

Actinide carbonate complexes

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Actinide carbonate complexes

Methodologies for estimating stoichiometries and stabilities



Introduction. For the management of radioactive wastes, Equilibrium speciation is studied in aqueous solutions for Actinides: **critical reviewing and measuring thermodynamic data, (see typically NEA TDB reviews, and corresponding methodologies and thermodynamics basis)**

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Carbonate complexes of M^{3+} , a well known system(?)

Differences between Eu, Am and Cm are less than experimental accuracy.

Sensitivity analysis.

Limiting complex(es)

Comparison with sulfate complexes

Carbonate complexes of M^{4+}

Actinide carbonate complexes

Methodologies for estimating stoichiometries and stabilities

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**Maximum possible stabilities
for non well established stoichiometries**

Carbonate complexes of M^{3+}

Methodologies for estimating stoichiometries and stabilities

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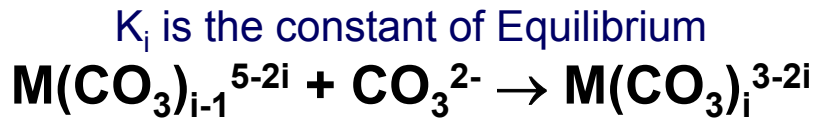
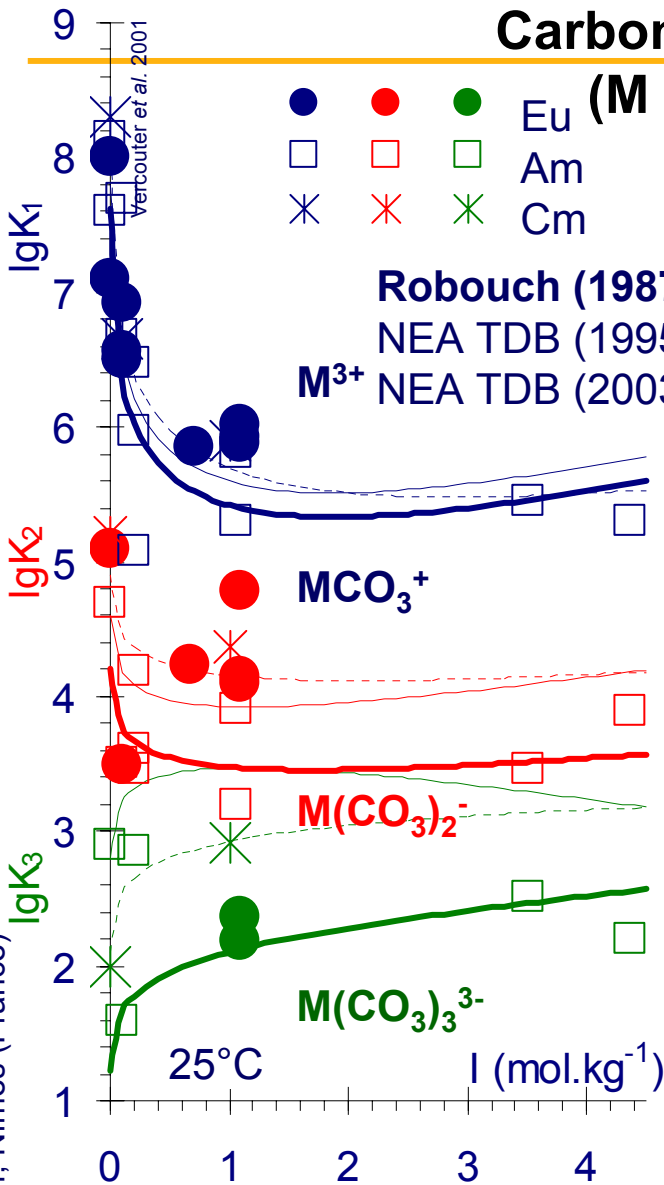
Comparison with sulfate complexes

Carbonate complexes of M^{4+}



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Carbonate complexes of M³⁺



→ Differences between Eu, Am and Cm are less than experimental accuracy

→ Consistency in stability data from different laboratories is obtained only for MCO₃⁺

Origins of differences in selected values:

- Giving more weight on selected measurements
- Experimental inconsistencies (typically activity coefficient, junction potentials)
- difficulty in decomposing the experimental observations into the contributions of each soluble the species *i.e.* in determining the **actual stoichiometries** (sensitivity analysis),

¹P.Robouch Thèse Université L.Pasteur, Strasbourg (France) 1987

²R.Silva *et al.* Chemical Thermodynamics of Americium NEA, Paris (France) 1995

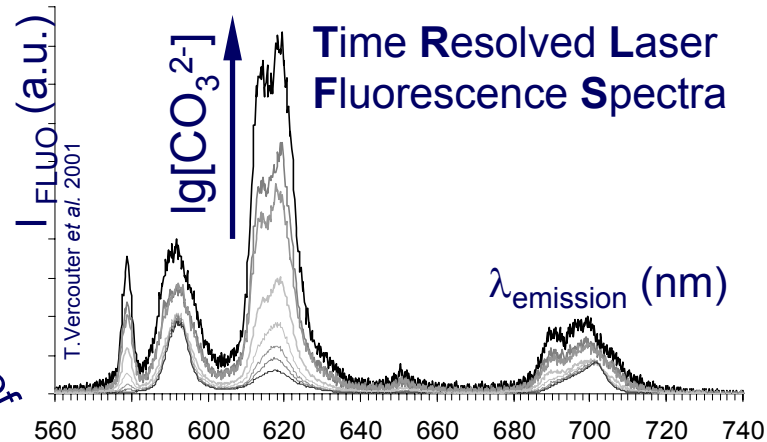
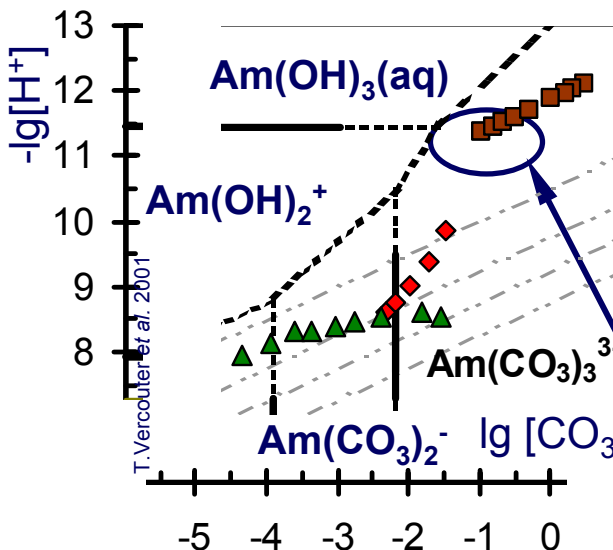
³R.Guillaumont *et al.* Update on the Chemical Thermodynamics of... NEA, Paris (France), Elsevier Ed. 2003



