Biogeochemistry (2018) 137:27–49
https://doi.org/10.1007/s10533-017-0410-1

SYNTHESIS AND EMERGING IDEAS

Calcium-mediated stabilisation of soil organic carbon

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Received: 7 August 2017 / Accepted: 10 December 2017 / Published online: 19 December 2017

Abstract Soils play an essential role in the global cycling of carbon and understanding the stabilisation mechanisms behind the preservation of soil organic carbon (SOC) pools is of globally recognised significance. Until recently, research into SOC stabilisation has predominantly focused on acidic soil environments and the interactions between SOC and aluminium (Al) or iron (Fe). The interactions between SOC and calcium (Ca) have typically received less attention, with fewer studies conducted in alkaline soils. Although it has widely been established that exchangeable Ca (Ca_{Exch}) positively correlates with SOC concentration and its resistance to oxidation, the exact mechanisms behind this relationship remain largely unidentified. This synthesis paper critically assesses available evidence on the potential role of Ca in the stabilisation of SOC and identifies research topics that warrant further investigation. Contrary to the common view of the chemistry of base cations in soils, chemical modelling indicates that Ca^{2+} can readily exchange its hydration shell and create inner sphere complexes with organic functional groups. This review therefore argues that both inner- and outer-sphere bridging by Ca^{2+} can play an active role in the stabilisation of SOC. Calcium carbonate ($CaCO_3$) can influence occluded SOC stability through its role in the stabilisation of aggregates; however, it could also play an unaccounted role in the direct sorption and inclusion of SOC. Finally, this review highlights the importance of pH as a potential predictor of SOC stabilisation mechanisms mediated by Al- or Fe- to Ca, and their respective effects on SOC dynamics.

Keywords Calcium · Soil organic carbon stabilisation · Sorption · Occlusion · Polyvalent cation bridging · Organo-mineral interactions

Introduction

Soil organic carbon stabilisation

Soils are the largest actively cycling terrestrial C reservoir and play an essential role in the global cycling of C. Improving our understanding of this C reservoir and modelling its dynamics are fundamental to predicting its sensitivity to future change (Brovkin and Goll 2015). However, current models suffer from

Responsible Editor: Marc G. Kramer.

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large uncertainties caused by the complexities of SOC and its physicochemical interactions with the soil matrix (Friedlingstein et al. 2006). Models require further mechanistic research on the variables that drive SOC dynamics to improve their accuracy (Campbell and Paustian 2015). Therefore, understanding the mechanisms behind the accumulation and persistence of SOC is of globally recognised importance.

Soil organic C stabilisation broadly refers to mechanisms believed to impede the decomposition of organic matter, promoting its accumulation and persistence in soils. Conversely, decomposition refers to the progressive oxidative transformation of organic inputs, during which a fraction of the organic matter is volatilised as carbon dioxide, while residues become increasingly laden with functional groups, such as carboxyl, phenol, or hydroxyl groups (Guggenberger and Zech 1993; Oste et al. 2002; Peinemann et al. 2005). Sollins et al. (1996) originally proposed three theoretical mechanisms that confer stability to SOC: (i) an inherent recalcitrance or thermodynamic stability of soil organic matter (SOM) and its subsequent selective preservation by decomposers, (ii) the physical occlusion of SOC from decomposers, and (iii) sorption of SOC to inorganic soil components resulting in organo-mineral or organo-cation complexes.

It was previously thought that the primary mechanism behind the persistence of SOC was the selective preservation of thermodynamically stable or recalcitrant substrates by decomposers (Aber et al. 1990; Sollins et al. 1996), causing their accrual within the soil matrix. However, as hypothesised by Oades (1988), there is little evidence for the preservation of complex cell-wall materials like lignin and suberin in stable SOC pools (Gleixner et al. 1999, 2002; Rumpel and Kögel-Knabner 2011; Schmidt et al. 2011). Contrarily, recent evidence suggests that selective preservation is only relevant at the beginning of the SOC decomposition continuum (Dignac et al. 2005; Gleixner et al. 1999, 2002; Lehmann and Kleber 2015; Schmidt et al. 2011) or within organic horizons (Lemma et al. 2007; Preston et al. 2009). The stabilisation and maintenance of SOC in mineral soil horizons, over medium- to long-time periods, is now predominantly thought to be driven by specific ecosystem properties rather than the inherent recalcitrance of SOC (Schmidt et al. 2011).

The established paradigm: ecosystem properties limiting SOC decomposition

Important ecosystem properties that contribute to SOC stabilisation include:

(i) the physical separation of substrates from decomposers over plurimetric to micrometric scales;
(ii) interactions between SOC and cations or minerals;
(iii) the occurrence of temperature or moisture conditions that are incompatible with enzymatic reactions;
(iv) toxicity effects of metal ions like Al^{3+}.

The first and second processes are the most widespread as they occur, theoretically at least, in all soils. The state of knowledge on these processes is briefly synthesised below.

Physical separation

Soil organic carbon (SOC) can be stabilised by its physical separation from decomposers, their enzymes, and the necessary components of aerobic decomposition, such as oxygen or moisture. This physical constrainment can occur over large spatial scales in biologically limiting environments, like those present in Histosols or Cryosols, where waterlogged or frozen conditions severely limit the oxidative degradation of organic substrates (Dörfer et al. 2013), but can also occur at smaller spatial scales. Mechanisms for small scale physical separation include hydrophobic interactions arranging substrates into a micellar structure (Chassin 1979), SOC inclusion within a mineral or co-genetic mineral assemblage (Bindschedler et al. 2016), SOC intercalation within phyllosilicates (Theng et al. 1986), and occlusion of SOC within pedogenic aggregates (Adu and Oades 1978). Thus, the physical constrainment of aerobic decomposition can occur over plurimetric to micrometric scales and stabilises SOC in nearly all soil environments.

Formation of soil aggregates is the most widespread microscale process that leads to the physical separation of SOC, typically labelled as occluded SOC. The relation between aggregation and the stability or accumulation of SOC has been repeatedly demonstrated (Denef et al. 2004; Moni et al. 2010; Monreal et al. 1997; Plante et al. 2002; Skjemstad et al. 1993; Virto et al. 2008, 2010). Formation of aggregates has conventionally been thought to involve the electrostatic flocculation of soil separates into stable domains 2–20 µm in size (Ghezzehei 2011), which are then bound by organic or inorganic cementing agents (Jastrow 1996; Six et al. 2004). Much emphasis has been placed on biological mechanisms that can control aggregation, such as the physical meshing of soil particles by roots and fungi or the excretion of extracellular polysaccharides/polymeric substances by microorganisms and roots (Balesdent et al. 2000; Chenu and Cosentino 2011; Six et al. 2002, 2004). In the theory of biological-controlled aggregate formation (Chenu 1989; Oades and Waters 1991; Oades 1993; Tisdall 1996), fresh SOC acts as an aggregate formation nucleus, stimulating localised activity of microorganism communities. These microorganisms excrete extracellular polysaccharide/polymeric substances that adhere to soil particles, which binds them together, creating a shell around the decomposing SOC nucleus and eventually occluding the SOC residue within (Chenu and Cosentino 2011). When driven by biology, soil structure is typically arranged into a spatial hierarchy, with distinct physical classes of aggregates that are often classified as macroaggregates (> 250 µm) or microaggregates (< 250 µm; Asano and Wagai 2014; Elliott 1986; Oades 1984; Six et al. 2000, 2004; Tisdall 1996; Tisdall and Oades 1982). These aggregate classes have different properties (size, structural stability, porosity, hydrophilicity), which confer different stabilities to the SOC occluded within (Chenu and Cosentino 2011; Dexter 1988; Kleber et al. 2007; Sutton et al. 2005; von Lützow et al. 2006; Zheng et al. 2016). It is largely accepted that in this hierarchy, microaggregates are formed within macroaggregates, which then break apart because of their weaker binding agents and larger planes of weakness, distributing microaggregates into the soil matrix (Oades 1984; Six et al. 2004; Tisdall 1996). These microaggregates are typically considered more stable because of their stronger binding agents and reduced macroporosity, increasing the stability of SOC occluded within (Denef et al. 2004; Tisdall and Oades 1982). Yet despite the recent emphasis on biological controls on soil aggregation, it should be noted that soil aggregation, its hierarchy, and the occlusion of SOC is also influenced by inorganic components of the soil matrix.

