Lanthanide and actinide inorganic complexes in natural waters. TRLFS* and ESI-MS** studies.

Advances in acquisition of thermodynamic data

* **T**ime-**R**esolved **L**aser-induced **F**luorescence **S**pectroscopy
** **E**lectro**S**pray **I**onization **- M**ass **S**pectrometry

Thomas VERCOUTER[1,2,3], Badia AMEKRAZ[2,3], Christophe MOULIN[3], Pierre VITORGE[2,3]

ANDRA

[1] **N**ational radioactive waste management agency

[2] **U**MR 8587 (Evry University - CEA - CNRS)

Université d'Évry-Val d'Essonne

[3] **N**uclear **E**nergy **D**ivision/ **D**epartment of **P**hysics and **C**hemistry
Service for the studies of the radionuclides behaviour
Molecules and **R**adionuclides **S**peciation **L**aboratory

Advances in acquisition of thermodynamic data

1- Sulphate complexation

ESI-MS (La)

TRLFS (Eu)

2- Carbonate complexation

TRLFS and solubility measurements (Eu)

3- Temperature influence on carbonate complexation

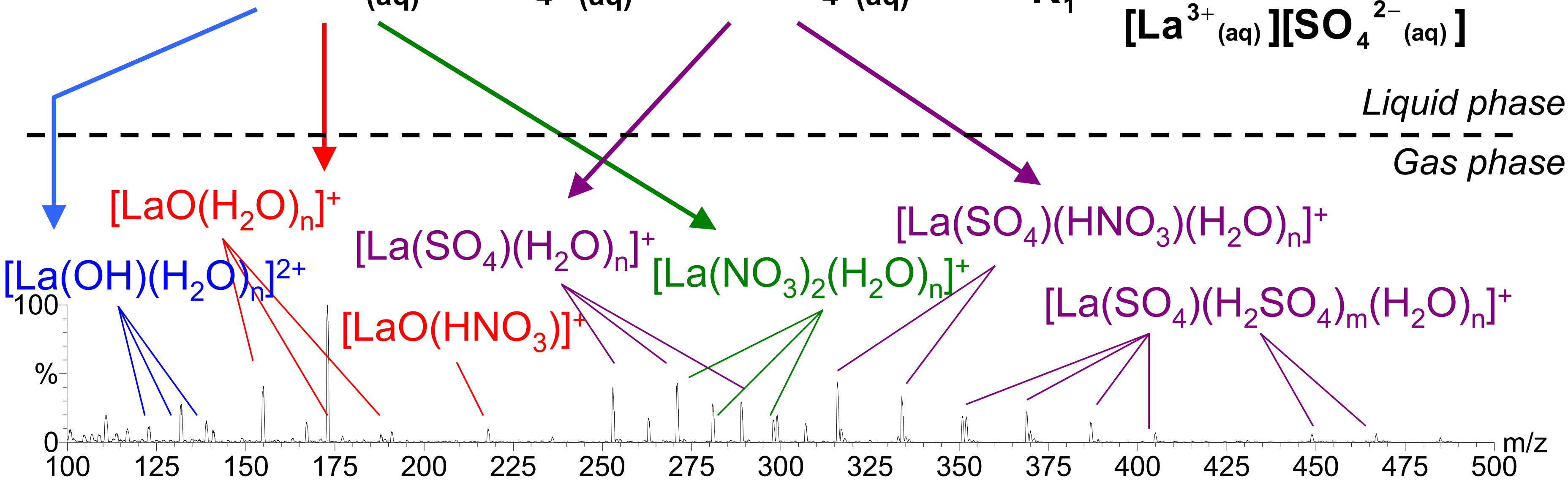
TRLFS (Cm)

Formation of $LaSO_4^+$: an ESI-MS study

➔ La has a very stable oxidation state +III

➔ The speciation in the **initial solution with pH =1-2** can be simply described

$$La^{3+}_{(aq)} + SO_4^{2-}{}_{(aq)} = LaSO_4^{+}{}_{(aq)} \qquad K_1 = \frac{[LaSO_4^{+}{}_{(aq)}]}{[La^{3+}_{(aq)}][SO_4^{2-}{}_{(aq)}]}$$



