Actinide Geochemistry

Pierre Vitorge

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***Not all the subject will be treated
you can ask further details (pierre.vitorge@cea.fr)
before, during or after the Summer School***

Acknowledgements to Thomas Vercouter for remarks and corrections on the slides.

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Last Lines of the Periodic Table

5 O	^{37}Rb	^{38}Sr	^{39}Y	^{40}Zr	^{41}Nb	^{42}Mo	^{43}Tc	^{44}Ru	^{45}Rh	^{46}Pd	^{47}Ag	^{48}Cd	^{49}In	^{50}Sn	^{51}Sb	^{52}Te	^{53}I	^{54}Xe
6 P	^{55}Cs	^{56}Ba	^{57}La	^{72}Hf	^{73}Ta	^{74}W	^{75}Re	^{76}Os	^{77}Ir	^{78}Pt	^{79}Au	^{80}Hg	^{81}Tl	^{82}Pb	^{83}Bi	^{84}Po	^{85}At	^{86}Rn
7 Q	^{87}Fr	^{88}Ra	^{89}Ac	^{104}Rf	^{105}Db	^{106}Sg	^{107}Bh	^{108}Hs	^{109}Mt	^{110}Ds	^{111}Rg	^{112}?		^{114}?		^{116}?		

^{57}La	^{58}Ce	^{59}Pr	^{60}Nd	^{61}Pm	^{62}Sm	^{63}Eu	^{64}Gd	^{65}Tb	^{66}Dy	^{67}Ho	^{68}Er	^{69}Tm	^{70}Yb	^{71}Lu
^{89}Ac	^{90}Th	^{91}Pa	^{92}U	^{93}Np	^{94}Pu	^{95}Am	^{96}Cm	^{97}Bk	^{98}Cf	^{99}Es	^{100}Fm	^{101}Md	^{102}No	^{103}Lr

I Fr^+

II Ra^{2+} Cf^{2+} Es^{2+} Fm^{2+} Md^{2+} No^{2+}

III Ac^{3+} U^{3+} Np^{3+} Pu^{3+} Am^{3+} Cm^{3+} Bk^{3+} Cf^{3+} Es^{3+} Fm^{3+} Md^{3+} No^{3+} Lr^{3+}

IV Th^{4+} Pa^{4+} U^{4+} Np^{4+} Pu^{4+} Am^{4+} Cm^{4+} Bk^{4+} Cf^{4+}

V $Pa(V)$ UO_2^+ NpO_2^+ PuO_2^+ AmO_2^+

VI UO_2^{2+} NpO_2^{2+} PuO_2^{2+} AmO_2^{2+}

VII $Np(VII)$ $Pu(VII)$

Highest oxidation number for each element = number of its group

Inside each d or f series: increase of the nucleus charges which contract electron density
slight decrease of the ionic radii
hardness slightly increase

From one line (of d or f series) to the next line: the same effect also results in better
shielding (by core electrons) of f and d valence electrons (from the nucleus):
softness slightly increases
high oxidation states are stabilized.

Relativistic effects
contraction of s (and p) orbitals : increasing their shielding effect of f (and d) ones
spin orbit coupling

Chemical **Analogues**

5 O	[37]Rb	[38]Sr	[39]Y	[40]Zr	[41]Nb	[42]Mo	[43]Tc	[44]Ru	[45]Rh	[46]Pd	[47]Ag	[48]Cd	[49]In	[50]Sn	[51]Sb	[52]Te	[53]I	[54]Xe
6 P	[55]Cs	[56]Ba	[57]La	[72]Hf	[73]Ta	[74]W	[75]Re	[76]Os	[77]Ir	[78]Pt	[79]Au	[80]Hg	[81]Tl	[82]Pb	[83]Bi	[84]Po	[85]At	[86]Rn
7 Q	[87]Fr	[88]Ra	[89]Ac	[104]Rf	[105]Db	[106]Sg	[107]Bh	[108]Hs	[109]Mt	[110]Ds	[111]Rg	[112]?		[114]?		[116]?	

[57]La	[58]Ce	[59]Pr	[60]Nd	[61]Pm	[62]Sm	[63]Eu	[64]Gd	[65]Tb	[66]Dy	[67]Ho	[68]Er	[69]Tm	[70]Yb	[71]Lu
[89]Ac	[90]Th	[91]Pa	[92]U	[93]Np	[94]Pu	[95]Am	[96]Cm	[97]Bk	[98]Cf	[99]Es	[100]Fm	[101]Md	[102]No	[103]Lr

I	Fr^+										
II		Ra^{2+}				Cf^{2+} Es^{2+} Fm^{2+} Md^{2+} No^{2+}						
III			Ac^{3+}	U^{3+} Np^{3+} Pu^{3+}	Am^{3+} Cm^{3+} Bk^{3+} Cf^{3+} Es^{3+} Fm^{3+} Md^{3+} No^{3+} Lr^{3+}							
IV				Th^{4+} Pa^{4+} U^{4+} Np^{4+} Pu^{4+} Am^{4+} Cm^{4+} Bk^{4+} Cf^{4+}								
V				$Pa(V)$ UO_2^+ NpO_2^+ PuO_2^+ AmO_2^+								
VI				UO_2^{2+} NpO_2^{2+} PuO_2^{2+} AmO_2^{2+}								
VII				$Np(VII)$ $Pu(VII)$								

Actinides form hard cations

they strongly bind with hard electronegative atoms or anions
in that case Chemical Reactivity is driven by Ratio (charge / ionic radius)
(this gives **chemical analogues**)
in environmental waters with typically OH_2, HO^-, CO_3^{2-}, $H_2PO_4^{2-}$, $H_nSiO_4^{n-}$, SO_4^{2-}, $S_2O_3^{2-}$, F^-
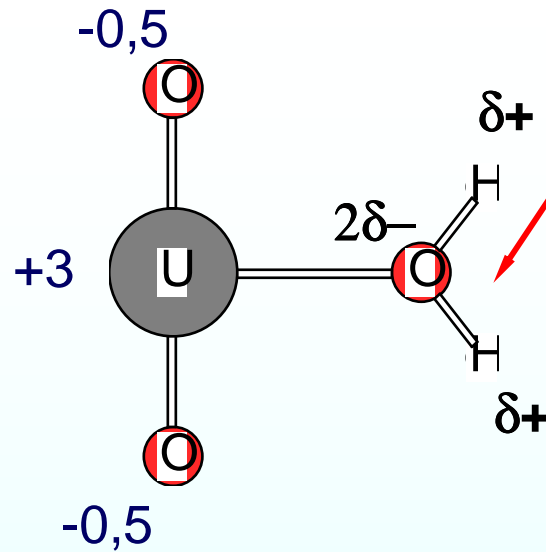
However, very positive charges **polarize** water
this promotes **Hydrolysis** (of cations)
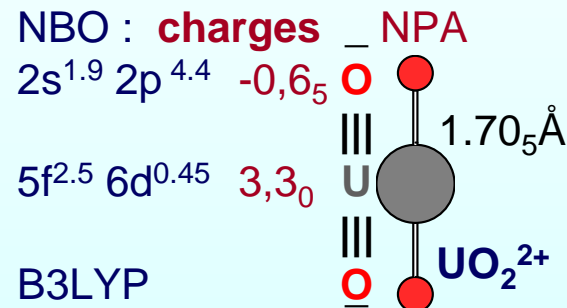even higher positive charge can promotes **charge transfer** (= **covalent** binding)
as typically in UF_6, UO_2^{2+}...

Polarisation and Charge Transfer

Transfer of e⁻ from O^{2-} to U^{6+} results in the **covalent** U-O bond

-0,5

$\delta+$

Transfer of e⁻ inside the H_2O molecule induced by the charge of U
= **polarisation** of the H_2O molecule

+3   U $2\delta-$ O

$\delta+$

-0,5

NBO : **charges** _ NPA

$2s^{1.9}\ 2p^{4.4}$ -0,6₅ O

1.70₅Å

$5f^{2.5}\ 6d^{0.45}$ 3,3₀ U

B3LYP   O UO_2^{2+}

DFT calculations by P.Vitorge and C.Marsden

Quantum mechanics give an insight of electronic configuration, specially for covalent binding.

Actinyl ions

AnO$_2^+$ and AnO$_2^{2+}$ are the stable chemical forms of most An(V) and An(VI) ions

An-O is probably a triple bond
the linear geometry is attributed to f electrons

Conversely **Th**O$_2$ is not linear and it is rather a d-like element.

U^{6+}(aq) is hydrolysed 4 times: U^{6+} + 2 H$_2$O $\rightarrow$ **UO$_2^{2+}$** + 4 H$^+$

**What are the structures
of Pa(V) aquo ions ?**   Pa^{5+} + n H$_2$O $\rightarrow$? + m H$^+$
B.Siboulet, P.Vitorge, C.Marsden (to be submitted)

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I	Fr$^+$								
II	Ra^{2+}					Cf^{2+} Es^{2+} Fm^{2+} Md^{2+} No^{2+}			
III	Ac^{3+}	U^{3+} Np^{3+} Pu^{3+}	Am^{3+} Cm^{3+} Bk^{3+} Cf^{3+} Es^{3+} Fm^{3+} Md^{3+} No^{3+}	Lr^{3+}					
IV	Th^{4+} Pa^{4+}	U^{4+} Np^{4+} Pu^{4+}	Am^{4+} Cm^{4+} Bk^{4+} Cf^{4+}						
V	Pa(V)	UO$_2^+$ NpO$_2^+$ PuO$_2^+$ AmO$_2^+$							
VI		UO$_2^{2+}$ NpO$_2^{2+}$ PuO$_2^{2+}$ AmO$_2^{2+}$							
VII		Np(VII) Pu(VII)							

Hydrolysis Constants for Ions of the last line of the Periodic Table

$$M(OH)_{i-1}^{z+1-i} + H_2O \leftrightharpoons M(OH)_i^{z-i} + H^+$$
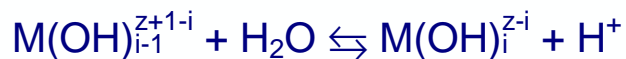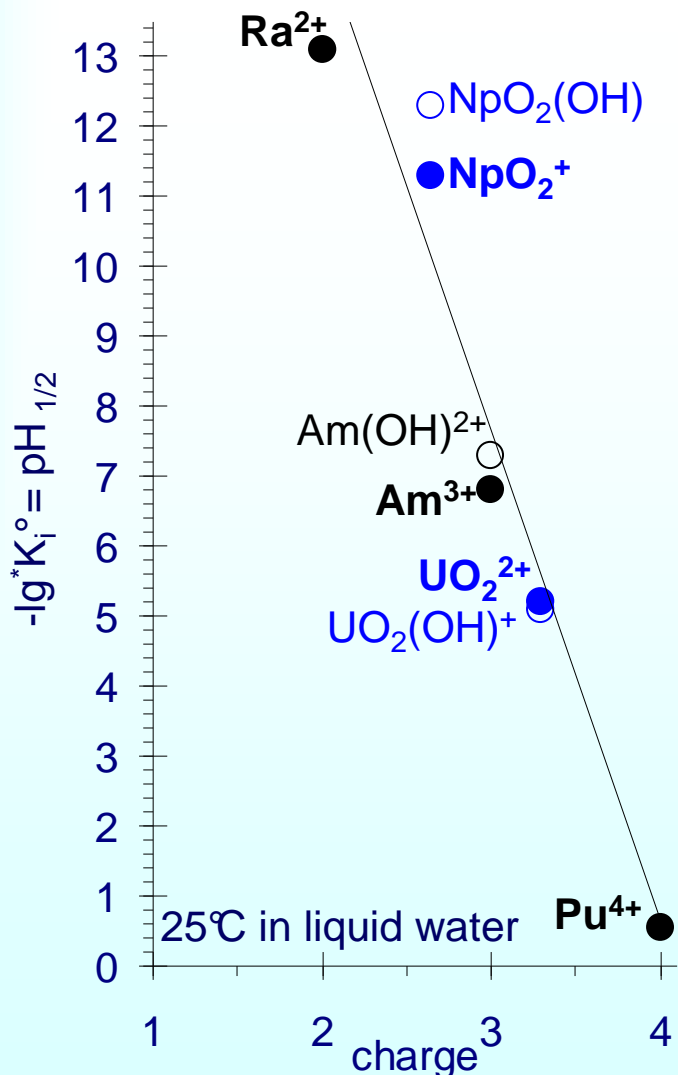
$$^*K_i^o = \frac{|M(OH)_{i-1}^{z+1-i}|}{|M(OH)_i^{z-i}|\,|H^+|} \quad \begin{array}{l}\text{for i = 1 or 2, |X| is X activity} \\ M^{z+} = Ra^{2+},\ Am^{3+},\ Pu^{4+}, \\ \qquad NpO_2^+ \text{ or } UO_2^{2+}.\end{array}$$

$$\Delta_r G^\circ_{m,i} = -R\,T\,\ln(^*K_i^o)$$
$$R\,T\,\ln(10) = 5.71 \text{ kJ.mol}^{-1} \text{ at } 25°C$$

Plot: $-lg\,^*K_i^\circ = pH_{1/2}$ (y-axis, 0 to 13) versus charge (x-axis, 1 to 4). Data points: Ra^{2+} (~13), $NpO_2(OH)$ (open circle, ~12), NpO_2^+ (filled, ~11.2), $Am(OH)^{2+}$ (open circle, ~7.3), Am^{3+} (~6.8), UO_2^{2+} (~5.3), $UO_2(OH)^+$ (~5.1), Pu^{4+} (~0.6). 25°C in liquid water.

The hydrolysis constants are correlated to the atomic charges;
nevertheless classical electrostatics is not enough to model aqueous chemistry:
correlations are not explanations
actually, several physical phenomena are driven by charges...

Charge is the atomic charge of the metal atom from quantum calculations *(B.Siboulet, P.Vitorge, C.Marsden)*, typically the charge of U in UO_2^{2+} or in $UO_2(OH)^+$.

lgβ₁ *vs.* pKa Correlation for Actinide Ions.

V. Phrommavanh, M. Descostes, P. Vitorge, C. Beaucaire, J.P. Gaudet

$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$
$$Ka = ([CO_3^{2-}][H^+]) / [HCO_3^-]$$

$$CO_3^{2} + UO_2^{2+} \rightarrow UO_2CO_3$$
$$\beta_1 = ([CO_3^{2-}[UO_2^{2+}]) / [UO_2CO_3]$$
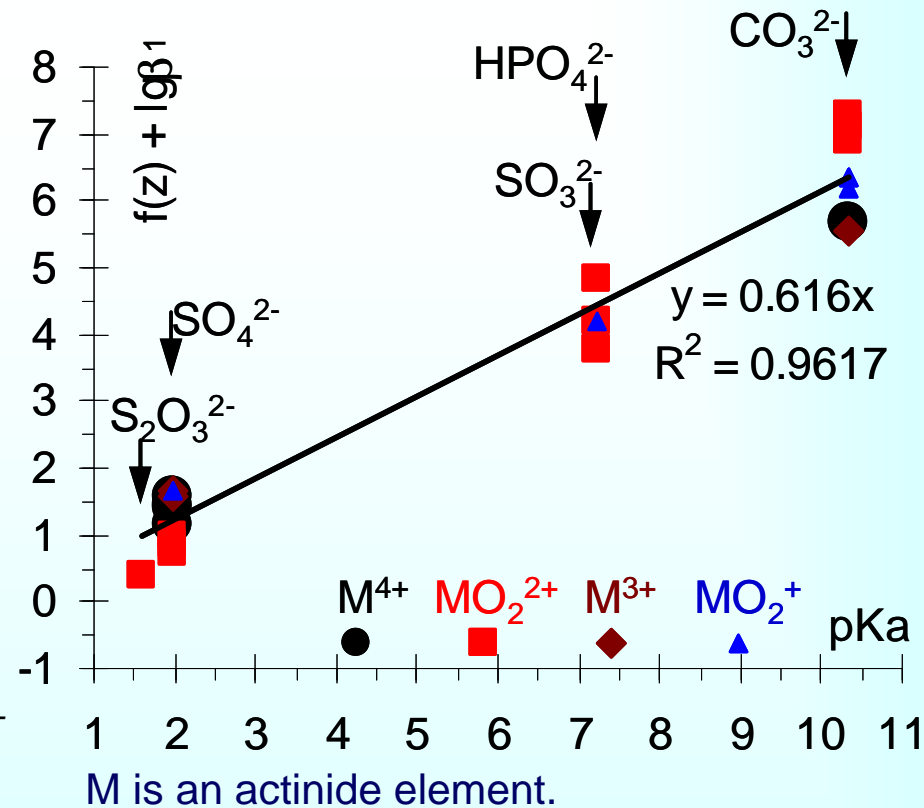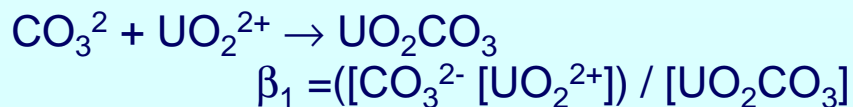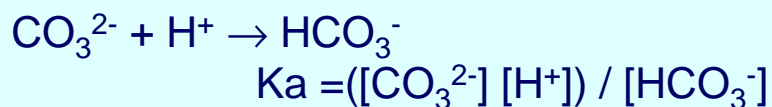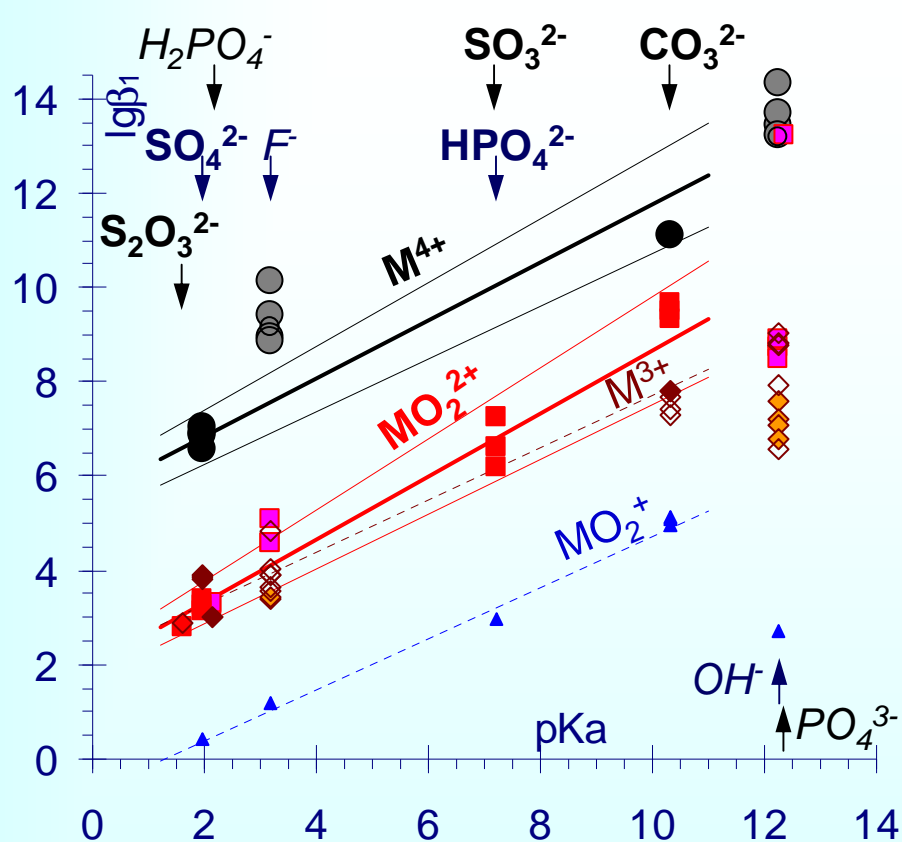
The values of the equilibrium constant are taken form the NEA TDB reviews.

M is an actinide element.

V. Phrommavanh, *et al.* PA3-9 at MIGRATION'05. September 18-23, 2005.Avignon, France

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Be^{2+} and UO_2^{2+}

U, Np, Pu and Am Pourbaix' (E_{SHE},pH) Diagrams

e^- notation

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Molecular Modelling (on PC's)

Hydrolysis of Be²⁺ and UO₂²⁺

$$Hydrolysis\ of\ Be^{2+}\ and\ UO_2^{2+}$$
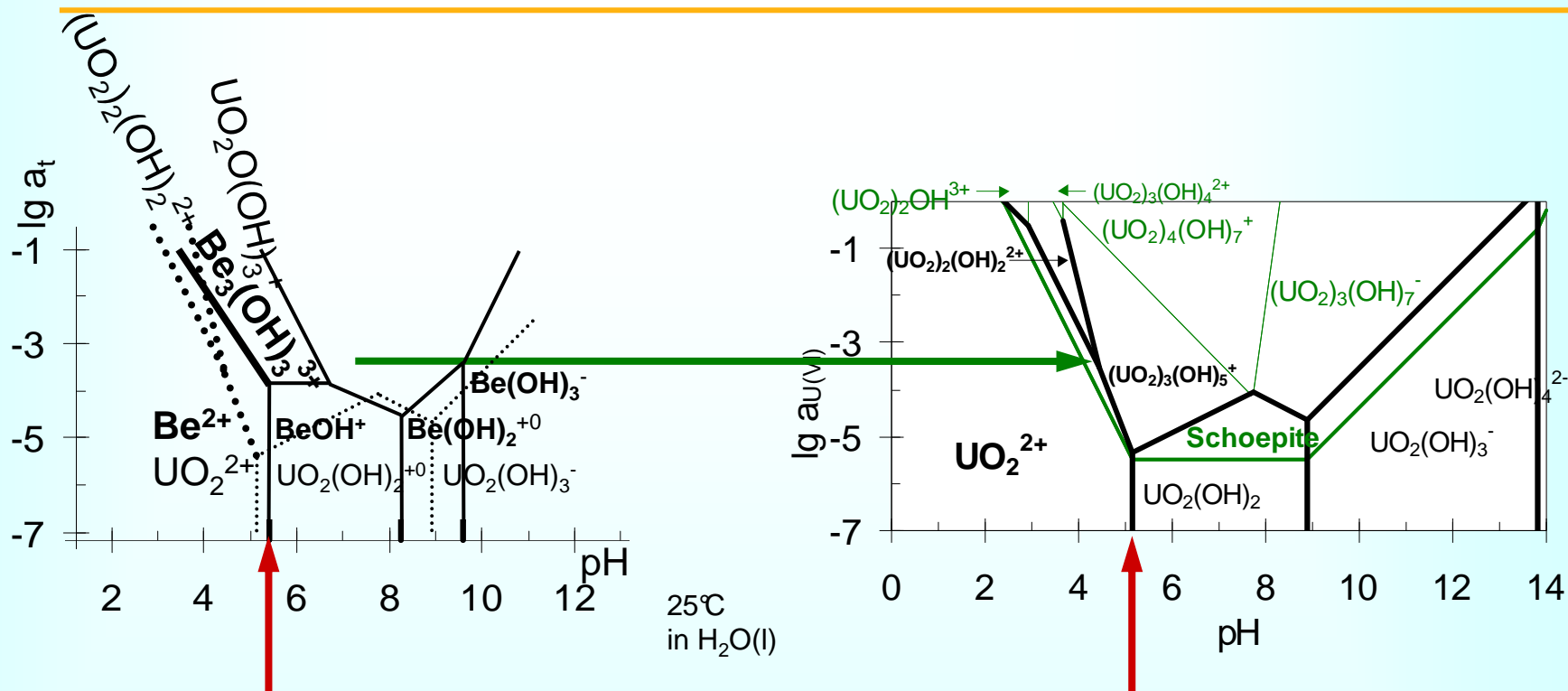
"Speciation" depends on

