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-µm size fraction)

Clay_{XRD} (<2-µm size fraction used for XRD analysis of minerals, treated with 2% H_2O_2)

Clay Minerals (all the identifiable minerals that reside in the <2-µm 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 μm but <2 mm.

XRD-measured Fe oxihydroxides in the clay fraction. These are the Fe oxidhydroxides measured by XRD in the <2-μm 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}C content.

We define our use of organic matter as follows:

Free Light Fraction (fLF) carbon: The organic carbon in material that floats in a solution with density 1.7 g cm^{-3}. (Questions by reviewer 2 about details of the density fractionation procedures are given below, this would be considered “free” light fraction based on the weakness of the sonication).

Root-free fLF carbon: The organic carbon remaining once visible roots have been picked out of the light fraction (please see Castanha et al. reference now added to the manuscript, and other comments below). We chose to pick out visible roots because the removal of roots earlier in sample preparation is highly variable.

Heavy Fraction (HF) carbon: The organic carbon in material that sinks in a solution with density 1.7 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 (Carbon in the 'non-clay-sized' fraction). 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 to each of the reviewers are given below. To ease reading, we have put our responses in red below the referee's comment.

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.

We understand the reviewer's frustration with the originally submitted manuscript and hope to convince them that the major errors were in communication rather than interpretation. We thank the reviewer for their patience in giving such a thorough review.

Major concerns:

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.

The text has been extensively revised with these concerns in mind. We hope we are now providing clear definitions and sticking to our terminology.

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.

We agree that the H_2O_2 treatment removes organic C from the clay fraction. However, our goal was to measure the radiocarbon in C that was in exactly the same fraction as was measured for mineralogy using XRD. As long as the H_2O_2 treatment was performed consistently, we do not agree that biases associated with differential efficiencies of removal of organic matter by H_2O_2 (e.g. surface Fe oxihydroxide coatings versus layered silicate minerals) make the measurements meaningless. In a revision, we will take care to point out that there **are** potential biases, but feel that the comparison of the minerals and age of carbon strongly associated with XRD-clay from the same fraction is useful information, especially as it is one place where we have radiocarbon and minerals determined in the same material.

Also, analysis of the mineral assemblage of the clay fractions is based entirely on X-ray diffraction with Cu Kα 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.

We do understand the point and have clarified throughout the text.

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.

We decided to measure only the so-called ‘free’ light fraction, i.e. the material that floats but not the material that requires strong sonication to destroy aggregates. The cutoff density of 1.7 g cm^{-3} is one that means most SRO minerals (i.e. lowest density mineral phases) will not float. Density separation is a technique that is adapted to the soils used and there is not really a standard protocol. It is very clear that the procedure used definitely influences the results (please see Castanha et. al, 2013 who discuss this in detail). As we used a common procedure for all samples, we assume that results can be compared within our study, though care must be taken when comparing with other studies that may have used other methods. .

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.

Often in clay-rich soils, there are some mineral phases that are attached to low density material, or that remain floating in the sodium polytungstate solution even after a very long time of centrifugation. Some of these can be siphoned on to the filter when removing the floating organic matter. Including the total weight of these phases and the C content is important for determining the yield of the procedure, and reported low C contents are not uncommon, especially in B horizons and (in our data set) in clay-rich soils. The presence of small amounts of mineral materials on the filter can dilute the C content overall but have a negligible effect on the C isotope signature. For example if 50% of the weight of isolated material is mineral-dominated with a concentration of 0.5%C, and the other 50% of the weight is free organic C with 40%C. then the overall %C of the mixture on the filter would be 20.25%, a large dilution. However if we combust and analyze the isotopic signature of the mixture, the part of the mixture with 0.5%C would contribute 0.5/25.25, or about 2%, of the total C in the sample. In the case of the basalt soils (which averaged about 10%C, the contribution from the mineral-associated C could be higher (in our example, .5/10, or 5%). Using our own data as an example, assuming ^{14}C signatures of free organic matter of 1.100 fraction modern and 0.8 fraction modern for the mineral-C, the total fraction modern we measure on the mixture would be 1.096 (instead of 1.100), and reduces the presumed TT by 1-2 years (either from 10 to 9 years, or 65 to 63 years).

For this reason, we are not concerned by the degree of dilution in reporting our isotopic signatures for the root-free fLF fraction. In a revision, we will point out that %C results are subject to uncertainties in the root-free fLF fraction due to the potential inclusion of mineral material on the filters.

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).

We choose the disputable and will clear up confusion throughout the text as detailed 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.

We recognize the confusion created here and note for the record that we do not believe that the DCB extractable Al is a useful indicator of mineral composition. We will remove Al from that sentence, and have generally removed Al(d) from the Tables as well (it is still given in the supplementary material).

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

As this reviewer points out the definition of SRO minerals is vague. Here we use the standard approach of evaluating the oxalate extract for the amounts of Fe and Al released during extraction. We assume that Fe release is due to decomposition of ferrihydrite or perhaps nano-crystalline goethite and that the Al release is due to decomposition of nano-crystalline aluminosilicates such as allophane and imogolite. We recognize that we may not have been clear about this operational definition and will clarify throughout the text.

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.

The reviewer is correct. We regret the sloppy short hand that crept into our text; it should be fixed now.

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

We completely rewrote and simplified the text in the introduction based on this and several other comments by the reviewer below.

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 “de- hydration 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 mechanisms. Did Masiello et al. (2004) really refer to crystalline Al and Fe sequioxides?

The reviewer is justified in not understanding our highly compressed text which tried to cover too much ground in a short space – something we think is not really important for the paper anyway, and therefore was rewritten to achieve greater simplicity and clarity.

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

Done.

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.

The reviewer is strictly correct in this point although those authors selected samples to analyze that ensured a dominance of crystalline alumino-silicate clays with or without crystalline Fe oxides.

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

We have re-written this section and now make the questions more explicit.

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

The Kruger sampling sites offer a unique landscape for soil sampling. All the streams that cross the park from west to east are maintained at the same erosional base level by a strata of rhyolite that is much more resistant to erosion than the granites and other volcanics that are upstream of it. Furthermore we are able to establish erosion rates on the granites using ^{10}Be accumulated in quartz sampled in this case from stream channels sands. As we state in the referenced citation (Chadwick et al., 2013): "Using average regolith depth and catchment-averaged erosion rate estimates, we infer long hillcrest regolith residence times of 0.11, 0.15, and 0.57 m.y. for the dry, intermediate, and wet sites, respectively." These data are corroborated by measured soil production rates (Heimsath et al. in prep.). The importance of the stream channel base level control is that it means that all landscapes regardless of whether they are underlain by granite or volcanic rocks are eroding at the same overall rate. This gives us confidence that the soil landscape is highly stable as one would expect for a craton in a non-glaciated environment and as a consequence mineral transformations can be expected to have moved past the meta-stable SRO stage toward a stable end product (given a specific climate condition). This approach to sample selection was also used by Wattel-Koekoek et al. (2003, 2004), except they used it a more global context without a specific local landscape context.

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?

As mentioned in the text, we used H_2O_2 that destroyed part of the organic matter in the clay fraction that was measured by XRD.

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

Done.

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

The reviewer is correct that “as stated” it appears that only characterization of clay minerals was attempted. There are several parts to that statement. First we specifically did not characterize sand and silt size mineralogies. We did use a separate approach to characterize the SRO minerals and Fe oxyhydroxide minerals. For these we conducted oxalate and DCB extractions on the <2-mm fine earth fraction. The reason for using the fine earth was that we were concerned that some of these minerals would be coating the sands and silts in ways that would be missed if we only conducted those extractions on the <2-μm (clay size) fraction. In the methods section we covered these extractions in the previous section on soil characterization which led to an artificial separation of the extraction quantification of the clay minerals from the XRD characterization.

We have attempted to rewrite the text to make it clear that we are relying on both the extractions and the XRD approaches to develop the quantitative understanding of the soil mineral composition. It should be noted that we recognize that mixing these approaches is not the best way to get a soil mineral compositions, but we also argue that there is no readily accepted single approach to full quantitative mineral characterization of soils. As a consequence, we are fully aware that our development of graphical relationships among mineral compositions and carbon turnover is flawed by our acceptance of specific operational approaches toward mineral quantification. However, we now keep the comparisons strictly between the same kinds of samples – e.g. bulk C and bulk TT versus the bulk Fe(d)-Fe(o) measures on the one hand, and C strongly associated with the Clay-sized fraction that was also used for XRD measuremnent of mineralogy.

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?

The manuscript has been clarified to state that "corundum" was used as the XRD standard. Corundum has sharp peaks in XRD spectra that overlap with relatively few phases common in soil (including gibbsite) and these peaks degrade minimally during the grinding process used to mix sample and standard. Preliminary processing of the XRD spectra did not suggest gibbsite was an important constituent of the clay mineral fraction and gibbsite is not considered to be a major sorber of organic matter in soils. The word "software" has been added to clarify that the Rockjock software was used to for the quantification of minerals from XRD spectra.

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

The density of 1.6 g/cm^3 is typically below those of all SRO minerals; so is 1.7 g/cm^3. We consulted with the author of the reference (Marion Schrumpf) about which density to use, and this was her suggestion. There is no general agreement on methods to use for density separations and many different density cut-offs can be found in the literature.

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?

The amount used was 10-15 grams, we did not feel the need to control the amount of sample extracted to better than within a few grams as the yield was determined based on the measured initial weight for each sample. We did estimate C recovered in each fraction (these data are given in Supplementary Table 1, and indeed they are not as beautiful as we could wish (recovery based on adding the fractions together ranges from 40-95% for surface soils). We are most confident of the % of total C in the HF-fraction as there are issues with weight change in filters and low masses with the quantification of the low-density fraction, and potentially loss of material when picking roots off of the filters). An additional amount of C is dissolved and not recovered in the dense liquid. We admit that our mass balance (as occurs in many density separation procedures) was not perfect. However, as outlined above, we do not think this affected isotopic results – or at least it affected them in the same systematic ways. Please see Castanha et al. (2008) for a detailed discussion of the various ways density fractions are affected by the procedures used.

*Castanha, C, S Trumbore, R Amundson (2008) Methods of separating soil carbon pools affect the chemistry and turnover time of isolated fractions
Radiocarbon, 50, 83-97.

p. 5, l. 26: What is meant with "ultrasonicated at 60 J mL-1 for 2.5. min"? Is 60 J/ml the total energy input? Did the authors control for proper dispersion, i.e., disaggregation? And if yes, how this was done?

60 J/mL is an estimate of the energy input, determined after calorimetrial calibration of the sonicator. This is a relatively low energy and not likely to disrupt strong aggregates. Schrumpf et al. 2013 used stepwise increases in energy input to determine the level at which all aggregates were dispersed (we are using the identical system that she used). They found that "Energy input of 100 J mL^{-1} was sufficient" (to destroy all aggregates) "for sandy soils (Bugac, Bordeaux), and between 300 and 450 J mL^{-1} for most other soils. For the clay-rich Hainich soil, the energy input had to be raised to up to 900 J mL^{-1}) . Clearly we did not destroy all aggregates with this procedure, and this was not our intent. Thus our mineral fraction may include low density material that was protected in aggregates. This is part of the general problem in such operationally defined fractionation methods, and one of the points of the paper is to explain the common observation that the heavy fraction is a mix of materials with different ^{14}C signatures.

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?

Castanha et al. (2008, reference above) demonstrated that the radiocarbon signature of the low density fraction is strongly affected by the presence of fine roots. Normally these are picked from samples as part of the sieving to <2mm; however, different people pick fine roots more or less diligently. Castanha et al. (2008) showed that picking the fine roots out of the low density fraction minimized variability among 'operators'. Also, we know (because we measured them) that the fine roots have mostly contemporary C, and wanted to know what the rest of the C in the low density fraction contained, especially as we would expect charred materials in these fire-prone regions.

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.

Figure 4 was intended to be transparent about the overlaps between isolated fractions. While we agree with the reviewer that it might be more satisfying to have all fractions isolated sequentially so that there is no such overlap, this is not what we did. One reason for this is that the density separation is expensive, and did not always yield enough clay for the mineralogy step, especially in granites, where clay content was very low. We would definitely do this differently in the future, but cannot change the past.

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

Actually carbonates are remarkably non-bonded to other mineral phases and tend to reside in soil as their own unique bodies (K fabric concepts). We do expect that acidification to pH 6 will remove the carbonates although there is the possibility that some carbonates could avoid decomposition if protected within aggregates. As pointed out in the text the carbonate in the horizons sampled was primarily in relatively large aggregates (sand and pebble size) whereas the bulk of the fine-earth fraction was non-calcareous (did not react to acid in the field). We do point out the one place where carbonates in the ClayXRD fraction could play a role – in all other samples, there was no measureable carbonate in the samples analyzed for 14C and reported in Table 4.

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.

Yes the reviewer is correct: to get at the crystalline Fe oxide phase we subtract the oxalate extracted Fe from the DCB extracted Fe. We have pointed out in the text that Fe(oxides)=Fe(d)-Fe(o) and create new columns in the appropriate Tables with output of that calculation; we have also made sure the Figures use the correct values as well (results do not change).

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

Right the DCB-extracted Al is meaningless in this context – have removed that sentence.

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

Increasing clay with depth through the solum is quite typical for soils due to hydrological transfer of colloids. Typically the downward transfer of colloids is countered by bioturbation which mixes profiles, but our observation is that more often than not soils have a subsurface accumulation of clay-size materials, often skewed to the small particle sizes.

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?

There was no evidence from the XRD data to suggest that the clay fraction harbored calcite. If the picrite soil was carbonate free or mostly so then the classification should be Typic Haplustert. This has been corrected in Table 1.

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.

The problem here is with the definition of non-clay C. We meant this to mean all C (including that oxidized by H_2O_2) that was not in the clay fraction measured for XRD. We are more careful with this definition in the revised text. The mass balance stands – the C removed included all non-clay sized material and all material removed by H_2O_2 from clay sized material.

