

Dynamic interactions at the mineral–organic matter interface

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Abstract | Minerals are widely assumed to protect organic matter (OM) from degradation in the environment, promoting the persistence of carbon in soil and sediments. In this Review, we describe the mechanisms and processes operating at the mineral–organic interface as they relate to OM transformation dynamics. A broad set of interactions occur, with minerals adsorbing organic compounds to their surfaces and/or acting as catalysts for organic reactions. Minerals can serve as redox partners for OM through direct electron transfer or by generating reactive oxygen species, which then oxidize OM. Finally, the compartmentalization of soil and sediment by minerals creates unique microsites that host diverse microbial communities. Acknowledgement of this multiplicity of interactions suggests that the general assumption that the mineral matrix provides a protective function for OM is overly simplistic. Future work must recognize adsorption as a condition for further reactions instead of as a final destination for organic adsorbates, and should consider the spatial and functional complexity that is characteristic of the environments where mineral–OM interactions are observed.

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The vast majority of organic carbon in the biosphere (5,410–6,545 PgC; including vegetation, permafrost, soils, coastal systems and marine sediments¹) occurs at solid earth interfaces in close spatial proximity to some form of mineral matter. For this reason, carbon flowing through the biosphere will, at some point, almost inevitably come into contact with mineral surfaces, as it undergoes the many transformations inherent in the carbon cycle. Consequently, the interactions between organic and mineral phases have long been the subject of scientific inquiry. For example, most soil organic carbon is associated with colloidal-sized minerals^{2,3}, prompting early suggestions that this association is critical for soil fertility and, by extension, is ‘vital to life’⁴. When toxic organic chemicals were found to be accumulating in the biosphere⁵, mineral phases were investigated for their ability to break down organic contaminants in the environment^{6–8}. More recently, interest has turned towards using soils and sediments as repositories for excess atmospheric carbon^{9,10}, resulting in intensive research into the mechanisms determining the formation, strength and durability of mineral–organic matter (OM) associations^{10–13}. These latter research efforts have confirmed that minerals can protect OM from degradation. However, observed correlations between individual predictor values such as clay content¹⁴ or abundance of poorly crystalline minerals¹⁵ tend to be specific to certain situations and soil types. To date, no carbon cycle model has succeeded in predicting carbon turnover dynamics

based on a generalized, broadly applicable set of mineral phase parameters.

Several principles are critical to understanding mineral–OM interactions. First, soils and sediments originate from a combination of destructive and constructive processes. Weathering processes and OM decomposition disassemble rocks and organic debris into basic molecular units, which combine to create micron-sized agglomerations¹⁶. Biotic and abiotic processes organize the resulting microfabric into a porous, internally structured medium¹⁷. Second, minerals generally dominate over OM in soils and sediments in terms of mass proportions, with organic materials (including living organisms) rarely contributing more than single-digit percentages to total mass^{18–20} (although exceptions are found in organic soils and organic surface horizons). Owing to the quantitative dominance of the mineral phase, particle size distribution serves as a major constraint on the physical shape of the pore system as it evolves over time²¹. Third, liquid water is the most abundant phase in pore systems²², enabling geochemical and biological processes^{23,24}. Therefore, it is useful to consider even unsaturated soils and sediments as fundamentally aqueous systems. Finally, the mineral phase, the organic phase and the pore system are habitats for biota, which constantly modify both the physical shape of pores and the biogeochemical activities within the system²⁵.

In this Review, we undertake a broad appraisal of the complexity of the mineral–organic matter

Key points

- Minerals enable the compartmentalization of soils and sediments into small yet clearly delineated spaces, such that different chemical, ecological and evolutionary processes can occur concurrently within a larger system context.
- Organic matter (OM) attachment to mineral surfaces is dynamic, sensitive to interfacial energies and topology, and exhibits features reminiscent of a partial wetting phenomenon.
- Mineral-derived reactive oxygen species represent overlooked but undeniably key reactants in the oxidation and transformation of OM within soils and sediments.
- Correlations between OM and fine-grained minerals, although generally interpreted as reflecting the impacts of minerals on OM, could additionally reflect impacts of OM on mineral nucleation, growth and transformation.
- Depending on system logistics and environmental setting, the same type of mineral could act as a sorbent, chemical reactant and catalyst for associated OM, enabling a vast portfolio of potentially opposing outcomes.
- Assessments regarding the fate of OM in the environment should not be derived from correlations with single predictor values, such as abundance of a certain mineral phase or specific surface area.

Colloidal

Molecules or polymolecular particles dispersed in a medium that have at least in one direction a dimension roughly between 1 nm and 1 μm .

Poorly crystalline

An operational term to distinguish crystalline structures with short-range order from others that exhibit order over longer distances.

Unsaturated soils

(Soil) pore systems that are only partially filled with water are unsaturated; pore systems entirely filled with water are considered saturated.

Adsorption

An increase in the concentration of a dissolved substance at the interface of a condensed and a liquid or gaseous phase.

Reactive oxygen species

(ROS). Short-lived oxygen-bearing molecules with half-lives that range from fractions of seconds to days, including hydrogen peroxide (H_2O_2), superoxide ($\text{O}_2^{\cdot-}/\text{HO}_2^{\cdot}$), hydroxyl radical (HO^{\cdot}), singlet oxygen ($^1\text{O}_2$) and carbonate radical ($\text{CO}_3^{\cdot-}$).

Compartmentalization

The division of a system into multiple subsystems with well-defined boundaries that provide a certain degree of process autonomy.

interface and derive a perspective for future research efforts. The diverse roles of minerals in the environment are described (FIG. 1a), including OM adsorption, catalysis, chemical reactions participation and reactive oxygen species (ROS) generation. The role of the mineral matrix in creating distinct reaction spaces, and the importance of this compartmentalization in the fate of OM, are examined (FIG. 1b). Finally, we urge the field to move towards considering mineral–OM interactions as multidimensional and multifaceted, and to reconsider the current notion of mineral protection of OM.

Fundamental properties

Mineral–organic interactions depend on several characteristic properties of the individual mineral and organic phases, which are briefly described below.

Organic phase. Organic molecules can be produced by abiotic processes^{26,27} and by chemotrophic microorganisms²⁸, but phototrophic algae in the oceans and vascular plants on land are responsible for the bulk of modern biomass production, in roughly equal proportions²⁹. Primary production in the oceans creates mostly lipids, proteinaceous materials and carbohydrates other than cellulose³⁰, whereas lignin and cellulose together account for around half of primary production on land¹⁸.

Heterotrophic organisms use the resulting biomass as a combined source of carbon, energy and nutrients. Because cell wall passage is restricted to molecules with relatively small molecular masses (<600–1,000 Da)³⁰, the size of biomacromolecules must be reduced before assimilation into the cell is possible. Depolymerization and oxidation reactions inherent to extracellular molecular disassembly add ionizable oxygen-containing functional groups to decomposition products³. The resulting increasing abundances of polar functional groups (FIG. 2) enhance the aqueous solubility of the products, as well as their chemical reactivity towards metal cations and mineral surfaces, particularly when these functional groups are ionized. Moreover, the smaller molecular size facilitates diffusion³¹ of solubilized, reactive organic fragments towards mineral microstructures, where they can become entrapped and adsorbed.

Once an organic molecule comes close to a mineral surface, the abundance and type of organic functional groups constrain options for further reactions between matrix surfaces and mobile organic adsorbates.

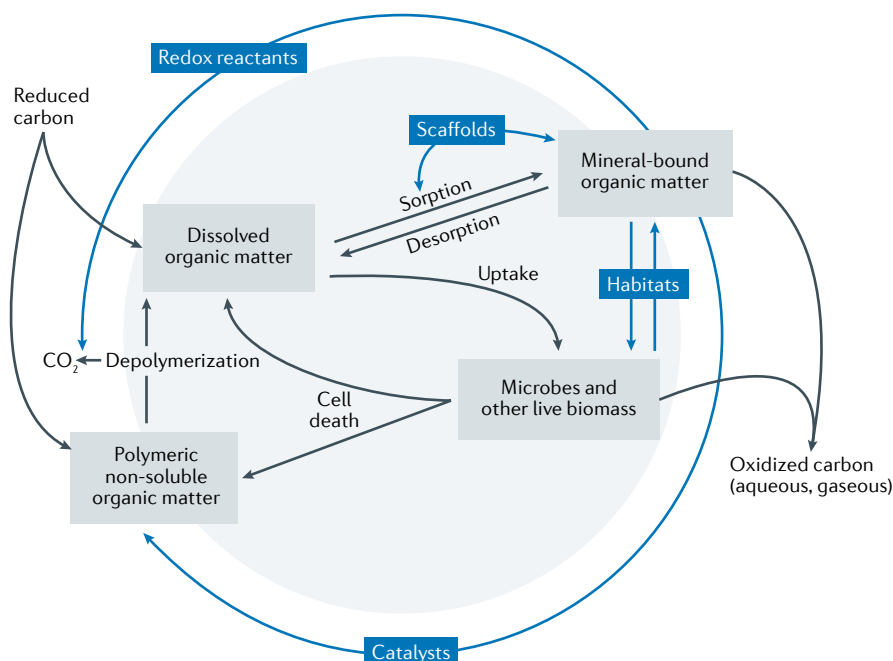
Mineral phase. A diverse suite of minerals occur in soils and sediments, including phyllosilicates and other aluminosilicates (collectively referred to as silicates); metal oxides, hydroxides and oxyhydroxides (collectively referred to as oxides); and metal carbonates and sulfides (FIGS 3,4). In most soils and sediments, phyllosilicates are the predominant component of the fine-grained fraction^{32,33}. Metal oxides are an order of magnitude less abundant than phyllosilicates except in highly weathered systems and metal-dominated marine benthic habitats (such as hydrothermal vent deposits and ferromanganese crusts), but they contribute distinct reactivity^{22,34} (FIG. 4).

Minerals possess both permanent (structural) and variable (pH-dependent and adsorbed-ion-dependent) surface charge distributions. Subsequent Coulombic interactions dictate many physical and chemical properties, such as dispersion behaviour, coagulation, colloidal stability, solubility and adsorptive bonding mechanisms^{35–37}. Mineral surface reactivity is also driven by surface topography³⁸, which results from deviations in atomic crystal structure (such as steps or vacancies), in tandem with particle shape and size. In altering the configuration and number of reactive surface groups per unit mass, topographic surface drivers (steps, edges and kinks, for example) can, thus, influence the composition, abundance and bond strength of compounds at the mineral surface. Surface defects can facilitate the formation of stronger surface complexes or reveal edges that offer unsaturated atoms available for direct complexation^{39–42}, and particle size modulates the relative number of reactive surface groups per unit mass of mineral. Finally, the presence and size distribution of pores within mineral grain assemblages also affect the available surface area for organic ligands, as well as exposure kinetics through steric constraints and diffusion limitation^{43–46}.

