Phosphorus, Calcium, and Sulfur in Two Ryugu Samples

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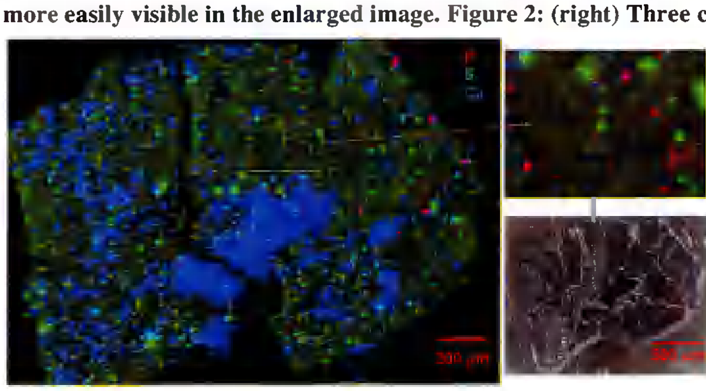
The Japanese Aerospace Exploration Agency (JAXA) Hayabusa2 spacecraft delivered the first samples of a primitive, carbonaceous asteroid to Earth. One of the objectives of the mission was to use the samples to characterize the formation and evolution of asteroid Ryugu or its parent body. The elemental compositions of some minerals, particularly apatite and, to a lesser extent, carbonate, are reflective of the composition of the fluid from which they were deposited. Because apatite, $Ca_{10}(PO_4)_6(OH,F,Cl)_2$, can host F, OH, or Cl in the anion position, its composition is a sensitive probe of the halogen and water content of the hydrothermal fluid from which it was deposited. However, the apatite structure is capable of tolerating relatively large structural distortions, allowing for diverse element substitutions, making other minor and trace elements in apatite a sensitive probe of fluid composition. Carbonate can also be deposited in hydrothermal processing, and some trace element contents can reflect fluid composition. In hydrous meteorites the carbonate crystals are generally much larger than the apatite crystals, so zoning from the interior to the rim in larger carbonates can indicate changes in the fluid composition during the formation. Sulfur, which condenses from the cooling Solar Nebula as schreibersite, an Fe-sulfide, interacts with an oxidizing fluid to alter to Fe-sulfate. In crystals where this alteration is incomplete the sulfide/sulfate ratio can indicate the degree of oxidation by the fluid. We are employing two synchrotron-based instruments to characterize the P, Ca, and S in hydrous meteorites and Ryugu samples to characterize the hydrothermal event(s) that occurred on the Ryugu parent body.

Samples and Instruments: We were loaned five samples of asteroid Ryugu from the Hayabusa2 collection to perform mineral identification, XRF mapping, and P, Ca and S X-ray Absorption Spectroscopy (XAS). The X-ray Fluorescence Microprobe (XFM) Beamline 4-BM of the National Synchrotron Light Source II at Brookhaven National Laboratory is a versatile XRF microscope for the characterization of elemental abundances and chemical speciation in heterogeneous materials, characterizing the K-, or L-lines of the heavier elements. XFM is an imaging beamline designed for spatially-resolved XAS spectroscopy in the 4-20 keV energy range, with a user-tunable spot size from 2 to 10 μm. The Tender Energy Spectroscopy (TES) Beamline 8-BM of the NSLS-II at Brookhaven National Laboratory, has a user-tunable spot size, varying from 10 x 25 μm, with a flux of up to 10^{11} photons/s, down to 1 x 2 μm, with a flux of up to 10^9 photons/s. A helium sample environment permits XRF element mapping down to 1 eV, for abundance mapping of elements as light as Na. The tunable monochrometer (2 to 5 keV) is optimized for K-edge XAS of elements from P to Ca.

Thus far, we have performed XRF maps of the polished surfaces of two of the five Ryugu samples using a 6 μm step size, at two energies; 7 keV, to provide maximum sensitivity for the low-Z elements while avoiding Fe K-edge fluorescence, in order to locate P-, S-, and Ca-bearing phases, particularly hydrothermal alteration products; and 13 keV, accessing heavier elements. The TES microprobe was then used to perform P, Ca, and S micro-XAS on targeted element hot-spots.

Results and Discussion: The initial XFM mapping (Figures 1 and 2) identified several likely effects of hydrothermal processing on the Ryugu parent body, some of which were characterized further by XAS using the TES instrument. The element distributions and associations were very similar to those we previously reported for several CM meteorites [1].

Figure 1: (left) Three color (P, S, Ca) map of Ryugu sample A0055-1, showing multiple Ca-rich grains (blue) including one a >0.5 μm in size, many S hot-spots (green), a few Ca and P bearing grains (purple), and several small P hot spots more easily visible in the enlarged image. Figure 2: (right) Three color (P, S, Si) map of Ryugu sample A0026-02.



