GAME CHANGER

Perspectives from the Fritz-Scheffer Awardee 2021: Soil organic matter storage and functions determined by patchy and piled-up arrangements at the microscale

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Abstract

Mounting evidence of recent spectromicroscopic insights have revealed that the distribution of mineral-associated organic matter (OM) at the microscale and nanoscale is organized heterogeneously in patchy and piled-up arrangements of varying thickness. Spectromicroscopic approaches could show local deterministic features of distinct OM and mineral composition that influence the heterogeneous lateral OM distribution. OM–OM interactions shape vertical and three-dimensional OM structures with potentially multilayered composition. Conceptualizing mineral-associated OM as patchy-distributed and piled-up has critical implications for our understanding of soil ecosystem functions as it defines their functional properties in compartmentalized regions at the microscale and nanoscale. The concentrated storage of OM associated to only a minor part of mineral surfaces implies that carbon sequestration may be decoupled from a direct limitation by the amount of fine mineral particles while sustaining mineral surface functionality in other parts. At the microscale and nanoscale, differences in altered surface properties, compartmentalized microhabitats, and biotic architectures shape a conceptual understanding where OM storage and other soil functions are driven by spatially resolved interactions. This novel conceptual framework warrants experimental approaches to incorporate the patchy and piled-up arrangement of OM and upscale potential effects of its heterogeneous arrangement to systematically understand the effectiveness of soil functions.

KEYWORDS
novel conceptual framework, organic carbon storage, spectromicroscopy, soil ecosystem functions, soil organic matter

1 | INTRODUCTION

The persistence of organic matter (OM) in soils is of globally recognized significance as soils harbor approximately three quarters of the terrestrial carbon pool (Scharlemann et al., 2014). The study of factors controlling OM storage has thus received considerable attention (e.g., Rasmussen et al., 2018; Stockmann et al., 2013; Wiesmeier et al., 2019). A majority (65%) of the OM in mineral soils globally is associated with minerals and is not found in particulate forms (Sokol et al., 2022). Various inherent soil properties and components have been identified to govern OM interactions with minerals in addition to external factors such as climate, management, and vegetation. Mineral

phases of clay minerals and Fe and Al (hydr)oxides are present as fine-sized particles with highly reactive surfaces that can enhance the physicochemical association of OM in soils (Kleber et al., 2021; Kleber et al, 2015; Torn et al., 1997). A higher content of fine mineral particles and surface is often linked with increased sequestration of OM (Carter et al., 2003; Feng et al., 2014; Stewart et al., 2008). This led to the notion of a limited 'protective' capacity of OM based on the content of fine mineral particles (Campbell & Paustian, 2015; Hassink, 1997; Six et al., 2002; Stewart et al., 2007). However, can a soil really run short of mineral surface area for OM, as might be deduced from such empirical concepts? This aspect is challenged by recent spectromicroscopic advances that provide direct evidence of the spatial arrangement of OM storage at the microscale and nanoscale. Such recent extensions call for a novel conceptual understanding relating the spatial arrangement of OM in complex soil structures with current notions of OM storage and soil functions.

The extent to which individual organic and mineral soil components influence OM persistence may be concerted by the actual spatial arrangement of soil components. Spatial arrangement is a key component of functional complexity, which also includes temporal variability and molecular diversity (Lehmann et al., 2020). As an overarching characteristic, the spatial arrangement of various mineral and organic components at biologically relevant scale in the soil matrix may attenuate or enhance their respective functions. For example, evidence of mineral–mineral interactions (Bucka et al., 2021) and OM–OM interactions (Possinger et al., 2020a) shows that not all the reactive surface areas of respective components contribute to organo–mineral interactions. The high diversity of mineral and organic soil components induces a multifunctionality of simultaneous and dynamic processes driving organo–mineral interactions (Kleber et al., 2021). At the global scale, the relative importance of specific OM stabilization mechanisms was found to vary depending on soil acidity and moisture availability (Rasmussen et al., 2018). At the other end of the scale from pedons to particles, the soil matrix may be organized in compartmentalized regions exerting different functions at the biologically relevant microscale and nanoscale.

The spatial arrangement of biotic processes adds an additional layer of complexity to the arrangement of organic and mineral components based on diverse microbial microsites across the soil matrix. Structural inaccessibility has been identified as a major conceptual mechanism of OM protection (Dungait et al., 2012; Sollins et al., 1996; von Lützow et al., 2006). The fact that much of the OM fate is governed by soil microbes and their spatial access to decompose it is increasingly underpinned by specifically designed experimental approaches (Patel et al., 2021; Ruamps et al., 2011; Shi et al., 2021) and modeling approaches (Ebrahimi & Or, 2015; Mbé et al., 2022; Zech et al., 2022). In fact, microbial hotspots, that altogether represent only approximately 5% of the soil volume, were related with microbial activity an order of magnitude higher than in other parts of the soil matrix while these account for up to 90% of soil CO_2 emissions (Kuzyakov & Blagodatskaya, 2015). While microbial hotspots are often related with a broad size range of a few mm down to a few μm, it is necessary to extend the size scale from a few μm to even finer scales to resolve soil structures where OM dynamics

are driven by structural inaccessibility and unravel underlying mechanisms. Beyond the mere abundance and allocation of individual mineral and organic soil components, it is imperative to gain a comprehensive understanding of how the microscale and nanoscale soil architecture interacts with the arrangement of biotic processes and affects the persistence of OM.

