

## Structure and Chemical Composition of Soil C-Rich Al–Si–Fe Coprecipitates at Nanometer Scale

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## <sup>1</sup> Structure and chemical composition of soil C-rich

## <sup>2</sup> Al-Si-Fe-coprecipitates at nanometer scale

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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 study34 provides chemical mapping down to a few nanometers of the structure of these associations,

leading to a new conceptualization of the latter with implications for their fate and stability insoils.

#### **37 INTRODUCTION**

Soil is the third largest reservoir of organic carbon (C) on Earth<sup>1</sup>. A large part of this organic 38 C is found in form of organic compounds bound to minerals $^{2-4}$ , thereby shielding them from 39 microbial mineralization<sup>5</sup>, which accounts for one of the mechanisms for long-term organic 40 carbon persistence <sup>6,7</sup>. These associations includes two interaction mechanisms at the molecular 41 scale: adsorption and coprecipitation<sup>3,8</sup>. Adsorption refers to accumulation of organic compounds 42 43 on primary or secondary mineral surface with various bond types (classified as chemisorption or physisorption). As for the formation of co-precipitates in soil, as defined by Kleber et al.<sup>3</sup>, it may 44 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 precipitation of organic compounds with secondary mineral phases or with elements derived 48 from mineral weathering containing Fe and Al<sup>9-12</sup>. Coprecipitates are thought to have a major 49 role in soil C sequestration<sup>12</sup>, yet their chemical composition and 3D atomic structure using 50 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.

The second challenge concerns lab experiments. As it is hard to extract intact coprecipitates 63 from soils, in many studies they have been characterized using synthetic coprecipitates obtained 64 by coprecipitating organic matter (OM) with two metals, i.e. with Fe<sup>15-25</sup> and sometimes with 65 Al<sup>26–28</sup>. The choice of these metals is linked to their high complexation capacity with OM (Figure 66 1), and also to the fact that they are major elements in terms of concentration in most soils. 67 However, the assumption that only these two metals are involved in coprecipitate formation in 68 soils is simplistic since many other chemical elements derived from the weathering of soil 69 minerals (e.g. Si, Mg<sup>2+</sup>, K<sup>+</sup>, Na or Ca) are also present in the soil solutions in which 70 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 spherical ferrihydrite nanoparticles<sup>3,23</sup>, whereas for Al, amorphous Al oxyhydroxide, imogolite 75 76 or allophane phases are often mentioned but barely represented by a conceptual model, except in Levard et al. (2012)<sup>29</sup> (Figure 1). There are two main reasons for this shortcoming in conceptual 77 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

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

82 Progress on the last two locking points has been achieved in recent laboratory studies. Tamrat et al. (2018, 2019)<sup>31,32</sup> synthesized coprecipitates from a biotite weathering solution. 83 They showed that the mono  $(K^+)$  and divalent  $(Mg^{2+})$  ions remained in solution while the 84 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 oligmers 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 oligomers with organics (nanoCLICs) concept. However, direct in situ characterization of 92 93 nanoCLICs has yet to be achieved.

94 Substantial advances have also been made in the in situ soil organo-mineral associations analysis field<sup>33</sup>. Transmission electron microscopy (TEM) is the tool of choice to probe 95 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 dispersion X ray (EDX) and electron energy loss (EELS)<sup>34,35</sup> spectroscopy can be used in 99 100 scanning TEM mode (STEM) to map the nanoscale elemental composition, with elemental colocation resolutions of 10 nm<sup>36,37</sup> and few Å<sup>34,35</sup>, respectively. While the spatial resolution of 101 102 EELS is higher, its sensitivity is not as good as EDX for heavy elements. These two imaging

spectroscopy tools can therefore be used advantageously in a complementary way, but they have yet to be markedly used in soil science research. EDX spectroscopy has mainly been used for spot analyses<sup>38,39,40</sup>. But recently Possinger et al. (2020)<sup>41</sup> took up the challenge of mapping C and N by EELS and revealed soil OM spatial heterogeneity patterns at the 1 nm scale. This latter research has opened a promising avenue for the simultaneous characterization of organic and 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 coprecitipates, denoted nanoCLICs<sub>Basalt</sub> and 118 nanoCLICs<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.