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

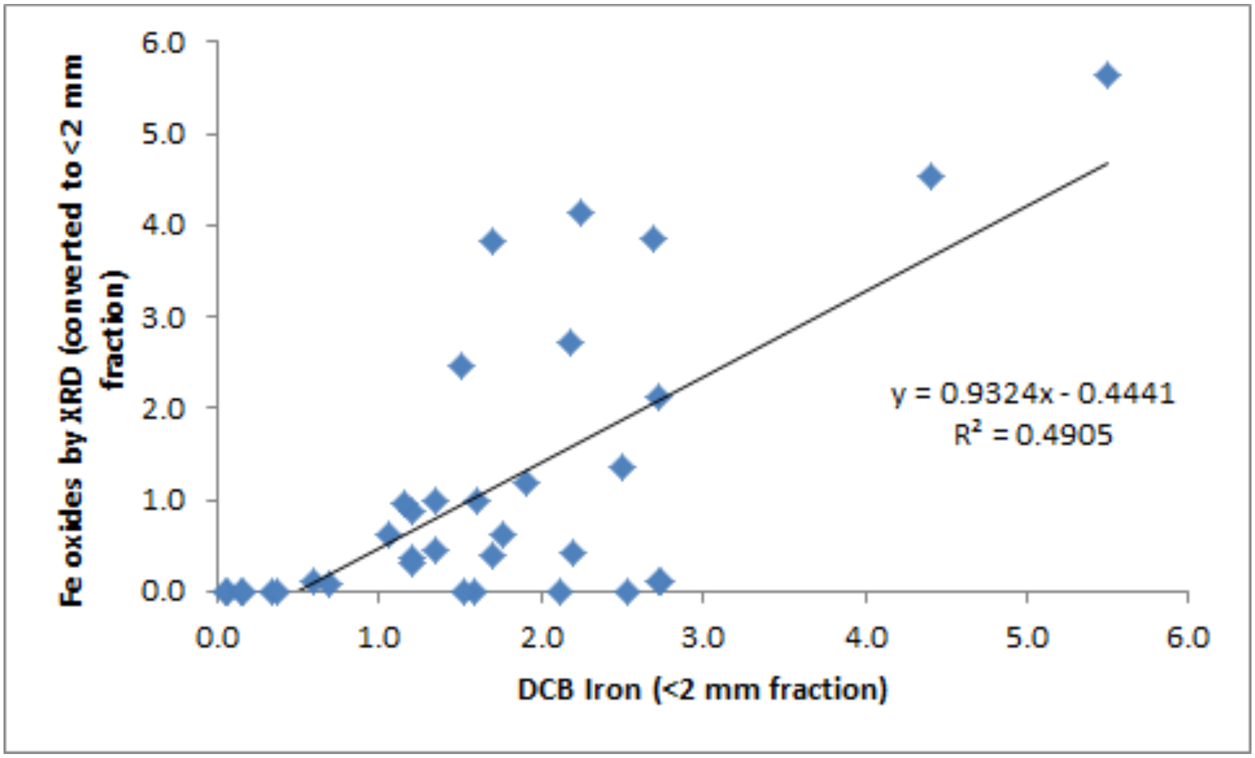
We now make clear in the text that subtracting the Feo from the Fed prior to determining the crystalline Fe oxide concentrations.

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

We agree, but also feel that we did point out in the text that we were speculating on this – effectively connecting the dots from pieces of the literature and our measurements.

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 Kα 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.

The only oxides quantified by XRD were Fe-bearing and included hematite, goethite, magnetite, maghemite and ilmenite. We agree that we create confusion when we also report data on crystalline Fe oxihydroxides based on the Fe(d) – Fe(o) for the bulk soil. In the plot below, we compare the DCB-oxalate Fe phases for the bulk soil (x- axis) to an upscaling of the Fe oxihydroxides measured with XRD corrected for the % of clay-sized material (y-axis). This plot is now given in the Supplemental Material as Figure 1. There is general correspondence, although we agree that the bulk extracts are a better measure since they also include things like coatings on sand or silt-sized materials. Also, we have far more data for the bulk extracts.



The clay minerals are important for the radiocarbon, where a small amount of old material has influence. The bulk of the C is stabilized by mechanisms that have timescales that yield similar 14C signatures. Something similar was found by Lawrence et al. (2015), so we thought it important to point this out.

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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).

We understand the problem and increased clarity throughout the text.

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.

We disagree that carbonates can be responsible for the old ages in smectite clays, expecially as no carbonates were found in the clay-sized fraction using XRD. To obtain an age of 2000 radiocarbon years, roughly 20% of the carbon in the sample would have to be radiocarbon-free. As the calcites we measured were not radiocarbon free, they would have to make up an even larger portion of the total C measured for isotopes. Of the the smectite-rich clays in Table 2, all but one had <1% Carbonate. It is highly unlikely that inclusion of carbonates can be possible for the low ^{14}C values we measured.

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.

We have revised and hopefully this is now better.

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.

The oxides presented here are for information only. We used the Fed-Feo data from the extractions to develop the Fe-oxide – carbon relationships because of concerns about loss of oxides (as coatings) during particle size separation.

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.

Please see the answer to this issue above. While we agree that there are likely mineral-bound (older) C diluting the low density C, (a) we can not absolutely rule out that the C conents of this fraction can be as low as 10%C and (b) dilution with mineral phases would contribute only a few per cent of the total C measured for isotopes, that would not have really big effects. We have not made strong interpretations of the fLF radiocarbon data in this paper, except to point out that they are different from the HF, and present them mostly for completeness.

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

We do not completely understand this comment. There is no 'enrichment factor' in the sense you would use for 13C isotopes. Radiocarbon data are all corrected for the 13C in the sample, and any such enrichment factors are corrected for. What is left is the mean age information that is given in the figure.

Anonymous Referee #2

Received and published: 15 June 2016

GENERAL COMMENTS

Summary: This manuscript investigates the controls on carbon turnover and C inven- tory across soils ranging in mineralogy in Kruger National Park, South Africa. The authors sampled soil across a variety of parent materials resulting in differing min- eralogical 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 13C and 14C 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 μm 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 have rewritten 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. However, we agree with the reviewer and have tried to remove this word throughout the text.

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 have changed this.

P1L21-24: This argument is confusing to me. The authors state that the fraction that is not clay (> 2 µm) has much shorter turnover time than the clay fraction. They then attribute the shorter TT in the > 2 µm 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 µm 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 have been 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 is fixed.

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

Removed from the 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 have rewritten the introduction

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

Agreed, we have changed 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 have tried to 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. We now have identified 3 research questions.

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; if the reviewers feels some of our tables can be moved to supplementary material, we will gladly do this.

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

We have fixed typos but prefer not to put mass of C in the text because we know there are such large issues with gravel content in many of our sites. These data are given in Supplemental Table 1 and used for profile-average calculations.

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.

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 have tried to remove extraneous references.

P9L23ff. On the issue of whether or not H2O2 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_2O_2 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_2O_2 still had organic C concentrations of 1-2%.

Discussion
P10L27: c.o.w. What are ‘C properties’?
We have changed this.

P12L6: c.o.w. ‘sorbers’ is not a word. It’s ‘sorbents’.
Agreed, and changed.

Timescales of C turnover in soils with mixed crystalline mineralogies

Lesego Khomo[1], Susan Trumbore[1,2,], Carleton R. Bern[3], Oliver A. Chadwick[4]

[1]Max Plank Institute for Biogeochemistry, Germany
[2]Department of Earth System Science, University of California, Irvine, USA
[3]U.S. Geological Survey, Denver, CO, USA
[4]Department of Geography, University of California, Santa Barbara, USA

Correspondence to: Susan Trumbore (trumbore@bgc-jena.mpg.de)

Abstract. Organic matter-mineral associations stabilize much of the carbon stored globally in soils. Metastable short-range-order (SRO) minerals such as allophane and ferrihydrite provide one mechanism for long-term stabilization of organic matter in young soil. However, in soils with few SRO minerals and a predominance of crystalline alumino-silicate or Fe (and Al) oxyhydroxides C turnover should be governed by chemisorption with those minerals. Here we evaluate the role of different minerals on the amount and mean turnover time (TT) of C estimated from radiocarbon data in ancient soils sampled in Kruger National Park, South Africa. We measured ^{14}C in bulk soil, and fractions separated by density into free particulate and mineral-associated components. In parallel, we used chemical extractions of bulk soils to quantify Fe oxyhydroxides and SRO minerals. Because of our interest in the role of silicate clay mineralogy, particularly smectite (2:1) and kaolinite (1:1), we separately quantified the mineralogy of the clay-sized fraction using XRD and measured radiocarbon on the same fraction. Density separation demonstrated that 40–70% of bulk soil C for granites, nephelinite and dry gabbro soils and >80% in other soils was associated with minerals in surface soils. The parallel separation by size demonstrated that 9-47% of the organic C in these soils was strongly associated with clay-sized minerals. Organic C from surface soils strongly associated with this clay-sized fraction had mean TT averaging 1020 ± 460 years; more than 40% of the minerals identified in the same fraction were smectite (2:1 clays). The mean TT of C in this fraction increased with the amount of smectite it contained, indicating that 2:1 clays were associated with C of greater ages than the other mineral phases present in clay-sized material. Summed over the bulk soil profile, we found that smectite content also correlated with the mean TT of bulk soil C across varied lithologies. Thus, carbon strongly associated with smectite (2:1) clays can explain much of the variation in the age of soil C.

The carbon not strongly associated with clay-sized minerals includes a combination of low density C, C associated with minerals of size between 2µm and 2cm (including Fe oxyhydroxides coatings), and C removed from clay-sized material by 2% hydrogen peroxide. Based on mass balance, the TTs estimated for organic C in this fraction averaged 190±190 years in surface horizons.

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SRO mineral content was generally very low in these soils (<0.5% by weight in all soils except those developed on gabbros under more humid climate). Soils with the most SRO had very high Fe and C contents, but surprisingly that C had short mean TT. In younger landscapes, SRO can be very stable and sorb Cover very long timescales. We hypothesize that in older landscapes SRO minerals are less stable, with that young C associated with them indicates that the minerals are short-lived. Across the varying lithologies and a precipitation gradient found in the KNP, we found Fe-oxyhydroxides (determined as the difference between Fe in dithionate citrate and oxalate extractions) to be the strongest predictor for soil C content. In contrast, mean TT of soil C was most related to the amount of smectite, whether measured in a single fraction (clay-sized material used for XRD mineralogy determination) or averaged over the whole soil profile. Combined with previous research on C turnover times in 2:1 versus 1:1 clays, our results hold promise for predicting C inventory and persistence based on intrinsic timescales of specific C-mineral interactions.

1 Introduction

The radiocarbon content of soil C provides a measure of how long C can persist in soils (Trumbore 2009). A working hypothesis is that the relative strengths of mineral-C interactions will be reflected in the radiocarbon content of the associated organic C. For example, 1:1 silicate clays with inherently low surface area, such as kaolinite, have limited sorptive capacity and retain C over relatively short timescales (Heckman et al., 2009; Sollins et al. 2009). In contrast, 2:1 clays with high charge density and high surface area, such as smectite, have higher affinity for C and thus retain it for relatively longer. In soils where the predominant minerals are smectites, organic C has older radiocarbon ages than in soils dominated by kaolinite (Wattel-Koekkoek et al., 2003; Poch et al., 2015). Soils in which much of the C is associated with high surface area short range order (SRO) minerals like Fe and Al oxyhydroxides contain organic C that has persisted for many millennia (Torn et al., 1997).

In soils of mixed mineralogy, several organic-mineral interaction mechanisms operate simultaneously, requiring multiple timescales for organic carbon persistence to explain radiocarbon measurements (e.g. Schrumpf and Kaiser 2014; Schrumpf et al. 2013; Wattel-Koekkoek and Buurman 2004).

The ability to quantitatively link specific mineral stabilization mechanisms with radiocarbon-based timescales of turnover is hampered because the operationally defined procedures used to quantify soil mineral content mostly differ from those used separate organic C into fractions that differ in radiocarbon content. Two main approaches are used to address this issue. One approach is to select samples for analysis from distinctly different global environments and use samples dominated by single mineral compositions (e.g. as described above; Wattel-Koekkoek et al. (2003)). Another approach is to sample soils along environmental gradients, and to correlate C age with the abundance of specific mineral stabilization mechanisms (e.g. Torn et al., 1997; Masiello et al., 2004; Lawrence et al. 2015), but often without full quantification of all the possible controls on C storage. Relatively few studies combine measures of the amounts and age of C in soil with quantitative measures of mineralogy. In particular, more studies

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are needed that focus on the C stabilization behaviour of mature soils where long-term depletion of primary minerals and ripening of secondary minerals provides an environment dominated by well crystallized compounds that have relatively low chemical reactivity (c.f. Wattel-Koekoek et al., 2003; Torn et al., 1997). In regions with long-term tectonic and climatic stability, such as parts of the tropics and subtropics (Paton et al., 1995), it is possible that the differences in C sorption between 2:1 and 1:1 clays could be one of the most important controls on C storage and turnover.

Here we analyse a lithosequence of arid to subhumid savanna soils developed on the Kaapval Craton and associated post-Gondwana breakup lavas in Kruger National Park (KNP) South Africa (SA). Low rates of landscape erosion and exceptionally long soil residence times (Chadwick et al., 2013) ensure that nearly all soil minerals have evolved past the metastable SRO stage and that there are few free trivalent metal ions available for direct sorption by organic ligands (Khomo et al., 2011; Khomo et al., 2013). We evaluate ^{14}C in bulk soil, and fractions separated by density into free particulate and mineral-associated components. In parallel, we used chemical extractions of bulk soils to quantify Fe oxyhydroxides and SRO minerals, and quantified allied properties such as cation exchange capacity. Because of our interest in the role of silicate clay mineralogy, particularly smectite (2:1) and kaolinite (1:1), we separated the clay-sized fraction for XRD analysis of mineralogy, and measured radiocarbon on the same fraction.

Our specific research questions reflect the inherent limitations in combining different methods to quantify minerals and organic matter: (1) how do the amount and radiocarbon content of bulk, low density (<1.7 g cm^{-3}) and dense (> 1.7 g cm^{-3}) fractions vary among soils developed on different parent materials present in the Kruger National Park?; (2) can we define relationships between minerals and the amount and mean TT (derived from ^{14}C) of carbon?; and (3) can such relationships be extrapolated from specific soil samples to entire soil profiles and across soils with contrasting mineralogy? Our overall goal is to find relationships that allow us to predict the amount and TT of carbon across broader landscapes with similar soil forming factors.