Recent advances of spectromicroscopic techniques have enabled novel insights into the distribution of organo–mineral associations in intact soil structures revealing a heterogeneous distribution. The advances have enabled visualizations of OM storage at biologically relevant scale, that is, resolving individual biotic entities such as fungal hyphae or bacterial cells (Pett-Ridge & Weber, 2022; Vidal et al., 2018; Wilpiszeski et al., 2019). Across the variety of spectromicroscopic techniques, each has unique resolution and dimensionality, and may be used to detect different OM properties (Weng et al., 2021). This article aims to summarize common findings on the OM distribution from recent spectromicroscopic advances and discuss implications for soil functioning and the soil carbon dynamics. A novel conceptual framework is developed to harmonize findings of the heterogeneous distribution of OM with current notions of the functioning of organic and mineral components in soils.

2 | SPECTROMICROSCOPIC INSIGHTS INTO THE COMPLEX SPATIAL ARRANGEMENT OF OM IN SOILS

2.1 | The patchy lateral distribution of soil OM and its diverse composition

Changing dynamics of OM storage have profound impacts at landscape or global scales and may originate in processes at the microscale and nanoscale. Various functional regions can be identified and imaged in the soil with spectromicroscopic techniques such as the interface of OM associated with mineral particles, particulate OM entrapped within aggregates, or microsites hosting active microhabitats of bacterial cells and fungal hyphae (Citeau et al., 2006; Lee et al., 2022; Schlüter et al., 2022; Wan et al., 2007; Watteau et al., 2012). Zooming into soil structures with novel applications of spectromicroscopic techniques provides direct evidence of the complex spatial arrangement of OM in soils at biologically relevant scales. Depending on the analytical power of various techniques, spectromicroscopic applications offer novel and diverse insights based on their resolution and specific detection characteristics of organic and mineral component properties.

Nanoscale secondary ion mass spectrometry (NanoSIMS) provides the distribution of up to seven ions simultaneously at a lateral resolution of approximately 50–150 nm depending on the application (Hatton et al., 2012; Keiluweit et al., 2012; Mueller et al., 2017). Based on the unique mass resolution of NanoSIMS, this can be used to trace ^{15}N-labeled or ^{13}C-labeled compounds in the soil (Hatton et al., 2012) and differentiate between mineral-dominated and patchy-distributed OM-dominated regions by detection of secondary ions (Schweizer et al., 2018). Using NanoSIMS-based imaging, freshly added OM was
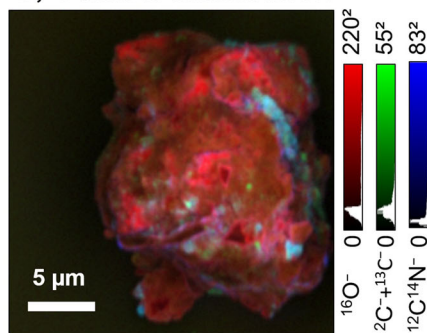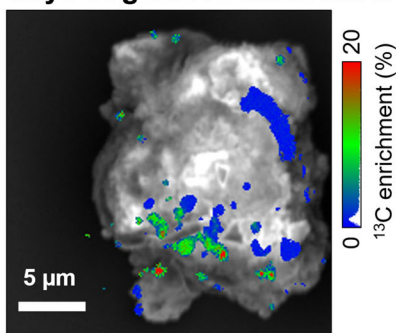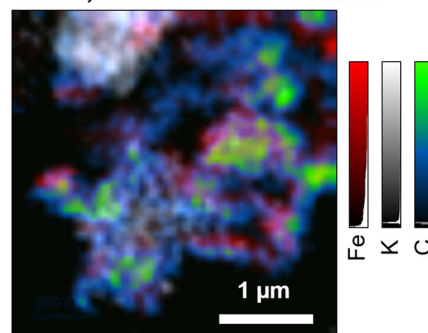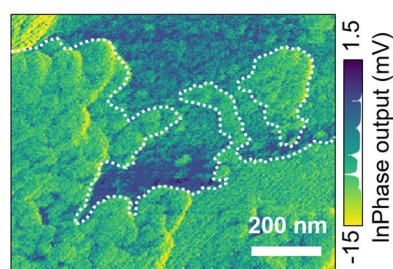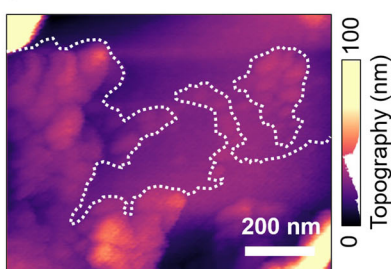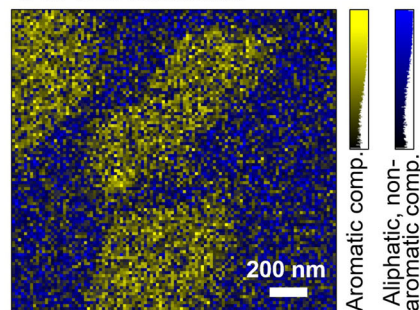
FIGURE 1 Patchy-distributed and piled-up arrangement of soil organic matter (OM) at microscale and nanoscale observed through different spectromicroscopic techniques. (A and B) Heterogeneous lateral distribution of OM (high in $^{12}C^-+^{13}C^-$ and $^{12}C^{14}N^-$) and colocalization with partially newly formed OM coatings derived from ^{13}C-labeled glucose incubation determined by nanoscale secondary ion mass spectrometry (NanoSIMS) (data by Wilhelm et al., 2022). (C) The patchy lateral distribution of OM (C distribution shown as heat map of black to blue to green) is confirmed by scanning transmission X-ray microscopy (STXM) and near-edge X-ray absorption fine structure (NEXAFS) (data by Asano et al., 2018). (D) Atomic force microscopy (AFM) providing nanomechanical properties and indications of the OM distribution (area below dotted line; OM less stiff and adhesive but with a rougher surface). (E) OM with different topographic extent with both thick and thin vertical arrangements at the nanoscale (data by Gazze et al., 2018). (F) Distinct OM composition of more aromatic components within a more aliphatic matrix reveals patchy OM–OM features by cryogenic scanning transmission electron microscopy and electron energy-loss spectroscopy (cryo-STEM-EELS) (data by Possinger et al., 2020b)

