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Study of uranium(VI) and radium(II) sorption at trace level on kaolinite using a multi-site ion exchange model

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Highlights

- sorption of trace U(VI) and Ra(II) on kaolinite was studied
- multi-site sorbent/multi-species sorbate ion exchange model used to describe sorption
- results provided U and Ra sorption equilibria stoichiometry and associated constants
- Ra^{2+} was the main adsorbed species over the pH range
- U negatively charged hydroxylated forms dominated sorption at $\text{pH} > 8$

1 Abstract

2 Uranium and the long-lived decay product radium-226 are abundantly present in mine
3 wastes produced during uranium extraction activities. In the case of release to the surrounding
4 environment, these radionuclides are at trace levels compared to groundwater solutes, and the
5 presence, content and properties of clay minerals in these subsurface environments influence
6 the extent of radionuclide sorption and, in turn, radionuclide migration. Since clays are known
7 to have the distinctive property of retaining ions, the aim of this work was to study the sorption
8 of trace uranium(VI) and radium(II) on a common phyllosilicate mineral, kaolinite, in the
9 presence of excess K, a common groundwater cation, in order to obtain a thermodynamic
10 database that describes the ion-exchange equilibria occurring at the mineral-solution
11 interface. The sorption of U(VI) and Ra(II) at trace level was obtained from pH 2 to 11
12 by measuring the distribution coefficient (K_d), and additional sorption isotherms were carried
13 out over a representative concentration range and at two different pH. The sorption data for
14 both elements was processed according to a general multi-site sorbent / multi-species
15 sorbate model and provided fundamental sorption equilibria stoichiometry and associated
16 equilibrium constants. Radium was sorbed from pH 2 to 10.5 on two main sorption sites as
17 Ra^{2+} . U sorption was observed on all the sorption sites of kaolinite governed by its solution
18 speciation, with positively charged hydroxylated species adsorbed between pH 2 and 4,
19 whereas its negatively charged forms dominated U sorption at pH > 8.

20 Keywords

21 Uranium(VI), radium, kaolinite, sorption, ion exchange

22

23 1. Introduction

24 Considerable large volumes of mill tailings are disposed every year near uranium mining
25 sites (Abdelouas, 2006). Since most of the ore deposits have low uranium content, the mill
26 tailings still comprise a small portion of the initial uranium and almost all of the daughter
27 radionuclides of the ^{238}U decay series, including ^{226}Ra (Déjeant et al., 2014; Nirdosh et al.,
28 1984). These decay products add to the environmental impact of uranium-waste, making the
29 mill tailings to be considered low-level radioactive waste. In particular, ^{226}Ra is of notable
30 relevance due to its long half-life (1600 y), degree of radiotoxicity and its short-lived

31 decayproducts, such as gaseous ^{222}Rn . The environmental concern of these tailings (and any
32 contaminated land) arises from the potential release of radionuclides into the groundwater, and,
33 as a result, contamination of subsurface environments in the vicinity of the mine
34 (Phrommavanh et al., 2013).

35 As thoroughly reviewed in Payne et al. (2013), a key factor on migration predictions is
36 the extent of radionuclide sorption onto the surfaces of solid phases found in natural
37 environments. These solid phases must be methodically characterised, with special emphasis
38 on the identification of sorption sites, the estimation of their concentration and their sorption
39 behaviour towards radionuclides under different conditions. The sorption of U(VI) and, in less
40 extent, Ra have been previously studied for different iron oxyhydroxide, carbonate and clayey
41 minerals (Catalano and Brown Jr, 2005; Jones et al., 2011; Payne et al., 2004; Sajih et al.,
42 2014; Stammose et al., 1992; Tachi et al., 2001; Turner et al., 1996). Clay minerals are
43 abundant in geological formations and soils, and have the distinctive property of retaining
44 ions, with high affinity for cationic species. The sorption process on clays is mainly via ion
45 exchange on the surface, becoming even more important with trace-level concentrations and
46 low ionic strength conditions, as the ones in natural environments. Catalano and Brown Jr
47 (2005) studied the sorption of U on montmorillonite and observed that the fraction of uranyl
48 sorbed via cation exchange under low ionic strength conditions was more important than
49 observed in previous studies, where only surface complexation was considered. Turner et al.
50 (1996) used an ion exchange model to describe sorption of uranyl on a smectite type clay, and
51 obtained equilibrium constants for the different sorption sites on the surface. An ion exchange
52 model (considering two types of sorption sites) was also more suitable than surface
53 complexation model to describe the retention of U(VI) at trace level on a clay mixture of
54 kaolinite and smectite (Stammose et al., 1992), and the sorption of Ra was also demonstrated
55 to happen via an ion exchange mechanism on purified smectite (Tachi et al., 2001).

56 When radionuclides are found at trace or ultra-trace level, major cations (found at higher
57 aqueous concentrations) are strong competitors for clay sorption sites in natural
58 environments (Tertre et al., 2011). Therefore, a full characterisation of the clay properties
59 towards the major ions is also required to describe the sorption of trace metals on clays. This
60 type of characterisation has already been carried out, for example, with argillaceous rock
61 (Motellier et al., 2003), beidellite (Robin et al., 2015) and kaolinite (Reinoso-Maset and Ly,
62 2014). In these three studies, the sorption of major ions was described using a multi-site ion

63 exchange model, and provided with a comprehensive and robust sorption data set that can be
64 applied when studying sorption of trace elements on these clays.

65 Therefore, the aim of this work was to study the sorption of trace level uranium(VI) and
66 radium(II) on a common phyllosilicate mineral, kaolinite, in the presence of excess K, a
67 common groundwater cation, in order to determine the ion-exchange equilibria occurring at
68 the mineral-solution interface. This work has followed a multi-site ion exchange model that
69 can describe chemical systems such as a multi-site sorbent/multispecies sorbate, and which
70 has already been applied in Reinoso-Maset and Ly (2014) to successfully characterise the ion
71 exchange properties of the same kaolinite used in this work. The model is presented in detail
72 therein, thus here we focused on the part of the model that describes sorption of a trace
73 element. Following a detailed experimental protocol using chemical and radiochemical
74 analytical techniques, batch experiments over a wide pH range (from 2 to 11) were carried out
75 to measure the distribution coefficient (K_d) of trace U(VI) and Ra(II) sorption on kaolinite.
76 Additionally, sorption isotherms of both elements were measured over a representative
77 concentration range and at two different solution pH. Finally, to obtain fundamental sorption
78 equilibria stoichiometry and associated constants, the sorption data for both elements was
79 processed according to the ion exchange model described here.

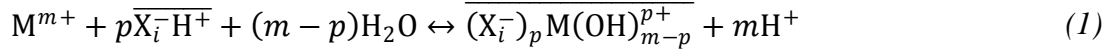
80 **2. Methodology**

81 Reinoso-Maset and Ly (2014) obtained the type and concentration of sorption sites of the
82 kaolinite used in this work, the related major ions sorption equilibria occurring at the mineral-
83 solution interface and their associated selectivity coefficients (expressed as the corrected
84 selectivity coefficients, K^*). The main formalisms and assumptions of the model are
85 present therein, hence we have focused this section on the part of the model describing
86 sorption of an element at trace level in the presence of two competitor ions.

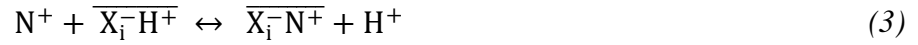
87 2.1 Adsorption on major sorption sites

88 The kaolinite crystal structure, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, presents permanent negatively charged
89 sites, X_i , and hydroxylated sites with pH-dependent charge, $Y_j\text{OH}$, that can result in different
90 sorption equilibria occurring at the solid solution interface. When the element M is found at
91 *trace level* compared to a major competitor N^+ and in the absence of other ligands than OH^- ,
92 the adsorption of M on a major sorption site can occur under its free M^{m+} form or as one of its
93 hydroxylated species, $M(\text{OH})_x^{m-x}$, depending on the solution pH.