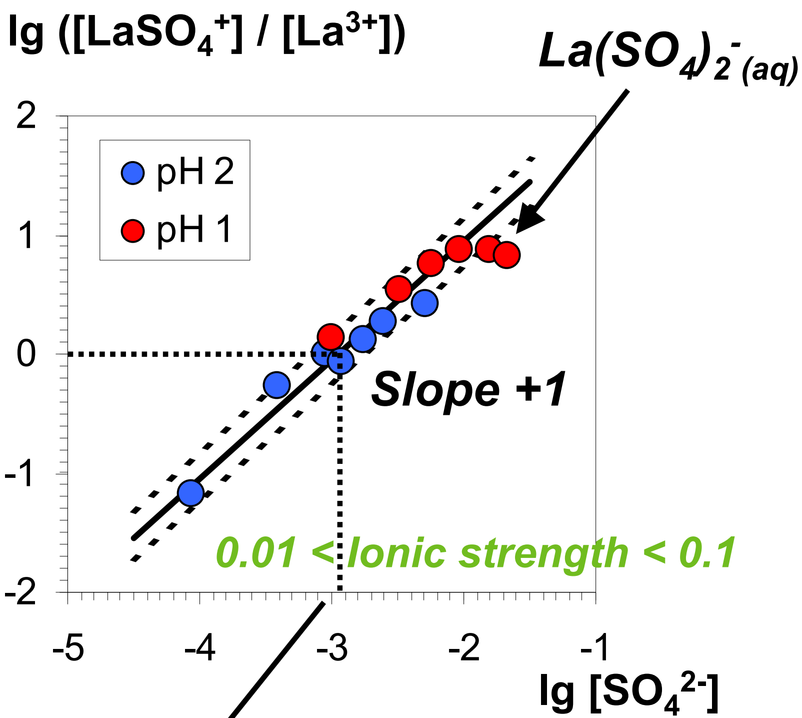
➔ **Numerous La(III) species** in the gas phase (positive-ion detection mode)

