Analysis of Ryugu Fluid Inclusions: An Update

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Introduction: The most direct and convincing evidence for the presence of water and organic molecules on protoplanetary bodies is provided by fluid inclusions trapped in secondary minerals [1]. Our previous work has demonstrated that early solar system fluids have survived as fluid inclusions in a Ryugu pyrrhotite crystal [2]. We hypothesize that the bulk molecular and isotopic composition of individual Ryugu fluid inclusions can be measured to provide ground truth for exploring and thermochemical modeling of the compositional and isotopic evolution of fluids in protoplanetary bodies including asteroids, comets and icy moons.

This presentation is an update on our efforts to make measurements of elemental, molecular and, in particular, isotopic compositions of individual aqueous fluid inclusions in Ryugu samples. The measurements we plan will permit us to (1) understand elemental composition of the aqueous fluids present on Ryugu's progenitor body, (2) track changes in the chemical and stable isotopic composition of altering fluids in small bodies over time, (3) verify the presence of organics in Ryugu fluids, (4) verify the reported significant CO_2 in Ryugu fluids, (5) measure O and H isotopes in preserved Ryugu fluids, (6) provide constraints on temperature range calculations for the mineralizing reactions being performed by other groups using mineral pairs, (7) measure sulfur/chloride and chloride/phosphorus ratios of Ryugu fluids. We note here that recent results from Enceladus reveal the importance of phosphorus in small body aqueous brines [3], indicating that our proposed research will benefit studies of all current ocean worlds.

Facilities: For the following XRCT and TOF-SIMS analysis, samples were prepared using the FEI Quanta 3D 600 Dual-beam Focused Ion Beam in the ARES -NASA-JSC Electron Beam Instrument Facility. For the X-ray Computed Tomography (XRCT) scans we used the Zeiss 620 XRM instrument at the University of Texas High-Resolution X-ray Computed Tomography Facility. For the Time of Flight-Secondary Ion Mass Spectrometry (TOF-SIMS) measurements we used the University of Texas Materials Institute's TOF-SIMS 6 instrument (ION-TOF GmbH) equipped with a pulsed Bi^+ analysis ion beam (30 keV ion energy) and a O_2^+ sputtering ion beam (1 kV ion energy). This TOF-SIMS instrument is capable of cooling the samples to -180ºC, and without this capability our measurements would be impossible.

Ryugu Fluid Inclusion Measurements: Our recent successful, coordinated, XRCT and TOF-SIMS analyses of individual fluid inclusions in a Ryugu pyrrhotite crystal demonstrated that they consist of water, CO_2, sulfur species, and organic material, with H^-, C^-, O^-, S^- and OH^- as the main fragments detected at these locations [2]. In addition, various amounts of F^-, Cl^- and Ni^- were found, together with Na^+, Mg^+, Al^+, Cr^+, K^+ and Ca^+. Larger organic fragments such as C_2^-, C_2H^-, C_3^-, CO^- and CN^- were also detected, indicating the presence in these inclusions of more complex organic molecules containing H, C, N and O. We can expect to see these and additional molecular fragments in other Ryugu fluid inclusions. TOF-SIMS breaks apart molecules - it does not make new ones. Therefore, all these identified species are fragments of once larger molecules which we can identify to some degree.

We made XRCT scans of Ryugu grains (A0175 and C0043) (Fig. 1). From these preliminary measurements we know that A0175 contains numerous pyrrhotite, carbonate, and, probably, apatite crystals with fluid inclusion candidates measuring at least 3-5 µm in diameter, which will permit our planned TOF-SIMS measurements.