2 Materials and Methods

2.1 Field sites

To evaluate mineralogical controls on C storage and turnover we sampled soils across gradients in geology, climate and topography in Kruger National Park (KNP). Soil residence times, estimated from average regolith depth and erosion rates determined using cosmogenic isotopes, are $>10^5$ yrs (Chadwick et al., 2013), providing ample time for crystalline mineral differentiation, ripening and depletion of metastable SRO minerals. In addition to strong geological differences across KNP, variation in clay mineralogy is imposed by a regional north-south gradient in rainfall that ranges from about 470 to 740 mm annually, and locally by differentiation of clay content along hillslopes. Under this setting, we can focus on

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organic matter – mineral interactions associated with differences in silicate clays and secondary Fe and Al oxyhydroxides in an environmental regime expected to have few SRO minerals.

We sampled soils underlain by five geological units: rhyolite, granite, an olivine-rich picrite basalt (black basalt), an olivine-poor basalt (red basalt), and nephelinite (Venter et al., 2003) (Table 1, Figure 1). Each of the lithologies were sampled in the northern, arid zone, with mean annual temperature of 23 °C and ~470 mm annual precipitation. We also sampled soils developed on granite, gabbro and mixed granite/gabbro parent materials in the south of the park where rainfall ranges from ~550–740 mm per year (Table 1). Samples were collected along watershed divides, i.e. hill crests in the gently rolling landscape, although we include data for soils collected along one toposequence at 550 mm of rain to increase the amount of mineralogical differentiation that develops along granitic catenas in the KNP (Khomo et al, 2011; Khomo et al. 2013, Bern et al., 2011).

2.2 Bulk Soil Characterization

Soil profiles were sampled by horizon to bedrock where possible and described and classified using standard techniques. Soil depth ranged from 30 cm to about 2 m. Following air-drying, the samples were sieved to < 2 mm to remove rocks and roots. Air-dried samples were homogenized and sub-sampled for physical, chemical, isotopic and mineralogical analyses. Bulk density was measured as the mass of oven-dry soil in a core of known volume. The amount of clay-sized material (<2 µm size fraction) was determined by the hydrometer method (Soil Survey Staff, 2014). The concentration of exchangeable base cations was determined by atomic absorption spectroscopy after extraction with 1M ammonium acetate buffered at pH 7. Cation exchange capacity (CEC) was determined by extracting the ammonium saturated samples with a 1 M potassium chloride solution and determining ammonium by Lachat autoanalyzer. We report CEC corrected for the contribution of organic matter by assuming a contribution of 200 cmol(+) per kg organic C (as measured using an elemental analyser; Soil Survey Staff, 2014).

SRO minerals (aluminosilicate or Fe oxyhydroxides that are minimally polymerized) were extracted from bulk soils using acid ammonium oxalate (AAO) in the dark (Schwertmann, 1973). Iron (Fe(o)) and Al (Al(o)) from the extract were measured by Inductively Coupled Plasma-Optical Emission Spectrometry. We also applied a standard dithionite citrate bicarbonate (DCB) extraction and report the Fe concentration in this solution as Fe(d) (Mehra and Jackson, 1960). Total crystalline Fe oxyhydroxides are defined as Fe(d) – Fe(o). Carbon and nitrogen content were determined by combustion on a Vario Max CN elemental analyser. To determine if soils contained pedogenic soil carbonates, inorganic carbon was determined on the residue after dry combustion of bulk samples at 450 °C for 16 h (Steinbeiss et al., 2008) and organic carbon was calculated as the difference between total carbon and inorganic carbon. Carbonates were present in the red basalt and two of the dry gabbro profiles; carbonates in upper horizons were mostly present as individual particles (i.e. not coatings) presumably derived from more massive carbonates in a Bc horizon below.

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Deleted: Vegetation across the entire park is mixed grass-tree savanna. In the northern part of the park the dominant tree species across all lithologies is *Colospermum mopane*, with greater grass coverage on the more basic igneous rocks and greater amounts of woody shrub sub-dominants on the more acid igneous rocks (granite, rhyolite) (Scholes et al., 2003). The vegetation growth forms interact with patterns of fire frequency and herbivory, with greater fire frequency and heavier grazing occurring on the grass-rich soils formed on the more basic igneous rocks (Scholes et al., 2003; Scholes and Walker, 1993). Vegetation at sampling localities on granite and gabbro parent materials in the southern (wetter) parts of the park consisted of grasses mixed with *Terminalia sericea* and *Sclerocarya birrea* (Scholes et al., 2003).

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2.3 Clay-sized material for XRD analysis

To isolate and prepare clay-sized material for XRD measurement of mineralogy, we started with bulk soil material. Sand-sized material was removed first by wet-sieving, and then the clay-sized (<2 µm) fraction for XRD was extracted following dispersion with 5% sodium hexametaphosphate and 2% H_2O_2, with three rounds of sedimentation and decantation in a 1L cylinder (Soil Survey Staff, 2014). The decanted material containing clay-sized material was evaporated and freeze-dried. The 2% H_2O_2 treatment, a standard pre-treatment for isolation of clay-sized material for XRD measurement, also removed organic C, and we waited for bubble formation (presumably from oxidation of organic matter) to cease before the first decanting procedure. Organic matter oxidized by this treatment included free particulate organic C, such as small plant fragments, that would also float in a solution of 1.7 g cm^{-3} (i.e. our low density fraction in 2.4 below). However, this treatment can also remove organic C that is weakly associated to clay-sized mineral surfaces. Thus we refer to material isolated this way as the "clay-sized XRD fraction" and assume that any C still in that fraction must be strongly associated with mineral surfaces. We estimate the C and C isotope content of C removed during isolation of the clay-sized XRD fraction using mass balance.

Splits of the clay-sized material were subjected to standard clay mineral identification routines including saturation with KCl and $MgCl_2$ before qualitative and quantitative analysis by X-ray diffraction (XRD). For mineral identification, peel-mounts of oriented clay-sized material were made by transferring the sample onto microprobe glass slides from 0.42 µm cellulose nitrate membrane filters where they had been oriented by vacuum (Pollastro, 1982). For mineral quantification, the clay-size fraction was micronized in methanol with 10% corundum by sample weight, dried, passed through a 50-µm sieve and placed into side-packed powder mounts (Eberl, 2003). XRD spectra were generated with a Siemens D500 diffractometer using Cu Kα radiation fitted with a graphite monochrometer configured to 35 mA and 40 kV. Mineral quantification was done using the Rockjock software (Eberl, 2003) and results were summed by mineral group. Additional mineralogy data for the clay-sized XRD fraction from select samples come from Khomo et al. (2011). All mineralogy data are normalized to sum to 100%.

2.4 Density Separation

For depth intervals identified as A horizons, where fresh plant inputs are largest, we performed a density separation on a sub-sample of soil. We used a heavy sodium polytungstate liquid (1.7 g cm^{-3}) to separate the sample into free light fraction (fLF) and heavy fraction (HF) (Schrumpf et al. 2013, modified to a density of 1.7 g cm^{-3}). A density of 1.7 g cm^{-3} is sufficient to separate minerals from fresh particulate organic material especially in soils with minimal SRO minerals that can have low densities (Castanha et al. 2007). Between 10 and 15 g of soil was added to 100 ml sodium polytungstate solution and gently shaken on a horizontal shaker for 10 min, ultrasonicated at 60 J ml-1 for 2.5 min, then centrifuged at 3500 rpm for 30 min. Because of the low energy used, we consider this fraction to be the "free" light fraction (fLF), i.e. there may still be some additional particulate material of low density trapped in aggregates that are not dispersed. The floating fLF was concentrated on filter paper (1.6 µm glass

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microfiber discs) using a light vacuum. The sinking material was re-suspended in the heavy solution, and the steps repeated without the ultrasonic disaggregation until no more floating fLF was observed (usually three times). The fLF was rinsed with a litre of water to remove the heavy liquid, then freeze dried. Visible very fine roots were removed by hand (Castanha et al. 2007); coarser roots were removed by sieving previously, but the efficiency of these procedures varies, so we used the density separation to ensure all fine roots were removed from the sample. The remaining root-free fLF was ground to homogenize it for C isotope measurements. Somewhat lower C contents in the root-free fLF fraction in this paper (compared to other published studies that used different procedures) are likely due to removal of roots, combined with small amounts of mineral inclusion that were unavoidable as small-sized material was difficult to separate using the centrifuge (no flocculants were added).

We estimated the overall mass balance of the procedure by combining the mass and C contents of the different fractions (roots, root-free fLF and HF) with the mass and C content of the original bulk sample (Supplemental Table 1); in A horizons we lost 2-15% of the original C (Suppl. Table 2), likely through dissolution in the dense liquid (Castnha et al. 2007)

Thus, our analyses of C and radiocarbon in fractions contain overlapping information. For example, we can assume that all of the C and ^{14}C found in the clay-sized XRD fraction (Clay_{XRD}) is also found in the HF. The C removed during isolation of Clay_{XRD}, contains a mixture of C associated with minerals larger than clay-sized (e.g. a component of HF) as well as root and root-free fLF C (see also Results, Figure 4). While it would have been preferable to do a sequential extraction, the separation of sufficient clay-sized material for mineralogy and C isotope analyses from the HF fraction would have been costly and required large amounts of material (particularly for sandy soils with low clay content).

Similarly, our mineralogical information has some overlapping components. For example, in the Clay_{XRD}, we report Fe oxyhydroxides as the sum of minerals such as goethite, magnetite, maghemite and ilmenite (Supplementary Table 1). We do not normally refer to this fraction, but rather to the bulk soil measurement of Fe oxyhydroxides, which we define as the Fe compounds that are dissolved by a standard dithionite citrate extraction but not by the standard oxalate extraction (i.e. Fe(d) – Fe(o)). These compounds are assumed to be pedogenic Fe (though some amount of geogenic Fe is possibly also dissolved), and includes the Clay_{XRD} Fe oxyhydroxides as well as coatings on minerals with sizes >2µm but <2mm.

2.5 Carbon isotopes

Radiocarbon (^{14}C) was determined by accelerator mass spectrometry (AMS). For determination of ^{14}C in organic samples, an amount of material (bulk soil, HF, fLF, or clay) needed to yield ~1 mg C was weighed into a pre-combusted quartz tube with CuO wire. The tube was evacuated, sealed with a torch and placed in a 900 °C furnace for 3 hours. The resulting CO_2 was purified on a vacuum line, and an aliquot was removed for determination of $^{13}CO_2$ using a gas bench coupled to an isotope ratio mass spectrometer (Xu et al. 2007). The remaining CO_2 was reduced to graphite using a sealed tube zinc reduction method (Xu et al. 2007), and isotopic compositions were measured at the WM Keck Carbon Cycle AMS facility at the University of California, Irvine. Samples which contained inorganic carbon were acidified with 1N HCl until the solution pH was

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below 6 and then dried and analyzed as above. Carbonates were normally present as distinct sand-sized or larger grains, and were present only in the black basalt and the dry gabbro samples; we also used the ^{13}C signature of the combusted sample to indicate that carbonate did not contribute significantly to the measured sample C. For one soil, we analyzed ^{14}C in pedogenic carbonates by collecting and purifying the CO$_2$ evolved during acidification, then reducing it to graphite as for organic C samples.

Radiocarbon data are reported as Δ^{14}C, the deviation from unity, in parts per thousand, between the ratio of ^{14}C /^{12}C in the sample divided by that of preindustrial wood (the standard). The potential influence of mass-dependent fractionation of isotopes is accounted for by reporting the ^{14}C /^{12}C ratio corrected to a common δ^{13}C value (-25‰), and assuming that ^{14}C is fractionated twice as much as ^{13}C by mass-dependent processes (Stuiver and Polach 1977). Therefore, differences in Δ^{14}C between samples reflect time or mixing rather than isotope fractionation. In these units, Δ^{14}C = 0‰ is equivalent to the standard. Values >0‰ indicate the presence of ^{14}C produced by atmospheric thermonuclear weapons testing in the early 1960s. Values <0‰ indicate that radiocarbon has had time to radioactively decay (half-life = 5730 years). Long-term accuracy for samples measured at the WM Keck CCAMS facility is ±3‰ for radiocarbon expressed as Δ^{14}C and ±0.1‰ for δ^{13}C.

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We also used the radiocarbon data to estimate the mean turnover time (TT) of soil C in the profile using a one-pool model that includes incorporation of bomb-^{14}C in the last decades and assumes steady state (see Torn et al. 1997; Trumbore 2009). Specifically, we used the SoilR package (Sierra et al. 2014) to calculate the predicted radiocarbon signature for such a one pool, steady state model in the year of sampling (R code used in included in Supplemental Material). For cases where two turnover times yielded the same ^{14}C in the year of sampling (for example, where Δ^{14}C is >0‰), we report both TT for the root-free fLF, but only the longer turnover time as more consistent with the fluxes of C into and out of the mineral associated and bulk fractions (see Gaudinski et al. 2000). The one-pool model is clearly an oversimplification, but is useful for translating radiocarbon data into average timescales of stabilization. The use of a mean TT also provides a way to compare data from samples collected in different years (2004–2011; Table 1). We want to emphasize that these TT only have meaning in the context of the assumptions used to generate them: they refer to C in a single, homogeneous pool at steady state.

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We report carbon concentration and isotope data for individual horizons as well as whole-profile averages (e.g. as in Masiello et al., 2004). Mean carbon isotope ratios and mean estimated turnover times for whole profiles were calculated as averages, carbon-mass-weighted by horizon and calculated from measured bulk soil ^{13}C and ^{14}C values.

2.6 Statistics

Graphs, including regression analyses, were produced with R (R Core Team, 2015). Correlation matrices were produced using the R package Hmisc (Harrell et al. 2016). TT were calculated with the SoilR package (Sierra et al. 2014).

