

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

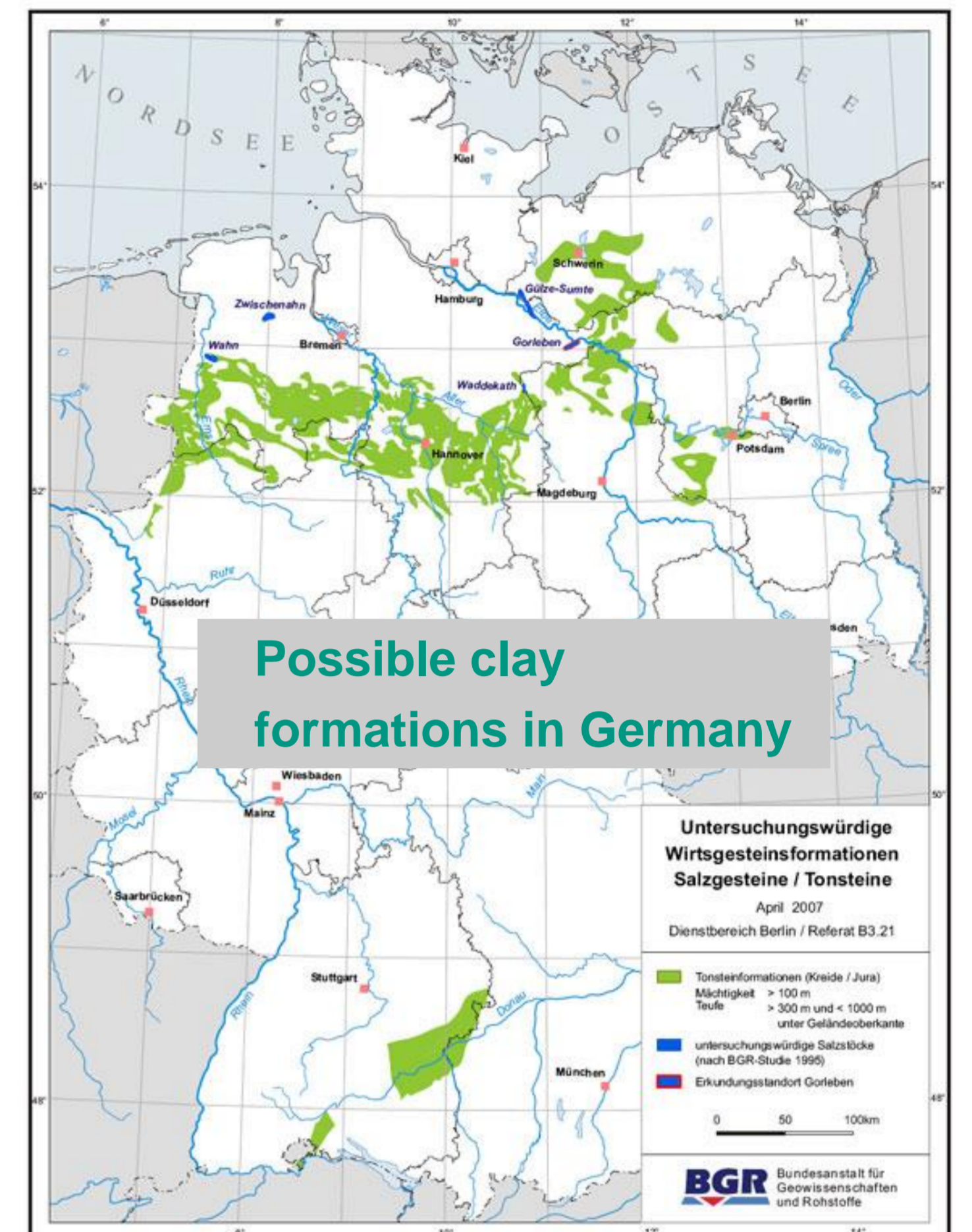
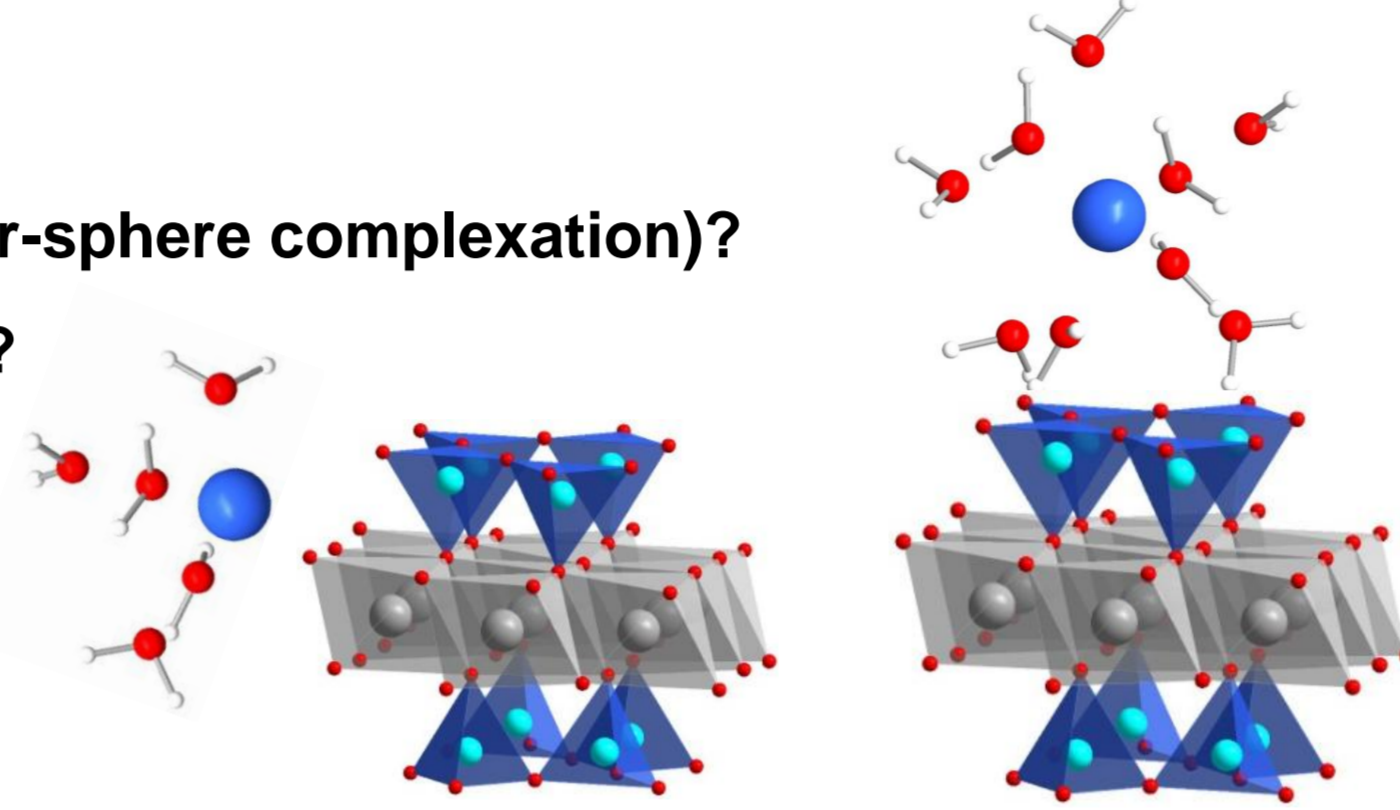
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Introduction

