Lamellar Self-Assembly and Crystal Polymorph Selection by a single protein fragment

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The formation of inorganic phases by living organisms, biomineralization, is an important and widespread phenomenon (1-4) that attracts the attention of scientists from a variety of disciplines. The development of biomineralized systems requires participation of macromolecular components, such as proteins, which chemically and physically interact with minerals to determine crystal polymorph, habit, and morphology. Hence, the role of proteins in biomineral formation must be crucial. The key to exploiting the materials construction strategies employed by biomineralizing organisms, such as nacre-forming ones, is to understand the interactions that occur at the organic-mineral interface (OMI) (5) and the function of key biomineral proteins.

We, along with several others (6-9), have taken the approach of creating model biomineral systems in which a limited number of molecular participants interact under controlled conditions. These in vitro systems provide a model for the role of individual proteins, allowing us to examine the OMI and function of individual proteins.

Using x-ray absorption near edge structure (XANES) spectromicroscopy, x-ray photoemission electron microscopy (X-PEEM), and scanning electron microscopy (SEM), we revealed that a 30-amino acid peptide, n16N, induces the nucleation of aragonite, even in calcite growth conditions. This is of particular interest because aragonite is thermodynamically less stable compared with calcite (both are CaCO$_3$ polymorphs) and, yet, aragonite appears in many mollusk shells and corals. The aragonite polymorph-selection function of the n16N peptide in a synthetic growth solution is evident in our experiments. We also revealed that n16N self-assembles into regularly spaced lamellar structure, similar to natural nacre and dramatically different than the control calcite crystals grown in the absence of peptide.

Many other proteins are present in natural nacre, thus, the functions exhibited by n16N here may be shared by other proteins. We cannot claim that n16 is the only protein with this function, but we can claim with certainty that the function exists, and a simple 30-amino acid peptide is sufficient to perform lamellar self-assembly of aragonite.

References: