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Chitosan as canvas for studies of macromolecular controls on $CaCO_3$ biological crystallization

BRENNA M KNIGHT[1], KEVIN J EDGAR[1], JAMES J. DE YOREO[2] AND **PROF. PATRICIA M DOVE**[1]

[1]Virginia Tech

[2]Pacific Northwest National Laboratory

Presenting Author: dove@vt.edu

Living organisms use macromolecules, typically as an organic matrix, to direct the formation of diverse mineral-organic composites collectively known as biominerals. Owing to the limitations of early extraction techniques, the biomineralization community traditionally assumed soluble, acidic proteins to be the primary regulators of crystallization. This motivated decades of research into the roles of proteins and negatively charged amino acids in biomineral formation. However, modern characterizations of the organic matrix indicate this perspective may be incomplete by showing sites of mineralization also contain acidic oligosaccharides and other polysaccharides, including glycoproteins and negatively charged proteoglycans (as carboxyl, sulfate, and phosphate groups). Long dismissed as inert, alpha-chitin is also frequently associated with $CaCO_3$ in ancient and modern biominerals; suggesting the success of this biopolymer-mineral combination as an evolutionary innovation. All of these glycomaterials can exhibit remarkable structural diversity with variations from simple monosaccharides and linear homopolymers to highly derivatized forms and extensively branched glycoproteins. These observations are raising new questions regarding the roles of macromolecular classes and functional groups in biomineralization processes and their influence on the recorded composition and morphometric signals. For example, are relationships between biomineral composition and components in the local organic matrix better understood through a palette of functional group density, conformation, and cooperativity, irrespective of macromolecular class?

To test these ideas, we use recent advances in biopolymer chemistry to prepare chitosan-based hydrogels with tailored compositions. Chitosan, a synthetically deacetylated chitin, is a promising and versatile material that can be derivatized for systematic, quantitative studies to design experiments that quantify the kinetics of $CaCO_3$ mineralization and the properties of the resulting products. By synthesizing (and characterizing) a series of chitosan materials as simple models for intracellular and extracellular organic matrices, systematic and hypothesis-based crystallization studies become possible. The figurative canvas provides a means to quantify relationships between $CaCO_3$ properties and degree of substitution (DS) of individual functional groups (sulfate, carboxylate, and hydroxyl groups) or through cooperative interactions. The findings suggest the overarching influence of functional group properties on mineralization and are consistent with conceptual and computational models while advancing our understanding of mineralization in hydrogel-hosted settings.