



Review

Impact of phyllosilicate mineralogy on organic carbon stabilization in soils: incomplete knowledge and exciting prospects



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ABSTRACT

Soil mineral phases strongly influence soil organic carbon (SOC) dynamics. Clay-size particles have been recognized as protecting SOC from microbial decomposition. Among clay-size minerals, phyllosilicates (clay minerals) have been shown to efficiently protect SOC. There is an important variety of phyllosilicate types present in soils which have contrasting surface properties (specific surface area, charge density). Although these differing surface properties should influence their ability in protecting SOC, this has not been clearly established yet. Publications comparing the ability of the different phyllosilicates to protect SOC are reviewed in this study. Relatively few studies dealing with the link between phyllosilicate mineralogy and SOC protection exist. The few existing studies have followed different methodologies and are based on various analytical techniques, such that direct comparisons among them are difficult. More problematic, they provide different conclusions. Indeed, if experiments conducted in suspension using pure clay phases and recent meta-analyses suggest that phyllosilicate mineralogy has a significant importance for SOC stabilization and SOC stock response to land-use change, these results are not clearly corroborated by studies conducted on a reduced number of soils. The recent technical developments which allow improving both quantitative and qualitative descriptions of the soil clay mineral assemblages, together with nano-scale investigations of phyllosilicate/OM interactions, offer exciting perspectives for determining more accurately the efficiency of the different phyllosilicate types in SOC protection. Such information may provide a much clearer understanding of the impact of phyllosilicate mineralogy on SOC dynamics in the coming years.

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1. Introduction

Soil organic matter (SOM) is of primary importance for soil functioning. SOM governs nutrient dynamics and binds mineral particles which contributes to soil structure therefore reducing erosion and regulating the role of soils in the water cycle. SOM is also a substrate for the huge diversity of heterotrophic organisms, and is of crucial importance for the global C cycle. Indeed, soils contain about three times more C than the atmosphere and it has been recognized that small changes of the soil C stock can have a significant impact on atmospheric CO₂ concentration (Eglin et al., 2010). Organic components can be stabilized in soils because of (1) their intrinsic chemical recalcitrance, (2) specific interactions with mineral surfaces and metal ions or (3) spatial inaccessibility due to physical occlusion within soil aggregates (e.g. Baldock and Skjemstad, 2000; Sollins et al., 1996, 2009; von Lützow et al., 2006). Apart from pyrogenic carbon, it is now agreed that intrinsic chemical recalcitrance alone does not explain long-term C persistence in soils (Schmidt et al., 2011) and that old SOM fractions with slow turnover rates are generally found in association with soil minerals (Marschner et al., 2008). Soil minerals, and especially finely divided minerals, i.e. mineral particles smaller than 2 μm that form the soil clay-size fraction, are therefore crucial for SOM dynamics as they provide surfaces that can adsorb organic molecules (stabilization mechanism 2), strongly affect soil microstructure and pore system and are involved in aggregate formation and dynamics (stabilization mechanism 3), which protect SOM from biodegradation. In other words, phyllosilicates may influence SOM biodegradation via surface interactions or via interactions at the scale of the soil microstructure (Chenu and Stotzky, 2002).

This crucial role of finely divided soil minerals has been demonstrated in numerous studies reporting that SOC content correlates well with the soil clay-size fraction content (i.e., with that of particles smaller than 2 μm). For instance, Martin et al. (2011) recently observed, on a dataset comprising 2200 measurements of SOC stocks over the French territory, that the clay content (i.e., clay-size mineral particle content) was the best or second-best predictor of SOC stocks. The importance of clay content on SOC dynamics is also recognized in most SOC models (e.g. Saffih-Hdadi and Mary, 2008). As an example, in the Century and Roth-C models, SOC mineralization rates decreases with increasing clay-size mineral particle content (Coleman et al., 1997; Parton et al., 1987). Moreover in the Century model, the amount of C entering the stable C pool increases with soil clay content. However, such models do not account for the actual mechanisms by which clay-size mineral particles stabilize organic matter. Several authors consider that the amount of fine mineral particles determines the “protective capacity” of a soil and defines ultimately the amount of C that can be stabilized in a soil (see the work by Hassink, 1996, 1997; developed by Six et al., 2002; Stewart et al., 2007, 2008, 2009; Feng et al., 2013).

