Solubilities of actinides in complex solutions

What are the solubility controlling phases in complex media?

Pierre Vitorge, Catherine Beaucaire, Marie-Hélène Fauré, Serge Maillard:
CEA-Saclay.CONTACT.pierre.vitorge(at)cea.fr.
Hélène Capdevila: CEA Cadarache.

1 - "Simple" case Na / Np(V) / carbonate system

Solubility *Ch.Dautel, P.Vitorge, I.Grenthe, D.Ferri*

Solid solution (NpO_2^+/Na^+ ionic exchange)?

P.Vitorge, M.-H.Fauré, S.Maillard

Sorption on a clayey sand (NpO_2^+/H^+ ionic exchange)

Ch.André (thesis), P.Vitorge, M.Sardin (LSGC CNRS ENSIC Nancy)

2 - Ligand competition in solid compounds

Am solubility in $OH^-/CO_3^{2-}/HCO_3^-/CO_2$ aqueous solutions

P.Vitorge, E.Giffaut (thesis), P.Robouch

3 - Redox reactions

Np(IV) solubility in $OH^-/CO_3^{2-}/HCO_3^-$ aqueous solutions

P.Vitorge (TDB NEA-OECD)

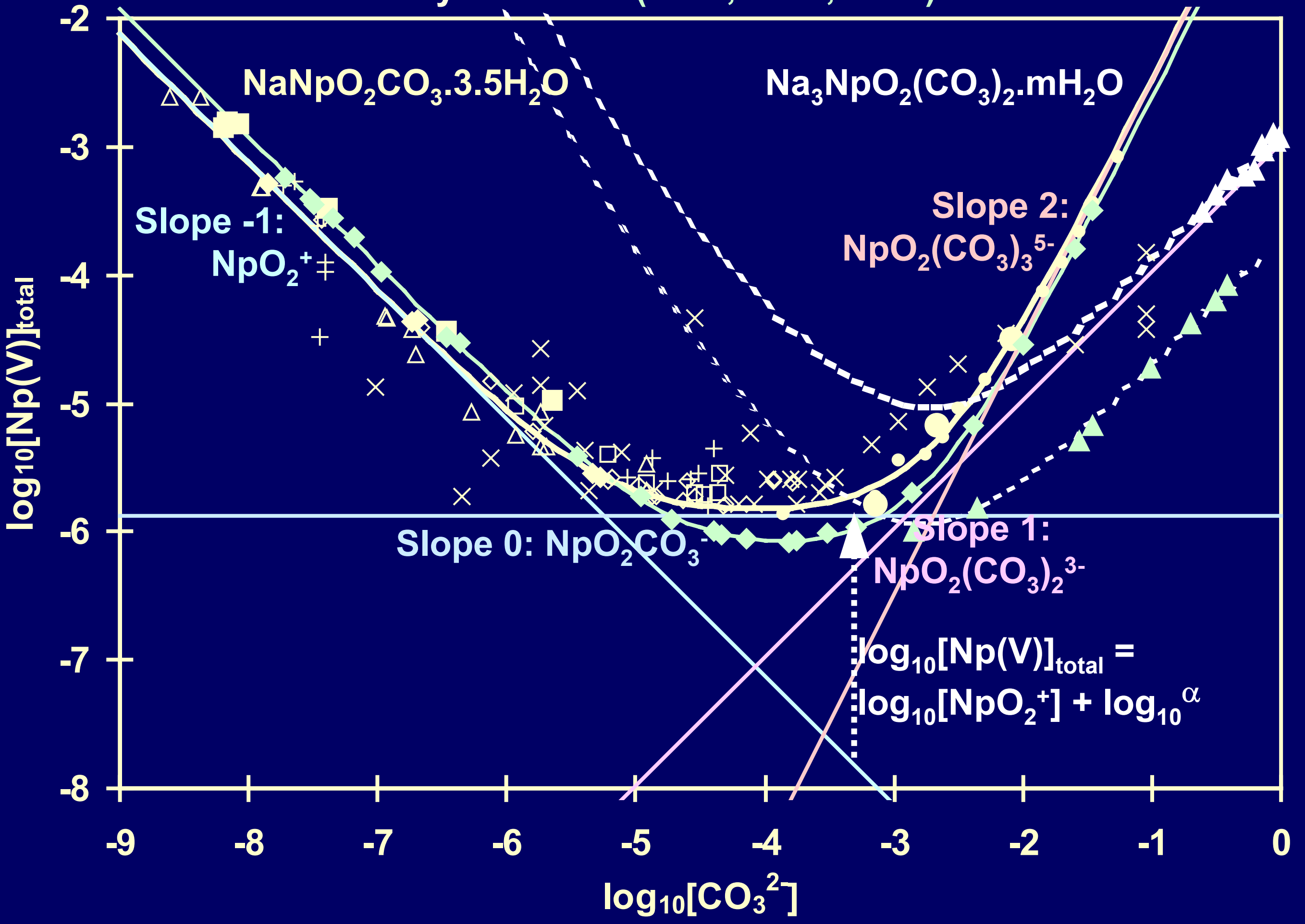
PuO_2(hyd,am) solubility product *H.Capdevila, P.Vitorge*

4 - Uranium in natural waters

Oklo and Pyrénées *M.-H.Fauré, C.Beaucaire*

Np(V) Solubility in 3M Na^+ aqueous solutions

measured by Simakin (1977), Vitorge *et al.* (1984, 1985, 1986, 1991,1998) and by Kim *et al.* (1991, 1994, 1995)



Wait for equilibrium achievement:
- Reach equilibrium from both sides, several times,
- Characterise solid phase (X-ray diffraction) when equilibrium is obtained.

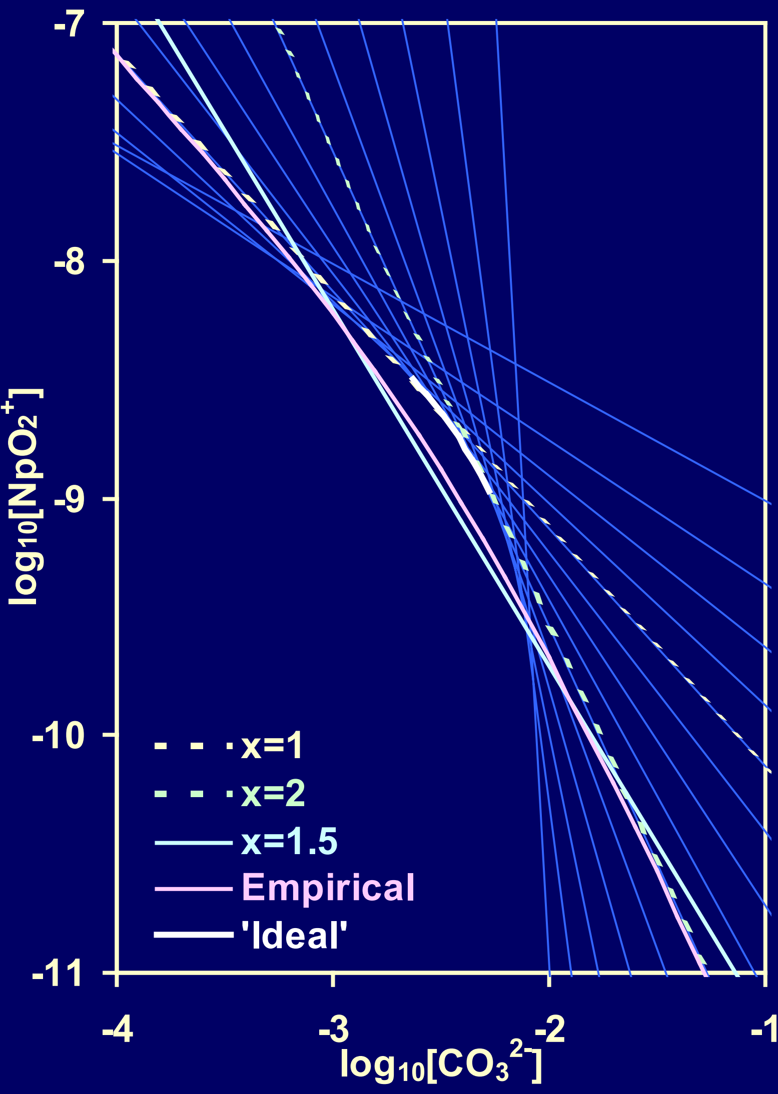
Control aqueous speciation (including activity coefficients, junction potential)

