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# Molecular-level understanding of metal ion retention in clay-rich materials

Xiandong Liu<sup>1†</sup>, Christophe Tournassat<sup>2,3†</sup>, Sylvain Grangeon<sup>4</sup>, Andrey G. Kalinichev<sup>5</sup>,  
Yoshio Takahashi<sup>6</sup>, Maria Marques Fernandes<sup>7</sup>

1. State Key Laboratory for Mineral Deposits Research and School of Earth Sciences and Engineering,  
Nanjing University, Nanjing, China

2. Institut des Sciences de la Terre d'Orléans, Université d'Orléans–CNRS–BRGM, Orléans, France

3. Earth and Environmental Sciences Area, Lawrence Berkeley National Laboratory, Berkeley, CA, USA

4. BRGM, Orléans, France

5. Laboratoire de physique subatomique et technologies associées , École nationale supérieure Mines-  
Télécom Atlantique Bretagne Pays de la Loire , Nantes, France

6. Department of Earth and Planetary Science, The University of Tokyo, Tokyo, Japan

7. Laboratory for Waste Management, Paul Scherrer Institute, Villigen, Switzerland

† Corresponding author: [xiandongliu@nju.edu.cn](mailto:xiandongliu@nju.edu.cn); [christophe.tournassat@univ-orleans.fr](mailto:christophe.tournassat@univ-orleans.fr).

## 18 Abstract

19 Clay minerals retain or adsorb metal ions in the Earth's critical zone. Rocks, sediments and  
20 soils rich in clay minerals can concentrate rare earth elements (REEs) in ion-adsorption type  
21 deposits and are similarly effective at metallic contaminant remediation. However, the  
22 molecular-scale chemical and physical mechanisms of metal retention remain only partly  
23 understood. In this Review, we describe the nature, location and energy requirements of metal  
24 retention at clay mineral surfaces. Retention originates mainly from electrostatic interactions  
25 during cation exchange at low pH and chemical bonding in surface complexation and  
26 precipitation at neutral and high pH. Surface complexation induces surface redox reactions and  
27 precipitation mechanisms including neof ormation of clay minerals layered structure. In ion-  
28 adsorption type deposits, outer-sphere adsorption is the major retention mechanism of REE  
29 ions. By contrast, the use of clay minerals in pollution control relies on various mechanisms  
30 that can coexist, including cation exchange, surface complexation and nucleation-growth. To  
31 more effectively leverage clay mineral-metal interactions in resource recovery and contaminant  
32 remediation, complex mechanisms such as surface precipitation and redox reactions must be  
33 better understood; for instance, by utilizing advances in quantum mechanical calculations,  
34 close combination between synchrotron and simulation techniques, and upscaling of  
35 molecular-level information in macroscopic thermokinetic predictive models.

36

## 37 [H1] Introduction

38 Clay minerals [G] play a major role in scavenging metal ions [G]<sup>1</sup> in Earth's critical zone [G].  
39 Metal immobilization processes are key aspects of natural biogeochemical cycles in surficial  
40 environments, as clay minerals can control the bioavailability of metal nutrients K<sup>+</sup> and Ca<sup>2+</sup>  
41 in temperate-zone soils<sup>2</sup>. In addition, the adsorptive properties of clay-rich materials [G] make  
42 them of economic interest, as they are crucial to concentrating rare earth elements (REEs) from  
43 weathered granites onto clay surfaces during the formation of ion-adsorption type deposits<sup>3</sup>.  
44 Clay-rich materials are also of growing industrial interest owing to their effective metal  
45 retention capacity and their cheap, widespread availability. For example, clay minerals are  
46 commonly used in pollution control and remediation applications, including as containment  
47 barriers in radioactive waste repository concepts<sup>4</sup>, as liner materials in landfills<sup>5</sup>, or as  
48 remediation agents for heavy metal-polluted soils<sup>6</sup>. The interaction of clay minerals and metal  
49 ions is therefore critical to environmental, industrial and economic applications. However, the  
50 complex and diverse nature of clay minerals and their surfaces mean that the mechanisms of  
51 metal retention remain debated.

52 The distinctive interaction of clay minerals with metal ions stems from their surface properties,  
53 which result from their layered crystal structure (Box 1 and Figure 1)<sup>7</sup>. Individual clay layers  
54 are formed of an octahedral sheet [G] sandwiched between two tetrahedral sheets [G], often

55 called **2:1 layers [G]** (Figure 1). When stacked together, these layers create inner, outer and  
56 edge surfaces onto which metal ions can be adsorbed. However, each layer can have varying  
57 compositions, meaning OH groups and cation exchange sites have a range of surface positions  
58 (Box 1). Various OH groups exist (such as those coordinated to Si, Al, Mg, Fe) and they are  
59 responsible for the chemical bonding of metal ions. This variety of surface positions, surface  
60 groups and layer compositions lead to a diversity of retention processes, such as cation  
61 exchange, surface complexation, structural incorporation in clay layers or through mineral  
62 growth by **epitaxial nucleation [G]**<sup>8</sup>.

63 Bulk measurements of metal retention in batch experiments do not always provide enough  
64 information to predict the fate of metal ions in practical or real-life applications in clay-rich  
65 media. Extrapolating the results of batch adsorption experiments (with timescales from hours  
66 to days) directly to radionuclide retention predictions in radioactive waste disposal in a  
67 geological formation (with timescales over hundreds and thousands of years) can lead to  
68 erroneous conclusions because the various retention processes do not have the same kinetic  
69 and reversibility characteristics. Consequently, molecular-level knowledge is crucial for  
70 understanding the physical-chemical mechanisms underlying experimental and field  
71 observations, and for developing predictive models for these environments<sup>6,9</sup>.

72 The emergence of several experimental techniques (such as **neutron diffraction**<sup>10</sup> **[G]**,  
73 **synchrotron X-ray reflectivity (XRR)**<sup>11</sup> **[G]** and **X-ray absorption spectroscopy (XAS)** **[G]**<sup>12,13</sup>)  
74 in the late 1980s, accompanied by the rapid development of computational modelling  
75 approaches (quantum mechanical, classical and multiscale)<sup>14</sup>, has provided the necessary tools  
76 for exploring clay mineral-metal ion interactions over different time scales. Because of the high  
77 surface heterogeneity of clay minerals, some of the basic properties controlling metal ion  
78 retention can be quantified only with the combination of advanced experimental and molecular  
79 simulation methods. Multiscale simulation methods in particular are a powerful tool for  
80 providing parameters that are impossible or very difficult for experiments to achieve, such as  
81 predicting the behavior of metal ions in clay-rich media over geological timescales<sup>15</sup>.

82 In this Review, we discuss advances in understanding metal ion-clay mineral interactions at  
83 the molecular scale. We first explore the macroscopic factors that affect the adsorptive  
84 properties of clay minerals, such as the composition and pH of the aqueous solution. Next,  
85 immobilization processes are described separately for basal and edge surfaces because they  
86 have fundamental differences in bonding mechanisms of with metal ions. We then review the  
87 importance of metal retention processes in ion adsorption REE ore formation and pollution  
88 control engineering, and we highlight possible future research directions in the molecular-level  
89 view of clay mineral-metal ion interactions for fundamental and applied research.

90

## 91 [H1] Macroscopic environmental factors

92 Under favourable conditions, 1 kg of smectite [G] such as montmorillonite can sorb up to 100  
93 g of metal cations, or equivalently about 1 mol of a monovalent metal cation. This capacity  
94 depends, of course, on local environmental conditions. Factors most impacting adsorption  
95 processes on clay mineral surfaces are pH and ionic strength. Depending on the chemical  
96 properties of the metal ions of interest, either one or both of these parameters can influence its  
97 overall retention (Box 2). For example, adsorption of alkaline and alkaline-earth metal ions in  
98 their cationic form such as rubidium ( $\text{Rb}^+$ )<sup>ref 16–19</sup>, cesium ( $\text{Cs}^+$ )<sup>ref 20,21</sup>, strontium ( $\text{Sr}^{2+}$ )<sup>ref 22,23</sup>,  
99 and barium ( $\text{Ba}^{2+}$ )<sup>ref 19</sup> is little impacted by pH, and strongly depends on ionic strength, while  
100 adsorption of more easily hydrolysed transition metals such as nickel ( $\text{Ni}^{2+}$ )<sup>ref 24,25</sup> and cobalt  
101 ( $\text{Co}^{2+}$ )<sup>ref 26–28</sup>, REEs, such as europium ( $\text{Eu}^{3+}$ )<sup>ref 26,29</sup>, and actinides<sup>ref 30</sup>, such as uranium ( $\text{UO}_2^{2+}$ )  
102<sup>ref 29</sup>, is affected by both parameters. Because adsorption can be a competitive process at surface  
103 sites, the chemical composition of the aqueous solution is also an important factor that  
104 contributes to the effectiveness of retention<sup>31–33</sup>. Also, the presence of dissolved and adsorbed  
105 organic molecules can be beneficial or detrimental to metal ions adsorption on clay mineral  
106 surfaces<sup>22,34</sup>.

107 Macroscopic quantification of cations retention on smectite and illite [G] surfaces amounts for  
108 countless studies in the literature (see references in<sup>35</sup>) whereas studies concerning the retention  
109 of anionic species are more limited. Repulsive electrostatic interactions are responsible for  
110 anions repelling from the surface, and thus many anionic element do not sorb substantially on  
111 illite and montmorillonite surfaces, such as iodide ( $\text{I}^-$ ), pertechnetate ( $\text{TcO}_4^-$ ), and selenate  
112 ( $\text{SeO}_4^{2-}$ )<sup>ref 36,37</sup>. Some anions, including metalloids, sorb weakly, but notably, such as selenite  
113 ( $\text{SeO}_3^{2-}$ )<sup>ref 36,38–41</sup>, arsenate ( $\text{AsO}_4^{3-}$ )<sup>ref 42–45</sup>, arsenite ( $\text{AsO}_3^{3-}$ ), antimony (in the forms  $\text{Sb}(\text{OH})_3$   
114 or  $\text{Sb}(\text{OH})_6^-$ )<sup>ref 46</sup>, and molybdate ( $\text{MoO}_4^{2-}$ )<sup>ref 47</sup>. Adsorption dependences on environmental  
115 parameters are also different, often opposite, for anions compared to cations. For example,  
116  $\text{SeO}_3^{2-}$  adsorption decreases with increasing pH, but is independent of ionic strength. For  
117  $\text{AsO}_4^{3-}$ , adsorption on illite and montmorillonite increases up to pH 5-6 and then decreases at  
118 higher pH. Because adsorption of anions is much less efficient than of cations, clay materials  
119 are not often studied as promising materials for applications relying on anion retention  
120 properties such as pollution control engineering. This statement must be however reconsidered  
121 if modifications of clay mineral surface properties are obtained through interactions with  
122 organic molecules. So-called organo-clay materials have proven to be very effective in  
123 removing oxyanions such as hexavalent chromium ( $\text{CrO}_4^{2-}$ )<sup>ref 48</sup>. This Review is focused on  
124 interactions of metal ions with unmodified clay materials. Consequently, it is also mostly  
125 focused on interactions with metal cations.

