

12.12 Mineral Matrices and Organic Matter

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Glossary

Adsorption A surface phenomenon where molecules from a gas, liquid, or dissolved state adhere to a surface. The process differs from absorption in which the sorbate permeates into the absorbent. Sorption encompasses both processes.

Aggregation Direct attraction between particles of soil or sediment via van der Waals forces or chemical bonding resulting in the structure of soils and sediments. Soil and sediment structure is determined by how individual soil granules clump or bind together and accumulate, and therefore, the arrangement of pores between them.

Bleb Small discrete units of organic matter often observed in sediments and soils to be located at joints and pore spaces between fine-grained phyllosilicate minerals. Often assumed to be of polysaccharide or protein composition and thought to play an important role holding clay minerals together to form primary aggregates.

Cation-exchange capacity The maximum quantity of total cations that a solid can hold, usually at a given pH value, and exchange with other cations in solution. It is expressed as milliequivalent of charge per 100 g (mEq + 100 g⁻¹) or as centimole per kilogram (cmol + kg⁻¹). The two units are coincident.

Clay An ambiguous term that refers to both size – generally smaller than 1–2 μm – and the mineral types that dominate in this size range – generally phyllosilicates.

Desorption The reverse of adsorption in which a molecule is released from a surface.

Exfoliation The removal from larger units of thin sheaths of clay mineral producing very thin lattice structures.

Exfoliation in the manner is hypothesized to produce thin ‘armoring’ coverings over microorganisms that can protect from predation and attack by higher organisms. Exfoliation in this sense is different from the larger-scale formation of joints in rocks that lead to the erosion and slumping of concentric slabs of rock.

Exudate Organic matter (usually polysaccharides) purposefully released by microorganisms for the purpose of creating or altering their immediate environment to suit their growth. Examples include exopolymeric substrates released by marine bacteria in order to produce flocculates and aggregates in sinking particles and sediments.

Humification Chemical changes to biochemicals that result in a decrease in their biologic availability. Many reactions have been hypothesized to lead to decreased availability, such as lipid oxidation and metal complexation. Resultant humified materials are often colored and acidic.

Intercalate The reversible inclusion of a molecule between two other molecules, used in this chapter to specifically define the sorption of small organic molecules into the interlamellar spaces of expandable phyllosilicate clays.

Mesopore Pores of diameter 2–50 nm.

Micropores Pores of diameter <2 nm.

Monolayer A single layer of adsorbed molecules.

Monolayer equivalent The amount of organic matter equivalent to that needed to create a single-layer coating

over all soil surfaces. It is not, and rarely has been, intended to refer to an actual monolayer. This amount depends on the nature of molecules putatively acting as a standard, but for most typical organic molecules of biologic origin, a monolayer equivalent would equal 0.5–1 mg-OC m⁻² of surface area.

Nanocomposite Generically, this term refers to any multiphase material in which at least one of the phases has nanometer-scale dimensions. In this chapter, we use the term to refer to a class of organic polymers containing exfoliated sheets of smectite with roughly unit cell thickness.

Occlusion The covering or blocking of organic matter within a mineral frame. In the marine literature, it often refers to protection of organic matter within a biomineral matrix such as the silicate walls of diatoms or the calcium carbonate shells of organisms such as foraminifera or corals. In the soil literature, it more often refers to protection within a matrix of small, nonbiogenic minerals.

Oxyhydroxide A generic term referring to a series of mixed hydroxide to oxide precipitates associated with metals such as iron and aluminum.

Phyllosilicate A generic mineral class containing tetrahedrally coordinated silicate sheets attached to octahedrally coordinated sheets of other metal oxides/hydroxides.

Remineralization The process of metabolically processing organic matter to return its elements to inorganic form in solution.

Smectite A class of layered aluminosilicate minerals, with unit cells containing two tetrahedral silicate sheets surrounding an octahedral sheet of varying composition. Isomorphous substitutions within these sheets lead to variable and intermediate net charge per unit cell, attracting exchangeable and hydrated cations of varying composition to populate the space between unit cells.

Sorption A physical and chemical process by which one substance becomes attached to another. Specific cases of

sorption are absorption – the incorporation of a substance into another, and adsorption – the physical adherence or bonding of solutes onto the surface of another phase. Two additional modes act in soils and sediments: multimode sorption – interaction of an organic macromolecule and a surface via more than one binding site. While this is typically considered to occur as multiple binding sites using the same mechanism (e.g., ligand exchange and cation exchange), the literature on multimode sorption in natural systems is currently poorly developed; multizone sorption – refers to the concept of sorption in differing layers where the inner layer closest to the mineral surface is called the ‘contact zone.’ In this zone, the formation of strong organomineral associations is favored by (1) polar organic functional groups of organic matter interacting via ligand exchange with singly coordinated mineral hydroxyls, forming stable inner-sphere complexes, or (2) proteinaceous materials that unfold upon adsorption. A secondary membrane-like bilayer contains a ‘hydrophobic zone,’ whose components may exchange more easily with the surrounding solution. Finally is an outer region, or kinetic zone, that is loosely retained by cation bridging, hydrogen bonding, and other interactions (Kleber et al., 2007).

Specific surface area A material property of solids that measures the total surface area. It is defined either by surface area divided by mass (with units of m² kg⁻¹) or surface area divided by the volume (units of m² m⁻³ or m⁻¹). The value obtained for specific surface area depends critically upon the method of measurement. In soils and sediments, the most common method for determining specific surface area is by N₂ adsorption and application of the BET (Brunauer et al., 1938) theory for calculating surface coverage of the gas. Despite common agreement among methods for many combinations of methods and solids, some combinations will systematically disagree with one another; one example is adsorption of N₂ gas versus ethylene glycol monoethyl ether (EGME) on solids containing smectite minerals.

12.12.1 Introduction

The three largest sinks of organic carbon on Earth are the stores in rock (70 million Gt of carbon), marine sediments (3000 Gt), and soils (2500 Gt; Hedges and Keil, 1995). Virtually all of this carbon is intimately mixed with minerals. The stabilization of organic matter in these mineral-rich systems receives interest from scientists both because of its relevance in the generation of fossil fuels and because of the role organic matter plays in the global cycles of many important elements. Over the past 100 years, both soil and marine researchers focused on the general topic, but in many respects, these researchers worked in isolation from each other (Hedges and Oades, 1997). For marine systems, Bader et al. (1960) summarized the importance of the research topic by noting that “interest in the organic matter in marine sediments began to develop about 35 years ago (e.g., 1920s). The concern of the original investigators revolved about the origin of petroleum. In recent years this area of investigation has received a new

surge of interest. Although the origin of petroleum is still a very important and vital issue, the role of organic matter in the processes of sedimentation including the formation of biomineral deposits, diagenesis of sediments, the accumulation of metallic ions in sediments and marine ecology is rapidly receiving increased interest.” Bader et al. (1960) then suggested that organic–mineral interactions, specifically sorption, are critical for promoting the preservation of organic matter in sediments. Similar stories can be culled from the soil literature (Kaiser and Zech, 1997). Jackson (1975), in comparing humic substances in soils and sediments, drew upon organic–mineral interactions as a major mechanism stabilizing humics in these systems. These sentiments still remain, and while much has been learned about organic–mineral interactions in soils and marine sediments, each new understanding brings a slew of new research questions.

As Waksman (1933), Bader et al. (1960), and many others have indicated, interactions between organic matter and minerals are frequently invoked as a major ‘reason’ that carbon is

preserved in these systems. In a very general sense, organic–mineral interactions can be considered to effectively protect organic matter against microbial degradation across an astonishing array of environmental settings, from deep-sea sediments to arctic tundra, but the mechanisms of the interactions vary greatly. Organic–mineral interactions can be broadly divided into three general types: (1) sorption of small molecules to surfaces via ‘classic’ mechanisms (e.g., ligand exchange), (2) sorption of larger organic molecules (e.g., proteins) via multiple points of interactions, and (3) aggregation/occlusion phenomena wherein complexes and aggregates create protective environments. The importance of organic–mineral interactions in preserving organic matter is well established. It competes with other preservation mechanisms, the most common of which is ‘selective preservation.’ Like organic–mineral interactions, selective preservation comes in a variety of flavors. Traditionally, selective preservation refers to the resistance of organic matter to degradation due to intrinsic properties of the organic matter itself (Huguet et al., 2008; Kokinos et al., 1998; Zonneveld et al., 2010); for example, it is too difficult for organisms to degrade. However, this hypothesis has occasionally been used too absolutely. Numerous lines of research have shown that (1) microbial communities are able to degrade any organic matter of natural origin; (2) the molecular recalcitrance of organic matter is relative, rather than absolute; and (3) ‘recalcitrance’ can be imparted to some organic compounds by sensitivity to electron acceptors (e.g., an oxygen effect) or by chemical alterations. A current definition for selective preservation is the preservation of organic matter in sediments and soils due to either sensitivity to oxygen (Amarson and Keil, 2007; Burdige, 2007; Hedges et al., 1999) or due to the secondary production of hard-to-degrade organic matter via abiotic (e.g., burning; Baldock et al., 2004) or biotic (e.g., reaction products of nonspecific oxidative attack) mechanisms. One version of selective preservation is the current embodiment of the 100+-year-old concept of humification in which chemical alterations to biochemicals reduce their

availability to organisms. It is most likely that for typical soils or sediments, all of these mechanisms and submechanisms are at work. How they interact, reinforce, or work against each other remains an important research topic for both soil and sediment geochemists.

Soils and sediments share many common characteristics despite large differences in the manner with which organic matter and minerals are delivered to or processed within the systems and the types of organic matter initially present (Baldock et al., 2004; Hedges and Oades, 1997). Although annual inputs of organic matter are typically orders of magnitude larger than standing stocks, organic carbon contents in soils and sediments show a remarkably small range, typically from 0.5 to 5 wt% organic carbon within the mineral-dominated matrix (Figure 1). Over the vast majority of the Earth’s surface, concentrations of organic matter in soils and sediments correlate tightly with those of fine-grained minerals (Baldock et al., 2004). This correlation holds especially well in the ocean (Premuzic et al., 1982), where organic matter and lithogenic mineral deposition are more strongly linked than in soils. The combination of similar bulk concentrations and correlation with fine-grained minerals argues for a similar ‘buffering’ or capacity-linked control on organic matter concentration in both types of environment. Because the mineral types are roughly similar between land and sea – indeed most marine minerals derive from land – organic geochemists must look for common mechanisms of stabilization of the different kinds of organic matter inputs into these zones.