94 Therefore, when considering H^+ as the reference competitor ion, the sorption of free or
 95 hydroxylated species of Mand N^+ on permanently charged sorption sites, X_i , can be described
 96 by Equations 1 and 3 respectively. Their associated equilibrium constants (as the corrected
 97 selectivity coefficients) have the form of Equations 2 and 4.



$$K_{M(OH)_{m-p}/mH}^{*i} = \frac{\left[\overline{(X_i^-)_pM(OH)_{m-p}^{p+}} \right] [H^+]^m \cdot (y_H)^m}{\left[\overline{X_i^-H^+} \right]^p [M^{m+}] y_M} \quad (2)$$



$$K_{N/H}^{*i} = \frac{\left[\overline{X_i^-N^+} \right] [H^+] \cdot y_H}{\left[\overline{X_i^-H^+} \right] [N^+] y_N} \quad (4)$$

98 where K^{*i} is the corrected selectivity coefficient for M^{m+} or N^+ and H^+ exchange on a
 99 surface site; i is the index number of the surface site; m is the cation
 100 charge; $\overline{(X_i^-)_pM(OH)_{m-p}^{p+}}$, $\overline{X_i^-N^+}$ and $\overline{X_i^-H^+}$ are the chemical forms describing the sorption
 101 state of M, N and H^+ on site X_i respectively; the square brackets [] indicate the concentration
 102 of species either in solution or adsorbed to site X_i (in mol L⁻¹ and mmol g⁻¹ of dry solid
 103 respectively); and y_H , y_M and y_N are the molar activity coefficients for H^+ , M^{m+} and
 104 N^+ quantified in the present work according to Davies expression, $\log y_i = -0.5 \cdot z_i^2 \cdot$
 105 $\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3 \cdot I \right)$, with ionic strength $I = \frac{1}{2} \cdot \sum_i C_i z_i^2$, where C_i and z_i are the molar concentration
 106 and charge of the species i respectively.

107 In the case of hydroxylated sorption sites, Y_jOH , the sorption of anions (L^- and anionic M
 108 hydroxylated species) must be also considered. Equations from 5 to 10 show all the chemical
 109 equilibria involved and their associated thermodynamic constants.

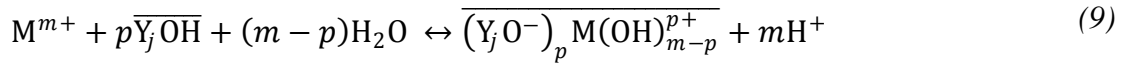


$$K_{N/H}^{*j} = \frac{[\overline{Y_j O^- N^+}][H^+]}{[\overline{Y_j OH}][N^+]} \cdot \frac{\gamma_H}{\gamma_N} \quad (6)$$

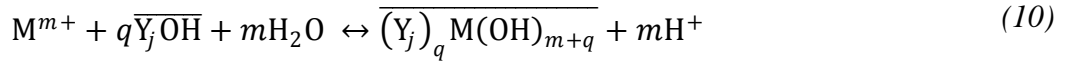


$$K_L^{*j} = \frac{[\overline{Y_j OH_2^+ L^-}]}{[\overline{Y_j OH}][L^-][H^+]} \cdot \frac{1}{\gamma_L \gamma_H} \quad (8)$$

-if $M(OH)_x^{m-x}$ are cationic species, $0 \leq x = m - p \leq m-1$ and $1 \leq p \leq m$, and thus:



-if $M(OH)_x^{m-x}$ are anionic species, $x > m$ and $q \geq 1$, and thus:



110 Since the exchange reactions of the element M are in competition with the ones involving
 111 N^+ , as well as L^- , the total concentration of sites X_i and $Y_j OH$ (SC_i and SC_j respectively) will
 112 be given by Equation 11 and 12.

$$SC_i = [\overline{X_i^- H^+}] + [\overline{X_i^- N^+}] + \sum_{p=m}^1 p [\overline{(X_i^-)_p M(OH)_{m-p}^{p+}}] \quad (11)$$

$$SC_j = [\overline{Y_j OH}] + [\overline{Y_j O^- N^+}] + [\overline{Y_j OH_2^+ L^-}] + \sum_{p=m}^1 p [\overline{(Y_j O^-)_p M(OH)_{m-p}^{p+}}] \\ + \sum_{q \geq 1} q [\overline{(Y_j)_q M(OH)_{m+q}}] \quad (12)$$

113 However, the concentration of sites occupied by the trace metal M (either in Equation 11
 114 or 12) can be considered negligible respect to the concentration of sites with adsorbed H^+ , N^+
 115 and L^- , and thus the distribution coefficient of the element M ($K_{dM} = [\overline{M}]/[M]$) can be
 116 expressed as a function of the corrected selectivity coefficients of M, N and L, the

117 concentration of sites i and j (SC_i and SC_j) and the solution pH by combining Equations 2, 4,
 118 6, 8 11 and 12. The final mathematical development yields to Equation 13.

$$\begin{aligned}
 K_{dM} = & \frac{1}{\alpha_M \cdot [H^+]^m \cdot \frac{(y_H)^m}{y_M}} \cdot \left(\sum_{\text{sites } i} \sum_{p=m}^1 \frac{K_{M(OH)_{m-p}/mH}^{*i} \cdot (SC_i)^p}{\left(1 + K_{N/H}^{*i} \cdot \frac{[N^+]}{[H^+]} \cdot \frac{y_N}{y_H}\right)^p} \right. \\
 & + \sum_{\text{sites } j} \left[\sum_{p=m}^1 \frac{K_{M(OH)_{m-p}/mH}^{*j} \cdot (SC_j)^p}{\left(1 + K_{N/H}^{*j} \cdot \frac{[N^+]}{[H^+]} \cdot \frac{y_N}{y_H} + K_L^{*j} \cdot [L^-] \cdot [H^+] \cdot y_L \cdot y_H\right)^p} \right. \\
 & \left. \left. + \sum_{q \geq 1} \frac{K_{M(OH)_{m+q}/mH}^{*j} \cdot (SC_j)^q}{\left(1 + K_{N/H}^{*j} \cdot \frac{[N^+]}{[H^+]} \cdot \frac{y_N}{y_H} + K_L^{*j} \cdot [L^-] \cdot [H^+] \cdot y_L \cdot y_H\right)^q} \right] \right) \quad (13)
 \end{aligned}$$

119 where α_M is the overall side-reaction coefficient expressed as

$$\alpha_M = \frac{[M]_{\text{total}}}{[M^{m+}]} = 1 + \sum_r \frac{\beta_r}{[H^+]^r} + \sum_s \beta_s \cdot [L^-]^s$$

120 to account for the aqueous chemical equilibria, including the complexation of M by hydroxide
 121 ion (effective formation constant β_r) and ligands L^- (effective formation constants β_s). The
 122 reactions and constants to calculate the side-reaction coefficient for U and Ra in this work are
 123 shown in the Supplementary Information, Table S1.

