



Visualizing Mineral-Associated Organic Matters in Long-Term Fertilization Treated Soils by NanoSIMS and SR-FTIR

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Formation of mineral-associated organic matters is essential for long-term soil organic carbon preservation. However, the regulation pathways of mineral-associated organic matters in soils remains largely undescribed, especially at the submicron scale. Using a well-controlled long-term (32 years) field experiment at the Jiangxi Institute of Red Soils, Jinxian, China, we showed that long-term manure fertilization significantly ($P < 0.05$) increased the available Al and Fe concentrations over one order of magnitude in soil water dispersible colloids compared to no fertilization and chemical fertilization. Nano-scale secondary ion mass spectrometry (NanoSIMS) images and region of interest (ROI) analysis provided direct evidence demonstrating that long-term manure fertilization increased the $^{27}\text{Al}^{16}\text{O}^{-}/^{12}\text{C}^{-}$, $^{27}\text{Al}^{16}\text{O}^{-}/^{12}\text{C}^{14}\text{N}^{-}$, $^{56}\text{Fe}^{16}\text{O}^{-}/^{12}\text{C}^{-}$, and $^{56}\text{Fe}^{16}\text{O}^{-}/^{12}\text{C}^{14}\text{N}^{-}$ ratios compared to no fertilization and chemical fertilization. This finding revealed that long-term manure fertilization may potentially enhance the stability of organic carbon and nitrogen. Synchrotron radiation based FTIR spectromicroscopy further supported that secondary minerals ($<950\text{ cm}^{-1}$) were co-localized with amines, lipids, and proteins in the long-term manure fertilization, but only co-localized with proteins in the no fertilization and chemical fertilization. To summarize, our findings highlight the importance of manure inputs in increasing formation of mineral-associated organic matters and thus potentially increasing soil carbon persistence.

Keywords: long-term fertilization treatment, manure, mineral-associated organic matters, NanoSIMS, soil carbon cycling, SR-FTIR

INTRODUCTION

Soils, which are a reservoir for carbon (C) and a source of atmospheric CO_2 , play important roles in the global C cycle and in the mitigation of global climate change (1, 2). Land use practices can improve soil quality and mitigate climate change via increases in soil C (3). Although the effects of land use practices on soil organic carbon (SOC), soil organic nitrogen (SON), and soil structure have been well-documented (4, 5), the responses of mineral-associated organic matters to land use practices remain largely unknown, which play an essential role in preserving SOC and SON (6). Among land use practices, long-term manure fertilization has been shown to markedly increase not only the contents and composition of SOC (7, 8) but also markedly influences the concentration of

reactive minerals (mainly nano-sized allophane and ferrihydrite) in a red soil in southern China (9–11), pointing to the fact that mineral composition can be affected by agricultural practices. However, the mineral availability to organic matters and whether they can effectively protect SOC *in-situ* remain largely unknown.

Nano-scale secondary ion mass spectrometry (NanoSIMS) is a powerful tool for studying organo-mineral associations at the submicron scale (12–17). These investigations include high lateral resolution (down to 50 nm) imaging, while maintaining a high mass resolution and high sensitivity (mg kg⁻¹ range) (17). However, NanoSIMS fails to provide information about all the mineral species and associated C groups (e.g., aromatic C and aliphatic C) in complexed soils. Complementary to NanoSIMS, synchrotron radiation-based Fourier transform infrared (SR-FTIR) spectromicroscopy allows to assess clay minerals, secondary minerals, and associated C functional groups with high sensitivity and micrometer spatial resolution (18–20). Because the effects of fertilization practices on the mineral-associated organic matter remain largely unexplored, visualizing mineral-associated organic matter in long-term fertilization treated soils by NanoSIMS and SR-FTIR may provide novel insights into soil C storage.