Arguments for a fine-grained mineral control on organic matter preservation are numerous and persuasive (Hedges and Keil, 1995; Kaiser and Guggenberger, 2003; Kaiser and Zech, 2000; Kalbitz et al., 2005; Kennedy et al., 2002, 2006; Kleber et al., 2007; Kögel-Knabner et al., 2008; Mikutta et al., 2009; Pichevin et al., 2004; Ransom et al., 1998; Wagai and Mayer, 2007). Nevertheless, a map of organic matter concentrations clearly indicates that most of the area of global sediment and

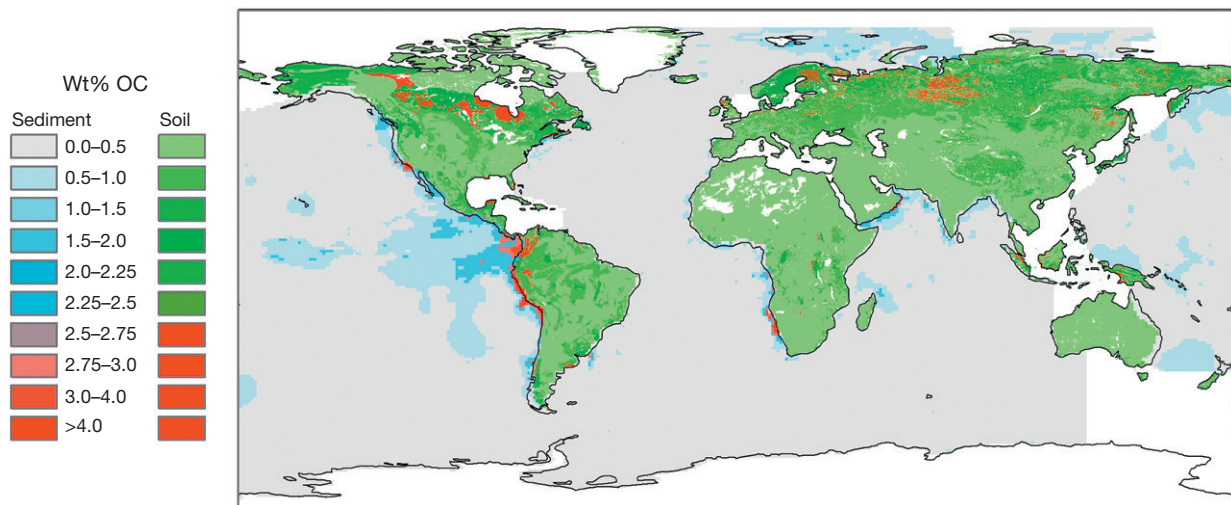


Figure 1 Weight percent organic carbon in soils and surface marine sediments. Soil data from Hiederer and Köchy (2011) and marine sediment data from Seiter et al. (2004). Organic matter content is a dynamic balance between organic matter inputs and soil or sediment development and delivery. In soils, the primary determinant of organic carbon content is rainfall and temperature (Hedges and Oades, 1997), while in sediments, it is a combination of lithogenic mineral and organic matter input (e.g., Premuzic et al., 1982). Color ramps highlight areas of exceptional carbon storage in northern forests and in continental margins of the west of the Americas and Africa.

soil contains organic matter in quantities far below the 'carrying capacity' of sediments (Figure 1), which is thought to equate to 2–3 wt% organic carbon (Hassink, 1997; Hassink et al., 1997; Hedges and Keil, 1995; Mayer, 1994a). Thus, large areas of the Earth accumulate or preserve little organic carbon, at least on time scales of millennia or longer (Baldock et al., 2004; Hedges and Keil, 1995). From a spatial perspective, many organic–mineral interactions are not necessarily at their 'maximal effectiveness.' However, the argument changes when deposition flux is considered. Both on land and in the sea, greatest carbon accumulation coincides with areas where organic–mineral interactions are poised at or slightly below the 'monolayer-equivalent' amounts of organic matter per unit mineral-specific surface area (Baldock et al., 2004). These areas include temperate and tropical forest and agricultural lands (Kögel-Knabner et al., 2008; Lutzow et al., 2006) and most continental margins of marine systems (Hedges and Keil, 1995).

Complementing these areas where carbon burial is either equal to or lower than expected based on mineral delivery are areas where carbon concentrations and burial flux are anomalously high. These areas of the Earth's surface have in common a lack of oxygen, which is thought to be protective of organic matter (Arnarson and Keil, 2007; Burdige, 2007; Hartnett et al., 1998). Examples include the oxygen-deficient zones of the ocean (Arabian Sea and Eastern Tropical Pacific) and the peatlands of North America and Russia (Figure 1). The oceanic examples show strong organic matter–mineral interactions, while the peat deposits lack any minerals. In nearly all examples of important organic carbon storage and burial, organic–mineral interactions are thought to play important roles in protecting organic matter from degradation. The nature of these roles presumably changes as a function of other controls, and it is not clear to what extent they are similar or vary among the different environments.

12.12.2 Evidence for Organic Matter Association with Minerals

12.12.2.1 Correlations with Grain Size and Mineral-Specific Surface Area

One of the more common approaches to identifying mechanisms controlling organic matter loadings in soils and sediments is to relate organic matter quantities to the physical characteristics of the deposits (Hedges and Keil, 1995; Hedges and Oades, 1997; Tisdall and Oades, 1982). Organic matter has long been known to be concentrated in marine sediments along continental margins containing fine-grained deposits (Bordovskiy, 1969; Waksman, 1933). A common mechanism inferred from this observation is sorption of organic matter to mineral surfaces, which leads to concentration of organic matter in finer deposits (Weiler and Mills, 1965 and many later papers). Suess (1973) and Muller and Suess (1977) demonstrated a direct correlation between the mineral surface area and the organic content of marine sedimentary particles, a relationship which suggested organic matter sorption. The observed loading of organic carbon per unit of surface area was comparable to the value reported by Arnold and Pak (1962) for single layers of protein associated with interfaces in aqueous systems, implying similar monolayer loading in

these sediments. Premuzic et al. (1982) showed strong correlations between proportions of clay-size material and organic matter content across large swaths of ocean bottom, implying generalized control between surface-rich minerals and organic matter. Coupled with similar correlations within size separates of sediments, and inability to physically remove organic matter of low density from higher-density minerals, these observations supported a focus on sorptive associations between minerals and organic material as fundamental to the latter's persistence, at least in marine depositional systems (Mayer, 1994a). Subsequent work was to show that this 'sorption' was likely not simple molecular attachments to surfaces.

Unlike marine sediments, soil systems present a less tidy correlation between mineral surface area and organic matter content (Hedges and Oades, 1997; Mayer, 1994b). Higher variance likely derives from several causes. First, terrestrial vegetation often deposits more organic detritus than in marine systems – to the extent that completely organic O-layer often forms at the soil surface and also adds nonmineral-associated organic detritus in significant concentrations to the underlying mineral-rich horizons. This contribution can be observed via density separations (e.g., Baisden et al., 2002). In the upper soil column, minerals associate with organic matter extensively via combinations of sorption and aggregation processes, which vary in their size, organic composition, and genesis (Chenu and Plante, 2006; Tisdall and Oades, 1982). Larger aggregates typically contain more discrete organic particulate material of plant origin (e.g., Verchot et al., 2011) and introduce variability into the grain size relationships (Six et al., 2002), despite positive correlations between clay content and formation of large aggregates (deGryze et al., 2006). Tilled agricultural soils show tighter grain size correlations because tilling selectively reduces this discrete organic particulate organic matter (Hassink et al., 1997; Kögel-Knabner et al., 2008). Second, moisture content and temperature affect microbial processing of soil organic matter more than for marine systems in which these two parameters are much less variable. Nonetheless, after accounting for the two primary determinants on soil organic content (temperature and water availability; Hedges and Oades, 1997), grain size correlations remain strong in many soil systems (Mikutta et al., 2009; Nagao et al., 2005). When soils are separated by size, fine silts and clay separates typically contain the highest organic matter contents (Shimel et al., 1994). The clay content, sometimes seen through the lens of surface area measurements, is sometimes regarded as a limitation on the soil carbon storage capability (e.g., Hassink, 1997).

12.12.2.2 Why Do Organic Matter and Minerals Stick Together?

The type of association between organic matter and mineral varies in response to organic molecular moiety, size, and shape, as well as to mineralogy and surface characteristics. Attachments vary along a continuum of mechanisms from simple adsorption to mineral surfaces to more physical incorporations into matrices of minerals – for example, occlusion within mineral grains (produced through either biotic or abiotic mechanisms) and aggregation of colloid- to particulate-sized organic materials with mineral grains at various levels of complexity.

12.12.2.2.1 Sorption

Sorption is influenced by the chemical properties of both the mineral and the organic matter. The main mineral determinant is its surface chemistry and its physical properties (e.g., shape, roughness, and specific surface area). The properties of the organic matter also strongly influence sorption, particularly the presence or absence of carboxyl or amine groups with which to interact with surfaces. Organic matter can be associated with mineral surfaces by a variety of binding mechanisms, such as ligand exchange, which is often considered to be the most important one (Feng et al., 2005; Kaiser et al., 2007; Kleber et al., 2007) and polyvalent cation bridges and weak interaction, which include van der Waals forces, hydrophobic interactions, and H-bonding. Excellent reviews of sorptive mechanisms are available: Derenne and Largeau (2001), Knicker (2007), Kögel-Knabner et al. (2008), Lutzow et al. (2006), Manjaiah et al. (2010), Schwarzenbach et al. (2003), and Six et al. (2002).

Six main mechanisms have been suggested to be involved in the sorption of organic matter to mineral surfaces: ligand exchange, ion exchange (cations and anions), cation bridging, van der Waals interactions, hydrogen bonds, and hydrophobic effects.

12.12.2.2.1.1 Ligand exchange

Ligand exchange involves the exchange of acidic hydroxyl groups of organic matter (e.g., carboxylic and phenolic) for hydroxyl groups on the surface. This mechanism is thought to dominate adsorption of humic substances and natural organic matter on hydrous aluminum and iron oxide surfaces in freshwater (Gu et al., 1994a). Ligand exchange occurs mostly in acid soils and soils that are rich in oxides. In marine systems, binding by ligand exchange can also be a major mechanism. The bonds by ligand exchange are very strong and can persist over 100 years (Lutzow et al., 2006).

12.12.2.2.1.2 Ion exchange

Ion exchange is the exchange of ions between a solution and a complex or surface. In soils and sediments, it typically occurs between singly coordinated OH groups on mineral surfaces and carboxyl groups (COOH) and phenolic OH groups of organic matter, for example, Fe-O-C bonds (Lutzow et al., 2006). Complexation of organic matter and mineral surfaces typically depends on solution ionic strength and pH (Mikutta et al., 2007). More organic matter is bound at lower pH values. For example, Gu et al. (1994b) found maximum sorption between pH 4.3 and 4.7 for carboxylic acids in soils. The pH determines the charge of both the mineral surface and the soil organic matter and thus the exact ion exchange binding mechanism. Ion exchange is considered to be one of the more important binding mechanisms in soils and sediments. In deep soil horizons, as much as 90% of the organic matter present has been attributed to ion exchange (Mikutta et al., 2009). This can be mineral-specific: for goethite, the majority of organic matter interacted with goethite via ligand exchange but not for pyrophyllite or vermiculite (Mikutta et al., 2009).

12.12.2.2.1.3 Cation bridging

Organic anions are normally pushed away from negatively charged surfaces. Binding is enhanced, however, in the

presence of polyvalent cations, which form positively charged bridges between the negatively charged mineral surface and the negatively charged acidic functional groups of the organic matter (COO⁻). In neutral and alkaline soils and in the oceans, these bridges form mostly via Ca²⁺ and Mg²⁺, whereas in acid soils, additionally, Fe³⁺ and Al³⁺ form cation bridges. The coordination complexes of the Fe³⁺ and Al³⁺ ions are considerably stronger in comparison to those with Ca²⁺ (Lutzow et al., 2006). However, the binding efficiency of organic matter, which is bound through cation bridges onto phyllosilicates, is lower than those of organic matter that is bound through ligand exchange at Al and Fe oxyhydroxide surfaces (Lutzow et al., 2006). Polyvalent cation bridges are found in soils with exchange phases that are dominated by Ca²⁺ or Al³⁺ cations. Though often reversible, they can last also for more than 100 years (Lutzow et al., 2006).

12.12.2.2.1.4 Van der Waals forces

Van der Waals forces are electrostatic forces caused by a temporarily fluctuating dipole moment arising from a brief shift of orbital electrons to one side of an atom or molecule, which creates a similar shift in adjacent atoms or molecules (Lutzow et al., 2006). Van der Waals forces are nonspecific interactions that can form between any kinds of molecules, regardless of chemical structure (Schwarzenbach et al., 2003). Individual van der Waals bonds are short-lived, but this form of bonding can achieve greater permanence if many such linkages are formed across both the adsorbing substance and the surface, because at any given time, sufficient van der Waals bonds can suffice to prevent desorption. This is sometimes important for binding of high-molecular-weight organic matter such as protein to surfaces (Rabe et al., 2011).

12.12.2.2.1.5 Hydrogen bonding

A hydrogen atom with a positive partial charge interacts with partially negative charged atoms (Lutzow et al., 2006). Hydrogen does not possess any inner electrons isolating the nucleus from the bonding electrons, it consists only of one proton. In hydrogen bonds with highly electronegative atoms, the bonding electrons are drawn to the electronegative atom, leaving the proton exposed at the outer end of the covalent bond. This proton can now attract another electron-rich center and form a hydrogen bond (Schwarzenbach et al., 2003). Like van der Waal's forces, hydrogen bonds are generally considered easily reversible and thus are not often considered important bonding mechanisms leading to long-term protection of organic matter in soils or sediments (Nguyen and Harvey, 2001; Plante et al., 2005).

