	<b>Experiment title:</b> High Resolution Powder Diffraction on Biomimetic Calcite Crystals	<b>Experiment number:</b> CH-3035
<b>Beamline:</b> ID31	<b>Date of experiment:</b> from: 05/11/2009 to: 09/11/2009	<b>Date of report:</b> 02.08.2010
<b>Shifts:</b> 12	<b>Local contact(s):</b> Andy Fitch	<i>Received at ESRF:</i>
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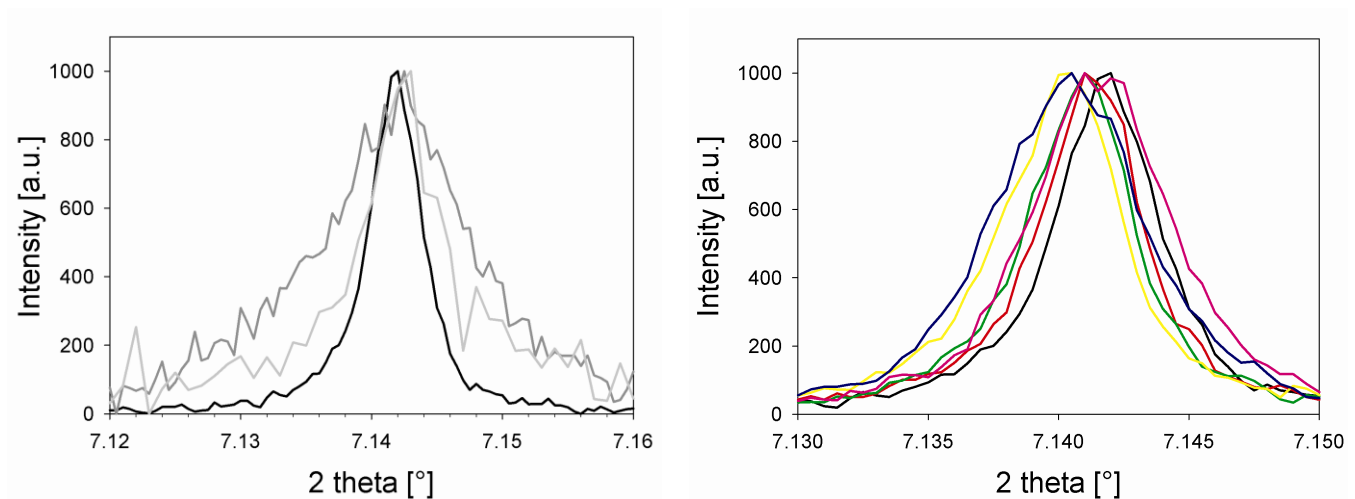
## Report:

Nature has evolved elaborate mechanisms for the growth of mineralized tissues with complex morphologies on different hierarchical levels (e.g. bone, glass sponges, mollusc shells).<sup>1</sup> Insoluble organic matrices as well as soluble biological macromolecules direct and regulate the growth of biominerals. The resulting composite materials often exhibit fascinating properties and act as a source of inspiration for materials science and nanotechnology. Recently even anisotropic lattice distortions have been reported for biogenic calcite and were attributed to the incorporation of organic macromolecules into the mineral crystals.<sup>2</sup> The study of simple model systems with a limited degree of complexity can provide valuable insights in the principles of macromolecule-mediated mineralization.

In this context we investigate the structure of bio-inspired calcite particles grown via a gas diffusion technique in the presence of a negatively charged polyelectrolyte (polystyrenesulfonate).<sup>3</sup> During the crystallization process the macromolecules are incorporated into the crystals and create inner surfaces between the mineral and the polymer phase.