Abiotic agents, such as the composition of the mineral soil matrix, can indeed play a dominant role in aggregate formation and stability and therefore, influence occluded SOC. Polyvalent cations are known to increase aggregation in soils by flocculating negatively charged soil separates (Bronick and Lal 2005; Érika et al. 2016; Grant et al. 1992). Inorganic components can also increase the stability of aggregates through cementation, with examples including poorly crystalline minerals (Rasmussen et al. 2005), well crystallised Fe oxides (Oades and Waters 1991; Zhao et al. 2017), or carbonates (Falsone et al. 2010; Fernández-Ugalde et al. 2011, 2014; Virto et al. 2011). Inorganic components have been documented to reinforce both macroaggregates (Fernández-Ugalde et al. 2011; Virto et al. 2013) and microaggregates (Falsone et al. 2010). Some authors have pointed out that when predominantly controlled by inorganic agents, like Fe oxides in Ferralsols (Oxisols; Oades and Waters 1991), soil structure may not display the hierarchical organisation commonly associated with biology. However, when compared to biotic processes, inorganic controls on SOC occlusion have received relatively little attention recently.

Sorption

SOC can also be stabilised through sorptive interactions. These interactions include adsorption to minerals, like phyllosilicate clays, Al-, Fe-, Mn-oxides, poorly crystalline minerals, or polyvalent cations forming bridges to mineral or other organic soil constituents. A positive relationship between the resistance of SOC to chemical oxidation and the presence of specific reactive mineral species was first described by Hosking (1932). Since then, the presence of reactive minerals or metals has been repeatedly shown to correlate with increased SOC stocks (Baldock and Skjemstad 2000; Grand and Lavkulich 2011; Sokoloff 1938; Torn et al. 1997) and the resistance of SOC to microbial degradation in incubation experiments (Minick et al. 2017; Rasmussen et al. 2006; Whittinghill and Hobbie 2012). Soil organic C complexed by minerals generally exhibits older ^{14}C-derived ages than other SOC pools (Kleber et al. 2011; Rasmussen et al. 2005; Schrumpf et al. 2013; Spielvogel et al. 2008; Trumbore 1993); thus adsorption plays a clear role in the stabilisation of SOC over long time periods. However, there is still some level of confusion within the field regarding the chemistry involved. Therefore, the main bonding mechanisms between organic and inorganic soil components are discussed briefly below.

Bonding mechanisms

There is a range of bonding mechanisms that can link organic molecules to minerals or metal cations (Table 1). The prevalence of each bonding mechanism will vary with soil texture, mineralogy, and concentration of cations. SOC can be stabilised through either inner- or outer-sphere interactions with minerals or metal cations (Sposito 2008; Sutton et al. 2005). Inner sphere complexes occur when a substance can closely approach a mineral's surface or metal ion, usually resulting in direct chemisorption; see Eq. 1 for an example. In outer sphere interactions, water molecules prevent the direct approach or sorption of a substance to a mineral's surface or metal ion; instead, the charges are countered through a diffuse charged zone (Oldham 2008). In soil, inner- and outer-sphere interactions act in combination to stabilise SOC over medium- to long-time periods, so that it becomes difficult, if not impossible, to ascribe SOC stabilisation in a given horizon to specific modes of interaction. However, a basic understanding of the fundamental chemical mechanisms at play is useful to inform our interpretation of operationally-defined SOC pools (see section below on sorption processes involving Ca).

$$\| - \mathrm{M} - \mathrm{OH} + \mathrm{HO} - \mathrm{R} \rightarrow \| - \mathrm{M} - \mathrm{O} - \mathrm{R} + \mathrm{H_2O}. \tag{1}$$

Equation 1: Ligand exchange between a mineral (M) and a hydroxyl functional group on an organic substrate (R) that results in the direct and strong adsorption of SOC. Equation adapted from Huang and Schnitzer (1986).

Stabilisation by sorption

SOC can be stabilised by organo-cation or organo-mineral interactions through several mechanisms. The primary SOC stabilisation mechanism of adsorption consists of the removal of SOC from solution and transfer to a solid phase. This transfer increases the stability of SOC by reducing the chance of diffusive encounter with degrading enzymes. It can occur whenever organic compounds become adsorbed to mineral surfaces (Kaiser and Guggenberger 2000; Kalbitz et al. 2005), but also when the concentration of cations becomes sufficient for soluble organic polymers to flocculate and precipitate (Baldock and Skjemstad 2000). Much of the research on flocculation thresholds has focused on acid soils dominated by Al chemistry (Boudot 1992; Matus et al. 2006; Rasmussen et al. 2006). In these soils, it has been shown that extensive flocculation and precipitation can be expected at a C:Al ratio in the order of 10–30 or lower (Jansen et al. 2003; Scheel et al. 2007; Skjemstad et al. 1992). The flocculation of dissolved organics by other cations in natural soils has not been as extensively studied.

Beyond the effect of sorption on the partition of SOC between the liquid and solid phase, substrates can also be stabilised by other mechanisms, such as the toxicity effects of certain metals, the inactivation of enzymes during sorption, or steric hindrance. It has been proposed that environmental cytotoxicity could result in the stabilisation of organics complexed by some metals such as Al (Tate and Theng 1980). $\mathrm{Al^{3+}}$ is toxic and is thought to limit decomposer activity in acidic soil environments (Tonneijck et al. 2010), although evidence for this can be contradictory (Marschner and Kalbitz 2003). The extra-cellular enzymes responsible for much of SOM decomposition can also be rendered inactive by adsorption onto mineral surfaces, due to structural modifications in their conformation at the adsorption interface (Quiquampoix and Burns 2007). Steric hindrance is a general mechanism involving the lack-of-fit between a substrate and a catalyst (an enzyme) caused by changes in tertiary structure, which is a common consequence of sorptive interactions in soil (Quiquampoix and Burns 2007; Zimmerman and Ahn 2010). Therefore, the spatial arrangement of adsorbed elements along the molecular interface plays an important role in the stabilisation of SOC during adsorption.

Although it was previously proposed that adsorption occurred uniformly over mineral surfaces, resulting in a monolayer coverage (Keil et al. 1994), this has now been challenged by empirical evidence suggesting that organic loading instead occurs in distinct reactive 'hotspots' (Hedges and Keil 1995; Kaiser and Guggenberger 2003; Vogel et al. 2014). Vogel et al. (2014) recently utilised scanning electron microscopy

Table 1 Mechanisms of interaction between soil organic carbon substrates and minerals or metal ions

