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On the study of Th(IV)-humic acid interactions by competition sorption studies with silica and determination of global interaction constants

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Summary. The influence of humic acids (HA) on the retention of thorium (IV) onto the surface of silica colloids is investigated. Thorium is considered as an analogue of tetravalent actinides (U, Np, Pu), except for the fact that it has no *f* electrons. Silica (SiO₂) is chosen as a model surface because it is a component of many minerals and because of its weak HA sorption properties. Retention experiments are performed by batch procedure at constant ionic strength (*I* = 0.1 M NaClO₄), at various pH (2 to 9) and HA concentrations (1–100 mg/L). The sorption of Th(IV) onto colloidal amorphous silica is characterised using a surface complexation model. The ternary system (*i.e.* HA-Th-Silica) clearly shows the influence of HA on Th(IV) retention. This can lead to a strong reduction of the amount of Th(IV) sorbed onto silica in the presence of HA compared to silica colloids without HA, due to a predominant part of thorium present in solution as humic complexes. In a pH range where no organic coating onto silica occurs, there is a competitive reaction between Th(IV) sorption onto the silica surface and onto HA reactive functional groups. In this case, Schubert's method is applied to obtain a global interaction constant for the Th(IV)-HA system. The large interaction constant values indicate a strong affinity of HA for Th(IV).

1. Introduction

The importance of colloidal matter on the facilitated transport of heavy metals in natural systems is now well accepted [1–4]. It is of particular importance to determine the influence of humic substances (HS, humic and fulvic acids, HA/FA), constituting nearly half of the dissolved organic matter present in groundwater [5–7], on the migration of radionuclides, particularly the actinide elements.

The complexation and sorption behaviour of mono, di or trivalent metal ions are now well documented. However, data on tetravalent cations, *e.g.* Th, Zr, Hf, are relatively scarce due to experimental difficulties met with their use: *i.e.* low solubility of the oxides [8, 9] and sorption on vessel

walls [10]. In deep groundwater, the redox potential (E_h) is expected to be negative inducing reducing conditions, so redox sensitive actinide elements are expected to be predominantly in their tetravalent form, *i.e.*, U(IV), Np(IV), Pu(IV). Knowledge of the tetravalent element behaviour in natural groundwater in the presence of humic substances is thus of a great importance. Moreover, Np(V), Pu(VI) and Pu(V) are reduced to Np(IV) and Pu(IV) by HS [11–15].

Thorium is regarded as an analogue for the other tetravalent actinides [16]. Investigations of Th(IV) sorption onto mineral surfaces have been reported in the literature [10, 17–23]. These studies indicate that the cation-mineral interaction is strong and the retention edge of Th(IV) on SiO₂, TiO₂, goethite, hematite or alumina is observed near pH 2–3. The silica-Th(IV) system has been previously studied by Östhols *et al.* [10], using a diffuse double layer surface complexation model (SCM) [24], and by Zaki and Kolta [25]. Literature data on the sorption of tetravalent elements on surfaces are scarce compared to *d* transition elements, mostly because of the experimental constraints related to these elements. As noted in [10], referring to [26], it is difficult to find any vessel material that would allow studies at pH ≥ 3, since tetravalent elements have strong affinities for any surfaces. Clear experimental evidences for a strong sorption of thorium onto silicate mineral surfaces in a large pH range are mentioned in [17, 27, 28]. In natural systems, tetravalent cations, including Th(IV), are associated with particulate or colloidal matter present in groundwater and their chemistries are not controlled by the precipitation of a single mineral phase [27–30].

The strong interaction of thorium with humic substances is known [31–34]. Data concerning the complexation of Th(IV) with humic substances have been compiled by Nash and Choppin [35] and revised by Choppin and Allard [36]. The authors described the increasing complexation strength of HA for Th(IV) with increasing pH using an operational equation as a function of HA ionisation [37, 38]. The log ^{HA} β value in [35] ranges from 10.6 at pH 3.5 to 13.2 at pH 5 (with ^{HA} β given in L/eq) referring to Baes and Mesmer hydrolysis data sets [39] and acetate complexation of Th(IV) [40]. Recently, Murphy *et al.* [41] deter-

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mined the complexation constant for the Th(IV)-HA system at pH 3.5 ($\log^{HA}\beta = 7.5$ with $^{HA}\beta$ given in L/eq) referring to Grenthe *et al.* hydrolysis data sets [42, 43]. Unfortunately, the data were obtained in a pH range which is irrelevant of natural media ($3.5 \leq \text{pH} \leq 5$) and caution must be taken for their application to conditions of natural waters ($6 \leq \text{pH} \leq 9$). Zuyi and Huanxin determined the constants for soil HA and FA at pH = 6 [44], the $\log^{HA}\beta$ values were comparable with [35]. Davis *et al.* [45] studied the Th(IV)-FA system between pH 5.3 and 6.5 ($5.6 \leq \log^{FA}\beta \leq 6.2$ with $^{FA}\beta$ given in L/g) and did not correct their data from hydrolysis.

Denecke *et al.* [46] and Schild and Marquardt [47] showed that under acidic conditions the Th-HA bonding occurs through carboxylate functions. However, the increasing complexing strength of HA with pH cannot be explained solely by complexation with HA carboxylate functions. This phenomenon has been interpreted to indicate that either mixed complexes form [48, 49] or an activation of other HA (phenolic) sites occurs [50]. Hence, it appears that, except for Davis *et al.* [45] whose experiments have been conducted up to pH 6.5 with FA, no studies on the complexation of Th(IV) by HA have been performed under natural groundwater conditions where competing reactions exist, in particular hydrolysis. The question emerges to what extent the extrapolation of data obtained under acidic conditions can be extrapolated to higher pH, where competing ligands are present and where ternary complexes (or mixed complexes) may form.

The presence of a competing ligand such as HA can strongly influence the retention of heavy metals onto mineral phases [51–56]. Although mechanisms involved in the sorption of HS onto mineral surfaces [57, 58] are not fully understood, many general trends are well known. Zachara *et al.* [53] have shown that when HA and the mineral are pre-equilibrated, cobalt (II) retention is more pronounced when the amount of HA is less than needed to saturate the mineral surface. When the concentration of HA surpasses the saturation of the mineral surface, Labonne-Wall *et al.* [54], Takahashi *et al.* [55] and Reiller *et al.* [56] reported that metal cation retention decreases with increasing pH. These effects depend upon the relative proportions of HA and mineral phase sorption sites.

The objective of this paper is to study the influence of HA on the sorption of a tetravalent actinide Th(IV) onto a mineral surface. The competition between HA and this surface is used to study the complexation of Th(IV) by HA, as pointed out by Vuceta and Morgan [59]. A silica colloidal suspension has been chosen as a model mineral surface because silica is one of the major components of colloidal matter in natural waters [60]. This study is focused on the system of a silica colloidal suspension, HA and thorium (IV), characterising it as a function of pH (2–8.5) and HA concentration (1–100 mg/L). The different equilibria involved in the binary (Th-SiO₂) system are described using a surface complexation model, SCM (without an electrostatic term). These results, combined with the experimental data for the Th(IV)-HA-SiO₂ ternary system, are used to determine apparent global interaction constants for Th-HA.

2. Experimental

2.1 Materials

The silica suspension is obtained from AEA Harwell [61]. The surface properties is taken from Brady [62]:



the point of zero charge pH_{pzc} is 2–3 [63]; C_e , the proton exchange capacity, PEC, is taken to be 0.3 meq/g.

