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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

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Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** The structure of biogenic vaterite	**Experiment number**: CH-2292
Beamline: ID13	**Date of experiment**: from: 14 May 2006 to: 16 May 2006	**Date of report**: 17/01/07
Shifts: 6	**Local contact(s)**: Dmitry Popov	*Received at ESRF:*

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Report:

We used the ID13 beam line in order to carry out the single-crystal diffraction measurements with biogenic vaterite, taken from the *Herdmania momus* ascidian spicules, as well as with geological vaterite. The experiments were aimed to clarify the structure of vaterite (the least stable non-hydrated polymorph of $CaCO_3$) which till now is debated on, and to compare the structures of vaterite of biogenic and geological origins. This latter point is of particular importance as we had already shown that the structures of biogenic aragonite and biogenic calcite (two more stable polymorphs of $CaCO_3$) slightly differ from those of their geological counterparts (Pokroy et al., 2004, 2006a, 2006b). If that is also valid for vaterite, then this phenomenon is not only widespread but actually ubiquitous within biogenic $CaCO_3$.

Individual crystals of biogenic vaterite, obtained from the spicules of the *Herdmania momus* ascidian (1-6 microns), and of geological origin (5-10 microns), were separated in each case by applying a slight force and attached to the end of a glass capillary using a micro-manipulator. The crystals were mounted onto the diffractometer and their diffraction images where recorded by means of an image plate.

All individual crystals of geological origin have diffracted X-rays as powder samples, producing Debye rings, which indicates that they are in fact composed of bundles of nanometer-sized crystallites. Unfortunately, we were not able to find a single crystal of geological vaterite suitable for single-crystal micro-diffraction. It should be mentioned that geological vaterite is extremely rare and its structural quality is poor. On the other hand, most of the biogenic vaterite crystals diffracted X-rays as single crystals as can be seen in Figure 1. However, in the measurements with biogenic vaterite, considerable diffuse scattering was detected (see Figure 2). The diffuse scattering, which has already been observed before (Meyer 1969), makes the refinement procedure complicated. If diffuse scattering is omitted, the collected data for biogenic vaterite fit better the model of Kamhi (1963), but a full-scale diffraction pattern (with diffuse scattering) fits better the model of Meyer (1969).

At this stage, we were unable to fully refine the structure of biogenic vaterite within the Meyer's model to achieve a good fit taking diffuse scattering into account. However, we were able to extract lattice parameters with high enough precision. By treating the diffraction data within the Meyer's model and comparing the obtained cell parameters with those of synthetic vaterite, we found that biogenic vaterite is also anisotropically distorted as compared to it's synthetic counterpart, namely:

a = 7.155(2); c = 16.936(7) Å for synthetic vaterite (Meyer, 1969);

a = 7.158(1); c = 16.9690(4) Å for biogenic vaterite (ID13).

A comparison between these numbers yields a magnitude of distortions: $\Delta a/a = 4.2*10^{-4}$; $\Delta c/c = 1.95*10^{-3}$, being very similar to those found in biogenic aragonite (Pokroy et al. 2004, Pokroy et al. 2006a) and biogenic calcite (Pokroy et al. 2006b).

At the moment, we know that individual thorns of the spicules of the *Herdmania momus* do diffract X-rays as single vaterite crystals. The obtained (preliminary) results indicate that the unit cell of biogenic vaterite is anisotropically distorted as compared to non-biogenic vaterite just as in the cases of biogenic aragonite and calcite. We think that these distortions are caused by intra-crystalline organic molecules entering the crystallites during biomineralization. However, additional experiments and the use of special programs handling the diffuse scattering are required in order to unambiguously refine the structure of both geological and biogenic vaterite. The difficulties in structure refinement come from poor quality of geological vaterite and the presence of diffuse scattering in biogenic vaterite.

References

Kamhi, S. R. *Acta Crystallographica,* **16**, 770-772 (1963)
Mayer, H. J. *Zeitschrift f. Kristallographie*, **128**, 183-212 (1969)
Pokroy, B. et al. *Nature Materials,* **3**, 900-902 (2004)
Pokroy, B. et al. *Journal Structural Biology*, **153**, 145-150 (2006a)
Pokroy, B. et al. *Journal Structural Biology*, **155**, 96–103 (2006b)

