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Evolution of calcium carbonate mineralogy during rapid avian eggshell calcification

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Eggshell calcium carbonate precipitates from the uterine fluid, which is highly supersaturated with respect to all calcium carbonate polymorphs. Surprisingly, even under these extreme conditions, eggshell mineralization occurs under precise control and produces a material with a well-defined ultrastructural organization (consisting of large columnar calcite crystal units arising from specific nucleation sites on the eggshell membrane) and monomineral composition (only calcite). Furthermore, the mineralization rate is modulated precisely during the phases of initiation, rapid growth and termination of eggshell formation. Avian eggshell mineralization is the fastest biogenic calcification process known in nature. How this is achieved while producing a highly crystalline material composed of large calcite columnar single crystals remains largely unknown. Though there many studies analyzing different aspects of the process of eggshell calcification, there is no detailed study of the evolution of the mineralogy and crystallinity of the eggshell at the early stages of its calcification, and during the phase of linear deposition. Here we report that eggshell mineral originates from the accumulation of flat disk-shaped amorphous calcium carbonate (ACC) particles on specific organic sites on the eggshell membrane, which are rich in proteins and sulfated proteoglycans. These structures known as mammillary cores promote the nucleation and stabilization of a amorphous calcium carbonate with calcitic short-range order which predetermine the calcite composition of the mature eggshell. The amorphous nature of the precursor phase was confirmed by the diffuse scattering of X-rays and electrons. The nascent calcitic short-range order of this transient mineral phase was revealed by infrared spectroscopy and HRTEM. The ACC mineral deposited around the mammillary core sites progressively transforms directly into calcite crystals without the occurrence of any intermediate phase. Ionic speciation data suggest that the uterine fluid is equilibrated with amorphous calcium carbonate, throughout the duration of eggshell mineralization process, supporting that this mineral phase is constantly forming at the shell mineralization front. On the other hand, the transient amorphous calcium carbonate mineral deposits, as well as the calcite crystals into which they are converted, form by the ordered aggregation of nanoparticles which progressively crystallize into calcite while preserving a granular nanostructure. The transformation front and crystallographic orientation propagates by secondary nucleation from previously formed calcite crystal seeds, yielding large calcite crystal units with have a coherent orientation. These growth mechanisms are very efficient and would explain the rapid calcification of the eggshell. Rapid growth eggshell calcite crystals by these mechanisms contrast the slow process of inorganic calcite growth by ion addition in atomically flat crystal faces. Better understanding of the mechanisms of formation of this biomaterial could lead to more efficient methods for the fabrication of synthetic crystalline materials.