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# Dynamic interactions at the mineral-organic matter interface

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**Abstract**

Minerals are widely assumed to protect organic matter (OM) from degradation in the environment, promoting the persistence of carbon in soil and sediments. In this Review, we describe the mechanisms and processes operating at the mineral-organic interface as they relate to OM transformation dynamics. A broad set of interactions occur, with minerals adsorbing organic compounds to their surfaces and/or acting as catalysts for organic reactions. Minerals can serve as redox partners for OM through direct electron transfer or by generating reactive oxygen species, which then oxidize OM. Finally, the compartmentalization of soil and sediment by minerals creates unique microsites that host diverse microbial communities. Acknowledgement of this multiplicity of interactions suggests 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 sediments<sup>1</sup>) 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<sup>2,3</sup>, prompting early suggestions that this association is critical for soil fertility and, by extension, is "vital to life"<sup>4</sup>. When toxic organic chemicals were found to be accumulating in the biosphere<sup>5</sup>, mineral phases were investigated for their ability to break down organic contaminants in the environment<sup>6-8</sup>. More recently, interest has turned towards using soils and sediments as repositories for excess atmospheric carbon<sup>9,10</sup>, resulting in intensive research into the mechanisms determining the formation, strength, and durability of mineral-OM associations<sup>10-13</sup>. These latter research efforts have confirmed that minerals can protect OM from degradation. However, observed correlations between individual predictor values such as clay content<sup>14</sup> or abundance of poorly **crystalline [G]** minerals<sup>15</sup> 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 agglomerations<sup>16</sup>. Biotic and abiotic processes organise the resulting microfabric into a porous, internally-structured medium<sup>17</sup>. Second, minerals generally dominate over OM in soils and sediments in terms of mass proportions, with organic materials (including living organisms) rarely contributing more than single-digit percentages to total mass<sup>18-20</sup> (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 time<sup>21</sup>. Third, liquid water is the most abundant phase in pore systems<sup>22</sup>, enabling geochemical and biological processes<sup>23,24</sup>. 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 system<sup>25</sup>.

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<sup>26,27</sup> and by chemotrophic  
109 microorganisms<sup>28</sup>, 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 proportions<sup>29</sup>. Primary  
111 production in the oceans creates mostly lipids, proteinaceous materials, and carbohydrates other  
112 than cellulose<sup>30</sup>, whereas lignin and cellulose together account for around half of primary  
113 production on land<sup>18</sup>.

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)<sup>30</sup>, 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 products<sup>3</sup>. 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 diffusion<sup>31</sup> 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]**<sup>32,33</sup>. 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<sup>22,34</sup> (**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 mechanisms<sup>35-37</sup>. Mineral surface reactivity is also driven by surface  
141 topography<sup>38</sup>, 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 complexation<sup>39-42</sup>, 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 limitation<sup>43-46</sup>.

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  
155<sup>47-49</sup>. 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<sup>50, 51</sup>.  
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 particles<sup>52</sup>.

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 atoms<sup>53</sup>. 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 chemistry<sup>34</sup>. 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 chemistry<sup>47</sup>. For example, poorly-crystalline ferrihydrite is often the initial product of  
169 Fe<sup>III</sup> 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 energy<sup>48</sup>.

## 172 173 **[H1] Adsorption**

174 Adsorption has long stood as an explanation for the spatiotemporal preservation of  
175 organic matter in soils and sediments<sup>54</sup>. However, mounting recognition of the dynamism  
176 occurring at the mineral-organic interface, buoyed by diversifying intersectionality in expertise

177 and analytical techniques<sup>14,55-58</sup>, 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 diversity<sup>59-61</sup>. Even among small organic compounds, this variety  
187 enables adsorption through a combination of multiple anchoring points and mechanisms<sup>62,63</sup>  
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<sup>64,65</sup>. 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 cations<sup>66</sup>.  
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<sup>3,67</sup> (**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<sup>68,69,70</sup> (**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 ions<sup>71</sup>, 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<sup>72,73</sup>. 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 spectroscopy<sup>74</sup>, temporal partitioning of organic ligands from solution onto the mineral surface  
218<sup>75,76</sup>, and detection of uneven structures at the mineral surface<sup>77-79</sup>.

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  
221<sup>80</sup>. 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]**<sup>45,65,81</sup>. Most kinetic datasets regarding OM sorption on soils and sediments come  
225 from studies conducted on **xenobiotic compounds [G]**<sup>65</sup>. 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<sup>82,83</sup>. 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 cations<sup>82-85</sup>, where adsorption rates are faster under conditions that promote  
232 weaker adsorption affinity, such as in alkaline solutions<sup>83</sup>. Notably, newly adsorbed organics  
233 might compete with and actually induce the release of previously adsorbed organic compounds<sup>86</sup>,  
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]**<sup>87,88</sup>. 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 groups<sup>89-91</sup>.