Beyond surface charge and topography, the key properties of fine-grained minerals that determine their interactions with OM (that is, mineral size, shape, charge and covalent reactivity) are fundamentally derived from their crystal structures (FIG. 3). Notably, interfacial energies of the different crystal facets have a strong influence on particle size and shape^{47–49}. For layer-type minerals (phyllosilicates, gibbsite and layered manganese (Mn) oxides such as birnessite), one facet carries only surface O atoms or OH groups that are fully saturated^{50,51}. The low interfacial energy of this crystal facet explains the tendency of the associated minerals to adopt a lamellar shape. In turn, this lamellar shape minimizes the tendency towards crystal growth and, hence, favours the persistence of small particles⁵².

The iron (Fe) oxides and framework Mn oxides are exceptions to the condition presented above, in that all their crystal facets carry under-coordinated or over-coordinated surface O atoms⁵³. One consequence of this imperfect surface O coordination state is that these minerals are primed for covalent reactions with appropriate organic functional groups. Another consequence

a Minerals may modulate the phase, transformation and turnover of organic matter by acting as scaffolds, catalysts, redox reactants and habitats.



Chemotrophic

The ability to use electron donors other than photons for the synthesis of organic compounds containing reduced carbon.

Phototrophic

The ability to capture photons as an energy source for the synthesis of organic compounds containing reduced carbon.

Heterotrophic

The ability to derive nutritional requirements from complex organic substances.

Depolymerization

The disassembly of a polymer into its constituent monomers or into a mixture of products.

Fine-grained fraction

Mineral grains with an average diameter smaller than 50/63 microns, depending on the classification system used.

Coulombic interactions

Interactions that result from the electric force between two charged entities.

Dispersion

A system in which particles of colloidal size of any nature (solid, liquid or gas) are dispersed in a continuous phase of a different composition (or state).

Coagulation

The formation of aggregates from a fluid colloidal system.

Steric constraints

Factors or effects that prevent the adoption of a certain spatial orientation that would be required for the reaction to proceed unhindered.

Crystal facets

Flat planes on a crystal.

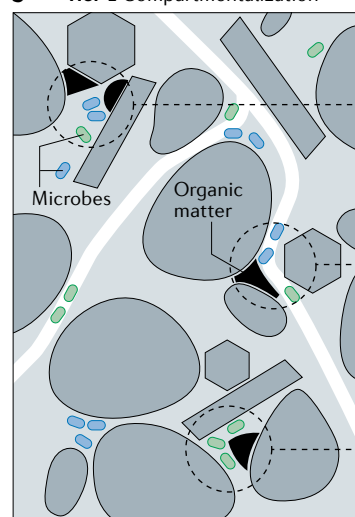
Interfacial energy

Excess free energy or work associated with the interface between two phases, per interfacial area.

Crystal growth

The addition of new atoms into the characteristic arrangement of the crystalline lattice, releasing thermal energy (enthalpy of crystallization).

b Tier 1 Compartmentalization



Tier 2 Physiochemical constraints

Substrate localization

Sorptive fixation and substrate dilution

Mobility filter

Preferential diffusion and transport pathways

Habitat definition

Constraining decomposer size, composition and metabolism

Tier 3 Molecular-level processes

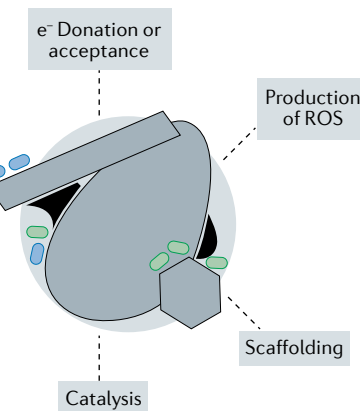


Fig. 1 | Organic matter cycling in soils and sediments and mineral–organic matter interactions. a | Historic representation of organic matter cycling in soils and sediments. Major organic matter pools and fluxes are represented as black boxes and arrows. Blue arrows represent processes and interactions discussed in this Review. **b** | Multiscale representation of mineral organic interactions. At the largest scale (Tier 1), the main function of the mineral matrix is to delineate compartmentalized space. As a consequence of compartmentalization, a number of static and dynamic constraints are imposed on smaller scales (Tier 2 functions). These constraints then determine the intensities and rates at which molecular-scale biogeochemistry could be able to proceed (Tier 3 functions). ROS, reactive oxygen species.

is that these minerals tend to grow and dissolve readily, and form particles in a variety of shapes, depending on the aqueous chemistry³⁴. Finally, the relatively high interfacial energy of these minerals enables the coexistence of multiple Fe oxides in most soils, as differences in surface and bulk energies cause reversals in the order of thermodynamic stability as a function of particle size and aqueous chemistry⁴⁷. For example, poorly crystalline ferrihydrite is often the initial product of Fe^{III}

crystallization, owing to its favourable surface energy. However, at sizes greater than ~5 nm, ferrihydrite becomes unstable relative to more crystalline goethite and hematite, owing to its less favourable bulk energy⁴⁸.

Adsorption

Adsorption has long stood as an explanation for the spatiotemporal preservation of OM in soils and sediments⁵⁴. However, mounting recognition of the




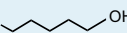

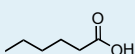
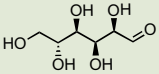
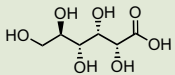
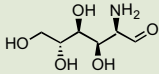
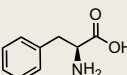
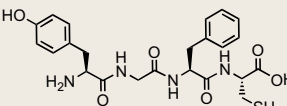
	Sensitivity to pH:	pH independent				
		pH independent		pH dependent		
	Functionality:	Nonpolar	Polar but neutral	(-) Charge	(+) Charge	Ability to unfold
	Mechanism of attachment:	Hydrophobic exclusion	H-bonding	Coulombic attraction	Coulombic attraction	Entropy gain
Aliphatic/aromatic moiety with minor functionalization						
Naphthalene		×				
Hexane						
Catechol		×	×	×		
Hexanol						
Benzoic acid		×		×		
Hexanoic acid						
Inherently polar moieties with additional functionalization						
Glucose			×			
Gluconic acid			×	×		
Glucosamine			×		×	
Compounds equipped with all major functionalities (usually N-containing)						
Phenylalanine		×	×	×	×	
Polypeptide/protein		×	×	×	×	×

Fig. 2 | **Organic multifunctionality.** Variation of functional group combinations on organic compounds allows for diverse modes of interaction with mineral surfaces.

dynamism occurring at the mineral-organic matter interface, buoyed by diversifying intersectionality in expertise and analytical techniques^{14,55–58}, has emerged in the last decade of biogeochemical research. Rather than a static and irreversible binding mechanism, it is increasingly clear that adsorption itself encapsulates a series of fundamentally kinetic processes: diffusion, competition and exchange reactions are concurrent and continuous as OM accumulates at the mineral surface. The dynamic mineral–OM interface evolves continuously with changes in the chemistry of aqueous phases, OM and mineralogy, and influences both magnitude and rate of OM adsorption.

Observed complexity in OM adsorptive processes is rooted in the inherent diversity of the reactants (FIG. 5a).

OM encompasses a complex, heterogeneous continuum of structure, processing and functional diversity^{59–61}. Even among small organic compounds, this variety enables adsorption through a combination of multiple anchoring points and mechanisms^{62,63} (FIG. 2). In tandem, a diverse suite of mineral phases occurs in soils and sediments, varying in surface charge and distribution, topography and particle size (FIG. 4). OM adsorption almost invariably involves a combination of several mechanisms. However, mechanisms of organomineral adsorption can be grouped by the surface chemistry of the mineral (FIG. 5b), as it affects surface ligand bond types, coordination state and spatial organization. These surface chemistries fall into three general groups: variably charged, non-charged and negatively charged.

Variably charged surfaces of metal oxides and phyllosilicate crystallite edges carry hydroxyl groups that are increasingly protonated with decreasing pH, thereby acquiring positive charge. This protonation, in turn,

enables the retention of organic ligands through rapid ligand exchange^{64,65}. In many phyllosilicates, substitution of octahedral aluminium (Al) and tetrahedral silicon (Si) with cations of lesser charge will generate permanently charged

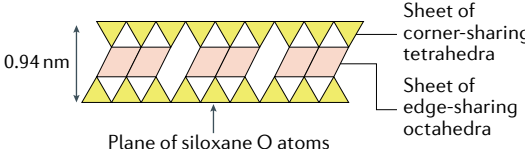
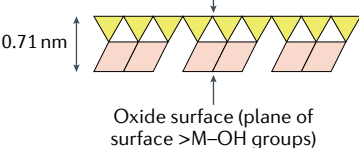
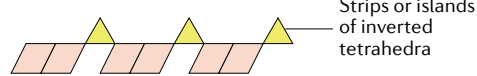
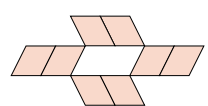
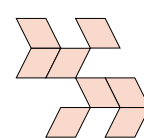
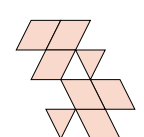

