Aragonite-Calcite phase transitions in scleractinian coral biominerals vs. minerals (experiment HS-3319)

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Reef-building scleractinian corals belong to the most extensive natural producers of $CaCO_3$. Modern scleractinian corals produce carbonate skeleton whose principal polymorph is aragonite. Besides $CaCO_3$ biogenic materials contain also a small amount of organic clusters which occupies about 1-3% of their mass. High resolution SR diffraction studies of mollusk shells have shown anisotropic elongations of the aragonite lattice parameters a, b and c as compared with reference geological aragonite [1,2]. These anisotropic elongations were observed for many species. It is believed that these distortions are due to the interactions between the $CaCO_3$ crystals and the surrounding organic clusters.

In order to get insight in the coral skeleton morphology high resolution SR diffraction studies were performed using the beamline ID31. Measurements were performed for skeletons of recent (Desmophyllum dianthus) and fossil (Isastrea cf. bernensis) scleractinian corals. As well as reference geological aragonite. All the studied biogenic and geological samples show relatively narrow Bragg peaks due to the aragonite phase [3] with $\Delta d/d$ values as low as 1×10^{-3}. Our studies with coral skeletons [3] have shown the same kind of anisotropic lattice elongations as those reported in the literature [1,2].

The same samples were also studied by several microscopic techniques including atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM).
The low FESEM magnifications of naturally fractured show linearly arranged skeletal fibers which are almost parallel to each other. The fibers show a bumpy surface exhibiting a discrete nanogranular morphology. However, the nanograins are not distinctly separated from each other and usually form clusters a few hundred nanometers in size. Also the AFM observations of polished and selectively etched samples reveal nanogranular texture with grains ca. 30–100 nm in diameter [4].

In order to characterize the microstructure of the samples we selected three groups of peaks with scattering vector **Q** direction along **a***, **b*** and **c*** directions. The Williamson-Hall plots in were used to show the square of the integral breadth β^2 as a function of the square of the scattering vector Q^2 for all three groups of Bragg peaks [4]. The microstrain fluctuations in each direction of the lattice are proportional to the slope of the lines. The microstrain fluctuations along the **a*** direction are smaller than those along the **b*** and **c*** directions for all biogenic samples. The microstrain fluctuations observed in geological aragonite differ considerably from those observed in all the biogenic samples.

The average grain size determined from SR diffraction data is in the order of 200–250 nm, i.e., considerably higher than the size of the nanograins observed in FESEM and AFM (30–100 nm). These seemingly contradicting results of microscopic and diffraction studies are reconciled within a new, minute-scale model of the coral skeleton structure [4]. Both SR diffraction and microscopic observations can be coherently interpreted assuming the model of nanocrystals interconnected by crystalline bridges. It is assumed that both the nanocrystalline "bricks" and the linking bridges are composed of atoms arranged in the same way as in a single crystal.

The intriguing aspect of our results is that both extant and fossil $CaCO_3$ biominerals, differing in age by about 150 millions of years, show a similar lattice distortion effect. Such a long-term preservation of the ''vital effect'' in the biomineral crystalline lattice may appear to be a valuable contribution to the research methodology for fossil samples.

Our studies have been also extended to other fossil coral specimens. We show that a well-preserved fossil coral, Coelosmilia sp. from the Upper Cretaceous (about 70 million years ago), has preserved skeletal structural features identical to those observed in present-day scleractinians. However, the skeleton of Coelosmilia sp. is entirely calcitic and it shows no trace of aragonite [3]. Its fine-scale structure and chemistry indicate that the calcite is primary and did not form from the diagenetic alteration of aragonite. This new result is an argument against the common belief that scleractinian corals form purely aragonitic skeletons [5]. This result implies that corals, like other groups of marine, calcium carbonate– producing organisms, can form skeletons of different carbonate polymorphs.

We have also performed *in situ* measurements in the range from RT to 500℃. 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. We have studied the thermal expansion of the biogenic aragonite and the detailed results were

obtained for the *Desmophyllum ingens* coral. 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 $CaCO_3$ host lattice and the organic inclusions entrapped during biomineralization [6].

Financial support was provided by the Polish Ministry of Science and Higher Education (Faculty of Physics University of Warsaw) as well as within projects N307-015733 and 155ESR263. We thank the European Synchrotron Radiation Facility for access to experimental facilities.

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