Minerals and carbon stabilization: towards a new perspective of mineral-organic interactions in soils

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Abstract

Classical models based on adsorption mechanisms are questioned as the only mechanisms involved in C stabilization in soils. An alternate three-dimensional functional view of carbon turnover dynamics at the microscale has gained ground in recent years. According to this view, soil consists of a multitude of largely independent microreactors formed around microbial cells, cell colonies and fungal hyphae. Mineral particles are conceptualised as components for the construction of small microstructures which are built around microbiota. This view is supported by abundant evidence that substantial parts of mineral surfaces are not covered by organic matter. In this alternate view, minerals may play an ecological function in relation to microbiota. Several experiments have pointed to the active role played by minerals in the functioning and structure of microbiota and their communities. As a result of differences in formation and breakdown processes, each particular type of mineral in soils can show great variation in its shape and size, kinetic and thermodynamic stability, abundance and extent of reactive surfaces. Hence each type is not constant in its ability to provide reactive surfaces and to serve as physical barriers or as suppliers of dissolved cations, which in turn may act as complexing and/or precipitating agents.

Key Words

OM mineralisation, carbon NEXAFS, microreactors, microhabitats, spatial, condensation nuclei.

The paradigm of mineral control: are minerals just adsorbents for organic C?

Significant debate surrounds the question whether the abundance of certain mineral phases might serve to predict the mean residence time of organic matter in soils. Iron oxides from identical soils, for example, may be positively correlated with carbon content in clay subfractions (Kahle *et al.* 2003) but negatively (Kahle *et al.* 2002b) with carbon contents of whole clay fractions. This raises the question if classical stabilization models based on adsorption mechanisms are capable of representing the whole breadth of the mineral-organic interactions involved in C stabilization. While minerals differ widely in the nature and extent of surface reactivity, long-term protection of organic molecules by sorptive interactions appears to be limited to those organic materials directly bonded to the protecting mineral surface (Kleber *et al.* 2005). Kalbitz *et al.* (2003) showed that sorption of soluble OM to subsoil material (Bw horizon) reduced OM mineralisation to 20% to 30% compared to mineralization in soil solution, but a detailed mechanistic understanding of why sorption to soil minerals reduces decomposition rates is lacking and is complicated by artefacts in the experiments.

A new perspective: minerals as rate controlling constituents of micro-bioreactors

