

Calcium carbonate formation in the presence of serum protein.

David C Bassett and Jake E Barralet

Faculty of Dentistry, McGill University, Montreal, Canada.

Calcium carbonate is an important mineral, it is responsible for fixing a majority of atmospheric carbon dioxide and has many industrial applications. Many species synthesise calcium carbonate for protective structures as well as components of aural organs. Biogenic forms may be found in various crystalline polymorphs such as calcite (the most stable), aragonite, vaterite and amorphous calcium carbonate (the least stable). Various acidic proteins are found in many mineralized tissues such as bone, teeth and shells and also in ectopic mineralisation. They can inhibit or promote mineralisation as well as alter the phases of the mineral formed.

In our experiments a well established gas diffusion biomineralisation technique was used to slowly precipitate calcium carbonate in the presence of protein. This method relies on the decomposition of ammonium carbonate to produce carbon dioxide and ammonia gas in a closed environment. Crystallisation is achieved via diffusion of the carbon dioxide gas into a well filled with calcium chloride solution with or without protein. In protein-free control experiments, the most stable form of calcium carbonate, calcite, formed in regular rhombohedral microcrystals. However in the presence of protein, 200nm fibres of calcium carbonate formed that were self assembled in conical shapes, or as blade-like calcite crystals arranged in parallel bundles. In addition to these fibres, floating crystals of vaterite, the least stable crystalline form, were observed from which fibrous processes protruded into the liquid and it was from these fibrous processes that the fibre bundles and conical shapes appeared to grow. In addition to these organised microscale fibres, randomly orientated nanofibers of calcium carbonate formed on the base of the reaction vessel. These nanofibres appeared to be calcitic.

The cones appeared to grow in a step-wise fashion, indicated by repeating layers of concentric rings observed along the length of the cones and consistently straight edges at the base. FTIR measurements of the conical structures indicated surface coating or integration of the protein molecule with the calcium carbonate. By attempting the reaction in a small vessel suspended upside-down we have determined that the formation of cones is gravity-dependant. Increasing viscosity increased the angle of the cones' apex such that at 0.014 Pa.s essentially flat discs of fibres radiating from a central point were formed.

Current explanations of templated nanostructures are 'hand-wavy' and suggest that protein-mineral nanoclusters are self assembled at fibre tips and lack quantitative support.

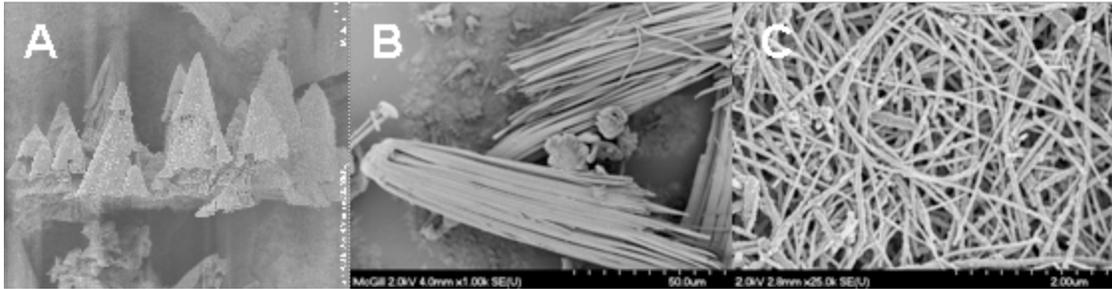


Figure 1. Microfibres of calcium carbonate arranged in conical (A), aligned bundles (B) and randomly oriented nanofibres (C) formed in the presence of protein.