. We hypothesize that within the coprecipitates at M:C lower
391 than 0.03, Al and Si may form small oligomers occluded in the Fe-OM matrix and that Al may
392 also bind OM.

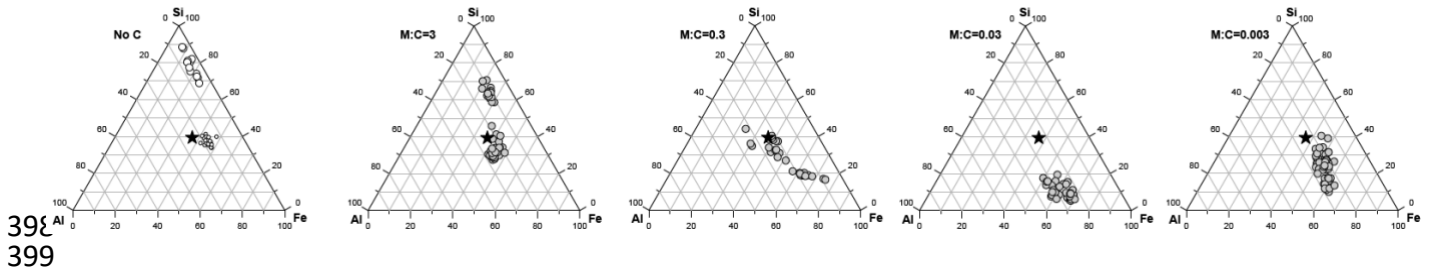
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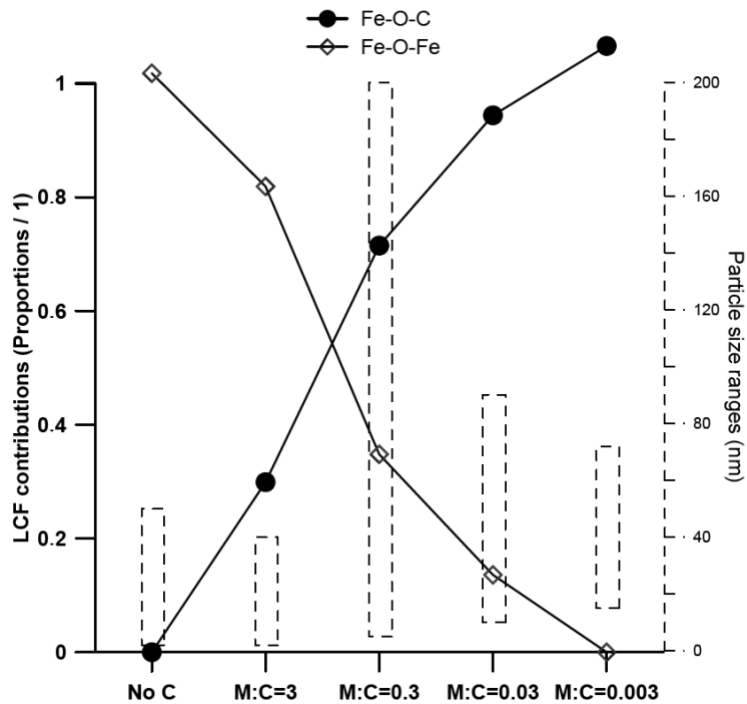
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398
399
400 **Figure 4: Ternary diagrams of Fe, Si and Al atomic proportions in the analyzed particles. White dots: smaller and larger**
401 **nanophases in the No C sample (Tamrat et al. 2018). Grey dots: coprecipitates for the four M:C ratios. The black star**
402 **represents the initial composition of the leachate solution.**

403



404
405 **Figure 5: Solid line: LCF contributions of Fe-O-Fe and Fe-O-C interactions. Fe-O-Fe represents contributions from Fe**
406 **dimers, $SRO_{Fe,Si}$ and 2L Ferrihydrite, while Fe-O-C represents contributions from Fe-C colloids and iron citrate reference**
407 **standards. Dashed bars: particle size ranges.**