Purified Aldrich HA is used in a protonated form. Characteristics of this HA are described by Kim *et al.* [64]. The PEC for HA-Aldrich was determined in [64] by potentiometric titration ($W_{\text{HA}} = 5.4 \times 10^{-3}$ eq/g) and by the Ba(OH)₂ adsorption and Ca-acetate methods (4.8×10^{-3} eq/g by (CH₃COO)₂Ca for carboxylic groups and 2.26×10^{-3} eq/g with Ba(OH)₂ for phenolic groups). The apparent acidity constant (determined as the pH at mid-equivalence) is $\text{p}K_a^{\text{HA}} = 4.52$.

The initial thorium solution (²²⁸Th in 2 M HNO₃) is obtained from Amersham. This solution is diluted in order to obtain a 1.09×10^{-9} M stock solution in 0.9 M NaClO₄ and 0.2 M HNO₃. All other chemicals are reagent grade and Millipore water is used.

2.2 Experimental

The sorption experiments are conducted in batch procedure at room temperature in polycarbonate vials sealed with screw caps. The silica suspension is prepared by diluting a stock solution with the background electrolyte to the desired concentration. Aliquots of HA are added and the pH is adjusted to the desired value with a TACUSSEL pH metre (PHM 220 MeterLab) equipped with a combined TACUSSEL electrode (Radiometer type XC 161, modified NaClO₄ 0.1 M, NaCl 10⁻² M), using HClO₄ (0.1 M) or freshly prepared NaOH (0.1 M). The combined electrode was calibrated against commercial pH buffers (pH = 4, 7, 9). The ionic strength is kept constant (NaClO₄ 0.1 M) through all of the experiments. HA concentration is measured spectrophotometrically at 254 nm (Shimadzu UV-2100), neglecting chromism effects [65]. The suspension is shaken for 24 hours to allow equilibration of the adsorbent. Enough Th(IV) solution is added to obtain a final concentration of 1.15×10^{-12} M and the pH is readjusted. The solution is shaken again for 24 hours. Three 1 mL aliquots of the suspension are sampled for thorium activity measurement (A_1), in order to get rid of Th(IV) adsorption on vial walls as described by Cromières *et al.* [23]. Colloids are separated from the liquid phase by ultracentrifugation (90 min, 50 000 rpm), the pH of the supernatant is measured and then three 1 mL aliquots are sampled from the supernatant for thorium activity measurement (A_2).

The activities of ²²⁸Th are measured by liquid scintillation counting. Sampled aliquots are added to 4 mL of liquid scintillator (Ultima Gold AB). The activity measurements are performed after one month in order to attain the secular equilibrium of ²²⁸Th with its daughters. In the initial solution thorium activity (A_0) is determined by direct addition into the liquid scintillator (Packard TRI-CARB 2700 TR).

The percent amount of Th(IV) sorbed, R (%), is calculated from the activities of the suspension (A_1) and of the

supernatant (A_2) according to the following equation:

$$R(\%) = \frac{A_1 - A_2}{A_1} \times 100. \quad (2)$$

The distribution coefficient, K_d , is given by:

$$K_d = \frac{C_{\text{Th sorbed}}}{[\text{Th}]_{\text{solution}}} = \left(\frac{A_1}{A_2} - 1 \right) = \frac{V(\text{ml})}{m_{\text{SiO}_2}(\text{g})} \\ = \frac{R}{100 - R} \times \frac{10^6}{C_{\text{SiO}_2}(\text{mg/L})}, \quad (3)$$

where V is the volume of the suspension, m_{SiO_2} is the mass of added silica.

2.3 Thorium chemistry

Th(IV) speciation diagrams for the conditions of these experiments are depicted in Fig. 1. Because of the low Th concentration, only the monomers induced by the hydrolysis need to be taken into account. Th(IV) hydrolysis constants are those determined by Baes and Mesmer [39] (Fig. 1a) and by Ekberg *et al.* [66] (Fig. 1b), as well as those determined by Grenthe *et al.* [42, 43] (Fig. 1c) in order to take into account for CO_3^{2-} complexation. Note that the constant for $\text{Th}(\text{OH})_4(\text{aq})$ neutral complex in these three references remains two to four orders of magnitude higher than the upper limit of this constant estimated by Ryan and Rai [8]¹. The cumulative constants of Th(IV), corrected for 0.1 M ionic strength using the Specific Interaction Theory (SIT), are reported in Table 1 ($\varepsilon_{\text{Th(IV)}}$ were taken as equal to $\varepsilon_{\text{U(IV)}}$ in Grenthe *et al.* [67]). The total carbonate concentration in our experimental closed system has been estimated by Labonne [68] and Cromières [69] to be 5×10^{-5} M. The carbonate complexes, $\text{ThCO}_3(\text{OH})_3^-$ and $\text{Th}(\text{CO}_3)_5^{6-}$, suggested by different authors [43, 70–72] have been taken into account. The pentacarbonatothorate(IV) limiting complex is of minor importance under our conditions. Tetravalent actinides are suspected to form silicate complexes but have not been yet quantified [73].

¹ $\log^* \beta_4 \leq -19.4$

Table 1. Complexation cumulative constants of Th(IV), corrected for 0.1 M ionic strength using SIT method.

Equilibrium	$\log^* \beta_i$	$\log^* \beta_i$	$\log^* \beta_i$
	[39] $I = 0.1 \text{ M}$	[42, 43] $I = 0.1 \text{ M}$	[66] $I = 0.1 \text{ M}$
$\text{Th}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})^{3+} + \text{H}^+$	-3.9	-3.8	-2.7
$\text{Th}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_2^{2+} + 2\text{H}^+$	-8.0	–	-7.7
$\text{Th}^{4+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_3^+ + 3\text{H}^+$	-13.0	-10.4	-12.7
$\text{Th}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_4 + 4\text{H}^+$	-17.4	-15.2	-18.3
$\text{Th}^{4+} + \text{CO} + 3\text{H}_2\text{O} \rightleftharpoons \text{ThCO}_3(\text{OH})_3^- + 3\text{H}^+$	–	-2.2	–
	$\log^* \beta_i$		
	[67]		
	$I = 0.1 \text{ M}$		
$\text{H}_4\text{SiO}_4 \rightleftharpoons \text{H}_3\text{SiO}_4^- + \text{H}^+$	-9.6		
$\text{H}_4\text{SiO}_4 \rightleftharpoons \text{H}_2\text{SiO}_4^{2-} + 2\text{H}^+$	-22.6		
$2\text{H}_4\text{SiO}_4 \rightleftharpoons \text{H}_5\text{Si}_2\text{O}_7^- + \text{H}^+$	-7.9		
$2\text{H}_4\text{SiO}_4 \rightleftharpoons \text{H}_6\text{Si}_2\text{O}_7^{2-} + 2\text{H}^+$	-18.4		

