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Solubility of $ThO_2 \cdot xH_2O(am)$ in carbonate solution and the formation of ternary Th(IV) hydroxide-carbonate complexes

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Summary. The solubility of X-ray amorphous Th(IV) hydroxide or hydrous oxide was determined in carbonate solution at $I = 0.5$ M ($NaHCO_3$-Na_2CO_3-NaOH-NaCl) and 22 °C. Two series of open system experiments were performed under CO_2 partial pressures of 1.0 and 0.1 bar at $-\log[H^+] = 4.5$–7.5. In three series of closed system experiments at constant total carbonate concentrations of $C_{tot} = [HCO_3^-] + [CO_3^{2-}] = 0.1$, 0.04 and 0.015 M, the H^+ concentration was varied in the range $-\log[H^+] = 8.5$–13.5. Some additional solubility data were determined in 0.25–2 M Na_2CO_3 containing 0.1 M NaOH. There was no indication for the formation of a thorium carbonate solid.

The simultaneous evaluation of the different sets of experimental data at $I = 0.5$ M shows that $Th(OH)(CO_3)_4^{5-}$ and $Th(OH)_2(CO_3)_2^{2-}$ are the most important ternary complexes. Further contributions to the Th(IV) solubility are coming from $Th(OH)_2(CO_3)(aq)$, $Th(OH)_3(CO_3)^-$ and $Th(OH)_4(CO_3)^{2-}$. Their formation constants, extrapolated to $I = 0$ with the SIT and combined with the solubility product of $\log K^\circ_{sp} = -47.8 \pm 0.3$, are calculated to be $\log \beta^\circ_{114} = 35.8 \pm 0.3$, $\log \beta^\circ_{122} = 37.0 \pm 0.4$, $\log \beta^\circ_{121} = 30.7 \pm 0.4$, $\log \beta^\circ_{131} = 38.5 \pm 0.6$ and $\log \beta^\circ_{141} = 40.6 \pm 0.5$. Pure carbonate complexes and other ternary complexes have no significant contributions to the solubility in the present studies at $I = 0.5$ M. Upper limits are derived for their formation constants. Using the SIT for ionic strength corrections, the evaluated set of equilibrium constants is also consistent with the solubility in Na_2CO_3-NaOH mixtures of higher ionic strength.

1. Introduction

Under natural conditions, the solubility of tetravalent actinides is controlled by amorphous oxyhydroxides $AnO_n(OH)_{(4-2n)} \cdot xH_2O(am)$, usually called hydroxide, $An(OH)_4(am)$, hydrous oxide, $AnO_2 \cdot xH_2O(am)$ or $AnO_2(am, hydr)$. Besides the strong tendency towards hydrolysis and colloid formation, the complexation of An(IV) with carbonate is one of the most important reactions in aqueous systems. Recent comprehensive reviews led to a consistent set of solubility and hydrolysis constants, which show systematic tendencies in the series Th(IV), U(IV), Np(IV) and Pu(IV) [1, 2]. However, there is still a lack of knowledge concerning An(IV) chemistry in carbonate solution. In the critical reviews of the OECD/Nuclear Energy Agency [2–4], equilibrium constants and thermodynamic data were only selected for the penta- and tetracarbonate complexes of U(IV), Np(IV) and Pu(IV). Contrary to the behaviour of trivalent and hexavalent actinides, where ternary hydroxide-carbonate complexes are negligible or of minor importance and solubility data in carbonate-containing solutions can be described by using exclusively pure hydroxide and pure carbonate complexes, the ternary hydroxide-carbonate complexes of the tetravalent actinides, $An(OH)_y(CO_3)_z{}^{4-y-2z} = (1yz)$, are known to become predominant aqueous An(IV) species under many natural conditions [2]. However, the complexes and speciation schemes proposed in the literature: (131) and (105) for Th(IV) [5–7], (131) and (141) for Np(IV) [9], (122) and (105) for U(IV), Np(IV), Pu(IV) [10–12], (122) and (142) for Np(IV) [13, 14] and Pu(IV) [15] were not considered as sufficiently ascertained [2]. In some cases, not only the calculated equilibrium constants but even the underlying experimental solubility data are conflicting [2].

A comprehensive investigation of the predominant complexes in the ternary system An(IV)-OH-CO_3 requires the variation of the concentrations of the ligands OH^- and CO_3^{2-} over wide ranges. To avoid experimental complications from possible redox reactions in the case of U(IV), Np(IV) or Pu(IV), the present studies are performed with redox-stable Th(IV) as surrogate for the tetravalent actinides. Uncertainties due to variations in the activity coefficient are minimized by keeping the ionic strength strictly constant at $I = 0.5$ M. This also facilitates the comparison and inclusion of $ThO_2 \cdot xH_2O(am)$ solubility data determined by Östhols *et al.* [5] at $I = 0.5$ M ($NaHCO_3$-Na_2CO_3-$NaClO_4$). Further solubility data for $ThO_2 \cdot xH_2O(am)$ have been measured by Rai *et al.* [6] in $NaHCO_3$ and Na_2CO_3-NaOH solutions (up to high carbonate concentrations) of variable ionic strength. The authors derived a thermodynamic model and ion interaction (Pitzer) parameters for the complex $Th(CO_3)_5^{6-}$ [7] which was later extended to Na_2CO_3 solutions containing 2.33 m or 4.67 m NaCl [8].

2. Experimental

2.1 Chemicals and analytical methods

$Th(NO_3)_4 \cdot 5H_2O$ (p.a.), NaCl (p.a.), $NaHCO_3$ (p.a.), Na_2CO_3 (p.a.) and HCl (Titrisol®) were purchased from Merck, carbonate-free NaOH solutions from Baker. All solutions

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were prepared with ultrapure water purified with a Milli-Q-academic (Millipore) apparatus. Thorium concentrations were determined by ICP-MS (ELAN 6100, Perkin Elmer). The background was about 0.001 ppb Th. As the 0.5 M NaCl aliquots must be diluted and acidified (2% HNO_3) for ICP-MS analysis, the detection limit for Th in the original solutions is about 10^{-10} mol/l.

Combination pH electrodes (type ROSS, Orion Co.) were calibrated against H^+ and OH^- concentrations in 0.5 M NaCl, *i.e.*, against freshly prepared standard solutions x M HCl/$(0.5-x)$ M NaCl and x M NaOH/$(0.5-x)$ M NaCl with x in the range of 0.001–0.1. Alkaline solutions were handled in an Ar glove box. Additional calibration against standard pH buffers (pH 1–11, Merck) yields the relations between the H^+ concentration and measured pH_{exp} value ($-\log[H^+] = pH_{exp} + A$, with $A = 0.00 \pm 0.02$ in 0.5 M NaCl). The experimental value of A includes the activity coefficient of the H^+ ion and a term, which results from the variation of the liquid junction potential when measuring dilute pH buffer solutions for calibration and 0.5 M NaCl test solutions [16]. In the case of strongly alkaline Na_2CO_3-NaOH-NaCl solutions ($[OH^-] > 0.01$ M), the H^+ concentration is calculated from the given NaOH concentration and the ion product of water ($\log K^\circ_w = -14.00$, $\log K'_w = -13.74$ in 0.506 m NaCl (molal scale) and -13.75 in 0.5 M NaCl (molar scale), c.f. NEA-TDB [2–4]).

The concentration $[CO_3^{\ 2-}]$ is calculated from $\log[H^+]$ and the equilibrium $CO_2(g)$ partial pressure and from $\log[H^+]$ and $C_{tot} = [HCO_3^{\ -}] + [CO_3^{\ 2-}]$ in the open and closed system experiments, respectively, by using auxiliary data and SIT coefficients of the NEA-TDB [2–4], *i.e.*, the equilibrium constants $\log K^\circ_2 = -10.33$ and $\log K^\circ_{H12} = -18.16$ at $I = 0$ and $\log K'_2 = -9.65$ and $\log K'_{H12} = -17.21$ in 0.5 M NaCl for the reactions:

$$HCO_3^{\ -} \Leftrightarrow CO_3^{\ 2-} + H^+ \qquad (K^\circ_2)$$

$$CO_2(g) + H_2O \Leftrightarrow CO_3^{\ 2-} + 2H^+ \qquad (K^\circ_{H12})$$

The experimental procedures have been confirmed by measuring consistent values of $\log K'_2 = -9.67 \pm 0.03$ and $\log K'_{H12} = -17.22 \pm 0.04$ at $I = 0.5$ M from NaCl-$NaHCO_3$-Na_2CO_3 and NaCl-$NaHCO_3$-H_2CO_3-$CO_2(g)$ buffer solutions as described in [16].