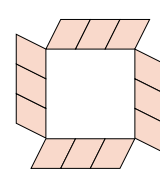

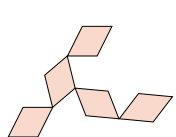



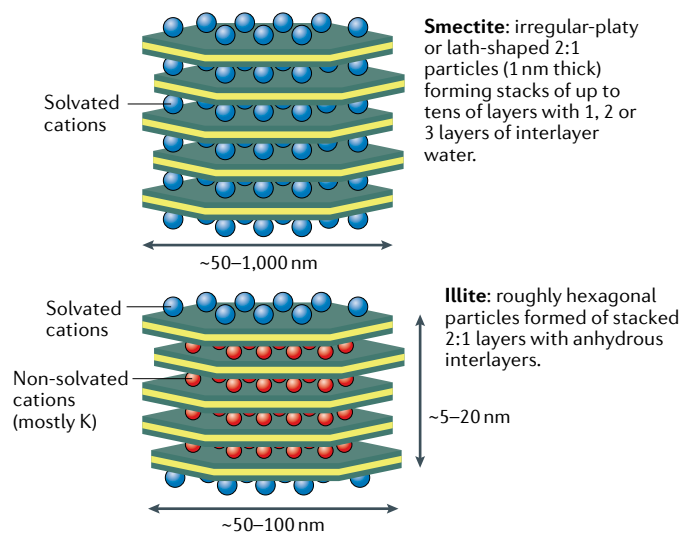
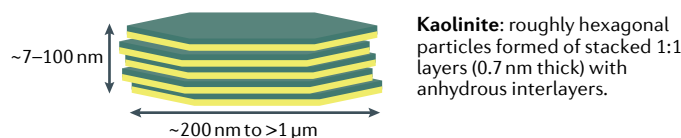
Mineral type	Crystal structure	Charge (σ , mmol _c g ⁻¹)	Area (a_s , m ² g ⁻¹)		
Phyllosilicates					
2:1 Layer type Illite ≥ smectite ≥ vermiculite, chlorite		Smectite: -0.7 to -1.2	Smectite: 740 to 780		
		Illite: -0.16 to -0.22	Illite: 20 to 200		
1:1 Layer type Kaolinite		Kaolinite: 0 to -0.02	Kaolinite: 7 to 80		
Modulated phyllosilicates Imogolite, allophane		Imogolite: 0.1 to 0.5 Allophane: 0 to -1.0	Imogolite: 600 to 900 Allophane: 700 to 900		
Metal oxides					
Fe oxides Goethite > hematite ≥ ferrihydrite > etc.	Goethite (FeOOH)		Chains of edge-sharing octahedra linked by corner sharing	Goethite: 0 to 0.15	Goethite: 40 to 90
	Hematite (Fe ₂ O ₃)		Pairs of face-sharing octahedra linked by corner and edge sharing	Hematite: 0 to 0.02	Hematite: 10 to 35
	Ferrihydrite (Fe ₁₀ O ₁₄ (OH ₂))		Tetrahedra and clusters of edge-sharing octahedra linked by corner sharing	Ferrihydrite: 0 to 1.3	Ferrihydrite: 200 to 800
Mn oxides Birnessite > todorokite > etc.	Birnessite (Na,Ca)Mn ₇ O ₁₄ • 2.8H ₂ O		Sheet of edge- sharing octahedra	Birnessite: -1.3 to -2.8	Birnessite: 1,200
	Todorokite (Ca,Na,K) _x (Mn ⁴⁺ ,Mn ³⁺) ₆ O ₁₂ • 3.5H ₂ O		Chains of edge-sharing octahedra linked by corner sharing	Todorokite: -0.15	Todorokite: ~1,200
Al oxides Gibbsite > boehmite, Al oxide gels	Gibbsite (Al(OH) ₃)		Sheet of edge- sharing octahedra	Gibbsite: 0 to 0.02	Gibbsite: 1 to 100
	Al hydroxide gel		Amorphous	Al(OH) ₃ gel: 0 to 0.4	Al(OH) ₃ gel: >200
<div> SiO₄ tetrahedron</div> <div> MO₄ tetrahedron (M = Al, Fe)</div> <div> MO₆ octahedron (M = Al, Fe, Mg, Mn)</div>					

Fig. 3 | **Key properties of fine-grained minerals and related solids.** The material referred to as allophane is a short-range-ordered phyllosilicate with imogolite-like local structure and highly variable stoichiometry; its distinguishing features are low crystallinity and transmission electron microscopy images suggestive of hollow spheres 3.5–5 nm in diameter, although multiple studies have noted that the interpretation of 3D structure from a 2D transmission electron microscopy image is ambiguous⁹⁵. Data based on REFS^{34,66,94,96,260–263}.

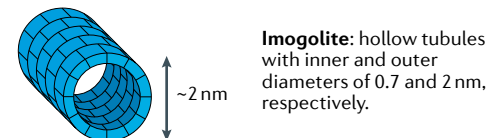
a 2:1 Layer type phyllosilicates



1:1 Layer type phyllosilicates

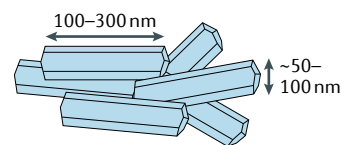


Modulated phyllosilicates

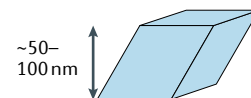


Fe oxides

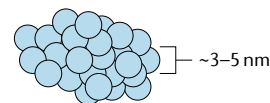
Goethite: rod-shaped crystals in roughly ordered clusters (also observed as oblong particles 3–5 nm in diameter, possibly stabilized by Al impurities).



Hematite: roughly rhombohedral crystals (tending towards a platy shape with increasing Al impurities).

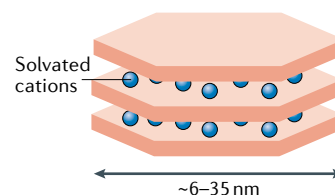


Ferrihydrite: aggregates composed of nanoparticles 3–5 nm in diameter.



Mn oxides

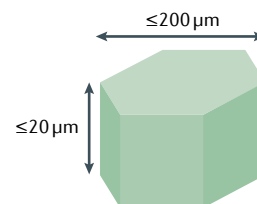
Birnessite: flake-shaped particles (0.7 nm thick) forming weakly ordered stacks with 0 or 1 layer of interlayer water.



Todorokite: platy or fibrous particles formed of intergrown hollow needles.

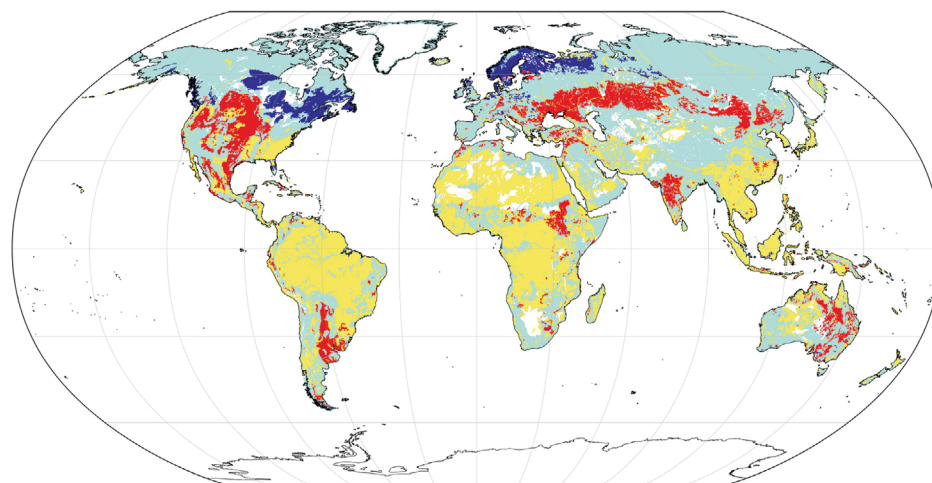
Al oxides

Gibbsite: rectangular crystals 50 to 100 nm long; larger crystals form pseudo-hexagonal plates or rods with dimensions up to ~200 µm.



Al oxide gels: amorphous polymeric network forming ~2-µm particles with internal porosity on length scales of ~20 nm to sub-nm.

b



Mineral	Abundance
Illite/mica	25%
Smectite	15%
Vermiculite	8%
Chlorite	5%
Kaolinite	28%
Gibbsite	4%
Fe oxides	3%
SRO phases (mostly allophane)	0.5%
Other (mostly framework silicates, such as quartz, feldspar)	11%

Solution

A homogeneous phase that results from the mixing of two (or more) phases.

surfaces. The prevailing negative charge of these surfaces allows for electrostatic attraction of metal cations⁶⁶. When isomorphic substitution is absent, as in some 2:1 phyllosilicates and kaolin group minerals, the resulting surfaces are electrostatically neutral and, thus, allow nonpolar organic molecules to accumulate via entropy-driven hydrophobic exclusion phenomena in combination with Lifshitz–van der Waals forces and H-bond formation^{3,67} (FIG. 5).

As organic ligands partition from solution to mineral surfaces, monolayer coverage of the mineral surface converges into a multilayer molecular architecture^{68–70} (FIG. 5c). Organic ligands tend to have a variety of functional groups (FIG. 2), thus, there can be multiple bonding mechanisms between the mineral and OM. This diversity of bonding reactions, paired with the competition of organic compounds for sorptive sites both between

◀ Fig. 4 | **Size, shape and global distributions of minerals.** **a** | Size and shape of minerals discussed here. **b** | Global map showing the most abundant fine-grained mineral in the subsoil (0.3 to 2 m depth) as a function of location, and average relative abundance of different fine-grained minerals in the upper 2 m of soil averaged over the Earth's land surface, with the exception of organic-rich soils (such as Mollisols) and ice-covered regions³³. SRO, short-range-ordered. Part **b** is adapted from REF.³³, CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>).

themselves and with inorganic ions⁷¹, results in complex multidimensional structures at the mineral surface (FIG. 5c). Ion concentrations are well known to modulate adsorption rates and extents, with variations amongst bonding mechanisms and ion composition^{72,73}. However, the importance of competition between organic compounds in structure-selective adsorption (molecular fractionation) is less well constrained.

The formation and structure of multilayer architectures over a range of timescales and length scales remains incompletely understood despite recent work involving nanometre-scale microscopy and spectroscopy⁷⁴, temporal partitioning of organic ligands from solution onto the mineral surface^{75,76} and detection of uneven structures at the mineral surface^{77–79}.

Adsorption of OM at the mineral–water interface occurs at a rapid rate and reaches equilibrium with the aqueous phase in 24 h for many organic moieties and non-porous minerals⁸⁰. The initial adsorption step is typically fast, and a majority of adsorption is completed within the first few hours after the solid phase is exposed to aqueous OM. Slow adsorption can follow this first step and is most likely caused by the diffusion of molecules into the intra-particle regions^{45,65,81}. Most kinetic datasets regarding OM sorption on soils and sediments come from studies conducted on xenobiotic compounds⁶⁵. However, studies carried out on organic molecules isolated from soil and aquatic environments suggest that the variables that control the magnitude of sorption also control its kinetics^{82,83}. Some of these variables include the size, charge, hydrophobicity, charge density and concentration of OM, solution composition (pH, ionic strength, ion type) and mineral type (such as metal oxides versus silicates). For example, rapid adsorption is more common at lower pH values, high OM concentration and in the presence of cations^{82–85}, where adsorption rates are faster under conditions that promote weaker adsorption affinity, such as in alkaline solutions⁸³. Notably, newly adsorbed organics might compete with and actually induce the release of previously adsorbed organic compounds⁸⁶, although this process is not well studied *in situ*.

Once bound to a mineral surface, an organic ligand only rarely remains undisturbed and, instead, is vulnerable to desorption and exchange processes, mineralization and catalytic transformations *in situ* (FIG. 6). During these processes, organic molecules on mineral surfaces might experience changes to their hydration, structure, isomerization, rotation and electron delocalization, depending on the type of chemical bonding at the mineral–water interface. The overall chemical or electronic state of the adsorbed molecule tends to be similar to the molecule in solution when the adsorbed molecules exhibit H-bonding, van der Waals interactions or retain their

solvated water (FIG. 6). Conversely, the adsorbed molecule tends to experience substantial changes to its chemical state if it forms covalent or ionic interactions and directly coordinates to the metal atoms at the mineral–water interface, such as during ligand exchange. These distinct responses are relevant to hydrolysis, electron transfer and radical-mediated reactions, as well as photochemical lability^{87,88}. Although electron transfer amongst weakly coordinated species can be limited in some of these complexes, for directly bound covalent complexes, not only the chemical state of the organic molecule is changed but also the electronic state of the metal atom on the surface (FIG. 6). Unlike alkali and alkaline earth elements, transition metal ions in solution or at mineral–water interfaces, such as Mn, Fe, Ni, Cu and Zn, play an important role in modifying the electronic states of the interacting organic functional groups^{89–91}.

