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A conceptual model of organo-mineral interactions in soils: self-assembly of organic molecular fragments into zonal structures on mineral surfaces

M. Kleber · P. Sollins · R. Sutton

Abstract In this paper, we propose a structure for organo-mineral associations in soils based on recent insights concerning the molecular structure of soil organic matter (SOM), and on extensive published evidence from empirical studies of organo-mineral interfaces. Our conceptual model assumes that SOM consists of a heterogeneous mixture of compounds that display a range of amphiphilic or surfactant-like properties, and are capable of self-organization in aqueous solution. An extension of this self-organizational behavior in solution, we suggest that SOM sorbs to mineral surfaces in a discrete zonal sequence. In the *contact zone*, the formation of particularly strong organo-mineral associations appears to be favored by situations where either (i) polar organic functional groups of amphiphiles interact via ligand exchange with singly coordinated mineral hydroxyls, forming stable inner-sphere complexes, or (ii) proteinaceous materials unfold upon adsorption, thus increasing adhesive strength by adding hydrophobic interactions to electrostatic binding. Entropic considerations dictate that exposed hydrophobic portions of amphiphilic molecules adsorbed directly to mineral surfaces be shielded from the polar aqueous phase through association with hydrophobic moieties of other amphiphilic molecules. This process can create a membrane-like bilayer containing a *hydrophobic zone*, whose components may exchange more easily with the surrounding soil solution than those in the contact zone, but which are still retained with considerable force. Sorbed to the hydrophilic exterior of hemimicellar coatings, or to adsorbed proteins, are organic molecules forming an outer region, or *kinetic zone*, that is loosely retained by cation bridging, hydrogen bonding, and other interactions. Organic material in the kinetic zone may experience high exchange rates with the surrounding soil solution, leading to short residence times for individual molecular fragments. The thickness of this outer region would depend more on input than on the availability of binding sites, and would largely be controlled by exchange kinetics. Movement of organics into and out of this outer region can thus be viewed as similar to a phase-partitioning process. The zonal concept of organo-mineral interactions presented here

M. Kleber (✉)
Earth Sciences Division, Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, CA, 94720, USA
e-mail: mkleber@lbl.gov

P. Sollins
Department of Forest Science, Oregon State University, Corvallis, OR, 97331, USA

R. Sutton
Department of Environmental Science, Policy and Management, University of California, #3114 Mulford Hall, Berkeley, CA, 94720-3114, USA

offers a new basis for understanding and predicting the retention of organic compounds, including contaminants, in soils and sediments.

Introduction

Decades ago, earth scientists acknowledged the ability of mineral particles to protect soil organic matter (SOM) from biological attack (Jung 1943; Allison et al. 1949). In temperate, cultivated soils, 50–75% of SOM exists within clay-sized organo-mineral particles (Christensen 2001), and numerous researchers have reported positive correlations between the contents of fine mineral particles and carbon in soils (Körschens 1980; Nichols 1984; Burke et al. 1989; Mayer and Xing 2001). As a consequence, it is widely assumed that the inhibiting effect of soil minerals on decomposition can influence strongly the turnover of SOM (Martin and Haider 1986; Theng et al. 1992; Hsieh 1996; Parfitt et al. 1997). It follows that understanding SOM stabilization requires knowledge of the processes operating at the organo-mineral interface. Of particular importance but great complexity are the questions of how strongly SOM may bind to mineral surfaces, how such bonds form and eventually break, and how the mechanisms of attachment of SOM to mineral surfaces affect its residence time in soils.

While the characteristics of mineral surfaces are reasonably well known, the chemical properties of SOM continue to be the subject of much debate. After all, while minerals crystallize towards or dissolve from a defined and comparatively simple crystal structure, SOM encompasses organic molecules representing both compounds released from living plant and microbial cells (e.g., extracellular enzymes, surface-active proteins, chelating compounds, and many others) and complex plant, microbial and animal residues in various stages of alteration due to both biotic and abiotic processes (Baldock and Skjemstad 2000). Considerable spectroscopic evidence (Chien et al. 1997; Engebretson and von

Wandruszka 1997, 1998; von Wandruszka 1998; von Wandruszka et al. 1999; Ferreria et al. 2001; Martin-Neto et al. 2001; von Wandruszka and Engebretson 2001; Nanny and Kontas 2002) indicates that soluble mixtures of organic molecules representing a significant fraction of SOM can form organized structures called micelles within aqueous solution, structures that consist of hydrophilic exterior regions that shield hydrophobic interiors from contact with water molecules (von Wandruszka 1998). Because amphiphilic molecules are requisite to the formation of micelles, the ability of SOM components to form these structures suggests that many of these molecules are amphiphilic. Significant to this insight, Wershaw (1993) previously developed a bilayer model of organo-mineral interactions (Fig. 1) that sharply contrasted with the traditional view of organo-mineral interactions (Stevenson 1985), which were visualized as associations of large, multifunctional polymers with mineral surfaces via a broad range of bonding mechanisms (Stevenson 1985; Leinweber and Schulten 1998). Further, Wershaw and Pinckney (1980) postulated that decayed organic materials are often bound to clay surfaces by amino acids or proteins, based on the observation that deamination of organo-mineral complexes with nitrous acid released organic materials from the clay.

