



Speciation, sorption, solubility and co-precipitation in a deep repository.

Kastriot Spahiu, Chalmers, SKB



Speciation of actinides in groundwaters

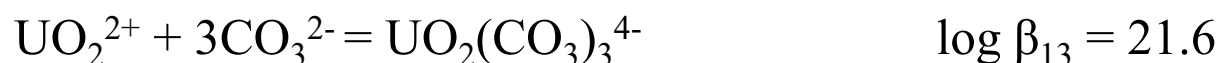
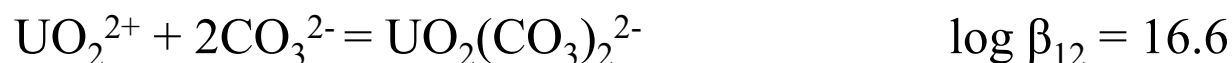
- Actinide cations are hard acid cations and form strongest complexes with ligands that are hard bases. The relative strength of complexes with ligands decrease in the order:



- Stabilities of actinide(An) complexes with the same ligand most often decrease in the order:

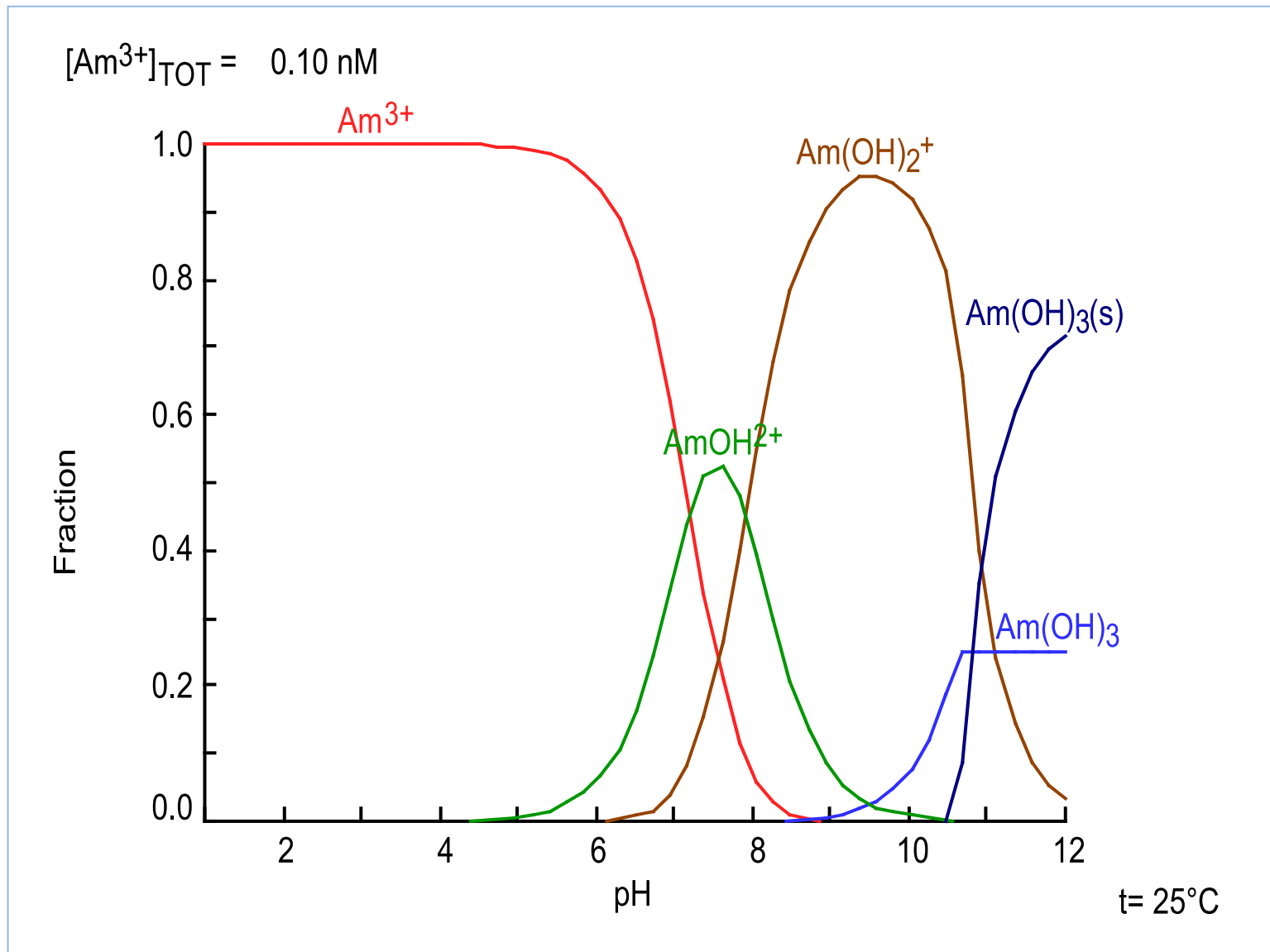


- Example: Uranyl ion UO_2^{2+} forms strong carbonate complexes



- Hydrolysis of U(IV) starts already at pH~2 and above pH~4 the species $\text{U}(\text{OH})_4$ dominates. Very narrow pH range to determine second and third hydrolysis species.

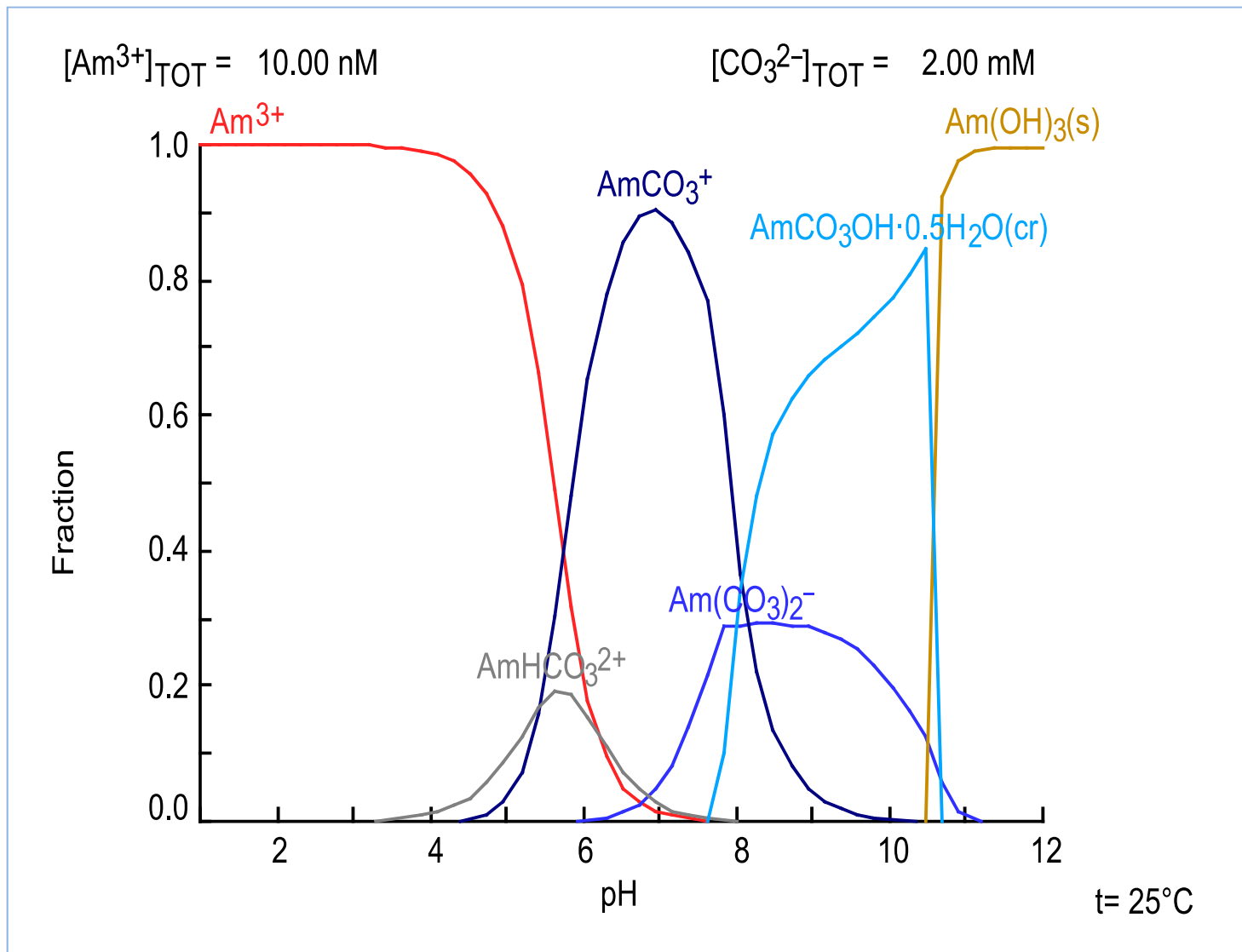
Speciation of Am(III) in water of various pH.