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T. Vercouter, P. Vitorge, C. Moulin.
 Communication O22-02 ATALANTE
 2004, Nîmes (France)

Carbonate complexes of Eu³⁺ a TRLFS study

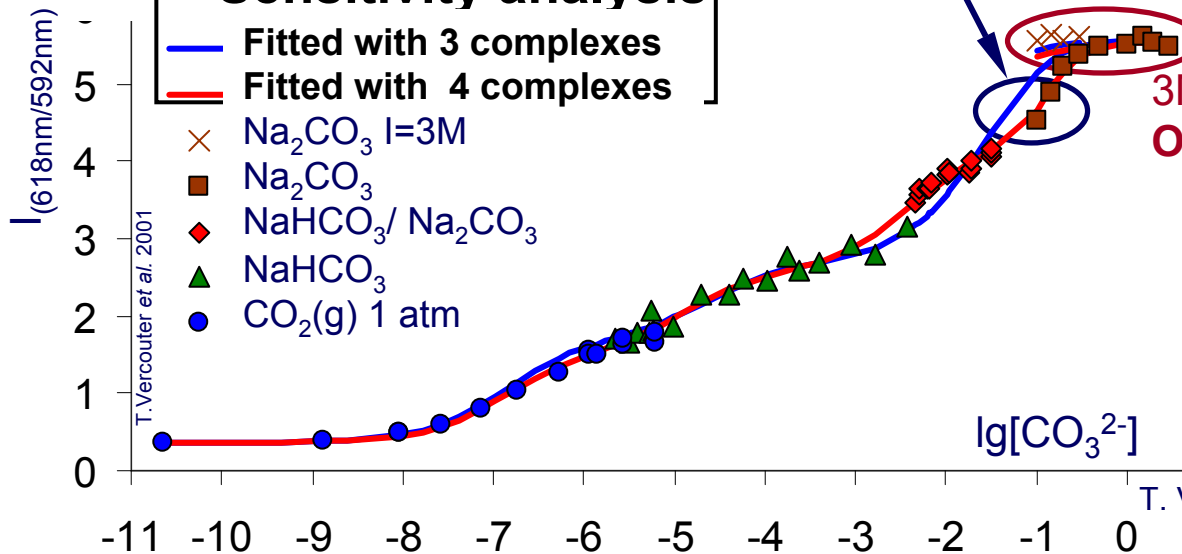


Possible formation of
 $\text{Eu}(\text{OH})_2^+$ or
 $\text{Eu}(\text{CO}_3)_i(\text{OH})_{3-2i}^-$?

Sensitivity analysis

- Fitted with 3 complexes
- Fitted with 4 complexes

- × Na_2CO_3 $I=3\text{M}$
- Na_2CO_3
- ◆ $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$
- ▲ NaHCO_3
- $\text{CO}_2(\text{g})$ 1 atm



3M (high) ionic strength.
One single species

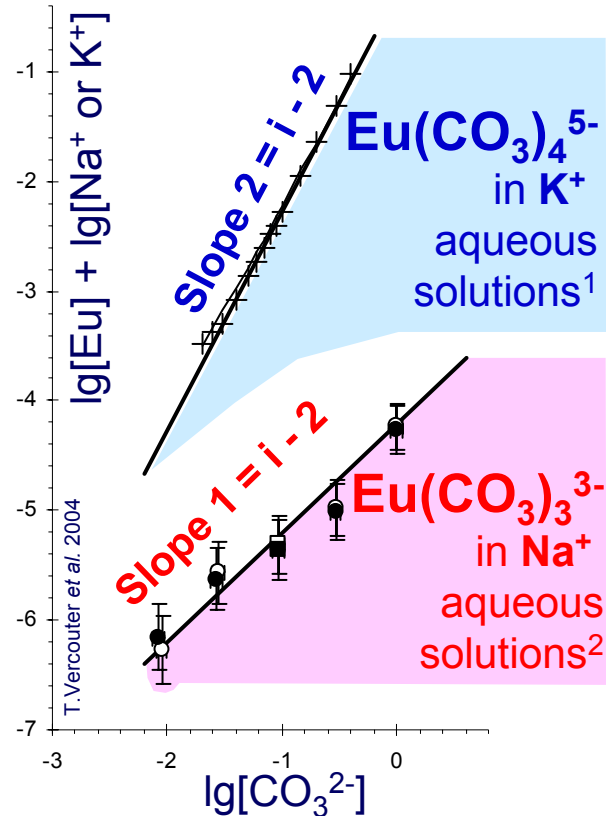
T. Vercoeur, P. Vitorge, C. Moulin. Communication
O22-02 ATALANTE 2004, Nîmes (France)

