INITIAL REE ANALYSES OF MM-SIZED, NON-AIR-EXPOSED RYUGU ROCK FRAGMENTS BY HIGH-ENERGY SYNCHROTRON XRF. B. J. Tkalcec[1*], B. Bazi[2], F. E. Brenker[1], E. De Pauw[2], M. Di Michiel[3], M. Lindner[1], P. Tack[2], B. Vekemans[2], K. Amano[4], E. Kagawa[4], M. Kikuiri[4], T. Morita[4], T. Nakamura[4], H. Naraoka[5], T. Noguchi[6], R. Okazaki[5], K. Sakamoto[7], S. Tachibana[7,8], Y. Tsuda[7], S-I. Watanabe[9], H. Yabuta[10], H. Yurimoto[11] and L. Vincze[2]. [1]Goethe University, Altenhöferallee 1, 60438 Frankfurt am Main, Germany; [2]Ghent University, Krijgslaan 281 S12 9000 Ghent, Belgium; [3]ESRF - The European Synchrotron, 71 Avenue des Martyrs, 38000 Grenoble, France; [4]Tohoku University, Sendai 980-8578, Japan; [5]Kyushu University, Fukuoka 812-8581, Japan; [6]Kyoto University, Kyoto 606-8502, Japan; [7]ISAS/JAXA, Sagamihara 252-5210, Japan; [8]The University of Tokyo, Tokyo 113-0033, Japan; [9]Nagoya University, Nagoya 464-8601, Japan; [10]Hiroshima University, Higashi-Hiroshima 739-8526, Japan; [11]Hokkaido University, Sapporo 060-0810, Japan. *tkalcec@em.uni-frankfurt.de

Introduction: Identification of the REE-bearing phases, and their distribution, within untouched mm-sized rock fragments returned in the Hayabusa2 mission can provide insight into the behaviour of the Ryugu REEs during the asteroid's aqueous alteration history. This will in turn help us to understand the asteroid's thermal and geological evolution. Three 2-mm-sized Ryugu rock fragments, A0055, C0033 and C0076, were analysed by high-energy synchrotron XRF (SXRF) at the ID15A beamline at the ESRF in Grenoble [1]. Rock fragment A0055 had been collected during the first touchdown, and rock fragments C0033 and C0076 from the second touchdown site could be from the asteroid's subsurface (ejecta of the Hayabusa2-made artificial crater). Prior to SXRF analysis no sample preparation was performed on the Ryugu rock fragments, apart from mounting on a sample holder pin. Not having yet been exposed to terrestrial air, all three rock fragments had been kept within a protective polyimide cap under N_2 conditions. The condition of non-exposure to air was maintained during synchrotron XRF analysis at the ESRF. Here we show some of the initial results of our high-energy SXRF analyses of 2-mm-sized Ryugu rock fragments.

Experimental Set-up: The Kirkpatrick-Baez (KB) mirror based system delivered a 0.5×0.5 µm² X-ray beam. The excitation energy E_0 was set at 90 keV. The induced fluorescent radiation was registered using two detectors, a Mirion Technologies (Canberra) HPGe detector for the high-energy and a Hitachi Vortex Si-drift detector for the low-energy XRF emissions from the rock fragment being analysed. SXRF tomographic overview scans of the 2-mm-sized Ryugu rock fragments, typically performed at a pixel size of 5 µm and an acquisition time of 0.2 s/point, provided the distributions of major, minor and trace elements, including REEs. Closer examination of selected regions of interest (ROIs) was performed by tomographic cross-section scans, point measurements and local ROI volume scans.

Results: Overview SXRF scans of the full rock fragments reveal that the spatial distribution of Ca not only coincides with that of Sr, Ba and Cs, but also partly coincides with the discrete enrichments of REEs such as Ce, Nd, Sm and Gd. An example is shown in Figure 1, where both Ca and Ce enrichments coincide in the same position, subsequently identified as apatite. In contrast, Ce, Nd, Sm and Gd enrichments were not observed in some other Ca-rich areas, subsequently identified as dolomite. The identification of these two distinct Ca-rich phases as apatite and dolomite, respectively, was inferred by comparison of the targeted point analysis data (Fig. 2) with data from subsequent trace element and SEM analyses which revealed Y and Mn to be the distinguishing elements present in apatite and dolomite, respectively.

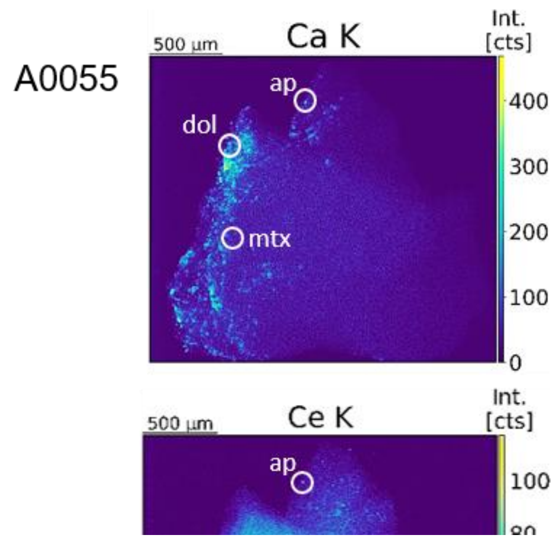

Figure 1: Ryugu fragment A0055: Ca-K map (top) showing Ca distribution as detected by the Ge-detector to the left of the sample. White circles show the positions of the point analyses of apatite, dolomite and matrix shown in Fig. 2. The Ce K map (bottom) serves to demonstrate an example of a REE enrichment of an apatite grain.