Medusa.kth, downloads. Install java version and read "short tutorial"



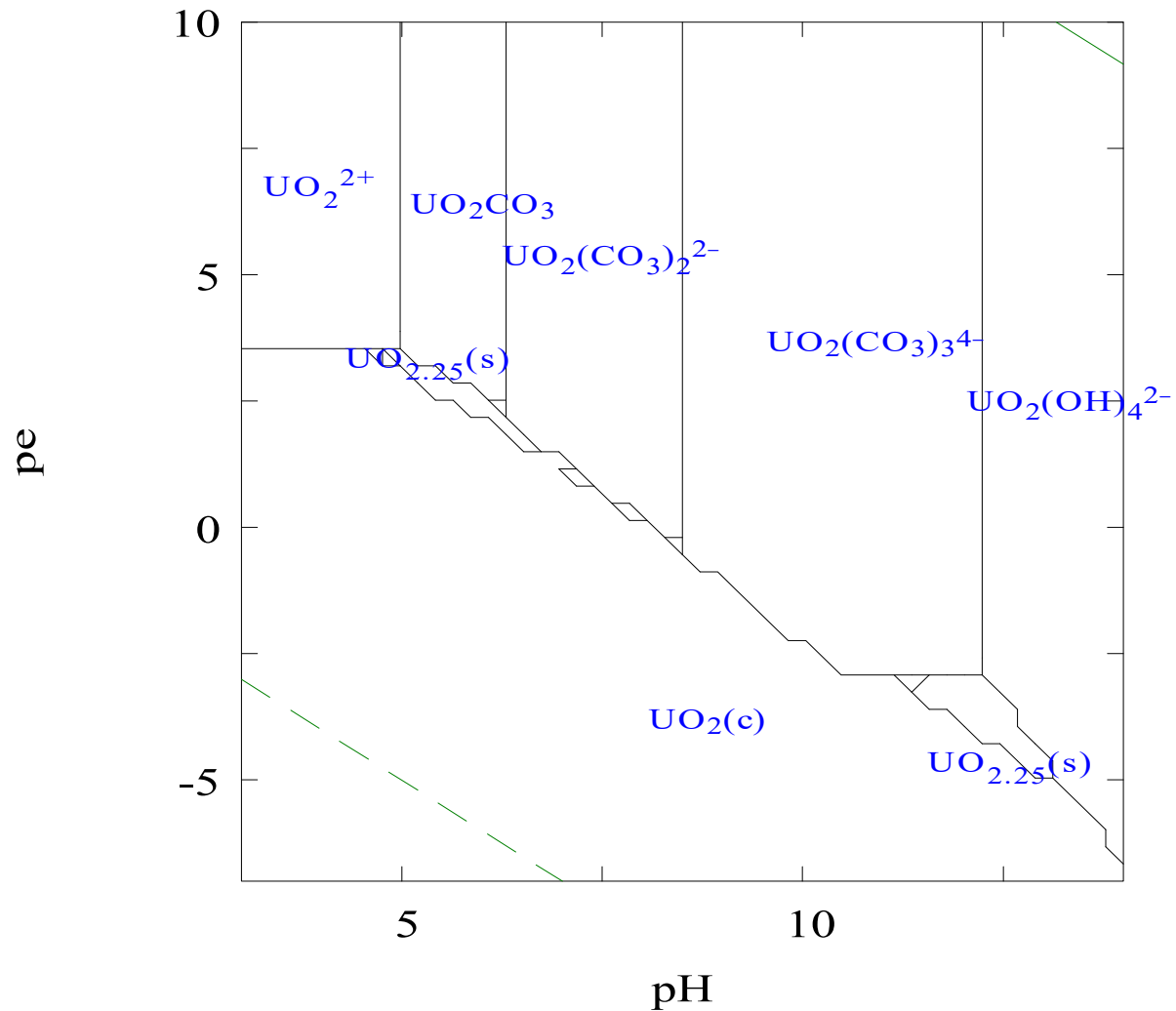
Speciation of Am(III) in presence of 2 mM CO_3^{2-} .



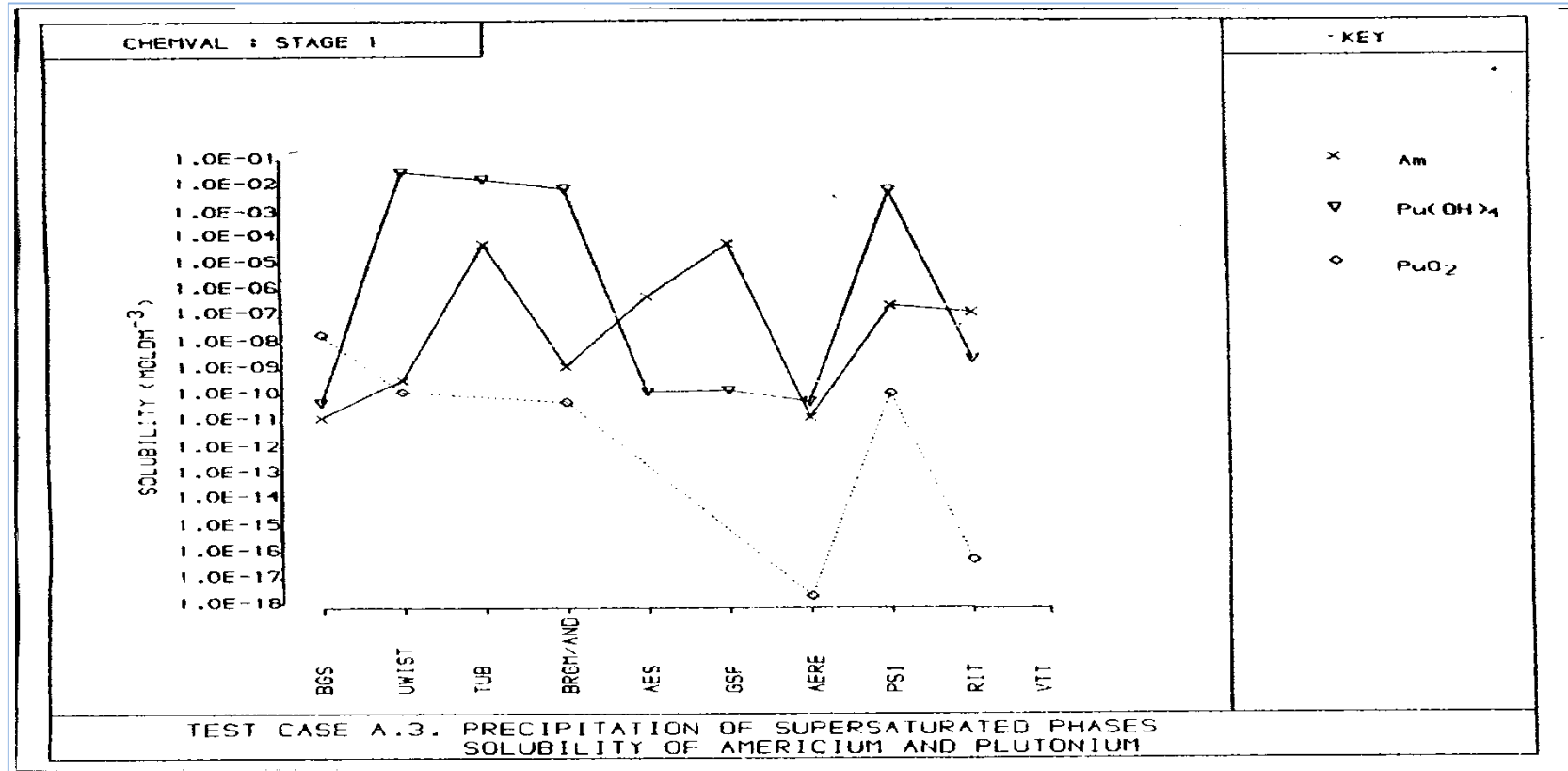
Uranium predominance diagram-1992 TDB

$[U^{4+}]_{TOT} = 0.10 \mu M$

$[CO_3^{2-}]_{TOT} = 1.80 mM$



The origins: The situation in the 1980's for data and codes



(From CEC Report EUR 12237 en (1989): CHEMVAL Project Stage 1: Verification of speciation models)

NEA TDB was launched in 1982 by the Data Bank and
Radioactive Waste Management Divisions of the NEA



Phase 0:
1982-86
"NBS DB
paradigm"

NEA:
Survey literature
Compile uncritical TDB

Literature +
Database software

Expert(s)
evaluate DB
for
EI_1

Expert(s)
evaluate DB
for
EI_2

Expert(s)
evaluate DB
for
EI_...