408 The mixtures of mononuclear metal-organic complexes and metal hydroxides has already
409 been described in many studies that synthesized Fe-coprecipitates, Al-coprecipitates and Fe-
410 Al-coprecipitates (Karlsson and Persson, 2010, 2012; Mikutta et al., 2010; Mikutta et al., 2014;
411 Nierop et al., 2002). Their proportions also varied as a function of the M:C ratios. For example,
412 Chen et al. (2016) described three types of local structures in Fe-coprecipitates: (1) in low C
413 systems, the ferrihydrite-like Fe domains were precipitated as the core and covered by the
414 OM shells; (2) in systems with intermediate C content, the emerging Fe-C bonding suggested
415 a more substantial association between Fe domains including edge- and corner-sharing Fe
416 octahedra and OM; (3) in systems with high C content, only corner-sharing Fe octahedra along
417 with Fe-C bond were found. In our system, even though the system was too complex to
418 perform shell by shell fitting to model the contributions of edges and corners, as we did for
419 the nanophases of the No C samples (Tamrat et al., 2018), we observed a similar trend for Fe
420 speciation. The level of Fe polymerization decreased with an increase in C content. However,
421 the main difference between this and the pure Fe system was the presence of Si (and to a

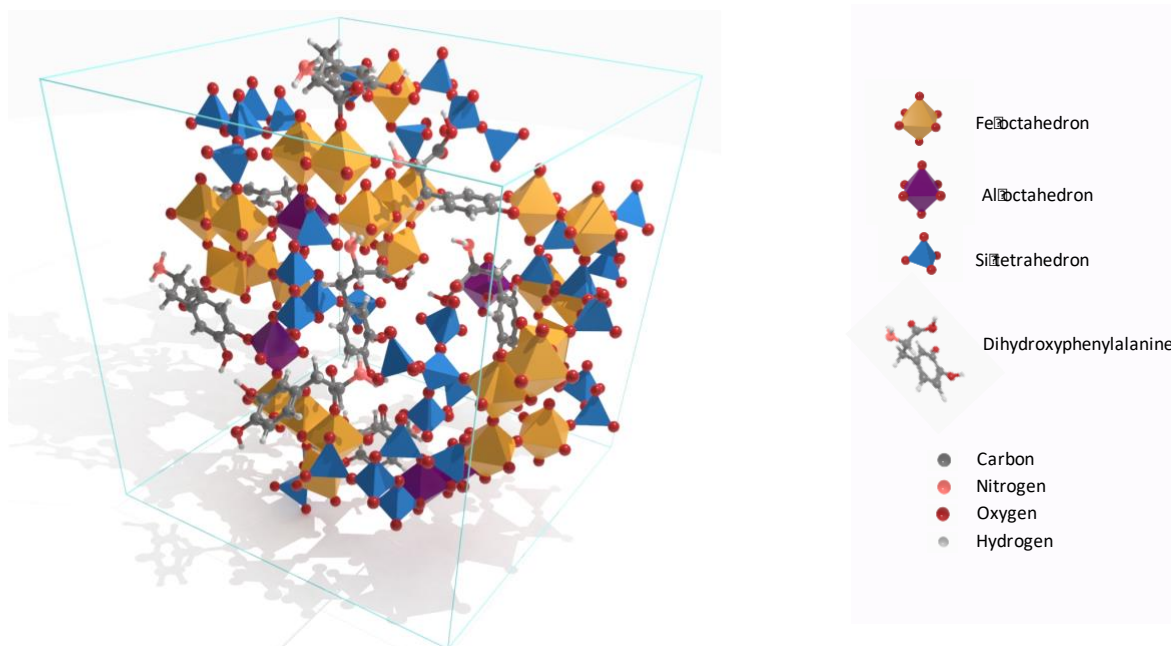
422 lesser extent of Al) that in particular prevents the polymerization of Fe into ferrihydrite
423 domains even at very low OM content. The second significant difference was the presence of
424 Si and Al in the coprecipitates, whatever the M:C ratio.
425

426 4.2 Conceptual model of coprecipitate structure in a Fe, Al, Si and OM system

427 4.2.1 Structure of Type II coprecipitates: “nanoCLICs”

