

Interactive comment on “Mineral physical protection and carbon stabilization in-situ evidence revealed by nano scale 3-D tomography” by Yi-Tse Weng et al.

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Reply to Reviewer#1: We have carefully prepared our response, it is lengthy, and we appreciate the patience of associate editor and reviewer #1. Revised manuscript is also attached (shown as a supplement file).

Abbreviation: organic carbon (OC), short-range-order (SRO), soil organic matter (SOM), soil organic carbon (SOC)

We use an old (3500 years) pyrogenic OC-mineral consortium to demo the in-situ OC-mineral interplay in a relatively simple mineralogy context. In-situ evidence reveals

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abundant mineral nano particles, in dense thin layers or nano-aggregates/clusters, instead of crystalline/micron/clay-size minerals on or near OC surfaces, the key working minerals for C stabilization are essentially SRO minerals and/or poorly crystalline sub-micron size clay minerals. Supported by spectroscopic results, the studied OC is not merely in criss-cross co-localization with reactive SRO minerals. There is a significant degree of binding between OC and minerals. We have other sets of unpublished 3-D tomography data for samples from various mineralogy background, and the minerals found associated with OC surface are coincidentally in line with nano particles/poorly crystalline minerals. ‘Mineral physical protection for OC stabilization may be more important than previously thought’ is not a solid conclusion, the statement is deleted.

Technology Progress for In-Situ Evidence:

This high resolution 3-D tomography tool we introduce has unprecedented resolution, is promising for new insight on in-situ organo-mineral association, the interior 3-D structure of microaggregates, and the fate of mineral nano particles including heavy metals in natural environment. Though some 3-D tomography research have been done on soil microstructure and porosity using X-ray micro-CT, the best achieved resolution only reaches tens of microns (Quin et al., 2014 (with biochar amendment, 70 microns); Kravchenko et al., 2015 (13 microns)), which exceeds the size of clay minerals (<2 microns), and not fit for capturing the microstructure of clay and the submicron assemblage of SRO minerals such as Fe oxyhydroxides. High resolution X-ray scanning and 3-D tomography is highly demanding in terms of technology, multidisciplinary and big-data analysis (Lafond et al., 2015). Except for the adoption of high resolution X-ray objective, fidelity of 3D tomography relies on the accurate alignment of the 2D projections in correct three-dimensional positions. However, non-negligible mechanical imperfection of the rotational stages at nanometer level, or the thermal effects may significantly degrade the spatial resolution of reconstructed tomography. We’ve developed a markerless image auto-alignment algorithm for fast projection matching (Faproma, Wang et al., 2017) to surpass these difficulties, and accomplished accurate reconstruction of

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3-D tomography down to nano meters.

Carbon Stabilization:

Soil organic C can be: (1) physically stabilized, or protected from decomposition, through microaggregation, or (2) intimate association with silt and clay particles in organo-mineral complexes, and (3) can be biochemically stabilized through the formation of recalcitrant SOC compounds (Six et al., 2002). Three main mechanisms of Soil organic matter stabilization are: (1) chemical stabilization, result of chemical or physiochemical binding between SOC and soil minerals (aka organo-mineral complexation), especially clay and silt in current opinions, (2) physical protection, which is predominantly at the microaggregate level, built on top of chemical organo-mineral complexation, and (3) biochemical stabilization, which is often experimentally defined, or equated to the nonhydrolyzable fraction (Stevenson, 1994; Christensen, 1996; Six et al., 2002). Experimentally to quantify C of different stabilized levels, a size/density fractionation approach with external force is routinely used for bulk soil, and three or more density fractions are divided: (a) free particulate OM, (b) occluded particulate OM, and (c) colloidal or clay associated OM, in the fine and dense fraction (Golchin et al., 1994, Sollins et al., 2009).

The stabilization of OC by the soil matrix is considered a function of the chemical nature of specific soil mineral fraction, the presence of multivalent cations, the presence of mineral surfaces capable of adsorbing organic materials, and the micro architecture of the soil matrix (Edwards and Bremner, 1967). The degree and amount of protection attributed by each mechanism depends on the chemical and physical properties of mineral matrix, the morphology, chemical nature and structure of organic matter (Baldock and Skjemstad, 2000). However, each mineral's unique capacity to stabilize organic C is rarely recognized in bulk sample analysis, or within size/density fractionation. Thus, quantifying the protective capacity of a soil requires a careful consideration of all mechanisms of protection and the implications of experimental procedures.