It is our intention to develop this earlier work into a generally applicable concept of the zonal structure of organo-mineral associations (Fig. 2), based on the amphiphilicity of SOM fragments, and the intimate involvement of proteinaceous compounds in stable organo-mineral associations. As defined here, a *zonal structure* is formed when the organic matter attached to a mineral surface is segregated into more than one layer or zone of molecules, such that not all adsorbed molecules are in contact with the mineral surface. Assuming such a zonal structure, we are able to account simultaneously for a number of phenomena observed in soils and sediments, including:

a) The decrease of C/N ratio with decreasing particle size (Hedges and Keil 1995; Aufdenkampe et al. 2001);
b) The decrease of C/N ratio with increasing particle density (Sollins et al. 2006);
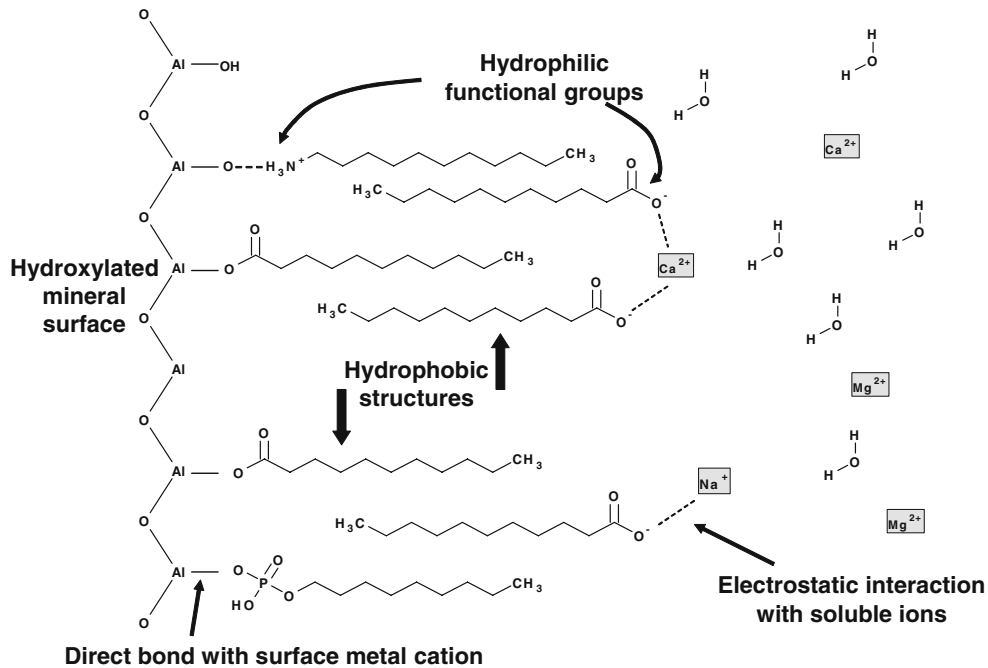
Fig. 1 The "Wershaw bilayer model" of organo-mineral interactions (Wershaw et al. 1996a). Figure adapted from Essington (2003). Accumulation of amphiphilic fragments on soil surfaces is initiated by electrostatic interactions between hydrophilic organic moieties and surface oxygens or hydroxylated surface-metal cations. The hydrophobic portions of these surface molecules are shielded from the polar aqueous phase by a second layer of amphiphiles, forming a bilayer

c) The decrease of ^{14}C content with decreasing C content in heavy fractions (Sollins et al. 2006);

d) The preferential sorption of large, hydrophobic organic compounds in sorption experiments with soils (Jardine et al. 1989; Guo and Chorover 2003) and in marine/estuarine sediments (Zhou et al. 1994);

e) The existence of at least two different C and N pools in heavy fractions: an older, more stable pool of C and N, and a more recent, fast cycling pool of C and N (Trumbore et al. 1989; Strickland et al. 1992; Swanston et al. 2005);

f) The observation that mineral-associated organic matter accumulates in A horizons beyond levels consistent with monolayer coverage (Eusterhues et al. 2005);

g) The correlation of concentrations of poorly crystalline mineral phases with amounts of oxidation-resistant SOM (Kleber et al. 2005);

h) Seasonal changes in water repellency in soils (Horne and McIntosh 2000).

To support the concept of zonal structure of organo-mineral complexes, we first discuss the idea of SOM as consisting of associations of organic molecules capable of micellar self-organization in aqueous solution. Given this important concept, it is appropriate to view a significant portion of SOM as consisting of a mixture of diverse but typically amphiphilic molecules. We will present empirical evidence that supports the idea of a zonal structure of organic accretions on mineral surfaces, demonstrate the special importance of proteinaceous compounds for the architecture of this structure, and show that the assumption of different zones of sorption implies differential exchange kinetics for organic fragments moving into and out of individual zones.

