Fitting a square peg in a round hole—the surprising structure of uranium bound in hematite

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New geochemical research clearly shows how toxic material like uranium binds with iron-bearing minerals like hematite in the soil, allowing scientists to predict long-term behavior. Credit: Environmental Molecular Sciences Laboratory

One promising approach to stabilize uranium contamination in soils is to envelop the radioactive uranium into iron-bearing minerals like hematite. But how well does uranium bind with hematite and for how long? Scientists have disagreed on the chemical structure of uranium bound in hematite, making long-term prediction difficult. By melding precise experimental characterization with molecular dynamics modeling, an international research team has discovered the answer. And it's not what anyone expected.

Uranium contamination lurks in groundwater and soils at U.S. Department of Energy (DOE) sites and under many industrial areas around the world, and some forms can readily transported. One approach for limiting the mobility of uranium is to enhance its binding with iron oxides or other minerals. Doing so could also enable scientists to better predict its long-term behavior to ensure uranium remains stabilized for thousands of years.

While scientists have been studying the binding of uranium to iron-bearing minerals for some time using X-ray spectroscopy, different researchers have interpreted similar data in drastically different ways. This has been a tough problem because uranium, like a square peg in a round hole, should not fit into the crystal structure of hematite, one of the most abundant iron minerals found in soils. The solution, developed by researchers at the Pacific Northwest National Laboratory and the University of Manchester, turns previous work on its head. With support from DOE's Office of Science, Office of Basic Energy Sciences, Geosciences Program at PNNL, and using the Cascade supercomputer at EMSL, the Environmental Molecular Sciences Laboratory, a DOE Office of Science user facility, the team calculated many possible atomic structures of uranium incorporated into the structure of this mineral.

They discovered that vacancies created in the atomic structure of hematite during its formation accommodate the uranium. Neither this accommodation nor the flexibility shown by the uranium was expected. This binding process had never before been identified, but the methods used to make this finding could explain a number of mysteries previously reported in the scientific literature. The work opens the door to new studies on how other radioactive contaminants bind to soil minerals and will lead to more accurate predictions of how these contaminants behave in the environment.

More information: Martin E. McBriarty et al. Iron Vacancies

Accommodate Uranyl Incorporation into Hematite, *Environmental Science & Technology* (2018). DOI: 10.1021/acs.est.8b00297