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1 Structure and chemical composition of soil C-rich  
2 Al-Si-Fe-coprecipitates at nanometer scale

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13

14 ABSTRACT. Soil carbon stabilization is mainly driven by organo-mineral interactions.  
15 Coprecipitates, of organic matter with short-range order minerals, detected through indirect  
16 chemical extraction methods, are increasingly recognized as key carbon sequestration phases.  
17 Yet the atomic structure of these coprecipitates is still rather conceptual. We used transmission  
18 electron microscopy imaging combined with EDX (energy dispersive x-ray) and EELS (electron  
19 energy loss spectroscopy) chemical mappings, which enabled direct nanoscale characterization  
20 of coprecipitates from Andosols. A comparison with reference synthetic coprecipitates showed  
21 that the natural coprecipitates were structured by an amorphous Al, Si and Fe inorganic skeleton  
22 associated with C, and were therefore even less organized than short-range order minerals  
23 usually described. These amorphous type of coprecipitates resembled previously conceptualized  
24 nanosized coprecipitates of inorganic oligomers with organics (nanoCLICs) with heterogeneous  
25 elemental proportions (of C, Al, Si and Fe) at nanoscale. These results mark a new step in the  
26 high-resolution imaging of organo-mineral associations, while shedding further light on the  
27 mechanisms that control carbon stabilization in soil, and more broadly in aquatic colloid,  
28 sediment and extraterrestrial samples.

29 KEYWORDS. Soil carbon cycle, organic matter, organo-mineral associations, coprecipitates,  
30 transmission electron microscopy, EDX, EELS.

31

32 SHORT SYNOPSIS STATEMENT.

33 Structural characterization of organo-mineral associations of soils remains limited. This study  
34 provides chemical mapping down to a few nanometers of the structure of these associations,

35 leading to a new conceptualization of the latter with implications for their fate and stability in  
36 soils.

## 37 **INTRODUCTION**

38 Soil is the third largest reservoir of organic carbon (C) on Earth<sup>1</sup>. A large part of this organic  
39 C is found in form of organic compounds bound to minerals<sup>2-4</sup>, thereby shielding them from  
40 microbial mineralization<sup>5</sup>, which accounts for one of the mechanisms for long-term organic  
41 carbon persistence<sup>6,7</sup>. These associations includes two interaction mechanisms at the molecular  
42 scale: adsorption and coprecipitation<sup>3,8</sup>. Adsorption refers to accumulation of organic compounds  
43 on primary or secondary mineral surface with various bond types (classified as chemisorption or  
44 physisorption). As for the formation of co-precipitates in soil, as defined by Kleber et al.<sup>3</sup>, it may  
45 involve several interacting processes (complexation, precipitation and adsorption) between OM  
46 and metal (mainly Fe and Al) species hydrolyzed, insolubilized and/or oxidized. In soils with  
47 acidic pH ( $\leq \sim 7$ ), organo-mineral associations mainly involve coprecipitates formed by  
48 precipitation of organic compounds with secondary mineral phases or with elements derived  
49 from mineral weathering containing Fe and Al<sup>9-12</sup>. Coprecipitates are thought to have a major  
50 role in soil C sequestration<sup>12</sup>, yet their chemical composition and 3D atomic structure using  
51 conventional geochemical techniques has been substantially hampered by three main challenges.

52 The first challenge relates to the analytical methods for detecting coprecipitates in soils.  
53 Coprecipitates, in terms of crystalline structure, are intermediate between allophane and metal-  
54 organic association. To detect this type of crystalline structure, wet-chemical extraction of soil is  
55 a standard procedure (e.g. extracted by Na-pyrophosphate and to some extent by ammonium  
56 oxalate–oxalic or hydroxylamine<sup>13,14</sup>). Following these chemical extractions, the ionic

57 concentrations in solution (e.g. Fe, Al or Si) are used to recalculate the quantities of phases  
58 initially present in the soil. Moreover, for some extractions (Na-pyrophosphate and  
59 hydroxylamine) the detection of C in solution is used to detect its association with this type of  
60 crystalline structure, presumably in the form of coprecipitates. However, no structural  
61 information on coprecipitates can be obtained as wet-chemical extractions destroy the phases of  
62 interest.

63 The second challenge concerns lab experiments. As it is hard to extract intact coprecipitates  
64 from soils, in many studies they have been characterized using synthetic coprecipitates obtained  
65 by coprecipitating organic matter (OM) with two metals, i.e. with Fe<sup>15-25</sup> and sometimes with  
66 Al<sup>26-28</sup>. The choice of these metals is linked to their high complexation capacity with OM (Figure  
67 1), and also to the fact that they are major elements in terms of concentration in most soils.  
68 However, the assumption that only these two metals are involved in coprecipitate formation in  
69 soils is simplistic since many other chemical elements derived from the weathering of soil  
70 minerals (e.g. Si, Mg<sup>2+</sup>, K<sup>+</sup>, Na or Ca) are also present in the soil solutions in which  
71 coprecipitation occurs.

72 The third challenge relates to the conceptual models used to represent coprecipitates at  
73 molecular scales. In the literature, coprecipitates are generally represented by OM in contact with  
74 well-known short-range order (SRO) minerals. For Fe, SROs are represented by aggregates of  
75 spherical ferrihydrite nanoparticles<sup>3,23</sup>, whereas for Al, amorphous Al oxyhydroxide, imogolite  
76 or allophane phases are often mentioned but barely represented by a conceptual model, except in  
77 Levard et al. (2012)<sup>29</sup> (Figure 1). There are two main reasons for this shortcoming in conceptual  
78 molecular scale coprecipitate models: (1) firstly, unlike adsorption models on mineral  
79 surfaces<sup>8,30</sup>, the surfaces reactivity of the inorganic part of coprecipitates is difficult to determine

80 and predict, and (2) secondly, carrying out in situ coprecipitate analyses at the nanometric scale  
81 with synthetic or natural soil samples is challenging.

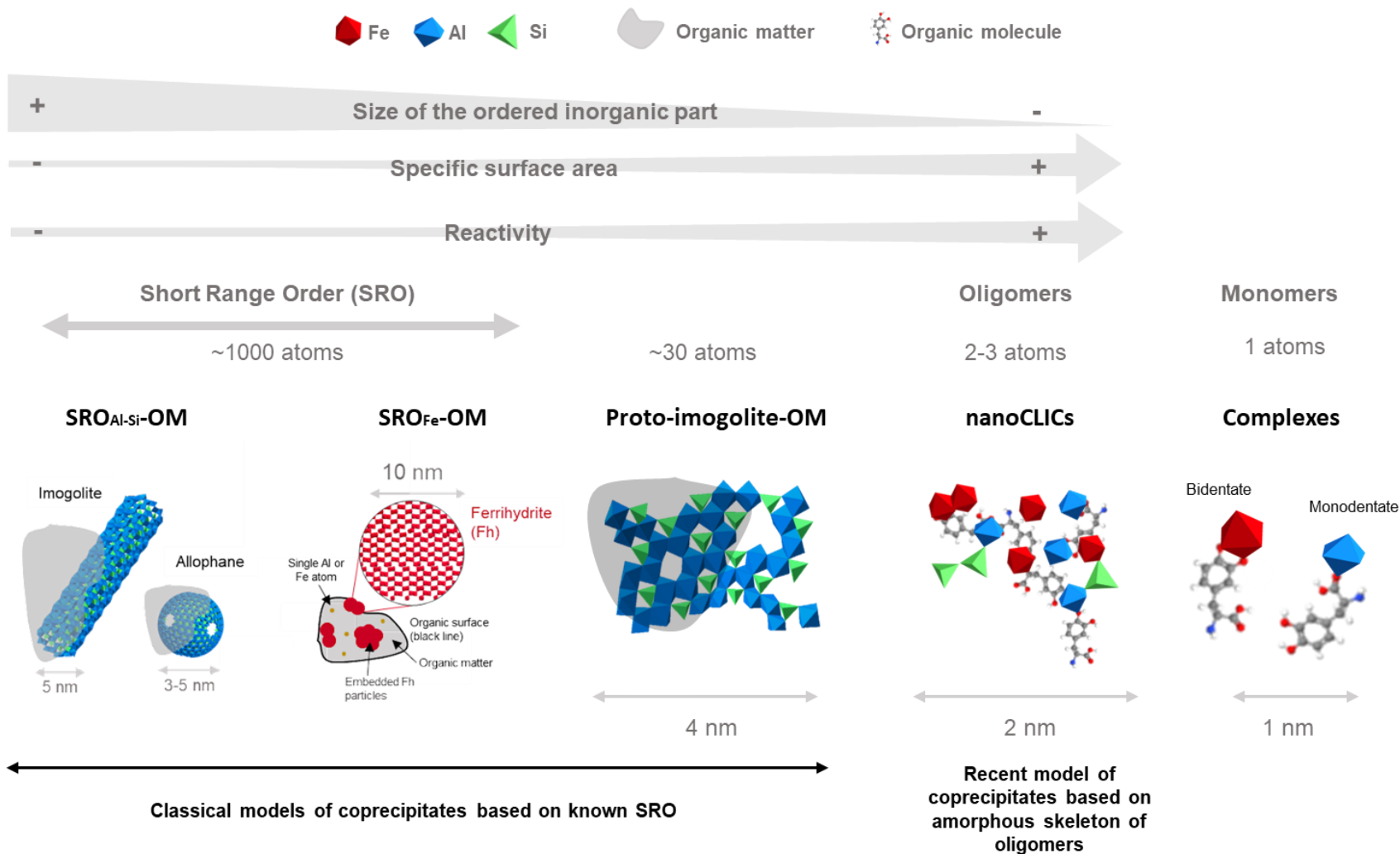
82 Progress on the last two locking points has been achieved in recent laboratory studies.  
83 Tamrat et al. (2018, 2019)<sup>31,32</sup> synthesized coprecipitates from a biotite weathering solution.  
84 They showed that the mono ( $K^+$ ) and divalent ( $Mg^{2+}$ ) ions remained in solution while the  
85 coprecipitates formed 5- to -200 nm nanoparticles containing OM, Fe, Al, as well as Si. Using Fe  
86 K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy, the local structure of  
87 the coprecipitates was modeled as a loose irregular 3D network of amorphous small Fe, Si and  
88 Al oligomers forming an amorphous and open-structured inorganic skeleton. Within this inorganic  
89 network, the organic compounds would be linked in the network pores by Fe and Al bonds of the  
90 skeleton, by monomeric Fe-O-C and Al-O-C, or by weak bonds with another organic molecule  
91 (Figure 1). These results gave rise to definition of the nanosized coprecipitates of inorganic  
92 oligomers with organics (nanoCLICs) concept. However, direct in situ characterization of  
93 nanoCLICs has yet to be achieved.