shown to be preferentially retained at preexisting mineral-associated OM patches (Vogel et al., 2014) and develops in successive spatial patterns with increasing coverage and connectivity of the patches over time (Schweizer et al., 2018). To analyze the influence of mineral soil components, the colocalization of OM patches with other ions (such as Fe, Al, or Si) can be assessed. For example, the colocalization of OM patches with Fe and Al phases in Andosol subsoils from a Hawaiian precipitation gradient was shown to result in a more N-rich composition of OM patches (Inagaki et al., 2020). After amendment with ^{13}C-labeled substrates, a higher extent of colocalization of the new organic carbon with mineral-dominated areas instead of OM-dominated areas was shown to correlate with a lower susceptibility and mineralization in a soil incubation experiment from the aforementioned Hawaiian precipitation gradient (Wilhelm et al., 2022; Figure 1A,B). Moreover, microbial processing was shown to have an important impact on the formation of mineral-associated OM since ^{15}N-labeled microsites were found in a Cambisol after an 8 h incubation with an amino acid (Hatton et al., 2012) and a 12-year incubation with plant leaves (Remusat et al., 2012). This was also reflected in NanoSIMS analyses of an Alfisol and

a Vertisol from Australia incubated with lucerne residue for one year, after ^{15}N-labeled microbial-derived N-rich OM patches were identified as potential local initial formation sites of mineral-associated OM (Kopittke et al., 2018). The NanoSIMS analysis of 40 different spots within the same aggregate structure revealed recurring architectures of three microdomain types potentially related to different functions (Steffens et al., 2017). Altogether, these studies demonstrate the patchy OM distribution across mineral surfaces and how the extent of the OM coverage as well as the N proportion may be related with the formation and susceptibility of mineral-associated OM.

Synchrotron-based scanning transmission X-ray microscopy coupled with near-edge X-ray absorption fine structure (STXM-NEXAFS) spectroscopy has revealed a high spatial molecular diversity of OM (Lehmann et al., 2008). In one of the first applications, the organic carbon in soil microaggregates of approximately 2 µm was found to be distributed in both dispersed and concentrated arrangements, which contained a wide range of aromatic, phenolic, and carboxylic functional groups as resolved at 30 nm for a Phaeozem and a Cambisol from Germany and an Ultisol from the USA (Wan et al., 2007). The analysis

of larger microaggregates of 20–250 μm was achieved using cryo-fixed thin sections of approximately 200–600 nm thickness scanned with a resolution of up to 50 nm and a step size of 50 nm (or occasionally also higher). A heterogeneous distribution of OM across soil aggregates with no consistent variation from exterior to interior was confirmed for aggregates from the USA, Kenya, and Brazil (Lehmann et al., 2007). However, the OM composition in coatings on mineral surfaces was found to contain more aliphatic and carboxylic C resembling microbial metabolites. In clay-sized fractions from a soil under pasture in the USA, aromatic C, carboxyl C, and polysaccharides were shown to be pervasive functional groups whereas aliphatic was only found in limited regions and C was similarly correlated with Fe, Al, and Si distribution (Chen et al., 2014). In another study, added ^{15}N-labeled amide N from chitinous fungal cell wall was preferentially found associated with Fe (hydr)oxide minerals in an O horizon where they were colocalized with aliphatic C indicating the accumulation of microbial lipids and proteins on these surfaces (Keiluweit et al., 2012). A comparison of soils from different tillage practices in Brazil observed more aliphatic C under no tillage than under conventional tillage (Arachchige et al., 2018). The application of STXM-NEXAFS in a 3-μm microaggregate from an allophanic Andosol indicated a dominance of amide and carboxyl C over aromatic and aliphatic C with poorly-crystalline mineral phases at 50 nm resolution (Asano et al., 2018). The heterogeneous abundance of OM (shown as heat map of black to blue to green in Figure 1C) also provides direct evidence for a patchy OM distribution, which was correlated with the Fe distribution (and also with Al distribution, data not shown; Asano et al., 2018). By taking advantage of a combination of C, N, Ca, Fe, Al, and Si STXM-NEXAFS, the composition of organic and mineral soil components was found to be equally complex at 50 nm resolution (Solomon et al., 2012). In summary, this illustrates that a high variety of organo–mineral interaction mechanisms coexist at the microscale and nanoscale, which are directly interwoven with the patchy distribution of OM.

