ESRF	**Experiment title:** Time resolved *in situ* study of the templated crystallisation of carbonate biominerals on self assembled monolayers	**Experiment number:** CH494
Beamline: ID 11	**Date of experiment:** from: 6 Dec 1998 to: 12 Dec 1998	**Date of report:** June 22, 2000
Shifts: 15	**Local contact(s):** Gavin Vaughan	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Ram Seshadri*, Gavin Vaughan*+, Wolfgang Tremel

Institut für Anorganische Chemie, Universität Mainz,
DuesbergWeg 10-14, Mainz D55099, Germany

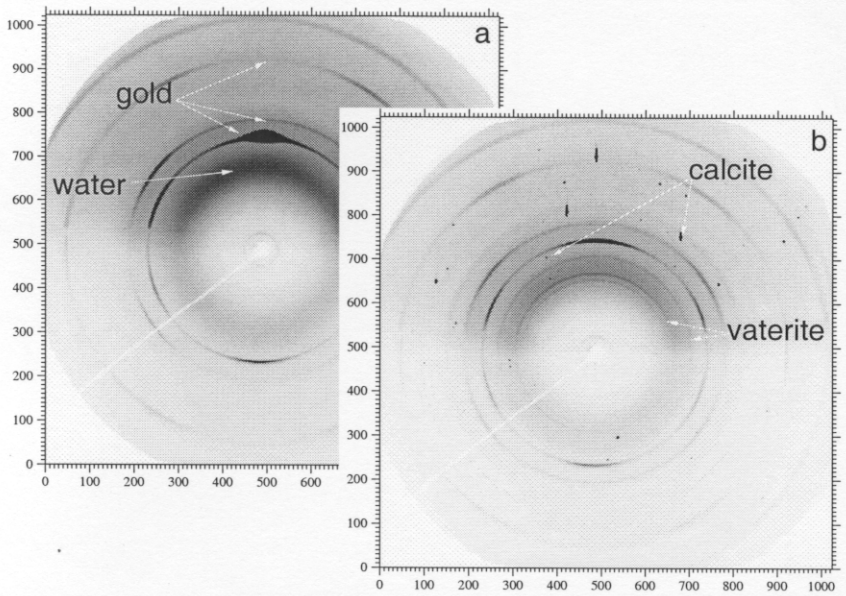
+ESRF

Report:

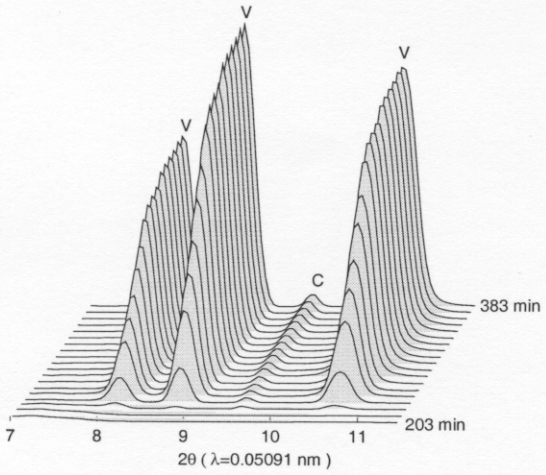
Calcium and strontium carbonates were allowed to crystallize on Self Assembled Monolayers (SAMs) of different long chain alkyl thiols on gold, *in situ* in a purpose built cell, on the ID11 beamline. Using a 0.5 Å monochromatic beam, it was possible to scatter through the 5 mm path length of solution in the cell at a grazing angle to the SAM substrate (held face down in solution), and to collect diffraction rings from the growing crystals on a Frelon image intensifier. The rings could then be integrated using Fit2D (Hammersley, ESRF) to obtain 1D diffraction patterns that were subject to Rietveld refinement using XND (Bérar, ESRF) in order to obtain scale factors for the different phases as a function of time. A sampling interval of the order of minutes was found sufficient, since the entire process took a few hours. The evolution of the scale factors with time could be fitted to the Avrami equation:

$$s = 1 - \exp(-kt^n)$$

While for the thermodynamically metastable $CaCO_3$ phases, vaterite and aragonite, the value of n was found to be around 1.5, for the stable phase calcite, the value of n was smaller, being around 0.75. The surprising result in the $CaCO_3$ crystallizations was that the different polymorphic phases appear nearly (within experimental resolution) concurrently. These results are being analysed, as are their implications for biomineralisation processes.



Typical frames from the image intensifier (a) before and (b) after crystallisation commences. Since calcite forms large, well-facetted crystals, diffraction spots are also seen. The substrate used here was a mercaptophenol thiol SAM.



Evolution of the calcite (C) and vaterite (V) peaks obtained by transforming frames such as the ones above into 1D diffraction patterns.