ISIS@MACH ITALIA

Science and Technology Facilities Council
ISIS Neutron and Muon Source

Experiment Proposal

Experiment number GP2023014

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Experiment title	Preparation of TEM lamellae of CaREE-flourcarbonates with the FIB lift-out technique		
MRF Instrument	**FIB-SEM GAIA 3**	**Days requested:** 3	
Access Route	Direct Access	**Previous GP Number:** no	
Science Areas	Environment	**DOI:** -	
Sponsored Grant	None	**Sponsor:** -	
Grant Title	-	**Grant Number:** -	
Start Date	-	**Finish Date:** -	
Similar Submission?	-		
Industrial Links	-		

Non-Technical Abstract CaREE-fluorcarbonates (CRFC) are main ore for rare earth elements (REE). REE are critical raw materials for electronics and green technologies and there is a global concern for their supply and recycling, Mineralogical and crystallographic studies on CRFC may shed light on their nature and genesis processes. The CRFC we are currently studying are systematically found in miarolitic cavities located in Cuasso al Monte (VA). These rocks, hydro-thermalized outcrops (not good for the market) and quarry wastes are rich of REE. The CRFC are normally less than 100 μm in size, and to be fully characterized a TEM is required. Before that, thin TEM lamellae must be extracted from such microscopic samples, a task sometimes more difficult than the TEM observation itself and possible only via the FIB lift-out technique.

Publications -

ISIS neutron and muon source	**IM@IT E-platform:** No
Instruments	**Days Requested:**
Access Route	**Previous RB Number:**
Science Areas	**DOI:**
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Sample record sheet

Principal contact Professor Giancarlo Capitani, University of Milano-Bicocca, ITALY
MRF Instrument **FIB-SEM GAIA 3** **Days Requested:** 3
Special requirements:

SAMPLE

Material	Ca and REE fluorcarbonate synchysite-(Ce) embedded in epoxy and polished	-	-
Formula	Ca(Ce,La, Nd)(CO3)2F with inclusions of hematite (Fe2O3) and thorite (ThSiO4) imbedded in epoxy	-	-
Forms	Solid		
Volume	7 cc		
Weight	9 g		
Container or substrate	Epoxy	-	-
Storage Requirements	-	-	-

SAMPLE ENVIROMENT

Temperature Range	room - K	-	-
Pressure Range	room - mbar	-	-
Magnetic field range	none - T	-	-
Standard equipment	None	-	-
Special equipment	none	-	-

SAFETY

Prep lab needed	Yes	-	-
Sample Prep Hazards	no	-	-
Special equip. reqs	TEM grids for FIB applications to fix the lamellae	-	-
Sensitivity to air	No	-	-
Sensitivity to vapour	No	-	-
Experiment Hazards	no	-	-
Equipment Hazards	-	-	-
Biological hazards	no	-	-
Radioactive Hazards	The amount of Th dispersed in the sample is so small that there is not detactable effect	-	-
Additional Hazards	-	-	-
Additional Details	-	-	-
Sample will be	Returned to user by instrument scientist (when inactive)	-	-

ISIS@MACH ITALIA Experimental Proposal – Preparation of TEM lamellae of CaREE-flourcarbonates with the FIB lift-out technique

1. Background and context

CaREE-fluorcarbonates (CRFC) are main ore for rare earth elements (REE). REE are critical raw materials for electronics and green technologies and there is a global concern for their supply and recycling, in particular from EC countries, which are completely dependent from China. Consequently, many efforts are being spent in geological exploitation, improvement of metallurgical processes and recycling REE from mine waste and RAEE (electronic waste). It is universally recognized, as well as often forgotten, that fundamental research is the nourishment of applied research. Mineralogical and crystallographic studies on CRFC may shed light on their nature and genesis processes, eventually suggesting more successful prospection routes, enhanced metallurgical processes and recycling strategies. In this context, since a few years, at the DISAT, we have undertaken a study of CRFC of the bastnäsite-synchysite series from several localities, in Italy (Cuasso al Monte (VA), Cinquevalli (TR)) and outside Italy (Malawi, Turkey), with the aim to contribute to the above issues. The study has been supported by university funding, both competitive (FAQC2022, 25'000 €) and non (FAQD) from 2017 to 2021 (total 7283 €) and a project has been submitted to MUR PRIN2022 (under evaluation). Over the years, the study has involved several bachelor and master degree students and it is currently the subject of a PhD thesis; it has produced three peer review papers on international journals [1-3] and two more are in preparation. The current proposal aims at finalizing the work in progress.