Expert(s)
evaluate DB
for
EI_n

Critically reviewed TDB

Selected
value tables

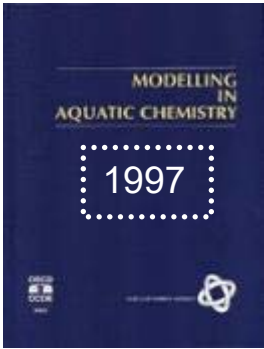
SKB



Phase I:
1986-98

NEA
Project
Coordinator

TDB
Advisory
Group



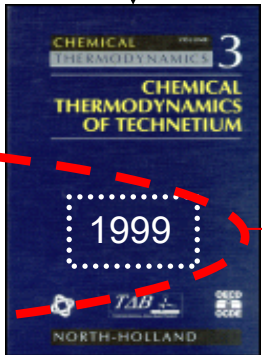
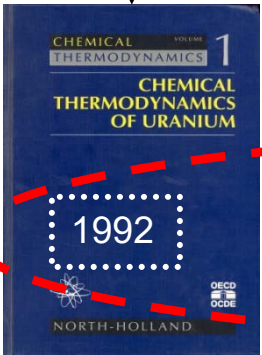
Review
Team
U

Review
Team
Np/Pu

Review
Team
Am

Review
Team
Tc

Critical review of
experimental
Literature
using
Guidelines



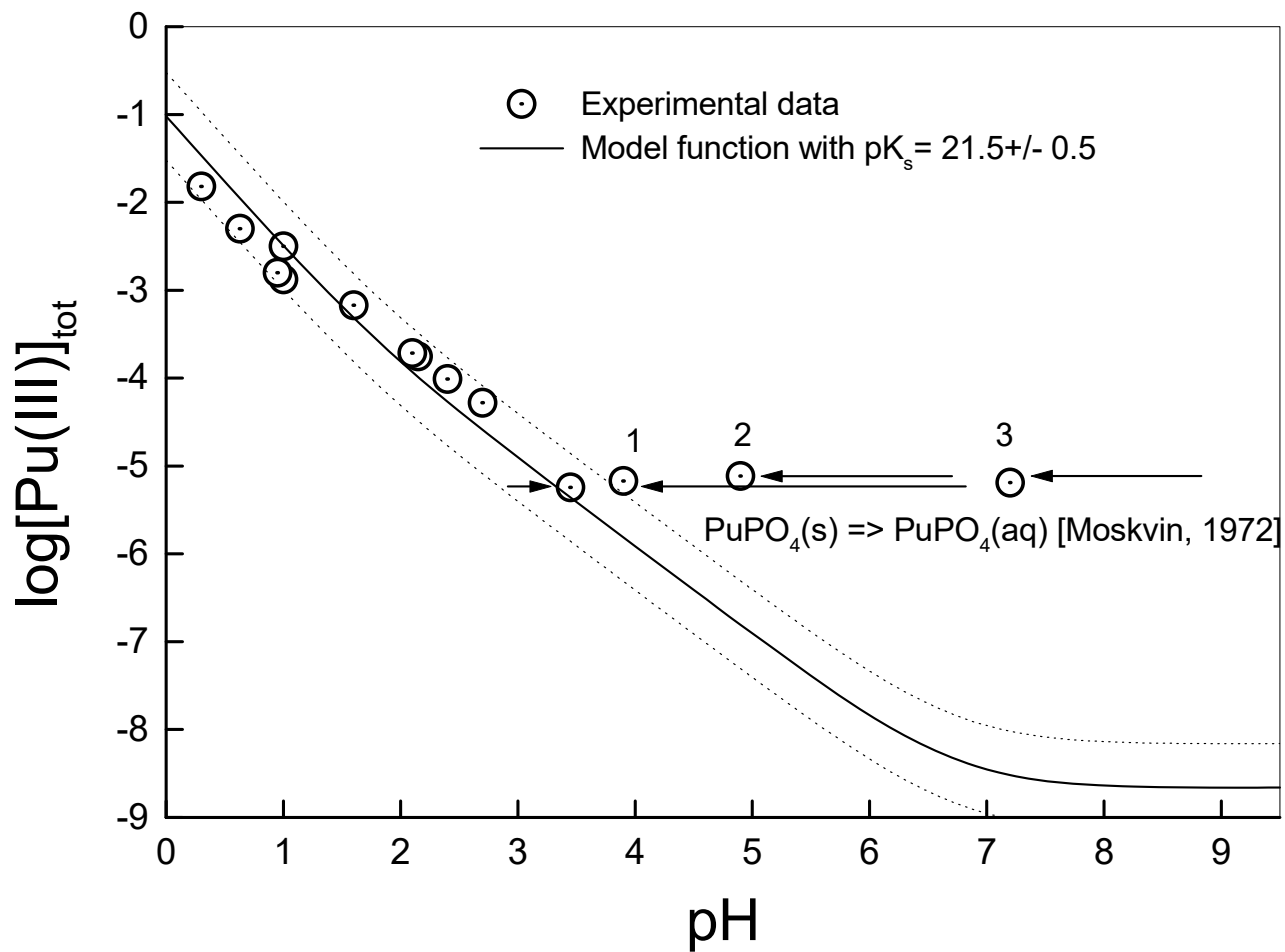
Large Delay

Critical reviews
Selected values
DB

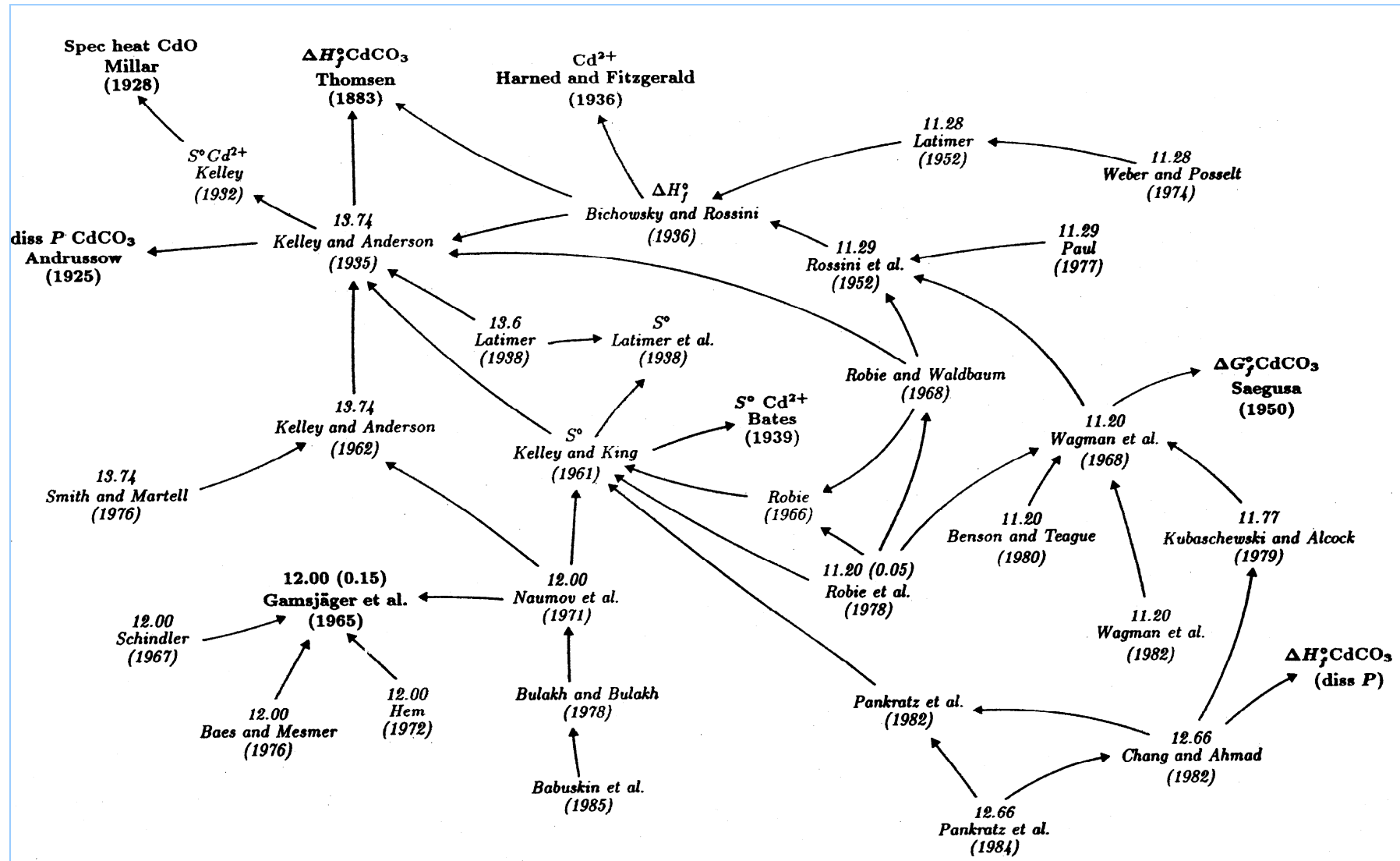
Lessons from the use of data in various project phases.

