

Sorption studies of actinides / lanthanides onto clay minerals under saline conditions

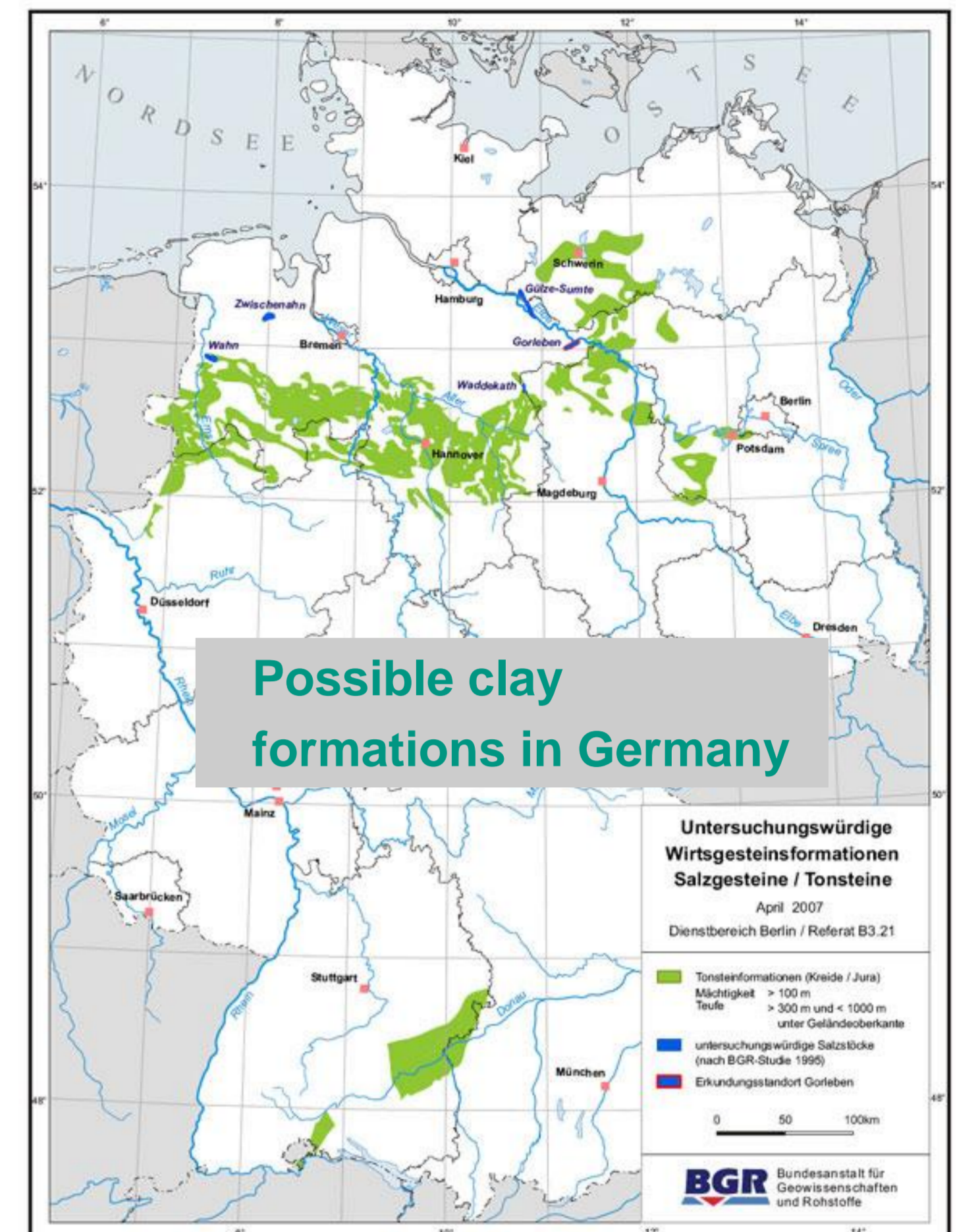
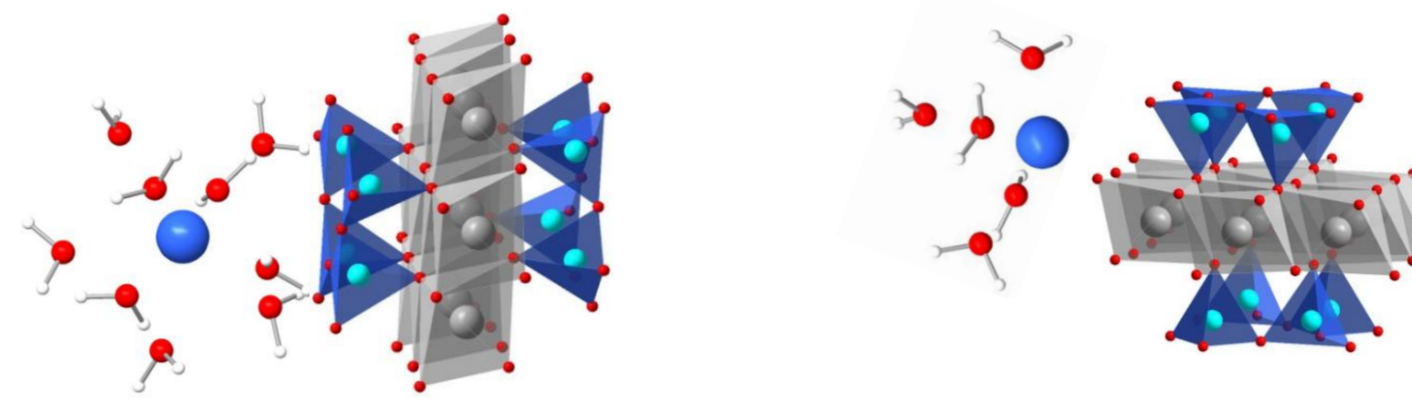
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Introduction