Amphiphilic molecules and the micellar association model of soil organic matter

Critical insights regarding organo-mineral complexes arose from studies probing the behavior of
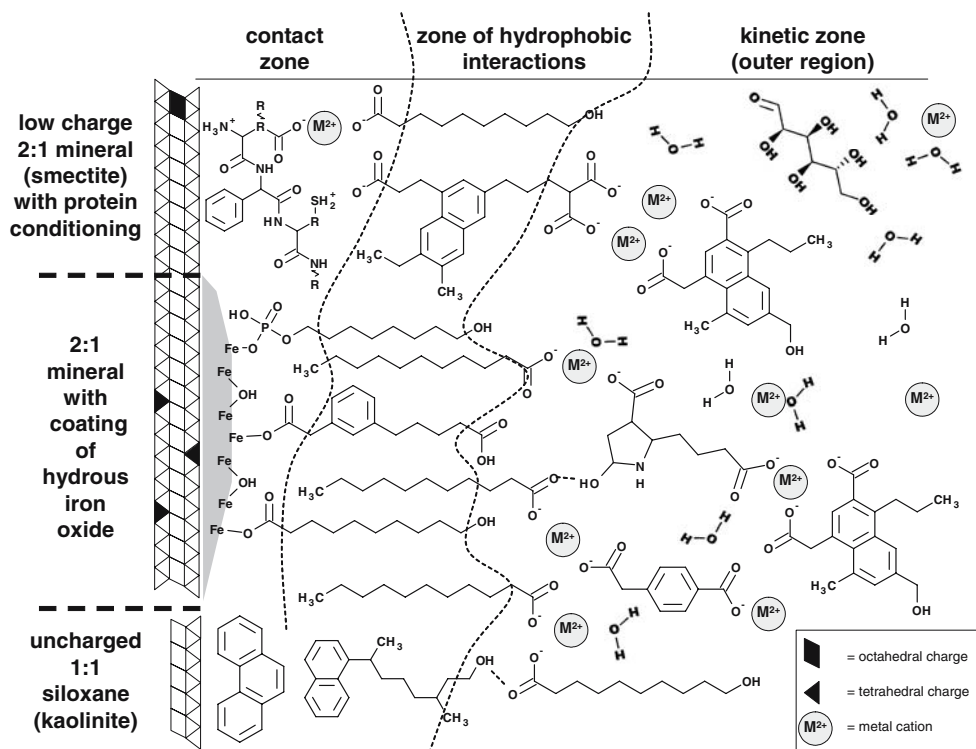
Fig. 2 The zonal model of organo-mineral interactions. The variety of surface types in soils is represented by a low-charge smectite, a hydroxylated Fe-oxide coating, and a hydrophobic kaolinite siloxane surface. This selection is meant to illustrate major bonding mechanisms, and is not intended to represent the full range of mineral surface types that may be encountered in soils. In the *contact zone*, amphiphilic fragments accumulate on charged surfaces through electrostatic interactions, directing hydrophobic portions outwards toward the polar aqueous solution. Proteins serve as a surface conditioner that adds polar functionality to low-charge siloxane surfaces. Some hydrophobic organic compounds may also associate with noncharged mineral surfaces. The *zone of hydrophobic interactions* is equivalent to the hydrophobic region formed as part of the Wershaw bilayer model, and results from the entropically driven shielding of the hydrophobic portions of adsorbed organic molecules from the polar aqueous phase by a second layer of amphiphilic molecules. The hydrophobic zone is thought to be discontinuous, as some proteins directly adsorbed to mineral surfaces may well expose ionized or polar functional groups towards the soil solution. In the outer region or *kinetic zone*, further accumulation of organic molecular fragments is possible, probably largely mediated by the presence of multivalent cations. Depending on stereochemical orientation, degree of amphiphilicity, cation content of the soil solution, pH, temperature, and perhaps several other controlling factors, a variety of modes of attachment of organic molecular fragments to the intermediate region appears to be possible. The thickness of the outer zone is likely to depend on input of organic materials and thus to be largely be controlled by exchange kinetics

natural organic fractions in aqueous solution. To examine and manipulate the behavior of these complex organic materials within a controlled laboratory environment, alkaline extraction is often used to solubilize a large portion of SOM, producing an operationally defined humic fraction. That alkaline extraction effectively removes between 50% (Rice 2001) and 80% (Scheffer and Schachtschabel 2002) of the organic material in soil samples indicates that while the humic fraction represents only a portion of SOM, it is a

significant portion of this organic material, and it contains many reactive polar or charged moieties that respond to pH. In addition, behavior consistent with micellar organization, observed using a diverse array of spectroscopic techniques including fluorescence (Engebretson and von Wandruszka 1997, 1998; von Wandruszka 1998; von Wandruszka et al. 1999; von Wandruszka and Engebretson 2001; Nanny and Kontas 2002), electron spin resonance (Ferreria et al. 2001; Martin-Neto et al. 2001), and nuclear magnetic resonance

(Chien et al. 1997), suggests that nonpolar moieties are also present within humic fractions. After all, it is the presence of hydrophobic functional groups within amphiphilic molecules that triggers entropically-driven self-organization to shield these nonpolar moieties from the polar aqueous medium through formation of a micelle. Thus, the observation of micellar structure within humic extracts representing a major portion of SOM indicates that a significant fraction of the molecules making up this complex organic material are amphiphilic in nature.

The components of decomposing SOM display a range of functional qualities based on chemical and structural composition (Sutton and Sposito 2005). We suggest that these chemical properties represent a continuum of amphiphilicity that ranges from molecules that are solely nonpolar and hydrophobic, to those that are predominantly amphiphilic because they also contain hydrophilic, highly polar or charged functional groups. Nonpolar, hydrophobic compounds are composed predominantly of alkyl and aromatic functional groups, and may derive from sources such as plant waxes and cutins. Occupying the mid-range of this chemical continuum are mildly polar materials, such as many carbohydrates and their derivatives, which feature functional groups like alcohols or ethers that do not ionize under typical soil and water pH conditions. In addition to hydrophobic functional groups, the amphiphilic compounds that populate the other extreme of this chemical spectrum contain more reactive functional groups like carboxyls and amines, which can develop charge under typical soil and water pH conditions. The dominant role of amphiphilic molecules in the behavior of complex organic mixtures within aqueous environments cannot be ignored when considering the mechanisms by which SOM adsorbs to mineral surfaces.