428 The three types of local structures described above represent three snapshots of an increasing
429 scale of C content in which we multiplied the concentration of OM by 10 at each step. On a
430 linear continuum of the M:C ratio, the local structure of the coprecipitates formed at pH 5
431 therefore gradually shifted from Type I to Type III with increasing C content. The Type I
432 structure resembles that of nanophases with no OM, and the structure of the nanophases is
433 detailed in Tamrat et al. (2018). At the opposite end of the M:C scale, in the Type III structure,
434 OM stabilization is dominated by monomeric metal-OM interactions. Beyond the fact that Si
435 oligomers are present in small amounts in the coprecipitates, the structure that stabilizes OM
436 is likely close to that of Fe and Al monomeric complexes described in previous papers (Chen
437 et al., 2016; Eusterhues et al., 2008; Karlsson and Persson, 2010, 2012; Karlsson et al., 2008;
438 Mikutta et al., 2010; Schwertmann et al., 2005). Between Type I and III, the range at which
439 Type II is observed is narrow and reduced to M:C between approximately 3 and 0.3. This range
440 could be an important range for C stabilization processes as it corresponds to the largest
441 particles that coprecipitated in our study (Figure 5). This range of M:C ratios also corresponds
442 to the values observed in andosols (Basile-Doelsch et al., 2005; Basile-Doelsch et al., 2007). As
443 Type II has never been described in previous work, we propose a model to represent a Type II
444 structure of the coprecipitates (Figure 6).

445
446 The frame of Type II coprecipitates could be formed by a loose and irregular 3D network of
447 amorphous small oligomers of Fe, Si and Al forming an “open” branched mineral skeleton. In
448 this network, the OMs are linked in three different ways: (1) OM binding to Fe (and Al)
449 octahedra that belong to the Al, Si, Fe oligomers network; (2) OM binding to Fe (and Al)
450 monomers, located in the porosity of this network; (3) OM interacting with other OMs by
451 weak bonds (such as Van der Waals or cation bridges (Lutzow et al., 2006)). It is important to
452 note that, in the particular case of DOPA, one molecule may bind simultaneously to two
453 different Fe octahedra (through carboxylate and catecholate bindings). Natural organic
454 compounds may behave in the same way. Together with Van der Waals electrostatic bindings,
455 covalent bindings likely help stabilize the structure of the whole 3D network. We define the
456 Type II structure as “Nanosized Coprecipitates of inorganic oLigomers with organiCs” with the
457 acronym “nanoCLICs”.
458



459

460 **Figure 6 : 3D conceptual model of Nanosized Coprecipitates of inorganic oligomers with organics ("nanoCLICs") in an**
 461 **Fe Al Si and DOPA system with initial $0.3 <M:C < 3$. H₂O molecules are not represented to simplify the visualization of**
 462 **the structure. The 3D model can be rotated with Adobe Acrobat using the pdf file provided in the Electronic Annex (a**
 463 **3D PDF basic function tutorial can be found on**
 464 **[https://www.qwant.com/?q=rotating%20object%20pdf%20adobe%20acrobat&t=videos&o=0:9860450d6f706f26d4](https://www.qwant.com/?q=rotating%20object%20pdf%20adobe%20acrobat&t=videos&o=0:9860450d6f706f26d49065218b7d1c03)**
 465 **[9065218b7d1c03](https://www.qwant.com/?q=rotating%20object%20pdf%20adobe%20acrobat&t=videos&o=0:9860450d6f706f26d49065218b7d1c03)).**

466 4.2.2 Comparison with previous models and limits of the model

467 This model of the structure of nanoCLICs differs from the models proposed in the literature.
 468 Previous models of coprecipitates included Fe only as ferrihydrite and monomeric Fe-OM
 469 (Eusterhues et al., 2014; Guenet et al., 2017; Kleber et al., 2015). In the model in Figure 6,
 470 other major elements potentially present in the soil solution are taken into account. These are
 471 mainly Si and Al in the synthetic samples studied here. In the conditions in which we formed
 472 the coprecipitates, K and Mg did not significantly contribute to the coprecipitates. However in
 473 soils, even if Fe, Si and Al are likely the main contributors, if other elements are present in
 474 sufficiently high concentrations and with appropriate physical-chemical conditions, they may
 475 also contribute to the structure of nanoCLICs.

