Long Term Project Report : Interim/Final

Summary Page

Proposal Number: ES1018

1. Beamtime Used

Please give a short summary of progress for each scheduling period for which beamtime has been allocated/used :

Scheduling period	Beamline(s) Used	Shifts Used	Summary of results obtained
2022/I	ID15A	15	Elemental distribution of Ca-phosphates and carbonates in mm-sized samples of CM2 meteorites embedded in epoxy, as analog material in preparation for analysis of Bennu asteroid material from NASA's OSIRIS-REx sample return mission.
2022/II	ID15A	15	Identification of the main mineral phases and high-Z trace elements, including rare earth elements (REEs) in Ryugu asteroid material brought to Earth in the JAXA's Hyabusa2 sample return mission.
2023/I			
2023/II			
2024/I			
2024/II			

2. **Resources Provided by User team (financial, personnel, technical...).** Please clearly indicate for each resource listed whether this resource remains permanently on the beamline or not, e.g. PhD student shared at 50% between user group and ESRF beamline, equipment purchased remaining permanently on the beamline or purchased for the user group only, etc:

A contribution to the LTP will be part the new high-resolution sample stage which ID15A is planning to acquire. In particular a set of combined xy and tilt stages for sample alignment on the rotation axis or a hexapod (which would serve as xy and tilt stages) will be acquired. The sample alignment stage will require moderate precision, see parameters below.

	Tilt X	Tilt Y	Translation X	Translation Y
Range (mm or mrad)	±150	±150	±5	±5
Max speed (mm/s or mrad/s)	20	20	1	1
Accuracy (µm or µrad)	100	100	5	5
Minimum incremental motion (µm or µrad)	20	20	1	1
Repeatability (µm or µrad)	50	50	1	1

Funding for the extra instrumentation (e.g. the above part of the new high-resolution sample stage at ID15A) for the XRF/XRD tomography experiments are being acquired from a parallel project proposal to the Belgian Research Foundation Flanders (FWO) amounting to 80 kEUR.
In terms of personnel, during the first year of the LTP, Ph.D. student B. Bazi (Ghent University) was permanently stationed at the ESRF DUBBLE beamline and closely collaborated with the ID15A group on site to improve on the detection conditions available for micro-XRF at ID15a.

3. **Technical and Scientific Milestones Achieved** (in relation to the milestones identified in the original proposal)**:**

Year 1
Two ID15A beamtimes were scheduled for the first year of our LTP: June 2022 and January 2023.

June 2022:
Due to the timing of sample allocation from JAXA's Hayabusa2 project, the dress rehearsal for the OSIRIS-REx project (originally scheduled in our LTP as a milestone in the first half of Year 3) was brought forward to our first LTP beamtime in June 2022. Here we measured Ca-phosphates and carbonates within two CM2 meteorites, as analogue material for the samples expected from the aqueously altered asteroid Bennu at the end of 2023. The Winchcombe meteorite is particularly interesting, since it is a meteorite that was seen to fall very recently (2021) in the UK and was recovered immediately for analysis before terrestrial weathering could occur.

One of the main technical aims of this beamtime was, for example, to determine the optimal orientation of the sample relative to the two detectors (one Si-based, one Ge-based) and the beam in order to reduce the noise-to-signal ratio for a similar sample size (1-2 mm) and mount (embedded within a 25 mm epoxy disc) to those expected in the Bennu samples. For this, two different orientation set-ups were employed (Fig. 1): Firstly with the sample at 45° to the beam and 45° to the two detectors; Secondly with the sample at 80° to the beam and 10° to the two detectors. Where the first option reduced the absorption on way to the Si-detector, absorption was greater on way through the epoxy towards the Ge-detector, the latter being important for the detection of rare-earth elements (REEs). It was determined that this measurement approach is sub-optimal, and instead efforts were made to allow sample surface mounting perpendicular to the beam direction, and instead place both detectors under ±10° angle with respect to the sample surface. Less shallow angles are unfortunately infeasible at the beamline due to mechanical constraints and the KB optic focal distance. With the second option, a regular adjusting of the sample ±20° allowed both detectors to have direct access to the sample without absorption through the epoxy disc which, however, required double scanning and time loss. In general overview scans of the samples were performed using 1-5 µm step sizes and 0.1-1s/pt acquisition rates. Subsequently, select regions of interest are identified and investigated following higher resolution scans and/or stationary point measurements with longer acquisition times, thus enhancing the sensitivity towards trace element identification and quantification.

