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

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

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:** Temperature-dependent structural changes in biogenic calcium carbonate	**Experiment number**: CH-2041
Beamline:	**Date of experiment**: from: 29/08/05 to: 02/09/05	**Date of report**: 01/02/06
Shifts:	**Local contact(s)**: Dr. Andy Fitch	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. Emil Zolotoyabko

Mr. Boaz Pokroy

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Report:

This research was focused on detailed investigation of anisotropic lattice distortions found by us in biogenic aragonite and calcite crystals, the two most widespread polymorphs of calcium carbonate. These distortions (as compared to geological minerals) are caused by intra-crystalline organic macromolecules entering into the crystallites during bimineralization. We carried out the x-ray powder diffraction measurements in different mollusk shells annealed at temperatures between 50 and 600 ^{0}C. We show that anisotropic lattice distortions, reaching in maximum a 0.1-0.2 %, are common in the mollusk phylum. Heat treatment at elevated temperatures leads to the pronounced lattice relaxation due to degradation of organic molecules. The obtained results which shed an additional light on the biomineralization problem were summarized in two papers:

1. B. Pokroy, A. Fitch, P. Lee, J. P. Quintana, E. N. Caspi, and E. Zolotoyabko. Anisotropic lattice distortions in the mollusk-made aragonite: A widespread phenomenon. J. Struct. Biology, v. 153, issue 2, pp. 145-150 (2006).

2. B. Pokroy, A. Fitch, F. Marin, M. Kapon, N. Adir, and E. Zolotoyabko. Anistropic lattice distortions in biogenic calcite induced by intra-crystalline organic molecules. J. Struct. Biology (2006, submitted).

Their abstracts are given below:

1. Abstract

In this paper, we present experimental results demonstrating systematic structural distinctions between biogenic and non-biogenic calcium carbonate. Specifically we show, by high-resolution X-ray powder diffraction on dedicated synchrotron beam lines, that the orthorhombic unit cell of the mollusk-made aragonite is anisotropically distorted as compared with that one of geological aragonite. In all investigated shells, belonging to different classes (bivalve, gastropod, and cephalopod) and taken from different habitat origins (sea, fresh water, and land), the maximum elongation of about 0.1 - 0.2 % was found along the *c*-axis. The lattice distortions along the *a*-axis were also of the positive sign (elongation) but lower than those along the *c*-axis, whereas lattice distortions along the *b*-axis were always negative (contraction). Supporting experiments, including structural analysis after a bleach procedure, measurements of temperature-dependent lattice relaxation, measurements of the CO_2 release at elevated temperatures, signify that the observed structural distinctions are most probably caused by the organic molecules intercalating into the aragonite lattice during biomineralization. Our findings show that in some sense organisms control the atomic structure of the crystals. Deeper understanding of this phenomenon will aid in the development of new approaches to grow biomimetic composites and tailor their properties on a molecular level.

2. Abstract

We have performed precise structural measurements on five different calcitic seashells by high-resolution X-ray powder diffraction on a synchrotron beam line and by laboratory single crystal x-ray diffraction. The unit cell parameters, *a* and *c*, of biogenic calcite were found to be systematically larger than those measured in the non-biogenic calcite. The maximum lattice distortion (about 0.2%) was detected along the *c*-axis. Under heat treatment above 200 ^{0}C, a pronounced lattice relaxation was observed, which allowed us to conclude that anisotropic lattice swelling in biogenic calcite is induced by organic macromolecules incorporated within the single crystal calcitic prisms during biomineralization. This conclusion is supported by the results of crystallization experiments in the presence of the specific protein extracted from one of the shells.