# A novel Surface Complexation Model approach to account for substitution in minerals: A case study of aluminum-ferrihydrites

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Surface Complexation Models (SCMs) have been utilized to describe charging and sorption on a host of mineral surfaces to great success. While SCMs have been updated to account for higher temperatures [1] and complex minerals such as ferrihydrite [2], they have not, for the most part, accounted for site defects and substitutions. Previous attempts to describe sorption on minerals containing impurities have utilized a uniform affinity constant for the mineral surface without breaking down the contribution of individual surface sites. The resulting models are constrained for a specific set of conditions and do not apply to the amalgam of scenarios found in the environment. In this study, we propose a new approach to building SCMs that takes into account the location of the substitution and demonstrate its applicability to aluminum (Al) substitution in ferrihydrite (Fh). Fh is a ubiquitous iron oxyhydroxide in natural environments. The debate around its structure is complicated by the presence of impurities, such as Al, that is known to substitute for Iron (Fe) in Fh.

Our approach situates the Al into octahedrally-coordinated reactive Fe1 sites that are bound to hydroxyls and are on the surface of the mineral. The Al substituted Fh (Al-Fh) samples synthesized have 12% and 24% Al, by molar weight. In the model, we modified the properties of the surface sites (site densities and affinity constants) to account for the presence of Al on the new surface. We used the Charge Distribution – MultiSite Complexation (CD-MUSIC) model paired with the Basic Stern layer model to describe the zeta potential of pure and Al-Fh as a function of solution pHs. The resulting model produced calculated values that satisfactorily fit the measured empirical data. We posit that this approach will serve as a foundation for building SCMs that account for environmental complexities.

REFERENCES

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