Adsorption potentially impacts not just the adsorbed OM but also the minerals: adsorption invariably lowers interfacial energy⁹², so accumulation of OM on mineral surfaces should both facilitate the nucleation of new particles and inhibit the growth of existing particles. This should favour the formation and persistence of smaller particles, a phenomenon observed experimentally in the apparent stabilization of short-range-ordered metal oxides (ferrihydrite) and aluminosilicates (proto-imogolite)^{93–96}. A logical consequence of this is that correlations between OM and fine-grained minerals, although generally interpreted as reflecting the impacts of minerals on OM, should additionally reflect (to an unknown extent) impacts of OM on mineral nucleation, growth and transformation.

The transformations summarized here, and the subsequent temporal persistence of adsorbed molecules, are critical to the parameterization of organic C cycling in environmental systems (FIG. 5c). Yet, comparatively few studies have assessed the susceptibility of organic ligands to desorption and exchange, despite widespread attribution of adsorptive temporal persistence^{12,58,97,98}. Even relatively short desorption experiments using minerals and whole soils reveal partial removal of adsorbed ligands from all surfaces except variable-charge hydrous oxides. However, it is likely that there is continuous exchange even with these minerals, masked by near-zero net solubility^{58,99}. Mineral transformation and dissolution could also mediate release of adsorbed compounds into the aqueous phase. Anoxic events and biotic reductive dissolution of oxides^{100–104}, acidity-driven deprotonation in low-Fe systems¹⁰⁵ and secretion of root exudates^{106,107} could all serve a weathering-like role in releasing adsorbed ligands.

A presumed link between particular bonding mechanisms and biotic mineralization of ligands has not been systematically addressed. Laboratory biodegradation studies suggest that OM adsorption, particularly to high-surface-area oxides in low-pH systems^{108–111}, can hinder decomposition. It is not clear, however, how such findings translate to natural soils and sediments, where dynamic weathering and solution chemistry will alter surface functionality, and where exoenzymes from fungi and bacteria can be abundant in solution. Indeed, whole-soil isotope tracer experiments suggest

Intra-particle regions

Any parts of a particle that are not participating in surface reactions.

Xenobiotic compounds

Substances that are foreign to a given natural environment or ecosystem; usually means that organisms in the system lack adaptations for the metabolic processing of a xenobiotic compound.

Ligand

Any atom or molecule attached to a central atom, usually a metallic element, in a coordination or complex compound; if regarding part of a polyatomic molecular entity as central, then the atoms, groups or molecules bound to that part are called ligands.

Photochemical lability

The tendency of a compound to undergo a chemical reaction when exposed to light.

Nucleation

The process by which nuclei are formed in solution.

Short-range-ordered

The regular and predictable arrangement of atoms over a very short distance; in crystals, order does not persist over distances of more than a few nanometres and often extends over a distance of just a few bond lengths; short-range-ordered minerals are often also referred to as poorly crystalline minerals.

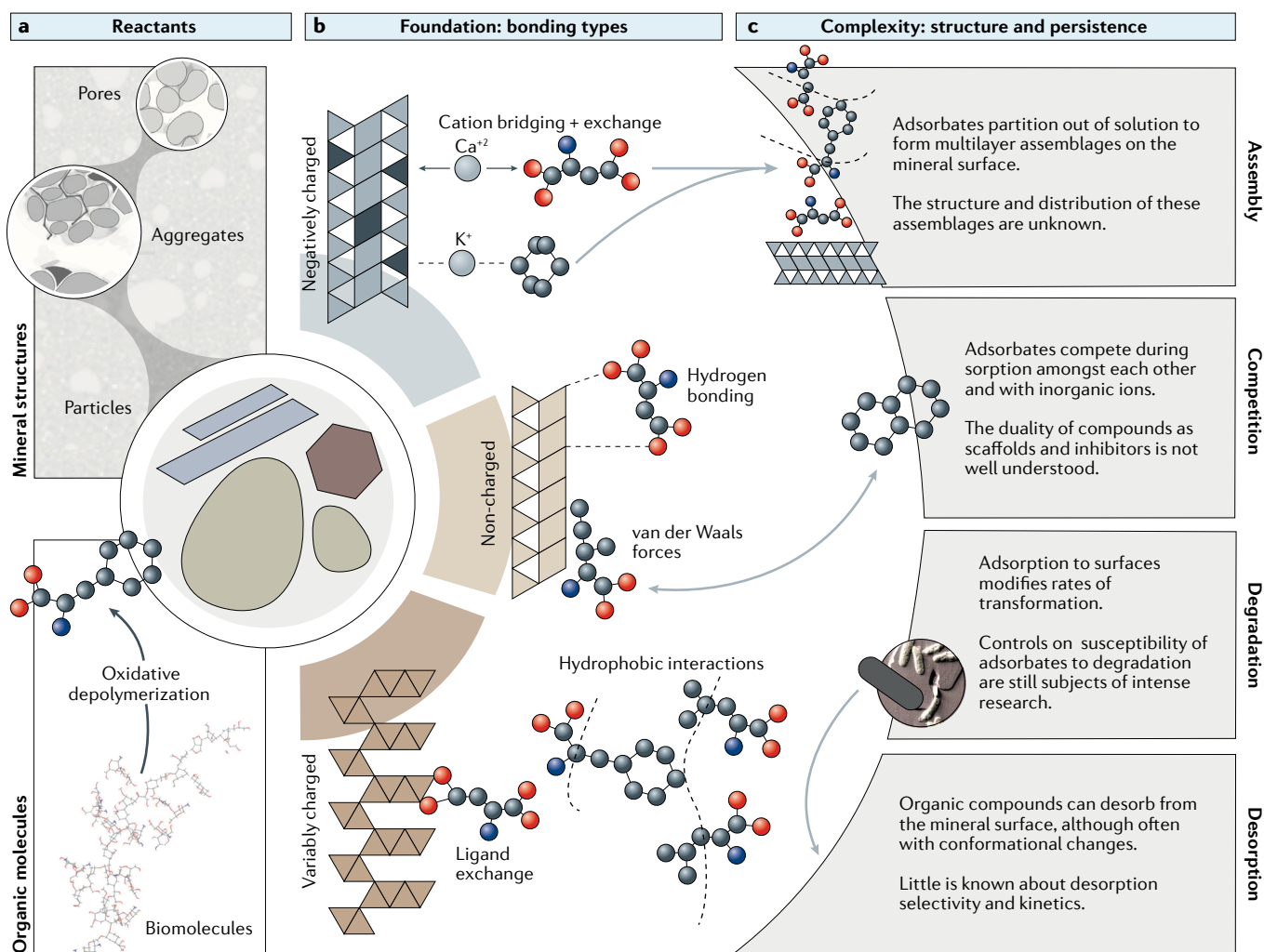


Fig. 5 | **Organic ligands at mineral interfaces.** **a** | Mineral interfaces occur at a variety of spatial scales and topography in soils and sediments, where a diversity of primarily low-molecular-weight, amphiphilic organic ligands may reach the solid–solution interface. **b** | Once proximal, ligands can bind to mineral surfaces through one or multiple complexation mechanisms, based on surface charge distribution and structural reactivity. **c** | Many fundamental components of adsorption, such as the assembly, bioavailability and downstream reactivity of adsorbed organic compounds on mineral surfaces, remain undefined in complex natural systems.

that metabolism of adsorbed ligands is continuous¹¹². Besides microbial degradation and consumption after direct desorption, displacement by biotic exudates can contribute to the decomposition of previously adsorbed molecules¹¹³, supported by observations that a substantial proportion of mineral-adsorbed OM is microbial in origin^{114–116}. Such evidence for the multifaceted role of biotic consumption, exchange and deposition of organic ligands highlights the uncertainty in underlying controls and their quantitative effect on mineralization rates.

Catalysis

The potential of a mineral surface to act as a catalyst and enhance reaction rates results from the combined action of multiple factors. For instance, minerals can concentrate organic compounds to several orders of magnitude higher than the bulk solution^{117,118}, thus, increasing the pre-exponential frequency factor in the Arrhenius equation. Association with a mineral

surface can reduce the degree of orientational freedom of an adsorbate by aligning monomers along two dimensions at planar surfaces¹¹⁹, thereby, facilitating recurring reaction patterns. Minerals also create centres of reactivity by providing coordinatively unsaturated sites and steric enhancement of reactions at surfaces with substantial topography³⁸. Furthermore, mineral surfaces can transfer protons to a sorbate, as well as offer empty electron orbitals for the reception of bonding electron pairs (Brønsted and Lewis acid/base functionalities¹²⁰). Lastly, minerals entirely made of transition metals (such as Fe and Mn oxides) or acting as solid supports for adsorbed transition metals at their surfaces and in interlayers (phyllosilicates) can contribute transition-metal-specific catalytic functionality^{121,122}.

Laboratory observations made on the catalytic reactivity of different minerals can be used to recognize three mineral types of chemical reactivity (FIG. 6), although the intensity of the organomineral interactions within

Catalyst

A substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction.

Orientational freedom

The absence of any physical restrictions to the movement and arrangement of a compound.

Steric enhancement

Factors or effects that facilitate the adoption of a certain spatial orientation that would be required for the reaction to proceed unhindered.

each class varies with changes in mineralogy, OM concentration and geochemistry of the environment.

Class I minerals are dioctahedral 2:1 clays that adsorb large organic molecules through cation bridging and through hydrophobic expulsion and aromatic ring π interactions with surfaces or Lifshitz–van der Waals forces. Direct complexation of OM can occur at edge sites. Because hydrophobic expulsion is the primary driver for adsorption, kinetics of adsorption are fast, macromolecular structures are rarely disturbed and limited electron transfer is expected. However,

heterogeneous oxidation of OM can occur on clay surfaces in the presence of adsorbed O_2 and transition metals^{123,124}. Overall, the catalytic activity of Class I minerals is expected to be low, with slow kinetics^{123,125}.

Class II minerals are metal oxides, silicates and 1:1 clays, and exhibit high adsorption capacity (FIG. 6). These minerals tend to catalyse moderate changes to the structure and electronic state of adsorbed molecules, primarily through direct bonding, hydrolytic breakdown from reactions with surface OH and heterogeneous oxidation with adsorbed O_2 (REFS^{123,126,127}).