- Sorption reactions are key processes for radionuclide retention
- Several countries have selected clay formations for deep geological disposal of high level radioactive waste (CH, BE, FR)
- Lower Cretaceous clay rocks in Germany are located in vicinity of rock salt formations showing saline pore water chemistry
- Only a few investigations related to radionuclide sorption under highly saline solutions are available in the literature [1]
- Applicability of available geochemical sorption models to high ionic strength condition has to be examined
- No surface speciation model of clay minerals for saline conditions available

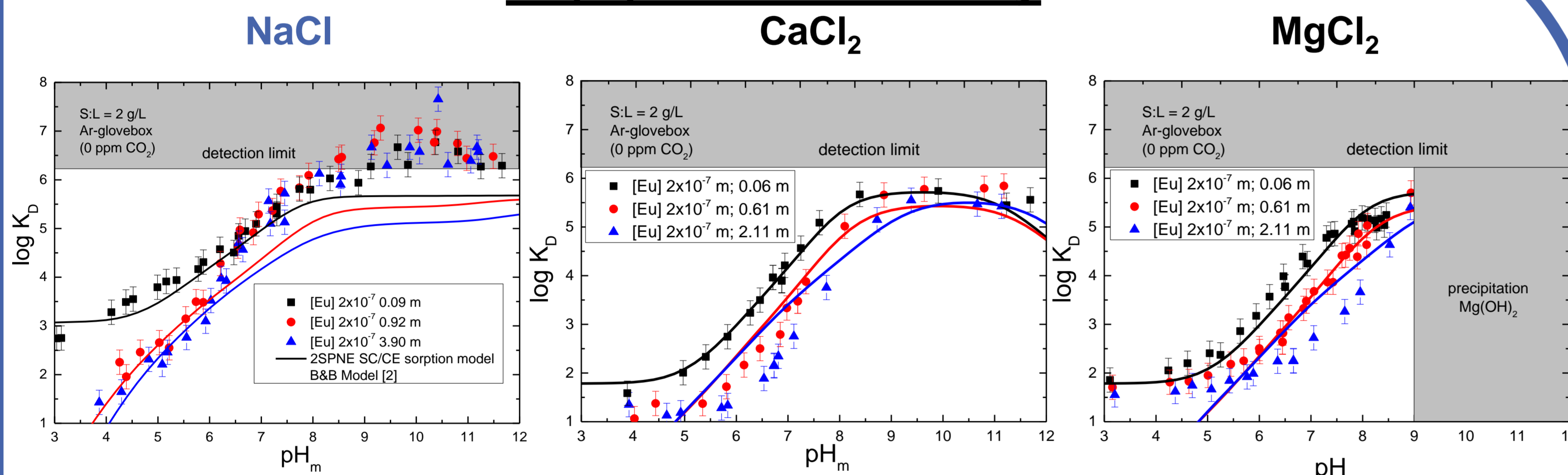
Focus of the present study

- Is there an ionic strength effect on pH dependent sorption/mechanism (outer or inner-sphere complexation)?
