MODELING GEOCHEMISTRY

ACS MEETING NEWS: Increasing computational power makes possible simulations of geology's nitty-gritty chemistry

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YOU MIGHT SAY that geochemistry can make a mountain out of a molecular molehill. The atomic-level descriptions of the chemical behavior of mineral surfaces and their interactions with aqueous solutions ultimately explain some of the planet's largest-scale phenomena.

As with many disciplines firmly planted in the macroscale, geoscience has only relatively recently been able to take significant advantage of computational molecular modeling. But in the past decade, geoscientists have been hungrily eyeing the ever-increasing computer power that's now making it possible to augment, verify, and fill gaps in geochemical experimental data. Molecular dynamics simulations of, for example, the interactions of clays with environmental contaminants, which were too expensive and time-consuming 10 years ago, can now be accomplished with supercomputing technologies (C&EN, April 13, 2009, page 52).

Last month's American Chemical Society national meeting in San Francisco saw the deployment of computational geochemistry forces that have been advancing for several years, with a symposium cosponsored by the Divisions of Geochemistry and Computers in Chemistry. The symposium's co-organizer, chemistry professor Andrey G. Kalinichev of Michigan State University, noted that geochemistry is in many ways similar to any field that considers computation a counterpart to experiment, such as biophysics or drug design. "We're using the same tools, but working on a different subject," he said.

But geochemistry also has some unique computational challenges, such as the imperfect crystal structures of clays and uncertainty in the composition and structure of soil humus molecules.

As much as any computational scientist would love to be able to describe, down to each electron, the dynamical behavior of a mélange of materials containing millions of atoms, that prospect is still out of reach. So-called ab initio methods, which generate computational descriptions of systems based only on the Schrödinger equation, are practical for hundreds of atoms only, and that's a bottleneck particularly pertinent to geosciences.

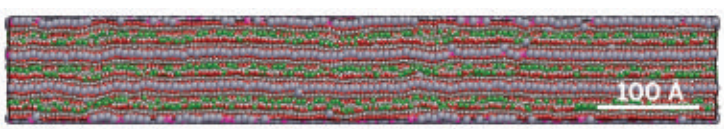
"Most geochemical problems are at the nanoscale with large numbers of atoms and long simulation times," Eric J. Bylaska, a computational chemist at Pacific Northwest National Laboratory, noted at the meeting.

IN ADDITION TO pure bulk, the materials that geochemists work with are particularly tough to characterize. Clays, composed of layers of fine-grained silicates, for example, are disordered, complex materials. In well-trodden computational realms, chemists frequently approximate the behavior of solvents, most notably water, as a force field, a potential function using empirical data that approximates interatomic interactions among molecules. But the properties of materials like clays are not yet as easily simplified.

"We're in the infancy of developing force fields for these materials," Randall T. Cygan of Sandia National Laboratories said at the meeting. Cygan, along with Kalinichev and other colleagues, created CLAYFF, a semiempirical force field that predicts, among other properties, how clays swell with water.

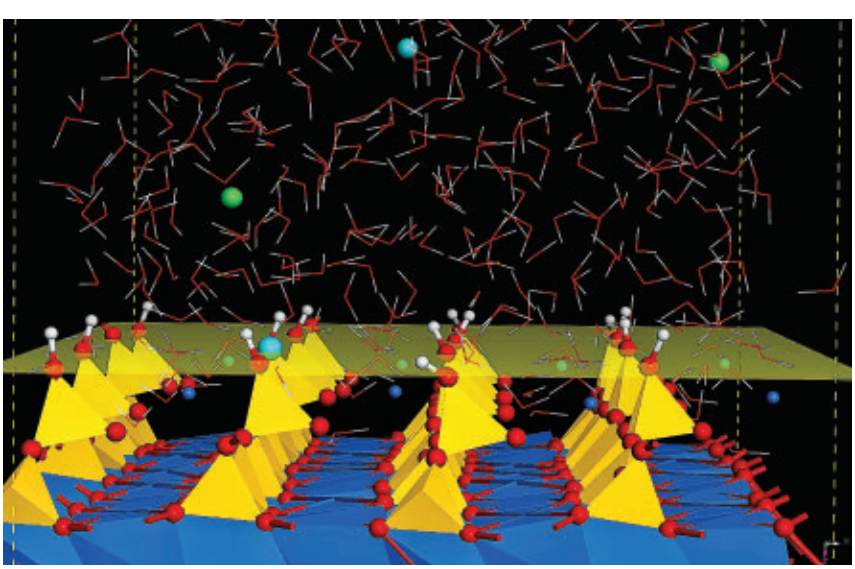
James R. Rustad, a geology professor at the University of California, Davis, has long

UP CLOSE A segment of a clay surface undulates in a molecular dynamics simulation. The length scale is expanded 15 times with respect to the height of the segment.