Mechanism	Nature	Type of interaction	Description
Ligand exchange (Mikutta et al. 2014) Ligand exchange is the formation of new coordination complexes with metals	Covalent to ionic bond	Inner sphere	Strong bonding to a metal via the direct substitution of one outgoing ligand (for instance, a hydroxyl group) by an incoming one (for instance, an organic molecule with a hydroxyl, phenol, or carboxyl functional group)—see Eq. 1. There is no change in oxidation state at the metal centre and charge is conserved during the reaction
Chelation (Ahmed and Holmström 2014) Chelation is the formation of polydentate coordination complexes with metals. Compared to monodentate complexes, they have a greater stability	Covalent to ionic bond	Inner sphere	A special case of ligand exchange, where the incoming ligand (usually an organic molecule) is polydentate and thus able to replace two or more of the simple outgoing ligands bound to the central metal.
Cation bridging (Iskrenova-Tchoukova et al. 2010) Cation bridging allows for the interaction of two negatively charged surfaces such as a phyllosilicate and an organic anion	Direct cation bridging Mostly ionic bond	Inner sphere	A bond formed when the hydration shell of a polyvalent cation is displaced. The organic anion becomes directly coordinated to the cation, as in ligand exchange
	Exchangeable (water) bridging Van der Waals forces (see below)	Outer sphere	Here water is not displaced and the cation interacts with the organic anion essentially through hydrogen bonding (see below). Both polyvalent and monovalent cations can participate in this type of interaction. It has sometimes been labelled 'water bridging', although this term remains ambiguous, as it has also been used to describe ligand exchange reactions. The term 'exchangeable bridging', which has been coined to describe the cation exchange phenomenon, may be more descriptive
Hydrophobic interactions (Spaccini et al. 2002) These occur whenever non-polar substances exist in a polar solvent, such as water	Entropy-driven structure	Outer sphere	Aggregation of non-polar substances caused by the repulsion of hydrophobic molecule by water. Hydrophobic interactions also take place during the clustering of amphiphillic molecules into bilayers and micelles (hydrophilic exterior protecting a hydrophobic core)
Other 'weak' interactions (van der Waals) (Israelachvili 2011) While weak, these forces are additive meaning that in complex substrates such as those commonly found in SOC, many van der Waals interactions can combine to create apparent strong sorption	Dipole–dipole force	Outer sphere	The electrostatic attraction between molecules with permanent polarity, arising from differences in the electronegativity of their atomic constituents
	Hydrogen bonding	Outer sphere	Hydrogen bonding refers to a specific type of dipole–dipole interaction, which occurs when a hydrogen atom bonded to a strongly electronegative atom (typically F, O, or N) interacts with another electronegative atom. These interactions are stronger than ordinary dipole–dipole forces
	London dispersion (induced dipole) force	Outer sphere	Temporary and weak attractive force arising from the unequal movement of electrons within a molecule, turning it momentarily into a dipole. Unlike dipole–dipole interactions, the London dispersion force does not arise from a difference in the electronegativity of component atoms, but merely the correlated movements of electrons in interacting molecules

The references point to one recent example of study in soil science and NanoSIMS to observe the direct adsorption of isotopically labelled SOM on a clay fraction during incubation. The authors found that SOM was preferentially associated with rough areas of nano-mineral clusters, including micropores, etch pits, and cracks. However, the preservation of organic C at these stabilisation 'hotspots' is difficult to ascribe to a single mechanism. As hypothesised by Kögel-Knabner et al. (2008), adsorption of SOC within these rough areas provides a twofold stabilisation of SOC, where the accessibility of the substrate to decomposers is reduced and the substrate is concomitantly stabilised by the aforementioned mechanisms of sorption. Therefore, at the molecular-scale, it seems that stabilisation by both physical separation and adsorption simultaneously co-occur (Fig. 1) and become indistinguishable (Chenu and Plante 2006; Kögel-Knabner et al. 2008; Vogel et al. 2014), thus questioning the conceptual segregation of the mechanisms enumerated by Sollins et al. (1996).

Ca-mediated SOC stabilisation

Ca–SOC interactions

Research into SOC stabilisation has typically focused on acidic soil environments and the effects of Al^{3+} or Fe^{3+} or their poorly crystalline forms on SOC (Grünewald et al. 2006; Kögel-Knabner et al. 2008). Basic soil environments, and potential interactions between the Ca and C cycles have received comparatively less attention (Grünewald et al. 2006). Yet, Ca is the most abundant alkaline earth metal in the Earth's crust, making up 2.94% of the upper continental crust (Wedepohl 1995). Furthermore, calcareous or Ca-rich

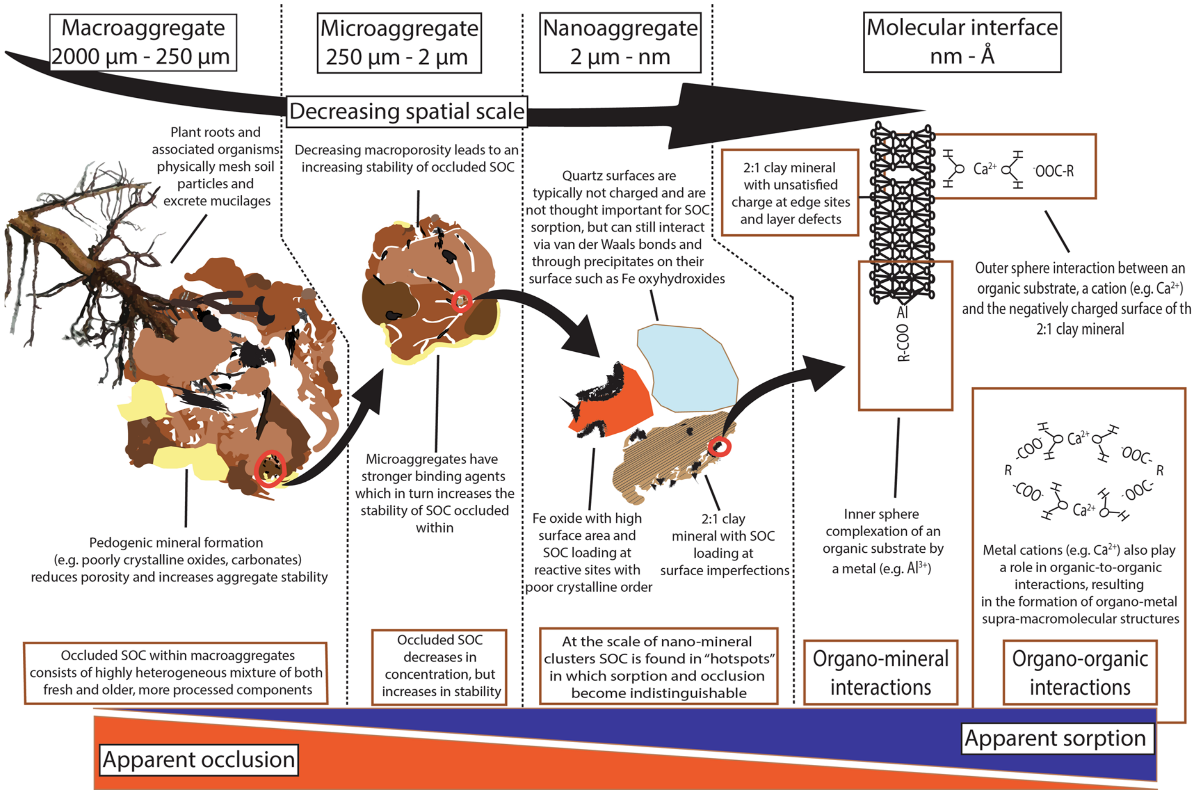


Fig. 1 Occlusion and sorption co-stabilise soil organic carbon at all spatial scales, but this co-occurrence becomes more apparent at the nano-scale where they become operationally indistinguishable