2.2 | Into another dimension: exploring the vertical structure of OM

The concept of a zonal vertical structure of organo–mineral associations was derived based on a range of observations using soil particle density and size fractionation techniques as well as sorption experiments (Gao et al., 2020; Kleber et al., 2007; Kleber et al., 2021). This concept describes the preferential accumulation of N-rich proteinaceous organic compounds to mineral surfaces and the formation of further overlying organic compounds forming a multilayer (among other possible types). Various direct insights into the vertical structure and composition of OM were obtained using spectromicroscopic investigation with techniques such as X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). These techniques provide information on the surface chemistry and morphology of organo–mineral associations in soils. XPS analyses of a glacial chronosequence over 120 years showed that the OM coatings grew in thickness from 0.5 to 1.6 nm on average across an area of 0.21 mm^2 since the mineral

phase was increasingly masked when assuming a homogeneous lateral distribution (Woche et al., 2017). AFM analyses of increasing amounts of water-extractable OM adsorbed to goethite indicated a preferential sorption of globular compounds with a diameter of 4–10 nm in addition to bulky agglomerations of fibrillary compounds with a thickness of 4–8 nm and a length of 20–100 nm (Kaiser & Guggenberger, 2007). Microbially mediated growth of OM coatings incubated over 21 days on modified glass wafers showed the increasing formation of thick mineral-associated OM, estimated to be 20–130 nm by applying XPS analyses with a lateral resolution of approximately 300 μm (Huang et al., 2020). While the quantification of the thickness of OM coatings measured by XPS may highly vary depending on the coverage (Gerin et al., 2003), thickening OM structures extend our mechanistic understanding of how OM sequestration may be decoupled from the lateral distribution and mineral surface area.

Further experimental evidence demonstrated how the vertical composition of OM coatings may also vary. The adsorption of water-extractable OM to goethite surfaces exhibited a temporal kinetic dynamic with an increasing C:N ratio in OM compounds over a time frame of 4 h according to electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (Coward et al., 2019). A preferred association of OM for aluminosilicate surfaces has been postulated based on XPS analyses comparing the relative signal intensity of Si and Al (Flogeac et al., 2005). A study of sequential sorption of peat-derived water-extractable OM onto either kaolinite, montmorillonite, and gibbsite indicated a successive layering with a potentially increasing role of OM–OM interactions as indicated by an increasingly similar composition of sorbed OM by ^{1}H high-resolution magic angle spinning nuclear magnetic resonance spectroscopy (Mitchell et al., 2018). Based on these studies, the thickness and vertical composition of OM seem to be highly interrelated indicating the importance of OM–OM interactions and multilayering for OM sequestration.

2.3 | Integrating the novel insights of a patchy lateral and a piled-up vertical arrangement of soil OM

How can we integrate the vertical structures of OM with the patchy lateral distribution in soils? Gao et al. (2020) estimated that the likelihood of a multilayer arrangement, instead of a monolayer, increases when the OM coverage across soil mineral surfaces is less than 50%. In a study where the OM coverage remained similar in fine mineral fractions with different C contents, increased organic C storage has been revealed within multilayers, inducing a piled-up OM storage mechanism (Schweizer et al., 2021). In another study using N_2-sorption measurements of the organic carbon loading and the C-constant related to the adsorption affinity, the research concluded that two different ways of arrangement, thinner "painted" and thicker globular forms, are found at different relative proportions (Wagai et al., 2009). Given that the spatial molecular diversity in soils is high, both arrangement types probably coexist demanding further spatial differentiation

using spectromicroscopic analyses. The vertical composition is postulated to differ depending on the types of mineral surface and organic compounds involved in the interaction. The patchy lateral distribution of OM extends this conceptual framework by providing insights under which circumstances and where in the soil architecture the OM storage may locally differ.

Approaches using AFM can provide topographical and mechanical properties of organo–mineral associations at the nanoscale. Recently, optimized imaging and probe selection enabled the analyses of intact aggregate structures sampled from a soil under grassland in Wales with an OM content of 56 mg g^{-1} (Gazze et al., 2018). While the presence of patchy-distributed OM was indicated by nanomechanical mapping using phase contrast imaging (area below dotted line; Figure 1D), the surface topography of OM had a considerable roughness of 13 nm on average with some sections sticking out up to 40 nm (area below dotted line; Figure 1E). The topography in such a sampled soil aggregate may be more heterogeneous than previously observed in a model montmorillonite amended with OM from a Histosol by phase-contrast imaging using AFM where the OM coverage appeared homogeneous (Rennert et al., 2012). When these studies are considered together, they provide direct evidence of different modes of OM with both thick and thin vertical arrangements coating soil minerals across a patchy lateral distribution at submicron scale.

