

## Review Discussion

The comments of both reviewers indicate that our manuscript was flawed due to poor definition and inconsistent use of a number of terms in the paper. For example, we clearly were not consistent or even always correct in our use of the 'clay' as a particle-size designator on the one hand and as a descriptor of crystalline layer silicates on the other. Given the topic of the paper the confusion created by our admittedly sloppy use of terms created understandable frustration for the reviewers. We recognize that a substantial revision of the manuscript is required before the validity of our interpretations can be fairly judged.

Reviewer 1 pointed out numerous instances of confusing terminology and further suggests that our confusion led to misinterpretations of the results. Reviewer 2 echoed many of those concerns but was a bit more open to following our line of argument even when our terms were imprecise. An example might be our use of the phrase "crystalline Fe and Al" which reviewer 1 rightly points out makes no sense. What we should have said was "DCB extracted Fe and Al oxide or hydroxide compounds from which oxalate extracted Fe and Al oxide or hydroxide compounds had been subtracted." Obviously the latter is too cumbersome but the former was too truncated. One can probably get the sense of what we meant from the former. However, such a lack of precision is inappropriate and annoying in a scientific paper.

We hope the editor will allow us to revise our manuscript. Among the things we will change will be to give clear definitions of all of the various terms used in the manuscript, as given below.

One of the major problems we have is that there is no universally agreed upon method to quantify the mineral components in soil. We quantified the crystalline aluminosilicates such as kaolinite and smectite, but also Fe oxihydroxide minerals like hematite and goethite using XRD on clay-sized material isolated from the bulk soil. Separately, we quantified the Fe oxihydroxides and SRO minerals using standard Dithionite citrate and oxalate extractions followed by measurement of Fe in the dithionite citrate extract and Fe and Al in the oxalate extract. A major problem with our originally submitted manuscript was that we did not clearly state in all cases which of the methods was used when we discussed results.

Here we define some of the "mineral" terms we use in this ms and note that we will use these definitions consistently in the revision:

Clay (<2- $\mu$ m size fraction)

Clay Minerals (all the identifiable minerals that reside in the <2- $\mu$ m fraction – this includes layer silicate minerals, Fe oxihydroxides, Al oxide, carbonates)

Layer Silicate Minerals (crystalline layered aluminosilicate minerals such as kaolinite and smectite)

Fe oxihydroxides (Fe compounds that can be dissolved using a standard dithionite citrate extraction but which are not dissolved by a standard oxalate extraction – these compounds are assumed to be pedogenic Fe molecules although it is possible that some geogenic compounds are also dissolved by the dithionite extraction). This fraction also includes coatings on minerals with size  $>2\text{ }\mu\text{m}$  but  $<2\text{ mm}$ .

XRD-measured Fe oxihydroxides in the clay fraction. These are the Fe oxidhydroxides measured by XRD in the  $<2\text{-}\mu\text{m}$  fraction, as goethite, hematite, goethite, magnetite, maghemite and ilmenite. We normally will not refer to this fraction, as the standard dithionite citrate and oxalate extractions were performed on more soils.

SRO minerals (aluminosilicate or Fe oxihydroxides that are minimally polymerized and tend to be linked to organic compounds or water – effectively these compounds are extracted using a standard oxalate extraction and quantified by measurement of Fe and Al in solution after extraction). In SRO minerals the crystallites are so small that they do not provide a coherent XRD signal

Al oxide or gibbsite is another component of clay minerals but one that we are not explicitly quantifying in this analysis – as noted below we used Al as an internal standard for the XRD quantification of the Layer Silicate Minerals.

A second issue was the nomenclature used to define the different organic matter fractions that were measured for C and  $^{14}\text{C}$  content.

We define our use of organic matter as follows:

Light Fraction carbon: The organic carbon in material that floats in a solution with density  $1.7\text{ g cm}^{-3}$ . (Questions by reviewer 2 about details of the density fractionation procedures are given below).

Root-free light fraction carbon: The organic carbon remaining once visible roots have been picked out of the light fraction (please see Castanha et al. and other comments below).

Heavy Fraction carbon: The organic carbon in material that sinks in a solution with density  $1.7\text{ g cm}^{-3}$ .

