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MS17-O4

The directing effects of bacterial EPS and artificial hydrogel matrices on calcite crystal organization in EPS-hydrogel-calcite composite aggregates

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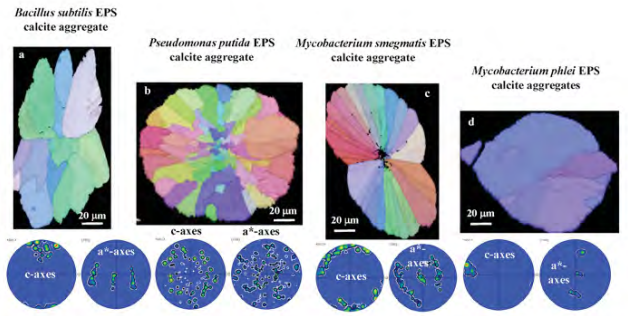
Mineralized structures generated under biological control are hierarchical composites that consist of two distinct materials: a compliant biopolymer matrix that is reinforced by stiff and hard minerals. In gastropod, bivalve, brachiopod shells the biopolymer matrix consists of two components: (i.) matrix membranes that subdivide space and influence shape and size of mineral units, (ii.) foam-like networks of fibrils occluded within the mineral units that control attachment and orientation of crystallites. Microbial cells surround themselves with a gelatinous coating: EPS (extracellular polymeric substances) that consists of polysaccharides, proteins, lipids and occurs in a wide range of molecular sizes, conformations, and physical/chemical properties. The EPS fabric is a three-dimensional fibrous scaffold that protects bacterial cells and allows them to orient themselves. Numerous bacteria precipitate carbonate as a by-product of their metabolic activity. The latter induces supersaturation with respect to carbonate phases in microenvironments within the EPS fabric[1].

Recent studies[2] have shown that in biocarbonate hard tissues organic membranes and fibres control mineral organization within the basic mineral units. The assembly pattern of the biomineral is adjusted according to the fabric of the preformed organics. In order to understand the influence of biopolymer membranes and fibres on mineral organization, we conducted EPS/agar gel/calcite growth experiments and investigated membrane formation, mineral/EPS/agar gel interlinkage and mineral organization in the composite aggregates. We used EPSs secreted by four different bacteria: the gram-positive bacterium *Bacillus subtilis* and the gram-negative bacteria *Pseudomonas putida*, *Mycobacterium phlei* and *Mycobacterium smegmatis*. Characterization was performed with HR-SEM imaging; patterns of mineral orientation were measured with electron backscatter diffraction (EBSD).

The EPS scaffold exerts a significant influence on aggregate morphology, the presence of membranes and their distribution within the aggregate and calcite crystal organization in the composites (Fig. 1). Membrane formation is extensive and is highly increased relative to composite aggregates grown without EPS. Rhombohedral morphologies are ab-

sent; aggregate and calcite crystal morphologies and surfaces are always rounded. The aggregates are radial mosaic crystals, with their individual subunits not being substructured (Fig. 1). Calcite crystal co-orientation strength and patterns range from markedly co-oriented (Fig. 1d) over graded (Figs. 1c, 1a), to very little co-oriented (Fig.1b). Hence, EPS incorporation within the calcite modulates the mineral microstructure and texture in a manner that is characteristic for the EPS of a specific bacterium. These characteristics could be used as a tool for identifying biologically induced calcification in the geological record[3].



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MS17-O5

Crystallographic characterisation of fluorapatite based glass-ceramics synthesised from industrial waste

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Apatite based glass-ceramics have been extensively studied in recent decades. They show excellent mechanical properties, bioactivity and compatibility for biomedical applications. They can form an apatite layer and strong chemical bonds at the bone or tooth interface with the implant [1]. The nano-crystalline structures, bioactivity and mechanical strengths of such glass-ceramics depend on their parent glass composition and the crystallisation processes during sintering.

A series of phase transformations of novel calcium fluoraluminosilicate (CFAS; SiO_2-Al_2O_3-P_2O_5-CaO-CaF_2) glasses forming a range of fluorapatite based glass-ceramics on sintering are reported. The sintering process induces formation of fluorapatite, mullite and anorthite phases within the amorphous silicate matrices of the glass-ceramics. The glasses are partially prepared from waste materials such as rice husk ash, pacific oyster shells and disposable aluminium cans. The thermally induced crystallographic and microstructure evolution of these glasses towards fluorapatite glass-ceramics, with applications in dental and bone restoration, are investigated by a range of techniques, including powder X-ray diffraction as well as small angle X-ray and neutron scattering techniques [2].

The observed phase transformations of glasses to glass-ceramics for the investigated compositions enhance our understanding of the effects of glass composition and sintering temperatures on the phase transitions in glass-ceramics. All investigated glasses produce fluorapatite glass-ceramics on sintering at temperature around 800 °C. The optimum glass compositions and sintering temperatures to produce fluorapatite-mullite, fluorapatite-anorthite and fluorapatite-albite glass-ceramics have been identified from PXRD analysis and will be presented. Formation of fluorapatite in glass-ceramics can also be identified from the far-infrared spectrum in agreement with the PXRD results. The fluorapatite glass-ceramics contain crystalline fluorapatite domains dispersed in an aluminosilicate glass matrix. This can be verified from FESEM imaging and the analysis of SANS data. The SANS results provide information about the average size of the fluorapatite domains in glass-ceramics. SANS data were interpreted using the correlation length model. The correlation length parameter obtained from the fit can be correlated with the average sizes of crystalline domains in these glass-ceramics.

The suitability of the investigated CFAS glasses to produce glass ionomer cements for dental restoration has been assessed and found to be comparable to the standard LG26 glass, thereby demonstrating the feasibility of using waste materials to develop biomaterials for bone and dental restoration.