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It is found that accumulation and subsequent loss of organic C were largely driven by changes in the millennial scale cycling of mineral-stabilized carbon (Torn et al., 1997, Nature). The protection of SOC by silt and clay particles in soils is well established for a positive relationship between old/stabilized organic C and the content of silt and/or clay in fine and dense fraction (Sorensen, 1972; Feller and Beare, 1997; Hassink, 1997; Trumbore, 1997). In addition to the clay content, clay type (2:1 vs 1:1 clay vs allophanic /short-range-order (SRO) minerals) has strong influence on the stabilization of organic C (Torn et al., 1997). Yet little is known about how spatial and temporal variation in soil mineralogy (especially type, phase, reactivity) controls C long term stabilization in terms of quantity and turnover (Oades, 1994, Torn et al., 1997). Quantification of interactive relationships is imperative, measurement and information using 2-D and 3-D quantitative tool will have great benefit in understanding soil C and aggregate dynamics (Six et al., 2004).

Very limited information is available on the in-situ distribution of clay-size or reactive minerals in soil, and subsequent organo-mineral micro assemblage in soils. For example, a substantial parts of mineral surfaces are considered likely not covered by organic matter (Ransom et al. 1998; Arnarson and Keil 2001; Mayer and Xing 2001; Kahle et al. 2002). Recently, nano scale two-dimensional mapping using Nano SIMS generated direct evidence, revealing that less than 19 percent of the clay-sized mineral surfaces co-localize with OC (Vogel et al., 2014, Nature Communication). Views of carbon sequestration in soils and the widely used carbon saturation estimates has been revolutionized to recognize likely only a limited proportion of the clay-sized surfaces contribute to OM sequestration in real soil environment. However, this research could underestimate the actual contact surface area between OC and mineral due to the limitation of sample treatment and two-dimensional approach. Exactly which reactive mineral in the clay-sized fraction interact with OC remains unknown. The cornerstone research done by Torn et al. (1997) revealed a positive relationship between non-crystalline minerals and organic carbon in soils through the climate gradient. In couple with extraction using ammonium oxalate and/or sodium dithionite-citrate-bicarbonate

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(DCB), SRO minerals, which may only be a small portion in the fine and dense fraction, are found of great importance for C stabilization, and further discovered preferentially associated with aromatic/lignin-like C (Kaiser et al., 2002; Eusterhues et al., 2005; Kleber et al., 2005; Mikutta et al., 2005, 2006, 2007; Rasmussen et al., 2005; Schneider et al., 2010; Cusack et al., 2012). The SRO minerals are known of high reactivity due to small size, large surface area and charges, their encounter with reactive OC surface may develop strong organo-mineral complexation (Eusterhues et al., 2008, 2011). Yet, the actual key mineral player (micron size clay vs nano scale SRO minerals) for interaction with OC, and the spatial and temporal variation of such minerals is not known in real soil environment (Vogel et al., 2014). On the other hand, a three-dimensional functional view of carbon turnover dynamics at the microscale has gained ground (Kleber et al., 2018), which consider a multitude of largely independent microreactors within soil. For example, anaerobic microsites are discovered of great importance for C stabilization (Keiluweit et al., 2017). New perspectives call for observational evidence on OC-mineral micro assemblage in nano scale details.

Using high resolution 3-D tomography and synchrotron-based spectroscopic approach, we unveil: i) There is a high heterogeneity within OC-mineral consortium, including many nano/micron size porosity and microsites. ii) Rare particulate OC surface is not coated by minerals. iii) The minerals on the OC-mineral interplay surface are essentially nano particles SRO minerals, or submicron/poorly crystalline minerals, which are highly reactive and carry large interactive surface for C absorption. iv) Very few micron size/clay-size, euhedral/crystalline minerals exist. v) The 3500-year-old pyrogenic OC is highly aromatic (1596 and 1386 cm^{-1}), and also has highly reactive carboxyl functional group (1706 cm^{-1}). vi) Broad FTIR bands points to a significant degree of organo-mineral association between OC and SRO minerals, which are not just criss-cross co-localization. vii) The OC surface is often coated by thin layers of SRO minerals, pointing to likely mineral absorption. viii) Within regions microns from particulate OC surface, abundant mineral nano particles develop nano-aggregates/clusters, pointing to likely co-precipitation of relatively free OC and SRO minerals.

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Our results suggest:

i) The coated particulate OC surfaces by SRO minerals are stabilized. ii) Minerals physical protection contributes to long term persistence of OC (3500 year old) in the sub-tropical environment. iii) Substantial mineral surfaces are likely available for C stabilization. iv) Large amount of nano-aggregates/clusters likely interact/co-precipitate with relatively free OC, which is difficult to prove directly. v) Current electron microscopy/spectroscopy/fractionation approach focusing on clay-sized may lead to underestimate C stabilization attributed by mineral physical protection.