➔ **Interpretation** : identification with the species in the aqueous solution

Stabilities of MSO_4^+ and $M(SO_4)_2^-$

ESI-MS

$La^{3+}_{(aq)} + SO_4^{2-}{}_{(aq)} = LaSO_4^+{}_{(aq)}$

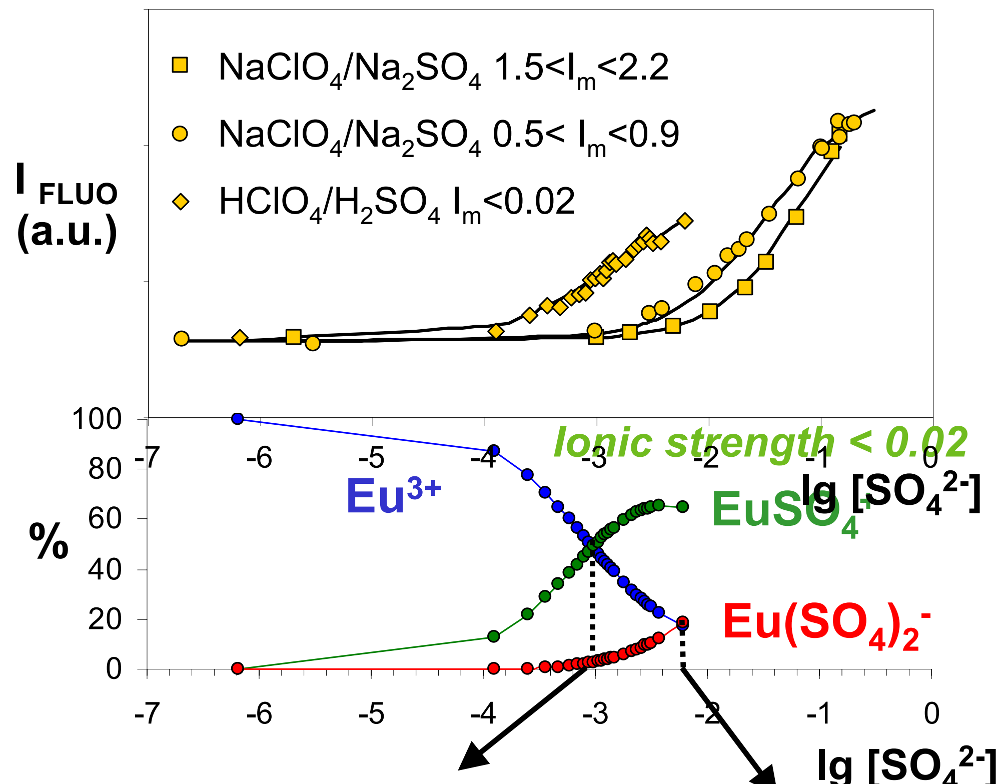


$\lg K_{1(La)} = 2.95 \pm 0.15$

TRLFS

$Eu^{3+} + SO_4^{2-} = EuSO_4^+$

$EuSO_4^+ + SO_4^{2-} = Eu(SO_4)_2^-$



$\lg K_{1(Eu)} = 3.0 \pm 0.1$

$\lg K_{2(Eu)} = 2.2 \pm 0.1$

$\lg K_1$ and $\lg K_2$ dependences with ionic strength, I_m

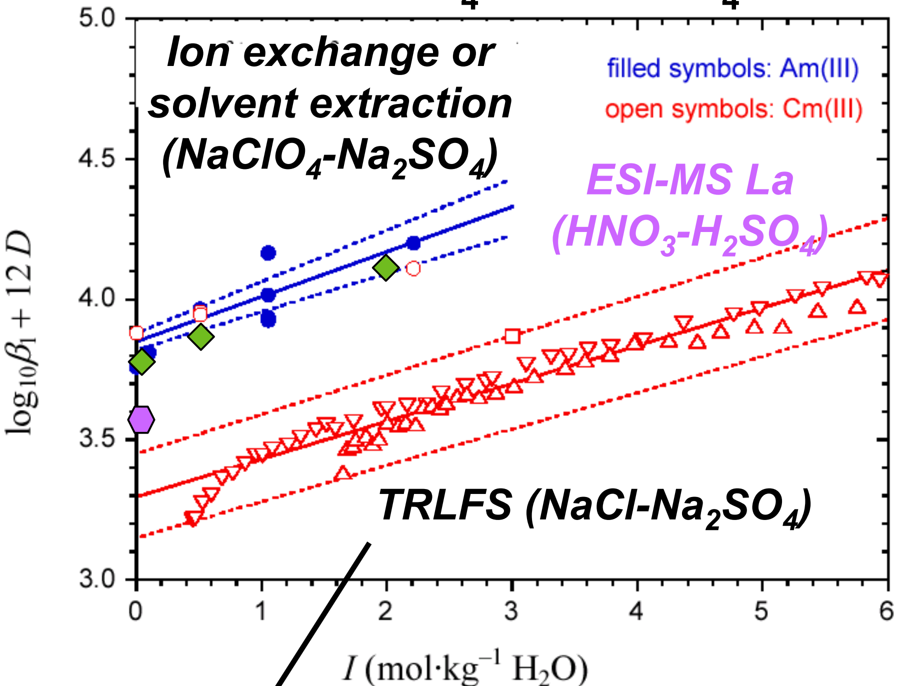
Comparison with selected literature data

➔ OECD-NEA critical reviews

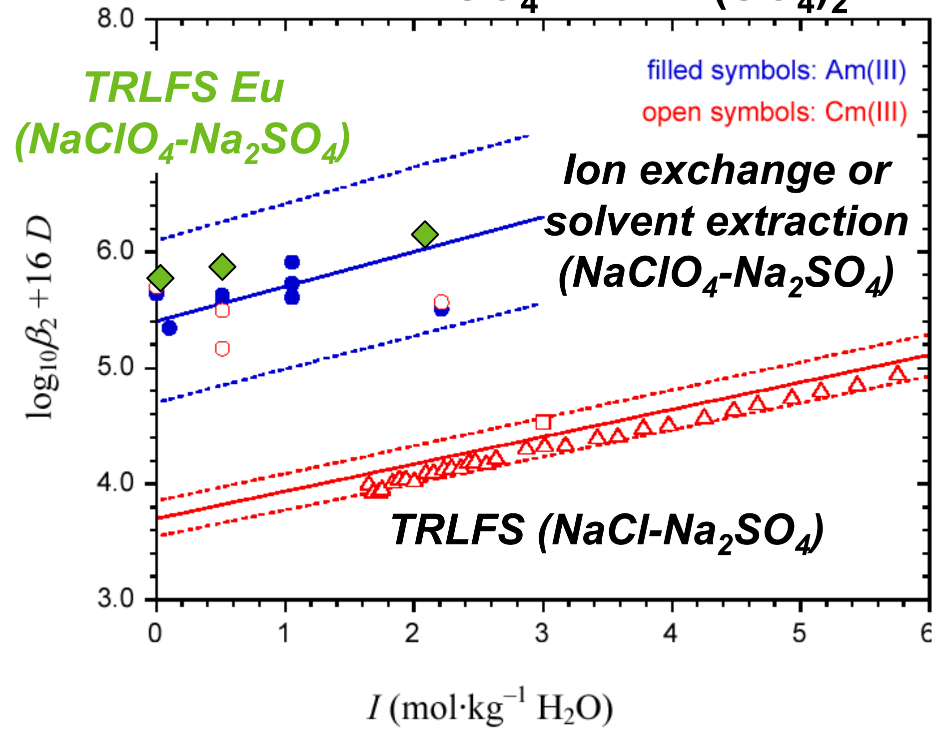
1995 R.J. SILVA, G. BIDOGLIO, M.H. RAND, P.B. ROBOUCH, H. WANNER, I. PUIGDOMENECH, *Chemical thermodynamics of Am*, Elsevier Science, Amsterdam, 374p.