94 Substantial advances have also been made in the in situ soil organo-mineral associations  
95 analysis field<sup>33</sup>. Transmission electron microscopy (TEM) is the tool of choice to probe  
96 coprecipitates at high spatial resolution through the analytical combinations offered by the  
97 different sensors available in a single instrument. Electron diffraction can be used to differentiate  
98 mineral-crystallized phases from poorly crystallized or even amorphous phases. Energy  
99 dispersion X ray (EDX) and electron energy loss (EELS)<sup>34,35</sup> spectroscopy can be used in  
100 scanning TEM mode (STEM) to map the nanoscale elemental composition, with elemental  
101 colocation resolutions of 10 nm<sup>36,37</sup> and few Å<sup>34,35</sup>, respectively. While the spatial resolution of  
102 EELS is higher, its sensitivity is not as good as EDX for heavy elements. These two imaging

103 spectroscopy tools can therefore be used advantageously in a complementary way, but they have  
104 yet to be markedly used in soil science research. EDX spectroscopy has mainly been used for  
105 spot analyses<sup>38,39,40</sup>. But recently Possinger et al. (2020)<sup>41</sup> took up the challenge of mapping C  
106 and N by EELS and revealed soil OM spatial heterogeneity patterns at the 1 nm scale. This latter  
107 research has opened a promising avenue for the simultaneous characterization of organic and  
108 inorganic coprecipitate phases at the nanoscale.

109 The aim of this study was to develop a conceptual molecular model of organo-mineral  
110 coprecipitates that contribute to soil C stabilization. We focused on an Andosol due the high  
111 abundance of these coprecipitates in this type of soil. We analyzed the crystallinity of inorganic  
112 phases obtained by electron diffraction and performed STEM-EDX and TEM-EELS imaging to  
113 collocate and quantify C, Al, Si and Fe at the nanometric scale. In support of our interpretations  
114 of coprecipitate formation in natural systems, we also relied: (1) on synthesized coprecipitates  
115 made with inorganic solutions from basalt and labradorite weathering to obtain solutions  
116 containing a diverse range of elements closer to the elemental diversity in natural soil solution  
117 (these two coprecipitates served as reference coprecipitates, denoted nanoCLIC<sub>Basalt</sub> and  
118 nanoCLIC<sub>Labradorite</sub>) and (2) on statistical approaches based on a Python code we specifically  
119 developed for TEM-EELS imaging. Our results demonstrate that the AAndosol coprecipitates  
120 are structured by an amorphous Al, Si and Fe inorganic skeleton, and are therefore even less  
121 organized than short-range order minerals usually described. These findings provide insights into  
122 the nanoscale mechanisms that control C stabilization in soils.

123



124  
 125 **Figure 1.** Molecular models of soil coprecipitates in the literature. Coprecipitates can be conceptualized with: (i) an inorganic phase of  
 126 one or several 100 to 1,000 atoms forming a more or less organized crystal lattice, or so-called short-range orders (SRO). These SRO  
 127 are imogolites or allophanes (composed of Si and Al) or ferrihydrate (composed of Fe; scheme adapted from Kleber et al.<sup>3</sup>); (ii) an



128 inorganic phase made up of only ~30 atoms with limited local organization, such as proto-imogolites (scheme adapted from Levard et  
129 al.<sup>29</sup>); and (iii) an inorganic phase involving the polymerization of only 2-3 atoms, the inorganic phase is composed of small  
130 amorphous oligomers, without local arrangement called nanosized coprecipitates of inorganic oligomers with organics (nanoCLICs)  
131 (scheme adapted from Tamrat et al.<sup>32</sup>); and (iv) an inorganic part involving only one atom (e.g. Fe, Al or Ca) complexed with organic  
132 molecules through a mono or bidentate bond.

## 133 2. MATERIALS AND METHODS

### 134 2.1. Synthetic nanoCLICs preparation

135 Synthetic nanoCLICs were obtained using a protocol similar to that of Tamrat et al. (2019)<sup>32</sup>,  
136 which consisted of two main steps: (1) silicate weathering to obtain a solution with dissolved  
137 elements, and (2) coprecipitation of the dissolved elements with an organic L-3,4-  
138 dihydroxyphenylalanine molecule (hereby referred to as DOPA). The DOPA molecule was  
139 selected due to its low molecular weight typical of organic compounds and because the DOPA  
140 has the main functional groups of MAOM<sup>42</sup>. Moreover, using DOPA also avoided fractionation  
141 uncertainty during coprecipitation<sup>32</sup>. This protocol was carried out using two types of minerals or  
142 rocks, i.e. basalt and labradorite, to obtain weathered solutions with various dissolved elements.

143 Briefly, the weathering solutions were obtained as follows: basalt or labradorite were crushed  
144 and particles between 50 and 100  $\mu\text{m}$  were isolated by dry sieving. Then, to mimic mineral  
145 weathering, 33 g of particles were agitated in 1 L of an  $\text{HNO}_3$  solution at  $10^{-2}\text{M}$ . After 3 months,  
146 the solutions were filtered using tangential flow filtration (KrosFlo®) with a 10 KDa pore size  
147 (corresponding to a pore size of about 2 nm). The dissolved elements were measured by ICP-  
148 AES (see results in SI1). The weathering solutions were then diluted to obtain an Al+Fe  
149 concentration of as low as 1.8 mM according to the protocol of Tamrat et al.<sup>32</sup> (4-fold dilution  
150 for the basalt weathering solution and 1.8-fold for the labradorite weathering solution). In a  
151 second step, L-3,4-dihydroxyphenylalanine (L-DOPA) was added to 150 ml of the weathering  
152 solutions to reach an atomic ratio of (Al+Fe):C = 1 (corresponding to an L-DOPA mass of 5.9  
153 mg). The coprecipitation step involved titration of the solutions with NaOH (0.1 M) at an  
154 hydrolysis rate of  $600 \mu\text{L}\cdot\text{min}^{-1}\cdot\text{L}^{-1}$ . Titrations were performed at a fixed temperature of  $25^\circ\text{C}$

155 using a thermostatic bath. Titrations were stopped when the pH reached 5 to be representative of  
156 acidic soil conditions (210 min titration time). The coprecipitates obtained were sub-sampled by  
157 the collection of a few ml of the solution. The sub-samples were kept at 4°C for microscopy  
158 analysis to avoid micro-organisms development during storage. As demonstrated by Tamrat et al.  
159 (2019)<sup>32</sup>, this procedure creates nanoCLICs, which is why these two coprecipitates obtained from  
160 basalt and labradorite weathering solutions were called nanoCLICs<sub>Basalt</sub> and nanoCLICs<sub>Labradorite</sub>.

