

## Introduction

- Actinides relevant in the context of deep geological disposal: Am(III), Pu(III)/Pu(IV) especially important (→ reducing conditions).

### AIM: comprehensive assessment of actinide solubility and speciation from dilute to highly concentrated brine solutions.

- Presence of boron under repository-conditions:

- Component of intruding brines.
- Part of the emplaced waste.

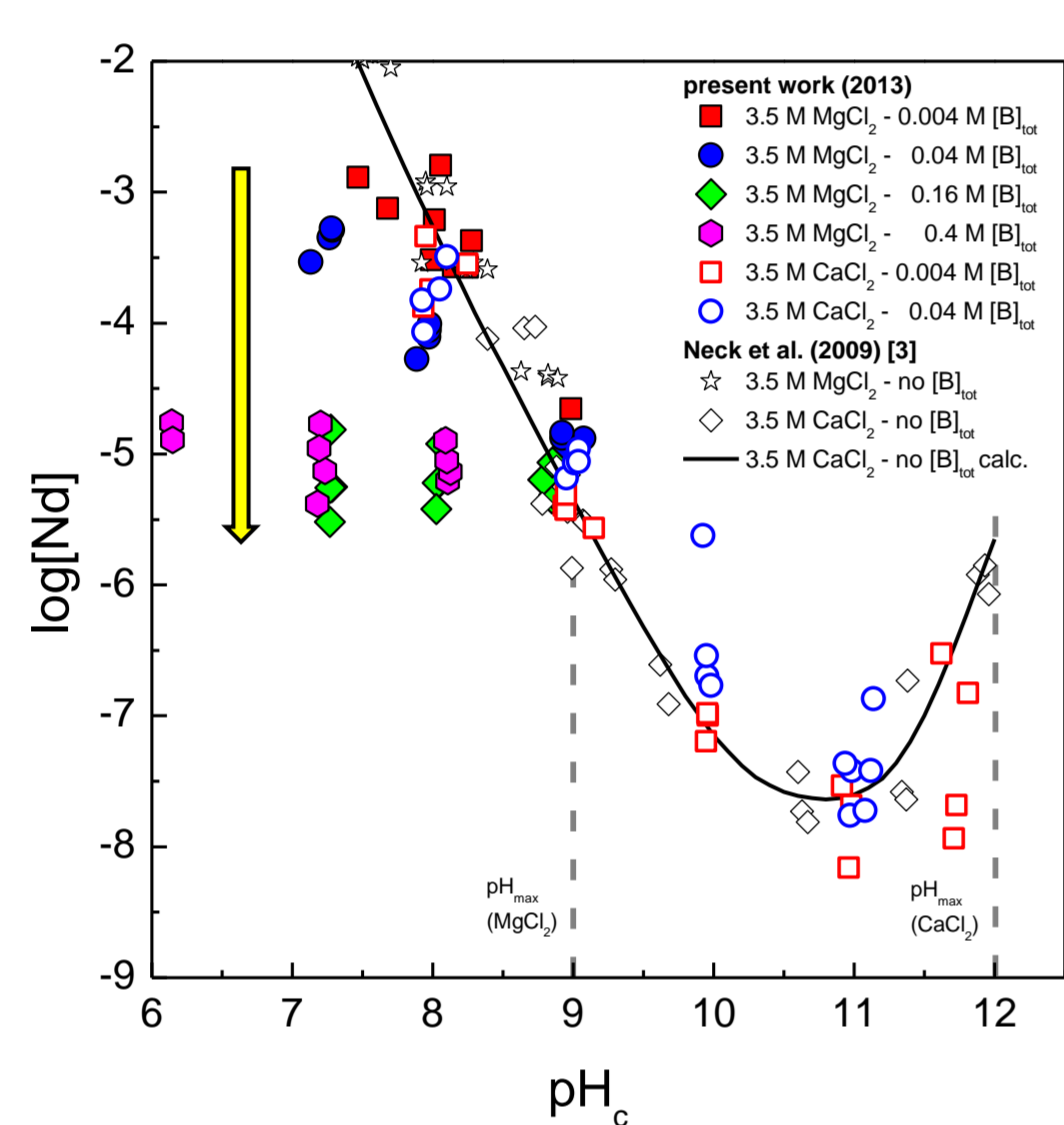
### This work: investigation of An-borate interactions relevant for assessing long-term safety of repository.