The objective of the present study was to visualize mineral-associated organic matter in long-term fertilization treated soils at the submicron scale using NanoSIMS and SR-FTIR. For this purpose, the effects of three contrasting treatments with triplicate plots in a well-controlled, long-term (32 years) fertilization experiment at the Jiangxi Institute of Red Soils, Jinxian, China, were selected: (1) without fertilization (Control), (2) farmyard manure fertilization (M), and (3) inorganic fertilization as nitrogen, phosphorus, and potassium fertilizer combination (NPK). Collectively, our results demonstrated that manure inputs can not only enhance soil C content but also promote formation of mineral-associated organic matters, providing implications for increase of soil carbon persistence. Knowledge about the regulatory effect of fertilization practices is critical for soil C storage and sequestration.

MATERIALS AND METHODS

Soil Samples

The well-controlled, long-term field experiment was initiated in 1986 at the Institute of Red Soil, Jinxian County (28°37' N, 116°26' E, 26 m above sea level), Jiangxi Province, China. This site has a typical subtropical climate with a distinct arid (July–September) and humid (March–June) season. The mean annual temperature and rainfall are 17.2°C and 1,549 mm, respectively. The soil was developed from Quaternary red clay. The soil sampled in 1,986 contained 9.4 g of organic C kg⁻¹, 0.98 g of total N kg⁻¹, 0.62 g of total P kg⁻¹, and 11.4 g of total K kg⁻¹, with an initial pH of 6.0.

The cropping system was a double corn (*Zea mays* L.) per year followed by winter fallow. The experiment was conducted using a randomized complete block design with three replicates (plot size 22.2 m²). Three contrasting treatments, i.e., Control, NPK, and M, were selected for the present investigation. The

application rates of inorganic fertilizers were 60 kg of N ha⁻¹, 13 kg of P ha⁻¹, and 33 kg of K ha⁻¹, respectively, for each corn growing season. Farmyard manure was applied at a rate of 15 Mg ha⁻¹ on a fresh weight basis for each growing season. All aboveground crop biomass was removed from the field following corn harvest. Soils were sampled by the core method after the harvest of the second corn in November 2018. In each plot, twelve cores were taken to a depth of 15 cm. Once in the laboratory, the field-moist soil was passed through a 5-mm sieve by gently breaking apart the soil, and it was then air-dried and stored at room temperature.

Soil Colloids Extraction

Soil colloids were isolated using the following procedure (21). Briefly, air-dried soil was suspended in deionized water at a ratio of 1:5 (W/V), shaken for 8 h at 25°C, and centrifuged for 6 min at 2,500 g. Aliquots of the supernatant suspensions containing the soil colloids were transferred into 50-mL glass vials, stored in the dark at 4°C, and analyzed within 1 week.

Scanning Electron Microscope (SEM) and NanoSIMS Analyses

SEM analysis was conducted using JSM-5610LV/NORAN-VANTAGE at the School of Earth System Science, Tianjin University, China. For SEM, the soil colloids solution mounted on stubs was sputter coated for 5 min with gold and platinum (30 nm) using a Cressington 208HR sputter coater (Ted Pella, Redding, CA, USA). Specimens were examined using an environmental scanning electron microscope (ESEM) (Philips XL30 ESEM FEG) operating at an accelerating voltage of 15 kV.

For NanoSIMS measurements, an aliquot of soil colloid solution was dropped onto a gold foil and then air-dried. The analyses were performed with a NanoSIMS 50L (Cameca, Gennevilliers, France) at the School of Earth System Science, Tianjin University, China. Prior to the analysis, the gold coating layer (~10 nm) and possible contamination of the sample surface were sputtered using a high primary beam current (pre-sputtering) (22). During the pre-sputtering step, the reactive Cs⁺ ions were implanted into the sample to enhance the secondary ion yields. The primary beam (~0.9 pA) was focused with a lateral resolution of 100–200 nm and was scanned over the samples. Secondary ion images of ¹²C⁻, ¹²C¹⁴N⁻, ²⁷Al¹⁶O⁻, and ⁵⁶Fe¹⁶O⁻ were simultaneously collected by electron multipliers with an electronic dead time of 44 ns (23, 24). The estimated depth resolution when using 16 keV Cs⁺ ions for the primary ion beam was approximately 15 nm. We compensated for the charging that resulted from the non-conductive mineral particles by employing the electron flood gun of the NanoSIMS instrument. All the measurements were performed in the imaging mode, with a dwell time of 1 ms pixel⁻¹ for all the acquisitions. The presence of ¹²C⁻ and ¹²C¹⁴N⁻ ions is an indicator of C and organic matters from soil, respectively. ²⁷Al¹⁶O⁻ ions can be attributed to aluminum minerals or oxides, while ⁵⁶Fe¹⁶O⁻ ions belongs to iron minerals or oxides. ROIs (numbered regions of interest) were chosen according to the distribution of the secondary ions of ¹²C⁻ and ¹²C¹⁴N⁻ using