2.2 Solubility experiments

The solids used, X-ray amorphous Th(IV) hydroxide or hydrous oxide, were already prepared and characterized in a previous study [17]. A gelatinous Th(IV) precipitate was obtained by slow titration of a thorium nitrate solution with carbonate-free NaOH (Baker) under Ar atmosphere up to pH 10. This precipitate, washed with water and stored as aqueous suspension, was used in most of the solubility experiments. A part of the experiments were performed with a solid obtained by drying the gelatinous precipitate for one week in a vacuum desiccator. The dried solid, similar to that used by Östhols *et al.* [5] may be called $ThO_2 \cdot xH_2O(am)$ with a water content of $x \approx 2.4$–2.5 [5, 17]. All solubility experiments were performed in PFA and polyethylene vials (Vol. 20–50 ml) at 22 ± 2 °C. The ionic strength of the solutions was kept strictly at $I = 0.5$ M ($NaHCO_3$-Na_2CO_3-NaOH-NaCl), except of some additional samples in 0.25–2 M Na_2CO_3 solutions containing 0.1 M NaOH. Each sample contained an appropriate amount of Th(IV) solid (~ 0.003–0.01 mol per liter solution).

Two series of solubility experiments were performed under CO_2 partial pressures of 1.0 and 0.1 bar (open system). A fine-dispersed gas stream of either 100% CO_2 gas or a mixture of 10% CO_2/90% Ar, pre-equilibrated with water vapour by passing the gas stream through 0.5 M NaCl, was bubbled through Th(IV) hydroxide suspensions in 0.5 M $NaHCO_3$-NaCl ($-\log[H^+] = 4.5$–7.5). The constant H^+ and Th concentrations measured after 5–20 days indicated that solid–liquid equilibria were reached. The equilibrium between $CO_2(g)$ and dissolved carbonate species was already reached after 1 day, as observed in some samples which were pre-equilibrated before the Th(IV) solid was added.

Three series of closed system solubility experiments were performed at constant total carbonate concentrations of $C_{tot} = [HCO_3^{\ -}] + [CO_3^{\ 2-}] = 0.1$, 0.04 and 0.015 M. The H^+ concentrations of $NaHCO_3$-Na_2CO_3-NaCl and Na_2CO_3-NaOH-NaCl solutions was varied in the range $-\log[H^+] =$ 8.5–13.5. These samples were stored in sealed vials in an Ar glove box. In order to observe a possible effect coming from ageing, alteration or transformation of the solid phase or from differences in the dried solid compared to the precipitate only washed, equilibration times were extended up to 130 days.

Special care was dedicated to the separation of colloids and solid particles. In each sampling, the thorium concentration was determined after ultracentrifugation for 60 minutes at 90 000 rpm, *i.e.*, at a mean relative centrifugal force of about 5×10^5 g. This method is known to be appropriate for the removal of even small Th(IV) colloids [17]. Within the open system experiments, additional efforts were undertaken to investigate the contributions from Th(IV) eigencolloids. For this purpose, in some cases the total concentration of dissolved Th was measured in parallel from aliquots taken after sedimentation of the solid phase a) from the clear supernatant, *i.e.*, without removal of colloids, b) after ultracentrifugation and c) after filtration at different pore sizes varying from 1.2 nm (1 kD) up to 450 nm. Membrane filters of different material and filter pore size were tested. Filtron polyether sulfone membrane filters (Microsept TM 1 kD, pore size *ca.* 1.2 nm or 300 kD, pore size *ca.* 20 nm) lead to a successful separation of colloids. The Th concentration measured after successive filtration of the filtrate remained constant and the results were consistent with those obtained by ultracentrifugation. The use of polypropylene and cellulose acetate membrane filters (*e.g.*, Gelman-GHP Acrodisc (polypropylene hydrophilic, pore size 200 nm) and Millipore-Millex SLHA0.25NB (cellulose acetate, pore size 450 nm) was not successful. In particular for samples in the solubility minimum region ($[Th] < 10^{-5}$ M), the measured Th concentrations are affected by the sorption of both colloidal Th(IV) species and neutral monomers $Th(OH)_2CO_3(aq)$. Despite of the larger pore sizes, the measured Th concentrations were much lower (partly at the background level of the ICP-MS) than those measured after 1.2 nm filtration with polyether sulfone filters or after ultracentrifugation.

3. Results and discussion

3.1 Open system experiments at $p_{CO_2} = 0.1$ and 1 bar

The Th(IV) solubilities determined in the present work in 0.5 M NaCl-$NaHCO_3$ solutions equilibrated with carbon dioxide partial pressures of $p_{CO_2} = 1$ and 0.1 bar are shown in Fig. 1 together with the data determined by Östhols *et al.* [5] for X-ray amorphous $ThO_2 \cdot xH_2O(am)$ in 0.5 M $NaClO_4$-$NaHCO_3$ solutions under the same CO_2 partial pressures. Fig. 1 also includes solubility data at pH < 4.5 determined in carbonate-free 0.5 M $NaClO_4$ [5] and 0.5 M NaCl [17] with $ThO_2 \cdot xH_2O(am)$ dried at room temperature. Comparable data were obtained in our previous study [17] by combining coulometric pH-titration and laser-induced breakdown detection (LIBD) to determine the initial formation of small (colloidal) solid particles when the solubility is just exceeded. These data points represent the solubility excluding colloids. The solid curve for $p_{CO_2} = 0$ is calculated with the corresponding solubility product of $Th(OH)_4(am)$, $\log K'_{sp} = -44.5 \pm 0.3$ in 0.5 M NaCl, and known hydrolysis constants for $Th(OH)_n{}^{4-n}$ $n = 1$–4 (mainly from Ekberg *et al.* [18], c.f. discussion in [17]). The contributions from oligomers $Th_x(OH)_y{}^{4x-y}$ with $(x, y) = (2, 2)$, (4,8), (4,12), (6,15) are negligible at the thorium and H^+ concentration along this solubility curve [17].

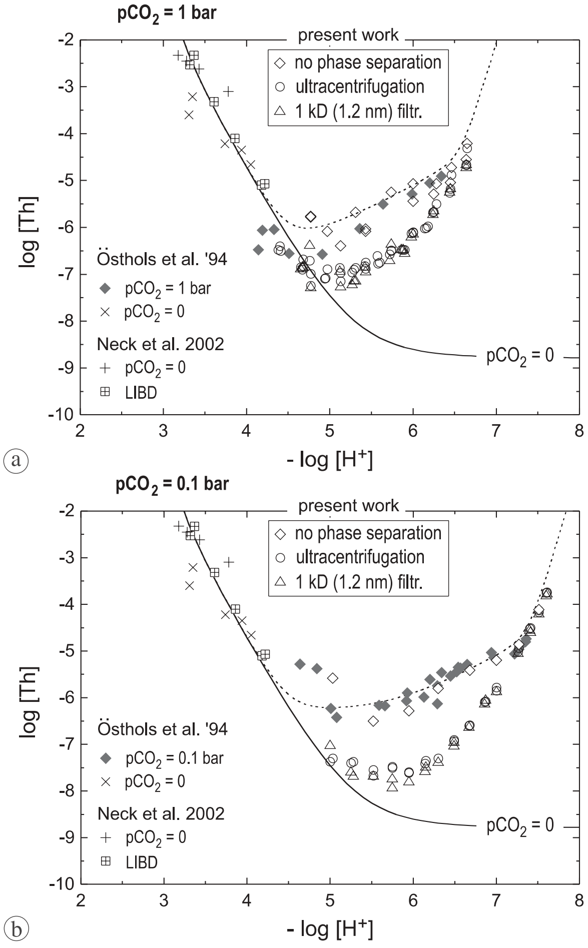

Fig. 1. Solubility of amorphous Th(IV) oxyhydroxide at $I = 0.5$ M in equilibrium with carbon dioxide partial pressures of (**a**) $p_{CO_2} = 1$ bar and (**b**) $p_{CO_2} = 0.1$ bar. Present results in comparison with experimental data and model calculations (- - - -) from Östhols *et al.* [5].