Figure 1. Molecular models of soil coprecipitates in the literature. Coprecipitates can be conceptualized with: (i) an inorganic phase of 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 are imogolites or allophanes (composed of Si and Al) or ferrihydrite (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

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#### 2.1. Synthetic nanoCLICs preparation

Synthetic nanoCLICs were obtained using a protocol similar to that of Tamrat et al.  $(2019)^{32}$ , 135 136 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 has the main functional groups of MAOM<sup>42</sup>. Moreover, using DOPA also avoided fractionation 140 uncertainty during coprecipitation<sup>32</sup>. This protocol was carried out using two types of minerals or 141 142 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 µm were isolated by dry sieving. Then, to mimic mineral 145 weathering, 33 g of particles were agitated in 1 L of an HNO<sub>3</sub> solution at 10<sup>-2</sup>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 concentration of as low as 1.8 mM according to the protocol of Tamrat et al.<sup>32</sup> (4-fold dilution 149 150 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 µL.min<sup>-1</sup>.L<sup>-1</sup>. Titrations were performed at a fixed temperature of 25°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  $(2019)^{32}$ , 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>.

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#### 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 high content in low-crystalline phases associated with organic matter<sup>9,29</sup>. X ray diffraction on this 169 170 horizon previously showed the predominant content of low-crystalline amorphous phase, with some gibbsite and feldspar<sup>9</sup>. Low-crystalline amorphous phases have been characterized by 171 172 indirect spectroscopic techniques, showing a lower degree of polymerization than imogolites, then referring to proto-imogolites in the papers by Basile-Doelsch et al. (2005, 2007)<sup>9,43</sup> and 173 Levard et al. (2012)<sup>30</sup>. The previous characterization of this horizon showed that it contains 60 174  $gC.kg^{-1}$  and had a pH of  $5.2^9$ . 175

The soil fine fraction was isolated as follows, in order to isolate them by a slight disaggregation but without modifying the coprecipitates' structure: up to 2 g of humid soil was dispersed in 100 ml of water by sonication (16 J.ml<sup>-1</sup> by immersion probe; in an ice bath). After 48 h of decantation, the supernatant brown gel, enriched in coprecipitates was collected and few µL were immediately deposited on microscopy grids and air-dried.

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

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

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

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

198the electrons and the material. This volume is hard to estimate, but in STEM mode, it199can be about 10 nm<sup>36,37</sup>. Yet the acquisition time necessary to obtain an exploitable200signal-to-noise ratio to compute the atomic proportions (at.%) remains long at the 10201mn scale, hence, atomic proportions are obtained in areas of several hundred 100 x202100 nm. The data were analyzed using Esprit software version 1.9 and atomic203proportions 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 underestimate heavier elements such as Si<sup>35</sup>. The analysis time per pixel is reduced as 212 213 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 alterations to elemental fine structure resulting from beam damage <sup>45,46</sup>, element 217 218 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

proportions calculated with power low fitted backgrounds and Hartree Slater cross
 sections. Energy ranges for power low fitted backgrounds and Hartree Slater cross
 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 SI4. Then elementary detection was done by computing the signal-to-noise ratio (SNR) adapted from Egerton (2011)<sup>35</sup>. The calculations are outlined in SI3. Finally, the script compiles all elementary multi-detections per pixel into a spreadsheet.

**3. RESULTS** 

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#### 3.1. Transmission electron microcopy (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.



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

#### **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 were negligible (1-3 at.%). Chemical maps of the Andosol fine fractions by EDX also showed 283 284 that C was heterogeneously detected throughout the sample with Al, Si ad 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.%).