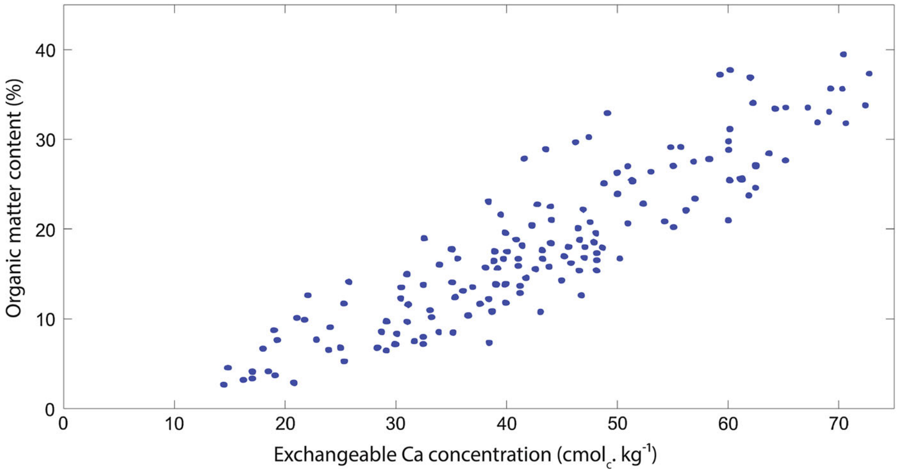
soils cover more than 30% of the Earth's surface (Bertrand et al. 2007; Chen and Barak 1982) and basic soils account for at least 12% of the world's soil resources (Grünewald et al. 2006). Ca^{2+} within a soil matrix typically originates from the weathering of lithosphere or surficial formations (Dijkstra et al. 2003; Likens et al. 1998), decomposition of Ca^{2+}-rich organic materials (Ranjbar and Jalali 2012), the lateral movement of Ca^{2+}-rich water (Clarholm and Skyllberg 2013), atmospheric dust deposition (Dijkstra et al. 2003; Pulido-Villena et al. 2006) or anthropogenic inputs. Ca^{2+} is weathered with relative ease from both primary and secondary minerals (Likens et al. 1998) and has therefore typically been thought to persist or accumulate chiefly in semi-arid to arid environments. However, Ca-rich environments also exist within temperate regions on soils developed from calcareous parent material, out-of-equilibrium with climate (Slessarev et al. 2016). High Ca concentrations are also commonly found in the topsoil of acid soils derived from crystalline lithologies due to biological cycling (Cailleau et al. 2004; Federer and Hornbeck 1985; Grand & Lavkulich 2013; Likens et al. 1998; Ross et al. 1991). Therefore, Ca^{2+} is an environmentally ubiquitous cation that could potentially play an unaccounted role in the stabilisation of SOC.

The first investigation into the interactions between Ca and SOC was published almost 80 years ago by Sokoloff (1938), who provided experimental evidence that organic matter solubility decreased upon addition of Ca when compared to Na addition. Since then, research in Ca-rich field environments has highlighted a positive correlation between exchangeable Ca^{2+} (Ca_{Exch}) and SOC concentration (see Fig. 2; Bertrand et al. 2007; Bruckert et al. 1986; Clough and Skjemstad 2000; Duchaufour 1982; Gaiffe et al. 1984; Oades 1988; Paul et al. 2003; Shang and Tiessen 2003). As an example, Yang et al. (2016) recently established that alpine grassland soils in the Neotropics contained nearly double the concentration of SOC (405.3 ± 41.7 t ha^{-1}) when developed on Ca-rich, calcareous lithology than their acidic counterparts (226.0 ± 5.6 t ha^{-1}). Similarly, O'Brien et al. (2015) and Li et al. (2017) demonstrated that Ca_{Exch} was the strongest explanatory variable for SOC concentration of grasslands. However, identification of the exact mechanisms responsible for this widespread correlation remain elusive.

A simple case of co-occurrence?

The positive correlation between Ca_{Exch} and SOC could be explained by their simple co-occurrence, as an increase in SOC concentration generally increases the cation exchange capacity (CEC) of a soil (Yuan et al. 1967). Calcium is a plant macronutrient and there is evidence that Ca also has a localised positive effect on net primary productivity (NPP) and SOM inputs through above-ground and below-ground biomass (Briedis et al. 2012b; Carmeis Filho et al. 2017; Paradelo et al. 2015). This localised effect on NPP has been shown to positively influence the accumulation of SOC in limed Ferralsols (Oxisols; Briedis et al.

Fig. 2 Positive relationship between exchangeable calcium (centimoles of charge per kg) and soil organic carbon concentration (%) in the Jura Mountain range, adapted from Gaiffe and Schmitt (1980)



2012b; Carmeis Filho et al. 2017) and could explain a portion of the differences in SOC concentration observed between acidic and calcareous soils. However, these explanations fail to account for the decrease in respiration rate (per unit C) associated with Ca prevalence and observed in multiple field studies (Groffman et al. 2006; Hobbie et al. 2002) or incubation experiments (Minick et al. 2017; Whittinghill and Hobbie 2012). These results are at first glance counter-intuitive since the addition of Ca^{2+} to an edaphic ecosystem is also linked to a change in decomposer communities composition from fungi- to bacterial dominance (Blagodatskaya and Anderson 1999; Rousk et al. 2009, 2010) and an improvement in conditions for bacterial decomposition (Illmer and Schinner 1991; Ivarson 1977; Zelles et al. 1987), at least partially due to the buffering of soil pH to circumneutral levels (Narendrula-Kotha and Nkongolo 2017). It would thus be expected that the rate of enzymatic decomposition of SOC would increase when Ca^{2+} saturates the exchange complex (Andersson et al. 1999; Chan and Heenan 1999; Thirukkumaran and Morrison 1996). This could be the case in the organic (litter) layer (Minick et al. 2017), but is generally not observed in the mineral soil. Contrary to hypotheses formulated in both studies, Hobbie et al. (2002) and Groffman et al. (2006) found that microbial respiration was actually lower in Ca-rich environments, even though physicochemical conditions for microbial activity were improved. Furthermore, lab experiments have shown that Ca_{Exch} concentration is correlated with a reduction in SOC leaching losses (Minick et al. 2017), photo-oxidation (7%; Clough and Skjemstad 2000) and respiration as CO_2 during incubation (Minick et al. 2017; Whittinghill and Hobbie 2012). Therefore, Ca_{Exch} seems to be linked to a reduction in the propensity of C substrates for decomposition that is not solely linked to its effects on NPP or microbial ecology.

Consequently, this review will investigate the potential mechanisms behind the stabilisation and accumulation of SOC mediated by Ca and its mineral forms, namely their influence on:

(i) aggregation and the occlusion of SOC;
(ii) inclusion of SOC within pedogenic- or biogenic-$CaCO_3$;
(iii) organo-mineral and organo-cation interactions.

Mechanisms for Ca-mediated SOC stabilisation

Occlusion: Ca and aggregation

The Ca ion and aggregates

It is widely accepted that Ca^{2+} has a significant positive effect on aggregation and soil structural stability and therefore, indirectly influences the accumulation and occlusion of SOC. Early authors demonstrated an influence of Ca^{2+} on soil aggregation (Martin et al. 1955; Peterson 1947). This dependence was further investigated by Gaiffe et al. (1984) who demonstrated that the removal of Ca_{Exch} and its replacement by K_{Exch} led to a disruption of aggregates. As theorised by Edwards and Bremner (1967), one of the main mechanisms thought to be behind this stabilisation is the flocculation of negatively charged separates by outer sphere interactions involving Ca^{2+}, which is explored further in the following section on sorption processes. This process operates in the bulk soil and it has also been hypothesised that Ca^{2+} could play a role in flocculating particles in the gut of certain earthworm species, leading to the formation of 'Ca humates' (Satchell 1967). This was supported by the results of Shipitalo and Protz (1989) who utilised micromorphology and chemical pre-treatments to infer that Ca probably played a role in flocculating particles within earthworm casts of certain species, stabilising the microaggregates within them. Another mechanism for the stabilisation of aggregates in Ca-rich environments involves the formation of complexes between Ca and high-molecular weight organic compounds such as root mucilages or microbial polysaccharides/polymeric substances. It has been shown that these substances readily complex Ca^{2+} and create gel-like structures that bind aggregates (Czarnes et al. 2000; de Kerchove and Elimelech 2007; Erktan et al. 2017; Gessa and Deiana 1992). In particular, galacturonic acids, a common root mucilage, display a high affinity towards Ca, which links polymer chains to form an adhesive matrix (de Kerchove and Elimelech 2007). Czarnes et al. (2000) also showed that these polygalacturonic acid gels increase the hydrophobicity of aggregates, thereby increasing their stability during wetting and drying cycles. Further investigation is needed to analyse the role that adhesive Ca-mucilage matrices play in aggregate stabilisation and the occlusion of SOC.