Carbonate complexes of Eu³⁺

Stoichiometries of the limiting complexes from solubility study



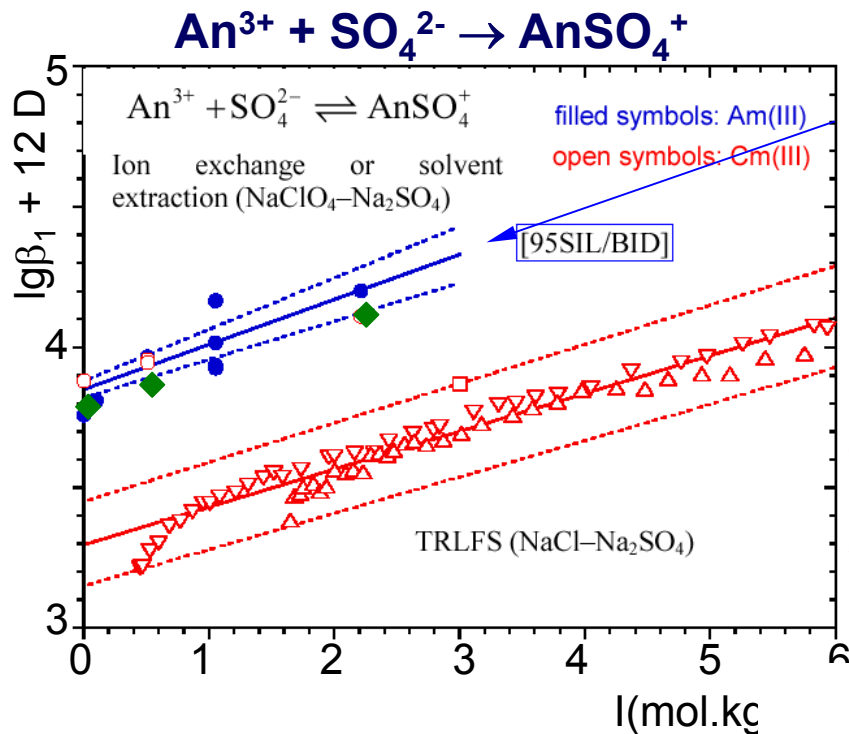
A⁺ = Na⁺ or K⁺



¹Faucherre *et al.*, *Rev. Chim. Minér.*, t3, 953 (1966)

²T. Vercouter, P. Vitorge, C. Moulin. Communication O22-02 ATALANTE 2004, Nîmes (France)

Comparison with sulfate complexes of M^{3+}



NEA 1995¹ Ion exchange or solvent extraction ($NaClO_4-Na_2SO_4$)

NEA 2003² from TRLF ($NaCl-Na_2SO_4$) data³

Inconsistency had been explained as follows: Spectroscopy would measure the stability of only **inner sphere complexes**, while other techniques would measure the stability of **in+outer sphere complexes**.

This is not consistent with Thermodynamics:
 $complex_{in} \rightarrow complex_{out} + n H_2O$

$$[complex_{out}] / [complex_{in}] = \text{Constant} (a_{H_2O})^n$$

Anyhow, our **TRLFS recent study⁴** rather confirms **NEA 1995 selection** for Eu ($NaClO_4-Na_2SO_4$)

¹R.Silva, G. Bidoglio, M.H. Rand, P.B. Robouch, H. Wanner, I. Puigdomenech. *Chemical thermodynamics of Am*. NEA Paris (France) 1995

²R. Guillaumont, T. Fanghänel, V. Neck, J. Fuger, D.A. Palmer, I. Grenthe, M.H. Rand. *Update on the chemical thermodynamics of U, Np, Pu, Am and Tc*, Elsevier, Amsterdam, 2003

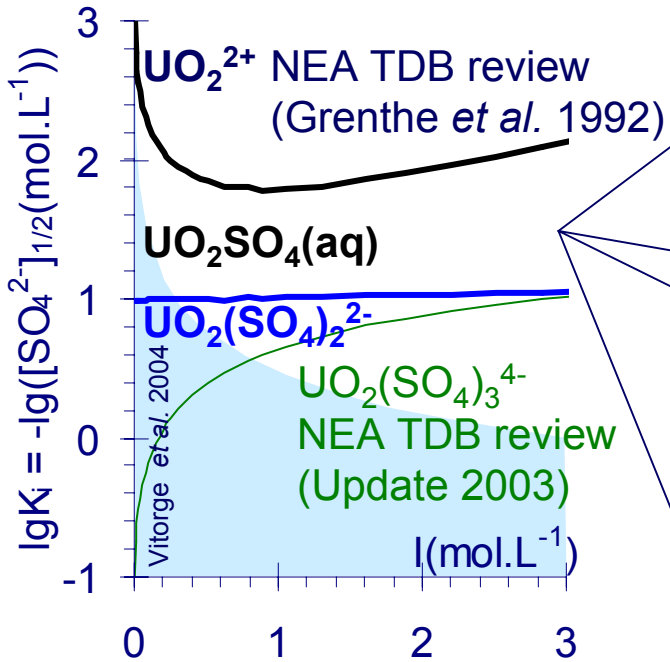
³P. Paviet, T. Fanghänel *et al.*, *Radiochim. Acta*, 74, 99-103 (1996) and V. Neck, T. Fanghänel *et al.*, Report, 1-108 (1998)

⁴T. Vercouter, P. Vitorge, C. Moulin. Communication O22-02 ATALANTE 2004, Nîmes (France)

Comparison with sulfate complexes of UO_2^{2+}



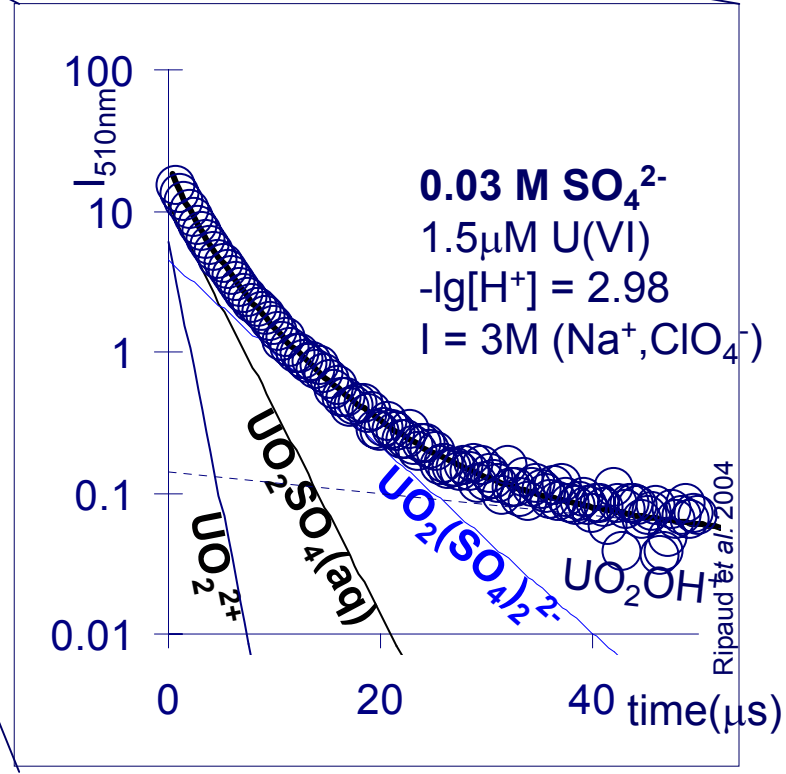
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a TRLFS study

