ESRF	**Experiment title:** Biomineralization and diagenesis in red coral: microstructure of present-day and fossil samples in reference to synthetic calcite and high magnesium calcite	**Experiment number**: HS/4820
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Report:

The project HS-4820 was a continuation the previous proposal HS-4398 entitled “Biomineralization and diagenesis in red coral: microstructure of present-day and fossil samples”. The results of the latter lead us to carry out new experiments in order to understand biogenic Mg-calcite properties.
This proposal HS-4820 aimed to obtain quantitative structural information 1) on red coral crystals from specifically identified annealed skeletons and 2) on synthetic high-magnesium calcite samples and thus
1) Compare biogenic crystals and synthetic high-magnesium calcite crystals
2) Understand and quantify the phase transitions occuring in biogenic crystals, characterize crystal structures, crystallite sizes and the microstrains along different crystallographic directions of the present phases.
3) Determine the contribution of the organic molecules within the red coral crystals in the annealing process.

Experimental:

The study were successfully carried out on three sets of samples: (1) red coral samples, preliminary annealed at different temperatures in a gas mixing furnace to control the oxygen fugacity on the phase transition observed during the first experiments (see report HS4398), (2) synthetic high magnesium calcites as prepared in high pressure vessel and 3) synthetic high magnesium calcites annealed as described in (1) for red coral samples. All samples were prepared in our own laboratory, ground gently in an agate mortar, then placed glass capillaries, 1mm in diameter.
High-resolution X-ray powder diffraction measurements were performed at 0.47 Å wavelength on ID31:
1) at room temperature to characterize the initial crystal structure, crystallite size, microstrains,
2) from RT to 700°C, using a hot air blower, in steps of 50°C, and again at RT after cooling to characterize the temperature-induced modifications (including loss of the organic component) to the crystal structure (lattice parameters, structural phase transition from magnesium calcite to dolomite), crystallite size, microstrains.

Results:

The overall results of the two studies **HS-4398 and HS-4820** was highly conclusive and has been submitted for publication to CRYSTAL GROWTH AND DESIGN**.**

Red coral produces biomineral skeletons and sclerites that are made of Mg-rich calcite nano components (9 to 15 mol.% $MgCO_3$) and organic matter (OM) (1.2 to 1.7 wt%). By contrast, synthetic magnesium calcite with 10% Mg prepared in high pressure vessel are large crystals free of organic matter.
The challenge of this structural study was to deal with the large magnesium calcite distribution specific to the red coral skeletons compared to other studied calcite biominerals. This work was successful and led to firm and conclusive results based on the large previous knowledge obtained on the red coral in various areas; but also owing to the concomitant data obtained on calcite and especially on the magnesium calcite at 10 Mg mol.% successfully synthetized. At first, the SXRPD study on our synthetized Mg calcite standard pointed out the problem of Mg quantification in magnesium calcites by Rietveld-based XRD analysis. As a result, SXRPD analysis is a good tool to obtain the accurate range of the Mg distribution of a biogenic material from diffraction peak profiles. Conversely, the average composition of biogenic Mg calcites is best determined from the lattice parameter *a*. In addition, the discrepancies of composition compared to chemical analysis measurements evidence the anisotropic distortion of a biogenic material compared to a geologic or synthetic one.
Accurate structural parameters obtained from high-resolution synchrotron radiation diffraction analysis in pure calcite, synthetic Mg calcite and different red coral skeletons pointed out 1) the general phenomenon of anisotropic unit cell distortions of the biogenic material, 2) its link to the intra-crystalline organic molecules trapped within individual crystallites attested by TG/DSC analyses and FTIR/ Raman spectroscopies. These structural properties unique to biogenic materials should have important implications on mechanical, optical, and other physical characteristics of biogenic crystals (dissolution, precipitation, ionic diffusion).
The thermal stability of the red coral skeletons is different from calcite and specifically from synthetic magnesium calcite at 10 Mg mol.% that is found stable up to 1073K. Thus, the red coral skeletons made of Mg calcite, with 10 to 15 mol.% Mg content, including trace elements (Na, S, Sr, P, K), are not stable above 823K in self-controlled CO_2 (*"in situ"* experiments). Their thermal decomposition is comparable to the dolomite (50 Mg mol.%) one. Furthermore, the presence of low Mg calcite phases as intermediate phases supports the formation of calcite via a magnesium calcite with a gradual release of Mg^{2+} ions. Besides, the produced calcite maintains a unit cell distortion along the *c* parameter probably linked to crystallinity defects due to the remaining trace elements. For instance, sulfate ions are still present within the calcite crystals according to the infrared spectroscopy results. Tetrahedral sulfate ions replacing planar carbonate ions may cause a distortion of the calcite unit cell along the *c* axis. This study gives very conclusive results that contribute to understanding the mechanisms of thermal decomposition of carbonates and the structure of carbonate skeletal structures of the living organisms.

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