Image J (1.45 h version) with the OpenMIMS plugin (http://www.nrim.s.hms.harvard.edu/NRIMS_ImageJ.php). Areas and sums of secondary ion counts for each ROI were extracted from all images. All ROIs with an area greater than 20 pixels were used for further calculations. The triangle algorithm was used for this measurement.

SR-FTIR Spectromicroscopy Analysis

Intact variably-shaped soil particles (50–100 μm) were picked with superfine tweezers from the soils and then frozen at -20°C followed by sectioning without embedding (19, 25). Thin sections ($\sim 1\ \mu\text{m}$ in thickness) were cut on a cryomicrotome (Cryotome E, Thermo Shandon Limited, UK) and transferred to infrared-reflecting MirrIR Low-E microscope Slides (Kevley Technologies, Ohio, USA). SR-FTIR spectromicroscopy was first obtained on the BL01B1 beamline at the Shanghai Synchrotron Radiation Facility (SSRF), China. Spectra were recorded in reflectance mode using a Thermo Nicolet 6700 FTIR spectrometer and a continuum infrared microscope with the following settings: spectral range 4,000–650 cm^{-1} , step size 1 μm , resolution 4 cm^{-1} , and 64 scans (26, 27). All spectral maps were processed using Omnic 9.0 (Thermo Fisher Scientific Inc.).

Chemical Analyses

The concentrations of SOC and total N (i.e., TN) were quantified using a CN analyzer (Vario EL, Elementar GmbH, Hanau, Germany). A soil:distilled water ratio of 1:5 was used to measure soil pH (28). The supernatant suspension was passed through a 0.45 μm polytetrafluoroethylene filter for DOC analysis. DOC was measured using a total organic carbon/total nitrogen analyzer (Multi N/C 3000, Analytik Jena AG, Germany) (20). The main metal ions in the colloids were quantified after digestion. The following procedure was performed: first, the soil colloids were mixed with 10% nitric acid at a ratio of 1:1 (v/v) on a heating plate, then, the mixture was heated to 150°C and heated for 2 h. After the digestion, the mixture was filtered through a filtration membrane (0.45 μm) and stored in a suitable container. In addition, soil samples that were passed through a 0.25-mm sieve were wet-digested with a concentrated acid mixture (HNO_3 , HClO_4 , and HF) to determine the total concentration of Al and Fe (29). The main mineral elements, namely, Fe and Al were quantified by inductively coupled plasma atomic emission spectroscopy (710/715 ICP-AES, Agilent, Australia).

Statistical Analyses

One-way analysis of variance (ANOVA) on the soil biogeochemical and taxonomic data was performed. Significances between fertilization treatments were determined using one-way ANOVA and the Tukey's HSD *post-hoc* tests, in which normality and homogeneity of variance were met. *T*-test was applied to data to test for differences between ROIs. All statistical analyses were performed using SPSS software (Version 19.0 for Windows).

RESULTS AND DISCUSSION

Associations Between Mineral Elements and C in Soil Water Dispersible Colloids

Compared to the Control and NPK treatments in the Jinxian experiment, the M treatment significantly ($P < 0.05$) enhanced SOC and TN contents (Table 1) and resulted in better corn growth (Figure 1A). These results are consistent with previous reports (5, 30). Notably, M treatment also enhanced Al and Fe concentrations more than one order of magnitude in soil water dispersible colloids when compared to Control and NPK treatments (Figures 1B,C). In contrast, M treatment slightly decreased the concentration of total Fe in the soil but did not change that of Al ($P > 0.05$) compared to Control and NPK treatments (Table 1). Taken together, these results suggest that the long-term application of organic manures can greatly increase the availability of Al and Fe minerals to C by mobilizing mineral elements and C.

