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Crystallization of $SrCO_3$ on a self-assembled monolayer substrate: an *in-situ* synchrotron X-ray study

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Self-assembled monolayers (SAMs) of alkanethiols on gold surfaces show great promise in controlling the nucleation and growth of inorganic minerals from solution. In doing so, they mimic the rôle of some biogenic macromolecules in natural biomineralisation processes. Crystallization on SAM surfaces is usually monitored *ex-situ*; by allowing the process to commence and to evolve for some time, removing the substrate from the mother solution, and then examining it using microscopy, diffraction *etc.* We present here for the first time, the use of high energy monochromatic synchrotron X-radiation in conjunction with a two dimensional detector to monitor *in situ*, in a time resolved fashion, the growth of $SrCO_3$ (strontianite) crystals on a SAM substrate.

Mineralisation processes in natural systems are complex and fascinating, and have captured the attention of researchers from a variety of backgrounds.[1] Living systems display a remarkable tendency to precipitate minerals from solution with exquisite control over phase, size, shape, and aggregation of the crystals. While insights into these are of importance for a better understanding of developmental processes in biology, there is also the imperative to understand how Nature manages to prepare high-performance materials from rather mundane crystalline phases such as calcium carbonate and that too under near-ambient conditions of temperature and pressure.[2] Concentrating on the key rôle played by thin organic layers, including the surfaces of macromolecules in natural mineralisation processes, a number of groups have attempted to crystallize materials under organic monolayers at the air–water interface[3] and on organic monolayers self-assembled on suitable metal or oxide substrates[4–9]—the organized monolayer being *ersatz* for the biogenic molecules.

Some of us have specifically focussed on the templated growth of $CaCO_3$ in all three common polymorphic modifications—calcite, vaterite and aragonite, on self assembled monolayers (SAMs) of alkylthiols assembled on gold substrates.[6–8] The use of ω-substituted thiols $X–(CH_2)_n–SH$ ($n=3$, 10, 12, 16) in forming the monolayer permits fine control of the surface presented by the monolayer to the growing crystal. For example, when n is large and X is H, the monolayer is non-polar and forms a crystalline 2D lattice. When n is small and X is a group such as $Na^+SO_3^-$ the lattice is poorly ordered and the surface is highly polar. Our studies have established that such modifications of the SAM substrate can indeed control the polymorphic modification of the precipitated $CaCO_3$ and crystal habit and morphology as well. None of these studies were made *in situ*. To date, all studies of crystallization of inorganic materials on SAMs have been performed by diffraction, spectroscopy and electron microscopy at the end of the crystallization process, on removing the substrate from the crystallizing solution.

In the present study, we have exploited the very high flux and high energies of the ID11 beamline at the European Synchrotron Radiation Facility, in conjunction with an advanced 2D detector (a 1024 × 1024 pixel image intensifier) to study the crystallization of $SrCO_3$ on a SAM substrate in an *in-situ* time-resolved manner. The use of a short wavelength (of the order of 0.5 Å) has permitted diffraction to be followed even after scattering through a 5 mm path of solution in a purpose-built cell mounted on the diffractometer. Debye–Scherrer rings collected on the 2D detector were integrated to obtain a 1D diffraction pattern. Suitable subtraction of the 1D patterns acquired at short times from the patterns acquired after the crystallization commences permitted the broad peak due to scattering from water, as well as the peaks from the gold substrate, to be subtracted (though the subtraction is less effective for the sharp gold peaks). The resulting 1D patterns correspond then to only the inorganic crystals that grow on the substrate and these patterns could be subject to further analysis including Rietveld refinement.