126 The reasons for these differences among cations, as well as between cations and anions, were  
127 early ascribed to differences in interaction mechanisms on basal and edge surfaces with two  
128 main mechanisms<sup>49</sup> (Figure 2). The first one is **inner-sphere complex [G]** reactions, in which  
129 metal ions compete with protons ( $\text{H}^+$ ) for the adsorption sites on edge surfaces, and the second  
130 is cation exchange reaction, in which metal ions replace layer charge compensating cations on

131 basal surfaces through, mostly, **outer-sphere complexes [G]**. Anions can also bind through  
132 ligand exchange [G] to form inner-sphere complex and in that case anions compete with edge  
133 hydroxyl and water surface groups. Because of the non-linearity of cation adsorption isotherms,  
134 it was soon necessary to subdivide edge surface complexation sites into two categories, the so-  
135 called strong and weak sites<sup>50</sup>, which made it possible to account for the higher affinity of some  
136 metal ions for the surface at low equilibrium concentration. Competitive adsorption  
137 experiments<sup>33</sup> evidenced the need to define sub-categories of strong sites, meaning sites that  
138 are least abundant but most energetically favourable to retention, for which some metal ions  
139 do compete and some others do not.

140 Macroscopic observations of metal ion retention on clay mineral surfaces can be understood in  
141 principle by considering two main types of surface complexes on basal and edge surfaces. The  
142 rationale behind most of these macroscopic modelling concepts remains very empirical, but  
143 can be verified by progresses made in the molecular level view of the adsorption processes.

## 144 **[H1] Molecular-level interaction mechanisms**

145 Multiscale experimental and modeling approaches rooted in molecular level information (Box  
146 3) are necessary to unravel the relative contributions of both the diverse array of metal ion  
147 retention mechanisms and the associated reactive sites on clay surfaces. Basal surfaces are  
148 terminated by saturated oxygen atoms whereas edge surfaces exhibit broken chemical bonds,  
149 leading thus in differences in reactivity between these two types of surfaces and metal ions.  
150 Hence, these interactions are discussed separately, and the influence of environmental  
151 parameters such as hydration state and the presence of organic matter are then introduced.

## 152 **[H2] Basal surfaces**

153 At basal surfaces, metal ions cannot form easily covalent bonding with surface atoms, which  
154 are already fully coordinated. Species adsorbed at basal surfaces are thus bound through weak  
155 long-range interactions such as electrostatics, which are the most effective for cations  
156 interacting with the negative potential created by the permanent negative charge of the layer.  
157 The adsorption state of cations largely depends on the Gibbs free energy of dehydration, that  
158 is, the cost in free energy of partial dehydration (such as, losing water ligand to form direct  
159 contact with the surface) makes the formation of inner-sphere complexes unfavourable.  
160 Therefore, most cations such as  $\text{Li}^+$ ,  $\text{Na}^+$  and those of higher valences form outer-sphere  
161 complexes while  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  form inner-sphere complexes due to lower dehydration free  
162 energy. The inner-sphere complexing sites include the positions above the center of ditrigonal  
163 cavity and above tetrahedron<sup>51-53</sup>. Adsorbed cations compete with other cations present in  
164 solution, hence the dependence of adsorption on ionic strength and on background electrolyte  
165 composition<sup>54</sup>.

166 The cation exchange thermodynamic theory makes it possible to conduct predictive  
167 quantifications without the need for molecular level understanding<sup>55,56</sup>. It has however several

168 drawbacks including the difficulty to derive true thermodynamic equilibrium constants and  
169 activity coefficient of exchanged species<sup>57</sup>. This problem often leaves exchange model  
170 parameters to the status of conditional constants that should not be applied without caution to  
171 conditions too different from the corresponding experimental conditions<sup>58</sup>.

172 Cation exchange models can be enriched with the consideration of multiple sites present on a  
173 same clay mineral particle, and having contrasting affinities for metal ions adsorption. Cs<sup>+</sup>  
174 exchange on illite surfaces represent certainly the best example for this need of a multiple sites  
175 description<sup>20,59,60</sup>. Cs<sup>+</sup> affinity for illite surface decreases by several order of magnitude with  
176 the increase of aqueous Cs<sup>+</sup> equilibrium concentration. The presence of at least three types of  
177 exchange sites is necessary to explain this behaviour. The least abundant site must have also  
178 the highest affinity for Cs<sup>+</sup> and is ascribed to the presence of so-called frayed edge sites<sup>60</sup>,  
179 which correspond to adsorption sites on basal surfaces neighbouring the edge of illite particles<sup>61</sup>.  
180 The two other sites have been ascribed to illite basal surfaces as the sum of their capacities  
181 matches illite cation exchange capacity, but the reason for their contrasted affinities for Cs<sup>+</sup>  
182 remains unclear<sup>60</sup>. This example illustrates the underlying complexity of adsorption processes  
183 on basal surfaces.

184 Quantitative techniques in numerical simulation are now available to evaluate the profiles of  
185 cation adsorption free energy as functions of their distance from the basal clay mineral  
186 surfaces<sup>62</sup>, and these techniques can take into account the effects of layer charge distribution  
187 on these surfaces and distinguish between several specific adsorption sites<sup>51</sup>. Molecular  
188 simulations coupled to X-ray reflectivity and resonant anomalous X-ray reflectivity  
189 measurements provided evidence of the importance of interfacial water structure on the affinity  
190 of cations such as Rb<sup>+</sup> and Cs<sup>+</sup> for outer basal surfaces of phyllosilicates<sup>51,63,64</sup>. Differences in  
191 the structure of water in the hydration shell lead to multiple adsorption positions for a single  
192 cation at a single surface, which could be a reason for the observed changes in macroscopic  
193 affinities as a function of cation concentration<sup>59,65–67</sup>.

194 In interlayer domains of **swelling [G]** clay minerals, cations and their hydration sphere interact  
195 with both bordering inner basal surfaces<sup>68</sup>. The layer-to-layer distance depends on the hydration  
196 of interlayer cations and on the external pressure applied to the clay-rich material<sup>69</sup>. Conversely,  
197 experimental values of montmorillonite interlayer affinity for Cs<sup>+</sup> increase with the pressure  
198 applied to the system, and hence with the change of interlayer occupancy from three water  
199 layers to two and one water layer(s)<sup>70</sup>. According to molecular dynamics simulations and  
200 microcalorimetric experiments, the main driving force for Cs<sup>+</sup> adsorption on clay mineral  
201 surface is not the a priori energetically favourable Cs<sup>+</sup>-clay mineral interaction, but the relative  
202 hydrophobicity of Cs<sup>+</sup> compared to its cationic competitors for the surface<sup>51,52,64,71,72</sup>. This  
203 molecular level information should help to build advanced cation exchange models that  
204 consider several energy terms to describe properly metal ions adsorption as a function of usual  
205 parameters such as concentrations, but also as a function of temperature, pressure and related  
206 hydration state encountered in underground clay-rich geological settings.

207 Most of the classical atomistic simulations of hydrated cation interactions with basal clay  
208 mineral surfaces only include the effects of molecular and ionic polarizability in an implicit

209 way through the effective parameters of interatomic interactions<sup>73</sup>. However, more advanced  
210 models explicitly including the polarizability effects into calculations are also emerging<sup>74,75</sup>.

211 Beyond the possibility to better describe and quantify metal ions affinity for basal surfaces,  
212 simulations and experiments at the molecular level offer a unique capability to study the  
213 mobility of surface species as a function of their location. The standard view of adsorbed  
214 surface species immobilized in the Stern layer is contradicted by evidences from molecular  
215 dynamics simulations<sup>76-79</sup> and spectrometric measurements, such as nuclear magnetic  
216 resonance<sup>79</sup>, which show substantial in-plane diffusion of species adsorbed on basal surfaces.  
217 Growing macroscopic experimental evidences about this coupling is also made available and  
218 macroscopic modelling of diffusive transport of metal ions in clay-rich materials has evolved  
219 accordingly since the early ~2010s' to take these coupled adsorption/diffusion processes fully  
220 into account<sup>14,80-82</sup>, with important implications for the modelling of the performance of  
221 radioactive waste storage concepts in clay-rich geological formations<sup>83-85</sup>. Because of the  
222 highly coupled nature of these processes, molecular level information is necessary to decipher  
223 the relative contributions of the various types of adsorbed species in interlayer, Stern layer and  
224 in the diffuse layer<sup>86</sup>.

225 Because of the chemistry and structure of clay mineral layers, electrostatics is the dominating  
226 interaction at basal surface, making the formation of outer-sphere complex the major metal  
227 retention mechanism, except for cations having low dehydration free energy, which can be  
228 adsorbed as inner-sphere complexes. This apparent simplicity of interaction mechanism  
229 description is however hiding additional complexity arising from coupling with environmental  
230 parameters, such as pressure, or with other physical processes such as ion mobility.

## 231 **[H2] Edge surfaces**

232 Higher chemical reactivity leads to the higher diversity of interaction processes on edge  
233 surfaces. Surface complexation first occurs when edge groups gradually become available for  
234 complexing cations upon proton dissociation as pH increases. Further accumulation at higher  
235 pH can cause surface nucleation and crystal growth. In the meanwhile, interfacial electron  
236 transfer processes can participate in the interactions of redox-active metal ions with Fe-  
237 containing clay minerals.

