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Interactive comment on "*In situ* interactive characteristics of reactive minerals in soil colloids and soil carbon preservation differentially revealed by nanoscale secondary ion mass spectrometry and X-ray absorption fine structure spectroscopy" *by* Jian Xiao et al.

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Response to Referee 1

We thank Referee 1 for the thoughtful and supportive comments. We have revised our manuscript in response to the suggestions. All of the revised parts were colored in red in the revised manuscript. Interactive comment on "In situ interactive characteristics of reactive minerals in soil colloids and soil carbon preservation differentially revealed

by nanoscale secondary ion mass spectrometry and X-ray absorption fine structure spectroscopy" by Jian Xiao et al.

Anonymous Referee #1 Received and published: 2 March 2016

The very interesting objective of the manuscript (ms) is that NPK + manure fertilization enhances the formation of reactive Fe and Al nano-minerals that may contribute to the soil carbon stabilization. The soil samples were collected from a 24 years fertilization field experiment and were compared to a control soil and a NPK fertilized soil. The authors applied a set of modern investigation techniques like NanoSIMS, HRTEM, SEAD, XANES, EXAFS and XPS to characterize the fractionated soil colloids. It remains however unclear in the ms if all these techniques used and the measured data are necessary for the achieved results and their rather poor discussion and the conclusion. The authors referred to some more and less relevant references in the discussion instead of a comprehensive interpretation of the results. In fact, this is a rather methodological paper and the (new) mechanistic insights are lacking.

Response: In the revised manuscript, we add an explanation about these techniques, strengthening their complementary properties. Also, we strengthened the discussion by a comprehensive interpretation of the results. In addition, the conclusion section was also revised.

Overall, some fundamental information about the manure application and SOC stocks could be included in the ms and useful for the discussion. (See also my comments below) The authors can find this information e.g. in a recent review paper by Maillard and Angers, 2014.

Response: Good suggestion! In the revised manuscript, we added some fundamental information about the manure application and SOC stocks in the Introduction, including two papers about meta-analysis (Maillard and Angers, 2014; Zhao et al., 2015).

Manure addition enhanced the org C binding of Al and Fe nano-minerals which was also shown in the previous papers of the authors like in Wen et al. 2014 a and b. The authors should clearly present what was achieved in that papers and what is really new in the ms besides the combination of applied modern investigation techniques.

Response: The results from our previous papers showed that manure amendments enhanced reactive components of minerals in soils, i.e., ferrihydrite and allophane. Because soil particles exhibit high heterogeneity, the in-situ characterization of the org C binding capability of Al and Fe nano-minerals at the submicron scale is urgent. To date, this information has not been explored in the contrasting fertilized soils. In the revised manuscript, we added this information in the Introduction section to strengthen the uniqueness of this manuscript.

Title: What are interactive characteristics? What about the other methods used in the manuscript? Response: In the revised manuscript, we removed "interactive" and the methods in the title. The title was changed to “New strategies for submicron characterization the carbon binding of reactive minerals in long-term contrasting fertilized soils: Implications for soil carbon storage”.

Introduction: The authors should add a paragraph about the effect of fertilization practices on SOM development of soils, especially about the effect of manure!

Response: Based on the suggestion of Referee 1, we added a paragraph to describe the effect of fertilization practices (e.g., manure amendments) on SOM development of soils in the Introduction section.

Line 115: ferrihydrite and allophanes.

Response: In the revised manuscript, we changed “allophane and ferrihydrite” to “ferrihydrite and allophone” (Lines 117-118 in the revised manuscript).

2.6 EXAFS and XANES: details of the data processing are missing. How was the data fitting procedure? How were they normalized and in which interval? How many single scans were used?... criteria for the best fit?

Response: In the revised manuscript, we added these missing details, which can be seen at Lines 174-199 in the revised manuscript.

Results: Line 207: significantly 217-219: the findings of SAED measurements are similar to the finding of Wen et al, 2014 paper. Why were the SAED experiments needed? What are the new knowledge and the benefit of these results for the ms?

Response: In the revised manuscript, we changed “Significant higher SOM concentrations patterned as under NPKM > NPK than > Control (Table 1). Significantly higher percentages of oxalate extracted Al (Alo), Fe (Feo), SRO Al (Alxps), Fe(Fexps), DOC ranked as under NPKM > Control > NPK, but, significantly higher ratios of DOC/Alxps and DOC/Fexps were under NPKM > NPK > Control (Table 1)” (lines 207-211 in the original manuscript) to “SOM concentrations in different fertilization treatments ranked as NPKM >NPK> Control (Table 1). Oxalate extracted Al (Alo), Fe (Feo), SRO Al (Alxps), Fe (Fexps), and DOC ranked as NPKM > Control > NPK, but ratios of DOC/Alxps and DOC/Fexps ranked as NPKM > NPK > Control (Table 1)”(lines 215-218 in the revised manuscript).

The samples of SAED measurements in Wen et al (2014) paper were dissolved organic matters, which are different from the samples in this manuscript. In this manuscript, we used SAED to characterize soil colloids. By using SAED, we want to illustrate the element composition of mineral particles. Our results from SAED demonstrated that the amorphous mineral species were dominated by Al, Si, and O, while the crystalline minerals were mainly composed of Fe and O (Fig. 1-c, d). This information is meaningful for the following NanoSIMS analysis, supporting that it is suitable to focus on Al and Fe and their binding with org C.

