

## ***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.***

**Jian Xiao et al.**

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Referee #4 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” Jian Xiao et al. yuguanghui@njau.edu.cn Received and published: 4 May 2016

Response to Referee #4

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We really thank Referee #4 for the exciting and thoughtful comments. We have revised our manuscript in response to these 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 #4 Received and published: 4 May 2016

This paper, by Xiao et al., presents a study about the influence of fertilization (organic vs inorganic) on the colloidal interactions between soil organic matter and Al-/Fe-rich minerals. The authors used top end micro- and nano- scale techniques to characterize the mineralogy, the redox and the amount of organic matter in their sample. The general topic of the study is well within the scope of biogeosciences. And this manuscript well written and that the study appears well designed. The abstract quality is good. The introduction provides a descent description of the scientific context of the study and presents the goal of this study. The sample and methods are well described. Nevertheless, I believe that the manuscript could really be improved before acceptance for publication. My main criticism is that I would expect the authors to discuss their data in more details. They seem to have acquired an impressive dataset, but the interpretation and discussion of the data, in addition to the insight we get from their comparison, is too short, to my sense. I'm sure there is much more to tell from their results. The authors should also present and discuss potential mechanistic processes that may explain their observations. Overall, this manuscript appears frustrating (we expect more in the discussion!).

Response: Great comments! In the revised manuscript, we strengthened the discussion. The revised parts were colored in red in the revised manuscript and not listed here for brevity.

In addition, I feel that some of the results should be presented in more details. For

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instance, the description of the NanoSIMS study, lines 208 to 211, is very short! I'm sure you have plenty of nice images. Please provide deeper description. Be more specific and indicate to the reader what the NanoSIMS brings to the study.

Response: We agree with the comments of Referee 4! In the revised manuscript, we presented the results in more details. The revised parts were colored in red in the revised manuscript.

There are few additional points that should be clarified : - lines 114-116: "In this study, we chose 6 spots ..." unclear, should be rephrased. What do you mean when you write organo-mineral complexes were included?

Response: Thanks! In the revised manuscript, we rephrased this sentence. Also, we deleted "organo-mineral complexes were included". The revised parts were colored in red in the revised manuscript and also listed as follows.

"In this study, we chose 6 spots from the NanoSIMS images to show the replicates of each soil colloid sample because the majority of particulate organo-mineral complexes were included and similar according to the characterization of natural colloids (Philippe and Schaumann, 2014; Xiao et al., 2015)"

was changed to

"In this study, we achieved 6 NanoSIMS images for each soil colloid sample to support the replicates of our results (Philippe and Schaumann, 2014; Xiao et al., 2015)".

- line 128: you claim that depth resolution of the Cs beam is 15 nm. Where does it come from? Is it a calculation? Was it measured by anyone? Please add the source for this number.

Response: We appreciate the comment of Referee 4. Vogel et al. (2014) calculated that "The estimated depth resolution with 16 keV Cs<sup>+</sup> ions as primary ion beam is about 15 nm." in their study. In the revised manuscript, we deleted this sentence after the discussion with one of the co-authors, Jialong Hao, who is responsible for the

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measurement of NanoSIMS.

Vogel, C., Mueller, C. W., Hoschen, C., Buegger, F., Heister, K., Schulz, S., Schloter, M., and Kögel-Knabner, I.: Submicron structures provide preferential spots for carbon and nitrogen sequestration in soils, *Nature communications*, 5, 2947, 2014

- line 131: it is ok to cite previous studies for details about analytical protocols, but the authors could at least provide their image size and resolution (i.e. number of pixels) as this is something that is adjusted from one study to the other.

Response: We were sorry for the incomplete information. In the revised manuscript, we added the details. The revised parts were colored in red in the revised manuscript and also listed as follows.

"Specific details describing NanoSIMS measurements can be found in previous publications (Vogel et al., 2014; Xiao et al., 2015)."

was changed to

"In this study, the NanoSIMS images sizes were 256 × 256 pixels, Control, no fertilization, 28 × 28 μm<sup>2</sup>; NPK, chemical nitrogen, phosphorus and potassium fertilization, 30 × 30 μm<sup>2</sup>; NPKM, chemical NPK plus swine manure fertilization, 25 × 25 μm<sup>2</sup>, respectively. Other specific details describing NanoSIMS measurements can be found in previous publications (Vogel et al., 2014; Xiao et al., 2015)."

- lines 134 and following: the sorting in 12C rich and less rich areas is unclear, and the authors should explain why they have different conditions (limit at 90 or 50 pixels) depending on the sample. How does it give comparable results if the conditions to different areas are different?