## 161 **2.2. Natural soil fine fraction preparation**

162 Natural soil was sampled on the island of Réunion, on the western side of the Piton des  
163 Neiges shield volcano, 1720 m ASL (55°21.530 E, 21°04.700 S). The mean annual temperature  
164 and precipitation are 13°C and 1,700 mm. The soil supports a forest composed predominantly of  
165 tamarinds (*Acacia heterophylla*), philippia (mainly *Philippia montana*), ferns (*Histiapteris*  
166 *incisa*) and bamboo (*Nastus borbonicus*). As a result of intermittent volcanic activity, this soil is  
167 an Andosol and consists of a modern surface layer overlying a series of buried horizons. We  
168 selected the sil-andic 4Bw horizon (90-190 cm depth, charcoal age of around 40 000 BP) for its  
169 high content in low-crystalline phases associated with organic matter<sup>9,29</sup>. X ray diffraction on this  
170 horizon previously showed the predominant content of low-crystalline amorphous phase, with  
171 some gibbsite and feldspar<sup>9</sup>. Low-crystalline amorphous phases have been characterized by  
172 indirect spectroscopic techniques, showing a lower degree of polymerization than imogolites,  
173 then referring to proto-imogolites in the papers by Basile-Doelsch et al. (2005, 2007)<sup>9,43</sup> and  
174 Levard et al. (2012)<sup>30</sup>. The previous characterization of this horizon showed that it contains 60  
175 gC.kg<sup>-1</sup> and had a pH of 5.2<sup>9</sup>.

176 The soil fine fraction was isolated as follows, in order to isolate them by a slight  
177 disaggregation but without modifying the coprecipitates' structure: up to 2 g of humid soil was  
178 dispersed in 100 ml of water by sonication ( $16 \text{ J.ml}^{-1}$  by immersion probe; in an ice bath). After  
179 48 h of decantation, the supernatant brown gel, enriched in coprecipitates was collected and few  
180  $\mu\text{L}$  were immediately deposited on microscopy grids and air-dried.

### 181 **2.3. TEM imaging, TEM-EDX and TEM-EELS chemical maps**

182 Solutions containing synthetic nanoCLICs or soil fine fractions were diluted with ultrapure  
183 water, at 1/50 and 1/100 ratio, respectively, to limit the number of particles likely to clump  
184 together on microscopy grids. Then 7  $\mu\text{L}$  of the sample solutions were directly deposited on a  
185 copper grid coated with a Lacey carbon film and air dried. This type of grid allowed us to  
186 investigate the structure and chemical compositions of particles located on the holes to prevent C  
187 signal from the Lacey C film.

188 Microscopic analyses were performed on and FEI OSIRIS transmission electron microscope  
189 (TEM) operating at 200 kV. TEM was used to image the sample from the micrometer to the  
190 nanoscale. The scanning transmission electron microscopy configuration was used to image the  
191 sample with a very resolved probe size of  $1.8 \text{ \AA}$  and a 0.3 nA current. Two chemical mapping  
192 techniques were used in STEM configuration, as detailed hereafter and in SI2, i.e. energy  
193 dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) techniques.

- 194 • Following electron beam scanning, EDX mapping uses the energy of photons emitted  
195 by a volume of the surface sample. EDX at 200 kV allows a wide range of elemental  
196 detection. In our study, we focused on C, N, Si, Al, Fe, Ca, K and Mg. However, the  
197 exact size of elementary collocations depends on the volume of interaction between

198 the electrons and the material. This volume is hard to estimate, but in STEM mode, it  
199 can be about  $10 \text{ nm}^{36,37}$ . Yet the acquisition time necessary to obtain an exploitable  
200 signal-to-noise ratio to compute the atomic proportions (at.%) remains long at the 10  
201 nm scale, hence, atomic proportions are obtained in areas of several hundred  $100 \times$   
202  $100 \text{ nm}$ . The data were analyzed using Esprit software version 1.9 and atomic  
203 proportions were calculated using the PB-ZAF interactive algorithm.

204 • Following the electron beam scan, EELS mapping uses the energy loss of the  
205 transmitted electron beam to detect elements. This technique allows us to attribute a  
206 very resolved elemental colocation size from a few Å to the nm scale, but the  
207 sensitivity is weak for heavy elements (Egerton 2011). This technique allows  
208 elementary detection on a range of up to 2000 eV. This range covers the C K-edge  
209 (284 eV), O K-edge (532 eV), Fe L-edge (708 eV), Al K-edge (1560 eV) and Si  
210 K-edge (1839 eV). However, this technique is more sensitive to light elements (e.g.  
211 more sensitive to C K-edge detection than to Si K-edge detection), so it may  
212 underestimate heavier elements such as Si<sup>35</sup>. The analysis time per pixel is reduced as  
213 much as possible to reduce beam damage, while ensuring elemental detection at the  
214 desired scales. EELS ranging from 250 to 1224 eV were acquired first with a pixel  
215 analysis time of 0.05 to 0.09 s. In a second step, EELS were acquired from 1,050 to  
216 2,074 eV with a time analysis of 0.1 to 1.5 s per pixel. However, due to the potential  
217 alterations to elemental fine structure resulting from beam damage<sup>45,46</sup>, element  
218 speciation is not interpreted in this paper. Data interpretation was done to obtain  
219 spatially resolved elemental detection (e.g. extracted core loss signal). EELS data  
220 were analyzed using Digital Micrograph software (version 2.32.888.0) and atomic

221 proportions calculated with power law fitted backgrounds and Hartree Slater cross  
222 sections. Energy ranges for power law fitted backgrounds and Hartree Slater cross  
223 sections are summarized in SI3.

224 EDX and EELS mappings are used as complementary methods rather than for comparative  
225 purposes, as the thicknesses of the probed zones are unknown (and variable). Furthermore  
226 performing EDX and EELS maps can lead to C deposition on the sample (electron-induced  
227 carbon fixation from residual gases and local volatilization and re-adsorption from and onto the  
228 sample)<sup>47</sup>. To quantify these possible deposits, we synthesized coprecipitates from basalt  
229 weathering solution without the addition of DOPA (referred to SRO<sub>Basalt</sub>), which therefore did  
230 not contain C. The EDX and EELS maps showed that the C atomic proportion was low (0.1-  
231 0.2%; SI4). Hence, the C deposits were considered negligible under the analysis conditions used.  
232 Moreover, TEM imaging, EDX and EELS mappings were carried out in chronological order, but  
233 on different particles to avoid any artifacts induced by the preceding analyses.

#### 234 **2.4. Nanoscale elemental colocation using EELS maps**

235 As explained above, the EELS technique allows elemental detection down to a few nm. In  
236 order to analyze the elemental colocations of C with inorganic elements at the nanometer scale,  
237 we detected the presence or absence of C, Fe, Al and Si elements in each pixel of about 10 nm  
238 (pixel lateral distance) of the EELS maps. To automatically perform these elementary multi-  
239 detections per pixel, we encoded a script in Python 3.9 that included the following steps:  
240 Localization of the elementary thresholds of C K-edge, O K-edge, Fe L-edge, Al K-edge and Si  
241 K-edge. Then a power law function fits and removes the background per elementary threshold,  
242 as defined by Egerton (2011)<sup>35</sup>. The energy range of the power law fits are mentioned in part

