ESRF	**Experiment title:** Temperature-dependent structure and microstructure changes and distinction between biogenic and geologic vaterite.	**Experiment number:** **CH-3257**
Beamline:	**Date of experiment:** from: 2/9/10 to:8/9/10	**Date of report:** 1/3/11
Shifts: 15	**Local contact(s):** Dr. Adrian Hill	*Received at ESRF:*

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Report:

Recently, by using high-resolution X-ray powder diffraction on a synchrotron beam line, Pokroy et al. found anisotropic lattice distortions both in biogenic aragonite[1,2] as compared to geological aragonite[3] as well as in biogenic calcite[4]. Since lattice distortions disappeared after a mild heat treatment, they were attributed to the incorporated organic molecules. They also observed a profound and surprising evolution of the microstructure of biogenic calcite and aragonite[5] upon heat treatments. More specifically they noticed that the diffraction peaks broaden as a consequence of the annealing treatments rather than narrowing. This is due to a decrease in the size of coherently scattered crystal blocks and an increase in the micro-strain fluctuations. These results imply that at least some of the organic/inorganic interfaces might be ordered prior to annealing.
Pokroy and Zolotoyabko demonstrated that not only is the lattice of biogenic calcite and aragonite distorted but in addition, by high-resolution neutron scattering, they were able to show that the atomic structure is distorted by intracrystalline organic molecules[6,7].

Peptides have also been incorporated within single crystals. Gilbert et al. have performed several studies in which a synthetic peptide with a sequence identical to a protein domain previously identified within a mollusk shell[8-10] were present in calcium carbonate crystallization solution. It was shown that such peptides can become incorporated into the calcite single crystals and distort the short and long-range order of the crystals. In addition such peptides can template lamellar aragonite growth.

Despite the research performed to date on the subject of intracrystalline organic molecules our understanding of the specific organic/mineral interactions, mechanisms of incorporation and influence of organic molecules on the structure of the inorganic phase is rather poor. Most of the basic science research has been carried out on biogenic crystals and not on synthetic crystals. The few studies that have been carried out on synthetic crystals have been carried out primarily on calcite crystals.

In the present study performed at the high-resolution powder diffraction beam-line ID31 we have successfully collected powder diffraction data on several biogenic vaterite samples. The main purpose of the experiment was to elucidate the structure and microstructure of biogenic vaterite as a function of in situ heat treatments.

Our fresh data indicate that similarly to biogenic calcite and aragonite the lattice of biogenic vaterite is also distorted (not yet calculated in detail) and these distortions seem to relax upon a mild annealing (see Figure 3). In addition, the microstructure also seems to evolve due to these heat treatments in a way which is similar to biogenic calcite and aragonite (Figure 3). This broadening of the diffraction peaks upon annealing is counterintuitive to what is known in conventional materials, and indicates interesting intracrystalline organic/inorganic interactions. As stated, these data are only preliminary and need to be performed again and analyzed by the Rietveld method and line-profiling fitting so as to obtain information on where the intracrystalline molecules are located and how they affect the long-range order of the crystals.

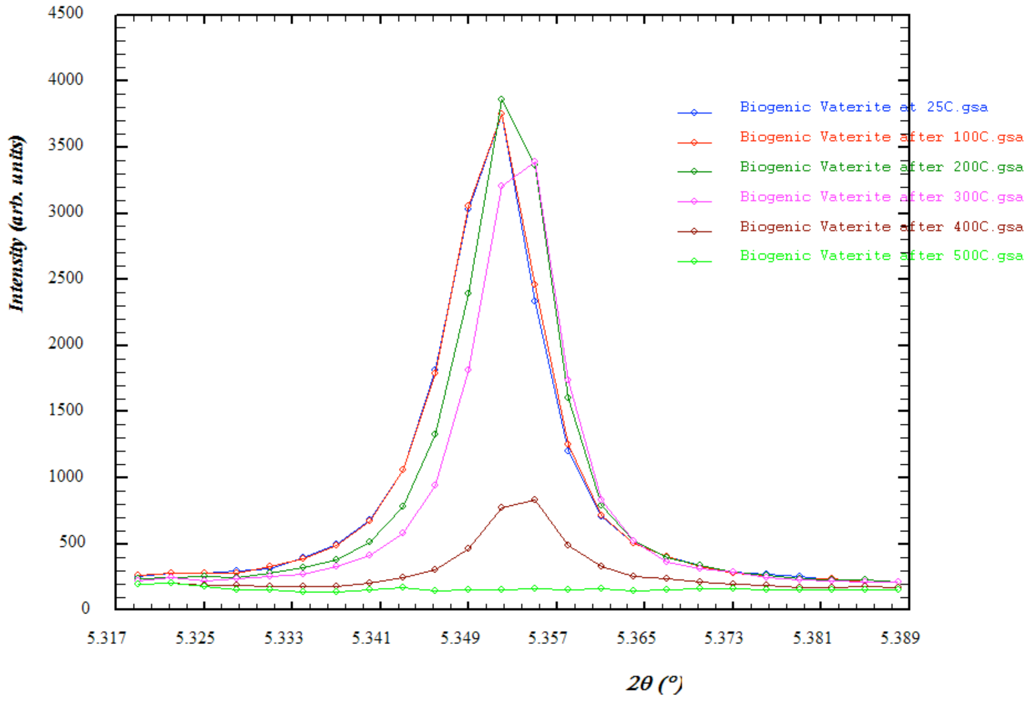

Figure 1: (001) Diffraction peak of biogenic vaterite taken at a wavelength of 0.3948 Å on the ID31 beamline of the ESRF after different annealing temperatures where applied. It can be seen that the diffraction peak shifts to a higher 2Θ angle (lower d-spacing). This indicates shrinkage of the c-lattice parameter. In addition broadening of the diffraction peak is observed. (blue line: room temperature, red line: after 100 deg C for 30 min, olive line: after 200 deg C for 30 min, magenta line: after 300 deg C for 30 min, brown line: after 400 deg C for 30 min, green line: after 500 deg C for 30 min).

In conclusion, by the use of the instrumentation provided by ID31 it was possible to resolve lattice distortions in biogenic vaterite crystals with intracrystalline inclusions of proteins.. Moreover, in-situ annealing allowed us to study temperature dependent effects on the diffraction of the composite crystals. 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.We are still analyiszing moer data and strated to write a reserch paper which will be submitted shortly to Advanced Functional Materials.

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