Stable isotope Measurements: In the past year we have begun isotopic measurements of standards. This task has required use of the few well-characterized standard materials that are isotopically homogeneous at the sub-micron scale. There are few of these available at the current time. In preparation for addressing the Ryugu samples, we first measured the hydrogen and oxygen isotopic composition of synthetic fluid inclusions in halite using the M6 TOF-SIMS instrument in high mass resolution mode. The halite standards were prepared by Bob Bodnar and have trapped fluids with D/H of 0.0005 but unknown $^{18}O/^{16}O$. With continued calibration effort we will determine the instrumental mass fractionation for this instrument, but already we have learned that the hydrogen isotopes are best measured by setting the analysis gun in "Fast Imaging" High Spatial Resolution Mode, while setting the analysis gun in "Spectrometry" mode and keeping the analyzer in "All Purpose" increasing the mass resolution in "All Purpose" mode

(All Purpose Resolution, an optimal setting between high mass and high spatial resolution) is best for oxygen. These results will now permit us to revisit the fluid inclusions found in halite in the Monahans (1999) and Zag meteorites, permitting new D/H measurements to be made (this was preciously done by S. Itoh, Y. Yurimoto and coworkers [4]).

For O isotope measurements in Ryugu samples will use the UWQ-1 quartz standard developed at the University of Wisconsin [5] and provided by John Valley and Noriko Kita. Our initial session with this standard resulted in a measurement standard deviation of 5‰ for ^{18}O and ^{16}O. Unfortunately, we probably cannot usefully measure ^{17}O in our samples because of mass interference with ^{16}OH. Measurements of oxygen at a high mass resolution mode might result in usable results for ^{17}O, however we cannot operate at that mode for individual fluid inclusions, which generally require measurements to be made in a high spatial resolution mode. Fortunately, the two oxygen isotopes we can measure are sufficient to permit comparisons to be made with ongoing work on Ryugu solid mineral pairs (see [6-8]), such as dolomite/magnetite, by other groups with whom we are in regular contact (e.g. H. Yurimoto's and R. Greenwood's groups). This is important as the results for Ryugu samples to date are either in conflict or indicate a rather wide range of mineralizing solution temperatures, namely ~25°C by Greenwoods group [9] and ~100°C by Yurimoto's group [8].

For hydrogen isotope measurements we are currently using MORB SR02 glass provided by Laurette Piani (Centre de Recherches Pétrographiques et Géochimiques (CRPG), Nancy), which was developed by Etienne Deloule. This sample has the following composition: H_2O = 2600 ± 110 wt. ppm and deltaD = -81.8 ± 5.3 ‰. Using the M6 TOF-SIMS we have succeeded in measurements of D/H in this glass with a measurement standard deviation of 33‰. This result is adequate for our purposes.

Next Steps: Thus, the isotopic measurements we propose will take effort, but we can successfully make them. In the next 6 months we will begin to measure hydrogen and oxygen isotope concentrations in individual Ryugu fluid inclusions, beginning with pyrrhotite crystals first scanned by XRCT by Romy Hanna (Univ. Texas). These sulfides contain no structural oxygen and are thus well suited for oxygen isotope measurements, since we will not have to analytically separate counts from the oxygen secondary ion signal in the host minerals from the oxygen signal in the trapped fluids during data reduction.

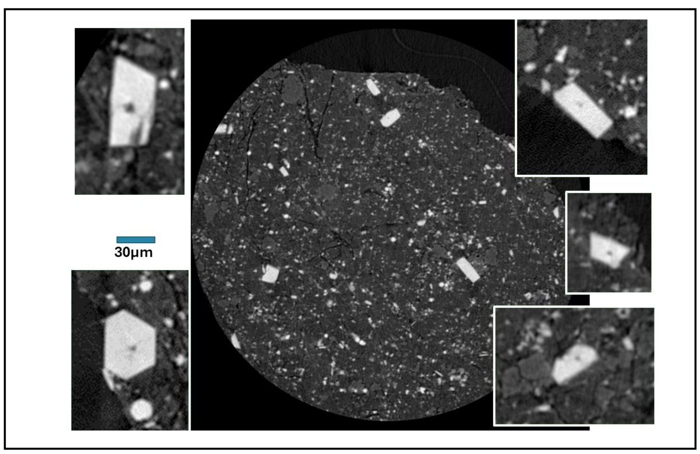

Figure 1. (Center) Portion of frame of the XRCT scan of Ryugu particle AO175, exhibiting numerous large pyrrhotite crystals (white). This sub-scan measures approximately 0.5 mm across. Set around the central image are higher magnification scans of pyrrhotite crystals identified in the particle, all at the same magnification. Probable fluid inclusions are visible as dark spots in the centers of each pyrrhotite crystal.

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