



HAL
open science

Dynamic interactions at the mineral–organic matter interface

Markus Kleber, Ian C Bourg, Elizabeth K Coward, Colleen M Hansel, Satish B. Myneni, Naoise Nunan

► **To cite this version:**

Markus Kleber, Ian C Bourg, Elizabeth K Coward, Colleen M Hansel, Satish B. Myneni, et al.. Dynamic interactions at the mineral–organic matter interface. *Nature Reviews Earth & Environment*, 2021, 2, pp.402-421. 10.1038/s43017-021-00162-y . hal-03225065

HAL Id: hal-03225065

<https://hal.science/hal-03225065>

Submitted on 12 May 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Dynamic interactions at the mineral-organic matter interface

Markus Kleber^{1*}, Ian C. Bourg², Elizabeth K. Coward³, Colleen M. Hansel⁴, Satish C. B. Myneni⁵, Naoise Nunan^{6,7}

¹Department of Crop and Soil Science, Oregon State University, Corvallis, OR, USA.

²Department of Civil and Environmental Engineering & High Meadows Environmental Institute, Princeton University, Princeton, NJ, USA.

³Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, CA, USA.

⁴Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA, USA.

⁵Department of Geosciences, Princeton University, Princeton, NJ.

⁶Sorbonne Université, CNRS, IRD, INRA, P7, UPEC, Institute of Ecology and Environmental Sciences—Paris, Paris, France.

⁷Department of Soil & Environment, Swedish University of Agricultural Sciences, Uppsala, Sweden

*email: Markus.Kleber@oregonstate.edu

42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57

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 the general assumption that the mineral matrix provides a protective function for organic matter 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.

[H1] Introduction

The vast majority of organic carbon in the biosphere (5410 - 6545 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 [G]**-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 environment⁶⁻⁸. 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-OM associations¹⁰⁻¹³. 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 [G]** 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 generalised, 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 organic matter decomposition disassemble rocks and organic debris into basic molecular units, which combine to create micron-sized agglomerations¹⁶. Biotic and abiotic processes organise 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 mass¹⁸⁻²⁰ (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 **[G]** 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 physical shape of pores and biogeochemical activities within the system²⁵

In this Review, we undertake a broad appraisal of the complexity of the mineral organic interface and derive a perspective for future research efforts. The diverse roles of minerals in the environment are described (**Fig. 1a**), including **OM adsorption [G]**, catalysis, chemical reactions participation, and **reactive oxygen species [G]** (ROS) generation. The role of the mineral matrix in creating distinct reaction spaces, and its importance of this **compartmentalization [G]** in the

98 fate of OM, are examined. Finally, we urge the field to move towards considering mineral-OM
99 interactions as multidimensional and multifaceted, and to reconsider the current notion of
100 mineral protection of OM.

101 102 103 **[H1] Fundamental properties**

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

106 107 **[H2] Organic phase**

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

114 **Heterotrophic [G]** organisms use the resulting biomass as a combined source of carbon,
115 energy, and nutrients. Because cell wall passage is restricted to molecules with relatively small
116 molecular masses (< 600-1000 Da)³⁰, the size of biomacromolecules must be reduced before
117 assimilation into the cell is possible. **Depolymerization [G]** and oxidation reactions inherent to
118 extracellular molecular disassembly add ionizable oxygen-containing functional groups to
119 decomposition products³. The resulting increasing abundances of polar functional groups (**Fig.**
120 **2**) enhance the aqueous solubility of the products, as well as their chemical reactivity towards
121 metal cations and mineral surfaces, particularly when these functional groups are ionized.
122 Moreover, the smaller molecular size facilitates diffusion³¹ of solubilized, reactive organic
123 fragments towards mineral microstructures where they can become entrapped and adsorbed.
124 Once an organic molecule comes close to a mineral surface, the abundance and type of organic
125 functional groups constrain options for further reactions between matrix surfaces and mobile
126 organic adsorbates.

127 128 **[H2] Mineral phase**

129 A diverse suite of minerals occur in soils and sediments, including phyllosilicates and
130 aluminosilicates (collectively referred to as silicates); metal oxides, hydroxides, and
131 oxyhydroxides (collectively referred to as oxides); and metal carbonates and sulfides (**Figs. 3 &**
132 **4**). In most soils and sediments, phyllosilicates are the predominant component of the **fine-**
133 **grained fraction [G]**^{32,33}. Metal oxides are an order of magnitude less abundant than
134 phyllosilicates except in highly weathered systems and metal-dominated marine benthic habitats
135 (such as hydrothermal vent deposits and ferromanganese crusts), but they contribute distinct
136 reactivity^{22,34} (**Fig. 4**).

137 Minerals possess both permanent (structural) and variable (pH-dependent) surface charge
138 distributions. Subsequent **coulombic interactions [G]** dictate many physical and chemical
139 properties, such as **dispersion [G]** behavior, **coagulation [G]**, colloidal stability, solubility, and
140 adsorptive bonding mechanisms³⁵⁻³⁷. Mineral surface reactivity is also driven by surface
141 topography³⁸, which results from deviations in atomic crystal structure (such as steps or
142 vacancies), in tandem with particle shape and size. In altering the configuration and number of
143 reactive surface groups per unit mass, topographic surface drivers (steps, edges, and kinks, for
144 example) can thus influence the composition, abundance, and bond strength of compounds at the
145 mineral surface. Surface defects can facilitate the formation of stronger surface complexes or
146 reveal edges that offer unsaturated atoms available for direct complexation³⁹⁻⁴², and particle size
147 modulates the relative number of reactive surface groups per unit mass of mineral. Finally, the
148 presence and size distribution of pores within mineral grain assemblages also affects the
149 available surface area for organic ligands, as well as exposure kinetics through **steric constraints**
150 **[G]** and diffusion limitation⁴³⁻⁴⁶.

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

160 The iron (Fe) oxides and framework Mn oxides are exceptions to the condition presented
161 above, in that all their crystal facets carry under- or over-coordinated surface O atoms⁵³. One
162 consequence of this imperfect surface O coordination state is that these minerals are primed for
163 covalent reactions with appropriate organic functional groups. Another consequence is that these
164 minerals tend to grow and dissolve readily, and form particles in a variety of shapes depending
165 on the aqueous chemistry³⁴. Finally, the relatively high interfacial energy of these minerals
166 enables the coexistence of multiple Fe oxides in most soils, as differences in surface and bulk
167 energies cause reversals in the order of thermodynamic stability as a function of particle size and
168 aqueous chemistry⁴⁷. For example, poorly-crystalline ferrihydrite is often the initial product of
169 Fe^{III} crystallization owing to its favorable surface energy. However, at sizes greater than ~5 nm
170 ferrihydrite becomes unstable relative to more crystalline goethite and hematite owing to its less
171 favorable bulk energy⁴⁸.

172 173 **[H1] Adsorption**

174 Adsorption has long stood as an explanation for the spatiotemporal preservation of
175 organic matter in soils and sediments⁵⁴. However, mounting recognition of the dynamism
176 occurring at the mineral-organic interface, buoyed by diversifying intersectionality in expertise

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

184 Observed complexity in OM adsorptive processes is rooted in the inherent diversity of
185 the reactants. Organic matter encompasses a complex, heterogeneous continuum of structure,
186 processing, and functional diversity⁵⁹⁻⁶¹. Even among small organic compounds, this variety
187 enables adsorption through a combination of multiple anchoring points and mechanisms^{62,63}
188 (**Fig. 2**). In tandem, a diverse suite of mineral phases occurs in soils and sediments, varying in
189 surface charge and distribution, topography, and particle size (**Fig. 4**). OM adsorption almost
190 invariably involves a combination of several mechanisms. However, mechanisms of
191 organomineral adsorption can be grouped by the surface chemistry of the mineral (**Fig. 5**), as it
192 affects surface-ligand bond types, coordination state, and spatial organization. These surface
193 chemistries fall into three general groups: variably-charged, non-charged, and negatively
194 charged.

195 Variably-charged surfaces of metal oxides and phyllosilicate crystallite edges carry
196 hydroxyl groups that are increasingly protonated with decreasing pH, thereby acquiring positive
197 charge. This protonation, in turn, enables the retention of organic ligands through rapid ligand-
198 exchange^{64,65}. In many phyllosilicates, substitution of octahedral aluminum (Al) and tetrahedral
199 silicon (Si) with cations of lesser charge will generate permanently charged surfaces. The
200 prevailing negative charge of these surfaces allows for electrostatic attraction of metal cations⁶⁶.
201 When isomorphic substitution is absent, as in some 2:1 phyllosilicates and kaolin-group
202 minerals, the resulting surfaces are electrostatically neutral and thus allow nonpolar organic
203 molecules to accumulate via entropy-driven hydrophobic exclusion phenomena in combination
204 with Lifshitz - van der Waals forces and H-bond formation^{3,67} (**Fig. 5**).

205 As organic ligands partition from **solution [G]** to mineral surfaces, monolayer coverage
206 of the mineral surface converges into a multilayer molecular architecture^{68,69,70} (**Fig. 5**). Organic
207 ligands tend to have a variety of functional groups (**Fig. 2**), thus there can be multiple bonding
208 mechanisms between the mineral and OM. This diversity of bonding reactions, paired with the
209 competition of organic compounds for sorptive sites both between themselves and with inorganic
210 ions⁷¹, results in complex multidimensional structures at the mineral surface (**Fig. 5**). Ion
211 concentrations are well known to modulate adsorption rates and extents, with variations amongst
212 bonding mechanisms and ion composition^{72,73}. However, the importance of competition between
213 organic compounds in structure-selective adsorption (molecular fractionation) is less well-
214 constrained.

215 Similarly, a plethora of recent work has probed the formation and structure of this
216 multilayer over a range of time and length scales based on nanometer-scale microscopy and

217 spectroscopy⁷⁴, temporal partitioning of organic ligands from solution onto the mineral surface
218^{75,76}, and detection of uneven structures at the mineral surface⁷⁷⁻⁷⁹.

219 Adsorption of OM at the mineral-water interface occurs at a rapid rate and reaches
220 equilibrium with aqueous phase in 24 hours for many organic moieties and non-porous minerals
221⁸⁰. The initial adsorption step is typically fast, and a majority of adsorption is completed within
222 the first few hours after the solid-phase is exposed to aqueous OM. Slow adsorption can follow
223 this first step and is most likely caused by the diffusion of molecules into the **intra-particle**
224 **regions [G]**^{45,65,81}. Most kinetic datasets regarding OM sorption on soils and sediments come
225 from studies conducted on **xenobiotic compounds [G]**⁶⁵. However, studies carried out on
226 organic molecules isolated from soil and aquatic environments suggest that the variables that
227 control the magnitude of sorption, also control its kinetics^{82,83}. Some of these variables include
228 the size, charge, hydrophobicity, charge density, and concentration of OM, solution composition
229 (pH, ionic strength, ion type), and mineral type (such as metal oxides versus silicates). For
230 example, rapid adsorption is more common at lower pH values, high OM concentration, and in
231 the presence of cations⁸²⁻⁸⁵, where adsorption rates are faster under conditions that promote
232 weaker adsorption affinity, such as in alkaline solutions⁸³. Notably, newly adsorbed organics
233 might compete with and actually induce the release of previously adsorbed organic compounds⁸⁶,
234 though this process is not well studied in situ.

235 Once bound to a mineral surface, an organic **ligand [G]** only rarely remains undisturbed
236 and instead is vulnerable to desorption and exchange processes, mineralization, and catalytic
237 transformations in situ (**Fig. 6**). During these processes, organic molecules on mineral surfaces
238 might experience changes to their hydration, structure, isomerization, rotation, and electron
239 delocalization, depending on the type of chemical bonding at mineral-water interface. The
240 overall chemical or electronic state of the adsorbed molecule tends to be similar to the molecule
241 in solution when the adsorbed molecules exhibit H-bonding, Van der Waals interactions, or
242 retain their solvated water (**Fig. 6**). Conversely, the adsorbed molecule tends to experience
243 substantial changes to its chemical state if it forms covalent or ionic interactions and directly
244 coordinates to the metal atoms at the mineral-water interface, such as during ligand-exchange.
245 These distinct responses are relevant to hydrolysis, electron transfer, and radical mediated
246 reactions, as well as **photochemical lability [G]**^{87,88}. Although electron transfer amongst weakly-
247 coordinated species can be limited in some of these complexes, for directly-bound covalent
248 complexes, not only the chemical state of the organic molecule is changed but also the electronic
249 state of the metal atom on the surface (**Fig. 6**). Unlike alkali and alkaline earth elements,
250 transition metal ions in solution or at mineral-water interfaces, such as Mn, Fe, Ni, Cu, and Zn,
251 play an important role in modifying the electronic states of the interacting organic functional
252 groups⁸⁹⁻⁹¹.

253 Adsorption potentially impacts not just the adsorbed OM, but also the minerals: adsorption
254 invariably lowers interfacial energy⁹², so accumulation of OM on mineral surfaces should both
255 facilitate the **nucleation [G]** of new particles and inhibit the growth of existing particles. This
256 should favor the formation and persistence of smaller particles, a phenomenon observed

257 experimentally in the apparent stabilization of **short-range-ordered [G]** (SRO) metal oxides
258 (ferrihydrite) and aluminosilicates (proto-imogolite)⁹³⁻⁹⁶. A logical consequence of this is that
259 correlations between OM and fine-grained minerals, though generally interpreted as reflecting
260 the impacts of minerals on OM, should additionally reflect (to an unknown extent) impacts of
261 OM on mineral nucleation, growth, and transformation.

