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"BIOLOGICAL CERAMICS" OR *ALL YOU WANTED TO KNOW ABOUT SHELLS**

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INTRODUCTION

Organisms fabricate a diverse array of biominerals or "biological ceramics". The most familiar of these types of hard tissues are the carbonated-hydroxyapatite used by animals for bone and teeth, mollusk shells and eggshells made of $CaCO_3$, and siliceous corals. However, more than 60 biominerals have been discovered to date[1-3]. Not only is there a great diversity of biominerals found in the animal kingdom, but an equal diversity in their morphology and microstructure. In this short paper, I will review a subset of ceramic-like biominerals with an emphasis on their microstructure.

EGGSHELLS

Perhaps the most familiar biological ceramic is the humble eggshell. A laying hen "in production" fabricates an egg every 24 hours and the typical egg sold in grocery stores has a $CaCO_3$ shell weighing about 5 gms. It is clear that a Ca source is an essential part of the diet of such productive chickens!

The shell contains a number of distinct components, as shown in a schematic drawing, Fig. 1[4]. The collagenous membranes are familiar to anyone who has eaten a hard boiled egg. The mineral portion of the shell, called the "palisade" in biological jargon, is calcitic $CaCO_3$; a typical shell is ~300 μm thick and contains grains ~20 μm in diameter[5]. The shell has a modest crystallographic texture, almost certainly due to a modest growth anisotropy. The shell is terminated by the cuticle, which ensures a sterile environment during development of the chick in a fertilized egg; interestingly, the cuticle containes fine needle-shaped particles of hydroxyapatite[4].

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* *Adapted from an article published in "Temas Actuales en Ciencia de Materiales" edited by A. Conde, A. Dominguez and J. Leal, University of Seville Press, honoring Professor Rafael Marquez on the occasion of his 70th Birthday*

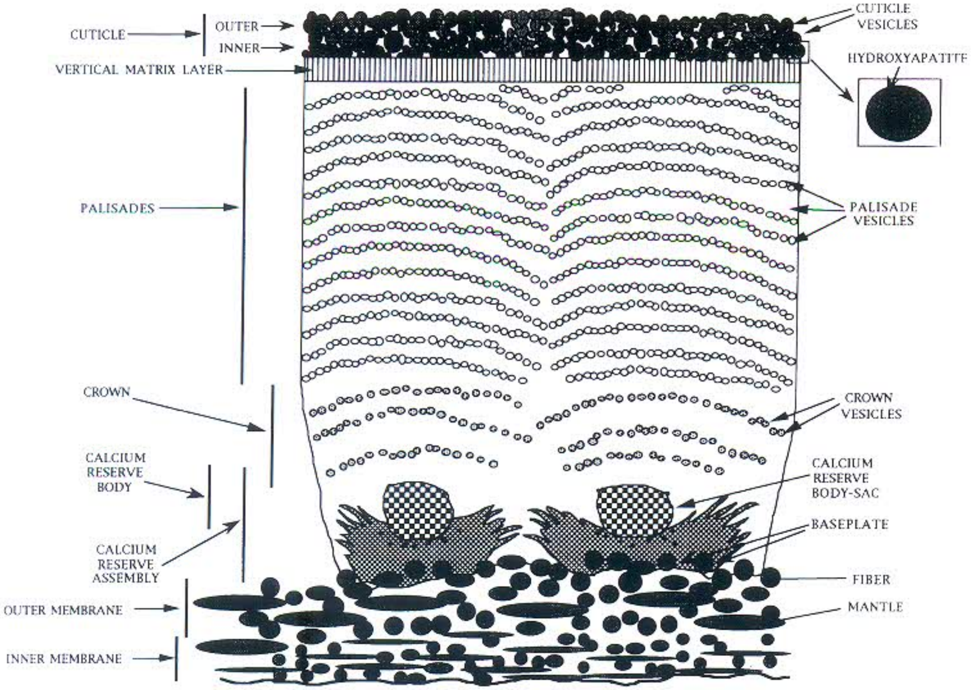

FIGURE 1 - Schematic drawing of the eggshell of the domestic chicken Gallus gallus (taken from ref. 4).