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3 Results

3.1 Mineralogy

With few exceptions, these ancient soils contained low amounts (<0.3%, expressed as weight percent (g Fe/100g soil) of oxalate extractable Fe and Al presumed to be derived from SRO minerals (complete data are given in Supplemental Table 1). Only nephelinite-derived 0.5-0.9%) and sub-humid gabbro soils had greater (2.9%) concentrations of oxalate extractable Al+Fe. Crystalline Fe oxyhydroxides determined as Fe(d) – Fe(o) ranged from 0% in a periodically anoxic "seep" zone in the granitic toposequence to 5.2% in the nephelinite-soil.

The clay-sized XRD fraction made up ≤15% of the <2-mm mass for soils developed at crest positions on granites and rhyolites, but up to 35 - 50% in the red and black basalt, low rainfall gabbro and nephelinite soils, and at the toeslope of the granitic toposequence (Table 2; Suppl. Table 1). With a few exceptions, the amount of clay-sized material increased with soil depth.

Within the clay-size XRD fraction, the sum of smectite, kaolinite, micas and chlorite and crystalline Fe minerals generally made up over 90% of the quantified mineralogy (Table 2). Smectite was present in all of the isolated clays except the granite crest under relatively high (740 mm) rainfall, and dominated the clay fraction in red (>90%) and black basalts (>99%; Table 2). Kaolinite was common in most soils but rare in the arid zone gabbro, and the two basalts. Crystalline Fe oxide minerals identified by X-ray diffraction made up 3-26% of the clay-sized fraction for most soils, but <1% in the smectite-dominated red and black basalts (Table 2).

Comparison of Fe oxyhydroxide abundance estimated by scaling quantitative XRD in the clay fraction to the whole soil (i.e multiplying the weight percent clay times the Fe oxide content measured by XRD) with that measured by extraction with DCB and oxalate in the bulk soil showed overall correspondence (see Supplemental Figure S1), but with much scatter. r

3.2 C in density fractions of A and B1 horizons

The root-free fLF isolated from A horizons had C concentrations of 10–37% (Table 3), with lower concentrations in the soils derived from rhyolite and the two basalts (10–16% C). As mentioned above, removal of roots and the inclusion of some clay-sized material during filtration can contribute lower values than expected if the root-free fLF is only fresh plant material. In general, carbon in the root free fLF made up only 10–20% of bulk C, even in surface soils (Suppl. Table 1). Mineral-associated heavy fraction (HF) had lower C concentrations but comprised more of the bulk soil mass, and represented 40–70% of bulk soil C for granites, nephelinite and dry gabbro soils and >80% in other soils (Table 3).

Root-free fLF δ^{13}C ranged from -24‰ to -14.5‰ (Table 3), reflecting a mixture of C3 and C4 vegetation sources. We found no relationship between root-free fLF δ^{13}C or HF δ^{13}C with rainfall, but mafic soils were consistently more enriched in δ^{13}C in both fractions compared to felsic

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soils (Figure 2a). Radiocarbon signatures of root-free fLF (that includes char as well as plant fragments) varied from values close to those measured in annual grasses in 2010 (+35‰ in Δ^{14}C) up to +145‰ (Figure 2b). For surface horizons, the one-pool model yielded two possible turnover times for most of the root-free fLF Δ^{14}C. Assuming the shorter of the two for soil A horizons (normally 0–2 cm), yielded TT's from <1 to 8 years, while assuming the longer TT yielded 45–185 years (Table 3). For the black basalt and dry gabbro soil A horizons, only longer root-free fLF TT's (125–185 yrs) were consistent with observed Δ^{14}C signatures. TT of both root-free fLF and HF increased with depth. Fine roots picked from root-free root-free fLF in the red basalt soil had radiocarbon signatures equivalent to TT <1 year regardless of depth (Suppl. Table 1), and δ^{13}C signatures of -12 to -16‰.

The δ^{13}C of HF averaged ~ 3–4 ‰ more enriched than δ^{13}C of root-free fLF from the same soil (Figure 2a). Radiocarbon signatures in mafic soil HF were generally much more depleted in ^{14}C than root-free fLF from the same horizon (Figure 2b). Felsic soils tended to have higher ^{14}C values in HF than mafic soils, though this was less the case for root-free fLF fractions.

3.3 Changes in C, ^{13}C and ^{14}C with depth

Soil depths increased with rainfall from north to south. In all soils, C and ^{14}C concentration decreased with depth. Differences in lithology and hence mineralogy were more important controls on C and C isotopes than differences in rainfall (Figure 3 and Supplemental Table 2). Notably, soils developed on nephelinite had the highest C concentrations, while felsic soils had the lowest (Figure 3). Patterns in δ^{13}C by depth followed two general patterns. Felsic, gabbro and nephelinite soils had large (2–6‰) increases in between the surface and ~10–30 cm depth then became depleted below (Figure 3). Red and black basalt soils experienced a ~2‰ enrichment in δ^{13}C with depth and then stayed constant. Radiocarbon declined with depth in all soils, but in wetter sites (>550 mm annual rainfall) shifted towards higher ^{14}C values at the very bottom of the profile (BC or C horizons; Suppl. Table 1). The ^{14}C signatures of organic C in the red and black basalt soils was lower (<0‰ at all depths, even at the surface) compared to the other soils, and were the most enriched in δ^{13}C at all depths (Figure 3).

The B horizons of the red basalt and the two dry gabbro soils contained pedogenic carbonates at concentrations of up to several percent with radiocarbon ages ranging from ~4500–25000 ^{14}C years, substantially lower in ^{14}C compared to organic C at the same depths (see Suppl. Table 1). The carbonates in B1 horizons were generally found as distinct small but visible fragments (with ^{14}C ages up to ~4500 y) and likely derived from fragmentation and upward mixing of older and more massive carbonates deeper in the soil. Carbonates do not influence radiocarbon or signatures reported for organic matter in these soils as they were removed prior to combustion; the efficiency of removal can be observed in the similarity between isotope signatures of organic C in red basalts (containing carbonate) and black basalts (that did not have carbonate).

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3.4 Carbon inventory and C strongly associated with clay-sized XRD fraction

The concentration of C strongly associated with the Clay$_{XRD}$- fraction ranged 1.0–4.7% across all soils Both the amount of C and its TT (ranging from 310-1330 years) increased with the amount of smectite measured in the same fraction (Table 4; Figure 5a). For Clay$_{XRD}$ samples where smectite made up >95% of the total mineral content, the mean TTs were in the range of 970-1250 years. C associated with Clay$_{XRD}$ samples where only ~45% of the mineral was smectites had the lowest TTs (340 years). We were unable to measure radiocarbon in samples from granites, due to the very low yield of clay-sized material in these soils.

Assuming bulk C has two components, a portion strongly associated with clay (Clay$_{XRD}$) and the rest of the soil C (“non-clay”), i.e. C that was removed with >2µm material (including coatings and organic matter associated with larger grains) or by the 2% H_2O_2 treatment (including much of the LF but also organic C weakly associated with clay sized material). We estimated the amount and radiocarbon signature of this “non-clay” component using mass balance:

$\%C_{\text{non-clay}} = (\%C_{\text{bulk}} - F_{\text{ClayXRD}} \times \%C_{\text{ClayXRD}}) / (1 - F_{\text{ClayXRD}})$ (1)

$\Delta^{14}C_{\text{non-clay}} = \Delta^{14}C_{\text{bulk}} - F_{\text{ClayXRD}} \times \Delta^{14}C_{\text{ClayXRD}})/(1 - F_{\text{ClayXRD}})$ (2)

where $F_{\text{clay-sized XRD}}$ is the fraction of bulk-C that is found in the clay-sized XRD fraction:

$F_{\text{clayXRD}} = (\%C_{\text{clayXRDy}} \times \%\text{ClayXRD})/(\%C_{\text{bulk}} \times 100\%)$ (3)

For the basalts, C in the Clay$_{XRD}$ fraction made up 40–47% of C_{bulk} in the top 2 cm, increasing to 80–86% in B horizons (see Suppl. Table 1). For all other soils, the amount of C strongly associated with Clay$_{XRD}$ accounted for <30% of bulk C. Other than the basalt-derived soils (and deeper B horizons in the gabbros; Suppl. Table 1), most bulk C was thus removed by the fractionation processes (size- and H_2O_2 treatment). As estimated from mass balance, the C removed ($\Delta^{14}C_{\text{non-clay-sized}}$) in the top 18 cm was (with one exception) dominated by C fixed in the last 50 years (Table 4). The estimated TT for non Clay$_{XRD}$ C ranged from 30-690 years, averaging 190±190 years; Table 4). The C strongly associated with Clay$_{XRD}$ (a fraction that includes not only clay minerals but up to 26% Fe oxides) for the same samples averaged 1020 ± 460 years.

As noted previously, the fractionation methods applied in this study, based on density and particle size, overlapped in what they measured (Figure 4). For example, all of the C in Clay$_{XRD}$ is a subset of HF. There is also overlap between the rfLF and the C removed when isolating Clay$_{XRD}$. The distribution of isotopes and C among the various fractions for one soil (illustrated as an example in Figure 4) demonstrate these variations and relationships, and show that the biggest differences in radiocarbon are between Clay$_{XRD}$ and rfLF fractionsE Fo.

3.5 Mineral – Carbon relationships at the profile scale

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Profile-averaged properties were calculated to emphasize the factors that controlled differences between soils at scales larger than the soil horizon to highlight variation across the landscape (Table 5). This calculation introduced errors associated with highly uncertain estimates of gravel and bulk density (see values in Suppl. Table 1), but as these errors are identical for the elements being compared (e.g. profile-averaged concentrations), the profiles being compared should share systematic biases (i.e. similar operator error). The calculation of total profile C inventories (Table 5) are included to demonstrate the importance of these factors in understanding profile-scale C storage and dynamics. For example, the nephelinite soil had the highest C concentrations (averaging 3.8 %C for the whole profile) but was estimated to have 80–90% gravel (Supplemental Table 1), so the estimated C inventory (1.1 kg C m^{-2}) is not the highest when compared to other soils (which ranged from a low of 0.6 kg C m^{-2} in the dry granite soils to 11.4 kg C m^{-2} in the black basalt soils). Thus it should be remembered that the relationships derived here are for the <2-mm component of soil.

Mass-weighted mean profile $\%C_{organic}$ correlated significantly with mineral CEC (i.e. CEC corrected for organic matter contribution), and bulk Fe oxyhydroxides determined from Fe(d)-Fe(o) (Figure 6 and Suppl. Table 2). Together, bulk Fe oxyhydroxides and non-organic CEC explained most of the variation in carbon inventory across all soils. We found a significant relationship between the amount of smectite (determined as the % of mass in the clay-sized XRD fraction times the fraction of that mass that was quantified by XRD as smectite minerals) and the mean TT (Figure 6); total clay-sized XRD fraction and the fraction of smectite each also correlated individually with the horizon averaged bulk ^{14}C, but not as well as their product (see complete correlation matrix in Supplemental material, Table 2). The only highly significant correlation for bulk profile ^{13}C was with ^{14}C (Figure 6), though less significant correlations were found between ^{13}C and average clay content, and pH and CEC (Suppl. Table 2).

4 Discussion

Geological, climatic and topographic variation in Kruger National Park give rise to soils of varying mineral compositions. Different strengths of association of organic C with these minerals lead to observed patterns in C inventory and TT across the sampled landscape. None of the soil properties we measured showed a significant relationship with mean annual precipitation (Suppl. Table 2), indicating that any influence of climate on C amount and TT was indirect, through mineralogy and possibly vegetation. This was true even for the fractions, like rfLF, that are expected to be controlled by vegetation and climate. Underlying lithology significantly influenced the amount of clay-sized material, the amount of smectite in this material, cation exchange capacity and the TT of bulk C (Suppl. Table 2).

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The mineral spectrum yielded by the broad environmental gradients sampled allowed us to determine whether there were simple, scalable relationships between measures of soil mineralogy with C amount and TT. Overall, we find that no single mechanism can explain both C inventory and TT, partly because our operationally defined fractions failed in most cases (all but the Clay$_{XRD}$ in basalts) to isolate pure mineral end members. We expected that in soils with low concentrations of SRO minerals, the ratio of smectite to kaoline would exert the strongest influence on C inventory and TT. We indeed observed that the C strongly associated with smectite minerals that made up >90% of the clay-sized minerals in basalts had TT averaging ~1000 years even in the top 2 cm, and overall the TT of C in the Clay$_{XRD}$ fraction correlated (weakly) with the amount of smectite (Figure 5a).

At the scale of the whole profile, the amount of smectite also correlated significantly with mean TT of C (Figure 5b). Hence, we conclude that the C strongly associated with smectite clay surfaces is responsible for the long TT of C in the clay-sized XRD fraction, and that the total amount amount of smectite clay in a soil profile exerts a control on the overall TT estimated from ^{14}C of bulk organic C. Soils at the toeslope of the granitic catena with HF C radiocarbon signatures +58‰ (i.e. TT of 130 yrs) still had 39–49% of their mass in the Clay$_{XRD}$ fraction. In that fraction, ~23–26% of the mass was identified as smectites and 53–57% as kaolin clay minerals; Table 2). This example demonstrates that it is not merely the amount of clay-sized material in the soil, but the amount of it that is smectite (i.e. 2:1 clay) that is key to long-term C storage in Kruger soils. These results are in accord with findings by Wattel-Koekkoek and Buurman (2004) that C stabilized on smectite in surface horizons has turnover times of 600-1400 years in soils from Africa and South America. Wattel-Koekkoek et al. (2003) also showed that the older C associated with smectite tends to be more aromatic, suggesting that 2:1 clays provide a long-term store for fire-derived C. The aging of LF C with depth in fire-prone soils was shown to be related to the presence of char in soils from other fire-adapted ecosystems (Koarashi et al. 2013; Heckmann et al. 2009); where we analysed this in the red basalt soils in this study we found increased age of LF C with depth as well (Suppl. Table 1). Though we did not measure the chemistry of root-free fLF C, the presence of charred materials provides one possible reason for its low TT, particularly in the red and black basalts where grass biomass is high and fires frequent (Govender et al. 2006).