476
 477 Within a network of oligomers on which OM can bind to a very large number of Fe (and Al)
 478 octahedra, the model of "core metal hydroxides embedded in an organic matrix" (Chen et al.,
 479 2016; Eusterhues et al., 2014; Mikutta et al., 2014) can no longer be applied. Interactions occur
 480 at the scale of monomers, dimers, trimers or very small Fe (or Al) oligomers. To represent
 481 these interactions, the model thus must be focused at a very local scale. Such a local scale was
 482 used by Schulten and Leinweber (2000) to perform molecular simulations. However their
 483 model considered large humic molecules and proposed well crystallized Fe oxides as
 484 pedogenic oxides. Since the 2000s, these two concepts has been revised (Schmidt et al., 2011),
 485 thereby invalidating the results of Schulten and Leinweber's molecular simulations.

486
 487 A similar local scale was used in the Kleber et al. (2007) conceptual molecular model to
 488 illustrate a conceptual view of OM organization at the interfaces with minerals. The model
 489 developed by these authors differed significantly from ours in the mineralogical structure of
 490 the interface. In their model, the authors considered theoretical mineral surfaces (kaolinite,

491 Fe oxides) to be flat and well crystallized. But it is likely that such theoretical surfaces only
492 occur exceptionally in soils, mainly because mineral surfaces are subject to alteration (Basile-
493 Doelsch et al., 2015; Churchman and Lowe, 2012). The concept of three superposed OM layers
494 covering the mineral surfaces (Kleber et al., 2007) is likely not strictly applicable to OM
495 interacting with oligomers in nanoCLICs.

496

497 It is important to point out that the model presented in Figure 6 also has its limitations. First,
498 it illustrates coprecipitates with a very specific OM, chosen because it can bind to metals in
499 different ways (COOH, phenol, catecholate). These functions are recognized as being
500 particularly conducive to co-precipitation (Mikutta, 2011). The structure of the nanoCLICs
501 could be a little different from that of other molecules of OM: some authors who tested
502 different types of OMs observed effects on the density of the coprecipitates for example
503 (Eusterhues et al., 2008; Mikutta et al., 2008). Furthermore, at pHs other than pH 5, the results
504 could also have differed slightly because inorganic oligomers have a different chemistry, with
505 in particular, less Si at pH 4.2 and 7 (Tamrat et al., 2018).

506

507 To sum up, the model proposed in Figure 6 provides one example of nanoCLICs with the aim
508 of illustrating the importance of taking at least Fe, Al as well as Si into account in the structure
509 of coprecipitates, even if Si does not bind directly to OM. In a mineral open network with Si in
510 the structure, it is indeed expected that the crystallinity of Fe (and potentially Al) will be lower,
511 implying (1) greater reactivity of Fe (and Al) for OM and (2) a very large specific surface area
512 of inorganic oligomers, forming an open-branched 3D network. These are two key factors in
513 soil OM stabilization (Eusterhues et al., 2014; Jones and Edwards, 1998; Mikutta et al., 2011;
514 Porras et al., 2018; Scheel et al., 2007b), but possibly also in interactions with other charged
515 species in soils.

516 4.3 Implications for soils

517 The role of Si in the mechanisms of OM stabilization by SRO have probably been largely
518 underestimated. Unlike Al and Fe, Si does not bind to OM. However, our work showed that its
519 presence limits the polymerization of Fe (and probably of Al) thus increasing the number of
520 Fe (and Al) octahedra available to bind OM. It can thus be expected that, for the same number
521 of Fe (and Al) atoms, a system that also contains Si will be much more reactive toward OM
522 than a system with no Si. The present work suggests that Si could therefore play an important
523 role in the quantities of OM stabilized by nanoCLICs in a soil profile. Future works should focus
524 on that hypothesis.

525

526 On the other hand, Si could also play a major role in the persistent reactivity of inorganic
527 oligomers. As proposed by Jones et al. (2009), the presence of Si may limit the progressive
528 aging of the Fe (and Al) phases towards better crystallized and more stable Fe (and Al) oxides.
529 As crystallized Fe oxides are less reactive to OM stabilization than Fe-oligomers (Basile-
530 Doelsch et al., 2007; Basile-Doelsch et al., 2009), the presence of Si would insure the
531 preservation of the very poorly polymerized state and maintain the high specific surface area
532 and high reactivity. Thus, the presence of Si in the structures of the coprecipitates may control
533 not only the amount of OM stabilized by the nanoCLICs, but also the persistence of this OM
534 stabilization potential in the longer term.

