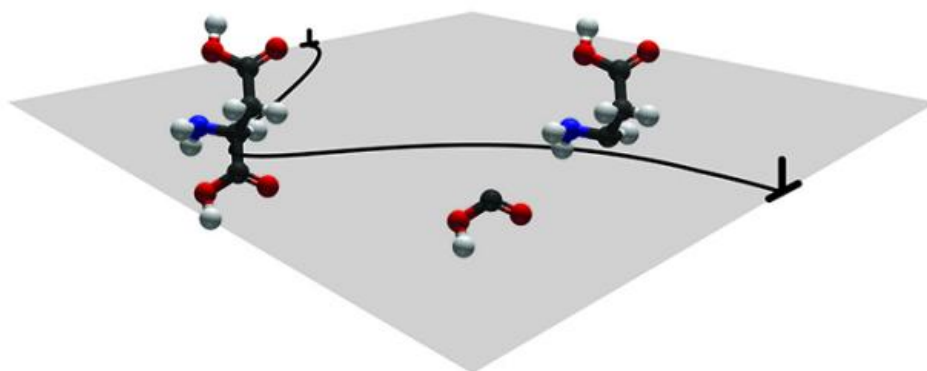
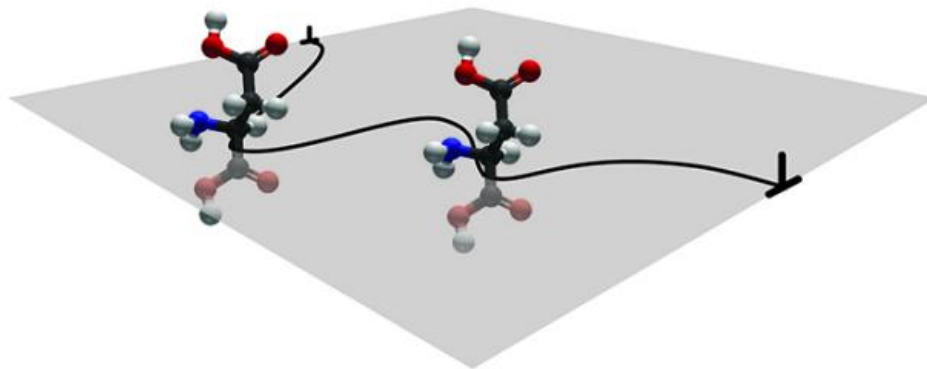
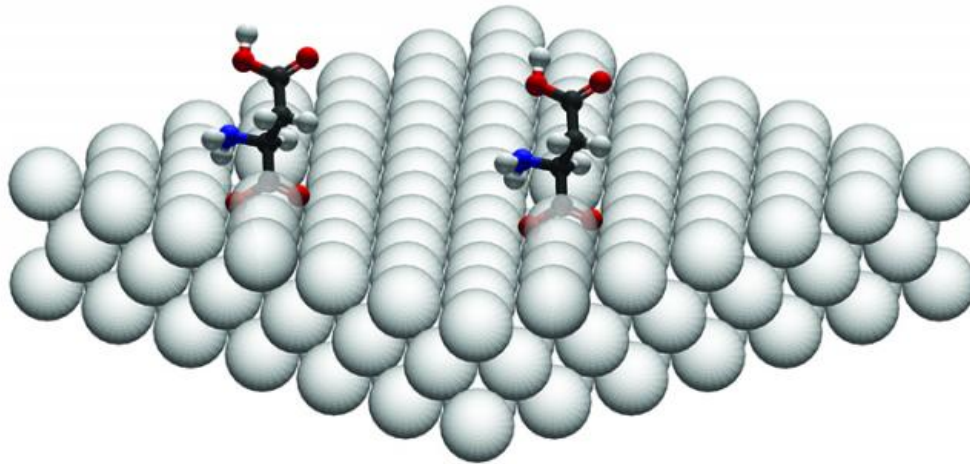


Calcite tuned to be mollusk-tough

May 3 2016, by Tom Fleischman



Top: Aspartic acid molecules embedded in a crystalline lattice. Middle: A

dislocation in the crystal, represented by the black line, gets hung up on the molecules. Bottom: The dislocation cuts one of the molecules. The strength of a covalent bond in the molecule ultimately determines the hardness of the crystal. Credit: Nicole Wiles

No self-respecting construction engineer would ever choose pure calcite – a weak, brittle mineral found in chalk – as a building material.