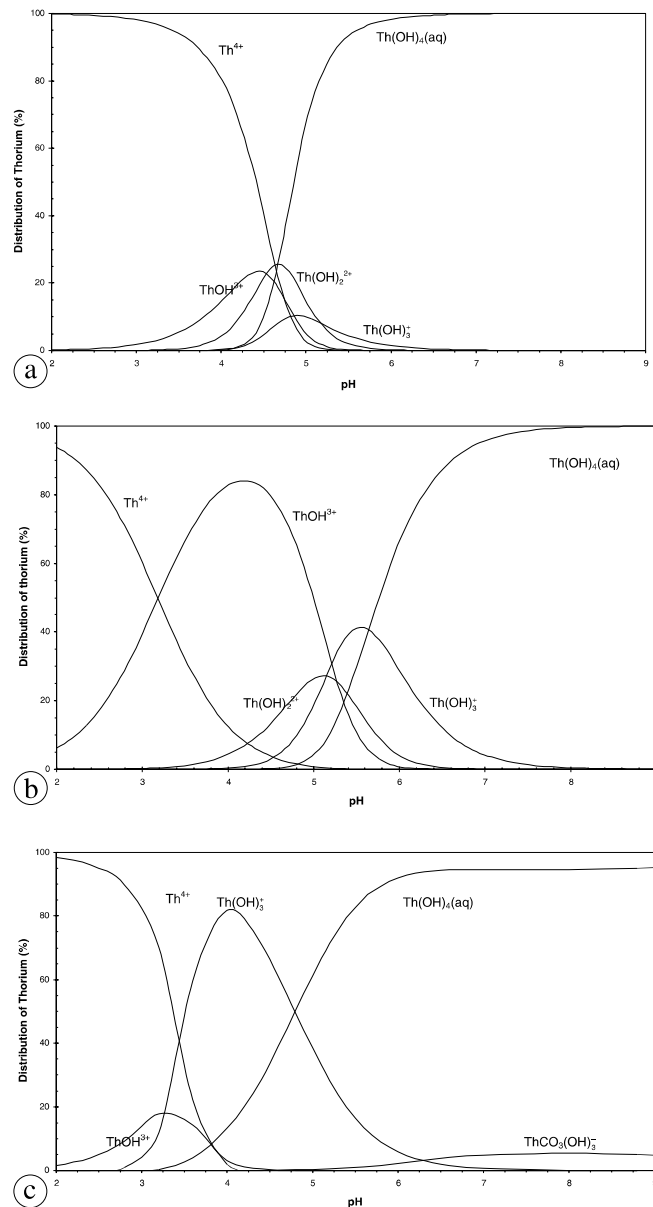


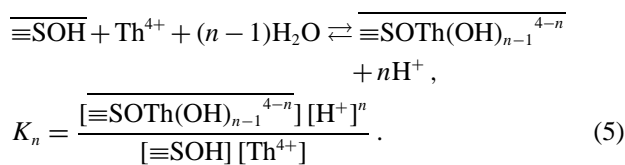
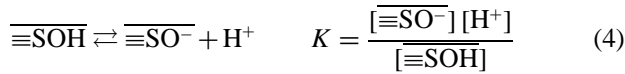
Fig. 1. Speciation diagram for thorium. $I = 0.1 \text{ M}$ (NaClO_4), $[\text{Th}] = 10^{-12} \text{ M}$, $[\text{CO}_3]_t = 5 \times 10^{-5} \text{ M}$, referring to: (a) [42, 43], (b) [39], (c) [66].

The experimental points of Th sorption experiment onto SiO₂ are fit using FITEQL 3.2 [74]. The criteria of the FITEQL code “SOS/DF” defined as the ratio of the sum of least squares on the degrees of freedom (7% relative error on Th_{ads}, and 2% relative error in pH) is used to determine the quality of the fit.

Binary system

Thorium retention by various minerals has been studied using SCM [19, 20, 22, 23, 43]. Laflamme *et al.* [19], Hunter *et al.* [20] and Cromières *et al.* [23] obtained comparable results for iron oxides. The authors determined surface complexation constants referring to the Baes and Mesmer [39] hydrolysis data sets.

The retention can be modelled following the assumption via the following reactions scheme and constants:



Ternary system

The formation of a complex between thorium and HA, to which the mass action law is applied, can be represented as follows:

$${}^{\text{HA}}\beta = \frac{[\text{ThHA}]}{[\text{Th}][\equiv\text{HA}]}, \quad (6)$$

where $\equiv\text{HA}$ can be considered as a site, ${}^{\text{HA}}\beta$ is an apparent global interaction constant where a formal stoichiometry is not necessary. The humic site concentration $[\equiv\text{HA}]$ is calculated as:

$$[\equiv\text{HA}] = W_{\text{HA}} (\text{eq/g}) \times C_{\text{HA}} (\text{g/L}).$$

Determination of ${}^{\text{HA}}\beta$ is straightforward assuming that there is no interaction between the mineral surface and HA. This is the case for silica at pH > 6.5, as shown on Fig. 2, as already shown in the case of silica surface [54, 55, 75], or on clay [76]. Furthermore, contrary to oxalic acids, humic acids do not appear to increase feldspar dissolution rate [77].

Combining Eqs. (3), (4) and (5), the portion of sorbed Th(IV) is obtained:

$$P = \frac{[\text{Th}_{\text{fixed}}]}{[\text{Th}_{\text{total}}]} = \frac{\sum_n K_n [\equiv\text{SOH}][\text{Th}^{4+}][\text{H}^+]^{-(n+1)}}{\left\{ \alpha_{\text{Th}} [\text{Th}^{4+}] + {}^{\text{HA}}\beta [\text{Th}^{4+}][\equiv\text{HA}] + \sum_n K_n [\equiv\text{SOH}][\text{Th}^{4+}][\text{H}^+]^{-(n+1)} \right\}}, \quad (7)$$

where α_{Th} is the Ringböm coefficient concerning inorganic complexation:

$$\alpha_{\text{Th}} = 1 + \sum_i \frac{{}^*\beta_i}{[\text{H}^+]} + \sum_j \beta_j [\text{CO}_3^{2-}]^j \dots \quad (8)$$

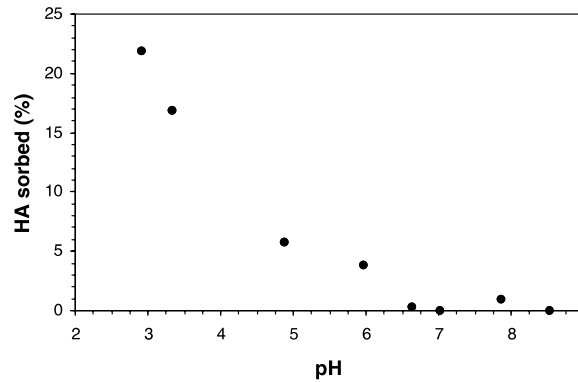


Fig. 2. Sorption of HA onto silica colloids, $[\text{HA}] = 0.01 \text{ g/L}$, $I = 0.1 \text{ M}$ (NaClO_4), $[\text{SiO}_2]_i = 0.25 \text{ g/L}$.

When the system can be considered as purely competitive ($\text{pH} \geq 6.5$), the following equation can be written:

$${}^{\text{HA}}\beta = \frac{\left((1-P) \sum_n K_n [\equiv\text{SOH}][\text{H}^+]^{-(n+1)} \right) - P\alpha_{\text{Th}}}{P[\equiv\text{HA}]}. \quad (9)$$

As the Th(IV) concentration is at trace level, the following equation is valid:

$${}^{\text{HA}}\beta = \frac{\left(\frac{(1-P)C_e}{\alpha_{\text{SiOH}}} \sum_n K_n [\text{H}^+]^{-(n+1)} \right) - P\alpha_{\text{Th}}}{P[\equiv\text{HA}]}, \quad (10)$$

where $\alpha_{\text{SiOH}} \cong (1 + 10^{-6.54+\text{pH}})$ neglecting the proportion of Th surface complexes.

The ${}^{\text{HA}}\beta$ can thus be estimated at a pH value where no HA sorption onto a mineral is assumed.

Competitive reaction systems are easily studied using the Schubert's method [78]. The following expressions are used to analyse the data from the ternary system to ultimately determine ${}^{\text{HA}}\beta$ of the Th(IV)-HA system.