Figure 3. Chemical mapping of synthetic nanoCLICs and AAndosol fine fractions using STEM-EDX. (A) imaging using a high angular dark field detector and chemical mapping showing elemental detection of C, Fe, Al and Si. (B) The atomic proportions on each sample are from an area of ~0.07  $\mu$ m<sup>2</sup>, 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 O2 and Cu. The
297	acquisition pixel size is of 4, 3 and 1 nm for nano $CLICs_{Basalt}$ , nano $CLICs_{Labradorite}$ and the
298	AAndosol fine fraction, respectively. Spectra used for atomic proportions are available in SI6.

300

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

301 Chemical EELS mapping results of NanoCLICs<sub>Basalt</sub> and nanoCLICs<sub>Labradorite</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). NanoCLICs<sub>Basalt</sub> showed C colocation (53 at.%) with mostly Al (16 at.%), Fe (24 at.%) 305 and Si (8 at.%), while nanoCLICs<sub>Labradorite</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.%).

At the nanometer scale of a single pixel (here from 6 to 10 nm of the lateral distance), the signal-to-noise ratio was too low to compute the atomic proportions. However, in a given pixel, we were able to obtain binary information (presence or absence of an element; method used outlined in part 5.4, SI3 and SI8). The inorganic element(s) colocated with C at 6-10 nm scales are summarized in Figure 5. The nanoCLICs<sub>Basalt</sub> results showed that 94% of C colocalized with Fe+Al+Si. Little C was measured alone or just with Al or Fe at ~10 nm scale. Otherwise nanoCLICs<sub>Labradorite</sub> showed that C was predominantly colocalized with Al alone (48%) and Al+Si (37%). Little C was measured alone (9%) at ~10 nm scale. Moreover, the Andosol fine fraction results showed that C was mostly colocalized with mixtures of inorganic elements in decreasing proportion, i.e. Al+Si (32%) > Al+Fe+Si (19%) > Al+Fe (19%) > Al (17%) > Fe+Si (2%) > Si (1%). Consistent with the synthetic nanoCLICs findings, little C was measured alone (6%) in the AAndosol fine fraction at the ~10 nm scale.



Figure 4. Chemical mapping of synthetic nanoCLICs and Andosol fine fractions using STEM-EELS. (A) image using an angular dark field detector and chemical mapping showing elemental detection of C, Fe, Al and Si. (B) Atomic proportions per sample on the whole images and atomic proportions on sub-areas of the AAndosol 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 nanoCLICs<sub>Basalt</sub>, nanoCLICs<sub>Labradorite</sub> and AAndosol fine fractions, respectively. Spectra
- 334 used for atomic proportion calculation are available in SI7.





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**Figure 5.** Nanoscale elemental colocalization through EELS mapping of 6-10 nm pixels size. The pixel sizes ranged from 6 to 11 nm (lateral distance). n stands for the number of analyzed pixels with C detection. For each sample, two EELS maps were acquired, this histogram summed the pixels of these two maps (including the EELS shown in Figure 4). A bar chart for each EELS map is shown in Figure SI8. This compilation includes 49 pixels of 8 nm (lateral 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 nanoCLICs<sub>labradorite</sub> and 276 pixels of 10 nm and 1517 pixels of 7 nm for the Andosol fine

346 fraction.

#### 347 **4. DISCUSSION**

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#### 4.1. First nanoCLICs model results on synthetic coprecipitates with multielemental solutions.

The nanoCLICs model proposed by Tamrat et al.<sup>32</sup> (Figure 1) describes coprecipitates in 350 351 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  $\sim 10$  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 range for various OM concentrations<sup>31,32</sup>. Our results confirmed that, regardless of the chemical 370

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 nanoCLICsLabradorite, 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 nanoCLICsLabradorite 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.