The solubility increasing effect of carbonate becomes evident at pH > 4.5. As expected, it is more pronounced at $p_{CO_2} = 1$ bar (Fig. 1a) than at $p_{CO_2} = 0.1$ bar (Fig. 1b). However, there are significant deviations between the results determined in the present study after ultracentrifugation or 1 kD ultrafiltration and those of Östhols *et al.* [5] who reported phase separation by 300 nm filtration. The dashed lines refer to the speciation model proposed by Östhols *et al.* [5], who ascribed the increased solubility at pH > 4.5 to the formation of $Th(OH)_3(CO_3)^-$ ($\log K'_{s,131} = -7.64 \pm 0.19$ [5]). The steep increase at higher pH comes from to the formation constant of $Th(CO_3)_5{}^{6-}$ ($\log K'_{s,105} = -12.9 \pm 0.3$ [5]), which was calculated from their closed system data at $I = 0.5$ M (Na_2CO_3-$NaHCO_3$-$NaClO_4$) and $C_{tot} = 0.1$ M.

The origin of the discrepancies between the data of Östhols *et al.* [5] and the present results becomes evident when the thorium concentrations measured after ultracentrifugation or 1 kD ultrafiltration are compared with those measured without removal of colloids, *i.e.*, in aliquots taken from the clear supernatant after sedimentation of the solid phase. In carbonate solutions where the solubility is relatively high ([Th] > 10^{-5} M), Th(IV) is dissolved predominantly as anionic hydroxide-carbonate complexes, which are neither kept back nor sorbed onto filters or removed by ultracentrifugation. The Th concentrations measured without phase separation, after ultracentrifugation or filtration with different filter materials and pore sizes were practically the same. Contrary to this, large differences are observed for samples in the solubility minimum region ([Th] < 10^{-5} M). The total Th concentrations measured without removal of colloids (open rhombs in Fig. 1) are significantly higher than those measured after 1.2 nm filtration (triangles) or ultracentrifugation (circles). Fig. 1 also shows that the data determined in the present study without removal of colloids (open rhombs) are comparable with those measured by Östhols *et al.* [5] after 300 nm filtration (filled rhombs). These significantly higher solubilities are obviously caused by colloidal species in the range of 1.2–300 nm, not by the complex $Th(OH)_3(CO_3)^-$ as supposed in [5]. It is further to note that in these carbonate-containing solutions, the colloidal Th concentration reaches values of $[Th]_{coll}$ up to 10^{-5} M, which significantly exceeds the values of $\log [Th]_{coll} = -6.3 \pm 0.5$ observed in carbonate-free solutions at comparable ionic strength and pH values [17, 19]. This may be an indication for the additional formation of ternary or carbonate bridged Th(IV) eigencolloids.

3.2 Closed system experiments at $C_{tot} = 0.1$, 0.04 and 0.015 M

The Th(IV) solubilities determined in Na_2CO_3-$NaHCO_3$-NaCl (pH 8.5–11) and Na_2CO_3-NaOH-NaCl (pH 11–13.5) solutions in the three series of closed system experiments at $C_{tot} = 0.1$, 0.04 and 0.015 M are shown in Fig. 2 together with comparable data determined by Östhols *et al.* [5] at $I = 0.5$ M, $C_{tot} = 0.1$ M and pH 8.2–10.5 in Na_2CO_3-$NaHCO_3$-$NaClO_4$ solutions. In order to illustrate the effect of carbonate, the solubilities measured in neutral and alkaline carbonate-free solutions after ultrafiltration or ultracentrifugation ($\log [Th(IV)] = -8.5 \pm 0.6$ [1, 17]) are shown for comparison as hatched area.

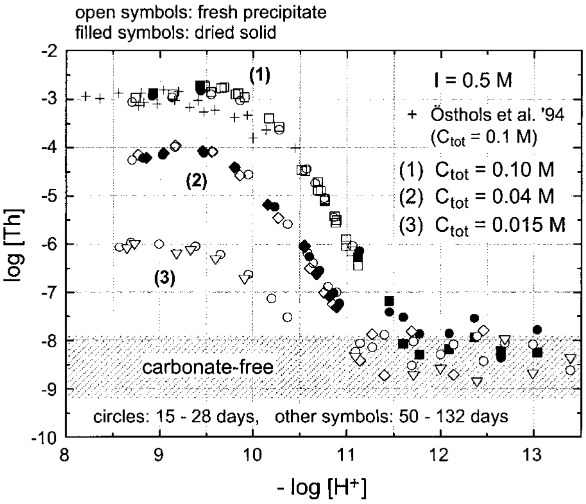

Fig. 2. Solubility of amorphous Th(IV) oxyhydroxide, either fresh precipitate only washed with water (open points) or dried $ThO_2 \cdot xH_2O(am)$ (filled points) at $I = 0.5\,M$ (Na_2CO_3-$NaHCO_3$-NaCl and Na_2CO_3-NaOH-NaCl) and $C_{tot} = [HCO_3^-] + [CO_3^{2-}] = 0.1$, 0.04 and 0.015 M (all data measured after ultracentrifugation). Experimental data for dried $ThO_2 \cdot xH_2O(am)$ from Östhols *et al.* [5] at $C_{tot} = 0.1\,M$ in 0.5 M Na_2CO_3-$NaHCO_3$-$NaClO_4$ (crosses) are included for comparison.

Increasing the total carbonate concentration from 0 to 0.1 M, the solubilities at pH 8–10 are raised up to 5 orders of magnitude. The values measured after 15–28 days (circles in Fig. 2) are not markedly different compared to those after 50–132 days (other symbols) which shows a) that equilibrium state was reached and b) that there was no solid transformation. The solubilities measured at $pH > 11$ are very close to those in carbonate-free solutions. The mean values ($\log [Th(IV)] = -8.0 \pm 0.3$ at $C_{tot} = 0.1\,M$, -8.2 ± 0.3 at $C_{tot} = 0.04\,M$, -8.35 ± 0.4 at $C_{tot} = 0.015\,M$) indicate a slight increase compared to $\log [Th(IV)] = -8.5 \pm 0.6$ at $C_{tot} = 0$.

In our previous study of Th(IV) hydroxide solubilities in carbonate-free solution [17], it was pointed out that fresh precipitates of "$Th(OH)_4(am)$" only washed with water lead to considerably higher solubility data at pH 3–5 than the X-ray amorphous solids dried at room temperature used in that study [17] and by Östhols *et al.* [5]. This might be due to an effect of differences in particle size. However, since the latter solubility data were consistent with the onset of colloid formation determined by LIBD, and since the presence of colloids could be demonstrated by EXAFS, it was concluded that the difference is caused by the dissolution of large amounts of colloidal particles already included in the gelatinous precipitates. In the closed system solubility studies at $C_{tot} = 0.1$ and 0.04 M and pH 8.5–11, the use of either a gelatinous precipitate only washed with water (open points in Fig. 2) or dried $ThO_2 \cdot xH_2O(am)$ (filled points), did not lead to noticeably different results. The thorium concentration coming from carbonate complexes is rather high and it may be assumed that small $Th(OH)_4(am)$ particles or colloids coming from the solid phase will be dissolved at first during the equilibration process. The final solid phase must have properties (crystallite size, molar standard Gibbs energy) comparable to the dried $ThO_2 \cdot xH_2O(am)$.

The formation of a thorium carbonate solid or a solubility limiting carbonate-containing surface layer can also be ruled out. The steep decrease of the solubility curve at pH 10.5–11.5 where $[CO_3^{2-}] = C_{tot} = \text{const.}$ (slope -3) cannot be explained with solubility control by $Th(CO_3)_2(s)$ or $Th(OH)_2CO_3(s)$. Assuming for instance that the solubility is given by

$$Th(OH)_2CO_3(s) + (z-1)CO_3^{2-} \Leftrightarrow$$
$$Th(OH)_y(CO_3)_z^{4-y-2z} + (2-y)OH^- ,$$

the slope of the plot log [Th] *vs.* pH would be $(y-2)$, *i.e.* the observed slope of -3 would correspond to $y = -1$, which does not make sense.