Strontium carbonate, itself not an important biomineral, is nevertheless interesting since its crystallization yields insights into the formation of the isostructural $CaCO_3$ phase, aragonite, which is what pearls and nacre largely comprise. It has a small solubility product, is highly crystalline, and only one polymorph is normally precipitated. These make it a suitable model biomineral. Since it has an orthorhombic crystal structure, there are no simple modes of epitaxy between $SrCO_3$ crystals and typical (hexagonal) close-packed SAM substrates. We have therefore chosen a SAM prepared from *p*-mercaptophenol as the substrate in the present experiments. This monolayer is too small and insufficiently rod-like to form an ordered monolayer. Details of *ex-situ* crystallization experiments on *p*-mercaptophenol SAMs can be found elsewhere.[10]

The manner in which a crystalline solid precipitates out of a homogeneous solution is a complex process that has been paid much attention. The availability of high-energy synchrotron radiation sources in recent years has made possible *in-situ*, time-resolved studies of various solid state transformations as well as studies of the crystallization of inorganic materials from solutions and from gels (and even under solvothermal reaction conditions).[11,12] The crystallization of molecular and inorganic crystals under Langmuir monolayers at the air–solution

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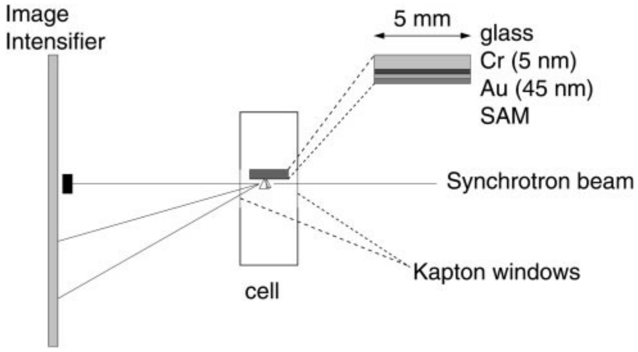

Fig. 1 Scheme of the experiment showing the Perspex cell, and its position relative to the synchrotron X-ray source and to the 2D detector.

interface has also been followed *in situ* using synchrotron XRD at grazing incidence.[13]

Experimental

Fig. 1 depicts a typical cell in which the crystallizations were carried out. The cell was constructed in a manner that permitted the gold-coated glass/SAM slide (20 mm × 5 mm) to lie face downward in a 100 mM solution of $SrCl_2$. The *p*-mercaptophenol monolayer was assembled on the gold slide using routine procedures.[6] The liquid path length in the cell was 5 mm and Kapton windows were employed to hold in the liquid. The cell was placed in the diffractometer and positioned so that the incident beam was in near grazing incidence and strong diffraction rings from the gold coating were observed on the 2D detector. Measurements were started as soon as bottles of solid $(NH_4)_2CO_3$ were placed within the cell, allowing the vapor to be in contact with the liquid surface. The advantage of this set-up is that there is no possibility of the cell moving during the experiment as there are no tubes going into or coming out of the cell. Frames from the Frelon 2D detector can be collected with time intervals of milliseconds but for this work, time intervals of the order of minutes between frames were deemed suitable for analysis, with each frame being exposed for (typically) 2 to 4 seconds.

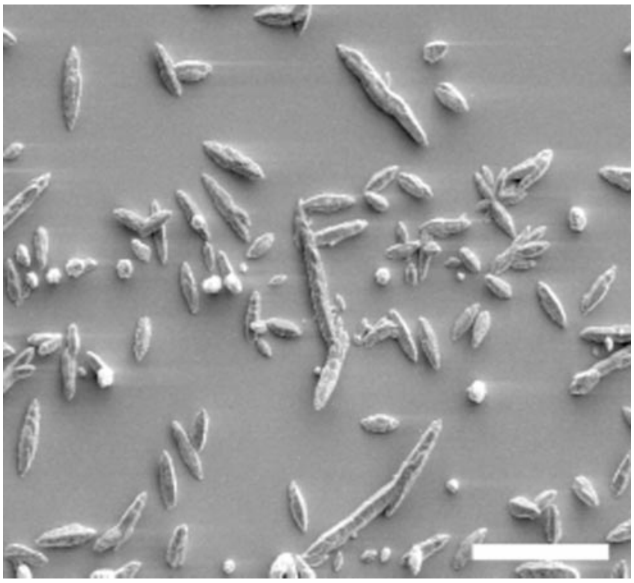

Fig. 2 Scanning electron micrograph of $SrCO_3$ crystals on a SAM substrate. The bar is 50 µm.

