Computational subcolloidal mineralogy

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Computation is now well established as a primary means of discovering and *understanding* chemical reactivity in aqueous and interfacial systems. Progress has not moved as quickly in the Earth sciences as it has in molecular biology because low-temperature Earth materials are so difficult to characterize. An important aspect of nano-Earth science is that while “small” is not necessarily different, “small” may be more precisely characterized. Recent advances in research on nanometer-sized aqueous poly(hydr)oxocations provide a particularly well defined path toward understanding surface reactivity in aqueous oxide systems. It has been possible to crystallize such ions as salts and determine their structure with single-crystal x-ray diffraction. These salts may then be redissolved in solution while preserving the complex ion for reactivity studies.

These ions can form an unusually tight link with computer simulation. This synergy is discussed in two case studies. The first of these involves water and hydroxide ligand exchange reactions in the ε-(Al, Ga, Ge)Al_{12} “Keggin” ion system. We find that the exchange mechanism is highly cooperative and not at all similar to mechanisms derived from the studies of octahedral substitution in aquo ions, which are often used in conceptualization of ligand exchange processes on oxide surfaces. For example, activation volume-mechanism relationships are completely opposite to those known for aquo ions. The second case study involves “*in silico*” acidometric titrations of model poly(hydr)oxocations in aqueous solutions. Here the reactivity of the Keggin $MO_4(OH)_{24}(H_2O)_{12}^{7+}$ structure is contrasted against that of the larger $M_{30}O_8(OH)_{56}(H_2O)_{26}^{18+}$ structure. The M_{30} structure has six triply-bridging hydroxide functional groups which might be expected to make the M_{30} ion more acidic than the M_{13} ion. The enhanced acidity of the M_{30} ion is indeed predicted by the model, but the contributing functional groups are unexpected and do not correlate at all with gas-phase acidity.

Controls of step length and direction on crystal solubility

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Solubility’s direction dependence is a fundamental property of anisotropic materials. For example, thermodynamics dictates that chemical potential necessary to maintain the growth of an individual crystal differs amongst faces that have different surface energies. This leads to the conclusion that multiple solubilities exist on anisotropic crystals where faces unrelated by any symmetry operations are present. Consider a step in the i^{th} direction, the direction-dependent solubility can be expressed by

$$\ln K_i = \ln K_{sp} + (2M_w/3RT\rho)[\gamma_i/l] \qquad (1)$$

where K_i and K_{sp} are step solubility and standard state solubility product, M_w and ρ are molecular weight and density, γ_i the surface energy of the step riser, l the step length, and RT have their usual thermodynamic meaning. Eq. (1) states that K_i is always greater than K_{sp}. However, a closer examination of the $\ln(K_i/K_{sp}) \sim l$ relationship reveals that all direction-dependent solubility converges to K_{sp} when l is infinitely large (in reality, a length of a few μm is sufficient). While this warrants the rationality of approximating solubility by K_{sp} in traditional studies of crystal growth and dissolution for larger crystals, it implies that direction-dependence cannot be ignored when dealing with nano-crystal growth/dissolution. In situ AFM experiments conducted on the cleavage face of calcite show that the $<\bar{4}41>\pm$ steps indeed exhibit direction and length dependent behaviour at nm to sub-μm scales. Whereas advance is observed in steps of μm-lengths in both directions at near equilibrium conditions defined by K_{sp}, nano steps (10-100 nm) do not grow until the solution saturation is up to 50% higher than that defined by K_{sp}. Furthermore, simultaneous growth and dissolution at the two directions are observed in a narrow range of saturation, providing a direct proof for the existence of direction dependent solubility in calcite.