124 If the terms in Equation 13 that are independent to i and j are arranged with the K_d , an
 125 equation with the form of a $Y = F(X, Z)$ function can be obtained (Equation 14):

$$\begin{aligned}
 Y = \log \left(\sum_{\text{sites } i} \sum_{p=m}^1 \frac{K_{M(OH)_{m-p}/mH}^{*i} \cdot (SC_i)^p}{\left(1 + K_{N/H}^{*i} \cdot 10^X\right)^p} \right. \\
 + \sum_{\text{sites } j} \left[\sum_{p=m}^1 \frac{K_{M(OH)_{m-p}/mH}^{*j} \cdot (SC_j)^p}{\left(1 + K_{N/H}^{*j} \cdot 10^X + K_L^{*j} \cdot 10^Z\right)^p} \right. \\
 \left. \left. + \sum_{q \geq 1} \frac{K_{M(OH)_{m+q}/mH}^{*j} \cdot (SC_j)^q}{\left(1 + K_{N/H}^{*j} \cdot 10^X + K_L^{*j} \cdot 10^Z\right)^q} \right] \right) \quad (14)
 \end{aligned}$$

126 where Y, X and Z contain factors that can be obtained experimentally or calculated
 127 (Equations 15-17).

$$\mathbf{Y} = \log \left(K_{dM} \cdot \alpha_M \cdot [\text{H}^+]^m \cdot \frac{(y_H)^m}{y_M} \right) \quad (15)$$

$$\mathbf{X} = \log \left(\frac{[\text{N}^+]}{[\text{H}^+]} \cdot \frac{y_N}{y_H} \right) \quad (16)$$

$$\mathbf{Z} = \log([\text{L}^-] \cdot [\text{H}^+] \cdot y_L \cdot y_H) \quad (17)$$

128 Equation 14 is a logarithm of a sum of different terms describing the following possible
 129 sorption processes occurring in the system:

130 - cation adsorption on permanently charged sites X_i

$$\mathbf{Y}_{i(p)} = \log \left[\frac{K_{M(OH)_{m-p}/H}^{*i} \cdot (\text{SC}_i)^p}{(1 + K_{N/H}^{*i} \cdot 10^{\mathbf{X}})^p} \right] = f_{i(p)}(\mathbf{X})$$

131 - cation adsorption on hydroxylated sites $Y_j\text{OH}$

$$\mathbf{Y}_{j(p)} = \log \left[\frac{K_{M(OH)_{m-p}/H}^{*j} \cdot (\text{SC}_j)^p}{(1 + K_{N/H}^{*j} \cdot 10^{\mathbf{X}} + K_L^{*j} \cdot 10^{\mathbf{Z}})^p} \right] = f_{j(p)}(\mathbf{X}, \mathbf{Z})$$

132 - anion adsorption on hydroxylated sites $Y_j\text{OH}$

$$\mathbf{Y}_{j(q)} = \log \left[\frac{K_{M(OH)_{m+p}/OH}^{*j} \cdot (\text{SC}_j)^q}{(1 + K_{N/H}^{*j} \cdot 10^{\mathbf{X}} + K_L^{*j} \cdot 10^{\mathbf{Z}})^q} \right] = f_{j(q)}(\mathbf{X}, \mathbf{Z})$$

133 Therefore, when $\mathbf{X} \rightarrow -\infty$, then $\mathbf{Y}_{i(p)} \rightarrow \log(K_{M(OH)_{m-p}/H}^{*i} \cdot (\text{SC}_i)^p)$, which results in a
 134 horizontal asymptote for the $\mathbf{Y}_{i(p)} = f_{i(p)}(\mathbf{X})$ curve that allows estimating the value of the
 135 corrected selectivity coefficient for M (K^{*i}). When $\mathbf{X} \rightarrow +\infty$, then $\mathbf{Y}_{i(p)} \rightarrow \log$
 136 $\left[\frac{K_{M(OH)_{m-p}/H}^{*i} \cdot (\text{SC}_i)^p}{(K_{N/H}^{*i})^p} \right] - p \cdot \mathbf{X}$, which is a linear asymptote with negative slope independently of the
 137 value of p , always a positive number ($1 \leq p \leq m$). This slope provides the stoichiometry of the
 138 adsorbed species and the associated chemical equilibrium.

139 In the same way, and if $K_{N/H}^{*j} \cdot 10^X \gg K_L^{*j} \cdot 10^Z$, $Y_{j(p)} \rightarrow \log \left[\frac{K_{M(OH)_{m-p}/H}^{*j} (SC_j)^p}{(K_{N/H}^{*j})^p} \right] - p \cdot X$ and $Y_{j(q)}$
140 $\rightarrow \log \left[\frac{K_{M(OH)_{m+p}/OH}^{*j} (SC_j)^q}{(K_{N/H}^{*j})^q} \right] - q \cdot X$ when $X \rightarrow +\infty$, defining linear asymptotes with negative
141 slopes ($1 \leq p \leq m$ and $q \geq 1$). Since X and Z vary in the opposite direction with increasing pH
142 (see Equations 16 and 17), the increase of Y with X (i.e. positive slope of the curve $Y = f(X)$)
143 implies that $K_{N/H}^{*j} \cdot 10^X \ll K_L^{*j} \cdot 10^Z$, which gives evidence of hydroxylated sorption sites that are
144 able to absorb anionic species of M.

145 The curves $Y = f(X)$ and $Y = g(Z)$ can be obtained experimentally by determining the
146 distribution coefficient of M in the presence of excess N^+ over a wide pH range. The
147 commonly used K_d vs. pH curve can then be converted to $Y = f(X)$ and $Y = g(Z)$ curves
148 representation, where the charge of the adsorbed species p and q can be determined through
149 the slopes of the curves, which consequently allows to write the stoichiometry of the sorption
150 reaction for the trace element M (Equations 1, 9 or 10). The corrected selectivity coefficient
151 associated to the reaction on each sorption site, $K_{M(OH)_{m-p}/H}^{*i}$, $K_{M(OH)_{m-p}/H}^{*j}$ and $K_{M(OH)_{m+p}/OH}^{*j}$,
152 can be obtained by nonlinear fitting of the experimental data. The values of SC_i , SC_j and $K_{N/H}^{*i}$,
153 $K_{N/H}^{*j}$, K_L^{*j} need to be determined a priori from saturation curves of major cations and anions
154 over pH. The clay material used in Reinoso-Maset and Ly (2014) is the same as the one used
155 in this work, therefore site concentrations and stability constants obtained therein were used in
156 the calculations presented here (see discussion).

157 2.2 Adsorption on minor sorption sites

158 Minor sorption sites (<0.001 mmol g^{-1} of dry clay) can have a significant affinity for
159 elements at trace level. Reinoso-Maset and Ly (2014) identified one minor sorption site on the
160 kaolinite after performing adsorption isotherms of Cs over a concentration range, at constant
161 pH and excess of Na^+ in solution (i.e. a competitor ion for the sorption sites). Therein, the
162 methodology and equations for the sorption of monovalent cations is fully explained. In this
163 work, the trace elements are present in solution mainly as their doubly charged species. The
164 equation to calculate the total adsorbed concentration, $[\bar{M}]_T$, of a doubly charged element M in
165 the presence of a monovalent competitor cation can be derived in the same manner and has
166 the final form of Equation 18.

$$\begin{aligned}
[\bar{M}]_T &= \sum_{i=1}^n [(X_i^-)_2 M^{2+}] = \\
&= \sum_{i=1}^n \left(\frac{SC_i}{2} + \frac{\left(1 + K_{N/H}^{*i} \cdot \frac{[N^+]}{[H^+]} \cdot \frac{y_N}{y_H}\right)^2}{8 \cdot K_{M/H}^{*i} \cdot \frac{[M^{2+}]}{[H^+]^2} \cdot \frac{y_M}{(y_H)^2}} \right) \\
&\quad - \sqrt{\left[\frac{\left(1 + K_{N/H}^{*i} \cdot \frac{[N^+]}{[H^+]} \cdot \frac{y_N}{y_H}\right)^2}{8 \cdot K_{M/H}^{*i} \cdot \frac{[M^{2+}]}{[H^+]^2} \cdot \frac{y_M}{(y_H)^2}} \right]^2 + SC_i \cdot \frac{\left(1 + K_{N/H}^{*i} \cdot \frac{[N^+]}{[H^+]} \cdot \frac{y_N}{y_H}\right)^2}{8 \cdot K_{M/H}^{*i} \cdot \frac{[M^{2+}]}{[H^+]^2} \cdot \frac{y_M}{(y_H)^2}}} \right)
\end{aligned} \tag{18}$$

167 This equation can then be used, along with the measured M concentration in solution at
168 equilibrium, [M], to obtain the distribution coefficient (K_d) of the element M. At a given pH
169 and constant N^+ concentration, and providing that M is at trace level compared to the
170 concentration of sites, $[\bar{M}]_T$ changes proportionally to [M] and thus the K_d tends to a constant
171 value. When $[\bar{M}]_T$ reaches the concentration of minor sorption sites, SC_s , a pronounced
172 decrease of K_d towards 0 occurs due to full saturation of the sorption sites. In Equation 18, the
173 solution pH and concentrations can be obtained experimentally, whereas the values of SC_i and
174 $K_{N/H}^{*i}$ were determined from the cation saturation curves over pH in Reinoso-Maset and Ly
175 (2014). By performing a nonlinear fitting of the adsorption isotherms ($\log K_d$ vs. $\log [\bar{M}]_T$), the
176 corrected selectivity coefficients associated to the adsorption equilibria reactions on minor
177 sorption sites can be calculated.