Mass action law is valid for this ideal system (Slope -1 for NpO_2^+):
- in solid (constant activity), and in solution (constant activity coefficient)

Slow transformation (for $\log_{10}[CO_3^{2-}] = -2.4$ at equilibrium):

$NaNpO_2CO_3.3.5H_2O + 2Na^+ \rightarrow Na_3NpO_2(CO_3)_2.mH_2O + 2CO_3^{2-} + (3.5-m)H_2O$
- Further slow transformations in both compounds

$Na_{(2-y)}(NpO_2)_yCO_3$ Solid Solution?



$K_{s1} = [Na^+]\ [NpO_2^+]\ [CO_3^{2-}]$

$K_{s2} = [Na^+]^3\ [NpO_2^+]\ [CO_3^{2-}]^2$

$K_{s1.5} = [Na^+]^2\ [NpO_2^+]\ [CO_3^{2-}]^{1.5}$

$v\ K_{s1} = [Na^+]\ [NpO_2^+]\ [CO_3^{2-}]$

$(1-v)\ K_{s2} = [Na^+]^3\ [NpO_2^+]\ [CO_3^{2-}]^2$

$$\frac{1}{v} = 1 + [Na^+]^2[CO_3^{2-}]\frac{K_{s1}}{K_{s2}}$$

$$K_y = \frac{\chi_{Na}^{2-y}\ \chi_{NpO_2}^{y}\ \chi_{CO_3}}{[Na^+]^{2-y}\,[NpO_2^+]^y\,[CO_3^{2-}]}$$

$K_y = K_1^{2-y}\,K_2^{y-1}$ (*see* Michard 1989)

$$D = \frac{\chi_{Na}\ [Na^+]}{\chi_{NpO_2}\ [NpO_2^+]} = \frac{K_2}{K_1}$$

$$\chi_{Na} = (2-y)\,\chi_{CO_3}$$

$$\chi_{NpO_2} = y\ \chi_{CO_3}$$

$$\chi_{CO_3} = \frac{1}{3}$$

$$K_1 = \frac{1}{9K_{s1}}$$

$$K_2 = \frac{0.1443}{\sqrt{K_{s2}}}$$

$$\left(\frac{\partial[NpO_2^+]}{\partial x}\right)_{[Na^+],[CO_3^{2-}]} = 0, \quad \text{where } x = \frac{1}{y}$$

$$\left(\frac{\partial \ln[NpO_2^+]}{\partial \ln[CO_3^{2-}]}\right)_{[Na^+]} = -x$$

Hypothesis: $\mu_{\overline{X}} = \mu_{\overline{X}}^o + RT\ln\chi_X$ for X = Na, NpO_2 and CO_3

Thermodynamics of coprecipitation for $Na_{2-y}(NpO_2)_yCO_3$

Eq.y: $(2\text{-}y)\ Na^+ + y\ NpO_2^+ + CO_3 \rightarrow Na_{2-y}(NpO_2)_yCO_3$

Eq.y = u Eq.y_1 +(1-u) Eq.y_2,

Eq.D = t (Eq.y_1 - Eq.y_2), $u = t\,(y - y_2)$, $t = 1/(y_1 - y_2)$

Eq.D: $Na_{2-y_1}(NpO_2)_{y_1}CO_3 + (y_2 - y_1)\ NpO_2^+ \rightarrow Na_{2-y_2}(NpO_2)_{y_2}CO_3 + (y_2 - y_1)\ Na^+$

Hypothesis: $\mu_{\overline{X}} = \mu^o_{\overline{X}} + RT\ln\chi_X$, for X = Na, NpO_2 and CO_3,

$\delta_X = \mu_{\overline{X}} - \mu_X$, χ_{Na} = (2-y) χ_{CO_3}, χ_{NpO_2} = y χ_{CO_3}, χ_{CO_3} = 1/3

Mass action law for stoichiometric compounds (fixed y_i)

$$0 = d\Delta_rG = \sum(\mu_i dn_i) = \left(\sum\mu_i\nu_i\right)d\xi,\quad 0 = \Delta_rG^o_{K_i} + RT\ln K_i$$

$$\Delta_rG^o_{Ki} = (2 - y_i)\delta^o_{Na} + y_i\delta^o_{NpO_2} + \delta^o_{CO_3} = -RT\ln K_i$$

$$K_i = K_{y_i} = (2y_i - 1)^{2y_i - 1}\,{y_i}^{y_i}\,\chi^3_{CO_3}\,K_{si}^{-y_i},\qquad K_{si} = [Na^+]^{2\frac{1}{y_i}-1}[NpO_2^+][CO_3^{2-}]^{\frac{1}{y_i}}$$

Mass action law for solid solution

$$0 = d\Delta_rG = \left(\sum\mu_i\nu_i\right)d\xi + \left(\sum\mu_i\frac{d\nu_i}{dy}\right)dy$$

$$\sum\mu_i\nu_i = \Delta_rG^o_{K_y} + RT\ln K_y = RT\ln(K_yK_1^{-u}K_2^{-1+u})$$

$$\Delta_rG^o_{K_y} = (2 - y)\,\delta^o_{Na} + y\,\delta^o_{NpO_2} + \delta^o_{CO_3} = -RT\ln\left(K_1^uK_2^{1-u}\right)$$

$$K_y = \left(\frac{\chi_{Na}}{[Na^+]}\right)^{2-y}\left(\frac{\chi_{NpO_2}}{[NpO_2^+]}\right)^{y}\frac{\chi_{CO_3}}{[CO_3^{2-}]}$$

$$\sum\mu_i\frac{d\nu_i}{dy} = \left(\Delta_rG^o_D + RT\ln D\right)dy = RT\ln(D\,K_2^t\,K_1^{-t})$$