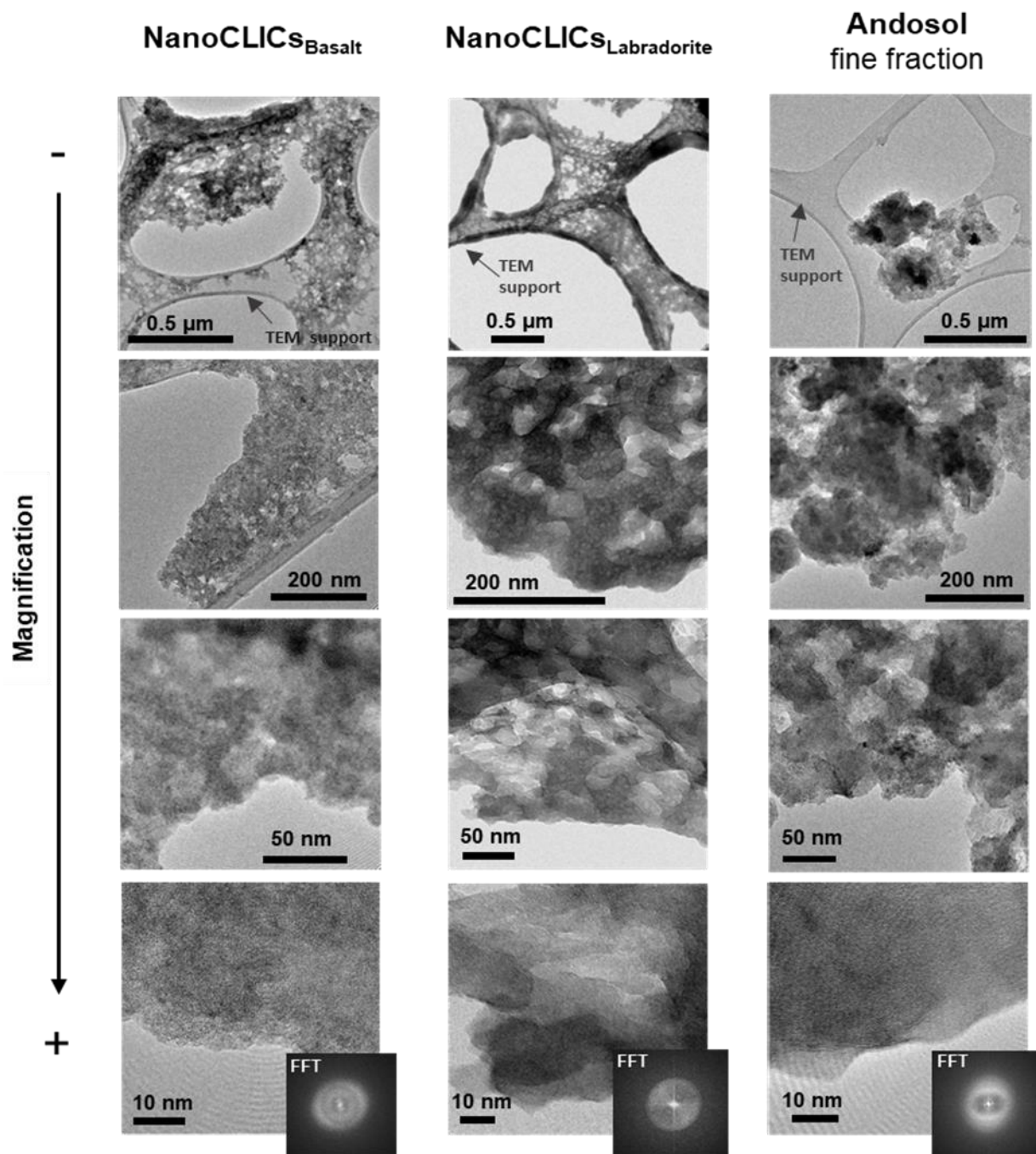
243 SI4. Then elementary detection was done by computing the signal-to-noise ratio (SNR) adapted  
244 from Egerton (2011)<sup>35</sup>. The calculations are outlined in SI3. Finally, the script compiles all  
245 elementary multi-detections per pixel into a spreadsheet.

## 246 **3. RESULTS**

### 247 **3.1. Transmission electron microscopy (TEM) imaging**

248 TEM imaging of nanoCLICs<sub>Basalt</sub> and nanoCLICs<sub>Labradorite</sub> (Figure 2; SI5) showed that they  
249 had a gel-like texture. No crystal planes were detected at the scale of a few nm using high  
250 resolution TEM. A fast Fourier transform (FFT) of the images at 10 nm scale did not show any  
251 diffraction pattern (indicated by bright dots), thereby suggesting the absence of crystal lattices  
252 (Figure 2). The local synthetic nanoCLICs structures were then very similar to each other and  
253 characterized as a gel-texture electron-amorphous phase. Moreover, TEM images of the Andosol  
254 fine fractions showed close similarities with the synthetic nanoCLICs—these fine fractions were  
255 mainly composed of a gel-textured phase (Figure 2) that was also electron amorphous (no atomic  
256 arrangement noted at the nanoscale by FFT). However, at microscale, Andosol fine fractions  
257 appeared to have greater differences in thickness or density than synthetic nanoCLICs (wider  
258 gray-scale contrast for Andosol fine fractions at microscale, Figure 2 and SI5). These differences  
259 may also be partly induced by sample preparation (dilution and drying, method 2.3).  
260 Furthermore, these analyses showed that these fine Andosol fractions did not have imogolite- or  
261 allophane-like arrangements.

262



263  
 264 **Figure 2.** Imaging and characterization of the structure of synthetic nanoCLICs and AAndosol  
 265 fine fractions using transmission electron microscopy (TEM). Scales range from the micrometer  
 266 scale to a few nanometers (high-resolution TEM). On high-resolution TEM images (10 nm  
 267 scale), the fast Fourier transform (FFT) shows electron diffractions characteristic of amorphous  
 268 structures for synthetic nanoCLICs and for the Andosol fine fraction.