When Th(IV) is sorbed onto silica, the distribution coefficient is written:

$$K_d^\circ = \frac{[\text{Th}_{\text{sorb}}]}{[\text{Th}_{\text{aq}}]} = \frac{\sum_n [\equiv\text{SOTh}(\text{OH})_n^{(4-n)+}]}{[\text{Th}_{\text{aq}}]} = \frac{\sum_n K_n \frac{[\equiv\text{SOH}]}{[\text{H}^+]^n}}{\left(1 + \sum_n \frac{{}^*\beta_n}{[\text{H}^+]^n} \right)} = \frac{\sum_n K_n \frac{[\equiv\text{SOH}]}{[\text{H}^+]^n}}{\alpha_{\text{Th}}}. \quad (11)$$

When the competition between silica and HA takes place, the distribution coefficient is:

$$K_d = \frac{[\text{Th}_{\text{sorb}}]}{[\text{Th}_{\text{aq}}]} = \frac{\sum_n [\equiv\text{SOTh}(\text{OH})_n^{(4-n)+}]}{[\text{Th}_{\text{aq}}]} = \frac{\sum_n K_n \frac{[\equiv\text{SOH}]}{[\text{H}^+]^n}}{\left(1 + \sum_n \frac{{}^*\beta_n}{[\text{H}^+]^n} + {}^{\text{HA}}\beta [\equiv\text{HA}] \right)}.$$

Thus, one can write:

$$K_d = \frac{\sum_n K_n \frac{[\equiv\text{SOH}]}{[\text{H}^+]^n}}{\alpha_{\text{Th}} + {}^{\text{HA}}\beta [\equiv\text{HA}]} \quad (12)$$

The resulting Schubert equation is:

$$\log \left[\left(\frac{K_d^\circ}{K_d} - 1 \right) \times \alpha_{\text{Th}} \right] = \log B \\ = n \log [\equiv\text{HA}] + \log {}^{\text{HA}}\beta, \quad (13)$$

where n is the number of ligand reacting per metal, α_{Th} is the Ringböm coefficient for hydrolysis of Th(IV), $[\equiv\text{HA}]$ is the concentration of HA sites given in eq/L (defined as the product of the HA concentration in g/L and the proton exchange capacity W_{HA}), and $\log {}^{\text{HA}}\beta$ is the apparent interaction constant of the Th-HA system (with ${}^{\text{HA}}\beta$ given in L/eq). Under the pH conditions studied here, all carboxylic sites are ionised. Silicate species are not considered to interact with HA, as only weak interactions are mentioned in the literature [79, 80], and no interactions with silanol groups occurs for $\text{pH} > 6.5$.

3. Results and discussion

3.1 Sorption of thorium onto silica

The results obtained for the retention of Th(IV) onto silica colloids versus pH in the range 2–9 are shown on Fig. 3 ($[\text{Th}]_{\text{ads}} = f(\text{pH})$). Error bars are the mean experimental uncertainty ($\cong 5\%$). As expected from former studies [19–23], the sorption edge is around pH 2–3. The sorption remains relatively constant up to pH 8–9. Using the amorphous silica solubility constant ($\log K_s = -2.71$) and orthosilicic acid hydrolysis constant recommended in Grenthe *et al.* [67] (Table 1), the experimental data can be modelled in the pH range 2–7, where the dissolution of silica is not extensive.

The main difference between our results and those of Östhols [10], is that the sorption of Th(IV) onto silica does not result in maximal sorption at a pH range 2–7.5. A progressive sorption edge is observed, similar to other oxides [19–21, 23]. Th(IV) is fixed onto silica in neutral pH media, as is it the case in natural medium [27, 28].

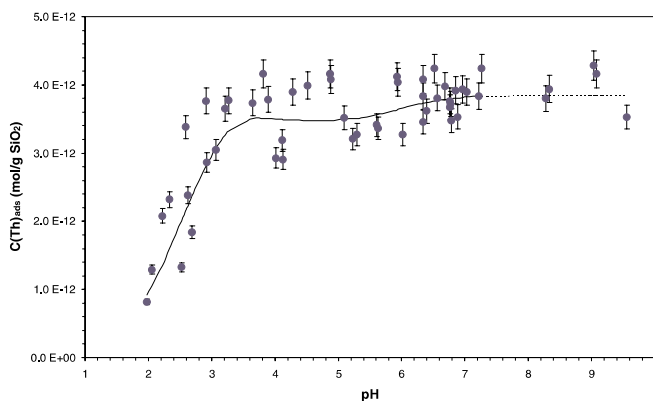


Fig. 3. $[\text{Th}]_{\text{ads}}$ (mol/g SiO_2) versus pH onto silica colloids. $I = 0.1 \text{ M}$ (NaClO_4), $[\text{SiO}_2]_i = 0.25 \text{ g/L}$ $[\text{Th}] = 1.5 \times 10^{-12} \text{ M}$.

From his sorption study of Th(IV) onto silica at $\text{pH} \leq 3.5$, and subsequent SCM fitting, Östhols [10] postulates a bidentate nature of Th(IV) sorbed species on colloidal silica. An EXAFS study of this system confirmed the results in the acidic pH range [81]. The surface coverage in the sorption study is four orders of magnitude higher than in our conditions (8.35×10^{-8} to $9.9 \times 10^{-6} \text{ mol Th/g SiO}_2$ in [10]; $4 \times 10^{-12} \text{ mol Th/g SiO}_2$ in this study). In the EXAFS study, the thorium concentration was high (10^{-4} – 10^{-2} M) and is not relevant to any natural situation, where Th(IV) is expected to be present at trace levels.

Using SCM many authors demonstrated the existence of two types of surface sorption sites: “strong” and “weak” sites [82]. Our experiments are performed at low Th concentrations so we assume that only strong binding sites are concerned here. The interaction constants obtained are only relevant to the “strong” binding sites of silica, due to trace metal concentration used (*i.e.* 10^{-12} M).

Monodentate surface complexes seem to be a justified approximation to describe our results. Under similar conditions, monodentate surface complexes have been used to successfully describe the sorption of Eu(III) onto hematite ($\alpha\text{-Fe}_2\text{O}_3$) [83] or Np(V) onto hydrargillite ($\text{Al}(\text{OH})_3$) [84]. As pointed out by Davis and Kent [85], in SCM the complexation exceeds the electrostatic contribution for strong adsorbing ions, including multivalent actinides. Furthermore, in our study, the very low coverage of surface silica by Th(IV) lowers the possible lateral coulombic interactions [86]. Hence, for our peculiar study, the use of a non-electrostatic SCM is justified.

The surface complexation constants describing the sorption of Th(IV) onto silica surface ($\equiv\text{SOH}$ groups) obtained from fits to the data are presented in Table 2. The fitting exercises are performed using hydrolysis constants of Baes and Mesmer [39], Grenthe *et al.* [42, 43] and Ekberg *et al.* [66]. Hydroxo surface complexes ($\equiv\text{SOTh}(\text{OH})_{n-1}^{(4-n)+}$ with n varying from 1 to 5) are needed to fully describe the sorption of thorium on silica colloids under our experimental conditions. The fit does not converge using a bidentate surface complex alone for Th(IV) sorption in acidic solution and the hydrolysis data recommended by Baes and Mesmer [39]. The use of the hydrolysis constants of Grenthe *et al.* [42, 43] and a bidentate surface complex yields a poor fit ($\text{SOS}/\text{DF} > 100$, data not shown). Fig. 3 compares experimental data to the model curve obtained using the surface complexation constants in Table 2.

Our fits are not in agreement with the assumption made in [10] that Th(IV) sorption onto silica is limited to a pH range between 2 and 7. However, Östhols studied Th(IV) sorption onto Aerosil OX 200 silica (pyrogenic) in acidic media. The pyrogenic silica can be compared to vitreous silica used by Rydberg and Rydberg [26] and to the substrate used by James and Healy [18]. Using his SCM results in acidic media ($\text{pH} \leq 3.25$), Östhols [10] successfully fit the results of [26] and [18] with a bidentate complex. These results, however, cannot be applied to the distribution of Th(IV) in groundwater rich in silica [27, 28]. One may also not directly compare data obtained using a pyrogenic silica substrate with a sol-gel silica [87]. It is known that precipitated silica (sol-gel) surface charge, BET surface density and total exchangeable protons are greater than

Table 2. Parameters for the surface complexation study of Th onto silica.

