Modeling plutonium sorption to kaolinite: accounting for redox equilibria and the stability of surface species

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Abstract. Plutonium with its particularly complex redox chemistry may be thermodynamically stable in the states +III to +VI depending on the redox conditions in the environment. Mineral surfaces can also affect Pu redox speciation. Therefore, the interpretation of Pu sorption data becomes particularly challenging, even for simplified laboratory experiments. The present study focuses on Pu sorption to kaolinite. Am(III), Th(IV), Np(V) and U(VI) literature sorption data are used as analogues for the corresponding Pu redox states to calibrate a simple surface complexation model, and the Nernst formalism is applied. Two independent pH-pe diagrams, one for the kaolinite surface and another for the aqueous phase, are constructed and superimposed. This allows visualization of the prevalent Pu redox state in both phases. The model suggests that the stability field of the most strongly adsorbing redox state is larger at the surface than in solution. Because Pu(V) weakly sorbs to kaolinite, it never prevails at the surface. Within the stability field of Pu(V) in 0.1M NaClO₄ solution, Pu(VI) and Pu(IV) prevail at the kaolinite surface under oxidizing and slightly reducing conditions, respectively. By contrast, the Pu(IV)/Pu(III) boundary is hardly affected because both redox states strongly sorb to kaolinite, especially for pH > 6. The present method is applied to literature data for Pu sorption to kaolinite. By estimating the pe from a Pu redox state analysis in solution, overall Pu uptake could be predicted. Generic equations are derived that are applicable to minerals and actinides other than kaolinite and Pu. The present study provides important progress in understanding Pu geochemistry, especially in the context of nuclear waste disposal where thermodynamic models are particularly necessary to predict Pu mobility.

Keywords: Plutonium, kaolinite, redox, surface complexation modeling.

39 **Highlights:**

- 40 • Data of actinide analogues are used to model Pu(III,IV,V,VI) sorption to kaolinite.
- 41 • Two pH-pe diagrams for Pu are drawn for (i) the solution and (ii) the surface.
- 42 • Pu sorption and redox speciation can be predicted.
- 43 • The redox potential is crucial information: it controls Pu overall sorption.
- 44 • This approach can be applied to other minerals and actinides.

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1. Introduction

Due to its radiotoxicity and the very long half-lives of several isotopes, plutonium (Pu) is an important element in the context of nuclear waste disposal as well as in remediation of areas contaminated by nuclear weapon testing or nuclear power-plant accidents. Geochemical behavior of Pu is particularly challenging since, in environmentally relevant conditions, Pu can be found in the oxidation states +III, +IV, +V or +VI. Pu(III) or Pu(IV) prevail under reducing conditions, which are particularly relevant for deep geological nuclear waste disposal. Pu(V) or Pu(VI) are more relevant under oxidizing conditions like oxygenated surface environments. The chemical behavior of Pu concerning complexation by organic and inorganic ligands, solubility, as well as sorption to minerals, strongly depends on the Pu redox state (e.g. Altmaier et al., 2013). Thus, Pu(V) weakly sorbs to minerals and is considered to be rather mobile (e.g. Geckeis et al., 2013). Pu(VI) and Pu(III) sorption is pH dependent and can be affected by the presence of carbonates (especially for Pu(VI)). Pu(IV) strongly sorbs to minerals, is sparingly soluble and, therefore, considered to be rather immobile. However, Pu(IV) also tends to form intrinsic colloids in neutral to alkaline conditions, which might enhance its mobility (Neck et al., 2007; Kersting, 2013; Walther and Denecke, 2013). Consequently, sound knowledge of the geochemical behavior of each Pu redox state is required to understand and predict Pu mobility in the environment. In this context, the development of geochemical models that predict Pu speciation accounting for all these processes are required.

Sorption to mineral surfaces can retard Pu migration or mediate its migration when Pu sorbs to mineral colloids (Kersting et al., 1999; Xie et al., 2013), if these colloids remain stable in aqueous suspension and can be transported by water flow. Because of the complexity of the mineral-water interface and of the heterogeneity of minerals in nature, laboratory studies with purified or synthetic minerals are carried out to unravel the underlying processes.

Even though such simplified systems have been widely investigated, the chemical behavior of Pu still remains unclear. In particular, although introduced in a single redox state to a mineral suspension, a mixture of Pu redox states rapidly emerges. For instance, when added either as Pu(VI) or Pu(V) under ambient (air) atmosphere, Pu(V) prevails in solution at the end of the experiment, but Pu(IV) is found at the surface of hematite, goethite, magnetite (Powell et al., 2004; 2005; Romanchuk et al., 2011; 2013; Hixon and Powell, 2014), quartz/silica (Kumar et al., 2012; Hixon et al., 2013) or montmorillonite (Zavarin et al., 2012). Similar observations were recently made in the case of neptunium (Np) interaction with illite (Marsac et al., 2015). Although initially introduced as Np(V) under oxygen-free argon atmosphere, a significant amount of Np(IV) was found at the surface, whereas a small fraction remained in solution as Np(V). Conversely, when Pu(IV) was added either under argon or ambient atmosphere, Pu(V) was found in solution in the presence of kaolinite (Banik et al., 2007). Pu(III) sorption to minerals has been probed less frequently, although it has high environmental relevance (Kaplan et al., 2007; Lujanienė et al., 2009; Kirsch et al., 2011). Buda et al. (2008) reacted Pu(III) with kaolinite in the presence of $\text{NH}_2\text{OH}\cdot\text{HCl}$ as reducing agent. A preliminary experiment, in the absence of kaolinite, showed that Pu(III) was not stable and Pu(IV) formed in solution in the presence of $\text{NH}_2\text{OH}\cdot\text{HCl}$ for $\text{pH} > 6$. In the presence of kaolinite, the pH-edges of Pu and Am(III) were found to be very similar, the sorption plateau being reached for $\text{pH} \approx 6$. This suggests that the Pu(IV)/Pu(III) redox couple is only weakly affected by sorption.

It appears from all these studies that mineral surfaces have a strong impact on Pu redox speciation, especially when the Pu(V)/Pu(IV) couple is involved. Furthermore, these studies also show that the prevalent redox state of the metal ion in aqueous solution can differ from that at the mineral surface. In principle, the overall redox potential of the system should determine the final redox state of Pu (Geckeis et al., 2013). It has been previously proposed that the strongly adsorbing Pu(IV) is thermodynamically favored at a mineral surface

compared to Pu(V) (Hixon et al., 2013; Hixon and Powell, 2014). With such an approach, the Np sorption to illite and redox speciation could recently be described in a quantitative way considering Np(IV) at the mineral surface and Np(V) in solution (Marsac et al., 2015). This approach might also be suitable in the case of Pu, because of the very similar chemistry of both actinides.

To determine the stability fields of different Pu redox states at a mineral surface, the sorption behavior of all redox states must be known separately. It appears that for Pu such experimental data will hardly ever become available because a mixture of redox states is found in most experimental studies. Fortunately, lanthanides/actinides (Ln/An) exhibit similar chemical behavior for the same redox state, even though thermodynamic constants may significantly differ between two elements (Altmaier et al., 2013). The use of these elements as chemical analogues might help to unravel the complex geochemical behavior of Pu in a first approach (Choppin, 1999).

The present study focuses on kaolinite because experimental sorption data for americium(III) (Am^{3+}), thorium(IV) (Th^{4+}), neptunium(V) (NpO_2^+) and uranium(VI) (UO_2^{2+}) are available (Buda et al., 2008; Banik et al., 2007; Amayri et al., 2011; Křepelová, 2007). These data are assumed to be representative for sorption of Pu(III, IV, V, VI), respectively, and used for each redox state of Pu to calibrate the simple surface complexation model developed by Tertre et al. (2008). By merging Pu redox chemistry with sorption processes, the resulting model is used to construct a predominance (pH-pe) diagram for Pu redox speciation at the kaolinite surface. The modeling results are compared with experimental data in order to test the capacity of the model to predict Pu sorption to kaolinite as a function of pH and pe. The present approach is subsequently tested on metal sorption on other minerals.

2. Materials and method

2.1. Geochemical speciation code and thermodynamic database

PHREEQC (version 2; Parkhurst and Appelo, 1999) is a computer code that can perform speciation (including surface complexation) and saturation-index calculations in water. Predominance (pH-pe) diagrams can be obtained using PhreePlot (Kinniburgh and Cooper, 2009), which contains an embedded version of PHREEQC. In the present work, thermodynamic constants for Pu aqueous speciation and solubility are taken from the NEA thermodynamic database (Guillaumont et al., 2003). Reactions and corresponding thermodynamic constants at 25°C and zero ionic strength are given in Table 1. In case of gaps in the Pu database, data for analogues were chosen and are included in Table 1. A redox reaction involving aqueous Pu^{4+} and PuO_2^+ is not given. It is calculated based on the reaction $\text{PuO}_{2(\text{am,hyd})} = \text{PuO}_2^+ + \text{e}^-$ with $\log K = -19.78$ at zero ionic strength (Guillaumont et al., 2003). The specific ion interaction theory (SIT; Ciavatta, 1980) accounts for ionic strength effects and the corresponding parameters for Pu (or the chosen analogue) from Guillaumont et al. (2003) are used.