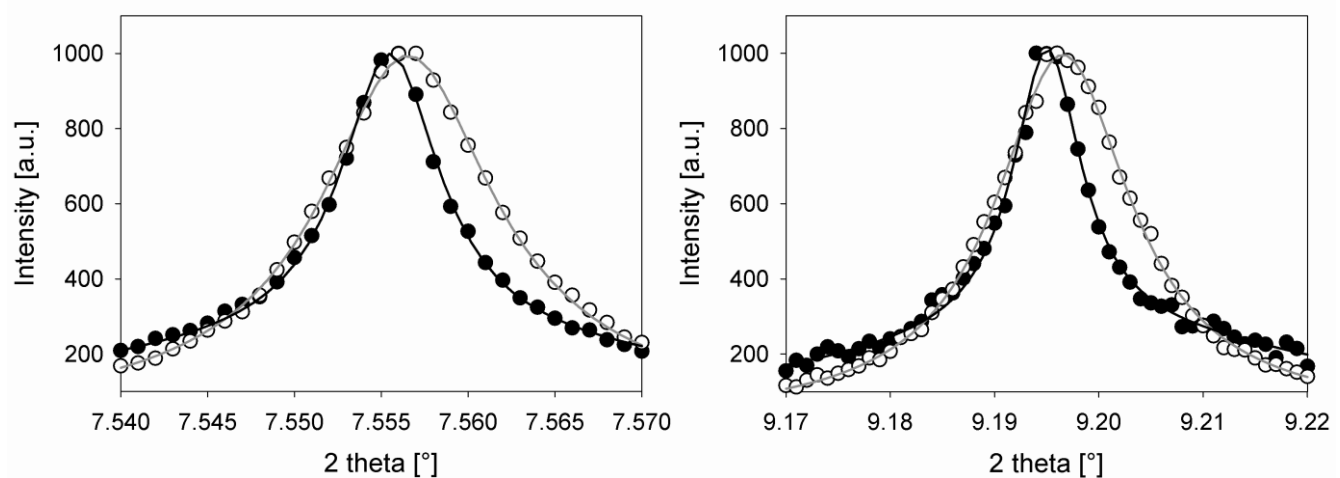
In the present study performed at the high resolution powder diffraction beam-line ID31 we have successfully collected powder diffraction data on several samples featuring different polymer/mineral ratios and polymer chain lengths (see fig. 1, left). The main purpose of the experiment was to elucidate whether or not a polyelectrolyte with a very simple chemical structure is capable of exerting effects on the mineral lattice of calcite. We observed variations in the width of the diffraction lines when samples prepared according to different reaction conditions were compared. By the use of the in-situ blower heater at the beam-line a selection of samples was annealed at different temperatures up to 500°C. Diffractograms recorded after the different temperature steps allowed the evaluation of lattice shifts induced by conformational changes and decomposition of the polymer, respectively (see fig. 1, right). Upon annealing at

moderate temperatures the lattice spacings were found to first increase (annealing up to 300°C) and subsequently decrease again when the sample had been exposed to a temperature of 500°C.



**Figure 1.** Profile of the (006)-diffraction peak of calcite. Left: Comparison between samples prepared under different conditions: black line:  $[\text{Ca}^{2+}] = 1.25 \text{ mmol/L}$ ,  $[\text{polymer}] = 0.5 \text{ g/L}$ , dark grey line:  $[\text{Ca}^{2+}] = 5 \text{ mmol/L}$ ,  $[\text{polymer}] = 1 \text{ g/L}$ , light grey line:  $[\text{Ca}^{2+}] = 1.25 \text{ mmol/L}$ ,  $[\text{polymer}] = 0.5 \text{ g/L}$ , polymer with an increased chain length. While the maximum position is maintained the peak width is influenced by the reaction conditions. Right: In-situ annealing of a sample prepared with the following reactant concentrations:  $[\text{Ca}^{2+}] = 1.25 \text{ mmol/L}$ ,  $[\text{polymer}] = 0.5 \text{ g/L}$ ; 25°C (black line), after annealing to 100°C (red), after annealing to 200°C (green), after annealing to 300°C (yellow), after annealing to 400°C (blue), after annealing to 500°C (magenta);