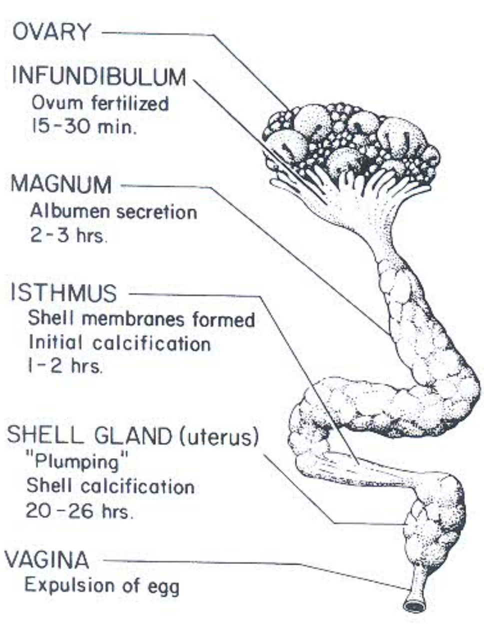

FIGURE 2 - Schematic drawing of the avian oviduct (taken from ref. 6).

Fig. 2 is a schematic drawing of the oviduct of the hen[6]. Shell development on the eggshell membrane occurs at particular sites called mammillae, which contact cells within the isthmus during "plumping"; it is these cells that secrete the shell-forming reagents. These regions also suffer the most extensive decalcification during chick development, as the shell provides the Ca needed for the chick's skeletal system. (They are also referred to as CRBs (calcium reserve bodies), as shown in Fig. 1.) The weakening of the shell induced by such decalcification is vital to the chick's ability to emerge from the shell when it is sufficiently developed.

Figs. 3 and 4 show two SEM fractographs of shells, one where the fracture proceeded from outside inwards and one from inside outwards. It is clear that the fracture surface morphology cannot be used to infer anything about biomineralization, as has been erroneously suggested in some biological literature. Rather, the features on the fracture surface arise from the vagaries of the dynamics of crack propagation in biogenic calcite containing ~5% organic matrix* (proteins, proteoglycans, etc.). The mammillae are clearly visible in Figs. 3 and 4 and are labeled M in these figures. Some of the organic matter is present in the form of fluid-filled vesicles (whose specific function is not known), which are readily seen in ion-thinned TEM foils (Fig. 5) and in the schematic drawing of Fig. 1. The grain boundary visible in Fig. 5 contains crystallographic facets, which clearly arise from crystallographic anisotropy in the calcite/calcite interfacial (grain boundary) energy.

MAGNETOTACTIC BACTERIA

The discovery in 1975 of microaerophillic or anaerobic bacteria** that contain single domain single crystal particles of magnetite (Fe_3O_4) constitutes one of the more interesting examples of biomineralization (Fig. 6). As organisms living in mud flats for which high levels of atmospheric oxygen can be toxic, they need to swim away from the surface of the Earth; the single domain ferromagnets allow them to swim along the weak magnetic flux lines of the Earth to avoid the atmosphere. In fact, such magnetotactic bacteria are found in the highest numbers at the oxic-anoxic transition zone (OATZ), which in many freshwater systems corresponds to the sediment-water interface.

As reported by Bazylinski[7], "Magnetotactic bacteria can have one of two magnetic polarities, north or south seeking, depending on the orientation

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Matrix is the term biologists use to refer to the organic component of hard or mineralized tissue.

***An anaerobic organism is one that can live without free oxygen. Microaerophilic bacteria require small amounts of oxygen but atmospheric levels of oxygen (20-21%) are toxic.*

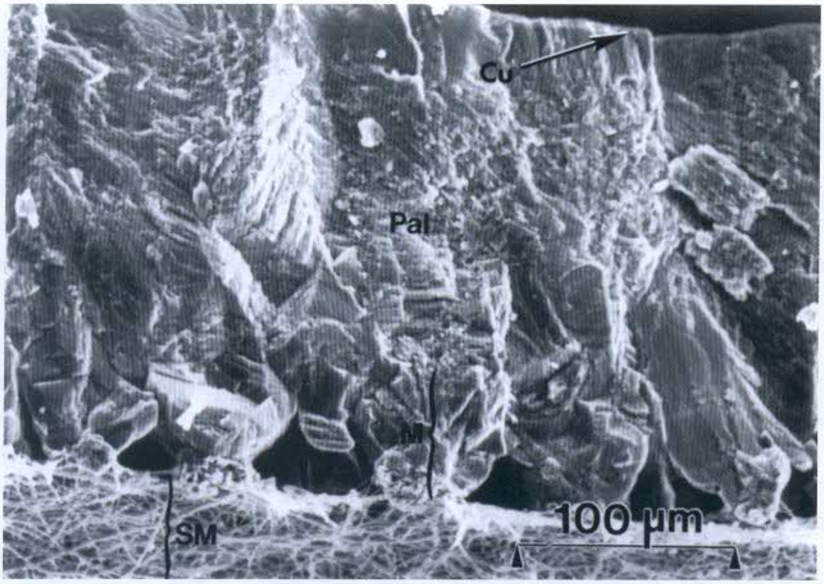

FIGURE 3 - Scanning electron micrograph of an eggshell fractured from the outside inwards. Cu, Pal, M, and SM refer to the cuticle, palisade, mamillary zone, and shell membranes, respectively (taken from ref. 4).