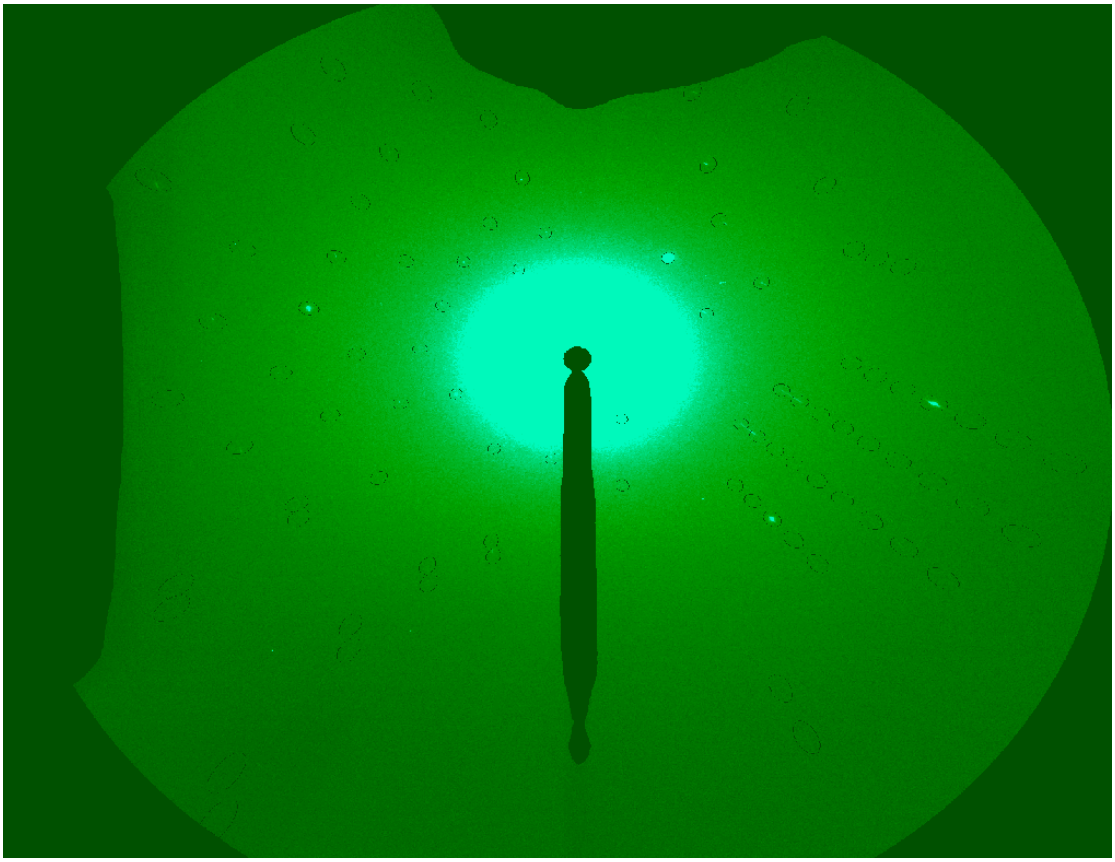

Figure 1. A typical CCD frame taken from a single crystal of biogenic vaterite.

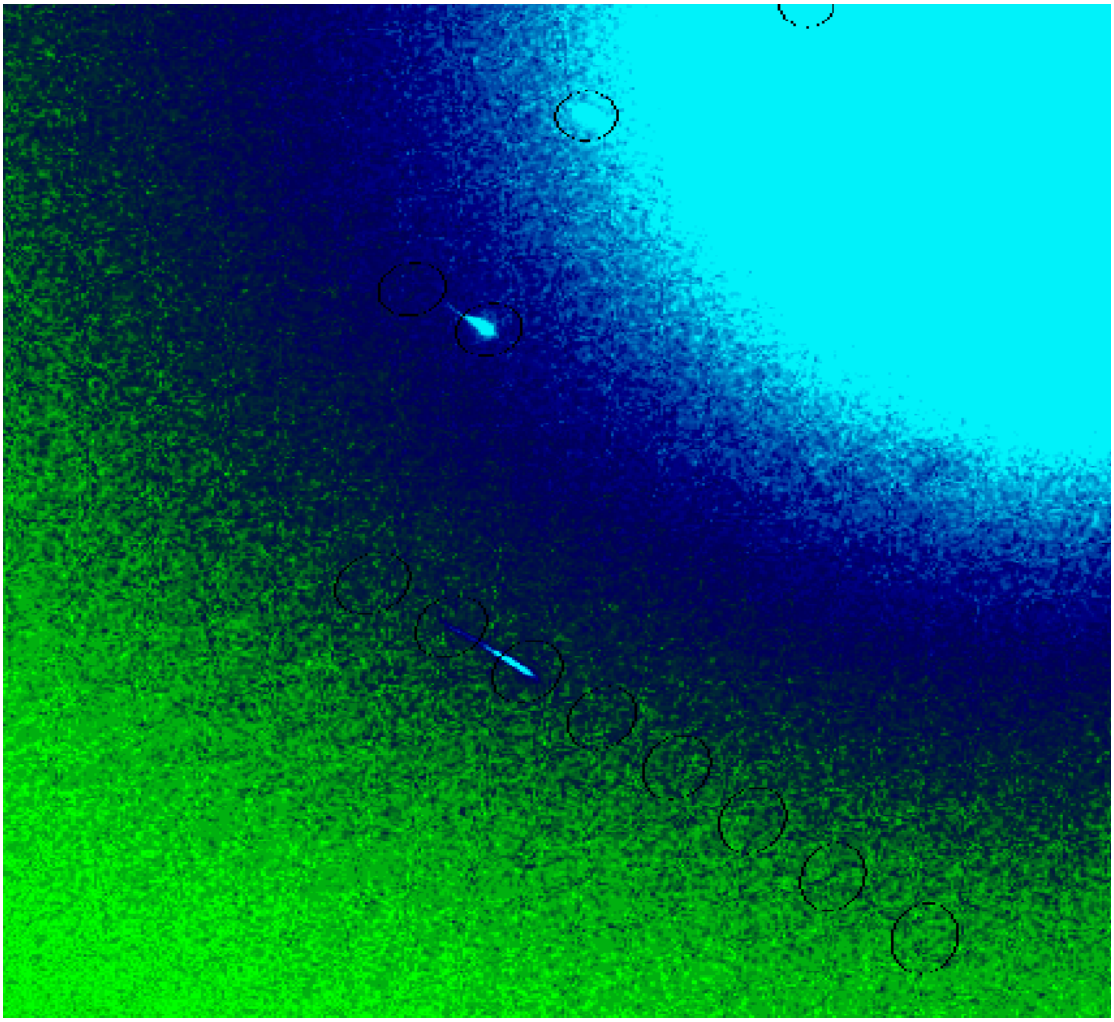

Figure 2. Zoom of Figure 1 revealing the diffuse X-ray scatering in biogenic vaterite.