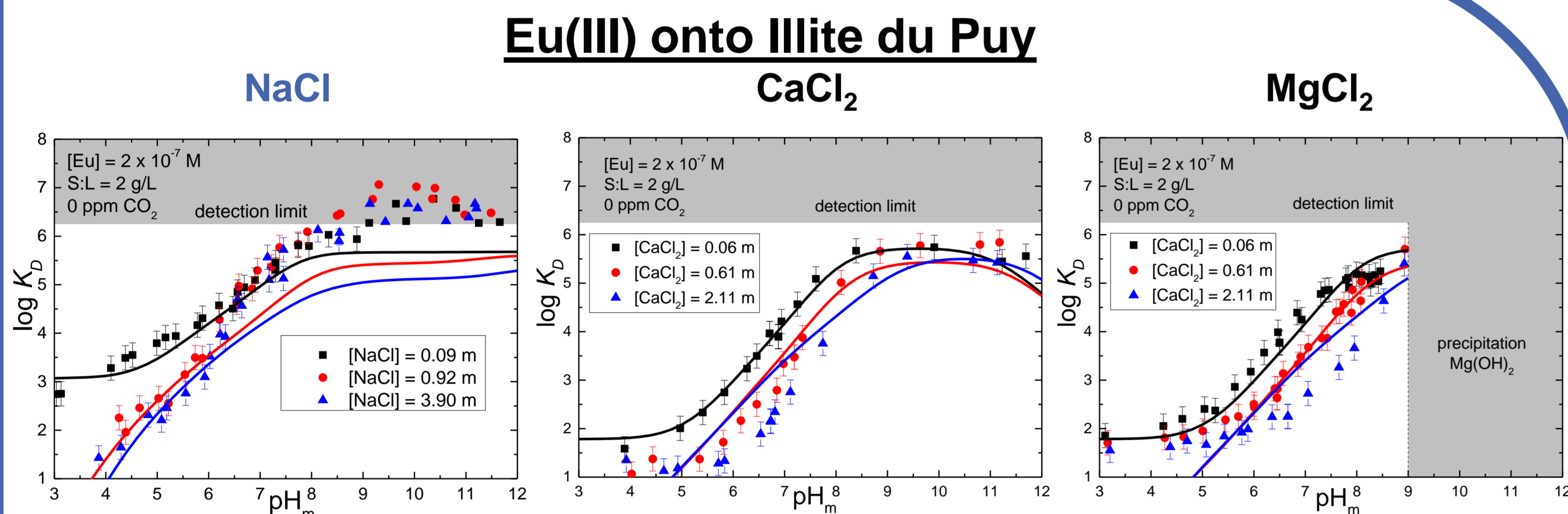
- Sorption reactions are key processes for radionuclide retention
- Several countries have selected clay formations for deep geological disposal of high level radioactive waste (CH, BE, FR)
- Lower Cretaceous clay rocks in Germany are located in vicinity of rock salt formations showing saline pore water chemistry [1]
- Only a few investigations related to radionuclide sorption under highly saline solutions are available in the literature [2]
- Applicability of available geochemical sorption models to high ionic strength condition has to be examined [3]
- 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 (inner- or outer-sphere complexation)?
- Different behaviour of tri- and hexavalent actinides/lanthanides at increasing salinity?
- Is sorption under highly 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?