Experimental evidence in support of a zonal structure of organic accretions on mineral surfaces

While mounting experimental evidence (Chien et al. 1997; Engebretson and von Wandruszka 1997, 1998; von Wandruszka 1998; von Wandruszka et al. 1999; Ferreria et al. 2001; Martin-Neto et al. 2001; von Wandruszka and Engebretson 2001; Nanny and Kontas 2002) supports the ability of complex natural organic substances to self-assemble into associations featuring regions with different chemical properties, similar behavior is not typically ascribed to SOM adsorbed to mineral surfaces. However, starting with the previously mentioned work by Wershaw and colleagues (Wershaw and Pinckney 1980; Wershaw 1986; Wershaw 1993), information from a broad range of scientific fields has provided numerous clues suggesting that SOM sorbs to minerals in layers or zones that may have different chemical or functional properties. In the following sections we use (i) the fate of organic pollutants in soils, sediments, and aquifers, (ii) the distribution of organic matter over mineral surfaces in natural systems, (iii) information from density fractionation experiments, (iv) evidence from the study of water repellency in soils, and finally, (v) data obtained through laboratory synthesis of layered organo-mineral structures, to draw inferences suggesting that organic accretions on minerals consist of multiple zones of self-assembling materials.

Sorption of organic compounds to organic coatings on mineral surfaces as a model of zonal organo-mineral architecture

The idea that organic matter covers mineral surfaces in a layered or zonal fashion (Fig. 2) is not new (Chassin 1979), with most early concepts of organics sorbing to mineral surfaces in two or more layers resulting from a wealth of studies on the fate of organic pollutants in soils, sediments, and aquifers. A review of this early work led Voice and Weber (1983) to conclude that, although hydrophobic bonding was a major sorption mechanism for hydrophobic compounds, no single sorption mechanism adequately explained all experimental observations. Instead, Weber et al. (1983) state that "*the organic carbon content of a solid appears to be the major factor in determining its sorptive capacity.*"

A step forward in advancing mechanistic knowledge about zonal arrangements of organic

molecules on mineral surfaces was taken by Murphy et al. (1990), who, following up on the work of Hunter and Liss (1982) among others, found that hydrophilic mineral particles exposed to humic fractions developed hydrophobic surfaces, rendering them more capable of sorbing hydrophobic organic compounds. Hydrophobic interactions bind the outer layer hydrophobic compounds to the inner layer organics because the total hydrocarbon surface that is exposed to water is reduced, and entropy maximized, when hydrophobic entities organize to reduce the nonpolar surface area exposed to water molecules. Jardine et al. (1989) provided additional support for the importance of hydrophobic interactions to adsorption of organic materials by comparing the sorption of dissolved organic carbon solutions that had been fractionated into operationally defined hydrophobic and hydrophilic organic portions. Hydrophobic organic solutes were preferentially adsorbed by soils relative to hydrophilic organic solutes, leading the authors to conclude that hydrophobic interactions driven by favorable entropy changes represent the primary mechanism of adsorption for these organic solutes. Murphy et al. (1990) further showed that the nature of the mineral surface, particularly the concentration and spatial distribution of hydroxyl sites, influenced the amount of hydrophobic organic C adsorbed to organic coatings. The chemical properties of the humic fraction used to coat the mineral particles influenced the amount of hydrophobic compounds adsorbed, with the most aromatic humic material being the strongest sorbent for hydrophobic material.

Patchy organic matter distributions on mineral surfaces indicate zonal architecture of sorbed materials

Further evidence for the zonal or layered sorption of organic matter to mineral surfaces comes from the examination of natural organo-mineral complexes taken from soil and marine systems. Both specific surface area (SSA) determinations and microscopic analyses indicate that the distribution of organic materials on the mineral surfaces of soils (Mayer and Xing 2001; Kahle

et al. 2002) and marine sediments (Ransom et al. 1998; Mayer 1999) is typically discontinuous. While organic matter loadings on sedimentary mineral surfaces are often on the order of the so-called monolayer equivalent of 0.5–1.0 mg organic C m^{-2} (Keil et al. 1994; Mayer 1994), the fact that organic material is not distributed evenly over the available mineral surface indicates that the material must instead be clustered in small patches with some vertical extension. Aluminosilicate sediments with low to moderate loadings of organic matter (<3 mg organic C m^{-2}) generally have less than 15% of their surfaces coated, with organic materials existing in discrete spots on the mineral surfaces (Arnarson and Keil 2001).

Speculations about a layered architecture of these patches have been voiced by Kaiser and Guggenberger (2003), who found that the reduction of SSA following sorption of increasing amounts of DOC was not uniform: the decrease in SSA was larger at smaller organic matter loadings than at larger ones. Among other potential explanations, they hypothesized that "*with increasing surface loading an increasing portion of the sorbing molecules did not attach to mineral surfaces but formed organic multilayers as a result of hydrophobic interactions or bridging by polyvalent cations between organic ligands of sorbed and soluted molecules*." This interpretation was subsequently supported by the work of Wang and Xing (2005), who found that, even under different organic matter loading levels, mineral surface coverage remained nearly constant, indicating that "*the coating must have increased in thickness while retaining practically the same surface coverage at a higher loading. In such a multilayer arrangement, the first several molecular layers close to the mineral surface may take a more compacted form due to the attractive forces of the mineral surface*." In addition, ocean sediment studies show a direct relationship between organic matter content and mineral surface area at organic loadings 2–5 times that of a monolayer equivalent (Hedges and Keil 1995), further supporting the existence of minerals coated with multiple layers of organic molecules.