Response: Good comments! This inspiration of sorting in 12C rich and less rich areas is from several excellent previous studies (Herrmann et al., 2007; Mueller et al., 2012; Rumpel et al., 2015; Vogel et al., 2014). For instance, Mueller et al. (2012) analyzed the spatial behavior of selected secondary ions along the line scans by choosing the

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single ROIs comprised between 100 and 1500 pixels corresponding to 0.2-4  $\mu\text{m}^2$  depending on particle size and ROI. Vogel et al. (2014) calculated the ROIs with an area greater than 10 pixels selected by the threshold option of the Image J software. In our study, the classification of sorting in 12C rich and less rich areas (limit at 90 or 50 pixels) were also based on the soil samples, which could represent the real intensity of ion mass. If we changed the conditions to a define area, the ratio between the 12C rich and less rich areas kept the same trend. In the revised manuscript, we added more details and marked them in red.

#### Reference

Herrmann, A. M., Ritz, K., Nunan, N., Clode, P. L., Pett-Ridge, J., Kilburn, M. R., Murphy, D. V., O'Donnell, A. G., and Stockdale, E. A.: Nano-scale secondary ion mass spectrometry-A new analytical tool in biogeochemistry and soil ecology: A review article, *Soil Biology and Biochemistry*, 39, 1835-1850, 2007.

Mueller, C. W., Kölbl, A., Hoeschen, C., Hillion, F., Heister, K., Herrmann, A. M., and Kögel-Knabner, I.: Submicron scale imaging of soil organic matter dynamics using NanoSIMS-From single particles to intact aggregates, *Organic Geochemistry*, 42, 1476-1488, 2012.

Rumpel, C., Baumann, K., Remusat, L., Dignac, M.-F., Barré, P., Deldicque, D., Glasser, G., Lieberwirth, I., and Chabbi, A.: Nanoscale evidence of contrasted processes for root-derived organic matter stabilization by mineral interactions depending on soil depth, *Soil Biology and Biochemistry*, 85, 82-88, 2015.

Vogel, C., Mueller, C. W., Hoeschen, C., Buegger, F., Heister, K., Schulz, S., Schloter, M., and Kögel-Knabner, I.: Submicron structures provide preferential spots for carbon and nitrogen sequestration in soils, *Nature communications*, 5, 2947, 2014.

- line 142 and following: what do you mean by “the ROIs of the AIO and FeO images were combined..”? Please provide more detail. Do you proceed this way to obtain a

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ROI corresponding to mineral rich regions?

Response: We were sorry for the confusing writing. In this study, we sorted the ROIs into 12C rich and less rich areas according to the pixels of 12C ion mass. Meanwhile, the ROIs of AIO and FeO ion mass were similar as the 12C ion mass because we were interested in studying the in situ location and correlation between the organic and mineral compositions in soil samples.

In the revised manuscript, we changed “The ROIs of the 27Al16O- and 56Fe16O-images were combined afterwards to obtain the ROIs according to the distribution of the 12C- rich ROIs and 12C- less rich ROIs under different fertilizations conditions (Table S2).” to “The same ROIs were simultaneously selected in the 27Al16O- and 56Fe16O- images. ”

- line 270: I'm not really convinced that Figure 3 shows what the authors claim.

Response: Sorry for the unclear statement. In the revised manuscript, we rephased this sentence. The revised parts were colored in red in the revised manuscript and also listed as follows.

“In this study, the ROI analyses of NanoSIMS in situ observation (Fig. 3) provided direct evidence that long-term organic fertilization strengthened the SOC binding and preservation capability of Al and Fe minerals in soil colloids as well as a highly spatial heterogeneity of soil colloids at the submicron scale.”

was changed to

“In this study, the ROI analyses of NanoSIMS observation (Fig. 3) indicated that despite of highly spatial heterogeneity of organo-mineral complexes at the submicron scale, long-term organic fertilization strengthened the SOC binding and potential preservation capability of Fe minerals for both the 12C- rich- or 12C- less rich- ROIs in soil colloids when compared to chemical fertilization. Meanwhile, long-term organic fertilization also strengthened the SOC binding and potential preservation capability

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of Al minerals for the 12C- rich- ROIs in soil colloids when compared to chemical fertilization. However, as for 12C- less rich- ROIs in soil colloids, fertilization regimes seemed to have no influence in the SOC binding with Al minerals.”

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/bg-2015-625/bg-2015-625-AC3-supplement.zip>

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Interactive comment on Biogeosciences Discuss., doi:10.5194/bg-2015-625, 2016.