2003 update R. GUILLAUMONT, T. FANGHANEL, 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 Science, Amsterdam, 919p.

$An^{3+} + SO_4^{2-} = AnSO_4^{+}$

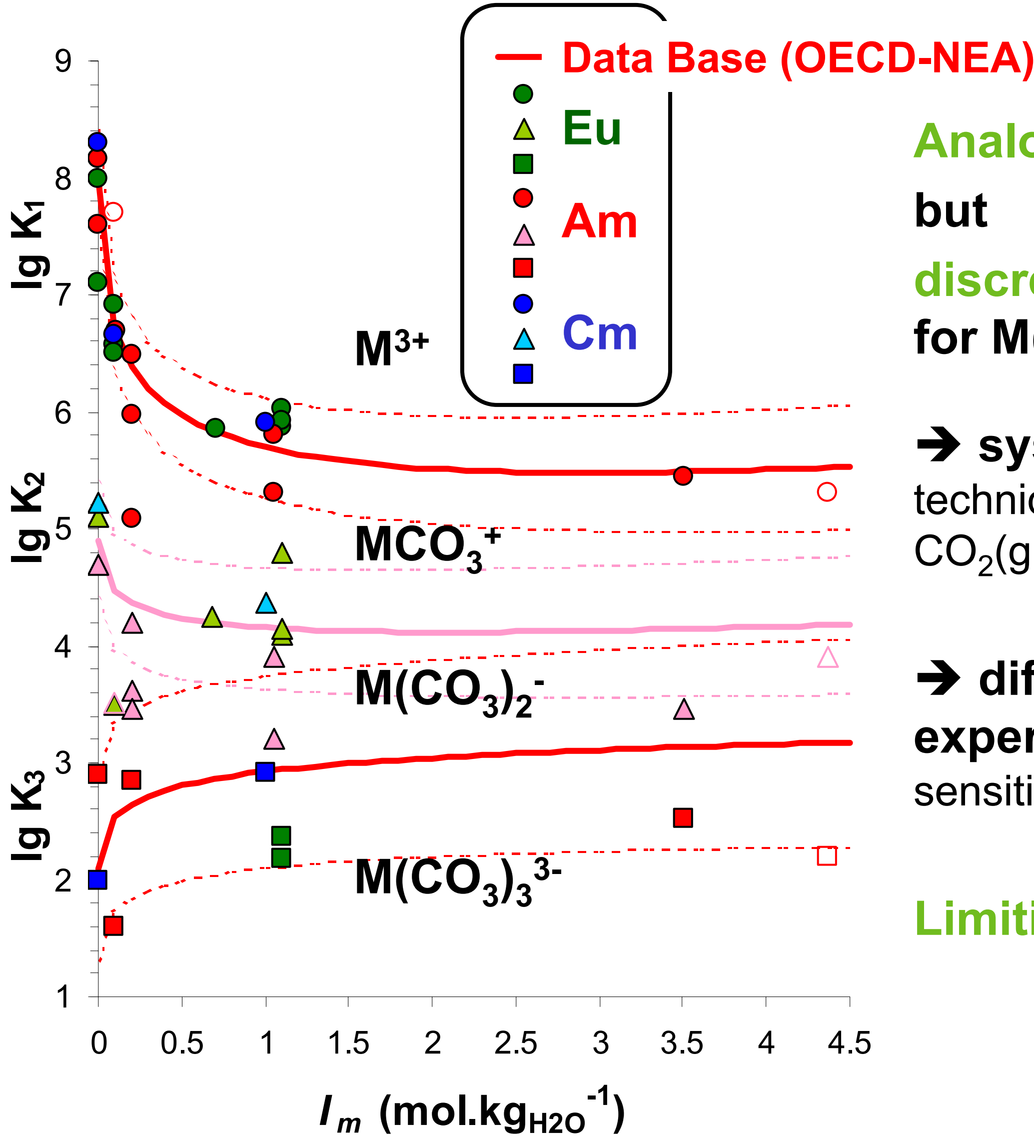


$An^{3+} + 2\ SO_4^{2-} = An(SO_4)_2^{-}$



P. PAVIET, T. FANGHANEL *et al.*, Radiochim. Acta, **74**, 99-103 (1996)
V. NECK, T. FANGHANEL *et al.*, Report, 1-108 (1998)

Carbonate complexation of M(III)



Analogy between M(III),

but

discrepancies in lg K_i values
for $M(CO_3)_i^{3-2i}$ with M = Eu, Am, Cm

➔ **systematic errors** (differences in the techniques, pH measurements, control of CO_2(g), [HCO_3^-] and [CO_3^{2-}], ...)