2.2. Surface complexation modeling

As for other clay minerals, the kaolinite surface is complex because of the presence of various types of hydroxyl surface groups, mainly silanols ($\equiv\text{SiOH}$) and aluminols ($\equiv\text{AlOH}$), that can bind cations. Furthermore, several faces with different charging properties occur (Miller et al., 2007) making the development of mechanistic models a challenging task. Tertre et al. (2008) showed that batch uptake data for the trivalent lanthanides to kaolinite can be relatively well modelled by the “Generalized Composite Approach” (Davis et al., 1998; Davies et al., 2004). In this approach, only one type of generic surface site ($\equiv\text{SOH}$) is

considered and no electrostatic term is included. As detailed by Tertre et al. (2008), for the modeling of the actinide sorption to kaolinite acid-base properties of the surface do not need to be treated explicitly. A similar approach was also used by Lützenkirchen (2012). The general reaction equation for the complexation of an actinide (An) cation with a charge “+n” to a monodentate generic surface group ($\equiv\text{SOH}$) can be written tentatively as:

where $i \geq 1$. The corresponding surface complexation constant will be noted $^sK_{X,(i-1)}$, where “X” denotes the redox state of the actinide. In the case of lanthanides (e.g. europium; Eu), Tertre et al. (2008) only consider the formation of the surface species $\equiv\text{SOEu}^{2+}$. Their study was restricted to $\text{pH} < 8$ and a decrease in the simulated sorption between pH 7 and 8 suggests that more (hydrolyzed) surface species (e.g. $\equiv\text{SOEuOH}^+$) need to be considered for $\text{pH} > 8$. This is similar to other clay minerals whenever a non-electrostatic model is used (e.g. for montmorillonite or illite: Bradbury and Baeyens 2005; 2009). In addition, cation exchange is a relevant sorption mechanism in the case of kaolinite. In PHREEQC, the Gaines and Thomas (1953) convention can be used, whereby cation exchange reactions, the thermodynamic exchange constant (K_{exch}), and selectivity coefficient ($^{An}_{Na}K_c$) are expressed as follows:

$$K_{\text{ex}} = \frac{N_{\text{An}}}{(N_{\text{Na}})^n} \times \frac{f_{\text{An}}}{(f_{\text{Na}})^n} \frac{[\text{Na}^+]^n}{[\text{An}^{n+}]} = \frac{^{An}_{Na}K_c}{(f_{\text{Na}})^n} \times \frac{f_{\text{An}}}{(f_{\text{Na}})^n} \quad (3)$$

Here, N_i are equivalent fractions, f_i are surface activity coefficients and brackets denote activities in solution. Tertre et al. (2008) also considered a H^+ - Na^+ exchange reaction with $\log ^H_{Na}K_c = -1$.

In the case of the original study of Tertre et al. (2006, 2008), the surface area of kaolinite is 10 m²/g, site densities for ≡SOH and exchange sites are 1.66 and 3.70 μmol/m², respectively.

2.3. Distribution coefficients (K_d)

As will be shown in the next sections, the use of distribution coefficients (K_d) to express An uptake by kaolinite is particularly convenient for the present purpose. K_d is defined as:

$$K_d = \frac{[An]_{surf}}{[An]_{tot,aq}} \times \frac{V}{S} \quad (4)$$

where [An]_{surf} and [An]_{tot,aq} refer to the total amount (i.e. the sum of all the species including various redox states) at the surface and in solution, respectively, and V/S is the liquid to solid ratio. S can be either expressed as the mass of solid (K_d in L/kg) or as the surface area (K_d in L/m²) in contact with a given solution volume. K_d is a highly conditional parameter that depends on the physico-chemical conditions (e.g. pH, I, T, ligands in solution, surface loading). As discussed later, this study focused on data obtained at room temperature, for 0.1 M NaClO₄, in the absence of complexing ligands other than OH⁻ and assuming ideal sorption behavior. Therefore, the evolution of K_d with pH can be calculated using the simple surface complexation model described above.

K_d is commonly experimentally determined to quantify actinide sorption to minerals. In the case of redox sensitive elements like Pu, several redox states (Pu(X); X = III, IV, V, or VI) might occur simultaneously both at the surface and in the aqueous phase, depending on the redox conditions. The overall (measured) K_d will be ultimately affected by the Pu redox state distribution. For a mixture, K_d is denoted K_{d,tot} and can be written as follows:

$$K_{d,tot} = \frac{\sum_X [Pu(X)]_{surf}}{\sum_X [Pu(X)]_{tot,aq}} \times \frac{V}{S} = \frac{\sum_X K_d(X) \times [Pu(X)]_{tot,aq}}{\sum_X [Pu(X)]_{tot,aq}} \quad (5)$$

$K_d(X)$ represents the measured K_d for the ideal case where only the redox state X is present both at the surface and in solution (i.e. when $K_{d,tot} = K_d(X)$):

$$K_d(X) = \frac{[Pu(X)]_{surf}}{[Pu(X)]_{tot,aq}} \times \frac{V}{S} \quad (6)$$

Such values can conveniently be obtained for redox insensitive analogues and applied to Pu.

2.4. Predominance pH-pe diagram

2.4.1. Construction of a simplified predominance diagram for aqueous species

For simplicity, in the remainder of the text, we used brackets to denote concentrations and K will refer to the conditional constant valid for a given ionic strength. In practice, appropriate corrections of the stability constants for $I = 0$ can be handled by speciation codes like PHREEQC applying appropriate activity corrections for example by using SIT. This study will only focus on experimental data obtained in non-complexing background electrolyte solutions ($NaClO_4$), under inert atmosphere or under atmospheric conditions where carbonate complexation was shown to be negligible (i.e. for sufficiently low pH). Furthermore, we restrict the study to sufficiently low Pu concentrations such that the formation of dissolved polycations is negligible. Under these premises, only the hydrolysis of Pu(III, IV, V, VI) are taken into account in the following equations. They are not valid in the presence of other complexing ligands (e.g. carbonates), but can be extended to include effects of aqueous speciation beyond bare hydrolysis in the absence of ternary surface complexes.

208 Free aqueous component species of Pu are Pu^{3+} , Pu^{4+} , PuO_2^+ and PuO_2^{2+} for the
 209 successive redox states. All relevant reactions are given in table 1. A generic redox reaction of
 210 an oxidized (Pu(Ox)) to a reduced (Pu(Red)) form can be written as:

$$212 \quad K_{\text{Ox/Red}} = \frac{[\text{Pu}(\text{Red})^{(n-q+m)}]}{[\text{Pu}(\text{Ox})^{n+}][\text{H}^+]^m[\text{e}^-]^q} \quad (8)$$

213 The simplified reaction 7, where “n” is the charge of the free Pu(Ox) cation, “q” is the number of
 214 electrons involved and “m” equals 0 or 4 depending on the redox states involved, is not
 215 entirely balanced because the “plutonyl oxygens” are not shown (see table 1). As an example,
 216 the reduction reaction of PuO_2^{2+} to Pu^{4+} involves two electrons and four protons ($q = 2$; $m = 4$)
 217 whereas Pu^{4+} reduction to Pu^{3+} involves only one electron ($q = 1$; $m = 0$). The mass law
 218 equation can be rearranged as follows:

$$219 \quad pe = \log K_{\text{Ox/Red}}/q + \log \left(\frac{[\text{Pu}(\text{Ox})^{n+}]}{[\text{Pu}(\text{Red})^{(n-q+m)}]} \right) / q - m/q \times pH \quad (9)$$

220 where pe equals $-\log a_{\text{e}^-}$ (the apparent activity of the electron). pe is related to the redox
 221 potential (in Volts, versus the standard hydrogen electrode) by the relationship: $pe = 16.9 \times E_{\text{h}}$,
 222 at 25°C. Applying the latter convention to eq. 9 would lead to the well-known Nernst
 223 equation. For standard conditions (25°C, pH = 0 and zero ionic strength) when $[\text{Pu}(\text{Ox})^{n+}] =$
 224 $[\text{Pu}(\text{Red})^{(n-q+m)}]$, the standard redox potential E^0 for a given couple is obtained.