253 Adsorption potentially impacts not just the adsorbed OM, but also the minerals: adsorption  
254 invariably lowers interfacial energy<sup>92</sup>, 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)<sup>93-96</sup>. 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<sup>12,58,97,98</sup>. 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<sup>58,99</sup>. Mineral transformation and dissolution could also mediate release of  
270 adsorbed compounds into the aqueous phase. Anoxic events and biotic reductive dissolution of  
271 oxides<sup>100-104</sup>, acidity-driven deprotonation in low-Fe systems<sup>105</sup>, and secretion of root exudates  
272<sup>106,107</sup> 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 systems<sup>108-111</sup>, 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 continuous<sup>112</sup>. Besides  
280 microbial degradation and consumption after direct desorption, displacement by biotic exudates  
281 can contribute to the decomposition of previously-adsorbed molecules<sup>113</sup>, supported by  
282 observations that a substantial proportion of mineral-adsorbed organic matter is microbial in  
283 origin<sup>114-116</sup>. 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<sup>117,118</sup>, 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 surfaces<sup>119</sup>, 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 topography<sup>38</sup>. 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 functionalities<sup>120</sup>). 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<sup>121,122</sup>.

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  $\pi$ -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 O<sub>2</sub> and transition metals<sup>123,124</sup>. Overall, the catalytic activity of Class I minerals is expected to be  
313 low with slow kinetics<sup>123,125</sup>.

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 O<sub>2</sub><sup>123,126,127</sup>.

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<sup>123,127-129</sup>. 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**<sup>129-131</sup>).

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<sup>123,132,133</sup>. 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<sup>74,134,135</sup>, 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<sup>133,136,137</sup>. 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 site<sup>38</sup> (**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<sup>38,85,130</sup>. 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.

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### 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 diversity<sup>138</sup>. 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 enzymes<sup>139</sup> or conductive **nanowires [G]**<sup>140,141</sup> 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 mineral<sup>142</sup>. 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 phyllosilicates<sup>123</sup>. 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 compounds<sup>143</sup>, including humic acids, phenols, anilines, low  
374 molecular weight organic acids (such as oxalate, pyruvate, citrate)<sup>7,144,145</sup>, and more recently  
375 proteins<sup>128,146</sup>. 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 molecule<sup>123</sup>.

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<sup>123,147</sup>. Despite typically lower adsorptive  
381 capacities, Mn oxides are stronger oxidants than Fe oxides, in large part owing to differences in  
382 redox potential<sup>123,148,149</sup>. 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 transformations<sup>143</sup>. 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  $\text{pH}_{\text{pzc}}$  of the oxide<sup>143</sup>.  
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 formation<sup>150</sup>, 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 loadings<sup>123</sup> and/or reaction products blocking reactive sites on the surface<sup>143</sup>.  
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<sup>113,149,151</sup>. In fact, the intimate and diverse  
400 association of OM with Mn oxides<sup>149,152</sup> leads to a continuum of reactions, including  
401 mineralization and polymerization within layers coating the oxide surface<sup>129</sup>. 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.

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## 407 **[H1] Reactive Oxygen Species**

408 Mineral-derived ROS<sup>153</sup>, particularly hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), superoxide ( $\text{O}_2^-/\text{HO}_2$ ),  
409 and hydroxyl radical ( $\text{HO}^\bullet$ ), represent likely important but currently underappreciated players in  
410 the transformation of soil and sediment organic matter<sup>154</sup>. Among various biological and  
411 (photo)chemical processes<sup>155,156</sup>, common soil and sediment minerals have also demonstrated  
412 the ability to produce ROS, including  $\text{H}_2\text{O}_2$  and  $\text{HO}^\bullet$ <sup>157-161</sup>. These ROS-producing minerals  
413 include primary silicates (such as plagioclase), oxides, sulfides, and clays, with the titanium  
414 dioxide phases rutile and anatase ( $\alpha$ - and  $\beta$ - $\text{TiO}_2$ ), iron oxide hematite ( $\alpha$ - $\text{Fe}_2\text{O}_3$ ), and Fe(II)-  
415 bearing clays such as biotite and chlorite having the highest ROS yields observed to date<sup>157,161</sup>.

