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### **Bio-Inspired Approaches to Crystals with Composite Structures<sup>1</sup>**

FIONA MELDRUM, University of Leeds

Advances in technology demand an ever-increasing degree of control over material structure, properties and function. As the properties of monolithic materials are necessarily limited, one route to extending them is to create a composite by combining contrasting materials. The potential of this approach is beautifully illustrated by the formation of biominerals where organic macromolecules are combined with brittle minerals such as calcite to create crystals with considerable fracture toughness. This talk will discuss how bio-inspired approaches can be used to generate single crystals with composite crystals through a simple one-pot method. By precipitating calcite crystals in the presence of “occlusion species” ranging from latex particles, to organic and inorganic nanoparticles and finally small molecules we demonstrate that high amounts of foreign species can be incorporated through control over the additive surface chemistry, and that this can lead to an enhancement of the mechanical properties of the calcite. Occlusion of 20 nm anionic diblock copolymer micelles was achieved at levels of over 13 wt%, and the properties of the resultant composite calcite crystals were measured using a range of techniques including IR spectroscopy, high resolution powder XRD and high resolution TEM. Incorporation of these macromolecules leads to crystals with structures and mechanical properties similar to those of biominerals. With sizes in the range of some intracrystalline proteins, the micelles act as “pseudo-proteins”, thereby providing an excellent model system for investigation of the mechanism of macromolecule insertion within biominerals. Extension of these studies to the incorporation of small molecules (amino acids) again demonstrated high levels of incorporation without any change in the crystal morphology. Further, occlusion of these small molecules within the calcite lattice again resulted in a significant increase in the hardness of the calcite, a result which appears to derive from an increase in lattice strain on molecular occlusion. Finally, the generality of this strategy is demonstrated by its extension to the incorporation of inorganic particles such as magnetite and gold within calcite, leading to the formation of inorganic-inorganic composites.

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