Prediction: $\text{UO}_2\text{SO}_4(\text{aq}) + \text{UO}_2(\text{SO}_4)_2^{2-} + \text{UO}_2(\text{SO}_4)_3^{4-}$

$\text{UO}_2(\text{SO}_4)_3^{4-}$, was not evidenced by our TRLF measurements in these chemical conditions.





When **intermediary species** are **stable in narrow domains** of experimental conditions, it is difficult to measure independently their physical properties (as typically molar absorbance), and their contribution to measured signals. Beside other difficulties, this can often explain **differences in the values determined by different authors** for equilibrium constants.

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Missing data on

Activity coefficients, specially for highly negative complexes,

Ion pairing? Structure of concentrated electrolytes?

Possible mixed complexes, *i.e.* $M(\text{CO}_3)_i(\text{OH})_j^{3-2i-j}$

(assuming no polynuclear complex).

Why no mixed complex have ever been evidenced?

Experimental difficulties?

Choice of experimental conditions?

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Carbonate complexes of M^{3+} , a well known system(?)

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Carbonate complexes of M^{4+}

$M(\text{CO}_3)_i$ $^{4-2i}$ stoichiometries for $i = 4$ and 5 , for several An(IV) and Ln(IV).

However, $i = 6$ was also proposed Th(IV) and Ce(IV).

Maximum possible values are proposed for the formation constants of possible $M(\text{CO}_3)_i(\text{OH})_j$ $^{4-2i-j}$ complexes based on published solubility data.

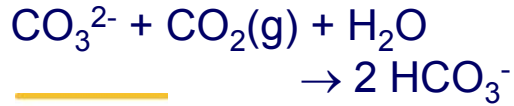


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Spectrophotometric study



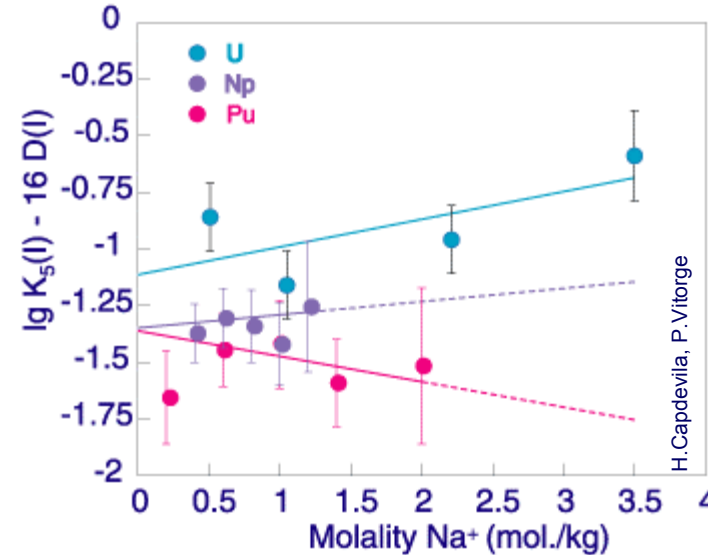
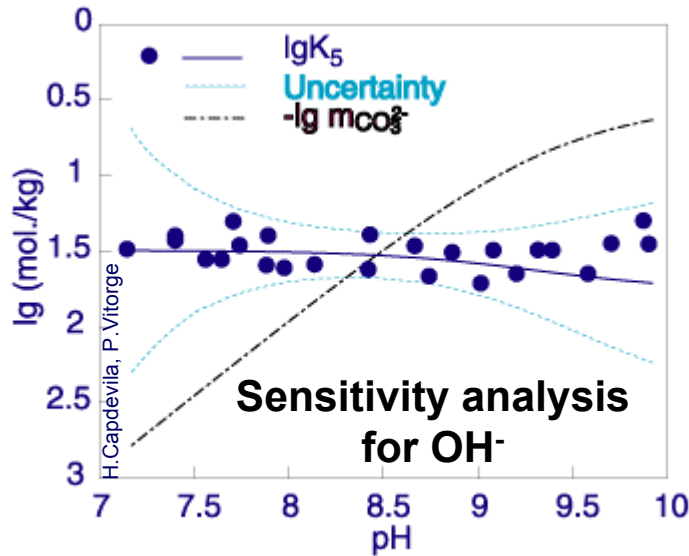
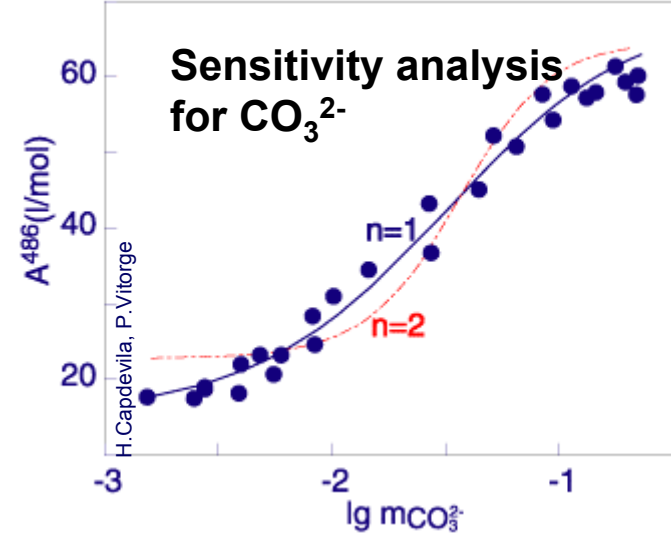
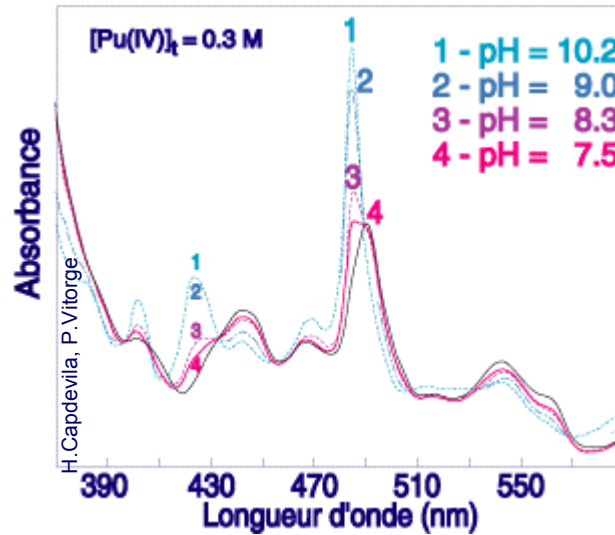
during titration