3.3 Evaluation of equilibrium constants

The equilibrium constants for the dissolution of $Th(OH)_4$ (or $ThO_2 \cdot xH_2O(am)$ with $x \approx 2$) and the formation of the complexes $(xyz) = Th_x(OH)_y(CO_3)_z^{4x-y-2z}$:

$$Th(OH)_4(s) \Leftrightarrow Th^{4+} + 4OH^-$$

and

$$xTh^{4+} + yOH^- + zCO_3^{2-} \Leftrightarrow Th_x(OH)_y(CO_3)_z^{4x-y-2z}$$

i.e., the conditional solubility product K'_{sp} and formation constants β'_{xyz} and the values at infinite dilution, K°_{sp} and β°_{xyz}, are defined by:

$$K'_{sp} = [Th^{4+}][OH^-]^4 = K^\circ_{sp}/(\gamma_{Th^{4+}})(\gamma_{OH^-})^4 , \quad (1)$$

and

$$\beta'_{xyz} = [Th_x(OH)_y(CO_3)_z^{4x-y-2z}]/[Th^{4+}]^x[OH^-]^y[CO_3^{2-}]^z$$
$$= \beta^\circ_{xyz}(\gamma_{Th^{4+}})^x(\gamma_{OH^-})^y(\gamma_{CO_3^{2-}})^z/\gamma_{(xyz)} \quad (2)$$

respectively, where [i] denotes the concentration of species i and γ_i its activity coefficient. The specific ion interaction theory (SIT) [3, 20] is used for the calculation of activity coefficients according to:

$$\log \gamma_i = -z_i^2 D + \sum \varepsilon_{ij} m_j , \quad (3)$$

where z_i is the charge of ion i, ε_{ij} is the interaction parameter for ion i and an oppositely charged ion j and m_j (mol/kg H_2O) is the molal concentration of ion j, D is the Debye–Hückel term at 25 °C: $D = 0.509\sqrt{I}/(1 + Bå\sqrt{I})$, with $Bå = 1.5$ and I (mol/kg H_2O) is the molal ionic strength. The interaction coefficients for H^+, OH^-, HCO_3^- and CO_3^{2-} are taken from the NEA-TDB [2, 4] and those for Th(IV) hydroxide complexes from [1, 17]. The unknown ion interaction coefficients $\varepsilon(Na^+, Th(OH)_y(CO_3)_z^{4-y-2z})$ used in the present study (0.1, 0.05, 0, −0.05, −0.1, −0.15, −0.2, −0.25 and −0.3 for Th(IV) complexes of charge 2, 1, 0, −1, −2, −3, −4, −5 and −6, respectively) are estimated according to known values for actinide complexes of analogous charge and similar size (c.f. ε_{ij} values given in the NEA-TDB reviews [2–4]). Uncertainties of the estimated SIT coefficients should not exceed ±0.3 and have thus no significant effect on the calculated activity coefficients at $I = 0.5$ mol/kg H_2O.

Under the conditions of the present study, the solubility of $Th(OH)_4(am)$ in carbonate free-solution [17] is increased by the formation of mononuclear complexes $Th(OH)_y(CO_3)_z^{4-y-2z}$ and colloidal Th(IV) species:

$$[\mathrm{Th}]_{\mathrm{tot}} = \sum x[\mathrm{Th}_x(\mathrm{OH})_y{}^{4x-y}] + \sum[\mathrm{Th}(\mathrm{OH})_y(\mathrm{CO}_3)_z{}^{4-y-2z}] + [\mathrm{Th(IV)}]_{\mathrm{coll}} . \quad (4)$$

The contributions from colloids are excluded by using only the data determined after ultracentrifugation or 1 kD ultrafiltration for the evaluation of equilibrium constants. As only the sums $\log K_{s,1yz} = (\log K_{sp} + \log \beta_{1yz})$ for the reactions

$$\mathrm{Th(OH)_4(am)} + z\mathrm{CO_3}^{2-} \Leftrightarrow \mathrm{Th(OH)}_y(\mathrm{CO_3})_z{}^{4-y-2z} + (4-y)\mathrm{OH}^-$$

can be determined from the solubility data, the evaluation of the formation constants β_{1yz} requires the knowledge of the solubility product of the solubility limiting solid phase.

3.3.1 Solubility limiting solid phase

In our previous review of the solubility and hydrolysis of Th(IV) [1], the available literature data in carbonate-free solution yielded a mean value of $\log K^\circ_{sp} = -47.0 \pm 0.8$ for the solubility product of amorphous Th(IV) oxide/hydroxide, while the value for dried $ThO_2 \cdot xH_2O(am)$ [5, 17], consistent with the onset of colloid formation determined by titration-LIBD method, was at the lower limit (-47.8 ± 0.3) [17]. The solubilities at pH > 4.5 at $p_{CO_2} = 1$ and 0.1 bar follow the solubility curve for $p_{CO_2} = 0$ calculated with this solubility product (Fig. 1). Moreover, the solubility was independent of the initial solid used, either gelatinous precipitates of $Th(OH)_4(am)$ or dried $ThO_2 \cdot xH_2O(am)$ (Fig. 2). Probably smaller solid or colloidal particles included in gelatinous precipitates will be dissolved at first during the equilibration process, so that the solubility is finally the same as that of the dried precipitate. The solubility product of $\log K^\circ_{sp} = -47.8 \pm 0.3$ ($\log K'_{sp} = -44.5 \pm 0.3$ in 0.5 M NaCl) [17] is therefore considered to be the correct value for the solubility data in carbonate solution.

3.3.2 Aqueous complexes $\mathbf{Th(OH)_y(CO_3)_z{}^{4-y-2z} = (1yz)}$

As the coordination number of the Th^{4+} ion is relatively high, *e.g.*, CN = 10 in the case of the known complex $Th(CO_3)_5{}^{6-}$, many different ternary complexes are theoretically possible. Therefore, it seems to be difficult to identify unequivocally the complexes formed in the present solubility experiments. However, it will be shown below, that although the concentrations of $CO_3{}^{2-}$ and OH^- were varied in wide ranges in the five sets of experimental data at $I = 0.5$ M, only a few complexes are predominant or give at least significant contributions to the solubility. As about 20 binary and ternary complexes are possible, an overall fit does not appear promising. Therefore, the solubility data at $I = 0.5$ M were evaluated in two steps.

In a first step, an upper limit was calculated for each complex ($1yz$) by increasing $\log K'_{s,1yz}$ until the calculated species concentration line exceeds one of the five sets of experimental data at any pH value (c.f., Appendix). In the case of the high solubility data at $C_{tot} = 0.1$ M, one has to take into account that the formation of $Th(OH)_y(CO_3)_z{}^{4-y-2z}$ has a slight effect on the free carbonate concentration ($[CO_3{}^{2-}] = C_{tot} - [HCO_3{}^-] - z[Th(OH)_y(CO_3)_z{}^{4-y-2z}]$). The calculated upper limit concentration lines show that the broad solubility maxima at pH 8–10 in the closed system experiments, followed by a steep solubility decrease are well described by the complex $Th(OH)(CO_3)_4{}^{5-}$ with $\log K'_{s,114} = 34.5 \pm 0.3$. Neither the limiting carbonate complex $Th(CO_3)_5{}^{6-}$ nor the complex $Th(OH)_2(CO_3)_4{}^{6-}$ (where one $CO_3{}^{2-}$ is replaced by two OH^- ligands) or any other complex or combination of other complexes can reproduce these data (c.f., Appendix, Fig. A1). The corresponding speciation lines for the complex (114) in the open system experiments fall together with the experimental solubilities at the highest pH values at $p_{CO_2} = 1$ and 0.1 bar. In the minima of the solubility curves at $p_{CO_2} = 1.0$ and 0.1 bar, further complexes are present. The upper limit calculations (c.f., Appendix, Fig. A2) show that the complex $Th(OH)_2(CO_3)_2{}^{2-}$ is necessary to describe the results in the open system experiments. They also show that the complexes (122) and others like (131) and (121), which may also be formed under these conditions, have no effect in the closed system experiments. The corresponding upper limits of $\log K'_{s,1yz}$ lead to species concentration lines which are orders of magnitude below the experimental data at

Table 1. Equilibrium constants and upper limits for the formation of Th(IV) complexes $Th(OH)_y(CO_3)_z{}^{4-y-2z} = (1yz)$ at $I = 0.5$ M and $I = 0$ (25 °C).