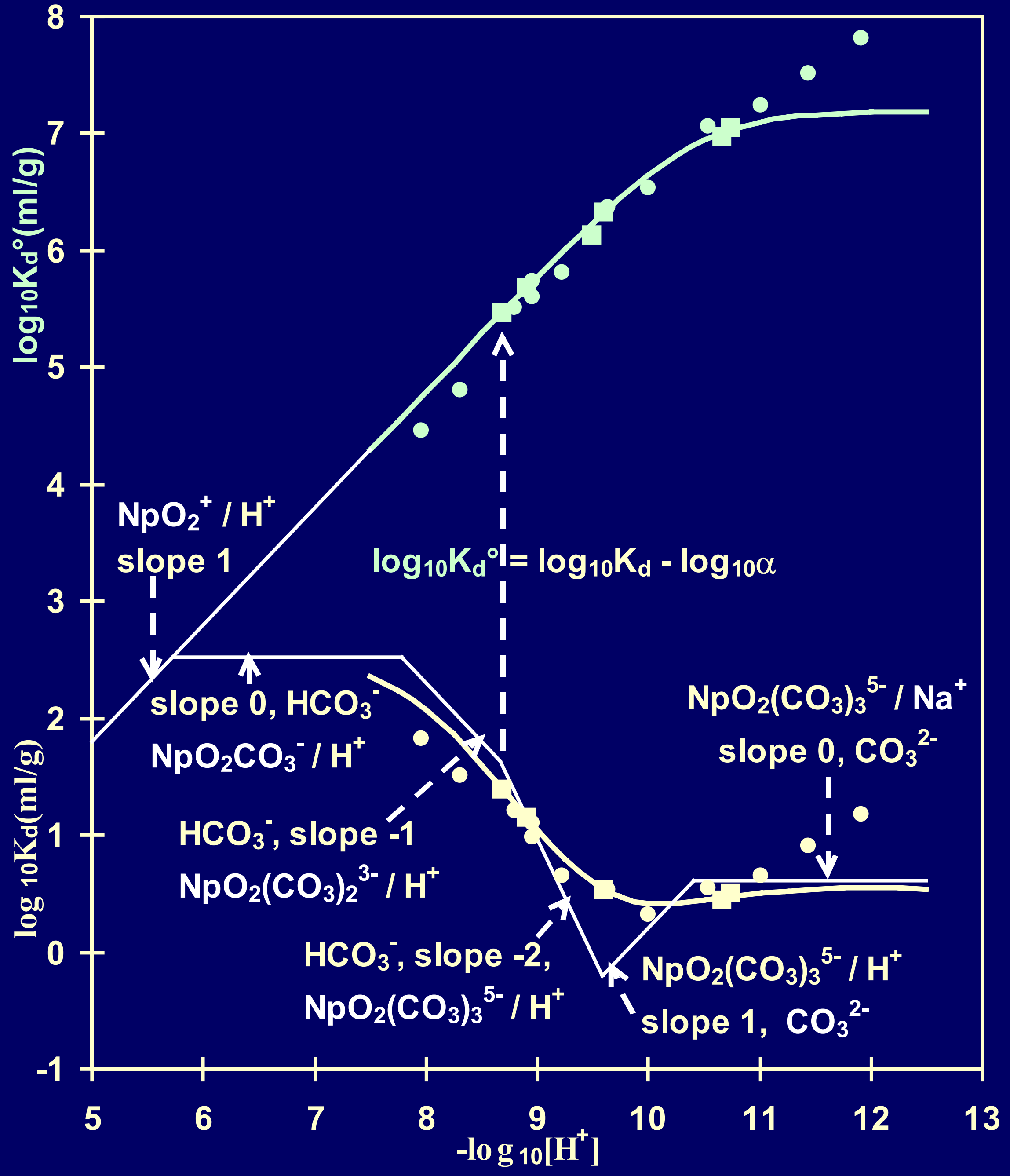
$$\Delta_rG^o_D = \delta^o_{NpO_2} - \delta^o_{Na} = t\,\Delta_rG^o_{K_1} - t\,\Delta_rG^o_{K_2} = -t\,RT\ln(K_1\,K_2^{-1})$$

$$D = \frac{[Na^+]\chi_{NpO_2}}{[NpO_2^+]\chi_{Na}} = \frac{K_1^t}{K_2^t}$$

$$0 = \ln\frac{K_y}{K_1^u\,K_2^{1-u}}d\xi + \ln\frac{D}{K_1^t\,K_2^{-t}}dy$$

Np(V) sorption on a clayey sand: NpO_2^+/H^+ ionic exchange

André 1997 (Thesis)

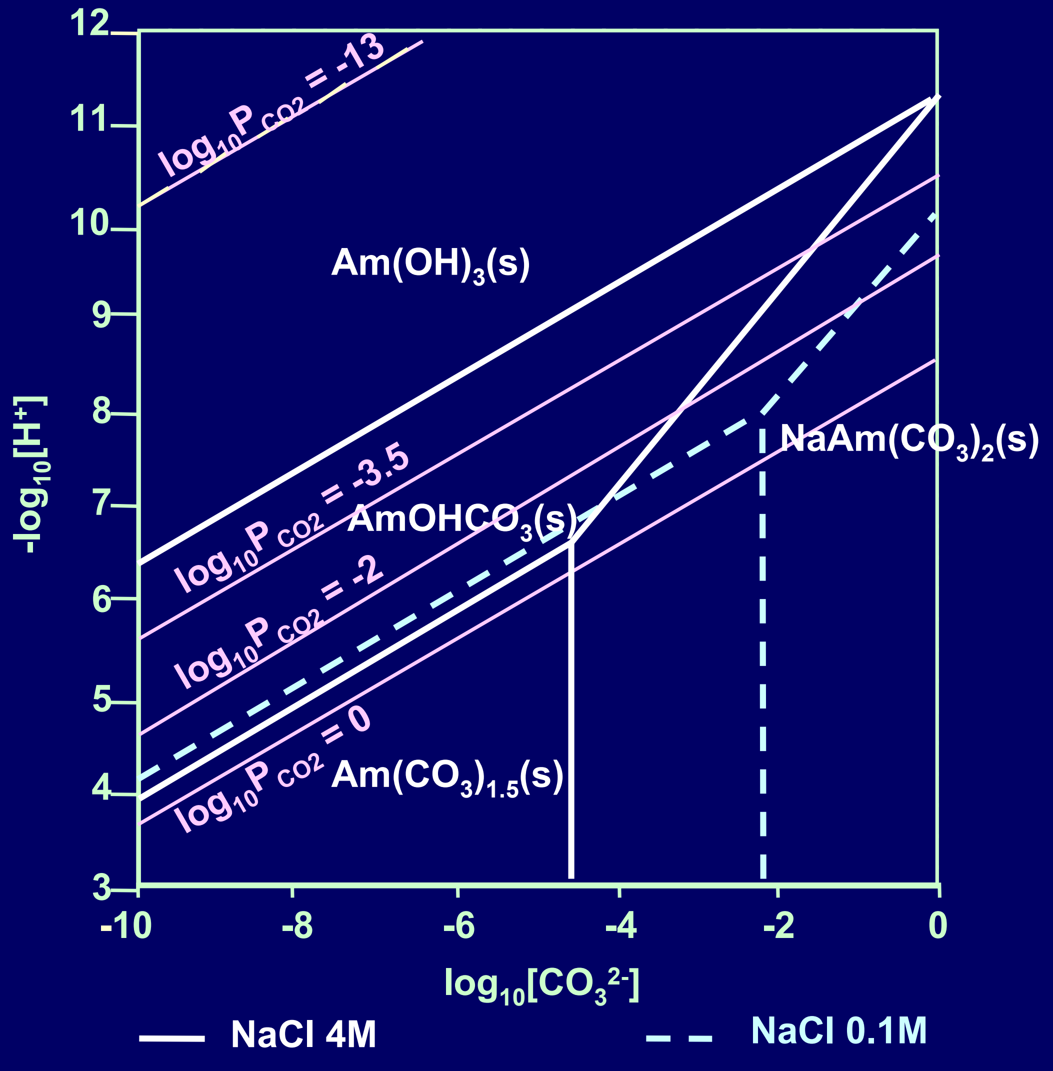


Np(V) is eluted with 1M Na^+, 0.2M (HCO_3^- + CO_3^{2-}), ClO_4^- aqueous solutions. Partition coefficient K_d, is measured by column experiments, $K_d°$ is NpO_2^+ partition coefficient obtained from K_d and the complexation coefficient α, calculated from complexation constants (known independently).