The effects of carbonate on aggregates

Interactions between Ca-bearing secondary minerals and soil structure have been extensively covered in the literature because of the use of liming ($CaCO_3$ addition) in agriculture. There have been many experiments that have documented the positive effects of the addition of calcite/aragonite ($CaCO_3$) or gypsum ($CaSO_4.2H_2O$) on the structure of non-calcareous soils (Armstrong and Tanton 1992; Baldock et al. 1994; Briedis et al. 2012a; Grant et al. 1992; Grünewald et al. 2006; Inagaki et al. 2017; Kaiser et al. 2014; Melvin et al. 2013; Muneer and Oades 1989a; Paradelo et al. 2016). Some authors have also assessed the effects of $CaCO_3$ removal from calcareous soils on aggregate stability, finding that the treatment reduced soil structural stability and increased porosity (Falsone et al. 2010; Muneer and Oades 1989c; Toutain 1974; Virto et al. 2011). Furthermore and reminiscent of the work of Oades and Waters (1991) on Fe oxides in Ferralsols (Oxisols), Fernández-Ugalde et al. (2011) demonstrated that the hierarchical model of aggregation was partially disrupted by carbonate. In the semi-arid Mediterranean soils of their study, the authors showed that the abundance of $CaCO_3$ controlled macroaggregate turnover and increased their stability, to the extent that the usual disruption of macroaggregates, leading to the release of constituent microaggregates, was prevented (Fernández-Ugalde et al. 2011; Oades 1984).

There are several mechanisms by which $CaCO_3$ could positively affect aggregate stability and the occlusion of SOC. $CaCO_3$ is easily weathered and acts as an abundant source of Ca^{2+}, thus encouraging the flocculation of soil separates and aggregation through the mechanisms listed above (Baldock and Skjemstad 2000; Clough and Skjemstad 2000; Wuddivira and Camps-Roach 2007). Carbonate ions are also capable of reprecipitation with Ca^{2+} under the right environmental conditions, forming secondary $CaCO_3$ crystals (from micrite to sparite) that cement aggregates (Fernández-Ugalde et al. 2011, 2014; Shang and Tiessen 2003; Virto et al. 2013). This mechanism was analysed in detail by Falsone et al. (2010), who utilised N_2 adsorption and Hg porosimetry to demonstrate that this formation of secondary $CaCO_3$ crystals decreased aggregate porosity in the 2–50 nm range and thus, decreased the accessibility of intra-microaggregate SOC to decomposers. Certain earthworm species have also been shown to cement particles that pass through their gut with a mixture of poorly crystalline biogenic carbonates (calcite, vaterite, aragonite) excreted from their calciferous glands (Brinza et al. 2014; Edwards and Bohlen 1995). The cementing effect of carbonates on aggregates is well-documented in arid soils in which large concentrations of pedogenic carbonates are found (Fernández-Ugalde et al. 2011, 2014; Virto et al. 2013). However, it may also play a role in humid or sub-humid environments where carbonate-rich parent materials are continually getting dissolved and locally reprecipitated, but this still needs to be investigated further.

Although it is widely accepted that the occurrence of $CaCO_3$ positively affects soil structure and offers favourable conditions for the stabilisation of SOC by occlusion, its actual consequence on occluded SOC stocks is less clear. In a recent review, Paradelo et al. (2015) concluded that while $CaCO_3$ addition had a clear positive effect on soil structure, its effect on occluded SOC stocks was uncertain. Positive (Egan et al. 2018; Muneer and Oades 1989a, b), non-existent (Paradelo et al. 2016) or negative effects (Chan and Heenan 1999) of $CaCO_3$-amendment on occluded SOC have indeed been reported. In some instances, it may be difficult to disentangle the integrative effects of agricultural management from the simple effects of $CaCO_3$ additions. In natural, unamended soils, Fernández-Ugalde et al. (2014) showed that carbonates had a positive effect on occluded SOC stocks. This finding needs to be replicated in a range of natural soils, as differences in initial conditions (e.g. texture, mineralogy, organic inputs and their distribution) could reasonably result in different outcomes.

Inclusion

Inclusion is defined as the envelopment of SOC within a mineral or cogenetic mineral assemblage that leads to its physical protection (Babel 1975). Stabilisation of SOC by inclusion works through a similar mechanism to intercalation or occlusion, by physically separating a substrate from decomposers. SOC may be trapped within any form of pedogenic carbonates, but its inclusion may not be quantitatively important when carbonate formation chiefly occurs through abiotic processes. Diaz et al. (2016) recently dated small concentrations of SOC (0.1–0.5%) included within pedogenic carbonate nodules in Cameroon with C^{14} measurement, recording ages ranging between 8000 and 13,000 years. This highlights the potential of this mechanism to stabilise SOC over long time periods, but probably only in small concentrations.

Calcium carbonate is one of the most abundant biominerals on Earth and can be synthesised by a wide range of terrestrial organisms (Skinner and Jahren 2007). Biomineralisation of $CaCO_3$ can either be induced within cells, mediated by biological activity that stimulates physicochemical precipitation, or initiated by the presence of an existing biological matrix that initiates crystal nucleation and growth in the extracellular environment (Bindschedler et al. 2016). During each of these forms of biomineralisation, SOC can become included and encapsulated within the crystal structure (Verrecchia et al. 1995). A few specific examples of biogenic carbonate forms include calcified root cells, fungal filaments and rhizoliths (calcified roots; e.g. Becze-Deàk et al. 1997; Jaillard et al. 1991; Monger et al. 1991), calcified earthworm biospheriods (Barta 2011), and the mineralisation of bacterial or fungal organic templates (Bindschedler et al. 2014; Cailleau et al. 2009). Another mechanism for the inclusion of SOC could be biomineralisation pathways such as the oxalate-carbonate pathway (Verrecchia 1990). The oxalate-carbonate pathway involves biomineralisation of $CaCO_3$ during the bacterial catabolism of calcium oxalate-rich SOC produced by plants or fungi. It thus intimately links SOC to the nucleation site of $CaCO_3$ biomineralisation and could allow its inclusion within the crystal matrix in both acidic (Cailleau et al. 2004, 2005; Verrecchia et al. 2006) and calcareous soils (Rowley et al. 2016). However, there has been very little direct quantification of the concentrations or ^{14}C ages of SOC included within biogenic carbonate forms, which could potentially contain much higher SOC concentrations than abiotically-formed pedogenic carbonates. Therefore, further investigation is now needed to quantify the inclusion of SOC within biogenic carbonate and its role in SOC dynamics.

Sorption: Ca, minerals and organics

Organo-mineral interactions with calcite

Lithogenic and pedogenic $CaCO_3$ could also play a key role in the stabilisation of SOC via adsorption. Most of the research into direct organo-calcite interactions has focused on the interactions between DOC and calcite in sorption experiments. Earlier work by Suess (1970) and Carter (1978) showed that DOC could be directly adsorbed onto $CaCO_3$, while Suzuki (2002) more recently showed that $CaCO_3$ was an effective adsorbant of DOC from black tea solutions, possibly due to its high point of zero charge (9.5; Grünewald et al. 2006). Thomas et al. (1993b) more specifically studied the affinity of different synthetic carbonates for common organic functional groups and demonstrated that calcite, dolomite, and magnesite all sorbed a wide range of organic compounds, which included carboxylic acids, alcohols, sulphates, sulfonates, amines, amino acids and carboxylated polymers. Interestingly, interaction with DOC has been shown to modify carbonate precipitation equilibria, by inhibiting either further crystal precipitation (Inskeep and Bloom 1986; Reddy et al. 1990; Reynolds 1978) or the dissolution of sorbent minerals (Thomas et al. 1993a). Jin and Zimmerman (2010) established that $CaCO_3$ obtained from aquifers preferentially adsorbed dissolved organic matter with a high molecular weight, which the authors attributed to a form of outer sphere interaction. It has been theorised that the kinetics of DOC adsorption by carbonates may be biphasic, occurring through an initial rapid phase of outer sphere interactions, which is then followed by a slower phase of inner sphere and hydrophobic interactions that in turn protect the carbonate surface from dissolution (Jin and Zimmerman 2010; Lee et al. 2005; Thomas et al. 1993b). While these DOC adsorption experiments have provided interesting insight into potential $CaCO_3$–SOC interactions, there has been relatively little direct research on the adsorption of SOC by different forms of calcite/aragonite in soils. Measurements of soil carbonate content commonly differentiate between a reactive and a total pool (Pansu and Gautheyrou 2006), but there is little evidence for the role of these operationally-defined pools in adsorption of SOC. Further research should focus on the effects of the supposedly reactive, poorly crystalline or amorphous $CaCO_3$ pool on the adsorption of SOC in natural environments.