- Different behaviour of tri- and hexavalent actinides at increasing salinity?
- Is sorption under saline conditions still a relevant retardation process?
- Are available thermodynamic models applicable for highly saline solutions?
- What is the influence of electrolyte composition on actinide/lanthanide sorption?



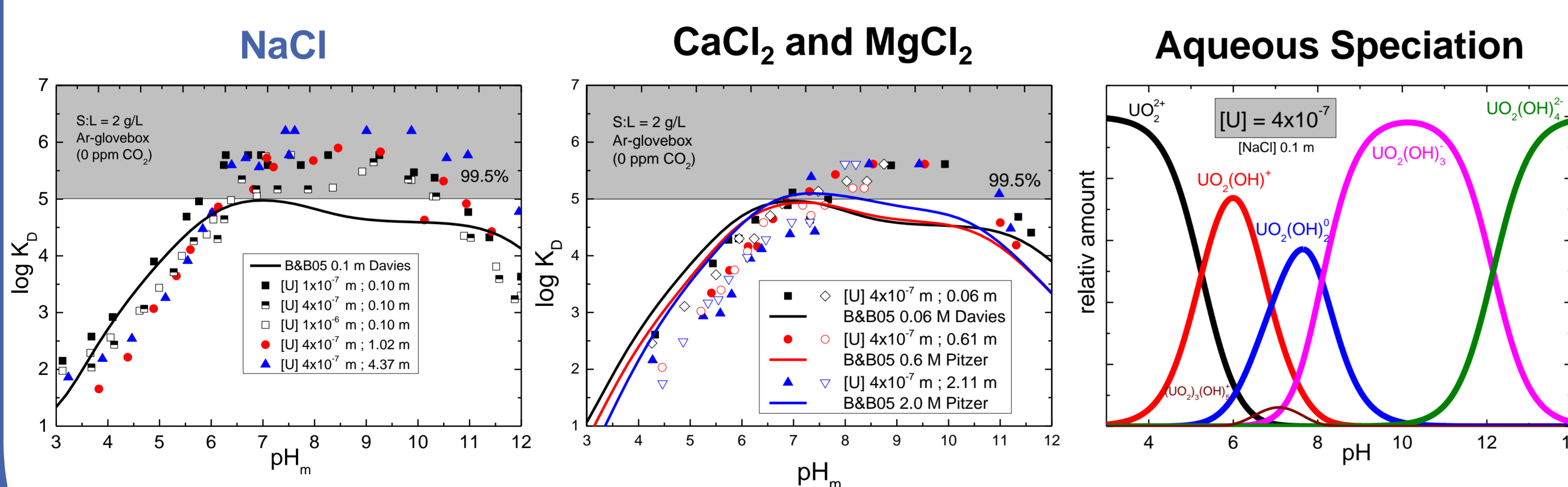
Batch sorption investigations

Eu(III) onto Illite du Puy



- Ionic strength effect visible at pH_m < 7
Explanation: Suppression of cation exchange at I > 0.92 m
- Almost quantitative uptake (> 99.5%) independent of ionic strength at pH_m > ~ 6.5 [3]
- Complete suppression of cation exchange even at low ionic strength in CaCl₂ and MgCl₂ system
- Estimated surface complexation constants for exchanged "Ca/Mg-illite" from Na-illite (similar Na-SWy-2 vs. Ca-SWy-2)