In line with the changes of Al and Fe concentrations, M treatment also enhanced the concentration of DOC over 3 times when compared to Control and NPK treatments (Figures 1B,C). Furthermore, Al and Fe concentrations were positively ($R^2 > 0.68$, $P < 0.05$) correlated with that of DOC (Figures 1B,C). This linearly relationship reveals that the storage or preservation of DOC may be controlled by Al and Fe minerals in soil water dispersible colloids.

Visualizing Mineral-Associated Organic Matter in Long-Term Fertilization Treated Soils by NanoSIMS

To explore whether Al and Fe minerals in soil colloids can effectively preserve soluble C and N, we used NanoSIMS to observe the associations between Al, Fe oxides, or minerals and soluble C and N *in-situ*. SEM image (Figure 2A) showed that soil colloids prepared for the following NanoSIMS images appeared to be heterogeneously distributed as a very thin coating or as patches upon golden foil, ruling out the effect of the topography on NanoSIMS images. NanoSIMS images from the soil in the long-term manure fertilization (Figure 2A) showed that $^{12}\text{C}^-$ and $^{12}\text{C}^{14}\text{N}^-$ were closely associated with $^{27}\text{Al}^{16}\text{O}^-$ and $^{56}\text{Fe}^{16}\text{O}^-$.

To better address the effects of long-term fertilization treatments on mineral-associated organic matter, we present the ratios of mineral elements and organic matter in violin with quartile plots with (Figure 2B). The 25–75% of the $^{27}\text{Al}^{16}\text{O}^-/^{12}\text{C}^-$ and $^{27}\text{Al}^{16}\text{O}^-/^{12}\text{C}^{14}\text{N}^-$ ratios were in the following order: M > Control > NPK. In contrast, the 25–75% of the $^{56}\text{Fe}^{16}\text{O}^-/^{12}\text{C}^-$ and $^{56}\text{Fe}^{16}\text{O}^-/^{12}\text{C}^{14}\text{N}^-$ ratios were in the following the order: NPK > M > Control (Figure 2B). Intriguingly, the $^{27}\text{Al}^{16}\text{O}^-/^{12}\text{C}^-$ and $^{27}\text{Al}^{16}\text{O}^-/^{12}\text{C}^{14}\text{N}^-$ ratios in the long-term manure fertilization were significantly higher than those in the long-term inorganic fertilization treatment, however, the $^{56}\text{Fe}^{16}\text{O}^-/^{12}\text{C}^-$ and $^{56}\text{Fe}^{16}\text{O}^-/^{12}\text{C}^{14}\text{N}^-$ ratios were similar in both fertilizations (Figure 2B). These results

TABLE 1 | Characteristics of soils from the different fertilization treatments at the Jiangxi Institute of Red Soils, Jinxian, China^a.

Treatment	SOC (%)	TN (%)	C/N	pH	Total Fe (%)	Total Al (%)
Control	0.76 ± 0.03 c	0.10 ± 0.00 c	7.75 ± 0.12 b	5.33 ± 0.08 b	3.54 ± 0.63 a	3.52 ± 0.10 a
NPK	0.93 ± 0.04 b	0.12 ± 0.01 b	7.96 ± 0.38 ab	4.60 ± 0.08 c	3.54 ± 0.16 a	3.61 ± 0.87 a
M	1.25 ± 0.06 a	0.15 ± 0.01 a	8.27 ± 0.26 a	5.94 ± 0.08 a	3.27 ± 0.08 b	3.11 ± 0.31 a

^aControl, no fertilization; M, farmyard manure fertilization; NPK, chemical fertilization. The different letter denoted statistically different (ANOVA; Duncan's test; $P < 0.05$).