at 25°C



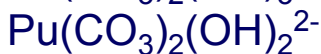
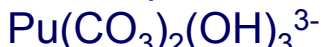
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H.Capdevila, P.Vitorge, E.Giffaut, L.Delmau. Radiochim. Acta 74, 93-98 (1996)

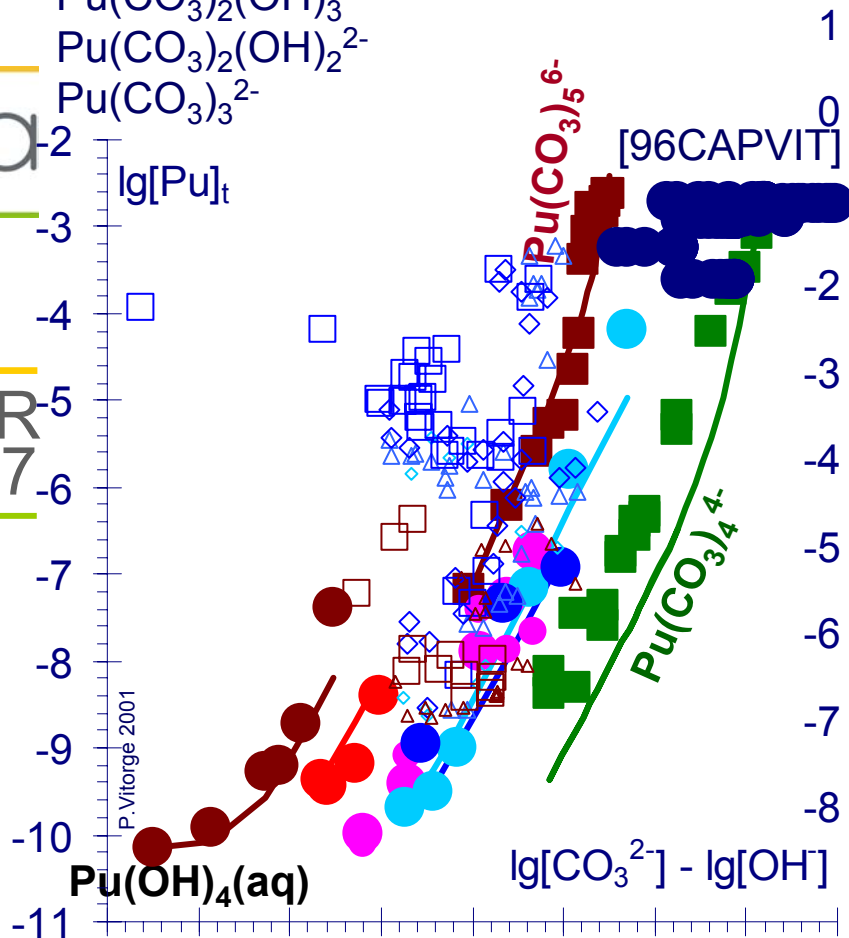
Pu(IV) solubility in carbonate media

Other possible species:

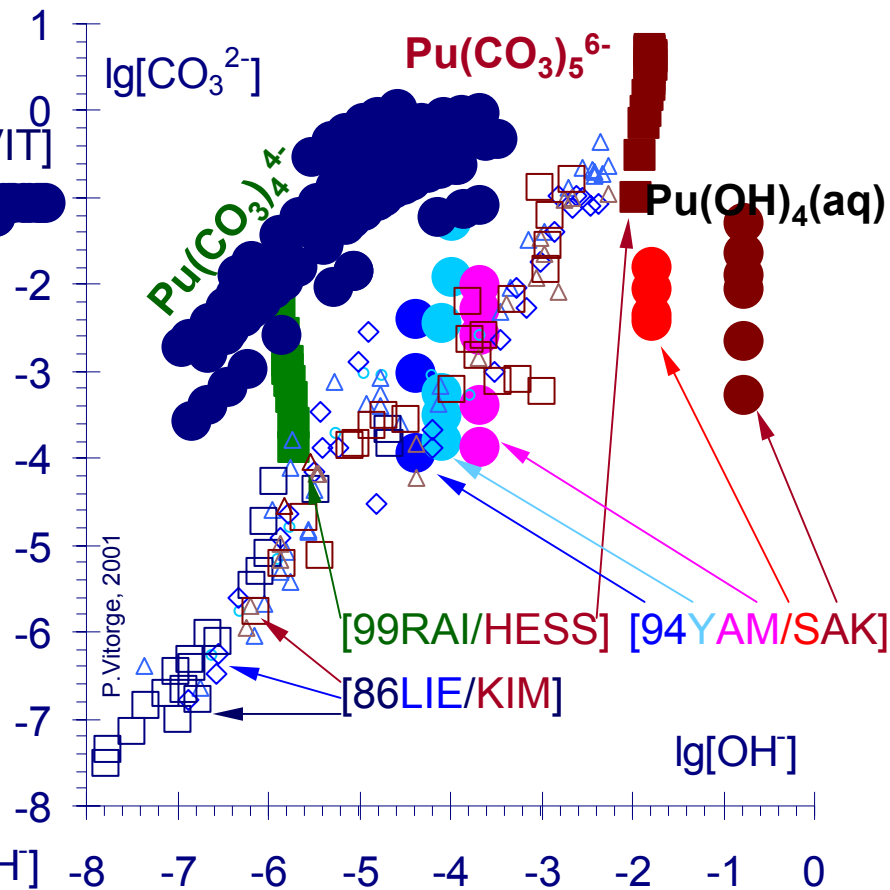


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Solubility

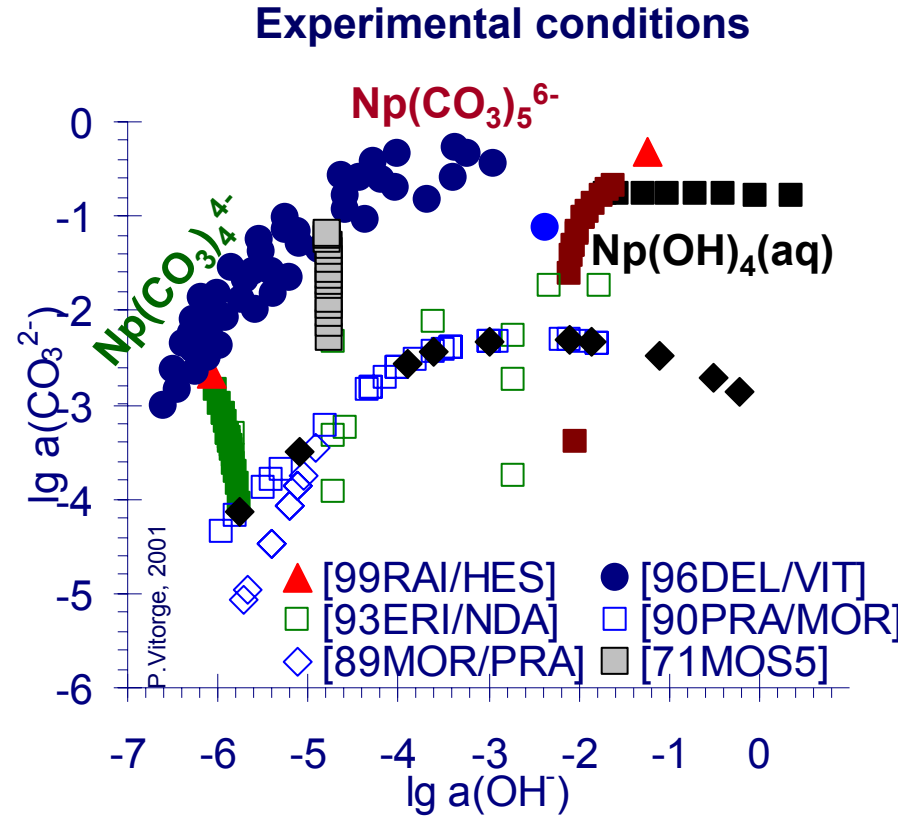
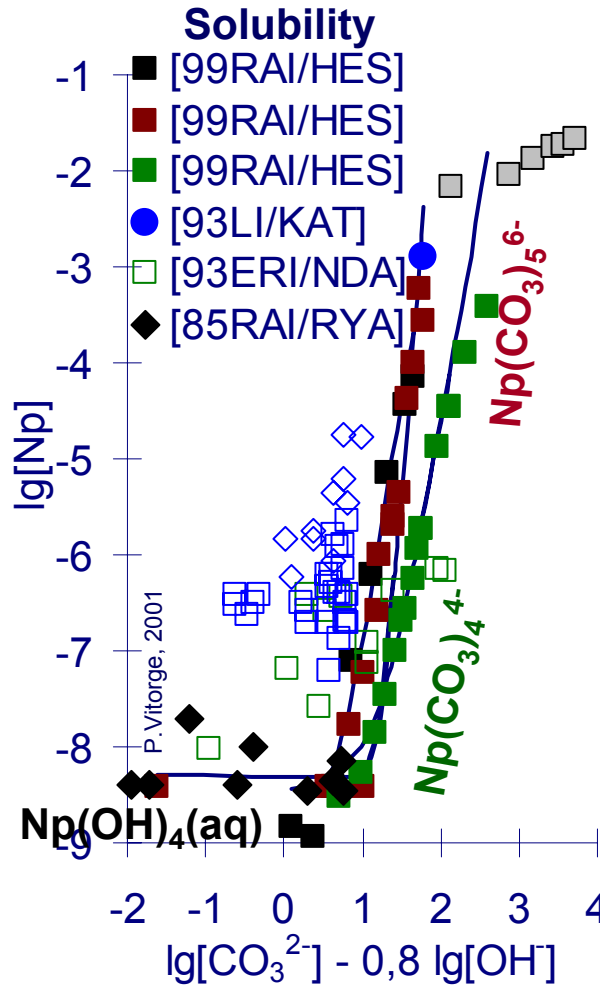


Experimental conditions



$\text{Pu}(\text{CO}_3)_5^{6-}$ + $\text{Pu}(\text{CO}_3)_4^{4-}$ are enough to account for experimental observation at high $\text{CO}_2(\text{g})$ partial pressure. Adding $\text{Pu}(\text{OH})_4(\text{aq})$ is enough to account for most of the other experimental data; however, **experimental solubilities are not consistent and activity coefficients were fitted.**

Np(IV) solubility in carbonate media



The way NEA TDB selected data

R. Lemire, J. Fuger, H. Nitsche, M. Rand, K. Spahiu, J. Sullivan, W. Ullman, P. Vitorge. *Chemical Thermodynamics of Neptunium and Plutonium*. Paris OCDE AEN, Elsevier (2001).

