

Weathering phenomena involving mineral nanoparticles, one of the last unexplored geochemical components in soils and sediments: A tribute to Art White

MICHAEL F. HOHELLA, JR.

Department of Geosciences, Virginia Tech, Blacksburg, VA, USA,
hochella@vt.edu.

Art White has made a difference in how we understand Earth. He has been a geochemist in the mold of Victor Goldschmidt in terms of a lifetime of deeply insightful thinking, and in Art's case, he has been a masterful unraveler of the critical zone. Remarkably, some of his experiments have lasted more than a decade. He is one of the best in the world at interpreting soil chronosequences, and is also a world authority on linking field- vs. laboratory-based weathering rates. In my career, he was the first to convince me that seemingly hopeless complicated Earth systems could be untangled and in fact understood.

Recently, we have realized that the field of nanoscience is important in weathering phenomena. Worldwide, soils blanketing the continents contain an estimated 10^7 to 10^8 terragrams (Tg = one million metric tons) of mineral nanoparticles, with roughly 10^3 to 10^4 Tg being transported to the continental margins annually via rivers. Nanoscience comes into play because experimental and theoretical evidence suggests that dissolution rate is a function of particle size in the nanoscale. Although quite difficult to measure, to date accelerated dissolution rates are associated with smaller nanoparticle sizes for silica, iron oxides/hydroxides, titanium dioxide, zinc oxide, and lead sulfide, and nanoscale clay edges dissolve much faster than basal surfaces. However, this is not the case for all minerals. Calcium phosphate minerals, in particular, may experience a dramatic retardation of dissolution rates at the nanoscale relative to larger crystals. This may be because there is a critical particle radius required for the formation of etch pits on these phosphates.

More recently, it has been clearly verified that there are other factors besides size that dramatically affect the dissolution rates of mineral nanoparticles. For example, the exact aggregation state is key: in tightly aggregated clusters, where water is reduced to nanofilms that we can now directly observe, dissolution rates can be reduced by orders of magnitude, essentially quenching the overall reaction per surface area available. In other words, even the fluids in this case are presenting dramatically different properties than in the bulk state, again the hallmark of nanoscience. Examples of mineral nanoparticles where this has been shown include goethite, lead sulfide, and zinc oxide. In addition, we have recently shown that nanotubular voids that intersect the surface of hematite nanoparticles act as highly reactive sites for reductive dissolution driven by organic acids. So again, acceleration and inhibition of dissolution can be dramatically manifested in different nanostructures of nanoparticles.

Such minute phenomena can have global consequences. For example, it has recently been realized that phytoplankton (key to CO₂ drawdown from the atmosphere) can acquire one of its vital limiting nutrients, iron, from iron oxide nanoparticles in the oceans that have been shed from the continents. This depends on iron oxide dissolution controlled by some of the factors described above.

Using pore-scale simulations to better quantify mixing and mass transformation in upscaled models

DAVID L. HOCHSTETLER^{1*}, MASSIMO ROLLE^{1,2}, PETER K. KITANIDIS¹

¹Department of Civil and Environmental Engineering, Stanford University, Stanford, CA, USA

²Center for Applied Geosciences, University of Tübingen, Tübingen, Germany

*(presenting author: dhochste@stanford.edu)

We perform pore-scale simulations of different transport scenarios in order to analyze irreversible bimolecular reactive transport with the objectives of: i) finding an empirical relationship that describes the effective kinetic rate constants in upscaled (Darcy scale) models; ii) determining the appropriateness of using intrinsic kinetic rate constants in upscaled models; iii) enhancing understanding of how compound-specific diffusivities affect mass transformation of reactive solutes at the pore-scale; and iv) quantifying the importance of accounting for compound-dependent mixing properties in predicting plume lengths and mass transformation at the Darcy scale. We evaluated transient displacement problems with a range of intrinsic kinetic rates as well as steady-state reactive plumes with a range of flow rates and “fast” and “slow” kinetics.

The results show that an empirical relationship can relate the ratio of the effective rate constant over the intrinsic rate constant to the inverse of the Damköhler; this is similar to what has been found for 1st-order [1] and biofilm [2] reactions. Furthermore, increasing Da does increase the amount of reactant segregation [3] but does not necessarily significantly increase mass overprediction because the reactant transformation may be mostly mixing limited. Thus, using an intrinsic rate constant in an upscaled model resulted in only about 10% overprediction of product mass for our problem set-up [4]. For the steady-state problems, we compare the adequacy of using the traditional linear parameterization for transverse dispersion to using a non-linear compound-specific parameterization [5] to predict reactive transport at the Darcy scale. We quantify the differences for product mass and plume lengths between the pore-scale results and the upscaled predictions using the linear and non-linear transverse dispersion coefficients.

[1] Dykaar and Kitanidis (1996) *Water Resour. Res.* **32**, 307-320.

[2] Wood et al. (2007) *Adv. Water Resour.* **30**, 1630-1647.

[3] Kapoor et al. (1997) *Water Resour. Res.* **33**, 527-536.

[4] Hochstetler and Kitanidis. (2012) (submitted).

[5] Rolle et al. (2012) *Transp. Porous Media* (in press).