We propose:

i) High resolution 3-D tomography is a powerful, suitable tool for nailing down the correct target (key working mineral) for C stabilization. ii) Two-dimensional TEM may be applicable in revealing nano particle, amorphous/poorly crystalline minerals, on certain focal plane, but not for a whole view. iii) XRD is powerful for crystalline minerals but very poor in resolving SRO, cautions should be taken in mineralogy pattern interpretation and sample preparation. iv) More research should be done to prove: i) whether it is a general phenomenon that the minerals interact with OC are essentially nano particle SRO minerals/poorly crystalline submicron minerals, ii) whether the major mineral for C stabilization is nano scale SRO minerals instead of clay-sized minerals. v) Perspective on SOM dynamics may have to take account the role of SRO minerals into modelling parameters, instead of drawing conclusion mainly on clay type and content (Kleber et al., 2010).

Carbon Models and Carbon Saturation:

Most current models of SOM dynamics try to describe soil heterogeneity by defining several pools, typically three to five, experimentally applicable with supposedly different intrinsic decay rates. Meanwhile, first order kinetics are assumed for the decomposition of different conceptual pools (Parton, et al., 1994; Paustian, 1994; McGill, 1996), which infers equilibrium C stocks are linearly proportional to C inputs (Paustian et al.,

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1997). These models predict that soil C stocks can theoretically be increased without limit, provided that C inputs increase without limit, leading to no assumptions of soil C saturation. Such models have been largely successful in representing SOM dynamics under some studied conditions and management practices, and native soils (e.g. Parton et al., 1987, 1994; Paustian et al., 1992; Powlson et al., 1996). Notably, the representation of the model pools (or quality spectrum) is primarily conceptual in nature (Christensen, 1996; Elliott et al., 1996; Six et al., 2002). The individual pools are generally only loosely associated with measurable quantities obtained with existing analytical methods.

The notion of carbon saturation is developed on the assumption that mineral physical protection could be limited by soil physicochemical characteristics such as silt and/or clay content, microaggregate, and surface area (Kemper and Koch, 1966; Hassink, 1997). Six et al. (2002) proposed a conceptual model which use the physicochemical characteristics inherent to soils to define the maximum protective capacity of different SOC pools, which may limit the increases in C sequestration with increasing organic residue inputs. This conceptual model includes four measurable pools: (1) a biochemically-protected C pool, (2) a silt and clay-protected C pool (less than 53 micron organomineral complexes) (3) a microaggregate-protected C pool (53 to 250 micron aggregates), and (4) an unprotected C pool. Each pool is supposed to has its own dynamics and stabilizing mechanism, which is in turn hypothesized to determine a level at which soil C becomes saturated. The silt and clay protected C pool, which is protected by association with the mineral particles, is defined as hydrolysable fraction and the biochemically-protected C pool is experimentally defined as nonhydrolyzable fraction. Biochemical stabilization is understood as the stabilization of SOM due to its own chemical composition (e.g. recalcitrant compounds such as lignin and polyphenols) and through chemical complexing processes (e.g. condensation reactions) in soil. The unprotected C pool is considered labile, an important nutrient source, which is very sensitive to management practices. Interestingly, the hierarchy for carbon stabilization based on protection capacity/level, from low to high has been ranked as: silt +

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clay protected pool, microaggregate protected pool, biochemically protected, and non-protected pool on the top to cap the maximum carbon saturation. Six et al. (2002) pointed that there are major gaps in knowledge and proposed a research priority in terms of soil C saturation on mechanistic level, if it exists, especially for unprotected and biochemically protection pools.

As an outsider, we share a few points:

i) The heterogeneity of microaggregates is little understood and minimal quantitative data is available. ii) The unprotected pool actually involves some mechanism separation and dispersion, which is not truly unprotected. iii) Six et al. (2000) shared our thought that non-hydrolyzable fraction is not only biochemically stabilized but is also partially stabilized by association with clay and silt particles, and the silt and clay protected pool could also be partially stabilized by incorporation in microaggregates. iv) Our studied aged pyrogenic OC (3500 years) is not only biochemically stable, but also partially stabilized by association with submicron minerals.

Reviewer #1 suggested some interesting research on biochemically stabilized organic compounds free of minerals, which appears a vast expansion to very solid organic geochemistry. Many models for SOM dynamics indeed incorporate a huge 'inert' pool, which may include biochemically stabilized organic compounds free of minerals. Perspective on carbon stabilization may have to expand to a much longer geological time scale, as common C saturation models are dealing with a time scale of millennials. Derenne et al. (1991) carried out research on biochemically stabilized organic compounds free of minerals, especially on kerogen/fossil-like organic compounds, in terms of kerogen/fossil formation/biochemical transformation/condensation process. We suggest research on biochemically protected pool also expand into black carbon/pyrogenic organic carbon, which are biochemically stable due to their high aromaticity and have similar structure with kerogen and coal, can persist over millennials under natural exposure. Long term abiotic/biotic degradation, aerobic/anaerobic alternation can render development of reactive surface functional groups (Liang et al.,

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2006), and lead to consequent mineral physical protection and C stabilization over millennia, even in the tropics (Liang et al., 2008).

Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2017-509/bg-2017-509-AC1-supplement.pdf>

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2017-509>, 2017.