12.12.2.2.1.6 Hydrophobic interactions

Nonpolar residues are excluded from water by entropy-related interactions that force the nonpolar groups together. Hydrophobic molecules in sediment pore waters tend toward surfaces or toward the production of micelles. Hydrophobic interactions become more favorable at low pH due to the protonation of carboxyl groups of organic matter (Lutzow et al., 2006). This type of sorption, though poorly studied, may in fact be a dominant form through which larger macromolecules interact with surfaces (at least initially; Rabe et al., 2011) and promote associations with other, presorbed organic molecules.

In general, the importance of the different mechanisms is thought to go from ligand exchange (strong stable bonds) to hydrogen bonds (weak and unstable) with the exact role of hydrophobic interactions relatively unknown. Mikutta et al. (2009) showed that organic matter bound to minerals mainly by ligand exchange was more resistant against mineralization than organic matter held by noncoulombic interactions (van der Waals forces). Furthermore, Ca bridges enhanced the stability of sorbed organic matter but less than the binding via ligand exchange (Mikutta et al., 2009; Table 1).

12.12.2.2.1.7 Multimode sorption

To better understand sorption to mineral surfaces, it is also important to focus on the molecular structure of the soil organic matter. Molecules with a high molecular weight, and those with aromatic structures, are often observed to be preferentially adsorbed from solution and also to be 'irreversibly' sorbed such that they cannot be retrieved from the surfaces they interact with (Ovesen et al., 2011). This observation has led several researchers to conclude that larger molecules are better stabilized against microbial respiration due to sorption at multiple locations along the molecule and mineral (Nguyen and Harvey, 2001; Ovesen et al., 2011; Rabe et al., 2011). Larger molecules, such as carbohydrates, proteins, and strands of DNA, are capable of interacting with surfaces in complex ways, including employing multiple sorption mechanisms and establishing multiple points of contact with the surface. They can also bind simultaneously with multiple mineral grains, creating exceedingly small aggregates (Wiseman and Puttmann, 2006).

One area of relatively poor knowledge is how proteins interact with surfaces. In studying polymer chemistry, Kim and Yoon (2002) noted that "It is not an exaggeration to say that nobody knows what exactly happens at the interfaces between proteins and particles. Proteins are so large that they cannot be treated as small solutes, and surfaces are variable, which makes quantification difficult." Because of its importance in medicine, the most studied type of multimode

sorption is that of protein to synthetic surfaces (Rabe et al., 2011). Protein sorption typically occurs in two steps, the first being sorption to surfaces via electrostatic charges, where the net positive charges of the proteins align loosely with the negative charges of the surface. During this stage of sorption, which can last from seconds to years, sorption is typically reversible and does not alter the three-dimensional (3D) structure of the protein. The second stage of sorption involves a change in the conformation of the proteins and is typically irreversible. The change involves denaturing the protein (unfolding and uncoiling) and arranging the chain along the surface to lower its entropy. When multiple proteins compete for surfaces, the general observed phenomenon is that of reversible sorption by the most abundant protein in solution followed by displacement of these proteins by ones of higher affinity in the denatured state. As a generality, larger proteins show greater affinity for irreversible sorption to surfaces (Kim and Yoon, 2002). The dominant interactive forces between proteins and surfaces are typically hydrophobic interaction, ionic (or electrostatic) bonding, hydrogen bonding, and van der Waals interactions (Asthagiri and Lenhoff, 1997; Wang et al., 2012). Proteins can readily be sorbed by clays and metal oxides (De Cristofaro et al., 1999; Ensminger and Gieseking, 1939; Ovesen et al., 2011). Smectites have been observed to sorb more than their own weight by intercalating the protein into the interlayer of the expandable clay (Ovesen et al., 2011; Theng, 1979). Studies of protein sorption to different surfaces indicate that in addition to the surface charge and distribution playing an important role in guiding protein placement and unfolding, an additional role is played by other proteins already sorbed nearby, which can interact with, and dictate, the nature and strength of sorption for the new protein, a process known as 'cooperative sorption' (Rabe et al., 2011). Although it is unknown how 'blebs' form ('blebs': small discrete units of organic matter often seen within pore spaces between fine-grained minerals; see next section), protein clusters and aggregates consisting of many hundreds of proteins are known to form in solution upon cell death and to then

Table 1 Mechanisms of sorption to mineral surfaces

Mechanism	Reactive groups/surfaces	Organic matter functionalities	Others
Ligand exchange	OH groups on edges of phyllosilicate minerals and on oxide minerals	Aliphatic or phenolic OH ⁻ groups, acid and amine groups on organic matter	
Ion exchange	Fixed ions or anions	Amines, amides, alcohol groups	
Cation bridging	Negatively charged functional groups such as OH ⁻ on expandable clays and clay edges	Carboxyl, carbonyl, alcohol, and organic acid moieties	Charged cations such as Na and Ca in solution
Van der Waals forcing	Nonexpandable clay surfaces, neutral surfaces of larger grains (quartz, gibbsite, etc.)	Uncharged, nonpolar organic moieties, such as alkyl and aromatic carbon	
Hydrogen bonding	Mineral with oxygen on surfaces, e.g., kaolinite	Carboxyl, carbonyl, phenolic, amines	
Hydrophobic interactions	Nonpolar, uncharged surfaces (top sheets of clays and quartz)	Nonpolar organic molecules	
Multimode sorption		Sorption of organic matter with more than one binding point using any of the aforementioned mechanisms	
Intercalation	Expandable phyllosilicates (smectites)	Organic molecules capable of creating or maintaining dipoles	
Occlusion in biominerals	Calcites and biogenic opal	Proteins and long-chain polyamine templates for opals, positively charged moieties for calcites (e.g., amino acids, peptides)	
Occlusion in oxide precipitates		Positively charged moieties such as amines	

cooperatively rearrange along surfaces such as to lower the net entropy of the entire cluster, resulting in some proteins being denatured and associated strongly with the surface while others interact (in 'multiple layers') with the sorbed proteins. Such surface-associated aggregations are known as protein 'coronas' (Sahoo et al., 2007; Wang et al., 2012) and can speculatively be considered candidates for 'blebs' that hold organic–mineral aggregates together.

12.12.2.2.1.8 Intercalation

A special type of sorption is intercalation within phyllosilicates (Lutzow et al., 2006). Organic ligands can intercalate into the interlayer spaces of expandable phyllosilicates (2:1 clays), particularly at low pH (Violante and Gianfreda, 2000). Organic cations can intercalate beyond the cation-exchange capacity of the clay if van der Waals forces play a major role in binding molecules to surfaces (Theng, 1979). Therefore, Theng et al. (1986) proposed intercalation of organic matter into interlayers of expandable phyllosilicates as a dominant stabilization process in acid soils (pH < 4). However, Eusterhues et al. (2003) found no indications of intercalation of organic matter into internal phyllosilicate surfaces in acid forest soils. One problem in this context is that there exist no specific methods to determine intercalated organic matter so that its chemical characterization and quantification is unreliable (Alexandre and Dubois, 2000; Kiersnowski et al., 2009). For example, the usual measurement of phyllosilicates by x-ray diffraction relies on unit cells separated by repeated, constant, organic interlayers, in order to achieve Bragg diffraction; it is unlikely that intercalation in nature would provide such repeating organic interlayers.

An extreme case of intercalation is the complete exfoliation, or splitting apart, of smectite crystallites. Organic cations are especially effective at exfoliation of smectites and might episodically appear in a soil or sediment to cause thin packets of smectite unit cells to exfoliate. Nanocomposite technology is based on this process in which various organic molecules are intercalated into smectite minerals to drive them apart into widely separated unit cells (Fukushima et al., 2010a,b; Kinyangi et al., 2006). This process can strongly reduce diffusive transport of, say, gases normal to the planes of the unit cells, with minimal use of mineral in the organic film. One implication from this literature is that intercalation in nature may lead to widely separated unit cells that would only show as smectite in x-ray diffraction if all of the organic matter is first removed and the unit cells allowed to reassemble; this possibility was discussed extensively in the so-called 'fundamental particle' literature (Nadeau, 2011; Nadeau et al., 1984). Although modified x-ray diffraction technologies to detect these aperiodic structures are being developed (Szczerba et al., 2010), the nanocomposite literature usually has more success using high-resolution TEM approaches (Alexandre and Dubois, 2000). While some of this type of TEM work has been done in natural systems (e.g., Chenu et al., 2009), more is needed in conjunction with organic matter detection capability.

12.12.2.2.2 Occlusion by biomineralization

Organic matter can be occluded into the mineral matrix of organisms (biominerals) during growth. This organic matter is then effectively trapped and preserved until the mineral coating is removed. The classic example of this is collagen

(protein) matrices upon which calcite bone is developed in mammals, but numerous examples of biomineralization and occlusion exist within sediment and soil. Protein and long-chain polyamine templates are used by diatoms to produce opaline shells (Bridoux and Ingalls, 2010), and amino acids are effectively trapped within calcite minerals of foraminifera, coccolithophores, and corals (Ingalls et al., 2003, 2004). Investigations of the composition and stability of organic matter in biominerals suggest that carbonates and silicates are important conveyors of relatively unaltered organic matter to sediments (Carter and Mitterer, 1978; Maita et al., 1982), and these materials are valuable for paleoceanographic investigations (Ingalls et al., 2003). Sediments underlying large swaths of the ocean are dominated by these biogenic minerals, and the organic matter trapped within their matrices dominates the total organic matter content of these systems (Bridoux and Ingalls, 2010). Much has been written on biomineralization, and readers are referred to works such as Baeuerlein (2000) and Dove et al. (2003) for extensive treatises on the subject (see also Chapter 10.4).

12.12.2.2.3 Secondary architectures: aggregation

The foregoing chemical forcings lead to direct contact between organic materials and mineral surfaces. The resultant organo-mineral associations serve as building blocks for associations at higher levels of complexity. In both aquatic and terrestrial environments, physical separations and microscopic examinations show aggregates consisting of many mineral grains and organic subunits. These aggregates show considerable persistence in their respective environments and indicate a role for these levels of organization on biologic availability.

The soil literature has explored the distribution and properties of aggregates more thoroughly than has been done in the sediment literature. Tisdall and Oades (1982) reviewed early suggestions that small aggregates coalesce to form larger ones, and that the properties of these secondary aggregates differ from those of the smaller ones. They and others (e.g., Christensen, 2001; Golchin et al., 1997; Six et al., 2002) have proposed classification schemes for soil aggregates, often based on operational separation methods. A guiding theme has been a hierarchy of associations, with different sizes, compositions, and lifetimes at the different levels of the hierarchy.