$$Am(OH)_3(s) + CO_2 \Leftrightarrow AmOHCO_3(s) + H_2O$$

$$AmOHCO_3(s) + 0.5\ CO_2 \Leftrightarrow 0.5\ Am_2(CO_3)_3(s) + 0.5\ H_2O$$

Vitorge (1992)



This diagram is from Giffaut *et al.* (1993, 1994), and accepted by TDB (1995)

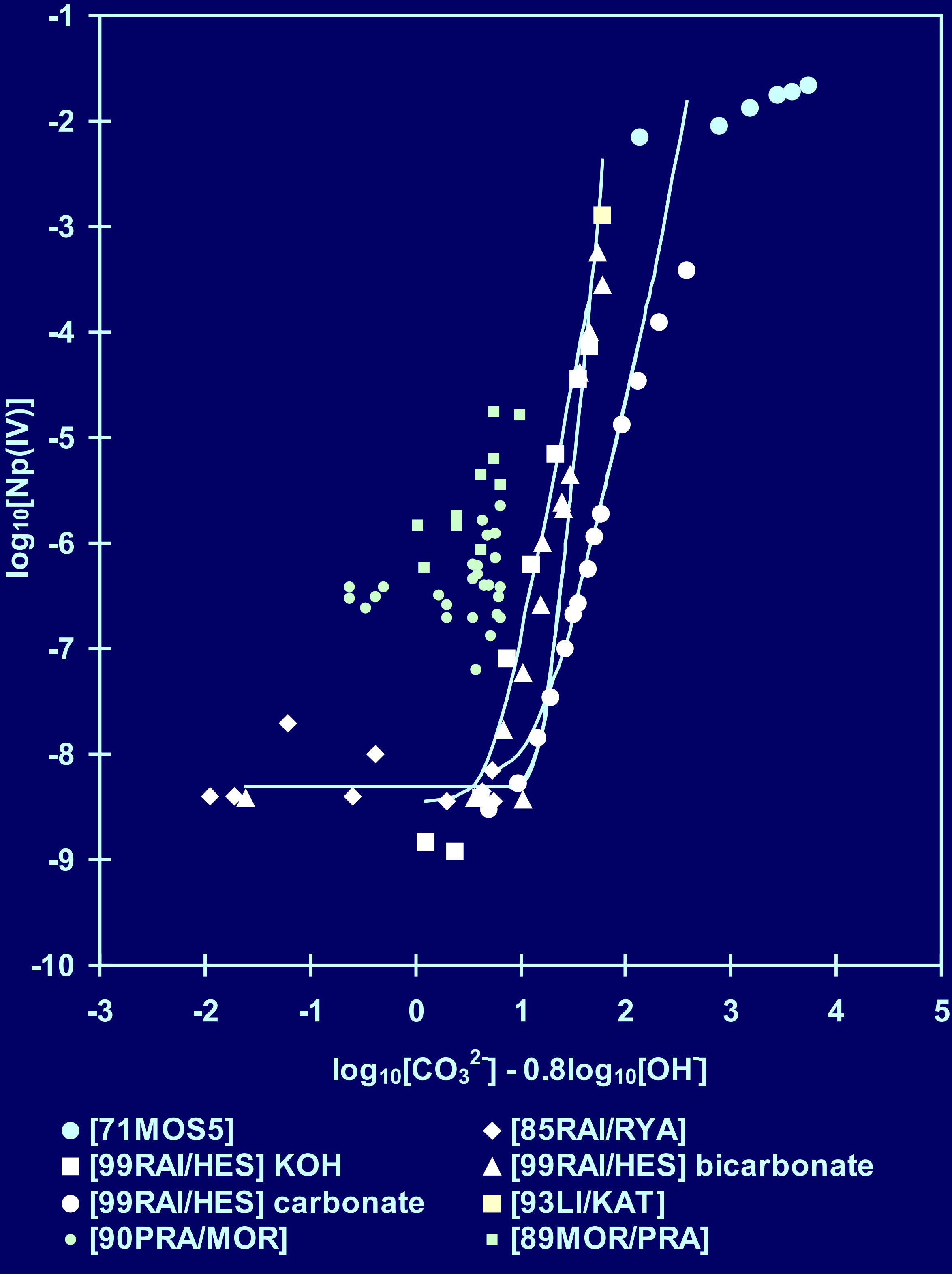
Ligand competition in solid phases,

CO_2 partial pressure (P_{CO2}, atm) is the key parameter.

Aqueous speciation cannot be deduced from solubility measurements equilibrated with air.

Np(IV) solubility in neutral and carbonate aqueous solutions

Measured by
Moskvin (1971), Rai *et al.* (1985, 1999), Prapoto (1989, 1990) and Li *et al.* (1993)



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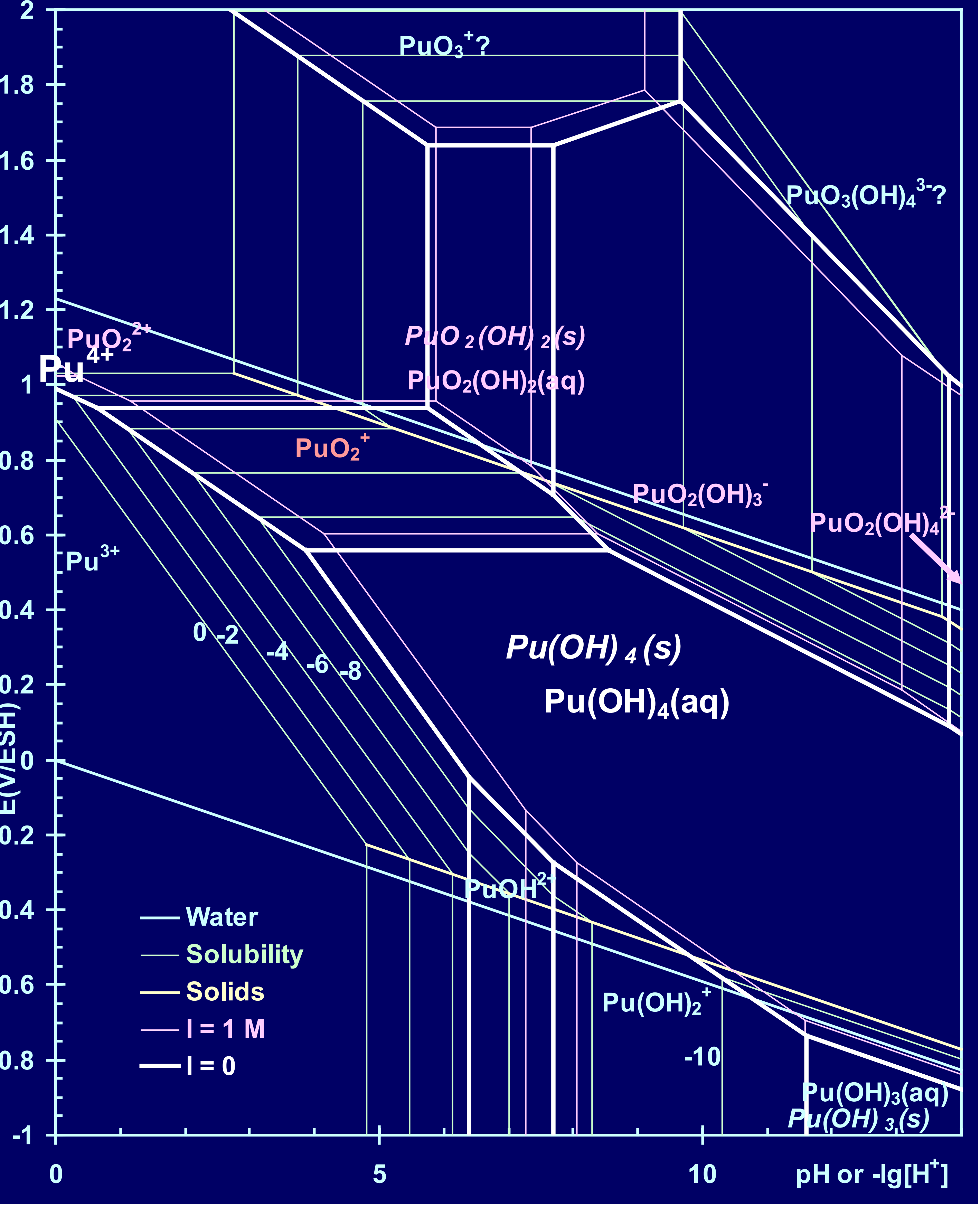
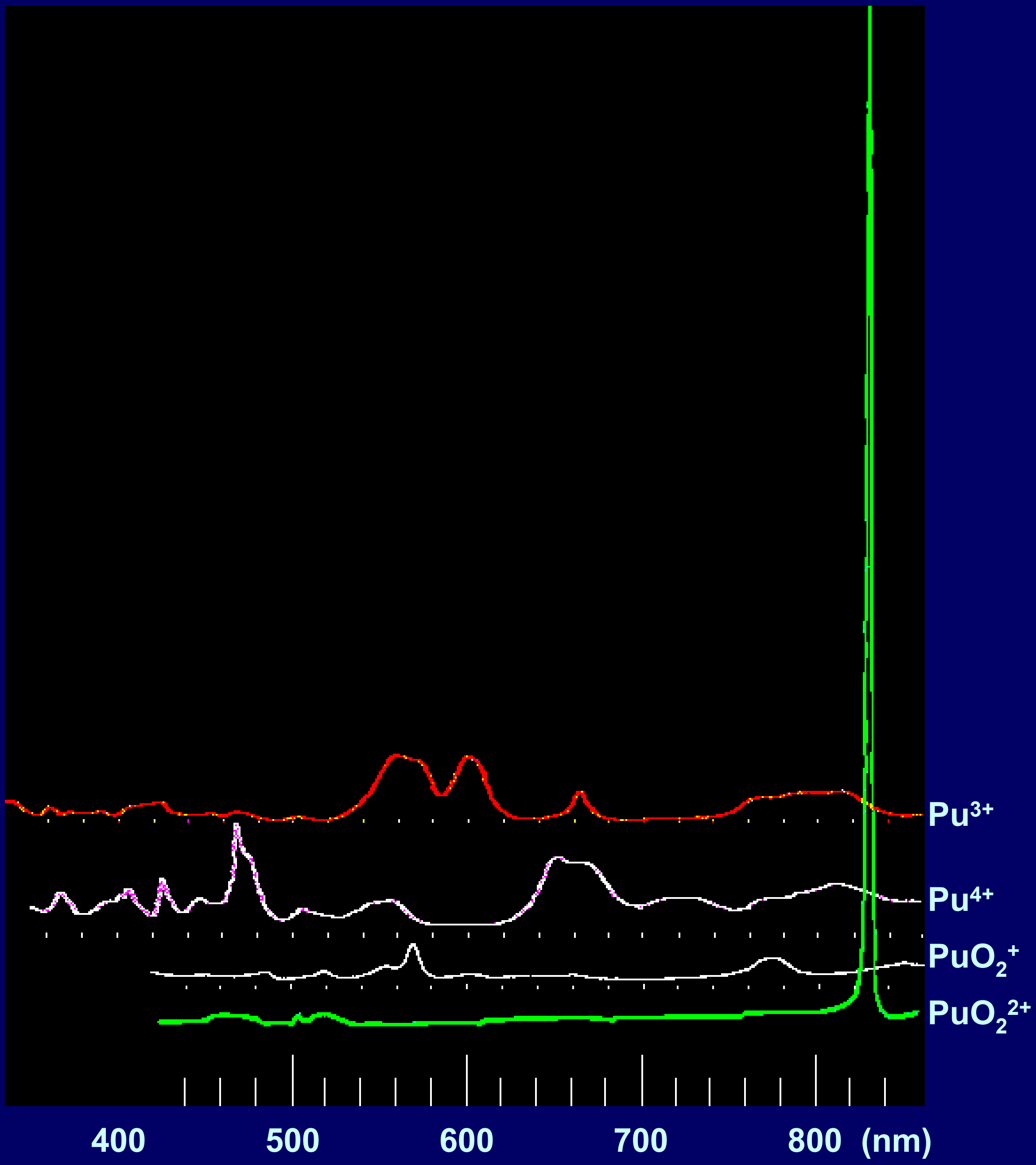
Vitorge (Chimie des actinides *in Techniques de l'ingénieur (1999 or 2000)*)



Pu absorption spectra in 1 M $HClO_4$ aqueous solutions



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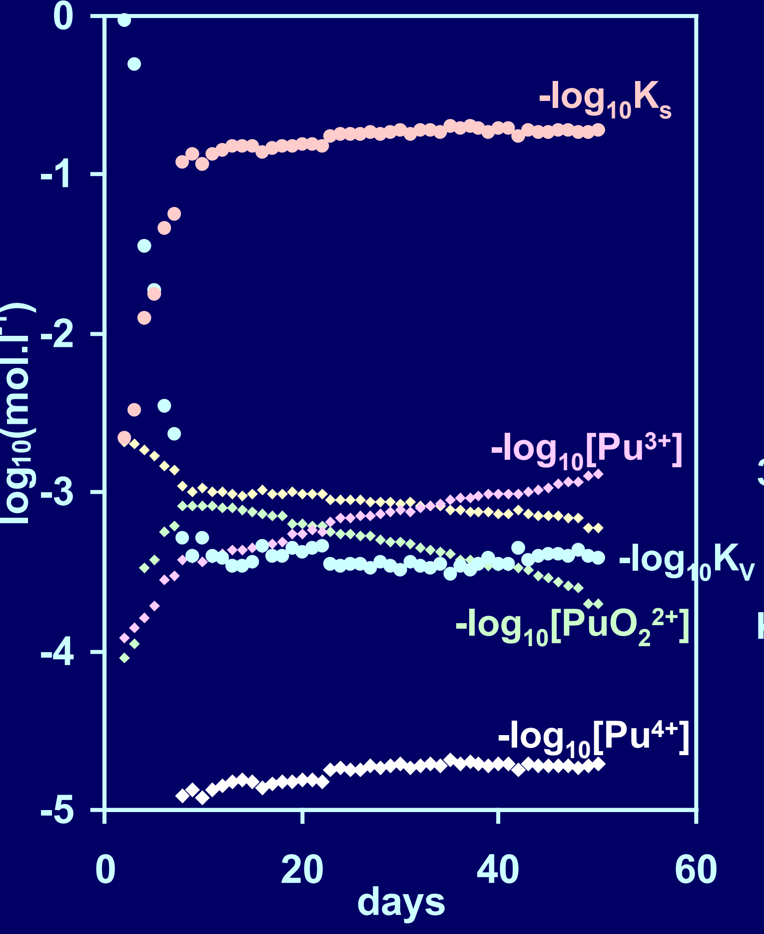
Pu(IV) solubility in acidic aqueous solutions