262 The transformations summarized here, and the subsequent temporal persistence of
263 adsorbed molecules, are critical to parameterization of organic C cycling in environmental
264 systems. Yet, comparatively few studies have assessed the susceptibility of organic ligands to
265 desorption and exchange despite widespread attribution of adsorptive temporal persistence
266^{12,58,97,98}. Even relatively short desorption experiments using minerals and whole soils reveal
267 partial removal of adsorbed ligands from all surfaces except variable-charge hydrous oxides.
268 However it is likely that there is continuous exchange even with these minerals, masked by near-
269 zero net solubility^{58,99}. Mineral transformation and dissolution could also mediate release of
270 adsorbed compounds into the aqueous phase. Anoxic events and biotic reductive dissolution of
271 oxides¹⁰⁰⁻¹⁰⁴, acidity-driven deprotonation in low-Fe systems¹⁰⁵, and secretion of root exudates
272^{106,107} could all serve a weathering-like role in releasing adsorbed ligands.

273 A presumed link between particular bonding mechanisms and biotic mineralization of
274 ligands has not been systematically addressed. Laboratory biodegradation studies suggest OM
275 adsorption, particularly to high-surface area oxides in low-pH systems¹⁰⁸⁻¹¹¹, can hinder
276 decomposition. It is not clear, however, how such findings translate to natural soils and
277 sediments, where dynamic weathering and solution chemistry will alter surface functionality, and
278 where exoenzymes from fungi and bacteria can be abundant in solution. Indeed, whole-soil
279 isotope tracer experiments suggest that metabolism of adsorbed ligands is continuous¹¹². Besides
280 microbial degradation and consumption after direct desorption, displacement by biotic exudates
281 can contribute to the decomposition of previously-adsorbed molecules¹¹³, supported by
282 observations that a substantial proportion of mineral-adsorbed organic matter is microbial in
283 origin¹¹⁴⁻¹¹⁶. Such evidence for the multifaceted role of biotic consumption, exchange, and
284 deposition of organic ligands highlights the uncertainty in underlying controls and their
285 quantitative effect on mineralization rates.

286 287 288 **[H1] Catalysis**

289 The potential of a mineral surface to act as a **catalyst [G]** and enhance reaction rates
290 results from the combined action of multiple factors. For instance, minerals can concentrate
291 organic compounds to several orders of magnitude higher than the bulk solution^{117,118}, thus
292 increasing the pre-exponential frequency factor in the Arrhenius equation. Association with a
293 mineral surface can reduce the degree of **orientational freedom [G]** of an adsorbate by aligning
294 monomers along two dimensions at planar surfaces¹¹⁹, thereby facilitating recurring reaction
295 patterns. Minerals also create centers of reactivity by providing coordinatively unsaturated sites
296 and **steric enhancement [G]** of reactions at surfaces with substantial topography³⁸. Furthermore,

297 mineral surfaces can transfer protons to a sorbate as well as offer empty electron orbitals for the
298 reception of bonding electron pairs (Broensted- and Lewis-acid/base functionalities¹²⁰). Lastly,
299 minerals entirely made of transition metals (such as Fe and Mn oxides) or acting as solid
300 supports for adsorbed transition metals at their surfaces and in interlayers (phyllosilicates) can
301 contribute transition metal specific catalytic functionality^{121,122}.

302 Laboratory observations made on the catalytic reactivity of different minerals can be used to
303 recognize three mineral types of chemical reactivity (**Fig. 6**), although the intensity of the
304 organomineral interactions within each class varies with changes in mineralogy, OM
305 concentration, and geochemistry of the environment.

306 Class I minerals are dioctahedral 2:1 clays that adsorb large organic molecules through
307 cation-bridging and through hydrophobic expulsion and aromatic ring π -interactions with
308 surfaces or Lifshitz - van der Waals forces. Direct complexation of OM can occur at edge sites.
309 Because hydrophobic expulsion is the primary driver for adsorption, kinetics of adsorption are
310 fast, macromolecular structures are rarely disturbed, and limited electron transfer is expected.
311 However, heterogeneous oxidation of OM can occur on clay surfaces in the presence of adsorbed
312 O₂ and transition metals^{123,124}. Overall, the catalytic activity of Class I minerals is expected to be
313 low with slow kinetics^{123,125}.

314 Class II minerals are metal oxides, silicates, and 1:1 clays, and exhibit high adsorption
315 capacity (**Fig. 6**). These minerals tend to catalyze moderate changes to the structure and
316 electronic state of adsorbed molecules, primarily through direct bonding, hydrolytic breakdown
317 from reactions with surface OH, and heterogeneous oxidation with adsorbed O₂^{123,126,127}.

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

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

331 The impact of mineral catalytic behavior on OM stability is expected to be greater where
332 there is direct organomineral interaction, or where there are monolayer coverages of OM (**Fig.**
333 **6**). As a consequence, the intensity of organomineral interactions should be strongest during
334 monolayer OM adsorption. In multilayer adsorption, conversely, the overall role of minerals as
335 catalysts should be comparatively diminished as OM-OM interactions increasingly predominate
336 over mineral-OM interactions (**Fig. 6**). Although a majority of molecular studies conducted on

337 soils or sediments belong to the latter category^{74,134,135}, the impact of layer thickness on OM
338 behavior remains relatively poorly understood because of the analytical difficulties in exploring
339 these systems.

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

355
356

357 **[H1] Redox reactions**

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

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

376 (hydr)oxide surface, transfer of electron(s) to the mineral-hosted metal, and subsequent
377 detachment of the reduced metal and oxidized organic molecule¹²³.

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

389 As mineral-OM redox reactions rely on surface complex formation¹⁵⁰, the efficacy of
390 mineral-induced organic matter oxidation and mineralization is ultimately determined by factors
391 controlling initial adsorption. Thus, the extent and rates of organic carbon transformation and
392 mineralization at mineral surfaces decline if surfaces become **passivated [G]**, for instance by
393 high organic matter loadings¹²³ and/or reaction products blocking reactive sites on the surface¹⁴³.
394 Further, mineral **ripening [G]** and recrystallization to less reactive phases during reaction can
395 constrain mineral surface reactivity over time. Extrapolation of the rates and products of mineral-
396 mediated OM transformations within natural systems from these reactions involving pure phases
397 is therefore limited and convoluted.

398 Nevertheless, correlations between oxidized Mn and oxidized OM point to a causal link
399 between Mn oxidation and carbon transformations^{113,149,151}. In fact, the intimate and diverse
400 association of OM with Mn oxides^{149,152} leads to a continuum of reactions, including
401 mineralization and polymerization within layers coating the oxide surface¹²⁹. Yet beyond
402 correlations, there is limited data directly linking natural Mn oxides (or any mineral) to OM
403 oxidation and transformation, pointing to a clear need for future investigations targeting mineral-
404 mediated OM redox mechanisms.

405
406

407 **[H1] Reactive Oxygen Species**

408 Mineral-derived ROS¹⁵³, particularly hydrogen peroxide (H_2O_2), superoxide (O_2^-/HO_2),
409 and hydroxyl radical (HO^\bullet), represent likely important but currently underappreciated players in
410 the transformation of soil and sediment organic matter¹⁵⁴. Among various biological and
411 (photo)chemical processes^{155,156}, common soil and sediment minerals have also demonstrated
412 the ability to produce ROS, including H_2O_2 and HO^\bullet ¹⁵⁷⁻¹⁶¹. These ROS-producing minerals
413 include primary silicates (such as plagioclase), oxides, sulfides, and clays, with the titanium
414 dioxide phases rutile and anatase (α - and β - TiO_2), iron oxide hematite (α - Fe_2O_3), and Fe(II)-
415 bearing clays such as biotite and chlorite having the highest ROS yields observed to date^{157,161}.

416 Minerals contribute to ROS production via water and O₂ reaction at defect sites or with mineral-
417 hosted or adsorbed Fe(II), and via photochemical electron transfer^{158,161,162} (**Fig. 7b-c**).
418 Alternatively, the reductive or oxidative dissolution of minerals leads to the release of metals
419 (particularly iron) or ligands (particularly sulfide) that can create ROS upon reaction with
420 oxygen¹⁵⁸ (**Fig. 7b**). Thus, albeit limited in number, these investigations of mineral-derived ROS
421 indicate that the mechanisms and pathways of ROS formation vary as a function of the mineral,
422 light, and aqueous environment.

423 Mineral-derived ROS within natural soils and aquifers have been measured in a limited
424 number of investigations. In subsurface soils and groundwaters, fluctuating redox conditions and
425 oxygenation of Fe(II)-bearing minerals are the primary contributors to ROS production^{161,163}.
426 Formation of ROS including O₂^{•-} and HO[•] has been linked to the oxidation of aqueous Fe(II)
427 emanating from subsurface marine¹⁶⁴ and lake sediments¹⁶⁵. Indeed, the oxygenation of reduced
428 soils, sediments, and waters results in a cascade of ROS pathways, including initial formation of
429 both O₂^{•-} and H₂O₂, ensuing dismutation of O₂^{•-} to H₂O₂, and ultimately formation of HO[•] via
430 reaction of aqueous Fe(II) and H₂O₂ (Fenton reaction)¹⁶⁶. In sunlit surface environments,
431 photochemical reactions at oxide surfaces have also been found to play an important role in ROS
432 (particularly O₂^{•-} and H₂O₂) formation, including in both desiccated and wet desert soils¹⁵⁹.
433 Production of ROS in soils pre-washed to remove photosensitizers such as nitrate point to direct
434 mineral-induced ROS generation upon irradiation¹⁵⁹. Superoxide and peroxides can be stabilized
435 within desiccated soils via complexation to metal oxide surfaces¹⁵⁹. These ROS are rapidly
436 released when soils are (re)saturated, leading to pulses of oxidants within pore waters. Thus,
437 several oxidants are formed upon oxygenation of soils and sediments, the species and flux
438 controlled by mineral composition and mechanism of ROS generation.

439 ROS vary in their selectivity and reactivity toward carbon functional groups, and react
440 with a wide range of organic compounds, including carbohydrates, fatty acids, and biomolecules
441 (such as DNA and proteins¹⁶⁷). The reaction progression upon interaction of DOM and ROS
442 ranges from partial oxidation of organic carbon compounds and formation of low molecular
443 weight organic acids to complete oxidation to CO₂, depending on the reactants and conditions
444 (such as pH). Aromatic moieties, such as quinones or humics, have been identified as primary
445 sinks for O₂^{•-} in marine DOM, the reaction of which could lead to a catalytic cycle regenerating
446 the original reactant and forming H₂O₂¹⁶⁸. Hydroxyl radical is a particularly unselective and
447 strong oxidant¹⁶⁹, having high reaction rates with DOM (10⁸ M C⁻¹ s⁻¹)¹⁷⁰ and the ability to
448 oxidize carbon compounds within the DOM pool that are otherwise difficult to photo- or
449 biodegrade^{171,172}.

450 Although indirect evidence points to probable contributions of mineral-derived ROS in
451 carbon processing, few studies to date have directly interrogated the role of ROS in carbon
452 transformation and degradation. Still, the potential for ROS to be quantitatively relevant in
453 carbon cycling was exemplified by a previous investigation where rates of CO₂ produced from
454 [•]OH (109 μmol CO₂ m⁻² d⁻¹) in Arctic soils were found to be on the same order of magnitude as
455 bacterial mineralization of DOM in surface waters¹⁶⁵. Similarly, DOM (including coloured

456 DOM) is a predominant sink of $O_2^{\cdot-}$ within several marine systems^{173,174}, and
457 photodecomposition of DOM in lake waters has been linked to ROS formation¹⁷⁵. One of the
458 first studies to directly link ROS to remineralization of carbon within soils showed that $\cdot OH$
459 derived from Fe(II) oxidation was responsible for DOM oxidation to CO_2 in Arctic soils¹⁵⁴.
460 Specifically, production of CO_2 in Arctic soil incubations scaled with $\cdot OH$ production stimulated
461 via H_2O_2 addition. Similarly, stimulation of carbon mineralization within aerobic incubations of
462 humid and tropical soils amended with Fe(II) pointed to contributions from Fenton based
463 reactions and ROS^{57,176}. In support of this, carbon mineralization decreased (8% less CO_2
464 compared to controls) within these incubations upon the addition of $\cdot OH$ scavengers, further
465 implicating $\cdot OH$ as a terminal oxidant of OM⁵⁷. Similarly, addition of superoxide alone or in
466 combination with Fe to soil incubations triggered $\cdot OH$ formation and concomitant degradation of
467 soil organic matter¹⁷⁷. Oxidation of tetracycline to CO_2 was also recently linked to $\cdot OH$
468 formation upon oxidation of sediments in lab incubations¹⁶¹. Lastly, soil organic matter
469 oxidation and decomposition in the absence of enzymatic activity (inactivation via autoclaving)
470 within soils implicated mineral-derived ROS^{56,178}; yet, the mechanism at play was not
471 elucidated.

472
473

474 **[H1] Definition of microbial habitats**

475 Mineral-organic matter associations play a critical role in structuring and
476 compartmentalizing the biological reaction space of soils and sediments into microsites [G],
477 and, in combination with the water potential, determine the extent to which the individual
478 microsites are connected¹⁷⁹ (**Fig. 8**). Pore connectivity, morphology, and size distribution at the
479 microsite scale either enhance or restrict microbial access to OM¹⁸⁰. They also determine the
480 conditions that microbial decomposers are exposed to, impacting the range and magnitude of the
481 microbial activities that occur. For instance, the compartmentalisation of space results in the
482 juxtaposition of microsites with different environmental conditions that can be mutually
483 exclusive (for example, oxic and anoxic) at very fine scales such as within a single aggregate
484^{171,172}. This juxtaposition leads to the emergence of gradients, allowing a range of processes to
485 proceed. It also facilitates the development and persistence of extensive microbial diversity,
486 because interactions that tend to reduce diversity, such as competition for resources or
487 antagonism, are attenuated in compartmentalised space^{173,174} (**Fig 8**). Understanding the link
488 between microbes and their environment is fundamental to understanding soil and sediment
489 microbial ecology, microbial activity and the involvement of microbial decomposers in OM
490 dynamics^{16,199,200}. As many of the functional properties of soils and sediments (nutrient cycling
491 and pollution degradation, for example) emerge from the diversity of their microbial inhabitants¹⁷⁵,
492 it is not unreasonable to suggest that this functioning is ultimately dependent on the minerals'
493 role in the structuring of space.