As is clear from our results, phyllosilicates provide just one mechanism for C storage in ancient soil. Given the very strong relationship between our bulk measure of crystalline Fe oxydroxides (i.e., Fe(d)-Fe(o)) and C concentration across our soils (Figure 6), it is reasonable to propose that Fe oxyhydroxides also provide important mechanisms for storing organic C, especially in soils with low smectite content. We cannot directly measure the TT of C removed by bulk extractions, due to the fact that both DCB and oxalate contain dissolved organic C. However, we can infer from the relatively short TT of C in soils with relatively smaller amounts of smectite minerals that the TT associated with the remaining mineral (kaolinite and Fe oxyhydroxides) is of the order of hundreds of years or shorter in A horizons. We thus expect millennial C associated with smectite to remain relatively insensitive to future changes in climate and land-use, while the decadal-centennial cycling C associated with the fLF, Fe oxyhydroxides and non-smectite clays like kaolinite should respond faster.

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Deleted: clay…lso correlated significantly with mean TT of C (Figure 6…b). Hence, we conclude that C…he C strongly associated with smectite clay surfaces is strongly stabilized, and that responsible for the long TT of C in the clay-sized XRD fraction, and that the total amount amount of smectite clay in a soil profile exerts a control on the overall age…T estimated from ^{14}C of bulk organic C in soil profiles of the KNP. We did not measure radiocarbon directly in kaolin-rich clays from our sites. However, soils … Soils at the toeslope of the granitic catena with HF C radiocarbon signatures > +50‰…+58‰ (i.e. TT of 130 yrs) still had 39–49% clay (... [41]

Deleted: ancient…he older C associated with smectite tends to be more aromatic, which suggests smectites…uggesting that 2:1 clays provide a long-term store for fire-derived C. The aging of LF C with depth in fire-prone soils was shown to be related to the presence of char in soils from other fire-adapted ecosystems (Koarashi et al. 2013; Heckmann et al. 2009); where we analysed this in the red basalt soils in this study we found increased age of LF C with depth as well (Suppl. Table 1). Though we did not measure the chemistry of LF…oot-free fLF C in this study… the presence of charred materials provides one possible reason for the…ts low TT o ... [42]

Deleted: Silicate clays …s is clear from our results, phyllosilicates provide just one way to stabilize …echanism for C storage in KNP…ncient soil. For soils other than those developed on basalts and the deep horizons in gabbro, <25% of the C was stabilized by silicate clay minerals (Table 4). …iven the very strong relationship between dithionite-extractable Fe and %C…ur bulk measure of crystalline Fe oxydroxides (i.e., Fe(d)-Fe(o)) and C concentration across our soils (Figure 6), it is reasonable to propose crystalline Fe and Al (oxyhydr)oxides as dominating other, non-clay mineral stabilization…hat Fe oxyhydroxides also provide important ... [43]

At the pedon scale, clay content was not the best predictor of the amount (r^2 =0.50, p=0.02) or TT (r^2 =0.59, p=0.03) of soil C, though this relationship improved when only smectite clay was considered (Figure 6; r^2 =0.75, p=0.001). Given the long TT associated with C stabilized by smectite, we conclude that even small addition of millennially-aged C strongly associated with smectite contributes substantially to the mean TT estimated from the bulk soil C. For example, mixing 75% C with a TT of 25 years with 25% C with a TT of 1200 years yields a bulk TT of ~320 years. Increasing the millenial pool to 35% changes the mean age of bulk C to ~450 years. The same is not true for C stocks, however, which are not significantly correlated with either clay (r^2 =0.50, p=0.08) or smectite clay (r^2 =0.45, p=0.12).

Somewhat unexpectedly, the subhumid gabbro and arid nephelinite soils with the highest concentration of SRO minerals (as determined from the Fe(o) and Al(o) extract concentrations), had younger C than would be predicted based on expected relationships between SRO minerals and C age found in other soils (c.f. Torn et al., 1997; Kramer et al., 2012). SRO minerals are particularly strong sorbers of C because their hydrated nano-crystals create intimate mixtures of mineral and organic material that - in the absence of drying and rewetting or redox pulses - tend to remain very stable (Chorover et al., 2004; Thompson et al., 2006b: Buettner et al., 2014). However, when SRO minerals are subjected to drying and rewetting or oxidation-reduction pulses, they reorganize into larger, more well-ordered crystalline compounds by ejecting C and water from the interior of their lattice structure (Ziegler et al., 2003; Thompson et al., 2006a). The wet gabbro and nephelinite soils had younger C, and only 9-17% of the C was associated with the clay-sized XRD fraction, even though they have >5% SRO mineral concentrations. The young C suggests that the SRO mineral phase is likely a relatively transitory phase that forms as primary minerals in the gravel and cobble fraction of the soil weather and ripen to kaolinite rapidly, with any C that was sorbed into the SRO mineral phase made available for microbial decomposition. In the same way, redox oscillations under seasonal wet-dry cycles promote crystallinity of Fe and we suggest that the Fe-bearing SRO minerals in these environments are likely short-lived giving way to crystalline Fe forms where C is sorbed to surfaces rather than within the less accessible lattice (Ziegler et al., 2003; Chorover et al., 2004). Thus, although the availability of a large surface area may promote stabilization of large amounts of C in these soils (e.g. nephelinite in Figure 3), the relatively rapid TT of that C may be a reflection of the short residence time of the minerals themselves and the short TT of C sorbed onto 1:1 clays and crystalline Fe oxyhydroxides. Studies of mineral-C interactions must consider not only the strength of C association with various mineral phases (e.g. strong for SRO and smectite, weak for kaolinite and oxyhydroxides)s, but also the timescale of mineral stability in the soil profile and pedogenic setting. Where SRO minerals and oxyhydroxides are stable, the associated C tends to be old, but in climates such as in Kruger the combination of a relatively short but strong rainy season and a long intervening dry season can lead to relatively rapid mineral transformation and hence rapid C turnover.

Factors that vary with soil depth exert controls on both C inventory and TT in KNP soils, as has been reported in many other areas. These affect the ^{14}C in all measured fractions. However, the rates at which age increased with depth differed between soils and C fractions. For soils with the largest amount of smectite clays (e.g. basalts), offsets in the TT for clay-sized XRD and the "non-clay-size" fractions were largest at the surface

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and smallest at depth. In contrast, in soils with little smectite clay, the offset between fractions was relatively uniform with depth. More work is required to understand the stability of the different mineral phases themselves, especially organic C associated with Fe (and Al) oxyhydroxides phases, and how they interact with transport mechanisms in soil (e.g. Schrumpf et al. 2013; Schrumpf and Kaiser, 2015).

There appears to be a mineral/lithologic control on ^{13}C variation in KNP soils. This control can operate in at least two ways. First, the root-free fLF δ^{13}C seem to indicate greater C3-derived vegetation inputs to soils with more felsic parent materials, and a predominance of C4 inputs in more mafic soils (Figure 2a). This is consistent with the vegetation patterns on the ground (Scholes et al. 2003), with C4 grasses dominating the basalt soil landscapes. These patterns are largely preserved in the mineral-associated C (Fig. 2a), although HF δ^{13}C is consistently enriched compared to the LF δ^{13}C. At the profile scale, the strongest predictor of δ^{13}C is Δ^{14}C (or TT; Fig. 6; r^2 =0.75, p=0.005), followed by pH (^{r2} =0.65, p=0.016) and clay content (r^2 =0.65, p=0.017). For the isolated clay fraction, the relationship between δ^{13}C and smectite was weak. Soils with the greatest amount of smectite are also those with the greatest C4 vegetation, so it is unclear whether lithologic control on C3 versus C4 plants, or fractionation associated with different mineral stabilization mechanisms, is responsible for the overall trends observed in δ^{13}C. Nonetheless, interpretations of paleo-vegetation from bulk soils must be undertaken with care, as variations in the mechanism of C stabilization across the landscape may affect the δ^{13}C signature as well as vegetation changes. More work is needed to disentangle these relationships at broader spatial scales encompassing climate and topographic gradients that will also involve changes in mineralogy.

Large parts of the land surface contain old soils with low concentrations of SRO minerals (Paton et al. 1995). We found good agreement in the age of C in the most smectite-rich (basalt soils) clay-sized XRD fraction, and those reported by Wattel-Koekek et al. (2003) from soils collected earlier at other sites in Africa and South America. Smectite clay content may thus provide a useful indicator for the fraction of C stabilized on millennial timescales over large areas. While quantitative clay mineralogy is not an easy measurement, the amount of smectite in our soils was broadly predictable from lithology and from more easily measured soil properties such as CEC (corrected for organic contributions), or pH (when below CaCO$_3$ saturation). Thus, across a range of landscapes and parent materials, one could predict how much of the C in soils is cycling on faster and slower timescales based on these parameters, while overall C inventory is more related to crystalline Fe and Al oxyhydroxides.

5 Conclusions

Differences in C cycling among soils differing in lithology, topography and rainfall are largely explained by varying mineralogy. Where SRO mineral concentration is low, the age of C in the clay-sized fraction depends on the concentration of smectite. However, this is only the case in basalts, for soils other than basalts, C TT averaged hundreds of years and is therefore weakly associated with the clay-sized fraction.

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Our data indicate that heavy fraction C in old soils consists of two major components: a relatively ‘passive’ pool that stabilizes C for millennia that we suggest is strongly bound to smectite , and a more dynamic pool stabilized for decadal to centennial timescales that includes C bound to kaolinite and/or associated with crystalline Fe and Al (oxy)hydroxides. Most C in surface horizons, even in basalt soils where clays are >95% smectite, is in this faster-cycling pool. A small but highly dynamic light fraction pool also occurs across all soils. Increases in age of C with depth in soil profiles may indicate rates of vertical mixing or the time required for repeated sorption/release of C as it moves downwards, or it may reflect changes in the stability of the minerals themselves as a function of soil depth. While more research will be needed to understand these issues, our results hold great promise for predicting C inventory and TT based on intrinsic timescales of C stabilization mechanisms.

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Table 1. Profile names used in the text, parent material lithology, mean annual precipitation (MAP), year of collection (Year), locations and classification of the soil profiles used for this study.

Profile name	Lithology	MAP (mm)	Slope Position	Year	Latitude (easting)	Longitude (northing)	Classification
GR-450-C	Granite	450	Crest	2004	322713	7452153	Haplocambid
GA-450-C	Gabbro	450	Crest	2010	321956	7449291	Calciustoll
RH-450-C	Rhyolite	450	Crest	2010	351375	7421676	Haplocambid
NE-450-C	Nephelinite	450	Crest	2010	336567	7398988	Ustorthent
BB-450-C	Black basalt)	450	Crest	2009	341888	7420588	Haplustert
RB-450-C	Red basalt)	450	Crest	2009	344120	7421754	Duritorrand
GR-550-C	Granite	550	Crest	2006	348678	7231971	Ustorthent
GR-550-S	Granite	550	Seepline	2006	348755	7231990	Dystrustept
GR-550-T	Granite	550	Footslope	2006	348831	7231986	Natrusalf
MG-550-C	Mixed granite	550	Crest	2010	341298	7232342	Ustorthent
MG-550-C2	Mixed granite	550	Crest	2010	341298	7232342	Ustorthent
GA-550-C	Gabbro	550	Crest	2005	333525	7230774	--
GA-740-C1	Gabbro	740	Crest	2010	329124	7218015	Haplotorrert
GA-740-C2	Gabbro	740	Crest	2010	329124	7218015	Haplotorrert
GR-740-C	Granite	740	Crest	2004	0326823	7211630	Dystrustept

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Table 2. Mineralogy determined on clay-sized XRD fraction for selected soils (mostly mafic soils that had higher clay contents). Abbreviations: Q= Quartz, F= Feldspars, C= Calcite, O= Oxides, K= Kaolins, S=Smectites, Ch= Chlorites, M= Micas. Complete data can be found in Supplemental Table 1.

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Identifier	Hor	Clay	Q	F	C	O	K	S	Ch	M
			--------------------% of clay-sized fraction ---------------------- -							
		(%)								
NE-450-C	A	30	1	1	0	15	24	47	0	12
NE-450-C	Bw1	40	1	1	0	14	26	48	0	9
BB-450-C	A1	39	1	0	0	0	6	92	0	0
BB-450-C	Bw1	43	2	0	0	0	5	93	0	0
RB-450-C	A1	36	1	0	0	0	0	99	0	0
RB-450-C	Bk2	46	2	0	0	0	0	98	0	0
GA-450-C*	A	15	2	2	0	7	0	67	0	22
GA-450-C*	Bw1	25	1	9	6	10	0	43	3	28
GA-740-C1	A	20	0	1	0	14	10	60	6	9
GA-740-C2	Bw1	25	0	1	0	8	16	68	6	1
GA-740-C3	Bw2	10	0	0	0	14	3	77	3	3
GR-550-C†	A	14	0	0	0	0	79	0	21	0
GR-550-C†	Bw2	17	0	0	0	0	79	1	21	0

GR-550-S†	A	6	0	0	0	0	76	17	7	0
GR-550-S†	Bw2	7	0	0	0	0	65	25	11	0
GR-550-T†	A	25	0	0	0	0	57	26	17	0
GR-550-T†	2Btn2	47	0	0	0	0	53	23	15	10

† Data are from Khomo et al. (2011).

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Table 3. Carbon and carbon isotope signatures of heavy (HF, >1.7 g/cc) and root-free free light fraction (root-free fLF) carbon. Turnover times (TT) were estimated using the steady state, one pool model described in the text. When two TT were possible, we show both options for the root-freef LF fraction, but only the longer one for the HD fraction.

