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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
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- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Micro-XANES and micro-XRD investigation of carbonatation processes for stone consolidation	Experiment number: HG-63
Beamline: ID21	Date of experiment: from: 29/01/2016 to: 05/02/2016	Date of report: 31/01/2020
Shifts: 18	Local contact(s): Wout De nolf	<i>Received at ESRF:</i>
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1. INTRODUCTION

The application of consolidants is a common practice for the preservation of limestones used in cultural heritage buildings and monuments against outdoor weathering processes.

Recently, inorganic treatments involving the *in situ* formation of CaCO_3 , have been proposed, being more suitable due to their higher physico-chemical compatibility and stability with respect to synthetic organic polymers (e.g., polyacrylates, polyvinylacetates and epoxies). [1]

The main issue of these Ca-based consolidants is the formation of different CaCO_3 phases, that may range from amorphous deposits to crystalline systems composed of either vaterite, or calcite, or their mixtures [1-3]. The formation of different phases of calcium carbonate has implication on the long term performance of a consolidation treatment.

In the context of our research, we have tested a newly developed calcium acetoacetate-based consolidant [4] and the commercially available products CaLoSiL IP-5 and IP-25 (IBZ-Salzchemie GmbH & Co.KG) product, as a precursor for deposition of CaCO_3 . At this regard, earlier studies have shown that different metastable calcium carbonate phases (i.e. first, amorphous CaCO_3 and then vaterite) can precede the formation of stable calcite during the carbonation of these calcium-based consolidants and that the formation of calcite is favored with increasing relative humidity (RH) conditions. [5-8]

Thus, for such systems, it becomes highly relevant providing detailed information about the nature and distribution of the newly formed crystalline and amorphous calcium carbonate phases directly in the stone porosity and to determine the environmental conditions at which they preferentially form.

To this purpose, in this experiment we have employed for the first time a multi-method approach based on synchrotron radiation-based 2D X-ray methods [(i.e., μ -XRD, μ -XRF and XANES at Ca K-edge)] for studying fragments of calcium acetoacetate-based and CaLoSiL consolidated limestone substrates (Lecce stone) treated at different relative humidity conditions.

Such approach permitted us to discriminate between amorphous calcium carbonate (herewith called ACC), vaterite and calcite and to map their distribution inside the stone matrix down to the (sub)micrometer scale length.

2. EXPERIMENTAL

The following materials have been investigated at the ID21 beamline:

a) Reference powders of different polymorphs and amorphous CaCO₃ (4 in total);

b) Calcium acetoacetate-based and CaLoSiL consolidated limestone substrates (Lecce stone) (10 in total) before and after exposure to different RH conditions.

For the analysis, a thin layer (thickness $\approx 10\text{-}20\ \mu\text{m}$) of the reference powders was fixed on sulfur-free tape, that was then covered with a foil of ultralene. Regarding the consolidated Lecce stone mock-ups, measurements were carried out on cross-sections prepared from fragments taken from the mock-ups themselves (sizes of *ca.* $3\times 2\ \text{mm}^2$), which have been embedded into polyester resin and then polished down to a thickness between $80\ \mu\text{m}$ and $150\ \mu\text{m}$.

Measurements were performed at the scanning $\mu\text{-XRD}/\mu\text{-XRF}$ end station and the scanning X-ray microscope (SXM) and full field (FF)-XANES end-stations. Investigations were carried out by means of a fixed exit double-crystal Si(111) monochromator at all the end-stations.

At the $\mu\text{-XRD}/\mu\text{-XRF}$ end station analysis were performed with an incident beam of $8.5\ \text{keV}$, which was focused by means of Kirkpatrick-Baez (KB) mirrors down to a size of *ca.* $2\times 2\ \mu\text{m}^2$ ($h\times v$). $\mu\text{-XRD}$ patterns were recorded using a taper FReLoN detector (2048×2048 pixels, pixel size $52\ \mu\text{m}$) and with an exposure time of $10\ \text{s/pixel}$. Data processing of XRD data has been done by XRDU software. [9]

At the SXM end-station, the incident beam was focused with KB mirrors down to a diameter of $0.7\times 0.3\ \mu\text{m}^2$ ($h\times v$). XRF signals were collected in the horizontal plane and at 69° with respect to the incident beam direction by means of either a photodiode or a silicon drift detector (Xflash 5100, Bruker).

Single point XANES spectra were acquired in XRF mode by scanning the primary energy around the Ca K-edge with the following energy step sizes (total points number: 549; exposure time: $0.1\ \text{s/point}$): i) $5\ \text{eV}$ in the $3938\text{-}4018\ \text{eV}$ and $4238\text{-}4398\ \text{eV}$ range, ii) $0.3\ \text{eV}$ in the $4018\text{-}4138\ \text{eV}$ region and iii) $1\ \text{eV}$ in the $4138\text{-}4238\ \text{eV}$ range.