- Previous solubility study at  $pH_c = 8.6$  indicated complexation of Nd(III) with tetraborate in dilute to concentrated NaCl solutions [1].
- Leaching experiments with boron-bearing glass showed no significant effect of An-solubility with borate [2].

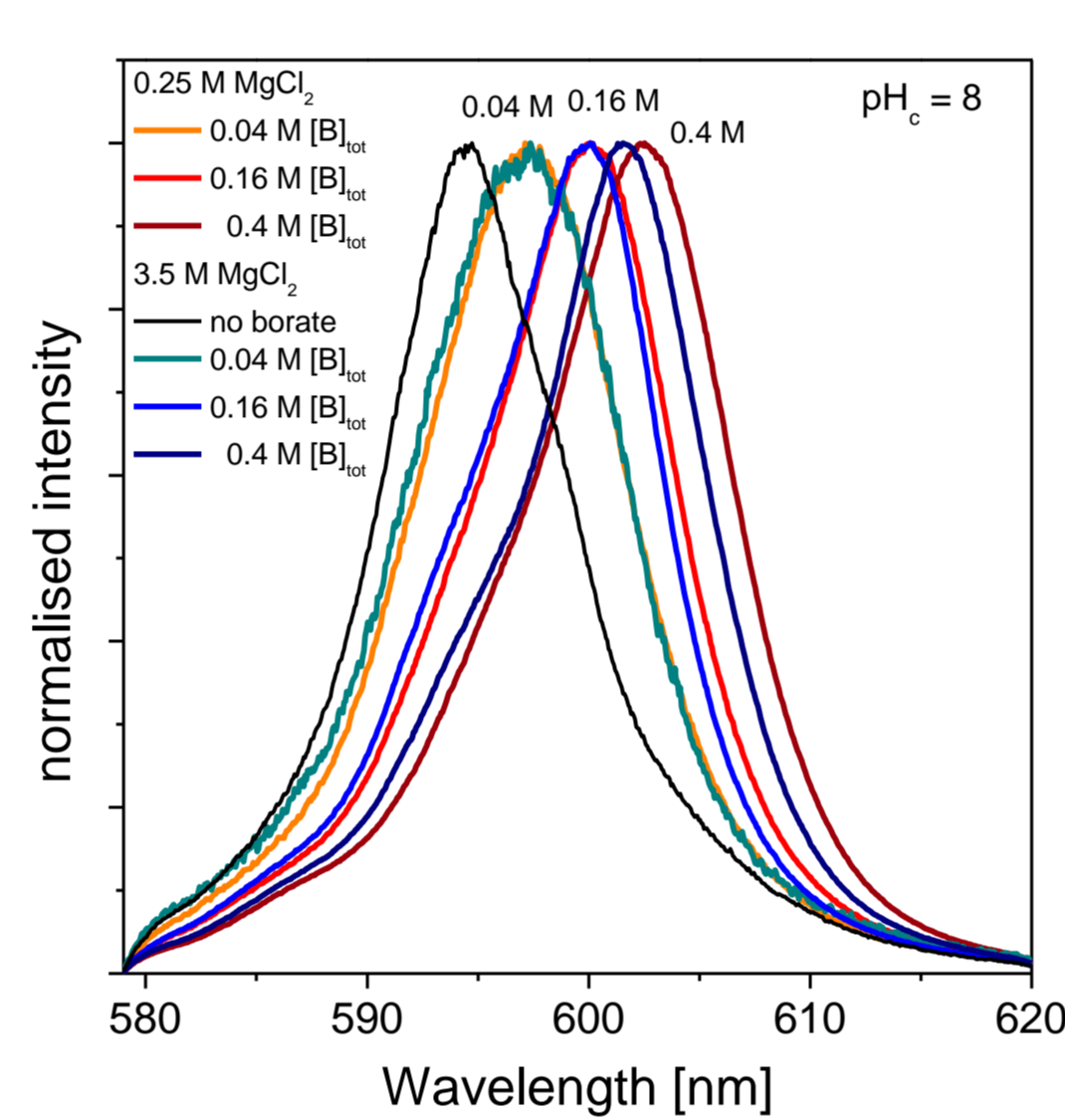
## Experimental

- All experiments conducted in Ar-glovebox
- $[B_4O_7]^{2-}_{init} = 0.001 \text{ M to } 0.1 \text{ M} \Rightarrow [B]_{tot} = 0.004 \text{ M to } 0.4 \text{ M}$
- Background electrolytes: NaCl : 0.1 to 5.0 M; MgCl<sub>2</sub>/CaCl<sub>2</sub>: 0.25 to 3.5 M
- Nd(III), Th(IV), Np(V) and U(VI) -Solubility experiments:**
  - ca. 2-10 mg Nd(OH)<sub>3</sub>(am), Th(OH)<sub>4</sub>(am), NpO<sub>2</sub>OH(am), UO<sub>3</sub>·2H<sub>2</sub>O(am) and Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub>·1.6H<sub>2</sub>O(cr) per experiment (characterized by XRD)
  - Equilibration time: 7d - 140 d
  - Phase separation: 10 kD (2-3 nm) ultrafiltration
  - Reference system without borate Nd(III) [3], Np(V) [4], U(VI) [5]
- Cm(III)-TRLFS experiments:**
  - [Cm] = 1·10<sup>-7</sup> M per sample
  - Equilibration time: spectra taken at < 1 d
- Np(V) UV-Vis:**
  - 900 ≤ λ [nm] ≤ 1200
  - Spectra taken after centrifugation