494 Indeed, we posit that the overriding function of mineral matrices (Tier 1 in **Fig. 1b**) should
495 be seen in their role in compartmentalizing the system. Microbially driven decomposition

496 requires decomposers and organic substrates to encounter one another²⁰¹. However, OM is
497 heterogeneously distributed at scales that are relevant for microbial decomposition²⁰², as are
498 microbial communities themselves²⁰³. This distribution results in a patchwork of cold and
499 hotspots of microbial activity²⁰⁴, which is a fundamental characteristic of soils. Furthermore,
500 there can be non-linear, concave relationships between the concentration of available organic
501 substrate and microbial activities. These can be particularly apparent in activity hotspots and are
502 possibly related to the saturation of cellular transport systems or local O₂ limitations¹³². A major
503 consequence of non-linear, concave relationships between the concentration of available
504 substrate and decomposition result is the lowering of overall organic matter decomposition
505 relative to when substrate and decomposers are homogeneously distributed¹³².

506 The variable connectivity of the microsites (**Fig. 8**) means that microbial communities
507 function and evolve more or less independently of communities in other microsites and under
508 different environmental conditions^{176,177}. Taxa that are better adapted to the prevalent microsite
509 conditions, such as through the capacity to use electron acceptors other than O₂ in anoxic
510 conditions¹⁷⁸, can competitively exclude other, less adapted taxa, with the potential loss of
511 metabolic capacity from the community. Metabolic capacity can also be lost when mutations
512 cause the inactivation of genes that are not maintained by selective pressure (in essence, the gene
513 does not provide any benefit to the microbe in the microsite) or genetic drift¹⁷⁹. Such losses of
514 capacity from microsites could have consequences for subsequent organic matter dynamics, as
515 they would allow organic molecules to persist over time, regardless of the intrinsic properties of
516 the molecules or the microsite conditions.

517 Just as plant roots affect and select microbial communities within their sphere of influence,
518 the rhizosphere, minerals also exert influence over the microbial communities within their
519 vicinity, and therefore the metabolic pathways and organic matter dynamics that are present in
520 microsites¹⁸⁵. The sphere of influence of minerals has been termed the “mineralosphere”¹⁸⁶. For
521 example, different types of minerals select different microbial communities¹⁸⁷⁻¹⁸⁹, and the
522 selective pressures exerted by minerals can even be greater than those associated with different
523 environmental conditions or in the presence of different organic matter sources^{188,190}. Minerals,
524 therefore, should not be viewed simply as supporting surfaces onto which microbial communities
525 arrive from the surrounding environment in a random and passive fashion. The selective pressure
526 exerted by minerals is likely derived from differences in resource availability at the surface or in
527 the vicinity of the minerals induced by their function as a mobilisation filter, from the mineral
528 acting as an electron acceptor or donor¹⁹¹, from differences in surface charge, area, or
529 topography¹⁹². Microbial attachment to mineral surfaces can also trigger wholesale changes in
530 microbial functioning, with metabolic activity being either stimulated or inhibited, or growth and
531 biofilm formation being promoted or suppressed, depending on the mineral type^{193,194} and
532 depending on the microorganism^{195,196}. The types of microbial metabolic pathways present at
533 mineral surfaces is likely to have a major impact on mineral-organic matter associations and,
534 indeed, a number of studies have suggested that a large part of mineral associated organic matter
535 has been processed by microbial communities^{109,197,181} particularly in agroecosystems or in

536 contexts where microbial communities flourish^{182,183}. Furthermore, the extent to which
537 microbially processed organic matter associates with minerals could even depend upon the
538 composition of the microbial communities¹⁹⁸. The mechanisms underlying the production of
539 mineral associated organic matter via microbial processing remain as yet un-elucidated however.
540 Nevertheless, the overriding message that emerges from these studies is that microbial
541 communities not only mineralise organic matter but are also agents in the generation of mineral-
542 organic matter associations.

543 Ultimately therefore, the properties, including the biotic composition, of the
544 compartmentalized space are intimately linked to microbial-mineral associations. These
545 properties affect the local environmental conditions, which, in turn, modulate subsequent
546 biogeochemical processes¹⁸⁴. This kind of functioning, in which feedback controls are
547 prominent and in which the overall performance of the system is not reflected in the properties of
548 the individual components, but emerges from the component interdependencies, is typical of
549 complex systems^{184,185}. The feedback controls impose a number of static and dynamic
550 constraints on the system (Tier 2 in **Fig. 1b**). These constraints then determine the intensities and
551 rates at which molecular scale biogeochemistry might be able to proceed (Tier 3 in **Fig. 1b**).
552 Depending on the extent to which higher level (Tier 1 and 2) constraints operate in different parts
553 of the system, different lower tier processes could occur simultaneously within the same system.
554 How the structuring of space into a network of more or less connected microsites affects the
555 assembly of microbial communities and determines local environmental conditions that modulate
556 the expression of microbial functions and, ultimately, ecosystem performance has not yet been
557 fully explored.

558

559 **[H1] Summary and future perspectives**

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

575

576 **[H2] Structure and prokaryotic performance**

577 Interactions within the mineral-organic matter complex not only have immediate and direct
578 effects on organic matter dynamics as described above but might also have indirect and longer
579 term consequences. **Metabolic dependency [G]**, when microbial cells lose the ability to produce
580 essential metabolites and instead use those released into the environment by other cells, is
581 common in natural microbial communities^{179,180}. Such metabolic dependency develops only if
582 communities remain spatially co-located long enough for coevolution to occur^{181,182}. Metabolic
583 dependency has been shown to evolve in experimental populations in 1000 to 2000 generations
584¹⁸⁶. In soils and sediments, the probability of such co-evolutionary interactions occurring is
585 greater if the physical structure of the microsite persists over time (**Fig. 8**). Microsite persistence
586 is related to the organic matter content¹⁸³, but could also be related to the mineralogy. For
587 example, there is evidence to suggest that 1:1 clays and oxides produce more persistent microsite
588 structures¹⁸³, probably owing to electrostatic interactions between the variable charged minerals
589¹⁸⁴. In view of the suggestion that the persistence of organic matter in soil is related to the
590 heterogeneous distributions of organic substrate and metabolic capacities^{187,188}, it would be
591 interesting to test the hypothesis that the mineral compartmentalizing the environment affects the
592 distribution of metabolic capacity at the microsite scale. This could be achieved using shotgun
593 metagenomics¹⁸⁹, at appropriate scales, in soils with different mineralogies.

594 595 **[H2] Adsorption, desorption and protection**

596 Decomposition of adsorbed OM is typically substantially slower than decomposition of the
597 same type of OM in a freely suspended or dissolved state¹⁹⁰, leading to the notion of ‘sorptive
598 protection’ of OM. However, desorption can be facilitated by changes in pH, electron
599 availability, or by modifications to sorbent surfaces¹⁰⁵. Indeed, evidence is mounting that plants
600 are equipped with tools to achieve this exact purpose, such as the exudation of organic
601 compounds designed to release bound organic matter from mineral surfaces¹⁹¹ and to adjust
602 patterns of microbial community composition for optimal functionality¹⁹². With these
603 developments in mind, we suggest that sorptive protection should be re-evaluated as an
604 explanation for organic matter persistence, especially in systems inhabited by plant roots.

605 More broadly, the idea that there is reduced bioavailability of adsorbed substrates must be
606 further scrutinized. Potentially, it is not that the adsorption process exerts overwhelming bonding
607 forces, preventing breakdown of sorbates. Instead, adsorption could temporarily fix the location
608 of an adsorbed substrate within a given pore network. Such localization would force the
609 decomposer community to overcome the resulting spatial complexity of substrate locations,
610 slowing the rate of decomposition^{187,193}. To understand the relationship between OM persistence,
611 bioavailability, and adsorption, enzyme activity experiments should be moved away from
612 traditional batch experiments conducted with phases dispersed in a slurry. Instead, investigations
613 must consider and preserve the three-dimensional microstructure of natural mineral-organic
614 interfaces^{46,194}.

615 Although the importance of various physicochemical variables in determining the magnitude
616 of OM adsorption to select phyllosilicates, metal oxides and carbonates are well understood, the

617 influence of these variables on the rates of adsorption and desorption is not. In addition, most
618 OM sorption and desorption kinetic studies have been conducted on clean minerals exposed to
619 aqueous phase OM. The kinetics of sorption onto realistic soils and sediments, where the newly
620 offered adsorbate could compete with and actually induce the release of previously adsorbed
621 organic compounds, have been studied on rare occasions⁸⁶, presumably because of the difficulty
622 in unequivocally attributing resulting observations to certain mechanisms when the sorbent is
623 complex¹⁹⁵.

624

625 [H2] Adsorption as a framework-stabilizing process

626 In addition to localizing the adsorbed substrate within a pore network, adsorption has the
627 potential to significantly influence the stability of this network, thus influencing the microbial
628 dynamics outlined above¹⁹⁶. For example, investigations of sediment dynamics demonstrate that
629 fine-grained minerals and mineral-OM assemblages have a controlling influence on the cohesive
630 nature of sediment. Detailed understanding of the relevant relationships, unfortunately, remains
631 elusive due to complexity of interparticle interactions in assemblages of fine-grained minerals.
632 Even in the absence of OM, colloidal interactions [G] involve a variety of interaction
633 mechanisms with different sensitivities to distance and particle shape and charge, such that
634 different interactions to predominate in different systems¹⁹⁷⁻¹⁹⁹. In particular, for layered
635 minerals, the combination of a long-range osmotic repulsion and a long-ranged attraction due to
636 configurational entropy enables the formation of extensive aggregates with relatively dilute yet
637 cohesive gel-like structures^{200,201 202,203}.

638 In the presence of OM, the stability of the mineral framework is further stabilized¹⁹⁶. One
639 conceptual model that could shed light into this stabilization is that the interaction of OM with
640 mineral surfaces, at the OM abundances that exist in most soils and sediments, should be
641 somewhat analogous to a wetting phenomenon. This analogy to wetting, in particular, is
642 qualitatively consistent with the existence of either patchy or uniform distributions of OM in
643 different systems^{16,204-206} (although patchy distributions can partly reflect microbial lifestyles
644^{207,208}, they are also observed in studies examining the uptake of dissolved organic matter on
645 pristine mineral surfaces in abiotic conditions as well as in soils^{135,209}), with observations of
646 preferential uptake of OM on rough surfaces or in colloidal aggregates^{79,207}, and with the
647 tendency of OM to induce lasting mineral aggregation^{94,96,210}. It also is consistent with the
648 hydrophobic character of the siloxane surface of phyllosilicate minerals in the absence of surface
649 charge^{211,212} or even, in the case of smectite, in uncharged surface patches resulting from the
650 non-uniform distribution of isomorphous substitutions^{62,67}. In the case of oxides, studies
651 indicating OM fractionation during uptake by Fe oxides suggest that the uptake of an initial
652 'contact layer' plays an important role in enabling mineral wetting by OM⁷⁶. A number of other
653 concepts developed in studies of wetting phenomena could prove useful in studies of mineral-
654 OM interactions, including theoretical representations of contact angles and thin films²¹³⁻²¹⁵ and
655 descriptions of the impacts of biosurfactants on microorganism distribution, carbon cycling, and
656 bioremediation^{45,216,217}.

657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674

[H2] Mineral-catalyzed 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^{218,219} and in prebiotic chemistry²²⁰. The fundamental ability of minerals to modify organic compounds has been confirmed in laboratory settings²²⁰⁻²²², 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 time scales, invoking serious experimental challenges. In the environment, mineral-catalyzed 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 substrates²²³. 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.

[H2] Redox and ROS

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 organic matter 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 is needed. These investigations will undoubtedly require new methods and approaches to specifically probe the OM-mineral 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,

697 chloride, bromide, or carbonates^{165,170,224}, and thus the contribution of ROS to OM cycling will
698 undoubtedly vary with local geochemical conditions, and between freshwater and marine
699 systems. Further the promiscuity of ROS such as O₂^{•-} and H₂O₂ to act as both reductants and
700 oxidants depending on the reactants and aqueous conditions leads to complex reaction networks
701 even within relatively simple systems. Investigations of dityrosine formation within marine
702 waters recently highlighted the potential for ROS-induced polymerization as a means to generate
703 less bioavailable "humic"-like fluorescent DOM in the ocean²²⁵, indicating that ROS can
704 mediate polymerization in addition to carbon mineralization. Thus, given the emerging
705 recognition of minerals as sources of high ROS fluxes within the subsurface and the well-known
706 role of ROS in organic carbon transformations, mineral-based ROS serve as a new frontier in
707 understanding the carbon cycle.

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

721
722

723 **References**

- 724
- 725 1 Friedlingstein, P. *et al.* Global Carbon Budget 2019. *Earth System Science Data* **11**, 1783-1838,
726 doi:10.5194/essd-11-1783-2019 (2019).
 - 727 2 Henin, S. & Turc, L. in *Transactions of the 4th International Congress of Soil Science. 4th*
728 *International Congress of Soil Science*. 152-154. (1950)
 - 729 3 Kleber, M. *et al.* in *Advances in Agronomy, Vol 130* Vol. 130 *Advances in Agronomy* (ed D. L.
730 Sparks) 1-140 (2015).
 - 731 4 Jacks, G. V. The biological nature of soil productivity. *Soils and Fertilizers* **26**, 147-150 (1963).
 - 732 5 Carson, R. *Silent Spring*. (Houghton Mifflin Company, 1962).
 - 733 6 Stone, A. T. & Morgan, J. J. Reduction and dissolution of manganese (III) and manganese (IV)
734 oxides by organics. 1. Reaction with hydroquinone. *Environmental Science & Technology* **18**,
735 450-456, doi:10.1021/es00124a011 (1984).
 - 736 7 Stone, A. T. & Morgan, J. J. Reduction and dissolution of manganese (III) and manganese (IV)
737 oxides by organics. 2. Survey of the reactivity of organics. *Environmental Science & Technology*
738 **18**, 617-624, doi:10.1021/es00126a010 (1984).