## 238 **[H3] Surface complexation**

239 Clay minerals edge surface structure is responsible for a wide range of possible adsorption sites  
240 and processes, with adsorbates having the possibility to interact by surface complexation or  
241 ligand exchange with tetrahedral sites, octahedral sites or both, and by different binding modes  
242 such as mono- or multi-dentate surface complexes. Depending on the chemical nature of these  
243 sites (for example Al octahedra versus Mg or Fe octahedra), binding affinities with adsorbates  
244 can also vary. In addition, site coordination depends on the crystallographic plane of each edge,  
245 which adds up this complexity<sup>87-89</sup>. The corresponding diversity of site types provides a  
246 reasonable explanation to the necessity to consider many sub-categories of edge adsorption



247 sites in surface complexation models. However, it highlights also the necessity to better  
248 constrain the nature of the surface complexation sites to understand competition processes.

249 Spectrometric techniques, such as X-ray absorption fine structure (EXAFS) spectroscopy, and  
250 diffractometric techniques, such as high-energy diffractometric methods, and more specifically  
251 differential X-ray pair distribution function (d-PDF), provide molecular level information to  
252 unravel retention processes on clay mineral edges. For example, d-PDF measurements  
253 evidenced the binding mode of Sb(V) on montmorillonite to be a bidentate complex attached  
254 to the edges of the octahedral sheet<sup>90</sup>. While d-PDF can be used to decipher the crystallographic  
255 nature of surface complexation adsorption sites on clay minerals, some limitations of the  
256 technique prevent its general use in adsorption studies. These limitations include the needs of  
257 a high adsorbed concentration of the element of interest, and an a priori knowledge of the  
258 structure of clay mineral edges, which must remain unaffected during the experiment. Such  
259 limitations are partly circumvented by the use of EXAFS spectroscopy that allows determining  
260 and quantifying the local environment of adsorbed elements.

261 In experimental conditions identified as being favourable to surface complexation on strong  
262 sites Ni<sup>2+</sup> adsorbs only in octahedral coordination in plane with the octahedral sheet on  
263 montmorillonite edges<sup>91</sup>. Adsorbed Zn exhibit a similar local environmental on  
264 montmorillonite strong edge sites. In conditions favourable to adsorption on weak sites, Zn had  
265 a more disordered configuration, possibly related to the presence of multiple adsorption sites,  
266 all being out of the clay mineral octahedral plane<sup>92</sup> and possibly being bidentate complexes<sup>93</sup>.  
267 For the adsorption of lanthanides, such as Eu, on illite and montmorillonite edge surfaces.  
268 Time-resolved laser fluorescence and EXAFS spectroscopy indicate the formation of inner-  
269 sphere surface complexes at pH >5 for both clay minerals<sup>29,94,95, 192-194</sup>. Correspondingly,  
270 surface complexation of Eu, other lanthanides and trivalent actinides on illite and  
271 montmorillonite can be modelled successfully with the same surface complexation model  
272 approach as that used for transition metals<sup>27,29,96</sup>.

273 While diffractometric and spectrometric methods give insightful details about adsorption  
274 processes, they are often limited by the presence of multiple surface complexes that cannot be  
275 probed individually, and by the impossibility to distinguish a site configuration from another  
276 because of a lack of sensitivity of the method. This limitation can be overcome by coupling  
277 molecular level simulation predictions with diffractometric/spectrometric information. For  
278 example, the combination of FPMD simulations with EXAFS spectroscopy results made it  
279 possible to assign the outermost **dioctahedral [G]** vacancy of dioctahedral layers to strong sites  
280 for Zn<sup>2+</sup> and 1<sup>st</sup> row transition metals<sup>93,97,98</sup>, while other sites are related to weak sites, such as  
281 aluminol, silanol, apical oxygen and their combination<sup>97</sup> (see principle in Figure 3). Another  
282 interesting example is the complexation of uranyl on montmorillonite surfaces, for which  
283 different macroscopic modelling approaches yielded different interpretations about the binding  
284 mode and the sites available for this species<sup>99,100</sup>, while being equally good at predicting  
285 available macroscopic retention observations as well as spectroscopic results. A possible  
286 physical basis was later provided by molecular level simulations. While multiple bidentate  
287 complexes were predicted by static density functional theory (DFT) calculations<sup>101-103</sup>, first

288 principles molecular dynamics (FPMD) simulations showed that they have similar binding  
289 affinity and therefore can be treated with a single stability constant in a macroscopic surface  
290 complexation model<sup>104</sup>. This example highlights that the determination of adsorption sites in  
291 case of surface complexation, both from microscopic and macroscopic points of view, is an  
292 extremely complex task, which requires the coupled use of several experimental and  
293 computational physical and chemical methods to obtain reliable results (Figure 3).

294 This identification of surface adsorption sites is made even more complicated in systems  
295 resembling to natural conditions with the possible interactions of aqueous components and  
296 surfaces in ternary (or more) surface complexes. The uranium-carbonate-montmorillonite case  
297 is very informative in this respect. This system has been investigated using EXAFS  
298 spectroscopy by several teams, yielding different interpretations of uranium binding  
299 mechanisms<sup>100,105,106</sup>, with the reported presence<sup>105</sup> or absence<sup>100</sup> of ternary uranyl-carbonate-  
300 montmorillonite complexes for experiments conducted in similar conditions. Additional  
301 constraints provided by molecular level simulations of ternary complexes adsorption processes  
302 would certainly help to resolve this apparent inconsistency.

### 303 **[H3] Nucleation and growth**

304 At high pH values and in the presence of high concentrations of metal ions, surface complexes  
305 can serve as nucleation sites, thus promoting (co-)precipitation of metal ions. Epitaxial  
306 nucleation or growth has been found for the 1<sup>st</sup> row transition metal including Zn<sup>2+</sup> ref 107,108,  
307 Ni<sup>2+</sup> ref 109,110, Co<sup>2+</sup> ref 111 and Fe<sup>2+</sup> ref 112,113. The neoformed phases can be a phyllosilicate or a  
308 layered double hydroxide (LDH). LDH, similar to hydroxalcite, is made up of stacked  
309 octahedral layers, where the partial substitution of trivalent for divalent cations results in a  
310 positive layer charge, compensated by anions located in interlayer space. Because of structural  
311 similarities between the neoformed octahedral layer and the octahedral sheet of TOT layer, it  
312 is reasonable to assume that these phases nucleate and grow as a continuation of the edges  
313 (Figure 2). FPMD simulations<sup>114</sup> evidenced that upon complexation in vacancy, these elements  
314 hydrolyse in normal pH range and thus provide complexing sites for subsequent metal cations,  
315 eventually yielding epitaxial nucleation. In contrast, cations with larger ionic radii like Pb<sup>2+</sup>  
316 hardly hydrolyse on clay mineral surfaces, prohibiting the multinuclear complexation and  
317 nucleation. Phyllosilicates would form in presence of considerable amount of Si in solution, in  
318 laboratory as well as in natural systems<sup>12,108,115-117</sup>. In samples from Zn-clay ores, transmission  
319 electron microscopy evidence was found for epitaxial growth of Zn-smectite from clay mineral  
320 edges which played a templating role<sup>118</sup>. FPMD study suggested that for the formation of  
321 phyllosilicates, the synchronous pathway (that is Si and metal ions co-precipitate at the same  
322 time, path G to H in Figure 2) is favourable over the stepwise pathway (that is the phyllosilicate  
323 is formed via silicification of neoformed hydroxide, path I to J in Figure 2)<sup>114</sup>.

324 Actinides and lanthanides can also form secondary mineral phases<sup>94</sup>. Because of obviously  
325 larger ionic radii of f-elements, actinides and lanthanides cannot form phyllosilicate/hydroxide  
326 phase resembling the structure of clay minerals. In these cases, clay minerals might only  
327 provide complexing ligands, for example, in the formation of coffinite (U(IV)SiO<sub>4</sub>), but have

328 no templating effect. Although classified as REEs together with lanthanides and Y, Sc can be  
329 incorporated into octahedral sheets, forming Sc-rich smectite<sup>119</sup>.

### 330 [H3] Surface redox reactions

331 Clay minerals often contain structural or adsorbed Fe<sup>ref 120</sup>, which participate in electron  
332 transfer reaction with adsorbed redox sensitive metal ions<sup>121</sup>, such as U<sup>ref 122–124</sup>, Np<sup>ref 124</sup>, Pu  
333 <sup>ref 125,126</sup>, Se<sup>ref 127,128</sup>, Tc<sup>ref 124,129–131</sup>, and Cr<sup>ref 131–135</sup>. The mobility of redox sensitive elements  
334 depends on their oxidation state, often through the contrasted solubility and adsorption  
335 properties of oxidized and reduced aqueous species of a given element. The study of surface  
336 enhanced reduction or oxidation of redox sensitive metal ions is made very difficult by the  
337 numerous mechanisms that were identified as a function of the elements of interest, but also as  
338 a function of the nature of the clay mineral and of the geochemical conditions. For example,  
339 naturally reduced ferrous clay minerals from subsurface redox transition zones exhibit  
340 minimal reactivity towards the oxyanions TcO<sub>4</sub><sup>-</sup> and CrO<sub>4</sub><sup>2-</sup> compared to those measured in  
341 previous studies on laboratory treated samples<sup>131</sup>. Their reduction capacity was enhanced by  
342 adsorbed Fe(II) although added Fe(II) was not detected as redox-reactive species within the  
343 outermost few nanometers of clay mineral surfaces. The adsorption of Se(IV) on  
344 montmorillonite is an another example of a surface-enhanced redox reaction. In the presence  
345 of dissolved Fe(II) and in the pH range (pH < 8) where Fe(II) is also sorbed onto  
346 montmorillonite, a reductive precipitation of Se(IV) to nano-particulate Se(0) in the pH range  
347 (pH < 8) is observed<sup>127,136</sup>. However, based on Mössbauer spectrometry and XANES  
348 measurements, Fe oxidation kinetic rate was much higher than Se reduction kinetic rate.  
349 Structural Fe(II) in a chemically reduced nontronite does not reduce As(V) or Sb(V), and when  
350 all structural Fe is Fe(III), it does not oxidize As(III) and Sb(III) neither. Also, Fe(III) within a  
351 Fe(II)–O–Fe(III) moiety is more reactive compared to that in Fe(III)–O–Fe(III) in oxidizing  
352 As(III) and Sb(III)<sup>ref 128,137</sup>, and so, Fe(II)–O–Fe(III) moieties at the edge sites are assumed to  
353 be the redox-active species in Fe-containing clay minerals.

