

would make this CMS workshop lectures volume much more durable and valuable to students of the field. Finally, one could hope for a frank assessment of the role molecular simulations can play in clay research, preferably coauthored by an experimentalist and a modeler. Molecular simulations probably remain over-hyped, due to general misunderstanding of their strengths and weaknesses. The authors of the current volume each attempt to educate us, but the overall lesson is not systematic and presents too few comparisons between simulation results and experimental data. Again, such a chapter would be hard to write, but for that reason would be valuable to students and to the progress of clay science.

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The Surface Chemistry of Natural Particles by Garrison Sposito. Oxford University Press, New York, 2004; x + 242 pages. [ISBN: 0-19-511780-8]. Price \$85 hardback.

In my heart-of-hearts, I've long suspected that some Earth scientists believe in magic. What other explanation accounts for our reflex to leap to a global cause for extraordinarily complicated phenomena from a tiny handful of experimental data? Remember our fascination with the one activated complex to explain the dissolution of all aluminosilicate minerals? Best forgotten. If we don't cleave to magic, then at least some of us hope for it. Perhaps our urge to leap ahead is natural because of the complexity of Earth materials and because there are so few of us. Certainly among the most complicated of reactions, and those dimly lit by experiment, are those at the surfaces of natural particles.

For two decades, Gary Sposito enlightened this subject through a series of books directing graduate students and researchers towards well-established concepts from chemistry that might aid in the interpretation of complicated data. Books such as *The Thermodynamics of Soil Solutions*, *The Surface Chemistry of Soils* and *Chemical Equilibria and Kinetics in Soils* lucidly laid out a framework for interpreting sorption data. These books introduced a generation of geochemists to Pearson's Hard-Soft treatment of ligand binding, Gouy-Chapman and DLVO theories, and basic statistical mechanics. These books often had a didactic tone because the concepts were well ahead of the data.

His new book *The Surface Chemistry of Natural Particles* is strikingly different. It seems to describe a mature field where concepts have fattened themselves on a porridge of spectroscopy and hard thinking, and now glean relatively little nourishment from pure chemistry. The vocabulary and data are much richer than a decade ago or, stated differently, the field now generates its own heat.

Most chapters in *The Surface Chemistry of Natural Particles* organize and comprise a *Summa Geochemica* where concepts are discussed using real data on Earth materials. Mercifully, we no longer have to start understanding surface charge (or proton-enhanced reaction rates) by figuring out what '>SOH' means – it is explained clearly and related to actual molecular structures. The first chapter, on the charged interface, gallops into view with adsorbates where structures are drawn in polyhedral or ball-and-stick form and include solvent cages, actual bond lengths, and coordination shells. These aren't 'sitting-in-the-armchair-doodling' structures, but are derived from someone's nasty spectroscopy.

Sposito's explanations glide seamlessly from this molecular-scale information to macroscopic changes in chemistry. The explanations may be more intuitive now

because the community (in this case, me) is more comfortable with the summation of molecular properties to yield familiar bulk reactivities. The experiments are also well integrated with theoretical methods which are themselves generated largely from within the geochemical community and are advancing quickly. There has been much thinking about how to assign thermodynamic properties to individual surface complexes, to estimate individual equilibrium constants, and the proper use of electronic-structure information.

Other chapters cover the subject at different scales and dimensions. After the first chapter comes more spectroscopy, kinetics, modeling and, finally, colloidal phenomenon. Sposito's familiar didactic tone reappears in the last chapter, on colloidal phenomenon, where he outlines the use of light scattering to gauge time scales and lengths scales (there are none) of aggregates suspended in solution. I know nothing about this subject and he does a fine job of introducing new, complicated material cogently.

Ultimately, the value of thermodynamic data lies in its ability to predict compositions and, in my opinion, the best chapter in the book concerns the modeling of ion adsorption. In it, the preceding detailed information is integrated into a presentation of methods of predicting the reactive properties of soils and colloids, starting with charge and size of the adsorbate but ending up with natural particles showing different affinities for interacting with extraneous chemicals. The discussion begins with Schindler diagrams that compare the proton charge of the surface with the charge of the adsorbate, then into Guoy-Chapman theory, weaknesses and strengths of the Triple-Layer Model and leading to thermochemistry and

ways to approximate temperature dependencies of equilibrium constants for surface reactions. Sposito then wades into the reactivities of real particles with many, and poorly characterized, functional groups, and methods of identifying and estimating the uptake and release of adsorbates.

How will the next edition differ? First, the advance and retreat of growth steps on a crystal can now easily be imaged directly and there are rich theories for explaining them. I suspect that 'step-flow' models will supplant much of the current interest in molecular-scale mechanisms; it is difficult to find a surface morphology that cannot be reproduced from random addition and detachment of cubes (making 'Cubonium') or spheres ('Spheronium') with simple bond rules. Secondly, it will have much new discussion of atmospheric particles and soot, since these are among the most chemically dynamic and poorly understood of natural particles. Atmospheric chemistry is the logical home for much of our *ab initio* and molecular-scale modeling because the molecular details are immensely important and hypotheses can be better tested than for a clay particle in water.

In summary, I love this book. I bought a copy for myself weeks ago and I am very happy to have an additional copy courtesy of *Clays and Clay Minerals*.

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