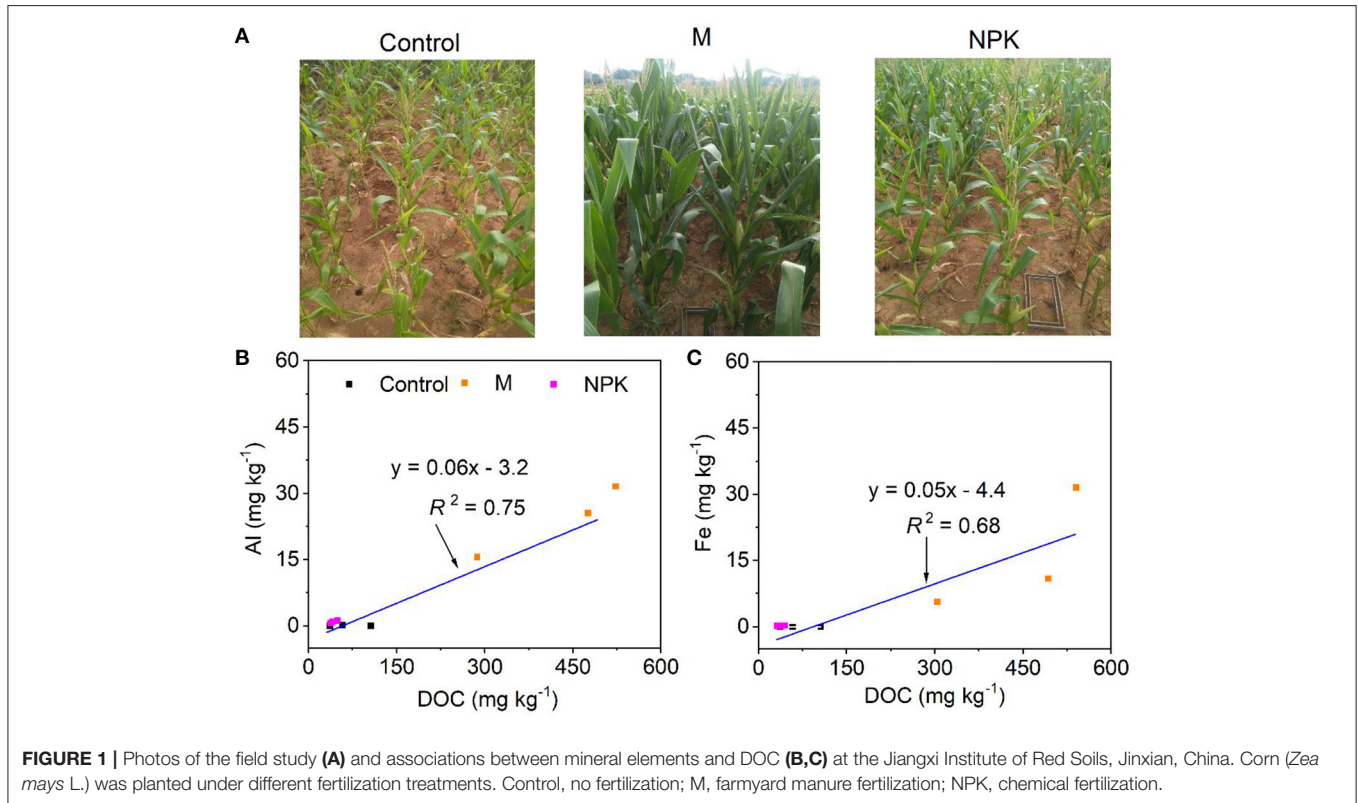
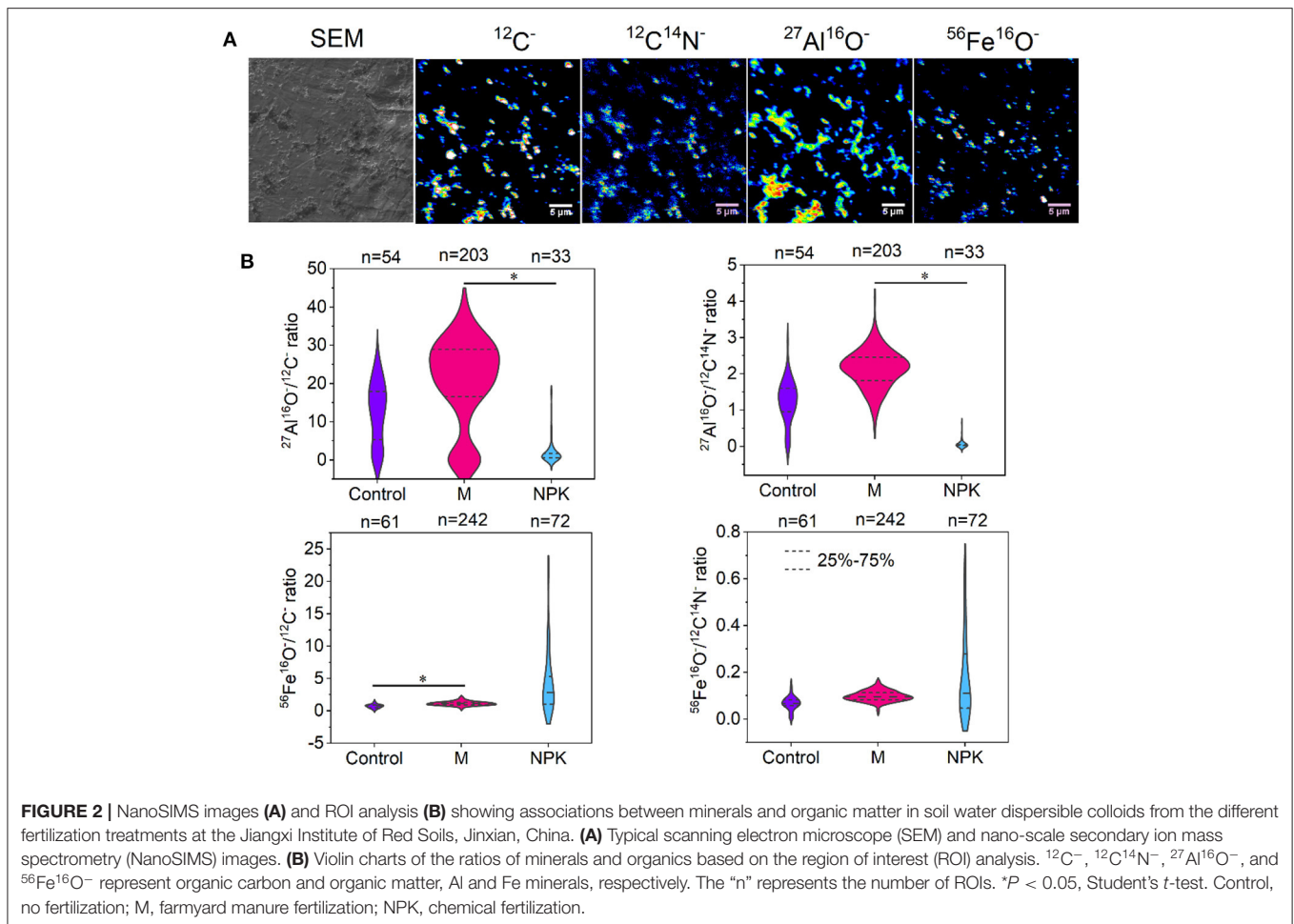