Results and discussion

Fig. 2 is an SEM image of $SrCO_3$ crystals grown on a SAM substrate. It is seen from this image that most crystals are needle like (due to trilling around a pseudohexagonal axis[8]) and the arrangement of the crystals does not suggest any mode of epitaxy or order with respect to the substrate. From present as well as earlier studies, we know that nucleation takes place at the SAM–liquid interface and that homogeneous nucleation in the solution is negligible, as is nucleation on the Perspex cell. When they appear, $SrCO_3$ reflections are superimposed on scattering from the gold substrate and are seen even when there is no precipitation in bulk solution (the solution remains clear). This lends confidence to the assumption that the process being followed is indeed crystallization on the surface.

A typical frame collected on the 2D detector during the later stages of $SrCO_3$ crystallization, visualized using the program FIT2D,[14] is displayed in Fig. 3a, with some of the characteristic reflections marked. The top–bottom asymmetry of the frame arises from scattering taking place from a surface rather than from homogeneous media. The various contributions to the scattering include a broad and very strong peak due to water and less strong but sharp peaks due to the gold substrate. The

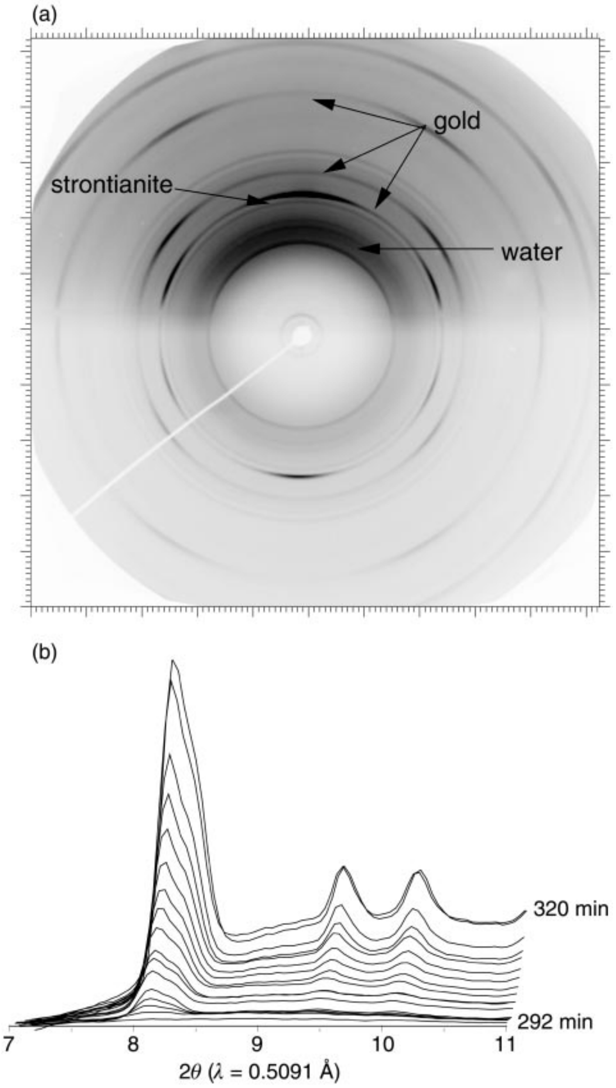

Fig. 3 (a) Typical 2D detector frame acquired late in the experiment. The diffraction rings corresponding to water, to the gold substrate and to $SrCO_3$ are indicated. (b) Time evolution of the 1D scattering patterns obtained by integrating the rings such as those seen in (a) and subtracting the scattering due to water. In the region shown, gold peaks do not appear.

analysis of the frames included corrections for the flatness of the detector and wavelength calibration. This was followed by "caking" and integrating the data in order to convert it to a 1D pattern. All these are achieved within the FIT2D program. Once a 1D pattern is obtained, subtraction of blank patterns (obtained at the beginning of the experiment) permits scattering due to water and gold to be subtracted revealing the scattering due to the overgrown crystals.

The absence of preferred orientation/epitaxy in the growth of the $SrCO_3$ crystals is attested to by the clean and spot-free Debye–Scherrer rings in the frames. Typical 1D data are displayed in Fig. 3b showing the growth of the $SrCO_3$ reflection starting after about 300 minutes for the conditions chosen here and shown at 2 minute intervals till there is almost no further growth of peak intensities.