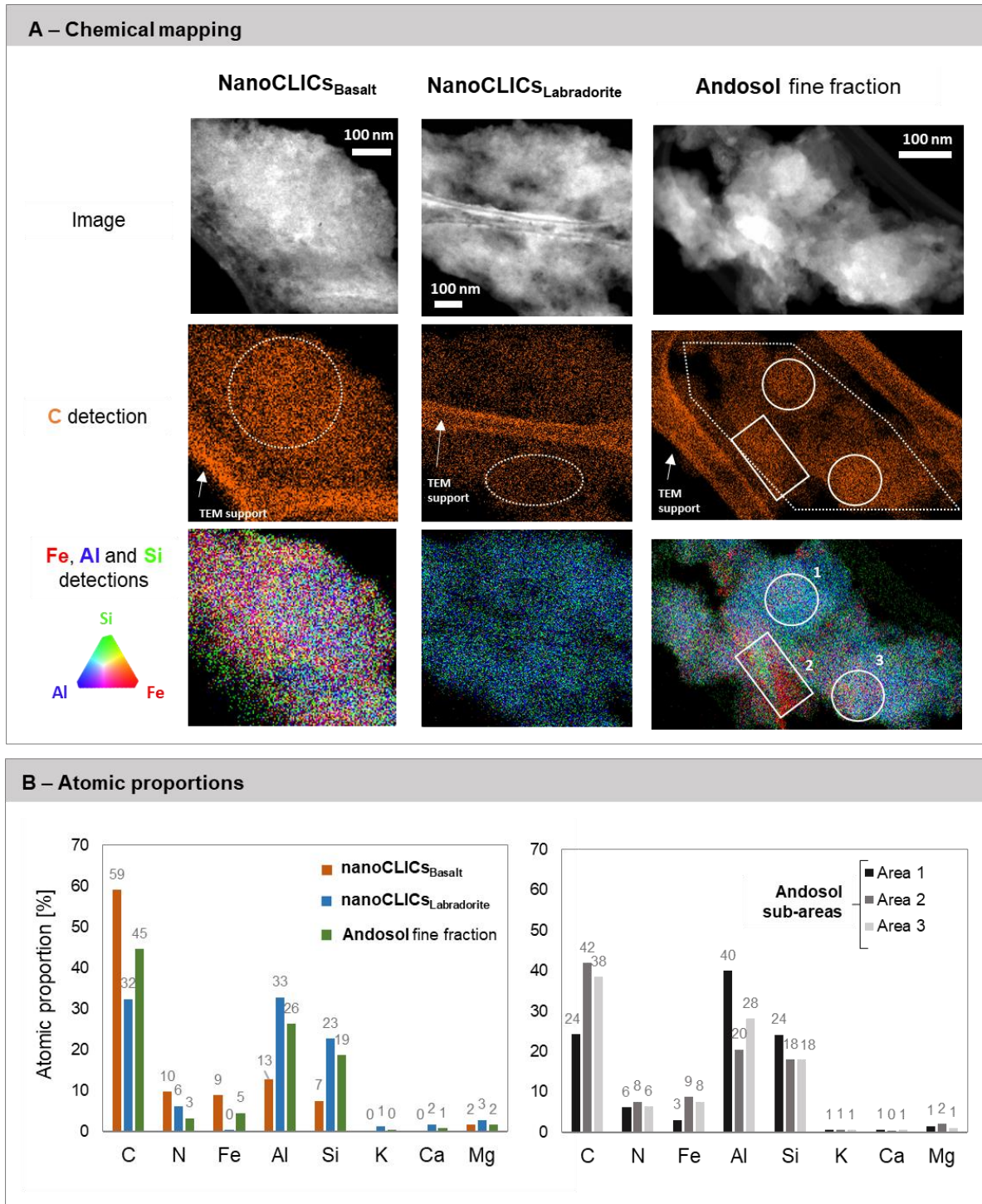


269  
270

### 3.2. Energy dispersive x-ray (EDX) mappings

271 Chemical EDX mappings of nanoCLICs<sub>Basalt</sub> and nanoCLICs<sub>Labradorite</sub> revealed a  
272 homogeneous distribution of C across the analyzed areas (Figure 3A; SI6). However, C was not  
273 detected alone, i.e., Al, Fe and Si were also jointly detected in all of the EDX maps. These  
274 inorganic elements (Al, Fe and Si) were also homogeneously distributed in the sample and did  
275 not form inorganic clusters. However, nanoCLICs<sub>Basalt</sub> and nanoCLICs<sub>Labradorite</sub> had different  
276 inorganic compositions when colocalized with C (Figure 3B): nanoCLICs<sub>Basalt</sub> showed C  
277 colocation (59 at.%) with mostly Al (13 at.%), Fe (9 at.%) and Si (7 at.%) whereas  
278 nanoCLICs<sub>Labradorite</sub> had C colocation (32 at.%) with mostly Al (33 at.%) and Si (23 at.%) and  
279 trace of Fe (0.3 at.%). These proportions demonstrated that coprecipitates could be formed with  
280 different inorganic elements derived from mineral weathering and that the presence of Fe is not  
281 necessary for nanoCLICs formation. Moreover, nanoCLICs<sub>Basalt</sub> and nanoCLICs<sub>Labradorite</sub>  
282 detections revealed other elements, including K, Ca and Mg, but their elemental proportions  
283 were negligible (1–3 at.%). Chemical maps of the Andosol fine fractions by EDX also showed  
284 that C was heterogeneously detected throughout the sample with Al, Si and Fe (Figure 3A).  
285 Overall, C (45 at.%; Figure 3B) was colocalized with Al (26 at.%) and Si (19 at.%) and Fe (5  
286 at.%), but unlike the synthetic nanoCLICs, elemental proportions were more spatially  
287 heterogeneous—some areas had a higher proportion of Al and Si (sub-area 1; Fe = 3 at.%), while  
288 others had more Fe, Al and Si (sub-areas 2 and 3; Fe = 8-9 at.%) and some areas had a lower  
289 proportion of C (sub-area 1; C = 24 at.%). In these sub-areas, the three predominant elements in  
290 the coprecipitate structures were C (24–42 at.%), Al (20–40 at.%) and Si (18–24 at.%).

291



292 **Figure 3.** Chemical mapping of synthetic nanoCLICs and AAndosol fine fractions using STEM-  
 293 EDX. (A) imaging using a high angular dark field detector and chemical mapping showing  
 294 elemental detection of C, Fe, Al and Si. (B) The atomic proportions on each sample are from an  
 295 area of  $\sim 0.07 \mu\text{m}^2$ , dotted shapes on (A); atomic proportions on sub-areas of AAndosol fine

296 fractions are shown with a solid line on (A); The proportions do not include O<sub>2</sub> and Cu. The  
297 acquisition pixel size is of 4, 3 and 1 nm for nanoCLIC<sub>SBasalt</sub>, nanoCLIC<sub>SLabradorite</sub> and the  
298 AAndosol fine fraction, respectively. Spectra used for atomic proportions are available in SI6.

299  
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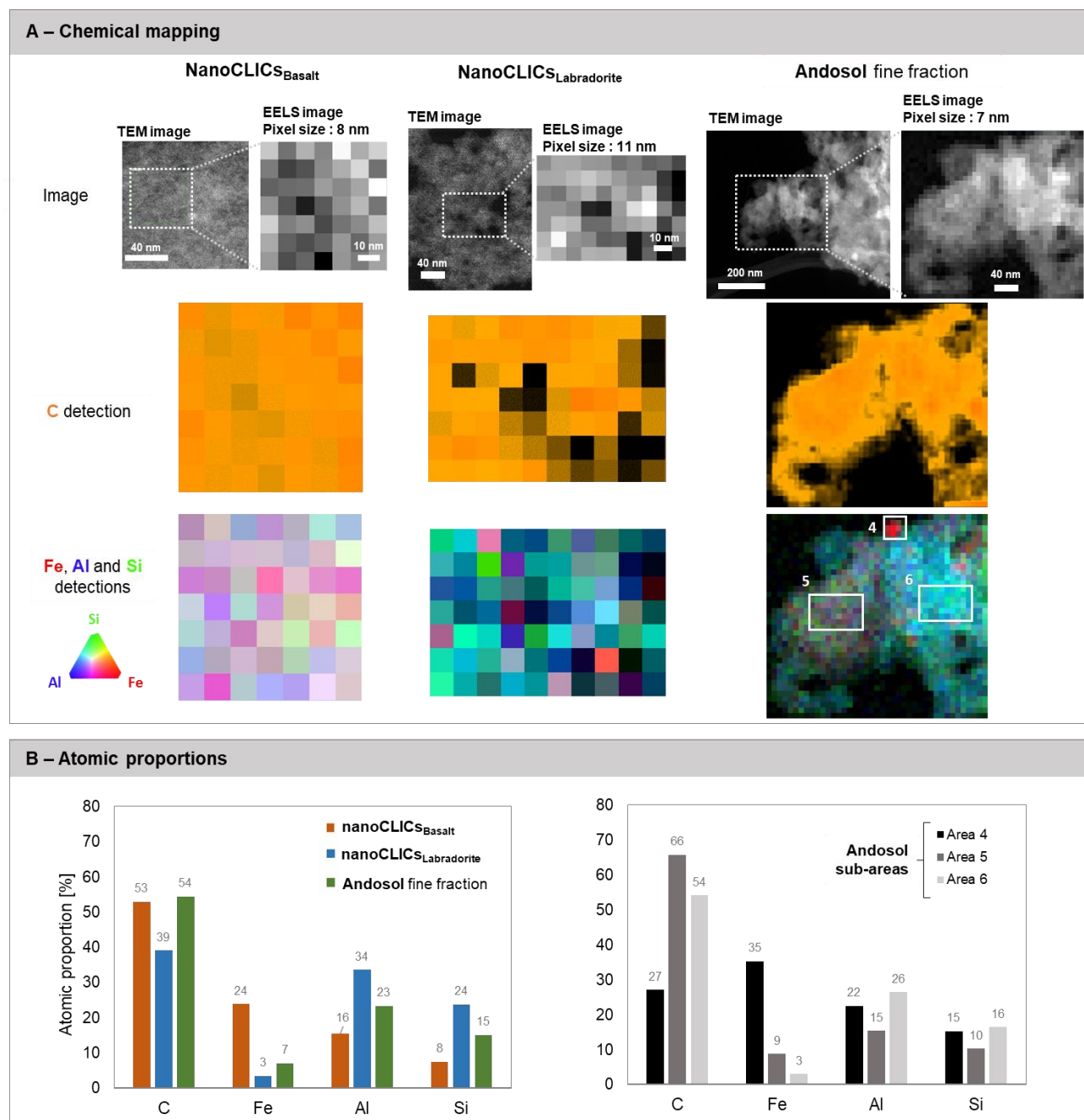
### 3.3. Electron energy loss spectroscopy (EELS) mappings

301 Chemical EELS mapping results of NanoCLIC<sub>SBasalt</sub> and nanoCLIC<sub>SLabradorite</sub> were similar to  
302 those obtained by EDX maps, i.e. an homogeneous distribution of C throughout all of the  
303 analyzed areas and colocation of C with Al, Si and Fe down to the pixel scale (7-11 nm) (Figure  
304 4A; SI7). NanoCLIC<sub>SBasalt</sub> showed C colocation (53 at.%) with mostly Al (16 at.%), Fe (24 at.%)  
305 and Si (8 at.%), while nanoCLIC<sub>SLabradorite</sub> had C colocation (39 at.%) with mostly Al (34 at.%)  
306 and Si (24 at.%) and little Fe (3 at.%). EELS maps results of the fine Andosol fractions were  
307 similar to those obtained by EDX maps, i.e. an heterogeneous detection of C throughout the  
308 sample (54 at.%), colocalized with Al (23 at.%), Si (15 at.%), and Fe (7 at.%). However, the  
309 elementary colocation proportions were noticeably heterogeneous (sub-areas 4-6), with sub-area  
310 4 rich in Fe (35 at.%) but it also included C (27 at.%), Al (22 at.%) and Si (15 at.%), while sub-  
311 area 5 included a C-rich mixture (66 at.%) with Al (15 at.%), Si (10 at.%) and Fe (9 at.%), and  
312 sub-area 6 included C-rich mixture (54 at.%) with Al (26 at.%), and Si (16 at.%) and little Fe (3  
313 at.%).