535

536 The formation of nanoCLICs containing Fe, Si and Al is very likely to occur in most soils, as
537 silicates are the main minerals in the Earth's crust. The "pure" Fe and Al coprecipitates, as
538 studied in synthetic systems, have made it possible to highlight different levels of Fe
539 polymerization (Chen et al., 2016; Eusterhues et al., 2008; Karlsson and Persson, 2010, 2012;
540 Karlsson et al., 2008; Mikutta, 2011; Mikutta et al., 2010; Nierop et al., 2002; Scheel et al.,
541 2007a; Schneider et al., 2010; Schwertmann et al., 2005), but may not be representative of
542 the majority of nanoCLICs in most soils. The occurrence of pure Fe-coprecipitates and Al-
543 coprecipitates is probably limited to very specific environments. In the case of Fe, for example,
544 Fe-coprecipitates may form in environments subjected to redox oscillations (Coward et al.,
545 2018). But in most soils, nanoCLICs likely incorporate a large number of major cations other
546 than Fe and Al, such as Si, Mn (Stuckey et al., 2018), or to a lesser extent more soluble species
547 such as Ca (Rasmussen et al., 2018), Mg or even monovalent species as K (Grand and Lavkulich,
548 2015), depending on the physical-chemical conditions (concentrations, pH, redox, etc.).
549 Recent studies showed in particular the important role played by Ca in ternary complexation
550 mechanisms (Rowley et al., 2018; Sowers et al., 2018) and its importance in stabilizing OM in
551 rather arid soils and in soils with a pH above 7 (Kramer and Chadwick, 2018; Rasmussen et al.,
552 2018).

553
554 Within a soil profile, nanoCLICs could also be characterized by high variability in space, over
555 time and in their structure. It is very likely that in a given soil profile, amorphous Fe Si Al
556 nanophase (Type I), nanoCLICs (type II) and monomeric Fe complex (type III) will be found
557 simultaneously at different microsites. Physical-chemical conditions at a microsite can also
558 vary over time, which may lead to time-dependent variations in the structure of nanoCLICs.
559 At some microsites, as proposed by Keiluweit et al. (2015) in the rhizosphere, the de-
560 structuration of SRO-OM may also occur upon biologic stimulation. The dynamics of nanoCLICs
561 structures should thus also be considered in future studies of OM stabilization.

562 5 Conclusion

563 Organo-mineral interactions are recognized as key factors in stabilizing organic matter (OM)
564 in soils, and short-range order minerals (SRO) are increasingly considered as key mineral
565 nanophases in the control of soil OM dynamics. In the present work, we have shown that:

- 566 - Fe-coprecipitate and Al-coprecipitate systems are likely not the only coprecipitates to
567 consider in SRO-OM stabilization issues, because they do not fit the complex chemical
568 composition of soil solutions that occur in soils;
- 569 - In soils in which silicate minerals are present and provide a range of cations upon
570 weathering ($\text{Fe}(\text{OH})^{2+}$, $\text{Al}(\text{OH})^{2+}$, $\text{Si}(\text{OH})_4$, Mg^{2+} , Ca^{2+} , K^{2+} etc.), at least Si may be an
571 important component in the mineral structure of the coprecipitates, whatever the
572 concentration of C;
- 573 - In the case of intermediate C contents, we propose a structural model of coprecipitates
574 in which amorphous small oligomers of Fe (~70%), Si (~20%), Al (~10%) form an
575 amorphous, open-branched 3D network. In this mineral skeleton, organic compounds
576 are linked either by bonds with Fe and Al to the network, by monomeric Fe-O-C in the
577 porosity of the network, or by weak bonds with OM. We propose to name the structure
578 "Nanosized Coprecipitates of inorganic oLligomers with organiCs" with the acronym
579 "nanoCLICs".
- 580 - In nanoCLICs, Si does not bind directly with OM. However, it prevents the
581 polymerization of Fe and Al phases into crystalline structures, thereby insuring large