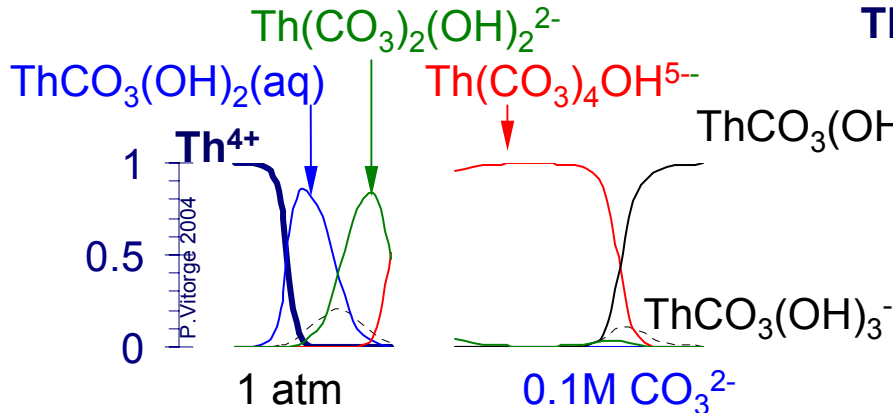
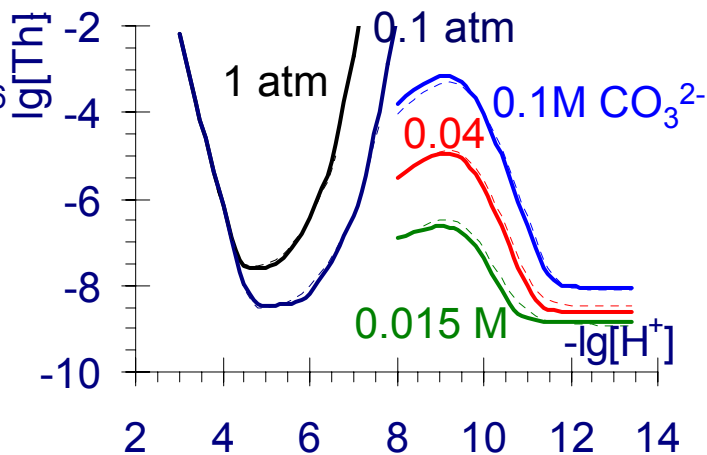
$\text{Np}(\text{CO}_3)_5^{6-} + \text{Np}(\text{CO}_3)_4^{4-}$ are enough to account for experimental observation at high $\text{CO}_2(\text{g})$ partial pressure. Adding $\text{Np}(\text{OH})_4(\text{aq})$ is enough to account for most of the other experimental data; however, **experimental solubilities are not consistent and activity coefficients were fitted.**

Th solubility in carbonate media

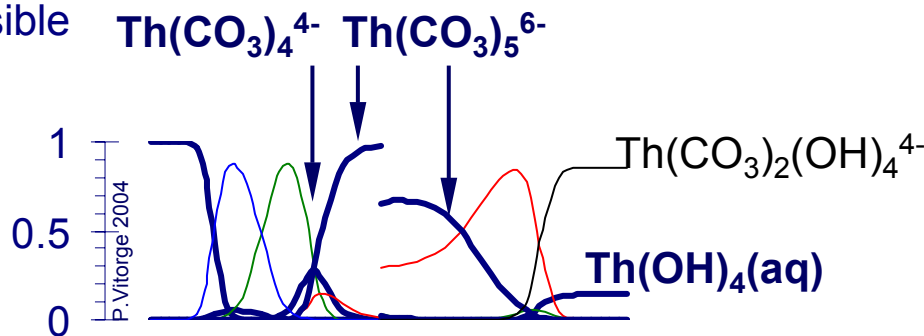
M. Altmaier, V. Neck, Th. Fanghänel NRC6 2004- O3



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Another possible interpretation



A possible interpretation; however: comparing with **other published data?**

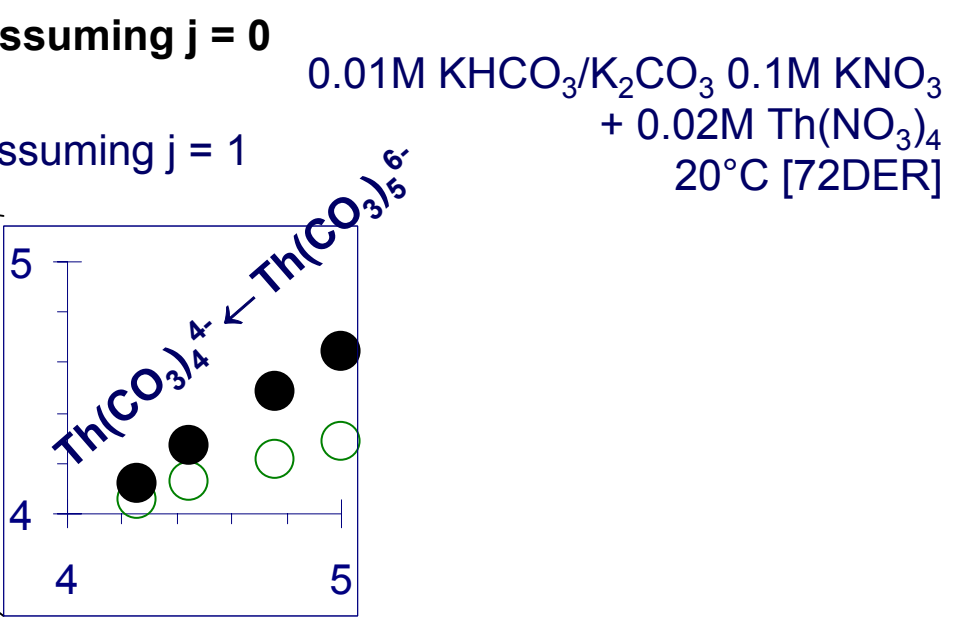
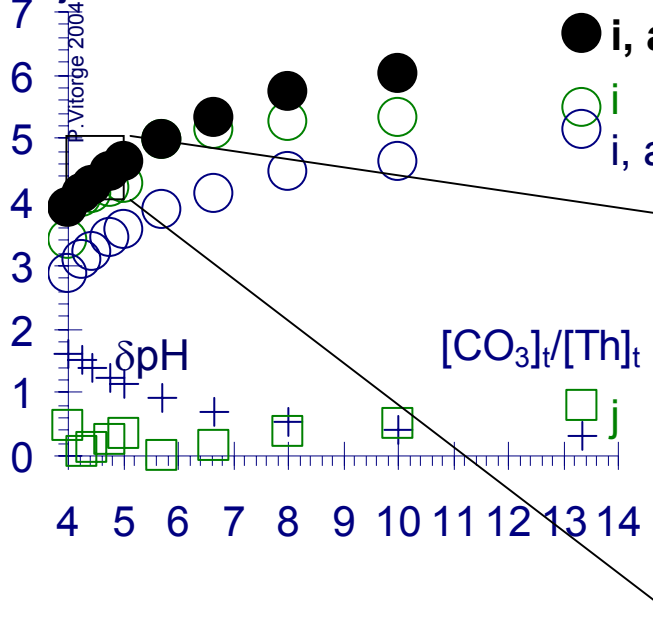
- D.Rai, D.Moore, C.Oakes, and M.Yui (2000)
- N.Hess, A.Felmy, D.Rai, and S.Conradson (1997).
- D.Rai, A.Felmy, D.Moore, M.Mason (1995)
- D.Rai, D.Moore, M.Yui (2000)
- D.Rai, N.Hess, A.Felmy, D.Moore, M.Yui (1999)
- D.Rai, L.Rao, H.Weger, A.Felmy, G.Choppin, and M.Yui (1999)
- D.Rai, A.Felmy, M.Mason, N.Hess (1996)