## Solubility of Nd(III) // Cm(III)-TRLFS studies in NaCl, MgCl<sub>2</sub> and CaCl<sub>2</sub> solutions

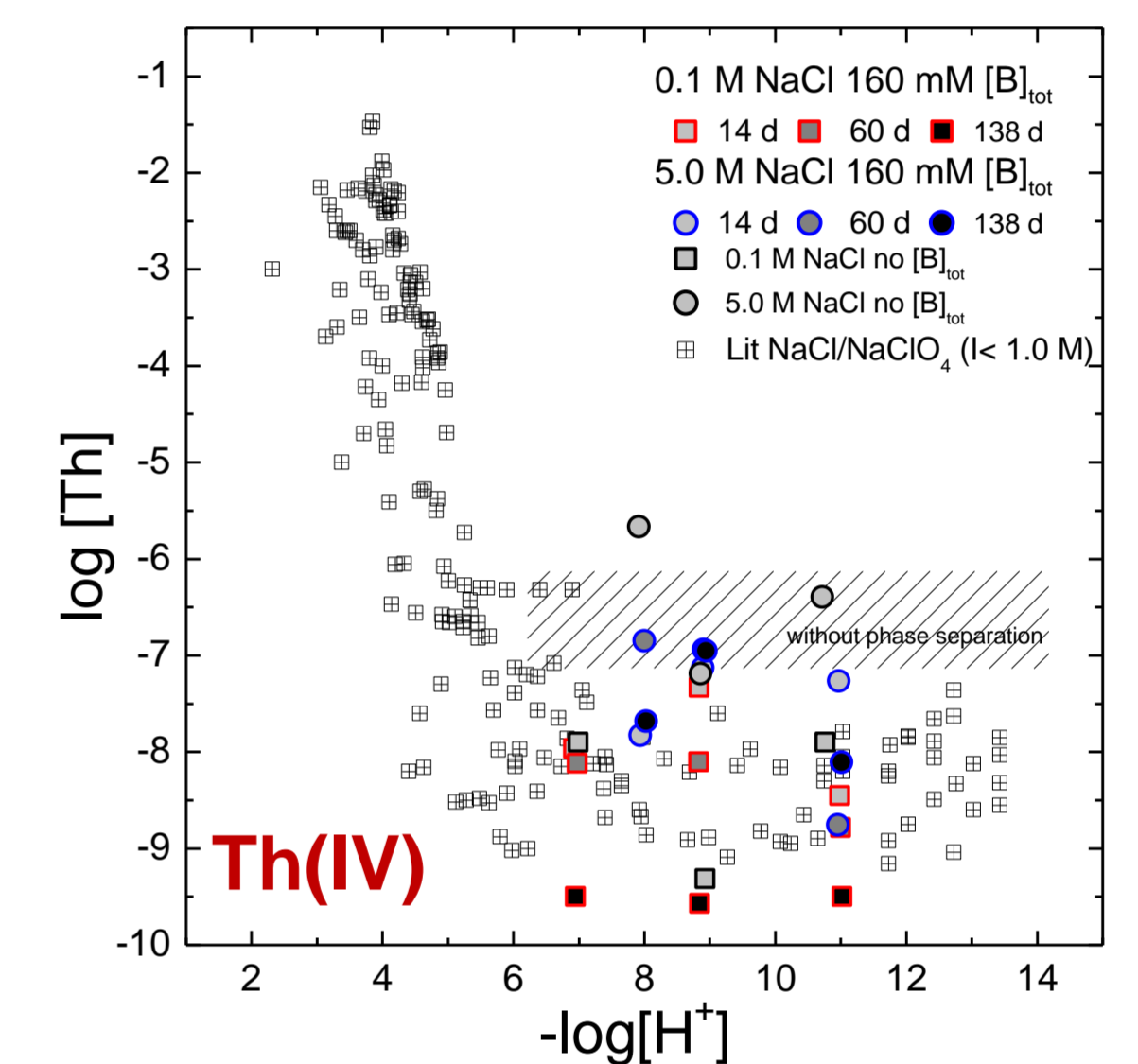


- Clear decrease in Nd(III) solubility at  $[B]_{tot} \geq 0.04 \text{ M}$  and  $pH_c = 7-9$ .
  - No effect of borate at higher  $pH_c$ -values.
  - Similar effects observed in dilute systems.
  - XPS confirms the presence of B in the solid phase (at  $[B]_{tot} \geq 0.16 \text{ M}$ )
