Modeling of surface complexation parameters of Eu-sorption under different geochemical conditions for muscovite and orthoclase

Susan Britz (GRS)

Overall scope

- Consideration of geochemical influences upon sorption processes: development of "smart K_d-concept"
  - K_d values variable in time and space
  - Based on thermodynamic parameters
  - Implementation in the transport code r^{3}t

Aim of this study

- Complementation of RES^{3}T (thermodynamic sorption data base)
- Surface complexation parameter (SCP) estimation through PhreeqC in combination with UCODE of Eu^{3+} for muscovite and orthoclase
- Batch experiments of Eu^{3+} on both minerals
- Validation of the chosen bottom-up approach through the application of a synthetic sediment

Experimental set-up & applied geochemical conditions

- Titration experiments of muscovite, orthoclase, and a synthetic sediment (80% quartz, 10% muscovite, 10% orthoclase)
- Particle size: 63 µm – 200 µm
- Solid/liquid ratio: 1/20, 1/80, 1/320
- adjustment to approx. pH 3 – 9)
- Eu^{3+} concentration: 10^{-5} mol/L – 10^{-8} mol/L
- Equilibration time: 24 h
- Solid-liquid separation (centrifuge, filtration 0.02 µm)
- ICP-MS measurements of equilibrium concentration

Application of the geochemical speciation code PhreeqC

- SOLUTION (background concentration of potentially released elements from both minerals)
- EQUILIBRIUM PHASES (equilibration with atmosphere)
- EXCHANGE (muscovite = K-exchanger)
- SURFACE_MASTER_SPECIES (strong sites (logK a), weak sites (logK b)
- SURFACE SPECIES (S_aOEu+2, S_bOEu+2)
- SURFACE (determination of surface site density - SSD, surface site area – SSA, protolysis constants – pK1, pK2)

Results

SCP	Muscovite	Orthoclase
SSA [m2g-1]	5.96	15.2
SSD [sites nm-1]	1.73	7.18
pK1	8.13	8.04
pK2	-6.7	-6.8
logK a	3.5	1.95
logK b	1.6	
logK_EuX	-0.6	

Muscovite Eu^{3+} batch-experiment

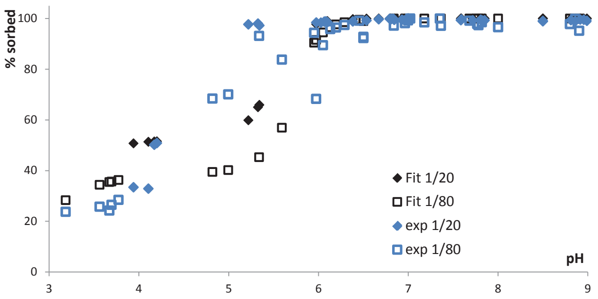

Fig. 1 Experimental data (blue) and fitted pH-dependencies (black) of Eu^{3+} muscovite batch-experiments, pH-edge between pH 4 and 6.

Orthoclase Eu^{3+} batch-experiment

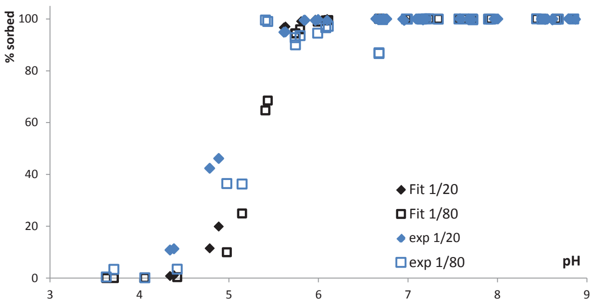

Fig. 2 Experimental data (blue) and fitted pH-dependencies (black) of Eu^{3+} orthoclase batch-experiments, pH-edge between pH 4 and 6.

Validation of the chosen bottom-up approach

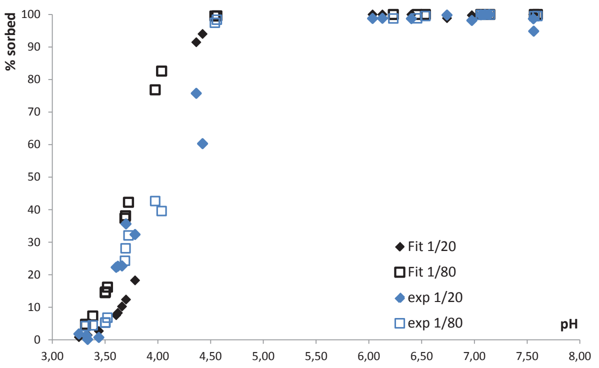

Fig. 3 Measured and simulated pH-dependencies of the Eu^{3+} synthetic sediment system with a pH-edge between pH 3 and 5.

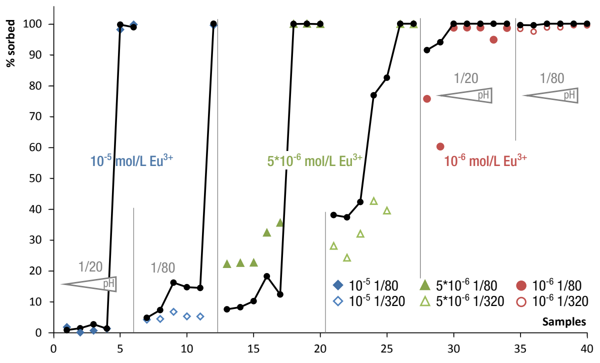

Fig. 4 Simulated (black characters) and experimental data (colored symbols) of the Eu^{3+} synthetic sediment system. Calculated data is obtained by applying the priorly determined SCP of muscovite and orthoclase. A SCP data set of quartz is obtained from literature (see Britz (2011)).

Conclusions

Muscovite and orthoclase batch-experiments

- Calculated data (black characters) represent measurements well (colored symbols)
- Muscovite plateau at low pH-values illustrate influence of exchangeable cations
- Minimum sorbat concentrations of orthoclase and muscovite differ due to the influence of cation exchange (min. sorbat concentrations muscovite equal 20%)
- Sorption edges are satisfactorily represented

Bottom-up approach

- Good correspondence between simulated and measured data sets by applying the determined SCP of both minerals to simulate sorption behavior of the synthetic sediment
- Bottom-up approach proves to offer satisfying results describing surface complexation reactions of a complex sediment by means of its constituents

Literature

Britz, S. (2011): Sorption studies of Eu^{3+} on muscovite and orthoclase, Diploma thesis, available at: GRS Braunschweig, Theodor-Heuss-Sr. 4, Abt. 401, 38122 Braunschweig.

Acknowledgements

This work was funded by the Federal Ministry of Economics and Technology of Germany under grant No. FKZ 02 E 10518.

Gesellschaft für Anlagen- und Reaktorsicherheit, Theodor-Heuss-Str. 4, 38122 Braunschweig, www.grs.de, e-mail: susan.britz@grs.de, Tel.: +49-531-8012-292