

Characterization Of Early Solar System Aqueous Fluids In Ryugu Samples

Michael Zolensky¹, Robert Bodnar², Andrei Dolocan³, JangMi Han⁴, Romy Hanna³, Iona Gearba³, Queenie Chan⁵, Trevor Ireland⁶, Megumi Matsumoto⁷, Akira Tsuchiyama⁸.

¹NASA JSC, Houston, TX 77058, USA (michael.e.zolensky@nasa.gov); ²Virginia Tech, Blacksburg VA 24060, USA; ³Univ. of Texas, Austin TX 78712, USA; ⁴University of Houston, Houston TX 77204, USA; ⁵Royal Holloway University, Egham Hill, Egham TW20 0EX, UK; ⁶University of Queensland, St Lucia 4072, Queensland, Australia; ⁷Tohoku University, Aoba-ku, Sendai, Miyagi, Japan; ⁸Ritsumeikan Univ., Kusatsu, Shiga, 525-8577, Japan

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. Our previous research has demonstrated that early solar system fluids have survived as fluid inclusions in a few astromaterials that escaped significant shock, terrestrial alteration, and invasive sample handling [1-3]. We hypothesize that the bulk molecular and isotopic composition of individual 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 isotopic compositions of individual aqueous fluid inclusions in Ryugu samples.

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 5 and TOF-SIMS 6 instruments (ION-TOF GmbH) equipped with a pulsed Bi⁺ analysis ion beam (30 keV ion energy) and a O₂⁺ sputtering ion beam (1 kV ion energy). The TOF-SIMS instruments are capable of cooling the samples to -160 and -180C, respectively, and without this capability our measurements would be impossible.

Aqueous Fluids: Studies of aqueous alteration in primitive meteorites, based solely on secondary mineral associations, have hinted that this process did not occur under a single set of conditions [4]. The temperatures of alteration that have been suggested are highly variable, from below 0 to ~250°C. The fluid compositions must have likewise varied, though this critical aspect is very poorly understood. Our previous molecular, O and H isotopic measurements of fluids in halite in the Monahans and Zag meteorites [2,5] have shown considerable variation in fluid composition even within individual crystals. For example, we suspect that early solar system aqueous fluids could alternate between being S-rich and S-poor, based on the alternating pyrrhotite-magnetite alteration assemblage observed in the Tagish Lake and Sutter's Mill chondrites [6]. We know from our previous studies of aqueous fluid inclusions in extraterrestrial halite and calcite in the Sutter's Mill C2 chondrite that the mineralizing fluids also contained a significant concentration of mineralizing cations such as Fe, Mg, Ca, and volatiles such as CO₂ and S-bearing compounds in variable abundances (though the abundances are not yet determined) [2,7]. We observed CN⁻, a molecular fragment of a larger nitrogenous compound, in the aqueous fluid inclusions in a Ryugu pyrrhotite crystal [1-3]. Nakamura et al. [3] reported that the earliest formed phyllosilicates in Ryugu were rich in Na, indicating significant compositional changes in the mineralizing fluid.

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, CO₂, sulfur species, and organic material, with H⁻, C⁻, O⁻, S⁻ and OH⁻ as the main fragments detected at these locations [1,3]. 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 C₂⁻, C₂H⁻, C₃⁻, 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.

Measurement of the stable isotopic compositions of aqueous fluid inclusions in Ryugu samples will enable a comparison with our measurements of a few fluid inclusions in carbonaceous chondrites (e.g. [7]), and fluids calculated to have reacted with other primitive samples (CI chondrites, OCs, HEDs, ureilites) which have δD ranging from ~0-3000‰. Actual direct measurements of preserved trapped fluids would thus inform us about fluid changes during aqueous alteration in a large suite of primitive bodies. Russell et al. [8] has suggested that CI materials form

two groups with distinct water/rock ratios, temperature ranges, and hydrogen isotope compositions. Are these truly distinct groups or do these just represent endmembers of a poorly sampled complete range (as also suggested by Russell et al., [8])? Our planned analyses of individual fluid inclusion oxygen and hydrogen isotope compositions in Ryugu samples will settle this issue as we will either observe narrow compositions or a compositional continuum.