314 At the nanometer scale of a single pixel (here from 6 to 10 nm of the lateral distance), the  
315 signal-to-noise ratio was too low to compute the atomic proportions. However, in a given pixel,  
316 we were able to obtain binary information (presence or absence of an element; method used  
317 outlined in part 5.4, SI3 and SI8). The inorganic element(s) collocated with C at 6-10 nm scales  
318 are summarized in Figure 5. The nanoCLIC<sub>SBasalt</sub> results showed that 94% of C colocalized with

319 Fe+Al+Si. Little C was measured alone or just with Al or Fe at ~10 nm scale. Otherwise  
320 nanoCLICs<sub>Labradorite</sub> showed that C was predominantly colocalized with Al alone (48%) and  
321 Al+Si (37%). Little C was measured alone (9%) at ~10 nm scale. Moreover, the Andosol fine  
322 fraction results showed that C was mostly colocalized with mixtures of inorganic elements in  
323 decreasing proportion, i.e. Al+Si (32%) > Al+Fe+Si (19%) > Al+Fe (19%) > Al (17%) > Fe+Si  
324 (2%) > Si (1%). Consistent with the synthetic nanoCLICs findings, little C was measured alone  
325 (6%) in the AAndosol fine fraction at the ~10 nm scale.

326

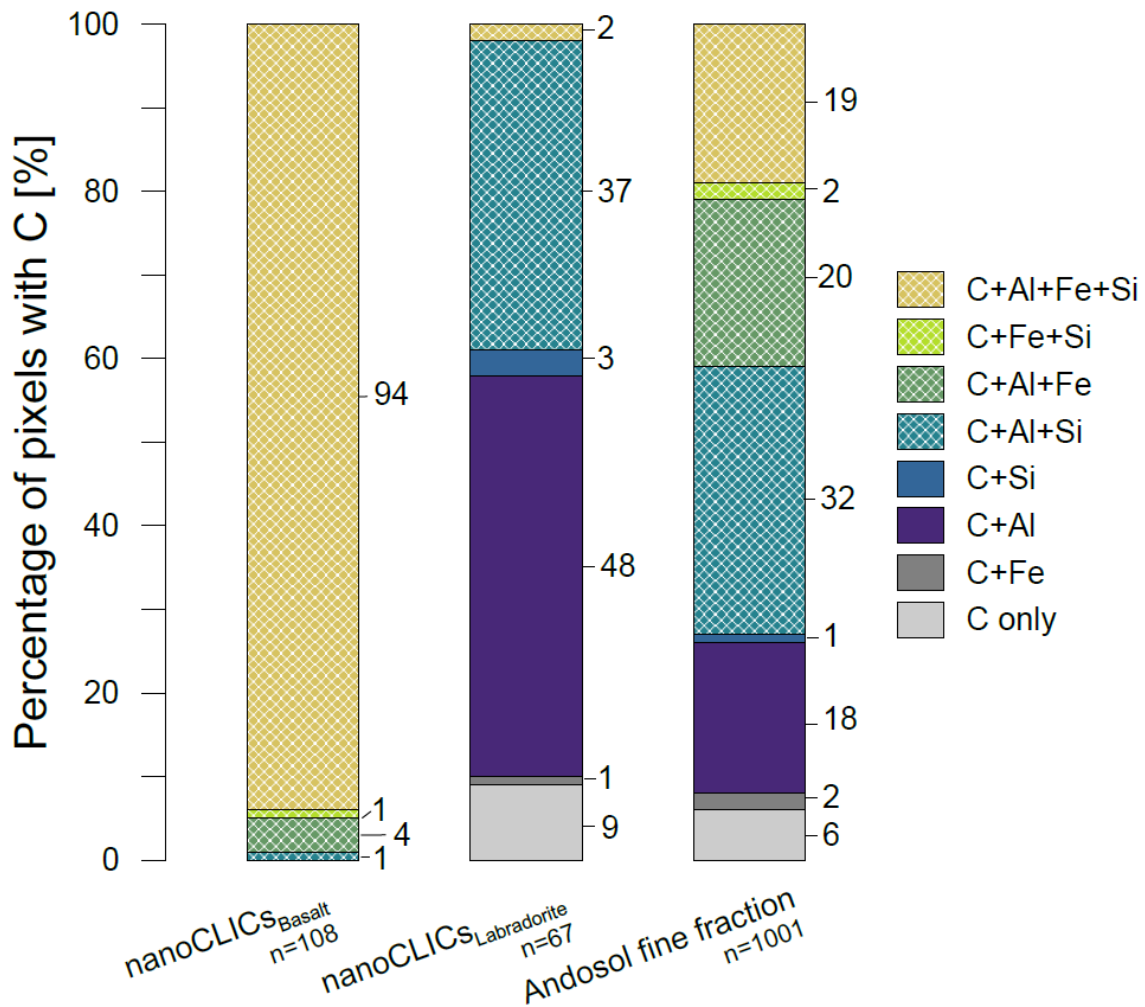


327

328 **Figure 4.** Chemical mapping of synthetic nanoCLICs and Andosol fine fractions using STEM-  
 329 EELS. (A) image using an angular dark field detector and chemical mapping showing elemental  
 330 detection of C, Fe, Al and Si. (B) Atomic proportions per sample on the whole images and  
 331 atomic proportions on sub-areas of the Andosol fine fraction (sub-areas displayed with solid

332 lines). The proportions do not take oxygen into account. The acquisition pixel size was 8, 11 and  
333 7 nm for nanoCLIC<sub>Basalt</sub>, nanoCLIC<sub>Labradorite</sub> and AAndosol fine fractions, respectively. Spectra  
334 used for atomic proportion calculation are available in SI7.

335



337

338

339 **Figure 5.** Nanoscale elemental colocalization through EELS mapping of 6-10 nm pixels size.

340 The pixel sizes ranged from 6 to 11 nm (lateral distance). n stands for the number of analyzed

341 pixels with C detection. For each sample, two EELS maps were acquired, this histogram

342 summed the pixels of these two maps (including the EELS shown in Figure 4). A bar chart for

343 each EELS map is shown in Figure SI8. This compilation includes 49 pixels of 8 nm (lateral

344 distance) and 64 pixels of 6 nm for the nanoCLIC<sub>basalt</sub>, 20 pixels of 10 nm and 70 pixels of 11 nm

345 for the nanoCLIC<sub>Slabradorite</sub> and 276 pixels of 10 nm and 1517 pixels of 7 nm for the Andosol fine  
346 fraction.



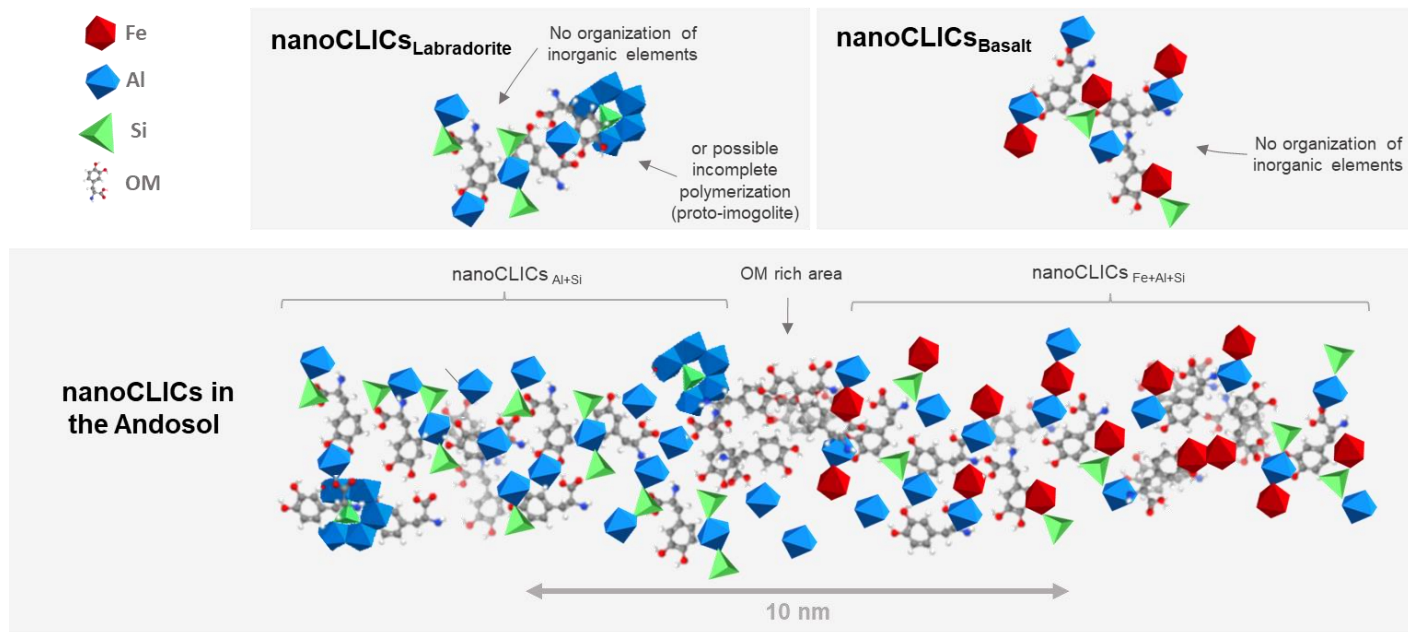
347 **4. DISCUSSION**

348 **4.1. First nanoCLICs model results on synthetic coprecipitates with multi-**  
349 **elemental solutions.**