Line 224: Fig. 1 and S2: not really clear what the authors want to demonstrate with the HRTEM and NMR (!!) spectra

Response: With the help of HRTEM (Fig. 1), we could directly visualize the differences in both morphology and elements compositions of soil particles, which is helpful for the reason that we choose Al and Fe for binding org C in the following NanoSIMS. Fig. 2 shows the spatial heterogeneity of 12C-, 27Al16O-, and 56Fe16O- ion masses in the soil colloids. Fig. S2 presents the distribution of region of interests (ROIs), i.e., the 12C- rich ROIs and the 12C- less rich ROIs.

Line 230: What is the relevance of Fig.S2 and Table S2 for 12C- rich or less rich ROIs? Table S2 is about metal composition! See also line 232

Response: Fig.S2 was a representative NanoSIMS image showing the position of region of interests (ROIs) among the several replicates of different fertilization treatments as listed in Table S2 (Control: 8 replicates; NPK: 6 replicates; NPKM: 6 replicates, respectively). Table S2 presents the quantification of 12C- rich (12C–R) and 12C- less-rich (12C–LR) ROIs. In the revised manuscript, we added the more detail description about the Fig. S2 and Table S2.

Line 233: why is the area of percentage similar for the Control and the NPKM?

Response: The area of percentage for the Control and the NPKM is similar but different from the NPK, suggesting that compared to the Control treatment, the NPK treatment can change organo-mineral associations at the submicron scale in soil colloids, but NPKM can restore these associations.

Lines 238-239: These results are expected. See paper Maillard and Angers, 2014.

Response: We agree with the comments of Referee 1. These results in Lines 238-239 are expected, but they provided in-situ observation evidence at the submicron scale demonstrating that more organic C had been bound by Al and Fe minerals under NPKM than under NPK. This information has not been shown by previous publications. In the revised manuscript, we removed "the first" and rewrote the sentence.

Line 241: present

Response: In the revised manuscript, we changed “presented” to “present”.

Lines245-251: the XANES results about Fe oxide species are interesting! But see my comments about EXAFS.

Response: The response about this question can be seen in the response of "EXAFS results".

Line 252-253: see my comments for lines 238-239, these results are expected!

Response: We agree with the comments of Referee 1. These results in Lines 252-253 are expected, but they provided in-situ observation evidence at the submicron scale. This information has not been shown by previous publications. In the revised manuscript, we added the comparison between this result and that from Maillard and Angers (2014).

EXAFS results (lines 254-279): The authors confirm the findings of XANES. Why were both EXAFS and/or XANES measurements needed? What is the benefit of the EXAFS or/and XANES results?

Response: XANES gives the quantitative composition of Fe minerals. Whereas EXAFS results can provide qualitative information about the structure of Fe minerals under different fertilization treatments. Furthermore, we use EXAFS results to show that the structure of Fe minerals under different fertilization treatments is really distinct. We believed that the EXAFS results are a helpful complementary to XANES. Combined XANES and EXAFS, we could get a complete understanding about the composition and coordination state of Fe minerals.

XPS: (lines 280-285): interesting results! Can a direct uptake of manure be distinguished?

Response: We really appreciate your interests. The previous investigation had shown that aromatic C in composted dairy manure accounted for approximately 30% of the total C, taking advantage of solid-state 13C nuclear magnetic resonance (NMR) spectroscopy (Liang et al., 1996). Another investigation showed that the addition of manure-based amendments, with or without chemical fertilizers, increased SOC and enhanced aggregate stability (Mikha et al., 2015). But it is unclear whether manure is direct contributed to aromatic C increase or first utilized by microbes and then contributed to aromatic C increase. In the revise manuscript, we added the above discussion in the Discussion section.

4.1. The discussion about the increased concentration of reactive Al and Fe minerals is missing in the chapter (the authors only cite previous works about this). Also a discussion of the org C content and composition is missing in lines 301-306.

Response: In the revised manuscript, we added the discussion about increased concentration of reactive Al and Fe minerals and the org C content and composition.

4.2: a discussion about the possible mechanism of the formation of reactive Al and Fe mineral is missing. It is further unclear why both XANES and EXAFS results are necessary and useful for the discussion. The author included in the Discussion part some recent papers and their statements and repeated the advantages of the used methods but this did not result in a comprehensive discussion about the formation of reactive Fe and Al minerals and their role for the SOC stabilization.

Response: In the revised manuscript, we added the discussion about the possible mechanism of the formation of reactive Al and Fe minerals. By measuring the composition of manure, Wen et al. (2014b) have shown that the reactive minerals introduced by the manures were very limited, ruling out the possibility that fertilizers introduced Al fractions. Therefore, we suggests that organic fertilization treatments enhance reactive minerals by the in-situ transformation of minerals. This is supported by the results from a simulated study that addition of oxalic acid to soil colloids can promote the transformation from Fe(III) to ferrihydrite (Huang et al., 2016). Another previous report also indicated that the low-molecular-weight (LMW) organic acid may incorporate into the network structure of SRO minerals, inhibiting further growth of SRO minerals (Xu et al., 2010).

In this study, XANES and EXAFS results provided quantitative and qualitative information about the composition of Fe minerals under different fertilization treatments, respectively. Both of them can support each other. Combined XANES and EXAFS, we could get a complete understanding about the composition and coordination state of Fe minerals. Moreover, we strengthened the discussion by a comprehensive interpretation of the results.

Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/bg-2015-625/bg-2015-625-AC1-supplement.zip

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