225 The general hydrolysis reaction of a given Pu redox state “X” is:

$$227 \quad {}^{\text{OH}}K_{\text{X},i} = \frac{[\text{Pu}(\text{X})(\text{OH})_i^{n-i}][\text{H}^+]^i}{[\text{Pu}(\text{X})^{n+}]} \quad (11)$$

228 where $^{OH}K_{X,i}$ is the corresponding equilibrium constant. The total aqueous concentration of
 229 Pu(X) ($[Pu(X)]_{tot,aq}$) can be calculated from the concentration of the free cation ($[Pu(X)^{n+}]$) via:

$$\begin{aligned}
 230 \quad [Pu(X)]_{tot,aq} &= [Pu(X)^{n+}] + \sum_i [Pu(X)(OH)_i^{n-i}] = [Pu(X)^{n+}] \times \left(1 + \sum_i \frac{^{OH}K_{X,i}}{[H^+]^i} \right) \\
 231 \quad &= [Pu(X)^{n+}] \times \alpha_X \quad (12)
 \end{aligned}$$

232 where α_X is the side reaction coefficient for Pu(X). Introduction in the Nernst equation (eq. 9)
 233 yields:

$$234 \quad pe = \log K_{Ox/Red} / q + \log \left(\frac{[Pu(Ox)]_{tot,aq}}{[Pu(Red)]_{tot,aq}} \times \frac{\alpha_{Red}}{\alpha_{Ox}} \right) / q - m/q \times pH \quad (13)$$

235 The pe corresponding to the borderline between two Pu redox states in solution (noted
 236 $\{Ox/Red\}_{aq}$) is found as follows:

$$237 \quad \{Ox/Red\}_{aq} = pe = \log K_{Ox/Red} / q + \log \left(\frac{\alpha_{Red}}{\alpha_{Ox}} \right) / q - m/q \times pH \quad (14)$$

238 $\{Ox/Red\}_{aq}$ evolves with pH and ionic strength. With eq. 14, a relatively simple
 239 predominance (pH-pe) diagram can be drawn. It will not show the speciation of a given redox
 240 state (e.g. hydrolyzed species) but the boundaries between redox states appear. In eq. 14, the
 241 side reaction coefficient ratio is driving $\{Ox/Red\}_{aq}$, i.e. the redox state of Pu with the
 242 strongest hydrolysis tends to enlarge its predominance area with increasing pH. Note that the
 243 precipitation of solid phases is not included in the present calculations. Therefore, the
 244 equations are only valid (i) below the saturation of relevant Pu-bearing minerals or (ii) for
 245 discussions restricted to the aqueous phase, independent of any solid phase (i.e. precipitates as
 246 well as adsorbing phase), as discussed by Schüring et al. (2000).

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2.4.2. Construction of a predominance diagram for the mineral surface

To take into account sorption processes in the Nernst equation, the expression of K_d (eq. 6) for two different redox states (i.e. $K_d(Ox)$ and $K_d(Red)$) can be included into eq. 13:

$$pe = \log K_{Ox/Red} / q + \log \left(\frac{[Pu(Ox)]_{surf}}{[Pu(Red)]_{surf}} \times \frac{\alpha_{Red}}{\alpha_{Ox}} \times \frac{K_d(Red)}{K_d(Ox)} \right) / q - m/q \times pH \quad (15)$$

and it becomes possible to calculate the predominance field for different Pu surface redox states. Because eq. 15 exclusively relates to the surface, such a plot is independent of that corresponding to solution: both must be superimposed for comparison. As stated before, K_d varies with pH and ionic strength.

On a pH-pe diagram, the borderline between two redox states at the mineral surface ($\{Ox/Red\}_{surf}$) can be directly compared with the one in solution:

$$\{Ox/Red\}_{surf} = \{Ox/Red\}_{aq} + (\log K_d(Red) - \log K_d(Ox))/q \quad (16)$$

At the mineral surface, the pH-pe predominance area of the redox state with the strongest sorption behavior (i.e. the highest K_d) is enlarged relative to the aqueous phase, similar to the effect of hydrolysis in solution. Hence, certain redox conditions will favor the stabilization of a given redox state in solution whereas the corresponding reduced or oxidized form is stabilized at the surface. The pe scale appears more appropriate than Eh since, for a reaction involving only one electron ($q = 1$), a difference of one order of magnitude between the K_d 's ($\Delta \log K_d = 1$) simply shifts the Ox:Red 1:1 borderline at the mineral surface compared to the one in solution by one pe unit (± 60 mV). Such uncertainties on pe are on the order of experimental errors (Altmaier et al., 2010).

2.5. Data selection

Because of its complex redox chemistry, the ideal pH-edges of Pu(III/IV/V/VI) for one redox state in the system are not readily available. Fortunately, f-orbital elements exhibit very similar chemical behaviors for a given redox state, and the nearest neighbors in the lanthanide and actinide series of the periodic table show sufficiently similar chemistries to serve as analogues. In this study, experimental uptake data on kaolinite for Am(III), Th(IV), Np(V) and U(VI) are assumed to be representative for the sorption of Pu in the corresponding redox state. These experimental data can then be directly used to calibrate the surface complexation model Pu(III/IV/V/VI). The subsequent predictions of this model will strongly depend on this approximation.

Experimental datasets for Am(III) (Buda et al., 2008; $[Am]_{tot} = 10^{-9}$ M), Th(IV) (Banik et al., 2007; $[Th]_{tot} = 6.6 \times 10^{-13}$ M) and Np(V) (Amayri et al., 2011, $[Np]_{tot} = 7 \times 10^{-12}$ M) are chosen. All these studies on actinide sorption involve kaolinite KGa-1b at 4 g/L, 0.1 M NaClO₄ background electrolyte and absence of CO₂. The above elements are very stable in the respective redox states for a wide range of pH-pe conditions. However, under inert atmosphere (i.e. Ar), Np(V) was partially reduced to Np(IV) in the presence of illite, leading to higher overall uptake compared to Np(V) sorption to illite in the presence of O₂ (Gorgeon, 1994; Marsac et al., 2015). Nevertheless, for pH < 7, where carbonates have no influence on Np(V) sorption to kaolinite, Amayri et al. (2011) found similar results under inert and ambient atmospheres. Therefore, their Np-kaolinite data can be confidently attributed to the sorption of Np(V) only. By contrast, U(VI) sorption to kaolinite, often studied in the presence of CO₂ (e.g. Payne et al., 2004; Gao et al., 2010), is strongly affected by U(VI)-carbonate complexation for pH > 8. Fortunately, Křepelová (2007) investigated U(VI) sorption to KGa-1b in 0.1 M NaClO₄ with CO₂ and in 0.01 M NaClO₄ in the absence of CO₂ ($[U]_{tot} = 10^{-6}$ M;

S/V = 4 g/L). Both data sets will be discussed, discarding the sorption data above pH = 8 in the presence of CO₂. The published data were digitized and recalculated to K_d (eq. 4).

The sorption of Am(III), Th(IV), Np(V) and U(VI) to kaolinite has been studied for different [An]_{tot} (from 6.6×10⁻¹³ to 10⁻⁶ M). Uptake of An on kaolinite may in principle be affected by the total An concentration due to the presence of low and high affinity sites in different amounts, causing non-ideal sorption behavior at the respective An to kaolinite ratios. A lower uptake was measured for Np(V) and U(VI) in the corresponding studies for higher [Np/U]_{tot} (~10⁻⁵ M), which can be attributed to a surface site saturation effect. The behavior of An at such high concentrations is not addressed in this study. The modeling of An uptake by kaolinite is restricted to the lowest [An]_{tot} available in the literature. Although ideal sorption behavior was established for low [An]_{tot} in the case of illite and montmorillonite (Bradbury and Baeyens, 2005; 2009), this observation cannot a priori be transferred to kaolinite due to the lack of sorption isotherms for each of the analogues of Pu(III, IV, V, VI) over sufficiently broad [An]_{tot} ranges (especially for very low [An]_{tot}). As a first approximation our treatment assumes ideal sorption behavior for all An. If the simulations result in reasonable prediction of the experimental data, this simplification is appropriate for the range of conditions of the calibration and simulation data sets. Any prediction made with this model for environmentally relevant Pu concentrations (e.g. ~10⁴ atoms/kg in Dai et al., 2002) should be considered with caution.

Banik et al. (2007) added Pu(IV) ($6.9 \times 10^{-9} < [\text{Pu}]_{\text{tot}} < 3.5 \times 10^{-7}$ M) to a KGa-1b suspension (S/V = 4 g/L) in 0.1 M NaClO₄ either under argon or ambient atmosphere. Detailed information on the experimental work can be found in Banik (2006). In that study, only small variations in Pu uptake were observed (i) with time between 63 and 209 h (Figure S1), (ii) with [Pu]_{tot} (Figure S2) and (iii) with changes of the atmosphere for pH < 9. However, speciation calculations suggested that significant amounts of Pu-carbonate complexes formed

for pH > 8 in the presence of CO₂. We will not discuss the effect of carbonate in the present study so the latter data for pH > 8 in the presence of CO₂ are not considered. Pu aqueous redox state analysis ($\pm 10\%$ uncertainty) in the solution on contact with kaolinite and subsequent phase separation (i.e. only the aqueous phase was analyzed) was performed at pH = 1, 4 and 9 ($[\text{Pu}]_{\text{tot}} = 3.5 \times 10^{-7} \text{ M}$), resulting in (i) for pH = 1, 38% of Pu(III) and 46% of Pu(IV), (ii) for pH = 4, 75% of Pu(V) and 14% of Pu(IV) and (iii) for pH = 9, 45% of Pu(IV) and 49% of Pu(IV) in form of intrinsic (or eigen-) colloids.