Complex	$\log K'_{s,1yz}$ ($I = 0.5$ M)	$\log K^\circ_{s,1yz}$	$\log \beta^\circ_{1yz}$ [a]
Hydroxide complexes			
(110)	-34.0 ± 0.4 [b]		11.8 ± 0.2 [b]
(120)	-25.4 ± 0.4 [b]		21.4 ± 0.2 [b]
(130)	-16.9 ± 1.0 [b]		30.6 ± 1.0 [b]
(140)	-8.8 ± 0.6 [b]		39.0 ± 0.5 [b]
Carbonate complexes			
(101)	< -35.3	< -35.8	< 12.0
(102)	< -27.7	< -26.8	< 21.0
(103)	< -21.5	< -20.6	< 27.2
(104)	< -17.1	< -17.6	< 30.2
(105)	< -13.2	< -16.6	< 31.2
	-12.9 ± 0.3 [c]	-16.4 ± 0.3 [c]	31.4 ± 0.5
		-18.4 [d]	29.4
Ternary hydroxide-carbonate complexes			
(111)	< -26.3	< -26.2	< 21.6
(112)	< -19.2	< -18.4	< 29.4
(113)	< -14.1	< -14.0	< 33.8
(114)	-10.0 ± 0.1	-12.0 ± 0.2	35.8 ± 0.3
(121)	-17.5 ± 0.2	-17.1 ± 0.3	30.7 ± 0.4
(122)	-11.2 ± 0.1	-10.8 ± 0.2	37.0 ± 0.4
(123)	< -8.9	< -9.9	< 37.9
(124)	< -7.8	< -11.6	< 36.2
		≤ -13.3 [e]	≤ 34.5
(131)	-9.7 ± 0.5	-9.3 ± 0.5	38.5 ± 0.6
(132)	< -7.7	< -8.0	< 39.8
		< -8.4 [e]	< 39.4
(133)	< -6.8	< -9.2	< 38.6
		< -10.9 [e]	< 36.9
(141)	-7.2 ± 0.3	-7.2 ± 0.3	40.6 ± 0.5
(142)	< -6.0	< -7.4	< 40.4
		< -9.1 [e]	< 38.7

a: The formation constants $\log \beta^\circ_{1yz}$ are related to $\log K'_{sp} = -44.5 \pm 0.3$ in 0.5 M NaCl and $\log K^\circ_{sp} = -47.8 \pm 0.3$ [17]. Uncertainties are given as 2σ;

b: Hydrolysis constants are taken from [17, 18];

c: Östhols *et al.*'94 [5];

d: Felmy *et al.*'97 [7];

e: Calculated in Sect. 3.4 from solubility data in 1 M Na_2CO_3-NaOH solutions.

$C_{tot} = 0.1$, 0.04 and 0.015 M (except of a minor contribution of (122) to the solubility at $C_{tot} = 0.015$ M).

In a second step, a least square fit program was used considering simultaneously all experimental data at $I = 0.5$ M. An approximation including only the complexes (114) and (122) was extended step by step by adding successively other possible complexes (1*yz*) and repeating the optimization procedure. This kind of sensitivity analysis clearly shows, whether the addition of a complex improves the fit and whether a significant value is obtained for its formation constant, *i.e.*, whether a complex has a significant contribution to the thorium concentration in at least one of the different series of solubility experiments. In addition to the most important complexes $Th(OH)(CO_3)_4{}^{5-}$ and $Th(OH)_2(CO_3)_2{}^{2-}$, there is evidence for significant contributions of $Th(OH)_2(CO_3)(aq)$ and $Th(OH)_3(CO_3)^-$ in the solubility minimum region of the open system experiments at $p_{CO_2} = 1$ and 0.1 bar. The slight solubility increase at pH > 11 when C_{tot} is increased from 0 to 0.1 M in the closed system experiments, is found to be caused by the formation of $Th(OH)_4(CO_3)^{2-}$. The sensitivity analysis gave no significant values for the pure carbonate complexes (10*z*) and the ternary complexes (111), (112), (113), (123), (124), (132), (133) and (142). Only upper limits could be derived for their formation constants.

The evaluated equilibrium constants und upper limits at $I = 0.5$ M (NaCl) are summarized in Table 1, together with the equilibrium constants at $I = 0$ calculated with the SIT. The formation constants $\log \beta'_{1yz}$ and $\log \beta^\circ_{1yz}$ are related to the solubility product of $\log K'_{sp} = -44.5 \pm 0.3$ in 0.5 M NaCl and $\log K^\circ_{sp} = -47.8 \pm 0.3$ [17]. The solubility curves calculated with the equilibrium constants for the complexes (114), (122), (121), (131) and (141) are shown in Fig. 3a and b. The set of equilibrium constants in Table 1 allows a reliable prediction of the solubility and speciation of Th(IV) under most conditions (pH and carbonate concentration) relevant for natural aquatic systems.

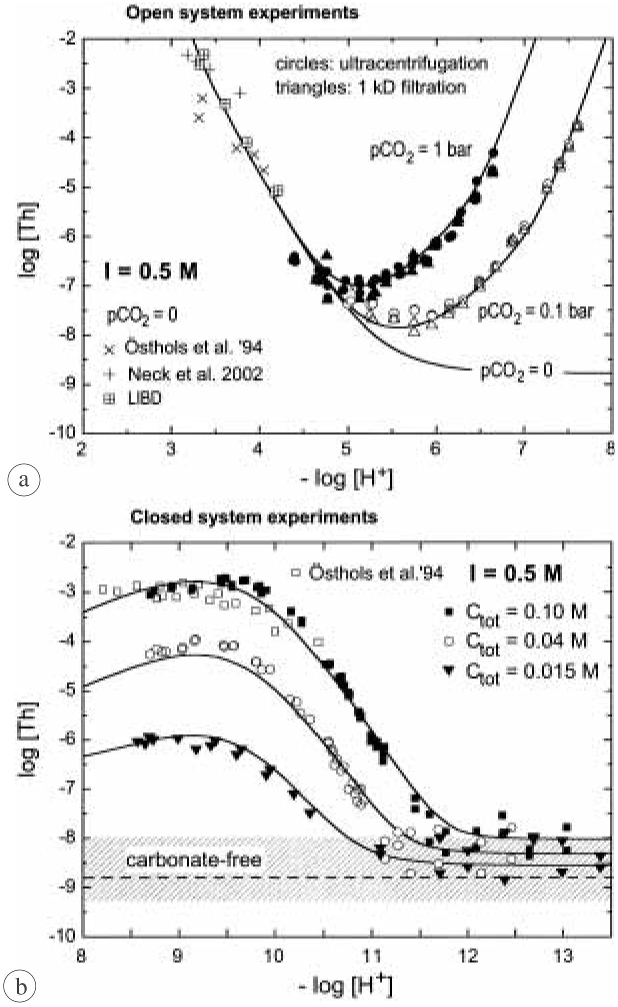

Fig. 3. Solubility of amorphous Th(IV) oxyhydroxide, (**a**) open system experiments at $p_{CO_2} = 1.0$ and 0.1 bar, (**b**) closed system experiments at $C_{tot} = 0.1$, 0.04 and 0.015 M. Solid lines are calculated with the equilibrium constants in Table 1.

3.3.3 Limiting carbonate complex $Th(CO_3)_5{}^{6-}$

The pentacarbonate complex $Th(CO_3)_5{}^{6-}$ is known to be formed at high bicarbonate and carbonate concentrations and characterized by EXAFS (extended X-ray fine structure spectroscopy) [7]. In the present studies at $I = 0.5$ M and $C_{tot} \leq 0.1$ M, the formation of $Th(CO_3)_5{}^{6-}$ is not significant. The upper limit of $\log K^\circ_{s,105} < -16.6$, which is close to the value calculated by Östhols *et al.* [5] from comparable data, is considerably too large. If the proposed equilibrium constant of $\log K^\circ_{s,105} = -16.4 \pm 0.3$ [5] is combined with the upper limit of $\log K^\circ_{s,104} < -17.6$ for the tetracarbonate complex, the stepwise constant for the reaction $Th(CO_3)_4{}^{4-} + CO_3{}^{2-} \Leftrightarrow Th(CO_3)_5{}^{6-}$ becomes $\log K^\circ_5 > 1.2$, which is about 2 log-units higher than the analogous values selected in the NEA-TDB for other tetravalent actinides ($\log K^\circ_5 = -1.1 \pm 0.2$ for U(IV) [3], -1.1 ± 0.3 for Np(IV) [4], -1.4 ± 0.1 for Pu(IV) [4]). According to known systematics in actinide carbonate complexation [22] the value of $\log K^\circ_5$ for Th(IV) is expected to be similar or somewhat lower than for U(IV).