Chemical Reactivity (as reflected in the numerical value of Equilibrium Constant K) and chemical conditions (here pH and $[M]_t$, M = Be or U(VI))

$pH_{1/2}$ (position of the line):
pH at the half point of Reaction $M^{z+} + H_2O \rightarrow MOH^{z-1} + H^+$ $K = \dfrac{[MOH^{z-1}]\,[H^+]}{[MOH^{z-1}]}$
namely for $[M^{z+}] = [MOH^{z-1}]$: **$lgK = lg[H^+]_{1/2}$**

Slope of the line = -j/(i-1) for Reaction $i\ M^{z+} + j\ H_2O \rightarrow M_i(OH)_j^{\,iz-j} + j\ H^+$

Np and Pu Hydrolysis (Pourbaix' Diagrams)

Chemical analogues at the same oxidation state;
but **Geochemical non-analogues** (in similar redox conditions)
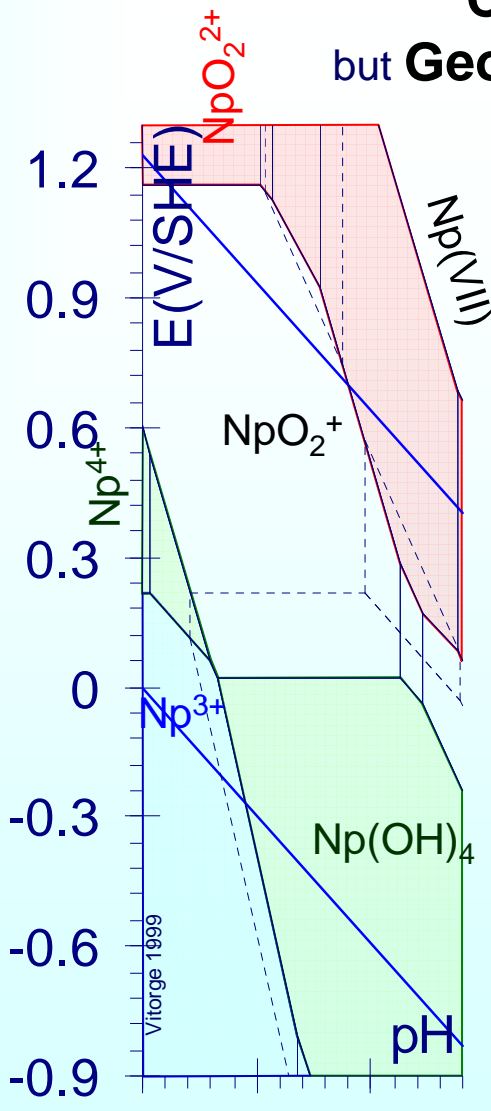
For the same oxidation state (of Np and Pu), the shape of the domains are similar.

This analogy is typically used for Pu(VII) from Np(VII), and conversely Pu(V) from Np(V).

The stability of each oxidation state is specific for each element: the vertical lengths and positions of the domains are different (for Np and Pu).

25°C
I = 0
<10^{-10} M
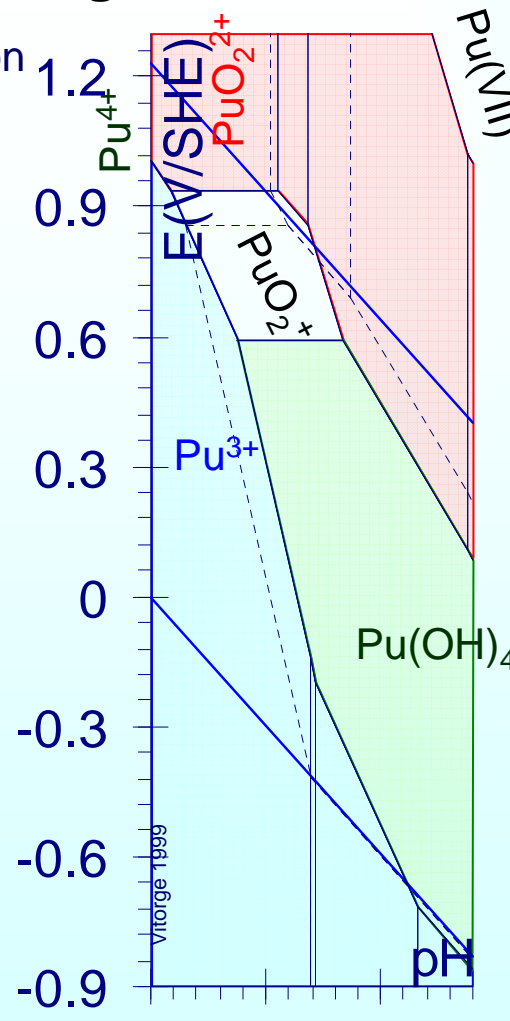
Notation e⁻
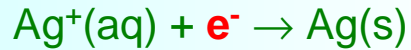
Ag⁺(aq) + **e⁻** → Ag(s)   Notation for Electrochemistry

H⁺(aq) + **e⁻** → 0.5 H₂(g)   Standard Hydrogen Electrode (SHE)

Ag⁺(aq) + 0.5 H₂(g) → Ag(s) + H⁺(aq)   Notation for Thermodynamics

ox + n **e⁻** → red   Corresponding equilibrium constant $K = \dfrac{[red]}{[ox]\, a_{e^-}^n}$

$\Delta_r G_{ox/red} = -R\, T\, \ln K_{ox/red} = -n\, F\, E_{ox/red}$

$\Delta_f G_e = R\, T\, \ln a_e = -F\, E$ **Corresponding e⁻ activity**

$0 = \Delta_r G_{SHE} = 0.5\, \Delta_f G_{H_2(g)} - \Delta_f G_{H^+(aq)} - \Delta_f G_{e^-}$, also $0 = \Delta_f G_{H_2(g)}$ (Reference State)

when $0 = \Delta_f G_{H^+(aq)}$ $\Delta_f G_{e^-} = 0$

similarly $\Delta_f H_{e^-} = 0$

and $S_{e^-} = 0.5\, S_{H_2(g)} - S_{H^+(aq)}$

➔ **e⁻** is not **e⁻(aq)**, neither **e⁻(s)**, it is rather **e⁻_SHE**

➔ Ag⁺(aq) → Ag⁺(s)   Actual mechanism[1] ?
however this notation does not include charge balance in each phase

[1]Eliezer Gileadi. Chem.Phys.Letters 393 (2004) 421–424

U, Np, Pu and Am Hydrolysis (Pourbaix' Diagrams)

Most usual order for the stabilities of actinide complexes and hydroxides:

$$An^{4+} \gg AnO_2^{2+} > An^{3+} \gg AnO_2^{+}$$

Precipitated solids ($[An]_t\ 10^{-5}$ mol.L^{-1}) not the high temperature solids:

$$MO_2(cr),\ MO_{2+x}(s),\ M_2O_5(cr)$$

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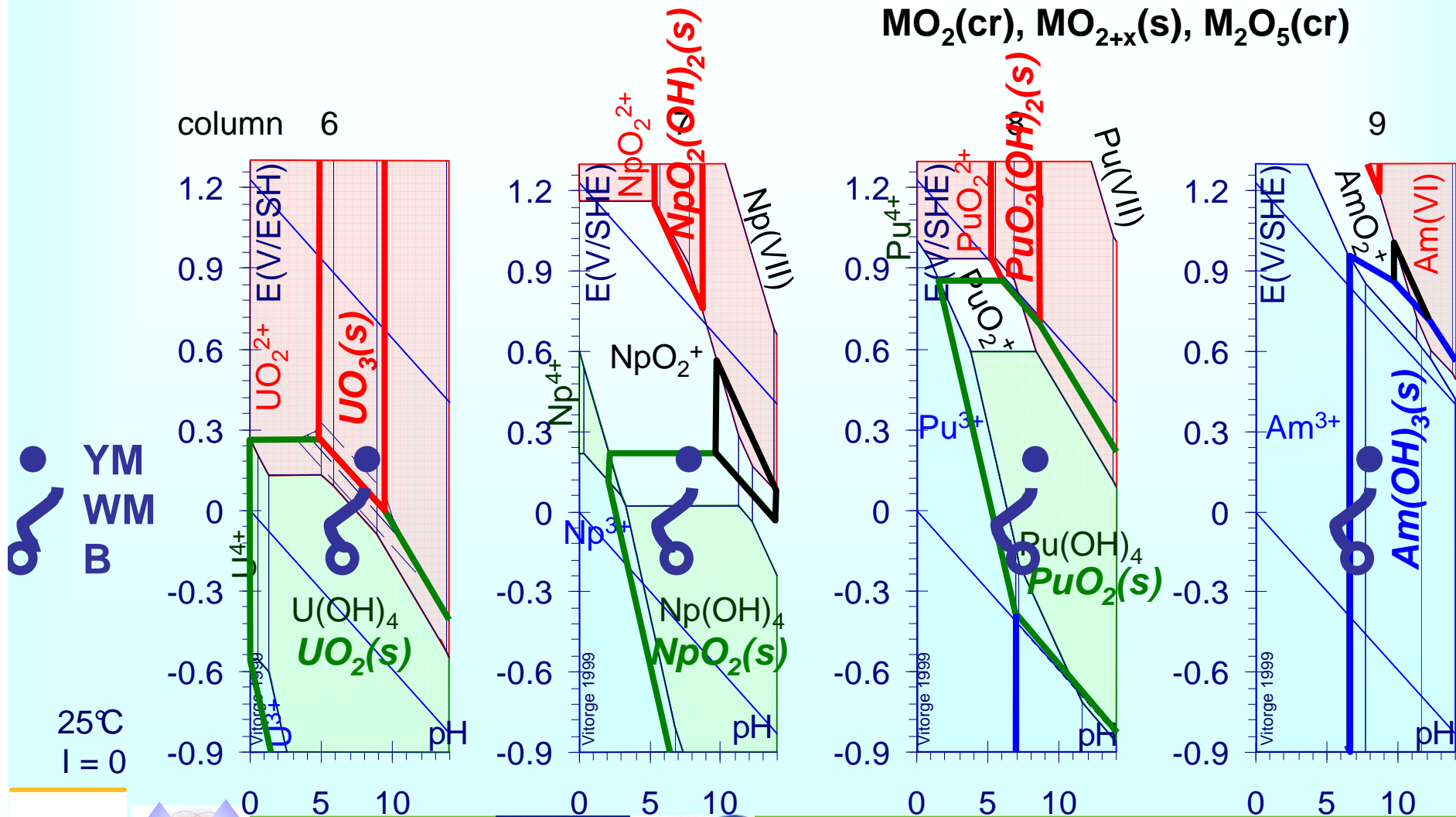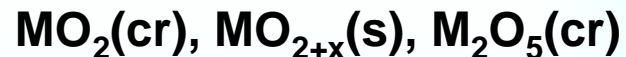
Complexes

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Carbonate complexes of actinides (0.01 atm CO$_2$)