3. Results and discussion

3.1. Surface complexation modeling

Figure 1 presents the experimental log K_d values (in L/kg) versus pH for Am(III), Th(IV) and Np(V) sorption to kaolinite (S/V = 4 g/L) in 0.1 M NaClO₄ and in the absence of CO₂ from the literature (Buda et al., 2008; Banik et al., 2007; Amayri et al., 2011). Both the U(VI) sorption data of Křepelová (2007) in 0.1 M NaClO₄ with CO₂ (pH < 8) and in 0.01 M NaClO₄ without CO₂ are shown. When plotted as log K_d , the two latter datasets are similar, showing that U(VI) sorption to kaolinite is barely affected by ionic strength. Only a slightly higher sorption is observed in 0.01 M NaClO₄. The pH-edges follow the effective charge of the cations Np(V) (+2.3) < Am(III) (+3) < U(VI) (+3.3) < Th(IV) (+4), as usual (Geckeis et al., 2013). Sorption reaches a plateau for all actinides at $3.5 < \log K_d < 4$, as well as for both ionic strengths investigated for U(VI). K_d values cannot be derived for U(VI) (pH < 4) and Np(V) (pH < 6) because no significant sorption occurred at the solid to liquid ratio of 4 g/L. For $2 < \text{pH} < 4$, K_d for Am(III) remains constant, due to cation exchange, and lower sorption is observed for pH < 2.

Am(III), Np(V), and U(VI) will provide a sound estimate for Pu(III/V/VI) sorption to kaolinite due to the similar hydrolysis constants of the respective analogues. Direct comparison between Th(IV) and Pu(IV) is hampered by the documented difference in their hydrolysis constants. An inaccurate description of Pu(IV) sorption might have consequences for the determination of the various boundaries between two Pu redox states on the kaolinite surface ($\{Ox/Red\}_{surf}$). However, the difference between Th(IV) and Pu(IV) sorption must be large (more than one $\log K_d$ unit) to significantly affect our interpretations, as discussed in section 2.4.2. From the sorption data and the Pu redox state analysis in solution as reported by Banik (2006), eq. 5 allows us to determine $K_d(IV)$, i.e. the K_d that is measured in the case where only Pu(IV) would be present both at the surface and in solution. If Pu(IV) and an additional redox state X prevail, eq. 5 becomes:

$$K_d(IV) = (K_{d,tot} - K_d(X) \times F_{X,aq}) / F_{IV,aq} \quad (17)$$

where $F_{IV,aq}$ and $F_{X,aq}$ represent the fractions of the respective redox states in solution. With equation 17, $K_d(IV)$ can be calculated for $pH = 1$, with $K_d(III)$ from Am(III). For $pH = 4$, although 75% of Pu(V) was present in solution ($F_{V,aq} = 0.75$), Pu(V) sorption is weak and $K_d(V) \times F_{V,aq}$ can be neglected. This leads to $K_d(IV) \approx K_{d,tot} / F_{IV,aq}$ (Figure 1). K_d values for Th(IV) and Pu(IV) are very similar for kaolinite, which supports the use of Th(IV) as a reliable analogue. For $pH = 9$, $K_d(IV)$ cannot be determined because Banik et al. (2007) observed Pu(IV) as monomers or eigen-colloids. However, we expect a constant K_d for $pH > 4$ since tetravalent actinides show no hydrolyzed aqueous species beyond $An(OH)_{4(aq)}$ (e.g. $An(OH)_5^-(aq)$). Therefore, in the absence of CO_2 , no additional complexation reaction for Pu(IV) in solution occurs that could decrease Pu sorption on kaolinite, relative to Th(IV), for high pH.

The surface complexation constant for $\equiv\text{SOPu(III)}^{2+}$ is set equal to the one for Eu(III) ($\equiv\text{SOEu(III)}^{2+}$) determined by Tertre et al. (2008) (Table 1), since Eu(III) is as well an analogue for trivalent actinides. All the other surface complexation constants are fitted to the K_d of the respective analogues and are listed in table 1. A good fit is achieved with this simple model (Fig. 1). The fitted surface complexation constants ($\log {}^S K_{X,(i-1)}$; eq. 1) for Pu(III/IV/V/VI) , when plotted against the corresponding hydrolysis constants ($\log {}^{OH} K_{X,i}$; eq. 10), yield a linear free energy relationship (LFER; Figure 2):

$$\log {}^S K_{X,(i-1)} = 0.97 \times \log {}^{OH} K_{X,i} + 5.65 \quad (R^2 = 0.99) \quad (18)$$

The correlation corroborates the self-consistency of our surface complexation constants. The $\text{Na}^+ \text{-Pu}^{3+}$ selectivity coefficient is found to be 10 ($\log {}^{Pu(III)}_{Na} K_c = 1$), in agreement with Tertre et al. (2008), and is relatively consistent with literature data of selectivity coefficients for An/Ln(III) with clay minerals (e.g. Bradbury and Baeyens, 2006; 2009) although it is found to be lower than for montmorillonite and illite ($\log {}^{Pu(III)}_{Na} K_c = 1.5$ and 1.9 , respectively). The rather weak Am(III) uptake at $\text{pH} = 1$ is relatively well simulated when taking into account the $\text{Na}^+ \text{-H}^+$ exchange reaction previously considered by Tertre et al. (2008). During preliminary tests, when using the $\text{Na}^+ \text{-UO}_2^{2+}$ selectivity coefficient reported for montmorillonite (Marques Fernandez et al., 2012), for 0.1 M NaClO_4 , the predicted $\log K_d(\text{VI})$ for $\text{pH} < 4$ remained below the experimental data for $\text{pH} = 4$, while for 0.01 M NaClO_4 too high values were predicted. Since reliable exchange constants cannot be determined for U(VI) and Np(V) from the selected datasets, the ion exchange mechanism is omitted in the present study. However, this has no significant consequence for the following discussions and the approach can be extended to include ion exchange once reliable selectivity coefficients become available. Furthermore, Bradbury and Baeyens (2005) observed no effect of the ionic strength between 0.1 and $1 \text{ M (NaClO}_4)$ for Th(IV) sorption to montmorillonite. Therefore, cation exchange for Pu(IV) is not considered. Kaolinite dissolution is not taken into account

in this study. Kaolinite dissolution could be affecting the amount of available surface sites or result in competitive effects from dissolved aluminium (Lützenkirchen et al., 2014), for instance. Finally, the present model is likely to be questionable for the very low pH values, especially for $\text{pH} \approx 0$, but (i) such low pH values are of minor environmental relevance and (ii) the equations derived in this study to describe Pu sorption and redox speciation at the kaolinite surface are based on K_d values, and therefore this should have no impact on the following discussions based on the results from laboratory experiments.

3.2. Predominance diagram: solution versus surface

Figure 3 shows the superimposed predominance diagrams for the different Pu redox states in solution (in black) and at the kaolinite surface (in gray), in 0.1 M NaClO_4 and in the absence of CO_2 . The ionic strength increases by a factor of about 10 between $\text{pH} = 1$ and 0 because of increasing $[\text{HClO}_4]$. Pu(IV) is found at intermediate redox conditions. Its predominance area is small at low pH due to the similar standard redox potentials for the different couples. When the pH increases, its stability field is enlarged because of its strong hydrolysis. Pu(III) shows the largest stability field in acidic condition, which is narrowed with increasing pH by hydrolyzed Pu(IV) species. Pu(VI) is only stable under oxidizing conditions. Its stability field is increased for $\text{pH} > 8$ because of its relatively strong hydrolysis. Pu(V) predominates in less oxidizing conditions than Pu(VI). Pu(V) shows very weak hydrolysis, which explains its confined predominance field for alkaline pH.

From a purely thermodynamic point of view, if hydrolysis controls the predominance area of the different redox states in solution, complexation reaction with the $-\text{OH}$ groups of the kaolinite surface should act similarly (see Figure 3, in gray). For $\text{pH} < 6$, Pu(IV) sorption to kaolinite is much stronger than Pu(III), narrowing the predominance area for surface Pu(III)

compared to solution. For $\text{pH} > 6$ both redox states exhibit similarly strong sorption, and $\{\text{Pu(IV)/Pu(III)}\}_{\text{surf}}$ is close to $\{\text{Pu(IV)/Pu(III)}\}_{\text{aq}}$.

In the range of pH presently discussed, Pu(V) sorption is always weaker than for the other redox states. Although present under some conditions, it never predominates and does not appear in Figure 3. Instead Pu(IV) and Pu(VI) prevail at the kaolinite surface (depending on the pe), even if Pu(V) is stable in solution.

$\{\text{Pu(VI)/Pu(IV)}\}_{\text{surf}}$ evolves in similar fashion as $\{\text{Pu(IV)/Pu(III)}\}_{\text{surf}}$: (i) the Pu(IV) stability field at the kaolinite surface is enlarged because of the lower Pu(VI) sorption at low pH , whereas for $\text{pH} > 6$ the Pu(VI)/Pu(IV) borderlines at the surface and in solution are similar due to the similar K_d for both redox states. While significant Am(III) sorption to kaolinite was experimentally observed in the pH range investigated, U(VI) sorption is insignificant for $\text{pH} < 4$, leading to highly uncertain $K_d(\text{VI})$. Therefore, the calculated $\{\text{Pu(VI)/Pu(IV)}\}_{\text{surf}}$ values for $\text{pH} < 4$ are probably inaccurate. Note also that $\{\text{Pu(VI)/Pu(IV)}\}_{\text{surf}}$ is found for almost constant redox conditions: $\text{pH} + \text{pe} \approx 18$.