178 3. Materials and methods

179 3.1 Reagents and solutions

180 All solutions were prepared with ultrapure water ($18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$, Milli-Q gradient
181 system, Millipore) and analytical grade reagents purchased from Sigma Aldrich (USA), Fisher
182 Scientific (UK), Fluka (Germany) or VWR (France). Solid phase masses and solution volumes
183 were always determined by weight using daily calibrated 4 decimal figure balances (Mettler
184 Toledo AT200 or XP504, France). Experiments were carried out at room temperature and
185 atmospheric CO_2 , except for the preparation of K hydroxide solutions (used to adjust the pH

186 of the clay suspensions) which was carried out in CO₂-free conditions to minimise additional
187 complexation processes.

188 Radioisotopes solutions of ²³²U and ²²⁶Ra were obtained from Isotope Products
189 Laboratories (USA). Due to the relatively short half-life of ²³²U (t_{1/2}= 68.9 years), the
190 formation of decay products (i.e. ²²⁸Th, ²²⁴Ra, ²²⁰Rn, etc.) can cause interferences in the
191 activity counting, therefore the source solution was first purified following the methodology
192 proposed by Kraus et al. (1956). Aliquot of the ²³²U source solution was loaded in an ion
193 exchange resin column (AG1X8, 100-200 mesh, chloride form; Biorad Laboratories,
194 USA) pre-conditioned with 8 M HCl. The decay products were washed out using 8 M HCl,
195 and to recover the more strongly retained ²³²U, the column was rinsed with 0.1 M HCl. The
196 eluted solution was neutralised with a small volume of 4 M KOH. This fresh ²³²U spiking
197 solution was used within 21 days to ensure that less than 2% of the total activity was due to
198 the accumulated decay products. In the case of ²²⁶Ra (t_{1/2}= 1600 years), the source and spiking
199 solutions were aerated under the fume hood before sampling to avoid any external
200 contamination by the daughter gas ²²²Rn (t_{1/2}= 3.825 days). The formation of other decay
201 products was not an issue for the type of experiments carried out in this study.

202 3.2 Clay preparation

203 The kaolinite clay mineral used in the work was 100% wt. pure kaolinite purchased from
204 Sigma-Aldrich (Germany). Its purity was verified by X-ray diffraction and its N₂-BET
205 specific surface area was 21.38 m²g⁻¹ (Reinoso-Maset and Ly, 2014). Prior to the batch
206 experiments, the raw pure kaolinite was conditioned to its K homoionic form as explained in
207 detail in (Reinoso-Maset and Ly, 2014). Briefly, raw kaolinite was first homoionized to Na-
208 kaolinite and then converted to K-kaolinite. A MilliQ water suspension was carried out to
209 eliminate any residual salt solution, and a final ethanol suspension was used to enhance the
210 drying process. The homoionic K-kaolinite was then gently ground to fine powder and stored
211 in a constant relative humidity container until use. The water content calculated after drying
212 few mg at 105°C was less than 1.30% and considered for the actual mass involved in each
213 individual batch.

214 3.3 Adsorption over pH experiments

215 The adsorption of U(VI) and Ra(II) at trace level was studied at room temperature for a
216 pH range between 2 and 12 in the presence of excess K. The U and Ra distribution coefficients
217 were determined using 0.1 g of K-kaolinite and 20 mL solution phase in tightly capped 30 mL

218 Nalgene centrifuge tubes. This experimental configuration offered a minimal headspace and
219 when sampling was needed the exposure to the laboratory air was for a short time, thus
220 limiting the introduction of atmospheric CO₂ to a negligible amount. In addition, other
221 potential sources of air CO₂ were prevented, e.g. KOH was prepared in a glove-box and added
222 to clay suspensions via an automatic burette.

223 In order to fully disperse and hydrate the clay material, it was first suspended with
224 MilliQ water and after > 16 h aliquots of KClO₄ solution were added accordingly to obtain
225 5·10⁻² M K. The potassium perchlorate salt was used to avoid any potential complexation of U or Ra
226 by the salt anion. After > 16 h equilibration time, the pH was adjusted with known aliquots of
227 concentrate HClO₄ and KOH (previously determined by titration of an equivalent clay
228 amount) and suspensions were shaken for > 20 h, a sufficient time to reach thermodynamic
229 equilibrium between solid and solution phases. The final solution pH was measured after
230 phase separation by ultracentrifugation (20 min, 20000 rpm), and two 1 mL and one 5 mL
231 supernatant aliquots were collected for anion, cation and dissolved Si analysis.

232 At this stage, an aliquot of known ²³²U and ²²⁶Ra activity was added to each batch
233 suspensions, corresponding to initial U and Ra concentrations of ca. 10⁻⁹ and 10⁻¹⁰ M
234 respectively. In both cases, the spiked suspensions were equilibrated overnight on a
235 TURBULA orbital mixer before solid and solution phases were separated by
236 ultracentrifugation. A 1 mL aliquot of the supernatant was taken from uranium batch
237 experiments for liquid scintillation counting (LSC) and 10 mL aliquot from Ra batch
238 experiments for gamma spectrometry. Based on the isotopic dilution principle of no-
239 fractionation between stable and radioactive M, determining the supernatant activity is a simple
240 approach to measure the distribution ratio between solid and solution phases, and
241 consequently the concentration of adsorbed U or Ra (Reinoso-Maset and Ly, 2014).

242 3.3 Adsorption isotherm experiments

243 The U(VI) and Ra(II) adsorption isotherms were obtained at two given pH using 0.15 g of
244 K-kaolinite. Buffer solutions of 2.5·10⁻³ M KOH and 5·10⁻³ M 2-[N-morpholine]ethane-
245 sulfonic acid (MES) or 3-[cyclohexylamino]-1-propane-sulfonic-acid (CAPS) were used to
246 fix the solution pH at 6.1 and 10.2 respectively. These reagents are known to have no
247 interaction with metallic elements (Yu et al., 1997) and their anionic forms are unlikely to be
248 adsorbed onto the clay surface, therefore, they will not interfere with the ion exchange
249 reactions. The buffer solutions also contained 5·10⁻² M KClO₄ to provide excess K in solution.

250 In order to avoid pH changes during the adsorption process, the K-kaolinite was first
251 washed with 20 mL of buffer solutions. The suspensions were mixed during 1 h and after
252 ultracentrifugation (20 min, 20000 rpm) the supernatant was carefully removed to avoid clay
253 loss. The buffer solution wash was repeated one more time. A final 20 mL buffer solution was
254 used to equilibrate the system overnight. Clay dissolution and K concentration were checked
255 after ultracentrifugation (20 min, 20000 rpm) by sampling 5 mL of the supernatant for
256 Sianalysis, and two 0.1 mL aliquots for cation and anion determination.