Polished Ryugu sample C00025 contains large sulfides, magnesite, magnetite and dolomite crystals (Fig 1). We have already FIBed several foils from this sample and subjected one of the FIB foils to TOF-SIMS measurements. We detected no filled fluid inclusions, however we were limited to analyzing inclusions larger than about 3 μm using the M5 TOF-SIMS instrument, and it appears the inclusions were far smaller (Fig.1). We plan to repeat the measurements of this sample using the newly-installed M6 TOF-SIMS, which has greatly expanded capabilities. We made XRCT scans of two additional Ryugu grains (A0175 and C0043) (Fig 2). 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.

The TOF-SIMS analytical data are counts under the peaks for each species. An example of the data is shown in Figure 3, which shows counts for OH- (indicative of H₂O) and C- (here indicative of CO₂). This sample was a synthetic fluid inclusion standard (quartz) prepared by Bob Bodnar where the inclusions contained a 1:1 mixture of H₂O and CO₂. As you can see from the included table, despite the fact that the sensitivity of the technique for CO₂ was much lower than for H₂O, 4/5 of the inclusions showed consistent counts for these species, meaning that with continued calibration we can produce quantitative composition measurements for some species. We note that the signals for CO₂ we observed in the Ryugu pyrrhotite crystal were more pronounced than those we obtained using the 50:50 standard, suggesting a very high abundance of CO₂ in the Ryugu mineralizing fluid. In fact, solid CO₂ sublimed rapidly in a vacuum at our measurement temperature, making quantification very difficult.

In the coming year we will begin isotopic measurements of standards in synthetic fluid inclusions and Ryugu pyrrhotites and carbonates we have already identified, as well as increasing our stock of pre-analyzed Ryugu crystals.

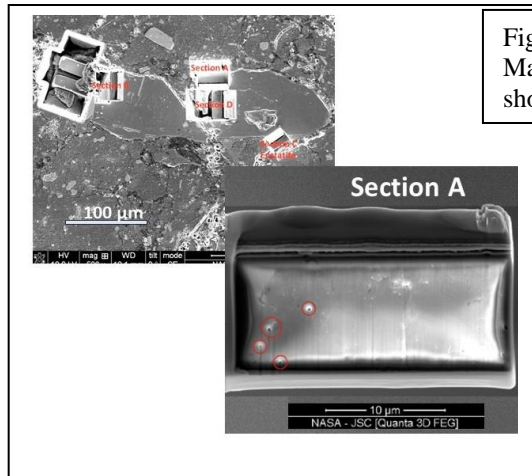
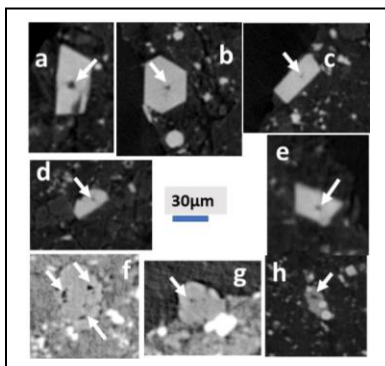


Fig. 1. Magnesite in Ryugu sample C00025 (left) BSE image of Magnesite showing FIB pits. (right) SEI image FIB A foil showing submicron-sized fluid inclusion candidates circled.

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References: [1] Zolensky et al. (2022) *85th Meeting of The Meteoritical Society*. Abstract 6011; [2] Bodnar et al. (2019) *50th LPSC Abstracts*; [3] Nakamura et al. (2022) *Science* **377**, 10.1126/science.abn8671; [4] Brearley (2005) In *Meteorites and the Early Solar System II*. D. S. Lauretta and H. Y. McSween Jr., Eds.; [5] Yurimoto et al. (2014) *Geochemical Journal* **48**, 1-12; [6] Zolensky et al. (2014) *MAPS* **49**, 1997-2016; [7] Tsuchiyama et al. (2021) *Science Advances* **7**, eabg9707; [8] Russell et al. (2022) *MAPS* **57**, 277–301.



(Left) Fig. 2. XRCT “slices” of Ryugu sample A0175. Fluid inclusion candidates are arrowed. (a-e) Pyrrhotite crystals. (f-g) Probable carbonates. (h) Possible apatite crystal.

(Right) Fig. 3. Results of TOF-SIMS measurements of synthetic fluid inclusion standard (quartz), with inclusions that contain a 1:1 mixture of H₂O and CO₂. Inclusions are numbered to match the table (e.g. ROI1=1). Counts = cts.