FIGURE 1 | Photos of the field study (A) and associations between mineral elements and DOC (B,C) at the Jiangxi Institute of Red Soils, Jinxian, China. Corn (*Zea mays* L.) was planted under different fertilization treatments. Control, no fertilization; M, farmyard manure fertilization; NPK, chemical fertilization.

suggested that compared to the Control treatment, long-term manure fertilization treatment increased the association between Al minerals (i.e., $^{27}\text{Al}^{16}\text{O}^-$) and organic matter (i.e., $^{12}\text{C}^-$ and $^{12}\text{C}^{14}\text{N}^-$). In contrast, long-term inorganic fertilization treatment seriously decreased the association of Al minerals (i.e., $^{27}\text{Al}^{16}\text{O}^-$) with organic matter (i.e., $^{12}\text{C}^-$ and $^{12}\text{C}^{14}\text{N}^-$). This result is consistent with previous observations that long-term inorganic fertilization treatment in red soils increased exchangeable Al, decreased soil pH, caused soil acidification, and decreased the sequestration of SOC (31–33). Meanwhile, both organic and inorganic fertilization treatments strengthened the association of Fe minerals (i.e., $^{56}\text{Fe}^{16}\text{O}^-$) with C (i.e., $^{12}\text{C}^-$) and organic matter (i.e., $^{12}\text{C}^{14}\text{N}^-$). This finding is supported by increased contents of short-range ordered (SRO) Fe minerals in organic and inorganic fertilization treatments compared to the Control treatment (8). These SRO Fe minerals have a strong adsorption on soil organic matter and thus promote formation of organo-mineral associations (6, 34, 35).