U, Np, Pu and Am Pourbaix' Diagrams

Most usual order for the stabilities of actinide complexes and hydroxides::

$$(An^{4+} ? >) \; AnO_2^{2+} > An^{3+} > AnO_2^+$$
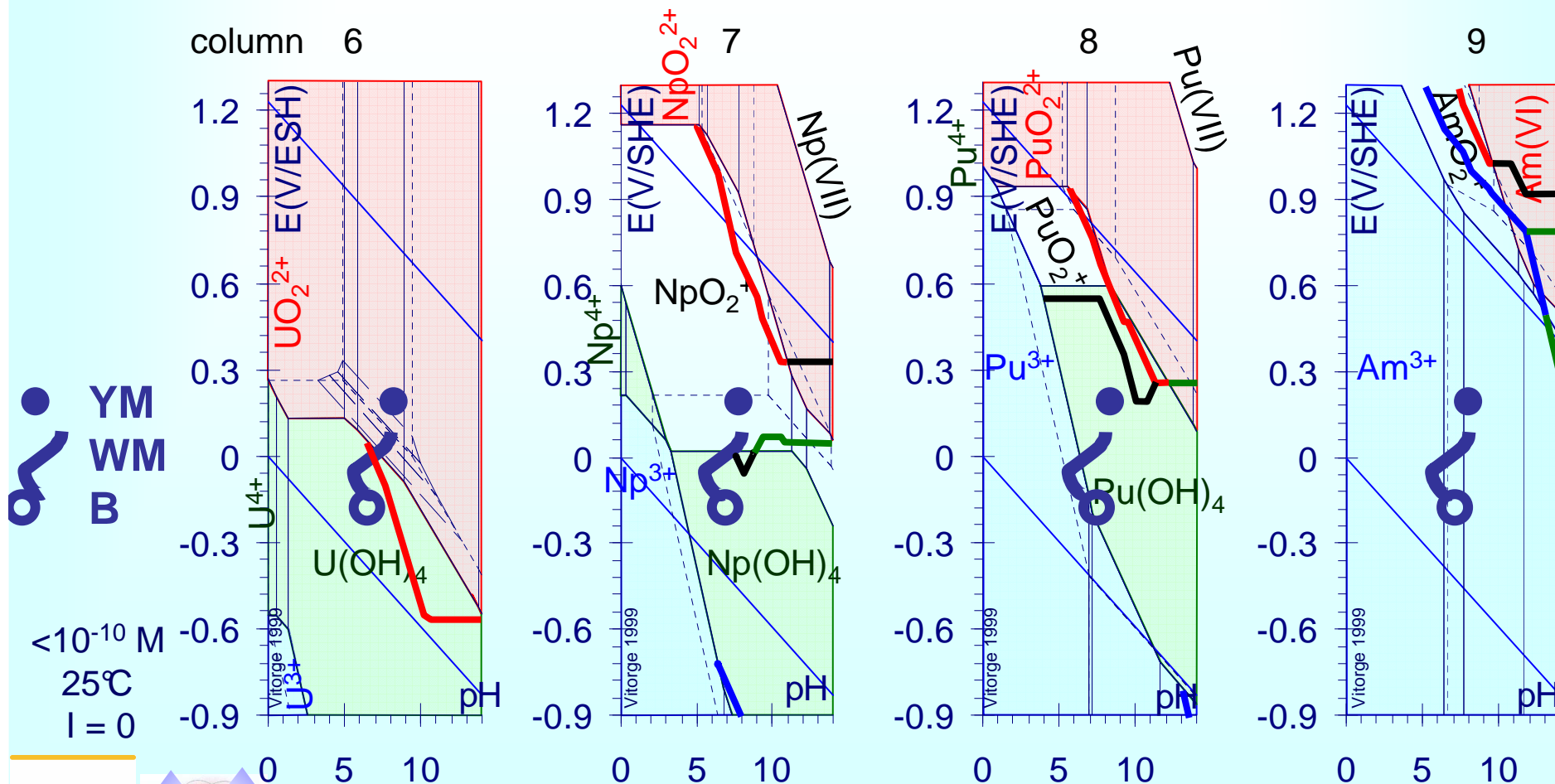
Carbonate complexes of Np and Pu (0.01 atm CO$_2$)

Sulfate complexes of M^{3+} T.Vercouter, P.Vitorge

$$An^{3+} + SO_4^{2-} \rightarrow AnSO_4^+$$
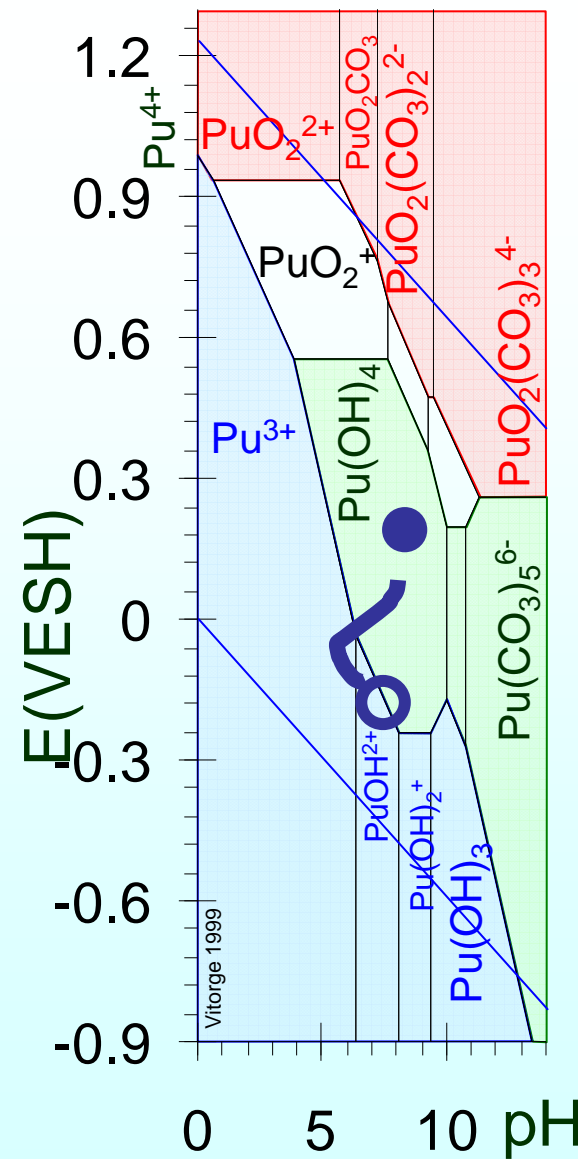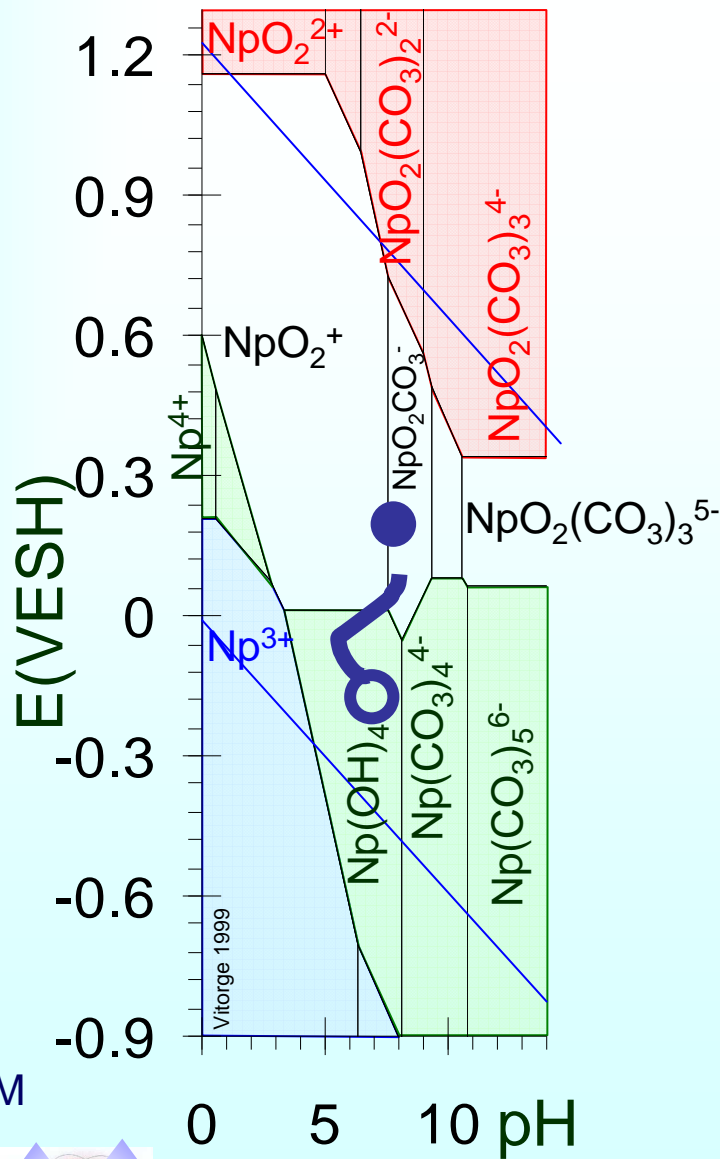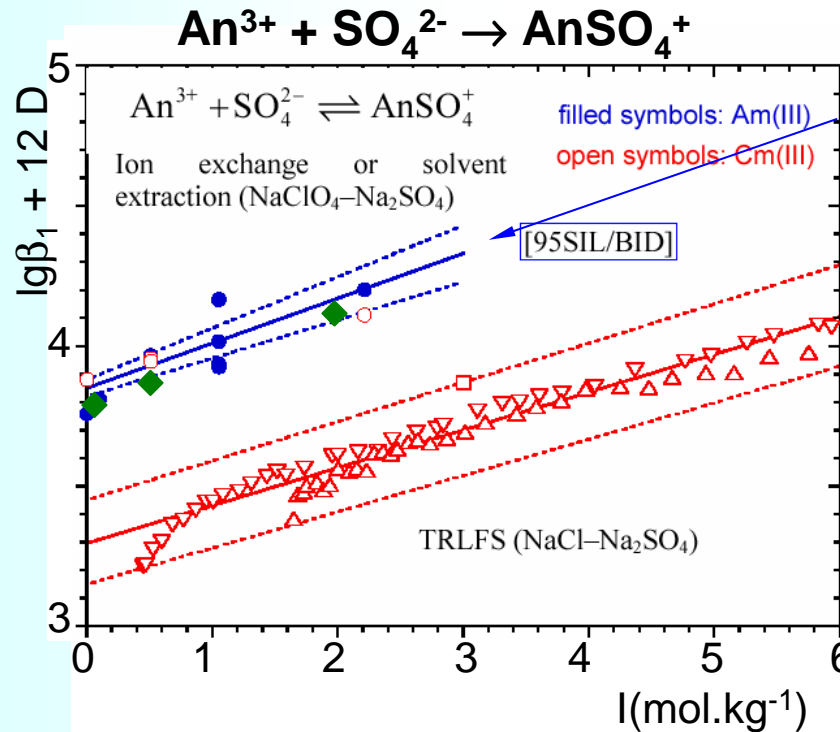
NEA 1995[1] Ion exchange or solvent extraction ($NaClO_4$-Na_2SO_4)

NEA 2003[2] from **TRLF** ($NaCl$-Na_2SO_4) data[3]

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$_{in}$] = Constant $(a_{H2O})^n$

TRLFS recent study[4] rather confirms NEA 1995 selection for Eu ($NaClO_4$-Na_2SO_4)

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

[2]R. 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

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

[4]T.Vercouter, P.Vitorge, B.Amekraz, E.Giffaut, S.Hubert, C.Moulin, Inorg. Chem., 2005, 44, 16, 5833-5843