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			Root-free fLF (free light fraction)				HF (Heavy fraction)			
Identifier	Depth (cm)	Total C in HF	C_{org} %	$\delta^{13}C$ ‰	$\Delta^{14}C$ ‰	TT yr	C_{org} %	$\delta^{13}C$ ‰	$\Delta^{14}C$ ‰	TT yr
GR-450-C	0-23	0.59	37.0	-23.7	99.3	5, 75	0.5	-19.5	30.1	195
	23-45	1.06*	24.6	-18.9	125.6	8, 50	0.4	-17.5	-35.9	510
GA-450-C1	0-2	na	34.2	-16.8	44.1	155	na	-13.6	6.2	275
	2-12	na	42.3	-15.0	34.4	180	na	-14.5	20.9	225
RH-450-C	0-3	0.81	16.6	-23.2	98.4	8, 75	0.7	-18.2	72.9	55
	3-15	0.83	1.9	-20.0	76.7	5, 100	0.5	-16.2	40.9	165
NE-450-C	0-2	0.65	31.3	-20.6	88.3	8, 85	4.2	-16.7	74.4	105
	2-18	0.76	30.8	-19.5	64.4	4, 120	2.4	-14.9	1.8	300
RB-450-C	0-4	0.82	11.6	-16.6	60.0	3, 125	1.8	-14.8	-23.1	425
	4-15	0.69	10.0	-16.6	30.0	195	1.4	-13.3	-95.2	985
	15-30	0.92	10.0	na	na	na	1.4	-13.3	-152	1560
	30-49	0.84	11.2	na	-53.0	330	1.3	-13.3	-216	2300
BB-450-C	0-3	n.d	10.0	-15.4	33.5	185	1.5	-13.7	-25.4	440
	3-11	0.78	7.5	-16.6	33.5	185	1.6	-12.9	-65.6	735
GR-550-C	0-15	0.70	16.0	-22.2	57.7	1, 130	0.5	-18.1	50.3	145
	15-41	na	14.5	-21.9	82.3	2, 95	0.4	-17.1	59.0	130
GR-550-S	0-2	0.72	22.5	-20.8	62.4	1, 120	0.5	-18.8	62.9	120
	2-10	1.1*	21.3	-20.2	82.1	4, 95	0.4	-19.1	96.1	80
GR-550-T	0-8	0.91	21.2	-18.0	54.7	1, 135	0.8	-16.7	58.0	130

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	8-15	0.69	15.2	-19.9	74.4	105	0.5	-17.4	79.0	100
MG-550- C	0-3	0.84	36.9	-22.3	71.7	5, 125	0.9	-16.6	60.2	125
	3-10	0.92	15.5	-20.6	80.5	6, 110	0.7	-15.3	54.1	135
GA-550-C	0-9	na	29.9	-28.2	98.3	5, 85	2.8	-14.4	45.8	140
	9-24	na	15.2	-13.2	88	4, 100	2.3	Na	38.4	175
GA-740-C1	0-3	0.70	34.7	-16.9	72.6	1, 100	1.6	-13.4	78.2	100
	3-9	0.73	23.2	-14.8	40.5	165	1.5	-11.8	6.1	275
GA-740-C2	0-4	0.85	35.7	-16.1	67.6	4, 135	1.5	-13.1	85.2	90
	4-24	0.76	35.3	-16.9	64.4	4, 140	1.8	-12.8	60.6	125
GR-740-C	0-8	0.41	32.7	-21.3	145.8	10, 45	1.0	-16.8	143.9	45
	8-17	0.66	18.6	-17.8	95.0	4, 80	0.3	-15.1	109.4	70

* Values >1 indicate the magnitude of errors associated with density separations.

Table 4. Measurements of C and isotopes in the bulk soil and clay-sized XRD fraction, the same fraction analyzed for quantitative mineralogy (Table 2). The fraction of bulk C in the clay-sized XRD fraction ($F_{clayXRD}$) and the characteristics of the C making up the rest of the bulk C are calculated using equations 1-3, given in the text. Bottom depths >10 cm indicate B1 horizons; we excluded data from sampled depths >20 cm. We cannot rule out the potential for carbonates making up a small fraction of the $Clay_{XRD}$ fraction for the dry gabbro (GA-450-C1) Bw horizon sample as these were not acidified prior to combustion and carbonates were found using XRD in this soil. All other $Clay_{XRD}$ samples did not contain measurable carbonates (Table 2).

	Bot.	Clay-sized (< 2-μm) XRD fraction				Bulk Soil					Remaining C ("non-clay")			
Identifier	Depth (cm)	C_{org} (%)	$\delta^{13}C$ ‰	$\Delta^{14}C$ ‰	TT (yr)	Corg (%)	$\delta^{13}C$ ‰	$\Delta^{14}C$ ‰	TT (yr)	$F_{clayXRD}$	C_{org} (%)	$\delta^{13}C$ ‰	$\Delta^{14}C$ ‰	TT (yr
NE-450-C	2	2.52	-16.9	-1.5	310	6.04	-17.8	65.0	110	0.13	6.5	-17.9	69	11
NE-450-C	18	1.14	-16.8	-129.5	1330	3.04	-15.4	8.0	270	0.15	3.4	-15.3	16	24

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GA-450-C1	2	4.69	-14.8	-64.6	730	3.28	-14.9	20.1	225	0.22	2.9	-14.9	58	130
GA-450-C1	12	2.35	-13.9	-145.0	1485	1.90	-13.9	-28.8	465	0.31	1.7	-13.9	43	160
RB-450-C	4	2.50	-14.1	-125.3	1275	1.94	-14.9	-16.0	385	0.47	1.5	-16.0	149	30
BB-450-C	3	2.48	-14.3	-91.7	955	2.41	-13.7	-25.4	440	0.40	2.4	-13.4	22	220
GA-450-C2	2	1.29	-16.3	-4.4	320	1.62	-16.6	22.0	220	0.12	1.7	-16.6	25	210
GA-740-C1	4	0.96	-17.6	-91.7	955	2.18	-11.8	-62.1	690	0.09	2.3	-11.6	-61	690
GA-740-C2	9	1.17	-19.1	-160.0	1650	1.76	-13.6	88.1	85	0.14	1.9	-12.9	122	55
GA-740-C2	24	1.10	-17.7	-116.1	1180	2.24	-13.4	70.0	110	0.10	2.4	-13.0	83	90

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Table 5. Profile-averaged (excluding BC /C horizons) properties for the soils sampled in this study. Averages for C and C isotopes are calculated from bulk values. C inventory (Cinv) is the sum for the profile in kgC m^{-2}. All averages are mass-weighted, except C isotopes, which are weighted by the mass pf C in each horizon. Smectite content (Smec.) is estimated from multiplying the fraction of total mass in the clay-sized XRD times the %Clay (denoted in the table as Clay and expressed as per cent of total mass) by the percent of the clay-sized XRD identified as Smectite (Smec.; Table 2). Profile averaged values for ditionite citrate extracted iron (Fe(d)) and oxalate extractable iron Fe(o) and Aluminumn (Al(o)), as well as their difference, a measure of Fe oxyhydroxides in bulk soil, are all expressed as weight% as in mass Fe per 100 gram soil.

Identifier	Depth (cm)	Cinv	pH	CEC*	Clay (%)	Smec.	Fe_d	Fe_o	Fe_d - Fe_o	Al_o	C_{org} (%)	C/N	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	TT (yr)
RH-450-C	30	1.3	6.8	5.5	1.0	10	2.7	0.1	2.6	0.1	0.66	9.9	-16.2	28.0	230
GR-450-C	23	0.6	6.1	7.7	6.3	46	0.6	0.0	0.6	0.0	0.78	11.9	-20.2	30.4	200
NE-450-C	18	1.1	6.8	61.8	38.7	48	5.4	0.3	4.9	0.2	3.85	11.8	-15.9	9.9	235
BB-450-C	49	11.4	7.7	44.3	42.0	98	1.7	0.2	1.5	0.2	1.56	14.2	-13.5	-140.4	1500
GA-450-C	34	8.6	8.3	25.7	9.9	50	1.9	0.2	1.7	0.2	1.66	na	-15.0	-37.0	550
RB-450-C	70	8.6	7.0	50.1	46.2	93	2.5	0.1	2.4	0.1	1.53	14.8	-12.3	-156.4	1720
GR-550-C	62	3.5	5.4	3.2	14.8	1	0.4	0.1	0.3	na	0.32	21.2	-15.3	12.2	430
GR-550-S	41	1.8	5.1	2.6	7.5	21	0.1	0.0	0.1	na	0.23	19.6	-18.6	51.8	150
GR-550-T	46	3.6	7.0	29.9	42.7	24	0.2	0.1	0.1	na	0.50	14.1	-14.7	24.8	225
MG-550-C	38	2.6	6.9	7.8	15.0	41	1.4	0.3	1.1	0.2	0.82	14.2	-13.8	-68.6	755
GA-740-C1	44	7.0	7.2	37.7	17.7	69	2.6	1.1	1.5	0.4	1.53	12.2	-13.9	-47.5	250
GA-740-C2	25	4.5	7.3	31.5	25.8	25	2.5	2.0	0.5	0.3	1.49	11.9	-13.3	26.9	150
GR-740-C	93	5.1	5.7	7.0	3.7	**10**	0.4	0.0	0.4	0.0	0.36	14.8	-18.5	88.8	240

Depth indicates the depth to which the in the profile averages were calculated (we excluded BC and C horizons).

Values in bold for smectite content (Smec.) were not measured but are assumed based on similar lithology values. We assumed average values for the horizons above and/or below to fill in data for smectite content for depths in a profile where no measurements were available (see Supplemental information).

Subscripts d and o represent dithionite and oxalate extracts for Fe and Al.

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Figure 1. Locations and lithology of parent materials where soils were sampled for this study. Rainfall decreases from ~740mm/a in the southern end of the park to ~450 mm/a in the northern end of the park.

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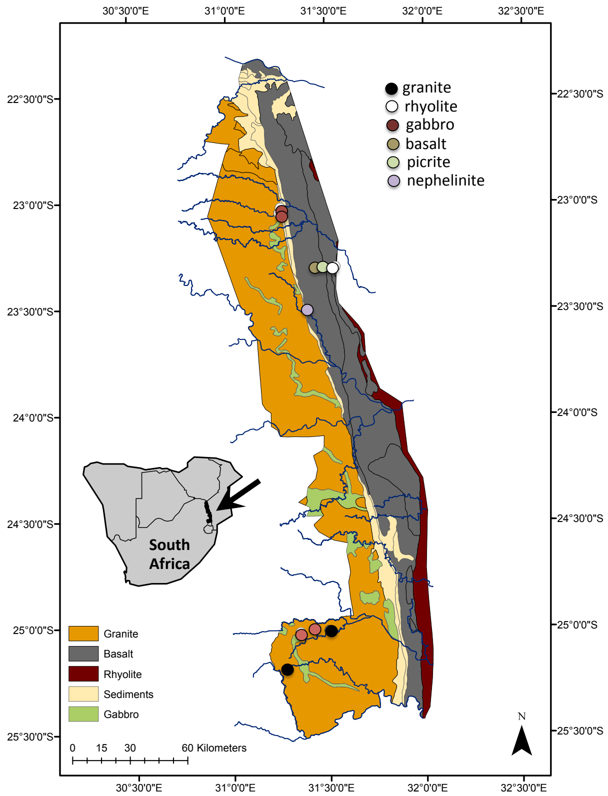

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Figure 2. Comparison of ^{13}C (2A) and ^{14}C (2B) in root-free free light fraction (root free-fLF) and heavy fraction (HF) organic C for individual samples from A horizons (see Table 3). Felsic lithologies (open circles) include soils developed on granite and rhyolite, mafic lithologies (filled circles) include soils developed on gabbros and basalts, and nephelinite. The 1:1 correlation line is plotted for reference.

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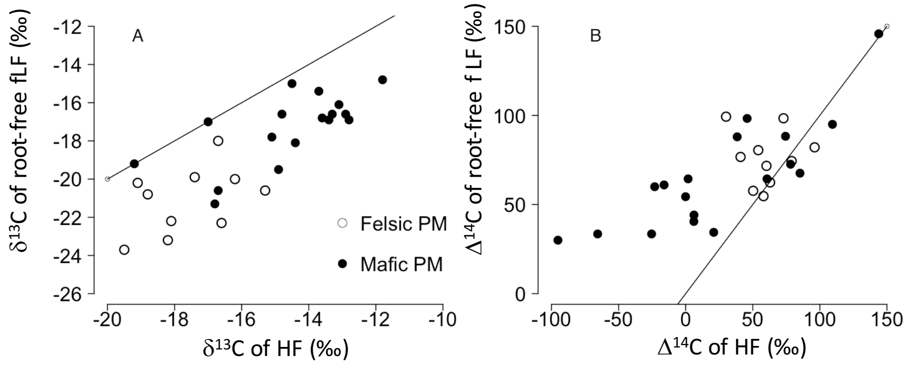

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Figure 3. Depth profiles of bulk C (top-left), and the δ^{13}C (top-middle), and Δ^{14}C (top-right) measured in bulk C for soil profiles developed on selected lithologies. Also shown in the lowr panel are other soil bulk properties, total Fe oxyghroxides (Fe(d)- Fe(o)) (bottom-left), total nitrogen (bottom middle) and cation exchange capacity (CEC) corrected for organic matter contributions (see text; bottom right).

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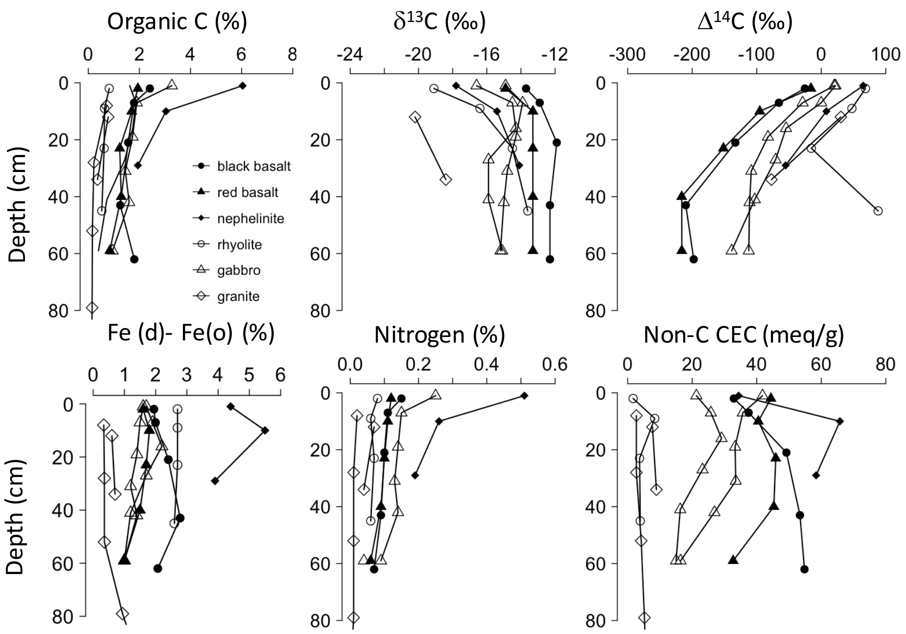

Figure 4. Comparison of C and C isotopes for a single soil sample (0-3 cm depth in GA-740-C (gabbro parent material) indicating the inter-relationships among the different process-defined organic C fractions. For each fraction we indicate the percent of total C (C_T) it contains; fractions for root-free fLF and HF do not add to 100% because of contributions from roots picked from the free ligh fraction (fLF) and C that dissolves in the polytungstate solution and is not recovered. Colors indicate overlaps between C among different fractions exist. For example, C strongly associated with the clay-sized fraction measured with XRD ($Clay_{XRD}$; orange) makes up part of the HF-C. Free low density C (fLF; light green, including both roots picked from the fLF and the root-free fLF fractions) makes up part of the non-clay-sized fraction. Most of the fLF is likely removed from the $Clay_{XRD}$ when it is treated with 2% H_2O_2.

