Coherent nanoparticles in calcite

A toughening strategy known to metallurgists is also used by the brittlestar

By **Dorothy M. Duffy**

Living organisms use a wide range of minerals to perform a variety of functions, including familiar examples such as bones (for support), teeth (for mastication) and shells (for protection), as well as other less common functions, such as optical, magnetic and gravity sensing. These biominerals are produced with elements that present in the local environment under ambient conditions. The ability to mimic biological strategies to improve current materials and processing methods is a longstanding goal of material scientists. On page xx of this issue, Polishchuk *et al.* (*1*) characterized the properties of a biomineral in the skeleton of the brittlestar, *Ophiocoma wendtii*. An array of microlenses on their skeletons focus light on to an optical receptor, enabling them to detect shadows and, hide from predators. Nanoprecipitates in these lenses also toughen the skeleton, an effect that is achieved in engineered metal alloys only through expensive heat treatments.

The lenses are made of single crystal calcite, ~ 50 μm in size, arranged in a hexagonal pattern on their dorsal arm plates. The microstructure of these brittlestar lenses has been known since 2002 (2), but until now, little was known about the nanostructure. Polishchuk *et al.* found that the single-crystal calcite lenses contained arrays of calcite nanoprecipitates, ~ 5 nm in diameter, that have a higher magnesium content than the host crystal. Further investigation revealed that these nanoprecipitates were coherent with the host, meaning that the crystal lattice planes were continuous as they passed through the nanoparticles. Coherent nanoparticles, sometimes referred to as Guinier Preston, or GP, zones (*3*, *4*) are well known in metallurgy, where they are used to increase the strength of the metal. The presence of GP zones had not previously been detected in biominerals.

The microlenses of the brittlestar have a dual function. Not only do they focus light onto a receptor, but they are also part of the skeleton and, as such, they need to have robust mechanical properties. Like all minerals, calcite is very brittle and it is susceptible to fracture. Organisms use a number of strategies to increase the toughness of biominerals. One of the most common, used in both bone (*5*) and seashells (*6, 7*), is the use of complex hierarchical structures of hard and soft materials (*8*). The combination of hard and soft material is also used in synthetic composites, such as the carbon-fiber reinforced–polymers widely used for high-strength, low-density applications.

Such complex structures would not be suitable for optical lenses, so these brittle stars required an alternative toughening strategy. The similarity of the Mg-rich nanoparticles in the calcitic lenses to coherent nanoparticles in metals suggest that they may play a role in the enhancement of the mechanical properties. In metals, GP zones increase the tensile strength by inhibiting dislocation motion but they also decrease ductility (increase brittleness) by the same mechanism.

Failure of brittle materials, such as calcite, occurs via a different mechanism than in metals, as dislocation mobility is limited. Brittle materials break catastrophically when a combination of the applied stress and the crack length reaches a critical value, known as the fracture toughness. The fracture toughness of a material is a measure of its resistance to fracture and it is related to the energy required to extend existing cracks in a material. Fracture toughness can be increased by introducing interfaces to the material, as in bones, shells and synthetic composites. It can also be increased by introducing a compressive stress, in order to counteract the applied tensile stress. Synthetic brittle materials that use such a strengthening mechanism include tempered glass and prestressed concrete.

The hypothesis put forward by Polishchuk *et al.* is that the Mg-rich nanoparticles induce a compressive stress in the host calcite material, which increases the fracture toughness. The stress originates from the smaller lattice parameters of Mg-rich calcite and the coherent nature of the lattice planes, which together create a tensile stress in the particles and a compensating compressive stress in the surrounding host crystal (see the figure). The hypothesis is supported by measurements of fracture toughness, which was found to be on the order of a factor of 2 higher than single-crystal geological calcite.

Coherent nanoparticles in metals, such as aluminium, are formed by cooling a molten mixture of aluminium and copper to produce a supersaturated solid solution of copper atoms in aluminum (*9*). The solid solution is then heated, or annealed, and nanoparticles of a second phase, which have a high concentration of copper atoms, precipitate from the solid solution. The size of nanoparticles is controlled by the annealing temperature, as growth is limited by the rate at which the copper atoms diffuse through the crystal.

Biominerals must form under ambient conditions, and many biominerals are known to form from an amorphous precursor. As the solubility of magnesium in amorphous calcium carbonate is high, this precursor may be rich in magnesium. Magnesium is much less soluble in crystalline calcite than in amorphous calcium carbonate, so crystallization results in a supersaturated solid solution. Over time, the excess magnesium atoms diffuse to form coherent magnesium rich precipitates. Such a formation mechanism of coherent nanoparticles in calcite is analogous to copper rich nanoparticles in aluminum, as both evolve from supersaturated solid solutions.

Polishchuk *et al.* identified a toughening mechanism that does not disrupt the primary function of the biomineral, that is, the focusing of light. It is possible that prestressing by coherent nanoparticles occurs in other dual function biominerals, where toughening with hierarchical structures is not an option, as it would disrupt the primary function of the biomineral. Future investigations should explore other dual function biominerals to determine the extent to which Nature employs such a strategy. Future research should also attempt to replicate the formation of coherent nanoparticles in minerals or ceramics by crystallization from an amorphous precursor, with the aim of developing in an energy-efficient process for increasing the fracture toughness of ceramic materials.

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