U(VI) onto Illite du Puy



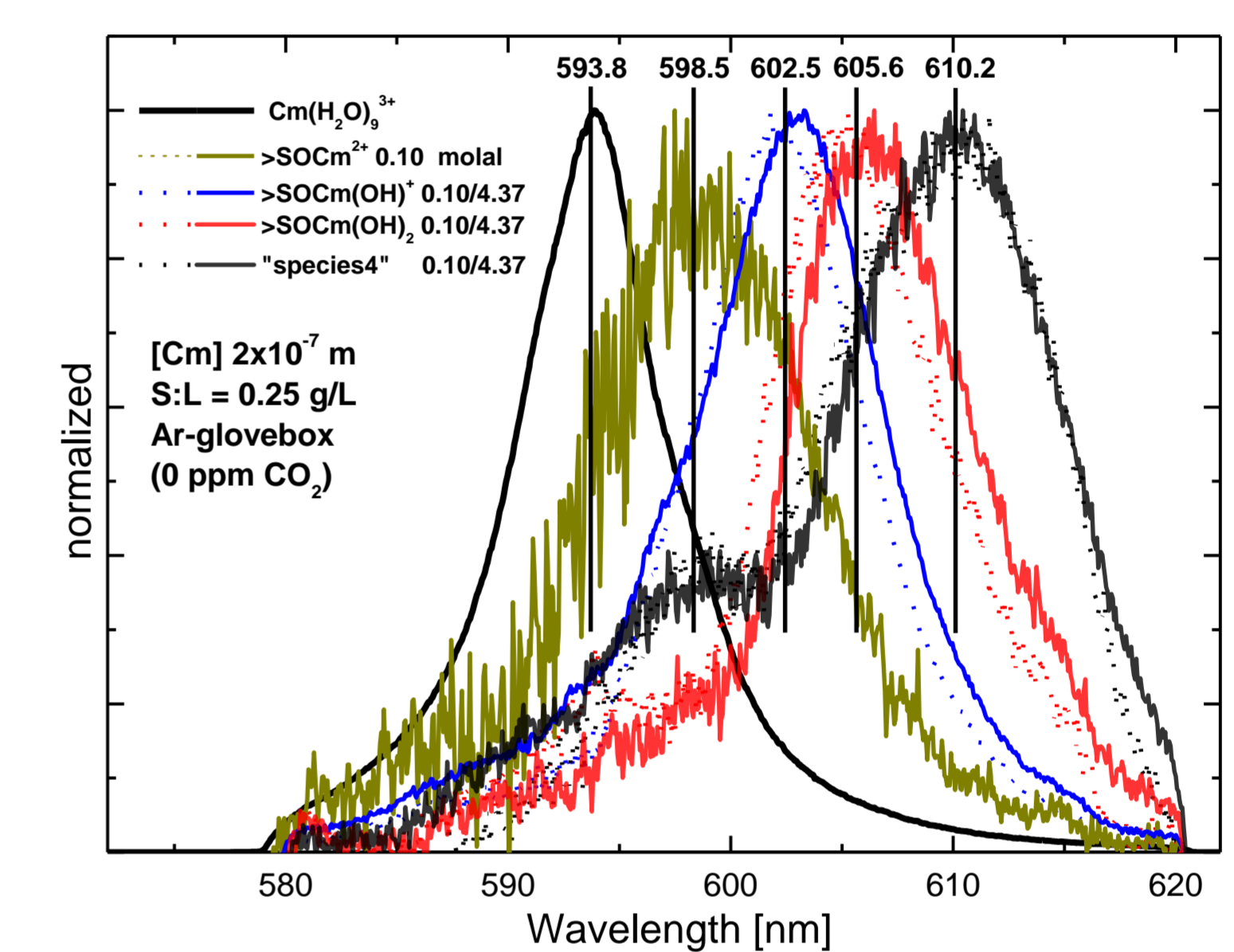
- No significant effect of ionic strength and electrolyte composition (NaCl, MgCl₂, CaCl₂)
- Almost quantitative U(VI) uptake (> 99.5%) for all ionic strengths at most "relevant" pH_m (7 < pH_m < 10)
- Decreasing sorption at very high pH_m (pH_m > 10) (predominance of negative aqueous species)

Conclusions

- Even high NaCl concentrations show only slight impact on Eu(III), U(VI) inner-sphere surface complexation
- Strong U(VI) retention takes place at environmental most "relevant" pH range (7 < pH_m < 10) independent of background electrolyte
- Eu(III) sorption in all NaCl solutions can be fairly well described using the 2SPNE SC/CE model and applying the Pitzer approach for considering ion-ion interactions in solution
- Nature of Cm(III) inner-sphere surface species independent of ionic strength as studied by TRLFS
- Identification of an additional "high pH surface species"
- Investigations point to formation of a curium-hydroxo-silicate-clay complex (further investigations necessary)