Carbon strongly associated with XRD-clay. The carbon in the same clay fraction measured by XRD for mineralogy. This is 'strongly bound' because the material measured for XRD was treated with hydrogen peroxide and presumably only material that has a strong association with minerals or aggregates survives this treatment. Carbon strongly bounded to clay is a subset of the Heavy Fraction carbon (which can include C associated with Fe oxihydroxides coating sand grains)

Carbon not strongly associated with XRD-clay. This is determined by mass balance between the Carbon strongly bound to XRD-clay and the Bulk soil C. It includes a heterogeneous mix of materials, from very fine roots to C associated with Fe oxihydroxides coating sand grains.

## Research Design

We know from a couple of decades of work that SRO minerals store a lot of carbon and hold that carbon for long periods of time. As noted by Reviewer 2 there has been far less work done evaluating carbon storage in soils where SRO minerals make up a very small proportion of the clay mineral fraction of the soil. Our goal in this paper was to evaluate carbon storage in soils with low concentrations of SRO minerals where we would expect the heavy carbon fraction to be associated with other clay mineral components.

We agree with both reviewers that overlaps among the different mineral and C fractions we analyzed can be confusing, and that a more streamlined procedure is advisable in the future. However, we also think that in reporting the data we have, we are able to draw robust conclusions about the role of smectite clays influencing the age of carbon in soils with few SRO minerals.

Detailed responses are given below. To ease reading, we have put our responses in red below the referee's comment.

## Anonymous Referee #2

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### GENERAL COMMENTS

Summary: This manuscript investigates the controls on carbon turnover and C inventory across soils ranging in mineralogy in Kruger National Park, South Africa. The authors sampled soil across a variety of parent materials resulting in differing mineralogical characteristics. Older soils with low contents of short-range order mineral phases were chosen to specifically test the impact of phyllosilicate clays on C turnover time and stocks. To elucidate mineral protection mechanisms, particle size and density fractionation was used in combination with  $^{13}\text{C}$  and  $^{14}\text{C}$  measurements. The main finding is that the content of high surface area, 2:1 phyllosilicates (i.e., smectite) is a better predictor for C turnover times in these soils than clay content (i.e.,  $< 2 \mu\text{m}$  size fraction). They conclude that analysis of phyllosilicate clay composition reveals clearer insights into C stabilization mechanisms than clay content alone.

Strengths: This manuscript provides a unique dataset in that it is one of very few that measured radiocarbon on different soil fractions (particle size and density) of the same soils. This approach puts the authors in a position to examine the usefulness of individual fractionation approaches for different soil system, and provides interesting insights into the mineral protection mechanisms responsible for C storage in low-SRO, phyllosilicate

clay dominated soil systems. This manuscript will be of broader interest to the SOIL readership and I support its publication.

Weaknesses: 1) The authors don't draw a clear line between two definitions for 'clay', i.e. clay as a particle size category and clay as phyllosilicates. It would be helpful to be consistent with this terminology throughout the manuscript  
2) The manuscript could use some editing. The introduction is not very concise and could state the research question more clearly. There are typos, somewhat confusing sentence structures and word choices, and mislabeled figures throughout (see specific comments below).

We will rewrite the introduction to make it more concise and to the point and will clarify the use of the term "clay" throughout.

#### SPECIFIC COMMENTS

##### Abstract

P1L18: What does 'stabilized' mean in this context? Adsorbed?

We use stabilized to refer to C that is retained in the soil without reference to any specific mechanism or timescale.

P1L19-20: This is a speculative argument informed by the data presented here and should be framed as such. It is a valid point to make, but it should not be framed as a result.

Agreed, we will change this.

P1L21-24: This argument is confusing to me. The authors state that the fraction that is not clay ( $> 2 \mu\text{m}$ ) has much shorter turnover time than the clay fraction. They then attribute the shorter TT in the  $> 2 \mu\text{m}$  fraction to weaker bonding of C to Fe and Al oxyhydroxides and kaolinite as well as the presence of more modern plant inputs (lightfraction). The part that's confusing to me here and throughout the manuscript is the fact that I would consider Fe/Al oxyhydroxides and kaolinite as clays. They could be clays either because of their small size (oxyhydroxides) or because they are phyllosilicates (kaolinite). I understand the authors' point in the discussion that some of these minerals may have stuck to larger grains and so were removed with the  $> 2 \mu\text{m}$  fraction. But I strongly suggest making sure you clearly separate when you talk about clays as size separates and when 'clay' means phyllosilicate.

All the above points will be incorporated into a revision of the introductory text material, the discussions above hopefully help clarify this.