Outer sphere processes

Irrespective of their carbonate content, many soils have significant concentrations of free Ca^{2+} which may also contribute to the stabilisation of SOC. The widely observed correlation between Ca_{Exch} and SOC has led to the implicit assumption that Ca^{2+} predominantly affects SOC through weak outer sphere interactions (von Lützow et al. 2006), such as those contributing to the retention of exchangeable cations (Table 1). This form of cation bridging by Ca^{2+} has been highlighted as an important component of SOC stabilisation by many authors and is well-documented (Clough and Skjemstad 2000; Edwards and Bremner 1967; Oades 1988). As illustrated in the lyotropic series, cations' outer sphere (exchangeable) behaviour is related to the size of their hydration shell and valence. This is confirmed by chemical modelling, which indicates that exchangeable bridges by Ca^{2+} typically have a larger residence time than those of monovalent cations, like Na^{+}, because the charge-to-hydration radius ratio of Na^{+} prevents it from efficiently countering the repulsion between negatively-charged surfaces (Iskrenova-Tchoukova et al. 2010; Sutton et al. 2005). Thus, Ca^{2+} is a fundamental flocculating agent of natural systems because of its ability to form efficient outer sphere bridge units.

However, it is interesting to note that Al^{3+} and H^{+} rate higher than Ca^{2+} on the lyotropic series and should thus cause similar or higher levels of apparent flocculation in soils in which they are abundant, such as most acid soils. Yet, it is widely observed that colloidal mobility is enhanced in acidic environments where Al^{3+} and H^{+} dominate and there is little or no Ca^{2+} present, such as those associated with the formation of Luvisols (Lavkulich and Arocena 2011). It is also worth considering that the innate reversibility of outer sphere interactions should mean that exchangeable Ca bridges would not be inherently persistent in natural soils. These considerations lead us to explore the possibility that interactions between Ca and SOC are not solely attributable to outer sphere (exchangeable) processes and that, despite its correlative association with SOC, Ca_{Exch} may not be solely responsible for the bulk of SOC stabilisation in Ca-rich soils.

Inner sphere processes

It is generally observed that each cation has a different range of interactions in soils. For instance, trivalent Fe is seldom found in large amounts as a free ion in soil, as it very readily hydrolyses to form insoluble precipitates under most environmentally-relevant conditions. Al^{3+} also hydrolyses into insoluble hydroxides at slightly acidic to basic pH, while in acidic soils, it is found to participate both in outer sphere, cation exchange and inner sphere, ligand exchange reactions. Ca^{2+} is thought to retain its hydration shell and behave strictly like an exchangeable cation, as are other 'base' cations such as Mg^{2+}, K^{+} and Na^{+} (Essington 2004). However in soil science, the fundamental controls on the propensity of each cation to form inner sphere complexes with SOM are not as well understood as the affinity of cations for non-specific exchange sites.

One of the reasons for this is that there are many factors that can influence inner sphere complexation of SOM by ions in the soil matrix, including characteristics of cations (ionic potential, electronegativity, polarisability of their electron cloud, hydrated radii, propensity to retain their hydration shell), of ligands (amount and type of organic functional groups) and of the environment (pH, ionic strength, solution composition, metal-to-ligand ratio, pressure and temperature conditions; Essington 2004). Cations can be broadly split into three classes (Class A, B, and intermediate/C) based upon the polarisability of their electron cloud, which in turn, indicates how likely they are to form inner sphere complexes with specific ligands (Ahrland et al. 1958; Pearson 1963; Schwarzenbach 1961). Class A cations are weakly polarisable and tend to form complexes with O-containing ligands, such as carboxylate functional groups through ionic bonding. On the other hand, Class B cations have a labile electron cloud and tend to form complexes with N- or S-bearing ligands through more covalent bonding (Langmuir 1997; Sposito 2008). Al^{3+} and the base cations, including Ca^{2+}, are considered group A cations, indicating that they may theoretically form inner sphere complexes with widely-occurring O-bearing ligands such as carboxylate groups (Sposito 2008). However, each cation's actual behaviour in soil cannot be predicted from one or a couple of first-principles only, as it results from the interaction of several factors. For instance, Na is not generally seen to engage in inner sphere complexation in soils, while

K only does so in the interlayer of specific phyllosilicates. Advanced chemical modelling can offer insight into these issues.

Authors have modelled the interactions between dissolved organic C (DOC) and Ca^{2+} in an attempt to investigate their molecular-scale interactions (Aristilde and Sposito 2008; Benedetti et al. 1995). These models suggest that Ca^{2+} can bind to SOC through both inner sphere and outer sphere processes (Bogatko et al. 2013; Iskrenova-Tchoukova et al. 2010; Kalinichev and Kirkpatrick 2007; Sutton et al. 2005). Sutton et al. (2005) modelled the complexation of deprotonated carboxyl groups by Ca^{2+} and found that their interactions were predominantly inner sphere (75%). The model of Kalinichev and Kirkpatrick (2007) also confirmed that Ca^{2+} could form direct cation bridges with carboxylate and to a lesser extent, phenolic and other –OH functional groups, unlike Mg^{2+}, whose hydration water is more tightly held (Dontsova and Norton 2002; Kalinichev and Kirkpatrick 2007; Tipping 2005). Chemical modelling thus indicates that Ca^{2+} can interact with SOC through inner- and outer-sphere processes, thereby potentially increasing SOC stability against decomposition or leaching (Minick et al. 2017).

Building empirical evidence for Ca–SOC interactions

While models predict that Ca^{2+} can form both inner- and outer-sphere bridges with SOC, empirical evidence of these associations in natural environments remains scarce. Density fractionation, which separates free, occluded and mineral-associated SOC (Golchin et al. 1994) has the potential to offer insight. When performed sequentially (Sollins et al. 2009), density fractionation can separate SOC fractions associated with different minerals; furthermore, because the method uses extremely concentrated salt solutions (usually Na polytungstate), outer sphere associations are not expected to survive the treatment, meaning that only strong (inner sphere) association with minerals are considered. Wen et al. (2017) recently showed that there was more SOC associated with calcite-rich than with dolomite-rich heavy fractions, possibly corroborating modelling predictions of stronger SOC association with Ca than Mg (Kalinichev and Kirkpatrick 2007). The occluded fraction was however not separated from the mineral-associated fraction, so that the results remain somewhat equivocal. Further density fractionation studies analysing the relative role of occlusion and sorption for SOC accumulation in Ca-rich soils would undoubtedly prove informative. Density fractionation is however a costly and time-consuming technique (Poeplau et al. In review) and may be difficult to use in calcareous soils, since polytungstate left in contact with free Ca for extended periods can precipitate as insoluble Ca-metatungstate. Methods applicable to the bulk soil would constitute useful complements to fractionation approaches.