Capdevila's thesis (1992), Capdevila *et al.* (1992, 1995, 1998)



◆ $-\log_{10}[PuO_2^{2+}]$

◆ $-\log_{10}[PuO_2^{+}]$

◆ $-\log_{10}[Pu^{4+}]$

◆ $-\log_{10}[Pu^{3+}]$

● $-\log_{10}K_V$

● $-\log_{10}K_s$

$$3PuO_2^+ + 4H^+ \rightarrow 2PuO_2^{2+} + Pu^{3+} + 2H_2O$$

$$K_V = \frac{[PuO_2^{2+}]^2[Pu^{3+}]}{[PuO_2^+]^3[H^+]^4} = 10^{3.44\pm0.08}$$

$$E = E^o_{6/5} + 0.05916\ \log_{10}\frac{[PuO_2^{2+}]}{[PuO_2^+]}$$

$$= 0.902 \pm 0.009,$$

$$[Pu^{4+}] = [Pu^{3+}]\,10^{\frac{E-E^o_{4/3}}{0.05916}} = 10^{-4.72\pm0.03}$$

$$K_{so} = \frac{[Pu^{4+}]}{[H^+]^4} = 10^{-0.72\pm0.03}$$

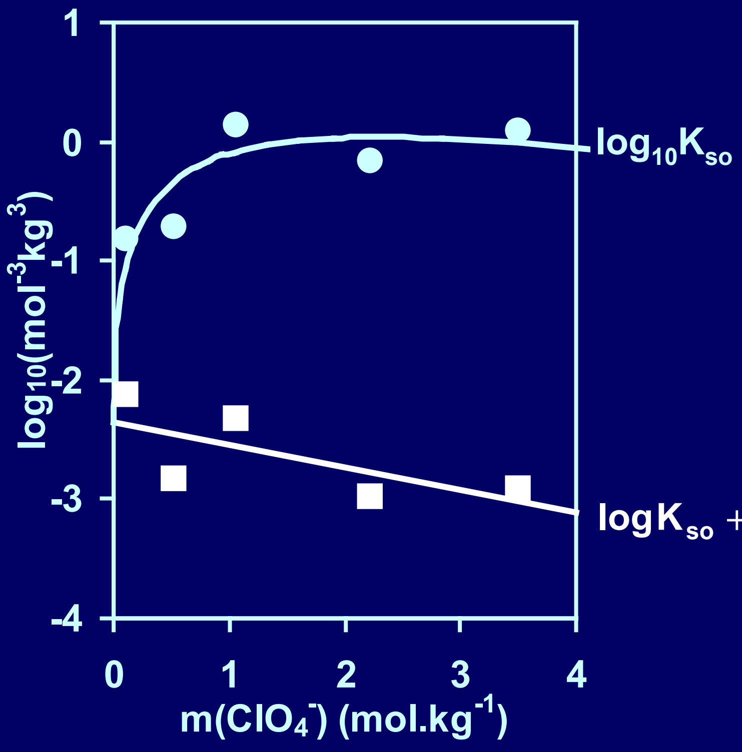
$$PuO_2(hyd,am) + 4H^+ \rightarrow Pu^{4+} + 2H_2O$$

$$\frac{E^o_{6/5} - E^o_{4/3}}{0.05916} - \log_{10}K^o_s = \log_{10}\frac{[PuO_2^+][H^+]^4}{[Pu^{3+}][PuO_2^{2+}]} = 10^{-0.64\pm0.03}$$

$$PuO_2^{2+} + Pu^{3+} + 2H_2O \rightarrow PuO_2^+ + PuO_2(am,hyd) + 4H^+$$

$PuO_2(am,hyd) + 4H^+ \rightarrow Pu^{4+} + 2H_2O$

Capdevila *et al.* (1998)



$$K_{so} = \frac{[Pu^{4+}]}{[H^+]^4}$$

$$\log K_{so} + 12\frac{0.509\sqrt{I_m}}{1+\sqrt{I_m}} = \log K^o_{so} - \Delta\varepsilon\ m_{ClO_4^-}$$

I_m = ionic strength (mol.kg^{-1})

Fitted values:

$\log K^o_{so} = -2.26 \pm 0.44$

$\Delta\varepsilon = 0.27 \pm 0.23$

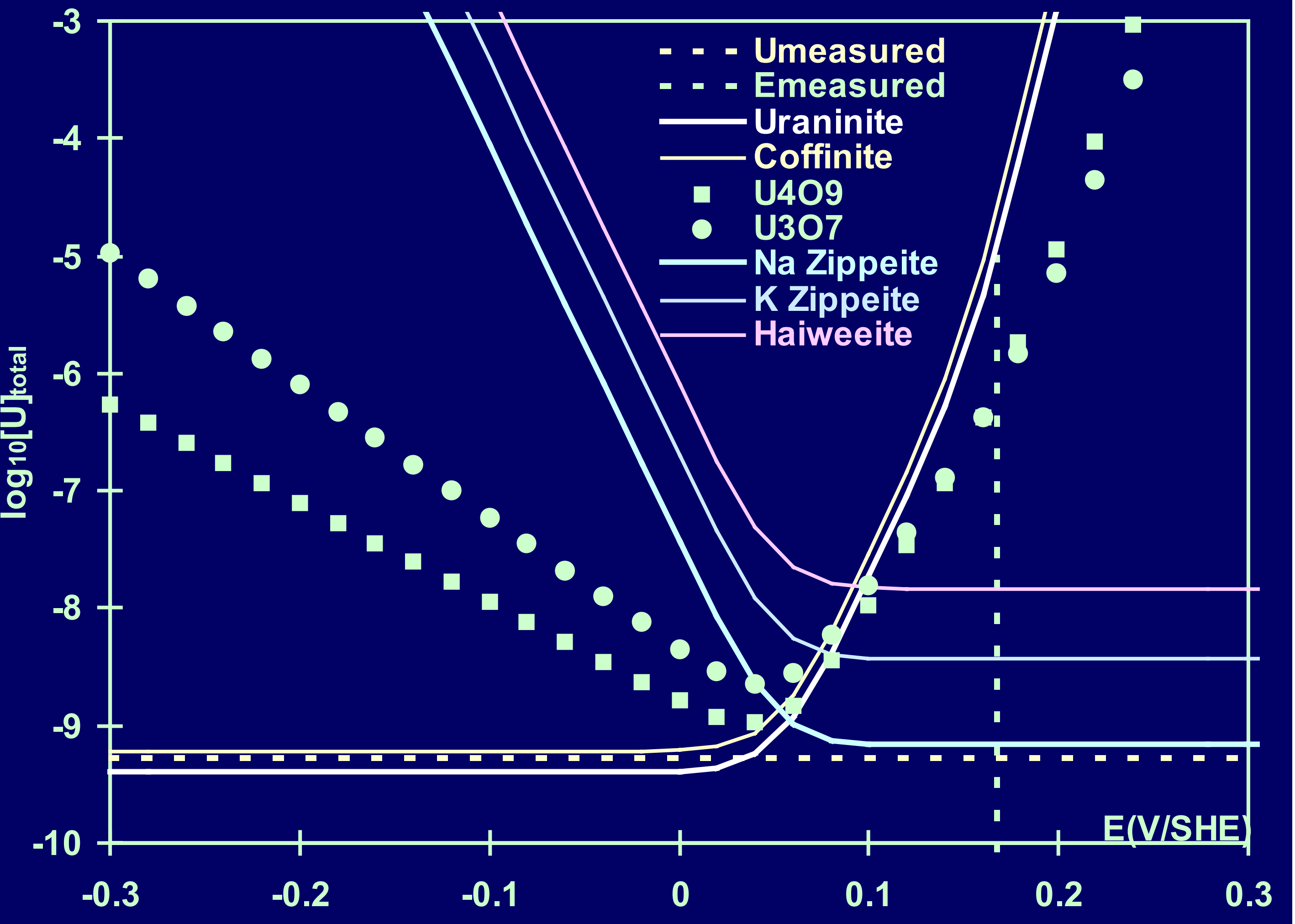
$\varepsilon(Pu^{4+}, ClO_4^-) = 0.89 \pm 0.27$