- Example: Pu-phosphate aqueous chemistry. Besides PuPO_4^0 , also $\text{Pu(IV)(HPO}_4)_x$; $x=1-5$, are rejected. No data on Pu(V), one study on Pu(VI). This does not mean complexes do not exist, but that further studies are needed.
- Other non existent species which live in databases: $\text{UO}_2(\text{H}_2\text{PO}_4)_2$ in EQ3/6 and Chemists Workbench: ~ 40 orders of magnitude error; $\text{Pu(IV)(CO}_3)_x$, $x=1-5$; D. Rai [1984] shows that they are ~ 35 orders in error; still they were included in Hatches TDB (2000).
- Avoids situations caused by lack of documentation, as e.g. in the case of published solubility data for $\text{CdCO}_3(\text{s})$.
- Estimation of Ni-S complexes need to be done by the users.

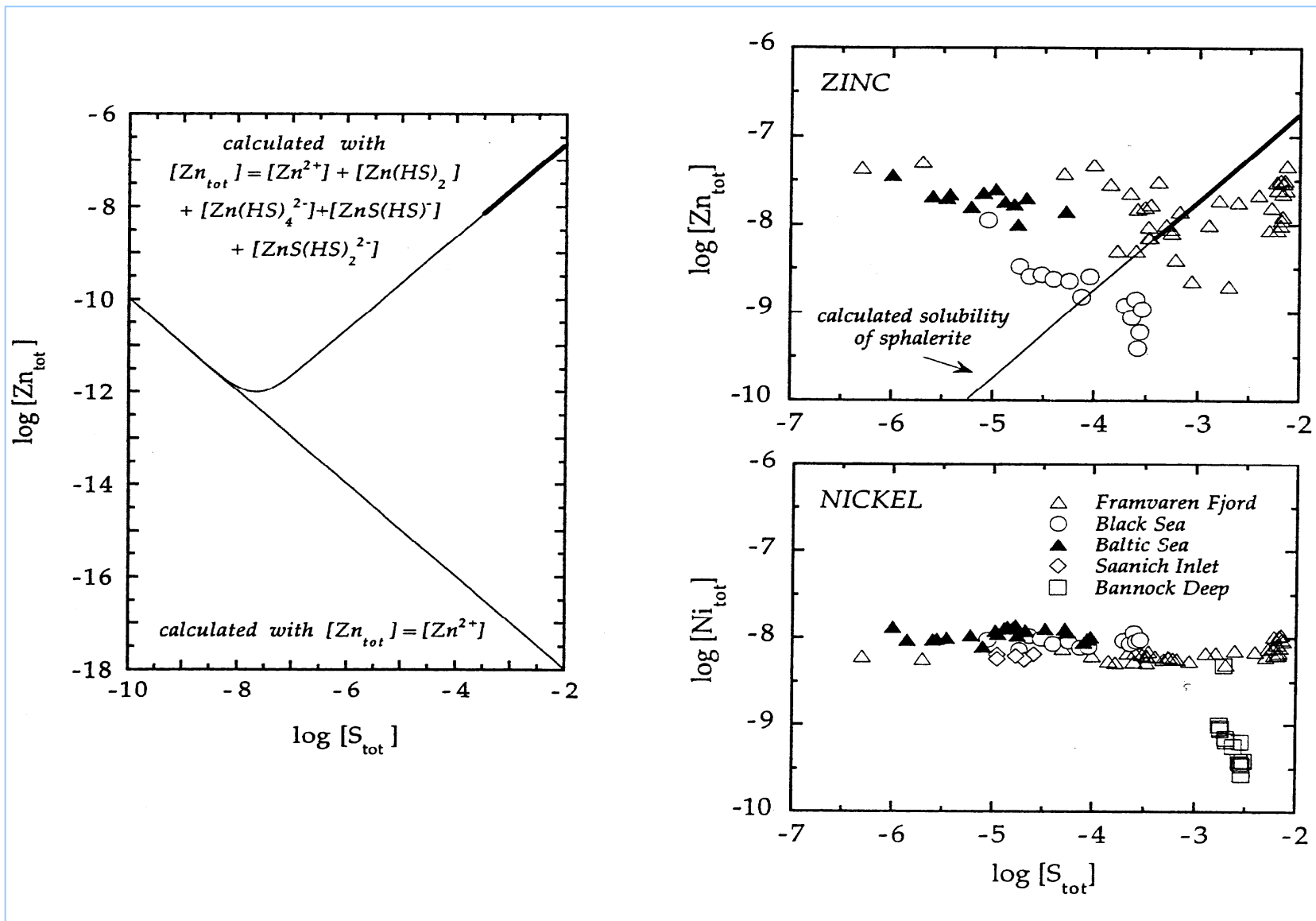
PuPO₄·xH₂O(s) solubility study



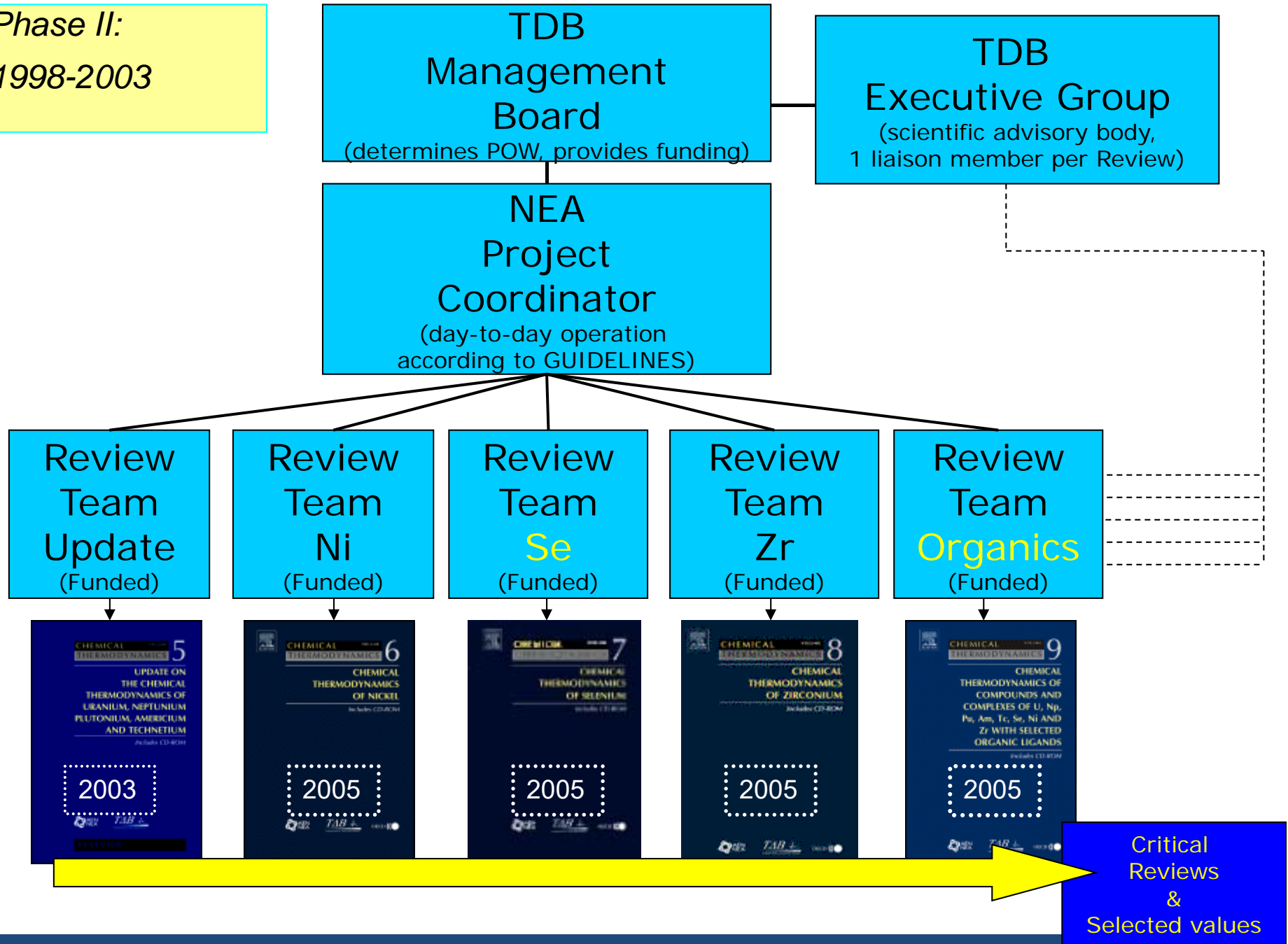
“Genealogical tree” of data on the solubility of $\text{CdCO}_3(\text{s})$ [1993STI/PAR]



NiS and ZnS solubilities [1999THO]-complete TDB.