- 739 8 McBride, M. B. Reactivity of adsorbed and structural iron in hectorite as indicated by oxidation
740 of benzidine. *Clays and Clay Minerals* **27**, 224-230, doi:10.1346/ccmn.1979.0270308 (1979).
- 741 9 Parton, W. J., Schimel, D. S., Cole, C. V. & Ojima, D. S. Analysis of factors controlling soil organic
742 matter levels in Great Plains grasslands. *Soil Science Society of America Journal* **51**, 1173-1179
743 (1987).
- 744 10 Oades, J. M. The retention of organic matter in soils. *Biogeochemistry*. **5** **35-70** (1988).
- 745 11 Jardine, P. M., Weber, N. L. & McCarthy, J. F. Mechanisms of dissolved organic carbon
746 adsorption on soil. *Soil Science Society of America Journal* **53**, 1378-1385 (1989).
- 747 12 Gu, B., Schmitt, J., Chen, Z., Liang, L. & McCarthy, J. F. Adsorption and desorption of natural
748 organic matter on iron oxide: mechanisms and models. *Environmental Science and Technology*
749 **28**, 38-46 (1994).
- 750 13 Hedges, J. I. The formation and clay mineral reactions of melanoidins. *Geochimica et*
751 *Cosmochimica Acta* **42**, 69-76 (1978).
- 752 14 Rasmussen, C. *et al.* Beyond clay: towards an improved set of variables for predicting soil
753 organic matter content. *Biogeochemistry* **137**, 297-306, doi:10.1007/s10533-018-0424-3 (2018).
- 754 15 Torn, M. S., Trumbore, S. E., Chadwick, O. A., Vitousek, P. M. & Hendricks, D. M. Mineral control
755 of soil organic carbon storage and turnover. *Nature* **389**, 170-173 (1997).
- 756 16 Chenu, C. & Plante, A. F. Clay-sized organo-mineral complexes in a cultivation chronosequence:
757 revisiting the concept of the 'primary organo-mineral complex'. *European Journal of Soil Science*
758 **57**, 596-607, doi:10.1111/j.1365-2389.2006.00834.x (2006).
- 759 17 Baveye, P. C. *et al.* Emergent Properties of Microbial Activity in Heterogeneous Soil
760 Microenvironments: Different Research Approaches Are Slowly Converging, Yet Major
761 Challenges Remain. *Frontiers in Microbiology* **9**, doi:10.3389/fmicb.2018.01929 (2018).
- 762 18 Oades, J. M. in *Minerals in soil environments. Second Edition*. Vol. Book Serie Nr.1 (eds J. B.
763 Dixon & S. B. Weed) 89-160 (SSSA, 1989).
- 764 19 Batjes, N. H. Total carbon and nitrogen in the soils of the world. *European Journal of Soil Science*
765 **47**, 151-163 (1996).
- 766 20 Jobbagy, E. G. & Jackson, R. B. The vertical distribution of soil organic carbon and its relation to
767 climate and vegetation. *Ecological Applications* **10**, 423-436 (2000).
- 768 21 Vereecken, H., Maes, J., Feyen, J. & Darius, P. ESTIMATING THE SOIL-MOISTURE RETENTION
769 CHARACTERISTIC FROM TEXTURE, BULK-DENSITY, AND CARBON CONTENT. *Soil Science* **148**, 389-
770 403, doi:10.1097/00010694-198912000-00001 (1989).
- 771 22 Sposito, G. *The Chemistry of Soils*. Third Edition edn, (Oxford University Press, 2016).
- 772 23 Ball, P. Water is an active matrix of life for cell and molecular biology. *Proceedings of the*
773 *National Academy of Sciences of the United States of America* **114**, 13327-13335,
774 doi:10.1073/pnas.1703781114 (2017).
- 775 24 Schimel, J. *et al.* in *19th World Congress of Soil Science, Soil Solutions for a Changing World*. 55-
776 58.
- 777 25 Meysman, F. J. R., Middelburg, J. J. & Heip, C. H. R. Bioturbation: a fresh look at Darwin's last
778 idea. *Trends in Ecology & Evolution* **21**, 688-695, doi:10.1016/j.tree.2006.08.002 (2006).
- 779 26 Miller, S. L. A production of amino acids under possible primitive earth conditions. *Science* **117**,
780 528-529 (1953).
- 781 27 Heck, P. R. *et al.* The fall, recovery, classification, and initial characterization of the Hamburg,
782 Michigan H4 chondrite. *Meteorit. Planet. Sci.*, **19**, doi:10.1111/maps.13584.
- 783 28 Lengeler, J. W., Drews, G. & Schlegel, H. G. *Biology of the Prokaryotes*. 984 (Wiley-Blackwell,
784 1999).

- 785 29 Field, C. B., Behrenfeld, M. J., Randerson, J. T. & Falkowski, P. Primary production of the
786 biosphere: Integrating terrestrial and oceanic components. *Science* **281**, 237-240,
787 doi:10.1126/science.281.5374.237 (1998).
- 788 30 Hedges, J. I. & Oades, J. M. Comparative organic geochemistries of soils and marine sediments.
789 *Organic Geochemistry* **27**, 319-361 (1997).
- 790 31 Anslyn, E. V. & Dougherty, D. A. *Modern physical organic chemistry*. (University Science Books,
791 2006).
- 792 32 Fagel, N. in *Developments in marine geology* Ch. Chapter 4, 139-184 (Elsevier, 2007).
- 793 33 Ito, A. & Wagai, R. Global distribution of clay-size minerals on land surface for biogeochemical
794 and climatological studies. *Scientific Data* **4**, doi:10.1038/sdata.2017.103 (2017).
- 795 34 Barron, V. & Torrent, J. in *EMU Notes in Mineralogy* Vol. 14 297-336 (2013).
- 796 35 Schulthess, C. P. & Sparks, D. L. A critical assessment of surface adsorption models. *Soil Science*
797 *Society of America Journal* **52**, 92-97, doi:10.2136/sssaj1988.03615995005200010016x (1988).
- 798 36 Heil, D. & Sposito, G. Organic matter role in illitic soil colloids flocculation. 2. Surface charge. *Soil*
799 *Science Society of America Journal* **57**, 1246-1253,
800 doi:10.2136/sssaj1993.03615995005700050015x (1993).
- 801 37 Quirk, J. P. in *Advances in Agronomy, Vol 53* Vol. 53 *Advances in Agronomy* (ed D. L. Sparks) 121-
802 183 (1994).
- 803 38 Brown, G. E. *et al.* Metal Oxides Surfaces and Their Interactions with Aqueous Solutions and
804 Microbial Organisms. *Chemical Reviews* **99**, 77-174 (1999).
- 805 39 Armanious, A., Aeppli, M. & Sander, M. Dissolved Organic Matter Adsorption to Model Surfaces:
806 Adlayer Formation, Properties, and Dynamics at the Nanoscale. *Environmental Science &*
807 *Technology* **48**, 9420-9429, doi:10.1021/es5026917 (2014).
- 808 40 Petridis, L. *et al.* Spatial Arrangement of Organic Compounds on a Model Mineral Surface:
809 Implications for Soil Organic Matter Stabilization. *Environmental Science & Technology* **48**, 79-
810 84, doi:10.1021/es403430k (2014).
- 811 41 Sander, M., Maddern, T. & Baldock, J. Similar composition but differential stability of mineral
812 retained organic matter across four classes of clay minerals. *Biogeochemistry* **121**, 409-424,
813 doi:10.1007/s10533-014-0009-8 (2014).
- 814 42 Mueller, C. W. *et al.* Microscale soil structures foster organic matter stabilization in permafrost
815 soils. *Geoderma* **293**, 44-53, doi:10.1016/j.geoderma.2017.01.028 (2017).
- 816 43 Deen, W. M. Hindered transport of large molecules in liquid-filled pores. *Aiche Journal* **33**, 1409-
817 1425, doi:10.1002/aic.690330902 (1987).
- 818 44 McBride, M. B. Mobility of small molecules in interlayers of hectorite gels -ESR study with an
819 uncharged spin-probe. *Clays and Clay Minerals* **42**, 455-461, doi:10.1346/ccmn.1994.0420412
820 (1994).
- 821 45 Pignatello, J. J. & Xing, B. S. Mechanisms of slow sorption of organic chemicals to natural
822 particles. *Environmental Science & Technology* **30**, 1-11, doi:10.1021/es940683g (1996).
- 823 46 Yang J.Q., Zhang X., Bourg I.C. & Communications, S. H. A. N. 4D imaging reveals mechanisms of
824 clay-carbon protection and release. *Nature communications*, in press (2021).
- 825 47 Navrotsky, A. Energetic clues to pathways to biomineralization: Precursors, clusters, and
826 nanoparticles. *Proceedings of the National Academy of Sciences of the United States of America*
827 **101**, 12096-12101, doi:10.1073/pnas.0404778101 (2004).
- 828 48 Waychunas, G. A., Kim, C. S. & Banfield, J. F. Nanoparticulate iron oxide minerals in soils and
829 sediments: unique properties and contaminant scavenging mechanisms. *Journal of Nanoparticle*
830 *Research* **7**, 409-433, doi:10.1007/s11051-005-6931-x (2005).

831 49 Zucker, R. V., Chatain, D., Dahmen, U., Hagege, S. & Carter, W. C. New software tools for the
832 calculation and display of isolated and attached interfacial-energy minimizing particle shapes.
833 *Journal of Materials Science* **47**, 8290-8302, doi:10.1007/s10853-012-6739-x (2012).

834 50 Sposito, G. *The Surface Chemistry of Natural Particles*. (Oxford University Press, 2004).

835 51 Pauling, L. The structure of micas and related materials. *Proc Natl Acad Sci U.S.A.* **16**, 123-129
836 (1930).

837 52 Chen, J. J. *et al.* Building two-dimensional materials one row at a time: Avoiding the nucleation
838 barrier. *Science* **362**, 1135-+, doi:10.1126/science.aau4146 (2018).

839 53 Venema, P., Hiemstra, T., Weidler, P. G. & Van Riemsdijk, W. H. Intrinsic proton affinity of
840 reactive surface groups of metal (hydr)oxides: Application to iron (hydr)oxides. *J. Colloid Interf.*
841 *Sci.* **198**, 282-295 (1998).

842 54 Sollins, P., Homann, P. & Caldwell, B. A. Stabilization and destabilization of soil organic matter:
843 Mechanisms and controls. *Geoderma* **74**, 65-105 (1996).

844 55 Abramoff, R. *et al.* The Millennial model: in search of measurable pools and transformations for
845 modeling soil carbon in the new century. *Biogeochemistry* **137**, 51-71, doi:10.1007/s10533-017-
846 0409-7 (2018).

847 56 Blankinship, J. C., Becerra, C. A., Schaeffer, S. M. & Schimel, J. P. Separating cellular metabolism
848 from exoenzyme activity in soil organic matter decomposition. *Soil Biology and Biochemistry* **71**,
849 68-75, doi:<http://dx.doi.org/10.1016/j.soilbio.2014.01.010> (2014).

850 57 Chen, C., Hall, S. J., Coward, E. & Thompson, A. Iron-mediated organic matter decomposition in
851 humid soils can counteract protection. *Nature communications* **11**, 1-13 (2020).

852 58 Leinemann, T. *et al.* Multiple exchange processes on mineral surfaces control the transport of
853 dissolved organic matter through soil profiles. *Soil Biology and Biochemistry* **118**, 79-90,
854 doi:<https://doi.org/10.1016/j.soilbio.2017.12.006> (2018).

855 59 Newcomb, C. J., Qafoku, N. P., Grate, J. W., Bailey, V. L. & De Yoreo, J. J. Developing a molecular
856 picture of soil organic matter–mineral interactions by quantifying organo–mineral binding.
857 *Nature communications* **8**, 1-8 (2017).

858 60 Ding, Y. *et al.* Chemodiversity of Soil Dissolved Organic Matter. *Environmental Science &*
859 *Technology* **54**, 6174-6184, doi:10.1021/acs.est.0c01136 (2020).

860 61 Kellerman, A. M. *et al.* Unifying Concepts Linking Dissolved Organic Matter Composition to
861 Persistence in Aquatic Ecosystems. *Environmental Science & Technology* **52**, 2538-2548,
862 doi:10.1021/acs.est.7b05513 (2018).

863 62 Teppen, B. J. & Aggarwal, V. Thermodynamics of organic cation exchange selectivity in
864 smectites. *Clays and Clay Minerals* **55**, 119-130, doi:10.1346/ccmn.2007.0550201 (2007).

865 63 MacKay, A. A. & Vasudevan, D. Polyfunctional Ionogenic Compound Sorption: Challenges and
866 New Approaches To Advance Predictive Models. *Environmental Science & Technology* **46**, 9209-
867 9223, doi:10.1021/es301036t (2012).

868 64 Ni, J. & Pignatello, J. J. Charge-assisted hydrogen bonding as a cohesive force in soil organic
869 matter: water solubility enhancement by addition of simple carboxylic acids. *Environmental*
870 *Science: Processes & Impacts* **20**, 1225-1233 (2018).

871 65 Schwartzbach, R. P., Gschwend, P. M. & Imboden, D. M. *Environmental Organic Chemistry*.
872 1024 (Wiley, 2016).