257 In the U batch experiments, and without exceeding the solubility limit of U at each pH
258 value, aliquots of stable U stock solutions prepared from an ICP-AES standard solution (1000
259 $\mu\text{g mL}^{-1}$ U in 4% HNO_3 , PlasmaCAL, SCP Science, Canada) were added to the suspensions
260 to obtain 10 concentrations between $2 \cdot 10^{-10}$ and $1 \cdot 10^{-7}$ M for the MES series (pH 6.1), and 12
261 concentrations up to $1.26 \cdot 10^{-6}$ M for the CAPS series (pH 10.4). The suspensions were placed
262 on an orbital shaker and left to equilibrate for > 20 h. Both series were finally spiked with 200
263 μL of ^{232}U spiking solution prepared as described above. The addition of ^{232}U was taken into
264 account in the total U concentration in solution. Stable Ra salts or solutions are not available,
265 thus the concentration range in the Ra batch experiments was obtained from a ^{226}Ra spiking
266 solution. The added activities corresponded to an initial Ra concentration between $1.82 \cdot 10^{-10}$
267 and $2.73 \cdot 10^{-7}$ M for the 10 MES batch experiments (pH 6.1), and between $1.12 \cdot 10^{-10}$ and
268 $3.47 \cdot 10^{-7}$ M for the 10 CAPS batch experiments (pH 10.4). In both set of experiments, the
269 spiked suspensions were shaken overnight on a TURBULA mixer before solution and solid
270 phases were separated by ultracentrifugation (20 min, 20000 rpm) and 1 and 10 mL aliquots
271 were taken for ^{232}U LSC and ^{226}Ra gamma spectrometry respectively.

272 3.4 Analytical methodology and experimental error

273 The solution pH, cation and anion concentration by ion chromatography and dissolved
274 silicon concentration by UV-Vis spectrometry were determined in the exact same manner as
275 the methodology followed in Reinoso-Masetand Ly (2014) and analytical details are
276 explained therein.

277 The activity of ^{232}U was measured on a Tri-CARB 2700TR liquid scintillation analyser
278 (Packard, USA) using the α/β discrimination mode to verify that the activity is originated by a
279 pure α emitter. Since the batch series contained high concentration of salt buffer solutions, 0.3
280 mL supernatant aliquots were diluted with 0.7 mL of acetate buffer (0.3 M final
281 concentration) before mixing with 4 mL scintillation cocktail. This resulted in an equal

282 quenching level for all samples with a constant counting efficiency. The counting was
283 performed during 15 min and only the α emission band (200 – 400 keV) was considered.

284 The γ activity of 10 mL supernatant aliquots containing ^{226}Ra was determined using a
285 gamma spectrometer equipped with an N-type coaxial high purity germanium detector
286 (ITECH-Instruments). The gamma spectra were collected from 0 to 2000 keV during 60 min
287 and treated with the InterWinner 6.0 software. The ^{226}Ra band was identified at 186 keV. This
288 band coincides with the ^{235}U energy band, but since U was not present in these batch
289 solutions, any registered activity at this specific energy was attributed to the Ra isotope.

290 The uncertainties reported in this work were calculated for each experimental batch by
291 the propagation of known measurement errors theory, as explained in detail in Reinoso-
292 Maset and Ly (2014).

293 **4. Results and discussion**

294 4.1 Adsorption of U and Ra over pH

295 The K_d distribution for trace U and Ra sorption on K-kaolinite was obtained over pH in
296 the presence of excess K (Figure 1). The U data shows a sorption edge at around pH 3.5
297 followed by a wide sorption plateau, that ends with a slight K_d increase and another two short
298 sorption edges are seen at the highest pH range of the experiments (pH 10-11). Radium
299 however was completely adsorbed at the highest pH, causing null K_d results and thus the data
300 points above pH 10.6 were excluded from the curve representation. Negligible sorption was
301 observed below pH 4, resulting in K_d values around 0. This data is shown in the graph for
302 reference, but it was not considered in the data treatment. Between pH 4 and 10, the K_d
303 increased gradually with increasing pH, as expected from the exchange reaction. However,
304 these results in this form do not provide further information about the charge of the adsorbed
305 species nor the stoichiometry of the reaction. Therefore, the experimental K_d data was
306 transformed to the $Y = f(X)$ and $Y = g(Z)$ functions and Y was represented against X for both
307 trace U and Ra sorption (Figure 1).

308 In the case of U, a small plateau is observed at $1 < X < 2.5$, followed by a decrease of the
309 curve with slope between -2 and -1, for then, at $X > 6$, increase with +1 and +2 slope up to X
310 = 10. The positive slope observed in the $Y = f(X)$ could be due to the precipitation of uranyl
311 silicate minerals formed with Si brought into solution by the inevitable dissolution of
312 kaolinite. However, special care was taken when choosing the U concentration for these

313 experiments, by working with considerable low total concentration of the radioisotope. The
314 non-precipitation was confirmed by the total U in solution at equilibrium for each
315 experimental batch falling below the calculated limiting solubility curves for three U mineral
316 phases at the experimental conditions (Figure S1 in SI). Another consideration is the formation
317 of uranyl carbonate species. Payne et al. (2004) studied the sorption of U over the pH on two
318 Georgia kaolinites and observed that at $\text{pH} > 8$ the complexation of U by dissolved carbonate
319 reduced the U uptake. It was elsewhere mentioned that uranyl carbonate species could be
320 adsorbed on another clay mineral surface, montmorillonite (Catalano and Brown Jr, 2005).
321 Both studies, however, were conducted on air-equilibrated clay suspensions, i.e. systems
322 containing more than about 10^{-5} M total dissolved carbonate. According to thermodynamic
323 predictions, this dissolved concentration will exponentially increase at pH higher than 5.5
324 (Figure S2 in SI) and would explain the observed uranium reactivity. As mentioned above, in
325 this work the amount of carbonate involved in each experiment was sufficiently small to
326 prevent a significant formation of uranyl carbonate complexes. Therefore, the positive slopes
327 were assigned to the sorption of negative uranyl species according with the dissolved species
328 distribution in the absence of carbonate, which shows that the main species at $\text{pH} > 8$ are
329 $\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{OH})_4^{2-}$ (Figure S3 in SI).

330 The $Y = f(X)$ representation for Ra shows a curve with two linear parts ($1 < X < 7$ and 7
331 $< X < 9$) both with slope -2, corresponding to a positively doubly charged species being
332 adsorbed on two different sorption sites. This speciation of Ra agrees with previous studies
333 (e.g. Sajih et al. (2014)) and with its solution speciation distribution of Ra, which is
334 dominated by Ra^{2+} up to pH 11.5 in the absence of carbonate or any other complexing agent
335 (Figure S3 in SI).

336 Once the charge of the adsorbed species were deduced, a nonlinear fitting of the $Y = F(X,$
337 $Z)$ representation for both U and Ra adsorption was performed using Equation 14. The
338 number and concentration of sorption sites on the kaolinite, as well as the constants describing
339 the ion exchange reaction for the major cation and anion (K and ClO_4 in these experiments)
340 were obtained in our previous work (Reinoso-Maset and Ly, 2014). Briefly, cation and anion
341 saturation curves revealed five major sorption sites on the kaolinite surface, of which two
342 were identified as permanently charged sites (X_3^- , X_4^-) and three as hydroxylated sorption
343 sites ($Y_1\text{OH}$, $Y_2\text{OH}$, $Y_5\text{OH}$). The sorption isotherms confirmed the presence of a minor
344 sorption site of lower concentration but higher affinity. Table S2 in SI shows all the solution
345 species, sorption sites and equilibrium constants used to resolve Equation 14 for each

346 system. After some trial and error fittings with all the possibilities, the calculated curves were
347 simplified to the sum of the curves corresponding only to the sorption equilibria that
348 contributed most at each pH interval (e.g. the sorption of negative uranyl species at low pH
349 was negligible compared to the positively charged species). The $Y = F(X, Z)$ fittings for U
350 and Ra were optimized by nonlinear regression using Excel Solver tool and are represented in
351 Figure 2. The stability constants, as corrected selectivity coefficients, obtained from the
352 optimized fittings are summarised in Table 1. These corrected selectivity coefficients for U
353 and Ra, along with constants previously obtained for K, ClO_4 and sorption site concentrations
354 (Reinoso-Maset and Ly, 2014) were subsequently used in Equation 13 to fit the $\log K_d$ vs. pH
355 graphs (Figure 1 for raw data). Figure 2 shows the individual curves for each U and Ra
356 species as well as the overall calculated K_d curve.