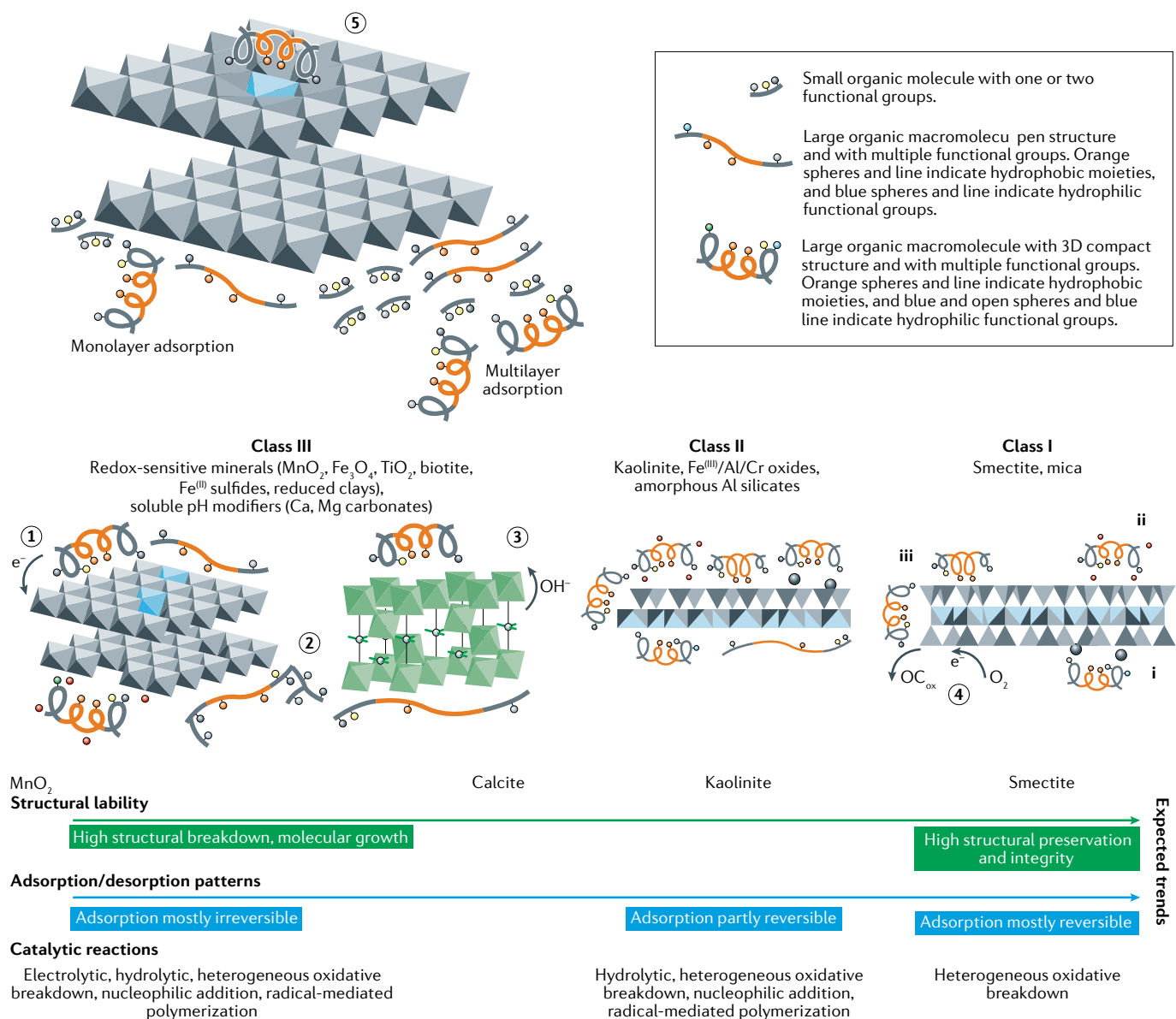


Fig. 6 | Molecular mechanisms of organic matter reactions at mineral–water interfaces. Cartoon at the top shows a mineral surface showing monolayer and multilayer (3D) sorption of small and large organic matter (OM). Molecular structures of organic molecules at mineral–water interfaces are: (i) cation bridging; (ii) H-bonded or Lifshitz–van der Waals interactions; and (iii) direct covalent interactions. Expanded views of OM interactions and expected trends for different mineral structures in soils and sediments are shown at the bottom. The nature of chemical reactions are (as numbered in the figure): (1) e^- transfer and electrolytic breakdown

of OM; (2) larger OM formation from nucleophilic addition and radical-mediated polymerization; (3) hydrolytic breakdown of molecules from pH changes at the interface; (4) heterogeneous OM oxidation from adsorbed O_2 ; and (5) chemical changes to substrate showing electron transfer and reduction of substrate atoms, and changes to the coordination environments of neighbouring atoms of the substrate surface. Based on their differences in chemical reactivity towards OM, we further classify minerals presented above into three classes (I–III). Expected trends for OM behaviour are included.

Finally, Class III minerals are highly reactive in terms of magnitude of sorption, and in terms of hydrolytic and electrolytic breakdown and heterogeneous oxidation (FIG. 6). Reduced clays (those with substituted transition metals), Mn oxides, sulfides and magnetite belong to this category^{123,127–129}. Mineral carbonates and sulfides, through major changes of surface acidity at the interface, play an important role in the hydrolytic breakdown of macromolecular organic molecules. Breakdown of large molecules into small molecules is possible, as is the subsequent transformation into larger molecules through nucleophilic addition, radical-mediated polymerization and large-molecule-formation reactions^{129–131} (FIG. 6).

Because of these changes, substantial alterations to mineral surface structure, including even eventual dissolution, are anticipated in the case of Class III minerals (FIG. 6). Strongest proof for all of these observations comes from solution studies, rather than from spectroscopic work directed at the interface^{123,132,133}. The solution studies reveal the progress of catalytic reactions and their rates, but not the reaction mechanisms at the interface.

The impact of mineral catalytic behaviour on OM stability is expected to be greater where there is direct organomineral interaction and monolayer coverage of OM (FIG. 6). As a consequence, the intensity of organomineral interactions should be strongest during monolayer OM adsorption. In multilayer adsorption, conversely, the overall role of minerals as catalysts should be comparatively diminished as OM–OM interactions increasingly predominate over mineral–OM interactions (FIG. 6). Although a majority of molecular studies conducted on soils or sediments belong to the latter category^{74,134,135}, the impact of layer thickness on OM behaviour remains relatively poorly understood because of the analytical difficulties in exploring these systems.

Metal atoms of mineral surfaces in the proximity of adsorbed molecules also tend to experience changes to the adsorbed water and surface hydroxyls, and to their electronic state. These can be threefold: changes in the metal–ligand coordination (and hydration and hydrolysis) environment; complete electron transfer and oxidation or reduction of surface metal atoms; and perturbations to the energy levels of valence electrons^{133,136,137}. Although changes are less notable during the formation of weak H-bonded complexes, the formation of direct ionic and covalent interactions impact the binding of metal atoms of the mineral surface strongly, with some additional impact to the buried atom layers next to the binding site³⁸ (FIG. 6). As a result, adsorption of OM to mineral surfaces often modifies the characteristics of both OM and mineral surfaces, and only on rare occasions are the chemical characteristics of each preserved at the interface during bonding^{38,85,130}. These considerations highlight the difficulty to distinguish between two fundamental functions (catalysis and redox reactions) of mineral surfaces when considering OM transformations at solid earth interfaces. At this time, it seems that there is considerable conceptual uncertainty regarding these functions, with the available evidence favouring a role as reactant.

Redox reactions

Electron transfer reactions between OM and minerals, directly or mediated by microbes, are a primary pathway contributing to the oxidation, transformation and mineralization of carbon within soils and sediments (FIG. 7a). Minerals and OM can serve as either electron donors or acceptors for a vast array of heterotrophic or mixotrophic microbial metabolisms spanning a broad ecological and taxonomic diversity¹³⁸. Various mechanisms are employed in the microbial coupling of organic carbon oxidation to the reduction of Fe and Mn oxides, including direct electron transfer via outer membrane enzymes¹³⁹ or conductive nanowires^{140,141} and indirect transfer via endogenously produced electron-shuttling molecules that are secreted by an organism, after which they adsorb to an oxide surface and transfer the bacterial-derived electron to the mineral¹⁴². The latter reaction pathway is a coupled biotic–abiotic pathway, whereby the second step is a direct electron transfer reaction between the organic molecule and mineral surface.

A variety of organic molecules can be transformed via direct electron transfer at the surface of minerals, including Fe and Mn oxides, sulfides and phyllosilicates¹²³. Within natural systems, metal oxides have garnered particular attention for their ability to serve as effective oxidants of a wide range of organic compounds¹⁴³, including humic acids, phenols, anilines, low-molecular-weight organic acids (such as oxalate, pyruvate, citrate)^{7,144,145} and, more recently, proteins^{128,146}. The overall reaction sequence involves adsorption of the organic reactant to the (hydr)oxide surface, transfer of electron(s) to the mineral-hosted metal and subsequent detachment of the reduced metal and oxidized organic molecule¹²³.

The adsorption, fractionation and oxidative transformation upon reaction of dissolved organic matter (DOM) with minerals are dependent on mineral surface chemistry, including the composition and abundance of terminal bonds^{123,147}. Despite typically lower adsorptive capacities, Mn oxides are stronger oxidants than Fe oxides, in large part owing to differences in redox potential^{123,148,149}. Indeed, Mn oxides are considered the strongest naturally occurring oxidants, and, thus, considerable attention has been paid to investigating the role of Mn oxides in organic carbon transformations¹⁴³. In general, organic compound oxidation rates increase with average oxidation state, redox potential and specific surface area of the Mn oxide and decrease with apparent activation energy of the overall reaction and the pH_{pzc} (pH at the point of zero charge) of the oxide¹⁴³. Furthermore, OM oxidation rates increase with decreasing pH, which has been primarily attributed to the higher redox potential at lower pH.

As mineral–OM redox reactions rely on surface complex formation¹⁵⁰, the efficacy of mineral-induced OM oxidation and mineralization is, ultimately, determined by factors controlling initial adsorption. Thus, the extent and rates of organic carbon transformation and mineralization at mineral surfaces decline if surfaces become passivated, for instance, by high OM loadings¹²³ and/or reaction products blocking reactive sites on the surface¹⁴³. Further, mineral ripening and recrystallization to less reactive phases during reaction can constrain

Mixotrophic

Deriving carbon and energy from a mix of different sources, typically, a combination of inorganic and organic compounds.

Nanowires

Proteinaceous appendages produced by microbes, particularly bacteria, that are electrically conductive.

Passivated

A surface that is unreactive owing to alteration or from the formation of a thin inert coating.

Ripening

Physical and/or structural alteration of a mineral to obtain a lower surface free energy and more energetically favourable state.