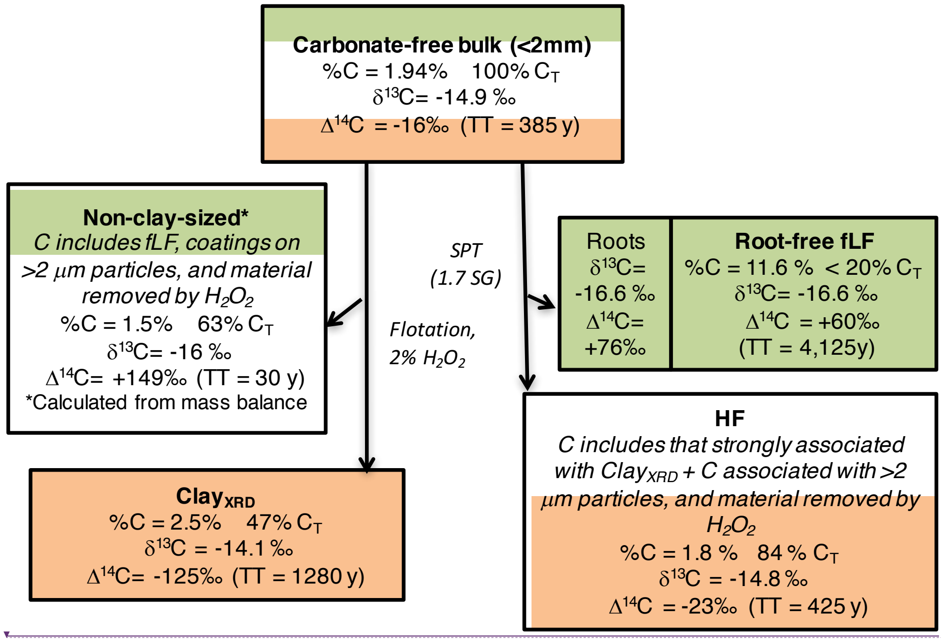

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Figure (left). Mean Turnover Time (TT) of C in the clay-sized XRD fraction increases with smectite concentration, the linear relationship for A horizon points (n=7) has R-squared =0.48 and p=0.08. (Right) Mean TT of bulk C averaged for each profile compared to the fraction of the total C that is found in the clay-sized fraction ($F_{clayXRD}$). The mean TT of bulk organic C correlates significantly with the fraction of organic matter strongly associated with the clay-sized XRD fraction. Here the linear relationship R-squared = 0.54 and p=0.004

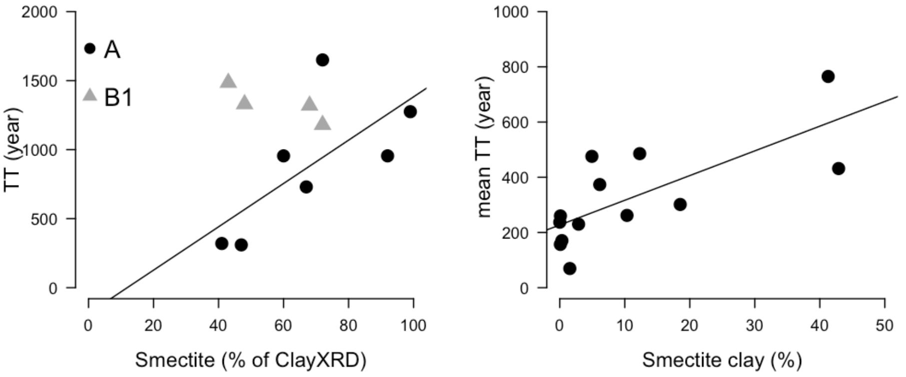

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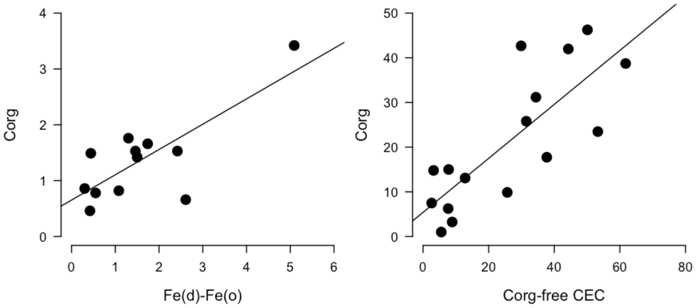
Figure 6. Across all the studied soils, the mean %C in the soil profile was best predicted by Fe(d)-Fe(o) (left; R-squared = 0.60, p=0.003), and cation exchange capacity (right; R-squared = 0.63, p=0.0003). The best predictors for profile-averaged C turnover times was the amount of smectite clay (Figure 5 (right)). Correlation matrices for other variables in Table 5 are given as Supplemental Table 2.



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carbon in a field setting designed to minimize the role of SRO by taking advantage of multiple lithologies

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material had average TT of 1020 ± 460 years in surface soils. The mean TT of this clay-associated C increased with depth and with fraction of clay

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was smectite. Because the C associated with smectite clay was so old, the amount of smectite (2:1 clays) controlled the age of

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Kruger landscapes. The TT of the majority of soil C –not stabilized by clays - was much shorter, 190±190 years in surface horizons. We suggest that this faster component reflects timescales of weaker C stabilization by crystalline Fe and Al oxyhydr)oxides and kaolinite (1:1) clays, as well as LF fractions not associated with minerals. Thus, bulk or HF carbon integrates C stabilized by mechanisms with inherently different TT, something that is often inferred from radiocarbon measurements. While SRO mineral concentrations were very low in these soils, the soils with most SRO had very high C content but also very young C. In other environments, SRO can be very stable and sorb C on very long timescales. We hypothesize that the seasonal wetting and drying in the KNP may reduce the age of SRO minerals as well as the C

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them. Across the varying lithologies and a precipitation gradient found in the KNP, we found mineralogy to be the most important explanatory factor for C content (related to crystalline Fe) and turnover time (related to the amount of smectite).

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range of interactions with inorganic compounds, but in the complex soil medium our understanding of the contributions of each mechanism is limited (von Lützow et al., 2007). For example, organic ligands can bond with trivalent metal ions such as iron (Fe) and aluminum (Al) or by dehydration bonding with metallic nano-(oxyhydr)oxides (Parfitt and Childs, 1988; Kaiser and Zech, 1996; Chorover et al., 2004). At high clay concentrations and soil surface area, organic ligands can be sorbed into the matrix of short-range-order (SRO) nanocrystalline aluminosilicates or metallic (oxyhydr)oxides (Torn et al., 1997; Kaiser and Guggenberger, 2003; Chorover et al., 2004; Kramer et al., 2012) or onto crystalline silicate clay minerals (Kaiser and Guggenberger, 2000; Sollins et al., 2009). However

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In addition, crystalline pedogenic Fe and Al sesquioxides are associated with C that has ages ranging from hundreds to thousands of years (Masiello et al., 2004).

Soil C can be operationally separated into a light fraction not

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(low density fraction; LF) and a heavy fraction associated with minerals (high density fraction; HF). Decomposition of the light fraction may be governed by interactions among decomposers and C substrate quality, as well as by occlusion within mineral aggregates. Stabilization mechanisms in HF can operate on a range of timescales (e.g.

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Schrumpf and Kaiser 2014; Schrumpf et al. 2013; Wattel-Koekkoek and Buurman 2004).

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Given the different strengths of mineral-C interactions, there is a need to measure carbon storage and age of C within the dense fraction of mixed mineralogy soils where the quantity of C-sorbing compounds including clay minerals has also been measured. With this information, we can attempt to predict C storage and timescales of stabilization from known amounts of mineral constituents (e.g. 2:1 versus 1:1 clays) or from readily available proxy measurements such as surface area or cation exchange capacity (Lawrence et al., 2015

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One approach to evaluate mineral controls on C storage and turnover is to select samples for analysis from distinctly different global environments to cover a suite of mineral compositions. For example, Wattel-Koekkoek et al. (2003) used this approach to document that larger quantities of crystalline 2:1 clays were associated with greater (and older) C storage, while 1:1 clays were not. Another approach is to sample soils along gradients of state factors to isolate specific soil property gradients and evaluate correlations among varying soil properties and C properties. The latter approach has proved useful (e.g. Trumbore et al., 1996; Torn et al., 1997; Masiello et al., 2004) but often without full quantification of all the possible controls on C storage. By contrast Lawrence et al. (2015) quantified virtually all reactive components along a humid, forested chronosequence formed on alluvium from andesitic volcanics and evaluated their correlations with C storage and turnover. They found a complex suite of controls for C storage and age related to depth-dependant C inputs and depth-dependant inorganic chemical properties. In surface horizons, they found increases in C storage but not its stability with increasing amounts of pyrophosphate extractable Fe and Al. In subsurface horizons they found increased C stability, but not increased storage, with increases in surface area and halloysite clay concentrations. In contrast with other studies cited above, they found little correlation between C storage or stability and the amount of smectite clays or SRO minerals. Although it would be ideal to be able to make predictions about C storage and stability based on chemical and mineralogical properties, this (Lawrence et al. 2015) and other studies (e.g. Masiello et al., 2004; Wattel-Koekoek et al., 2003; Wattel-Koekoek et al., 2004) indicate that there may be significant C-storage trade-offs occurring within soils of differing mineral compositions. Therefore we need more case studies that cover a broad range of environmental, ecological and soil chemical conditions. Our long-term goal is to refine understanding of the sensitivity of mineral-associated organic matter to climate and land-use change.

Few studies have focused

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the bulk soil. Experience has shown the greatest contribution from LF to bulk soil C in A horizons; in deeper horizons, we did not perform density separations and instead assumed that the bulk fraction approximates HF for properties such as C and C isotope concentrations.

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-associated and non-clay associated, we

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- $F_{clay} \times \%C_{clay}$

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While depth-related increases in C TT may be partly controlled by changes in the age of C associated with the millenial C fraction and with changes in the relative amount of C stabilized on smectite versus sesquioxides, much more

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Kaiser, K. and Guggenberger, G.: Mineral surfaces and soil organic matter. European Journal of Soil Science 54, 219-236, 2003.

Kaiser, K. and Zech, W.:Defects in the estimation of aluminum in humus complexes of podzolic soils by pyrophosphate extraction, Soil Sci. 161, 452-458, 1996.

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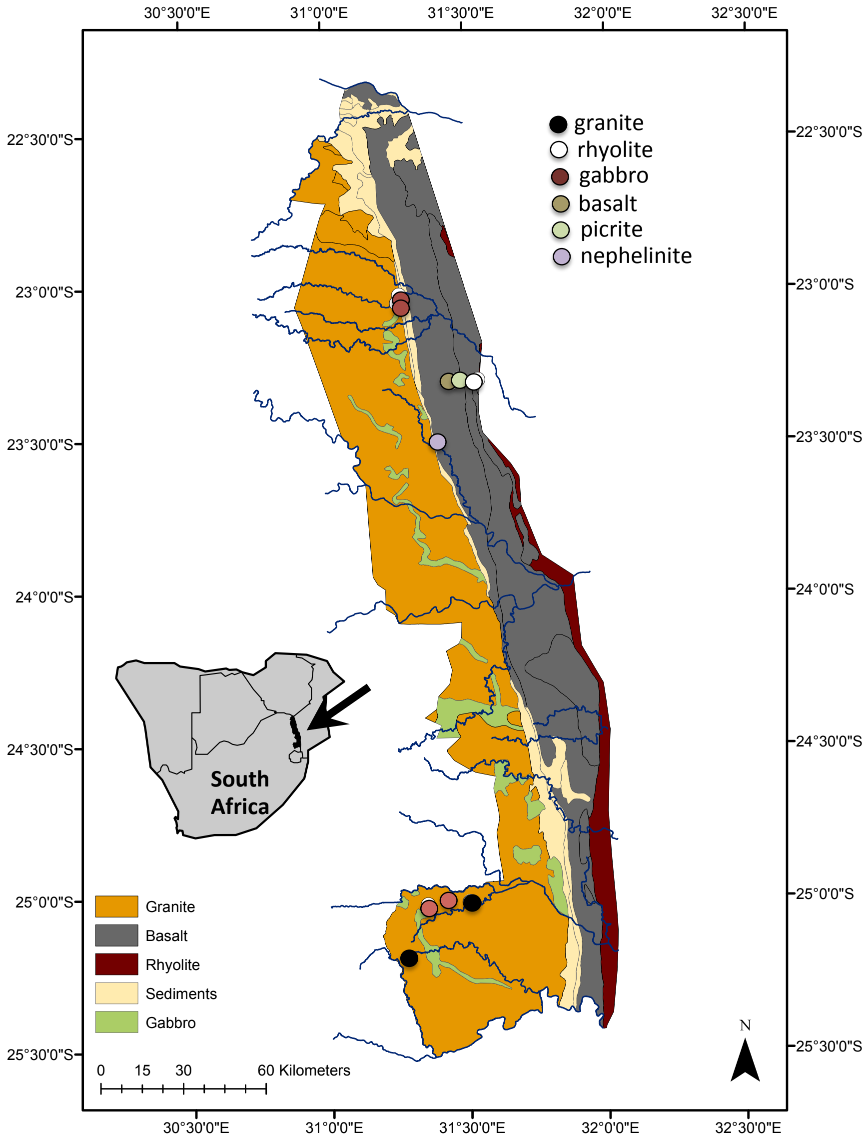