357 For U, the sorption of the free uranyl (UO_2^{2+}) was dominant at $\text{pH} < 5$ on sorption site
358 Y_2OH but also presented considerable sorption on X_4 at circumneutral pH. The positively
359 charged hydroxylated form, $\text{UO}_2(\text{OH})^+$, adsorbed mainly on site X_3 . The negatively charged
360 species, $\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{OH})_4^{2-}$, were the predominant species adsorbed on site Y_5OH at
361 $\text{pH} > 7$. This distribution of the adsorbed species over pH highly agrees with the speciation in
362 solution (Figure S2 in SI), and the overall calculated K_d curve fits satisfactorily well to the
363 experimental data (see comparison of calculated vs experimental data in Figure 1). In the case
364 of Ra, the lower number of experimental points limited the fitting to only few possible
365 modelling assumptions. Despite higher uncertainty (see calculated vs experimental in Figure
366 1), the fitting reveals that the sorption of Ra^{2+} over pH occurred more importantly on sites
367 Y_2OH and X_4 , behaviour that resembles the sorption of divalent cations, Ca and Mg, on the
368 same kaolinite material (Reinoso-Maset and Ly, 2014).

369 4.2 Adsorption isotherms of U and Ra

370 Figure 3 shows the experimental adsorption isotherms of U and Ra at trace level at pH
371 6.1 and 10.4. Regardless the variability on the pH 10.4 series for U, a significant difference on
372 the coefficient distribution was observed between the different pH series. This difference was
373 more remarkable between the Ra series, demonstrating that as the pH increases higher
374 sorption is observed, as seen in the saturation curves.

375 For both elements and both pH series, a decrease of sorption at around $\log[M] = -4.5$
376 mmol g^{-1} proves the existence of a low concentration site, which was saturated as the
377 concentration of U or Ra increased in solution. Since all series showed the same inflexion

378 point, the concentration of this site is hence independent of the solution pH and solution
379 speciation. Moreover, this estimated concentration ($0.082 \mu\text{mol g}^{-1}$) agrees with the minor site
380 (X_s) identified on the Cs isotherm in Reinoso-Maset and Ly (2014). Therefore, at the time of
381 calculating the U and Ra isotherm curves by non-linear fitting, this value was used to
382 determine the contribution of a minor site on the overall U and Ra sorption. In both cases, the
383 contribution of a major site (i.e. $Y_1\text{OH}$) was also taken in account, along with the corrected
384 selectivity coefficients for K that had been obtained in previous experiments (Reinoso-Maset
385 and Ly, 2014).

386 The calculated isotherms curves are shown in Figure 3. For trace U at both pH and Ra at
387 pH 10.4, the major contribution to the sorption was by the minor site, X_s , while for Ra at pH
388 6.1 the major site, $Y_1\text{OH}$, had a significant contribution to the sorption. From the non-linear
389 fitting, the best estimated of the corrected selectivity coefficients for U and Ra sorption on the
390 minor site X_s were calculated as well as the U sorption on site $Y_1\text{OH}$, which had not been
391 revealed in the saturation curve (Table 2). The comparison of calculated and experimental K_d
392 values shows a satisfactory agreement for both elements (Figure 3).

393 5. Conclusions

394 The treatment of common experimental K_d values using the multi-site ion exchange
395 model presented here provided with extra information about the speciation of sorbed U and
396 Ra at trace level on kaolinite over a wide pH range. Moreover, the thermodynamic constants
397 of the sorption equilibria were also obtained during optimisation of the model. Table 3
398 compiles the chemical equilibria for U and Ra and their associate equilibrium constants (as
399 corrected selectivity coefficients). Ra was sorbed as its free form, Ra^{2+} , from pH 2 to 10.5 on
400 two main sorption sites, comparably to the behaviour of Ca and Mg sorption on kaolinite.
401 Uranium, on the other hand, showed a more complicated speciation with positively charged
402 species (free and hydroxylated forms) dominating the sorption at pH below 7, while
403 negatively charged uranyl species were sorbed at higher pHs on the most basic sorption site.
404 The sorption isotherms proved the existence of minor sites, which have lower concentration
405 but high affinity for elements at trace level concentrations.

406 The sorption equilibria and associated constants reported here complete the major ions
407 sorption equilibria obtained previously (Reinoso-Maset and Ly, 2014) and consolidate the
408 multi-site ion exchange model as a reliable approach to obtain a robust thermodynamic
409 database describing the sorption of trace elements in the presence of major cations on

410 kaolinite, and in any other similar multi-site ion exchanger. Consequently, this fundamental
411 thermodynamic database will improve the knowledge on radionuclide behaviour in
412 environments containing clayey minerals, which are extremely relevant for migration
413 predictions at contaminate sites.