873 66 Sposito, G., Skipper, N. T., Sutton, R., Park, S.-H., Soper, A. K. Greathouse, J. A. Surface
874 geochemistry of the clay minerals. *Proceedings of the National Academy of Sciences USA* **96**,
875 3358-3364 (1999).

876 67 Willemsen, J. A. R., Myneni, S. C. B. & Bourg, I. C. Molecular Dynamics Simulations of the
877 Adsorption of Phthalate Esters on Smectite Clay Surfaces. *Journal of Physical Chemistry C* **123**,
878 13624-13636, doi:10.1021/acs.jpcc.9b01864 (2019).

- 879 68 Wershaw, R. L. Model for Humus in Soils and Sediments. *Environmental Science and Technology*
880 **27**, 814-816 (1993).
- 881 69 Kleber, M., Sollins, P. & Sutton, R. A conceptual model of organo-mineral interactions in soils:
882 self-assembly of organic molecular fragments into zonal structures on mineral surfaces.
883 *Biogeochemistry* **85**, 9-24 (2007).
- 884 70 Huang, X. Z. *et al.* Direct evidence for thickening nanoscale organic films at soil biogeochemical
885 interfaces and its relevance to organic matter preservation. *Environmental Science-Nano* **7**,
886 2747-2758, doi:10.1039/d0en00489h (2020).
- 887 71 Ohno, T. & Kubicki, J. D. Adsorption of Organic Acids and Phosphate to an Iron (Oxyhydr)oxide
888 Mineral: A Combined Experimental and Density Functional Theory Study. *Journal of Physical*
889 *Chemistry A* **124**, 3249-3260, doi:10.1021/acs.jpca.9b12044 (2020).
- 890 72 Bowden, J. W., Posner, A. M. & Quirk, J. P. Ionic adsorption on variable charge mineral surfaces.
891 Theoretical charge development and titration curves. *Soil Research* **15**, 121-136 (1977).
- 892 73 Riedel, T., Biester, H. & Dittmar, T. Molecular Fractionation of Dissolved Organic Matter with
893 Metal Salts. *Environmental Science & Technology* **46**, 4419-4426, doi:10.1021/es203901u (2012).
- 894 74 Possinger, A. R. *et al.* Organo-organic and organo-mineral interfaces in soil at the nanometer
895 scale. *Nature communications* **11** (2020).
- 896 75 Mitchell, P. J., Simpson, A. J., Soong, R. & Simpson, M. J. Nuclear Magnetic Resonance Analysis of
897 Changes in Dissolved Organic Matter Composition with Successive Layering on Clay Mineral
898 Surfaces. *Soils* **2**, 8 (2018).
- 899 76 Coward, E. K., Ohno, T. & Sparks, D. L. Direct Evidence for Temporal Molecular Fractionation of
900 Dissolved Organic Matter at the Iron Oxyhydroxide Interface. *Environmental Science &*
901 *Technology* **53**, 642-650, doi:10.1021/acs.est.8b04687 (2019).
- 902 77 Hatton, P.-J., Remusat, L., Zeller, B., Brewer, E. A. & Derrien, D. NanoSIMS investigation of
903 glycine-derived C and N retention with soil organo-mineral associations. *Biogeochemistry* **125**,
904 303-313, doi:10.1007/s10533-015-0138-8 (2015).
- 905 78 Lehmann, J. *et al.* Spatial complexity of soil organic matter forms at nanometre scales. *Nature*
906 *Geoscience* **1**, 238-242, doi:10.1038/ngeo155 (2008).
- 907 79 Vogel, C. *et al.* Submicron structures provide preferential spots for carbon and nitrogen
908 sequestration in soils. *Nature Communications* **5**, doi:10.1038/ncomms3947 (2014).
- 909 80 Shaker, A., Komy, Z., Heggy, S. & Elsayed, M. Kinetic Study for Adsorption Humic Acid on Soil
910 Minerals. *The journal of physical chemistry. A* **116**, doi:10.1021/jp3078826 (2012).
- 911 81 Koopal, L., Tan, W. F. & Avena, M. Mixed ad/desorption kinetics unraveled with the equilibrium
912 adsorption isotherm. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **577**, 709-
913 722, doi:10.1016/j.colsurfa.2019.06.033 (2019).
- 914 82 Avena, M. J. & Wilkinson, K. J. Disaggregation kinetics of a peat humic acid: Mechanism and pH
915 effects. *Environmental Science & Technology* **36**, 5100-5105, doi:10.1021/es025582u (2002).
- 916 83 Li, W. L. *et al.* Real-time evaluation of natural organic matter deposition processes onto model
917 environmental surfaces. *Water Res.* **129**, 231-239, doi:10.1016/j.watres.2017.11.024 (2018).
- 918 84 Avena, M. J. & Koopal, L. K. Kinetics of humic acid adsorption at solid-water interfaces.
919 *Environmental Science & Technology* **33**, 2739-2744, doi:10.1021/es981236u (1999).
- 920 85 Lee, S. S., Fenter, P., Park, C. & Nagy, K. L. Fulvic acid sorption on muscovite mica as a function of
921 pH and time using in situ X-ray reflectivity. *Langmuir* **24**, 7817-7829, doi:10.1021/la703456t
922 (2008).
- 923 86 Lilienfein, J., Qualls, R. G., Uselman, S. M. & Bridgman, S. D. Adsorption of dissolved organic
924 carbon and nitrogen in soils of a weathering chronosequence. *Soil Science Society of America*
925 *Journal* **68**, 292-305 (2004).

- 926 87 Mostovaya, A., Hawkes, J. A., Dittmar, T. & Tranvik, L. J. Molecular Determinants of Dissolved
927 Organic Matter Reactivity in Lake Water. *Frontiers in Earth Science* **5**,
928 doi:10.3389/feart.2017.00106 (2017).
- 929 88 Chacon, S. S. *et al.* Mineral Surfaces as Agents of Environmental Proteolysis: Mechanisms and
930 Controls. *Environmental Science & Technology*, doi:10.1021/acs.est.8b05583 (2019).
- 931 89 Haas, K. L. & Franz, K. J. Application of Metal Coordination Chemistry To Explore and Manipulate
932 Cell Biology. *Chemical Reviews* **109**, 4921-4960, doi:10.1021/cr900134a (2009).
- 933 90 Christl, I. & Kretzschmar, R. C-1s NEXAFS spectroscopy reveals chemical fractionation of humic
934 acid by cation-induced coagulation. *Environmental Science & Technology* **41**, 1915-1920,
935 doi:10.1021/es062141s (2007).
- 936 91 Edwards, D. C. & Myneni, S. C. B. Hard and soft X-ray absorption spectroscopic investigation of
937 aqueous Fe(III)-hydroxamate siderophore complexes. *Journal of Physical Chemistry A* **109**,
938 10249-10256, doi:10.1021/jp053349n (2005).
- 939 92 Radke, C. J. Gibbs adsorption equation for planar fluid-fluid interfaces: Invariant formalism.
940 *Advances in Colloid and Interface Science* **222**, 600-614, doi:10.1016/j.cis.2014.01.001 (2015).
- 941 93 Schwertmann, U. Inhibitory effect of soil organic matter on crystallization of amorphous ferric
942 hydroxide. *Nature* **212**, 645+, doi:10.1038/212645b0 (1966).
- 943 94 Eusterhues, K. *et al.* Characterization of Ferrihydrite-Soil Organic Matter Coprecipitates by X-ray
944 Diffraction and Mossbauer Spectroscopy. *Environmental Science & Technology* **42**, 7891-7897,
945 doi:10.1021/es800881w (2008).
- 946 95 Levard, C. *et al.* Structure and distribution of allophanes, imogolite and proto-imogolite in
947 volcanic soils. *Geoderma* **183**, 100-108, doi:10.1016/j.geoderma.2012.03.015 (2012).
- 948 96 Chen, C. M., Kukkadapu, R. & Sparks, D. L. Influence of Coprecipitated Organic Matter on Fe-
949 (aq)(2+)-Catalyzed Transformation of Ferrihydrite: Implications for Carbon Dynamics.
950 *Environmental Science & Technology* **49**, 10927-10936, doi:10.1021/acs.est.5b02448 (2015).
- 951 97 Kaiser, K. & Zech, W. Release of natural organic matter sorbed to oxides and a subsoil. *Soil*
952 *Science Society of America Journal* **63**, 1157-1166 (1999).
- 953 98 Oren, A. & Chefetz, B. Sorptive and Desorptive Fractionation of Dissolved Organic Matter by
954 Mineral Soil Matrices. *J. Environ. Qual.* **41**, 526-533, doi:10.2134/jeq2011.0362 (2012).
- 955 99 Lippold, H. & Lippmann-Pipke, J. Effect of humic matter on metal adsorption onto clay materials:
956 Testing the linear additive model. *Journal of Contaminant Hydrology* **109**, 40-48,
957 doi:<https://doi.org/10.1016/j.jconhyd.2009.07.009> (2009).
- 958 100 Eusterhues, K. *et al.* Reduction of ferrihydrite with adsorbed and coprecipitated organic matter:
959 microbial reduction by *Geobacter bremsensis* vs. abiotic reduction by Na-dithionite.
960 *Biogeosciences* **11**, 4953-4966, doi:10.5194/bg-11-4953-2014 (2014).
- 961 101 Eusterhues, K., Rumpel, C., Kleber, M. & Kogel-Knabner, I. Stabilisation of soil organic matter by
962 interactions with minerals as revealed by mineral dissolution and oxidative degradation. *Organic*
963 *Geochemistry* **34**, 1591-1600 (2003).
- 964 102 Grybos, M., Davranche, M., Gruau, G. & Petitjean, P. Is trace metal release in wetland soils
965 controlled by organic matter mobility or Fe-oxyhydroxides reduction? *Journal of Colloid and*
966 *Interface Science* **314**, 490-501, doi:10.1016/j.jcis.2007.04.062 (2007).
- 967 103 Pan, W., Kan, J., Inamdar, S., Chen, C. & Sparks, D. Dissimilatory microbial iron reduction release
968 DOC (dissolved organic carbon) from carbon-ferrihydrite association. *Soil Biology and*
969 *Biochemistry* **103**, 232-240, doi:10.1016/j.soilbio.2016.08.026 (2016).
- 970 104 Poggenburg, C., Mikutta, R., Schippers, A., Dohrmann, R. & Guggenberger, G. Impact of natural
971 organic matter coatings on the microbial reduction of iron oxides. *Geochimica et Cosmochimica*
972 *Acta* **224**, 223-248, doi:<https://doi.org/10.1016/j.gca.2018.01.004> (2018).

- 973 105 Thompson, A., Chadwick, O. A., Boman, S. & Chorover, J. Colloid mobilization during soil iron
974 redox oscillations. *Environmental Science & Technology* **40**, 5743-5749 (2006).
- 975 106 Collignon, C., Ranger, J. & Turpault, M. P. Seasonal dynamics of Al- and Fe-bearing secondary
976 minerals in an acid forest soil: influence of Norway spruce roots (*Picea abies* (L.) Karst.).
977 *European Journal of Soil Science* **63**, 592-602, doi:10.1111/j.1365-2389.2012.01470.x (2012).
- 978 107 Ochs, M., Brunner, I., Stumm, W. & Cosovic, B. Effect of root exudates and humic substances on
979 weathering kinetics. *Water Air and Soil Pollution* **68**, 213-229, doi:10.1007/bf00479404 (1993).
- 980 108 Fang, L., Cao, Y., Huang, Q., Walker, S. L. & Cai, P. Reactions between bacterial exopolymers and
981 goethite: A combined macroscopic and spectroscopic investigation. *Water Res.* **46**, 5613-5620,
982 doi:<http://dx.doi.org/10.1016/j.watres.2012.07.046> (2012).
- 983 109 Goynes, K. W., Chorover, J., Zimmerman, A. R., Komarneni, S. & Brantley, S. L. Influence of
984 mesoporosity on the sorption of 2,4-dichlorophenoxyacetic acid onto alumina and silica. *J.*
985 *Colloid Interf. Sci.* **272**, 10-20 (2004).
- 986 110 Johnston, C. T., Premachandra, G. S., Szabo, T., Lok, J. & Schoonheydt, R. A. Interaction of
987 Biological Molecules with Clay Minerals: A Combined Spectroscopic and Sorption Study of
988 Lysozyme on Saponite. *Langmuir* **28**, 611-619, doi:10.1021/la203161n (2012).
- 989 111 Hunter, W. R. *et al.* Metabolism of mineral-sorbed organic matter and microbial lifestyles in
990 fluvial ecosystems. *Geophysical Research Letters* **43**, 1582-1588, doi:10.1002/2016gl067719
991 (2016).
- 992 112 McGhee, I., Sannino, F., Gianfreda, L. & Burns, R. G. Bioavailability of 2,4-D sorbed to a chlorite-
993 like complex. *Chemosphere* **39**, 285-291, doi:10.1016/s0045-6535(99)00109-5 (1999).
- 994 113 Keiluweit, M. *et al.* Long-term litter decomposition controlled by manganese redox cycling.
995 *Proceedings of the National Academy of Sciences*, 201508945 (2015).
- 996 114 Kallenbach, C. M., Frey, S. D. & Grandy, A. S. Direct evidence for microbial-derived soil organic
997 matter formation and its ecophysiological controls. *Nature Communications* **7**,
998 doi:10.1038/ncomms13630 (2016).
- 999 115 Malik, A. & Gleixner, G. Importance of microbial soil organic matter processing in dissolved
1000 organic carbon production. *Fems Microbiology Ecology* **86**, 139-148, doi:10.1111/1574-
1001 6941.12182 (2013).
- 1002 116 Simpson, A. J., Simpson, M. J., Smith, E. & Kelleher, B. P. Microbially Derived Inputs to Soil
1003 Organic Matter: Are Current Estimates Too Low? *Environmental Science & Technology* **41**, 8070-
1004 8076 (2007).
- 1005 117 Ferris, J. P. Montmorillonite catalysis of 30-50 mer oligonucleotides: Laboratory demonstration
1006 of potential steps in the origin of the RNA world. *Origins of Life and Evolution of the Biosphere*
1007 **32**, 311-332, doi:10.1023/a:1020543312109 (2002).
- 1008 118 Aldersley, M. F., Joshi, P. C., Price, J. D. & Ferris, J. P. The role of montmorillonite in its catalysis
1009 of RNA synthesis. *Applied Clay Science* **54**, 1-14, doi:10.1016/j.clay.2011.06.011 (2011).
- 1010 119 Duval, S. *et al.* On the why's and how's of clay minerals' importance in life's emergence. *Applied*
1011 *Clay Science* **195**, doi:10.1016/j.clay.2020.105737 (2020).
- 1012 120 Laszlo, P. Chemical reactions on clays. *Science* **235**, 1473-1477,
1013 doi:10.1126/science.235.4795.1473 (1987).
- 1014 121 McBride, M. B. Adsorption and oxidation of phenolic compounds by iron and manganese oxides
1015 *Soil Science Society of America Journal* **51**, 1466-1472 (1987).
- 1016 122 Sheng, F. *et al.* Rapid Hydrolysis of Penicillin Antibiotics Mediated by Adsorbed Zinc on Goethite
1017 Surfaces. *Environmental Science & Technology* **53**, 10705-10713, doi:10.1021/acs.est.9b02666
1018 (2019).
- 1019 123 Chorover, J. & Amistadi, M. K. Reaction of forest floor organic matter at goethite, birnessite and
1020 smectite surfaces. *Geochimica et Cosmochimica Acta* **65**, 95-109 (2001).