416 Minerals contribute to ROS production via water and O<sub>2</sub> reaction at defect sites or with mineral-  
417 hosted or adsorbed Fe(II), and via photochemical electron transfer<sup>158,161,162</sup> (**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 oxygen<sup>158</sup> (**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<sup>161,163</sup>.  
426 Formation of ROS including O<sub>2</sub><sup>•-</sup> and HO<sup>•</sup> has been linked to the oxidation of aqueous Fe(II)  
427 emanating from subsurface marine<sup>164</sup> and lake sediments<sup>165</sup>. Indeed, the oxygenation of reduced  
428 soils, sediments, and waters results in a cascade of ROS pathways, including initial formation of  
429 both O<sub>2</sub><sup>•-</sup> and H<sub>2</sub>O<sub>2</sub>, ensuing dismutation of O<sub>2</sub><sup>•-</sup> to H<sub>2</sub>O<sub>2</sub>, and ultimately formation of HO<sup>•</sup> via  
430 reaction of aqueous Fe(II) and H<sub>2</sub>O<sub>2</sub> (Fenton reaction)<sup>166</sup>. In sunlit surface environments,  
431 photochemical reactions at oxide surfaces have also been found to play an important role in ROS  
432 (particularly O<sub>2</sub><sup>•-</sup> and H<sub>2</sub>O<sub>2</sub>) formation, including in both desiccated and wet desert soils<sup>159</sup>.  
433 Production of ROS in soils pre-washed to remove photosensitizers such as nitrate point to direct  
434 mineral-induced ROS generation upon irradiation<sup>159</sup>. Superoxide and peroxides can be stabilized  
435 within desiccated soils via complexation to metal oxide surfaces<sup>159</sup>. 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 proteins<sup>167</sup>). 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 CO<sub>2</sub>, 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 O<sub>2</sub><sup>•-</sup> in marine DOM, the reaction of which could lead to a catalytic cycle regenerating  
446 the original reactant and forming H<sub>2</sub>O<sub>2</sub><sup>168</sup>. Hydroxyl radical is a particularly unselective and  
447 strong oxidant<sup>169</sup>, having high reaction rates with DOM (10<sup>8</sup> M C<sup>-1</sup> s<sup>-1</sup>)<sup>170</sup> and the ability to  
448 oxidize carbon compounds within the DOM pool that are otherwise difficult to photo- or  
449 biodegrade<sup>171,172</sup>.

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 CO<sub>2</sub> produced from  
454 <sup>•</sup>OH (109 μmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>) in Arctic soils were found to be on the same order of magnitude as  
455 bacterial mineralization of DOM in surface waters<sup>165</sup>. Similarly, DOM (including coloured

456 DOM) is a predominant sink of  $O_2^{\cdot-}$  within several marine systems<sup>173,174</sup>, and  
457 photodecomposition of DOM in lake waters has been linked to ROS formation<sup>175</sup>. 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 soils<sup>154</sup>.  
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<sup>57,176</sup>. 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 OM<sup>57</sup>. 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 matter<sup>177</sup>. Oxidation of tetracycline to  $CO_2$  was also recently linked to  $\cdot OH$   
468 formation upon oxidation of sediments in lab incubations<sup>161</sup>. Lastly, soil organic matter  
469 oxidation and decomposition in the absence of enzymatic activity (inactivation via autoclaving)  
470 within soils implicated mineral-derived ROS<sup>56,178</sup>; yet, the mechanism at play was not  
471 elucidated.

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#### 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 connected<sup>179</sup> (**Fig. 8**). Pore connectivity, morphology, and size distribution at the  
479 microsite scale either enhance or restrict microbial access to OM<sup>180</sup>. 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<sup>171,172</sup>. 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<sup>173,174</sup> (**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<sup>16,199,200</sup>. 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 inhabitants<sup>175</sup>,  
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 another<sup>201</sup>. However, OM is  
497 heterogeneously distributed at scales that are relevant for microbial decomposition<sup>202</sup>, as are  
498 microbial communities themselves<sup>203</sup>. This distribution results in a patchwork of cold and  
499 hotspots of microbial activity<sup>204</sup>, 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 O<sub>2</sub> limitations<sup>132</sup>. 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 distributed<sup>132</sup>.