414

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418

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Figures

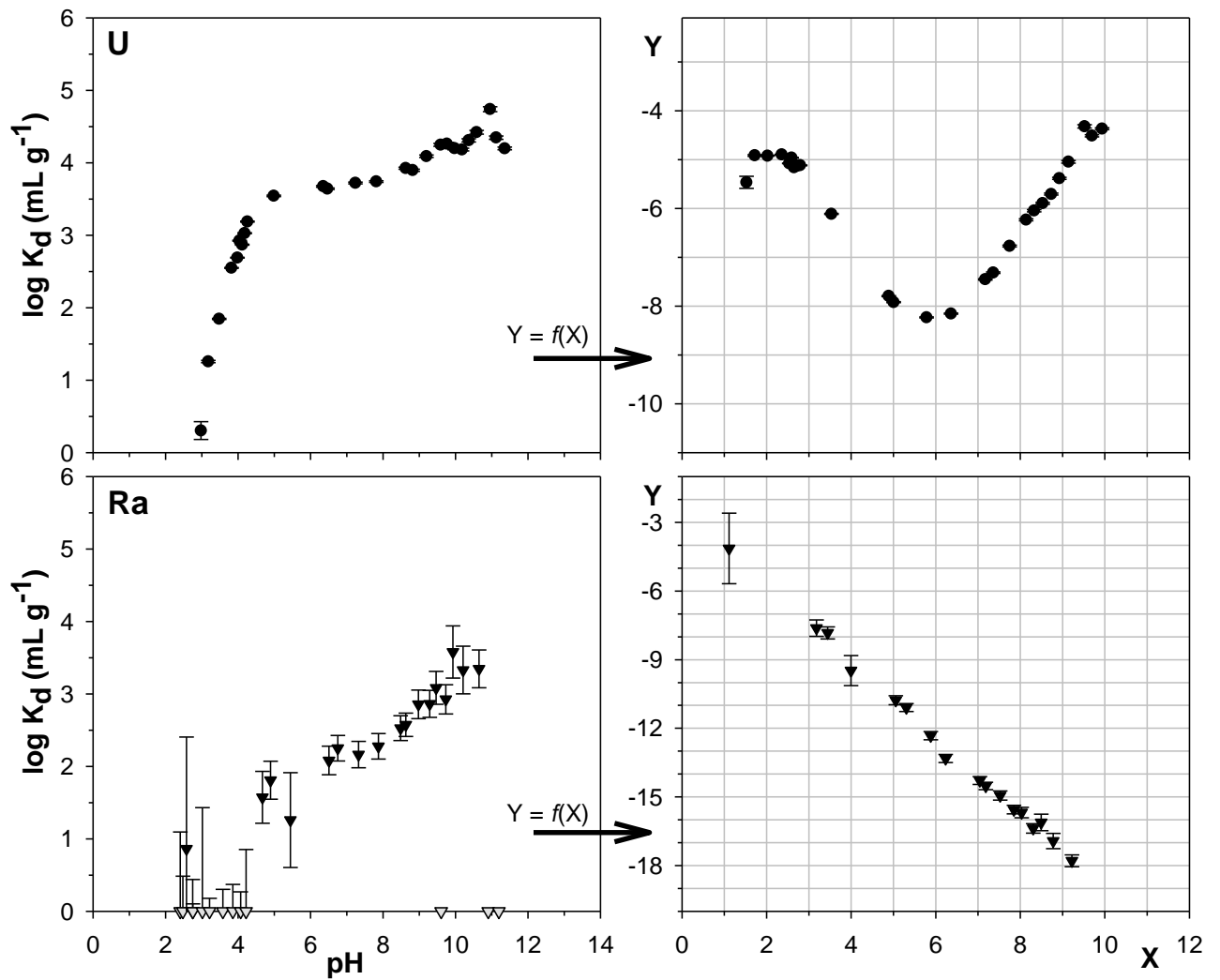


Figure 1. *Left:* Experimental distribution coefficient (K_d) over pH for U (*top*) and Ra (*bottom*) sorption on K-kaolinite in the presence of $5 \cdot 10^{-2}$ M K. Grey triangles were excluded for further data analysis. *Right:* $Y = f(X)$ representation of the same U and Ra sorption data following Equation 14. Grey lines are 1:1 grids to help visualize the slopes. In all cases, the error bars represent $\pm 1 \sigma$.

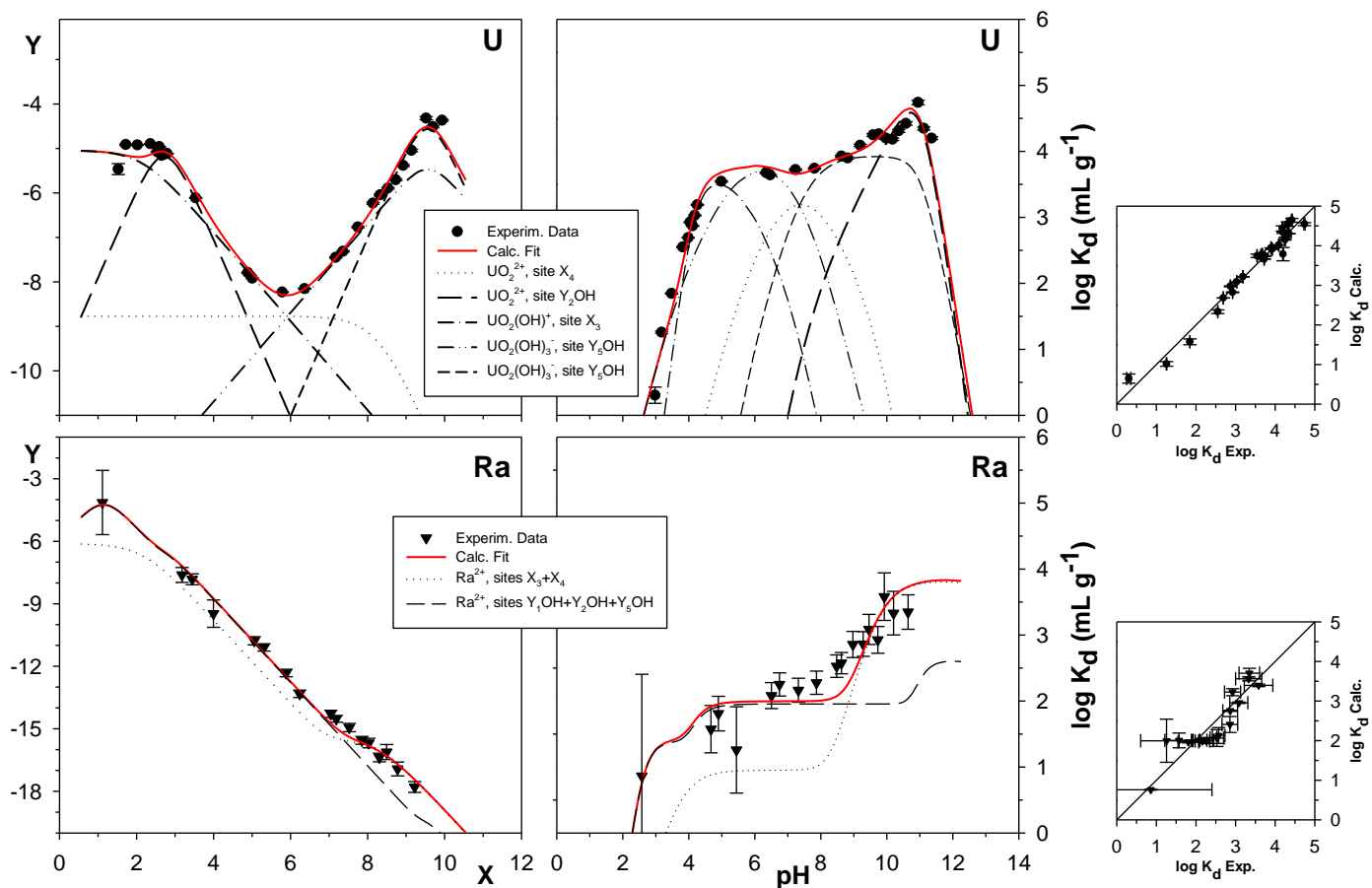


Figure 2. Left: Non-linear fitting of the $Y = f(X)$ representation for trace U (top) and Ra (bottom) sorption. Centre: Fitting of experimental distribution coefficient (K_d) for U (top) and Ra (bottom) sorption on K-kaolinite using Equation 13. In both graphs, the dotted and dashed lines correspond to individually calculated fit for the sorption of U and Ra species on different sorption sites, while full red lines are the overall sum of U and Ra species and sorption sites fits. Right: Comparison of experimental and calculated distribution coefficient of U (top) and Ra (bottom) on kaolinite. In all cases, the error bars represent $\pm 1 \sigma$.

