EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal: *https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do*

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report")*,
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- 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.

ESRF	**Experiment title:** Investigating the effect of amino acid incorporation into the crystal lattice of magnetite: from structure to magnetic properties	**Experiment number**: ES-1118
Beamline: ID-22	**Date of experiment**: from: 26/04/2021 to: 30/04/2021	**Date of report**: 24/07/2022 *Received at ESRF:*
Shifts: 12	**Local contact(s)**: Giorgia Confalonieri	

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Report:

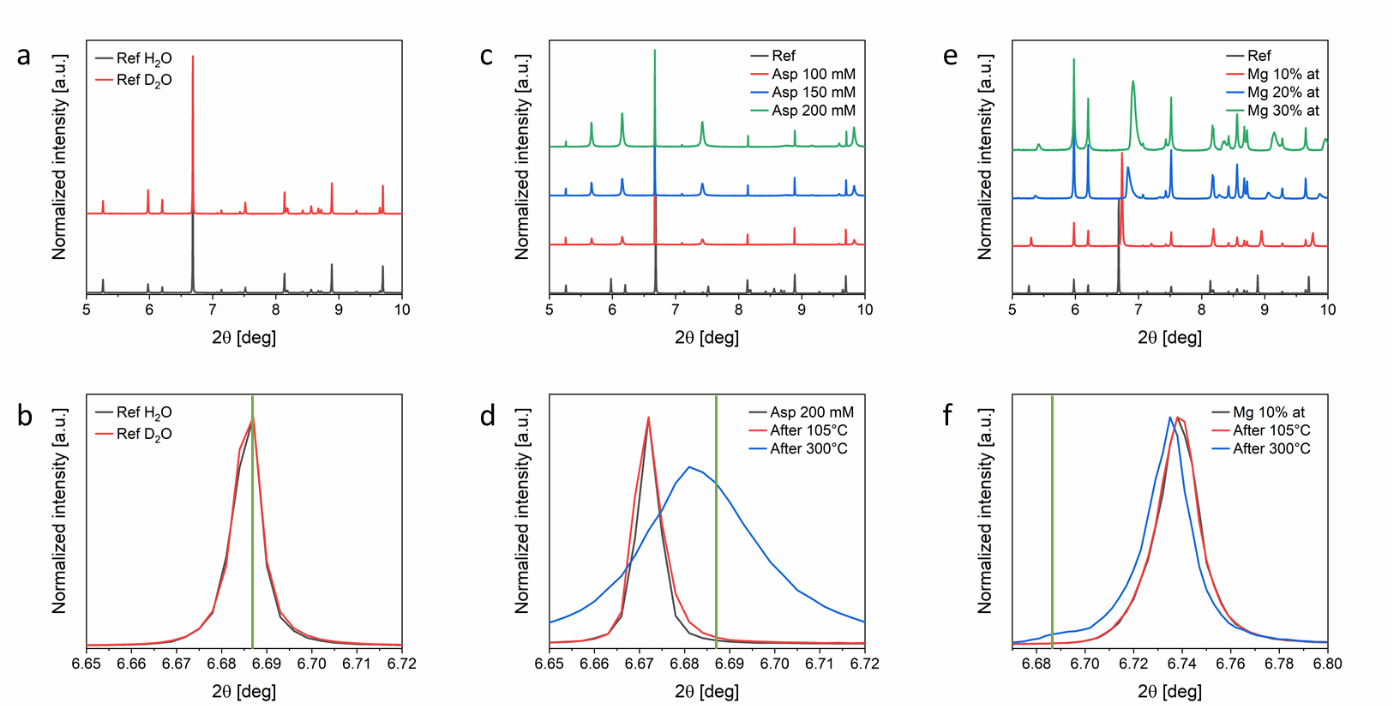

Figure 1. HR-PXRD results: (a) Diffraction patterns of reference CaCO$_3$ grown in H$_2$O and D$_2$O. (b) The (104) reflection in (a), Showing no change. (c) Diffraction patterns of CaCO$_3$ grown in D$_2$O in the presence of different concentrations of aspartic acid. (d) The change in the (104) reflection of the Asp-incrporated calcite after annealing. (e) Diffraction patterns of CaCO3 grown in D$_2$O in the presence of different concentrations of Mg. (f) The change in the (104) reflection of the Mg-incrporated calcite after annealing. Green vertical lines mark the position of the (104) reflection of pure calcite.

