Study: Pulsating dissolution found in crystals

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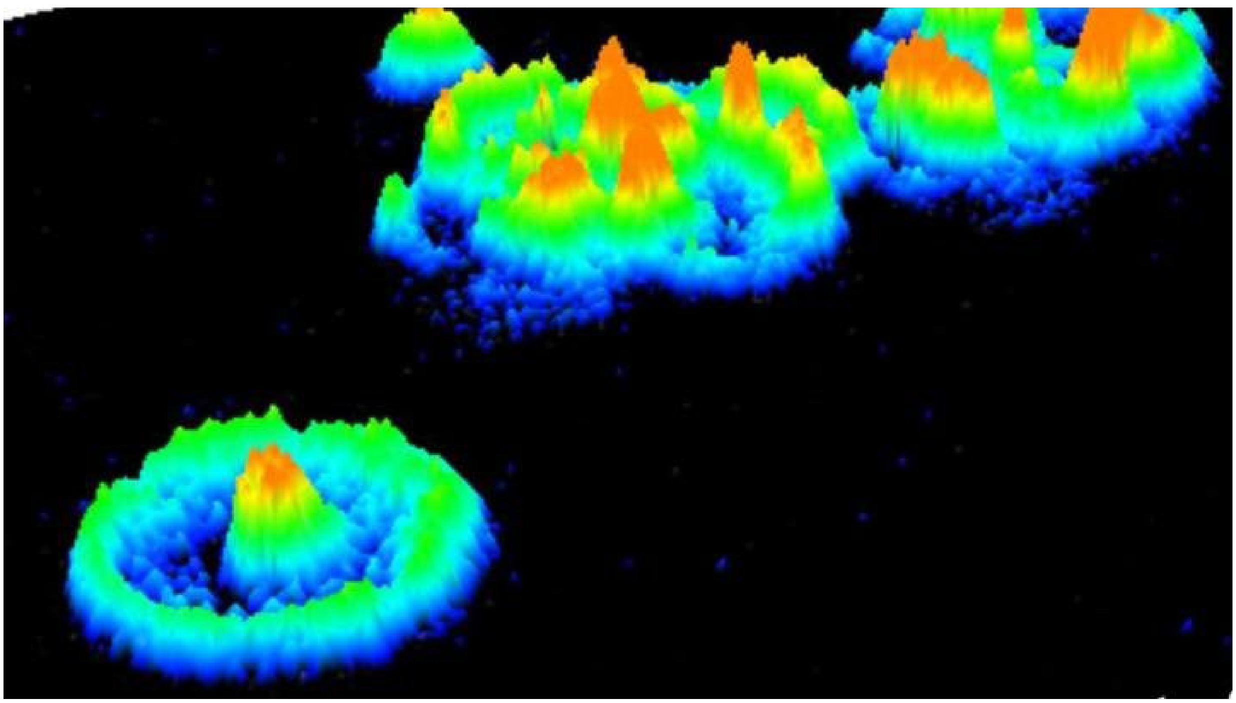

Dissolution of crystals happens in pulses, marked by waves that spread just like ripples on a pond. Credit: MARUM - University of Bremen

When German researchers examined time-lapse images of dissolving crystals at the nanoscale, they found a surprise: Dissolution happened in pulses, marked by waves that spread just like ripples on a pond.

"What we see are waves or rings," said lead investigator Cornelius Fischer, who conducted this research at the University of Bremen in the group of Prof. Andreas Lüttge. "We have a pit in the middle, and then around these pits are rings of mass removal." The research has been published in the *Proceedings of the National Academy of Sciences*. Fischer and Lüttge specialize in studying minerals-fluid interactions, and have collaborated for more than 15 years in the US and Germany.

In everyday life, dissolving crystals is as simple as stirring sugar into a glass of water. And as any child who has made rock candy knows, the process also works in reverse: Crystals of sugar will form as water evaporates from the glass. Lüttge said scientists have long known that crystals form through a continuous process as molecules are deposited from solution into the regular crystal lattice of the solid they're forming.

"We always thought dissolution was a continuous process, kind of like crystal formation in reverse, and we were astonished when these experiments showed this was not a continuous process," Fischer said. "Instead, what we saw were pulses occurring around these pits."

The pulses show up clearly in rate maps, high-resolution still images that capture the rate at which material dissolves over time from the surface of a crystal. In experiments at MARUM, Cornelius Fischer modified an imaging technique called "vertical scanning interferometry" that Lüttge pioneered at Rice University (Houston, U.S.) in the early 2000s to make "surface reaction rate maps."

"The maps show the distribution of the material flux and thus illustrate the surface reactivity," said Fischer, a former MARUM postdoctoral researcher who's now head of a research group at the independent German research laboratory Helmholtz-Zentrum Dresden-Rossendorf. "During the routine analysis of rate-map data, we discovered the existence of a remarkable pattern of surface reactivity. This was the starting point for a systematic analysis of pulsating rate map features."

Using samples of first zinc oxide and later calcium carbonate, Fischer made maps that showed every dip and rise on the surface of the crystal to a resolution of 1 nanometer, or 1 billionth of a meter. Each scan collected more than 4 million measurements from a surface measuring no more than a square centimeter. Taking subsequent snapshots of a crystal's surface as it dissolved allowed them to measure the rate at which the crystal dissolved as a function of surface height.

Scientists have long understood the importance that tiny surface defects play in crystal dissolution. Miniscule divots called "etch pits" expose crystal edges and increase the likelihood that a solvent, like water, will chemically react with atoms from the crystal. The process is similar to how rust eats away at iron or steel.

When they examined their rate maps for dissolving calcite and zinc oxide crystals, Lüttge and Fischer found "rhythmic fluctuations of the reactive surface site density," or dissolution pulses that spread like rings from etch pits and screw dislocations, much like ripples that spread from the point where a pebble is dropped into a pond.

"The complex superimposition of pulses defines the overall result, and we are now able to understand—and, most importantly, to quantify—such patterns as the starting point for the formation of porosity in solid materials during dissolution," Fischer said. Lüttge said the discovery adds to scientists' fundamental understanding of crystal dissolution and could aid researchers in fields as diverse as corrosion prevention and pharmaceutical manufacturing.

More information: Cornelius Fischer el al., "Pulsating dissolution of crystalline matter," *PNAS* (2018).
www.pnas.org/cgi/doi/10.1073/pnas.1711254115