At the smallest scale, much organic matter in many soils and sediments associates with clay-size minerals to form what are often called organomineral complexes. If chemical sorption is the driving mechanism for this association, then it will be optimized for smaller mineral sizes due to surface area:volume considerations. These primary organomineral complexes are often thus seen with clay minerals and metal oxyhydroxides of submicrometer to micrometer dimensions. The two mechanisms that are most likely to create such a primary complex are (1) sorption of dissolved organic molecules to mineral surfaces or (2) aggregation of macromolecular (colloidal) organic matter with minerals. It is often hard to distinguish between these two phenomena in finer grained fractions where most organic matter resides, especially because colloidal organic matter is 'dissolved' by operational definitions. High resolution microscopy results imply that the organic matter in these associations is not an evenly spread film of small organic molecules, but instead more often consists of colloid-sized 'blebs' of organic

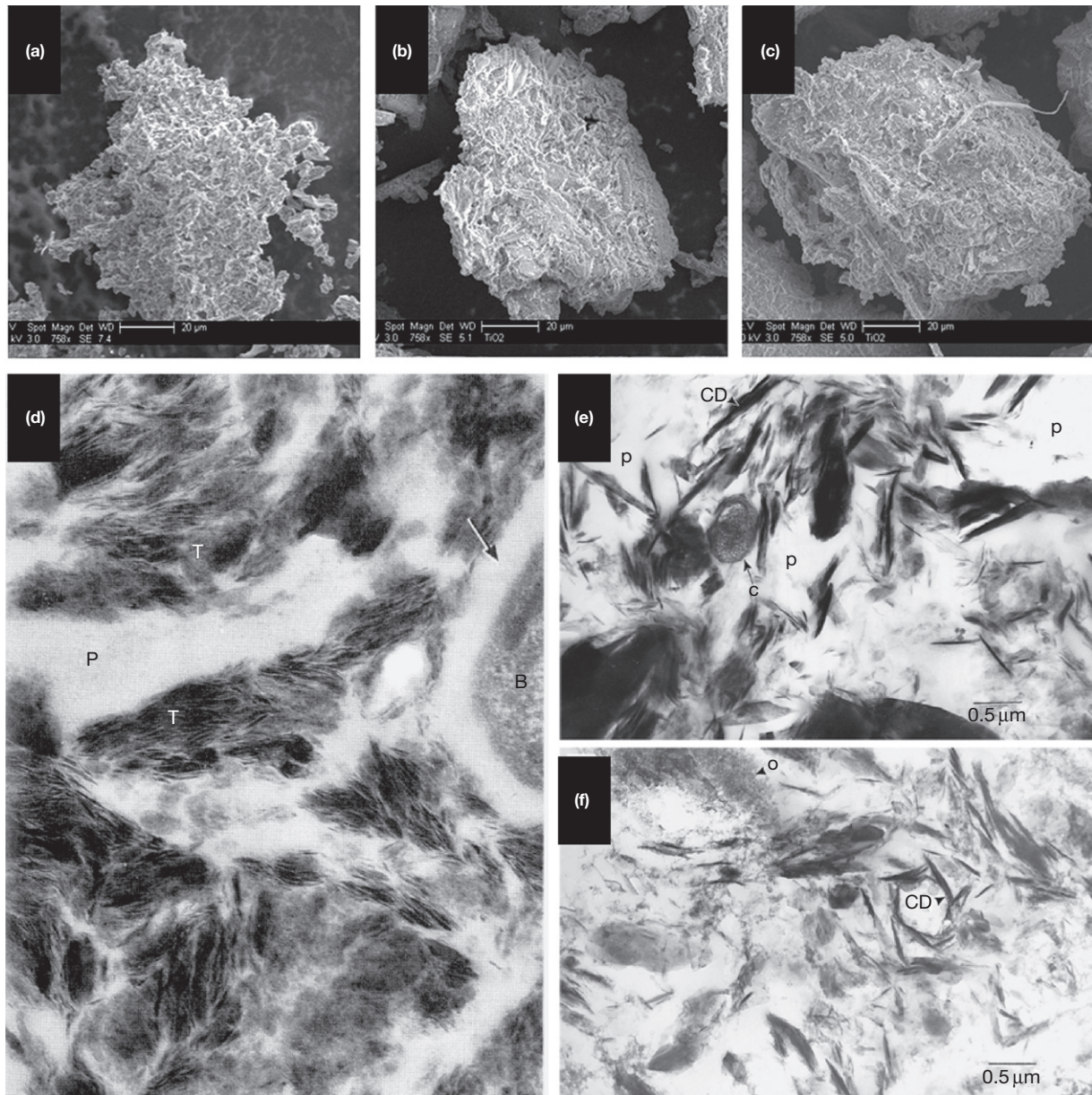


Figure 2 Scanning and transmission electron microscope images illustrating similarities in the general shape and morphology of organomineral complexes in soils, river suspended sediments, and marine sediments. SEM images (bar = 20 μm) of (a) an aggregate from the Washington margin (~ 2000 m water depth; [Arnarson and Keil, 2007](#)), (b) suspended particles in the upper Amazon River (unpublished data), and (c) soil from Clayoquot Sound, British Columbia (unpublished data). Finer scale TEM images of (d) the Weisenboden clay-rich soil illustrating tactoids (T) with pores filled with polysaccharides (P) and a bacterium (B) surrounded by exudates (extracellular polysaccharide, ECP; from [Foster, 1985](#)). Images (e) and (f) illustrate clay fabric and a prokaryotic cell (c) from a marine sediment. P denotes pore spaces. O denotes organic matter. The arrangement of clay domains (cd) is reminiscent of the particle arrangements that commonly occur around single bacterial cells in soils and sediments. Reproduced with permission from [Bennett RH, Ransom B, Kastner M, et al. \(1999\) Early diagenesis: Impact of organic matter on mass physical properties and processes, California continental margin. *Marine Geology* 159: 7–34.](#)

matter located among the sub-micrometer clay grains ([Lehmann et al., 2007; Wan et al., 2007](#)). These results imply significance for a colloidal aggregation mechanism.

Attempts to achieve full dispersion of these primary organomineral complexes is extremely difficult, and usually results in a significant fraction of clay and organic matter persisting as multi-grain assemblages with dimensions of severalfold greater than their primary, submicrometer clay crystallites. For

example, [Emerson \(1959, 1977\)](#) noted parallel clay crystallites often grouping closely together and apparently behaving as a single unit. These associations, variously called 'domains' or 'tactoids' ([Bennett et al., 1999; Emerson et al., 1986](#)), ultrafines ([Coppola et al., 2007](#)) or organoclays ([Plante and Chenu, 2006](#)), usually contain face-to-face arrangements of primary clay crystals. They are evident in soil and sediment systems, and comprise an extremely common secondary level of

organization (though perhaps less appreciated and studied in sediment systems).

As seen in Figure 2(d-f), intimate associations between these tactoid/domain structures and connecting organic matter (e.g., polysaccharides) are observed in soils, sediments, and sedimentary rocks (e.g., Emerson et al., 1986; Ransom et al., 1999; Salmon et al., 2000). Association of patches of organic matter with these tactoids/domains is clearly evident via careful transmission electron microscopy (Chenu and Plante, 2006; Furukawa, 2000). Despite this patchiness, the concentration of organic matter at this scale of aggregation often falls into a relatively constant ratio to the mineral surface area – the so-called ‘monolayer-equivalent’ level of $0.5\text{--}1\text{ mg-OC m}^{-2}$. Based on appropriate mineral and organic matter densities and clay surface area:mass ratios, this $0.5\text{--}1\text{ mg-OC m}^{-2}$ loading predicts aggregate densities of roughly $1.9\text{--}2.3\text{ g cm}^{-3}$ (Bock and Mayer, 2000; Chenu and Plante, 2006), and these so-called ‘mesodensity’ associations are therefore separable by high-density liquids. Clay-rich, mesodensity aggregates contain important fractions of organic matter in soils and sediments (Arnarson and Keil, 2007; Bock and Mayer, 2000; Chenu and Plante, 2006; Virto et al., 2008).

Observed prior to separations, domain structures are generally joined into larger aggregations, at a variety of scales (Figure 3). Aggregations to the scale of several micrometers are commonly observed both in situ and after separations, implying resistance to breakup in nature or the laboratory. Aggregation of these domains occurs via gluing by organic matter and/or metal oxyhydroxides, with the latter more common in highly weathered environments such as oxisols (Kiem and Kögel-Knabner, 2002; Kinyangi et al., 2006). Elevated organic matter concentrations have long been found in the fine silt size range of particle size separations, for soils and sediments (e.g., Catroux and Schnitzer, 1987; Tanoue and Handa, 1979; Tiessen and Stewart, 1983). Recent attention is focusing on aggregates in this size fraction as an important contributor to carbon storage in soils (Virto et al., 2008). Fine silt-sized fractions in marine sediments can contain as much organic matter by weight as clay fractions and are accompanied by high clay contents and surface area values (Keil et al., 1994a,b) – again suggesting aggregation of finer clays into this size range. It is notable that the mesodensity aggregates in Arnarson and Keil’s (2007) exploration of margin sediments fall into this fine silt size class (cf. their Figure 2(c)).

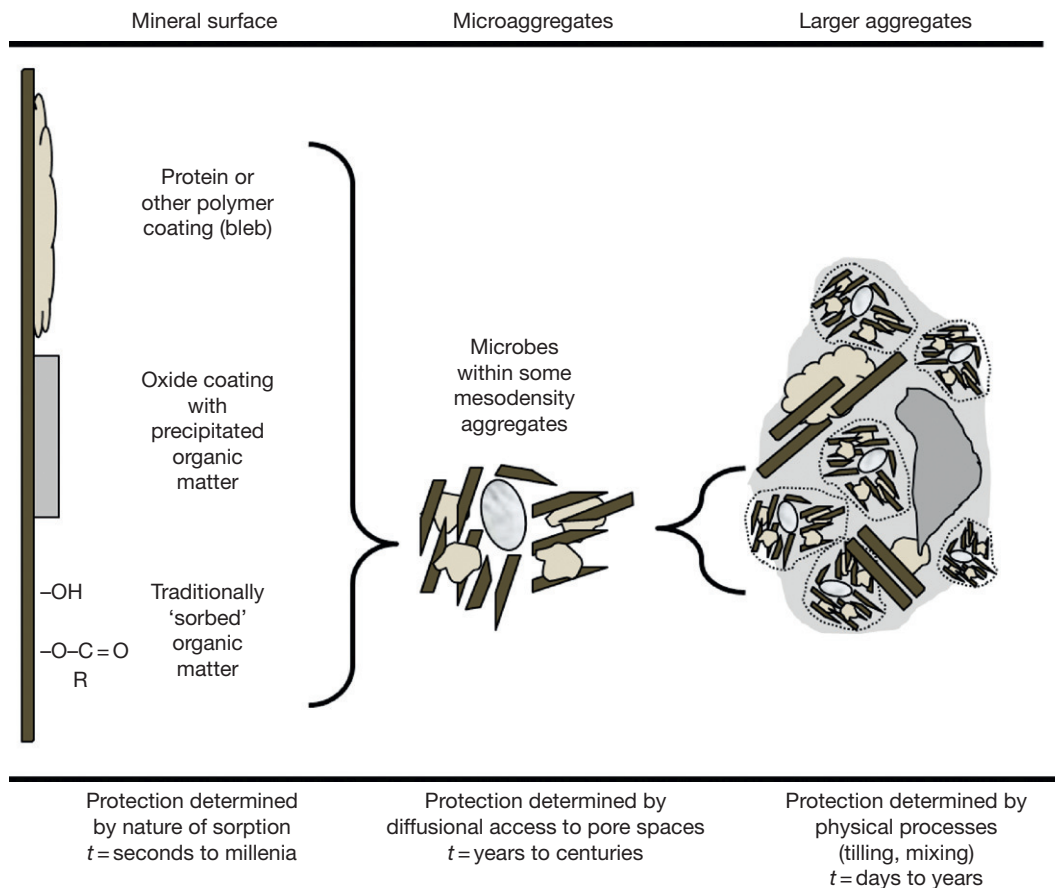


Figure 3 Schematic representation of the development and protective power of organomineral complexes in soils and sediments. Initial contact via surface phenomenon can be protective and leads to the development of mesodensity aggregates composed largely of organic ‘blebs’ and fine-grained minerals. Some mesodensity aggregates contain microbes, which may play an active role in conditioning and structuring their surroundings. Most mesodensity aggregates contain ^{14}C -depleted organic matter, which is presumed to be older and more resistant to degradation than the organic matter that holds larger aggregates together. Large aggregates contain many mesodensity aggregates, additional bacteria, and the youngest and most bioreactive organic matter within the system.

Aggregation continues to sizes well beyond the fine silt range. The soil literature has built various classifications to these varying sizes, commonly terming aggregates of $<250\ \mu\text{m}$ 'microaggregates' and those of $>250\ \mu\text{m}$ as 'macroaggregates,' although this terminology varies. Many are based on the 'aggregate hierarchy' theme developed by Tisdall and Oades (1982) and Oades (1984); see reviews in Jastrow and Miller (1998) and Six et al. (2004). Many aggregates can be destroyed by ultrasonic vibration, but microaggregates are remarkably robust and resilient to disaggregation. Very little analogous work has been done to examine organic matter–aggregate relationships in sediments, at the methodological, classification, or process levels. There are many sightings of aggregates containing various kinds of organic matter (Arnason and Keil, 2007; Pichevin et al., 2004; Ransom et al., 1998) but little of the size- or category-based quantification reported for soils.

