The Advanced Photon Source

A Rare Mineral from Rocks Found in Mollusk Teeth

Northwestern University researchers have, for the first time, discovered a rare mineral called santabarbaraite hidden inside the teeth of a chiton, a large mollusk found along rocky coastlines. Before this surprising discovery, this iron mineral had been found only in rocks in very tiny amounts and never before in a biological context. The new finding, using data obtained at the U.S. Department of Energy's Advanced Photon Source (APS), helps us understand how the whole chiton tooth, not just the ultrahard, durable cusp, is designed to allow them to chew on rocks to feed. Based on minerals found in chiton teeth, the researchers developed inks for three-dimensional (3-D) printing of bioinspired composites. The study, lead by Derk Joester at Northwestern, was published in the *Proceedings of the National Academy of Sciences of the United States of America*.

One of the hardest known materials in nature, chiton teeth are attached to a soft, flexible, tongue-like radula, which scrapes over rocks to collect algae and other food. Having long studied chiton teeth, Joester and his team most recently turned to *Cryptochiton stelleri*, a giant, reddish-brown chiton that is sometimes affectionately referred to as the "wandering meatloaf."

X-ray absorption spectro-microscopy at the iron K-edge was performed at the GeoSoilEnviroCARS x-ray microprobe beamline 13-ID-E where x-ray fluorescence maps were recorded to determine regions of interest for subsequent micro-x-ray absorption near edge structure measurements. Additionally, x-ray computed microtomography was performed on the DuPont-Northwestern-Dow Collaborative Access Team beamline 5-BM-C at the APS and synchrotron Mössbauer spectroscopy (SMS) (Fig. 1) was performed at the X-ray Science Division beamline 3-ID-B. This kind of mineralogical mapping using the newly developed Mössbauer microscopy for the first time has allowed them to follow a biomineralization process.

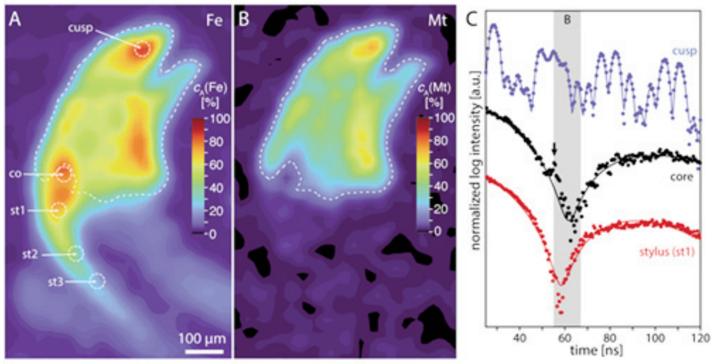

Fig. 1. (A) SMS image of iron distribution, (B) Mineral selective SMS image, showing the magnetite concentration, and (C) SMS spectra od magnetite in the cusp, as well as non-magnetic iron in the core and stylus.

The results showed that santabarbaraite is dispersed throughout the chiton's upper stylus, a long, hollow structure that connects the head of the tooth to the flexible radula membrane. The stylus, which is like the root of a human tooth, is composed of a tough material composed of extremely small santabarbaraite nanoparticles in a fibrous matrix made of biomacromolecules, similar to bones in our body. Since mechanical structures are only as good as their weakest link, it's interesting to learn how the chiton solves the engineering problem of connecting its ultrahard tooth to a soft underlying structure. This remains a significant challenge in modern manufacturing, so it is useful to look to organisms like the chiton to understand how this is done in nature.

(This report is based upon a Northwestern University press release.
See the entire APS science highlight here.)

See: Linus Stegbauer[1], E. Ercan Alp[2], Paul J. M. Smeets[1], Robert Free[1], Shay G. Wallace[1], Mark C. Hersam[1], and Derk Joester[1]*, "Persistent Polyamorphism in the Chiton Tooth: From a New Biomineral to Inks for Additive Manufacturing," Proc. Natl. Acad. Sci. USA **118** (23) e2020160118 (June 8, 2021).
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Information on access to beam time at the APS is at http://www.aps.anl.gov/Users/apply_for_beamtime.html or contact Dr. Dennis Mills, DMM@aps.anl.gov, 630/252-5680.

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