1021 124 Faure, P., Schlepp, L., Burkle-Vitzthum, V. & Elie, M. Low temperature air oxidation of n-alkanes
1022 in the presence of Na-smectite. *Fuel* **82**, 1751-1762, doi:10.1016/s0016-2361(03)00133-9 (2003).

1023 125 Mitchell, P. J. *et al.* Solution-state NMR investigation of the sorptive fractionation of dissolved
1024 organic matter by alkaline mineral soils. *Environmental Chemistry* **10**, 333-340 (2013).

1025 126 Riedel, T., Zak, D., Biester, H. & Dittmar, T. Iron traps terrestrially derived dissolved organic
1026 matter at redox interfaces. *Proceedings of the National Academy of Sciences of the United States*
1027 *of America* **110**, 10101-10105, doi:10.1073/pnas.1221487110 (2013).

1028 127 Chacon, S. S., Garcia-Jaramillo, M., Liu, S. Y., Ahmed, M. & Kleber, M. Differential capacity of
1029 kaolinite and birnessite to protect surface associated proteins against thermal degradation. *Soil*
1030 *Biology & Biochemistry* **119**, 101-109, doi:10.1016/j.soilbio.2018.01.020 (2018).

1031 128 Reardon, P. N. *et al.* Abiotic Protein Fragmentation by Manganese Oxide: Implications for a
1032 Mechanism to Supply Soil Biota with Oligopeptides. *Environmental Science & Technology* **50**,
1033 3486-3493, doi:10.1021/acs.est.5b04622 (2016).

1034 129 Johnson, K. *et al.* Towards a mechanistic understanding of carbon stabilization in manganese
1035 oxides. *Nature Comm.* **6**, 7628 (2015).

1036 130 Cleaves, H. J. *et al.* Mineral-organic interfacial processes: potential roles in the origins of life.
1037 *Chemical Society Reviews* **41**, 5502-5525, doi:10.1039/c2cs35112a (2012).

1038 131 Soma, Y. & Soma, M. CHEMICAL-REACTIONS OF ORGANIC-COMPOUNDS ON CLAY SURFACES.
1039 *Environmental Health Perspectives* **83**, 205-214, doi:10.2307/3430656 (1989).

1040 132 Norde, W. My voyage of discovery to proteins in flatland..... and beyond. *Colloids and*
1041 *Surfaces B-Biointerfaces* **61**, 1-9, doi:10.1016/j.colsurfb.2007.09.029 (2008).

1042 133 Hoarau, M., Badieyan, S. & Marsh, E. N. G. Immobilized enzymes: understanding enzyme -
1043 surface interactions at the molecular level. *Organic & Biomolecular Chemistry* **15**, 9539-9551,
1044 doi:10.1039/c7ob01880k (2017).

1045 134 Maurice, P. A. & Namjesnik-Dejanovic, K. Aggregate structures of sorbed humic substances
1046 observed in aqueous solution. *Environmental Science and Technology* **33**, 1538-1541 (1999).

1047 135 Myneni, S. C. B., Brown, J. T., Martinez, G. A., Meyer-Ilse, W.,. Imaging of humic substance
1048 macromolecular structures in water and soils. *Science* **286**, 1335-1337 (1999).

1049 136 Denton, J. K. *et al.* Molecular-level origin of the carboxylate head group response to divalent
1050 metal ion complexation at the air-water interface. *Proceedings of the National Academy of*
1051 *Sciences of the United States of America* **116**, 14874-14880, doi:10.1073/pnas.1818600116
1052 (2019).

1053 137 Liu, W., Tkatchenko, A. & Scheffler, M. Modeling Adsorption and Reactions of Organic Molecules
1054 at Metal Surfaces. *Accounts of Chemical Research* **47**, 3369-3377, doi:10.1021/ar500118y
1055 (2014).

1056 138 Nealson, K. H. & Saffarini, D. Iron and manganese in anaerobic respiration: Environmental
1057 significance, physiology, and regulation. *Annu. Rev. Microbiol.* **48**, 311-343 (1994).

1058 139 Shi, L. *et al.* Extracellular electron transfer mechanisms between microorganisms and minerals.
1059 *Nature Rev. Microbiol.* **14**, 651-662 (2016).

1060 140 Gorby, Y. A. *et al.* Electrically conductive bacterial nanowires produced by *Shewanella oneidensis*
1061 strain MR-1 and other microorganisms. *Proc. Nation. Acad. Sci.* **103**, 11358-11363 (2006).

1062 141 Reguera, G. *et al.* Extracellular electron transfer via microbial nanowires. *Nature* **435**, 1098-
1063 1101, doi:10.1038/nature03661 (2005).

1064 142 Marsili, E. *et al.* *Shewanella* Secretes flavins that mediate extracellular electron transfer.
1065 *Proceedings of the National Academy of Sciences of the United States of America* **105**, 3968-
1066 3973, doi:10.1073/pnas.0710525105 (2008).

1067 143 Remucal, C. K. & Ginder-Vogel, M. A critical review of the reactivity of manganese oxides with
1068 organic contaminants. *Environ. Sci.: Processes Impacts* **16**, 1247 (2014).

- 1069 144 Sunda, W. G. & Kieber, D. J. Oxidation of humic substances by manganese oxides yields low-
1070 molecular weight organic substrates. *Nature* **367**, 62-64, doi:10.1038/367062a0 (1994).
- 1071 145 Ma, D., Wu, J., Yang, P. & Zhu, M. Q. Coupled Manganese Redox Cycling and Organic Carbon
1072 Degradation on Mineral Surfaces. *Environmental Science & Technology* **54**, 8801-8810,
1073 doi:10.1021/acs.est.0c02065 (2020).
- 1074 146 Russo, F., Johnson, C. J., McKenzie, D., Aiken, J. M. & Pedersen, J. A. Pathogenic prion protein is
1075 degraded by a manganese oxide mineral found in soils. *Journal of General Virology* **90**, 275-280,
1076 doi:10.1099/vir.0.003251-0 (2009).
- 1077 147 Heckman, K., Vazquez-Ortega, A., Gao, X. D., Chorover, J. & Rasmussen, C. Changes in water
1078 extractable organic matter during incubation of forest floor material in the presence of quartz,
1079 goethite and gibbsite surfaces. *Geochimica et Cosmochimica Acta* **75**, 4295-4309,
1080 doi:10.1016/j.gca.2011.05.009 (2011).
- 1081 148 Lehmann, R. G., Cheng, H. H. & Harsh, J. B. Oxidation of phenolic acids by soil iron and
1082 manganese oxides. *Soil Sci. Soc. Am. J.* **51**, 352-356 (1987).
- 1083 149 Stuckey, J. W. *et al.* Impacts of hydrous manganese oxide on the retention and lability of
1084 dissolved organic matter. *Geochem. Trans.* **19**, 6 (2018).
- 1085 150 Suter, D., Banwart, S. & Stumm, W. Dissolution of hydrous iron(III) oxides by reductive
1086 mechanisms. *Langmuir* **7**, 809-813, doi:10.1021/la00052a033 (1991).
- 1087 151 Jones, M. E. *et al.* Manganese-driven carbon oxidation at oxic-anoxic interfaces. *Environ. Sci.*
1088 *Technol.* **52**, 12349-12357 (2018).
- 1089 152 Estes, E. R., Andeer, P. F., Nordlund, D., Wankel, S. & Hansel, C. M. Biogenic manganese oxides
1090 as reservoirs of organic carbon and proteins in terrestrial and marine environments. *Geobiol.* **15**,
1091 158-172 (2016).
- 1092 153 Fridovich, I. Oxygen toxicity: A radical explanation. *Journal of Experimental Biology* **201**, 1203-
1093 1209 (1998).
- 1094 154 Trusiak, A., Treibergs, L. A., Kling, G. W. & Cory, R. M. The role of iron and reactive oxygen
1095 species in the production of CO₂ in arctic soil waters. *Geochimica Et Cosmochimica Acta* **224**, 80-
1096 95, doi:10.1016/j.gca.2017.12.022 (2018).
- 1097 155 Hansel, C. M. & Diaz, J. M. Reactive oxygen species production by marine biota. Annual Review
1098 of Marine Science. *Annual Review of Marine Science*, doi:doi:10.1146/annurev-marine-041320-
1099 102550 (2021).
- 1100 156 Blough, N. V. & Zepp, R. G. in *Active Oxygen in Chemistry* (eds C.S. Foote, J.S. Valentine, A.
1101 Greenburg, & J.F. Liebman) 280-333 (1995).
- 1102 157 Xu, X. *et al.* Characteristics of desert varnish from nanometer to micrometer scale: A photo-
1103 oxidation model of its formation. *Chem. Geol.* **522**, 55-70, doi:10.1016/j.chemgeo.2019.05.016
1104 (2019).
- 1105 158 Schoonen, M. A. A. *et al.* in *The Emergent Field of Medical Mineralogy and Geochemistry* Vol. 64
1106 (eds N. Sahia, M.A.A. Schoonen, & H.C.W. Skinner) 59-113 (Geochemical Society, 2006).
- 1107 159 Georgiou, C. D. *et al.* Evidence for photochemical production of reactive oxygen species in
1108 desert soils. *Nature Comm.* **6**, 7100, doi:10.1038/ncomms8100 (2015).
- 1109 160 Gil-Lozano, C., Davila, A. F., Losa-Adams, E., Fairen, A. G. & Gago-Duport, L. Quantifying Fenton
1110 reaction pathways driven by self-generated H₂O₂ on pyrite surfaces. *Scientific Reports* **7**, 43703
1111 (2017).
- 1112 161 Tong, M. *et al.* Production of Abundant Hydroxyl Radicals from Oxygenation of Subsurface
1113 Sediments. *Environmental Science & Technology* **50**, 214-221, doi:10.1021/acs.est.5b04323
1114 (2016).