Phase II:
1998-2003



TDB-III: 2003-2007

- NIRAS/ONDRAF (B)
- OPG (CAN)
- RAWRA (CZ)
- POSIVA (FIN)
- ANDRA (F)
- CEA (F)
- FZK INE (D)
- JAEA (JAP)
- ENRESA (E)
- SKB (S)
- SKI (S)
- HSK/NAGRA/PSI (CH)
- Nexia Solutions (UK)
- NIREX (UK)
- DOE (US)

TDB Management Board
(determines POW, provide funding)

TDB Executive Group
(scientific advisory body, 1 liaison member per Review)

NEA Project Coordinator
(day-to-day operation according to GUIDELINES)

Review Team Th
(Funded)
Publ. 2008

Review Team Sn
(Funded)
Publ. 2012

Review Team Fe part I
(Funded)
Publ. 2013

Expert Team SAR Solid Solutions
(Funded)
Publ. 2007



TDB-IV: 2008-2013

- NIRAS/ONDRAF (B)
- NWMO (CAN)
- RAWRA (CZ)
- POSIVA (FIN)
- ANDRA (F)
- CEA (F)
- FZK INE (D)
- JAEA (JAP)
- KAERI (KOR)
- ENRESA (E)
- SKB (S)
- HSK/NAGRA/PSI (CH)
- NDA (UK)
- DOE (US)

TDB Management Board
(determines POW, provide funding)

TDB Executive Group
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NEA Project Coordinator
(day-to-day operation according to GUIDELINES)

Review Team Fe vol.2
(Funded)

Review Team Mo
(Funded)

Review Team Ancilliary data
(Funded)

Expert Team SAR Cement systems
(Funded)



Thermodynamics, NEA-TDB

- OECD-NEA Thermochemical Database Project (<http://www.oecd-nea.org/dbtdb>) established international standard for aqueous actinide thermodynamics and solution chemistry.
- Thermodynamic data for solids, aqueous complexes and gas phases
- Use of transparent, traceable and well documented guidelines.
- Standards, conventions, symbols, nomenclature strictly defined and applied.
- SIT used to account for ion-interaction processes and to derive standard-state thermodynamic data.
- → NEA-TDB is highly consistent basis for reliable thermodynamic modeling.

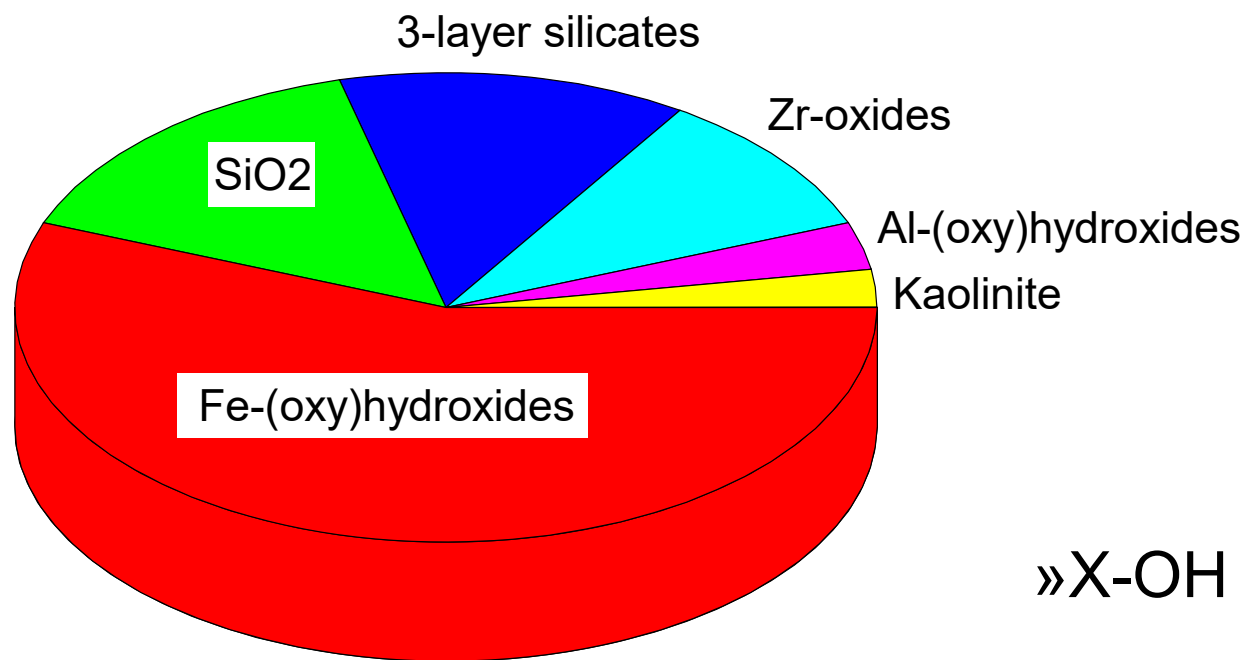
Title	Vol., Year
Chem. Thermodyn. of Uranium	Vol. 1 (1992)
Chem. Thermodyn. of Americium	Vol. 2 (1995)
Chem. Thermodyn. of Technetium	Vol. 3 (1999)
Chem. Thermodyn. of Np and Pu	Vol. 4 (2001)
Update on the Chem. Thermodyn. of U, Np, Pu, Am and Tc	Vol. 5 (2003)
Chem. Thermodyn. of Ni	Vol. 6 (2005)
Chem. Thermodyn. of Se	Vol. 7 (2005)
Chem. Thermodyn. of Zr	Vol. 8 (2005)
Chem. Thermodyn. of Compounds and Complexes of U, Np, Pu, Am, Tc, Se, Ni, Zr with Sel. Organic Ligands	Vol. 9 (2005)
Chem. Thermodyn. of Solid Solutions	Vol. 10 (2007)
Chem. Thermodyn. of Thorium	Vol. 11 (2009)
Chem. Thermodyn. of Tin	Vol. 12 (2012)
Chem. Thermodyn. of Iron	Vol. 13 (2014)

Sorption

- CEC or cation exchange capacity is the quantity of cations a mineral can accommodate in its negatively charged surface, units mol/kg or meq/100g. In the case of bentonite clay, both cation exchange, anion exclusion and sorption at the edge sites of clay platelets takes place.
- Sorption occurs mainly on silanol (Si-OH) or aluminol (Al-OH) groups of bentonite clay or aluminosilicate minerals of the rock. Usually the radionuclides which have strong hydrolysis (strong binding with OH-groups of water) also sorb strongly. Such are the low valence states or reduced forms of actinide ions, which have also strong sorption. Most of the mineral surfaces are negatively charged at near neutral pH, typical for groundwaters. This is the reason why anions do not sorb and become a problem in PA.
- Distribution coefficient $K_d = C_{\text{solid}} / C_{\text{solution}}$, characterises sorption on specific sorption sites. C_{solid} is given in mol/kg and C_{soln} in mol/m³, thus K_d units are m³/kg. Sorption isotherm is: $C_{\text{solid}} = K_d C_{\text{soln}}$
- K_d depends on: Aqueous and solid phase composition, temperature, ionic strength, contact time etc.
- Models: single value K_d , parametric K_d , mass action models (i.ex.) and surface complexation models. The last two difficult to use with transport codes.
- NEA Sorption Modelling Forum-Sorption database with several thousand R_d . Aims at the use of mechanistic models to support chosen R_d or uncertainty range.
- If the chemical properties of a species are well known, one can predict also its sorption properties. However, in most cases the K_d needed for PA have to be determined at the specific site chosen.

SCM Data Overview – Mineral coverage

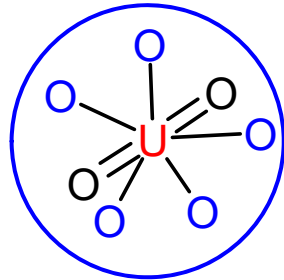
- The actual RES³T database lists more than 600 log K records for U(VI) – compared to only 11 for U(IV).