The present approach, which separates Pu redox speciation in solution and at the surface, has the advantage of being insensitive to the solid to liquid ratio within a sufficiently low $[\text{Pu(X)}]_{\text{tot}}$ range where K_d values remain constant (i.e. ideal sorption behavior). We may simultaneously visualize the prevalent redox states in solution and at the surface. Such an approach was also shown to be useful when mineral phases can form (Schüring et al., 2000). It also turns out to be particularly useful to understand overall Pu uptake by kaolinite. Common predominance diagrams would not separate Pu redox speciation in solution and at the surface and only the prevalent species in the total system, either on the surface or in solution, will appear. Such a diagram is shown in figure 3b for our experimental conditions ($\text{S/V} = 4 \text{ g/L}$; 0.1 M NaClO_4). In our model, the comparison between Figure 3a and 3b shows that although Pu(VI) is stable at the kaolinite surface under oxidizing conditions (Fig. 3a), it

represents only a small proportion of Pu because, below $\text{pH} < 7$, Pu(VI) sorption is weak and Pu(V) prevails in solution (Fig. 3b). This strongly limits overall Pu sorption.

3.3. Pu(V) versus Pu(IV)

3.3.1. Modeling Pu-kaolinite sorption data

Our model is applied to the experimental data of Banik et al. (2007) where 6.6×10^{-9} M of Pu(IV) was contacted with 4 g/L kaolinite in 0.1 M NaClO_4 . The experimental percentage of Pu uptake reported by Banik et al. (2007) in air (only for $\text{pH} < 8$) and in argon atmosphere are shown in Figure 4a together with Th(IV) data ($[^{234}\text{Th}]_{\text{tot}} = 6.6 \times 10^{-13}$ M). Pu overall uptake is systematically lower than Th(IV). Overall Pu uptake increases from 10 to 80% for $0 < \text{pH} < 3$, decreases down to $\sim 60\%$ for pH around 4 and reaches again $\sim 80\%$ above $\text{pH} = 7$. The dip at intermediate pH is unusual and cannot be explained by Pu(IV) alone, which becomes clear from a redox state analysis of Pu in the aqueous phase.

No redox potential measurements were performed by Banik et al. (2007), which would have been crucial information for the present study. Instead of using the measured p_e , we here attempt to estimate the p_e via the Nernst equation and by using the Pu redox state analysis in solution after reaction with kaolinite and subsequent phase separation. This approach has been previously applied by Yun et al. (2007). However, those authors investigated acidic conditions ($\text{pH} < 2.5$) and observed some discrepancies between calculated and measured p_e . Therefore, we might obtain a p_e value with a relatively large uncertainty. In the modified Nernst equation (eq. 13), the experimental total concentration of two Pu redox states and the pH can be directly used to estimate the p_e . We obtain $p_e \approx 15.7$ for $\text{pH} = 1$ and $p_e \approx 11.6$ for $\text{pH} = 4$, i.e. almost constant redox conditions (constant $\text{pH} + p_e \approx 16.1$). The redox state analysis data cannot be used in eq. 13 for $\text{pH} = 9$ because only Pu(IV) was detected.

464 Additionally, the redox speciation has only been performed for the samples studied under
465 ambient conditions. Therefore, although a steady state was reached, as deduced from Pu
466 sorption behavior (Fig. S1), its redox speciation was obviously not controlled by the reaction
467 $0.25 \text{ O}_{2(\text{g})} + \text{H}^+ + \text{e}^- = 0.5 \text{ H}_2\text{O}$ (i.e. $\text{pH}+\text{pe} = 20.6$ for $p_{\text{O}_2} = 0.21 \text{ atm}$).

468 Calculations of Pu uptake on kaolinite are performed for the experimental conditions
469 of Banik et al. (2007). Constant redox conditions are considered. Only the results obtained for
470 $\text{pH} < 5$ will be discussed here. Regarding the uncertainty in the $\text{pH}+\text{pe}$ value, it is adjusted to
471 provide the best fit to the experimental data (Figure 4a). A relatively good fit is achieved for
472 $\text{pH}+\text{pe} = 16.2$, consistent with the estimate from the redox state analysis ($\text{pH}+\text{pe} \approx 16.1$).
473 Figure 4b shows a predominance diagram restricted to relevant pH-pe conditions for the study
474 of Banik et al. (2007). Only the aqueous redox speciation is shown because only Pu(IV) is
475 calculated to prevail at the kaolinite surface for $14 < \text{pH}+\text{pe} < 18$ (see Fig. 3a). Here, the
476 predominance diagram is plotted as $\text{pH}+\text{pe}$ versus pH (instead of pe versus pH) to visualize
477 constant redox conditions as a horizontal line. The comparison between the $\text{pH}+\text{pe} = 16.2$ line
478 and $\{\text{Pu(IV)}/\text{Pu(III)}\}_{\text{aq}}$ or $\{\text{Pu(V)}/\text{Pu(IV)}\}_{\text{aq}}$ can explain the features observed in the Pu uptake
479 curve. For $\text{pH} < 5$, Pu(III) and Pu(V) weakly sorb to kaolinite. Therefore, maximum uptake is
480 found when Pu(IV) dominates in solution, i.e. when physico-chemical conditions approach a
481 pure Pu(IV) system ($\text{pH} \approx 2$). The decreased uptake with increasing pH from 2 to 5 is due to
482 the predominance of Pu(V) in solution, which is very well predicted. Minimum uptake is
483 found when the difference between the line of the redox condition ($\text{pH}+\text{pe} = 16.2$) and the
484 line of $\{\text{Pu(V)}/\text{Pu(IV)}\}_{\text{aq}}$ reaches a maximum (shown as a double arrow in figure 4b; $4 < \text{pH}$
485 < 5). The present approach allows the description of overall Pu uptake on kaolinite, by
486 applying thermodynamic concepts and by simultaneously taking into account the complete Pu
487 redox chemistry and the respective sorption behavior. The calculations are very sensitive to pe,
488 as illustrated on figure 4 by considering $\text{pe} \pm 0.5$ (corresponding to $\pm 0.03 \text{ V}$). This result

clearly shows that without any information concerning the redox conditions in the experiment, it is almost impossible to predict Pu uptake by kaolinite.

Above pH = 5, information about pe is not available. Simulations are made assuming pH+pe = 16.2 as before. Because of the strong assumption, the following simulations and discussion should be considered with caution. For pH = 9, Pu(IV) is the dominant redox state in solution (see Fig. 4b), consistent with redox state analysis. For pH > 5, the solution is oversaturated with respect to PuO_{2(am,hyd)}: total aqueous [Pu(IV)]_{tot,aq} equals approximately 10⁻⁹ M for pH = 9, whereas the Pu(IV) solubility limit is 10^{-10.4±0.5} M (Neck et al., 2007). The break in the simulated curve (Fig. 4a) is due to the inclusion of Pu precipitation in the calculations. Experimentally, precipitation (both homogeneous and heterogeneous) is difficult to distinguish from the surface uptake processes. This leads to an overestimation of the overall Pu uptake for pH > 5. Preliminary test calculations showed that this cannot be attributed to the assumed redox conditions, as illustrated in Figure 4a when considering pe ± 0.5. Neck et al. (2007) found that formation of Pu(IV) intrinsic (eigen-) colloids (PuO_{2(am, coll, hyd)}) leads to an increased apparent solubility of Pu up to 10^{-8.3±1.0} M. Removal of these colloids from the aqueous phase requires either ultrafiltration at 3-10 kDa or ultracentrifugation. Banik et al. (2007) only performed phase separation by centrifugation at 3000g, which is not sufficient to remove Pu(IV)-colloids. Furthermore, Banik et al. (2007) performed experiments for approximately 10 and 50 times higher [Pu]_{tot} (6.6×10⁻⁸ M and 3.2×10⁻⁷ M). Experimentally observed Pu uptake does not change but the corresponding calculations lead to an enhanced uptake with increasing [Pu]_{tot} because of the increased amount of precipitated PuO_{2(am,hyd)} (see Fig. S2). Although Pu(IV)-colloids interact with mineral surfaces (Reich et al. 2007; Powell et al., 2011; Schmidt et al., 2012), a small fraction of Pu(IV)-colloids remained in the supernatant in the experiments of Banik et al. (2007) because of insufficient phase separation. It is also possible that, although thermodynamically favorable, PuO_{2(am,hyd)} was not formed

within 209 h in the presence of kaolinite. This is illustrated in Figure 4a (bold dashed line) where we neglect the precipitation of $\text{PuO}_{2(\text{am,hyd})}$, which then leads to a better fit for $\text{pH} > 5$. Indeed, as observed experimentally for $\text{pH} > 5$, an increasing Pu uptake with increasing pH is predicted because the redox conditions approach the stability field of $\text{Pu(IV)}_{\text{aq}}$. Above $\text{pH} = 8$, only Pu(IV) is found in solution for $\text{pH} + \text{pe} = 16.2$ and Pu uptake is predicted to be equal to Th(IV). Unfortunately, the sorption of Pu-colloids to kaolinite cannot be simulated yet using a mechanistic model without making additional assumptions. However, overall Pu uptake for $\text{pH} = 8$ is similar to Th(IV), although significant amounts of Pu(IV)-colloids are present, and is independent of $[\text{Pu}]_{\text{tot}}$ (Figure S2). Eq. 5 suggests that the respective K_d for aqueous Pu(IV) and Pu(IV)-colloids are similar for $\text{pH} = 8$. This might be because $\text{Pu(OH)}_{4(\text{aq})}$ (i.e. the prevailing aqueous Pu(IV) species) and $\text{PuO}_{2(\text{am, coll, hyd})}$ are both uncharged species at $\text{pH} = 8$ (Neck et al., 2007). However, the sorption of Pu(IV)-colloids to minerals needs to be studied in further experiments.