Organo-mineral associations isolated through density fractionation may also suggest a zonal architecture of sorbed materials

In addition to the ocean sediments described above (Hedges and Keil 1995), soil particles isolated through density fractionation have also provided evidence indicating that organic material is sorbed to minerals through both direct and indirect interactions with mineral surfaces. Eusterhues et al. (2005) found that organic matter loadings in heavy fractions (>2 g cm^{-3}) from a series of topsoils were greater than could be explained solely by direct attachment to the available mineral surfaces area in a monolayer fashion. They hypothesized that interactions between organic molecules leading to greater than monolayer coverage would be necessary to explain the large amounts of sorbed organic material (Eusterhues et al. 2005).

Organic C in the heavy fraction of soils is commonly seen as being closely associated with minerals and typically more depleted in ^{14}C than light-fraction material, which is not intimately bound to minerals (Trumbore and Zheng 1996). However, when Swanston et al. (2005) traced an atmospheric ^{14}C pulse into a forest ecosystem, they noticed that the elevated ^{14}C signal appeared not only in the light fraction, but also in the strongly mineral-associated dense fraction. They interpreted this observation as indicating the existence of at least two different C pools in the organo-mineral fraction: an older, more stable pool of C, and a younger, fast cycling C pool. Strickland et al. (1992) found similarly that ^{15}N-labeled inorganic N was incorporated rapidly into dense (organo-mineral) fractions of five soils of greatly differing mineralogy, then released as both inorganic and organic N during a subsequent incubation. The existence of rapidly cycling C and N in the dense or mineral-associated fraction can satisfactorily be explained by a zonal structure of organic accretions on mineral surfaces. While the organic materials directly adsorbed to the mineral surface are likely to be tightly bound and well protected from microbial degradation, the materials sorbed in outer regions of the organo-mineral complex, and lacking direct interaction with the mineral surface, are presumably more loosely bound and more readily desorbed or decomposed. That only part of the mineral-bound carbon is protected from oxidation is corroborated by experiments that subject subsoils to chemical oxidation. The resulting C solubilization and mineral dissolution show that most of the organic matter in subsoils is associated with mineral surfaces (Eusterhues et al. 2003; Mikutta et al. 2006). Thus mild chemical oxidation leaves an organic residue with a mass that correlates significantly with mineral surface F$^-$ reactivity, and a Δ^{14}C value lower than that of the original organic matter pool (Kleber et al. 2005).

Seasonal water repellency explained through presence of organic material sorbed to mineral surfaces in a zonal fashion

Seasonal changes in soil water repellency may also be explained by alterations to the zonal architecture of sorbed organic matter induced by seasonal changes in the soil environment. Non-seasonal water repellency in soils has often been attributed to the presence of hydrophobic moieties such as those found in long-chain fatty acids (Ma'shum et al. 1988). The presence of hydrophobic compounds alone, however, does not explain *seasonal* changes in water repellency. Using the 'molarity of ethanol droplet' method to measure repellency, combined with a set of organic extractions, Horne and McIntosh (2000) attributed seasonal changes in soil wettability to the existence of multiple, functionally different layers of organic matter on sandy grains. In their model, an inner layer of more hydrophobic compounds is covered by a layer of amphiphilic compounds. When the soil is wettable, the hydrophobic material is effectively screened, especially if the outer surface is well hydrated. Repellence occurs when the hydrophobic compounds making up the inner layer are more exposed. This can be linked to seasonal moisture differences through a combination of factors: during the wet season, the outer layer will be well hydrated, amphiphilic compounds will be arranged in such a fashion as to have their polar portions oriented outwards, the carboxylate anion will predominate, and hydrophobic groups will be effectively screened by more hydrophilic groups. With the onset of the dry season, a more

hydrophobic outer surface develops as the amphiphilic compounds change in orientation, the carboxylate groups are protonated, and contraction of the amphiphilic 'surface screen' exposes the interior hydrophobic layer.

Laboratory and industrial synthesis of multilayer organic assemblages

Multilayered organo-mineral structures are routinely manufactured and studied in the laboratory, mainly for biomedical (Galeska et al. 2001) and biotechnical purposes (Halthur et al. 2004). Because these artificial organo-mineral structures likely form as a result of some of the same adsorption mechanisms active in soils, they may be viewed as potential analogs of natural organo-mineral complexes. In one such study of artificial organo-mineral assemblages, Spaeth et al. (1997) sorbed protein multilayers to hydrophobic silanized silicon wafers using alternating incubations with poly-streptavidin and bovine serum albumin. They found that the thickness of the organic layers increased 18.75 nm per incubation, yielding a final protein multilayer thickness of 350 nm.

