Rock: Electrons run through it

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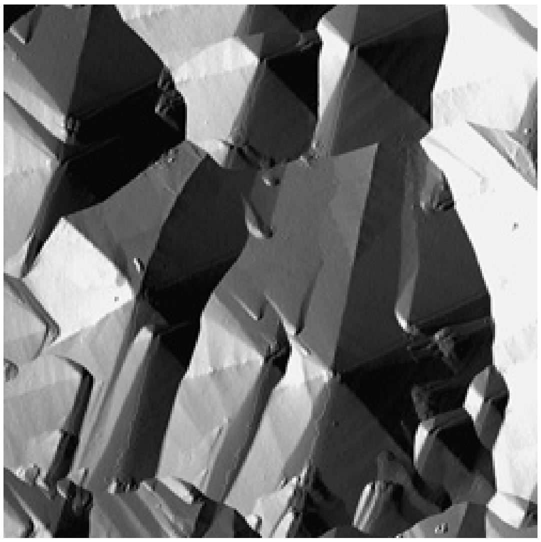

Rocky growth: Iron building up into pyramids on one face of a hematite crystal sends electrons to another face, which slowly dissolves. Credit: PNNL

If the Flintstones had electricity, their wires might have been made of rock. New results in Science Express show that a chunk of hematite can conduct electrons under certain chemical conditions. In addition, the current causes some mineral surfaces to build up while others degrade. These results with iron oxide might be important for water quality, soil evolution, and environmental cleanup.

"Considering iron as an important nutrient, the finding could help us understand how soils evolve from nutrient rich to nutrient poor," says lead investigator Kevin Rosso, a chemist at the Department of Energy's

Pacific Northwest National Laboratory. "And it has implications for other common minerals such as pyrite and manganese oxides -- even particles in the atmosphere."

Scientists have long known that electrons can travel through some iron oxides when a voltage is applied, but they have assumed that electrons stemming from chemical reactions alone won't move spontaneously through the mineral's bulk. That long-standing assumption has caused chemists to treat different faces of a hunk of mineral as independent entities that don't 'communicate' with each other. New results, published online March 6, 2008 in *Science Express*, suggest otherwise.

"Now we know reactions at different faces of these minerals can couple together and yield behavior unique to semiconducting minerals," says Rosso.

Minerals often exist as individual crystals in rocks at a stream's bottom, where they keep busy reacting with the water flowing around them. Understanding this chemistry is central to understanding how elements move through sediments, maintaining good water quality, and cleaning up pollution. To elicit the details, scientists study what effect acids and other forms of chemicals have on mineral surfaces.

When Rosso and PNNL colleague Svetlana Yanina immersed a cube-shaped hematite crystal in an acid solution in the absence of oxygen, they expected all surfaces to degrade. But when the chemists examined the surfaces at high magnification, they found one surface that didn't. This surface grew pyramid-like mounds rising from the top. "The whole crystal wants to dissolve, thermodynamically," says Rosso. "So we didn't expect to see that growth."

No one had previously reported this buildup, so the team modified their experiments to try to prevent the pyramids from growing. "In fact, we spent a year trying to get rid of it," Rosso says.

One path to getting rid of something is to understand how it got there in the first place, so they decided to explore how the pyramids formed. The researchers performed atomic force, scanning electron and transmission electron microscopy at the DOE's Environmental Molecular Sciences Laboratory on the PNNL campus, as well as electrical potential measurements of the individual surfaces.

Because hematite is a crystal of iron oxide, the sides and the top (and bottom) are structurally different, and therefore have different chemical properties. The team wondered if the iron being deposited on the top came from iron dissolving from the sides, building up in solution, and then redepositing.

To test this, they separated the six cube surfaces into groups: They took two cubes, protected four sides from the solution on one, and on the other, protected the top and bottom. The acidic solution chewed away the unprotected surfaces, as expected. But the chemists didn't see any buildup on the unprotected top and bottom faces and instead saw degradation. This indicated the breakdown and buildup were not independent of each other.

"The hematite won't grow pyramids without that surface being connected to the dissolving ones," says Rosso.

The required physical connection hinted at electron conduction. Iron in solution, or Fe(II), contains one more electron than the iron in the crystal, Fe(III). If Fe(II) landed on the top, it might react with the surface, incorporate into the crystal and give up its electron. The electron could then flow through the crystal to the sides, where an atom of Fe(III) could pick up the electron and dissolve into the solution.

To prove this, the chemists connected the electron flow with a wire. When they repeated the first experiment but connected the two cubes with a dab of silver, the team restored the pyramid buildup. Additional experiments allowed them to measure the electrical potential driving the current flow, which came out to 200 millivolts -- about 6% of the power needed for a keychain LED light, or about twice as much as in a nerve cell.

Citation: S. V. Yanina and K. M. Rosso, "Linked reactivity at mineral-water interfaces through bulk crystal conduction," published online at *Science Express*, March 6, 2008, 10.1126/science.1151614.

Source: PNNL