Visualizing Mineral-Associated Organic Matter in Long-Term Fertilization Treated Soils by SR-FTIR

To further identify the types and spatial distribution of functional groups of mineral-associated organic matter in the contrasting fertilization treatments, the high resolution of spatially-related SR-FTIR spectromicroscopy (with the fine scan model, $1\ \mu\text{m}\ \text{step}^{-1}$) was used to collect the spectra through the soil particles (Figure 3). Obviously, the N-H stretching of amines ($\sim 3,200\text{--}3,400\ \text{cm}^{-1}$) (36, 37), C-H stretching of lipids ($\sim 2,920\ \text{cm}^{-1}$) (36), and aromatic C=C vibrations and amide N-C stretch ($\sim 1,650$ and $1,530\ \text{cm}^{-1}$, respectively) (37) were stronger in the long-term manure fertilized soil (i.e., M) than those in the long-term inorganic fertilized soil (i.e., NPK) (Figure 3). Notably, the strong absorbance of functional groups from secondary minerals ($<950\ \text{cm}^{-1}$) (38) supported that secondary minerals (e.g., Fe-O and Al-O) played a vital role in the SOC storage, which was supported by the results from NanoSIMS images (Figure 2). Therefore, these results indicated



that secondary minerals were co-localized with amines, lipids, and proteins in the long-term manure fertilized soil (i.e., M) but only co-localized with proteins in the long-term inorganic fertilized soil (i.e., NPK), supporting that long-term manure fertilization may be benefit for the formation of mineral-associated organic matter and thus potentially long-term C stability in soils.

Environmental Implications

Collectively, long-term (i.e., 32 years) application of manures could increase the bioavailability of minerals to C and accelerate formation of mineral-associated organic matter. In line with our results, Yan et al. (30) also found that there were much more oxalate-soluble Fe in the M treatment (2.35 g kg^{-1}) than Control (2.16 g kg^{-1}) and NPK (1.80 g kg^{-1}) treatments at the Jiangxi Institute of Red Soils.

Importantly, we provided direct evidence demonstrating that fertilization practices could alter the potential preservation capability of Al and Fe minerals for C and organic matters by the combination of NanoSIMS and SR-FTIR analyses.

In the short-term, the enhancement of bioavailable minerals will facilitate crop production with higher yields (5, 30). This enhancement may also increase mineral exports from agricultural ecosystems to the surrounding aquatic ecosystems, which in turn can partially compensate for the bio-available mineral depletion in agricultural ecosystems (39). Meanwhile, the enhancement of bioavailable minerals will facilitate the stability and preservation of organic C and N in soil by strengthening the associations between minerals and organics. In the long-term, although some investigators have suggested that the enhancement of mobile minerals may increase cation losses via leaching, surface runoff or drainage in an agricultural ecosystem (39, 40), we demonstrated that the amount of Al was almost stable, but the amount of Fe was slightly decreased (Table 1). This result eliminated the possibility of cation loss, which was also supported by previous investigations in the Qiyang experiment (10, 20, 32, 41). Finally, our results may provide unique opportunities to manage soil C storage or preservation by fertilization practices. Further research is needed to explore the regulatory mechanisms of mineral-associated organic matters in soil.