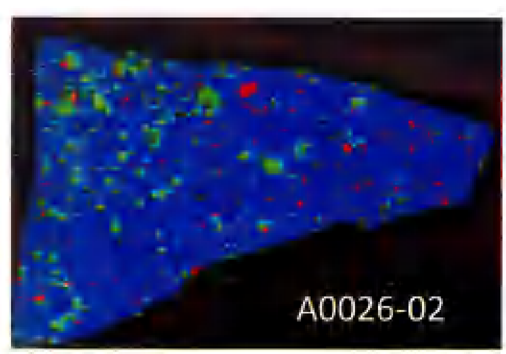
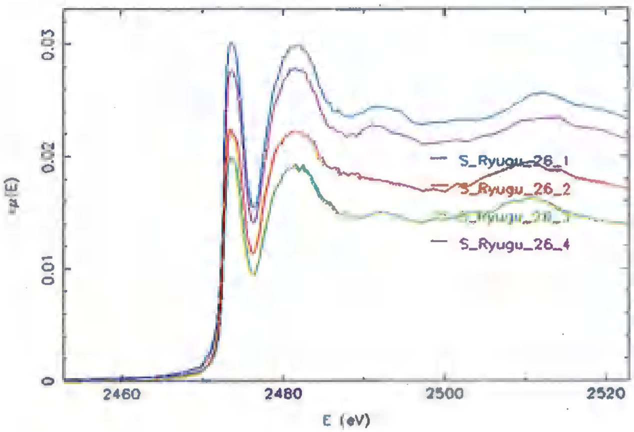
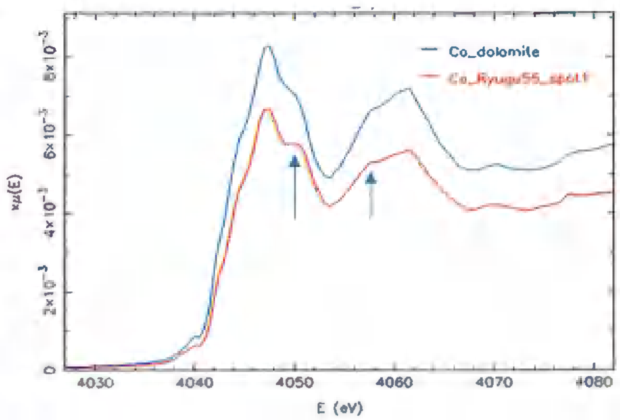


Figure 3: (left) P-XAS of three P hot-spots in A0055-1 that exhibit apatite spectra. Figure 4: (right) Ca-XAS of the large Ca hot-spot in A0055-1. The arrows indicate Ca-XANES features that distinguish dolomite (a bilayered carbonate) from calcite or magnesite (monolayered carbonates).





Apatite: Small P hot-spots were found in both A0026-02 and A0055-1. This P appeared in three distinct element associations (Figure 1): spots with both P and Ca (appearing pink), most likely apatite grains, small P hot-spots without Ca (red in the enlarged insert in Figure 1), which will be further analyzed by XAS, and spots with both S and P (yellowish green), potentially the high-P sulfides found in CM meteorites by Nazarov [2]. Three of the most intense P hot-spots in A0055-01 each have P-XAS spectra consistent with apatite (Figure 3), which is believed to be a hydrothermal alteration product in CM chondrites. These will be studied further to investigate their compositions.

Carbonate: Both samples contained Ca-bearing minerals, most likely carbonates >5 mm in size. One large carbonate, >0.5 mm in size , in A0055-1 was selected for further study. This large carbonate was identified as a dolomite by XAS (Figure 4). The dolomite area of interest contains a significant amount of Mn. Mn-XAS indicated the Mn is in the 2+ oxidation state, consistent with Mn in a bilayered carbonate. Element mapping of this large carbonate will be performed to search for zooning.

Sulfur: Sulfur hot-spots were identified in both samples. All four S hot-spots analyzed thus far in A0026-02 show XAS spectra consistent with pyrrhotite, with no detectable sulfate, consistent with models of Solar Nebular condensation which indicate that S condenses from the cooling gas as an iron-sulfide, resulting in the subsequent incorporation of this iron-sulfide into the Ryugu parent body. However, three of the largest S hot-spots in A0055-1 show mixed sulfide and sulfate in the same grain.

This suggests the sulfides in A0055-1 experienced significant hydrothermal alteration to produce sulfate. This observation is consistent with the alteration of sulfide to sulfate reported in six CM chondrites, where O-isotopic analysis indicated the alteration of sulfide to sulfate occurred on the asteroidal parent body (Airieau et al., GCA, 2005). We also identified an Fe-rich grain in A0055-1 that has an XAS spectrum consistent with magnetite, another mineral believed to be produced by interaction of Fe-metal with an oxidizing fluid. The presence of oxidized S in A0055-1 but only sulfide in A0026-02 may suggest different alteration histories for these two samples collected from the same site.

References

[1] Flynn, G. J. et al. 2022. Abstract #6290, 85th Annual Meeting of The Meteoritical Society. [2] Nazarov et al. 2008. Petrology, 17, 101–123. [3] Airieau et al. 2005. Geochimica et Cosmochimica Acta, 69 (16), 4167-4172.