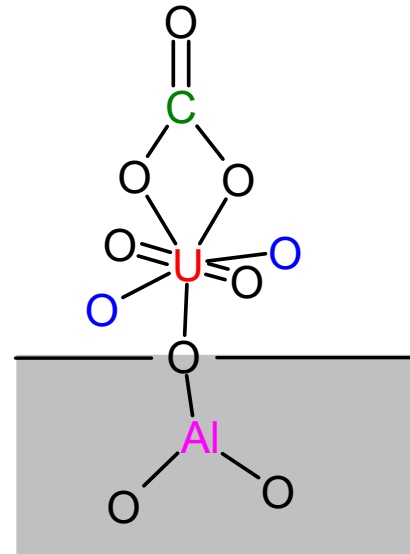
Distribution of SCM log K values among mineral groups

Surface complex categorization

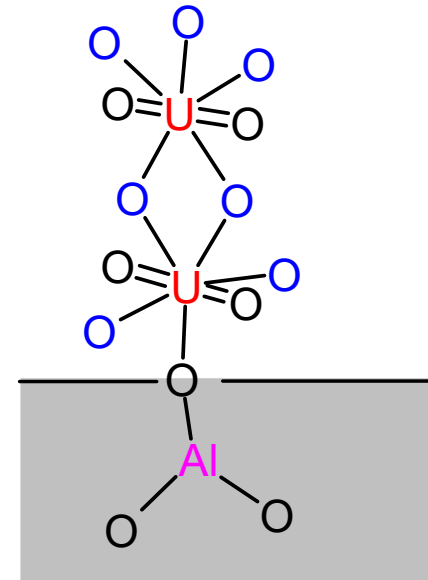
- Type of binding
- Denticity
- Oligomerization
- # components



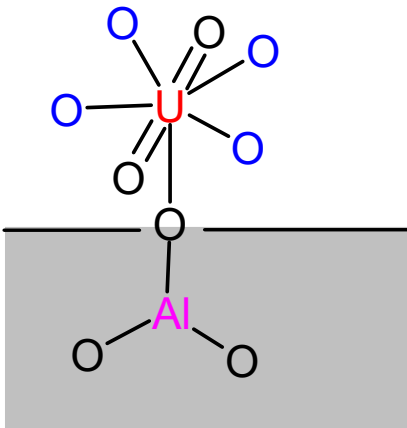
Outer-sphere



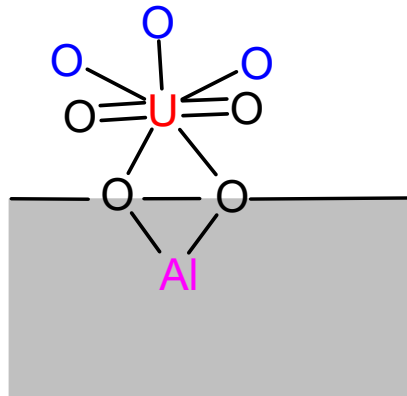
Inner-sphere, monodentate, ternary



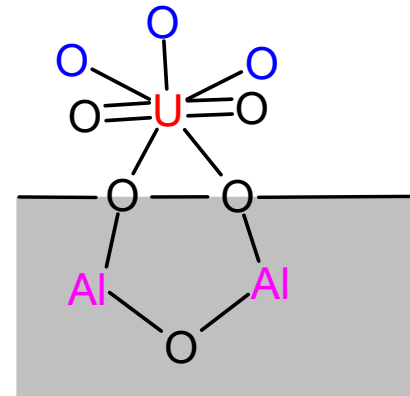
Inner-sphere, monodentate, binuclear



Inner-sphere, monodentate, mononuclear



Inner-sphere, bidentate, mononuclear

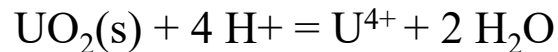


Inner-sphere, bidentate, mononuclear

Radionuclide solubilities

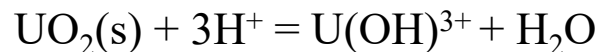
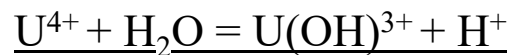
- Radionuclide solubilities are very important both for determining solubility limits to be used in performance assessment and for judging about experimental results on fuel dissolution.
- Very often a constant concentration of a radionuclide in time indicates that it is probably in equilibrium with a solid phase of the given element.
- The solubility of e.g. $\text{UO}_2(\text{s})$ is usually plotted as the concentration of total U in solution as a function of pH or $-\log[\text{H}^+]$.

The solubility product for $\text{UO}_2(\text{s})$ can be written:



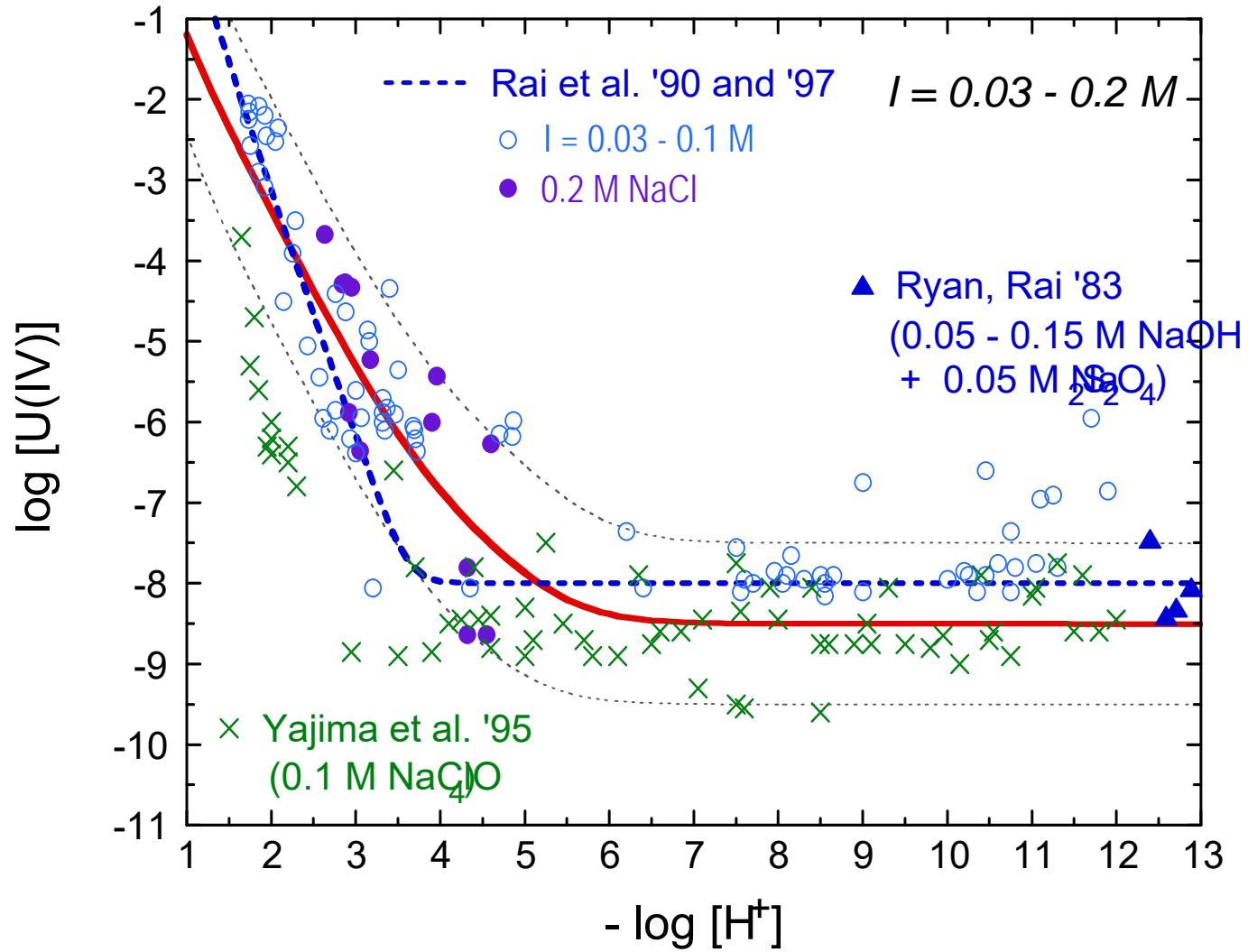
In this case $K_{\text{sp}} = \{\text{U}^{4+}\} \{\text{H}_2\text{O}\}^2 / \{\text{H}\}^4$ or $\log [\text{U}^{4+}] = \log K_{\text{sp}} - 4 \text{pH} + 2 \log a_{\text{w}}$.