Felmy *et al.* [7] applied the ion interaction approach of Pitzer [21] to solubility data for $ThO_2 \cdot xH_2O(am)$ in 1–2 M Na_2CO_3-NaOH solutions [6] and calculated a value of $\log K^\circ_{s,105} = -18.4$, which is two orders of magnitude lower than the value of Östhols *et al.* [5]. The proposed model is based on quite reasonable binary Pitzer parameters for Na^+-$Th(CO_3)_5{}^{6-}$ ($\beta^{(0)} = 1.31$, $\beta^{(1)} = 30$) [7], but solubility data in Na_2CO_3 solutions containing 2.33 m or 4.67 m NaCl (for which no experimental details and pH values are given) required the addition of large mixing parameters, $\theta(Th(CO_3)_5{}^{6-}$-$Cl^-) = 1.8$ and $\Psi(Th(CO_3)_5{}^{6-}$-Cl^--$Na^+) = 0.3$ [8]. An even larger value of $\theta(Th(CO_3)_5{}^{6-}$-$ClO_4{}^-) = 5.5$ was used in [7] to reproduce the solubility data of Östhols *et al.* [5] at $C_{tot} = 0.1$ M in 0.5 M Na_2CO_3-$NaHCO_3$-$NaClO_4$. However, as shown above, the predominant complex in these solutions is $Th(OH)(CO_3)_4{}^{5-}$, not $Th(CO_3)_5{}^{6-}$.

In similar studies Rai *et al.* measured the solubility of $UO_2 \cdot xH_2O(am)$ [10], $NpO_2 \cdot xH_2O(am)$ [11] and $PuO_2 \cdot xH_2O(am)$ [12] in concentrated carbonate solutions. Based on analogous thermodynamic models they determined $\log K^\circ_{s,105}$ values of −22.2, −21.15 and −22.7 for the pentacarbonate complexes of U(IV), Np(IV) and Pu(IV), respectively. On the other hand, in the recent NEA-TDB review [2] the predominance of the limiting carbonate complex $An(CO_3)_5{}^{6-}$ at high $CO_3{}^{2-}$ concentrations and pH > 12 has been questioned. The predominance of $An(CO_3)_5{}^{6-}$ would yield a slope of -4 ($\log[An(IV)]$ *vs.* $\log[OH^-]$), while the solubilities of $UO_2 \cdot xH_2O$(am) in alkaline 3 m K_2CO_3 [6, 10] and of $NpO_2 \cdot xH_2O$(am) in alkaline 1.78 m K_2CO_3 [11] decrease with a slope of about -2 at OH^- concentrations in the range of 0.01 to 0.1 M, *i.e.*, at approximately constant ionic strength. The same holds for the solubility of $ThO_2 \cdot xH_2O$(am) in alkaline 1 M Na_2CO_3 solutions (c.f., Fig. 5 in [6]). The stoichiometry of the thorium complexes formed under these conditions is discussed in the following section, where experimental solubility data of $ThO_2 \cdot xH_2O$(am) in Na_2CO_3-NaOH solutions are compared with calculations based on the formation constants and upper limits derived from the solubility experiments at $I = 0.5$ M (Table 1).

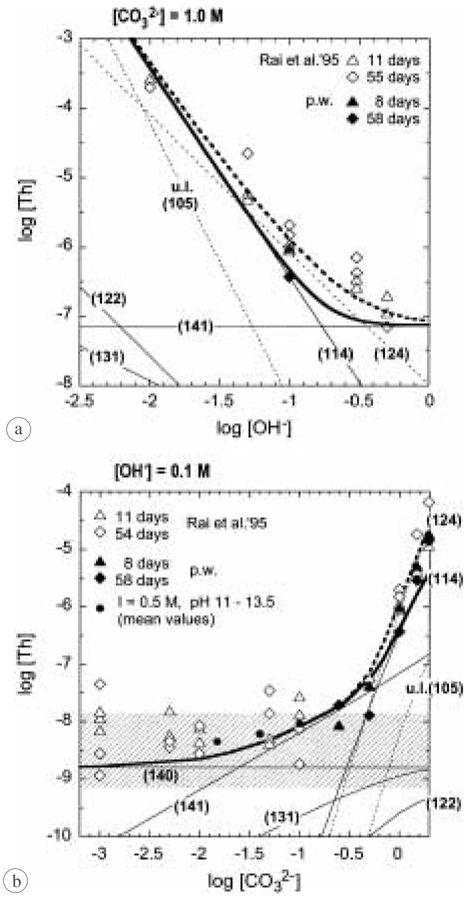

Fig. 4. Solubility of amorphous Th(IV) oxyhydroxide in Na_2CO_3-NaOH solutions (data from present work and Rai *et al.* [6, 7]), (**a**) in 1.0 M Na_2CO_3/0.01–0.5 M NaOH, (**b**) in 0.001–2.0 M Na_2CO_3/0.1 m NaOH. The species concentration lines are calculated with the equilibrium constants and upper limits (u.l., dotted lines) from Table 1, extrapolated to the corresponding ionic strength with the SIT. The fat lines represent the calculated total Th concentration (solid line: without (124), dashed line: including (124)).

3.4 Solubility of $ThO_2 \cdot xH_2O$(am) at high $CO_3{}^{2-}$ concentrations and $[OH^-] \geq 0.01$ M

The solubility of $ThO_2 \cdot xH_2O$(am) in Na_2CO_3-NaOH mixtures is shown in Fig. 4. The present experimental results are in reasonable agreement with those of Rai *et al.* [6, 7]. Species concentration lines for the complexes (114), (122), (131) and (141) are based on the equilibrium constants given in Table 1 and activity coefficients calculated with the SIT according to Eq. (3). In the case of 1 M Na_2CO_3 solutions containing 0.01–0.5 M NaOH, the estimated uncertainties of ± 0.3 for the interaction coefficients $\varepsilon(Na^+, (1yz))$ correspond to uncertainties of ± 0.6 log-units for the $\log K'_{s,1yz}$ values in 1 M Na_2CO_3. Application of the SIT to Na_2CO_3 solutions above 1 molar ($I > 3$ mol/kg H_2O) may include larger uncertainties. As $\log K'_{s,1yz}$ varies to a certain extent with the ionic strength, the species concentration lines in Fig. 4 are not strictly linear.

Fig. 4a shows solubility data in 1 M Na_2CO_3 containing 0.01–0.5 M NaOH, *i.e.*, $\log[Th]$ plotted as a function of $\log[OH^-]$ at approximately constant ionic strength. The thorium concentration calculated with the $\log K'_{s,1yz}$ values for the complexes $Th(OH)(CO_3)_4{}^{5-}$ and $Th(OH)_4(CO_3)^{2-}$ reproduce very well the experimental data at the lowest and highest NaOH concentrations. The dotted maximum concentration line for $Th(CO_3)_5{}^{6-}$, calculated with the upper limit of $\log K^\circ_{s,105} < -31.2$ and $\varepsilon(Na^+, Th(CO_3)_5{}^{6-}) = \varepsilon(Na^+, U(CO_3)_5{}^{6-}) = -0.30 \pm 0.15$ [2–4], does not reflect the experimental data. The solubility in 1 M Na_2CO_3 is described best (fat dashed line in Fig. 4a) by introducing the complex $Th(OH)_2(CO_3)_4{}^{6-}$ with an equilibrium constant of $\log K'_{s,124} = -8.1 \pm 0.4$, corresponding to

$$\log K^\circ_{s,124} = -13.3 \pm 0.7 \text{ and } \log \beta^\circ_{124} = 34.5 \pm 0.8 .$$

This value is considerably lower than the upper limit in Table 1 and hence compatible with the experimental results at $I = 0.5$ M. However, $\log K^\circ_{s,124}$ should rather be considered as an upper limit, because the experimental data are rather scattered and contributions from the complexes (133) and (142) to the solubility under these conditions cannot be excluded (c.f. Appendix, Fig. A3).

Fig. 4b shows the solubility of $ThO_2 \cdot xH_2O$(am) in 0.1 M NaOH containing 0.001–2 M Na_2CO_3, *i.e.*, $\log[Th]$ plotted as a function of $\log[CO_3{}^{2-}]$. Up to $[CO_3{}^{2-}] = 0.1$ M, the thorium concentrations remain at a low level ($\log[Th] < -8$). The effect of carbonate complexation is negligible within the scatter of the solubility data, which is probably due to the more or less complete removal of colloids [17]. The solubility increase in the range $[CO_3{}^{2-}] = 0.1$–0.5 M is consistent with the reaction $Th(OH)_4(am) + CO_3{}^{2-} \Leftrightarrow Th(OH)_4(CO_3)^{2-}$ (slope 1). The steep increase of the solubility curve at $[CO_3{}^{2-}] \geq 1$ M is well described with the formation constant of $Th(OH)(CO_3)_4{}^{5-}$ and the upper limit for $Th(OH)_2(CO_3)_4{}^{6-}$ derived from the solubility data at $I = 0.5$ M and in 1 M Na_2CO_3/0.01–0.5 M NaOH, respectively. The concentration line calculated with the upper limit for $Th(CO_3)_5{}^{6-}$ (Table 1) is about 2 orders of magnitude below the experimental data.

