FINAL REPORT:
"PREDICTIVE SURFACE COMPLEXATION MODELING"

Surface complexation plays an important role in the equilibria and kinetics of processes controlling the compositions of soilwaters and groundwaters, the fate of contaminants in groundwaters, and the subsurface storage of CO_2 and nuclear waste. Over the last several decades, many dozens of individual experimental studies have addressed aspects of surface complexation that have contributed to an increased understanding of its role in natural systems. However, there has been no previous attempt to develop a model of surface complexation that can be used to link all the experimental studies in order to place them on a predictive basis. In turn, this would enable modeling of surface protonation and adsorption of metallic cations, anions and organic species for the wide range of fluid compositions, minerals, and temperatures and pressures that exist in nature.

My research has shown that all the parameters in the extended triple-layer model (ETLM) can be predicted for alkalis and alkaline earths, enabling prediction of proton surface charge for oxides in 1:1 and 2:1 electrolyte solutions and mixtures of these (Sverjensky and Sahai, 1996; Sahai and Sverjensky, 1997a, b, 1998; Sverjensky, 2003, 2005, 2006). Two significant advances involved the development of rigorously-defined standard states for surface species and the quantitative treatment of the effects of cation and anion solvation on adsorption. The equilibrium constants in the ETLM were placed on sensible, well-defined standard states for the surface species by including specific recognition of the surface area and solid concentration, which had previously been ignored. This research enabled direct comparison of the equilibrium constants for different minerals or different samples of the same mineral with different surface areas (Sverjensky, 2003). Solvation was treated quantitatively for the removal of water dipoles from cations as they approached a mineral surface. This enabled placing cation adsorption on a predictive basis through correlations involving the dielectric constants of the solids (Sverjensky, 2005, 2006). The critical role of the release of water dipoles during inner-sphere ligand binding was also quantified (Sverjensky and Fukushi, 2005, 2006). In turn, this quantification enables an interpretation of the number of inner-sphere points of attachment for ligand binding on mineral surfaces (Fukushi and Sverjensky, 2007a, b). Several applications are listed below.

Using the advances described above, the attachment of rare earth elements and organic acid anions to mineral surfaces was studied in detail. The major goal was to integrate experimental uptake data and spectroscopic results with a predictive model. Using X-ray studies of yttrium surface coordination on titanium dioxide, I developed a model for rare earth element adsorption applicable to many oxides minerals. The results indicate the importance of a single hydrolysis state for rare earth elements on oxide surfaces (Piasecki and Sverjensky, 2008). In the case of organic acid anion attachment to oxides, it was found that this typically happens with a state of protonation different from that in aqueous solution at the same pH. Furthermore, the organic species typically adsorb in at least two ways simultaneously, which can be accounted for if experimental data refer to a wide enough range of conditions and if sufficiently general predictive theories are available (Jonsson et al., 2009, 2010; Estrada et al., 2015; Feuillie et al., 2015). The results of my studies indicate that Born solvation theory can help the development of very general linear free energy correlations for both organic and inorganic species. In this way, results for inorganic systems previously studied in this project can help generalize the results for the organic species.

Progress was also made in extending the predictive ETLM for oxides to 1:2 electrolytes involving oxyanions such as carbonate, enabling surface chemistry calculations more relevant to natural waters than previously possible (Kanematsu et al., 2011). Second, by applying the ETLM to oxyanionic organic acids such as glutamate and aspartate, it was demonstrated that prediction of surface species with the ETLM was consistent with independently-measured ATR-FTIR spectra and quantum chemical modeling (Parikh et al., 2011).