2. Proposed experiments

The CRFC we are currently studying are systematically found in miarolitic cavities in a granophyre located in the Western Southern Alps (Cuasso al Monte (VA)). These rocks have been never regarded as ore for REE, but rather as dimension stones. Nevertheless, hydro-thermalized outcrops (not good for the market) and quarry wastes are rich of REE. The CRFC are normally less than 100 µm in size, have hexagonal prismatic habit, reddish color and an evident zonation (Fig. 1). The latter microstructural aspect is very intriguing, since unveiling inhomogeneous REE distribution, with a Ce-rich core and a Y-rich rim. The rim is also enriched in Th and plenty of Fe-oxides (hematite, determined by Raman). This microstructure may convey information about the minero-genesis, which may potentially guide any ore prospection operation. Moreover, since the difficulty affecting the separation of REE in metallurgical processes, it would be of paramount importance to understand the Ce/Y fractionation process operated by nature. The last but not the least, given the huge environmental problem caused by the association of Th to every REE deposit, the understanding of the processes underlying the Th mobility may help in the design of cleaner metallurgical processes. To get access to all this information, the investigation must move down to the nanometer scale, a dimension accessible exclusively by transmission electron microcopy (TEM). Before that, thin TEM lamellae must be extracted from such microscopic samples, a task sometimes more difficult than the TEM observation itself and possible only via the FIB lift-out technique [4]. Basically, a wedge shaped lamella ~20 µm in length must be cut out across the core-rim interface and extracted, welded on a special TEM-FIB grid and further thinned down to electron transparency (Fig. 2), then we are ready to go to TEM!

3. Summary of previous experimental proposals or characterisation

The proposal has never been submitted before but the samples have been characterized by a variety of techniques, including scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), single crystal X-ray diffraction and Raman spectroscopy. Overall, these techniques revealed that the CRFC are synchysite-(Ce), with inclusions of hematite (Fe_2O_3) and thorite ($ThSiO_4$) and with the microstructure and chemical zoning described above. A TEM investigation focused on the core/rim interface would complement these information, possibly leading to a genesis model. Previous TEM studies on similar samples from other localities have shown syntactic (crystallographically oriented) intergrowths of different CRFC, compositional and polytypic faults and new polymorphs. All together, these observations have contributed to better define the bastnäsite-synchysite series and to speculate on the formation of the ore.

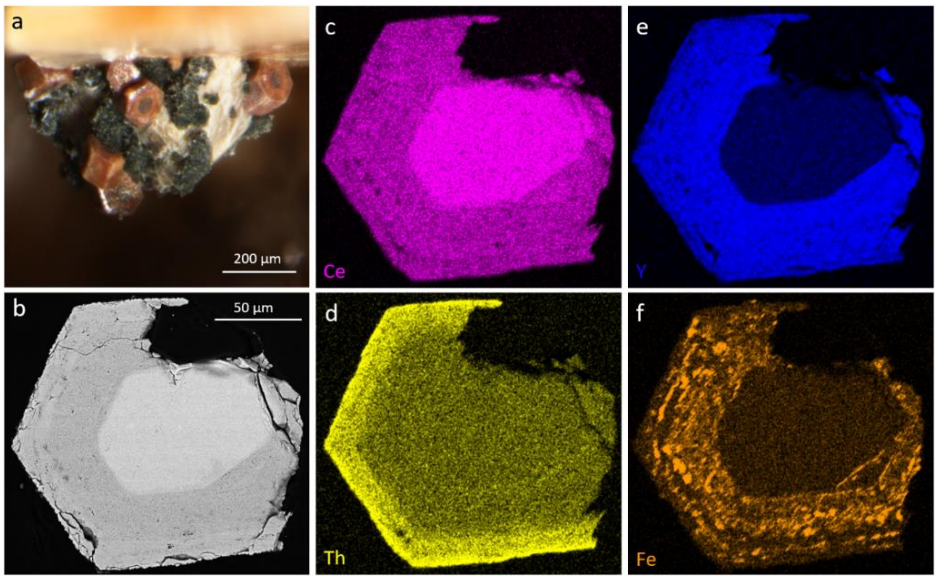

Figure 1. (a) Optical micrograph showing the Ca-REE fluorcarbonates samples within a miarolitic cavity. (b-f) SEM-EDS images showing the chemical zonation. The Ce content is greater in the core with respect to rim (c), whereas Y and Th show an opposite trend (e,d). Fe-oxides inclusions are present only in the rim (f).