354 Electron transfer processes at mineral interfaces can in principles be modeled by using DFT  
355 based free energy calculation methods<sup>138,139</sup>. However, the delocalization error caused by the  
356 poor description of the exchange energy in generalized gradient approximation (the commonly  
357 currently used DFT level) usually leads to errors in the estimates of redox levels and redox  
358 potentials, with the underestimate in redox potential reaching 1 eV<sup>140</sup>. The estimate of redox  
359 levels and redox potentials could be improved to some extent by using the *beyond DFT*  
360 *technique*, such as Hubbard+U<sup>141</sup> and constrained DFT<sup>142</sup>. These techniques have also been  
361 used to estimate the rate of self-exchange type electron transfer<sup>143</sup>. However, such ad hoc tricks  
362 can bring about other problems. Advanced functionals such as hybrid/double-hybrid functional  
363 are able to obviously improve the predictions, for aqueous transition metal cations<sup>144</sup>, liquid  
364 water<sup>145</sup> and solid-water interfaces<sup>146</sup>. Unfortunately, FPMD using these functionals are easily  
365 tens of times more expensive than that with generalized gradient approximation. The  
366 computational cost has now been a major obstacle to the application on the mineral interfaces  
367 of geochemical/environmental interest. Understanding the redox properties and the associated  
368 electron transfer mechanisms in clay minerals is thus a key but also challenging issue on an  
369 experimental as well as from a computational point of view.

## 370 [H2] Influence of environmental parameters

### 371 [H3] Water saturation and surface hydration

372 Clay mineral surfaces are hydrated in conditions relevant to the critical zone. Water molecules  
373 are adsorbed through interactions with both adsorbed cations and clay surface atoms. A 43 %  
374 relative humidity is sufficient for external basal surface to be covered by a complete water layer,  
375 which corresponds to dry conditions in Earth's surficial environments. Relative humidity of  
376 only 0.2 % and 9 % are sufficient to establish fully hydrated smectite interlayer space with  
377 monolayer and double layer states respectively<sup>147,148</sup> because of strong water attraction under  
378 nanosized confinement. Previous simulation and experimental studies indicate that under  
379 partially saturated conditions, outer-sphere complexes can transform into inner-sphere, that is,  
380 the adsorption is stronger compared to water saturated condition<sup>76,149</sup>. On the opposite,  
381 adsorption of Cs<sup>+</sup> on the outer-basal of montmorillonite decreases with decreasing water  
382 saturation levels in adjacent interlayer spaces<sup>67</sup>, thus evidencing also possible long-range  
383 interactions influencing cation adsorption from one surface to another surface in clay mineral  
384 particles. This effect seems, however, to have a minor influence on cation mobility in clay-rich  
385 materials compared to the effect of pore connectivity decrease with decreasing water saturation  
386 levels<sup>150</sup>.

### 387 [H3] Natural organic matter

388 In soil and sedimentary rock systems, the presence of organic matter brings in additional  
389 complexity on retention of metal elements<sup>151</sup>. Natural organic matter and clay minerals form  
390 organo-clay association through the bonding of active groups, such as carboxylate, phosphate,  
391 and ammonium groups, and hydrophobic interactions with aliphatic or aromatic moieties<sup>152</sup>.  
392 Organic matters can bind on outer basal and edge surfaces and can also intercalate into the  
393 interlayer region of clay minerals<sup>153</sup>, with binding location and mechanism varying as a  
394 function of factors such as pH, ionic strength<sup>152</sup>.

395 Because of the multifunctionality of natural organic matter, they can alter surface  
396 hydrophilicity, cover surface sites while they bring in active groups which can serve as  
397 complexing sites for metal cations, and they can take part in interfacial electron transfer  
398 processes with redox-active groups<sup>154</sup>. Consequently, the effect of organic matters on metal  
399 cation retention in clay-rich materials can be extremely complicated, and the presence of  
400 organics can promote or inhibit the retention of metal ions depending on investigated metals  
401 and experimental conditions<sup>22,34</sup>.

402 The molecular-level mechanisms that are responsible for organic matter – metal ions – clay  
403 minerals interactions are still far from being fully understood. Natural organic matter are now  
404 described as supramolecular associations of a group of small molecules<sup>155,156</sup> rather than  
405 macromolecules<sup>157</sup> or polymers<sup>158</sup>, as evidenced by both experiments<sup>159,160</sup> and molecular  
406 simulations<sup>161</sup>. By taking advantage of this new description of organic matter structure,  
407 molecular level models of organo-clay associations have been developed, which can explicitly  
408 take account of experimentally measured properties of organics and clay minerals<sup>162,163</sup>. Such  
409 models together with multiscale simulation techniques can thus serve as a starting point to

410 explore microscopic interactions and develop predictive approaches for multicomponent  
411 systems.

412 Clay mineral edge surface reactivity is responsible for very diverse interaction processes with  
413 metal cations, including surface complexation, co-precipitation and redox reactions, which  
414 cannot be unravelled on the basis of batch chemical characterization only. Because the kinetics,  
415 reversibility, and thus efficiency of these retention processes are not the same depending on  
416 environmental conditions, deciphering their respective contributions is necessary to make  
417 useful predictions for industrial and environmental applications. Multiscale experimental and  
418 modeling approaches rooted in molecular level information have proved to be effective to do  
419 so (Figure 3), but many technical challenges remain, especially to model crystal growth and  
420 redox reactivity.

## 421 **[H1] Industrial and environmental implications**

422 Major advances in the ability to characterize and model interaction processes and mechanisms  
423 have important practical applications to several environmental and industrial processes. Below  
424 we briefly describe the current understanding of clay mineral-metal ion retention processes in  
425 both metallic waste pollution control and REE ion-adsorption deposits as examples.

## 426 **[H2] Pollution control engineering**

427 Clay minerals have exceptional thermal, mechanical, hydraulic and chemical properties, they  
428 are abundant in nature and reasonably cheap. Because of these features, clay-rich materials are  
429 commonly used as natural buffers to remediate contaminated soils and waters and to inhibit the  
430 migration of pollutants in disposal facilities for hazardous wastes including radioactive  
431 waste<sup>9,164-169</sup>. Clay minerals are also increasingly finding new applications in materials science,  
432 biotechnology and clay mineral-based nanocomposites development<sup>166,170</sup>.

433 Adsorption is one of the most efficient mechanisms to remove metal ions, which is why clay  
434 minerals have been used since the ~1970-1980s as a less toxic alternative for environmental  
435 remediation. However, in the face of increasing pollution from industrial and anthropogenic  
436 activities, increasing efforts have been made since the ~2000s to develop new types of clay  
437 mineral-based adsorbents modification of natural clay-rich material to increase its adsorption  
438 capacity, such as modified clay minerals and nanocomposites. Clay mineral-based adsorbents  
439 are used for the removal of toxic organic and inorganic (metal) contaminants from polluted  
440 waters. The removal efficiency of clay minerals towards pollutants can be increased through  
441 treatments of the material such as thermal and acid treatment, exfoliation, pillaring of cations,  
442 and modification with surfactants, polymers and organosilanes<sup>171-173</sup>.

443 Clay mineral supported nanoparticle have high potential for use in the development of high-  
444 capacity adsorbents and photocatalyst. Montmorillonite supported zero-valent iron is very  
445 effective in removing highly toxic arsenic from aqueous solutions<sup>174</sup>. The combination of many  
446 type of modification and the use of clay minerals of various morphologies (tubed, fibrous,

447 stacked) has led to the development to tailored made clay mineral based nanomaterial(s) with  
448 extreme high and selective adsorption properties<sup>175–177</sup>. For instance, polymer-functionalized  
449 clay mineral nanocomposites combine the remarkable features of both nanoparticles and  
450 polymers. The use of clay mineral as a nanofillers in polymer matrixes confer the polymer  
451 desirable interfacial properties<sup>178,179</sup>.

452 Most studies published in the field of pollution control engineering focus on aqueous  
453 contaminant removal efficiency of raw and treated clay-rich materials, and on the associated  
454 favorable environmental or engineered conditions. In proportion of the total number of studies,  
455 few gain insights from basic molecular understanding about retention processes. Notable  
456 exceptions to this dominant empiricism driven approach are found in the areas of radioactive  
457 waste storage<sup>9,180</sup>, and of the study of mobility of metals in soils<sup>59,181,182</sup>, for which cation  
458 exchange, surface complexation, surface precipitations, electron transfer, as well as  
459 interactions with natural organic matters have been identified as important clay mineral related  
460 processes in the understanding of metals mobility and biogeochemical cycling.

461 Geological disposal, which is presently the internationally preferred option for the storage of  
462 radioactive waste, relies on a multi-barrier concept, which is a combination of engineered  
463 barriers (waste form and canister, backfill, seal) and natural barriers (host rock), to ensure the  
464 containment and long-term isolation of the highly radio- and chemo- toxic waste from the  
465 biosphere. Clay minerals are key components of such most multi-barrier systems. The retention  
466 of (radio-)contaminants on clay minerals surfaces along potential transport paths is the main  
467 retardation mechanisms on which the safety assessment of deep geological repositories relies  
468 (Figure 3).

469 Because of the time- and length scales envisioned for radioactive waste storage, the prediction  
470 of contaminant migration in performance and safety assessments are commonly based on  
471 models using a limited set of macroscopic parameters, on which sensitivity analysis are  
472 conducted. These macroscopic parameters loop together many basic processes (Figure 3). For  
473 example, all retention mechanisms explored in this review are often up-scaled in the form of a  
474 single numerical parameter for a given radionuclide. In this respect, the safety case must  
475 demonstrate a detailed understanding of the physical–chemical phenomena governing retention  
476 processes, in order to confirm the consistency of the chosen up-scaling approach<sup>9</sup> (Figure 3).

