

Interactive comment on “Timescales of C turnover in soils with mixed crystalline mineralogies, Kruger National Park, South Africa” by L. Khomo et al.

Anonymous Referee #1

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General comments

The idea of the present work was to test the organic carbon accumulation and turnover as related to crystalline mineral phases. To do so, soils low in short range order (SRO) mineral phases were studied. The authors report differential effects of certain mineral phases on accumulation and turnover.

I am not convinced that their assumptions are valid. Major misconceptions as well as serious methodological flaws question the entire study. I therefore cannot recommend publication.

Major concerns:

C1

Throughout the manuscript there is a tendency to mix up “accumulation” and “stabilisation” of organic matter. These are no synonyms. Please try to be specific.

There is also an overall tendency of imprecise expressions and mixing up of concepts. The result is a partly confused text hard to read and understand.

The definition of SRO phases used by authors is rather vague and changes throughout the text. Sometimes it is based in oxalate-extractable Fe and Al, sometimes it seems also the dithionite-citrate-bicarbonate (DCB)-extractable Fe and Al is included.

Analyses of the clay fraction where carried out after treatment with H₂O₂. This will remove part of the light fraction-type material but also part of the mineral-associated material. Since the exact share of mineral-associated organic carbon removed by the H₂O₂ may vary, all data organic carbon data obtained on the clay fraction are biased, thus, need to be dropped. Since much of the conclusions are based on the clay fraction-related data this questions the overall meaning of the work. Justifying the analyses of carbon in H₂O₂-treated material by claiming that some carbon survived the treatment is not valid.

Also, analysis of the mineral assemblage of the clay fractions is based entirely on X-ray diffraction with Cu K α radiation. Thus, there is no proper estimate of possible contents of SRO phases and oxides of the clay fractions. Several sections of the manuscripts left me under the impression the authors are not aware that the clay fraction is not composed entirely of clay minerals but also contains other phases capable to interact with organic matter.

The density separation used is also rather strange. The cut-off density of 1.7 g/cm³ is not justified, at last not by the reference given. In addition, the sonication energy used was little, thus, total dispersion of samples with stable aggregates has to be questioned. Especially, the more oxide and kaolinite-rich samples may not disperse completely, thus, the heavy fraction likely still may contains light fraction-type material. In turn, undispersed aggregates may still contain enough light material to make them float.

C2

The rather variable and often very small contents of organic carbon in the light fractions point at major problems with the separation. In summary, the density separation has been carried out in a hardly reproducible manner.

Minor concerns:

Title: As written, the title suggests a study of only local importance. The authors may consider changing it into "Timescales of C turnover in soils with mixed crystalline mineralogies".

p.1, l. 17-18: The conclusion that the enrichment of OC in the clay fraction is due to stabilisation by clays is either trivial (in case of the authors refer to clay as size fraction) or disputable (in case of referring to clay minerals; see above and below).

p. 1, l. 23: What made the authors believe that crystalline Al oxyhydroxides contributed to the accumulation of faster turning over fraction? Is that based on DCB-extractable Al? If yes, please note that the extractant is not capable of extracting much Al from crystalline Al phases such as gibbsite.

p. 1, l. 26: What does SRO refer to? Seemingly it refers to the observed relationship between DCB-extractable Fe and organic carbon. Dithionite-citrate-bicarbonate-extractable Fe includes Fe from crystalline Fe oxides, such as goethite and haematite.

p.1, l. 29-30 (and elsewhere in the manuscript): Expressions such as "crystalline Fe" are nonsense and misleading. Iron is an element. Please refer to the correct mineral phase, e.g., Fe oxides.

p. 2, l. 3-5: Some references given do not refer to physical protection or recalcitrance. Please be re-consider.

p. 2, l. 7-16: Somehow, I am under the impression the authors have some problems with mechanisms involved in organic-mineral interactions. For example, what is "dehydration bonding"? Also, the choice of references is a bit strange. For instance, two references are on methods for estimating mineral phases but do not address binding

C3

mechanisms. Did Masiello et al. (2004) really refer to crystalline Al and Fe sesquioxides?

p. 2, l. 10: Replace "metallic" by "metal".

p. 3, l. 13-16: Note, the studies of Wattel-Koekoek et al. (2003, 2004) include no proper estimates of possible contents of oxides, thus, do not allow for distinguishing of effects by clay minerals and other phases, including SRO phases.

p. 3, l. 17-23: I suggest adding proper research questions and/or hypotheses.

p. 3, l. 27-28: What is "soil residence time"? Please explain.

p. 4, l. 24-25: Please give more information on the determination of the clay contents. Did the procedure involve pre-treatments such as destruction of organic matter and oxides?

