Parameter determination of thermodynamic sorption models

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Since the last quarter of the past century multiple theories concerning the composition of the solid-solution interface during sorption processes at mineral water interfaces have been developed, e.g. the constant capacitance (CCM), diffuse double layer (DDLM), Basic Stern (BSM), or triple layer (TLM) model. The theories were partially build on one another and represent the basis of modern thermodynamic sorption models (TSM) to describe retardation processes of e.g. potential contaminants on mineral surfaces.

At first sight, the application of mechanistic TSMs seems straightforward: Acid-base properties of mineral surfaces are determined via titration experiments, specific surface areas (SSAs) and surface site densities (SSDs) are estimated, sorption experiments provide the basis to define element-specific surface complexation constants and distribution coefficients. At second glance, however, the complexity becomes obvious: Which approach is best to describe surface protolysis reactions (1-pK vs. 2-pK model)? How do we actually know that results from titration experiments are not biased by mineral surface impurities and how do we obtain best estimates of counter-ion affinity constants? How should the point of zero charge be determined for mineral surfaces other than pure metal-oxide interfaces? How do we correctly assess SSDs[1]? Which surface complexes realistically describe sorption data under constraints of surface charge measurements and collected spectroscopic data?

We examined natural quartz and feldspar mineral surfaces, performed titration and Eu(III)-batch experiments, determined SSA and SSD. We applied the DDLM, a non-electrostatic model, and CD-MUSIC type approach (BSM) with PHREEQC[2] to describe experimental Eu(III) sorption and mineral surface charge data. Model approaches, applied theoretical assumptions, data analysis of collected and literature data yielded insight into the complexity of some of the problems posed above. We offer a critical discussion of the applied models, required parameters, collected data, and benefits as well as drawbacks of implemented assumptions and boundary conditions.

[1] Barrón and Torrent (1995) J. Colloid Interface Sci. (177), 407-410, [2] Parkhurst, Appelo (1999) U.S. Geological Survey, 312 pp.