Equilibrium				
$\equiv\text{SOH} \rightleftharpoons \equiv\text{SO}^- + \text{H}^+$	-6.54			
Surface site concentration	0.3 meq/g			
Hydrolysis data set	[42, 43]	[39]	[66]	
$\equiv\text{SOH} + \text{Th}^{4+} \rightleftharpoons \equiv\text{SOTh}^{3+} + \text{H}^+$	1.6 ± 0.1	1.6 ± 0.1	1.6 ± 0.1	1.7 ± 0.1
$2\equiv\text{SOH} + \text{Th}^{4+} \rightleftharpoons (\equiv\text{SO})_2\text{Th}^{2+} + 2\text{H}^+$	—	2.3 ± 0.5	—	—
$\equiv\text{SOH} + \text{Th}^{4+} + \text{H}_2\text{O} \rightleftharpoons \equiv\text{SOThOH}^{2+} + 2\text{H}^+$	—	—	—	1.55 ± 0.3
$\equiv\text{SOH} + \text{Th}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \equiv\text{SOTh(OH)}_2^+ + 3\text{H}^+$	-5.1 ± 0.3	—	—	—
$\equiv\text{SOH} + \text{Th}^{4+} + 3\text{H}_2\text{O} \rightleftharpoons \equiv\text{SOTh(OH)}_3 + 4\text{H}^+$	—	-9.9 ± 0.3	-12.0 ± 0.4	—
$\equiv\text{SOH} + \text{Th}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \equiv\text{SOTh(OH)}_4^- + 5\text{H}^+$	-15.9 ± 0.3	-16.3 ± 0.6	-18.2 ± 0.5	-19.1 ± 0.4
SOS/DF	5.2	5.3	5.3	5.8

for pyrogenic silica [87]. Furthermore, the hydroxylation of the pyrogenic silica sample used by Östhols [10], was performed in neutral to strongly acidic media. This treatment undoubtedly minimises the formation of polysilicates induced by the dissolution of the surface ([10], p. 1237). In our experiments, the silica suspension is stored in slightly alkaline medium, similar to the experiments reported by Yates and Healy [87]. Under these conditions, the total hydroxylation of the surface, considering the hydration kinetics of heat-treated silica [88], and the formation of polysilicates are then possible. These polynuclear complexes of orthosilic acid are suspected to complex thorium in solution [73], and could be responsible of the enhancement of the retention onto silica surface compared to the vitreous silica.

3.2 Effect of the presence of HA on the sorption of thorium onto silica

The effect of HA on the sorption of Th(IV) onto silica with varying HA concentration (1, 10, 50 and 100 mg/L) is presented in Fig. 4. As expected, retention of Th(IV) onto silica decreases with increasing HA concentration. As in the case of Th(IV) sorption onto hematite [56] and Zr(IV) onto kaolinite and silica [55], the presence of HA has a strong impact on the sorption even in slightly basic media. This is likely due to the formation of soluble thorium organic complexes.

As silicate ions are not known to be associated with HA [79, 80], the interaction constant of Th(IV)-HA complex can be estimated using the surface complexation data determined at a pH value where no sorption of HA onto silica occurs, *i.e.*, pH = 7–8. Under these conditions, an apparent global interaction constant, referring to [39], is estimated

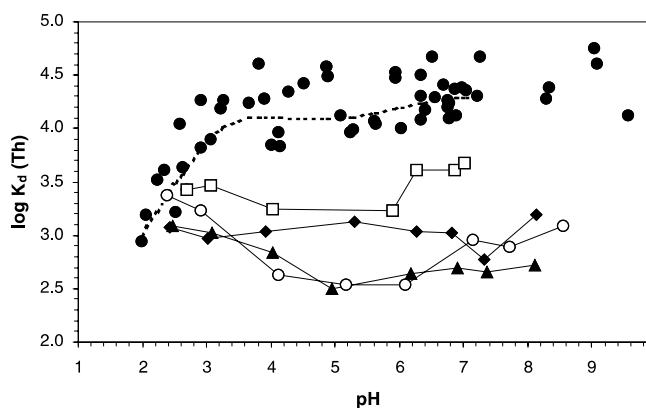


Fig. 4. Influence of HA on the sorption of Th(IV) onto silica colloids vs. pH: [Th] = 1.15×10^{-12} M, [SiO₂] = 0.25 g/L, $I = 0.1$ M (NaClO₄); ● [HA] = 0, □ [HA] = 10^{-3} g/L, ◆ [HA] = 10^{-2} g/L, ▲ [HA] = 5×10^{-2} g/L, ○ [HA] = 0.1 g/L.

(Table 3). These values are compared with the $\log {}^{\text{HA}}\beta(\text{Th}^{4+})$ calculated from the following equation [36]:

$$\log {}^{\text{HA}}\beta(\text{Th}^{4+}) = 7.1 {}^{\text{HA}}\alpha + 9.2, \quad (14)$$

where ${}^{\text{HA}}\alpha$ is the ionisation coefficient of Lake Bradford HA (${}^{\text{HA}}\beta = 0.9$ for pH = 7, and ${}^{\text{HA}}\alpha = 0.99$ for pH = 8) [37].

The $\log {}^{\text{HA}}\beta$ estimated clearly show that the Th(IV)-HA complexes are strong, which is in agreement with [36]. However, our values are larger than those that can be extrapolated from [36] for the same hydrolysis constant data set. The different HA used within these two works may not totally explain this discrepancy (Aldrich versus Lake Bradford) as Nash and Choppin determined very close value of $\log {}^{\text{HA}}\beta$ for these two different humic acids at pH ≈ 4 [35].

Table 3. Global interaction constants for the Th-HA system calculated from the constants in Table 2 referring to [39].

[HA] (mg/L)	100 mg/L			50 mg/L			10 mg/L			1 mg/L			$\log \overline{{}^{\text{HA}}\beta}_{\text{BM}}}$
	pH	P (%)	$\log {}^{\text{HA}}\beta$	pH	P (%)	$\log {}^{\text{HA}}\beta$	pH	P (%)	$\log {}^{\text{HA}}\beta$	pH	P (%)	$\log {}^{\text{HA}}\beta$	
pH ≈ 8	8.1	27.8	21.0	8.1	11.5	21.7	8.1	27.8	22.0	—	—	—	21.6 ± 1.3
pH ≈ 7.5	—	—	—	—	—	—	—	—	—	7.6	54.5	20.2	—
pH ≈ 7	6.8	21.1	15.8	6.9	10.9	16.9	6.8	21.1	16.8	6.9	50.4	17.6	16.8 ± 1.2

3.3 Competition between silica and HA at constant pH using

Fig. 5 presents the results of complexing behaviour of HA towards Th(IV) using silica colloids as a competing agent at constant pH values 6.7 ± 0.2 , 7.2 ± 0.1 and 7.9 ± 0.1 . The concentration range chosen for this experiment covers the widest range which HA are encountered in natural media. It can be seen this competitive system behave like the ternary system Th, α -Fe₂O₃ and HA [56], where the sorption minimum is around pH = 7.

These results are plotted according to Eq. (13) in Fig. 6, using [42, 43] data sets for hydrolysis and carbonate complexation. The following linear relations satisfactorily represent the points:

$$\log B_{\text{pH}=6.7} = (1.3 \pm 0.2) \log[\equiv\text{HA}] + (18.2 \pm 1.0);$$

$$r^2 = 0.9612;$$

$$\log B_{\text{pH}=7.2} = (1.1 \pm 0.3) \log[\equiv\text{HA}] + (19.4 \pm 1.1);$$

$$r^2 = 0.9387;$$

$$\log B_{\text{pH}=7.9} = (1.0 \pm 0.1) \log[\equiv\text{HA}] + (21.3 \pm 0.6);$$

$$r^2 = 0.9757;$$

using a 95% confidence interval.