Selective extractions on bulk soil have typically been used to analyse the effects of cation pools on SOC stocks. As indicated in Fig. 2, the operationally defined Ca_{Exch} pool, extracted by salt solutions, represents a reactive and abundant pool of Ca^{2+} that is regularly correlated with SOC concentration (Bruckert et al. 1986; Gaiffe and Schmitt 1980; Li et al. 2017; O'Brien et al. 2015), thus highlighting its potential as an indicator variable for the measurement of Ca^{2+} interacting with SOC. However, by definition, Ca_{Exch} only represents Ca^{2+} engaged in outer sphere interactions. The selective chemical extraction of the inner sphere Ca pool, corresponding to pyrophosphate extractions for Al and Fe in acidic soil environments (Bascomb 1968; Parfitt and Childs 1988; Rasmussen et al. 2006), is challenging due to the insolubility of most chelating agents once complexed by Ca (e.g., Ca-pyrophosphate or Ca-oxalate). In a recent study, van der Heijden et al. (2017) isolated a "non-crystalline pool of Ca" in acidic, base-poor soils, which may have included a significant contribution of Ca complexed by SOM, but the extract (dilute oxalic + nitric acid) was not specific to organic complexes. Extraction with other chelating agents that remain soluble in their Ca form (e.g. ethylenediaminetetraacetic acid, EDTA; Bélanger et al. 2008) or with salts of strong cation complexants (e.g. copper chloride; Barra et al. 2001; Juo and Kamprath 1979) may be informative; however, these extractants could also attack the mineral $CaCO_3$ pool, making their use difficult in calcareous soils.

Alternatively, X-ray absorption spectroscopy (XAS) could eventually be used to investigate the coordination environment of Ca^{2+}–SOC complexes under different environmental conditions. As an example, Martin-Diaconescu et al. (2015) have recently successfully probed the coordination environment of synthetic Ca complexes. While powerful, these direct spectroscopic techniques require the use of synchrotron light source and can only be applied to small amounts of samples with limited compositional complexity. We are still lacking a method that allows for the routine assessment of inner sphere Ca–SOM complexes and their relative importance in different soils, which constitutes a significant research gap given the potential for inner sphere interactions to stabilise SOM with increased efficiency (Mikutta et al. 2007), and perhaps through ecosystem disturbance events (Basile-Doelsch et al. 2009; Grand and Lavkulich 2012).

Implications for conceptual models of SOC cycling

Despite the growing body of evidence supporting a major role for specific soil minerals and cations in SOC stabilisation (Doetterl et al. 2015), soil mineralogy and geochemistry are largely absent from leading models of SOC cycling. The following section will discuss a few processes that have the potential to improve representations of SOC stabilisation, with particular emphasis on Ca-rich soils.

Digressing from the expected profile-scale depth distributions

In addition to their influence on the total amount of SOC retained in soil, polyvalent cations are suspected to influence its vertical distribution in soil profiles. Current pedometric approaches to mapping soil C acknowledge the importance of accounting for soil type when estimating the vertical distribution of SOC (Kempen et al. 2011; Wiese et al. 2016). Polyvalent cations can indeed cause departures from the generally assumed exponential decline of SOC concentration with depth (Hilinski 2001). A classical example involves Podzols characterised by the effective translocation of Al–SOC complexes to deep soil horizons (Ferro-Vázquez et al. 2014; Grand and Lavkulich 2011). Contrastingly, Calcisols have an accumulation of Ca-saturated SOC in surface horizons (Yang et al. 2016). This accumulation of Ca-saturated SOC is likely caused by the complexation, flocculation, and precipitation of organic acids and clays in the presence of Ca, precluding their translocation to subsoil horizons. Two of the most common low molecular weight organic acids (oxalic and citric acids) in soil notably form sparingly soluble salts in the presence of Ca (calcium oxalate $K_{sp} \approx 10^{-8.5}$; Certini et al. 2000), preventing their translocation, whereas their Al and Fe counterparts are highly soluble (Gadd 1999). The fundamental differences in how polyvalent cations modulate SOC inputs, stability and depth distributions highlight the critical importance of accounting for geochemical factors when modelling SOC dynamics.

Preferential sorption

Integrating a geochemical dimension into conceptual models of SOM dynamics is also important because the formation of organo-mineral complexes appears to be a preferential process, with selectivity exhibited by both the organic and mineral component (Spielvogel et al. 2008). Very little is actually known about the preferential nature of organo-mineral interactions in soils. To date, there is some evidence within the literature that specific organic compounds such as N-rich microbial metabolites, microbial cell-wall fragments, and possibly pyrogenic C may be selectively sorbed by soil minerals (Brodowski et al. 2007; Jin and Zimmerman 2010; Miltner et al. 2012; Scheel et al. 2008; Schurig et al. 2013; Spielvogel et al. 2008). Furthermore, it has been suggested that some reactive mineral surfaces, such as those of Al and Fe phases, may be disproportionally involved in the sorption of specific classes of organics, such as proteins, lignin, and phenolic compounds (Heckman et al. 2013; Kögel-Knabner et al. 2008; Xiao et al. 2015). However, there have been very few studies looking at the potential preferential sorption of organic compounds in Ca-rich edaphic environments.

If molecular scale stabilisation of SOC by Ca^{2+} predominantly occurs through inner- or outer-sphere cation bridging, then it should preferentially target functional groups such as carboxyls and phenols. Römkens and Dolfing (1998) and Kaiser (1998) accordingly demonstrated that Ca^{2+} preferentially flocculated and precipitated high molecular weight DOC compounds, which contained higher proportions of carboxylic and phenolic functional groups. There is also evidence for the preferential adsorption of negatively charged products of lignin degradation (syringyl units; Grünewald et al. 2006) and DOC (Jin and Zimmerman 2010; Jin et al. 2014) by calcite. The implications of this hypothesis for our understanding of SOC dynamics could be profound. It could

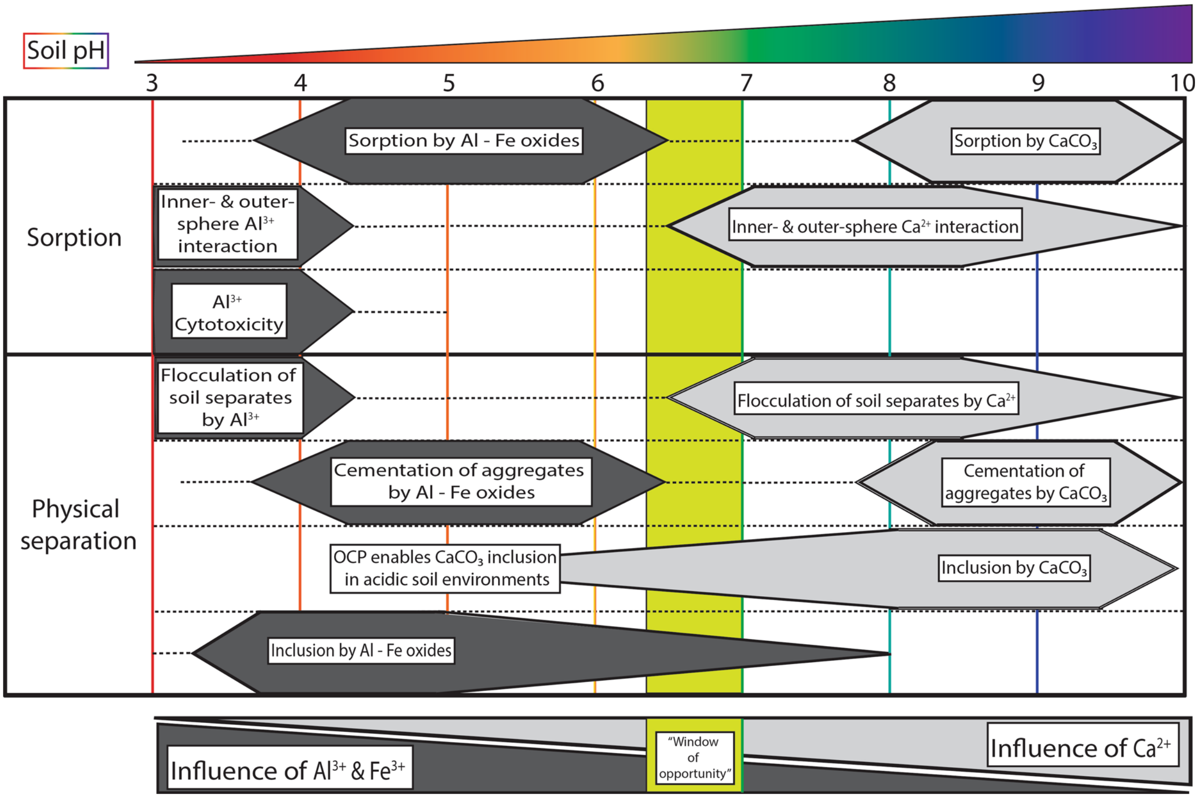


Fig. 3 The shifting role of polyvalent cations in the stabilisation of SOC with increasing pH. A 'window of opportunity' for microbial decomposition is highlighted in green according to the proposition of (Clarholm and Skyllberg 2013). Thresholds are based on values available in the literature and it is expected that adjustments will occur as more results become available. Al–Fe oxides refer to true oxides as well as oxyhydroxides and their poorly crystalline forms. *OCP* oxalate-carbonate pathway