The large contribution of microbial-derived residues to mineral-associated OM (Angst et al., 2021; Liang et al., 2019; Ludwig et al., 2015) warrants further investigation to the extent bacterial or hyphal fragment structures (Mayerhofer et al., 2021; Silhavy et al., 2010) influence the lateral and vertical arrangement of organo–mineral associations at the microscale and nanoscale. AFM analyses showed that the coverage of bacterial cells and biofilms on clay surfaces vary depending on the nutrient conditions, whereas nanoscale heterogeneities of bacterial cell wall biopolymers and mineral surface roughness and composition might explain differences between observed attraction forces and predictions based on theoretical colloidal dispersion stability (Huang et al., 2015). The application of AFM to single molecules provides important insights to unravel organo–mineral interactions as affected by different composition, orientation, and conformation of organic compounds, kinetic and thermodynamic processes, as well as ion and pH effects (Newcomb et al., 2017; Zhai et al., 2019; Zhai et al., 2021). Measurements of adhesion forces between Fe (hydr)oxides-coated tips and water-extractable OM by chemical force microscopy indicated that carboxyl-rich aromatic and N-containing aliphatic compounds may compose the initial layer (Chassé et al., 2015). Such ways of integrating biotic processes into spatial investigations could be crucial to unravel the formation and functioning of soil architectures at the microscale and nanoscale.

2.4 | OM–OM interactions

Scanning transmission electron microscopy coupled with electron energy-loss spectroscopy (STEM-EELS) provides analytical opportunities that are particularly useful for light element analyses. An example

is the C and N K-edge analysis with high lateral resolution of approximately 1–20 nm, which can be extended down to subangstrom scale for atomic structure investigations (Archanjo et al., 2017; Krivanek et al., 2010). Recent advances by cryogenic thin-sectioning coupled with additional thinning by focused ion beam milling provided the opportunity to image electron transparent soil sections of <100–200 nm from a Hawaiian Andosol (Possinger et al., 2020a). The imaging revealed a submicron architecture within an OM-rich soil structure consisting of a distinct aromatic-rich C and lower-N component (yellow) within an alkyl-rich C and higher-N matrix (blue; Figure 1F). The disordered vertical structure of OM was found to be potentially layered as indicated by variations of the C/O and C/N composition at the scale of several nm, which may resemble proteinaceous compounds (Possinger et al., 2020a). These results provide direct evidence of vertical and three-dimensional architecture of OM at mineral surfaces consisting of OM–OM interactions in addition to organo–mineral interactions.

The presence of OM–OM interactions is also supported by batch adsorption experiments that showed a surface conditioning effect of mineral and OM-coated mineral surfaces by amino acids to enhance the adsorption of more hydrophobic and less polar OM compounds such as phenolic acids (Gao et al., 2017; Gao et al., 2018). The piled-up arrangement of OM could thus be explained by multiple layers of OM compounds that could be stacked upon each other whereas direct in-situ observations of the actual formation of such OM–OM interactions are needed at high resolution to get a better understanding of how vertical structuring interferes with OM sequestration.

3 | CONSEQUENCES FOR SOIL FUNCTIONS

3.1 | Carbon storage and dynamics

The patchy and piled-up distribution of mineral-associated OM at the microscale and nanoscale has extensive repercussions on various soil functions. Integration of spectromicroscopic evidence into a novel conceptual framework induces various hypotheses that warrant further experimental studies to quantify the magnitude of the influence of varying lateral and vertical arrangements of OM on its sequestration and functional behavior in soils (Figure 2).