$\mu\text{-XRF}$ mapping investigations were carried out by employing a monochromatic primary beam of fixed energy around the Ca K-edge. Maps of the same region of interest were recorded using $50\ \text{ms/pixel}$ at the following three energies: i) $4043.5\ \text{eV}$ to favor the excitation of vaterite and amorphous CaCO_3 , ii) $4064\ \text{eV}$ to obtain the XRF intensity of calcite and iii) $4400\ \text{eV}$ for promoting that of all Ca-based species.

PyMCA was used to fit the XRF spectra and to separate the contribution of different elements.

The normalization of single point XANES spectra was performed by means of the ATHENA software. [10]

Full-spectral (FS) $\mu\text{-XANES}$ mapping investigation of a region of interest of one cross-section was performed by recording a stack of $74\ \mu\text{-XRF}$ maps (exposure time: $40\ \text{ms/pixel}$), while tuning the X-ray energy across the Ca K-edge with the following steps: i) $4\ \text{eV}$ in the $4012\text{-}4040\ \text{eV}$ and $4080\text{-}4120\ \text{eV}$ range, ii) $0.5\ \text{eV}$ in the $4040\text{-}4046\ \text{eV}$ region, iii) $1\ \text{eV}$ in the $4046\text{-}4074\ \text{eV}$ range, iv) $2\ \text{eV}$ in the $4074\text{-}4080\ \text{eV}$ range and v) $6\ \text{eV}$ in the $4120\text{-}4198\ \text{eV}$ region.

Ca K-edge FF-XANES imaging in transmission mode was carried out using an unfocused beam (size of $\sim 1.5\times 1.5\ \text{mm}^2$). A $\text{Lu}_2\text{SiO}_5\text{:Tb}$ scintillator (located at a distance less than $2\ \text{mm}$, downstream the sample) was used to convert X-ray transmission images into visible images. A $10\times$ optical objective was employed to magnify the image onto a CMOS camera (PCO edge, Germany) with a pixel size of $\sim 0.65\times 0.65\ \mu\text{m}^2$ and giving a lateral resolution of $\sim 1.4\ \mu\text{m}$. The maximum field of view (FOV) was around $1000\times 1000\ \mu\text{m}^2$. A stack of 549 X-ray radiographs was recorded, while tuning the X-ray energy across the Ca K-edge with the same following step sizes used for recording the single point XANES spectra. The dark and flat field correction and the images alignment were performed by employing the Spectrocrunch library.

The TXM-Wizard software package [11] was used to process the FS $\mu\text{-XANES}$ and FF-XANES data-sets, thus to produce the chemical state maps of different calcium-based compounds and CaCO_3 polymorphs.