350 The nanoCLICs model proposed by Tamrat et al.<sup>32</sup> (Figure 1) describes coprecipitates in  
351 which organic molecules are bound (by covalent or weak bonds) to oligomers of 2-3 inorganic  
352 atoms (Fe, Al, Si) structured in a loose irregular 3D network. The representation of this 3D  
353 structure was deduced from EXAFS spectroscopy measurements and could be roughly 5 nm in  
354 size. For the coprecipitates obtained from the basalt and labradorite weathering solutions, the  
355 TEM approaches used in the present study helped validate this nanoCLICs structure model based  
356 on the following results. Firstly, the chemical mappings with ~10 nm-pixel-size (from 6 to 8 nm  
357 size for nanoCLICs<sub>basalt</sub> and from 10 to 11 nm size for nanoCLICs<sub>Labradorite</sub>) detected C in  
358 majority (91–100%) along with one or more inorganic elements (Al, Si, Fe, see Figures 3, 4 and  
359 5). Furthermore, the electron diffraction results (Figure 2) indicated that the atoms formed an  
360 amorphous phase (hence without any electron-detectable crystalline arrangement). The  
361 nanoCLICs model results regarding the size, composition or crystal structure criteria were thus  
362 consistent for coprecipitates formed from the basalt and labradorite weathering solutions. Yet  
363 beyond their common structure, nanoCLICs<sub>Basalt</sub> and nanoCLICs<sub>Labradorite</sub> were not identical in all  
364 aspects. Prior to coprecipitation, basalt and labradorite weathering solutions contained dissolved  
365 Al, Fe and Si, but also Mg and Ca (see Methods, no Fe in labradorite weathering solutions).  
366 However, EDX and EELS chemical maps of nanoCLICs<sub>Basalt</sub> and nanoCLICs<sub>Labradorite</sub> did not  
367 show any substantial presence of Mg and Ca in the synthetic coprecipitates (Figures 3 and 4).  
368 These divalent elements thus did not appear to coprecipitate with OM up to pH ~5. A similar  
369 trend had also been documented in coprecipitates from biotite weathering within the 4-7 pH  
370 range for various OM concentrations<sup>31,32</sup>. Our results confirmed that, regardless of the chemical

371 composition of the initial solution, mono and divalent cations did not enter the synthetic  
372 nanoCLICs structure under acidic to neutral conditions. Otherwise, Al, Si and/or Fe were highly  
373 present in nanoCLICs<sub>Basalt</sub> and nanoCLICs<sub>Labradorite</sub>. However, coprecipitation of nanoCLICs<sub>Basalt</sub>  
374 was incongruent since, relative to the initial solution, it contained a higher proportion of Al and  
375 C, an equivalent or even slightly lower proportion of Fe, but a lower proportion of Si (SI6). In  
376 nanoCLICs<sub>Labradorite</sub>, however, the proportions of C, Al and Si present in the solution before  
377 coprecipitation remained almost identical in the coprecipitates (SI9), thus reflecting congruent  
378 coprecipitation. Based on these results, Figure 6 illustrates the nanoCLICs<sub>Basalt</sub> and  
379 nanoCLICs<sub>Labradorite</sub> structures which could account for the possible heterogeneity of the  
380 inorganic part of the nanoCLICs model (Figure 6). These nanoCLICs models may be used as  
381 benchmarks to study, by direct comparison, natural coprecipitates in Andosols.

382



383 **Figure 6.** Conceptual molecular models of nanoCLICs' local structure observed in  
 384 nanoCLICs<sub>Basalt</sub>, nanoCLICs<sub>Labradorite</sub> and in the Andosol. For the Andosol fine fraction, note that  
 385 the model represents an elemental mix of C+Al+Si+Fe or C+Al+Si detected above 10 nm scale.  
 386 Atomic proportions are deduced from larger-scale analyses from Figure 3 and 4 and should be  
 387 taken with caution as it is not possible to represent all compositional variability at this scale.  
 388 Also, organic matter is represented in this scheme by an identical small organic molecule,  
 389 however, co-precipitated organic matter is most likely heterogeneous in composition and size.

#### 4.2. Coprecipitates in Andosol fine fractions: are they natural nanoCLICs?

The local structure of the inorganic part of the Andosol coprecipitates analyzed in this study was characterized in a previous study<sup>29</sup>, highlighting the absence of allophane spheres and imogolite tubes as well as very limited local organization of Al and Si atoms. The authors therefore concluded that the mineral part was likely rather poorly ordered proto-imogolites. Our results confirmed that the Andosol fine fraction consisted of an electron amorphous phase (Figure 2), indicating that the atoms were not organized in a crystallographic lattice. From a local structure perspective, the Andosol fine fraction coprecipitates were therefore very similar to synthetic nanoCLICs in which inorganic elements are structured in a loose irregular 3D structure of small amorphous oligomers forming an amorphous and open-structured mineral skeleton<sup>32</sup>. Otherwise, regarding their elemental composition (from EDX and EELS mappings), the Andosol fine fraction coprecipitates contained C, Al, Fe and Si in proportions quite similar to those of synthetic nanoCLICs (SI9). Our results thus suggested that the natural Andosol coprecipitates were mainly composed of organic molecules bound to an inorganic network of amorphous small oligomers (See SI10 for further clarification). However, it is likely that the organic compounds may also have simply been complexed with unpolymerized Al and Fe (monomers) within the coprecipitates. Figure 6 illustrates the Andosol coprecipitate structures, as done for the nanoCLICs<sub>Basalt</sub> and nanoCLICs<sub>Labradorite</sub>. In conclusion, the local structure and chemical nature of the Andosol coprecipitates were similar to those of both synthetic coprecipitates (no crystalline structure and elemental mix of C, Al, Si and  $\pm$ Fe down to 7 nm), thereby showing that the inorganic part that stabilized C in the studied Andosol could be assimilated to nanoCLICs. We hence propose to qualify the Andosol coprecipitates as ‘natural nanoCLICs’.

### 4.3. Heterogeneity of natural nanoCLICs in Andosol

413 The EELS and EDX results (Figure 3-6) showed that the composition of natural nanoCLICs  
414 was somewhat heterogeneous. For example, the C+Al+Fe+Si mix was mainly located in sub-  
415 area 5 (Figure 4), while the C+Al+Si mix was more prevalent in sub-area 6. Several non-  
416 exclusive assumptions could be put forward to explain this heterogeneity: (i) It could be the  
417 result of coprecipitation from locally different soil solutions since in the two synthetic systems  
418 studied we found that the variability of elements present in the starting solution could create  
419 nanoCLICs with inorganic phases of different compositions (i.e. Al+Si+Fe for nanoCLICs<sub>Basalt</sub>  
420 and Al+Si or Al only for nanoCLICs<sub>Labradorite</sub>, Figure 5). Indeed, soil solutions can show  
421 variations in element concentrations depending on their proximity to different types of minerals  
422 of varying chemical compositions; (ii) Soil solution concentration heterogeneity could be related  
423 to the extent of weathering of the minerals that provide the dissolved elements, particularly for  
424 non-congruent weathered mineral phases<sup>31</sup>; (iii) Also, this degree of mineral weathering could be  
425 locally variable depending on the biotic environment of the mineral (presence of root exudates,  
426 microorganisms, etc.) and physicochemical (moisture, pH, Eh<sup>48-50</sup>) conditions. For Fe especially,  
427 in an Andosol at the micrometer scale, coprecipitates were previously found to have less C  
428 collocated with Fe when there were marked redox fluctuations<sup>51,52</sup>. Redox fluctuations might  
429 therefore induce Fe migration out of nanoCLICs. Fe could then migrate into re-oxidation  
430 clusters, as observed in Figure 4..(iv) Finally, even if the speciation of organic matter could not  
431 be probed here, different proportions of C were detected (at the centi-nanometric scale; Figure 3  
432 and 4). These variations could result from different types of organic molecules or matter which  
433 have more or less affinities for a given metal, and thus, could give elementary mixture  
434 heterogeneities. These multiple factors would likely induce the formation of natural nanoCLICs  
435 that could present very small-scale variations in Al, Si and/or Fe composition. In the Andosol,  
436

437 natural nanoCLICs were thus mainly composed of nanoCLICsC+Al+Si (32%),  
438 nanoCLICsC+Al+Si+Fe (19%), nanoCLICsC+Al+Fe (19%), nanoCLICsC+Al (18%). The local  
439 variability in natural nanoCLICs is schematically illustrated in 2D in Figure 6, where Al, Si and  
440 Fe might play different roles in the organic compound stabilization process.