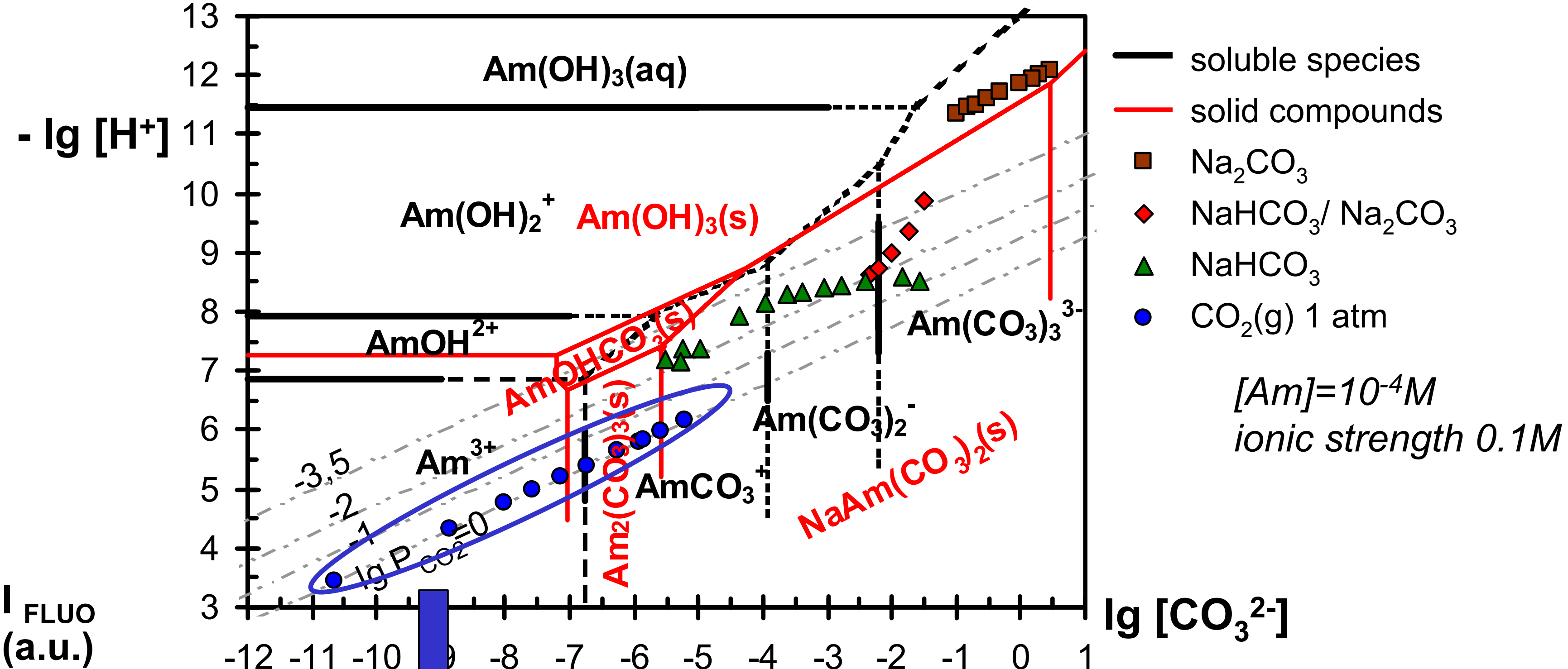
➔ **difficulties in the interpretations of experimental data** (nature of solid phases, sensitivity analyses, …)

