

**Experiment title:**

Understanding where intracrystalline organic molecules are located within an inorganic crystal host

Experiment number:

CH 3915

Beamline:**Date of experiment:**

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Received at ESRF:

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Report:**Introduction:**

In biomineralization processes, organisms use biological mechanisms in order to control polymorph formation. As part of the effort to understand this phenomenon, we incorporate amino acids, as they are the foundation elements for proteins, into the most abundant mineral on earth, calcium carbonate. One of the most interesting reactions between the amino acid and the mineral is the interaction between the sulphur atom in the cysteine and methionine amino acids. In this experiment, we want to understand how the amino acid interacts with the carbonate in the different phases.

Experimental:

Three polymorphs of calcium carbonate, calcite, aragonite and vaterite, were crystallized with cysteine and methionine amino acids and were examined by using X-ray Absorption Spectroscopy (XAS) monitoring the sulphur K-edge at ID26 beamline by using a crystal spectrometer. The scanned energy range was 2450-2650 eV. The spectroscopy measurements were conducted under vacuum conditions.

During the data collection, some pure phases bearing Sulphur cations with different valence were used as references to interpret the sample's spectra:

- Organic Phases: Cysteine and Melatonin
- Inorganic S⁻²: CaS and ZnS
- Inorganic Sulphate (SO₄²⁻): CaSO₄ and ZnSO₄

The spectra of CaCO₃ samples crystallized with cysteine or methionine were compared with the reference spectra to understand the sulphur coordination and valence state after the crystallization.

Results:

The experimental spectra of the calcium carbonate with Methionine and Cysteine are reported in figure 1 and figure 2 respectively. For the pictures, it is possible to highlight some occurrences:

- The sulphur oxides CaSO_4 is present in all samples except in the vetarite with cysteine
- Unreacted methionine is always present in all three samples crystallized with this aminoacid
- In the spectra of vetarite sample there is a strong peak 2475 eV that is difficult to attribute to a specific phase, but it seems to be due to a phase with sulphur charge between -2 and 6
- The aragonite with cysteine spectra shows that sulphur is partially unreacted in cysteine and partially oxidized to CaSO_4 .
- Calcite and vetarite with cysteine show that the peak of Sulphur atom in the aminoacid is split, suggesting a possible reaction of this molecule with the Ca^{2+} cation.

The chemical consequence of these result are still under analysis

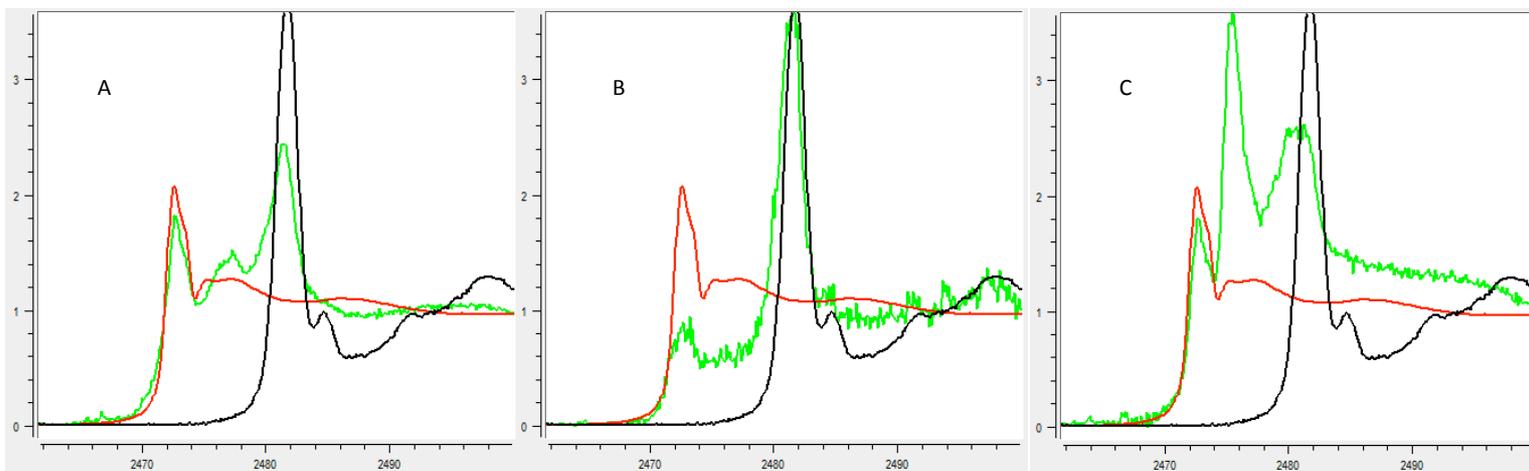


Figure 2 CaCO_3 with Methionin, red Methion spectra, black CaSO_4 spectra, green A Calcite, B Aragonite, C Veterite spectra

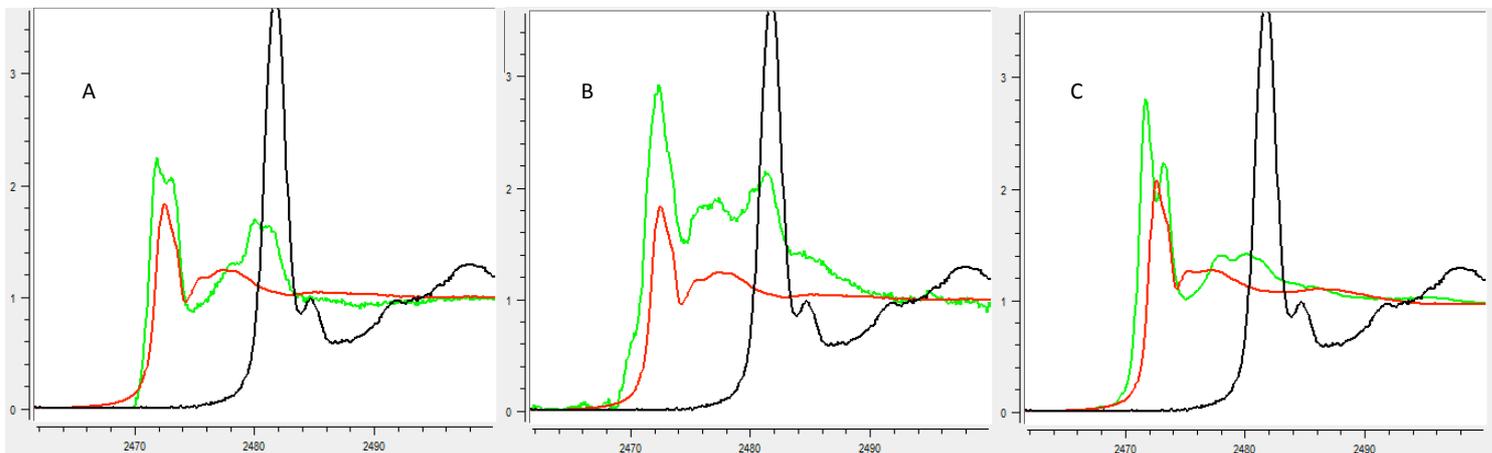


Figure 1 CaCO_3 with Cystein, red Cystein spectra, black CaSO_4 spectra, green A Calcite, B Aragonite, C Veterite spectra