



# Nanoscale evidence of contrasted processes for root-derived organic matter stabilization by mineral interactions depending on soil depth



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## ABSTRACT

Up to now stabilization of organic matter (OM) in soils due to mineral interactions has been assessed mainly by correlations between carbon and iron and/or aluminum oxides evidencing that metal oxides may be principal stabilization agents. The nature and morphology of stabilized OM are poorly known. Taking advantage of a field experiment, the aim of our study was to analyze the fate of <sup>13</sup>C and <sup>15</sup>N labeled root material at 30 and 90 cm depths after three years of incubation and to characterize the nature of OM stabilized by interactions with metal oxides. Our methodological approach included isolation of metal oxides by physical fractionation and visualization of their interaction with OM using NanoSIMS. We concentrated metal oxides in a fraction corresponding to our objectives: the heavy fraction (>3 g cm<sup>-3</sup>) of fine silt. NanoSIMS analyses of this fraction allowed us to locate unlabeled OM and OM either double labeled or carrying one single label in association with metal oxides. Our results suggest that decoupling of C and N may have happened during OM stabilization within the timeframe of the 3 year field experiment. Scanning electron microscopy (SEM) after NanoSIMS analyzes, indicated that <sup>15</sup>N labeled OM at 90 cm were well-defined ovoid OM particles resembling to microbial cells in interaction with Fe, Al and Ti oxides. At 30 cm depth, OM associated with metal oxides was <sup>13</sup>C and <sup>15</sup>N labeled unstructured material, possibly derived from plant debris. We suggest that at the two soil depths under investigation different processes might be at work, leading to association of OM with mineral compounds of the isolated fraction: in upper soil layers, decomposed plant material may directly interact with metal oxides, whereas in deep mineral soil, OM could mainly interact with metal oxides after microbial turnover. Both types of interactions may be fairly stable as they persisted after ultrasonication and salt extraction.

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## 1. Introduction

Soil organic matter (SOM) stability is governed by accessibility rather than recalcitrance (Dungait et al., 2012). In particular, interaction with the mineral phase was identified as the only mechanism able to stabilize a significant proportion of SOM for long timescales by adsorption of OM onto Fe and Al oxides (Kögel-

Knabner et al., 2008). These processes were made responsible for the extremely long residence times of OM stored in subsoil horizons (Eusterhues et al., 2003; Kleber et al., 2005). The nature of mineral interactions has long been discussed and SOM adsorption was hypothesized to occur as monolayer equivalent (Mayer, 1994) as well as patchy distribution (Ransom et al., 1998; Vogel et al., 2014). The composition of SOM stabilized by mineral interactions has also been a matter of debate up to date: while aromatic lignin molecules were found to be preferentially sorbed onto metal oxides (Kaiser and Zech, 1998; Kramer et al., 2012), other studies showed no correlation between lignin and Fe oxides in subsoil horizons (Spielvogel et al., 2008). The absence of lignin stabilization through

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mineral interactions was recently hypothesized to be a methodological artifact (Hernes et al., 2013). Easily available polysaccharides are stabilized by the mineral phase in top- (Kiem and Kögel-Knabner, 2003) and subsoil horizons (Liang and Balser, 2008; Rumpel et al., 2010). A recent theory postulates the adsorption of nitrogen rich material onto mineral surfaces (Kleber et al., 2007), suggesting that in particular microbial material would be stabilized by interaction with the mineral phase. This is in agreement with recent findings on the importance of microbial material for SOM formation (Miltner et al., 2012). However, the nature of OM interacting with the mineral phase may depend on soil depth, since the nature of mineral-associated OM was found to be different in top- and subsoil horizons, with plant-derived compounds prevailing in topsoil and microbial material dominating in subsoil (Rumpel et al., 2012). All these findings are mainly based on statistical relationships between C and dense particles as well as Fe- and/or Al-oxides. Few studies were carried out to directly show these interactions.

This is mainly due to the fact that interaction between OM and the mineral phase of soil takes place at much finer scales than those studied in general. Due to technical limitations, the micrometer-scale complexity of soil has been rarely addressed up to date although organo-mineral interactions occur at these scales. With the development of nanoscale techniques, such as nanoscale secondary-ion mass spectrometry (NanoSIMS), the observation of organo-mineral interactions has become possible (Herrmann et al., 2007). NanoSIMS was developed to enable the differentiation between several stable isotopes at high mass resolving power and at high lateral resolution. The technique provides isotopic maps in addition to elemental maps. It allows therefore the tracking of labeled compounds and elucidating nano-scale interaction between OM and clay as well as iron oxides. For example, Mueller et al. (2012) used NanoSIMS to show heterogeneous utilization of  $^{13}\text{C}$  and  $^{15}\text{N}$  labeled proteins by microorganisms located on aggregate surfaces. So far most studies using NanoSIMS have been carried out in the laboratory with model compounds (e.g. Liu et al., 2013) or after laboratory incubation with natural organic material (Keiluweit et al., 2012; Vogel et al., 2014). These studies indicated patchy distribution of OM on mineral surfaces, with preferential adsorption of new OM to pre-existing organo-mineral clusters (Vogel et al., 2014). Recently, Remusat et al. (2012) used NanoSIMS *in situ* to image intact soil particles and to detect spots of isotopic enrichment a decade after  $^{15}\text{N}$  litter labeling. They concluded preservation of OM after microbial processing through interaction with the mineral phase. By using Scanning transmission X-ray microscopy in addition to NanoSIMS, they were able to show that the organic compounds consisted of microbial products, which may include microbial cells as well as extracellular polymeric substances (Remusat et al., 2012). The protein fraction of extracellular polymeric substances was found to be sorbed preferentially on Al as well as Fe oxides (Mikutta et al., 2011; Keiluweit et al., 2012; Liu et al., 2013). However, it was also shown that sorption affects only minor parts of the extracellular polymeric substances (Liu et al., 2013).