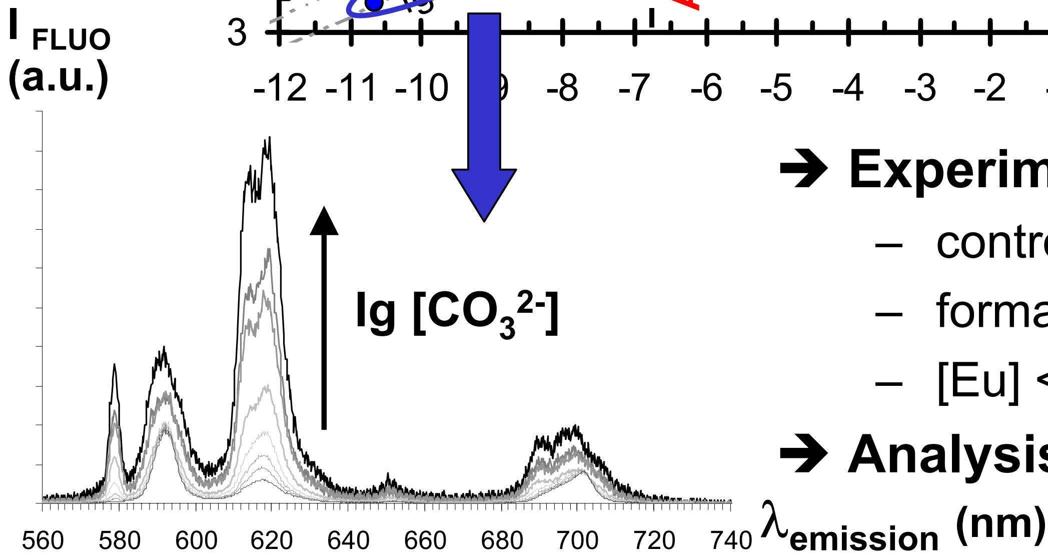
Limiting carbonate complex

$M(CO_3)_3^{3-}$ and/or $M(CO_3)_4^{5-}$?

Analogy ?

Planning of TRLFS experiments on Eu solutions





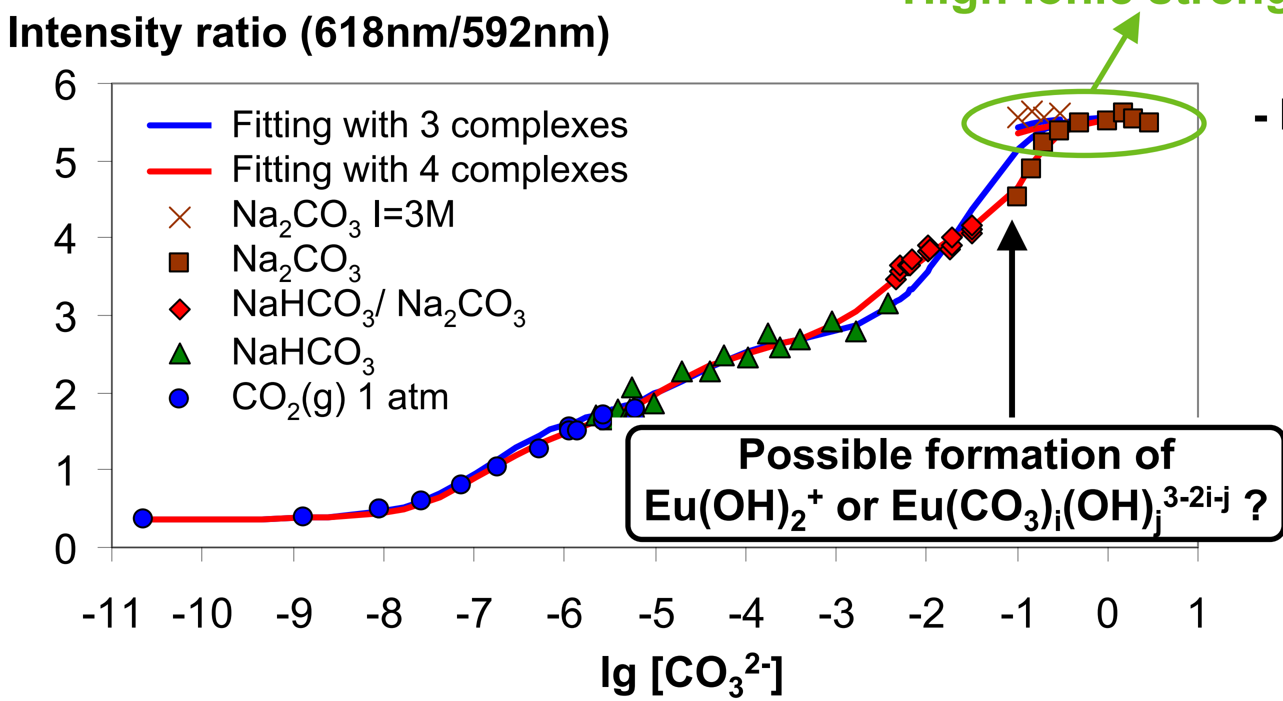
➔ Experimental conditions :