But what if you could somehow strengthen [calcite](#) by a factor of two or more, the way a mollusk has done through the evolutionary process to protect itself from sharp-toothed predators?

Well, you still might not choose hardened calcite to build your home, but it might have other applications that, by virtue of its availability, could make it an attractive option for low-strength fabrication needs.

Cornell researchers, together with a team from the University of Leeds (U.K.), have jointly led an expansive, years-long international collaboration that has resulted in a paper detailing the ability to control and increase resistance to deformation in pure calcite through the introduction of amino acids.

The paper, "Tuning hardness in calcite by incorporation of amino acids," is published on May 2 in *Nature Materials*.

"Why is it that a mollusk at the bottom of the ocean can make a single crystal of calcite that's solidly twice as hard as a naturally occurring, pure geologic calcite?" asked Shefford Baker, Cornell associate professor in the Department of Materials Science and Engineering.

That was the question he and colleague Lara Estroff, also an associate

professor of materials science and engineering and a member of the Kavli Institute at Cornell for Nanoscale Science, had sought to answer through approximately six years of research.

Estroff and Baker worked with an international team. Fiona Meldrum and Yi-Yeoun Kim from Leeds co-led the study; additional collaborators included current Cornell graduate student Joseph Carloni and former grad student Miki Kunitake, both jointly advised by Estroff and Baker, and nine others from the United Kingdom and Israel.

"I don't think there's any way that all of these teams, having done their parts in isolation, could have come up with this paper," Baker said. "I don't think all the connections would have been understood."

The answer lies in aspartic acid (Asp) and glycine (Gly), amino acids that – when added in precise, controlled amounts – increased single-crystal calcite's hardness to values equivalent to biogenic calcite.

To create the model biominerals, the Meldrum group grew single-crystal calcite samples in a solution containing either Asp or Gly, the amount of amino acid present in the mineral dependent on the concentration of molecules in the solution.

"This was really a breakthrough," Estroff said, "to be able to have controlled and very well quantified amounts of amino acids within single crystals."

The structural characterization of these crystals required highly specialized techniques and the expertise of multiple researchers. Kirsty Penkman's group (University of York) precisely quantified the concentration of amino acids within the [calcite crystals](#), and Melinda Duer's group (University of Cambridge) demonstrated that the molecules were distributed individually rather than in clumps.

In parallel, a group led by John Harding (University of Sheffield) conducted atomistic computer simulations to determine how the [amino acid molecules](#) were fit into the calcite lattice, and Kim, along with Boaz Pokroy (Technion) and researchers at the Diamond Light Source (U.K.), characterized the distortions the molecules induced in the calcite lattice.

Using this data, the Cornell team determined how far apart in nanometers the molecules were from each other. Then by comparing hardness measured by nanoindentation, they showed hardness was determined by the force needed to cut, or break, the covalent bonds within the [amino acids](#).

The hardness of the model biominerals were the largest reported to date in man-made synthetic calcite and are consistent with those measured in naturally occurring biogenic calcites.

"This certainly opens up the door for us to think about how hard calcite could be made," Baker said. "Now that we're starting to understand the control mechanisms, the question is, could we make a system in which we go further than this?"

More information: Yi-Yeoun Kim et al. Tuning hardness in calcite by incorporation of amino acids, *Nature Materials* (2016). [DOI: 10.1038/nmat4631](#)

Provided by Cornell University

Citation: Calcite tuned to be mollusk-tough (2016, May 3) retrieved 30 April 2024 from <https://phys.org/news/2016-05-calcite-tuned-mollusk-tough.html>

This document is subject to copyright. Apart from any fair dealing for the purpose of private

study or research, no part may be reproduced without the written permission. The content is provided for information purposes only.