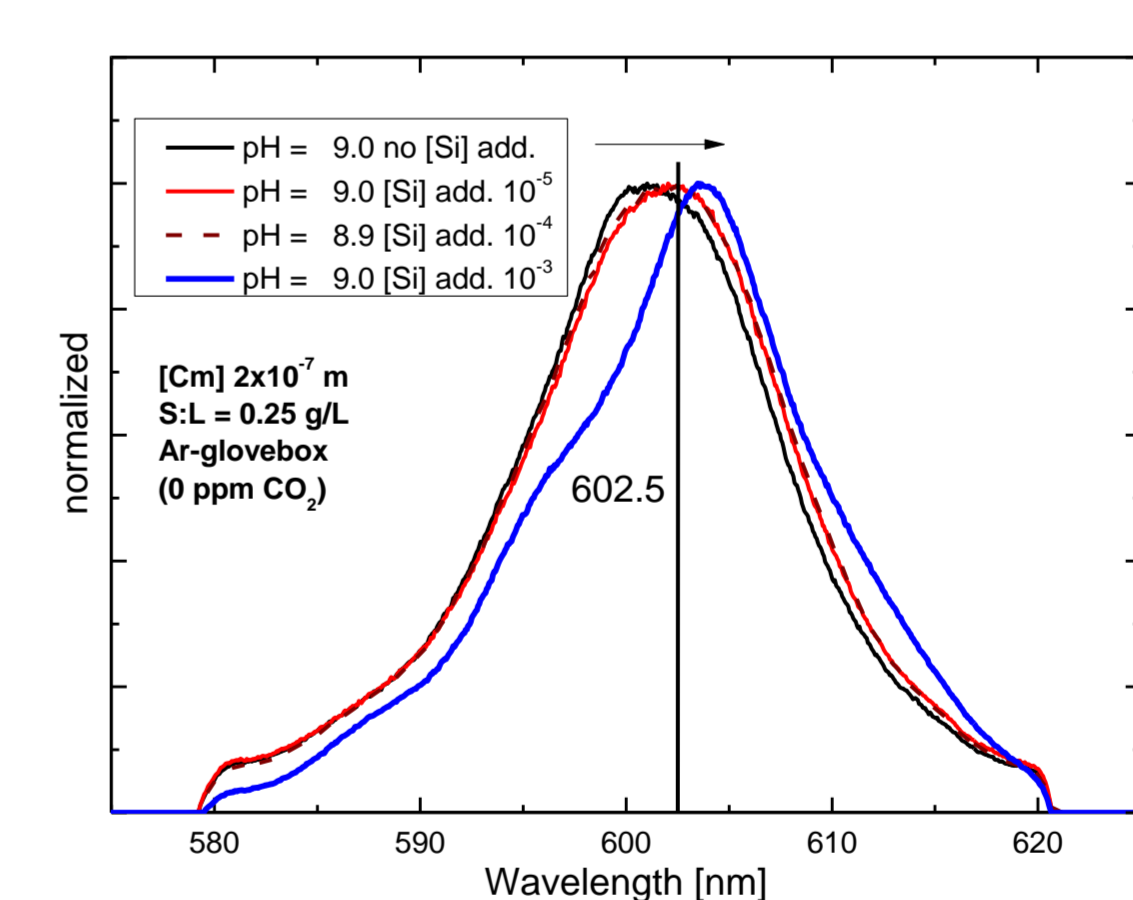
TRLFS experiments

Cm(III) sorption to Illite du Puy



- Four different surface-complexes identified [3]
- Peak positions (of the first three) agree with previous studies [4]
- Same species observed at all ionic strength conditions

Investigations on "4th surface species"



- Increased [Si] leads to an additional inner-sphere surface complexation
- Due to clay dissolution at high pH (>10) an increased [Si] (10⁻³) is expected [2]

➔ Indication of a possible formation of a curium-hydroxo-silicate-clay complex [5]

Acknowledgements

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