- In the horizontal part, the reaction is $\text{UO}_2(\text{s}) + 2\text{H}_2\text{O} = \text{U}(\text{OH})_4(\text{aq})$
- If the first hydrolysis complex dominates in solution, we have:

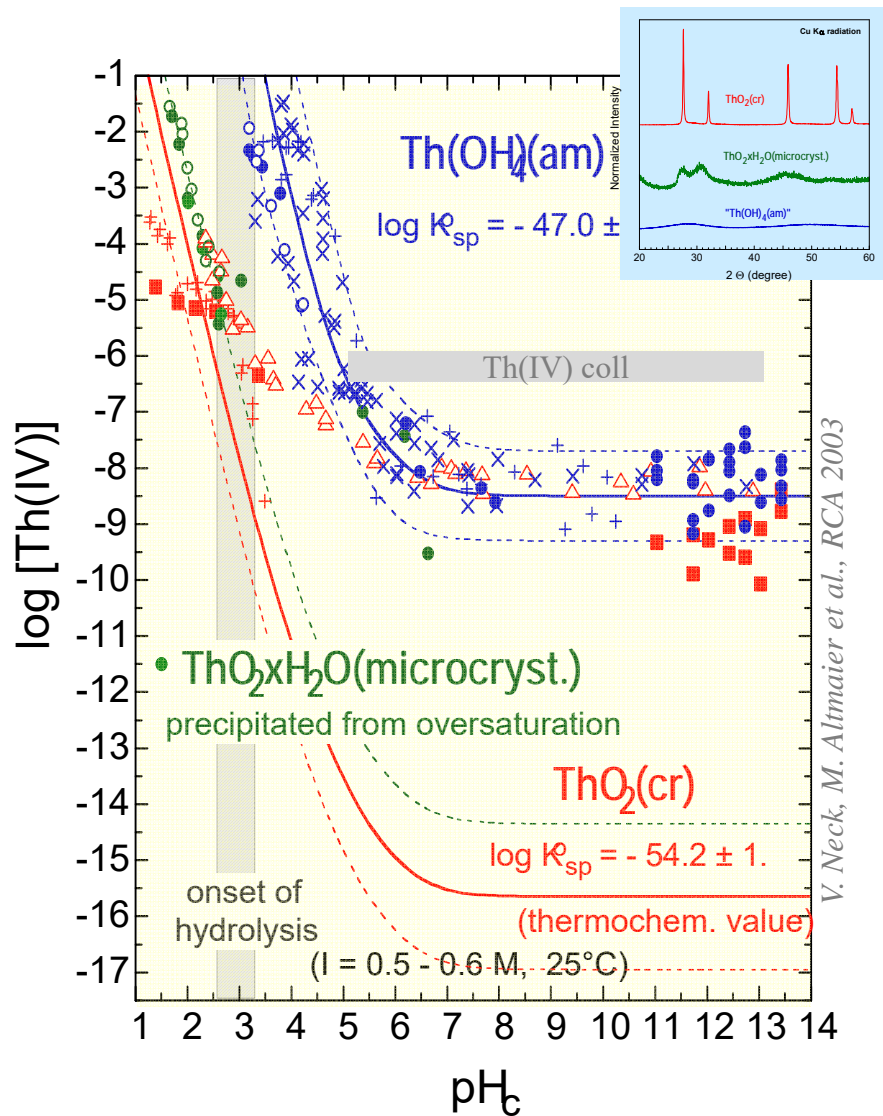


--This plots as a line of slope -3!

Solubility of U(IV) at 25°C



Solubility of different Th(IV) solid phases



- Distinct differences between amorphous and crystalline thorium oxohydroxides.

- Rather good agreement with calculated solubility curves at acidic conditions.

- Solubility of $\text{ThO}_2\text{(cr)}$ in neutral to alkaline range significantly higher than calculated.

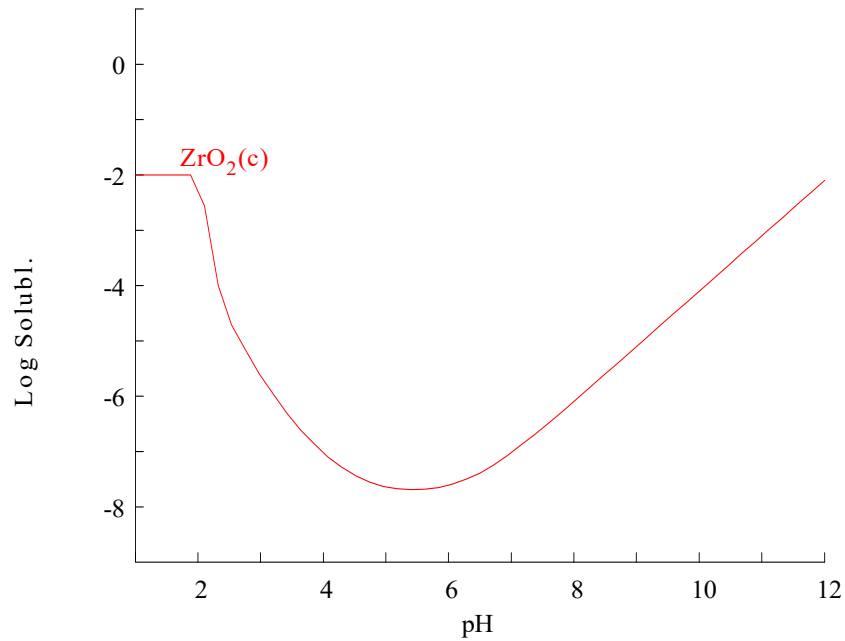
- $\text{ThO}_2\text{(cr)}$ solubility slightly lower than for amorphous phase.

- Intrinsic colloids found at $[\text{Th}] \sim 10^{-6} \text{ M}$ concentration level.

Large differences in Th(IV) solubility data clearly related to chemical processes (e.g. characteristics of solid phases) and not due to any “basic uncertainties”.

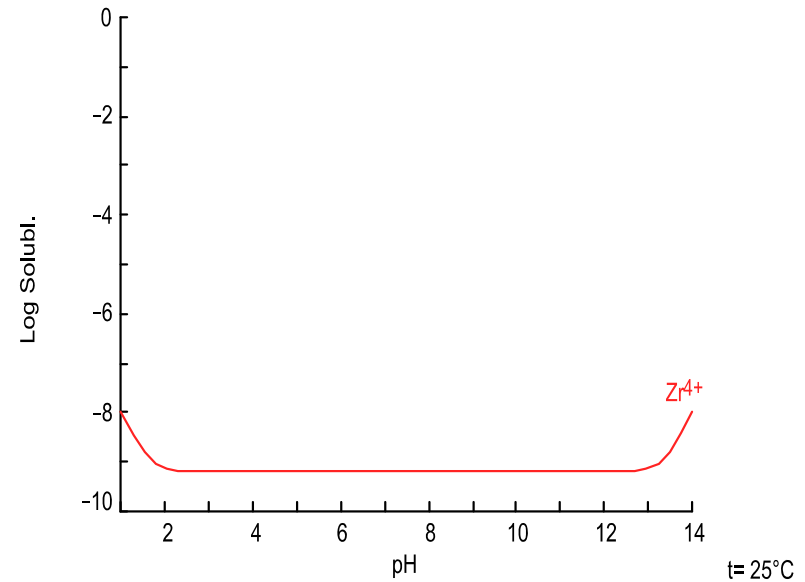
Importance of databases.