- 1115 162 Xu, J., Sahia, N., Eggleston, C. M. & Schoonen, M. A. A. Reactive oxygen species at the
1116 oxide/water interface: Formation mechanisms and implications for prebiotic chemistry and the
1117 origin of life. *EPSL* **363**, 156-167 (2013).
- 1118 163 Yuan, X. *et al.* Production of hydrogen peroxide in groundwater at Rifle, Colorado. *Environ. Sci.*
1119 *Technol.* **51**, 7881-7891 (2017).
- 1120 164 Sutherland, K. M. *et al.* Spatial heterogeneity in particle associated, light-independent
1121 superoxide production within productive coastal waters. *JGR - Oceans*, In review (2020).
- 1122 165 Page, S. E. *et al.* Dark Formation of Hydroxyl Radical in Arctic Soil and Surface Waters.
1123 *Environmental Science & Technology* **47**, 12860-12867, doi:10.1021/es4033265 (2013).
- 1124 166 Rose, A. L. The influence of extracellular superoxide on iron redox chemistry and bioavailability
1125 to aquatic microorganisms. *Frontiers in Microbiology* **3**, doi:10.3389/fmicb.2012.00124 (2012).
- 1126 167 Waggoner, D. C., Wozniak, A. S., Cory, R. M. & Hatcher, P. G. The role of reactive oxygen species
1127 in the degradation of lignin derived dissolved organic matter. *Geochimica Et Cosmochimica Acta*
1128 **208**, 171-184, doi:10.1016/j.gca.2017.03.036 (2017).
- 1129 168 Goldstone, J. V. & Voelker, B. M. Chemistry of superoxide radical in seawater: CDOM associated
1130 sink of superoxide in coastal waters. *Environmental Science & Technology* **34**, 1043-1048,
1131 doi:10.1021/es9905445 (2000).
- 1132 169 Voelker, B. M. & Sulzberger, B. Effects of fulvic acid on Fe(II) oxidation by hydrogen peroxide.
1133 *Environmental Science & Technology* **30**, 1106-1114, doi:10.1021/es9502132 (1996).
- 1134 170 Buxton, G. V., Greenstock, C. L., Helman, W. P. & Ross, A. B. CRITICAL-REVIEW OF RATE
1135 CONSTANTS FOR REACTIONS OF HYDRATED ELECTRONS, HYDROGEN-ATOMS AND HYDROXYL
1136 RADICALS (.OH/.O-) IN AQUEOUS-SOLUTION. *Journal of Physical and Chemical Reference Data*
1137 **17**, 513-886, doi:10.1063/1.555805 (1988).
- 1138 171 Goldstone, J. V., Pullin, M. J., Bertilsson, S. & Voelker, B. M. Reactions of hydroxyl radical with
1139 humic substances: Bleaching, mineralization, and production of bioavailable carbon substrates.
1140 *Environ. Sci. Technol.* **36**, 364-372 (2002).
- 1141 172 Pullin, M. J., Bertilsson, S., Goldstone, J. V. & Voelker, B. M. Effects of sunlight and hydroxyl
1142 radical on dissolved organic matter: Bacterial growth efficiency and production of carboxylic
1143 acids and other substrates. *Limnol. Oceanogr.* **49**, 2011-2022 (2014).
- 1144 173 Wuttig, K., Heller, M. I. & Croot, P. L. Pathways of Superoxide (O₂⁻) Decay in the Eastern
1145 Tropical North Atlantic. *Environmental Science & Technology* **47**, 10249-10256,
1146 doi:10.1021/es401658t (2013).
- 1147 174 Heller, M. I., Wuttig, K. & Croot, P. L. Identifying the Sources and Sinks of CDOM/FDOM across
1148 the Mauritanian Shelf and Their Potential Role in the Decomposition of Superoxide (O₂⁻).
1149 *Frontiers in Marine Science* **3**, doi:10.3389/fmars.2016.00132 (2016).
- 1150 175 Scully, N. M., Cooper, W. J. & Tranvik, L. J. Photochemical effects on microbial activity in natural
1151 waters: the interaction of reactive oxygen species and dissolved organic matter. *Fems*
1152 *Microbiology Ecology* **46**, 353-357, doi:10.1016/s0168-6496(03)00198-3 (2003).
- 1153 176 Hall, S. J. & Silver, W. L. Iron oxidation stimulates organic matter decomposition in humid
1154 tropical forest soils. *Global Change Biology* **19**, 2804-2813, doi:10.1111/gcb.12229 (2013).
- 1155 177 Xiao, Y. H., Carena, L., Nasi, M. T. & Vahatalo, A. V. Superoxide-driven autocatalytic dark
1156 production of hydroxyl radicals in the presence of complexes of natural dissolved organic matter
1157 and iron. *Water Res.* **177**, doi:10.1016/j.watres.2020.115782 (2020).
- 1158 178 Bach, C. E. *et al.* Measuring phenol oxidase and peroxidase activities with pyrogallol, L-DOPA,
1159 and ABTS: Effect of assay conditions and soil type. *Soil Biology & Biochemistry* **67**, 183-191,
1160 doi:10.1016/j.soilbio.2013.08.022 (2013).
- 1161 179 Carson, J. K. *et al.* Low Pore Connectivity Increases Bacterial Diversity in Soil. *Applied and*
1162 *Environmental Microbiology* **76**, 3936-3942, doi:10.1128/aem.03085-09 (2010).

- 1163 180 Negassa, W. C. *et al.* Properties of Soil Pore Space Regulate Pathways of Plant Residue
1164 Decomposition and Community Structure of Associated Bacteria. *Plos One* **10**,
1165 doi:10.1371/journal.pone.0123999 (2015).
- 1166 181 Miltner, A., Bombach, P., Schmidt-Brucken, B. & Kastner, M. SOM genesis: microbial biomass as
1167 a significant source. *Biogeochemistry* **111**, 41-55, doi:10.1007/s10533-011-9658-z (2012).
- 1168 182 Angst, G., Mueller, K. E., Nierop, K. G. J. & Simpson, M. J. Plant- or microbial-derived? A review
1169 on the molecular composition of stabilized soil organic matter. *Soil Biology and Biochemistry*,
1170 doi:<https://doi.org/10.1016/j.soilbio.2021.108189> (2021).
- 1171 183 Liang, C., Amelung, W., Lehmann, J. & Kastner, M. Quantitative assessment of microbial
1172 necromass contribution to soil organic matter. *Global Change Biology* **25**, 3578-3590,
1173 doi:10.1111/gcb.14781 (2019).
- 1174 184 Young, I. M. & Crawford, J. W. Interactions and self-organization in the soil-microbe complex.
1175 *Science* **304**, 1634-1637 (2004).
- 1176 185 Levin, S. A. Ecosystems and the biosphere as complex adaptive systems. *Ecosystems* **1**, 431-436,
1177 doi:10.1007/s100219900037 (1998).
- 1178 186 D'Souza, G. & Kost, C. Experimental Evolution of Metabolic Dependency in Bacteria. *Plos*
1179 *Genetics* **12**, doi:10.1371/journal.pgen.1006364 (2016).
- 1180 187 Lehmann, J. *et al.* Persistence of soil organic carbon caused by functional complexity. *Nature*
1181 *Geoscience* **13**, 529-534, doi:10.1038/s41561-020-0612-3 (2020).
- 1182 188 Nunan, N., Schmidt, H. & Raynaud, X. The ecology of heterogeneity: soil bacterial communities
1183 and C dynamics. *Philosophical Transactions of the Royal Society B-Biological Sciences* **375**,
1184 doi:10.1098/rstb.2019.0249 (2020).
- 1185 189 Wilhelm, R. C., Pepe-Ranne, C., Weisenhorn, P., Lipton, M. & Buckley, D. H. Competitive
1186 Exclusion and Metabolic Dependency among Microorganisms Structure the Cellulose Economy
1187 of an Agricultural Soil. *Mbio* **12**, doi:10.1128/mBio.03099-20 (2021).
- 1188 190 Kalbitz, K., Schwesig, D., Rethemeyer, J. & Matzner, E. Stabilization of dissolved organic matter
1189 by sorption to the mineral soil. *Soil Biology & Biochemistry* **37**, 1319-1331 (2005).
- 1190 191 Keiluweit, M. *et al.* Mineral protection of soil carbon counteracted by root exudates. *Nature*
1191 *Climate Change* **5**, 588-595 (2015).
- 1192 192 Zhalnina, K. *et al.* Dynamic root exudate chemistry and microbial substrate preferences drive
1193 patterns in rhizosphere microbial community assembly. *Nature Microbiology* **3**, 470-480,
1194 doi:10.1038/s41564-018-0129-3 (2018).
- 1195 193 Woolf, D. & Lehmann, J. Microbial models with minimal mineral protection can explain long-
1196 term soil organic carbon persistence. *Scientific Reports* **9**, doi:10.1038/s41598-019-43026-8
1197 (2019).
- 1198 194 Borer, B., Tecon, R. & Or, D. Spatial organization of bacterial populations in response to oxygen
1199 and carbon counter-gradients in pore networks. *Nature Communications* **9**, doi:10.1038/s41467-
1200 018-03187-y (2018).
- 1201 195 Barzen-Hanson, K. A., Davis, S. E., Kleber, M. & Field, J. A. Sorption of Fluorotelomer Sulfonates,
1202 Fluorotelomer Sulfonamido Betaines, and a Fluorotelomer Sulfonamido Amine in National Foam
1203 Aqueous Film-Forming Foam to Soil. *Environmental Science & Technology* **51**, 12394-12404,
1204 doi:10.1021/acs.est.7b03452 (2017).
- 1205 196 Grabowski, R. C., Droppo, I. G. & Wharton, G. Erodibility of cohesive sediment: The importance
1206 of sediment properties. *Earth-Science Reviews* **105**, 101-120,
1207 doi:10.1016/j.earscirev.2011.01.008 (2011).
- 1208 197 Israelachvili, J. & Wennerstrom, H. Role of hydration and water structure in biological and
1209 colloidal interactions. *Nature* **379**, 219-225, doi:10.1038/379219a0 (1996).

1210 198 Sushko, M. L. & Rosso, K. M. The origin of facet selectivity and alignment in anatase TiO₂
1211 nanoparticles in electrolyte solutions: implications for oriented attachment in metal oxides.
1212 *Nanoscale* **8**, 19714-19725, doi:10.1039/c6nr06953c (2016).

1213 199 Shen, X. Y. & Bourg, I. C. Molecular dynamics simulations of the colloidal interaction between
1214 smectite clay nanoparticles in liquid water. *Journal of Colloid and Interface Science* **584**, 610-621,
1215 doi:10.1016/j.jcis.2020.10.029 (2021).

1216 200 Michot, L. J. *et al.* Liquid-crystalline aqueous clay suspensions. *Proceedings of the National
1217 Academy of Sciences of the United States of America* **103**, 16101-16104,
1218 doi:10.1073/pnas.0605201103 (2006).

1219 201 Underwood, T. R. & Bourg, I. C. Large-Scale Molecular Dynamics Simulation of the Dehydration
1220 of a Suspension of Smectite Clay Nanoparticles. *Journal of Physical Chemistry C* **124**, 3702-3714,
1221 doi:10.1021/acs.jpcc.9b11197 (2020).

1222 202 Pignon, F. *et al.* Yield stress thixotropic clay suspension: Investigation of structure by light,
1223 neutron, and x-ray scattering. *Physical Review E* **56**, 3281-3289, doi:10.1103/PhysRevE.56.3281
1224 (1997).

1225 203 Bourg, I. C. & Ajo-Franklin, J. B. Clay, Water, and Salt: Controls on the Permeability of Fine-
1226 Grained Sedimentary Rocks. *Accounts of Chemical Research* **50**, 2067-2074,
1227 doi:10.1021/acs.accounts.7b00261 (2017).

1228 204 Mayer, L. M. Surface area control of organic carbon accumulation in continental shelf
1229 sediments. *Geochimica et Cosmochimica Acta* **58**, 1271-1284 (1994).

1230 205 Ransom, B., Dongsom, K., Kastner, M. & Wainwright, S. Organic matter preservation on
1231 continental slopes: Importance of mineralogy and surface area. *Geochimica et Cosmochimica
1232 Acta* **62**, 1329-1345 (1998).

1233 206 Kaiser, K. & Guggenberger, G. Mineral surfaces and soil organic matter. *European Journal of Soil
1234 Science* **54**, 219-236, doi:doi:10.1046/j.1365-2389.2003.00544.x (2003).

1235 207 Barker, W. W., Welch, S. A., Chu, S. & Banfield, J. F. Experimental observations of the effects of
1236 bacteria on aluminosilicate weathering. *American Mineralogist* **83**, 1551-1563, doi:10.2138/am-
1237 1998-11-1243 (1998).

1238 208 Watteau, F. & Villemin, G. Soil Microstructures Examined Through Transmission Electron
1239 Microscopy Reveal Soil-Microorganisms Interactions. *Frontiers in Environmental Science* **6**,
1240 doi:10.3389/fenvs.2018.00106 (2018).

1241 209 Namjesnik-Dejanovic, K. & Maurice, P. A. Conformations and aggregate structures of sorbed
1242 natural organic matter on muscovite and hematite. *Geochimica Et Cosmochimica Acta* **65**, 1047-
1243 1057, doi:10.1016/s0016-7037(00)00542-1 (2001).

1244 210 Moreau, J. W. *et al.* Extracellular proteins limit the dispersal of biogenic nanoparticles. *Science*
1245 **316**, 1600-1603, doi:10.1126/science.1141064 (2007).

1246 211 Jaynes, W. F. & Boyd, S. A. Hydrophobicity of siloxane surfaces in smectites as revealed by
1247 aromatic hydrocarbon adsorption from water. *Clays and Clay Minerals* **39**, 428-436 (1991).

1248 212 Rotenberg, B., Patel, A. J. & Chandler, D. Molecular Explanation for Why Talc Surfaces Can Be
1249 Both Hydrophilic and Hydrophobic. *Journal of the American Chemical Society* **133**, 20521-20527,
1250 doi:10.1021/ja208687a (2011).

1251 213 Radke, C. J. & Prausnitz, J. M. THERMODYNAMICS OF MULTI-SOLUTE ADSORPTION FROM
1252 DILUTE LIQUID SOLUTIONS. *Aiche Journal* **18**, 761-+, doi:10.1002/aic.690180417 (1972).

1253 214 Degennes, P. G. WETTING - STATICS AND DYNAMICS. *Reviews of Modern Physics* **57**, 827-863,
1254 doi:10.1103/RevModPhys.57.827 (1985).

1255 215 McGinley, P. M., Katz, L. E. & Weber, W. J. A DISTRIBUTED REACTIVITY MODEL FOR SORPTION BY
1256 SOILS AND SEDIMENTS.2. MULTICOMPONENT SYSTEMS AND COMPETITIVE EFFECTS.
1257 *Environmental Science & Technology* **27**, 1524-1531, doi:10.1021/es00045a006 (1993).