Orders of magnitude for $\Delta_f G°$ and $\Delta_r G°$

For aqueous solution chemistry, the best $\log_{10}K$ uncertainty can be ± 0.01, i.e. $\Delta_r G \pm 0,06$ kJ.mol^{-1}.
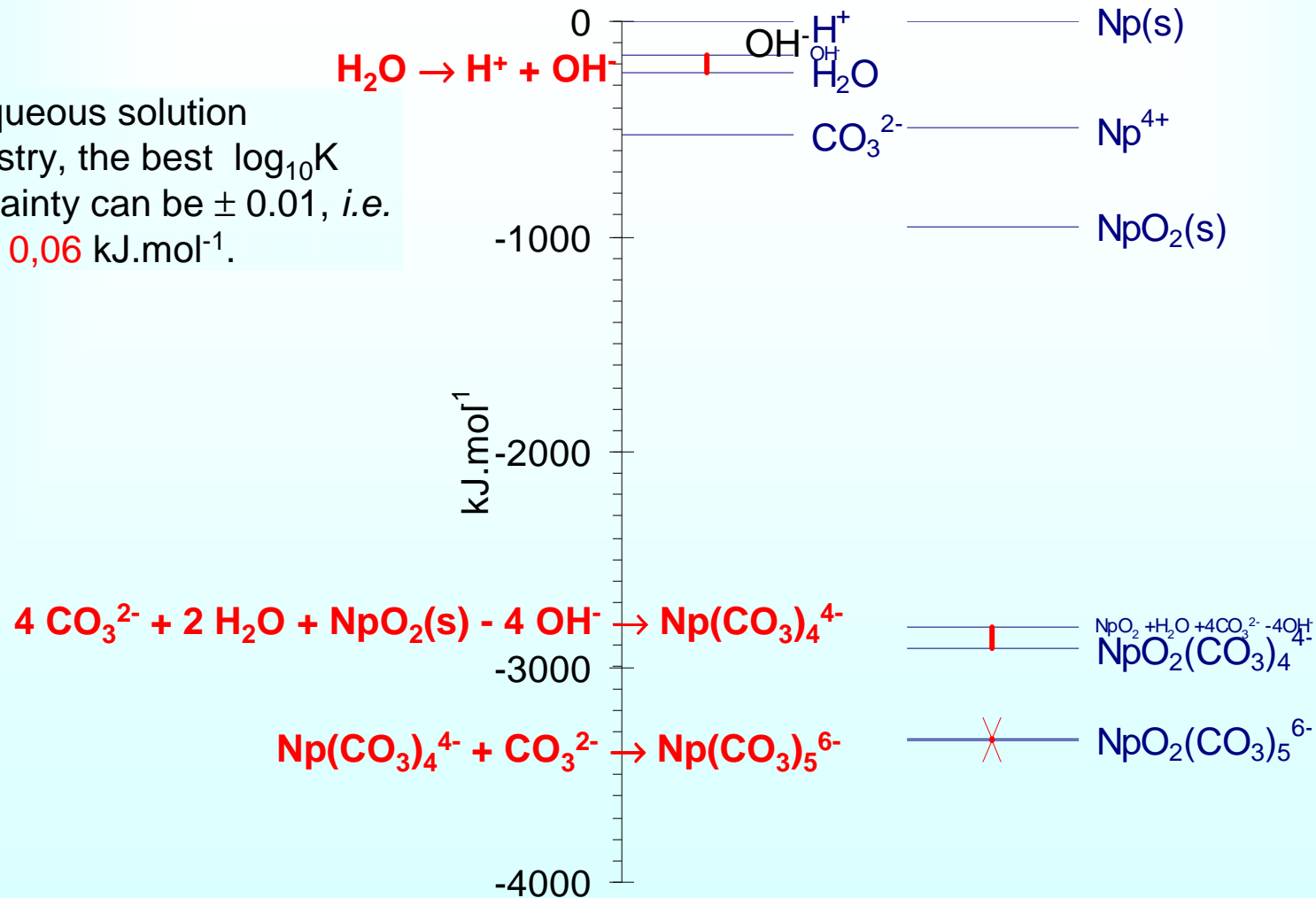
$H_2O \rightarrow H^+ + OH^-$

$4\ CO_3^{2-} + 2\ H_2O + NpO_2(s) - 4\ OH^- \rightarrow Np(CO_3)_4^{4-}$

$Np(CO_3)_4^{4-} + CO_3^{2-} \rightarrow Np(CO_3)_5^{6-}$

kJ.mol^{-1}

0

-1000

-2000

-3000

-4000

$OH^-\ H^+$
OH
H_2O
CO_3^{2-}

Np(s)

Np^{4+}

$NpO_2(s)$

$NpO_2 + H_2O + 4CO_3^{2-} - 4OH^-$
$NpO_2(CO_3)_4^{4-}$

$NpO_2(CO_3)_5^{6-}$

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> ***Measurements***
>
> **M^{3+}/CO_3^{2-}**
>
> **M^{4+}/CO_3^{2-}**

Molecular Modelling (on PC's)

Experimental techniques

C.Moulin, B. Amekraz

"Speciation" : determination of the different forms under which a chemical agent is present in a media. Each form is defined by :
- its chemical composition and/or
- its detailed physics characteristics and/or
- its biochemical and toxicological effects

Important not only to have the concentration but to know the speciation in order to evaluate the impact

Need for spectrometric methods :

NMR, EXAFS,   ES-MS,   TRLIF, HPLC-ICP/MS

10^{-2} M 10^{-5}M 10^{-8}M

Principles for measuring equilibrium constants

- Checking **Mass Action Law** by using physical measurements varying with "Speciation"
  - = checking the stoichiometric coefficients of the equilibrium (sensitivity analysis)
  - = and measuring K

- Requirements:
  - Definition of the system (limits, **number of independent concentrations** / reactions)
  - Ideal system ("**constant ionic strength, I**")
  - Definition of the Standard State (pure solvent, typically pure water, or any constant I)
    - (activity coefficients:
    - empirical **SIT formula** and corresponding symmetric mixing rule = extended DH.. +vdW)
  - Ensemble (n_i, P, T) since P, T and c_i are intensive variables ($\mu = \mu° + R\,T\,\ln(c_i/c_i°)$)
    - consequently Equilibrium Constants vary with γ_i, P and T
    - Concentrations units are linked to the Standard Sate:
      - **Molality** (mol/kg of solution –solution is not solvent-) is an intensive concentration unit
        - while Molarity (mol.L^{-1}), mole fraction (Mixtures), surface concentrations... are not

- Solutions are not Mixtures (for Thermodynamics)
  - different standard states (the pure components / 1 component = the solvent)
  - different concentration units (mole fraction / mole per quantity of matrix)
  - coprecipitation or solid solutions = solutions
    - solubility of solid solutions = a 2 advancement variable reaction (set of 2 equations)
      - (non stoichiometric) dissolution of the matrix + the associated ionic exchange
        - including sorption (see Jacques Ly's lecture) providing known m/V

- Bibliography

Carbonate complexes of M^{3+} (M = Eu, Am and Cm)

Vercouter et al. 2001

● (blue)	● (red)	● (green)	Eu
□ (blue)	□ (red)	□ (green)	Am
✳ (blue)	✳ (red)	✳ (green)	Cm

Robouch (1987)[1] ——
NEA TDB (1995)[2] ——
M^{3+} NEA TDB (2003)[3] - - - - -

MCO_3^+

$M(CO_3)_2^-$

$M(CO_3)_3^{3-}$

25℃   I (mol.kg^{-1})

K_i is the constant of Equilibrium

$$M(CO_3)_{i-1}^{5-2i} + CO_3^{2-} \rightarrow M(CO_3)_i^{3-2i}$$
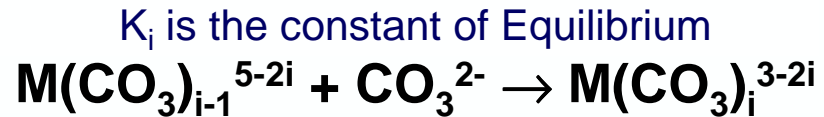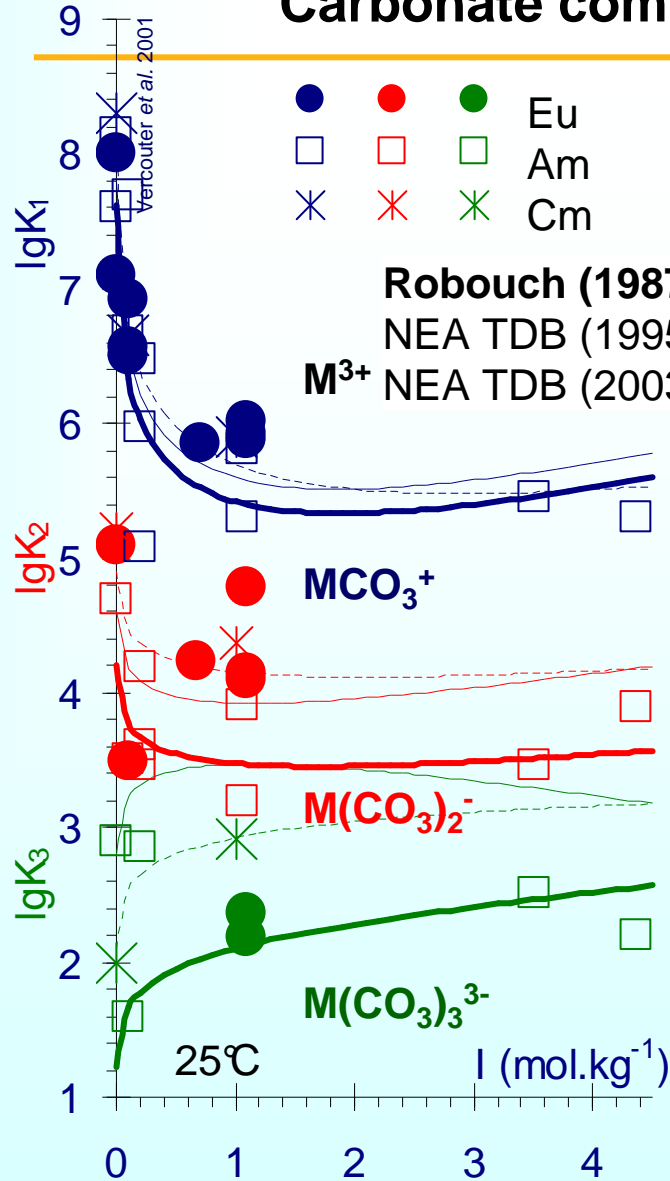
➔ **Differences between Eu, Am and Cm are less than experimental accuracy**

➔ Consistency in stability data from different laboratories is obtained only for MCO_3^+

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),

[1]P.Robouch Thèse Univesité L.Pasteur, Strasbourg (France) 1987
[2]R.Silva *et al.* Chemical Thermodynamics of Americium NEA, Paris (France) 1995
[3]R.Guillaumont *et al.* Update on the Chemical Thermodynamics of… NEA, Paris (France), Elsevier Ed. 2003