#### 441 **4.4. Different roles of Fe, Al and Si in organic compound stabilization in** 442 **nanoCLICs**

443 In the studied Andosol, Fe is not the major element expected to stabilize C in coprecipitates,  
444 but rather Al and Si, often described in the form of allophane and imogolites<sup>54,55</sup>. However, a  
445 slight amount of Fe is detected in the coprecipitates of this andosol (up to 3 to 8 at.% in Figures 3  
446 and 4, excepted area 4). In literature, Fe has long been identified for its high affinity to organic  
447 molecules and put forward as playing a primary function in stabilizing OM in soils<sup>56-59,17,19-</sup>  
448 <sup>21,23,24</sup> as well as in sediments<sup>60,61</sup>, and even in some Andosols<sup>62,63</sup>. The short-range order form of  
449 Fe, i.e. ferrihydrite (Figure 1), has been widely cited for its high reactivity, mainly related to its  
450 large specific surface. This ferrihydrite + OM association was represented by Kleber et al.<sup>3</sup> with  
451 an interaction model that showed Fe octahedrons organized in spherical clusters of a few  
452 thousand Fe atoms, and these clusters were aggregated together to form Fe oxy-hydroxide phases  
453 of several tens of nanometers<sup>3</sup>. In the Andosol studied here, despite the presence of Fe, the TEM  
454 maps did not highlight any such high Fe-rich zones over several tens of nanometers. Moreover,  
455 the proportion of pixels in which C was only associated with Fe was very small (2%). Hence, we  
456 concluded that Fe in form of ferrihydrite was not involved in the Andosol fine fraction  
457 stabilization process. Most of the Fe was associated with Al or Si and the rest was locally more  
458 concentrated in some areas (area 2 in Figure 3, areas 2 and 4 in Figure 4). This indicates that,  
459 despite the fact that Fe was not expected in the coprecipitate of this andosol, it is important when  
460 it is associated in nanoscale elementary mixtures as Fe+Al+Si, Fe+Al and Fe+Si (41% of the ~10

461 nm pixels had Fe+Al+Si, Fe+Al and Fe+Si detections). Similar results were obtained by  
462 NanoSIMS on ferromanganese concretions in a Stagnosol<sup>53</sup>. These authors showed that Fe and C  
463 were not necessarily collocated at the submicron scale, confirming the necessity of spatially  
464 resolved studies along with, a more frequent than previously thought, decoupling of Fe and  
465 organic matter. As for Fe, Al has also long been recognized for its affinity to organic  
466 molecules<sup>64,65,28</sup>. Our results showed that Al appeared to play a major role in stabilizing organic  
467 matter in Andosol fine fractions. Indeed, Al was colocalized with C in 89% of the pixels (Figure  
468 5). 18% of the pixels showed collocation of C with Al alone. Al associated with C was also  
469 mainly associated with Si (32%), with an Al/Si ratio of close to 2, potentially in a proto-  
470 imogolite type of structure as described previously<sup>29</sup>. Yet Al was also associated with Fe in the  
471 presence (19%) or absence (20%) of Si. However, Si detection was probably underestimated by  
472 EELS mapping (see Methods). Al hence appeared to play a central role in interactions with OM  
473 within Andosol natural nanoCLICs. Unlike Al and Fe, Si is known to have low affinity to OM<sup>66</sup>.  
474 However, it was present to a substantial extent in the structure of nanoCLICs and, in most of the  
475 nanoCLICs analyzed (except for nanoCLICs<sub>Basalt</sub>), in a larger proportion than Fe. The presence  
476 of Si in coprecipitates is described as being a factor that disrupts Al and Fe oxy-hydroxide  
477 polymerization, thereby preventing their crystal growth into gibbsite, ferrihydrite or goethite<sup>67-</sup>  
478 <sup>69,9,43,70</sup>. The presence of Si could therefore maintain amorphous Al and Fe structures in the  
479 oligomeric state, hence ensuring greater accessibility of reactive OH groups<sup>70</sup>. Si would favor the  
480 preservation of the very poorly polymerized state, maintaining the high specific surface area and  
481 high reactivity of the inorganic skeleton of nanoCLICs<sup>32</sup>. Si would also limit the progressive  
482 aging of Fe (and Al) phases towards better crystallized and more stable Fe (and Al) oxides<sup>71</sup>,  
483 thereby ensuring OM stabilization within natural nanoCLICs.

## 484 5. ENVIRONMENTAL IMPLICATIONS

485 The findings of this study showed that, using solutions containing various elements, the  
486 coprecipitates formed are of the nanoCLICS type and so even less organized than SRO-OM  
487 usually described. Thus, depending on the element concentrations and pH levels of these  
488 solutions, the amorphous nanoCLICs-type of coprecipitates are likely to be formed in many  
489 types of soils and environments at pH ~4–6, and not SRO-OM, as usually conceptualized in the  
490 literature. In addition to their potential presence, their amorphous structure might lead to their  
491 rapid fluctuations in ecosystems. In soils, the physicochemical conditions of a microsite can  
492 change over time, especially in the rhizosphere<sup>72–75</sup>. These changes disrupt some organo-mineral  
493 associations and thereby allow access to OM (and thus nutrients as Fe and Si) previously  
494 unavailable to microorganisms and plants. This sensitivity to disruption is higher for organo-  
495 mineral associations with a lower crystalline inorganic part<sup>76</sup>. Considering the amorphous and  
496 heterogeneous nature of the inorganic part of nanoCLICs, nanoCLICs could be fairly unstable in  
497 soil microsites and subject to disruption, particularly in the rhizosphere. NanoCLICs could thus  
498 have a predominant role in plant and microorganism nutrient cycles. Moreover, the role of  
499 coprecipitates has recently been highlighted in the maintenance of soil aggregates via their glue-  
500 like properties<sup>77,78</sup>. By their gel-like texture observed in this study, nanoCLICs could also be  
501 involved in soil aggregate formation. However, nanoCLICs are hard to detect because it depends  
502 on costly nanoscale analytical methods (hard to extrapolate to large scales). Despite these  
503 obstacles, future research could be geared towards quantifying nanoCLICs in various  
504 environments to gain further insight into their importance in rapid soil C stock dynamics, as well  
505 as in other environments such as sediments.

506



507 ASSOCIATED CONTENT

## 508 **Supporting Information**

509 SI 1. Measurement of dissolved elements in the basalt and labradorite weathering solutions  
510 obtained by ICP-AES.

511 SI 2. Table of microscopic analysis parameters used for TEM imaging and chemical mapping.

512 SI 3. Determination of the signal-to-noise ratio for the detection of C, O, Fe, Al and Si elements  
513 per pixel.

514 SI 4. C contamination survey: EDX and EELS mapping on SRO<sub>Basalt</sub>.

515 S I5. TEM images and EDX and EELS mapping summary.

516 SI 6. EDX spectra used in Figure 3 for atomic proportions.

517 SI 7. EELS spectra used in Figure 4 for atomic proportions.

518 SI 8. Summary of the acquired EELS data and bar plot of all acquired EELS maps with a lateral  
519 pixel size of 6-10 nm.

520 SI 9. Comparison of atomic proportions between Al-Fe-Si and Al-Fe-C before coprecipitation  
521 and in the nanoCLICS<sub>Basalt</sub>, nanoCLICS<sub>Labradorite</sub> and the Andosol fine fraction.

522 SI 10. Detailed information to interpret the inorganic part of co-precipitates as predominantly  
523 oligomers.

524

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528 574).

## 529 **Notes**

530 Data is available upon request to the corresponding author. The code used for nanoscale  
531 elemental colocation through EELS mapping is available at the following link:

532 [https://github.com/FlorianeJamoteau/EELS\\_elemental\\_detection\\_and\\_multi-detections](https://github.com/FlorianeJamoteau/EELS_elemental_detection_and_multi-detections).

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