However, if the importance of clay content for SOC stabilization in soils is broadly accepted, only few authors attempted to go a step forward to discuss the importance of the mineralogy of clay fractions on OC stabilization in soil conditions. Indeed, soil clay fractions most often contain a mixture of mineral phases with highly contrasting surface properties. Considering that the content of clay-size mineral particles is an acceptable proxy to describe the protection that these minerals can provide to SOM as it is done in SOC dynamic models means that the influence of the surface properties (surface area and surface chemistry) and that of the microstructure of these minerals on SOC dynamics can be neglected. This postulate needs to be discussed.

Soil clay-size fractions can contain six main types of minerals: phyllosilicates (known as clay minerals), metallic oxides and hydroxides (ferrihydrite, goethite ...), primary minerals (quartz, feldspars ...), and in some soils carbonates, gypsum or short-range order alumina-silicate minerals (allophane, imogolite). Apart from gypsum, all these types of minerals have been shown to efficiently protect SOM from decomposition. Sollins et al. (2009) showed for instance that if little OC was associated to primary minerals, this OC had been stabilized for centuries. It has been shown that short-range order alumina-silicate minerals developed on volcanic ash efficiently protect SOM (Basile-Doelsch et al., 2009; Torn et al., 1997) which explains the high C stocks often observed in soils developed on this type of materials. Metallic oxy-hydroxides have been shown to stabilize SOC efficiently, particularly in acidic forest soils (Mikutta et al., 2006). The role of carbonates has been studied to a lesser extent, but the presence of carbonates has been recognized to stabilize SOC in early models of SOM decomposition (Hénin and Dupuis, 1945). In agreement with this, some authors have found that carbonate-rich soils tend to accumulate more SOC than other soil types under similar environmental and management conditions (Baldock and Skjemstad, 2000; Fernandez-Ugalde et al., 2011). In calcareous arable soils of the Mediterranean region, the SOC content correlated better with carbonate content than clay content (Romanyà and Rovira, 2011).

Our present review attempts to link the mineralogy of phyllosilicates (also known as clay minerals) to SOM stabilization. We consider that this contribution is needed in that (1) phyllosilicates are the main component of clay fractions in numerous soils and (2) even though there is a variety of phyllosilicates in soils (from discrete phyllosilicate phases such as kaolinite and illite to a wide variety of interstratified phyllosilicate phases) with contrasting surface properties, there is to our knowledge no review dedicated to the link between phyllosilicate mineralogy and SOC dynamics. Similar work on short-range order minerals or oxides would be of interest but is beyond the scope of our present work. Similarly, this review does not aim at comparing the relative efficiency of phyllosilicate and non-phyllosilicate minerals towards SOC stabilization.

Initially, we present briefly the characteristics and diversity of phyllosilicates that can be found in soils, their characteristics relevant to an understanding of their impact on SOC biodegradation via surface interactions, and the complexity of their isolation and identification. We then review the studies dedicated to the link between phyllosilicate mineralogy and SOC protection, classifying them into four main approaches. Finally, we discuss the knowledge gaps and the potential of new methods that can be used to address them.

2. The diversity of soil phyllosilicates and soil phyllosilicate properties

2.1. Soil clay-size fractions contain most often a mixture of different phyllosilicates

Soil phyllosilicates have been studied for decades, which has generated many books, reviews and case studies (e.g. Jackson, 1964; Millot, 1964; Velde, 1995; Wilson, 1999). The purpose of the present work is not to describe soil phyllosilicates in extenso but to give some insights needed to understand why soil phyllosilicate mineralogy can be an important parameter when studying soil C dynamics. For an extensive description of soil phyllosilicates, the reader can refer to the variety of textbooks dedicated to the subject (e.g. Moore and Reynolds, 1997; Velde, 1992).

Soil phyllosilicates can have three different origins: they can be inherited from parent materials, transformed from other minerals in

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