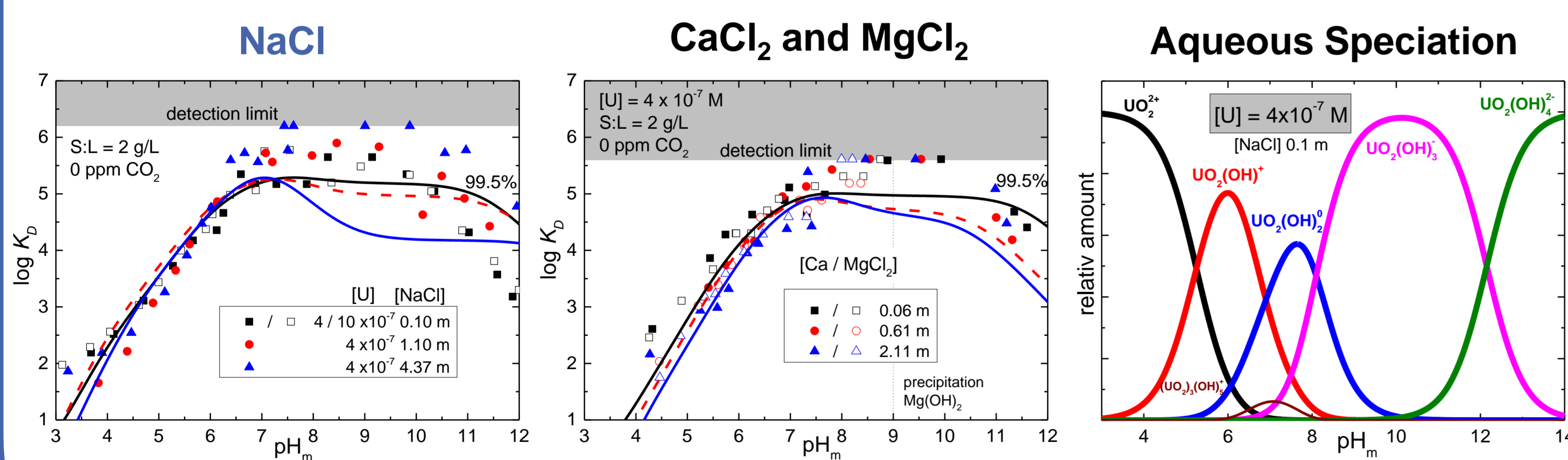


Batch sorption investigations



- Ionic strength effect visible at $\text{pH}_m < 7$;
- Due to more strongly suppression of cation exchange at $I > 0.92 \text{ m}$
- Almost quantitative uptake ($> 99.5\%$) independent of ionic strength at $\text{pH}_m > \sim 6.5$ [4]
- Complete suppression of cation exchange even at low ionic strength in CaCl_2 and MgCl_2 system
- Estimated surface complexation constants for exchanged "Ca/Mg-illite" from Na-illite [5]
- 2SPNE SC/CE model (solid lines) applicable to high ionic strength conditions [3]