Initiated largely by the work of Chenu and collaborators (Chenu and Plante 2006; Chenu and Stotzky 2002) and seconded by recent imaging and X-ray spectroscopic work (Lehmann *et al.* 2007; Lehmann *et al.* 2008; Wan *et al.* 2007), an alternate functional view of carbon turnover dynamics at the microscale has gained ground over the last years. In this view, the two-dimensional concept of soil as a system composed of adsorbent (mineral surface) and adsorbate (soil organic matter) has been extended to a three-dimensional view of soil consisting of a multitude of largely independent microreactors formed around microbial cells, cell colonies and fungal hyphae. Figure 1 illustrates how microbial cells might act as condensation nuclei for soil microstructures, effectively inverting purported causal relationships by suggesting that rather than viewing organics as adsorbates on mineral adsorbents, a better representation of observational evidence would be to conceptualise mineral particles as components for the construction of small microstructures which are built around microbial cells or cell colonies (Spectrum 1 in Figure 1 is archetypical for microbial cells). This view is supported by abundant evidence that substantial parts of mineral surfaces are not covered by organic matter (Arnarson and Keil 2001; Kahle *et al.* 2002a; Mayer and Xing 2001; Ransom *et al.* 1998). This fact is difficult to reconcile with a chromatographic view of soil, where the mineral matrix is conceptualized as an adsorbent and soil organic matter as an adsorbate that is dissolved and/or suspended in the soil solution.
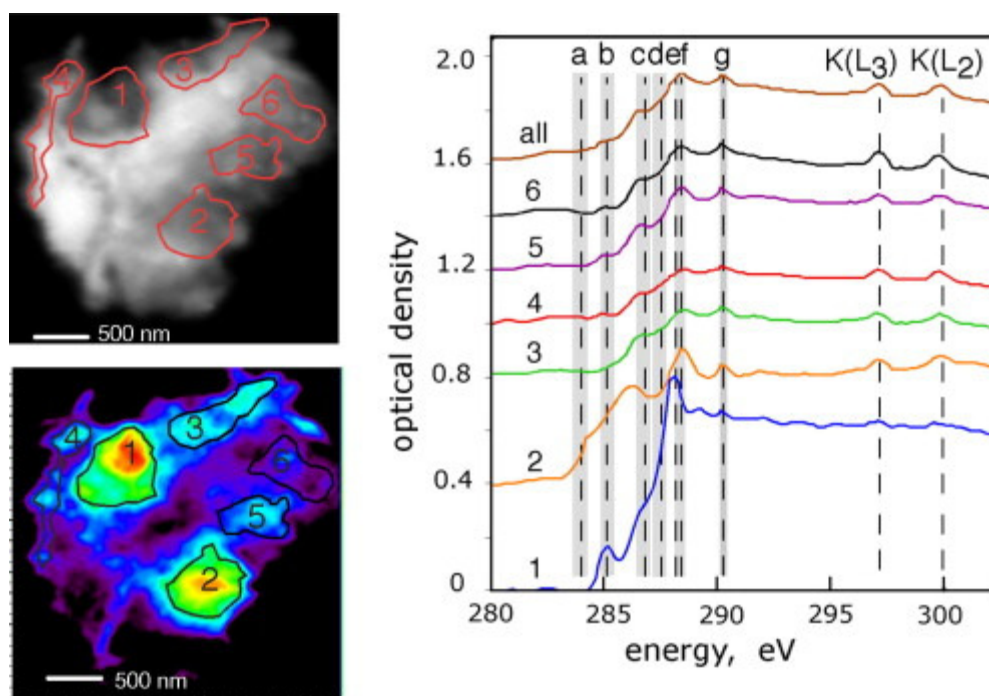
Figure 1. Variations of organic matter composition in close proximity to mineral surfaces within a microaggregate. Carbon NEXAFS spectra obtained within selected areas (regions numbered 1 through 6), and for the whole sample. Spectral features identified by the vertical dashed lines correspond to C in (a) quinonic, (b) aromatic, (c) phenolic, (d) aliphatic, (e) peptidic, (f) carboxylic, and (g) carbonate/carbonyl functional groups. The shaded gray bands indicate energy ranges attributed to each functional group. The peaks at the higher energies result from small amounts of K^+, and correspond to its L_3 and L_2 edges. Figure adopted from Wan *et al.* (2007).

The new view of minerals as building blocks of microbial microreactors raises the question whether minerals simply have structural roles ("bricks") in such microstructures, or whether they have any ecological function, for example, serving as nutrient sources or as alternate electron acceptors at times when oxygen is scarce. Historic knowledge about the role of the microbiota in weathering processes (Barker *et al.* 1998) together with more recent publications on microbial-mineral interactions leave little doubt that the microbiota actively interact with mineral surfaces for a number of purposes. One well known process is the reduction of structural Fe(III) by bacteria on the surface of smectite clay minerals (Kostka *et al.* 2002). The presence of smectite has also been shown to be a key stimulus to the rapid growth of biofilms in a laboratory setting (Alimova *et al.* 2006), with evidence that the microbiota actively create composite organo-clays (Alimova *et al.* 2009). In another recent example, altering the mineral composition of soil caused a shift in microbial community structure (Carson *et al.* 2007), prompting Kotani-Tanoi *et al.* (2007) and Carson *et al.* (2009) to state that the structure of bacterial communities in soil is influenced by the mineral substrates in their microhabitat and that minerals in soil play a greater role in bacterial ecology than simply providing an inert matrix for bacterial growth.

Outlook

Evidence is accumulating that the role of the mineral matrix in carbon stabilization needs to be viewed in a new light. In the past, the effect of mineralogy on SOM turnover has typically been viewed as a matter of variations in surface reactivity. But differences in mineralogy are not just differences in surface chemistry. As minerals are either weathered into fragments or crystallize from solution, they vary in shape and size, kinetic and thermodynamic stability, abundance and extent of reactive surfaces. Consequently, differently sized specimens of the identical mineral can not be considered constant in their ability to provide reactive surfaces, their ability to serve as physical barriers or as suppliers of dissolved cations, which in turn may act as complexing and/or precipitating agents. It appears that scientific progress will require us to add spatial complexity to the classical sorbent-sorbate model of mineral-organic interactions.

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