477 Retardation factors ( $R_f$ ), which quantify the delayed aqueous transport of adsorbed  
478 contaminants compared to a perfect tracer, are major input parameters in performance and  
479 safety assessments<sup>83</sup>.  $R_f$  values for strongly adsorbing tracers are commonly derived from  $K_D$   
480 values measured from batch adsorption experiments. Since the ~2000s, evidence of coupled  
481 transport-retention processes through surface-enhanced diffusion have accumulated, which  
482 questions the adequacy of this equivalence between real  $R_f$  values and  $R_f$  values derived from  
483 batch  $K_D$  values. Related experimental and modelling study at all scales from molecular  
484 level<sup>15,81</sup> to in situ tests<sup>183–185</sup> gave rise to changes in modelling paradigms with consideration  
485 of emergent coupled processes<sup>82,83</sup>, in which part of adsorbed species is not immobilized on  
486 the surface, but, on the contrary, participates to an enhancement of the overall diffusion flux<sup>186–  
487 188</sup>. Adsorption must be seen as a process that both slows down metal ion transfer because of

488 accumulation on the surface, and also that accelerates their transfer through surface-enhanced  
489 diffusion. Consequently, a detailed understanding of adsorption process must be made  
490 available to use retention parameters obtained in static systems for the prediction of  
491 contaminants diffusive mobility.

## 492 [H2] Ion-adsorption REE ores

493 REEs ion-adsorption type deposits (IADs) have been known as an important source of REEs  
494 in the world in particular for heavy REEs<sup>189–194</sup>. IADs are characterised by high recovery rate  
495 of REEs simply by leaching of REEs with an ammonium sulphate solution at normal  
496 temperature, and low leachable amounts of U and Th, which can cause problems in other REEs  
497 sources in terms of environmental problems and working environment. Thus, IADs are ideal  
498 REE resources, which are critical to society due to its use in modern technologies<sup>195,196</sup>.

499 IADs are mainly found in weathered profile of felsic igneous rocks with a variety of clay  
500 minerals. In most cases, weathered granite has been developed, but IADs can also be found in  
501 felsic volcanic rocks in the world<sup>191,193,197–199</sup>. IADs typically consist of a strongly weathered  
502 zone at the surface layer, and an enriched zone of REEs in the subsurface layer accumulated  
503 mainly by adsorption through outer-sphere complexation of hydrated REE trivalent cation to  
504 clay minerals (Figure 4a,b)<sup>189,199,200</sup>. The surface layer exhibits a positive Ce anomaly in REE  
505 patterns due to the removal of the other REEs and fixation of Ce by its oxidation to insoluble  
506 Ce(IV) species<sup>201,202</sup>, whereas the subsurface REE-enriched layer generally shows a negative  
507 Ce anomaly due to the fixation of REEs, except for Ce (Figure 4c-e).

508 REE species in the enriched zone have been revealed by EXAFS spectroscopy<sup>189,200</sup>, showing  
509 that the outer-sphere surface complex to clay minerals is main REE species, and the species is  
510 responsible for the high recovery rate of REE by the ion-exchange reaction<sup>192,203</sup>. These results  
511 are consistent with laboratory studies on the formation of outer-sphere complex to various clay  
512 minerals, such as montmorillonite, as evidenced by EXAFS spectroscopy<sup>189,200,204</sup> and by laser-  
513 induced fluorescence spectroscopy<sup>205,206</sup>. The enriched zones are usually located in acidic  
514 environment ( $\text{pH} < 6$ )<sup>138</sup>. The lower pH is unfavorable for dissociation of groups of edge  
515 surfaces, thus suppressing the formation of REE inner-sphere complexes. Although the  
516 identification of phyllosilicates at the nm-scale is possible by transmission electron microscopy,  
517 the detection of REEs in the same view presented a challenge, which inhibited the attainment  
518 of clear identification of the REE host phase. In such cases, secondary ion mass spectrometry  
519 (SIMS) can bring additional insights<sup>207</sup>. Identification of the host mineral is primarily important,  
520 since the type of host mineral is related to the degree of weathering depending on temperature  
521 and rainfall<sup>208</sup>, which is crucial information for the survey of IADs, and the recovery rate of  
522 REE from the IADs.

523 High REEs extractable property of IADs is very contrastive to marine REEs resources such as  
524 marine ferromanganese oxides with low extractability of REEs ( $< 1\%$ ) due to the formation of  
525 inner-sphere surface complex of REEs<sup>209–212</sup> and deep-sea REEs-rich mud with REEs  
526 incorporated as phosphate phases<sup>213</sup>. However, IADs cannot be formed under marine  
527 environment due to high salinity of seawater, which shows that IADs are specific to land areas.

528 The difference between IADs and marine ferromanganese oxides originated from the different  
529 REE retention mechanisms: the former is mainly through electrostatics which is hindered by  
530 high ionic strength, whereas the latter is through chemical bonding. This example clearly shows  
531 that molecular-level studies allow systematic understanding of ion retention that occurs in  
532 natural systems, and to develop its application such as extraction of useful metals.

533 Retention reversibility and adsorbed cation mobility are two key aspects of resources extraction  
534 efficiency in industrial processes and contaminant mobility in pollution control engineering.  
535 Both properties are linked with the speciation of metal cations at clay mineral surfaces, with  
536 the presence of outer-sphere complexes enhancing reversibility and mobility.

## 537 **[H1] Summary and future directions**

538 The accurate predictions of metal ion – clay mineral interactions over long time- and large-  
539 spatial scales in natural and engineered systems necessitates the development of a continuum  
540 of macroscopic models that are able to consider a large range of environmental conditions, as  
541 well as temporal and spatial changes. Such predictions are currently hampered by the diversity  
542 of interaction processes of metal ions with clay mineral surfaces, and by the difficulty to  
543 unravel their respective contributions in the results of macroscopic experiments that are used  
544 to calibrate retention models, such as surface complexation models. This limitation is currently  
545 being addressed by implementing retention models with molecular level characterization to  
546 better understand adsorption and related processes.

547 The highly complex nature of clay mineral-metal ion interactions requires the application of  
548 multiple techniques to reach insightful conclusions. Important progress has been made since  
549 the ~2000s in this direction, with important breakthroughs in deciphering mechanisms of  
550 adsorption and of incorporation of elements, with applications to the formation mechanisms of  
551 economically important metal deposits, as well as to the containment of hazardous materials  
552 by clay-rich barriers. Since the 2010s, the emerging coupling of quantum mechanics simulation  
553 predictions with molecular level synchrotron-based characterization techniques proved to be  
554 very powerful to better constrain the nature and location of adsorption sites, binding  
555 mechanisms, as well as the energy associated to binding reactions, thus allowing further  
556 development of macroscopic models with a reduced number of empirically fitted parameters.  
557 It is now also possible to obtain quantified information on surface nucleation and growth  
558 mechanisms that are yet not integrated into geochemical modelling approaches.

559 With the application of higher quantum mechanical levels (such as advanced density functional  
560 and perturbation theory), more accurate estimates can be made, approaching chemical accuracy  
561 (about 1 kJ mol<sup>-1</sup>). Multiscale modelling will allow the system size and time scale to be  
562 expanded substantially towards ~µm and ~s respectively, enabling the direct simulation of slow  
563 processes, such as nucleation and dissolution, and promoting the combination with  
564 experimental results. Therefore, one can expect that the continuous development of efficient  
565 algorithms and increases in computing power will greatly advance the predictive capability of



566 microscopic simulation, which is going to play an ever more important role in guiding  
567 industrial and engineering applications.

568 Concerning adsorption processes, the quantification of surface ternary complex formation (in  
569 particular, in the presence of carbonated metal ions species) and a better understanding of  
570 metal-organic matter-clay mineral surface interactions, are needed to model conditions relevant  
571 to natural systems. Surface nucleation and growth clearly deserves more mechanistic research  
572 for their fundamental importance in both pollution control engineering and transition metal  
573 enriched clay deposits, such as zinc clay ores<sup>118</sup> and nickel laterite ores<sup>214</sup>.

574 Surface induced redox reactions have important implications for the containment performance  
575 of engineered and natural clay-rich barriers in pollution control applications, but also for  
576 bioremediation applications. The detailed understanding of surface induced redox reactions  
577 with respect to the retention of redox sensitive metals still requires extensive research before  
578 implementation in geochemical models, particularly with respect to the redox properties of  
579 iron. In particular, further research is needed for the identification of electron transfer paths  
580 and efficiency; for the assessment and thermodynamic description of intrinsic redox potential  
581 of structural and adsorbed Fe; for the identification of relationship between changes in Fe  
582 oxidation state and surface chemistry; and, for the quantification of Fe redox reactivity as a  
583 function of its abundance and location in the crystal structure.

584 The growing scientific interest in the quantification and understanding of clay mineral retention  
585 properties must be put in perspective with industrial and environmental applications that rely  
586 on the ability of clay minerals to scavenge metal ions. Bulk characterization of retention  
587 properties is necessary to study the effectiveness of clay-rich materials for such applications,  
588 but still is not sufficient to quantify these processes over long timescales. Process  
589 understanding at the molecular level combined with multiscale simulation approaches has  
590 proved to be essential to predict parameters such as resource extractability and contaminant  
591 mobility.

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## 1177 **Author contributions**

1178 XL and CT were responsible for the design and compilation of the article. All authors contributed to the  
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1181 The authors declare no competing interests.

1182

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1190 **Key points:**

1191 • Clay minerals have a diverse array of chemical structures and layer types that lead to a range  
1192 of metal ion retention mechanisms in Earth's critical zone. The metal retention capabilities of  
1193 clay minerals can concentrate rare earth elements (REEs) in ion adsorption type deposits and  
1194 can also be exploited for metallic industrial waste disposal.

1195 • Basic metal ion-clay mineral interaction mechanisms include cation exchange, surface  
1196 complexation, ligand exchange, structural incorporation, surface precipitation (with or  
1197 without epitaxial growth of neoformed minerals), and precipitation induced by surface redox  
1198 reactions.