- Transformation of Nd(OH)<sub>3</sub>(am) into a "Nd-borate" solid phase.



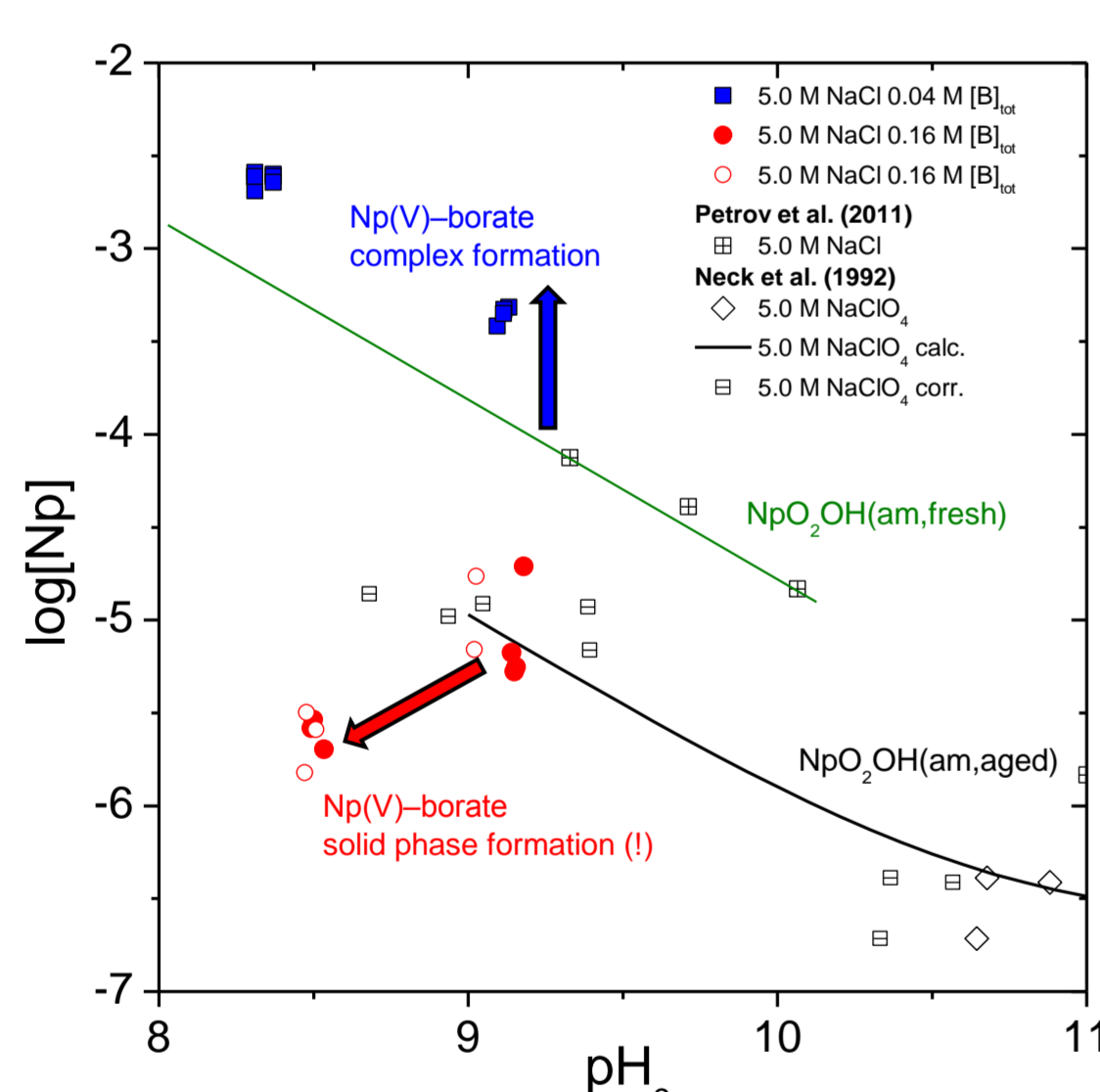
- $[B]_{tot} \leq 0.04 \text{ M}$ : only slight peak shifts compared to the borate free system → very weak borate complexation.
- $[B]_{tot} \geq 0.16 \text{ M}$ : clear red shift compared to low  $[B]_{tot}$  → increasing Cm(III)-borate complex formation.