Galeska et al. (2001) sorbed layers of the Aldrich commercial humic fraction onto silicon wafers, noting that the expansion of the organic film could be significantly altered by the incorporation of salt, with the charge screening effect contributing to thicker film deposition irrespective of pH. Further experimentation indicated that the permeability of simple carbohydrates through the humic coating was a function of the number of self-assembled layers of organic material. That the probe glucose penetrated thick films composed of many layers of organic matter more readily than thin films made up of few layers suggests that organic molecules, including both SOM and xenobiotic substances, may not be tightly bound to outer regions of organo-mineral complexes.

Alkylated silicon oxide surfaces were used by Schmidt et al. (1990) in studies of protein adsorption on hydrophobic surfaces. They found that a model with at least three classes of adsorbed molecules was necessary to adequately describe their experimental results. A first layer was formed by the molecules that adsorbed within a short time after the beginning of the incubation. These molecules made up approximately 65% of the final coverage. They were irreversibly adsorbed and did not measurably exchange with bulk solution molecules. A second layer reached equilibrium after several hours of incubation and showed a pronounced and temperature-dependent exchange with bulk molecules. A third layer consisted of molecules that exchanged rapidly with the bulk solution, but comprised only about 10% of the total coverage. An important implication of this work is that a protein-based multilayer structure allows occurrence of both hydrophobic adsorption on a stable inner layer, as well as phase-partitioning into a dynamic outer layer, thus explaining experimental results suggesting the coexistence of both kinds of sorption mechanisms in the same system.

Reconciling the evidence for zonal structures on mineral surfaces

The evidence compiled above suggests that SOM may attach to mineral surfaces in a zonal or layered fashion. In conjunction with the work of Wershaw et al. (1995; 1996a; b) on adsorption of compost leachates to aluminum oxide, studies of the amounts or spatial distributions of organic materials bound to mineral particles, and of variations in C turnover time and seasonal water repellency, have provided a wealth of direct and indirect information supporting the concept of an organized, zonal architecture for SOM sorbed to mineral surfaces. Experiments and observations in the laboratory prove that organic multilayers on mineral surfaces can even be manufactured to serve specific purposes. Ecologically speaking, the work of Schmidt et al. (1990) is especially significant, as it assigns different exchange kinetics to molecules making up different parts of the organo-mineral complex, with molecules of the inner zone being the most stable, and molecules of the outermost zone having the fastest exchange with the soil solution. Such differential, zone-dependent kinetics could explain why organo-mineral isolates from soils can contain C and N pools with different turnover times (Trumbore et al. 1989; Strickland et al. 1992; Swanston et al. 2005).

Table 1 Relative composition of vascular plants, algae, bacteria, and fungi, compiled using data from Knicker (2004) and White (1997)

	Vascular plants	Algae	Bacteria	Fungi
	% Dry matter			
Lignin	5–30			
Cellulose	15–60			
Hemicellulose	10–30			
N-containing compounds	2–15	24–50	50–60	14–52
Lipids		2–10	10–35	1–42
Carbohydrates		40	4–32	8–60
	Ratio			
C:N ratio	20–50 (tree leaves) 25–80 (herbaceous plants)	6	5–8	≈10

The role of proteins in organo-mineral associations

Mineral-associated SOM exhibits C/N ratios of 7–14, whereas water-extracted SOM has C/N ratios of 26–55 (Aufdenkampe et al. 2001), indicating N enrichment of adsorbed organic materials. Numerous observations, made in both soils and marine/freshwater environments (Aufdenkampe et al. 2001), similarly suggest that the adsorption of nitrogenous compounds to mineral surfaces may be a broadly relevant ecological process. Thus, a model of organo-mineral associations should account for the body of evidence suggesting preferential adsorption of N-containing moieties over other organic compounds to mineral surfaces (Omoike and Chorover 2006; Hedges and Oades 1997).

Certainly, the relatively high strength of protein adsorption to mineral surfaces (Theng 1979; Chevallier et al. 2003; Wershaw 2004) is a long-established (Ensminger and Gieseking 1942)—and often technologically exploited (Gougeon et al. 2003)—chemical phenomenon, and one that has proved relevant to the laboratory synthesis of multilayer organo-mineral complexes, as discussed previously (Schmidt et al. 1990). We suggest that proteinaceous materials play a prominent role in the formation and structure of organo-mineral complexes due to both the relatively high abundance of such compounds in soils, and the ability of these materials to adsorb irreversibly to mineral surfaces.

Protein availability at soil mineral surfaces—^{15}N-NMR analysis has demonstrated that a significant amount of soil nitrogen is present in amide form (Almendros et al. 1991 Knicker et al. 1995; Knicker and Lüdemann 1995; Knicker 2000, 2002; Leinweber and Schulten 2000; Mahieu et al. 2000, 2002; Mathers et al. 2000; Zang et al. 2000), and thus most likely in the form of proteins or protein residues. Tremblay and Brenner (2006) showed in a 4-year decomposition experiment that on average 60–75% of the N in highly decomposed detritus was derived from heterotrophic bacteria, rather than plant tissues. As the smallest organisms in the soil, bacteria and fungi are able to enter small, confined pore spaces and die and decompose there, and also contain far more N than vascular plant materials or surface litter (Table 1). In fact, bacteria are known to actively use proteins to attach to surfaces (Bashan and Levanony 1988; Dufrene et al. 1999). Mycelial fungi also secrete a broad class of surface-active glycoproteins (Wright and Upadhaya 1996). Abundant evidence indicates that microbial products accumulate in fine clay fractions of soils (Leinweber and Schulten 1995; Kleber et al. 2004; Mertz et al. 2005), further corroborating the supposition that the more proteinaceous microbial residues are likely to make initial contact with mineral surfaces, rather than the less proteinaceous plant residues.