In the soil-based schema, microaggregates have different properties than macroaggregates. The former contain organic matter that is typically more reflective of extensive microbial processing and is perhaps more humified in the sense of having undergone alteration of the original chemical makeup (e.g., production of nonprotein amino acids in sediments; Cowie and Hedges, 1992). Macroaggregates, on the other hand, are more likely to contain larger organic matter fragments of more recent origin, such as roots or fungal hyphae, which can often nucleate the formation of the aggregate. Because terrestrial detritus often has a relatively high C:N ratio, macroaggregates often have higher C:N than microaggregates. Likewise, this detritus can impart a highly aliphatic character to the organic matter, though this character varies among soils. Detritus can be separated via density separation protocols as the 'occluded' light fraction (see review in Wagai et al., 2009). Microaggregates are thought to form both inside and outside of macroaggregates and can survive breakup of macroaggregate hosts. Breakup due to physical disturbances, such as tilling, preferentially leads to decay of these occluded materials, reducing the soil to the more resistant clay–organic matter subunits that dominate the fine silt-sized aggregates discussed earlier (Hassink, 1997; Six et al., 2000).

While inorganic glues can cause aggregation in some environments, it is clear that biologic processes and their attendant organic glues dominate aggregate formation (e.g., Tisdall, 1993; and see review in Kögel-Knabner et al., 2008). Mucilages from fungi, plant roots, or even animal gut passage can glue materials at the macroaggregate scale in soils. As noted earlier, a microaggregate–macroaggregate systematization is lacking for the marine realm, and likely animals and protists are the major contributors to larger aggregate formation in sediments. At finer scales in both terrestrial and marine realms, there is abundant evidence that bacteria cause aggregation via their capsular envelopes. Clay sheaths around bacterial cells are commonly seen in field-collected soils and sediments (Chenu and Plante, 2006; Ransom et al., 1999). Smectites are especially important in this regard (Bennett et al., 1999). Similar structures can be formed in the laboratory (Dorioz et al., 1993; Lünsdorf et al., 2000).

12.12.2.2.4 The role of mineral surface area and geometry

Strong correlations between mineral surface area and organic matter content, especially in sediments, beg the question as to

whether surface area is indeed indicative of the sorptive capacity of a system or whether it simply reflects the relative abundance of fine clay-sized material in samples. The idea of monolayer sorption of organic matter as precursor to its protection goes back to at least Emerson (1959) and was continued with the observations of monolayer-equivalent concentrations of organic matter by Muller and Suess (1977), Suess (1970), and Suess (1973). The possibility that surface area indeed reflected the sorptive capacity of a system, and that its measurement was predictive of a soil's or sediment's capacity to store carbon, was considered by many (e.g., Keil et al., 1994a,b; Mayer, 1994a,b), but subsequent research did not support a monolayer of evenly distributed organic matter over all surfaces (Arnason and Keil, 2001; Mayer, 1999; Ransom et al., 1997). Alternatively, it was considered that organic matter was concentrated in smaller mesopore volumes ($<10\ \text{nm}$ diameter) that were proportional to surface area and which could exclude digestive enzymes (Mayer, 1994a,b), but this mesopore exclusion hypothesis was also rejected in later research (Mayer et al., 2004). The term monolayer equivalent is now known to express only a ratio of organic matter to fine-grained minerals and not an indication of sorptive coverage. Submicrometer clay and oxyhydroxide phases are the only ones experimentally shown to associate physically with organic matter (Coppola et al., 2007; Kaiser and Guggenberger, 2003), leading to the understanding that the surface area measurement focuses on the reactive phases without specifically identifying sorption as the physical mechanism causing the observed relationships.

In sorption experiments, there is preferential uptake of organic matter into small pores, especially micropores (Kaiser and Guggenberger, 2007; Mikutta et al., 2004). The types of organic matter contained within micropores are different than those on exposed surfaces. In addition, pores can provide multiple interaction sites for single organic molecule. The role this actually plays in the environments remains an active area of research.

Taken together, the soil and sediment literature suggests a common occurrence of organic matter in the pore spaces between fine-grained sediments, with most of the exposed (nonpore) surface area clear of detectable organic matter. These small mesodensity aggregations are often further aggregated into larger units, with younger and 'fresher' organic matter 'gluing' the larger units together (Figure 3). The role of aggregates of various sizes in protecting organic matter from degradation is taken up in the following section.

12.12.3 Impact on Organic Matter

12.12.3.1 Compositional Variations Among Different Mineral Associations

The organic matter interacting with mineral surfaces comes in a myriad of molecular compositions and sizes/weights (Kleber et al., 2007). Two complementary approaches have been used to determine the organic matter composition: direct analysis of molecular composition such as lignin and amino acids (Bergamaschi et al., 1997) and synoptic analyses that evaluate the entire organic matter pool (e.g., nuclear magnetic resonance – NMR; Baldock et al., 2004). Direct analysis of biochemicals typically only identifies half the organic matter, likely because compounds fall out of the 'analytical window'

as they are modified during degradation (Hedges et al., 2000; Panagiotopoulos and Sempere, 2005). Conversely, holistic analyses, such as solid state ^{13}C NMR, offer no direct measure of the molecular composition of the organic matter examined (Baldock et al., 2004). Additional techniques such as Fourier transform-ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) are somewhat in between direct analysis and holistic, offering a nontargeted molecular approach that provides molecular formula but not quantization or positive identification among isomers (Kujawinski et al., 2009).

In both marine and soil settings, analysis of size and density separates yields consistent trends in identifiable organic matter content and composition (Coppola et al., 2007; Kaiser et al., 2004; Keil et al., 1998; Knicker, 2004; Mikutta et al., 2009). Amino acids, which contain the 'internal diagenetic indicator' of the production of nonprotein amino acids (Cowie and Hedges, 1992), are typically enriched in fine-grained and meso-density fractions, as is the mole percentage of nonprotein amino acids, indicating both preferential association of nitrogen-containing materials with clays and also of extensive diagenetic alteration of the material (Amarson and Keil, 2007; Bergamaschi et al., 1997; Keil et al., 1998). Carbohydrates are similarly enriched in fine-grained sediments (Bergamaschi et al., 1997; Chenu and Plante, 2006; Curry et al., 2007; Kögel-Knabner et al., 2008; Kovac et al., 2004), consistent with their being potentially important glues holding aggregates together (Kovac et al., 2004; Solomon et al., 2005). Kinyangi et al. (2006) found oxidized, carboxylate-dominated materials in thin layers within microaggregates, consistent with secretion of acidic polysaccharides by microbes (Emerson et al., 1986), and more aromatic/aliphatic, larger materials in larger pores between grains. Conversely, lignin is typically associated with larger grains or present as floatable (distinct) debris (Adams and Bustin, 2001; Bergamaschi et al., 1997; Kögel-Knabner et al., 2008). The lignin that does associate with fine-grained clays is highly degraded (Amarson and Keil, 2001; Keil et al., 1998) and potentially associated via sorption of monomers and not polymers (Aufdenkampe and Hedges, 2005; Hernes et al., 2007).

While identifying only a subset of the total organic matter, molecular-level analyses are in general agreement with more synoptic approaches (Baisden et al., 2002; Baldock et al., 2004; Dickens et al., 2006). Clay-rich (loamy) soils generally have higher contributions of polysaccharide-like chemical moieties, whereas sandy soils and fractions are more aliphatic (Kaiser et al., 2002; Kögel-Knabner et al., 2008). Phenolic components are usually depleted in clay-dominated samples and subsamples, consistent with what is observed for lignin (Kaiser et al., 2004).

According to Kaiser and Guggenberger (2003, 2007a), at higher organic matter loadings at the mineral surface, fewer organic ligands per organic molecule are involved in the bonding, making the organic molecules more flexible. They can thus extend into the soil solution, making them more susceptible to microbial decomposition. Ellerbrock et al. (2005) assumed that interaction between hydrophilic functional groups within organic matter and polyvalent cations located at mineral surfaces mainly account for organic matter–mineral complexes and protect organic matter against decomposition. If correct, then the organic matter-to-clay ratio, the presence (or absence) of polyvalent cations, and the organic matter composition may influence distribution and conformation of organic matter on

mineral surfaces. Sollins et al. (2006) and Kleber et al. (2007) provided an alternative explanation stating a zonal structure for organic matter associated with mineral surfaces, with the outer layers of the organic matter having a more rapid turnover than the inner ones. In the zonal scheme, the contact zone between organic and mineral strong is stabilized by organo-mineral associations dominated by either polar organic functional groups of organic matter interacting via ligand exchange with singly coordinated mineral hydroxyls, forming stable inner-sphere complexes, or proteinaceous materials that unfold upon adsorption. A secondary layer containing a 'hydrophobic zone' consists of other organic matter, which may be absorbed into the first layer and whose components may exchange more easily with the surrounding solution. An outer (third) region, or kinetic zone, contains organic matter loosely retained by cation bridging, hydrogen bonding, and other interactions (Kleber et al., 2007). This zonal hypothesis is consistent with sequences of organic matter accumulation in chronosequence studies (e.g., Dümig et al., 2012), showing early attachment of proteinaceous materials to surfaces followed by accumulation of microbial carbohydrates. Several investigators have found indirect evidence supporting the role of an outer layer in protecting organic matter from decay (Carrington et al., 2012), but more work needs to be done to determine whether zonal structures are common in soils or sediments.

12.12.3.2 Organic Matter Stabilization and Destabilization

12.12.3.2.1 Abiotic and biotic roles of minerals in organic matter decay

There is evidence that some minerals can enhance decomposition of organic matter. One candidate mechanism would be direct oxidation by electron-poor elements in minerals. Reactive manganese dioxide phases, such as birnessite, have been shown to perform such oxidations in soils (e.g., Miltner and Zech, 1998) and in marine settings (Sunda and Kieber, 1994).

Organisms have evolved to use various minerals as electron acceptors, expanding the importance of electron-poor minerals in organic matter decomposition beyond those reactions that occur in the absence of biota. Such reactions generally have a lower energy yield than those involving oxygen, restricting biologic success of these processes to environments in which oxygen becomes depleted. These reactions are also restricted to bacteria and are not known to be employed by other kingdoms of organisms. The most common minerals used by such bacteria are the range of oxides to hydroxides of iron and manganese (Lovley and Phillips, 1998). Classic zonations of respiration in sediments lacking oxygen therefore show successive respiration of manganese and iron oxyhydroxides, respectively. Within these broad families of minerals, those forms with the least crystallinity and highest specific surface area typically are used most easily.

12.12.3.2.2 Minerals as organic matter stabilizers

The observation that interacting with minerals helps protect organic matter from degradation was made more than 100 years ago (Scheiner and Shorey, 1908). Since then, numerous lines of evidence have supported this inference (e.g., Waksman, 1933). Pinck and Allison (1951) evaluated protein–montmorillonite complexes and observed decreased aerobic

degradation. Estermann et al. (1959) extended the work by evaluating protein–silica complexes, suggesting that it was not the montmorillonite specifically that leads to the protection of the organic matter, but perhaps the small size of the particles. Inferring that these experiments led to the formation of mesodensity microaggregates, we can surmise that it was the aggregation effect itself that likely protected the organic matter. Many other experiments support this supposition. ‘Sorption’ experiments lead to protection of organic matter from microbial attack (Arnarson and Keil, 2005; Kalbitz et al., 2005), and yet when released into solution, particle-associated organic matter can be rapidly degraded (Keil et al., 1994a,b), suggesting that something about the mineral interaction is protective. Sorption to minerals generally reduces the susceptibility of organic matter toward oxidative attack (Eusterhues et al., 2003; Kaiser and Guggenberger, 2003) and the bioavailability (Kalbitz et al., 2005). Interactions between soil minerals and dissolved organic matter result in a distinct stabilization as indicated by increased mean residence times after sorption to a mineral subsoil (Kalbitz et al., 2005), soil minerals (Mikutta et al., 2007), and after precipitation by Al (Scheel et al., 2007). Almost all these controlled experiments result in the formation of mesodensity aggregates, leaving the question whether it is the sorption itself or the aggregation that helps protect the organic matter.