Th(CO₃)_i⁴⁻²ⁱ complexes are stable for i = 4, 5 (and 6?) at high I and [CO₃²⁻]; measured **activity coefficients** are needed for comparisons.

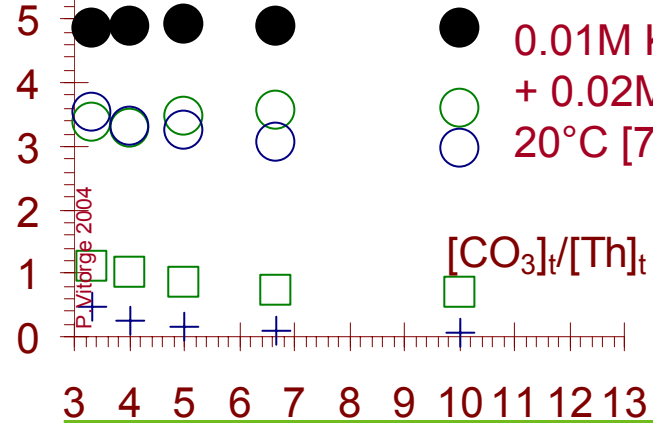
Evidence of **Th(CO₃)₅⁶⁻** in **0.16-0.3 M K₂CO₃ (2M Na⁺)**, in **0.2-1 M KHCO₃ (2M Na⁺)**, and in **0.1 M K₂CO₃ or KHCO₃ (0.08M K⁺)**
 Dissociation into **Th(CO₃)₄⁴⁻**? Also proposed at low ionic strength in **0.001 M K₂CO₃**, and in **0.01 M KHCO₃ + <0.01M K₂CO₃ aqueous solutions [72DER]**.



Th limiting carbonate complex



0.01M KHCO₃/K₂CO₃ 0.1M KNO₃
+ 0.02M Th(NO₃)₄
20°C [72DER]



● 0.01M KHCO₃/K₂CO₃ 0.1M KNO₃
○ + 0.02M Th(OH)₂(NO₃)₂
○ 20°C [72DER]

0.01 M KHCO₃ + <0.01M K₂CO₃
aqueous solutions [72DER].

Th and Pu(IV) possible (hydroxo-)carbonate complexes

$M(\text{CO}_3)_i(\text{OH})_j^{(4-2i-j)+}$	$\lg\beta_{ij}^0(\text{Pu})^1$	$\lg\beta_{ij}(\text{Th})^2$	$\lg\beta_{ij}(\text{Th})^3$
M^{4+}			
MOH^{3+}	13.2		<8.7
$M(\text{OH})_4(\text{aq})$	< 47.9		27.4
$M\text{CO}_3(\text{OH})_2(\text{aq})$	<<42	27.0	26.9
$M\text{CO}_3(\text{OH})_3^-$	<<47.7	34.8	
$M(\text{CO}_3)_2\text{OH}^-$	<40.5		<25.6
$M\text{CO}_3(\text{OH})_4^{2-}$	<<51.8	37.4	<34
$M(\text{CO}_3)_2(\text{OH})_2^{2-}$	<46.2	33.3	33.3
$M(\text{CO}_3)_3^{2-}$	<37.6		<22.6
$M(\text{CO}_3)_2(\text{OH})_3^{3-}$	<50.5		<36.6
$M(\text{CO}_3)_3\text{OH}^{3-}$	<42		<31.4
$M(\text{CO}_3)_2(\text{OH})_4^{4-}$			38.4
$M(\text{CO}_3)_3(\text{OH})_2^{4-}$	<<41		<35.7
$M(\text{CO}_3)_4^{4-}$	37		27.4
$M(\text{CO}_3)_3(\text{OH})_3^{5-}$	<<40.5		<39.5
$M(\text{CO}_3)_4\text{OH}^{5-}$	<<39	34.4	34.1
$M(\text{CO}_3)_3(\text{OH})_4^{6-}$	<<38.5		<39.3
$M(\text{CO}_3)_4(\text{OH})_2^{6-}$	<<37		<36.4
$M(\text{CO}_3)_5^{6-}$	35.6		31.5

→ Maximum possible stabilities estimated for Pu complexes¹ are **consistent** with the values proposed or estimated for Th.

→ Depending on their stoichiometries, many possible mixed complexes would be more stable **in the experimental conditions of the Th study: corresponding estimation of the upper limits of their stability constants are closer to the actual value.**

→ However not all published experimental data have been taken into account for Th.

¹P.Vitorge, H.Capdevila. Radiochim. Acta 91, 623–631 (2003)

²M. Altmaier, V. Neck, Th. Fanghänel NRC6 2004- O3

³Another possible interpretation of experimental data from Ref.²



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**Maximum possible possible values for stabilities,
a conservative approach
a way for comparing published experimental data**



Actual stabilities

**Coordination chemistry
(including mixed hydroxo-carbonate complexes)**

**Bridging ligands?
(polynuclear complexes)**

**Activity coefficients
(ion pairing and structure of concentrated electrolytes)**

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