U(VI) onto Illite du Puy



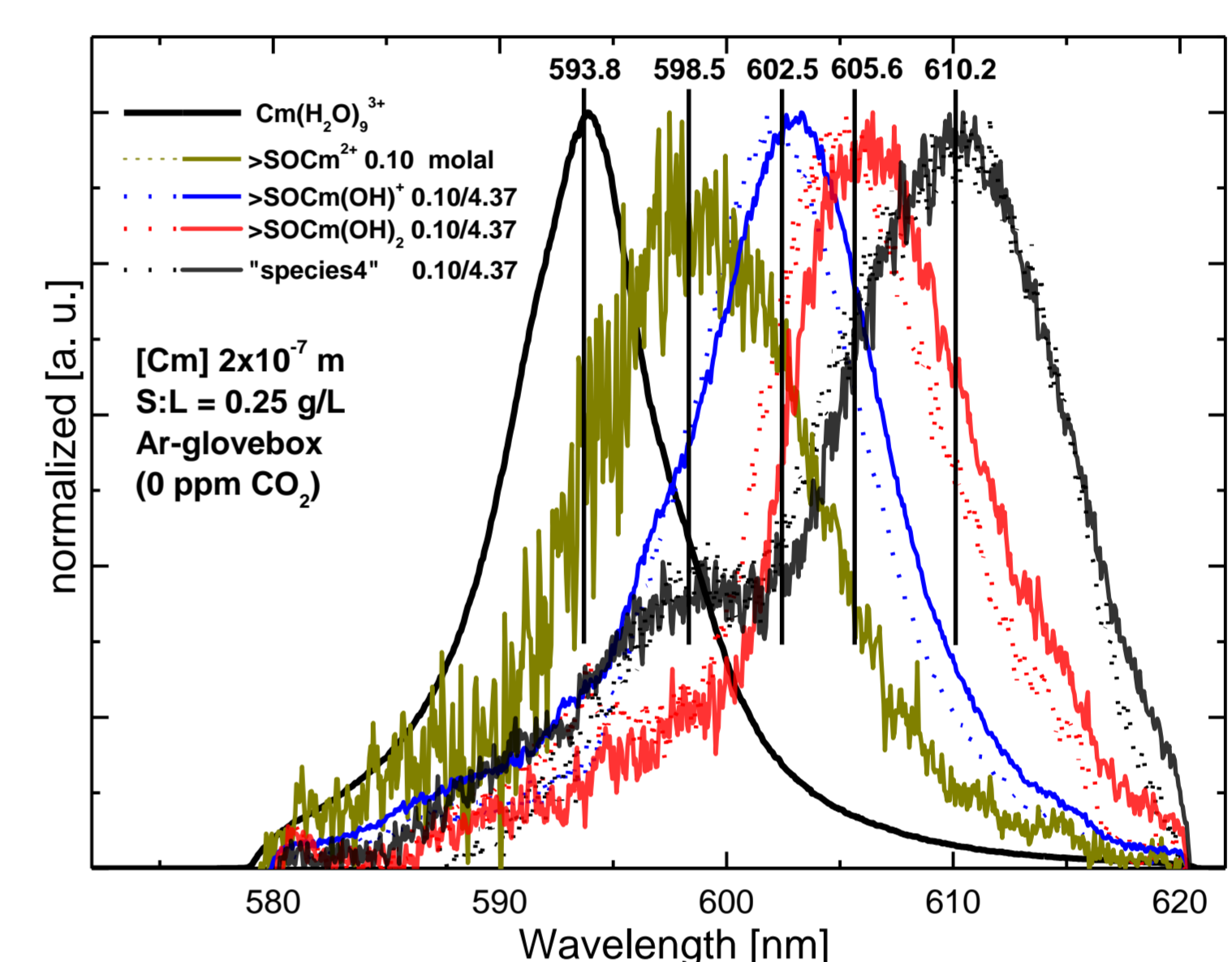
- No significant effect of ionic strength and electrolyte composition (NaCl , MgCl_2 , CaCl_2)
- Almost quantitative U(VI) uptake ($> 99.5\%$) for all ionic strengths at most "relevant" pH_m ($7 < \text{pH}_m < 10$)
- Decreasing sorption at very high pH_m ($\text{pH}_m > 10$) (predominance of negative U(VI) aqueous species)

