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A solution to the 'calcite-aragonite problem'

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We suggest that the acidic shell matrix protein Aspein identified from Pinctada fucata is an agent controlling the shell calcium carbonate crystal polymorphism in this pearl oyster species. Aspein is made up of 413 amino acids, including a high proportion of Asp (60.4%), Gly (16.0%), and Ser (1 3.2%), and the predicted isoelectric point is 1.45; this is one of the most acidic of all known proteins on earth. The main body of Aspein is occupied by (Asp)2?10 sequences punctuated with Ser?Gly dipeptides. Crystallization experiments using recombinant Aspein (rAspein) showed that rAspein can control the CaCO3 polymorph (calcite/aragonite) in vitro. While aragonite is preferentially formed in Mg2+-rich solutions imitating the extrapallial fluids of marine molluscs, Aspein exclusively induced calcite precipitation in such a solution. Our results indicate that Aspein is involved in the specific calcite formation in the prismatic layer. Experiments using truncated Aspein demonstrated that the aspartic acid rich domain (D domain) is crucial for the calcite precipitation. Comparisons of Aspein sequences between P. fucata and a congeneric species P. maxima indicated that the length and the amino acid sequence of the D domain is variable and may not be so important for their functions, while sequences in the N-terminal region are well conserved and may have important roles. The variable D domain sequences suggest that the control may not be achieved by a three-dimensional match between protein and crystal structures, but by some other mechanisms, including a kinetic effect caused by a local increase of Ca/Mg ratio. A causal link between an Asp-rich matrix protein and calcite precipitation is manifested also in a soft coral species (Azizur Rahman and Oomori, 2009), implying that the mechanisms are not restricted to pteriomorph molluscs.

Keywords: biomineralization, shell matrix proteins, crystal polymorphism