4. Justification of experimental proposals request

Based on the above, it should appear clear that this study requires a TEM investigation to complement the data so far acquired. The size and shape of the sample require a dual beam instrument to prepare TEM lamellae. Whereas we can rely on a 200 kV TEM for the observations, we do not have a dual beam instrument to prepare the TEM lamellae at our facility. So, in the first instance, we only need TEM lamellae to proceed with our study. However, we do not exclude a priory to apply in the future for TEM observations. Considering the dimension of the sample and the volume affected by the extraction of the lamella, the preparation of 4 lamellae appears feasible. Four lamellae seems a reasonable number, considering the poor stability of the CRFC under the electron beam and the diversity of TEM techniques planned (analytical TEM, high resolution, diffraction tomography). On the basis of previous experiences, a three-day working time should be enough to accomplish the mission.

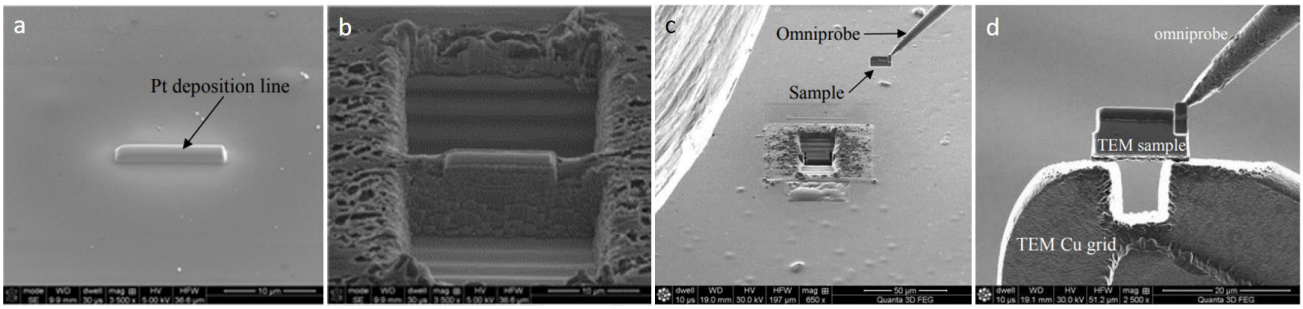

Figure 2. SEM images of lamella preparation steps: (a) Deposition of a Pt strip to protect the extraction area; (b) Cut out the lamella with the ion beam; (c) Lamella extraction with a micromanipulator; (c) Welding the lamella on a TEM grid for further milling.

[1] Capitani, G. HRTEM Investigation of Bastnäsite–Parisite Intergrowths from Mount Malosa (Malawi): Ordered Sequences, Polysomatic Faults, Polytypic Disorder, and a New Parisite-(Ce) Polymorph. *ejm* **2019**, *31* (3), 429–442. https://doi.org/10.1127/ejm/2019/0031-2824. [2] Capitani, G. Synchysite-(Ce) from Cinquevalli (Trento, Italy): Stacking Disorder and the Polytypism of (Ca,REE)-Fluorcarbonates. *Minerals* **2020**, *10* (1), 77. https://doi.org/10.3390/min10010077. [3] Conconi, R.; Fumagalli, P.; Capitani, G. A Multi-Methodological Study of the Bastnäsite-Synchysite Polysomatic Series: Tips and Tricks of Polysome Identification and the Origin of Syntactic Intergrowths. *msam* **2022**. https://doi.org/10.2138/am-2022-8678. [4] Hyun Jung, K.; Sang, H., C.; Hung-Bin, B.; Tae Woo, L. Transmission Electron Microscopy (TEM) Sample Preparation of Si1-XGex in c-Plane Sapphire Substrate. *NASA/TM–2012-217597* **2012**, 39 pp. https://ntrs.nasa.gov/citations/20120013304.