According to $\log K^\circ_{s,122} = -10.8 \pm 0.2$, $\log K^\circ_{s,131} = -9.3 \pm 0.5$ and the upper limit of $\log K^\circ_{s,123} < -9.9$ (Table 1), neither $Th(OH)_2(CO_3)_2{}^{2-}$ nor $Th(OH)_3(CO_3)^-$ and $Th(OH)_2(CO_3)_3{}^{4-}$ have significant contributions to the total thorium concentration in the solubility experiments shown in Fig. 4a and b. The same holds for the complexes (113) and (132), because the maximum concentrations calculated with the upper limits from Table 1 are much lower than the experimental data. Contributions from the complexes (133) and (142) cannot be excluded under these conditions (c.f. Appendix, Fig. A3). The solubility data in 1 M $Na_2CO_3/0.01–0.5$ M NaOH and (0.001–2) M $Na_2CO_3/0.1$ M NaOH set new upper limits for $\log K^\circ_{s,124}$, $\log K^\circ_{s,132}$, $\log K^\circ_{s,133}$ and $\log K^\circ_{s,142}$ which are up to 1.7 log-units lower than those derived under the conditions of the studies at $I = 0.5$ M (c.f. Table 1).

The present evaluation of Th(IV) solubilities at high carbonate concentrations and $[OH^-] \geq 0.01$ M indicates, that (due to the competition between hydroxide and carbonate ligands) the speciation depends on the ratio $[OH^-]/[CO_3^{2-}]$, even at carbonate concentrations of 1–2 M. The pentacarbonate complex (105) is expected to be predominant in concentrated carbonate solutions at pH 7–10, but increasing pH to values above 11–12 leads to the formation of ternary hydroxide-carbonate complexes.

4. Conclusions

The present study contains a comprehensive investigation of the solubility and complex formation of Th(IV) in carbonate solution. The formation constants $\log \beta^\circ_{1yz}$ of analogous complexes $An(OH)_y(CO_3)_z{}^{4-y-2z}$ are expected to increase systematically from Th(IV) to U(IV), Np(IV) and Pu(IV), similar as in the case of the pentacarbonate complex and hydroxide complexes [1, 2]. The present results in the ternary system Th(IV)-OH-CO_3 are helpful as qualitative analogues to understand the chemical behaviour of U(IV), Np(IV) and Pu(IV).

As illustrated in Fig. 5, the most important ternary Th(IV) complexes, $Th(OH)(CO_3)_4{}^{5-}$ and $Th(OH)_2(CO_3)_2{}^{2-}$, are on a diagonal line between the limiting mononuclear hydroxide complex $Th(OH)_4(aq)$, which is predominant (together with $Th(OH)_4$ colloids) at pH > 5 and low carbonate concentrations, and the limiting carbonate complex $Th(CO_3)_5{}^{6-}$ (black fields). Further complexes with significant contributions to the Th(IV) solubility, $Th(OH)_2(CO_3)(aq)$, $Th(OH)_3(CO_3)^-$ and $Th(OH)_4(CO_3)^{2-}$ (grey fields), are close to this diagonal line. At high carbonate concentrations, the highly charged complexes $Th(CO_3)_5{}^{6-}$, $Th(OH)(CO_3)_4{}^{5-}$ and possibly $Th(OH)_2(CO_3)_4{}^{6-}$ are formed, depending on pH, *i.e.*, on the ratio of the $CO_3{}^{2-}$ and OH^- concentrations.

The model proposed by Rai *et al.* [10–12] for U(IV), Np(IV) and Pu(IV) includes only the ternary complexes (122) and the pentacarbonate complexes (105) as the major species at moderate and high carbonate concentrations, respectively. This is certainly an oversimplification but a helpful approximation for the calculation of solubilities in carbonate solution. The formation of (122) at $C_{tot} = 0.01–0.1$ M and pH 8–10 and the formation of (141) and/or (142) at pH > 11, as suggested for Np(IV) [9, 14] and Pu(IV) [15], is compatible with the results for Th(IV). However, the experimental solubility data and equilibrium constants $\log K^\circ_{s,122}$ reported by Rai *et al.*for Np(IV) [11] and Pu(IV) [12] are about 1.5 log-units lower than those determined by Kitamura and Kohara [14] and Yamaguchi *et al.* [15], respectively. These discrepancies need further investigation [2].

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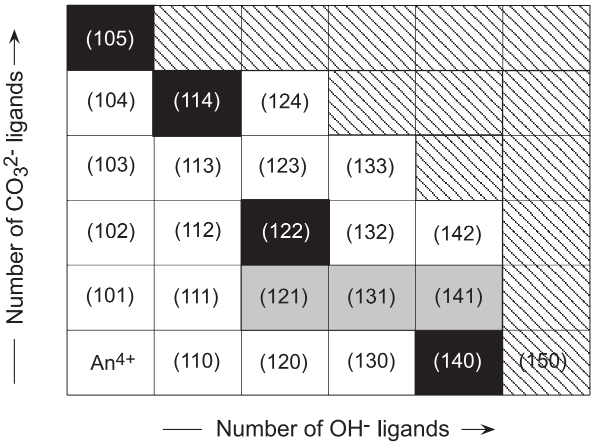

(105)					
(104)	(114)	(124)			
(103)	(113)	(123)	(133)		
(102)	(112)	(122)	(132)	(142)	
(101)	(111)	(121)	(131)	(141)	
An^{4+}	(110)	(120)	(130)	(140)	(150)

Fig. 5. Possible mononuclear complexes $(1yz) = An(OH)_y(CO_3)_z{}^{4-y-2z}$. Black fields indicate the most important species in neutral and alkaline solutions of low to high carbonate concentration. Grey fields indicate further Th(IV) complexes quantified in the present work.

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Appendix

Upper limits for the equilibrium constants $\log K'_{s,1yz}$ refering to the reactions

$$Th(OH)_4(am) + zCO_3^{2-} \Leftrightarrow Th(OH)_y(CO_3)_z^{4-y-2z} + (4-y)OH^-.$$

