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The bond-valence method - another perspective on crystal surface reactions

A. Mutter[1], M. Schindler[2] and A. Putnis[1]

[1] Wilhelms-Universität Münster, (mutteran@nwz.uni-muenster.de)
[2] Lakehead University, Canada

The basic principles of the bond-valence theory of BROWN[1] (1981) have lately been extended[2,3] and are now suitable to be used to discuss crystal growth and dissolution features on crystal surfaces.

The crystal composition of minerals with a sheet like structure, such as uranyl-sheet minerals can be divided into a structural unit and an interstitial complex[4]. In such cases the structural unit is parallel to the prominent basal face of these minerals and dominates the crystal morphology. The structural unit itself can be subdivided into chains of polyhedra, so called edges, which are terminated by anions. According to the bond-valence method the bond-valence deficiency of these anion terminations per unit length can be calculated. The differences in the individual bond-valence deficiencies of these polyhedral chains corresponds well with the intrinsic acidity constant pKa and the free energy ΔGat of corresponding acid-base reactions. Furthermore the Point of Zero Charge (PZC) can be calculated for each individual polyhedral chain. Therefore the bond-valence deficiency is a valuable tool to compare and predict the stability of different edges on a crystal surface with respect to the pH and the saturation of the aqueous solution in contact with the mineral surface.

Detailed analysis of the structural unit e.g. of schoepite even yielded a connection between the abundance of aqueous species of different uranyl-complexes in solution and the termination of different polyhedral chains. The most stable polyhedral chains have a termination, which corresponds with the most abundant aqueous species. As these complexes also can be used to build up the whole structural sheet we call them principal-building units (PBU).

Recently the calculation of bond-valence deficiencies of anion terminations was extended and is now applied to crystal faces. As a preliminary result there is again a good agreement between the crystal morphology and the bond-valence deficiency of the individual crystal face, with respect to the pH and the saturation of the mother liquid of the crystal.

References

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The role of organic molecules and microbial organisms in metal ion sorption processes

G.E. Brown, Jr.[1,2], T.H. Yoon[1], S.B. Johnson[1], A.S. Templeton[3], T.P. Trainor[4], B.C. Bostick[5], T. Kendelewicz[1], C.S. Doyle[1] and A.M. Spormann[6]

[1] Surface & Aqueous Geochemistry Group, Department of Geological & Environmental Sciences, Stanford University, Stanford, CA 94305-2115, USA (gordon@pangea.stanford.edu)
[2] Stanford Synchrotron Radiation Laboratory, SLAC, 2575 Sand Hill Road, MS 99, Menlo Park, CA 94025, USA
[3] Marine Biology Research Division, Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093, USA
[4] Department of Chemistry & Biochemistry, University of Alaska, Fairbanks, CA 99775, USA
[5] Department of Earth Sciences, Dartmouth College, Hanover, NH 03755, USA
[6] Department of Civil & Environmental Engineering, Stanford University, Stanford, CA 94305, USA

Organic matter and microbial organisms compete with mineral surfaces for metal ions in soils and aquatic systems in complex ways (no pun intended). Organic matter can form both inner- and outer-sphere complexes on mineral surfaces as will be illustrated by the results of ATR-FTIR spectroscopy studies of the interaction of simple dicarboxylic acids and natural fulvic acid with Al-oxyhydroxide surfaces. Organic matter may also participate in the sorption of metal ions on mineral surfaces, resulting in the formation of ternary surface complexes. ATR-FTIR and Pb L_{III}-edge EXAFS studies from the Pb(II)/oxalic acid/boehmite system will be used to illustrate such complexes. Organic coatings on mineral surfaces can complete for aqueous metal ions with mineral surfaces, as will be shown by the results of x-ray standing wave-fluorescence yield studies of the Pb(II)/polyacrylic acid (CH_2=CHCOOH)/α-Al_2O_3 system. Similarly, microbial biofilm coatings compete with mineral substrates for metal ions, as shown by our recent XSW-FY and GI-EXAFS spectroscopy studies of the interaction of aqueous Pb(II) with *Burkholderia cepacia*-coated corundum and hematite single crystal surfaces. Biomineralization processes involving microbial organisms on mineral surfaces also result in the sequestration of metal ions through the formation of precipitates. These processes will be illustrated by the formation of pyromorphite in the Pb(II)/*B. cepacia*/iron oxide system and by the formation of goethite and schwertmannite in the *Thiobacillus ferrooxidans*/*Thiobacillus thiooxidans*/ pyrite system.