Clay mineral weathering in shales and soils in the critical zone

S. MacDonald, R.H. April* and D.M. Keller

Geology Department, Colgate University, Hamilton, NY 13346 (*correspondence: rapril@colgate.edu)

As part of the Shale Hills Critical Zone Observatory (SHCZO) research project, we studied the weathering characteristics of Clinton group (Silurian) shale and overlying soils in a research site in central New York State. This site is the northern-most of six SHCZO satellite sites making up a N-S climate-transect that extends from New York to Puerto Rico. We were especially interested in the weathering characteristics of the clay minerals of these deposits, some of which tend to undergo mineralogical transformations via mixed-layer intermediates. X-ray diffraction analysis (XRD) of bulk shale samples reveals that the shale is composed of quartz, Fe-rich chlorite and illite (mica). Some shale beds contain calcite or dolomite, or both, and feldspar is present in minor amounts. Modelling with NEWMOD© [1] suggests that illite is the most abundant phyllosilicate in the <2μm clay-size fraction (~90%), with chlorite constituting the remainder. Both phyllosilicates are well crystallized.

Soils at our study site contain abundant fragments of Clinton group shale. [Most soils in central New York have developed from glacial sediments (e.g. till and stratified drift) comprising aggregates of sand, silt, clay, and rock fragments derived from ice-scoured bedrock units. The mineralogy of the glacial debris is often heavily influenced by the mineralogy of the local bedrock.] XRD reveals that the bulk soil contains abundant quartz with lesser amounts of feldspar, mica and chlorite. The <2μm clay-size fraction contains illite, illite-vermiculite, chlorite (possibly chlorite-vermiculite) and vermiculite with hydroxy-aluminum interlayers. Kaolinite may be present in minor amounts. Modelling with NEWMOD© reveals that the proportions of soil clays change with depth in the soil profile. For example, illite consitutes 60% of the clay fraction in the 65-70 cm depth interval and decreases in abundance to about 45% in the 0-5 cm interval where near-surface weathering is more intense. Artificial weathering experiments with the shale show that the Fe-rich chlorite is more susceptible to decomposition in a weak acid solution than illite. Clays exfoliated (by sonification) from the surface of shale fragments collected from the soil were analyzed by XRD and show incipient weathering of clay minerals.

[1] Moore & Reynolds (1997) *X-Ray Diffraction and the Identification & Analysis of Clay Minerals*, Oxford, p.378.

Towards an accurate prediction of surface protonation equilibria: Quantifying interfacial structure via the bond valence-MUSIC model framework

M.L. Machesky[1]*, M. Předota[2], L. Vlcek[3], J. Rosenqvist[4], A. Skelton[5], P.T. Cummings[5], M.K. Ridley[6], J.D. Kubicki[7], J.O. Sofo[7], N. Kumar[7], A.V. Bandura[8] and D.J. Wesolowski[3]

[1]University of Illinois, Champaign, IL 61820, USA (*correspondence: machesky@illinois.edu)
[2]University of South Bohemia, 370 05 Ceske Budejovice, Czech Republic
[3]Oak Ridge National Lab, Oak Ridge, TN 37831, USA
[4]University of Leeds, Leeds LS2 9JT, UK
[5]Vanderbilt University, Nashville, TN 37235, USA
[6]Texas Tech University, Lubbock, TX 79409, USA
[7]Penn State University, State College, PA 16802
[8]St. Petersburg State University, St. Petersburg, Russia

Our understanding of the static and dynamic properties of mineral-water interfaces is coming into clearer focus thanks to increasingly sophisticated experimental and computational probes. An invaluable use of this information will be to place the prediction of surface protonation equilibria on a firm theoretical footing. A useful, albeit empirical, framework that is able to explicitly utilize interfacial structural information is the bond valence-MUSIC model.

We will summarize how we utilize the bond valence-MUSIC model framework to predict surface protonation constants for the (110) surfaces of rutile and cassiterite that take into account surface Ti-O and Sn-O bond lengths from DFT calculations and x-ray reflectivity measurements, as well as H-bond configurations derived from ab initio and classical molecular dynamics simulations. The principal conclusion from these predictions is that the bridged oxygen is more acidic than the terminal hydroxyl group on the rutile (110) surface, while the reverse is true for cassiterite. Moreover, this order of relative acidities is consistent with DFT calculations that indicate a greater tendency for associative water adsorption on rutile (110), and dissociative water adsorption on cassiterite (110).

We have also begun to investigate quartz-aqueous solution interfaces, and our initial efforts at predicting quartz surface protonation constants will also be presented.