Conclusions

- Even high background electrolyte concentrations show no or only slight impact on Cm(III)/Eu(III), U(VI) inner-sphere surface complexation
- Very strong Cm(III)/Eu(III), U(VI) retention at environmental most "relevant" pH conditions ($7 < \text{pH}_m < 10$)
- Eu(III) and U(VI) sorption 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 An(III)/Ln(III) inner-sphere 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)

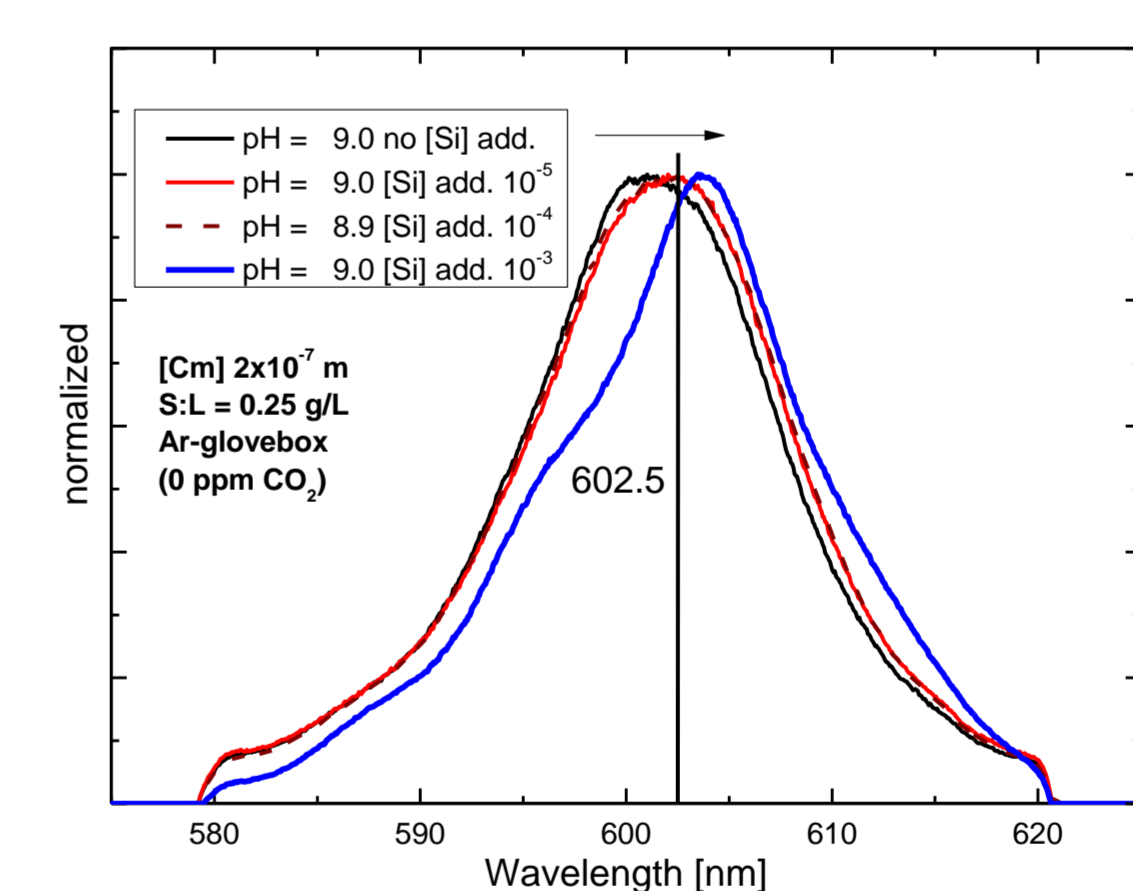
TRLFS experiments

Cm(III) onto Illite du Puy



- Four different surface-complexes identified [4]
- Same species observed at all ionic strength conditions
- Peak positions (of the first three) agree with previous studies [6]

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 [3]

➔ Indication of a possible formation of a curium-hydroxo-silicate-clay complex [7]

Acknowledgements

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