1199 • Such diversity of retention mechanisms originates from the distinct structures and properties  
1200 of basal and edge surfaces. Cation exchange on basal surfaces occurs mainly through  
1201 electrostatics while other mechanisms occur through chemical bonding on edge surfaces.

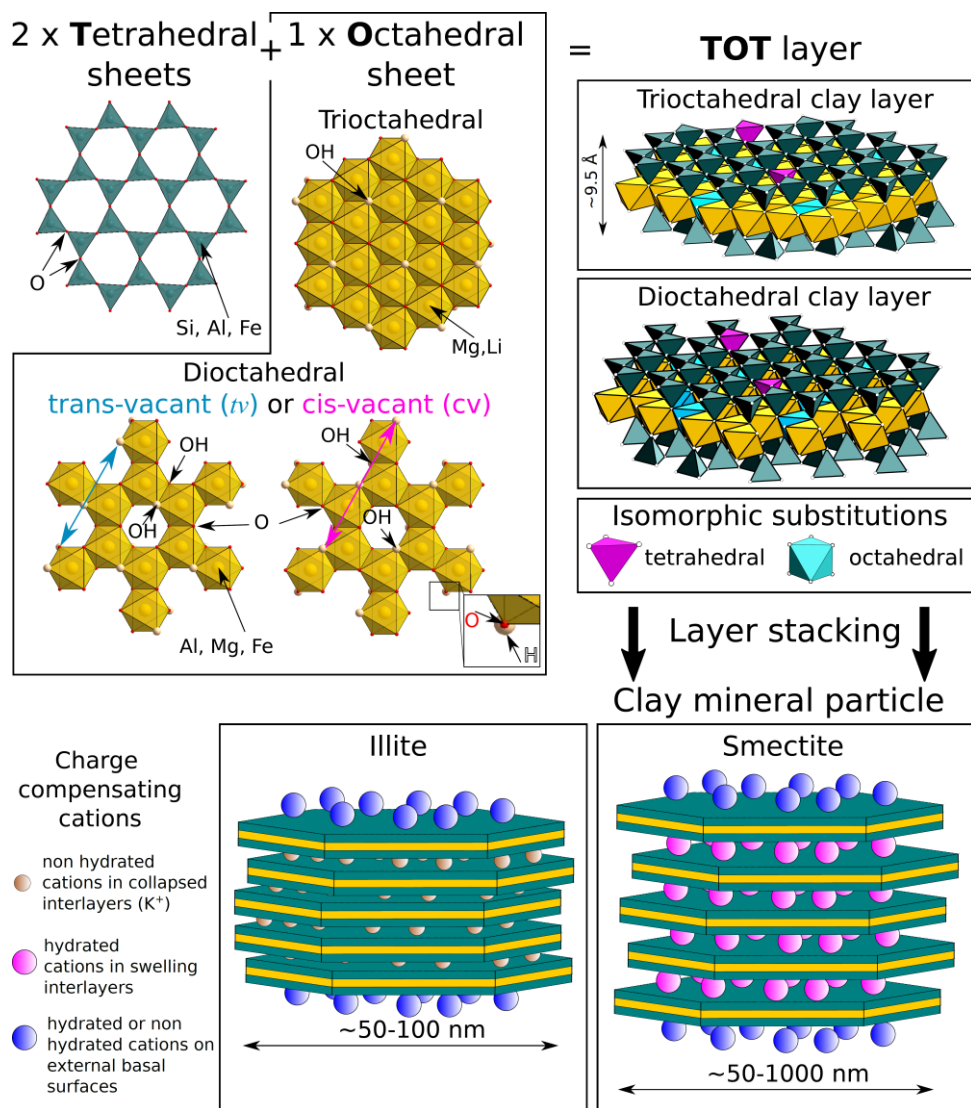
1202 • REEs in ion adsorption type deposits are mainly physically adsorbed on basal surfaces, which  
1203 are responsible for the high REE extractability (> 50 %) through ion exchange.

1204 • Both cation exchange and surface complexation processes occur during the retardation of  
1205 metallic pollution plumes in waste management applications (radioactive and conventional  
1206 industrial wastes as well as landfill leachate).

1207 • Understanding and quantification of the multifaceted and multiscale nature of clay mineral-  
1208 metal ion interactions necessitates the close combination of experimental and modelling  
1209 techniques at the molecular-level.

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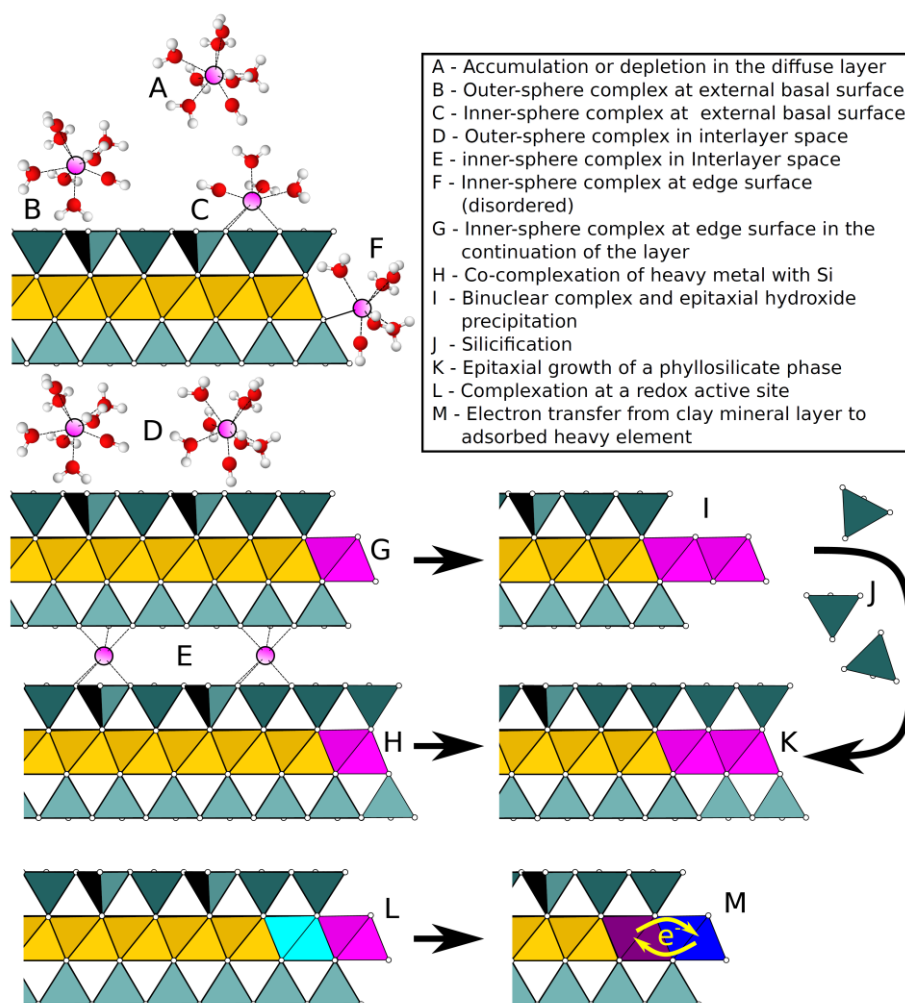


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1214 **Figure 1. Clay mineral sheet, layer and particle structures.** Two tetrahedral sheets  
 1215 sandwiching an octahedral sheet form a tetrahedral-octahedral-tetrahedral (TOT) layer. The  
 1216 thickness of a TOT layer, ~9.5 Å, corresponds to the distance between two planes of apical  
 1217 oxygen atoms, ~6.6 Å, plus the ionic radii of two oxygen atoms. Isomorphous substitutions  
 1218 (where one structural cation is replaced for another of similar size, see magenta tetrahedral and  
 1219 cyan octahedral) are responsible for a permanent negative structural layer charge that is  
 1220 compensated by cations present in the interlayer spaces and on external surfaces of clay mineral  
 1221 particles. In water-saturated conditions, charge compensating cations can be hydrated (red and  
 1222 blue cations) or not (yellow cations), depending on the nature of the cation, the type of layer  
 1223 isomorphous substitutions, the layer charge, and the type of neighbouring surfaces (interlayer  
 1224 versus external). Layer structure and negative charge are responsible for the high metal cation  
 1225 retention capability of clay minerals.

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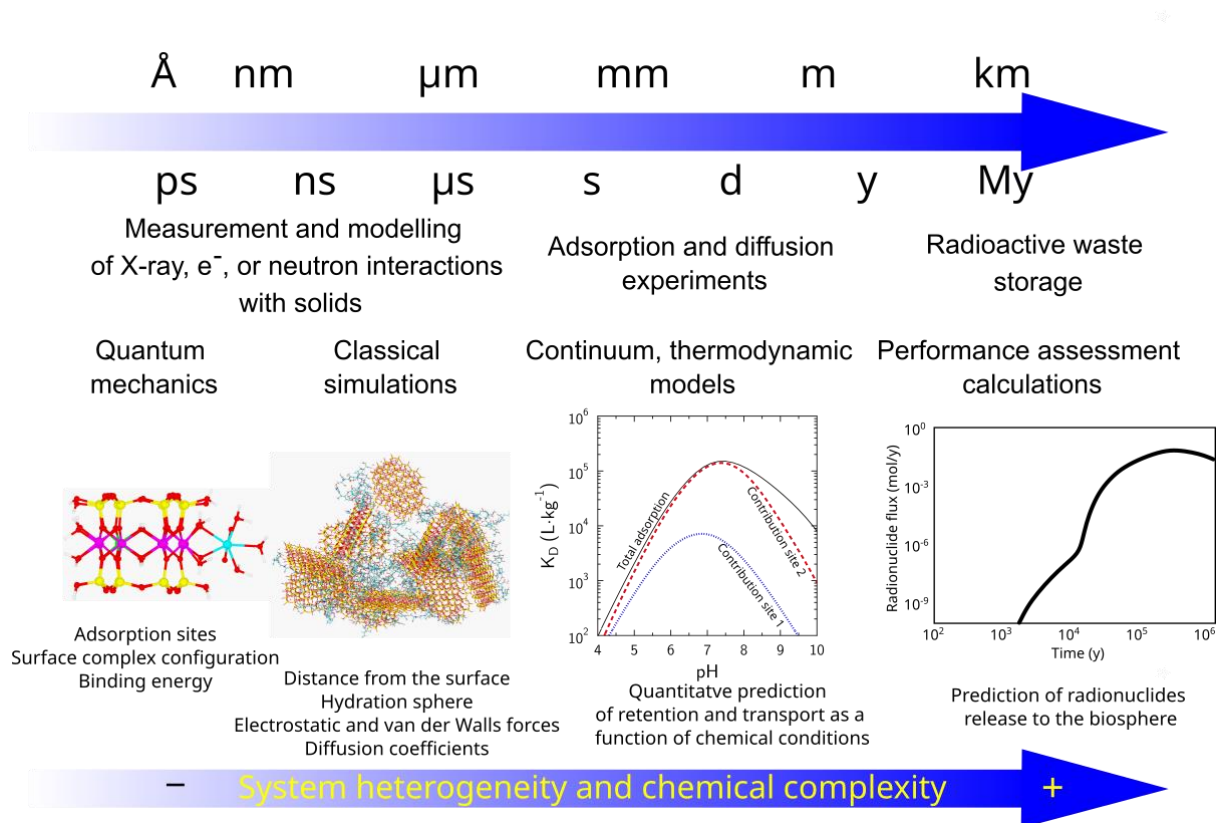