Experiments using high-intensity light allow evaluation between the two mechanisms. Much of the organic matter in soils cannot be degraded in the lab by intense UV light (Skjemstad et al., 1993), suggesting that the organic matter occupies a protected internal location. If it is not simply sorption providing protection from light, could it specifically be sorption within pores of mineral grains? Though there is abundant indirect evidence used to infer a ‘pore space’ argument for why aggregates are protective, there is relatively little direct evidence to show that organic matter is protected by residence within the micropores (<2 nm) or small mesopores (2–10 nm) of mineral grains that can exclude enzymes (Mayer, 1999, 2004). In fact, intragranular pore spaces are a small component of the pore space in soils and sediments, and most micro- and mesopore space is interstitial between grains. These pore spaces develop when primary complexes aggregate to form microaggregates, and it is perhaps these tightly packed spaces that provide significant protection from degradation. That is, because the space between most sediment and soils is contained within pores too small for bacteria and their enzymes, aggregation should protect organic matter from microbial degradation (Chevallier et al., 2010; McCarthy et al., 2008; Mikutta et al., 2009).

As preferential sorption sites the mouth of micropores (<2 nm) or smaller mesopores (2–10 nm) of Fe oxides have been suggested (Kaiser and Guggenberger, 2003). These small pores represent the surface roughness resulting from defects in the surface structure of goethite crystallites (Weidler et al., 1998). Consequently, micropores are sites of increased reactivity and thus best suited for sorptive interactions with organic acids and polyelectrolytes (Kaiser and Guggenberger, 2003; Mikutta et al., 2004). There, organic matter can form strong multiple bindings that disfavor both the desorbability and the oxidative removal of organic matter, respectively (Kaiser and Guggenberger, 2007). Similarly, Zimmerman et al. (2004)

observed greater irreversibility of desorption of nitrogenous compounds following adsorption to mesoporous sorbents compared with their nonporous analogues. However, in soil and sediment environments, the importance of molecular-sized pores within the mineral matrix for the stabilization of organic matter is not yet understood. Mayer et al. (2004) concluded that other factors than association with mesopores must be responsible for the accumulation of organic matter in marine sediments because only 10–20% of organic matter was found to be actually contained in 2–10 nm pores that are small enough to prevent access of hydrolytic enzymes and microbes. Similar results were reported for the soil mineral goethite (Kaiser and Guggenberger, 2007).

Presence at the boundary between fine mineral grains may not be the only mechanism that protects organic matter. Aggregated minerals may also induce network effects that lead to functionally similar protection. Diffusion through networks of pores is limited to molecules smaller than the smallest pore in the network path, so that diffusional access to organic molecules held within a network can be limited by a small number of small pores (called ‘throats’). Small, plate-like clays provide especially effective barriers to diffusion of enzymes in the direction normal to the plate (Nielsen, 1967) and may be important parameters controlling oxygen availability in some situations (Bolton et al., 2006). Further, arrays of these plates can produce small pore throats that inhibit diffusion around their edges. Nanocomposite structures deriving from exfoliation and orientation of these plates can thus reduce diffusion normal to the direction of plate orientation (Alexandre and Dubois, 2000; Kiersnowski et al., 2009). As a result, biodegradation of the organic matter that inhabits the spaces among the plates can be inhibited (Lee et al., 2002), though the direction of this change can depend on a variety of factors (Fukushima et al., 2010a,b).

Microaggregates are very stable (Oades, 1993), so the lifetime of the pore system that traps organic matter must be considered ‘long’ (Lutzow et al., 2006). Chenu and Stotzky (2002) demonstrated that 15% of the soil porosity in a sandy soil and 52% in a clayey soil is inaccessible to passage by microorganisms, because the diameters of the pore necks are smaller than 0.2 μm . Calculations made by van Veen and Kuikman (1990) indicate that perhaps up to 95% of the pore spaces in a silt loam are too small to be accessible to bacteria. However, it is not known if and at what rate organic matter trapped in pores of about 1–100 nm is diffusing out again and to what extent organic matter in such pores can be reached by exoenzymes. As noted earlier, exoenzyme diffusion may be limited by small pore throats of sizes (less than 5–10 nm). Nevertheless, the secretion of exoenzymes is metabolically expensive for bacteria, and the benefit/cost ratio decreases with distance from the bacterial cell (Vetter et al., 1998). Thus, lengthening of diffusion distances by tortuosity in aggregates may also reduce the ability of microbes to profitably attack substrates held within mineral aggregates (Mayer et al., 2004). If coupled to the inferior energetic yields obtained from anaerobic metabolism, these diffusional limitations by clays may act in synergy with oxygen availability (see next section). While anoxic microzones are well known in sedimentary environments (Brandes and Devol, 1995), even aerobic soils can exhibit anaerobic microzones as indicated by the presence of obligate anaerobic bacteria in clay particle size fractions (Sessitsch et al., 2001).

Growth of bacterial cells may orient clay grains into concentric arrays that enhance mineral protection of the core region by armoring the cells. These concentric arrays are frequently seen in transmission electron microphotographs of soil and sediment bacteria (Figure 2; Bennett et al., 1996; Dorioz et al., 1993; Ransom et al., 1997). For example, McCarthy et al. (2008) found that microaggregates accumulated organic matter primarily in pores of similar sizes as bacterial cells and suggested encapsulation by the surrounding mineral matrix as a protective barrier that effectively excluded further biologic mineralization from remineralizing some fraction of this bacterial production (Knicker 2007). Miltner et al. (2012) described a role for colloid-sized bacterial cell fragments to account for the bulk of organic matter production in soils. This idea of 'necromass' occurs in sediments as well (Lomstein et al., 2012). Because more than 60% of the organic matter in sediments remains uncharacterized at the molecular level, it is hard to identify and quantify with clarity the organic matter present in a system that is derived from dead microbial biomass. Branched fatty acids, a characteristic of bacterial production, are found enriched in clay relative to coarser size fractions (e.g., Barouxis et al., 1988). If significant necromass is held in collapsed residues of the concentric clay layers produced by some bacteria, then organic matter with relatively impermeable clay walls should result.

12.12.3.2.3 Does mineralogy influence protection?

The strong relationships between very fine-grained minerals and organic matter in soils and sediments leads to the question of whether or not mineralogy plays a significant role in affecting protection of organic matter. Field associations between fine-grained minerals and organic matter point our attention toward those minerals that occur in the fine-grained fraction – largely phyllosilicates and Al-Fe oxyhydroxides. The surface reactivity of a mineral may play a role. For example, iron oxyhydroxides with high surface area are commonly associated with elevated organic matter concentrations, but little such enrichment has been reported for sediments with high levels of high surface area manganese oxyhydroxides. Empirically then, the oxyhydroxides of iron and aluminum and various micrometer-sized aluminosilicate minerals (usually called clay minerals) are particularly important in the stabilization of organic compounds (Greenland, 1971; Hassink, 1995; Theng and Tate, 1989). These minerals generally have high specific surface area and usually carry significant charge, enabling them to bind, and thereby potentially chemically stabilize, organic matter. As noted, however, even amorphous silica – a relatively nonsorptive solid phase – can protect organic matter in laboratory experiments (Estermann et al., 1959), so that surface reactivity cannot be the only variable of importance.

A variety of nonphyllosilicate, clay-sized minerals are often associated with elevated organic matter concentrations. A common trait for these minerals is high surface area and low crystallinity, which are often seen in organomineral associations of intermediate weathering sections of soil chronosequences on volcanic terrain (Mikutta et al., 2009; Torn et al., 1997). Besides iron oxyhydroxides, which are especially important in subsurface horizons of acidic soils (Mikutta et al., 2005), aluminum analogues are also important in many soils. There is recent evidence for iron control on organic matter preservation in marine sediments

(Lalonde et al., 2012), but it is not yet clear if the stabilized organic matter is associated with an iron mineral phase or instead consists of precipitated iron-organic matter complexes. In some volcanically derived soils (Andosols), the aluminosilicate minerals allophane and imogolite have very high surface area and bind considerable organic matter (e.g., Basile-Doelsch et al., 2007), but other minerals can also dominate organic matter sequestration in volcanic terrains (Egli et al., 2008). While manganese oxyhydroxides can also have high surface areas, they do not seem to be as effective in stabilizing organic matter (Miltner and Zech, 1998).

Phyllosilicate minerals of approximately micrometer size dominate the literature of organic matter stabilization for both soils and sediments. This class of minerals ranges widely in surface reactivity and surface area, and yet most of its members have been reported as strong correlates of organic matter concentration in various environments. This strong representation suggests that the plate-like morphology of most of these minerals is central to their ability to protect organic matter against biologic attack, perhaps via the diffusional arguments made earlier. Numerous studies have addressed the relative efficacy of different phyllosilicates at organic matter preservation. These studies are hampered by the fact that mineral names apply to families of minerals having variations in morphology, genesis, chemistry, and biologic interactions. Analytical tools are sometimes misleading. For example, analysis by x-ray diffraction yields mass concentrations when perhaps morphological parameters such as areal extent are more relevant parameters. Likewise, surface area analysis by gas adsorption does not capture the very high interlamellar surface area of smectites, while sorption by ethylene glycol monoethyl ether (EGME; Kennedy et al., 2002) is sensitive to these surfaces.

Mineralogy may affect both bulk organic matter preservation and the types of organic matter preserved, each by a variety of mechanisms. Simple sorptive associations will vary according to principles described in the preceding text. Conversely, minerals may 'adsorb' onto organic particulates subject to similar principles and promote aggregate formation. At colloidal size scales, the terms 'sorption' and 'aggregation' become ambiguous and exchangeable. Different minerals will participate in aggregation processes for reason of chemical attractions and morphology. Mineralogy affects microbial community structure (Carson et al., 2007; Stotzky, 1986), which will affect types of organic matter produced and aggregation processes.

Laboratory experiments have long examined ability to adsorb various organic solutes. Many have focused on kaolinite versus smectite sorption (Bader et al., 1960; Feng et al., 2005; Hedges and Hare, 1987; Wang and Lee, 1993). This comparison has been driven by the abundance of these two structurally different mineral types in soils and sediments, plus the availability of relatively pure end-members. Smectite has often been found to be more sorptive, due to some combination of higher charge, greater surface area, and likely other factors such as iron content. Irreversibility of adsorption has suggested reduced biologic availability (Bader et al., 1960; Kahle et al., 2004). Particularly strong attraction has been found between smectites and components of bacterial cell-surface compounds, such as acidic polysaccharides (Dontsova and Bigham, 2005; Walker et al., 1989). This attraction facilitates formation of clay-rich biofilms, which are protective

structures for bacteria living within (e.g., Alimova et al., 2009) and may promote bacterial ‘hutch’ structures as observed by Lünsdorf et al. (2000). Because smectite can reduce diffusion more effectively than kaolinite, it can affect oxygen status in microzones and perhaps alter microbial communities between bacteria and fungi (Stotzky and Rem, 1967).

Dissection of relationships among field abundances of these phyllosilicates and organic matter concentrations has been ambiguous. Smectite-containing soils and sediments have often been found to contain elevated organic matter (e.g., Kennedy et al., 2002; Ransom et al., 1998; Wattel-Koekkoek et al., 2003). Furukawa (2000) found elemental composition adjacent to organic matter in sediments to be implicative of preferential association with smectite. Virto et al. (2008) found 2:1 clays, which include smectite, to be especially abundant in microaggregates relative to other clay minerals. On the other hand, Wattel-Koekkoek et al. (2001) found that the total amount of organic carbon in the clay-size fraction in tropical soils from seven countries to be independent of the kaolinite versus smectite composition, despite differences in organic matter binding mechanisms; Wattel-Koekkoek and Buurman (2004) extended this finding to the mean residence time of organic matter. Bruun et al. (2010) found organic matter in smectite-containing soils to be more bioavailable than that in kaolinite-containing ones.

Smectites are the phyllosilicates most prone to exfoliation, which may explain some instances of enhanced protection. If organic cations capable of exfoliation of smectites, or even some proteins that can induce delamination (Kiersnowski et al., 2009), are episodically produced in a soil or sediment, thin laminae might accumulate as a powerful protective mechanism. An inorganic mechanism for delamination of smectites was proposed by Brockamp (2011), who found smectites from one river sediment to delaminate at low salinities in estuarine mixing, while smectite from another river did not. Whether or not this mechanism is important, it does suggest that the suite of minerals called ‘smectite’ has internal variations that will behave differently – in this case with respect to delamination but also perhaps with respect to protection of organic matter (Fukushima et al., 2010a,b; Kinyangi et al., 2006). Thus, differences in mineralogies and their interactions with local conditions may explain the ambiguity of this literature.