Protein polyfunctionality and adsorption to mineral surfaces—Proteins are a special class of amphiphilic molecules with a strong tendency to bind to surfaces and to resist desorption (Hlady and Buijs 1996). They consist of chains of amino acids with both apolar and polar (either neutral or charged) side chains, folded into a conformation in which as many apolar residues as possible are packed into the interior, leaving mainly polar and charged residues at the surface.

Given the diversity of functional groups making up proteins, no single process dominates protein adsorption to mineral surfaces. Instead, three subprocesses drive adsorption behavior: (i) structural rearrangement of the protein molecule; (ii) dehydration of parts of the sorbent and protein surfaces; and (iii) redistribution of charged groups at the organo-mineral interface (Haynes and Norde 1994). Numerous electrostatic bonds can form between reactive mineral sites and organic amide and other polar or charged functional groups during the adsorption process (Brash and Horbett 1995). Due to their large size and coiled structure, proteins gain considerable conformational energy by unfolding at the solid/liquid interface, an entropically driven rearrangement that produces numerous organo-mineral interactions and distinguishes protein adsorption from that of other available biomolecules (Haynes and Norde 1994). With adsorption to a mineral, proteins may increase the number of reactive sites on the newly coated surface by exposing their abundant polar functional groups to the soil solution. This effect is known as support preconditioning (Dufrene et al. 1996), and is considered a routine step preceding the adhesion of microorganisms to mineral surfaces (Bos et al. 1999; Bakker et al. 2004). The surface charge densities of both protein and surface can vary with pH, and adsorption is typically greatest at the isoelectric point of the protein (Ramsden 1995).

Proteinaceous compounds can bind especially stably to mineral surfaces over long time periods, as illustrated by the fruitless attempts of archaeologists to remove protein from archaeological artifacts for further study (Craig and Collins 2002). Amelung et al. (2006) used changes in chirality of aspartic acid and lysine to show that some soil proteins achieve residence times of centuries. Sorption experiments (Hedges and Hare 1987; Wang and Lee 1993) as well as observational data from marine sediments and riverine particles (Hedges and Hare 1987; Wang and Lee 1993; Mayer et al. 1995; Arnarson and Keil 2001; Aufdenkampe et al. 2001) also indicate strong and stable binding of amino acids to clay minerals. Glycoproteins secreted by arbuscular mycorrhizal fungi (Wright and Upadhaya 1996) stabilize soil aggregates (Baveye 2006), likely due to their ability to bind to both hydrophilic and hydrophobic mineral surfaces. Strong adsorption of defined proteins on clean clays is well documented in the laboratory, with the amount of adsorbed material varying over nearly five orders of magnitude with the nature of the sorbate, sorbent, and experimental conditions (Theng 1979; Burchill et al. 1981; Wang and Lee 1993; De Cristofaro and Violante 2001; Ding and Henrichs 2002).

N-containing biomolecules as contact materials within a zonal organo-mineral complex

The proposed special role of proteins in the organo-mineral contact zone has implications for the attachment of additional organic compounds, or the *zonal architecture* of organic materials adsorbed to mineral surfaces. Organo-mineral complexes featuring multiple layers of proteins have been synthesized using a variety of experimental methods (Schmidt et al. 1990; Spaeth et al. 1997; Halthur et al. 2004). The amounts of proteins that may eventually sorb to mineral surfaces can be large, approaching 1 g protein g^{-1} clay for clean clays (e.g., Burchill et al. 1981; De Cristofaro and Violante 2001) and buried ceramics (Craig and Collins 2002), with record values of 2.4 g g^{-1} (Greenland 1965) on montmorillonite, implying a soil C concentration greater than that allowed for a mineral soil horizon according to Soil Taxonomy (Soil Survey Staff 1999).

However, observations from natural systems provide more compelling evidence regarding the critical role proteins play within soil organo-mineral complexes. Physical fractionation data led Sollins et al. (2006) to postulate that sorption of proteins might create a basal layer to which other amphiphilic molecular fragments would adsorb more strongly than they would to clean clay surfaces, creating a zonal effect, with N-rich compounds more abundant near mineral surfaces, and C-rich compounds more abundant farther from the surface. Physical fractionation reveals the tendency for the C/N ratio to decrease with increasing particle density (Turchenek and Oades 1979; Young and Spycher 1979). Lighter fractions (<1.8 g cm^{-3}) have high C/N ratios because they are rich in plant structures high in lignin and cellulose. The continued downward trend in C/N

ratios at densities beyond 2.2 and even 2.4 g cm^{-3} has previously been attributed to the accumulation of proteinaceous material (Oades 1988), and is consistent with our suggestion that N-rich compounds have a high probability of remaining sorbed to mineral surfaces.

Sollins et al. (2006) further suggested that sequential density fractionation combined with ^{14}C analysis might offer a way to assess the role of N-rich compounds in the formation of organo-mineral complexes. They pointed out that variation in particle density correlated well with the percentage of C in the particles, and thus that C loadings decreased with increasing particle density, suggesting thinner coatings of organics, and in turn a more protein-rich inner layer. Assuming these thin inner coatings were more stable, ^{14}C age should increase with particle density. This proved to be true for an Andic forest soil they examined. However, large differences in mineralogy of the density separates from this soil precluded ascribing the increase in ^{14}C age solely to coating thinness.