We synthesized $CaCO_3$ using a previously reported hydrothermal method.[1] Here, the Ca^{+2} and CO_3^{-2} solution were prepared in D_2O. The percipitaiton solution, containing the Ca-CO_3 mix, together with a known amount of additives (aspartic acid or Mg) was sealed in bottles prior to placing in the autuclave, in order to minimize the penetration of H_2O from the autoclave itself.

First, we wanted to see whether replacing H_2O with D_2O has an effect on the resulting $CaCO_3$. **Figure 1a** demonstrates that in both cases the resulting phase is calcite, with some aragonite impurities (as expected from high-temperature gron $CaCO_3$).[2] Morover, zooming-in on the (104) reflection (**Figure 1b**) proves that both samples have the same lattice parameters, as it is positioned exactly in the same 2θ value.

To study how the water content in calcite is affected by organic incorporation, which tends to induce lattice expansion, we synthesied $CaCO_3$ in the presence of aspartic acid (Asp) – the amino acid with the highest incorporation level in calcite.[1,3] As predicted, the addition of Asp promotes the formation of vaterite:[4] **Figure 1c** shows that the more Asp is added to the percipitation solution, the higher the amount of vaterite in the sample gets. Moreover, as demonstrated in **Figure 1d**, Asp incorporation induces lattice excpansion, *i.e.*, shift of the diffraction peaks to smaller 2θ values. This shift is relaxed upon thermal annealing at 300ºC, which is also accompannied by a massive peak broadning (due to new defects appear during organics decomposition). Note, that annealing at 105ºC does not affect the diffraction peak position, hence does not provide a method to monitor the evaporation of water from within the crystal.

Next, to study how the water content in calcite is affected by inorganic incorporation, we synthesized $CaCO_3$ in the presence of Mg anions, which are known to induce lattice contractions.[5] **Figure 1e** indeed demonstrate the shift of the diffraction peaks to higher 2θ values. However, for Mg concentration higher than 10% at, the dominant phase is aragonite.[2] For Mg-calcite, thermal annealing at 300ºC induced a small diffraction peak relaxation (**Figure 1f**), as some of the Mg goes out of the calcite structure to form MgO. Again, in this case, annealing at 105ºC does not result in any observable change.

Future work:

Next, after collection of HR-PXRD data, we plan to perform Rietveld refinement (using GSAS-II[6]) to calculate the structural parameters of our calcite samples. Then, we will use time of flight secondary ions mass spectroscopy (ToF-SIMS) in order to measure the amount of water trapped in our crystal. The use of D_2O during synthesis should allow to distinct the trapped water originate from the crystallization process, from water from other sources (washing and humidity, for example). Finally, we hope to correlate between these two features, and understand how additives, which induce changes in the crystal structure of calcite, affet the amount of trapped water in the crystal.

References:

[1] S. Mijowska, I. Polishchuk, A. Lang, E. Seknazi, C. Dejoie, S. Fermani, G. Falini, N. Demitri, M. Polentarutti, A. Katsman, B. Pokroy, *Chemistry of Materials* **2020**, *32*, 4205.
[2] N. A. J. M. Sommerdijk, G. de With, *Chemical Reviews* **2008**, *108*, 4499.
[3] S. Borukhin, L. Bloch, T. Radlauer, A. H. Hill, A. N. Fitch, B. Pokroy, *Advanced Functional Materials* **2012**, *22*, 4216.
[4] H. Tong, W. Ma, L. Wang, P. Wan, J. Hu, L. Cao, *Biomaterials* **2004**, *25*, 3923.
[5] N. Bianco-Stein, I. Polishchuk, A. Lang, G. Atiya, J. Villanova, P. Zaslansky, A. Katsman, B. Pokroy, *Acta Biomaterialia* **2021**, *130*, 362.
[6] B. H. Toby, R. B. von Dreele, *Journal of Applied Crystallography* **2013**, *46*, 544.