known value : 0.82 ± 0.06

Composition of an Oklo natural water Okelobondo (OK195-46)

E	0.167	V/SHE
pH	6.4	
Alkalinity	0.917	mM
U	$5.46\ 10^{-10}$	M
F	0.789	µM
Cl	9.00	µM
S	21.5	µM
P	0.161	µM
Si	0.406	mM
Li	1.45	µM
Na	0.198	mM
K	20	µM
Mg	0.181	mM
Ca	0.125	mM
Ba	0.0874	µM
Fe	0.234	mM
Al	2.68	µM

Uranium solubility in an Oklo natural water (OK195-46)



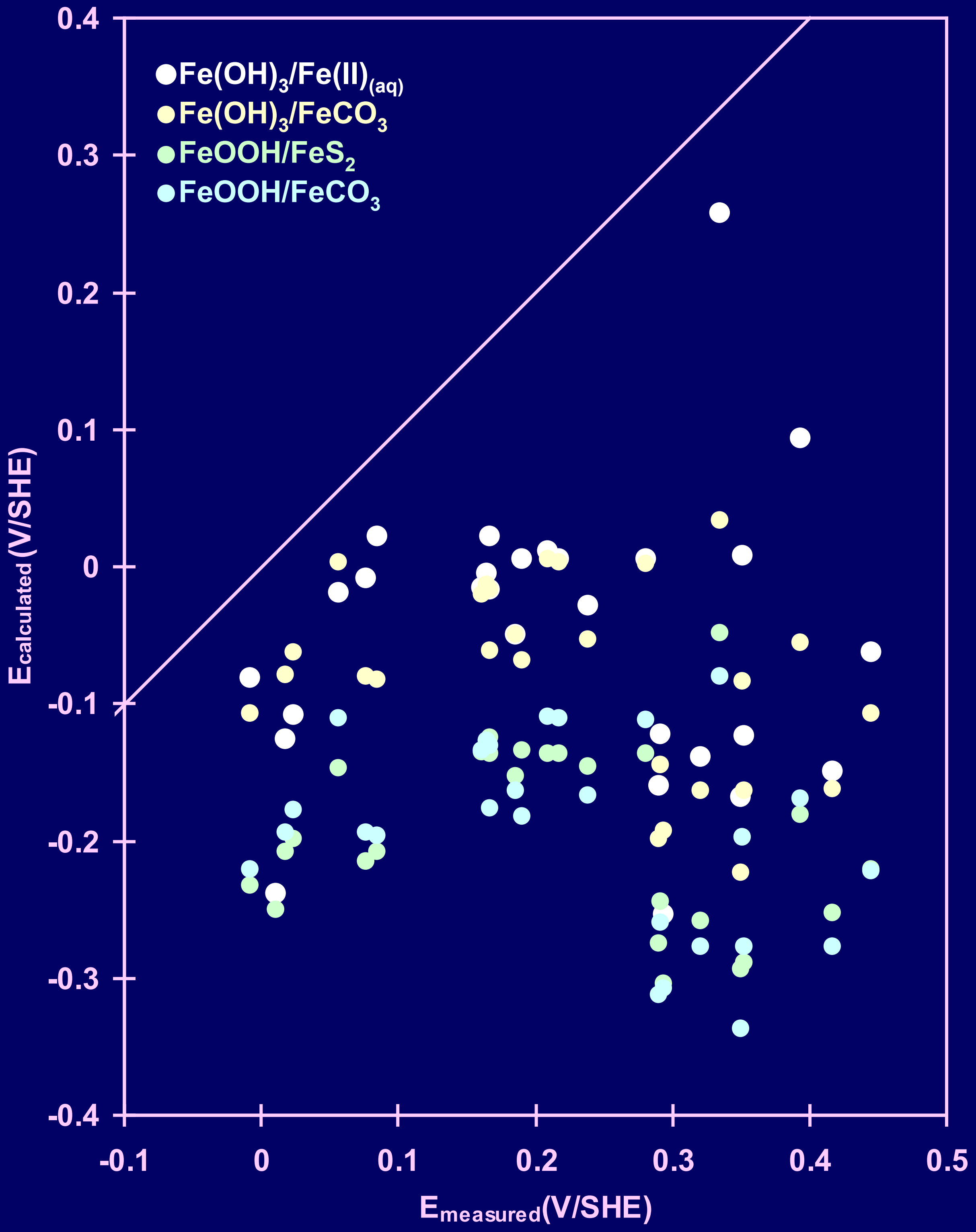
$UO_3(\alpha)$
$UO_3(\beta)$
$UO_3.2H_2O$
$Ca(UO_2)_6O_4(OH)_6.8H_2O$ (becquerilite)
$Ca_3Mg_3(UO_2)_2(CO_3)_6(OH)_4.18H2O$ (rabbittite)
$Ca_3NaUO_2(CO_3)_3F(SO_4).10H_2O$ (schroeckingite)
$Na_4(UO_2)_6(SO_4)_2.4H_2O$ (Na zippeite)
$K_4(UO_2)_6(SO_4)_3(OH)_{10}.4H_2O$ (K zippeite)
$Ca(UO_2)_2(Si_2O_5)_3.5H_2O$ (haiweeite)
$Na_2(UO_2)_2(Si_2O_5)_3.4H2O$ (Na-weeksite)
$Ca(UO_2)_2(SiO_3OH)_2$ (uranophane)

UO_2CO_3 (Rutherfordine)
$UO_2CO_3.H_2O$ (sharpite)