Eu³⁺ / HCO₃⁻ / CO₃²⁻ / HO⁻

T.Vercouter *et al.*

LaC**O₃O**H(H₂O)₅
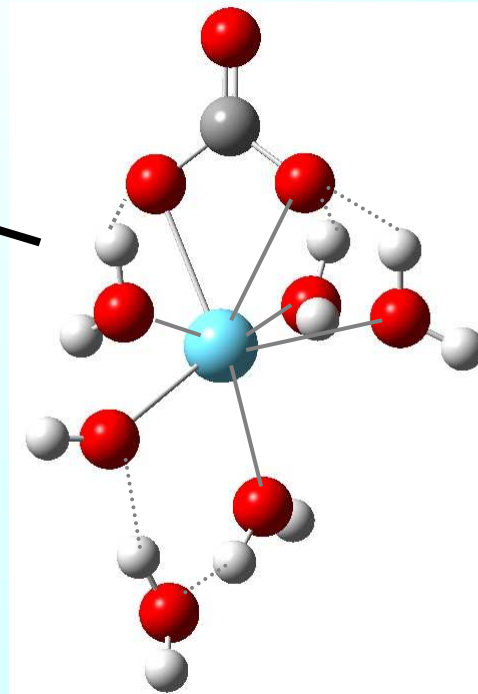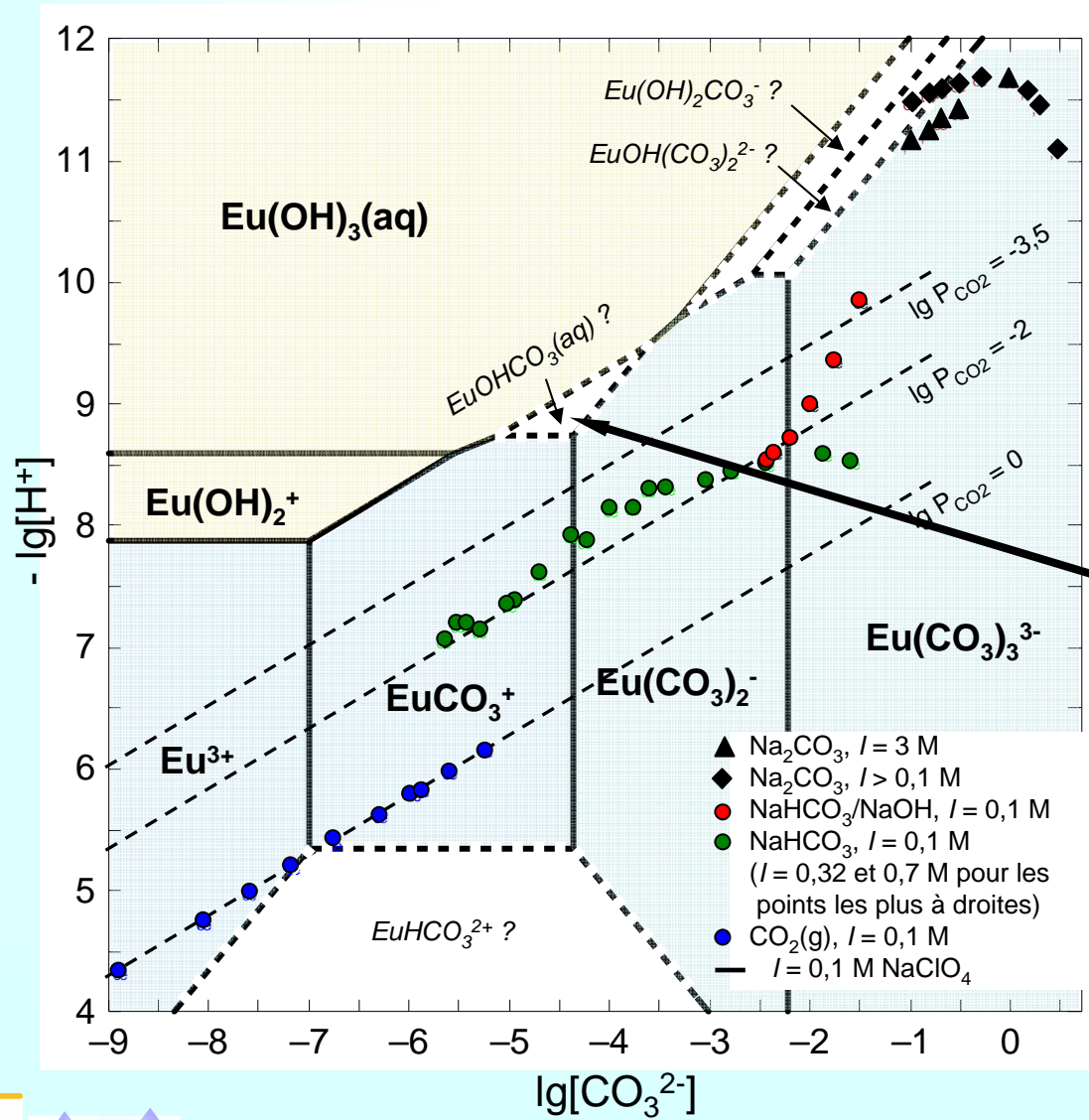
Limiting carbonate complex of Eu(III)
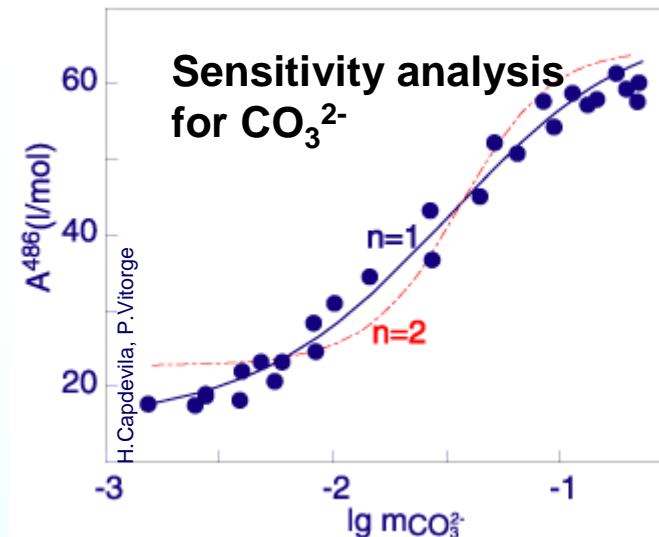
T.Vercouter *et al.*

Solubility study

$$NaEu(CO_3)_2(s)$$
$$\downarrow$$
$$Eu(CO_3)_i^{3-2i} + Na^+ + (2-i)CO_3^{2-}$$

Time **R**esolved **L**aser **F**luorescence **S**pectra

lg $[CO_3^{2-}]$

Sensitivity analysis

- 3 comp
- 4 comp
- × Na2CO3 I=3
- ■ Na2CO3 I>0,1
- ◆ HCO3/CO3
- ▲ NaHCO3
- ● 100% CO2

Slope 2 = i - 2

$Eu(CO_3)_4^{5-}$ in K^+ aqueous solutions

Slope 1 = i - 2

$Eu(CO_3)_3^{3-}$ in Na^+ aqueous solutions
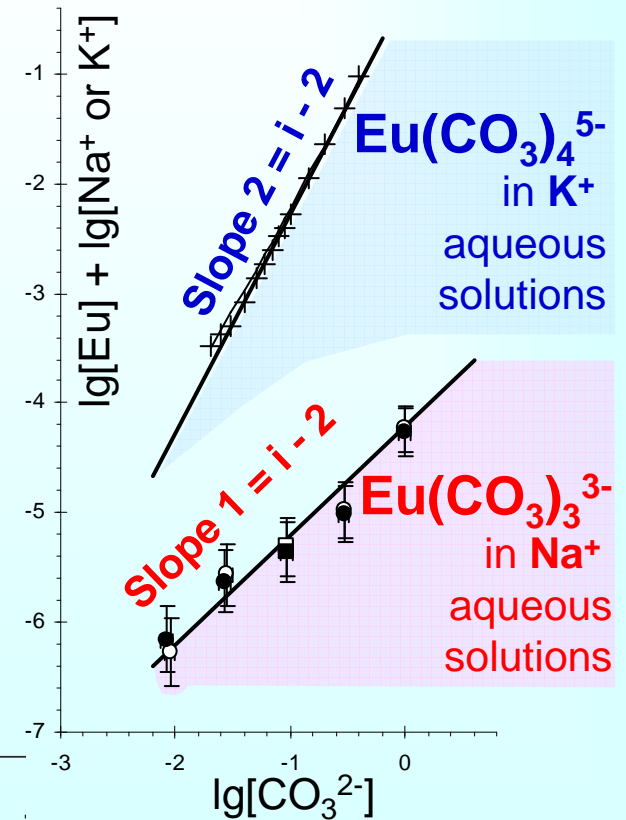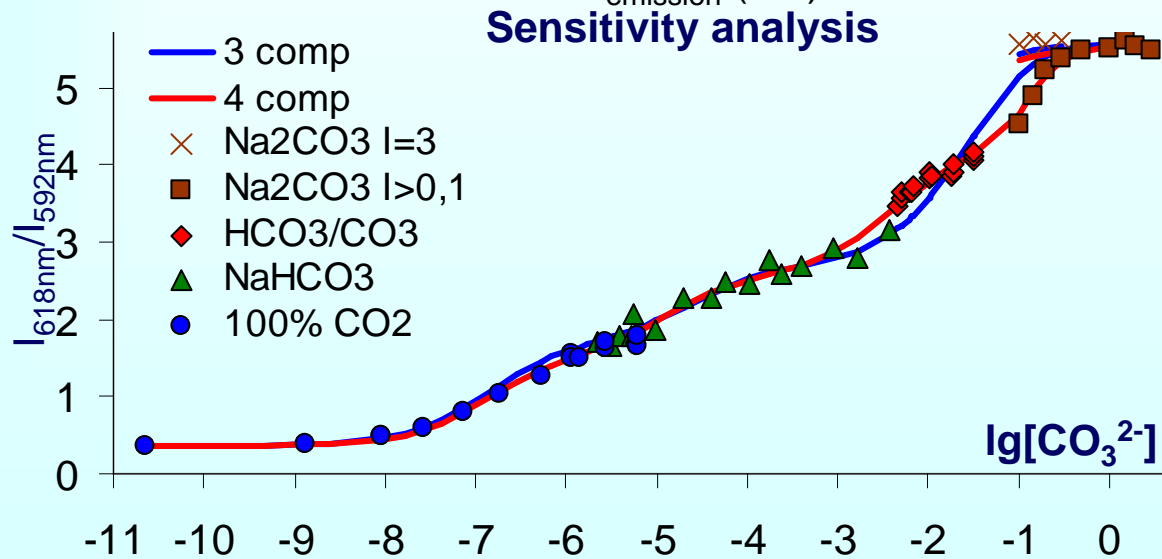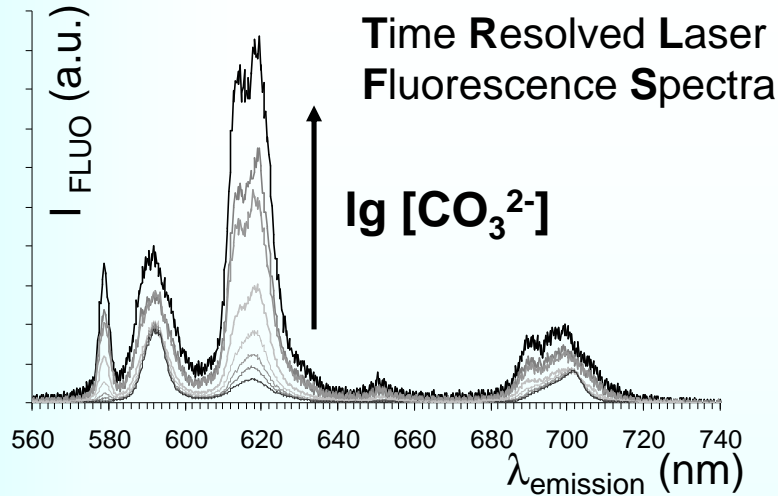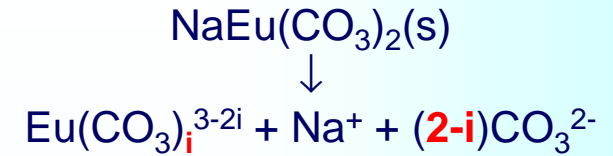
Spectrophotometric study $\quad Pu(CO_3)_4^{4-} + CO_3^{2-} \leftarrow Pu(CO_3)_5^{6-}$

