

## ***Interactive comment on “Multidecadal persistence of organic matter in soils: investigations at the submicrometer scale” by Suzanne Lutfalla et al.***

### **Anonymous Referee #1**

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The topic, a potential special role of smectites in adsorbing/preserving soil OM, is still not well understood and of interest to the readers of BG. Analytical techniques with a high spatial resolution such as STXM may in fact be crucial to answer the underlying questions here. Therefore, the scientific approach is generally valid and of scientific significance. The presentation is concise and well structured. Language seems appropriate as far as I can judge as a non-native speaker. However, many details concerning data analysis and interpretation remain unclear.

The final outcome of my review is not very positive, because the main conclusion of the manuscript (smectites protect associated OM more effectively than other clay minerals) is not well supported by the given data and because the discussion of the data is rather weak:

P7 L23-26: A high C content in the fine clay fraction and about 100% smectite in this fraction are used to argue for a special role of smectites. This is not convincing as all investigated clay fractions are dominated by smectites. Especially the IC fraction has a much lower C-content, but only small contributions of illite and kaolinite. The smaller particle size and larger surface area of the finest clay fraction may also explain the higher C content in the FC fraction. If possible, the paper should distinguish between “dominantly smectites show an OM cover” and “smectites show a larger C-signal because they are usually much thinner than illite particles”. If not possible the issue should be discussed.

Figures 5, 6, 7, i.e. the STXM stacks: The origin of the four spectra (Figure 5) is unclear. Have they been extracted from one of the stacks or are these references?

Clay mineral identification using only these C stack is unclear. All spectra of Figure 5 used to reconstruct spectra of the stacks (presumably) by linear combination fitting (LCF) show considerable contributions from K (including the “OM+K+Ca”). What is its origin, if not an illite component? Potassium does not occur in smectite and kaolinite, but in illite and mixed layer illite/smectites so that the spectrum “OM+K+Ca” can be in accordance with illite and mixed layer illite/smectite, but not with a pure smectite. However, as far as I understand the XRD data, all samples are dominated by smectites, while mixed layer phases make up for only a minor amount (if wrong, please explain!). Can K-feldspar be excluded?

Even the OM-rich fraction shows a considerable contribution of K. What is this, if not a lot of OM on illite?

Most smectites contain Ca, illites and kaolinites do not. However, it remains unclear why the spectrum “OM+K+Ca” used to represent OM-covered smectites is assumed to contain any Ca. Only at the end of the paper (P7 L29) it is mentioned that smectites were identified by the presence of Ca. HOW was that done? The Ca L-edge has its strongest peaks at 349.2 eV (L3) and 352.5 eV (L2), i.e., outside of the recorded

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energy range (according to the methods sections in paper and SI).

STXM stacks are supposed to show that smectites are always associated with OM, while illites become increasingly free with the duration of bare fallow. However, only three stacks of  $\sim 4$   $\times$   $1.5 \mu\text{m}$  size are shown, two of them (2008 CC and 1951 CC) show illites (according to the LCF) with no C signal (red, but not pink areas). This is not enough to show a trend with time or mineral composition. The paper can easily accommodate a larger Figure 6/7. I suggest to show at least 10 stacks (instead of 5) in a combined figure with two columns (two size fractions) and 5 rows (sampling times). As the fine clay does not contain much illite, the IC fraction might be more interesting than the FC fraction. If there are more stacks add them to the SI.

In addition to the RGB images of components please show the residuals plus a number of fits for different ROIs. LCF will always give a result but only the residuals and the actual fits allow to judge if the result is meaningful and if the right set of components has been chosen.

I also suggest to show the calculated C concentration as separated images. This will help to visualize where OM is located with respect to the particles.

Why is the component “OM+K” not shown in Figure 6? Does not it exist? If so, please show that LCF with the three other components can reproduce the measured spectra without the “OM+K” component.

Legend of Figure 6: should not the color of “K” be red? (Please correct.) If so, only two small separate spots with that signature remain. Can you exclude that these spots are K-feldspars? At least discuss!

Figure 7: if the fine clay fraction contains only smectites (or if only smectites were imaged by STXM), how can the authors use Figure 7, to conclude that illites carry less OM than illites?

P6 L7-9: here you mention that N K-edge stacks have also been done. If so, show

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them, don't withhold them! Do they fit the C/N-data? If the clay associated OM is rich in N, should not the main peak at the C K-edge be discussed as at least partly be originating from amides?

Do you have any explanation of the small peak at  $\sim 290$  eV (which only appears in the OM+K+Ca component)? What is the origin of the small peak at  $\sim 283$  eV and the trough at  $\sim 284$  eV? What is the interpretation of the peak at  $\sim 291$  eV in FC\_10 and FC\_22 (Figure 4)? Comparison between bulk NEXAFS data and STXM NEXAFS data is missing. How can differences be explained?

The discussion is overall rather weak. Related work is often not considered. A different interpretation (as given in the named paper by Chen) is discussed in a way that the completely different conclusions drawn from a correlation between Ca and OM by two studies does not become clear. Reasons for a potentially higher reactivity (as sorbents) of smectites relative to illites are not mentioned.

SI: I cannot judge, whether the proposed (new?) method for spectra normalization is meaningful.

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