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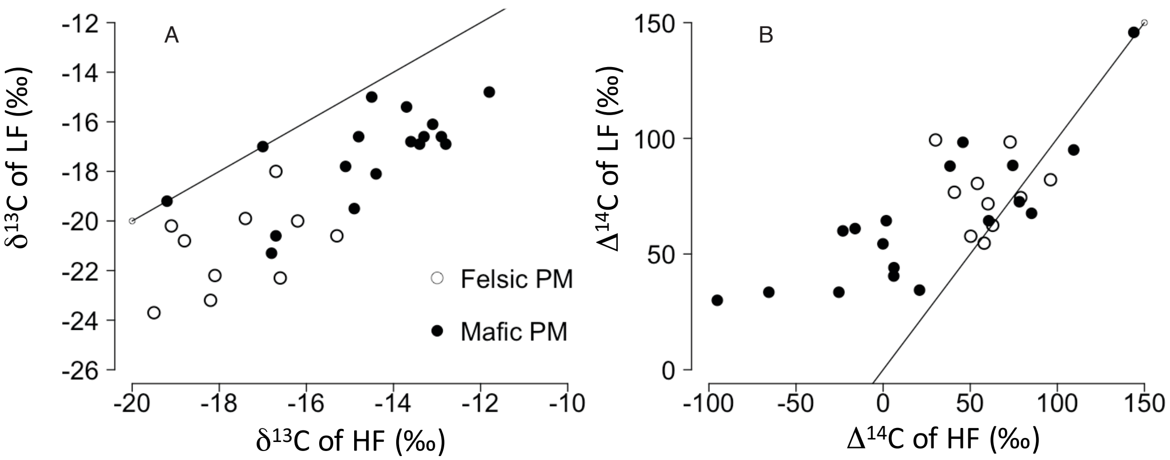

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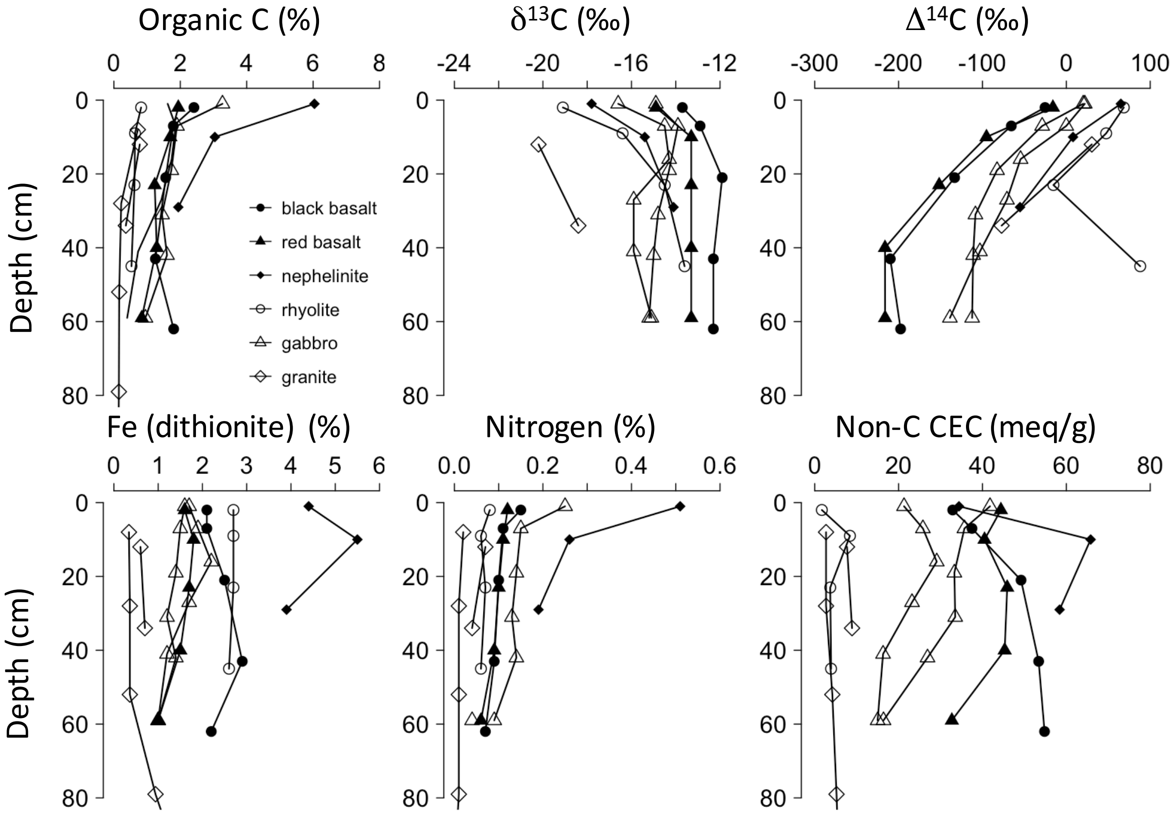

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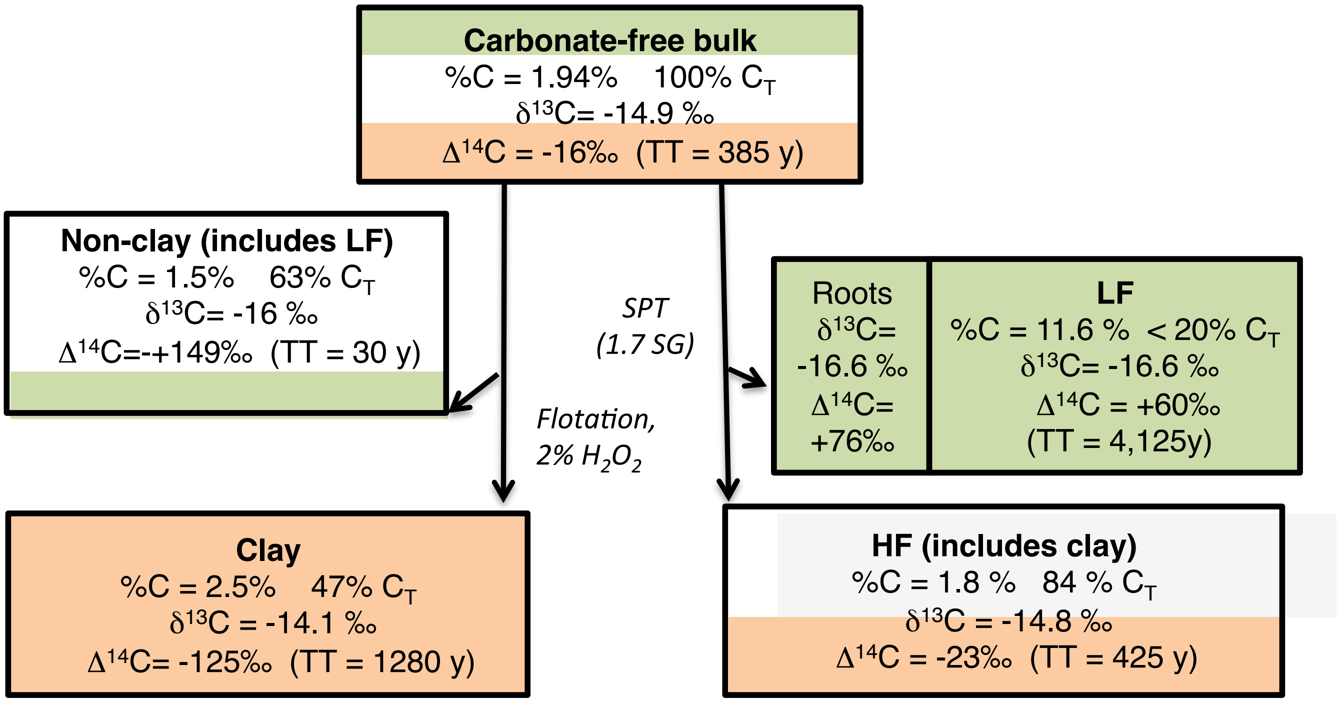

Figure 4.

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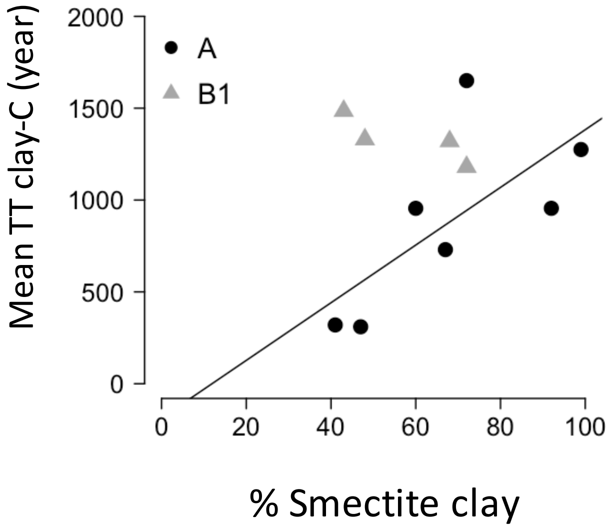

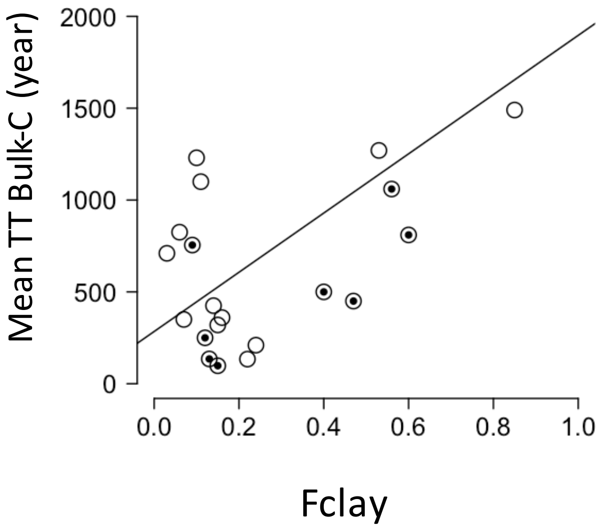

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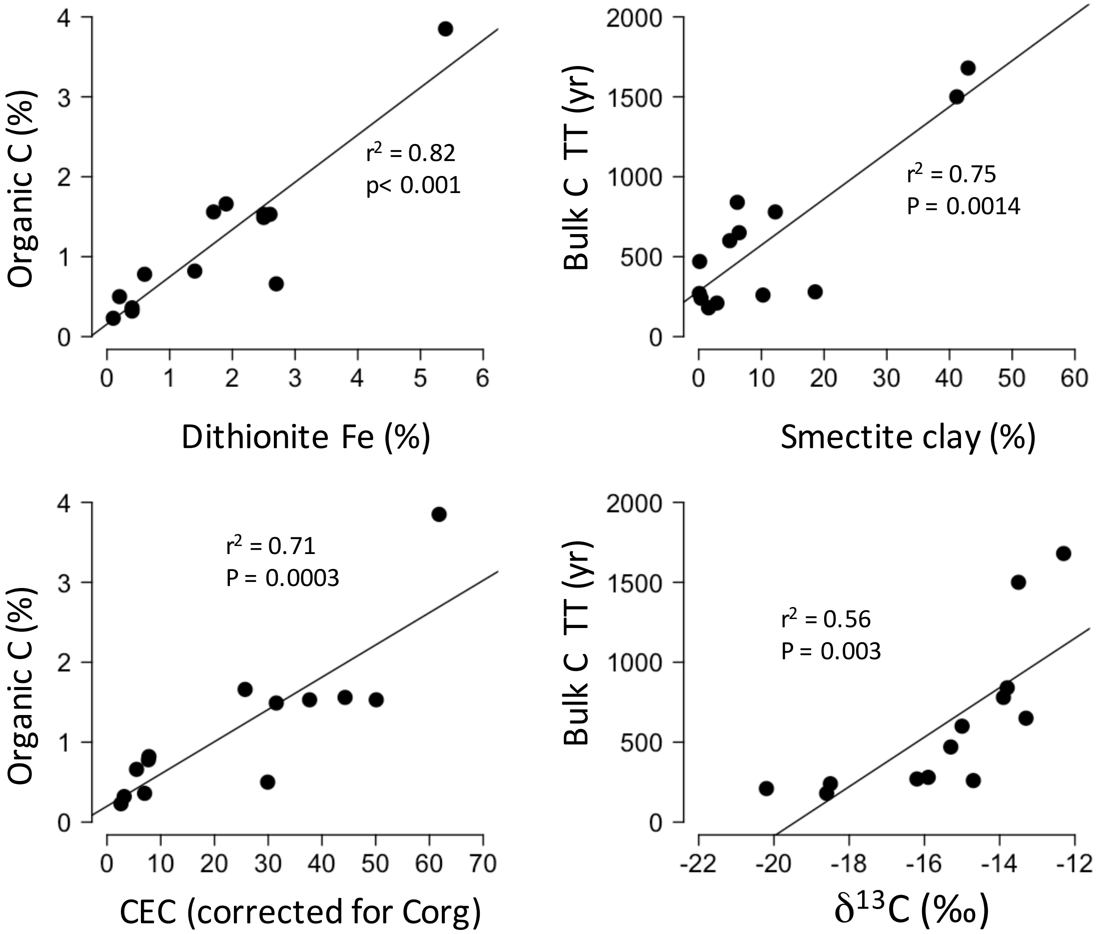
Organic C (%)
0
1
2
3
4
0
1
2
3
4
5
6
Dithionite Fe (%)
r² = 0.82
p< 0.001
Bulk C TT (yr)
0
500
1000
1500
2000
0
10
20
30
40
50
60
Smectite clay (%)
r² = 0.75
P = 0.0014
Organic C (%)
0
1
2
3
4
0
10
20
30
40
50
60
70
CEC (corrected for Corg)
r² = 0.71
P = 0.0003
Bulk C TT (yr)
0
500
1000
1500
2000
-22
-20
-18
-16
-14
-12
δ¹³C (‰)
r² = 0.56
P = 0.003