The zonal structure of organo-mineral complexes: a hypothesis

Recent spectroscopic evidence suggests that the decomposing organic residues in soils can be viewed as a mixture of largely amphiphilic fragments (Chien et al. 1997; Engebretson and von Wandruszka 1997, 1998; von Wandruszka 1998; von Wandruszka et al. 1999; Ferreria et al. 2001; Martin-Neto et al. 2001; von Wandruszka and Engebretson 2001; Nanny and Kontas 2002). The amphiphilicity of many of these molecular fragments, and the polarity of the aqueous soil solution in which they are contained, cause them to self-assemble into micellar associations when suspended at high concentrations, and into layered or zonal structures when in contact with mineral surfaces. Based on the evidence presented above, we propose that the self-assembly of SOM on mineral surfaces creates a layered or zonal structure with regular features (Fig. 2).

The contact zone—When brought into contact with a mineral surface, amphiphilic SOM compounds form a contact zone whose structural properties depend mainly on the type, density, and chemical reactivity of the mineral functional groups, and on the pH of the soil solution. Organic fragments directly attached to mineral surfaces are protected against decomposition and do not participate in significant exchange with organic compounds in the soil solution. This can be explained in part by the strong, ligand-exchange bonding of charged or polar heads of amphiphilic molecules to hydroxylated mineral surfaces (Tiberg et al. 1999). Proteins, a special class of amphiphilic molecules, can bind particularly strongly to mineral surfaces because they reinforce the initial organo-mineral bonds that form with entropically favorable conformational changes that produce further opportunities for more numerous adsorption interactions (Haynes and Norde 1994).

The hydrophobic zone—Amphiphilic molecules adsorbed directly to mineral surfaces tend to mask the physicochemical properties of these surfaces (Bos et al. 1999), to the extent that an outwardly oriented region of high hydrophobicity may be created, especially when the underlying mineral surface has high densities of reactive, singly coordinated hydroxyls (Murphy et al. 1990). The hydrophobic zone thus formed provides a suitable region for sorption of hydrophobic moieties, including the hydrophobic portions of amphiphilic molecules in the soil solution, leading to formation of a bilayer structure on the surface of the mineral. In contrast, the direct adsorption of proteins to a mineral surface may lead to an increase in the number of reactive surface sites, rather than hydrophobic sites. Direct adsorption of proteins may not result in formation of a hydrophobic zone or a bilayer structure, but instead enable the attachment of SOM components through electrostatic interactions. Thus, the hydrophobic zone must not be considered an essential and continuous layer present within all organo-mineral associations, but rather a zone likely to be found to varying degrees in many of these associations.

The kinetic zone—Depending on stereochemical orientation, degree of amphiphilicity, cation content of the soil solution, pH, temperature, and perhaps several other controlling factors, a variety of modes of attachment of further organic

molecules appears to be possible. No common principle governing these associations is apparent. However, there is reason to assume that the organic compounds trapped in this outer region are partitioned rather than sorbed, and that their residence times within the outer region are shorter than the residence times of compounds in the intermediate or inner regions. Because "*Crowded conditions promote selfassembly*" (Goodsell 2004), the thickness of the outer layer is likely to depend more on input of organic materials than on the availability of binding sites, and to be largely be controlled by exchange kinetics. This suggests that more material will be sorbed to kinetic zones in topsoil A horizons than in subsurface B and C horizons. Movement of organics into and out of this outer region may thus resemble a phase-partitioning process, rather than classical adsorption.

Conclusions

With the proposed zonal model, we attempt to reconcile information from different natural and artificial systems and from various scientific fields into an integrated view of the organo-mineral complex and its most important properties. Our model encompasses interdependent hypotheses regarding (i) the formation of organo-mineral associations, (ii) the specific architecture of the zones of adsorbed organic matter, and (iii) the exchange kinetics of these organic materials with the surrounding soil solution.

We suggest a zonal structure for organic matter accretions on mineral surfaces by recognizing that SOM consists largely of amphiphilic molecular fragments with the thermodynamic impetus to self-assemble into micellar structures on mineral particle surfaces suspended in a polar liquid (Fig. 2). We further propose that microbial proteins are better able to bind to mineral surfaces, as well more likely to arrive at these surfaces, than are residues of vascular plants, thus explaining the proposed existence of a particularly stably bound, N-rich inner layer of organic material. Hydrophobic portions of these surface-bound molecules can be protected from contact with aqueous solution by the additional accumulation

of amphiphiles arranged such that the polar portions point towards the aqueous phase, creating a bilayer structure with a discrete hydrophobic zone. Empirical evidence for organic surface loadings of 2–5 times the monolayer equivalent (Hedges and Keil 1995) suggests that further attachment of organics in a third region or kinetic zone is possible, although for this outer zone or region, exchange rates of organic compounds with the soil solution are likely high, and residence times brief.

The arguments in support of the zonal hypothesis of organo-mineral complexes are indirect in nature. We invite the scientific community to join us in future attempts to challenge the zonal concept and to help us further elucidate the structure and dynamics of organo-mineral associations. If experimentally and empirically validated, the zonal model for organo-mineral associations in natural systems should not only open up a new road towards improved understanding of organic C and N dynamics in soils and sediments, but also facilitate the modeling of the fate and transport of contaminants.

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