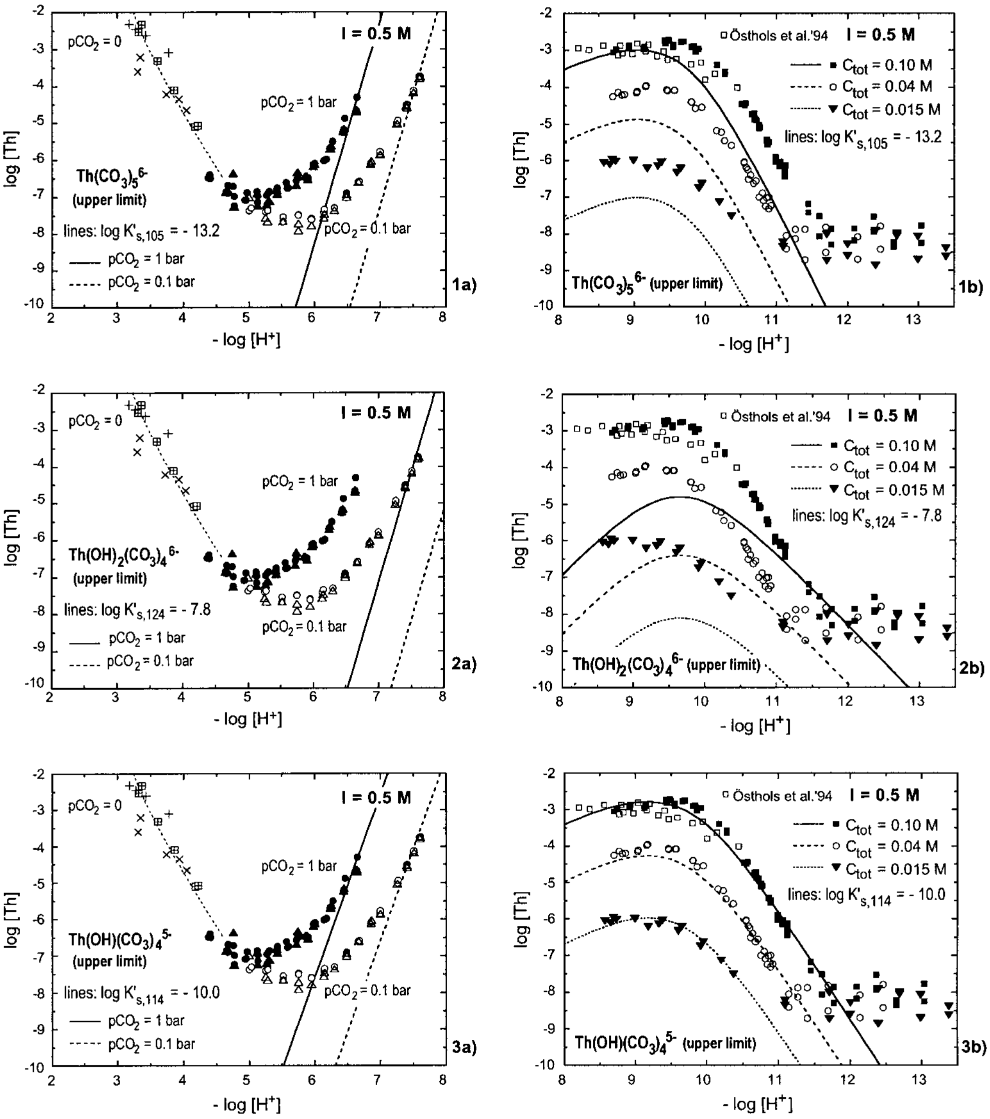

Fig. A1. Upper limits for $Th(CO_3)_5^{6-}$ (1), $Th(OH)_2(CO_3)_4^{6-}$ (2) and $Th(OH)(CO_3)_4^{5-}$ (3), considering simultaneously the 5 sets of solubility data at $I = 0.5$ M: (**a**) open system experiments at $p_{CO_2} = 1.0$ and 0.1 bar (left side) and (**b**) closed system experiments at $C_{tot} = 0.1$, 0.04 and 0.015 M (right side).

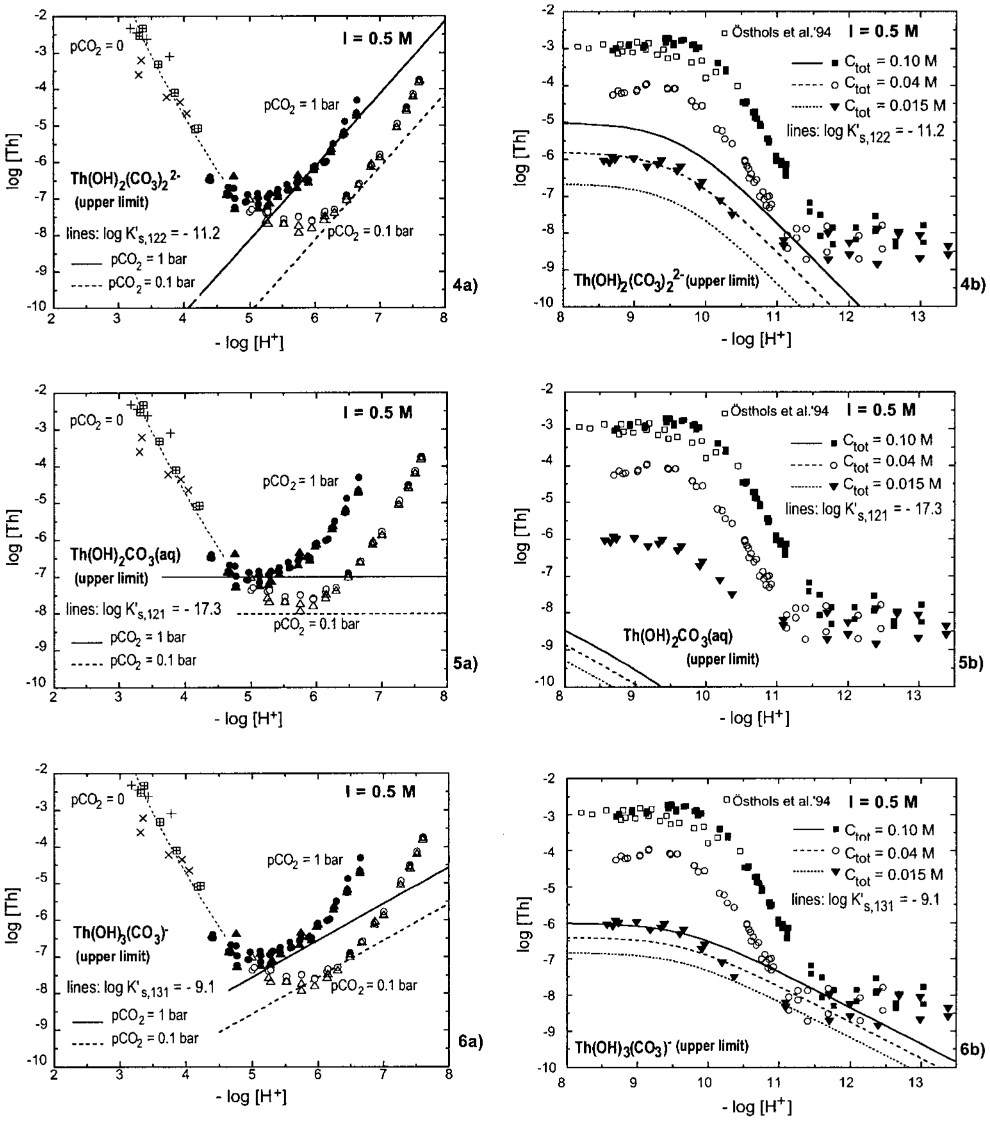

Fig. A2. Upper limits for $Th(OH)_2(CO_3)_2^{2-}$ (4), $Th(OH)_2CO_3(aq)$ (5) and $Th(OH)_3(CO_3)^-$ (6), considering simultaneously the 5 sets of solubility data at $I = 0.5\,M$: (**a**) open system experiments at $p_{CO_2} = 1.0$ and 0.1 bar (left side) and (**b**) closed system experiments at $C_{tot} = 0.1$, 0.04 and 0.015 M (right side).

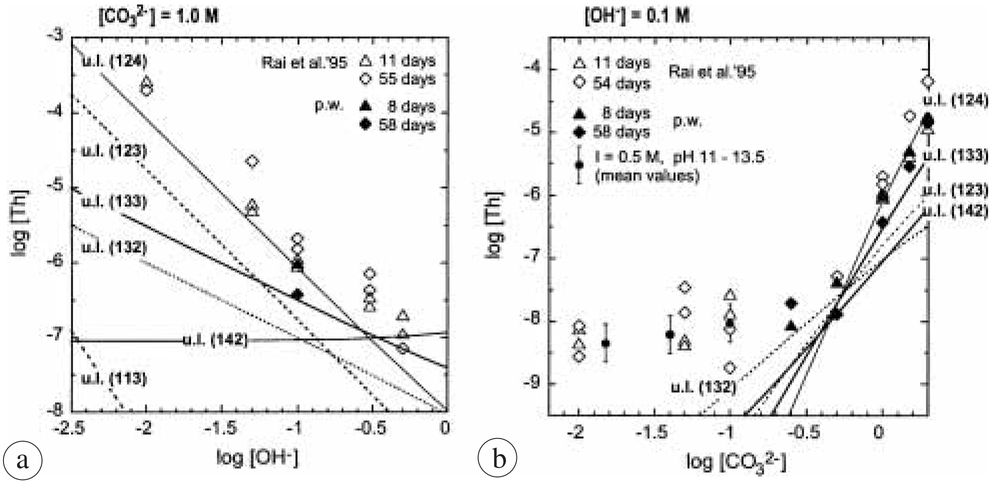

Fig. A3. Upper limits for $Th(OH)(CO_3)_3^{3-}$ and $Th(OH)_2(CO_3)_3^{4-}$ (given by the $\log K^\circ_{s,123}$ and $\log K^\circ_{s,123}$ maximum values derived at $I = 0.5\,M$) and for $Th(OH)_2(CO_3)_4^{6-}$, $Th(OH)_3(CO_3)_2^{3-}$, $Th(OH)_3(CO_3)_3^{5-}$ and $Th(OH)_4(CO_3)_2^{4-}$ given by the solubility of $Th(OH)_4(am)$ in either 1.0 M Na_2CO_3/0.01–0.5 M NaOH (left side) or 0.001–2.0 M Na_2CO_3/0.1 M NaOH (right side).