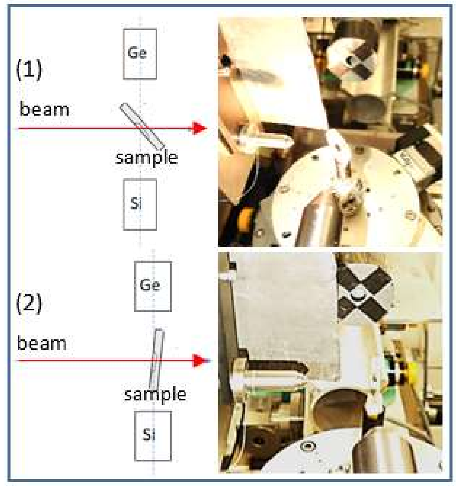

Fig. 1: Two sample orientation set-ups for relative to the detectors and incoming beam.

Scientifically, we were able to analyse Ca-phosphates and carbonates observed within these two samples, including the observation and analysis of a Ca-phosphate-rich rim (around a phyllosilicate nodule) that was revealed to be also Y- and REE-rich (Fig. 2). This appears to be a rare occurrence and testifies to intense aqueous alteration on the parent asteroid and possibly a change in acidic conditions. Like the material from the asteroid Ryugu that we analysed in the preceeding (inhouse) beamtime in 2021, this confirms Ca-phosphates to be the main REE-bearing minerals in this CM2 carbonaceous material. These data are currently being presented at the LPSC conference in Houston [1] and a manuscript is currently being prepared.

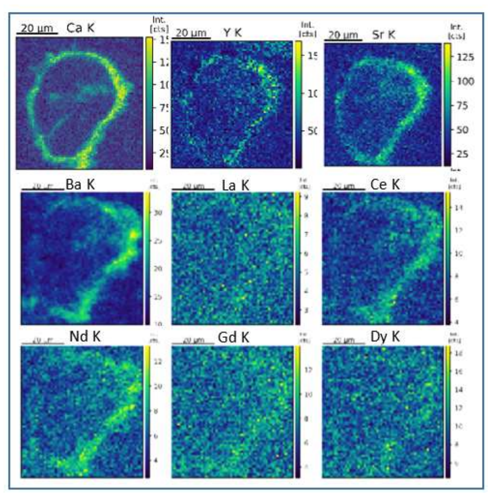

Fig. 2: Elemental maps of Ca-REE-rich rim of a phyllo-silicate nodule in the Winchchombe meteteorite.

January 2023

Further to our initial-stage analysis at ID15A (during the inhouse beamtime in July 2021) of mm-sized particles from the asteroid Ryugu as part of JAXA's Hayabusa2 sample return mission, the results of which have been presented at two conferences [2,3,4,5] and published in two international journals [6,7], we were able to deepen our investigation of Ryugu material with much smaller particles (100-500 µm). These particles were mounted onto glass capillaries 100 µm in diameter. In accordance with the milestone scheduled for the second half of Year 1 of the LTP, we were able not only to identify the main mineral phases but to determine the distribution of high-Z trace elements, including REEs. In particular, Ca-phosphates, the main REE-bearing mineral, were scanned with an aim to understanding more about their REE-concentrations. While quantitative data processing is still ongoing, qualitative results show the presence of large Ca-phosphates (20-25 µm) that are clearly REE-enriched (Fig. 3). Further data processing will determine the REE concentrations and trends within these Ca-phosphates and reveal whether these are single grains or clusters of smaller grains. Two publications are currently being prepared for submission to the main meteoritic journal, Meteoritics and Planetary Science, at the end of March for inclusion in their special edition regarding Ryugu.