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<sup>176,177</sup>. Taxa that are better adapted to the prevalent microsite  
509 conditions, such as through the capacity to use electron acceptors other than O<sub>2</sub> in anoxic  
510 conditions<sup>178</sup>, 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 drift<sup>179</sup>. 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 microsites<sup>185</sup>. The sphere of influence of minerals has been termed the “mineralosphere”<sup>186</sup>. For  
521 example, different types of minerals select different microbial communities<sup>187-189</sup>, 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<sup>188,190</sup>. 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 donor<sup>191</sup>, from differences in surface charge, area, or  
529 topography<sup>192</sup>. 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<sup>193,194</sup> and  
532 depending on the microorganism<sup>195,196</sup>. 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<sup>109,197,181</sup> particularly in agroecosystems or in

536 contexts where microbial communities flourish<sup>182,183</sup>. Furthermore, the extent to which  
537 microbially processed organic matter associates with minerals could even depend upon the  
538 composition of the microbial communities<sup>198</sup>. 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 processes<sup>184</sup>. 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<sup>184,185</sup>. 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.

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## 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.

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## 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<sup>179,180</sup>. Such metabolic dependency develops only if  
582 communities remain spatially co-located long enough for coevolution to occur<sup>181,182</sup>. Metabolic  
583 dependency has been shown to evolve in experimental populations in 1000 to 2000 generations  
584<sup>186</sup>. 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 content<sup>183</sup>, 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 structures<sup>183</sup>, probably owing to electrostatic interactions between the variable charged minerals  
589<sup>184</sup>. 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<sup>187,188</sup>, 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 metagenomics<sup>189</sup>, at appropriate scales, in soils with different mineralogies.

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

595 Decomposition of adsorbed OM is typically substantially slower than decomposition of the  
596 same type of OM in a freely suspended or dissolved state<sup>190</sup>, leading to the notion of ‘sorptive  
597 protection’ of OM. However, desorption can be facilitated by changes in pH, electron  
598 availability, or by modifications to sorbent surfaces<sup>105</sup>. Indeed, evidence is mounting that plants  
599 are equipped with tools to achieve this exact purpose, such as the exudation of organic  
600 compounds designed to release bound organic matter from mineral surfaces<sup>191</sup> and to adjust  
601 patterns of microbial community composition for optimal functionality<sup>192</sup>. With these  
602 developments in mind, we suggest that sorptive protection should be re-evaluated as an  
603 explanation for organic matter persistence, especially in systems inhabited by plant roots.

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

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

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 occasions<sup>86</sup>, presumably because of the difficulty  
622 in unequivocally attributing resulting observations to certain mechanisms when the sorbent is  
623 complex<sup>195</sup>.

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## 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 above<sup>196</sup>. 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 systems<sup>197-199</sup>. 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<sup>200,201 202,203</sup>.

638 In the presence of OM, the stability of the mineral framework is further stabilized<sup>196</sup>. 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<sup>16,204-206</sup> (although patchy distributions can partly reflect microbial lifestyles  
644<sup>207,208</sup>, 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<sup>135,209</sup>), with observations of  
646 preferential uptake of OM on rough surfaces or in colloidal aggregates<sup>79,207</sup>, and with the  
647 tendency of OM to induce lasting mineral aggregation<sup>94,96,210</sup>. It also is consistent with the  
648 hydrophobic character of the siloxane surface of phyllosilicate minerals in the absence of surface  
649 charge<sup>211,212</sup> or even, in the case of smectite, in uncharged surface patches resulting from the  
650 non-uniform distribution of isomorphous substitutions<sup>62,67</sup>. 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 OM<sup>76</sup>. 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 films<sup>213-215</sup> and  
655 descriptions of the impacts of biosurfactants on microorganism distribution, carbon cycling, and  
656 bioremediation<sup>45,216,217</sup>.

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## [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<sup>218,219</sup> and in prebiotic chemistry<sup>220</sup>. The fundamental ability of minerals to modify organic compounds has been confirmed in laboratory settings<sup>220-222</sup>, 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 substrates<sup>223</sup>. 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<sup>165,170,224</sup>, 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 O<sub>2</sub><sup>•-</sup> and H<sub>2</sub>O<sub>2</sub> 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 ocean<sup>225</sup>, 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.

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### **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**

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### **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 ambiguous<sup>95</sup>. Data based on Refs<sup>34,66,94,96,226-229</sup>.

**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 regions<sup>33</sup>. Part X is adapted from ref<sup>33</sup>, 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<sup>-</sup>-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 O<sub>2</sub>; 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<sup>230,231</sup>. 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 community<sup>232</sup> (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  $\mu$ 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 (H<sub>2</sub>O<sub>2</sub>), superoxide  
1482 (O<sub>2</sub><sup>•-</sup>/HO<sub>2</sub>), hydroxyl radical (HO<sup>•</sup>), singlet oxygen (<sup>1</sup>O<sub>2</sub>), and carbonate radical (CO<sub>3</sub><sup>•-</sup>).  
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.

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