## Solubility of Th(IV) and U(VI) in NaCl and MgCl<sub>2</sub> solutions

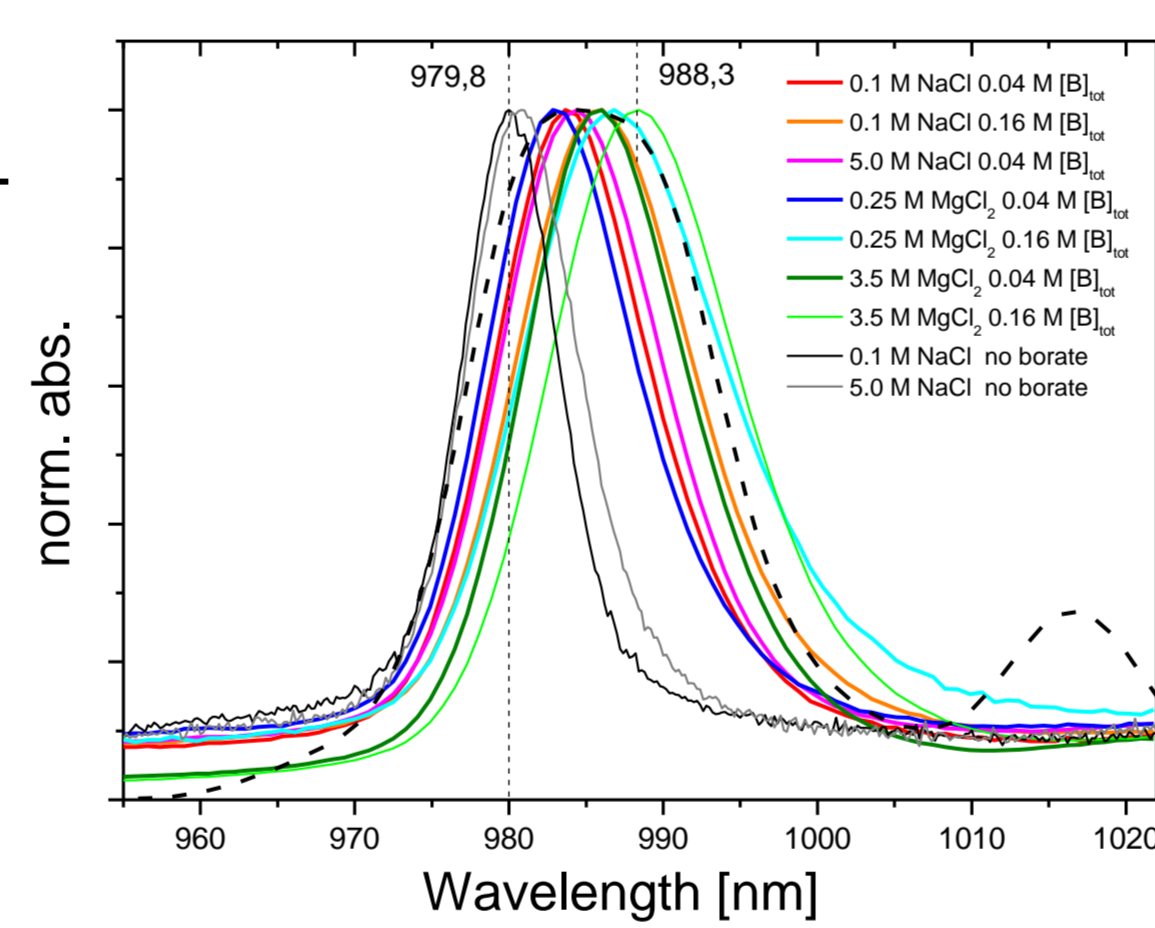


- No significant effect of borate on Th(IV) solubility.
- Further studies in NaCl borate-free systems at elevated ionic strength needed.