COURTESY OF PETER COVENEY

SURFACE ACTION Snapshot of a molecular dynamics simulation shows how water interacts with the surface of a mineral, tobermorite. (Red is oxygen, white is hydrogen, green is chloride ion, blue is potassium ion. Gold tetrahedra represent the SiO_4 crystal structure elements, at the center of which is a silicon atom.)



COURTESY OF ANDREY KALINICHEV

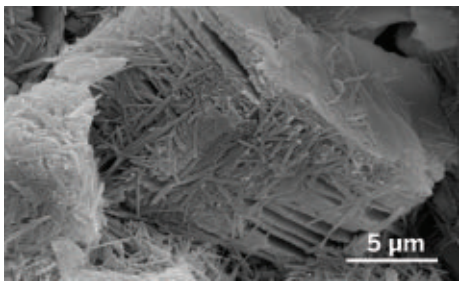
been developing and studying a computational model that allows for the dissociation of water molecules at the surfaces of minerals. Scientists need more fine-grained information about what goes on with mineral-water interactions than can be obtained by computationally perturbing a bulk force field, he said at the meeting.

Rustad pointed out that the chemistry at the edges of a mineral particle can be quite different from that of a flat surface—a property that needs to be taken into account in computational models.

Although considerable work remains to be done on force-field models, explosive increases in computing power and technology have allowed geochemists to make computation a standard part of their methodological repertoire. Petaflop-scale supercomputers such as IBM's Roadrunner at Los Alamos National Laboratory and the Cray Jaguar at Oak Ridge National Laboratory are popular workhorses for intensive computations.

SCIENTISTS ARE increasingly turning to distributed, or grid-based, computing, harnessing the potential of many connected computers to solve scientific problems. Peter V. Coveney, theoretical chemistry professor at University College London, described his studies of numerous systems, including the thermal fluctuations of clay sheets, using grid-based supercomputing systems such as the National Science Foundation's TeraGrid.

NOT SO SIMPLE Clays, like the example of halloysite shown, are difficult to model.



COURTESY OF ZAINUDDIN YUSOFF/U OF EDINBURGH

And to find the next big thing in scientific computing, one needs to look no further than the nearest gaming machine. Graphical processing units (GPUs), with their highly parallel structure, were originally developed for video games but are now recognized as powerful tools for solving some types of scientific problems (C&EN, Sept. 22, 2008, page 88).

For instance, Ivan Ufimtsev, a graduate student in the lab of chemistry professor Todd J. Martinez of Stanford University, touted one of Nvidia's consumer GPUs as a tool for studying charge transfer at mineral-water interfaces.

Such new technologies could help solve some pressing environmental problems. For example, the toxic uranyl ion is a problematic environmental contaminant near nuclear power plants (C&EN, Jan. 21, 2008, page 10). Cygan reported that models of uranyl sorption on sediments show that high carbonate levels can hinder the ion's sorption.

Humic substances, or natural organic matter (NOM), are a ubiquitous, complex component of soil and surface waters that's formed when plant and animal matter decays. Although it's pervasive, it's unknown whether NOM is composed of large macromolecules or of supramolecular aggregates of smaller fragments. Yet its penchant for forming complexes with metals carries environmental implications. Scientists have pieced together a prototype NOM structure, which contains a number of carboxylic groups.

Eugenia Iskrenova-Tchoukova, a postdoc in Kalinichev's lab, described at the meeting molecular dynamics simulations that showed that calcium ions encourage NOM aggregation, and that two possible mechanisms may be at work: Either a calcium ion causes bridging by grabbing carboxylates of two different NOM molecules, or calcium may attach to a single NOM carboxylate, lowering the complex's charge, making it easier for these complexes to aggregate in aqueous solutions.

Kalinichev and colleagues continue to raise the profile of computational molecular chemistry. Ultimately, they hope to organize an international consortium for computational geochemistry and environmental chemistry that will provide a disciplinary framework for scientists and students. "There is a strong feeling in the community that we need something like this," he said. ■