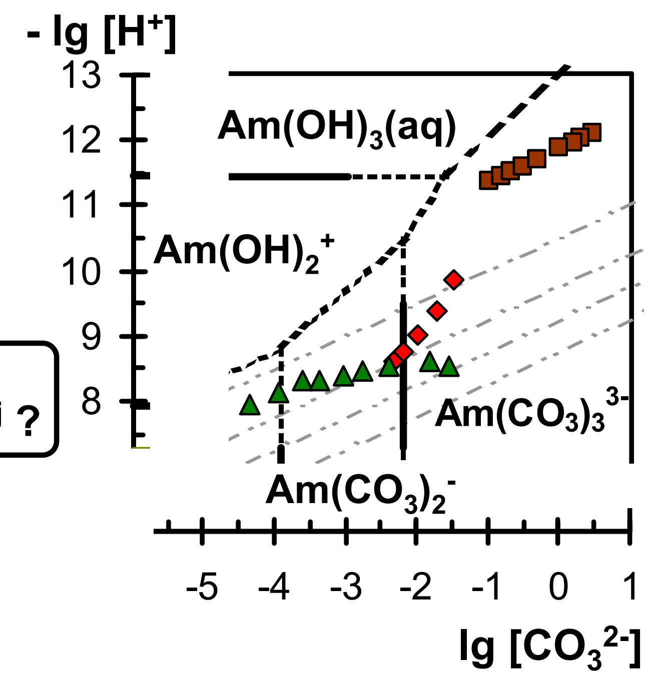
- control of the carbonate speciation
- formation of Eu carbonate complexes
- [Eu] < solubility limit

➔ Analysis of fluorescence spectra

Sensitivity analysis

High ionic strength (3M) : unique species





- ➔ Characterization of the formation of $EuCO_3^+$, $Eu(CO_3)_2^-$, $Eu(CO_3)_3^{3-}$ ($Eu(CO_3)_4^{5-}$?)
- ➔ **Sensitivity analysis** : possible other complexes
- ➔ Isolation of the **limiting complex at high ionic strength**

Stoichiometry of the limiting complex is not straightforward

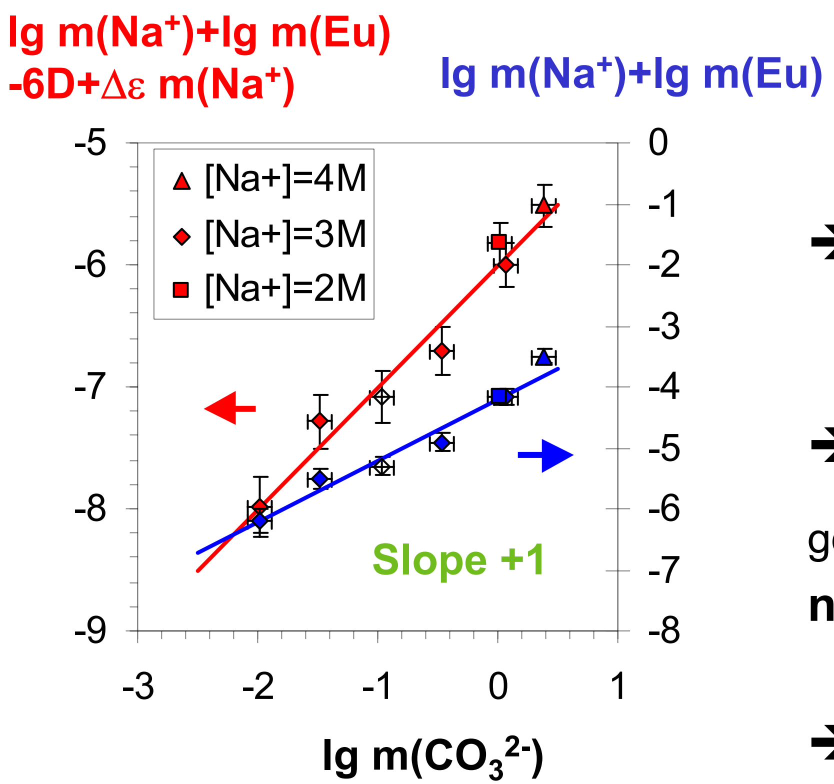
Limiting complex $Eu(CO_3)_3^{3-}$

Solubility experiments at high ionic strength :

synthesis of $NaEu(CO_3)_2,xH_2O(s)$ (confirmed by XRD)