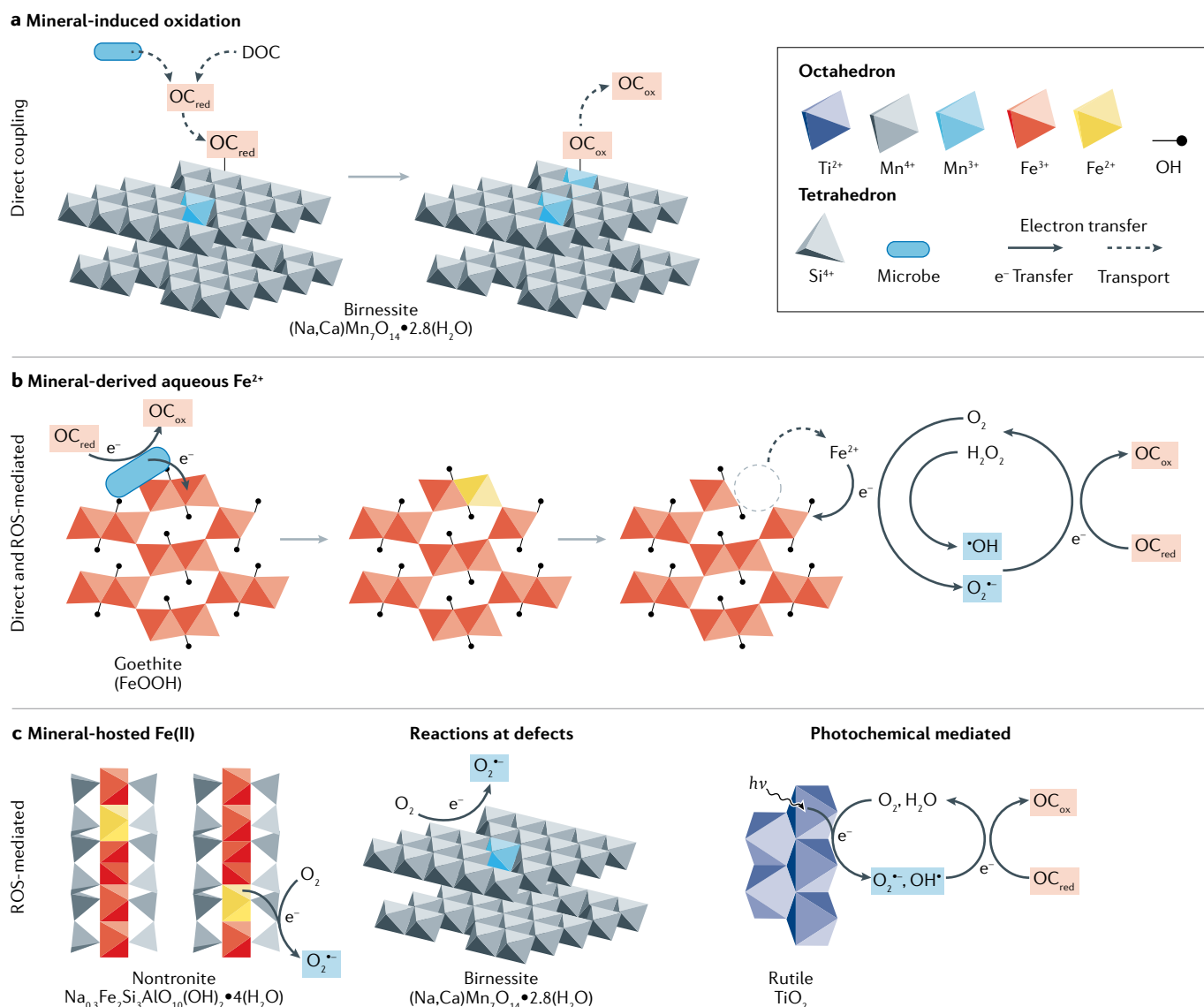


Fig. 7 | Mineral-induced organic carbon redox pathways. a | Mineral-induced oxidation, which represents direct coupling. **b** | Mineral-derived aqueous Fe(II), which involves both direct and reactive oxygen species (ROS)-mediated reactions. **c** | ROS-mediated reactions. In panels **b** and **c**, the fate of mineral-derived ROS includes reaction of ROS with organic carbon (OC) or transformation of one ROS to another (dismutation of superoxide to hydrogen peroxide, formation of hydroxyl radical from ferrous iron and hydrogen peroxide via the Fenton reaction) — for simplicity, all these fates are not shown here. The illustrations are meant to show general processes, not mechanistic details, and the list of reactions is not exhaustive. DOC, dissolved organic carbon.

mineral surface reactivity over time. Extrapolation of the rates and products of mineral-mediated OM transformations within natural systems from these reactions involving pure phases is, therefore, limited and convoluted.

Nevertheless, correlations between oxidized Mn and oxidized OM point to a causal link between Mn oxidation and carbon transformations^{149,151,152}. In fact, the intimate and diverse association of OM with Mn oxides^{149,153} leads to a continuum of reactions, including mineralization and polymerization within layers coating the oxide surface¹²⁹. Yet, beyond correlations, there are limited data directly linking natural Mn oxides (or any mineral) to OM oxidation and transformation, pointing to a clear need for future investigations targeting mineral-mediated OM redox mechanisms.

Reactive oxygen species

Mineral-derived ROS¹⁵⁴, particularly hydrogen peroxide (H₂O₂), superoxide (O₂^{•-}/HO₂) and hydroxyl radical (HO•), represent likely important but currently underappreciated players in the transformation of soil and sediment OM¹⁵⁵. Among various biological and (photo)chemical processes^{156,157}, common soil and sediment minerals have also demonstrated the ability to produce ROS, including H₂O₂ and HO• (REFS^{158–162}). These ROS-producing minerals include primary silicates (such as plagioclase), oxides, sulfides and clays, with the titanium dioxide phases rutile and anatase (α-TiO₂ and β-TiO₂), iron oxide hematite (α-Fe₂O₃) and Fe(II)-bearing clays such as biotite and chlorite having the highest ROS yields observed to date^{158,162}.

Minerals contribute to ROS production via water and O₂ reaction at defect sites or with mineral-hosted or mineral-adsorbed Fe(II), and via photochemical electron transfer^{159,162,163} (FIG. 7b,c). Alternatively, the reductive or oxidative dissolution of minerals leads to the release of metals (particularly iron) or ligands (particularly sulfide) that can create ROS upon reaction with oxygen¹⁵⁹ (FIG. 7b). Thus, albeit limited in number, investigations of mineral-derived ROS indicate that the mechanisms and pathways of ROS formation vary as a function of the mineral, light and aqueous environment.

Mineral-derived ROS within natural soils and aquifers have been measured in a limited number of investigations. In subsurface soils and groundwaters, fluctuating redox conditions and oxygenation of Fe(II)-bearing minerals are the primary contributors to ROS production^{162,164}. Formation of ROS, including O₂^{•−} and HO[•], has been linked to the oxidation of aqueous Fe(II) emanating from subsurface marine¹⁶⁵ and lake sediments¹⁶⁶. Indeed, the oxygenation of reduced soils, sediments and waters results in a cascade of ROS pathways, including initial formation of both O₂^{•−} and H₂O₂, ensuing dismutation of O₂^{•−} to H₂O₂, and, ultimately, formation of HO[•] via reaction of aqueous Fe(II) and H₂O₂ (Fenton reaction)¹⁶⁷. In sunlit surface environments, photochemical reactions at oxide surfaces have also been found to play an important role in ROS (particularly O₂^{•−} and H₂O₂) formation, including in both desiccated and wet desert soils¹⁶⁰. Production of ROS in soils pre-washed to remove photosensitizers such as nitrate point to direct mineral-induced ROS generation upon irradiation¹⁶⁰. Superoxide and peroxides can be stabilized within desiccated soils via complexation to metal oxide surfaces¹⁶⁰. These ROS are rapidly released when soils are (re)saturated, leading to pulses of oxidants within pore waters. Thus, several oxidants are formed upon oxygenation of soils and sediments, the species and flux controlled by mineral composition and mechanism of ROS generation.

ROS vary in their selectivity and reactivity towards carbon functional groups, and react with a wide range of organic compounds, including carbohydrates, fatty acids and biomolecules (such as DNA and proteins¹⁶⁸). The reaction progression upon interaction of DOM and ROS ranges from partial oxidation of organic carbon compounds and formation of low-molecular-weight organic acids to complete oxidation to CO₂, depending on the reactants and conditions (such as pH). Aromatic moieties, such as quinones or humics, have been identified as primary sinks for O₂^{•−} in marine DOM, the reaction of which could lead to a catalytic cycle regenerating the original reactant and forming H₂O₂ (REF. 169). Hydroxyl radical is a particularly unselective and strong oxidant¹⁷⁰, having high reaction rates with DOM (10⁸ M C^{−1} s^{−1})¹⁷¹ and the ability to oxidize carbon compounds within the DOM pool that are otherwise difficult to photodegrade or biodegrade^{172,173}.

Although indirect evidence points to probable contributions of mineral-derived ROS in carbon processing, few studies to date have directly interrogated the role of ROS in carbon transformation and degradation. Still, the potential for ROS to be quantitatively

relevant in carbon cycling was exemplified by a previous investigation where rates of CO₂ produced from [•]OH (109 μmol CO₂ m^{−2} per day) in Arctic soils were found to be on the same order of magnitude as bacterial mineralization of DOM in surface waters¹⁶⁶. Similarly, DOM (including coloured DOM) is a predominant sink of O₂^{•−} within several marine systems^{174,175}, and photodecomposition of DOM in lake waters has been linked to ROS formation¹⁷⁶. One of the first studies to directly link ROS to remineralization of carbon within soils showed that [•]OH derived from Fe(II) oxidation was responsible for DOM oxidation to CO₂ in Arctic soils¹⁵⁵. Specifically, production of CO₂ in Arctic soil incubations scaled with [•]OH production stimulated via H₂O₂ addition. Similarly, stimulation of carbon mineralization within aerobic incubations of humid and tropical soils amended with Fe(II) pointed to contributions from Fenton-based reactions and ROS^{57,177}. In support of this, carbon mineralization decreased (8% less CO₂ compared with controls) within these incubations upon the addition of [•]OH scavengers, further implicating [•]OH as a terminal oxidant of OM⁵⁷. Similarly, addition of superoxide alone or in combination with Fe to soil incubations triggered [•]OH formation and concomitant degradation of soil OM¹⁷⁸. Oxidation of tetracycline to CO₂ was also recently linked to [•]OH formation upon oxidation of sediments in lab incubations¹⁶². Lastly, soil OM oxidation and decomposition in the absence of enzymatic activity (inactivation via autoclaving) within soils implicated mineral-derived ROS^{56,179}, yet, the mechanism at play was not elucidated.