L24: HF and LF are not defined

Thank you, this will be fixed

P2L8: What is "dehydration bonding"? Do you mean ligand exchange?

Yes, we will clarify if the material remains in the revised introduction.

P2L13-15: Poch et al. seems an odd reference here. It's work on clays on Mars.

**We will remove this reference.**

P2L15-16: Masiello et al found correlations between pyrophosphate extractable Fe and Al and turnover time. I thought that pyrophosphate extracts poorly or amorphous Fe and Al phases, not crystalline sesquioxides as the authors state here.

**Yes it is correct that it does not extract crystalline sesquioxides – probably more likely Fe and Al oxides bound to organic ligands. Actually the line between pyrophosphate and oxalate extracted material is pretty fuzzy.**

P2L17-24: This argument seems very convoluted to me. Isn't the argument that organics on different mineral phases may exchange at different rates and therefore have different turnover times. Fractionation techniques average across a number of these interactions, and so there is a need to look into mineral composition of these fractions more closely to gain insights into what mineral phases provides the most protection (and thus the longest turnover time)? I see where the authors are headed with this argument, but this paragraph could be more concise.

**We will tackle this paragraph in a new introduction with the aim to streamline and clarify.**

P2L28: What is 'older C storage'. Choice of words (c.o.w.) is odd.

**Agreed, we will change this.**

P2L32: Lawrence et al provide a large dataset, but it's not true they 'virtually' measured 'all' reactive components in the system.

**We concede that point although we do think that they did better than most papers when it comes to field-based sampling, lab characterization and correlation analysis of the results.**

P3L2-4: These two sentences makes little sense to me. I think it would help to frame the argument in terms of C stocks and turnover times, rather than 'storage' and 'stability'. That applies to the remainder of the paragraph.

**Thank you for this suggestion, we should adopt this throughout the manuscript.**

P3L8: 'Trade-offs" of what?

**The idea relates back to the sentence starting on the first line of the page, but we recognize that there were a long few lines between the two points – we will clarify in a rewrite.**

P3L9-10: I agree with this statement, but that is not a research question.

It was not meant to be a research question but we can understand why the reviewer would be yearning for a pithy purpose statement by now.

P3L10: Having this very broad goal stated here seems a bit misplaced. I think the authors should state the specific research question here.

Right.

Methods

P3L28: 105 yrs? I might be wrong, but shouldn't it be longer?

It was a typo, should be 10,000 (i.e.  $10^5$ )

P4L31: Typo, should be Plasma

Thanks

Results

P7L19-20: where does it go up to 26%. The values in Table 2 range from 0-15%?

In Table 2, the % smectite (S) column has 23% and 26% for GR-550-T soils. The column labeled O (oxides) is the one that ranges from 0-15%. What is written in the text is, as far as we can tell, consistent with the Table.

Table 2 was also published previously, better in the SI?

Only three of the samples (GR-550) in Table 2 were published in Khomo et al. – we would prefer to keep the new data in the text, but acknowledge that perhaps some of our many tables could be moved to supplemental material and will review this.

Table 3: I would include total C in HF (mass of C). There are also a few typos in the table header.

We will fix this.

P9L7: I think the authors are referring to Fig. 5. The authors should check what figures are referred to in the following. It didn't always seem to match up.

This will be done.

P9L21-29: Why does every sentence refer to Fig. 4? I'm not sure what is said here refers to anything I can see in Fig. 4.

We felt that Figure 4 was crucial to provide clarity about the overlapping nature of the organic C fractions we measured. The idea was to illustrate how these varied with one sample, but we will revisit this and clarify it and remove extraneous references.

P9L23ff. On the issue of whether or not H<sub>2</sub>O<sub>2</sub> oxidizes mineral bound OM. I think it does, and it's a mute point to argue it doesn't. But the authors could at least find some refs to support the claim that it has minor impacts.

We agree that H<sub>2</sub>O<sub>2</sub> oxidizes some mineral bound OM, and did not mean to imply that it did not. Our point was that a lot of C still remained, as most of the clay samples treated with H<sub>2</sub>O<sub>2</sub> still had organic C concentrations of 1-2%.

#### Discussion

P10L27: c.o.w. What are 'C properties'?

We will find a clearer way to express this.

P12L6: c.o.w. 'sorbers' is not a word. It's 'sorbents'.

Agreed, this will be changed.