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1229 **Figure 2. Interaction mechanisms of metal ions with clay minerals.** Clay layers are made of  
 1230 octahedral (orange) and tetrahedral (blue) sheets, depicted along the stacking direction.  
 1231 Adsorbed metal ions are shown in purple, and water molecules in red and white. a| Metal ions  
 1232 (purple) in complexes with water molecules (red-white) can be adsorbed onto external basal  
 1233 surfaces or accumulate in diffuse layers. The transitions from panels b to d highlight the  
 1234 continuum from adsorption on edge surfaces to clay mineral nucleation and growth. b| outer-  
 1235 sphere complexes can be adsorbed in the interlayer space. Inner-sphere complexes can attach  
 1236 onto the edge of the octahedral layer, or c| in the interlayer space. If complexation of the edge  
 1237 surface occurs at the same time as silicification, the clay mineral undergoes epitaxial growth.  
 1238 d| A cation adsorbed by complexation at an active redox site on an edge surface can undergo  
 1239 electron transfer with the clay mineral layer, which in turn changes the redox state of both the  
 1240 octahedral sheet and adsorbed metal ions (blue-purple colour change). The duality of surface  
 1241 types (basal vs. edge) and the redox reactivity of the inner atoms in the layer are responsible  
 1242 for multiple modes of interactions with metal cations.

1243



1244

1245 **Figure 3. Upscaling of information in modeling of radionuclide storage.** a| Quantum  
 1246 mechanical simulation of a metal ion complexed on clay mineral surface. b| Classical  
 1247 simulation of metal ions at a clay mineral-aqueous solution interface. c| An example of a  
 1248 surface complexation model for metal ion adsorption on clay mineral surfaces using a two-site  
 1249 model. Information about binding energy and the nature of adsorption sites can be constrained  
 1250 by molecular level studies. d| generic example of a simulation of radionuclide flux at the outlet  
 1251 of a radioactive waste storage site over 1000-100,000 year time scales. Retention and diffusion  
 1252 parameters used in these simulations are usually obtained in laboratory experiments that last  
 1253 from days to years. Using these parameters to make upscaled predictions to million year time  
 1254 scales must be justified by process understanding and quantification. Effective upscaling of  
 1255 molecular-level information from measurements and simulations enables practical applications  
 1256 in macroscopic studies.

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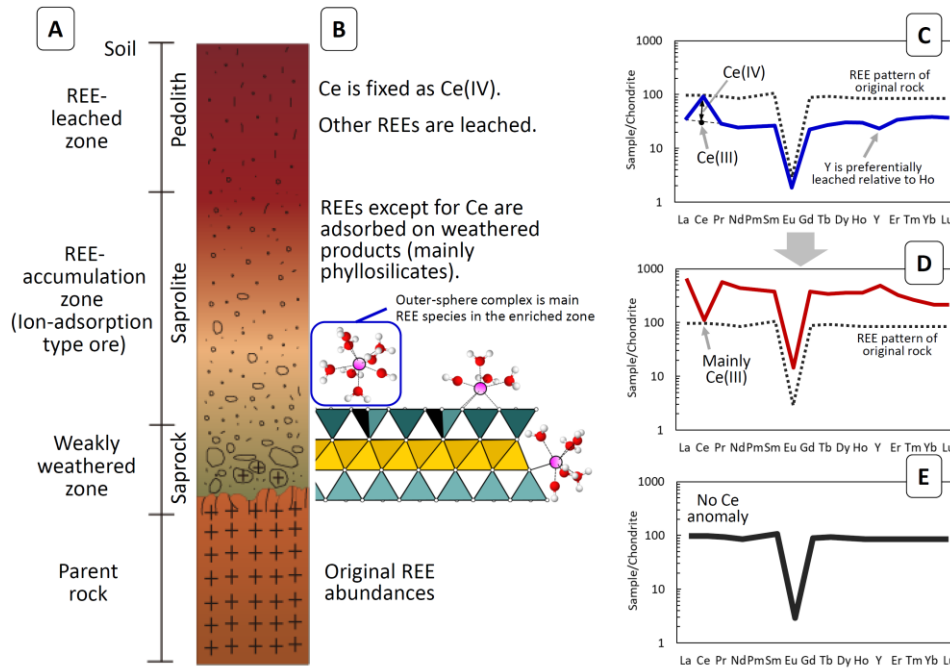
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1266 **Figure 4. Ion-adsorption type rare earth element (REE) deposits. a** | Typical vertical profile  
 1267 of weathered zone hosting ion-adsorption deposit (IAD). Granite is a typical parent rock for  
 1268 IADs. **b** | Rare earth elements, excluding Ce, are leached from the top layer in the profile (the  
 1269 pedolith). REE accumulation occurs in saprolite deposits, below the pedolith but above the  
 1270 weathered parent rock. Adsorption of REEs in the accumulation zone mainly occurs as outer-  
 1271 sphere complexes on external basal clay layers. **c** | the REE-leached zone is characterized by a  
 1272 positive cerium (Ce) anomaly and relatively low REE abundances. Y is preferentially leached  
 1273 relative to Ho. **d** | the REE-accumulation zone is characterized by a negative Ce anomaly and  
 1274 enrichment of the other REEs. Y is enriched relative to Ho. **e** | the weakly weathered zone has  
 1275 a similar REE pattern to the parent rock, but does not have the Ce anomaly. Adsorption on clay  
 1276 minerals as outer-sphere complex is responsible for the enrichment and high extraction rate of  
 1277 REEs in IAD.

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## 1286 **Boxes**

### 1287 **Box 1. Clay mineral structures and surfaces**

1288 Clay minerals are phyllosilicates. They are made up of stacked layers consisting of an  
1289 assemblage of sheets. Chemical composition, spatial arrangement of sheets, and layer stacking  
1290 mode are the main criteria that identify clay mineral family members<sup>215</sup>.

1291 Layers of dioctahedral smectite and illite, two groups of clay minerals of interest for their metal  
1292 ions retention properties, are made of two tetrahedral sheets sandwiching an octahedral sheet,  
1293 forming so-called 2:1 layers (Figure 1).

1294 Tetrahedral and octahedral sheets of smectite and illite contain mostly Si and Al (or Fe) atoms.  
1295 A range of other minor elements are incorporated through isomorphic substitutions, which  
1296 create a local charge imbalance if the substituted element does not bear the same formal charge  
1297 as the incorporated element (for example, Mg<sup>2+</sup> for Al<sup>3+</sup>). This local charge is not compensated  
1298 for in the layer structure, which creates a permanent negative structural charge in the clay layer.  
1299 This negative charge is compensated by the positive charge of cations in the interlayer space  
1300 and on external surfaces.

1301 Interlayer spaces can be hydrated and accessible to aqueous species as in the case of smectite,  
1302 or collapsed and mostly inaccessible to water and aqueous species as in the case of illite, in  
1303 which adjacent tetrahedral sheets are bonded by non-hydrated K<sup>+</sup> ions (Figure 1). Na<sup>+</sup>, K<sup>+</sup>,  
1304 Ca<sup>2+</sup>, Mg<sup>2+</sup> are the most common charge compensating cations, but they can be exchanged  
1305 easily on external and hydrated interlayer surfaces by other metal cations<sup>68</sup>. Differences in  
1306 hydration properties of interlayer cations results in the common phenomenon of clay mineral  
1307 swelling, which corresponds to changes of interlayer spacing as a function of the nature of  
1308 interlayer cations and water chemical potential<sup>216</sup>.

1309 Crystal faces of clay minerals can be grouped into basal and edge surfaces, which are parallel  
1310 and perpendicular to the basal plane respectively<sup>68</sup>. Smectite and illite layers thickness is  
1311 approximately 1 nm, while their lateral dimensions range from 50 nm to 1 μm (Figure 1). These  
1312 dimensions result in very large specific surface areas, up to 800 m<sup>2</sup> g<sup>-1</sup> for smectites. The vast  
1313 majority of the surface area is born by the basal surfaces, while edge surface area account for  
1314 only 5 to 30 m<sup>2</sup> g<sup>-1</sup>.

1315 Atoms present at basal surfaces are fully coordinated and form a siloxane terminated surface,  
1316 while oxygen atoms present at edge surfaces have fewer metal neighbours than in bulk (Figure  
1317 1). Edge surfaces are covered by chemically adsorbed water, forming amphoteric charged  
1318 surface hydroxyl groups (>OH groups, where the > sign is indicative of a surface coordination),  
1319 having contrasted acidity constants (pK<sub>a</sub>) as a function of coordination, surface crystallographic  
1320 orientation and nature of the central metal bonded to the >OH group<sup>88</sup>. Consequently, edge  
1321 surface chemical properties are strongly pH-dependent, by contrast, basal surface properties  
1322 are little or not.