- 1258 216 Davey, M. E., Caiazza, N. C. & O'Toole, G. A. Rhamnolipid surfactant production affects biofilm
1259 architecture in *Pseudomonas aeruginosa* PAO1. *J. Bacteriol.* **185**, 1027-1036,
1260 doi:10.1128/jb.185.3.1027-1036.2003 (2003).
- 1261 217 Zhang, Y. M. & Miller, R. M. ENHANCED OCTADECANE DISPERSION AND BIODEGRADATION BY A
1262 PSEUDOMONAS RHAMNOLIPID SURFACTANT (BIOSURFACTANT). *Applied and Environmental*
1263 *Microbiology* **58**, 3276-3282, doi:10.1128/aem.58.10.3276-3282.1992 (1992).
- 1264 218 Myneni, S. C. B. Chemistry of Natural Organic Matter-The Next Step: Commentary on a Humic
1265 Substances Debate. *Journal of Environmental Quality* **48**, 233-235,
1266 doi:10.2134/jeq2019.02.0002c (2019).
- 1267 219 Kleber, M. & Lehmann, J. Humic Substances Extracted by Alkali Are Invalid Proxies for the
1268 Dynamics and Functions of Organic Matter in Terrestrial and Aquatic Ecosystems. *Journal of*
1269 *Environmental Quality* **48**, 207-216, doi:10.2134/jeq2019.01.0036 (2019).
- 1270 220 Hazen, R. M. & Sverjensky, D. A. Mineral surfaces, geochemical complexities, and the origins of
1271 life. *Cold Spring Harb. Perspect. Biol.* **2**, a002162 (2010).
- 1272 221 Huang, P. M. & Hardie, A. G. in *Biophysico-Chemical Processes Involving Natural Nonliving*
1273 *Organic Matter in Environmental Systems* (eds N. Senesi, B. Xing, & Huang P. M.) 41-109 (John
1274 Wiley & Sons, Inc., 2009).
- 1275 222 Huang, P. M. & Hardie, A. G. in *Handbook of soil sciences: Properties and processes* (eds P.M.
1276 Huang, Y. Li, & M.E. Sumner) 18.11 - 18.40 (CRC Press, 2012).
- 1277 223 Van Loosdrecht, M. C. M., Lyklema, J., Norde, W. & Zehnder, A. J. B. Influence of interfaces on
1278 microbial activity *Microbiological Reviews* **54**, 75-87 (1990).
- 1279 224 Lipson, D. A., Jha, M., Raab, T. K. & Oechel, W. C. Reduction of iron (III) and humic substances
1280 plays a major role in anaerobic respiration in an Arctic peat soil. *Journal of Geophysical*
1281 *Research-Biogeosciences* **115**, doi:10.1029/2009jg001147 (2010).
- 1282 225 Paerl, R. W., Claudio, I. M., Shields, M. R., Bianchi, T. S. & Osburn, C. L. Dityrosine formation via
1283 reactive oxygen consumption yields increasingly recalcitrant humic-like fluorescent organic
1284 matter in the ocean. *Limnology and Oceanography Letters* **5**, 337-345, doi:10.1002/lol2.10154
1285 (2020).
- 1286 226 Guggenheim, S. *et al.* Summary of recommendations of nomenclature committees relevant to
1287 clay mineralogy: Report of the Association Internationale pour l'Etude des Argiles (AIPEA)
1288 Nomenclature. *Clays and Clay Minerals* **54**, 761-772, doi:10.1346/ccmn.2006.0540610 (2006).
- 1289 227 Theng, B. K. G. & Yuan, G. Nanoparticles in the soil environment. *Elements* **4**, 395-399 (2008).
- 1290 228 Tournassat, C., Bourg, I. C., Steefel, C. I. & Bergaya, F. in *Developments in Clay Science* Vol. 6 (eds
1291 Christophe Tournassat, Carl I. Steefel, Ian C. Bourg, & Faqza Bergaya) 5-31 (Elsevier, 2015).
- 1292 229 Hansel, C. M. *et al.* Secondary mineralization pathways induced by dissimilatory iron reduction
1293 of ferrihydrite under advective flow. *Geochimica Et Cosmochimica Acta* **67**, 2977-2992,
1294 doi:10.1016/s0016-7037(03)00276-x (2003).
- 1295 230 Treves, D. S., Xia, B., Zhou, J. & Tiedje, J. M. A two-species test of the hypothesis that spatial
1296 isolation influences microbial diversity in soil. *Microbial Ecology* **45**, 20-28, doi:10.1007/s00248-
1297 002-1044-x (2003).
- 1298 231 Biesgen, D., Frindte, K., Maarastawi, S. & Knief, C. Clay content modulates differences in
1299 bacterial community structure in soil aggregates of different size. *Geoderma* **376**,
1300 doi:10.1016/j.geoderma.2020.114544 (2020).
- 1301 232 Pascual-Garcia, A., Bonhoeffer, S. & Bell, T. Metabolically cohesive microbial consortia and
1302 ecosystem functioning. *Philosophical Transactions of the Royal Society B-Biological Sciences* **375**,
1303 doi:10.1098/rstb.2019.0245 (2020).
- 1304
1305

1306
1307
1308
1309
1310
1311
1312
1313
1314
1315
1316
1317
1318
1319
1320
1321
1322
1323
1324
1325
1326
1327
1328
1329
1330
1331
1332
1333
1334
1335
1336
1337
1338
1339
1340
1341
1342
1343
1344
1345
1346

Acknowledgements

We acknowledge the constructive suggestions of three anonymous reviewers. ICB was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Geosciences Program under Award DE-SC0018419. SCBM was supported by the NSF (CHE; Award: 1609927). CMH's contribution was supported by NSF award EAR 1826940.

Author contributions

All authors participated in developing the concept. Figures were developed by E.C. (Figures 1 and 5), M. K. (Figure 2), I.C.B. (Figures 3 and 4), S.M. (Figure 6), C.M.H. (Figure 7) and N.N. (Figure 8). All authors contributed to writing and editing.

Competing interests

The authors declare no competing interests.

Peer review information

Nature Reviews Earth & Environment thanks M. Aeppli, L. Aristilde and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

Publisher's note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Key points

- Minerals enable the compartmentalisation 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, though 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.

Figure Captions

Figure 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 (OM) 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).

Figure 2. Organic Multifunctionality. Variation of functional group combinations on organic compounds allows for diverse modes of interaction with mineral surfaces.

Figure 3. Key properties of fine-grained minerals and related solids. The material referred to as allophane is a short-range-ordered (SRO) phyllosilicate with imogolite-like local structure and highly variable stoichiometry; its distinguishing features are low crystallinity and transmission electron microscopy (TEM) images suggestive of hollow spheres 3.5 to 5 nm in diameter, though multiple studies have noted that the interpretation of three-dimensional structure from two-dimensional TEM image is ambiguous⁹⁵. Data based on Refs^{34,66,94,96,226-229}.

Figure 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. Part X is adapted from ref³³, CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>).

Figure 5. Organic ligands at mineral interfaces. 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. Once proximal,

1386 ligands can bind to mineral surfaces through one or multiple complexation mechanisms based on
1387 surface charge distribution and structural reactivity.

1388
1389 **Figure 6. Molecular mechanisms of OM reactions at mineral-water interfaces.** Cartoon at
1390 the top shows a mineral surface showing monolayer and multilayer (3-dimensional) sorption of
1391 small and large OM. Molecular structures of organic molecules at mineral-water interfaces are: i:
1392 cation bridging, ii: H-bonded or Lifshitz -Van der Waals interactions, and iii: direct covalent
1393 interactions. Expanded views of OM interactions and expected trends for different mineral
1394 structures in soils and sediments are shown at the bottom. The nature of chemical reactions are
1395 (as numbered in the figure): 1: e⁻-transfer and electrolytic breakdown of OM; 2: larger OM
1396 formation from nucleophilic addition and radical mediated polymerization; 3: hydrolytic
1397 breakdown of molecules from pH changes at the interface; 4: heterogeneous OM oxidation from
1398 adsorbed O₂; and 5: chemical changes to substrate showing electron transfer and reduction of
1399 substrate atoms and changes to the coordination environments of neighboring atoms of substrate
1400 surface. Based on their differences in chemical reactivity towards OM, we further classify
1401 minerals presented above into 3 classes (I-III). Expected trends for OM behavior are included.

1402
1403 **Figure 7. Mineral-induced organic carbon redox pathways.** a| Mineral induced oxidation,
1404 which represents direct coupling. b| Mineral-derived aqueous Fe(II), which involved both direct
1405 and reactive oxygen species (ROS) mediated reactions. c| ROS mediated reactions.
1406 In **b** and **c**, the fate of mineral-derived ROS includes reaction of ROS with organic carbon (OC)
1407 or transformation of one ROS to another (dismutation of superoxide to hydrogen peroxide,
1408 formation of hydroxyl radical from ferrous iron and hydrogen peroxide via the Fenton reaction) –
1409 for simplicity, all these fates are not shown here. The illustrations are meant to show general
1410 processes, not mechanistic details, and the list of reactions is not exhaustive.

1411
1412 **Figure 8. Compartmentalization and mineral-organic matter-microbe interactions.** Top
1413 panel shows structure with high clay content that is compartmentalized and relatively constant
1414 over time and lower panel shows structure with low clay content that is relatively dynamic over
1415 time. The compartmentalization and constant micro-environmental conditions results in greater
1416 niche differentiation, which allows a greater microbial diversity to co-exist through reduced
1417 competitive interactions^{230,231}. The magnified insets show potential evolutionary consequences
1418 in microsites that form constant habitats. The capacity to use organic substrate present is
1419 subjected to strong selective pressure and preserved but other pathways could be lost (insets i.
1420 and iii.). Less competitive species do not compete for organic substrate present, but exploits
1421 metabolic by-product of more competitive species, resulting in a better use of available resources
1422 by the microsite community²³² (insets ii. and iv.).

1423 1424 1425 Glossary Terms

1426

1427 **Adsorption** - An increase in the concentration of a dissolved substance at the interface of a
1428 condensed and a liquid or gaseous phase due to the operation of surface forces.

1429 **Catalyst** - A substance that increases the rate of a reaction without modifying the overall
1430 standard Gibbs energy change in the reaction

1431 **Chemotrophic** – the ability to use electron donors other than photons for the synthesis of
1432 organic compounds containing reduced carbon

1433 **Coagulation** - the formation of aggregates from a fluid colloidal system

1434 **Colloid** - molecules or polymolecular particles dispersed in a medium that have at least in one
1435 direction a dimension roughly between 1 nm and 1 μ m

1436 **Colloidal interactions** - interactions that are enabled when particles become so small (equivalent
1437 diameter < 1-2 micron) that surface borne electric forces between particles can effectively
1438 control their behavior in a suspension (for instance, prevent them from settling)

1439 **Compartmentalization** - the division of a system into multiple subsystems with well defined
1440 boundaries that provide a certain degree of process autonomy

1441 **Coulombic interactions** - interactions that result from the electric force between two charged
1442 entities

1443 **Crystal facet** - a flat plane on a crystal

1444 **Crystal growth** - the addition of new atoms into the characteristic arrangement of the crystalline
1445 lattice, releasing thermal energy (enthalpy of crystallization)

1446 **Depolymerization** - the disassembly of a polymer into its constituent monomers or into a
1447 mixture of products

1448 **Dispersion** - A system in which particles of colloidal size of any nature (solid, liquid or gas) are
1449 dispersed in a continuous phase of a different composition (or state).

1450

1451 **Fine-grained fraction** - mineral grains with an average diameter smaller than 50/63 microns,
1452 depending on classification system used

1453 **Heterotrophic** - the ability to derive nutritional requirements from complex organic substances

1454 **Intra-particle region** - any part of a particle that is not participating in surface reactions

1455 **Interfacial energy** - excess free energy or work associated with the interface between two
1456 phases, per interfacial area

1457 **Ligand** - any atom or molecule attached to a central atom, usually a metallic element, in a
1458 coordination or complex compound; if regarding part of a polyatomic molecular entity as
1459 central, then the atoms, groups or molecules bound to that part are called ligands.

1460 **Metabolic dependency** - a form of adaptation that leads to the absence or loss of the ability to
1461 synthesize a certain metabolite essential for the organism, usually in response to an
1462 abundance of said compound in the environment

1463 **Microsite** - a clearly delineated space within an environment with unique conditions or features
1464 in which specific microbial processes can occur.

1465 **Mixotrophic** – deriving carbon and energy from a mix of different sources, typically a
1466 combination of inorganic and organic compounds
1467 **Nanowire** – proteinaceous appendage produced by microbes, particularly bacteria, that is
1468 electrically conductive
1469 **Nucleation** - the process by which nuclei are formed in solution
1470 **Oriental freedom** - the absence of any physical restrictions to the movement and
1471 arrangement of a compound
1472 **Passivated** - a surface that is unreactive owing to alteration or from the formation of a thin inert
1473 coating
1474 **Photochemical lability** - the tendency of a compound to undergo a chemical reaction when
1475 exposed to light
1476 **Phototrophic** - ability to capture photons as energy source for the synthesis of organic
1477 compounds containing reduced carbon
1478 **Poorly crystalline** - an operational term to distinguish crystalline structures with short range
1479 order from others that exhibit order over longer distances
1480 **Reactive oxygen species** - ROS are short-lived oxygen-bearing molecules with half-lives that
1481 range from fractions of seconds to days, including hydrogen peroxide (H₂O₂), superoxide
1482 (O₂^{•-}/HO₂), hydroxyl radical (HO[•]), singlet oxygen (¹O₂), and carbonate radical (CO₃^{•-}).
1483 **Ripening** – physical and/or structural alteration of a mineral to obtain a lower surface free
1484 energy and more energetically favorable state
1485 **unsaturated soil** - a (soil) pore system that is only partially filled with water is unsaturated; a
1486 pore system entirely filled with water is considered saturated.
1487 **Short-range ordered** - the regular and predictable arrangement of atoms over a very short
1488 distance; in crystals, order does not persist over distances of more than a few nanometers
1489 and often extends over the distance of just a few bond lengths; Short range ordered
1490 minerals are often also referred to as poorly crystalline minerals.
1491 **Solution** - a homogeneous phase that results from the mixing of two (or more) phases
1492 **Steric constraints** - factors or effects that either prevent the adoption of a certain spatial
1493 orientation that would be required for the reaction to proceed unhindered
1494 **Steric enhancement** - factors or effects that facilitate the adoption of a certain spatial orientation
1495 that would be required for the reaction to proceed unhindered
1496 **Xenobiotic compound** - a substance that is foreign to a given natural environment or ecosystem;
1497 usually means that organisms in the system lack adaptations for the metabolic processing
1498 of a xenobiotic compound

1499

1500 **Table of contents summary**

1501 Minerals and organic matter interact in soils and sediments, impacting biogeochemical
1502 cycling and ecosystem functioning. This Review describes the major and emerging
1503 environmental mineral-organic interactions observed, and their implications for organic matter
1504 persistence.

1505

1506

1507

1508

1509