Thus, while it is clear that some members of some mineral groups – for example, smectites and iron oxyhydroxides – can rise to the occasion to enhance organic matter protection under certain conditions, it is also clear that presence of these minerals does not always lead to enhanced protection.

12.12.3.3 Crosscutting Themes

12.12.3.3.1 Microbial roles

Given what is known about organic–mineral interactions, a number of scientists have proposed models of how soils and sediments operate (e.g., Baldock et al., 2004; Kleber et al., 2007; Tisdall and Oades, 1982). Bringing these views together into a single conceptual model highlights the role each mechanism and process plays in soils and sediments. Classic models where sorption completely drives the preservation of carbon (Bader et al., 1960) or soil structure (Chefetz and Xing, 2009; de Jonge et al., 2009) do not adequately describe what is known, and a ‘three-dimensional’ view (Kleber, 2010) where

aggregates and the processes within aggregates (including sorption) drive carbon stability and hierarchical system structures are now more common (Tisdall and Oades, 1982). Sediments and soils are increasingly thought to consist of a multitude of partially independent aggregates and ‘microreactors,’ some of which are active in carbon remineralization and microbial growth and some of which are less reactive and serve a preservative function (Brandes and Devol, 1995; Kleber, 2010).

Mineral particles are conceptualized as components for the construction of small microstructures that are built around microbiota (see also Brandes and Devol, 1995). This view is supported by abundant evidence that substantial parts of mineral surfaces are not covered by organic matter. In this alternate view, minerals serve an ecological function for microbiota. Several experiments have pointed to the active role played by minerals in the functioning and structure of microbiota and their communities. Each 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.

In soils, Lünsdorf et al. (2000) developed the idea of bacterial–clay mineral ‘hutches’ held together using exopolymer polysaccharides. The biofilms that developed consisted of a dense lawn of clay aggregates, each one of which contained one or more bacteria, phyllosilicates, and grains of iron oxide material, all held together by bacterial exudates. The clay leaflets were arranged in the form of ‘houses of cards’ and gave the aggregates the appearance of ‘hutches’ housing the bacteria. Metals can shift orientation of clays around bacterial cells from radial (edge contact) to tangential (face contact) (Walker et al., 1989), which would affect ability to armor cellular organic matter.

Microorganisms can precondition mineral surfaces to their needs (Bos et al., 1999; Duffrene et al., 1999), which seems to promote mineral–organic associations through the deposition of extracellular polysaccharides and proteins as adhesives (Chenu and Plante, 2006). In natural aqueous environments, pristine mineral surfaces become coated rapidly by biogenic organic films (Bos et al., 1999). The formation of these ‘conditioning films’ moderates eventual differences in the surface chemistry of the underlying substrate and can thus be seen as an adaptation mechanism that allows microorganisms to colonize highly variable types of mineral surfaces. These ‘conditioning’ mechanisms can lead to the development of aggregates as observed in many field experiments.

Small-sized fractions contain much of the microbial biomass in different soils (Kanazawa and Filip, 1986; Monrozier et al., 1991). For example, cellulose-feeding bacteria attach closely with their substrate in these microhabitat, which minimizes the loss of enzymes into the soil solution by diffusion (Alexander, 1977). Therefore, enzymes involved in the hydrolysis of high-molecular-weight organic substrates reflect the location and perhaps the quality of organic matter in agricultural soils (Speir and Ross, 2002). The bacterial dominance in the finer fraction was also shown by high abundance of bacterial-derived phospholipid fatty acids, high diversity of 16s rRNA gene fragments, and high activities of enzymes involved in the cycling of N and P (Kandeler et al., 2000; Poll et al., 2003). Kögel-Knabner et al. (2008) found that silt- and

clay-sized fractions favor a greater richness of bacterial species (Kirchmann et al., 2004; Selesi et al., 2007; Sessitsch et al., 2001). Thus, bacterial colonization seems to be at the heart of creation of organoclay aggregates that stabilize so much organic matter in soils and sediments.

12.12.3.3.2 Oxygen effects on bulk organic matter persistence

Exposure to oxygen adds a superimposed control on the role of minerals in the preservation of organic matter. It is thought that some organic macromolecules can be recalcitrant to degradation depending on the prevailing depositional conditions (Gelin et al., 1996, 1999; Keil et al., 1994a; Nguyen and Harvey, 2001). This class of protection would include organic matter that is stable only under reducing conditions, a type of selective preservation referred to as *oxygen-sensitive material* (Hedges et al., 1999). Cumulative oxygen exposure has been hypothesized to override physical protection mechanisms at time scale of centuries to millennia (Hartnett et al., 1998; Hedges and Keil, 1995; Hedges et al., 1999; Keil et al., 2004). While the exact mechanisms for oxic degradation of organic matter in sediments remain poorly understood, 'oxygen exposure time' has been proposed as a proxy for the oxic degradation history of marine sediments (Keil et al., 1994a). This concept has been more thoroughly explored in the sediment literature relative to soils.

A general scenario relating organic–mineral matrices and oxygen exposure time in marine systems is that organic matter–mineral interactions are predominantly established in the benthic boundary layer (Thomsen et al., 2002), where new inputs of organic matter interact with lithogenic mineral material resulting in aggregates of low density and high organic matter content. Analogous situations occur in soils (Six et al., 2000). Degradation by benthic organisms removes organic matter and results in aggregates of greater density. Aggregate density and organic matter composition are thus correlated by the fact that changes in both result from degradation (Arnarson and Keil, 2007; Chenu and Plante, 2006). Over time, as fresh organic matter is continually added to the system, organic matter will accumulate along a continuum of differing quantity, quality, and density, with the freshest material in the lightest fractions and the most degraded in the densest fractions. This trend is observed in many soils (Eusterhues et al., 2003; Kaiser et al., 2002; Kögel-Knabner et al., 2008; Lutzow et al., 2006; McCarthy et al., 2008; Mikutta et al., 2004; Six et al., 2002) and sediments (Adams and Bustin, 2001; Burdige, 2007; Coppola et al., 2007; Keil et al., 1994a,b, 1998; Ransom et al., 1998). Trends can become partially obscured when high-density fractions (containing remnant survivor OC from prior diagenesis) contribute to the creation of new lower-density aggregates (Six et al., 2000).

Along continental margins, most organic matter is found in mesodensity fractions (2–2.3 g cm⁻³) (Bock and Mayer, 2000) corresponding to small aggregates. These mesodensity aggregates slow the oxic degradation of organic matter within them (Arnarson and Keil, 2005), perhaps because of the previously mentioned processes.

Marine sediments of similar origin but spanning large differences in oxygen status allow for a naturally controlled test for how oxygen exposure affects organic–mineral interactions. In such systems, there is a well-established shift in the organic matter–mineral relationship (Cowie et al., 1995; Hedges et al.,

1999). This shift as a function of oxygen exposure can be used to differentiate between protective processes (e.g., mineral interactions and biomineral protection; Arnarson and Keil, 2005; Nguyen and Harvey, 2001) and destructive processes (e.g., oxygen exposure). Organic matter is present in low-density isolates (i.e., not greatly associated with minerals) in virtually all samples, regardless of oxygen exposure, implying that factors creating stable low-density aggregates (e.g., organic shielding and selective preservation; Nguyen and Harvey, 2001) may be important in all conditions. However, the quantities of low-density material are dramatically diminished after long oxygen exposure, suggesting that oxygen exposure leads to loss of material protected in this way. Fine-grained and high-density microaggregates are also found in all samples, but with increasing oxygen exposure, they become more important (Arnarson and Keil, 2007; Burdige, 2007; Hedges et al., 1999; Keil et al., 1994a,b; Mayer, 2004; Rothman and Forney, 2007). Researchers have interpreted these changes in natural laboratories as evidence that several potential preservation mechanisms are at work within marine sediments, and that as a function of oxygen exposure certain mechanisms become less important and others assume a more predominant role (Figure 4). Arnarson and Keil (2007) suggested for marine sediments a scheme wherein, as a function of oxygen exposure, the organic matter that resists degradation is 'moved' along a continuum where it is progressively both degraded and more associated with mineral grains in the form of primary complexes. During the early stages of degradation, most organic matter is predominantly recently deposited, low-density organic debris, and undergoing remineralization. At intermediate oxygen exposure times (estimated to be 40–400 years for continental margin sediments; Figure 4), aggregates dominate the system, organic matter is protected within aggregate matrices, and degradation slows. After long exposure to oxygen, aggregates are degraded away and the residual organic matter is primarily associated with individual mineral grains as primary complexes.

Chronosequences in soils provide similar trends in composition with time, often beginning with low-density terrestrial organic detritus either free or loosely associated with minerals, followed by aggregate formation and finally resulting in organic matter tightly associated with more crystalline mineral grains (Baisden et al., 2002; Mikutta et al., 2009). In soils, however, the exposure is dominantly oxic, which likely inhibits the relative preservation of the early stage, low-density organic matter. Counteracting this difference, however, terrestrially derived organic matter is somewhat less degradable than the algal organic matter input to oceanic sediments.

Generalizing these findings for soils and sediments under oxic conditions suggests a progression through different protection mechanisms over time (Figure 4) where during initial soil or sediment formation the dominant form of organic matter present is 'selectively preserved' in the sense that it is undergoing decay slower than other types of molecules (Canuel and Martens, 1996; Hedges and Keil, 1995; Hedges et al., 1999; Hulthe et al., 1998; van der Weijden et al., 1999). This material is rapidly lost from soils and sediments and is quantitatively important only in systems where other factors (lack of oxygen and very rapid deposition rates) bury the material before it can be degraded. Typical soils and sediments,

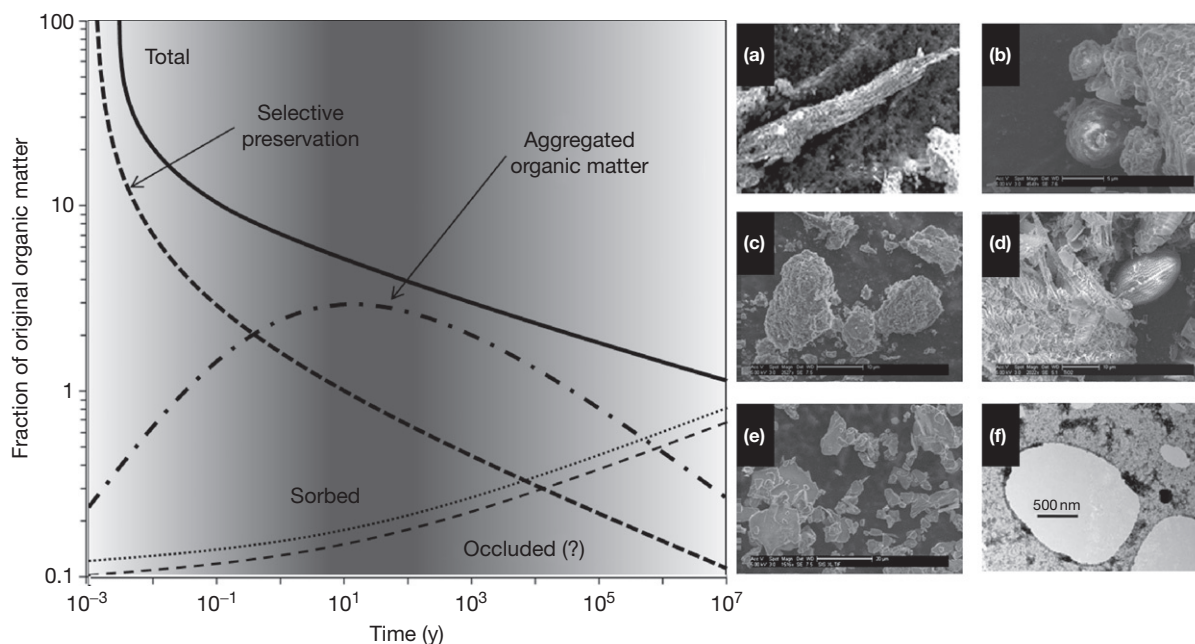


Figure 4 Idealized diagram illustrating the succession and overlaying of various protection mechanisms on soil and sediment organic matter. The fraction of original organic matter (y -axis) is marked as a function of oxygen exposure time. When degradation time is short (days to years), the majority of organic matter is preserved in its initial state via some form of selective preservation (e.g., oxygen sensitivity and naturally slow decay constants), after which aggregation occurs and becomes the major protective mechanism. The majority of soils and sediments are poised at the point where aggregation (micro and macro) is the dominant physical form of organic matter present in the system. At longer reaction times, the relative importance of sorption increases. Recent evidence suggests that occlusion in biominerals (especially in the ocean) and coprecipitation (occlusion) with iron oxide minerals can be an important protective mechanism at long time scales. The gray background color identifies the 'protective zone' in which fall most soils and marine sediments that are actively accumulating carbon. This diagram does not attempt to account for all preservation pathways or to quantitate their relative importance, but rather makes the point that the majority of organic matter preserved out to different time scales likely proceeds through successional overlays of various protection mechanisms. Modified from Mayer LM (2004) The inertness of being organic. *Marine Chemistry* 92(1–4): 135–140. SEM micrographs illustrating (a) lignin-rich woody debris off the Washington margin, (b) organic spheres of marine origin preserved in the anoxic sediments underlying the Eastern Tropical North Pacific (Arnarson and Keil, 2007), (c) typical aggregates, (d) diatom shell with occluded organic matter, (e) aggregate-poor sediments where sorption is thought to dominate after long oxygen exposure (Arnarson and Keil, 2007), and (f) iron oxide and humic acid aggregates formed in controlled lab experiments (Baalousha et al., 2008).