Definition of microbial habitats

Mineral–OM associations play a critical role in structuring and compartmentalizing the biological reaction space of soils and sediments into *microsites*, and, in combination with the water potential, determine the extent to which the individual microsites are connected¹⁸⁰ (FIG. 8). Pore connectivity, morphology and size distribution at the microsite scale either enhance or restrict microbial access to OM¹⁸¹. They also determine the conditions to which microbial decomposers are exposed, impacting the range and magnitude of the microbial activities that occur. For instance, the compartmentalization of space results in the juxtaposition of microsites with different environmental conditions that can be mutually exclusive (for example, oxic and anoxic) at very fine scales, such as within a single aggregate^{182,183}. This juxtaposition leads to the emergence of gradients, allowing a range of processes to proceed. It also facilitates the development and persistence of extensive microbial diversity, because interactions that tend to reduce diversity, such as competition for resources or antagonism, are attenuated in compartmentalized space^{180,184} (FIG. 8). Understanding the link between microbes and their environment is fundamental to understanding soil and sediment microbial ecology, microbial activity and the involvement of microbial decomposers in OM dynamics^{17,185,186}. As many of the functional properties of soils and sediments (nutrient cycling and pollution degradation, for example) emerge from the diversity of their microbial inhabitants¹⁸⁷, it is

Microsites

Clearly delineated spaces within an environment with unique conditions or features in which specific microbial processes can occur.

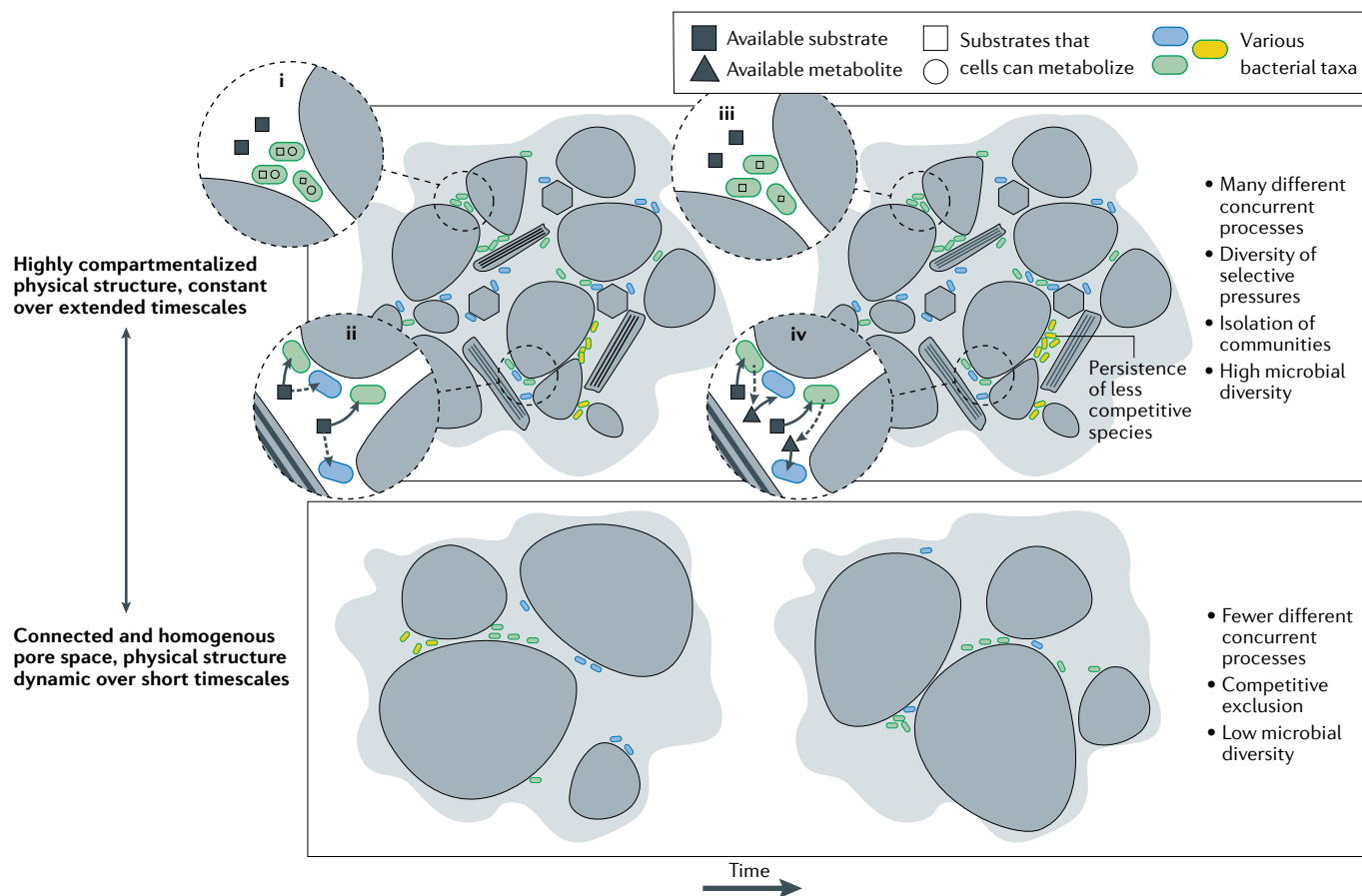


Fig. 8 | **Compartmentalization and mineral-organic matter-microbe interactions.** The top panel shows structure with high clay content that is compartmentalized and relatively constant over time and the lower panel shows structure with low clay content that is relatively dynamic over time. The compartmentalization and constant microenvironmental conditions result in greater niche differentiation, which allows a greater microbial diversity to coexist through reduced competitive interactions^{184,264}. The magnified insets show potential evolutionary consequences in microsites that form constant habitats. The capacity to use organic substrate present is subjected to strong selective pressure and preserved, but other pathways could be lost (insets i and iii). Less competitive species do not compete for organic substrate present but exploit the metabolic by-product of more competitive species, resulting in a better use of available resources by the microsite community²¹⁷ (insets ii and iv).

not unreasonable to suggest that this functioning is, ultimately, dependent on the minerals' role in the structuring of space.

Indeed, we posit that the overriding function of mineral matrices (Tier 1 in FIG. 1b) should be seen in their role in compartmentalizing the system. Microbially driven decomposition requires decomposers and organic substrates to encounter one another¹⁸⁸. However, OM is heterogeneously distributed at scales that are relevant for microbial decomposition¹⁸⁹, as are microbial communities themselves¹⁹⁰. This distribution results in a patchwork of cold spots and hotspots of microbial activity¹⁹¹, which is a fundamental characteristic of soils. Furthermore, there can be non-linear, concave relationships between the concentration of available organic substrate and microbial activities. These can be particularly apparent in activity hotspots and are possibly related to the saturation of cellular transport systems or local O₂ limitations¹⁹². A major consequence of non-linear, concave relationships between the concentration of available substrate and decomposition is

the lowering of overall OM decomposition relative to when substrate and decomposers are homogeneously distributed¹⁹².

The variable connectivity of the microsites (FIG. 8) means that microbial communities function and evolve more or less independently of communities in other microsites and under different environmental conditions^{193,194}. Taxa that are better adapted to the prevalent microsite conditions, such as through the capacity to use electron acceptors other than O₂ in anoxic conditions¹⁹⁵, can competitively exclude other, less adapted taxa, with the potential loss of metabolic capacity from the community. Metabolic capacity can also be lost when mutations cause the inactivation of genes that are not maintained by selective pressure (in essence, the gene does not provide any benefit to the microbe in the microsite) or genetic drift¹⁹⁶. Such losses of capacity from microsites could have consequences for subsequent OM dynamics, as they would allow organic molecules to persist over time, regardless of the intrinsic properties of the molecules or the microsite conditions.

Just as plant roots affect and select microbial communities within their sphere of influence, the rhizosphere, minerals also exert influence over the microbial communities within their vicinity and, therefore, the metabolic pathways and OM dynamics that are present in microsites¹⁹⁷. The sphere of influence of minerals has been termed the ‘mineralosphere’¹⁹⁸. For example, different types of minerals select different microbial communities^{199–201}, and the selective pressures exerted by minerals can even be greater than those associated with different environmental conditions or in the presence of different OM sources^{200,202}. Minerals, therefore, should not be viewed simply as supporting surfaces onto which microbial communities arrive from the surrounding environment in a random and passive fashion. The selective pressure exerted by minerals is likely derived from differences in resource availability at the surface or in the vicinity of the minerals induced by their function as a mobilization filter (FIG. 1b), from the mineral acting as an electron acceptor or donor²⁰³ or from differences in surface charge, area or topography²⁰⁴. Microbial attachment to mineral surfaces can also trigger wholesale changes in microbial functioning, with metabolic activity being either stimulated or inhibited, or growth and biofilm formation being promoted or suppressed, depending on the mineral type^{205,206} and depending on the microorganism^{207,208}. The types of microbial metabolic pathways present at mineral surfaces are likely to have a major impact on mineral–OM associations and, indeed, a number of studies have suggested that a large part of mineral-associated OM has been processed by microbial communities^{114,209,210}, particularly in agroecosystems or in contexts where microbial communities flourish^{211,212}. Furthermore, the extent to which microbially processed OM associates with minerals could even depend upon the composition of the microbial communities²¹³. The mechanisms underlying the production of mineral-associated OM via microbial processing remain as yet unelucidated, however. Nevertheless, the overriding message that emerges from these studies is that microbial communities not only mineralize OM but are also agents in the generation of mineral–OM associations.

Ultimately, therefore, the properties, including the biotic composition, of the compartmentalized space are intimately linked to microbial–mineral associations. These properties affect the local environmental conditions, which, in turn, modulate subsequent biogeochemical processes²¹⁴. This kind of functioning, in which feedback controls are prominent and in which the overall performance of the system is not reflected in the properties of the individual components but emerges from the component interdependencies, is typical of complex systems^{214,215}. The feedback controls impose a number of static and dynamic constraints on the system (Tier 2 in FIG. 1b). These constraints then determine the intensities and rates at which molecular-scale biogeochemistry might be able to proceed (Tier 3 in FIG. 1b). Depending on the extent to which higher level (Tiers 1 and 2) constraints operate in different parts of the system, different lower-tier processes could occur simultaneously within the same system. How the structuring of

space into a network of more or less connected microsites affects the assembly of microbial communities and determines local environmental conditions that modulate the expression of microbial functions and, ultimately, ecosystem performance has not yet been fully explored.