3. RESULTS

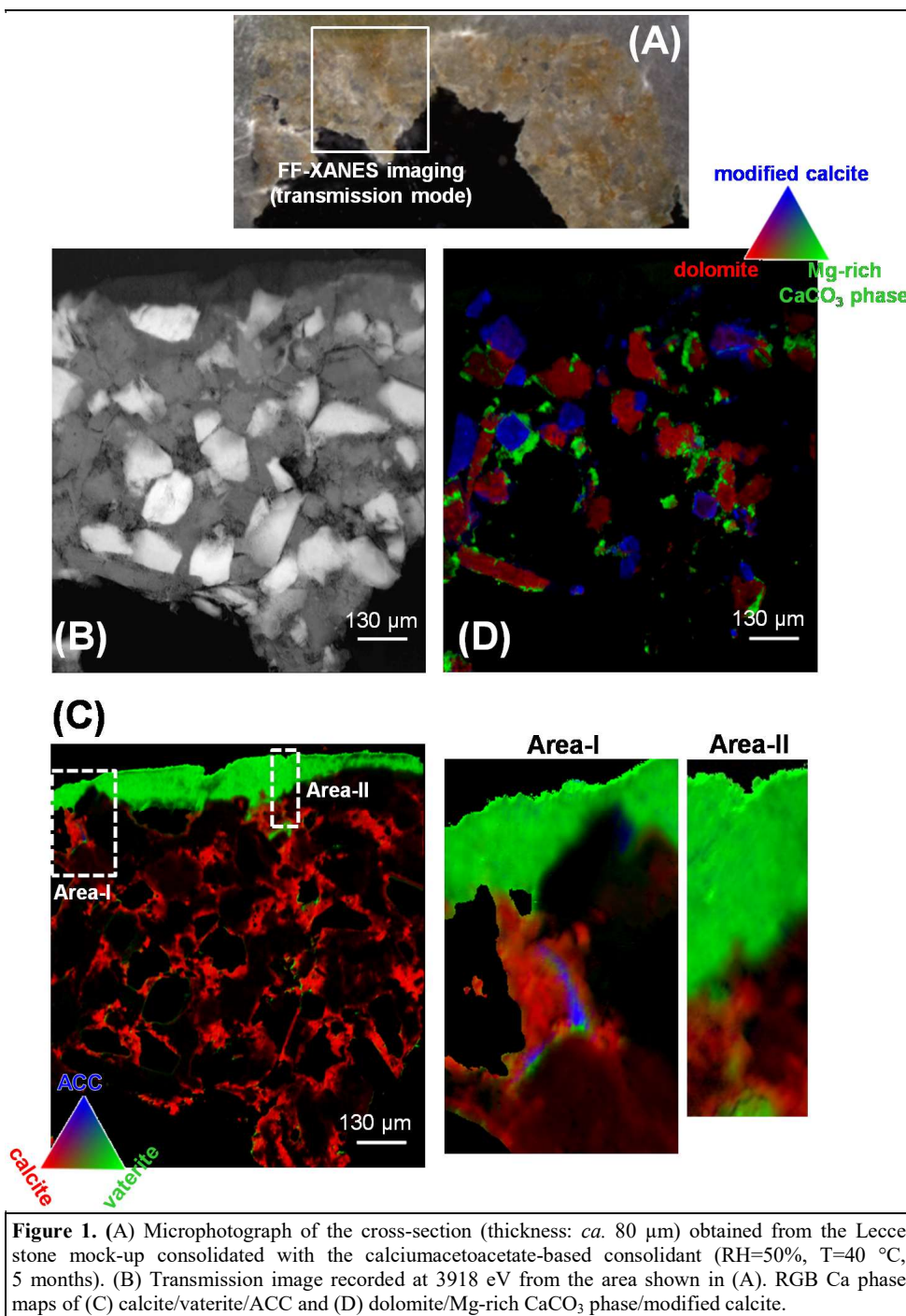


Figure 1. (A) Microphotograph of the cross-section (thickness: *ca.* 80 μm) obtained from the Lecce stone mock-up consolidated with the calcium acetoacetate-based consolidant (RH=50%, T=40 $^{\circ}\text{C}$, 5 months). (B) Transmission image recorded at 3918 eV from the area shown in (A). RGB Ca phase maps of (C) calcite/vaterite/ACC and (D) dolomite/Mg-rich CaCO_3 phase/modified calcite.

been also confirmed by $\mu\text{-XRD}$ mapping in a smaller region of interest of the sample (results not shown).

Overall, our results reveal that Ca K-edge FF-XANES imaging in transmission mode can be successfully used to study heterogeneous limestone samples, thus permitting to distinguish various CaCO_3 -based compounds with high specificity, high lateral resolution ($\sim 1.4 \mu\text{m}$) and large field of view (orders of mm^2).

However, the spectra extracted from the FF-XANES imaging data-set obtained from thicker cross-sections (thickness of 100-150 μm) show strong distortions, thus making impossible to obtain any meaningful information about the identification and spatial distribution of various Ca-based phases (results not reported). For such thicker, non transparent samples, problems encountered in transmission mode spectroscopy could be overcome by performing fluorescence mode XANES analysis, thus by combining the acquisition of multiple energy $\mu\text{-XRF}$ maps with single point $\mu\text{-XANES}$ analysis and/or by carrying FS $\mu\text{-XANES}$ mapping of smaller region of interest of the samples.

The results obtained from this experiment will be published soon.

As an example, Figure 1 shows the results obtained by Ca K-edge FF-XANES imaging of a region of interest of the cross-section (thickness: $\sim 80 \mu\text{m}$) obtained from one of the analyzed Lecce stone mock-up treated with the calcium acetoacetate-based consolidant.

Ca-phase maps confirm that the Lecce matrix is mainly composed of calcite (Figure 1C: red) with crystals of variable shape and size of dolomite (Figure 3D: red), a Mg-rich CaCO_3 phase (green), and one additional Ca-based compound of uncertain attribution (blue).

Measurements carried out on the untreated Lecce stone mock-up (results not shown) did not reveal the presence of either vaterite or ACC, meaning that they can be monitored for evaluating the penetration depth and chemical evolution of the calcium acetoacetate consolidant in the CaCO_3 -based substrate.

As Figure 1C shows, vaterite (green), formed by the consolidant application, is present as a uniform layer (thickness of *ca.* 60-100 μm) at the surface of the sample (Area-II). In the porosities of the calcite-based matrix (red), both ACC (Area-I: blue) and vaterite have been found. The presence of both vaterite and calcite has

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