

Nanoparticles in natural systems: Oxides and organic matter interaction

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Nanoparticles, either oxides or natural organic matter, are often dominantly determining the chemical reactivity of natural systems as result of the extremely large surface / mass ratio. Characterization of nanoparticles is difficult and often proxies have been used to improve the understanding of relevant surface characteristics and corresponding reactivity that will determine the tendency to react with compounds that are naturally present such as phosphate and calcium ions, and various types of natural organic substances. The interaction of cations, anions, and organic molecules with oxide nanoparticles will determine properties such as colloidal stability and mobility which is of relevance for the fate of cycling of elements in the environment.

Modeling of the surface reactivity of oxide particles requires information on the surface structure if the challenge is to use mechanisms that are based on the microscopic reality. For small particles, this is a challenge considering the difficulty to identify the structure of the mineral core of such nanoparticles. As will be discussed, surfaces may strongly contribute to the overall composition of the mineral phase as evidenced in macroscopic properties such as molar mass and mass density.

For oxides, application of surface complexation models (SCM) to natural systems will face the problem of quantifying the interaction of natural organic matter with the oxide fraction. Advanced adsorption models such as the Ligand and Charge Distribution (LCD) model have been developed to account for this. Simplified approaches based on LCD modeling results will be discussed. Application to natural systems requires also information about the size and reactive surface areas of the nano oxide particle (s) and for this an experimental approach is suggested. Application of the method to top soils provides data that suggest that nano-oxide particles are embedded in a matrix of soil organic matter. In subsoils, the particles of the natural oxide fraction may be larger for reasons discussed.

Scanning Probe Microscopy and mineral-water interfaces: Have we reached a limit?

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The spatial resolution of scanning probe microscopes (SPM) over the last two decades has provided new data on kinetics and thermodynamics of mineral-water interfaces. With its maturity in surface science, the question that often arises is: Have we learned everything that we can from SPM? Review of new developments in SPM instrumentation reveals an emphasis on ultra-high vacuum applications, yet fundamental questions remain in mineral surface science that are best addressed *in situ*. We present some of these developments and discuss potential impacts on *in situ* mineral-water interface science as well as present new prospects for SPM applications from recent work conducted in our laboratories. Whereas significant effort to improve resolution in SPM has led to advancements, efforts to enhance the chemical sensitivity of SPM have seen fewer successes. Lateral Force Microscopy (LFM) studies on cleaved calcite sections in contact with solutions supersaturated with respect to calcite-otavite solid solutions revealed important chemical sensitivities of the lateral force properties of thin films yet the complexities of surface structure, composition and contact mechanics may impose limits in the application of LFM as a nanometer-scale mineral surface composition mapping technique. In addition to the LFM work, a new high-pressure SPM is under development enabling the interrogation of mineral-fluid interfaces in supercritical fluids.