Summary and future perspectives

The mechanisms underlying mineral–organic matter interactions have a long tradition of being explored through adsorption experiments conducted with defined phases in tightly controlled laboratory environments. However, we strongly urge that this research take a more holistic, multidimensional view (FIG. 1b). We advise the scientific community to resist the temptation to attribute given manifestations of carbon dynamics to a single predictor value, such as the abundance of a certain mineral species, phyllosilicate clay content or operationally determined specific surface area values, as has been frequent practice in the past. Rather, soils and sediments should be investigated as multidimensional entities, whose overall functional performance depends on the extent to which the structure of the matrix supports molecular-scale reactions. Translating this insight into novel modelling approaches will be key to improved predictions of global biogeochemical cycles. Quantitative information about pore size, pore morphology and pore connectivity can be obtained from modern multidimensional imaging techniques, such as computed tomography, rendering an explicit consideration of architectural features fundamentally possible. In this final section, we examine some of the outstanding questions and pressing research needs in organomineral interaction research.

Structure and prokaryotic performance. Interactions within the mineral–OM complex not only have immediate and direct effects on OM dynamics as described above but might also have indirect and longer term consequences. Metabolic dependency, when microbial cells lose the ability to produce essential metabolites and, instead, use those released into the environment by other cells, is common in natural microbial communities^{196,216}. Such metabolic dependency develops only if communities remain spatially co-located long enough for co-evolution to occur^{217,218}. Metabolic dependency has been shown to evolve in experimental populations in 1,000–2,000 generations²¹⁹. In soils and sediments, the probability of such co-evolutionary interactions occurring is greater if the physical structure of the microsite persists over time (FIG. 8). Microsite persistence is related to the OM content²²⁰, but could also be related to the mineralogy. For example, there is evidence to suggest that 1:1 clays and oxides produce more persistent microsite structures²²⁰, probably owing to electrostatic interactions between the variable charged minerals²²¹. In view of the suggestion that the persistence of OM in soil is related to the heterogeneous distributions of organic substrate and metabolic capacities^{222,223}, it would be interesting to test the hypothesis that the mineral compartmentalizing of the environment affects the distribution of metabolic capacity at the microsite scale. This could be achieved

Metabolic dependency

A form of adaptation that leads to the absence or loss of the ability to synthesize a certain metabolite essential for the organism, usually in response to an abundance of said compound in the environment.

Colloidal interactions

Interactions that are enabled when particles become so small (equivalent diameter <1–2 microns) that surface-borne electric forces between particles can effectively control their behaviour in a suspension (for instance, prevent them from settling).

using shotgun metagenomics²²⁴, at appropriate scales, in soils with different mineralogies.

Adsorption, desorption and protection. Decomposition of adsorbed OM is typically substantially slower than decomposition of the same type of OM in a freely suspended or dissolved state²²⁵, leading to the notion of ‘sorpative protection’ of OM. However, desorption can be facilitated by changes in pH, electron availability or by modifications to sorbent surfaces¹⁰⁵. Indeed, evidence is mounting that plants are equipped with tools to achieve this exact purpose, such as the exudation of organic compounds designed to release bound OM from mineral surfaces¹¹³ and to adjust patterns of microbial community composition for optimal functionality²²⁶. With these developments in mind, we suggest that sorptive protection should be re-evaluated as an explanation for OM persistence, especially in systems inhabited by plant roots.

More broadly, the idea that there is reduced bioavailability of adsorbed substrates must be further scrutinized. Potentially, it is not that the adsorption process exerts overwhelming bonding forces, preventing breakdown of sorbates. Instead, adsorption could temporarily fix the location of an adsorbed substrate within a given pore network. Such localization would force the decomposer community to overcome the resulting spatial complexity of substrate locations, slowing the rate of decomposition^{222,227}. To understand the relationship between OM persistence, bioavailability and adsorption, enzyme activity experiments should be moved away from traditional batch experiments conducted with phases dispersed in a slurry. Instead, investigations must consider and preserve the 3D microstructure of natural mineral-organic matter interfaces^{46,228}.

Although the importance of various physicochemical variables in determining the magnitude of OM adsorption to select phyllosilicates, metal oxides and carbonates is well understood, the influence of these variables on the rates of adsorption and desorption is not. In addition, most OM sorption and desorption kinetic studies have been conducted on clean minerals exposed to aqueous phase OM. The kinetics of sorption onto realistic soils and sediments, where the newly offered adsorbate could compete with and actually induce the release of previously adsorbed organic compounds, have been studied on rare occasions⁸⁶, presumably because of the difficulty in unequivocally attributing resulting observations to certain mechanisms when the sorbent is complex²²⁹.

Adsorption as a framework-stabilizing process. In addition to localizing the adsorbed substrate within a pore network, adsorption has the potential to significantly influence the stability of this network, thus, influencing the microbial dynamics outlined above²³⁰. For example, investigations of sediment dynamics demonstrate that fine-grained minerals and mineral-OM assemblages have a controlling influence on the cohesive nature of sediment. Detailed understanding of the relevant relationships, unfortunately, remains elusive due to the complexity of interparticle interactions in assemblages of fine-grained minerals. Even in the absence of

OM, colloidal interactions involve a variety of interaction mechanisms with different sensitivities to distance and particle shape and charge, such that different interactions predominate in different systems^{231–233}. In particular, for layered minerals, the combination of a long-range osmotic repulsion and a long-ranged attraction due to configurational entropy enables the formation of extensive aggregates with relatively dilute yet cohesive gel-like structures^{234–237}.

In the presence of OM, the stability of the mineral framework is further strengthened²³⁰. One conceptual model that could shed light onto this stabilization is that the interaction of OM with mineral surfaces, at the OM abundances that exist in most soils and sediments, should be somewhat analogous to a wetting phenomenon. This analogy to wetting, in particular, is qualitatively consistent with the existence of either patchy or uniform distributions of OM in different systems^{16,238–240} (although patchy distributions can partly reflect microbial lifestyles^{241,242}, they are also observed in studies examining the uptake of DOM on pristine mineral surfaces in abiotic conditions as well as in soils^{135,243}), with observations of preferential uptake of OM on rough surfaces or in colloidal aggregates^{79,241}, and with the tendency of OM to induce lasting mineral aggregation^{94,96,244}. It is also consistent with the hydrophobic character of the siloxane surface of phyllosilicate minerals in the absence of surface charge^{245,246} or even, in the case of smectite, in uncharged surface patches resulting from the non-uniform distribution of isomorphic substitutions^{62,67}. In the case of oxides, studies indicating OM fractionation during uptake by Fe oxides suggest that the uptake of an initial ‘contact layer’ plays an important role in enabling mineral wetting by OM⁷⁶. A number of other concepts developed in studies of wetting phenomena could prove useful in studies of mineral-OM interactions, including theoretical representations of contact angles and thin films^{247–249} and descriptions of the impacts of biosurfactants on microorganism distribution, carbon cycling and bioremediation^{45,250,251}.

Mineral-catalysed polymerization. There is substantial interest in the ability of minerals to both induce molecular growth (such as polymerization and large-molecule formation) and contribute to molecular fragmentation, as it has implications for the global carbon cycle^{252,253} and in prebiotic chemistry²⁵⁴. The fundamental ability of minerals to modify organic compounds has been confirmed in laboratory settings^{254–256}, but the catalytic synthesis of novel organic compounds has not yet been observed in the environment. To investigate this phenomenon, observations need to occur simultaneously on extremely small spatial scales but on very long timescales, invoking serious experimental challenges. In the environment, mineral-catalysed synthesis could occur but could be counterbalanced by mineral-catalysed disassembly as soon as the newly made product diffuses away from its compartment of origin. Moreover, the same type of mineral can assume opposite functions in the microbial conversion of adsorbed substrates²⁵⁷. Directing greater research effort at the quantitative relevance of these phenomena in natural systems would be

particularly useful to settle the ongoing debate regarding the importance of mineral-induced catalysis in the environment.

Redox and reactive oxygen species. In direct opposition to the expectation that minerals act as stable repositories for OM, the close association of mineral and organic compounds also enables electron transfer and coupled redox reactions. It is now well established that a plethora of microbial taxa and biochemical pathways couple the decomposition of OM to the oxidative or reductive transformation of minerals. Yet, despite tremendous progress in understanding the biogeochemical underpinnings of mineral-dependent life, the taxonomy of, enzymatic machinery employed by and ecological controls on mineral-transforming microbes remain active and essential areas of inquiry. Importantly, the thermodynamic and kinetic constraints on operative metabolisms within natural soils and sediments remain poorly constrained, and, yet, are essential components for the efficacy of qualitative and quantitative biogeochemical models.

Further, despite some direct and indirect evidence of abiotic reactions mediating carbon transformation and mineralization at mineral surfaces, investigations of these interactions are sparse and, for those that have been conducted, conclusions are often based on correlations and/or anecdotal evidence. Moving forward, systematic and targeted investigations specifically linking OM cycling with direct and indirect reactions at mineral surfaces are needed. These investigations will undoubtedly require new methods and approaches to specifically probe the mineral–OM interface and track reaction products, such as incorporation of isotope labels and/or utilization of sophisticated imaging and spectroscopic techniques.

Acquisition of a clearer understanding of ROS-mediated carbon decomposition in soils and sediments has been hindered by several obstacles, including the difficulty in measuring short-lived ROS and identifying the fate of ROS among the numerous potential decay pathways within complex matrices. In fact, OM competes

with numerous other ROS sinks, such as metals, chloride, bromide or carbonates^{166,171,258} and, thus, the contribution of ROS to OM cycling will undoubtedly vary with local geochemical conditions, and between freshwater and marine systems. Further the promiscuity of ROS such as O₂^{•−} and H₂O₂ to act as both reductants and oxidants depending on the reactants and aqueous conditions leads to complex reaction networks, even within relatively simple systems. Investigations of dityrosine formation within marine waters recently highlighted the potential for ROS-induced polymerization as a means to generate less bioavailable ‘humic’-like fluorescent DOM in the ocean²⁵⁹, indicating that ROS can mediate polymerization in addition to carbon mineralization. Thus, given the emerging recognition of minerals as sources of high ROS fluxes within the subsurface and the well-known role of ROS in organic carbon transformations, mineral-based ROS serve as a new frontier in understanding the carbon cycle.

Disentangling the complex network of mineral-based redox reactions is a necessary next step to understanding the controls on carbon processing and availability within soils and sediments. These reactions will likely be most relevant at redox interfaces and in fluctuating redox environments. Under these conditions, fresh precipitates free of significant surface coatings and prior to ripening will have increased surface reactivity. Further, (re)generation of mineral-bound and aqueous redox reactants will lead to new mineral reactive sites and (re)generation of ROS and other reactive intermediates (such as reactive DOM). Teasing out the relative contributions of light-dependent and light-independent reactions on ROS formation and DOM decomposition is also required within sunlit environments. Thus, an improved understanding of OM cycling in soils and sediments also requires quantification of fluxes of solid-phase and aqueous reactants across light and redox gradients, likely requiring the use of spatially resolved techniques and thermodynamic and kinetic modelling to tease out the network of reactions at play.

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Competing interests

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