The patchy lateral distribution of mineral-associated OM at the microscale and nanoscale induces that the capacity and activity of soil functions related to OM is also distributed heterogeneously. Functions like the sequestration, turnover and persistence of OM are regulated in compartmentalized units meaning that OM storage and its dynamics are consolidated to specific patchy-distributed sites of mineral surfaces. The lateral distribution of mineral-associated OM storage has been shown to extend during initial soil formation and OM accrual over decadal to centennial timescales and develop from a patchy distribution into more connected OM coatings based on NanoSIMS-imaging (Schweizer et al., 2018). In that study, the coverage of OM did not reach more than the maximum of 55% in the oldest site of <700 years since deglaciation. The investigation of a clay content gradient of 5–37% with similar agricultural management and mineral
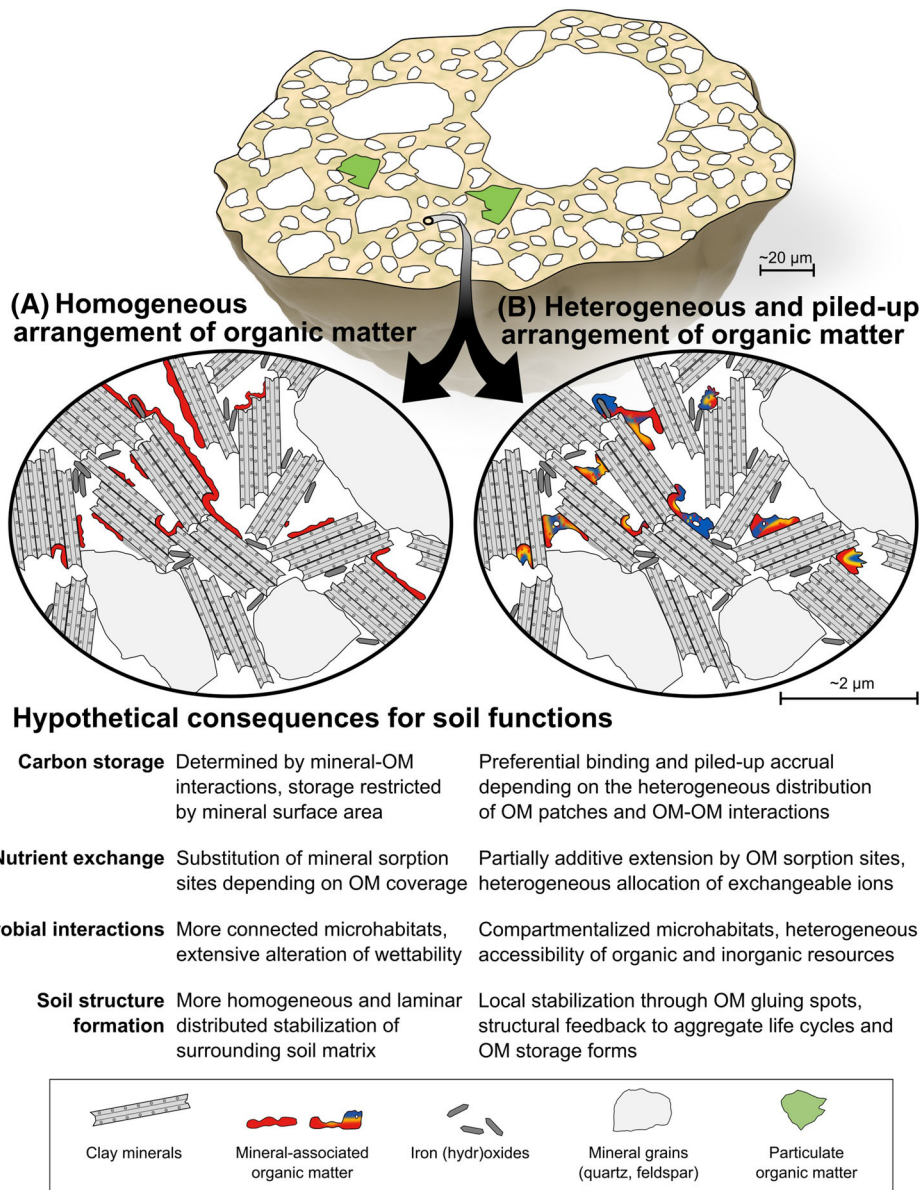
FIGURE 2 Schema of the novel conceptual framework based on patchy-distributed and piled-up soil organic matter (OM) associated to minerals. The hypothetical consequences of different OM arrangements for our understanding of key soil functions. (A) More homogeneous and less selective arrangement of OM as related with potential restrictions of carbon storage by the mineral surface area, a substitution of mineral sorption sites depending on OM coverage, more connected microhabitats as well as more extensive and homogeneous surface alteration and stabilization. (B) Based on the spectromicroscopic evidence of Figure 1, a more heterogeneous OM distribution induces preferential binding depending on OM–OM interactions decoupling OM storage from mineral surface area, an extension of sorption sites by OM, microhabitats with compartmentalized resource availability as well as locally stabilizing OM gluing spots that may generate structural feedback on OM storage forms

composition indicated a thicker accrual of mineral-associated OM in the low clay soils (<18%), whereas the OM coverage was similar at approximately 10.5% in the coarse clay-sized fraction (Schweizer et al., 2021). These analyses show that the storage of mineral-associated OM may be decoupled from most of the mineral surface area. Radiocarbon measurements of mineral-associated organic carbon in the coarse-clay sized fraction indicated a slower turnover in low clay soils with a higher organic carbon loading revealing that the thicker vertical arrangement of OM may enhance organic carbon persistence. Direct evidence of

OM–OM interactions (Possinger et al., 2020a) illustrate the important effect of reactive OM surface area and properties beyond mineral surfaces. Increased OM–OM interactions invoke the notion of a biophysical protection mechanism in which the accrual of OM at OM interfaces may enhance the persistence of the buried OM compounds possibly inducing a vertical age gradient of layered OM (Figure 2).

The storage of OM in a patchy and piled-up arrangement calls for a novel conceptual understanding of carbon storage including the limited extension of OM across mineral surfaces and the sequestration in

piled-up and potentially layered OM assemblages. This means that the capacity of soils to increase and maintain their organic carbon storage may not be necessarily restricted by the mineral surface area and clay content, but the properties of the native and fresh OM may increasingly govern organic carbon storage through OM–OM interactions (Figure 2). While the potential storage dynamics for particulate OM are addressed in Section 3.4, the heterogeneity of patchy-distributed and piled-up OM may explain contrasting observations on dissolved OM sorption. While various studies found that a higher organic carbon content of soils led to a higher adsorption of dissolved OM (Jagadamma et al., 2014; Mayes et al., 2012; Moore & Turunen, 2004), other works indicated that sorption sites may be blocked inhibiting the uptake of dissolved OM (Guggenberger & Kaiser, 2003; Jardine et al., 1989; Kothawala et al., 2009). However, direct spectromicroscopic quantification to which extent OM–OM interactions may decouple the persistence of fresh OM compounds from mineral surface interactions remain unresolved. Depending on the surface properties of the organic sorbate and sorbent (Jagadamma et al., 2014), the patchy-distributed and piled-up arrangement of OM at the microscale and nanoscale demonstrates that the distribution of mineral-associated organic carbon may shape its varying susceptibility to mineralization as affected by global change.