3.3.2. Comparison with other systems

Various experimental studies were dedicated to Pu sorption on oxidic minerals. Under oxidizing conditions (e.g. ambient air) Pu(V) was initially introduced (e.g. Powell et al., 2005; Zavarin et al., 2012; Hixon et al., 2013: for goethite, hematite, montmorillonite and quartz, respectively). These studies report a relatively fast and strong Pu uptake, which is due to the presence of Pu(IV) on the surface whereas Pu(V) remained in solution. Equation 16 implies that the thermodynamic stability field of the more strongly adsorbing Pu redox state is enhanced at a mineral surface compared to the aqueous phase. The actinide pH-edge sequence $\text{An(V)} < \text{An(III)} \approx \text{An(VI)} < \text{An(IV)}$ (Geckeis et al., 2013) is generally obtained for all minerals with surface $-\text{OH}$ groups. Therefore, the Pu(V)/Pu(IV) boundary at a mineral surface can be expected to be most strongly shifted to higher pe, especially in the low pH

region where An(V) sorption to minerals is weak. Furthermore, equation 16 exhibits a rather generic form, since it is based on K_d values, and is not restricted to Pu, kaolinite or to a specific surface complexation model. However, the present approach is based on thermodynamic concepts and might only be applicable when equilibrium or steady states are reached. For our treatment, the p_e is required, which is often not experimentally determined for various reasons. Finally, sorption data for analogues are required, but not always available. Therefore, the more general applicability of the present approach can only be tested on a limited number of available studies.

Np sorption and redox speciation in the presence of illite was recently investigated (Marsac et al., 2015). When added as Np(V) to an illite suspension under argon atmosphere, higher Np uptake was measured compared to a previous study under ambient atmosphere (Gorgeon, 1994). X-ray Absorption Spectroscopy and redox state analysis revealed a significant amount of Np(IV) at the illite surface whereas Np(V) prevailed in solution. By taking into account the experimental p_e and surface complexation of both Np(V) and Np(IV) to illite edge sites, the results of these Np sorption experiment could be modeled. In that study, the 2 Site Protolysis Non-Electrostatic Surface Complexation and Cation Exchange (2 SPNE SC/CE; Bradbury and Baeyens, 2009) model was used. For instance, for $pH = 7$ and an ionic strength of 0.1 M NaCl, $\log K_d(Np(V)) \approx 1.5$ L/kg and $\log K_d(Np(IV)) \approx 6$ L/kg. In agreement with eq. 16, $\{Np(V)/Np(IV)\}_{surf}$ was found approximately 4.5 p_e units higher than $\{Np(V)/Np(IV)\}_{aq}$ for these conditions. This simple calculation provides evidence that our equations are applicable to another actinide, another mineral and another surface complexation model.

Hixon et al. (2013) observed the reduction of Pu(V) to Pu(IV) at the quartz surface, when working under ambient air conditions, and proposed that the strongly adsorbing Pu(IV) is thermodynamically favored at the mineral surface compared to Pu(V), in agreement with

our approach. Hixon et al. (2013) more precisely calculated that, on quartz for $\text{pH} = 7$, $\{\text{Pu(V)}/\text{Pu(IV)}\}_{\text{surf}}$ would need to be 0.28 V (4.7 pe units) higher than $\{\text{Pu(V)}/\text{Pu(IV)}\}_{\text{aq}}$ to observe significant amounts of Pu(IV). Although a surface complexation model has been used in the above cases to obtain a numerical equation describing $K_d(\text{IV})$ and $K_d(\text{V})$ versus pH, eq. 16 can directly be applied to empirical (measured) K_d values when available for the same mineral and the same physico-chemical conditions. Since we did not find data for An(V) and An(IV) sorption to quartz to quantitatively support the findings of Hixon et al. (2013), sorption data for amorphous silica ($\text{SiO}_{2(\text{am})}$) are used as an estimate. In addition, even though K_d values for Th(IV) can directly be used for Pu(IV) sorption to kaolinite, this must be proven to be true for other minerals because both elements show significantly different hydrolysis. Consequently, the following estimates are based on strong assumptions and involve the concomitant uncertainties. Equation 16, based on K_d , is empirical and it is recommended to restrict its application to sorption data obtained for minerals of the same origin. This avoids for instance handling variations in the surface area of the mineral used between separate studies. To follow up on the quartz example, Righetto et al. (1991) studied both Th(IV) and Np(V) sorption to amorphous silica ($\text{SiO}_{2(\text{am})}$) in 0.1 M NaClO_4 . Their data were recalculated to K_d (L/kg) and are presented in figure S3. Th(IV) sorption data were recorded only up to $\text{pH} = 3.5$, where a constant K_d is reached ($\log K_d = 4.7$ L/kg). Reiller et al. (2003) investigated Th(IV) sorption to $\text{SiO}_{2(\text{am})}$ and observed constant K_d up to $\text{pH} = 9$. Therefore, we can safely assume constant K_d values for Th(IV) for $\text{pH} > 3.5$. Np(V) sorption is weak and $\log K_d(\text{Np(V)}) = 1.7$ L/kg for $\text{pH} = 7$. From this, we estimate $\{\text{Pu(V)}/\text{Pu(IV)}\}_{\text{surf}} - \{\text{Pu(V)}/\text{Pu(IV)}\}_{\text{aq}} = 3$, for $\text{pH} = 7$, i.e. the Pu(V)/Pu(IV) boundary at the $\text{SiO}_{2(\text{am})}$ surface is approximately 0.18 V above the one in solution. Despite the large uncertainties discussed above, our simple estimate is qualitatively consistent with Hixon et al. (2013).

Interestingly, the shift in the pe, $\{An(V)/An(IV)\}_{surf} - \{An(V)/An(IV)\}_{aq}$, is shown to depend on the nature of the mineral, which equals +4.5 for illite, +2.5 for kaolinite (as can be calculated from Np(V) and Th(IV) sorption to kaolinite data; figure 1) and +3 for $SiO_{2(am)}$. We cannot provide a convincing explanation for this observation at present. Clearly this issue will require a larger dataset for various minerals and more advanced calculations. In general, all minerals discussed above consistently show the stabilization of Pu(IV) at their surface, highlighting the importance of Pu(IV) even under slightly oxidizing conditions.

Because of its weak interaction with minerals, Pu(V) is known to be rather mobile. The opposite is true for Pu(IV). Therefore, an accurate knowledge of the Pu(V)/Pu(IV) redox couple is particularly important to predict Pu mobility in the environment. Although kinetic aspects might be required in order to predict Pu mobility, the present study supports previous experimental and modeling studies dedicated to the transport of Pu in (partially) oxygenated soils or sediments (e.g. Kaplan et al., 2004; Powell et al., 2014) where Pu(V) was found to be the mobile form of Pu (i.e. in the aqueous phase), whereas Pu(IV) was found at the surface of the solids, being strongly bound and decreasing the amount of dissolved Pu(V) and consequently limiting Pu transport. The strong interaction of Pu with minerals via the stabilization of Pu(IV) at their surfaces over a wide range of pH-pe conditions also agrees with the idea of colloid-facilitated transport of this element (Kersting et al., 1999; Xie et al., 2013).

3.4. Pu(IV) versus Pu(III)

Buda et al. (2008) studied Pu(III) sorption to kaolinite, compared it to Am(III) data and found the pH-edges to be very similar. The authors used $NH_2OH \cdot HCl$ as a reductant to maintain the trivalent redox state of Pu. This was not efficient for $pH > 6$ and Pu(IV) was

formed in the absence of kaolinite. Therefore, above $\text{pH} = 6$, the redox potential falls within the stability field of $\text{Pu(IV)}_{\text{aq}}$. Buda et al. (2008) could well describe Pu redox chemistry in the presence of kaolinite, assuming the presence of Pu(IV) for $\text{pH} > 6$. The present study shows that, different from other redox couples, $\{\text{Pu(IV)}/\text{Pu(III)}\}_{\text{surf}}$ is not significantly different from $\{\text{Pu(IV)}/\text{Pu(III)}\}_{\text{aq}}$ for $\text{pH} > 6$ in 0.1 M NaClO_4 . For reducing conditions, the previous discussions about Pu redox chemistry in contact with kaolinite based on the stability fields of Pu(IV)/Pu(III) in solution might be correct, even if sorption processes are disregarded.