$[\text{ZrO}_2(\text{c})]_{\text{TOT}} = 10.00 \text{ mM}$



Solubility of $\text{ZrO}_2(\text{s})$ calculated
with Phreeqc TDB

$[\text{Zr}^{4+}]_{\text{TOT}} = 10.00 \mu\text{M}$



Solubility of $\text{ZrO}_2(\text{s})$ calculated
with NEA TDB

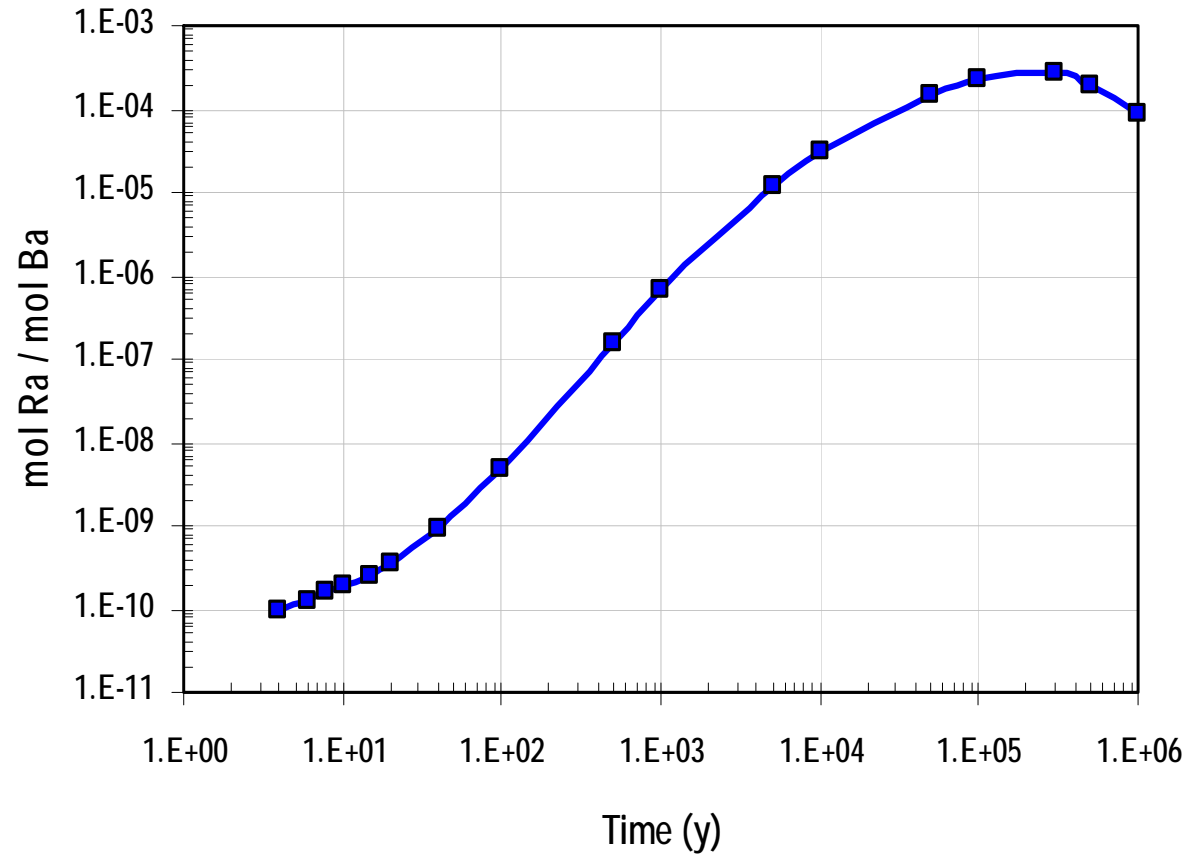


Spent fuel as source of Ra and Ba.

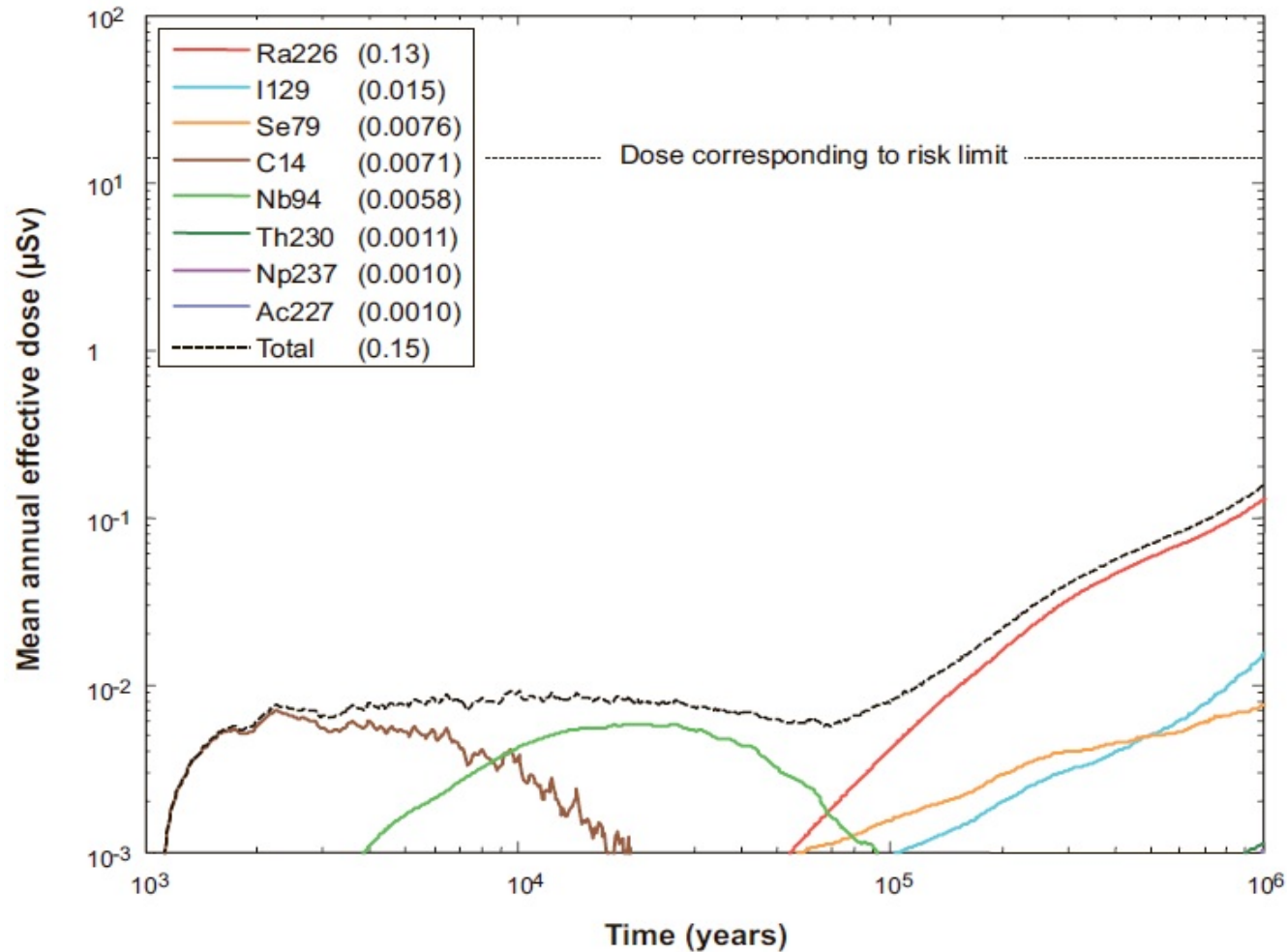
- Fuel dissolution rate: log-triangular distribution (10^{-8} , 10^{-7} , 10^{-6})/ year, i.e. about 0.2 g. fuel per container and year dissolves and releases U, other actinides and fission products, as well as Ra and Ba.
- Two sources of Ra: From dissolution of pristine fuel and from the precipitated $\text{UO}_2(\text{s})$ accumulated during all years. In the presence of sulfate, most of the released Ba precipitates as barite (BaSO_4).
- All experimental data indicate that even pre-oxidized U is reduced and precipitates on fuel surface. The low U concentrations indicate for a more crystalline phase than that formed in natural UO_2 solubility tests. We conservatively assume that all precipitated UO_2 contributes to Ra releases.
- The concentration of Ra released during fuel dissolution is governed by the solubility of $\text{RaSO}_4(\text{s})$:
$$\text{RaSO}_4(\text{s}) = \text{Ra}^{2+} + \text{SO}_4^{2-} \quad \log K_{\text{RaSO}_4}^0 = \log(a_{\text{Ra}} \cdot a_{\text{SO}_4}) = -10.26$$

Means that for 1 mM sulfate ($\log [\text{SO}_4] = -3$), Ra concentration is $10^{-7.26}$ M.
- It is well known that Ra and Ba in the presence of sulfate ions form mixed $(\text{Ra,Ba})\text{SO}_4$ precipitates (they **co-precipitate**) forming so-called solid solutions.

Time evolution of the molar ratio Ra/Ba in unaltered spent fuel.



Ra dominates dose after 100 kyears.



SKB (2011). *Long-term safety for the final repository for spent nuclear fuel at Forsmark: Main report of the SR-Site project. Sweden: SKB TR 11-01.*



(Ra,Ba)SO₄ co-precipitation

- In case an ideal mixed (Ra,Ba)SO₄ solid solution is formed with a mole fraction of Ra equal to x , the activity of RaSO₄(s) end member in the solid solution is nearly equal to its mole fraction: $a_{\text{RaSO}_4} \cong x_{\text{RaSO}_4}$. Then from definition of solubility product:

$$K^0_{\text{RaSO}_4} = (a_{\text{Ra}} \cdot a_{\text{SO}_4}) / x_{\text{RaSO}_4} \quad \text{or} \quad a_{\text{Ra}} \cdot a_{\text{SO}_4} = x_{\text{RaSO}_4} \cdot K^0_{\text{RaSO}_4}$$

- It follows that e.g. for $x = 10^{-3}$ - 10^{-4} , Ra concentration in equilibrium with the solid solution is 1000 to 10000 times lower than for equilibrium with pure RaSO₄(s).

Thank you!