## Solubility and UV-vis of Np(V) in NaCl and MgCl<sub>2</sub> solutions



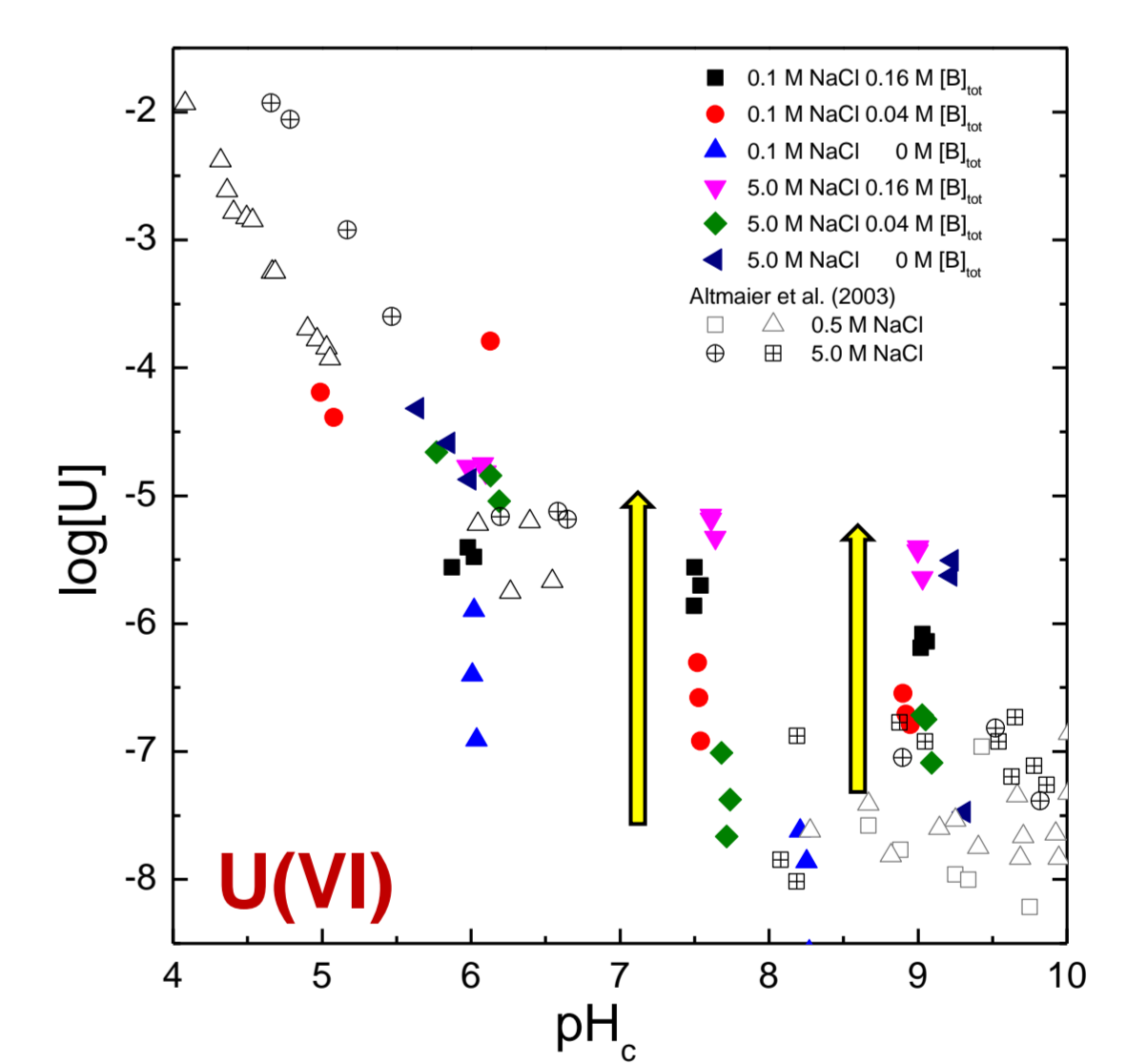
- Clear indications of Np(V)-borate complex formation in conc. NaCl solutions.
- Weaker complexation taking place in MgCl<sub>2</sub> solutions => competition with Mg<sup>2+</sup>?