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

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

391 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 392 393 imogolite tubes as well as very limited local organization of Al and Si atoms. The authors 394 therefore concluded that the mineral part was likely rather poorly ordered proto-imogolites. Our 395 results confirmed that the Andosol fine fraction consisted of an electron amorphous phase 396 (Figure 2), indicating that the atoms were not organized in a crystallographic lattice. From a local 397 structure perspective, the Andosol fine fraction coprecipitates were therefore very similar to 398 synthetic nanoCLICs in which inorganic elements are structured in a loose irregular 3D structure 399 of small amorphous oligomers forming an amorphous and open-structured mineral skeleton<sup>32</sup>. 400 Otherwise, regarding their elemental composition (from EDX and EELS mappings), the Andosol 401 fine fraction coprecipitates contained C, Al, Fe and Si in proportions quite similar to those of 402 synthetic nanoCLICs (SI9). Our results thus suggested that the natural Andosol coprecipitates 403 were mainly composed of organic molecules bound to an inorganic network of amorphous small 404 oligomers (See SI10 for further clarification). However, it is likely that the organic compounds 405 may also have simply been complexed with unpolymerized Al and Fe (monomers) within the 406 coprecipitates. Figure 6 illustrates the Andosol coprecipitate structures, as done for the 407 nanoCLICs<sub>Basalt</sub> and nanoCLICs<sub>Labradorite</sub>. In conclusion, the local structure and chemical nature of 408 the Andosol coprecipitates were similar to those of both synthetic coprecipitates (no crystalline 409 structure and elemental mix of C, Al, Si and  $\pm$ Fe down to 7 nm), thereby showing that the 410 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'. 411

#### 4.3. Heterogeneity of natural nanoCLICs in Andosol

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

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

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

443 In the studied Andosol, Fe is not the major element expected to stabilize C in coprecipitates, but rather Al and Si, often described in the form of allophane and imogolites<sup>54,55</sup>. However, a 444 445 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 molecules and put forward as playing a primary function in stabilizing OM in soils 56-59,17,19-447 <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 448 449 Fe, i.e. ferrihydrite (Figure 1), has been widely cited for its high reactivity, mainly related to its large specific surface. This ferrihydrite + OM association was represented by Kleber et al.<sup>3</sup> with 450 451 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 NanoSIMS on ferromanganese concretions in a Stagnosol<sup>53</sup>. These authors showed that Fe and C 462 were not necessarily collocated at the submicron scale, confirming the necessity of spatially 463 464 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 molecules<sup>64,65,28</sup>. Our results showed that Al appeared to play a major role in stabilizing organic 466 467 matter in Andosol fine fractions. Indeed, Al was colocalized with C in 89% of the pixels (Figure 468 5). 18% of the pixels showed colocation 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 protoimogolite type of structure as described previously<sup>29</sup>. Yet Al was also associated with Fe in the 470 471 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 within Andosol natural nanoCLICs. Unlike Al and Fe, Si is known to have low affinity to OM<sup>66</sup>. 473 474 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 polymerization, thereby preventing their crystal growth into gibbsite, ferrihydrite or goethite<sup>67–</sup> 477 478 <sup>69,9,43,70</sup>. The presence of Si could therefore maintain amorphous Al and Fe structures in the oligomeric state, hence ensuring greater accessibility of reactive OH groups<sup>70</sup>. Si would favor the 479 480 preservation of the very poorly polymerized state, maintaining the high specific surface area and high reactivity of the inorganic skeleton of nanoCLICs<sup>32</sup>. Si would also limit the progressive 481 aging of Fe (and Al) phases towards better crystallized and more stable Fe (and Al) oxides<sup>71</sup>, 482 483 thereby ensuring OM stabilization within natural nanoCLICs.

#### 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  $\sim$ 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 change over time, especially in the rhizosphere <sup>72–75</sup>. These changes disrupt some organo-mineral 492 493 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 gluelike properties<sup>77,78</sup>. By their gel-like texture observed in this study, nanoCLICs could also be 500 501 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.

#### 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 <u>https://github.com/FlorianeJamoteau/EELS\_elemental\_detection\_and\_multi-detections.</u>

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