3.5. Pu(VI) at the kaolinite surface?

Our calculations suggest that Pu(VI) can be stable at the kaolinite surface for $\text{pH} + \text{pe} > 18$. This is not supported by any experimental results. To obtain Pu(IV) as the dominant redox state at the kaolinite surface under $p_{\text{O}_2} = 0.21 \text{ atm}$, $\{\text{Pu(VI)}/\text{Pu(IV)}\}_{\text{surf}}$ must be at least ~ 2.5 log units higher than the presently calculated one, i.e. $\log K_{\text{d}}(\text{IV}) - \log K_{\text{d}}(\text{VI})$ must be about 5 (two electrons are involved). Obviously, this is beyond experimental uncertainties. As discussed previously (see e.g. fig. 3b), even though prevailing at the surface, the overall amount of Pu adsorbed to kaolinite can be low for a large range of pH under oxidizing conditions. Furthermore, the present calculations are made in the absence of CO_2 whereas experiments under oxidizing conditions are generally made under ambient atmosphere. U(VI) sorption to kaolinite decreases from $\sim 95\%$ to $\sim 10\%$ between pH 8 and 9 in the presence of carbonate (e.g. Payne et al., 2004; Křepelová 2007; Gao et al., 2010), which would, by analogy, further limit Pu(VI) sorption to kaolinite although ternary kaolinite-Pu(VI)-carbonate surface complexes might form. Such complexes have for instance been observed for U(VI) on montmorillonite (Marques Fernandez et al., 2012). Consequently, the presence of Pu(VI) at the kaolinite surface might be of limited relevance. Nevertheless, the fate of Pu(VI) at mineral surfaces appears elusive at present. For instance, Romanchuk et al. (2011; 2013) observed partial reduction to Pu(IV) in contact with hematite. Kumar et al. (2012) contacted Pu(IV)

with alumina and found some Pu(VI) in solution. Olsson et al. (2003) were able to stabilize Pu(VI) in contact with TiO₂ and determined its pH-dependent sorption. Further work is required to clarify the role of Pu(VI) under oxidizing conditions. Our survey of the available data would suggest a dependence on the type of sorbing mineral.

3.6. Further development required

The present study focusses on experimental studies, where An sorption to kaolinite was investigated in the absence of complexing ligands other than OH⁻, i.e. under conditions different from the complexity of natural waters. For instance, carbonates and humic substances are known to strongly affect An speciation and sorption to minerals. Reiller (2005) evaluated the impact of both carbonates and humic acids (HA) on the redox speciation of U/Np/Pu by applying thermodynamic calculations. Based on a similar approach (i.e. speciation calculations at equilibrium), Reiller (2005) predicted a narrow predominance field for Pu(V) due to strong Pu(VI)-carbonate and Pu(IV)-HA complexation, as in the present case, where the predominance field arises from strong sorption of Pu(VI) and Pu(IV) at the kaolinite surface. While metal ion complexation by various ligands can in principle be included in the side reaction coefficient (eq. 12), no attempt is made here for the sake of simplicity. The approach can be extended to account for the effect of other ligands in the future. However, to predict Pu sorption and redox speciation at a mineral surface in the presence of carbonates and HA, the formation of ternary surface complexes must be taken into account. Such complexes were included in models for instance by Marques Fernandez et al. (2008; 2012) for the Eu(III)- and U(VI)-monmorillonite-carbonate ternary systems. The prediction of An sorption to minerals in the presence of humic substances is even more

661 complex and relies on an accurate description of the mechanisms controlling humic
662 substances sorption to minerals and the identification of the ternary complexes formed, which
663 is still under debate (see e.g. Reiller, 2012).

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665

4. Conclusion

It is well known that Pu redox speciation has a strong impact on its mobility in the environment. Various experimental studies have shown that mineral surfaces affect Pu redox speciation. In the present study, Pu redox speciation at the kaolinite surface is interpreted based on the thermodynamic stability of the respective Pu redox state at the surface. To overcome difficulties in the interpretation of results related to the sensitivity of Pu to redox conditions, uptake data on kaolinite of the more redox-stable Am(III), Th(IV), Np(V) and U(VI) - chemical analogues for Pu(III,IV,V,VI) - are used to calibrate a surface complexation model. To fully understand Pu redox chemistry in the aqueous kaolinite suspension, the system is treated separately for the aqueous solution and the kaolinite surface, and the two resulting Pu predominance diagrams are superimposed. This method visualizes how the prevailing Pu redox states can differ between solution and surface for given pH/pe conditions. Notably, the kaolinite surface has no impact on the Pu(IV)/Pu(III) distribution in neutral to alkaline conditions, in the absence of aqueous ligands other than OH⁻. Therefore, the study of Pu(III) sorption to minerals is relevant for the reducing conditions encountered in deep geological nuclear waste repository sites. Under slightly oxidizing conditions, Pu(IV) can be stabilized at the kaolinite surface within the stability field of Pu(V) in solution, which significantly increases overall Pu uptake. The present model predicts overall experimental Pu uptake when the Pu(V)/Pu(IV) redox couple is involved. This suggests that Pu-mineral interaction is strong, even under slightly oxidizing condition. Also Pu(VI) can be stabilized at the kaolinite surface within the stability field of Pu(V) in solution, under oxidizing conditions. Its impact on overall Pu uptake is limited to redox conditions in equilibrium with ambient air atmosphere (O₂), by the weak Pu(VI) sorption to kaolinite for pH < 5 and the strong Pu(VI)-carbonate (due to atmospheric CO₂) complexation in alkaline conditions. Independent experimental data for other minerals with Pu and with Np corroborate our approach. The

derived equations are of rather generic form making them easily applicable yet to other adsorbant/adsorbat systems.

Based on the thermodynamic stability of the sorbed Pu species, the exact redox mechanism does not need to be explicitly considered but the redox potential of the system must be known. Measurement of redox potential is rarely simple and often bears large uncertainties, but the pe (or Eh) strongly affects overall Pu uptake by kaolinite. A redox state analysis of aqueous Pu can provide information on pe, when a steady state is reached. The determination of pe from Pu redox state analysis heavily relies on the accuracy of the available thermodynamic database for aqueous complexes, i.e. their capability to describe the speciation of the different Pu redox states in presence of various ligands. This fact becomes more important for natural samples that are more complex than the systems considered in this work.

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872

873 Table and figure caption

874 **Table 1.** Thermodynamic constants at zero ionic strength used in the present study
 875 (Guillaumont et al., 2003). The missing hydrolysis constants for Pu are taken from the
 876 corresponding analogues (in brackets). Surface complexation constants for Pu(III, IV, V, VI)
 877 are obtained assuming that the experimental uptake data of Am(III), Th(IV), Np(V) and U(VI)
 878 by kaolinite are representative for the uptake of the corresponding Pu redox states. (*)
 879 Exchange and surface complexation constants have been determined by Tertre et al. (2008).
 880 Some constants could not be determined since no appropriate experimental data were
 881 available. According to Tertre et al. (2006, 2008), the surface area of kaolinite is 10 m²/g, site
 882 density for ≡SOH and exchange sites are 1.66 and 3.70 μmol/m², respectively.

883 **Figure 1.** Experimental sorption data (K_d , in L/kg) on kaolinite versus pH for actinides with
 884 different redox states (Am(III)/Th(IV)/Np(V); data from Buda et al. (2008), Banik et al. (2007)
 885 and Amayri et al. (2011), respectively) for 0.1 M NaClO₄. Data for U(VI) are taken from
 886 Křepelová (2007) for 0.1 M NaClO₄ in the presence of CO₂ (closed diamonds; pH < 8) and
 887 0.01 M NaClO₄ in the absence of CO₂ (open diamonds). The elements are considered as
 888 chemical analogues for Pu(III/IV/V/VI). Pu(IV) data are recalculated from the sorption data
 889 and Pu redox state analysis of Banik (2006) using eq. 17 (two large white circles). Curves
 890 represent the modeled result for each Pu redox state.

891 **Figure 2.** Linear free energy relationship (LFER) between surface complexation $^sK_{X,(i-1)}$ and
 892 hydrolysis constants $^{OH}K_{X,i}$. “X” is Pu redox state and “i” is the number of OH⁻ involved in
 893 the complex, within the present model for kaolinite obtained by fitting Pu(III), Pu(IV), Pu(V)
 894 and Pu(VI) surface complexation constant to the experimental Am(III), Th(IV), Np(V) and
 895 U(VI) sorption to kaolinite data from the literature. All in 0.1 M NaClO₄.