[Eu] measured by ICP-AES

$$NaEu(CO_3)_2,xH_2O(s) + (i-2)\ CO_3^{2-} = Na^+ + Eu(CO_3)_i^{3-2i} + xH_2O$$



➔ **Slope analysis** => **i = 3**

thus **$Eu(CO_3)_3^{3-}$**

➔ **Ionic strength corrections**

good agreement between the data at different $[Na^+]$

no $Eu(CO_3)_4^{5-}$ is observed up to $[CO_3^{2-}]$ = 2M

➔ Influence on other lg K values

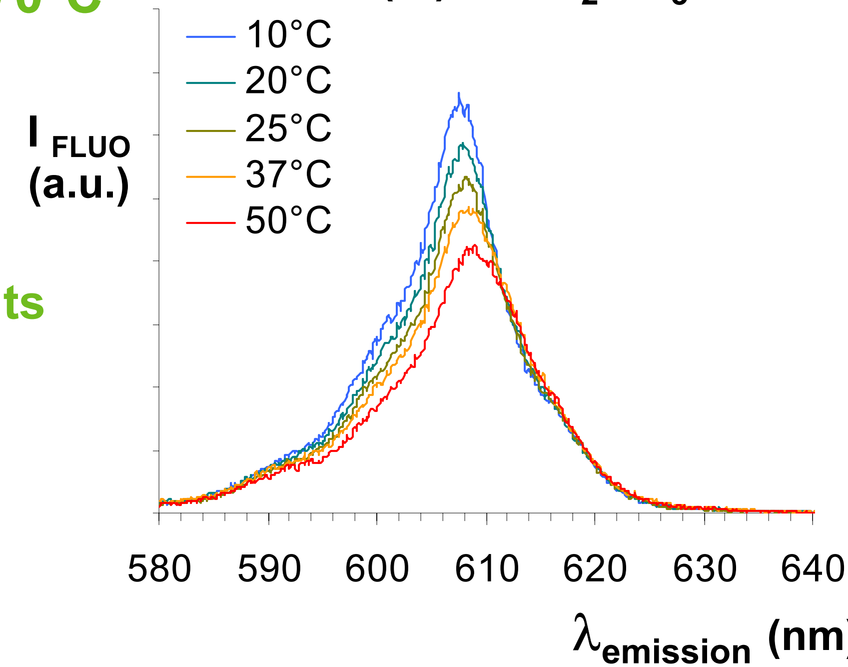
T° dependence on $Cm(CO_3)_i^{3-2i}$ formation

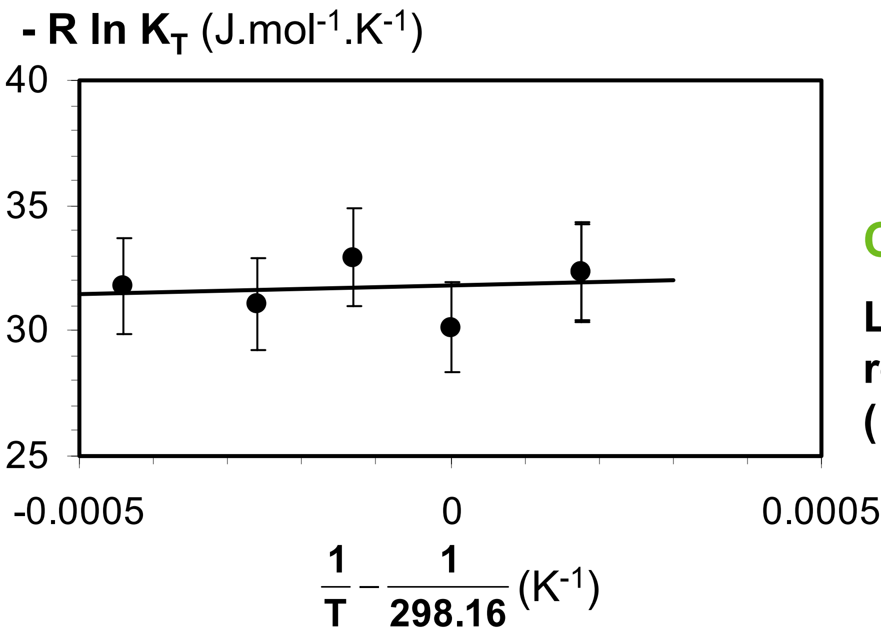
TRLFS on ^{248}Cm solutions **from 10°C to 70°C**

- ➔ effect of T on the fluorescence
- ➔ lg K_i by spectral decomposition
- ➔ determination of **thermodynamic constants**

$$R \ln K_T = R \ln K_{T°} - \Delta_r H\left(\frac{1}{T} - \frac{1}{T°}\right)$$

Cm(III) in Na_2CO_3 1M





$Cm(CO_3)_2^- + CO_3^{2-} = Cm(CO_3)_3^{3-}$

Linear regression (± 1.96 σ)

- $\Delta_r H = -1 \pm 4$ kJ.mol^{-1}
- $R \ln K_{25°C} = 32 \pm 1$ J.mol^{-1}.K^{-1}

➔

- $\Delta_r G_{25°C} = -9.5 \pm 0.3$ kJ.mol^{-1}
- $\Delta_r S_{25°C} = 30 \pm 14$ J.mol^{-1}.K^{-1}

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