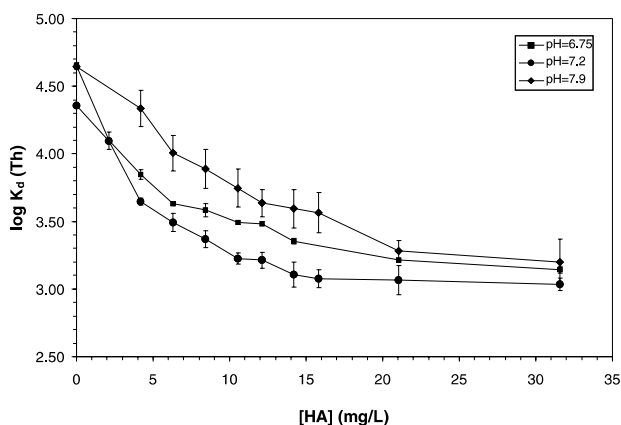


Fig. 5. Plot of the distribution coefficient K_d for Th(IV) in the competing system silica colloids-HA-Th at constant pH. $[\text{SiO}_2]_i = 0.25 \text{ g/L}$, $[\text{Th}] = 10^{-12} \text{ M}$, $[\text{NaClO}_4] = 0.1 \text{ M}$: ■ pH = 6.7 ± 0.2 ; ● pH = 7.2 ± 0.1 ; ◆ pH = 7.9 ± 0.1 .

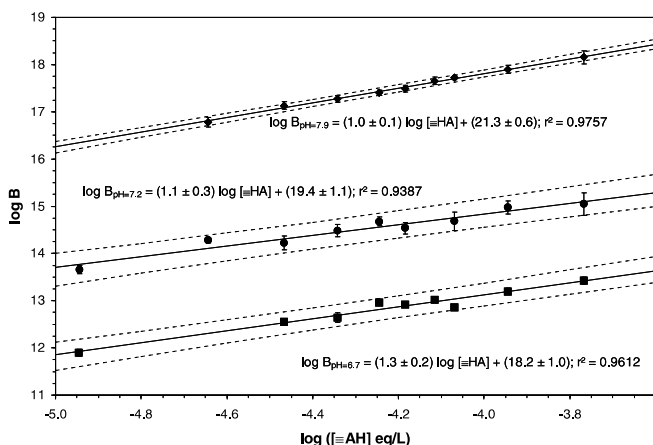


Fig. 6. Plot of Eq. (13) for Th(IV)-HA system, using silica colloids as competitor, referring to [42, 43]. $[\text{NaClO}_4] = 0.1 \text{ M}$: ■ pH = 6.7 ± 0.2 ; ● pH = 7.2 ± 0.1 ; ◆ pH = 7.9 ± 0.1 .

The slope of the plots in Fig. 6 are near unity, indicating that n is 1 at all pH values. The values obtained for $\log \frac{\text{HA}}{N} \beta(\text{Th}^{4+})$ (the indice N refers to the hydrolysis constants data set used, *i.e.*, GL for Grenthe *et al.* [42, 43], BM for Baes and Mesmer [39] and EK for Ekberg *et al.* [66]) from extrapolation of the plots to the y-axis intercept are summarised in Table 4.

The differences between the $\log \frac{\text{HA}}{N} \beta(\text{Th}^{4+})$ values come from the differences in $\log \alpha_{\text{Th}}$, since different Th hydrolysis constant data sets are used. In the pH range used in this study, $\text{Th}(\text{OH})_4(\text{aq})$ is the dominant species. Hence Eq. (13) can be rewritten:

$$\log \left(\frac{K_d^{\circ}}{K_d} - 1 \right) + \log \alpha_{\text{Th}} = n \log[\equiv\text{HA}] + \log \frac{\text{HA}}{N} \beta. \quad (15)$$

Using this equation, $\log \frac{\text{HA}}{N} \beta$ can be calculated for any Th hydrolysis constant data sets, as for example those proposed in [89, 90].

These $\log \frac{\text{HA}}{N} \beta$ results are comparable to the estimated values in the previous section and are about two to four orders of magnitude higher than those reported at $\text{pH} \leq 5.5$ [35, 36] and ten logarithmic units more than those determined at $\text{pH} = 3.5$ [41]. The different results obtained in this study, referring to the same Th(IV) inorganic complexation data set from Baes and Mesmer [39], are summarised on Fig. 7, where the $\log \frac{\text{HA}}{N} \beta$ values are compared

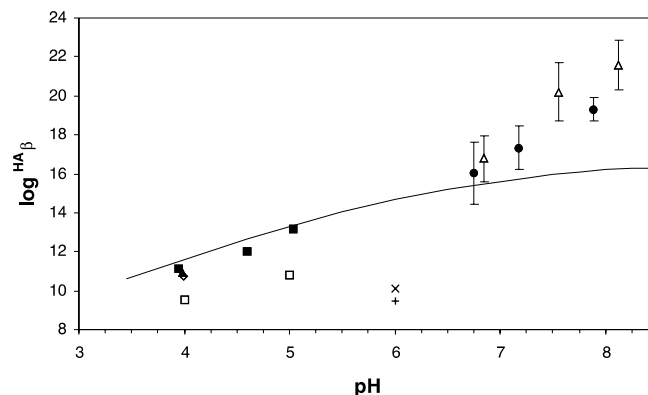


Fig. 7. Variation of the global stability constants $\log \frac{\text{HA}}{N} \beta$, referring to [39], for Th(IV) humic complexes as a function of pH; plain line Eq. (14) proposed by [36]: ■ Lake sediment HA, ◇ Soil HA, ▲ Aldrich HA, □ Aldrich FA from [35]; × Soil HA, + Soil FA from [44]; this study, ● [HA] isotherm (Table 4), △ pH isotherm (Table 3).

Table 4. Global interaction constants for the Th(IV)-HA system determined at pH 6.75, 7.2 and 7.9 (from Fig. 6) – $I = 0.1 \text{ M NaClO}_4$.

Hydrolysis constants set	pH	$\log \frac{\text{HA}}{N} \beta$ this work	$\log \frac{\text{HA}}{N} \beta$ from Eq. (14) [36, 37]
[39]	6.75	16.2 ± 1.0	15.4
	7.2	17.3 ± 1.1	15.8
	7.9	19.3 ± 0.6	16.2
[42, 43]	6.75	18.2 ± 1.0	
	7.2	19.4 ± 1.1	
	7.9	21.3 ± 0.6	
[66]	6.75	16.4 ± 1.0	
	7.2	17.5 ± 1.1	
	7.9	19.5 ± 0.6	

to the experimental values obtained in [35, 44]. The plot of Eq. (14) proposed in [36] versus pH is also mentioned. It can be seen that the importance of humic complexation is higher than previously postulated extrapolating expression Eq. (14). The linear trend observed for Th(IV) is in agreement with observations made on other metals as noted by Hummel *et al.* [91]. Further studies are needed to ascertain this point.

Fig. 8 presents the percent of thorium in humic complexes plotted versus the concentration of HA (g/L and eq/L assuming 5.4×10^{-3} eq/g) at pH 7.2 (Fig. 8a) and 7.9 (Fig. 8b) using $\log \frac{HA}{BM}\beta$ values. It can be seen that, if the humic complexation of Th(IV) is important at pH 7.2 for $[HA] = 100$ mg/L, it is apparently unimportant for the same humic concentration at pH 7.9 when $\log \frac{HA}{BM}\beta$ from [36] is used. These results are not in agreement with field observations (Table 2 in [92], and Table 1 in [93]) where thorium appears to be associated with humic substances as already discussed in [94]. Using the global interaction constants $\log \frac{HA}{BM}\beta$ determined in this study, referring to [39], humic complexation is still predominant down to 10^{-4} g/L

at pH = 7.2, and 10^{-3} g/L at pH = 7.9. In the latter case, Th(IV) is quantitatively associated to HA at 0.1 g/L which is in agreement with field observations [30, 32, 33, 92, 93] for the same conditions, even if the type of HA are not the same in both cases.