during titration

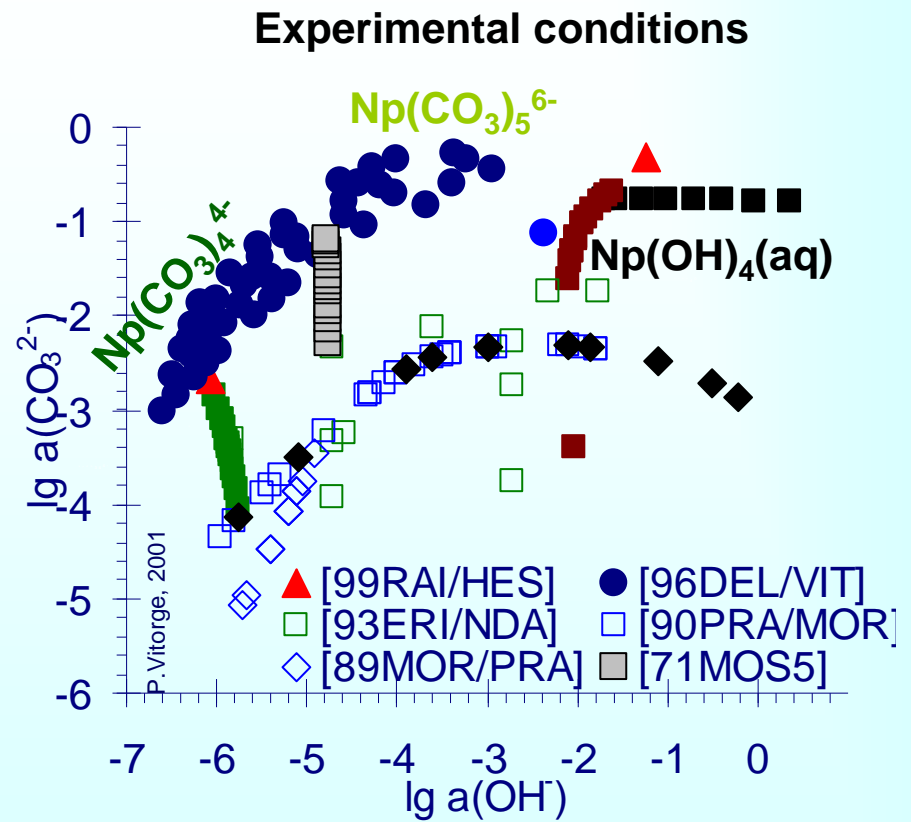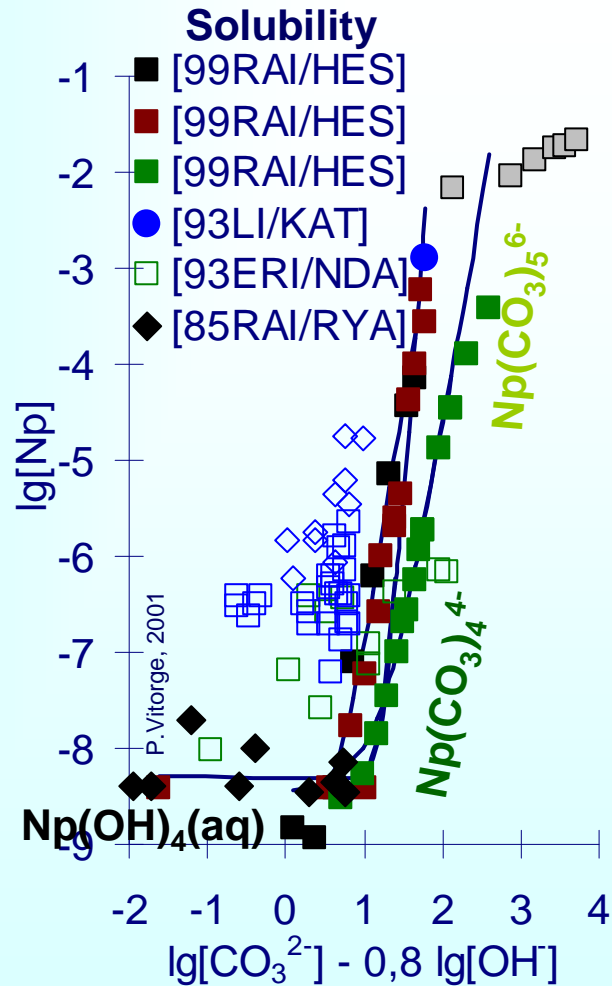$$CO_3^{2-} + CO_2(g) + H_2O$$
$$\rightarrow 2\ HCO_3^-$$
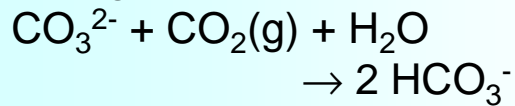
at 25°C
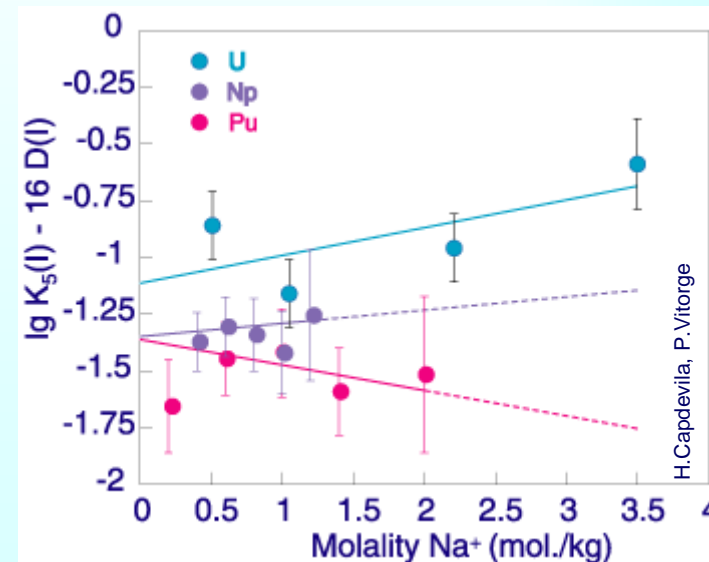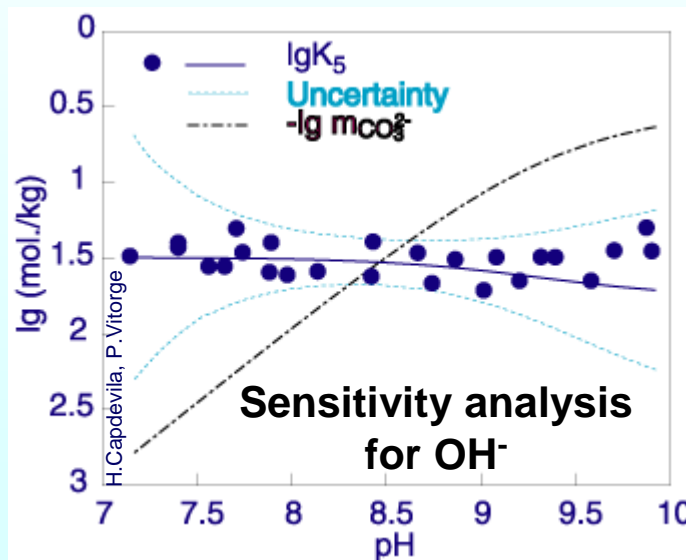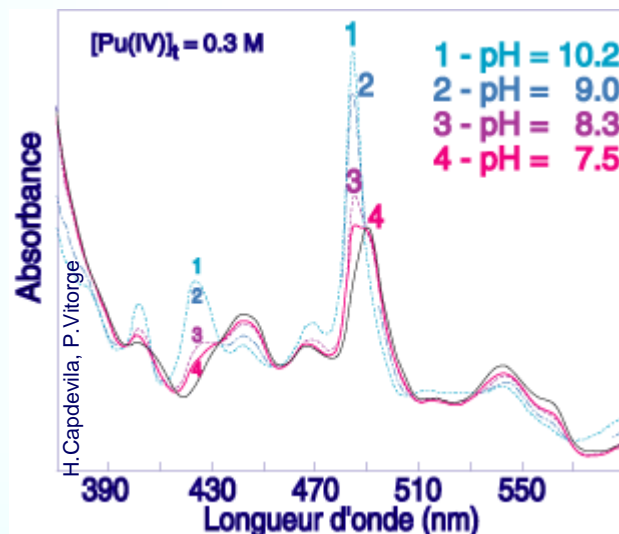
H.Capdevila, P.Vitorge, E.Giffaut, L.Delmau. Radiochim. Acta 74, 93-98 (1996)

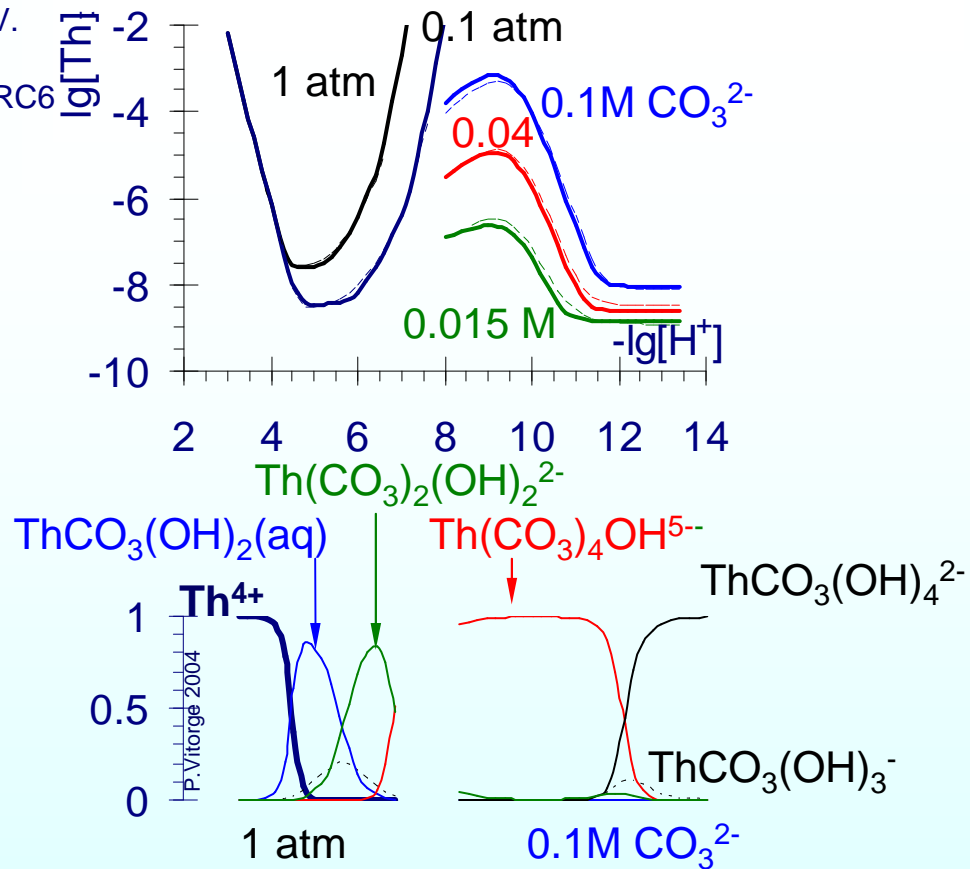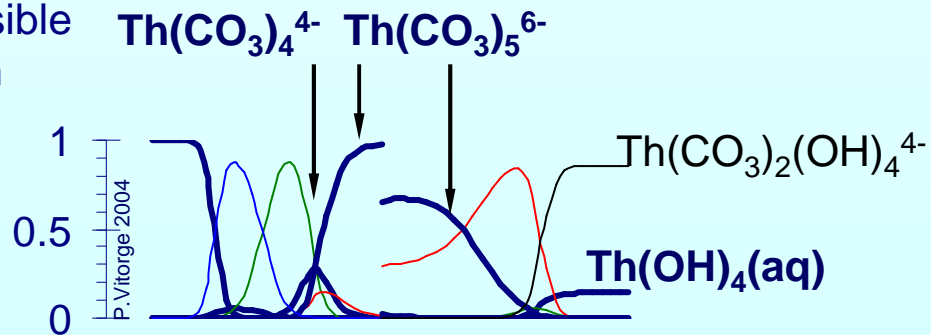# Pu(IV) solubility in carbonate media

Other possible species:
$Pu(CO_3)_2(OH)_3^{3-}$
$Pu(CO_3)_2(OH)_2^{2-}$
$Pu(CO_3)_3^{2-}$

Solubility

Experimental conditions

$Pu(CO_3)_5^{6-}$

$lg[Pu]_t$

$Pu(CO_3)_4^{4-}$

$Pu(OH)_4(aq)$

$lg[CO_3^{2-}] - lg[OH^-]$

P. Vitorge 2001

$lg[CO_3^{2-}]$

$Pu(CO_3)_5^{6-}$

$Pu(CO_3)_4^{4-}$

$Pu(OH)_4(aq)$

$lg[OH^-]$

P. Vitorge, 2001

$$PuO_2(s) + 2H_2O + \mathbf{4}CO_3^{2-} \rightarrow \mathbf{Pu(CO_3)_4^{4-}} + \mathbf{4}OH^-$$

Np(IV) solubility in carbonate media

Solubility
- [99RAI/HES]
- [99RAI/HES]
- [99RAI/HES]
- [93LI/KAT]
- [93ERI/NDA]
- [85RAI/RYA]