with ages in the upper soil or sediment horizon of up to 10^3 years, are often dominated by organic matter in the form of aggregates. For soils and sediments that remain in place for longer, larger complex aggregates give way to smaller and more primary ones, and the residual organic matter then becomes dominated by sorbed organic matter (Figure 4; Arnarson and Keil, 2007).

Saturation with oxygen appears to minimize residence time in the earlier stages, while removal of oxygen from the system retards the progression of mineral–organic matter association, in the process leaving higher concentrations of organic matter. Evidence for this oxygen effect can be seen in burial fluxes and types of organic matter in different depositional regimes. Burial at monolayer-equivalent loadings typically occurs in continental shelf sediments that have oxic conditions at the sediment–water interface, underlain by anoxic regimes within millimeter to centimeter, but often accompanied by occasional mixing into the oxic surface layer. These sites have organic matter primarily in mesodensity and aggregate forms (Arnarson and Keil, 2007; Bock and Mayer, 2000; Pichevin et al., 2004). Sedimentation under anoxic water column, on the other hand, can be accompanied by significant preservation of recognizable organic matter fragments (Pichevin et al., 2004).

This progression of organic matter–mineral interactions under varying oxygen conditions is consistent with several lines of evidence. An alternative possibility, however, is provided by the strong surface area correlations with organic carbon found for black shales (Kennedy et al., 2002). This relationship raises the possibility that the smectitic clays that account for the high surface area values measured by the EGME method are alone responsible for the elevated organic matter preservation and that anoxia is but an incidental factor. More work is needed in modern systems to ground truth this idea.

12.12.3.3.3 Physical disturbance

If diffusional access to substrates within hierarchical aggregate structures restricts biologic usage of these substrates, then physical access can be enhanced via various forms of physical disturbance. In soils, tilling clearly leads to reduction of macroaggregate structures, while microaggregates and primary organoclay structures, such as tactoids, survive much better (Tisdall and Oades, 1982). These impacts lead to the strong organic carbon–clay correlations that are common in agricultural lands (e.g., Nichols, 1984).

In the ocean, lower ratios of organic carbon to surface area are common in shallow water, deltaic systems (Mayer, 1994a).

Because these environments are unusual in maintaining clay-rich sediments at depths prone to frequent wave resuspension, they are considered to be analogous to mobile fluidized reactors in industry (Aller, 1998). It is unclear if the mechanism of enhanced organic matter decay in these environments is due to physical disruption of aggregates or simply a continued renewal of energetically more effective oxidants (e.g., oxygen and metal oxyhydroxides).

Over recent decades, the ocean has also become increasingly tilled, as on land, by commercial fishing activities that drag heavy gear across sediments (Duplisea et al., 2001). The level of physical disturbance of major fractions of ocean margin sedimentary environments is comparable to that in agricultural systems – once to several times per year to a depth of several centimeters. There are as yet no studies of the impact of this dragging on long-term organic matter preservation.

In both land and sedimentary environments, animals ingest bulk soil or sediment in order to obtain nutrition. In the process, there is reformation of the fabric of the organo-mineral assemblages. In this case, there lies the possibility that gut passage induces organic matter associations with minerals as well as breaking them up, as substantiated by microscopic examination of fecal material (Needham et al., 2005). Depending on the environment and types of animals, the balance between macroaggregates and microaggregates is strongly affected by gut passages (reviewed in Six et al., 2004).

12.12.4 Future Directions

Epistemological considerations: Despite more than 100 years of research, we are still only scratching the surface (pun intended) of understanding regarding the ways in which organic matter and minerals interact in the natural world. Future progress can be enhanced through continued integration of the soil and marine communities (Hedges and Oades, 1997) and by further expanding the fields to bring developments in the nanotechnology and surface structure fields to bear on geochemical issues. Many research areas are prime for further research.

In order to make progress, we argue that research needs to move away from single-explanation arguments and move toward integrated views and understandings of the organic–mineral complex within geochemical processes. We propose the following:

Geoscientists would be wise to shun single-explanation arguments for what is known to be a complex interplay of mechanisms. The geochemical literature is full of papers, including some written by the authors of this chapter, that apply Occam's razor to data sets and conclude that a single mechanism or process controls the studied environment. The razor asserts that one should proceed to simpler theories until simplicity can be traded for greater explanatory power. The simplest available theory need not be most accurate, which we argue is the current state of much research on organic–mineral interactions in the natural environment. For the razor to truly work, simple explanations that rely on a single mechanism (sorption, aggregation, and oxygen effects) must be carefully balanced against the preponderance of evidence, suggesting that the vast majority of sediment and soil systems studied are the result of multiple interactions occurring across multiple spatial and temporal scales.

As an example of multiple processes being important to creating an environmental system, Chenu and Plante (2006) evaluated cultivated loamy soils and suggested that (1) even clay-sized fractions are dominated by aggregates and (2) aggregation, in combination with sorption, controls protection. They state “the distribution of organic matter in clay-sized fractions was patchy and that many of the so-called <2 μm ‘particles’ were in fact nanometer- to micrometer-sized microaggregates in which organic matter was encrusted by minerals or coated minerals.” They concluded that true primary organo-mineral complexes cannot be isolated from typical environmental samples, and very small microaggregates are major sites of organic matter stabilization, both by adsorption and by entrapment of organic matter. Coarse clay–fine silt aggregates are difficult to separate, which might account for why neither natural processes nor even ultrasonication seems to knock them apart. This is because mechanical stability derives from the difference between cohesive and destructive forces. For cohesion, aggregate strength increases with the sum of strong and weak forces (e.g., van der Waals; Post-its will hang on to a surface only if enough area is in contact), and aggregate bonding forces should increase with size of particles in contact.

Thus, mineralogical influences on organic matter protection may not be monomineralic. As an example, frequent correlations of iron with organic matter contents may reflect not so much a direct adsorptive, complexation, or occlusion role for iron oxyhydroxides as a cementation of other minerals that more directly contact organic matter. Iron oxyhydroxides are clearly agents of binding in some aggregates, particularly in highly weathered soils (Barbera et al., 2008), and therefore may serve to bind clay aggregates and sequester organic matter in other situations (Wagai and Mayer, 2007; Wiseman and Puttmann, 2006). Because kaolinite often predominates over smectite in highly weathered soils, the interaction of iron oxides with kaolinite-rich aggregates enhances organic matter stabilization preferentially in kaolinite-rich soils, confounding a possibly greater capacity of smectite over kaolinite to stabilize organic matter in the absence of iron oxides. Experimental work substantiates a complex interaction among clay minerals, iron oxyhydroxides, and organic matter stabilization (Saidy et al., 2012).

Explicit incorporation of biology: Further research into organic matter stabilization by minerals should proceed on a basis that explicitly incorporates the biology of the process. The preservation, or stabilization, of organic matter is at root a question of bioavailability. Purely abiotic destruction of organic matter in mineral-rich systems is probably rare. Organic matter accumulates because it is not digested and metabolized by any organisms. Digestion generally proceeds via dissolution, so that stabilization is enhanced by mechanisms that prevent dissolution. Organisms promote dissolution generally via enzymatic attack. If enzymes exist to digest virtually any type of organic matter, then prevention of dissolution should be caused by either absolute or kinetic inhibition of enzyme access to substrate (Adu and Oades, 1978). We have reviewed mechanisms by which either inhibition can occur – for example, pore throats causing absolute exclusion of enzyme passage or tortuosity causing extended diffusion path lengths that reduce benefit–cost ratios. We suggest that more laboratory and field work be done that directly test these biotic access issues.

To the extent that bacteria are principal agents of organic matter decay, then constraints on their success in digestion and in reproduction within clay-rich microzones need more attention. Besides the question of enzyme diffusion, there is the need to understand how bacteria can propagate spatially in a clay-rich matrix, to access new substrate after a local microzone becomes depleted. Organic- and clay-rich microzones lose pore space upon compaction of sediments during burial, so the ability of bacteria to colonize microcaches of organic matter (e.g., necromass) must also decrease.

Size of organic matter in protected zones: If organic matter occurs as 'blebs,' then what are their sizes? Would they remain insoluble even without their mineral partner? The nature of sorption for larger biomolecules is poorly understood, as is the role this might play in aggregate formation. Do parts of adsorbed macromolecules dangle in solution and, if so, are they more available to enzyme attack? When and how is macromolecular sorption protective?

The mineralogy effect: While controlled lab experiments typically identify mineral-specific sorption, field data remain ambiguous. The role of specific mineralogies within mixed sediments and the role of oxide coatings on larger mineral grains are especially poorly understood. The experience gained from nanocomposite engineering suggests a role for exfoliated smectites in nature, as they can serve as protective minerals with a very high ratio of diffusional inhibition per unit weight of mineral. It suggests further research into natural exfoliation processes and recombination of thin smectite crystallites with bacteria and other forms of organic matter.

Metals and metal oxyhydroxides: The influence of dissolved and precipitated metals and metal oxyhydroxides, particularly in sediments, and their potential interactions with, or enhancements of, competition with organics for surface binding sites. There have been few studies that have coevaluated metal and organic binding to minerals in either soils or sediments. Recent evidence for marine systems suggests a larger role for oxide minerals and for occlusion within precipitated minerals than previously appreciated (Lalonde et al., 2009, 2012). Similarly and related, the influence of redox status on sorption and aggregation processes is essentially unknown. Do changes in Eh influence organic matter sorption, aggregate formation, or organic-metal interactions?

Zonal structure: The exact structure and influence of organic surface coatings in the creation and stability of aggregates is poorly constrained. The 'zonal structure' hypothesis of Kleber et al. (2007) is interesting and worthy of being followed upon, especially with regard to integrating it into 3D heuristic models of microreactors and stable aggregates. The literature on organic contaminants in soils and sediments is rich with examples of xenobiotic compounds, especially hydrophobic ones, attaching to preexisting natural organic matter rather than to mineral surfaces.

12.12.5 Conclusion

While we still do not understand fully the factors that limit and control the development of organic-mineral interactions, the merging and sharing of different perspectives on the role of

oxides, aggregates, and microbes has led to a new vision of how and why soils and sediments develop and change. This critical knowledge has been vital in helping develop strategies for predicting changes to Earth surface properties and global cycles in the Anthropocene (Certini and Scalenghe, 2011; Grunwald et al., 2011).

Acknowledgments

RK thanks AC Belcher for creating the initial database for this review, MG Logsdon for helping in constructing Figure 1, and J Neibauer for helping in editing. LM thanks M Kennedy and R Bennett for many stimulating discussions. RK and LM thank NSF Chemical Oceanography for support throughout the development of the theses described here.

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