3.2 | Nutrient exchange

The ability of soils to hold cations and anions depends on the abundance and surface properties of mineral particles and OM (Oades et al., 1989; Parfitt et al., 1995). The cation exchange capacity (CEC) is critical to describe soil functions related to nutrient retention and the fate of heavy metals or organic pollutants. The arrangement of mineral-associated OM at the microscale and nanoscale may influence the CEC as sorption sites of mineral surfaces may be partially covered and substituted by OM sorption sites. An influence of the arrangement of mineral-associated OM on CEC was invoked early on by studies based on OM removal by H_2O_2 oxidation, where a partial coverage of mineral and OM sorption sites was assumed (Burford et al., 1964; Dudas & Pawluk, 1969; Sequi & Aringhieri, 1977; Syers et al., 1970; Wilding & Rutledge, 1966).

Our novel understanding of a patchy and piled-up arrangement of mineral-associated OM induces that sorption sites of mineral surfaces are extended rather than substituted by OM. A partially additive extension of mineral-associated OM to the CEC of mineral surfaces means that OM sorption sites would add to a higher total CEC independent of the individual CEC of OM or mineral surfaces. Only a limited portion of mineral sorption sites would become unavailable after OM association (Figure 2).

Estimates of the CEC of OM are mostly based on multivariate regressions involving the clay content and total organic carbon content as factors without differentiating between particulate and mineral-associated forms. The large variation of the computed contributions of OM to the total CEC (43–78% in Asadu et al., 1997; 50–95% in Soares and Alleoni, 2008; 10–85% in Turpault et al., 1996; 66–97% in Yuan

et al., 1967) was explained with differences in pH and ionic strength, clay content, clay mineral composition, and OM composition. To explain why soils with comparable properties could differ (Krull et al., 2004; Meyer et al., 1994; Murphy, 2015) may be explained by differences in the patchy and piled-up arrangement of OM at the microscale and nanoscale.

Size fractionation has shown that especially in the clay size and silt size range, the CEC contributions of OM and mineral surfaces are high and highly variable (Caravaca et al., 1999; Oorts et al., 2003; Skjemstad et al., 2008), which makes their arrangement even more decisive. Spectromicroscopic techniques may help advance our understanding of how a patchy and piled-up arrangement influences the CEC as shown previously at the mm scale (Leue et al., 2019). Sorption sites of mineral surfaces and OM were indicated to differ in their affinity for cations, with OM preferably adsorbing divalent cations over Na and Ca over Mg compared with fine mineral surfaces (Curtin et al., 1998, 1995). Accordingly, a heterogeneous arrangement of OM may induce a more discrete allocation of different exchangeable cations as indicated for Zn (Sun et al., 2019).

3.3 | Microbial interactions

From a microbial perspective, the patchy and piled-up arrangement of mineral-associated OM at the microscale and nanoscale in soils induces a heterogeneous microenvironment characterized by a varying local accessibility of organic and inorganic resources. While OM may serve as a source of, for example, C, N, and P (Jones et al., 2018), access to mineral surfaces and inorganic nutrients may be equally important to provide, for example, Fe, Mn, Mg, P, Ca, and Na (Carson et al., 2009; Cuadros, 2017; Mauck & Roberts, 2007). The interaction distance between soil microbes and their microenvironment may be limited to up to several tens of µm (Dechesne et al., 2008; Dechesne et al., 2010; Gantner et al., 2006) so a patchy arrangement of OM exerts a directional influence on the probability of microbial interaction and activity (instead of an omnidirectional transmission). This imposes various physicochemical constraints on soil microbes. These constraints are determined by a restricted encounter of resources and microbial consumption, which depends on the allocation of microbes across compartmentalized units (Kleber et al., 2021; Pot et al., 2022).

In addition to the segregation of the soil volume by pore structure and water distribution (Erktan et al., 2020; Tecon & Or, 2017), the patchy distribution of OM may influence microbial ecology. Diverse microenvironmental conditions were related with functionally diverse specialized microbial communities resulting in distinct metabolic activities (Bickel & Or, 2020; Nunan et al., 2020; Wilpiszeski et al., 2019). The connectivity of different habitats and the distance of substrate diffusion pathways have been shown to influence the mineralization of organic carbon (Bailey et al., 2017; Ruamps et al., 2011). An innovative experimental approach using compartmentalized 3D-printed cylinders could show that the spatial substrate heterogeneity at the scale of mm can delay microbial activity (Shi et al., 2021). Further insights into natural resource gradients at the microscale and nanoscale are

needed to better understand the effect of the patchy-distributed OM on microbial ecology.

The distribution of soil water may be influenced by the OM distribution since an increased coating of mineral surfaces with OM was shown to increase the contact angle and lead to more hydrophobic surface properties at water drop scale (Woche et al., 2017). Interactions between bacteria or bacterial residues and mineral surfaces were shown to decrease the surface wettability (Achtenhagen et al., 2015). Using confocal laser scanning microscopy, an increasing water repellency was shown to lead to a more disconnected water phase at the microscale (Muehl et al., 2012). Since in turn the soil wettability has a major influence on organic carbon persistence (Goebel et al., 2011), the patchy distribution of OM may induce a heterogeneous distribution of the local water repellency at the microscale and nanoscale. Differences in the OM distribution and its local alteration of wettability and porosity (also see Section 3.4) may explain why the response of the bulk soil water-holding capacity to increasing OM content is not always clearly positive (Minasny & McBratney, 2018; Rawls et al., 2003).