Selected point analyses of Ca-rich spots confirm clear REE peaks, specifically La, Ce, Pr, Nd, Sm, Gd, Dy, Er and Yb in apatite, but neither in carbonate nor in the matrix (Fig. 2). In addition, a clear Y peak is

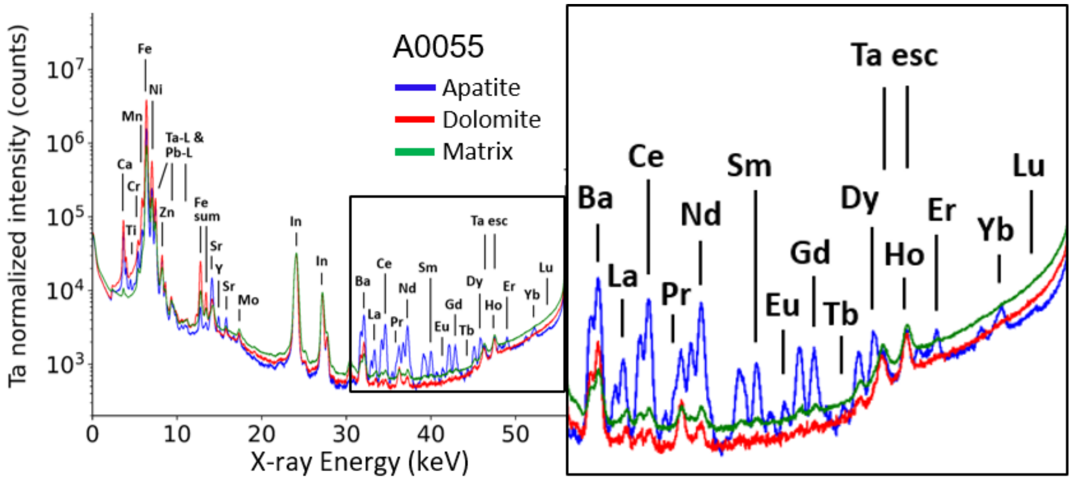

Figure 2: Results of point analyses (left) of three points of interest (an apatite grain, a carbonate grain and a point in the matrix, all marked by white circles in Fig. 1) in Ryugu rock fragment A0055. Ta, In and Pb are artefacts from detector shielding material. The intensity counts are thus normalised to Ta. The X-ray energy region for REE peaks is enlarged for visual clarity (right).

observed in the apatite grain but is absent in both the dolomite and matrix analyses. Mn is present in dolomite but absent in apatite. Sr is present in both apatite and dolomite, as it is characterized by a clear correlation with the Ca signal [2].

In the three rock fragments examined in this study apatite is observed to occur primarily as discrete grains dispersed throughout the samples. The distribution of discrete apatite grains appears to be random throughout the matrix as well as in a magnetite-rich vein [3]. Trace element quantification of the apatite grains reveals a noticeably flat REE profile some two orders of magnitude greater than that of the matrix and lacking any anomalies, such as Eu or Gd.

Discussion: These initial results of high-energy synchrotron XRF analyses of the three Ryugu rock fragments examined confirm apatite to be the main REE-bearing phase. This is in agreement with previous observations that Ca-phosphates are the main REE-bearing phases in meteoritic material [4,5]. The magnitude of REE enrichment in apatite relative to the matrix is roughly consistent with previous reports for chondrites [4]. Various REE patterns for Ca-phosphate grains in CI chondrites have been reported ranging from relatively flat to LREE-enriched to HREE-enriched and either with or without a (negative) Gd or (negative or positive) Eu anomaly [5]. The flat REE pattern observed in the Ryugu rock fragments examined here indicates that they had previously experienced no significant mass-dependent fractionation inducing process on the asteroid Ryugu. The lack of an Eu anomaly attests to the absence of plagioclase [e.g. 4]. The random distribution of discrete apatite grains throughout the matrix appears to be maintained also within an observed magnetite-rich vein [3].

The vast amount of data collected by high energy SXRF from the three 2-mm-sized Ryugu rock fragments are still being processed and next steps will include comparisons of the REEs in apatite grains from within the matrix with those found in the veins. Finally, it is noted that all the reported experiments were performed at high excitation energy with a microscopic beam, providing 2D and 3D information with microscopic resolution within the mm-sized rock fragments without compromising the integrity of the non-air-exposure protection cap, nor physically altering the rock fragments.

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