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"Interfacial Forces Are Modified by the Growth of Surface Nanostructures" by Chongzheng Na and Scot Martin, Harvard University, School of Engineering and Applied Sciences, 2008, 42 (18), 6883-6889; DOI 10.1021/es800839a.

Scot Martin and Chongzheng Na of Harvard University published a study about a simple method that has shed new light on the variability that nanostructures create on mineral surfaces. This work is part of a series of studies examining the interfaces of minerals common to some soils. The nanostructure maps, described in one of ES&T's best papers of 2008, could lead to new ideas about how sorption and other interactions in soils actually work.

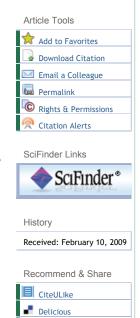
"I happened to be at the right place at the right time," says Na, a postdoctoral researcher in Martin's group and coauthor of the paper. "Scot has been working on these nanostructures for many years, and the team had been modeling what they saw in the lab with atomic force microscopy, or AFM. AFM is very good at picking up contrasts" for electrical properties, surface morphology, and more, Na says.

The method uses a tiny cantilevered arm, with a probe at one freely moving tip and the other end anchored. As the forces at the surface change, the probe is deflected, and the atomic force microscope arm bends. A laser reflecting off the back side of the arm measures that movement, producing vertical profiles that allow the researchers to map the forces acting at the surface of the samples. In this case, the team was sampling the mineral rhodochrosite, MnCO₃, which is common in anoxic soils. The researchers' interests focused on the interface between anoxic rhodochrosite and the oxic structures (MnO_x) that form on top, several nanometers high.

Differences in forces allowed Na and Martin to minutely map out the surface of the rhodochrosite and to monitor the shifts in those forces caused by the nanostructures sitting on top. The resulting images look like continents of MnO_x atop an ocean of MnCO₃. "When we look at the map, we are looking for contrast," Na says, both in forces working at the surface, such as van der Waals attraction, and in structures.

"This is basic research on fundamental science: we used a system that we think is relevant to geochemistry," Na continues. The surfaces that they've mapped are highly heterogeneous. These differences could help to elucidate the fundamental physics of how contaminants sorb to soil surfaces, for example, or the mechanics of filtration in soils. Because nanomaterials have features in the same size range, the same heterogeneity may apply, the team hypothesizes. Martin and Na also suggest that the tiny probe tip can stand in for many different materials that might interact with soil surfaces $|\mathbf{x}|$ even bacteria, theoretically.

The nanostructures "are so tiny, they may not affect bacterial adhesion," says Tracy Bank, a biogeochemist at the University at Buffalo, State University of New York. "But bacteria often



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have fimbria or different appendages that are often nanometers in diameter," she continues, and "the heterogeneity of the surfaces that they've documented may still influence" bacteria's interactions with soil surfaces.

The new work shows with extreme detail the size of these nanostructures and how they may have oxidized differently. This could lead to a more realistic view of minerals and how they weather, as well as "why they sorb species we don't expect," Bank explains. Until now, hints of this heterogeneity at soil surfaces existed only because certain behaviors did not seem to fit into the expected fate and transport of materials. "At the nanoscale, surfaces aren't anything like what you expect at the larger scale," Bank says.

The finding that surface charges differ radically between nanoscale versus bulk particles of ${\rm MnO_x}$ "is important when you wish to understand how certain contaminants or pathogens will move through an aquifer," says Steven Lower of Ohio State University.

"It's really cool how they used this [atomic force microscope] to determine" the shifts in forces at the mineral surface, Bank adds. "I can't think of any other way to do it," she says, "to actually measure the heterogeneous charges on [a] surface only nanometers in size. And they've done it so simply why didn't we think of that before?"



Chongzheng Na (left) and Scot Martin, pictured during a whale-watching trip in Boston, mapped the nanostructures of soil minerals for the first time by using AFM. The images revealed canyons and plateaus of heterogeneous force potential on the surface.

COURTESY OF CHONGZHENG NA AND SCOT MARTIN

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