ALS SCIENCE HIGHLIGHT

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The Molecular Ingenuity of a Unique Fish Scale

Arapaima's fish-scale armor could inform the design of other types of armor. Ritchie believes that the unique mechanism of conferring toughness could be mimicked and built into synthetic structural materials to yield enhanced damage tolerance. For example, heavy Kevlar armor used by the U.S. military and police officers could be replaced with armor that would be every bit as effective but much lighter in weight.

Arapaima gigas, a freshwater fish found in the Amazon Basin, has a remarkable ability to resist predation by piranhas through the strength and toughness of their scales, which act as natural dermal armor. Arapaima scales consist of a hard, mineralized outer shell surrounding a more ductile core. This core region is composed of aligned mineralized collagen fibrils arranged in a fine, plate-like structure. To study how these scales respond to applied stresses at the molecular level, researchers used the small angle X-ray scattering (SAXS) facilities at ALS Beamline 7.3.3. Mechanical tensile tests allowed researchers to observe deformation mechanisms in the fibrils, and to see how the arrangement of the fibrils plays a key role in the scales' unique protective properties.

The novel assembly of mineralized collagen fibrils in Arapaima's special "armored" scales is the first line of defense. During mechanical tensile tests at the ALS, researchers found that the scales can literally re-orient themselves in real time to resist force, in essence creating an adaptable body armor. SAXS imaging revealed that the collagen fiber in the fish-scale core is arranged in what researcher Robert Ritchie of Berkeley Lab's Materials Sciences Division describes as a "Liberace-type spiral staircase." When subjected to stress, the lamellae in this spiral staircase re-orient themselves to accommodate excess deformation and resist fracturing.

Remarkably, most lamellae re-orient toward the tensile axis and deform in tension through stretching/sliding mechanisms, whereas other lamellae sympathetically rotate away from the tensile axis and compress, thereby enhancing the scale's ductility and toughness to prevent fracture. Under *in situ* tensile loading at the beamline, researchers found that most of the lamellae rotate toward the direction of the applied stresses to better resist the applied loads.

Most hard biological materials, such as bones, antlers, and teeth, derive their structural integrity from their hierarchical architecture. Such hierarchical assembly allows a damage-tolerant material to be created from the basic building blocks of ductile, but soft, collagen molecules and stiff, but brittle, mineral nanocrystals: strength comes primarily

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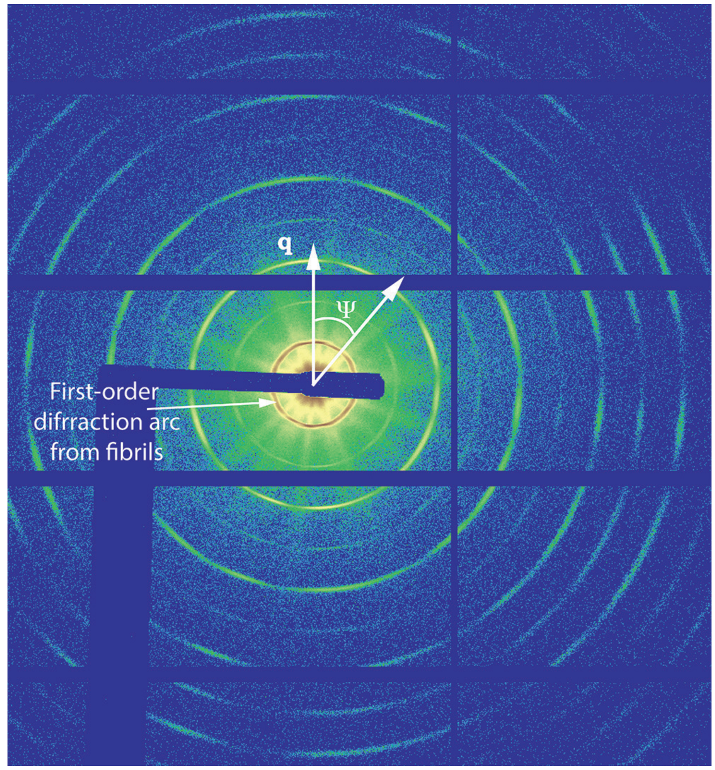
Diffraction Patterns in Fish Armor

When exposed to X-rays, the inner lamellar layer of the Arapaima scales creates a diffraction pattern that consists of distinct sets of concentric arcs, with each set appearing at a different angular orientation. These arcs result from the interaction of X-rays with the structure of the collagen fibril, which consists of a quarter-staggered array of collagen molecules with mineral nanoparticles within the gap regions situated between the heads and tails of the collagen molecules. In the presence of X-rays, the entire fibril acts as a molecular diffraction grating due to the periodicity of the collagen–mineral composite structure.

The fact that concentric arcs appear at multiple distinct angles indicates that the scale has an architecture in which collagen fibrils exist in a number of specific orientations. Each set of concentric arcs corresponds to one distinct fibril orientation in the scale, with the angle of orientation in the fibril being given by the angle at the center of the corresponding arc. On the basis of the fibrils being arranged in multiple distinct orientations, researchers concluded that the lamellae have a Bouligand-type (twisted plywood) arrangement.



Diffraction patterns from the inner layer of the *A. gigas* scales were collected at ALS Beamline 7.3.3. A representative diffraction pattern is shown here, where the periodicity in the mineralized collagen fibrils diffracts the incident X-rays at a small angle toward the detector.

from the ability to absorb energy at small length-scales through composite deformation of the mineral and protein phases, whereas toughness primarily originates from larger length-scales that are able to influence crack growth.

The protective scales of the Arapaima fish are a prime example of a biological material's evolution for a particular function. The scales specifically resist the bite of piranhas through multiple levels of defense provided by the scale's hierarchical architecture. First, the scales' aspect ratio (that is, length/thickness) and degree of imbrication (that is, exposed length/total length) not only provide flexibility during movement but also determine how much an individual scale will bend in response to a predatorial attack. Second, scales commonly have graded material properties throughout their thickness to resist both puncture and bending. For *Arapaima gigas* scales, there are two distinct macro-level regions: a hard, highly mineralized outer shell and a collagen inner core region. The highly mineralized outer shell provides hardness to minimize local plasticity and promote tooth fracture at the point of penetration by the predator; however, it also reduces tensile or compressive stresses during flexure through its corrugated morphology, which limits how much of the scale is under high stress during bending. As the scales will deform and bend in response to a predatory attack, the graded material properties through the scale thickness ensure that the larger deformations are in the inner core region, which can support greater amounts of plastic deformation than the hard but more brittle outer shell.

Arapaima's fish-scale armor could inform the design of other types of armor. Ritchie believes that the unique mechanism of conferring toughness could be mimicked and built into synthetic structural materials to yield enhanced damage tolerance. For example, heavy Kevlar armor used by the U.S. military and police officers could be replaced with armor that would be every bit as effective but much lighter in weight.