The individual data can be Rietveld analysed permitting the extraction of scale factors. The result of a typical Rietveld refinement (as implemented in the XND Rietveld program[15]) is displayed in Fig. 4a, showing the data as points, the fit and the difference profiles. The orthorhombic strontianite structure of $SrCO_3$ was used for the refinement and the markers at the top of the plot show the expected peak positions at the wavelength used. For the refinement, the cell parameters, scale factor, and three profile parameters were left free. Repeating this analysis on a number of frames starting from where the $SrCO_3$ reflections become visible in the difference spectra, permits scale factors to be plotted as a function of time (Fig. 4b). A non-linear least-squares fit of this evolution (after rescaling the scale factor to run between zero and unity) to the Avrami form:[16]

$$s = 1 - e^{-(k(t-t_0))^n}$$

yields a value of 2.7 for the exponent n when t_0 is taken as the time when crystallization is first seen as a Bragg peak, which is $t_0 = 302$ min. Much better fits are obtained when the t_0 value is decreased to about 280 min. In that case, $n = 5.8$ and $k = 0.02\ \mathrm{min}^{-1}$. The justification for doing this is that when the crystals have just started growing, they might be too small and too few to scatter. The fit is not very good at longer times, and in the manner in which the curve saturates. This is perhaps because of the number of different steps in the data analysis procedure with each step introducing some error. We are unable to simultaneously free k, n and t_0 in the fitting procedures. These large values of n suggest that the process is, in keeping with expectation, not diffusion controlled, and nucleation might continue even through the growth phase.[16]

The present experiments demonstrate that a process as complicated as the crystallization from solution of a mineral on a substrate can be monitored in an *in situ* time-resolved fashion. The nucleation and growth follow Avrami type kinetics and are indicative of the growth of crystals being auto-catalytic. $SrCO_3$ does not fully require the power of *in situ* diffraction as it does not display polymorphism. $CaCO_3$ is different in that it has three biologically important polymorphs forming under nearly the same conditions of temperature and supersaturation. Time-resolved scattering from $CaCO_3$ crystallization is presently being examined.

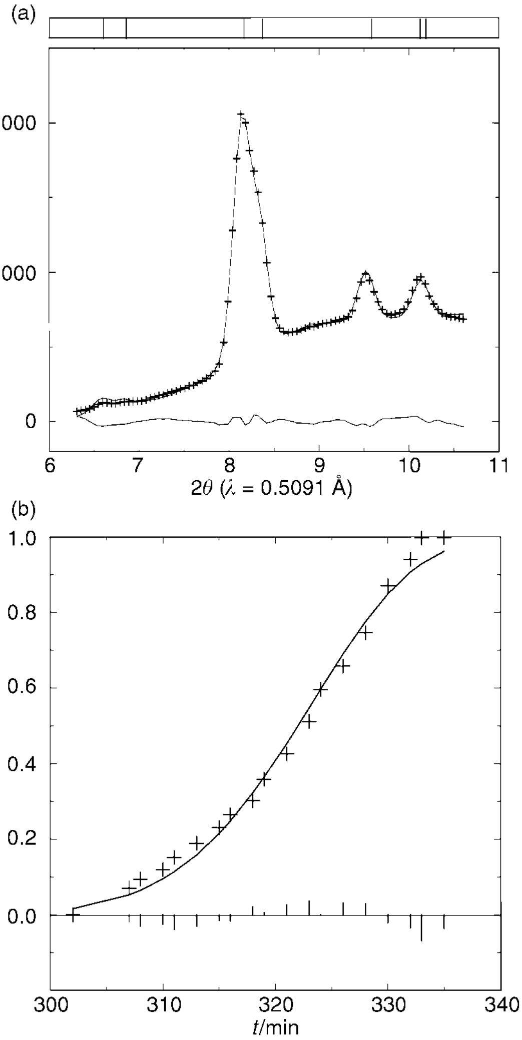

Fig. 4 (a) Rietveld analysis of a typical 1D diffraction pattern of the $SrCO_3$ crystals showing data (+), the Rietveld fit and the difference profile. The vertical lines at the top of the figure indicate expected peak positions. (b) Time evolution of relative scale factors (+) from Rietveld refinement fitted to the Avrami equation (line) as explained in the text. The vertical lines below are the residuals from the fit.

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