In this study, we went a step further in the characterization of organo-mineral complex formation *in situ*. We used NanoSIMS in combination with scanning electron microscopy (SEM) to investigate the morphology of labeled OM in association with metal oxides after three years of field incubation of  $^{13}\text{C}$  and  $^{15}\text{N}$  labeled root litter. This experiment, in which labeled root material was mixed with soil and exposed in litterbags at different soil depths, was carried out to investigate the influence of depth on decomposition and stabilization of root litter. We observed contrasting decomposition dynamics in the different soil depths with a lag-phase occurring in deep soil (Sanaullah et al., 2011). However, in contrast to our expectations, the magnitude of root litter

decomposition and stabilization was similar after 3 years at 30 and 90 cm depth (Sanaullah et al., 2011), which was in line with the similar temperature and water contents recorded at both soil depths (Sanaullah et al., 2011).

A major proportion of the remaining labeled  $^{13}\text{C}$  and  $^{15}\text{N}$  (about 40% of initial) was contained after 3 years in the heavy fraction ( $>1.8\text{ g cm}^{-3}$ )  $<50\text{ }\mu\text{m}$  (Sanaullah et al., 2011), being composed of organic matter stabilized by mineral interactions (Schrumpf et al., 2013). We hypothesized that labeled organic compounds are stabilized in this fraction due to association with Fe or Al oxides, which were shown to be the main stabilizing agents in the investigated soil (Moni et al., 2010). Moreover, we hypothesized that the nature of compounds associated with these minerals differs at 30 and 90 cm depth. In order to obtain a soil fraction containing Fe and Al oxides, we isolated the  $>3\text{ g cm}^{-3}$  fraction from fine silt by density fractionation. For elemental distribution and to identify regions of interest (ROI) the material in this fraction was analyzed by scanning electron microscopy (SEM) prior to NanoSIMS. NanoSIMS analyses were carried out to determine locations of labeled  $^{13}\text{C}$  and  $^{15}\text{N}$ . After NanoSIMS analyzes, we characterized the morphology and isotopic composition of the OM by SEM. The aims of the study were to.

- Demonstrate stabilization of SOM by interaction with Fe and Al oxides at different soil depths by studying one specific physical fraction
- Investigate if such a stabilization occurs within the timeframe of the field experiment
- Determine if stabilized compounds differ in contrasting depths of the soil profile

## 2. Materials and methods

### 2.1. Field incubation

The field incubation was carried out during three years at Lusignan (France) in a Cambisol soil with loamy texture (Chabbi et al., 2009) and grassland vegetation. Briefly, soil cores were excavated by an auger sampler ( $\varnothing 7.5\text{ cm}$ ) from 30 to 90 cm depth, corresponding to well defined pedogenic horizons, i.e. A (ploughing horizon) and B2 (horizon containing red clay). Thereafter, we prepared litterbags containing labeled root material and soil from the two different soil depths. Root material was isolated from labeled wheat, which had been grown hydroponically in a growth chamber under 2 atom%  $^{13}\text{C}$ - $\text{CO}_2$  atmosphere with a nutrient solution containing  $^{15}\text{NH}_4^{15}\text{NO}_3$  (10%  $^{15}\text{N}$  atom excess) for 16 weeks. After harvest, the roots had been dried at  $40\text{ }^\circ\text{C}$  before 2 g were cut into 1 cm pieces and mixed with 100 g of soil. The soil root mixture was put in  $10 \times 10\text{ cm}$  litter bags (mesh size  $100\text{ }\mu\text{m}$ ), placed at the original soil depth and covered with material from the original soil core. During the experiment the site was managed as grassland, including regular cutting as well as N fertilization. After 36 months of incubation, the litterbags were retrieved and the material inside was air-dried. Total as well as labeled C showed little variation especially in the stable isotope content between the three field replicates. Therefore, one sample of each depth was used for this study for further analyses. The experimental scheme used in this study is presented in Fig. 1.

### 2.2. Bulk soil analyzes

The organic carbon (OC), nitrogen (N) and stable isotope ( $^{13}\text{C}$  and  $^{15}\text{N}$ ) content of bulk soil, and the fraction  $<50\text{ }\mu\text{m}$  were measured in a single analysis using a CHN auto-analyzer (CHN NA

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