p. 4, l. 32-33: The location of the CN analyser is probably of no importance. Omit.

p. 5, l. 3: As stated, it seems only the characterisation of clay minerals was attempted.

p. 5, l. 14-16: What was the idea behind adding Al oxide to the clay fractions before X-ray diffractometry? Why not quartz? The addition of Al oxide limits estimation of Al oxide phases. Was the quantification of X-ray diffraction data supplemented by data on the elemental composition? What software was used?

p. 5, l. 24: Why a density-off of 1.7 g/cm³ was used? The reference given refers to 1.6 g/cm³.

p. 5, l. 25: What was the reason of using varying amounts of sample for the density separation? Why no standard protocol was used? Did the authors attempt estimating the carbon recovery?

p. 5, l. 26: What is meant with "ultrasonicated at 60 J m⁻¹ for 2.5. min"? Is 60 J/ml the total energy input? Did the authors control for proper dispersion, i.e., disaggregation?

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And if yes, how this was done?

p. 5, l. 29-30: What is the idea behind removing visible roots from the light fraction? Actually, dead roots are part of the debris material that makes up the light fraction. Why the authors did not remove living roots from fresh samples?

p. 6, l. 1-4: Due to the bias in the clay and density separation I do not think the data set to be solid and comprehensive. I am wondering why the authors did not try a more logic approach, such as first separating all light material, then, separating the clay fraction from the heavy fraction.

p. 6, l. 13-14: Is acidification to pH 6 really enough remove all carbonate, including that bonded to other mineral phases? I doubt.

p. 7, l. 13: No, DCB does not extract only crystalline Fe oxide phases but all Fe oxide phases, including ferrihydrite. In turn, oxalate extracts only the poorly crystalline portion of DCB-extractable Fe.

p. 7, l. 14: Note, DCB-extractable Al does not represent Al oxide phases.

p. 7, l. 18: Is there are reason why the clay contents increased with depth?

p. 8, l. 27-32: Is it correct, the soils containing pedogenic carbonates are those rich in smectite? So, could it be that their radiocarbon signature was affected by carbonate? By the way, the picrite (back basalt)-derived soil is classified as Calciustert but not listed as containing carbonate? Isn't that illogic?

p. 9, l. 8-9. Due to the H₂O₂ treatment of the clay fraction, I doubt that proper estimates on non-clay carbon are possible.

p. 10, l. 9-15: These correlations need to be re-considered bearing in mind that the clay fraction contains most of the oxides.

p. 11, l. 9-17: The discussion here is rather speculative since composition of organic matter was not addressed.

C5

p. 11, l. 18-29: Here, it becomes clear the authors partly equal clay-sized particles and clay minerals. They relate the estimated non-clay fraction carbon to "other, non clay mineral stabilization mechanisms". This is simply wrong, since the clay fraction holds also most if not all oxide phases (even the Cu K α X-ray diffraction, despite of being rather insensitive to Fe oxides, indicated their presence). Also, I have problems with the authors' logic. The organic carbon of all study soils relates well to the DCB-extractable Fe. Seemingly, the clay mineral type does not matter much to the accumulation of organic carbon. So, there is no reason for all the clay mineral discussion. I am also wondering, why the authors did not comment on the rather small contents of organic carbon in the smectite-rich soils. There is much writing on organic matter stabilisation by smectites. The results presented, however, suggest that smectites are rather poor organic carbon accumulators.

By the way, why do the authors consider "crystalline Fe and Al (oxyhydr)oxides" as controlling carbon accumulation? The close relationship is for DCB-extractable Fe and not for any Al. Also remember, DCB extracts all non-crystalline Fe oxides (see above).

Assuming that the relationship between organic carbon and Fe oxides is also valid for the smectite-rich soils, i.e., Fe oxides do the accumulation; it is absurd to assume that the smectites make the organic carbon turning over slowly. As already pointed out, I assume an issue with incomplete removal of carbonates to be the reason of the radiocarbon signature of the smectite-rich soils.

Tables and Figures (general): Please give proper dimensions. Percentages of smectite, organic carbon, smectite likely refer to weight-%. Consider giving instead g/kg. What is the dimension of the cation exchange capacity (CEC)?

None of the tables and figures is truly self-explanatory.

Table 2: I am wondering if the "oxides" included also Al phases. The little clay content of the non-mafic soils is no good reason for not analysing the composition of their clay fractions.

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Table 3: The rather low organic carbon contents of some of the light fractions support my concerns on issues with the density separation. The light fractions with little carbon may contain a good portion of mineral-bound (older) carbon, thus, suggesting a slow turnover.

Figure 5: Giving an enrichment factor for clay fractions treated with H₂O₂ is not valid.

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