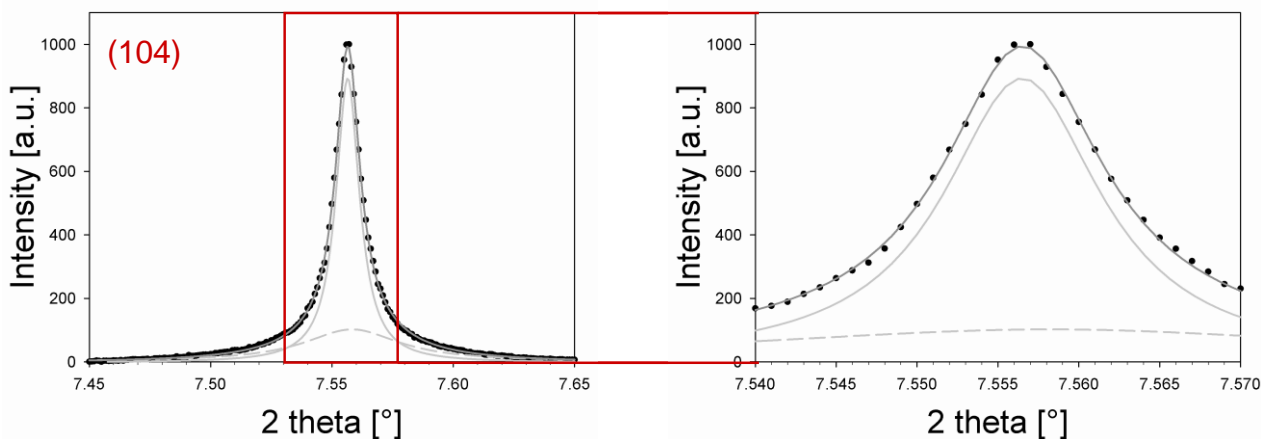
Since the polyelectrolyte, which we typically apply in our synthesis, was purchased as a sodium salt, we additionally checked for the influence of sodium ions introduced into the calcite lattice. Therefore control calcite samples prepared in the presence of defined sodium chloride additions have been investigated in the framework of an additional beamtime in May 2010. Moreover, a sample of bio-inspired calcite was synthesized using a polymer solution which had been dialyzed against water prior to the gas diffusion reaction in order to exclude sodium ions. When compared to a (sodium-free) calcite reference powder the diffraction peaks of the sodium-free polymer-mineral sample were shifted to higher angles. This effect was particularly pronounced for the two reflections shown in figure 2 ( $(\Delta d)/d = -1.3347\text{e-}4$  for the (104)-reflection and  $(\Delta d)/d = -1.6276\text{e-}4$  for the (110)-reflection). The lattice distortions we measured were found to be small, but significant. However they did not reach the same magnitude as those reported for biogenic calcite.



**Figure 2.** The diffraction peaks of bio-inspired particles prepared from a crystallizations solution containing  $[\text{Ca}^{2+}] = 1.25 \text{ mmol/L}$ ,  $[\text{polymer}] = 0.5 \text{ g/L}$  (white circles) are shifted to higher angles when compared to a control sample of pure calcite (black circles). The polymer solution has been dialyzed against water prior to the application in the particle synthesis in order to prevent sodium related effects. In the figure the (104)- [left] and the (110)- [right] reflections are shown.

Due to the very small sample quantities and the dimension of the observed lattice shifts, only the use of high brilliance synchrotron radiation in combination with the high angular resolution at the beam-line enabled us to study the effects we were aiming at.

The profiles of the diffraction peaks were best described by a sum of two Lorentzians (see figure 3)). It seems that generally for our samples there is a broad Lorentzian peak underneath a narrow one, indicating the presence of two structurally different components.



**Figure 3.** The peak profiles can be described as a sum of two Lorentzians. For the (104)-reflection obtained from a control calcite measurement (black circles) the fit (dark grey line) and its two Lorentzian components (light grey lines solid and dashed) are shown.

In conclusion, by the use of the instrumentation provided by ID31 it was possible to resolve lattice distortions in bio-inspired calcite crystals with intracrystalline inclusions of polymer. We investigated the influence of variations in polymer chain length and polymer/mineral ratio in the crystallization solution on the reflections. Moreover, in-situ annealing allowed us to study temperature dependent effects on the diffraction of the composite particles. We observed small, but significant lattice shifts. Profiling of the peaks is still in progress and will be subject to further analysis. We are currently preparing the data for publication.

## References:

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