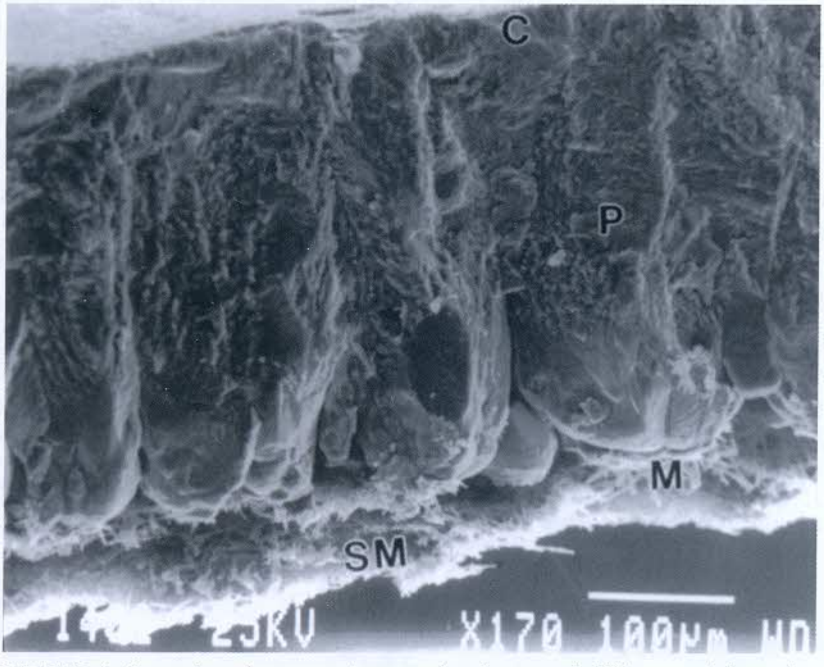

FIGURE 4 - Scanning electron micrograph of an eggshell fractured from the inside outward. C, P, M, and SM in this figure are the cuticle, palisade, mammillae, and shell membrane respectively.

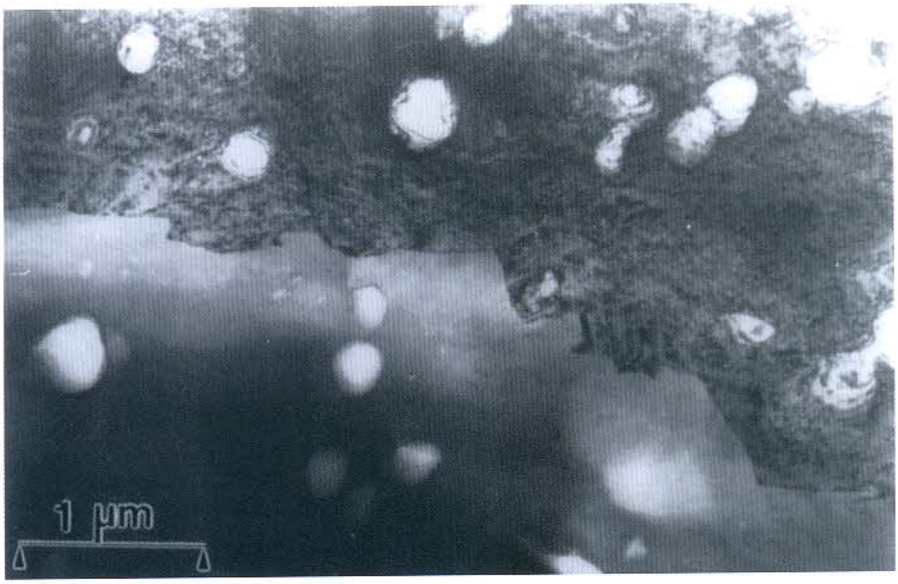

FIGURE 5 - Transmission electron micrograph of an intact ion-thinned specimen. The facetted grain boundary and fluid-filled vesicles (the white roughly spherical "blobs") are clearly visible (taken from ref. 4).

of the magnetic dipole in the cell. North-seeking magnetotactic bacteria predominate in the Northern Hemisphere, while south-seeking magnetotactic bacteria predominate in the Southern Hemisphere. The vertical component of the inclined geomagnetotactic field appears to select the predominate polarity in each hemisphere by favoring those cells whose polarity leads them towards sediments and away from potentially toxic concentrations of oxygen in surface waters. At the Equator, where the vertical component of the geomagnetic field is zero and the field is horizontal, approximately equal numbers of both polarities exist. Thus, the magnetosome chain constitutes a biomagnetic compass needle that is a masterpiece of permanent magnetic engineering. Magnetotactic bacteria have solved the problem of designing a magnetic dipole that is small enough to be assembled within the cell yet is robust enough so that the cell will be oriented in the geomagnetic field as it swims."