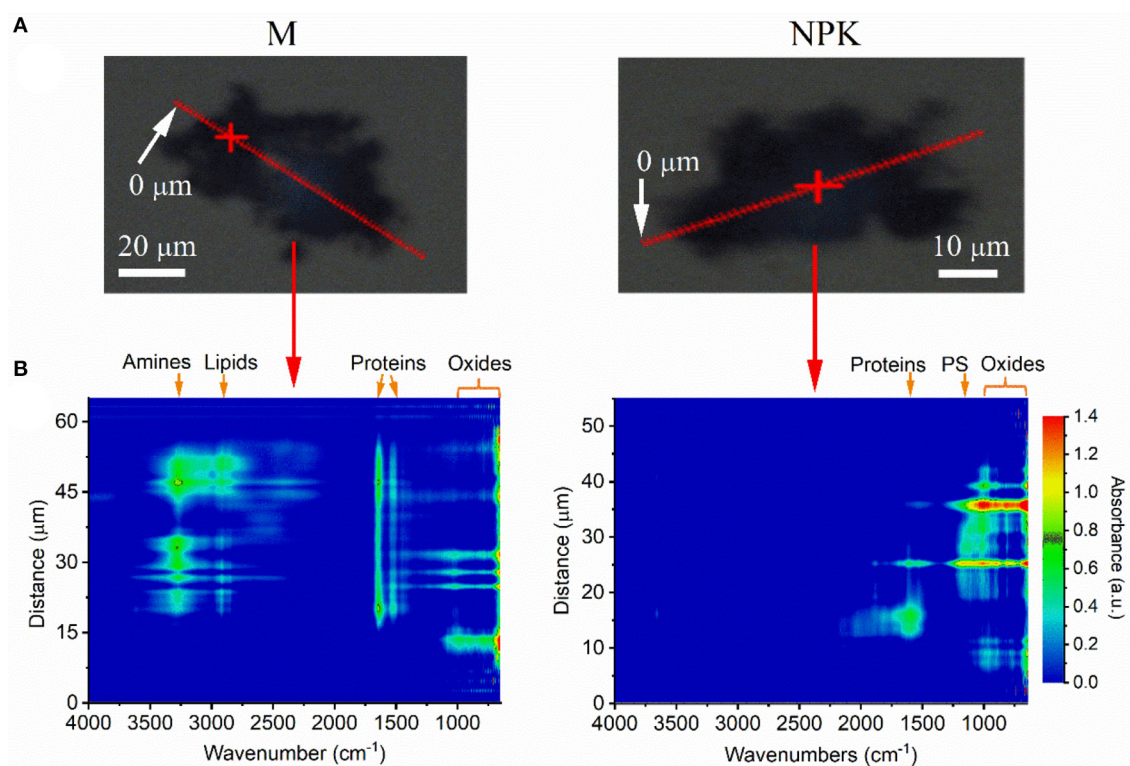


FIGURE 3 | Optical images (A) and the spatial related SR-FTIR spectroscopy (B) of soil particles in the contrasting fertilization treatments. M, farmyard manure fertilization, NPK, chemical fertilization. PS, polysaccharides. The μ -FTIR spectra peaks noted with white dashed lines represent the functional groups of N-H stretching of carboxylic acids ($\sim 3,400$ – $3,200$ cm^{-1}), C-H stretching of lipids ($\sim 2,920$ cm^{-1}), aromatic C=C vibrations and amide N-C stretch ($\sim 1,650$ and $1,530$ cm^{-1} , respectively), and secondary minerals (<950 cm^{-1}), respectively. The color is relative for μ -FTIR peak height and does not allow quantitative comparisons between peaks.

CONCLUSIONS

Taking advantage of a well-controlled long-term (32 years) field experiment at the Jiangxi Institute of Red Soils, Jinxian, China, we demonstrated that long-term farmyard manure input significantly increased the available Al and Fe concentrations more than one order of magnitude in soil colloids compared to no fertilization and chemical fertilization treatments. NanoSIMS images and SR-FTIR analyses provided direct evidence demonstrating that fertilization practices could regulate the associations between organic matters and minerals at the submicron scale. Our results highlight the importance of agricultural practices, e.g., manure inputs, as a driver to improve mineral-associated organic matters and potentially increase soil C persistence.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding author/s.

AUTHOR CONTRIBUTIONS

G-HY proposed the concept, designed the experiments, and supervised the project. SL carried out the experiment. Both authors wrote the manuscript and discussed the final manuscript. Both authors contributed to the article and approved the submitted version.

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