The increase in $\log \frac{HA}{BM}\beta$ with pH raises the question of the type of bonding between Th(IV) and HA in natural media. The works of Denecke *et al.* [46] (EXAFS) and Schild and Marquardt [47] (XPS) clearly showed that the carboxylate functional groups are primarily responsible for an important role in the humic complexation of Th(IV) in acidic media. However, this would not be entirely the case for Th-HA bonding in neutral to slightly acidic media. The increase in $\log \frac{HA}{BM}\beta$ with pH may indicate that mixed Th(IV)-humate complexes form, similar to observations made for cobalt [49], uranium [49, 95], cadmium, europium [48], americium and curium [96, 97]. This could be related to the chemistry of Th(IV), *i.e.*, formation of hydrolysed forms at high pH, or to the role of phenolic functional groups in HA in metal binding as well as conformational changes in HA molecules with increasing pH [50, 98].

3.4 Consequences on thorium mobility

Extent of Th-HA complexation

As discussed previously [94], the extent of tetravalent elements complexation by HA is still under debate [41, 56, 91, 99, 100]. To explore this, the extent of Th-HA complexation is calculated using our global interaction constant and data for natural groundwater reported in the literature. The first illustrative example is an argillaceous groundwater defined in [94] (Table 5), with a concentration of HA varying from 10^{-5} g/L to 10 g/L ($W_{HA} = 5.4 \times 10^{-3}$ eq/g) and a total Th concentration of 10^{-10} M. Only the complexation data of [42, 43] were used to take into account for Th(IV) carbonate complexation.

Fig. 9 shows the percent Th(IV) present as humate complexes obtained at pH 7.2 using $\log \frac{HA}{GL}\beta(Th^{4+}) = 19.4$ and at pH 7.9 with $\log \frac{HA}{GL}\beta(Th^{4+}) = 21.3$, with or without considering the complexation of Th(IV) by carbonate ions (Fig. 9a and 9b respectively). The percent Th(IV) fixed to humic acids calculated using $\log \frac{HA}{BM}\beta$ (Fig. 8), and $\log \frac{HA}{GL}\beta$, neglecting carbonate complexation (Fig. 9a), are the same since

Table 5. Composition of the argillaceous water considered in Reiller *et al.* [94].

T ($^{\circ}C$)	16.9
E (mV)	-155
Total inorganic carbon (M)	4.75×10^{-3}
Na (M)	6.15×10^{-2}
K (M)	7.20×10^{-4}
Ca (M)	4.70×10^{-3}
Mg (M)	7.70×10^{-3}
Fe (M)	4.00×10^{-7}
Al (M)	5.00×10^{-8}
Silicate (M)	1.80×10^{-4}
Cl (M)	4.28×10^{-2}
Total Sulphur (M)	9.50×10^{-3}

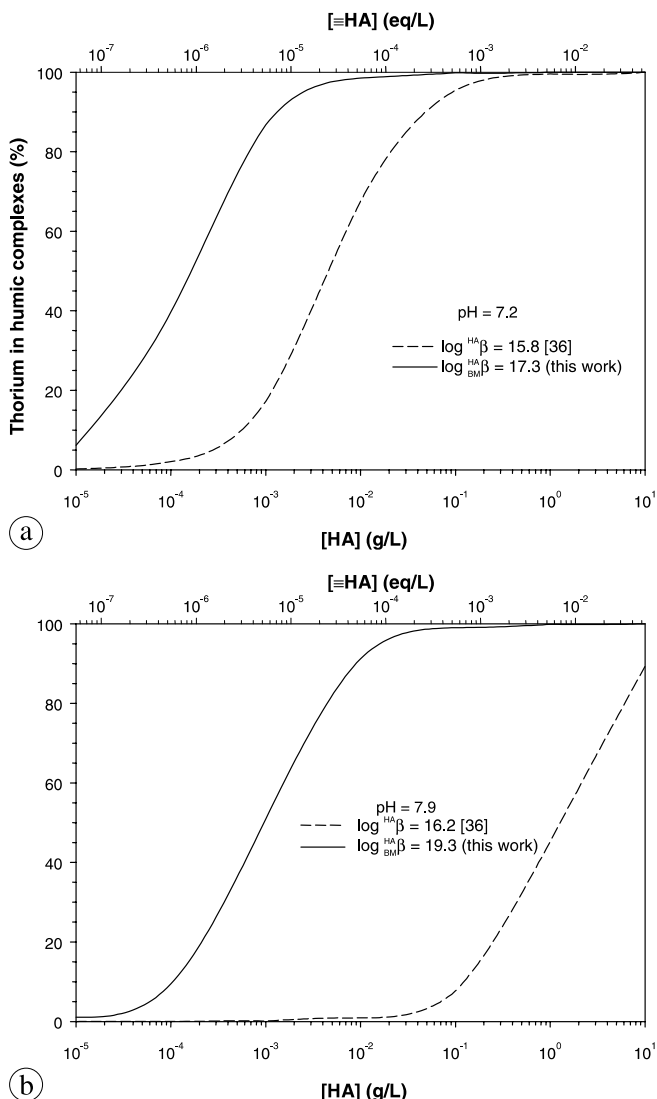


Fig. 8. Percent thorium in humic complexes as a function of HA concentration at fixed pH, values are referring to [39]: (a) pH = 7.2, (b) pH = 7.9; plain line this work, dashed lines [36].

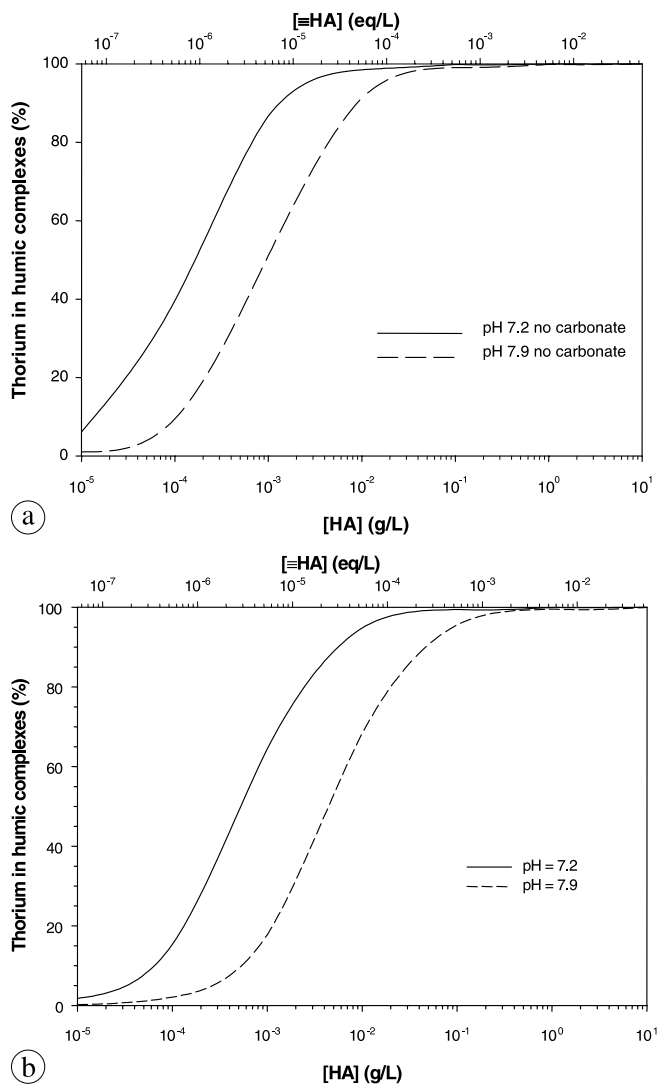


Fig. 9. Percent thorium in HA complexes as a function of HA concentration, $[Th] = 10^{-10}$ M at pH 7.2 and 7.9, in clayey water (defined in Reiller *et al.* [94]), $\log_{GL}^{HA}\beta$ values (referring to [42, 43] constant set): (a) no competition with carbonate ions; (b) competition with carbonate ions.

inner coherent data base are used. Using our results in Fig. 9 obtained with our determined global interaction constants, humic complexation of thorium is more important than estimated from other data.