- Very clear shift of peak position in dil. and conc. NaCl and MgCl<sub>2</sub> solutions compared to borate-free systems => strong complex formation.

- Very relevant drop in solubility (up to 3 log-units) observed in conc. NaCl and dil. MgCl<sub>2</sub> solutions in the presence of  $[B]_{tot} \geq 0.16 \text{ M}$ . New Np(V)-borate solid phase forming.

- Strong shift in peak position for conc. MgCl<sub>2</sub> systems => formation of ternary Mg-Np(V)-Cl species suspected [4] => competition with Np(V)-borate complex formation.



- Significant solubility increase at  $pH_c = 7.5-9$
- Minor effect at  $pH_c = 5-6$  => key role of polyborates in complex formation (?)

## Conclusions

- Actinide-borate interactions impact radionuclide solubility and speciation under repository relevant conditions.
- Cm(III)-TRLFS and Np(V) UV-vis indicate the formation of borate complexes with Cm(III) and Np(V) at  $pH_c = 8-9$ , although these have only a minor impact on solubility. Hydrolysis outcompetes borate complexation at higher pH values.
- Borate has a minor impact on Th(IV) solubility. On the contrary, the solubility of U(VI) is significantly increased at  $pH_c = 8-9$ .
- Strong decrease of An(III) and An(V) solubility within  $7 \leq pH_c \leq 9$  related to formation of Ln/An(III)-borate and An(V)-borate solid phases [→ new retention mechanism].

## Outlook

### Ln/An-borate interactions

- Comprehensive quantitative thermodynamic description of Ln/An-borate chemistry, including Ln/An-borate aqueous species and solid compounds forming in NaCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> solutions.
- Continuation of <sup>11</sup>B-NMR studies under saline conditions to achieve a better understanding of aqueous borate speciation in these systems.

### References:

- [1] Borkowski, M., Richmann, M., Reed, D. T., Xiong, Y., Radiochimica Acta 98, 577-582 (2010).
- [2] Kienzler, B., Luckscheiter, B., Wilhelm, S. Waste Management 21, 741-752 (2001).
- [3] Neck, V., Altmaier, M., Rabung, T., Lützenkirchen, J., Fanghänel, T., Pure and Applied Chemistry 81, 1555-1568 (2009).
- [4] V. G. Petrov, X. Gaona, D. Fellhauer, K. Dardenne, S. N. Kalmykov, M. Altmaier, Vortrag, Migration 2011, Peking, China.
- [5] M. Altmaier, V. Neck, V. Metz, R. Müller, M. Schlieker, T. Fanghänel, Vortrag, Migration 2003, Gyeongju, Korea