The biotic influence on the patchy and piled-up distribution of OM is probably quite high as suggested by recent insights into the importance of in vivo microbial turnover (Kallenbach et al., 2016; Sokol et al., 2019). Mineral-associated OM can comprise microbial cell wall fragments as well as plant cell fragments or agglomerations of differently sized molecules such as extracellular polymeric substances such as polysaccharides and proteins as adhesives (Chenu & Stotzky, 2002; Hu et al., 2020; Kleber et al., 2015). According to the distinct structure of biogenically excreted OM (Guhra et al., 2022; Huang et al., 2015), the lateral and vertical OM heterogeneity may be partially inherited from biotic formation depending on further fragmentation and transformation. To disentangle the formation and the effects of the spatial heterogeneity of OM, novel spectromicroscopic approaches are warranted to locally differentiate between biotic and abiotic formation and processing of mineral-associated OM. These processes are probably closely associated at the microscale and nanoscale.

3.4 | Stabilization of soil structure

The patchy distribution of mineral-associated OM induces preferential gluing spots that locally stabilize aggregate structures and connect the structural scaffold of soils. Even if the heterogeneous local stabilization is formed at the microscale and nanoscale, its effect would be disseminated according to the hierarchical interactions of aggregate building units with larger aggregate structures (Chenu et al., 1998; Tisdall & Oades, 1982; Totsche et al., 2018). While it is well established that an increasing OM content is related to increasing soil aggregate stability (Chaney & Swift, 1984; Haynes, 2000; Krull et al., 2004), the local temporal dynamics of gluing spots and how the surface properties are locally altered when OM undergoes decomposition remains uncertain.

Patchy-distributed OM gluing spots with different relative stabilization of the surrounding soil matrix may determine the planes of weakness upon aggregate disruption. Spatially resolved nanomechanical measurements (Gazze et al., 2018) could provide necessary insights

needed to advance the delineation of aggregates in intact soil structure (Koestel et al., 2021). The local formation or enhancement of some patchy-distributed OM gluing spots by addition of biomass, which may then supersede other local stabilization mechanisms, may also explain why aggregate turnover is enhanced after C addition (Peng et al., 2017). Whether the patchy lateral distribution of OM across mineral surfaces occurs in a more dispersed or a more connected arrangement could influence the local mechanical stability and its persistence in soil aggregates over time.

When an increasing amount of mineral-associated OM is accompanied by higher coverage or enhanced stabilization of OM gluing spots, the OM storage form within the soil structure may also be altered, that is, enhanced OM storage in particulate forms. Such structural feedback defined by local OM gluing spots might also contribute to the disproportionate increase of particulate storage forms with higher OM content at the expense of mineral-associated forms (Cotrufo et al., 2019). The shift toward more particulate OM is usually related to the empirical concept of a limited 'protective' capacity of OM by fine mineral particles (Six et al., 2002; Stewart et al., 2007). Since the alteration of soil structure by patchy-distributed OM also depends on how many fine mineral particles are present, the effect of OM gluing spots may also be related to the observed correlations between soil structure and the organic carbon:clay ratio (Prout et al., 2021). Other stabilizing agents and aggregate formation processes related to mineral components may also influence the effectiveness of patchy-distributed OM gluing spots on aggregate stability, aggregate life cycles and organic carbon storage.

4 | IMPLICATIONS

Recent evidence on the patchy and piled-up arrangement of OM implies a novel conceptual understanding of OM storage dynamics and interrelated soil functions. Various spectromicroscopic investigations consistently demonstrated how the patchy lateral distribution of OM at the microscale and nanoscale is related to the heterogeneous composition of OM such as local differences in N content or aromatic, aliphatic, and carboxylic C. Insights into the vertical structure and composition of OM revealed a thickness of a few nm to several tens of nm with a potentially multilayered structure explained by OM–OM interactions. Combining the conceptualization of patchy-distributed OM with vertical structural insights indicates that different modes of OM with thick and thin vertical arrangements may be associated to soil mineral surfaces decoupling OM storage from the mineral surface area.

According to these insights, various novel conceptual hypotheses arise toward key soil functions. The capacity of organic carbon storage may not be capped by the abundance of mineral surface area. Instead, the ability to form OM–OM interactions may become locally important, which could induce a vertically layered and three-dimensional protection mechanism. The heterogeneous storage of OM at the microscale and nanoscale induces a partially additive extension of OM sorption sites for nutrient exchange meaning that sorption sites of mineral surfaces are extended rather than substituted by OM. The

access of microbes to various elements from inorganic and organic compounds is highly regulated by the patchy and piled-up OM distribution. Heterogeneous microenvironmental conditions induce locally diverse microbial communities with diverse functions, activities, and ranges. Furthermore, variable surface conditions and wettability may also alter and segment the microbially relevant water distribution and attachment. Potential influence of inherited biotic architectures requires further disentangling of the formation pathways at the microscale and nanoscale. Patchy-distributed OM may locally stabilize larger soil structures as gluing spots which in turn could lead to an increased storage of occluded particulate OM. The conceptualized framework of patchy-distributed and piled-up OM in mineral soils opens up new perspectives of spatially resolved interactions that determine soil functions such as the fate of OM locally. A better understanding of the joint functioning of the soil architecture at the microscale and nanoscale may help to better predict the contribution of individual soil components as well as the susceptibility of functional regions within a dynamic soil architecture to soil amendments and disturbances.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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