Further testing of the predictive capabilities of the ETLM were made with the amino acid DOPA (dihydroxyphenlyalanine). This molecule has a very strong signal spectroscopically using surface-enhanced Raman spectroscopy (SERS). SERS has the great advantage that the spectroscopic signal arises only from that part of the molecule which is directly attached to the mineral surface. No signal arises from the dissolved ligand or the solid substrate. In this way, the precise modes of attachment can be inferred. An experimental study of the adsorption of DOPA on rutile was carried out and modeled with the ETLM. The surface complexation modeling of the adsorption data revealed two attachment mechanisms. One involved DOPA lying down on the mineral surface and the other involved DOPA standing up on the mineral surface (Bahri et al., 2011). In a subsequent, SERS study (Lee et al., 2012), these two modes of attachment were confirmed. Even the change in adsorption with pH of the two surface complexes was confirmed.

Building on the surface complexation modeling described above, it became clear that there was considerable evidence of a preference of oxyanions for low site-densities on oxide minerals. Consequently, further research was carried out to identify the oxyanion adsorption sites on rutile. The ETLM analysis of the surface speciation of amino acids on a single sample of well-characterized rutile requires a surface site density of 3.0 sites.nm^{-2} compared to a tritium exchange value of 12.4 sites.nm^{-2} and a theoretical site density value of 5.4 sites.nm^{-2} for singly coordinated oxygen atoms. It should be noted that this is the same sample of rutile studied for the adsorption of Ca^{2+} and many other studies of cation adsorption and proton surface charge (Sverjensky, 2006). In all the cation adsorption studies, a site density of 12.4 sites.nm^{-2} was used. A detailed examination of the rutile sample used for all the above studies was made using electron microscopy to produce high-resolution atomic-scale images of the rutile crystals (Livi et al., 2013). A key finding was that rutile crystal surfaces are far rougher than previously assumed, with almost one-third of all sites on the large, prismatic (110) faces possessing steps. By counting sites all the way around a single crystal, and assuming uniformity across the (110) faces, it was established that the steps have an abundance of about 3.3 sites.nm^{-2}, almost identical to the distinctively low site density of 3.0 sites.nm^{-2} established by surface complexation modeling of amino acid adsorption on this particular sample of rutile. This result points to the need to include different surface sites for organic oxyanions and metals in surface complexation adsorption models.

Following up on the discovery of the need for different sites for organic oxyanions and metals, a new predictive two-site ETLM successfully predicted the complex behavior in a mixed cation-organic oxyanion system. This is important because the key feature of the geologic complexity affecting the chemistry of mineral-water interactions in shallow subsurface conditions involves the fact that most near-surface and shallow subsurface waters on the continents are predominantly Ca-bicarbonate-silica waters. Consequently, it is essential to be able to model the chemistry of the mineral-water interface in such waters. Remarkably, there is not much experimental information about how such waters behave at the surfaces of minerals. As a first step, I investigated the effect of adding Ca^{2+} to a previously well-characterized system involving an organic oxyanion (glutamate) and rutile (Lee et al., 2014).

A remarkable enhancement of the adsorption of glutamate on rutile with added Ca^{2+} was measured experimentally. For example, without any Ca^{2+} the adsorption of glutamate has the usual maximum at a pH of about 4. In contrast, with 3 mM added Ca^{2+} there is an additional broad adsorption peak for glutamate at alkaline pH values, maximizing at a pH of about 10 units. The

additional adsorption of glutamate at high pH values is a consequence of the co-adsorption of Ca^{2+} which reverses the surface charge of the rutile from negative to positive, which in turn promotes the adsorption of the negatively charged glutamate. Cooperative effects such as the above example illustrates the need to account for the chemical and geologic complexity of the mineral-water interfaces in natural systems. Surface complexation calculations summarized in showed that the ETLM was able to successfully predict the reversal of the surface charge and the additional adsorption of glutamate at high pH values (Lee et al., 2014).

Overall, my research has successfully integrated the results of the work of many experimentalists published over several decades. For the first time in studies of the geochemistry of the mineral-water interface, a practical predictive capability for modeling has become available. The predictive correlations developed in my research now enable extrapolations of experimental studies to provide estimates of surface chemistry for systems not yet studied experimentally and for natural and anthropogenically perturbed systems.

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