ESRF	**Experiment title:** Physicochemical effects of inorganic oxyanions on the calcite formation	**Experiment number**: 30 02 927
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Shifts: 15	**Local contact(s)**: Denis Testemale	*Received at ESRF:*

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Report:

Scientific background

An international increase in interest in factors which control the nucleation and growth of carbonates was observed. The role of impurities, both inorganic and organic, has been the subject of much speculation over the years, and has generated various models of how such foreign ion or molecules may adsorb/incorporate on/in a growing surface and modify growth mechanisms and rates. At the present time, a multi-analytic approach from molecular to macroscopic scale can be used to elucidate clearly the fixation mechanisms of impurities in/on crystal surfaces by using sophisticated spectroscopic, microscopic and diffractometric measurements. For example, the x-ray absorption spectroscopy (XAS and μ-XAS) can be used to characterize the atomic organization, the oxidation state of ions and, impurity fixation mechanism into the crystals. High resolution transmission electron microscopy (HRTEM) coupled to energy dispersive spectroscopy (EDS) can be used to characterize the structural nano-domains organization and crystallinity of particles. Field emission gun scanning electron microscope (FEG-SEM) and focused ion beam milling (FIB) can be used to characterize the nanoparticles distribution throughout the micrometric crystal cross-sections. X-ray diffraction can be used to determine the coherent domain average size of nanometric particles. In the present experiment, we have coupled XRD, TEM-EDS, HRTEM and XAS to study the incorporation of Se and As in calcite grown in hydrothermal conditions.

Experiment (XAS measurements)

Twenty two samples (calcite containing different concentration of selenium and arsenic and five material references) were characterized by EXAFS and XANES on the Beamline FAME at the ESRF. Spectra were recorded in fluorescence mode using the 30-element Canberra detector and at 15 K using the He cryostat to limit possible radiation damage effects.

The XAS measurements were used to characterize the atomic organization, the oxidation state of chemical elements and, impurity fixation mechanisms into the crystals. The analysis of XAS data were performed

using the IFEFFIT package including ATHENA for data extraction and linear combination fits (LCFs) and ARTEMIS for the shell fitting. For example, in this study on the calcite growth in presence of seleno-L-cystine, the linear combination fits (LCFs) of EXAFS spectra were successfully used to determine the selenium species on/in the calcite composite (Figure 1).

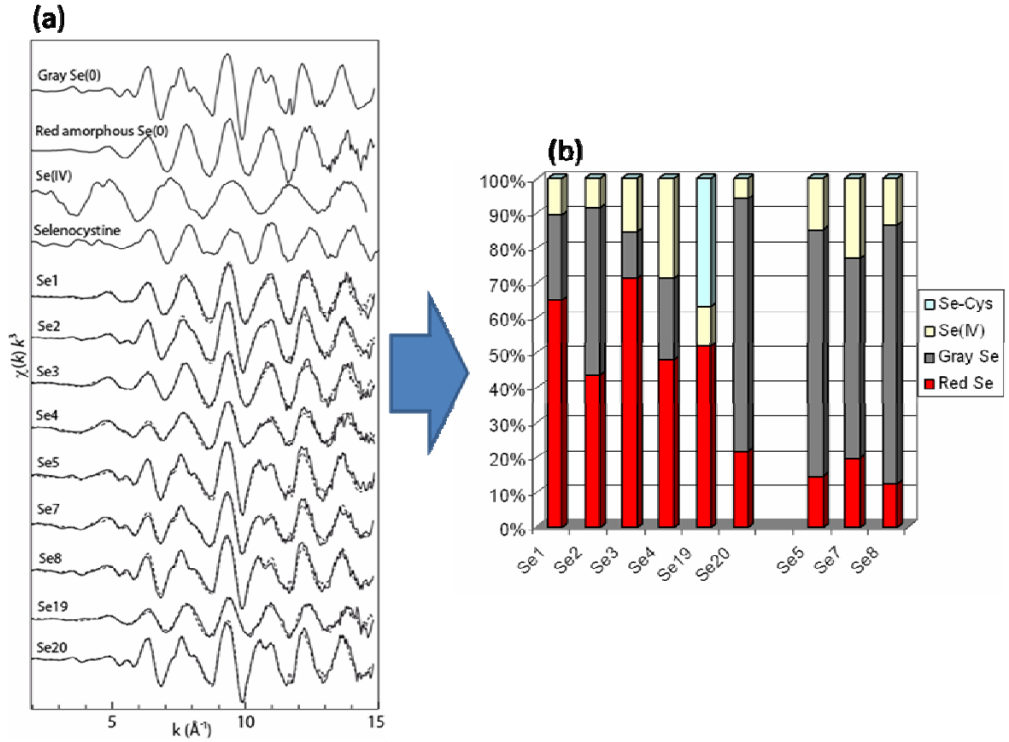

Figure 1. (a) k^3-weighted EXAFS spectra for references compounds and calcite samples produced in presence of seleno-L-cystine. Plain lines: experimental, dashed lines: linear combination. (b) Proportion of Se species determined by LCFs of EXAFS spectra after normalization to 100% (Montes-Hernandez, Sarret et al. 2010). The precision on the percentages was estimated to ±10%

On the other hand, the shell fitting using ARTEMIS software has revealed that incorporation of selenite (SeO_3^{2-}) into single crystals of calcite; i.e. a partial structural substitution of ion carbonate by ion selenite during nucleation-growth of calcite was directly associated to a c-axial elongation of rhombohedral calcite crystals and a retarding of the CO_2 transfer in triphasic gas-liquid-solid systems. Moreover, an atypical aggregation/agglomeration of calcite particles, leading to star and shell-like forms was also observed in presence of unstable seleno-L-cystine.
These nice results will be shared via one international publication, now in preparation:

G. Montes-Hernandez, G. Sarret, R. Hellmann, D. Testemale, L. Charlet, F. Renard (**2010**) Evidences of selenite (SeO_3^{2-}) incorporation into sub-micrometric crystals of calcite produced in a triphasic gas-liquid-solid system. XAS and HRTEM measurements (to be submitted *to GCA*)

<u>Perspectives</u>

A similar experiment will be proposed to the Beamline FAME at the ESRF. But, for this case, the calcite samples will be dopped with arsenic impurities because only four samples containing arsenic were studied.