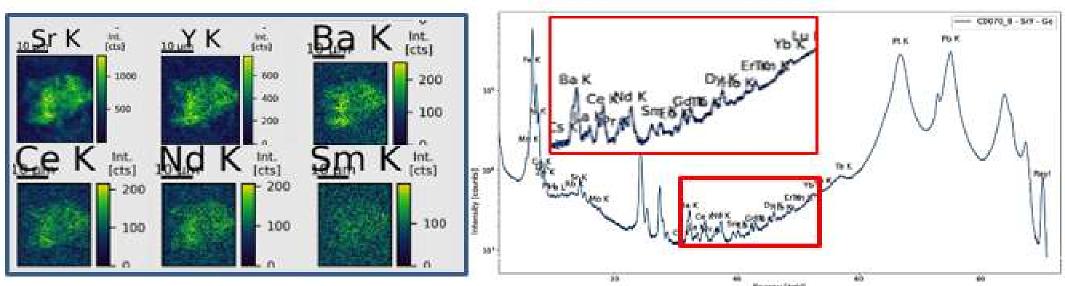

Fig. 3: Elemental maps (including REEs) and spectra of a Ca-phosphate grain in Ryugu sample C0070-8.

During these experiments, similar measurement conditions as previous tests were applied, aside from the implementation of the improved detection geometry where the detectors are mounted under shallow angles with respect to the sample surface, whereas the latter is mounted perpendicular to the primary excitation beam. Additionally, a specialised dual-pinhole detector collimator was designed for use with the Ge detector, thus restricting the detector field of view to a narrow volume (approx. 1mm diameter) surrounding the sample-beam point of incidence, and reducing unwanted spectral contribution originating from the surrounding instrumentation. The application of such a collimator has a positive effect on the signal-background ratio compared to alternatively available collimators. These findings are envisioned to be published in the scope of a more methodological manuscript (Analytical Chemistry, Spectrochimica Acta B).

Year 2

Year 3

4. List of publications directly resulting from beamtime used for this Long Term Project:

[1] **Tkalcec et al.** (2023). REE-rich, Ca-phosphate rim around a phyllosilicate nodule in the Winchcombe carbonaceous chondrite – witness of intense aqueous alteration on the parent body. Abstract #1485, 54th Lunar and Planetary Science Conference, Houston, Texas, USA.

[2] **Brenker et al.** (2022). Synchrotron-based trace element analyses of a magnetite vein cross-cutting a mm-sized Ryugu rock fragment. Abstract #6169, 85th Annual Meeting of The Meteoritical Society, Glasgow, Scotland.

[3] **Tkalcec et al.** (2022). Rare earth element analysis by SXRF of two Ryugu rock fragments collected during the Hayabusa2 space mission. Abstract #6238, 85th Annual Meeting of The Meteoritical Society, Glasgow, Scotland.

[4] **Brenker et al.** (2022). Synchrotron-based trace element analyses of a magnetite vein cross-cutting a mm-sized Ryugu rock fragment. Abstract #1264, 53rd Lunar and Planetary Science Conference, Houston, Texas, USA.

[5] **Tkalcec et al.** (2022). Initial REE analyses of mm-sized, non-air-exposed Ryugu rock fragments by high-energy synchrotron XRF. Abstract #2130, 53rd Lunar and Planetary Science Conference, Houston, Texas, USA.

[6] **Nakamura et al.** (2022). Formation and evolution of carbonaceous asteroid Ryugu: Direct evidence from returned samples. *Science,* 379:3364, https://doi: 10.1126/science.abn8671

[7] **Tack et al.** (2022). Rare earth element identification and quantification in millimetre-sized Ryugu rock fragments from the Hayabusa2 space mission. *Earth Planets and Space,* 74:146, https://doi.org/10.1186/s40623-022-01705-3