When the complexation of Th(IV) by carbonate ions is taken into account (Fig. 9b) in the clayey water, the association of Th(IV) with HA remains significant. Th(IV) humic complexes are predominant when C_{HA} is above 5×10^{-4} g/L at pH = 7.2 and 5×10^{-3} g/L at pH = 7.9. For $C_{HA} = 0.1$ g/L, Th(IV) is quantitatively fixed to HA at pH = 7.2, and the percent Th bound to humic complexes is greater than 95% at pH = 7.9.

Validation on independent data

As a validation, calculations could be performed using PHREEQC [101] on independent data, with the composition of two Gorleben groundwaters (Germany, Gohy-573 and Gohy-2227 given in [64, 92, 93, 102]) and with the Mont-Terri Opalinus clay extracts (Switzerland, [103]). In the case

of Gorleben groundwater, significant amount of Th(IV) is bound to HS. A weak influence of organic matter was evidenced in the case of Opalinus clay extracts.

In the case of Gorleben, C_{HA} , in grams of carbon per liter, and pH are given in [93, 102] (0.096 g C/L, 56 wt. % of carbon, pH = 7.9 for Gohy-573; 0.080 g C/L, 56.6 wt. % of carbon, pH = 7.8 for Gohy-2227), and W_{HA} are available in [93, 104] (4.91×10^{-3} eq/g for Gohy-2227; 5.38×10^{-3} eq/g for Gohy-573). The global interaction constant used is $\log_{GL}^{HA}\beta(Th^{4+}) = 21.3$ from our present study. The constants recommended by [67] are used for carbonate and silicate systems, and WATEQ4F data base for other auxiliary data (complexation of other metals). The thorium concentration in these groundwater was $1.6 \mu\text{g/L}$ in Gohy-2227 ([93] Table 1) and $3.7 \mu\text{g/L}$ in Gohy-573 ([92] Table 2). The concentration of humic sites is thus calculated as:

$$[\equiv HA] = W_{HA} \times \frac{C_{HA}(\text{mg C/L})}{\text{wt. \% carbon}}$$

Under these assumptions, $1.56 \mu\text{g Th/L}$ is found to be bound to HA (Fig. 10) in the case of Gohy-2227 groundwater, which is in agreement with the experimental value ($1.51 \mu\text{g/L}$; Table 1 in [93]). In the case of Gohy-573 groundwater, $3.2 \mu\text{g/L}$ of thorium is complexed by HA, which is also in agreement with experimental data ($3.5 \mu\text{g/L}$; Table 2 in [92]).

In the case of the Opalinus clay, Glaus *et al.* [103] studied the influence of water extracted organic matter on the sorption of Th(IV) onto an ion exchange resin. The obtained K_d values evidenced a weak influence of organic matter on the sorption of Th(IV). For their experiments, six extracts were used: 3 extracts from Mont-Terri security gallery (MT) and 3 extracts from Benken borehole (BE), with the ionic compositions available in Table 3 in [103]. For these six extracts, the maximum possible fractions of HA were estimated to be 5% of the total organic carbon ($5.5\text{--}12 \times 10^{-3}$ g C/L) from the UV-Visible spectra. This allows us to estimate the humic site concentrations as:

$$[\equiv HA] \approx 0.05 \times [HA](\text{g C/L}) \times 5.4 \times 10^{-3} (\text{eq/g}).$$

As the pH of these extracts were in the range 8.2–8.4, the $\log_{GL}^{HA}\beta(Th^{4+})$ value of 23 was used to calculate the speciation.

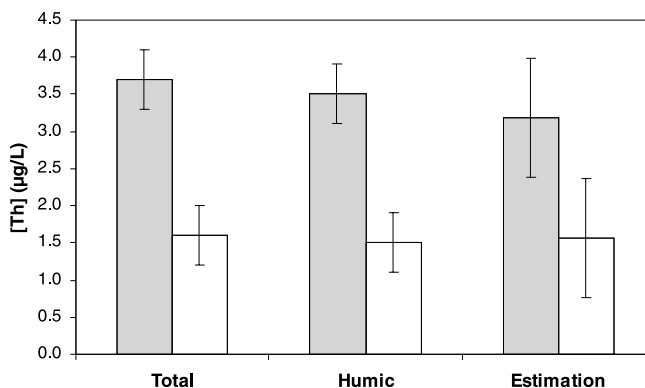


Fig. 10. Experimental [92 Table 1, 93 Table 2] and calculated distribution of Th(IV) bound to HA in Gohy-573 (shaded columns) and Gohy-2227 (empty columns) groundwaters; using $\log_{GL}^{HA}\beta(Th^{4+}) = 21.3$.

With these assumptions, the Th(IV) percent bound to HA is always under 5% showing a weak influence of organic matter on the speciation of Th(IV). This result is in agreement with the experimental results in [103].

The results obtained using the values determined here, demonstrate that thorium is predominantly bound to HA when the concentration of humic sites [$\equiv\text{HA}$] is larger than 2×10^{-5} eq/L (corresponding roughly to 5×10^{-3} g/L) for $\text{pH} \leq 8$, and the Th(IV)-HA complexes percent is still above 10% at 2×10^{-6} eq/L (corresponding roughly to 5×10^{-4} g/L). Such concentrations may be encountered in natural waters, even in sedimentary conditions [94].

Hence the complexation of Th(IV) (considered as an analogue of tetravalent actinides) by HA, should not be neglected *a priori* in speciation calculations, in particular for applications in natural water conditions.

4. Conclusions

The technique we have used to investigate the complexation of Th(IV) by humic substances (in particular, HA) is based on the study of a ternary system involving the cation, HA and a mineral surface (silica colloids) considered as a competitor for HA.

In the case of the binary system Th(IV)-silica, the surface complexation constants obtained allowed to quantify the sorption of Th(IV) onto amorphous silica using SCM without electrostatic term and taking into account the different hydroxo complexes of thorium.

HA have an important effect upon the sorption of tetravalent actinides onto silanol surface groups of silica, even in the pH range of groundwater ($\text{pH} \geq 6$). A strong decrease of Th(IV) sorption onto silica is observed due to the formation of humate complexes in solution. Using the ternary system (silica, Th(IV), HA), a quantification of the complexation of Th(IV) by HA has been performed in a pH range relevant of natural media, allowing the determination of global interaction constants ($^{HA}\beta$) for the system Th(IV)-HA. These values are dependent of the Th hydrolysis constant data sets, and are higher than other reported values in the literature. The possible formation of mixed complexes (hydro-humate complexes) or the implication of different complexing sites may explain these high interaction constants obtained in the neutral-basic pH range. Further studies are in progress to determine more precisely the nature of the complexes formed. The proposed global interaction constants also allow representation or comparison of independent experimental data obtained by other authors.

Moreover, this study allows exploring the potentially strong influence of HA in natural systems onto the chemistry of tetravalent elements in general, and of tetravalent actinides in particular at the laboratory scale. In the case of Th(IV), cation binding is apparently important even at relatively low HA concentration (10^{-3} g/L) in the neutral to slightly alkaline pH range. This is indicative of the importance of humic complexation reactions in a large variety of natural waters.

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