Experimental conditions

$Np(CO_3)_5^{6-}$

$Np(CO_3)_4^{4-}$

$Np(OH)_4(aq)$

lg[Np]

$lg[CO_3^{2-}] - 0,8 \, lg[OH^-]$

P.Vitorge, 2001

lg a(CO_3^{2-})

lg a(OH^-)

[99RAI/HES]   [96DEL/VIT]
[93ERI/NDA]   [90PRA/MOR]
[89MOR/PRA]   [71MOS5]

Th solubility in carbonate media

Another possible interpretation

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

$M(CO_3)_i(OH)_j^{(4-2i-j)+}$	$lg\beta^o_{i,j}(Pu)$[1]	$lg\beta_{ij}(Th)$[2]	$lg\beta_{ij}(Th)$[3]
M^{4+}			
MOH^{3+}	**13.2**		<8.7
$M(OH)_4(aq)$	**<47.9**		27.4
$MCO_3(OH)_2(aq)$	<<42	27.0	26.9
$MCO_3(OH)_3^-$	<<47.7	34.8	
$M(CO_3)_2OH^-$	<40.5		<25.6
$MCO_3(OH)_4^{2-}$	<<51.8	37.4	**<34**
$M(CO_3)_2(OH)_2^{2-}$	<46.2	33.3	33.3
$M(CO_3)_3^{2-}$	<37.6		<22.6
$M(CO_3)_2(OH)_3^{3-}$	<50.5		<36.6
$M(CO_3)_3OH^{3-}$	<42		<31.4
$M(CO_3)_2(OH)_4^{4-}$			38.4
$M(CO_3)_3(OH)_2^{4-}$	<<41		<35.7
$M(CO_3)_4^{4-}$	**37**		27.4
$M(CO_3)_3(OH)_3^{5-}$	<<40.5		<39.5
$M(CO_3)_4OH^{5-}$	<<39	34.4	34.1
$M(CO_3)_3(OH)_4^{6-}$	<<38.5		<39.3
$M(CO_3)_4(OH)_2^{6-}$	<<37		<36.4
$M(CO_3)_5^{6-}$	**35.6**		31.5

[1] P.Vitorge, H.Capdevila. Radiochim. Acta 91, 623–631 (2003)
[2] M. Altmaier, V. Neck, Th. Fanghänel NRC6 2004- O3
[3] Another possible interpretation of experimental data from Ref.[2]

➔ Maximum possible stabilities estimated for Pu complexes[1] 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.

Contents

Actinides in the Periodic Table

Chemical analogues – MO_2^{z+} – HO..H – Atomic Charges – $lg^*\beta_1$ vs.r – $lg\beta_1$ vs. pKa –

Hydrolysis

Be^{2+} and UO_2^{2+} – U, Np, Pu and Am Pourbaix' (E_{SHE},pH) Diagrams – e^- notation –

Complexes

CO_3^{2-} – SO_4^{2-}, a problem in thermodynamic data –

Thermodynamic Data

Measurements – M^{3+}/CO_3^{2-} – M^{4+}/CO_3^{2-} –

Molecular Modelling (on PC's)

Limits of modelling approaches

ab initio and DFT static methods

1st hydration shell... and a little further; but PES becomes flat.
Calculations at "0 K" with temperature corrections within the harmonic approximations, not relevant in liquids of for flat PES

Classical Molecular Dynamics

Choosing physics *v.s.* empirical models, and corresponding parameterisation
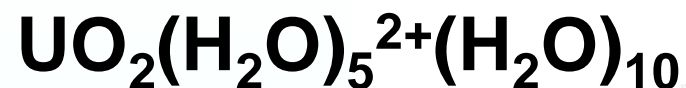Parameters often need rescaling to reproduce experimental results
Simulations of less than 10 nanoseconds
No bond formation / breaking, even no charge transfer,
not relevant for typically $H_2O......\mathbf{H}OH \rightarrow H_2O\mathbf{H}^+......^-OH$

CPMD ...

umr

8587

DFT studies of UO_2^{2+} hydration
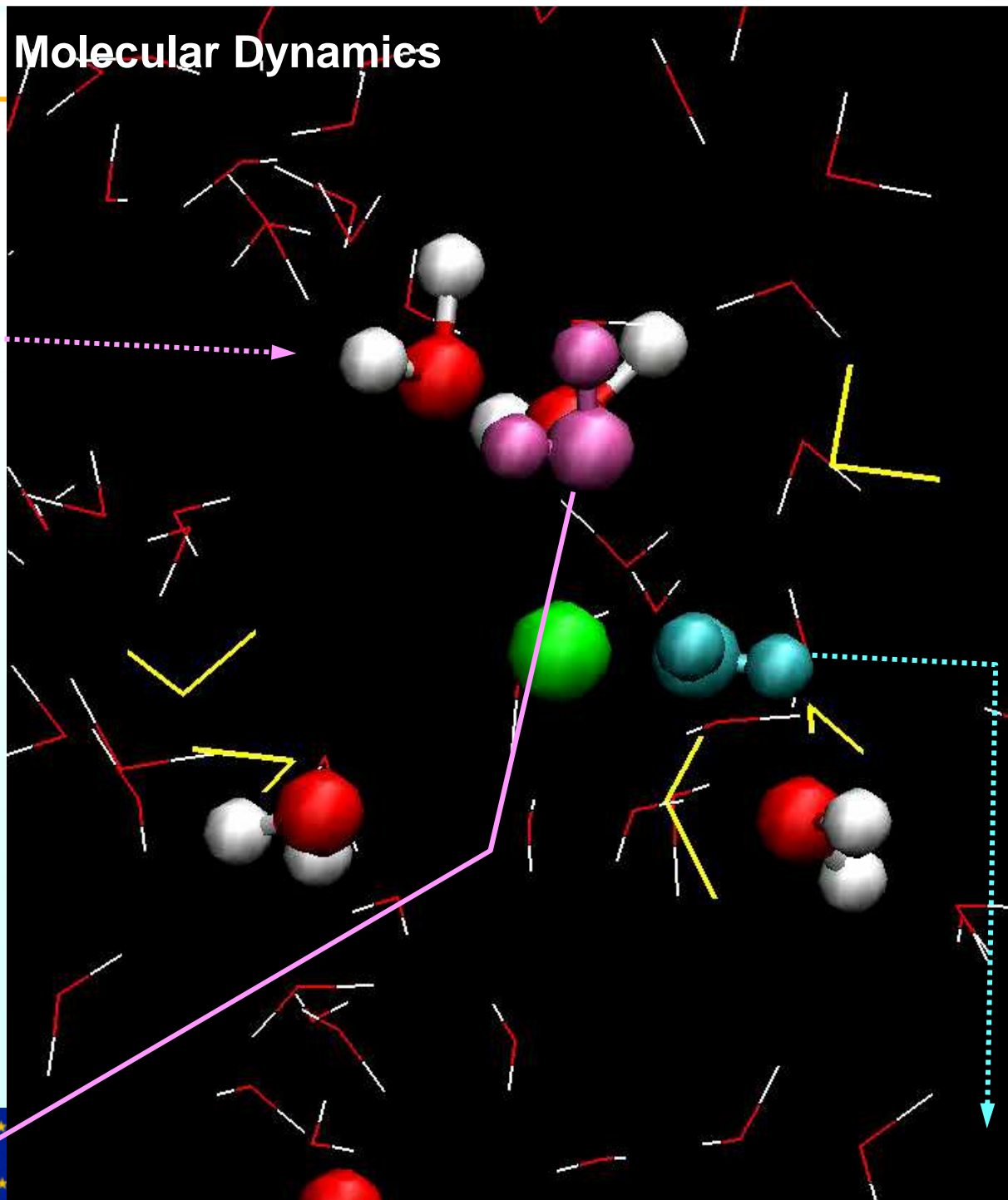
$UO_2(H_2O)_5^{2+}(H_2O)_{10}$

The 2nd hydration layer modifies charge transfers in UO_2^{2+} via H bounds, this is reflected in the corresponding parts of the IR spectrum.
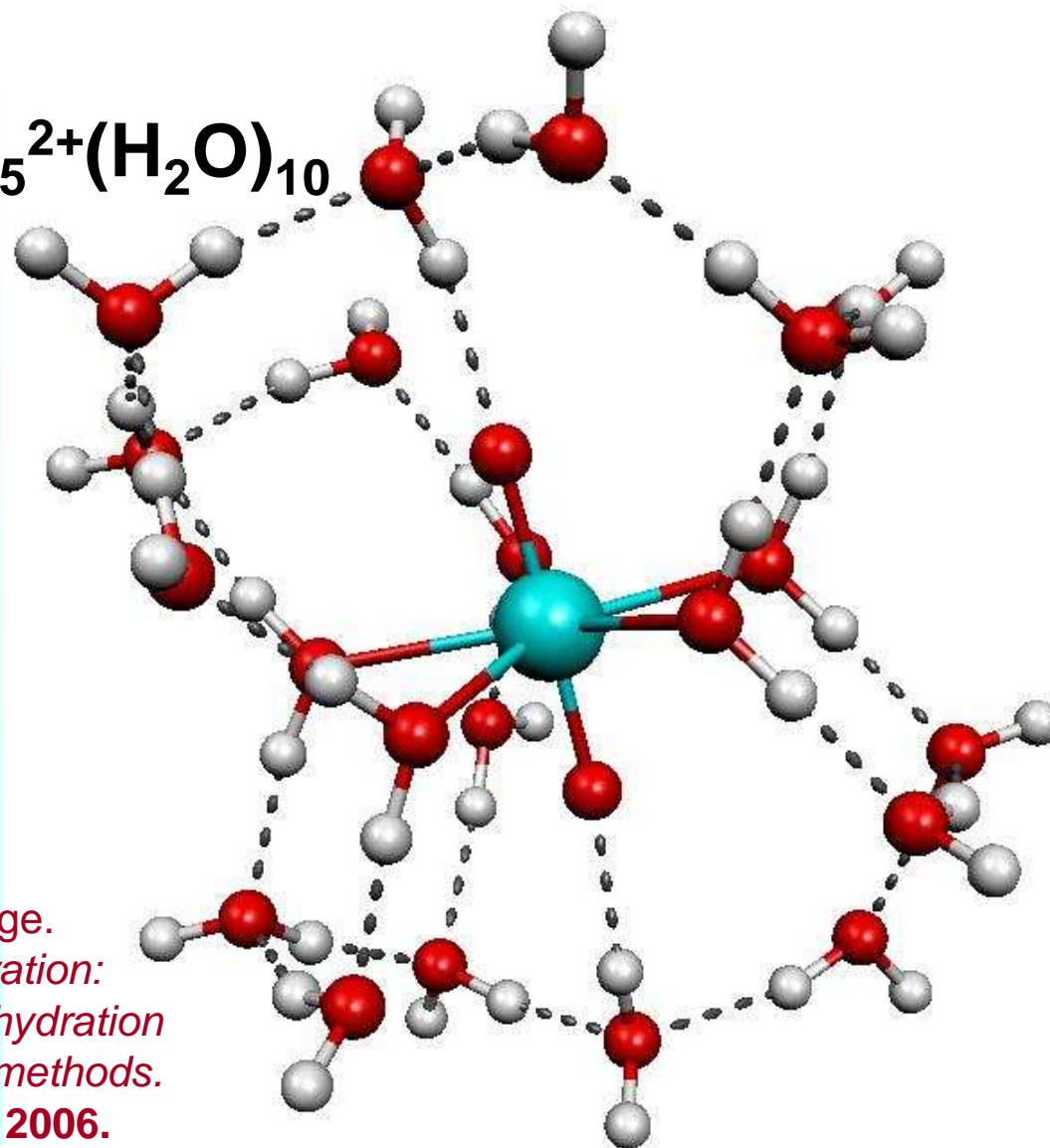
B.Siboulet, C.J.Marsden, P.Vitorge.
A theoretical study of uranyl solvation: explicit modelling of the second hydration sphere by quantum mechanical methods.
Accepted in **Chemical Physics, 2006.**