896 **Figure 3.** (a) Overlay of Pu predominance plots in solution (thin black lines) and at the
 897 kaolinite surface (bold gray lines). Only the predominance field of each redox state is shown,
 898 not the detailed speciation (e.g. hydrolyzed species). (b) More common predominance
 899 diagram where only the dominant Pu redox state can be seen for the total system (S/V = 4 g/L;
 900 [NaClO₄] = 0.1 M; [Pu]_{tot} = 10⁻¹¹ M).

901 **Figure 4.** (a) Percentage uptake of Pu and Th by kaolinite ([Pu]_{tot} = 6.6 × 10⁻⁹ M / [Th]_{tot} = 6.6
 902 × 10⁻¹³ M; 0.1 M NaClO₄; S/V = 4 g/L; either under ambient air below pH = 8 or argon
 903 atmosphere) experimentally obtained by Banik et al. (2007) and calculated for pH+pe = 16.2,

904 considering (bold line) or not (bold dashed line) the precipitated $\text{PuO}_{2(\text{am})}$ to be removed from
905 the aqueous phase with the kaolinite. The model sensitivity to pe is illustrated applying ± 0.5
906 uncertainty on the pe: $\text{pH} + \text{pe} = 15.7$ (dashed line) and 16.7 (dashed-dotted line); precipitated
907 $\text{PuO}_{2(\text{am})}$ is considered to have been removed with kaolinite. (b) Predominance diagram for the
908 aqueous solution plotting $\text{pH} + \text{pe}$ versus pe to visualize constant redox conditions horizontally.
909 The legend is valid for (a) and (b).

910

	Reaction	Log K (I = 0)
Solubility	$\text{PuO}_{2(\text{am,hyd})} + 2 \text{H}_2\text{O} = \text{Pu}^{4+} + 4 \text{OH}^-$	-58.33
Redox	$\text{PuO}_2^{2+} + \text{e}^- = \text{PuO}_2^+$	15.82
	$\text{PuO}_2^{2+} + 4 \text{H}^+ + 2 \text{e}^- = \text{Pu}^{4+} + 2 \text{H}_2\text{O}$	33.27
	$\text{PuO}_2^+ + 4 \text{H}^+ + \text{e}^- = \text{Pu}^{4+} + 2 \text{H}_2\text{O}$	17.45
	$\text{Pu}^{4+} + \text{e}^- = \text{Pu}^{3+}$	17.69
Hydrolysis	$\text{PuO}_2^{2+} + \text{H}_2\text{O} = \text{PuO}_2\text{OH}^+ + \text{H}^+$	-5.50
	$\text{PuO}_2^{2+} + 2 \text{H}_2\text{O} = \text{PuO}_2(\text{OH})_2 + 2 \text{H}^+$	-13.20
	$\text{PuO}_2^{2+} + 3 \text{H}_2\text{O} = \text{PuO}_2(\text{OH})_3^- + 3 \text{H}^+$	-20.25 (U)
	$\text{PuO}_2^{2+} + 4 \text{H}_2\text{O} = \text{PuO}_2(\text{OH})_4^{2-} + 4 \text{H}^+$	-32.40 (U)
	$\text{PuO}_2^+ + \text{H}_2\text{O} = \text{PuO}_2\text{OH} + \text{H}^+$	-11.30 (Np)
	$\text{PuO}_2^+ + 2 \text{H}_2\text{O} = \text{PuO}_2(\text{OH})_2^- + 2 \text{H}^+$	-23.60 (Np)
	$\text{Pu}^{4+} + \text{H}_2\text{O} = \text{PuOH}^{3+} + \text{H}^+$	0.60
	$\text{Pu}^{4+} + 2 \text{H}_2\text{O} = \text{Pu}(\text{OH})_2^{2+} + 2 \text{H}^+$	0.60
	$\text{Pu}^{4+} + 3 \text{H}_2\text{O} = \text{Pu}(\text{OH})_3^+ + 3 \text{H}^+$	-2.30
	$\text{Pu}^{4+} + 4 \text{H}_2\text{O} = \text{Pu}(\text{OH})_4 + 4 \text{H}^+$	-8.50
	$\text{Pu}^{3+} + \text{H}_2\text{O} = \text{PuOH}^{2+} + \text{H}^+$	-6.90
	$\text{Pu}^{3+} + 2 \text{H}_2\text{O} = \text{Pu}(\text{OH})_2^+ + 2 \text{H}^+$	-15.10 (Am)
	$\text{Pu}^{3+} + 3 \text{H}_2\text{O} = \text{Pu}(\text{OH})_3 + 3 \text{H}^+$	-26.20 (Am)
Exchange	$2 \text{X-Na} + \text{PuO}_2^{2+} = \text{X}_2\text{-PuO}_2 + \text{Na}^+$	nd
	$\text{X-Na} + \text{PuO}_2^+ = \text{X-PuO}_2 + \text{Na}^+$	nd
	$3 \text{X-Na} + \text{Pu}^{3+} = \text{X}_3\text{-Pu} + \text{Na}^+$	1
	$4 \text{X-Na} + \text{Pu}^{4+} = \text{X}_4\text{-Pu} + \text{Na}^+$	nd
	$\text{X-Na} + \text{H}^+ = \text{X-H} + \text{Na}^+$	-1 ^(*)
Surface complexation	$\equiv\text{SOH} + \text{PuO}_2^{2+} = \equiv\text{SO-PuO}_2^+ + \text{H}^+$	0.2
	$\equiv\text{SOH} + \text{PuO}_2^{2+} + \text{H}_2\text{O} = \equiv\text{SO-PuO}_2\text{OH} + \text{H}^+$	-6.9
	$\equiv\text{SOH} + \text{PuO}_2^{2+} + 2 \text{H}_2\text{O} = \equiv\text{SO-PuO}_2(\text{OH})_2^- + 3 \text{H}^+$	-14.5
	$\equiv\text{SOH} + \text{PuO}_2^+ = \equiv\text{SO-PuO}_2 + \text{H}^+$	-4.0
	$\equiv\text{SOH} + \text{Pu}^{4+} = \equiv\text{SO-Pu}^{3+} + \text{H}^+$	nd
	$\equiv\text{SOH} + \text{Pu}^{4+} + \text{H}_2\text{O} = \equiv\text{SO-PuOH}^{2+} + 2 \text{H}^+$	6.0
	$\equiv\text{SOH} + \text{Pu}^{4+} + 2 \text{H}_2\text{O} = \equiv\text{SO-Pu}(\text{OH})_2^+ + 3 \text{H}^+$	3.2
	$\equiv\text{SOH} + \text{Pu}^{4+} + 3 \text{H}_2\text{O} = \equiv\text{SO-Pu}(\text{OH})_3 + 4 \text{H}^+$	-3.0
	$\equiv\text{SOH} + \text{Pu}^{3+} = \equiv\text{SO-Pu}^{2+} + \text{H}^+$	-0.5 ^(*) (Eu)
	$\equiv\text{SOH} + \text{Pu}^{3+} + \text{H}_2\text{O} = \equiv\text{SO-PuOH}^+ + 2 \text{H}^+$	-9.3

911

912

Table 1

Figure 1

Figure 2

Figure 3

Figure 4

Supporting information.

Figure S1. Percentage of Pu uptake in presence of kaolinite versus the pH for different equilibration time (63, 120, 137, 209 hours). The results for $t = 120$ h were obtained for an independent set of experiments. Experimental conditions: $S/V = 4$ g/L; $[Pu]_{tot} = 3.5 \times 10^{-7}$ M ; 0.1 M $NaClO_4$; ambient air atmosphere. Curves are simulations with the present model when considering or not the precipitation of $PuO_{2(am)}$ as an uptake process ($pH+pe = 16.2$). The effect of carbonate is not considered in the calculations.

Figure S2. Percentage of Pu uptake in presence of kaolinite versus the pH for different total Pu concentrations ($[Pu]_{tot} = 6.9 \times 10^{-9}$; 6.6×10^{-8} ; 3.5×10^{-7} M). Experimental conditions: $S/V = 4$ g/L; 0.1 M $NaClO_4$; 120 h equilibration time; ambient air atmosphere. Curves are simulations with the present model when considering or not the precipitation of $PuO_{2(am)}$ as an uptake process ($pH+pe = 16.2$). The arrow shows the effect of increasing $[Pu]_{tot}$ on the simulations. When no precipitation is considered, the same simulated results are obtained for all $[Pu]_{tot}$. The effect of carbonate is not considered in the calculations.

Figure S3. Th(IV) and Np(V) sorption to amorphous silica versus the pH in 0.1 M $NaClO_4$ taken from Righetto et al. (1991) and recalculated as $\log K_d$ (L/kg). Experimental conditions: $[Th]_{tot} = 10^{-11}$ M; $S/V = 60$ mg/L / $[Np(V)]_{tot} = 10^{-14}$ M; $S/V = 1200$ mg/L. The double arrow illustrates $\log K_d(Th(IV)) - \log K_d(Np(V))$ for $pH = 7$ (see the main article).

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Figure S1

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Figure S2

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Figure S3