582 amounts of Fe and Al are available to bind with OM and hence for C stabilization. The
583 presence of Si may also limit the progressive aging of the Fe and Al phases into better
584 crystallized oxides, thus insuring the preservation of the very poorly crystallized state
585 and maintaining the high C stabilization potential of inorganic oligomers.
586
587

588 6 Acknowledgements

589 We would like to thank the European Synchrotron Radiation Facility (ESRF) (Grenoble, France)
590 and ELETTRA synchrotron (Trieste, Italy) and their respective teams at the FAME and 11.1
591 beam lines for their kind and expert assistance during the EXAFS measurements. We also
592 thank Patrice Thauhay (CIRAD) who designed the nanoCLICs 3D illustration.
593

594 7 Funding:

595 This work was supported by Aix-Marseille University doctoral school ED251, ANR (NanoSoilC
596 ANR-16-CE01-0012-02 project) and the *Institut Universitaire de France*.

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819 **FIGURE CAPTIONS**

820 Table 1: Proportions of Fe-O-C and Fe-O-Fe bounds estimated by linear combination fitting.
821 Proportions under the three reference standards designated “Fe-O-Fe” show contributions to fit
822 from pure Fe to Fe interactions. Fe-C colloids represent higher Fe to C interaction with a low but
823 significant Fe to Fe interaction. Fe citrate represents pure Fe to C interactions. The error in the
824 proportions was estimated at around 15%. R-factor indicates the relative goodness-of-fit between
825 the data and the model (values close to 0 represent the best fits, see supplementary information
826 for details).

827 Figure 1: TEM electron micrographs of coprecipitate series at pH=5: (a) ‘No C’, (b) M:C=3, (c)
828 M:C=0.3, (d) M:C=0.03 and (e) M:C=0.003. Electron diffraction patterns are shown in the upper
829 right of the 50 nm scale pictures. In the No C sample (a), LP stands for areas of larger particles and
830 and SP for smaller particles.

831 Figure 2: TEM-EDX chemical analysis of nanophases (No C) and coprecipitates at the four M:C ratios
832 expressed in stoichiometric atomic % (excluding C and O). The “box-and-whisker” plots represent
833 median values, the upper and lower quartiles, as well as the min and max of the data. Number of
834 analyzed particles: No C n=33; M:C=3 n= 42; M:C=0.3 n=30; M:C=0.03 n=40; M:C=0.003 n=60. For
835 the purpose of comparison, the chemical composition of the leachate solution (Leachate S.) is also
836 shown as dashed lines with their respective error values.

837 Figure 3: (a) EXAFS/k-space plots and (b) FTF/R-space plots. FTF peaks between 1.2-2Å correspond
838 to the first coordination sphere of oxygen atoms. On references, markers of Fe-C interactions (red
839 arrows) occur between ~2.2 and ~2.5 Å and Fe-Fe octahedra (black arrows) at ~2.7 and ~3.0 Å (for
840 edge (E) and double corner (DC) interactions respectively). Radial distances are not corrected for
841 phase shift.

842 Figure 4: Ternary diagrams of Fe, Si and Al atomic proportions in the analyzed particles. White
843 dots: smaller and larger nanophases in the No C sample (Tamrat et al. 2018). Grey dots:
844 coprecipitates for the four M:C ratios. The black star represents the initial composition of the
845 leachate solution.

846 Figure 5: Solid line: LCF contributions of Fe-O-Fe and Fe-O-C interactions. Fe-O-Fe represents
847 contributions from Fe dimers, $\text{SRO}_{\text{Fe,Si}}$ and 2L Ferrihydrite, while Fe-O-C represents contributions
848 from Fe-C colloids and iron citrate reference standards. Dashed bars: particle size ranges.

849 Figure 6 : 3D conceptual model of Nanosized Coprecipitates of inorganic oLlgomers with organiCs
850 (“nanoCLICs”) in an Fe Al Si and DOPA system with initial 0.3 <M:C <3. H₂O molecules are not
851 represented to simplify the visualization of the structure. The 3D model can be rotated with Adobe
852 Acrobat using the pdf file provided in the Electronic Annex (a 3D PDF basic function tutorial can be
853 found <https://www.qwant.com/?q=rotating%20object%20pdf%20adobe%20acrobat&t=videos&o=0:9860450d6f706f26d49065218b7d1c03>).
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