potentially provide a mechanism to bridge the two competing hypotheses of SOC persistence, i.e. biochemical recalcitrance *vs.* mineral association, since organic compounds with different compositions could have different probabilities for sorptive preservation. This perspective is highly relevant to SOC modelling. As an example, the CENTURY model assumes universal preservation of lignin in stable SOC pools (Parton 1996; Parton et al. 2015), which has been questioned by experimental evidence (Gleixner et al. 1999, 2002). Accruing evidence on selective sorption of specific compounds to minerals or cations, including lignin derivatives, could speak in favour of considering SOC biochemical composition as a predictor of residence time, but the parametrisation would have to be adjusted for different geochemical environments.

Conversely, Minick et al. (2017) demonstrated that high additions of Ca at the Hubbard Brook experimental forest specifically reduced the mineralisation of ^{13}C-depleted SOC, which should represent a relatively fresh pool, little affected by oxidative transformation (Rumpel and Kögel-Knabner 2011), thus contradicting the hypothesis that Ca^{2+} preferentially stabilises oxidised SOC. Yet stabilisation of ^{13}C-depleted SOC could simply imply that occlusion was the predominant mechanism of SOC stabilisation at the Hubbard Brook forest. SOC occlusion could limit the mineralisation of ^{13}C-depleted sources because aggregates occlude a heterogeneous mixture of both ^{13}C-enriched, decomposed and relatively fresh, ^{13}C-depleted particulate-organic matter (Poeplau et al. In review). However, this still requires further evidence. Future investigation should specifically focus on the relative importance of occlusion and adsorption for SOC stabilisation, as influenced by the geochemical environment (dominant free cation) and the composition of organic components (esp. prevalence of functional groups).

pH: the master variable for SOC stabilisation mechanisms?

As pH shifts from acidic to basic conditions, so does the importance of SOC stabilisation by different polyvalent cations and their mineral forms, moving from Al^{3+} or Fe^{3+} to Ca^{2+}, respectively (Tipping 2005). The prevalence of each cation is indeed largely linked to soil pH due to the buffering capacity of primary and secondary minerals, notably calcite and Al oxides (Oste et al. 2002; Slessarev et al. 2016). As each cation is associated with different SOC stabilisation mechanisms (Fig. 3), this shift in pH could arguably be used to predict the concentration and types of SOC being stabilised in each environment. Therefore, we propose the following conceptual model: in acidic environments, complexation of organic ligands by free Al^{3+} and Fe^{3+} as well as their mineral forms (Kalbitz and Kaiser 2008; Scheel et al. 2008) and the cementation of aggregates by Fe oxides (Oades and Waters 1991; Zhao et al. 2017) are likely to control SOC stabilisation. There could also be a localised effect of Ca in the topsoil of these acidic environments caused by biological cycling and resulting accumulation of Ca (Clarholm and Skyllberg 2013). As soil pH increases above 6, Ca^{2+} becomes more prevalent and consequently, there should be increased evidence of SOC stabilisation by inner- and outer-sphere Ca^{2+} bridging or Ca-mediated aggregation (Kayler et al. 2011). As soil pH increases further to $pH > 8.3$, excess Ca^{2+} will begin to precipitate as $CaCO_3$, reducing the stabilisation by free Ca^{2+} at the expense of $CaCO_3$-mediated mechanisms (Lindsay 1979). When soil pH starts to increase beyond pH 9.5, soils will become increasingly sodic and dominated by Na^+, which tends to disperse soil separates, reducing occlusion (Wong et al. 2010) and sorption of SOC (Iskrenova-Tchoukova et al. 2010; Sutton et al. 2005), and consequently weaken SOC stabilisation.

As indicated by Fig. 3, stabilisation of SOC by polyvalent cations is expected to be weakest at near-neutral levels of pH, which also coincides with optimum conditions for bacterial mineralisation (Groffman et al. 2006; Illmer and Schinner 1991; Ivarson 1977; Whittinghill and Hobbie 2012; Zelles et al. 1987). This was suggested previously by Clarholm and Skyllberg (2013) as a “window of opportunity” (highlighted in green; Fig. 3) for C mineralisation. Taking this reasoning a step further, we hypothesize that low and high pH environments will afford different capacities for SOC stabilisation. Given the documented efficiency of sorption by Al and Fe forms and of aggregation by Ca, we postulate that adsorption by Al–Fe oxides generally dominates SOC stabilisation at low pH, stabilising SOC for long time periods; but as the pH increases beyond the “window of opportunity”, it could be expected that the dominant stabilisation mechanism would be occlusion within aggregates, potentially involving larger amounts of SOC but for shorter durations. However, due to the relatively limited body of work on Ca-mediated SOC stabilisation mechanisms, these hypotheses currently remain speculative; the dominant SOC stabilisation mechanisms associated with each cation, the amount of SOC they can affect and the relative strength of the conferred protection still require confirmation. Nonetheless, pH has the potential to act as a fundamental indicator of the mechanisms controlling SOC stabilisation. Therefore, this review suggests that SOC models should consider incorporating pH as a master variable to represent the effects of different stabilisation mechanisms by polyvalent cations and their mineral forms on the accumulation and persistence of SOC.

Conclusions

Although an addition of Ca^{2+} generally improves microbial conditions for decomposition by increasing pH and reducing stress from H^+, it can counter-intuitively reduce respiration rates through the stabilisation of SOC. The main mechanisms behind Ca-mediated SOC stabilisation are likely linked to the ability of Ca^{2+} to bridge negatively charged surfaces. Chemical modelling indicates that Ca^{2+} can bridge SOC and minerals through both inner- and outer-sphere interactions, but this still requires empirical confirmation. When scaled up, Ca bridging also positively affects soil structure; yet surprisingly little is known about the implication for the amount and stability of occluded SOC. The relative prevalence of occlusion and adsorption for SOC stabilisation in Ca-influenced soils needs to be determined, as it could have important consequences for the stabilisation of SOC in terms of its maximum amount, mean residence time but also composition. Indeed, there is some evidence that adsorption could preferentially involve some classes of organic compounds whereas occlusion may be relatively indiscriminate, at least at the macroscopic level. Soil pH could also play a fundamental role in predicting the occurrence of these stabilisation mechanisms and should be considered for inclusion in current SOC models. In order to better represent interactions between the C and Ca cycle in conceptual and numerical models of SOC cycling, we suggest that further mechanistic investigation should focus on the quantification of the relative prevalence and strength of each stabilisation mechanism and their variation across pH thresholds.

Acknowledgements A special acknowledgement must be paid to Dr. Michèle Gaiffe for allowing us to modify her previous diagram and include it in the paper. Thanks also to Dr. Pascal Vittoz, Dr. David Sebag, Prof. Jasquelin Peña, Magali Matteodo, Dr. Nathalie Diaz, Finaritra Randevoson, and Fabienne Dietrich for enjoyable and profitable conversations regarding the manuscript. Special thanks to the Canton de Vaud and IDYST for financially supporting this work and the "*Conseil de coordination scientifique du Vallon de Nant*" for research permissions.

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