



<b>Experiment title:</b> Aragonite-Calcite phase transition: scleractinian coral biominerals vs. minerals	<b>Experiment number:</b> HS-3319	
<b>Beamline:</b> ID-31	<b>Date of experiment:</b> from: 02/03/2007 to: 05/03/2007	<b>Date of report:</b> 27/08/2007  <i>Received at ESRF:</i>
<b>Shifts:</b> 9	<b>Local contact(s):</b> M. Brunelli	

**Names and affiliations of applicants** (\* indicates experimentalists):

**Radosław PRZENIOSŁO(\*) and Dariusz WARDECKI**  
Institute of Experimental Physics, University of Warsaw, Poland

**Jarosław STOLARSKI(\*)**  
Institute of Paleobiology, Polish Academy of Sciences, Warsaw, Poland

**Maciej MAZUR (\*)**  
Laboratory for Electrochemistry, Dept. of Chemistry, University of Warsaw, Poland

## Report:

We have performed high resolution SR diffraction studies of biogenic aragonite and calcite samples. We have also used reference mineral and synthetic aragonite and calcite samples. The measurements were done at ambient conditions on the samples that were in their native state or that were thermally annealed. We have also performed *in situ* measurements in the range from RT to 500°C. The biogenic samples were studied either in form of a small piece of material detached from a larger specimen (so called *en-bloc*) or powder (*pulverized*) placed in a glass capillary.

Our studies performed for several coral skeletons confirm that the aragonite lattice parameters are systematically different as compared with reference mineral and synthetic aragonite samples [1]. Our results confirm previous observations by Pokroy et al. [2,3] of biogenic aragonite from other species. It seems that substantially similar a/b/c lattice parameter ratios observed in biogenic aragonite from different species are due to some general phenomena that occur during the biomineralization process.

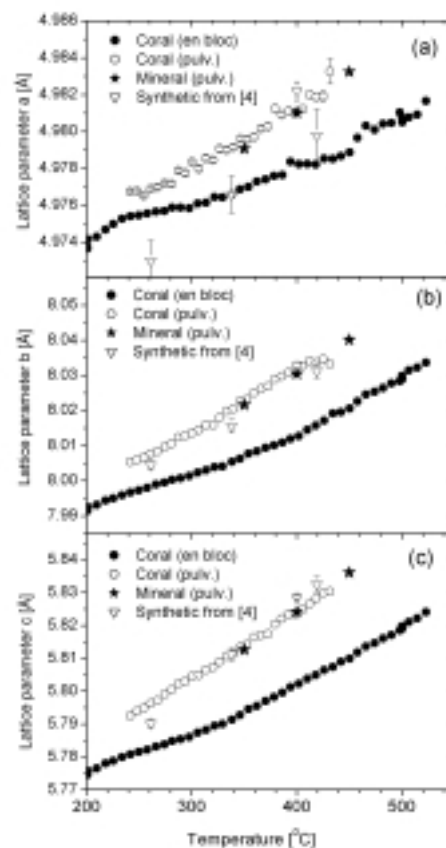
In the biogenic aragonite samples that were transformed to calcite by annealing *ex-situ* at 500°C [1], we observe considerable increase of the internal strain in the material. Microstrain fluctuations of

annealed samples are ca. twice larger as compared to samples before annealing [1]. Moreover, we observe that the microstrain fluctuations in calcite are strongly anisotropic.

The character of the aragonite-calcite phase transition is also different for biogenic samples studied *en-bloc* and *pulverized*. In both cases this process proceeds gradually with increasing temperature. The beginning of the transformation for the *pulverized* sample occurs at about 280°C and is entirely completed at 410°C. However, for the *en-bloc* coral the transformation starts at 350 °C and is not completed even at 500°C (at this temperature there is only 75% of the calcite phase and 25% of the volume remains in the aragonite structure). Please note here that the transition for a reference mineral aragonite is very sharp and occurs at 440°C.

We have also studied the thermal expansion of the biogenic aragonite and the detailed results were obtained for the *Desmophyllum ingens* coral. We performed measurements for both *en-bloc* and *pulverized* samples as shown in Fig. 1. The lattice parameters of the *pulverized* sample agree well with these of reference mineral aragonite. However, the results of coral skeletons studied *en-bloc* are surprising: the lattice parameters are systematically smaller as compared with the *pulverized* and reference mineral samples. The possible reason of this discrepancy is the interaction between the CaCO<sub>3</sub> host lattice and the organic inclusions entrapped during biomineralization.

The experimental findings reported here will be submitted to J. Phys.: Cond. Matter [5].



**Fig. 1** Temperature dependence of the lattice parameters of aragonite a,b and c derived from SR diffraction studies for several aragonite samples. Results are shown for biogenic coral sample extracted *en-bloc* (solid circles) and *pulverized* (empty circles) as well as for mineral aragonite (stars). Our results are compared to results from laboratory X-ray diffraction studies (triangles) of synthetic aragonite [4].

Further studies of the unusual thermal expansion of biogenic CaCO<sub>3</sub> materials are planned in the near future.

## References

- [1] Stolarski, J., Przeniosło, R., Mazur, M., & Brunelli, M., J. Appl. Cryst. (2007) **40**, 2-9.
- [2] Pokroy, B., Quintana, J.P., Caspi, E.N., Berner A. & Zolotoyabko, E. (2004). Nature Mat. **3**, 900-902.
- [3] Pokroy, B., Fitch, A.N., Lee, P.L., Quintana, J.P., Caspi, E.N. & Zolotoyabko, E. (2006). J.Struct. Biol. **153**, 145–150.
- [4] Lucas, A., Mouallem-Bohout, M., Carel, C., Gaudé, J. & Matecki, M. (1999). J. Solid State Chem. **146**, 73–78.
- [5] Wardecki, D., Przeniosło, R., Stolarski, J., Mazur, M., & Brunelli, M. J. Phys.: Cond. Matter (in preparation)