1323

1324 **Box 2. Quantification of metal ion immobilisation**

1325 Macroscopic quantification of metal ion retention on a given mass of clay minerals ( $m_{clay}$  in  
 1326 kg) can be obtained from experimental adsorption isotherms (see figure). The concentration of  
 1327 an adsorbed element ( $C_{ads}$  in  $\text{mol kg}^{-1}_{clay}$ ) can be quantified by the difference between a total  
 1328 concentration added in the system ( $C_{tot}$  in  $\text{mol L}^{-1}$ ) and an aqueous concentration measured at  
 1329 steady-state, which is assumed to be representative of thermodynamic equilibrium ( $C_{eq}$  in  $\text{mol}$   
 1330  $\text{L}^{-1}$ ).

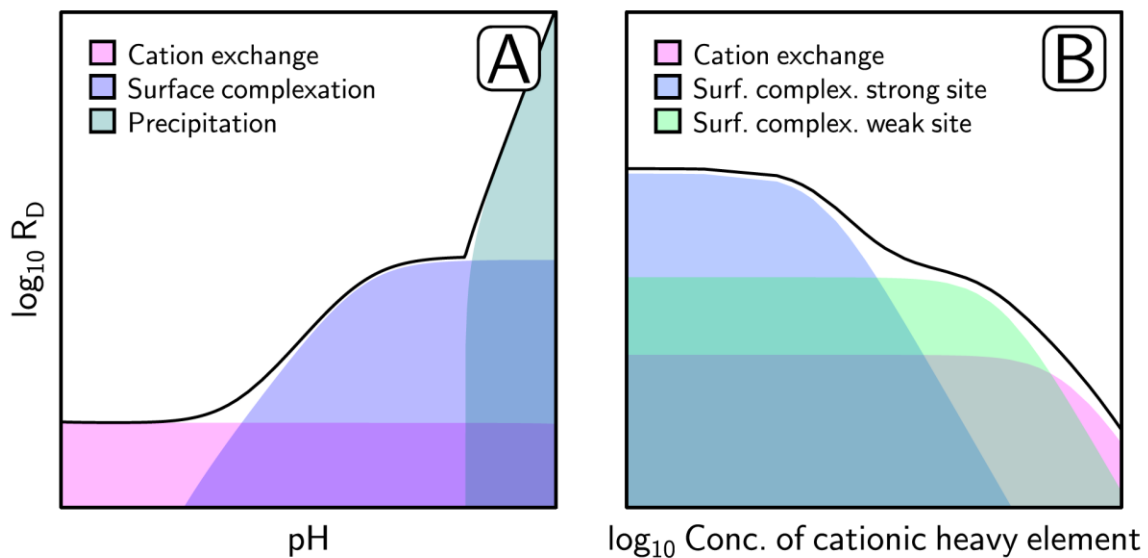
1331  
 1332 Retention is usually quantified as a percentage of total added concentration, or as a distribution  
 1333 coefficient  $R_D$ , or  $K_D$  (in  $\text{L kg}^{-1}$ ), which quantify the partitioning of the metal ions between the  
 1334 solution and the surface:

$$C_{ads} = \frac{C_{tot} - C_{eq}}{m_{clay}} V_{sol} \quad 1$$

$$R_D \text{ or } K_D = \frac{C_{ads}}{C_{eq}} \quad 2$$

1335 where  $V_{sol}$  is the volume of solution (in L).

1336 The  $R_D$  value does not give any insight into the physical and chemical processes responsible  
 1337 for the observed retention (such as adsorption, incorporation, and precipitation). However, in  
 1338 a first approach, the shape of the adsorption isotherms plotted as a function of pH and metal  
 1339 ion concentration (see figure), allows the difference between major adsorption sites and other  
 1340 retention mechanisms to be determined.



1341

1342 The figure shows: **a**| retention processes shown as a function of pH and constant metal cations  
 1343 concentration, and **b**| as a function of metal cations concentration and fixed pH. Superposition  
 1344 of coloured areas is indicative of a mixed contribution of several mechanisms to the overall  
 1345 retention.

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### 1348 **Box 3. Predictive approaches at different scales**

#### 1349 **Quantum mechanics simulation**

1350 Density functional theory (DFT)<sup>217,218</sup> has been the workhorse of quantum mechanics  
1351 calculation. By transforming the 3N-dimensional Schrodinger equation to 3-dimensional  
1352 Kohn-Sham equation, DFT makes it affordable to calculate energy and atomic forces of  
1353 realistic systems. First principles molecular dynamics (FPMD)<sup>219</sup>, a combination of DFT and  
1354 molecular dynamics (MD), generates dynamical trajectories at limited temperatures and is thus  
1355 able to explore the properties of aqueous and interfacial systems. FPMD can calculate free  
1356 energy by integrating with enhanced sampling techniques (such as the method of constraint,  
1357 metadynamics). However, the expensive computational costs badly limits the system size and  
1358 time FPMD can access: for current supercomputing architecture the typical length and time  
1359 scales are only ~10 angstroms and ~10 picoseconds.

#### 1360 **Classical simulation**

1361 Classical simulation calculates energy and forces based on a force field that is a set of  
1362 parameters describing atomic interactions<sup>220</sup>. Classical MD produces dynamical trajectories by  
1363 using the forces calculated from a force field. The length and timescale of classical simulation  
1364 can reach second and micrometer.

#### 1365 **Multiscale simulation**

1366 Classical mechanical simulation and thermodynamic models are necessary to build direct link  
1367 to macroscopic experiments. These models are usually based on a set of empirical/fitted  
1368 parameters. Multiscale simulation plays the role of a bridge by translating the information  
1369 generated by quantum mechanics into parameters of upscaling modelling, thus overcoming the  
1370 temporal and spatial limits of quantum mechanics modelling, such as it provides constraints  
1371 for geochemical modeling and the force field used in classical simulation<sup>221</sup>.

#### 1372 **Geochemical thermodynamic modeling**

1373 Surface complexation and cation exchange models apply mass balance, surface charge balance  
1374 and thermodynamic chemical equilibrium concepts to predict, quantitatively, the partitioning  
1375 of chemical species between an aqueous solution and mineral surfaces<sup>222</sup>. Surface  
1376 complexation and cation exchange models can be coupled to fluid transport models at large  
1377 scale (aquifers, rivers, water catchment) to build defensible predictions in the environmental  
1378 sciences<sup>223,224</sup>. Since the ~2000s, model parameters have been obtained from fitting  
1379 macroscopic adsorption, while microscopic and spectroscopic observations helped  
1380 constraining the main mechanisms responsible for the observed metal ions retention. Since the  
1381 ~2010s, advances in molecular level modelling and multiscale simulations provide new

1382 possibilities to reduce the number of empirical fitting parameters in surface complexation and  
1383 cation exchange models.

## 1384 **Glossary terms:**

1385 **Metal ions:** metal cation (M) in aqueous solution with the chemical formula  $[M(H_2O)_n]^{z+}$ ,  
1386 metal ions include rare earth elements (REEs), actinides, transition metals, and alkaline and  
1387 alkaline-earth metals.

1388 **Clay mineral:** signifies a class of hydrated phyllosilicates making up the fine-grained fraction  
1389 of rocks, sediments, and soils, which this Review is focused on.

1390 **Clay-rich materials** refers to materials containing clay minerals, such as sediments, soils and  
1391 weathered rocks, and with physical and chemical properties dominated by their clay mineral  
1392 fraction.

1393 **Earth's Critical zone:** The oxygenated and hydrated layer at Earth's surface and shallow  
1394 subsurface, spanning from the tops of tree canopies to the bottom of groundwater.

1395 **Complex:** a compound consisting of a central atom or ion that is bonded to other atoms or ions,  
1396 which are called ligands.

1397 **Ligand exchange:** A type of reaction in which a ligand of a complex is replaced by a different  
1398 ligand.

1399 **Tetrahedral sheet:** A 2-dimensional sheet formed by tetrahedral units, each consisting of a  
1400 metal cation coordinated by four oxygen atoms and linked to three neighbouring tetrahedra by  
1401 shared oxygen.

1402 **Octahedral sheet:** A 2-dimensional sheet formed by octahedral units, each consisting of a  
1403 metal cation coordinated by six oxygen atoms, linked to six neighbouring octahedra by shared  
1404 edges.

1405 **Diocahedral:** A common type of octahedral sheet where most of the metal cations are of +3  
1406 valence, two-thirds of the octahedra are occupied while the other third is vacant.

1407 **2:1-type clay mineral:** clay mineral which has a structural layer made of one octahedral sheet  
1408 sandwiched by two tetrahedral sheets.

1409 **Smectite:** A group of 2:1-type clay minerals with expandable interlayer space

1410 **Illite:** A group of 2:1-type clay minerals with non-expandable interlayer space.

1411 **Inner-sphere complex:** where the cation is adsorbed on a clay layer with direct chemical  
1412 contact to the mineral layer surface.

1413 **Outer-sphere complex:** where the cation is adsorbed on a clay layer surface, but is separated  
1414 by one or more water molecules.

1415 **Epitaxial nucleation:** formation of a crystalline nucleus on a substrate, where the new  
1416 crystalline layers form with one or more well-defined orientations fixed by that of the substrate  
1417 lattice.

1418 **Neutron diffraction:** an experimental technique used to probe the crystallographic properties  
1419 of materials, including the position of hydrogen atoms, notably by taking advantage of the  
1420 contrasting interactions of neutrons with hydrogen and deuterium.

1421 **Synchrotron X-ray reflectivity (XRR):** an experimental technique used to study the detailed  
1422 surface properties of solids, based on the analysis of X-rays reflected by a surface.

1423 **X-ray absorption spectroscopy (XAS):** an experimental technique used to study oxidation  
1424 state and local environment of an atom in a sample, based on analysis of variations in X-ray  
1425 absorption over a range of photon energies.

1426

### 1427 **Website summary:**

1428 Clay minerals can retain metal ions, concentrate rare earth elements and be exploited for  
1429 industrial waste disposal. This Review discusses the molecular-level mechanisms of metal ion  
1430 retention in clay minerals and their importance for environmental and industrial applications.

1431