SEA URCHIN SPINES

Sea urchins belong to the class of Echinoderms, which also includes sea lillies, sea stars, brittle stars, and sea cucumbers. All of these organisms share a common trait -the rheology of their connective tissue is mutable (i.e. variable)

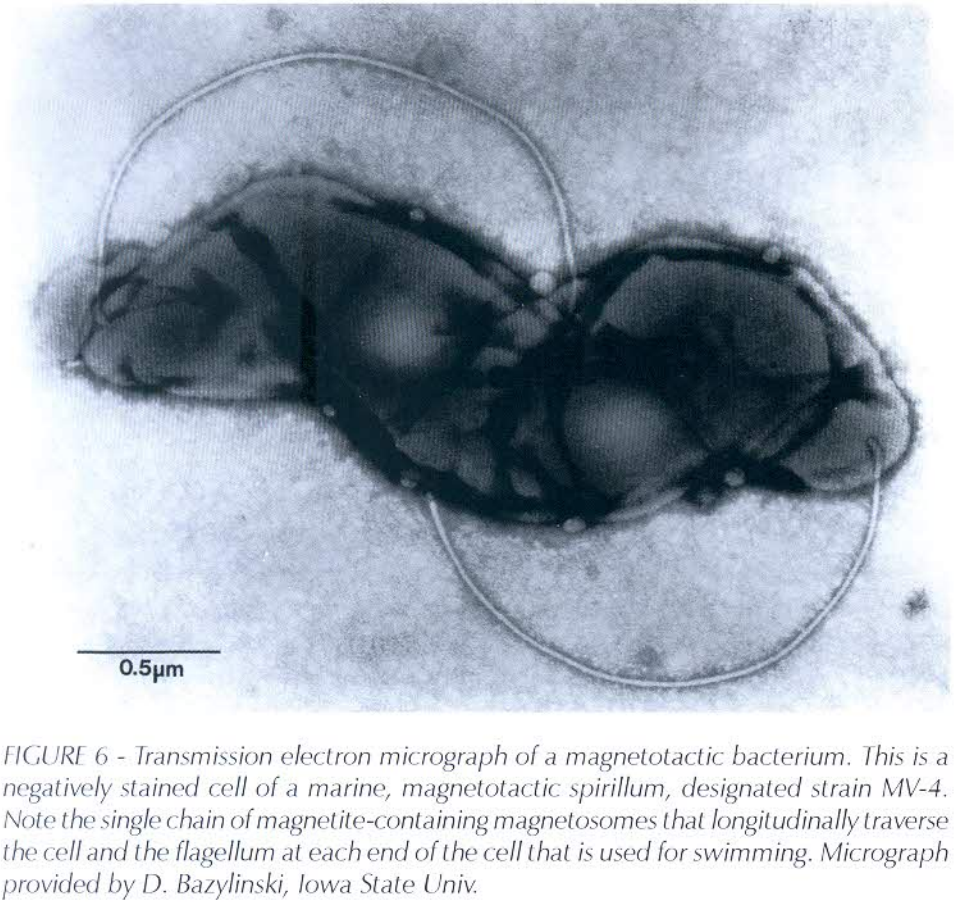

FIGURE 6 - Transmission electron micrograph of a magnetotactic bacterium. This is a negatively stained cell of a marine, magnetotactic spirillum, designated strain MV-4. Note the single chain of magnetite-containing magnetosomes that longitudinally traverse the cell and the flagellum at each end of the cell that is used for swimming. Micrograph provided by D. Bazylinski, Iowa State Univ.

on physiologic time scales ($0 \leq 1$ sec). Anyone who has experienced the rigidity assumed by sea urchin spines when disturbed by a possible predator will have experienced a practical manifestation of such mutable connective tissue.

The spines of sea urchins (Fig. 7) have another, even more remarkable, property - they consist of $\geq 99\%$ of Mg-rich calcite ($Ca_{1-x}Mg_xCO_3$) but in the form of crystallographically perfect, macroscopic single crystals! The internal structure of such single crystal spines can be assessed most readily from a fracture surface, Fig. 8 (the average strength of the spines shown in Fig. 7 is 26 MPa[8]). The low magnification image, Fig. 8a, reveals a "radiating spoke" structure, with the center of the spine showing large macropores, which can be seen at high magnification in Fig. 8b. Laue X-ray back reflection photographs (Fig. 9) reveal that the c axis is parallel to the spine axis[8], and TEM foils show no crystallographic defects but a high density of very small protein inclusions