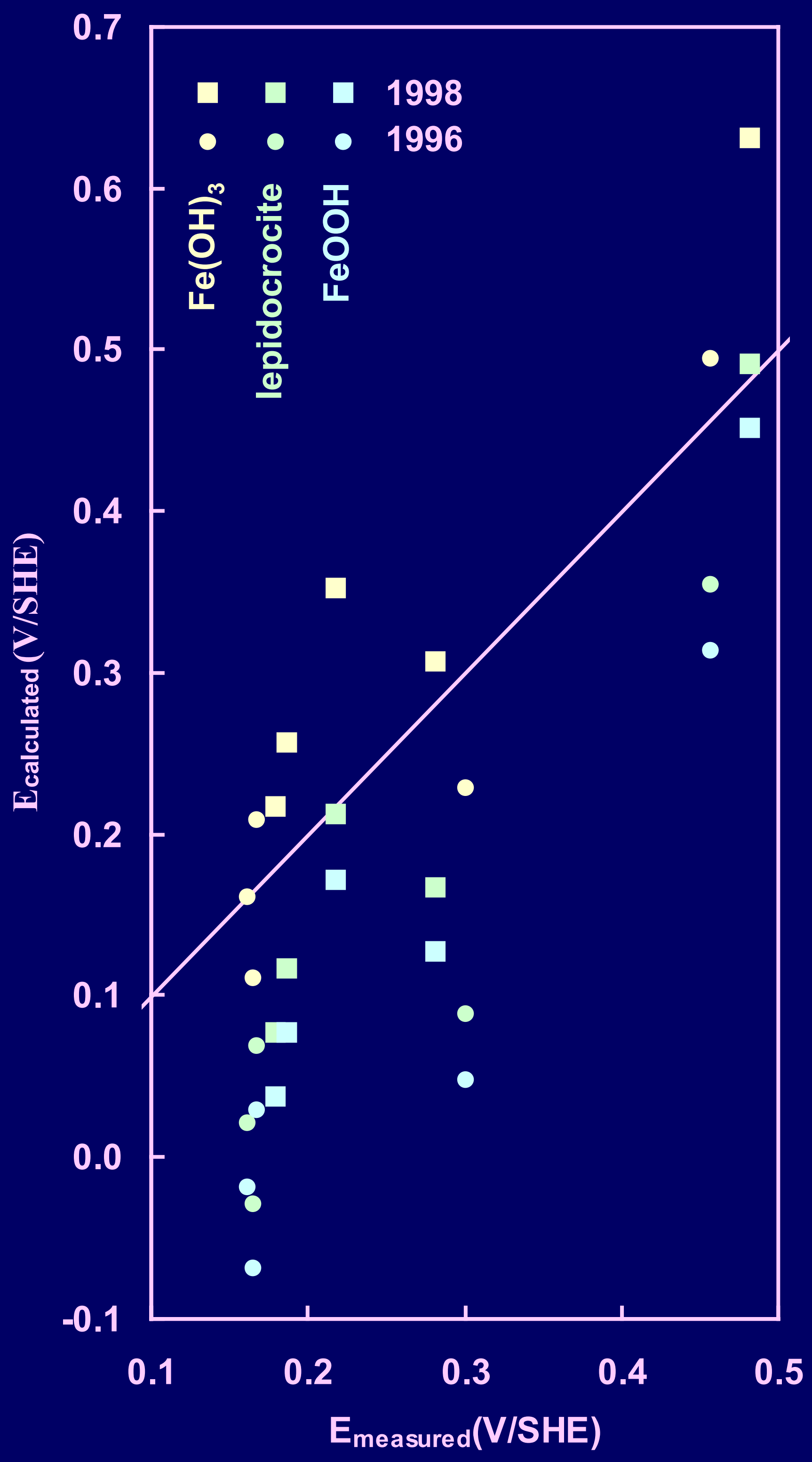
$Mg_2UO_2(CO_3)_3.18H_2O$ (bayleyite)
$CaMgUO_2(CO_3)_3.12H_2O$ (swartzite)
$Ca_2UO_2(CO_3)_3.10H_2O$ (liebigite)
$CaNa_2UO_2(CO_3)_3.6H_2O$ (andersonite)
$K_3NaUO_2(CO_3)_3.H2O$ (grimselite)
$(UO_2)_3(OH)_2(SO_4)_2.8H_2O$
$UO_2SO_4.3H_2O$
$(UO_2)_2SiO_4.2H_2O$ (soddyite)
$NaH_3OUO_2SiO_4.2H_2O$ (naboltwoodite)

U_3O_8 U_3O_7 U_4O_9 UO_2(Uraninite) $USiO_4$ (coffinite)

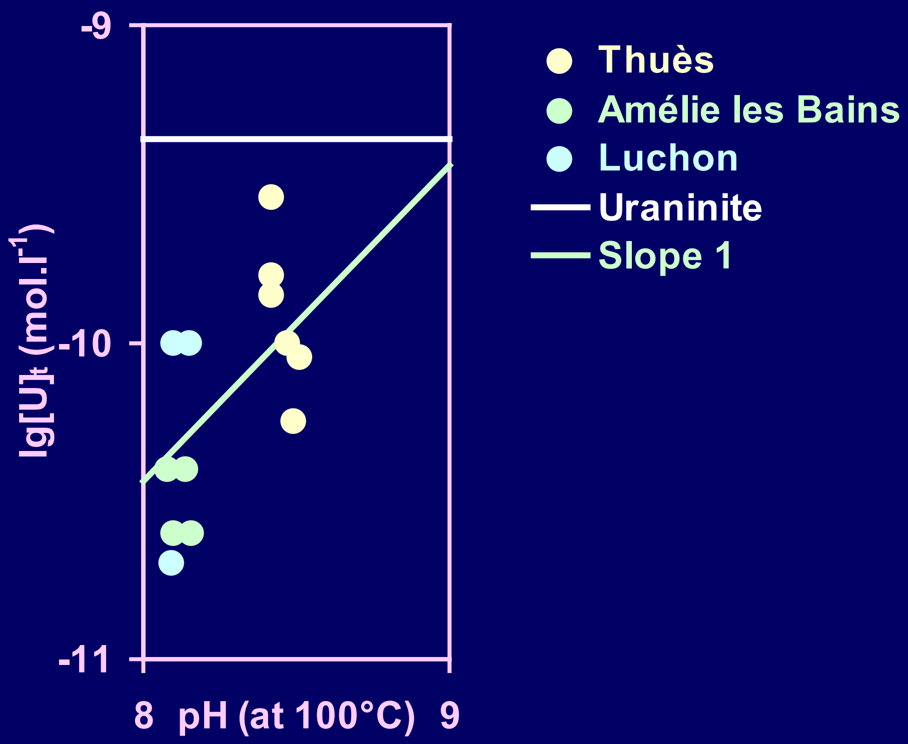
Redox potential in an Oklo natural water (Okelobondo)



Redox potential in an Oklo natural water (Bagombe)



Uranium solubility in Pyrénées waters



$UO_2(cr) + 2\ H2O \rightarrow U(OH)_4(aq)$

Experimental solubility is lower: sorption? New solid phase?

Slope 1?

$UO_2(cr) + 2\ H2O \rightarrow U(OH)_5^-$? + H^+ not confirmed, other anonic complex?

Typically:

$UO_2(cr) + 2\ SiO_2(cr) + 2\ H_2O \rightarrow U(SiO_2(OH)_2)(SiO_3OH)^-$? + H^+

$UO_2(cr) + 3\ SiO_2(cr) + 4\ H_2O \rightarrow U(SiO(OH)_3)(SiO_2(OH)_2)_2^-$? + H^+