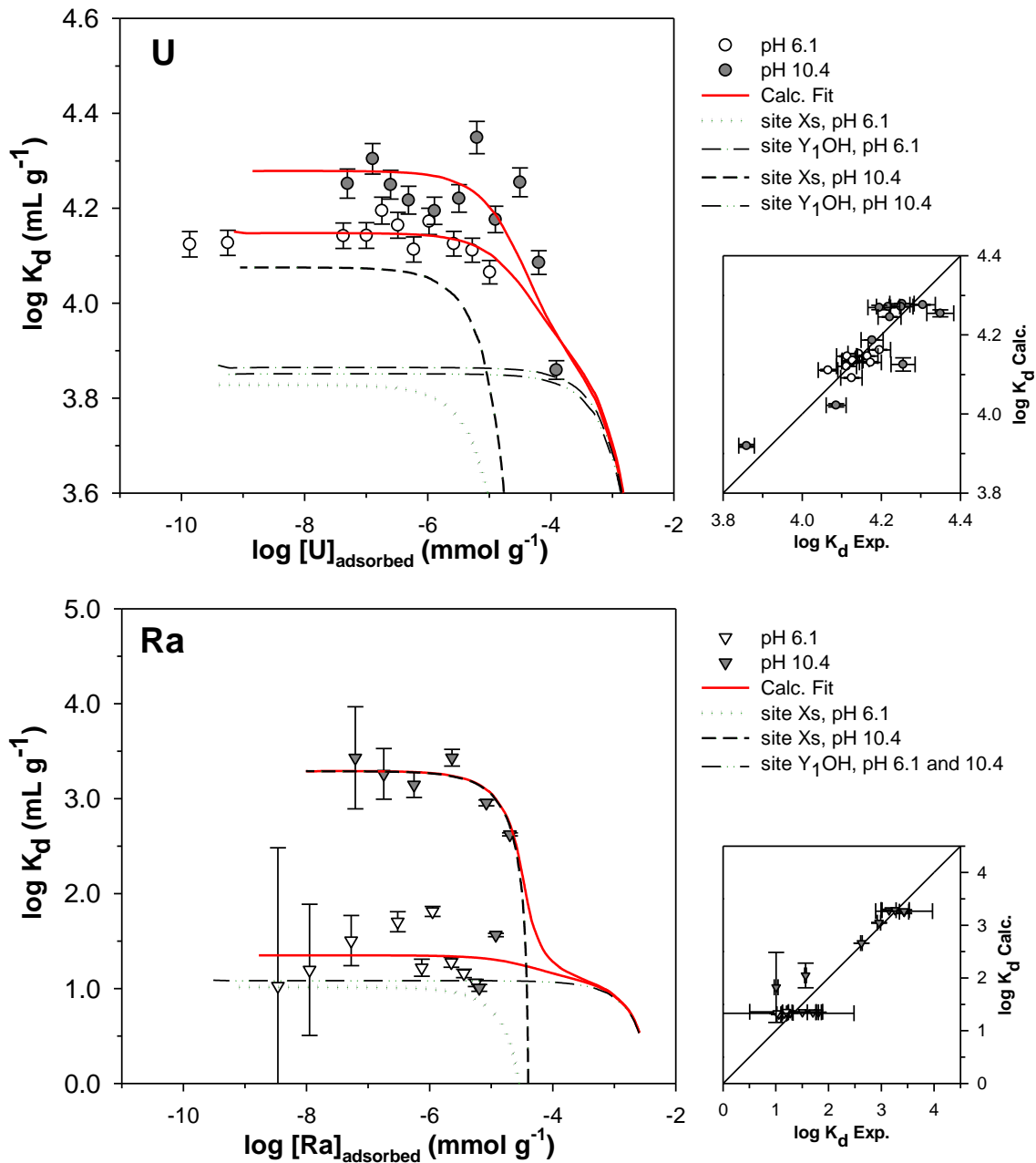


Figure 3. Adsorption isotherms of U (*top*) and Ra (*bottom*) on K-kaolinite. The distribution coefficient is represented as a function of adsorbed U or Ra concentration at pH 6.1 (empty symbols) and 10.4 (filled symbols), in the presence of $4.75 \cdot 10^{-2}$ M K. The dotted and dashed lines correspond to the calculated adsorption isotherms on a minor sorption site, Xs, and a major sorption sites, Y₁OH; and the full red lines are the overall U and Ra adsorption isotherms fittings. Graphs on the right are the comparison of experimental and calculated distribution coefficients. In all cases, the error bars represent $\pm 1 \sigma$.

Tables

Table 1. Type and concentration of major sorption sites, charge of the adsorbed species and the associated corrected selectivity coefficients, $K_{[M(OH)_x]^{m-x}/(m-x)H}^{*i} K_{[M(OH)_x]^{m-x}/(m-x)OH}^{*j}$ describing the sorption of trace U(VI) and Ra(II) on K-kaolinite in the presence of $5 \cdot 10^{-2}$ M K. The values of the constants were determined after non-linear fitting of the $Y = F(X, Z)$ representation of the U and Ra sorption (Equation 14).

Sorption sites X_i, Y_jOH	Site conc. (mmol g ⁻¹)	$K_{K/H}^{*i}$	Charge ($m-x$)	Adsorbed Species	Corrected selectivity coefficients K^{*i} / K^{*j}
Y ₂ OH	0.0190*	6.91e-03*	2	UO ₂ ²⁺	1.21 ± 0.01
X ₃	0.0069*	6.91e-03*	1	UO ₂ (OH) ⁺	(1.03 ± 0.06) · 10 ⁻³
X ₄	0.0107*	5.21e-09*	2	UO ₂ ²⁺	(1.98 ± 0.07) · 10 ⁻⁵
Y ₅ OH	0.0089*	2.16e-09*	-1	UO ₂ (OH) ₃ ⁻	(6.05 ± 0.04) · 10 ⁻³
			-2	UO ₂ (OH) ₄ ²⁻	95.8 ± 4.7
Y ₁ OH	0.0108*	1.83*	2	Ra ²⁺	1292 ± 20
Y ₂ OH	0.0190*	6.91e-03*	2	Ra ²⁺	(1.61 ± 0.02) · 10 ⁻²
X ₃	0.0069*	6.91e-03*	2	Ra ²⁺	(1.65 ± 0.10) · 10 ⁻²
X ₄	0.0107*	5.21e-09*	2	Ra ²⁺	(2.88 ± 0.02) · 10 ⁻¹⁴
Y ₅ OH	0.0089*	2.16e-09*	2	Ra ²⁺	≤ 3.70 · 10 ⁻¹⁴

*values previously obtained (Reinoso-Maset and Ly, 2014)

Table 2. Type and concentration of sorption sites and their associated corrected selectivity coefficients ($K_{M/mH}^{*i}$) describing the sorption of trace U(VI) and Ra(II) on K-kaolinite in the presence of excess K. Values were determined after non-linear fitting of the U and Ra isotherms at pH 10.4 and 6.1 and [K] = $5 \cdot 10^{-2}$ M using Equation 18.

Sorption Sites	Concentration (mmol g ⁻¹)	Corrected selectivity coefficients		
		$K_{UO_2/H}^{*i}$	$K_{Ra/H}^{*i}$	$K_{K/H}^{*i}$
X _s	0.000082 ± 0.000002*	35.4 ± 0.2 (pH 6) 50.3 ± 0.2 (pH 10)	0.121 ± 0.004 (pH 6) 17.5 ± 0.2 (pH 10)	(12.7 ± 0.5) · 10 ⁻⁵
Y ₁ OH	0.0108 ± 0.0001*	3.56 · 10 ⁻⁵	1292 ± 20*	(1.83 ± 0.05)*

*values taken from Table 1 and Reinoso-Maset and Ly (2014)

Table 3. Stoichiometry and associated corrected selectivity coefficients of trace level U(VI) and Ra(II) adsorption equilibria on kaolinite.

<i>Adsorption equilibria</i>	<i>logK*</i>
Uranium	
$UO_2^{2+} + 2 \overline{X_5H} - 2H^+ \leftrightarrow \overline{(X_5)_2UO_2}$	1.55 / 1.70
$UO_2^{2+} + 2 \overline{Y_1OH} - 2H^+ \leftrightarrow \overline{(Y_1O)_2UO_2}$	5.55
$UO_2^{2+} + 2 \overline{Y_2OH} - 2H^+ \leftrightarrow \overline{(Y_2O)_2UO_2}$	0.08
$UO_2^{2+} + \overline{X_3H} + H_2O - 2H^+ \leftrightarrow \overline{(X_3)UO_2OH}$	-2.99
$UO_2^{2+} + 2 \overline{X_4H} - 2H^+ \leftrightarrow \overline{(X_4)_2UO_2}$	-4.70
$UO_2^{2+} + \overline{Y_5OH} + 2H_2O - 2H^+ \leftrightarrow \overline{(Y_5)UO_2(OH)_3}$	-2.22
$UO_2^{2+} + 2 \overline{Y_5OH} + 2H_2O - 2H^+ \leftrightarrow \overline{(Y_5)_2UO_2(OH)_4}$	1.98
Radium	
$Ra^{2+} + 2 \overline{X_5H} - 2H^+ \leftrightarrow \overline{(X_5)_2Ra}$	-0.92 / 1.24
$Ra^{2+} + 2 \overline{Y_1OH} - 2H^+ \leftrightarrow \overline{(Y_1O)_2Ra}$	3.11
$Ra^{2+} + 2 \overline{Y_2OH} - 2H^+ \leftrightarrow \overline{(Y_2O)_2Ra}$	-1.79
$Ra^{2+} + 2 \overline{X_3H} - 2H^+ \leftrightarrow \overline{(X_3)_2Ra}$	-1.78
$Ra^{2+} + 2 \overline{X_4H} - 2H^+ \leftrightarrow \overline{(X_4)_2Ra}$	-11.54
$Ra^{2+} + 2 \overline{Y_5OH} - 2H^+ \leftrightarrow \overline{(Y_5O)_2Ra}$	-13.43