DIRECT MEASUREMENT OF THE COMPOSITION OF AQUEOUS FLUIDS FROM THE PARENT BODY OF ASTEROID 162173 RYUGU. M. Zolensky[1], A. Dolocan[2], R. Bodnar[3], I. Gearba[2], J. Martinez[4], J. Han[5], T. Nakamura[6], A. Tsuchiyama[7,8], J. Matsuno[8], M. Sun[7], M. Matsumoto[6], Y. Fujioka[6], Y. Enokido[6], K. Uesugi[9], A. Takeuchi[9], M. Yasutake[9], A. Miyake[10], S. Okumura[10], I. Mitsukawa[10], A. Takigawa[11], T. Mikouchi[11], S. Enju[12], T. Morita[6], M. Kikuiri[6], K. Amano[6], H. Yurimoto[13], T. Noguchi[10], R. Okazaki[14], H. Yabuta[15], H. Naraoka[14], K. Sakamoto[16], S. Tachibana[11,16], S. Watanabe[17], Y. Tsuda[16]

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Introduction: Imaging using X-ray absorption contrast by synchrotron nano-computed tomography (47.4 nm/voxel, 7keV) of a Ryugu pyrrhotite crystal (C0002-FC012 - from the second touch-down site) revealed probable fluid inclusions (Fig. 1A,B) [1]. The inclusions were completely encapsuled in pyrrhotite, suggesting the fluids were trapped in the early stages of crystal growth, and filled with low-Z material. We performed Time-of Flight-Secondary Ion Mass Spectrometry (TOF-SIMS) depth profiling and high-resolution mapping at -120°C to exposure and measure the composition of the trapped fluids in a frozen state.

Procedures: **We used a TOF-SIMS** 5 instrument (ION-TOF GmbH) at the Texas Materials Institute, equipped with a pulsed Bi^+ analysis ion beam (3 pA sample current, 30 keV ion energy) and a Cs^+ sputtering ion beam (40 nA measured sample current, 500 V ion energy). To ensure the stability of the sample during the TOF-SIMS data acquisition, which involves continuous sputtering, we moved the pyrrhotite sample to an Au coated Si wafer and welded it flat with Pt. A Fisher Scientific Scios 2 HiVac Dual Beam FIB/SEM system was used for this process. To access the inclusions in the pyrrhotite sample we continuously sputtered an area of 300 x 300 μm^2, centered around the fluid inclusion locations, with the Cs^+ ion beam while monitoring the high-resolution secondary ion maps of C^- (organic material marker) and OH^- (water marker) at the sample surface for signs of inclusion breaches. The Cs^+ sputtering rate was estimated at 0.07 nm/s based on the sputtering time needed to reach the largest inclusion and the depth of the inclusion beneath the surface based on the CT scans. The Cs^+ sputtering was stopped each time a major inclusion was breached and high resolution secondary ion mapping of areas of 30 x 30 μm^2 and 20 x 20 μm^2 was performed at the sample surface in both negative and positive polarities to identify the chemical species in the exposed inclusions. The analysis beam was set in the fast-imaging, burst alignment mode (<80 nm lateral resolution, ~0.4 pA sample current, mass resolution ~100) to achieve high spatial resolution. The TOF-SIMS experiments were performed at a base pressure of $1x10^{-9}$ mbar while the sample was cooled by flowing liquid nitrogen to approximately -120° C to prevent immediate sublimation of the frozen aqueous fluids upon opening in the vacuum of the sample chamber. Additional analytical details and results for other fluid inclusions are given in [2-3]. **Scanning Electron Microscopy** (SEM) was performed with a Supra 55 variable pressure field emission SEM and Bruker EBSD system, at NASA JSC, with no applied conductive coating.

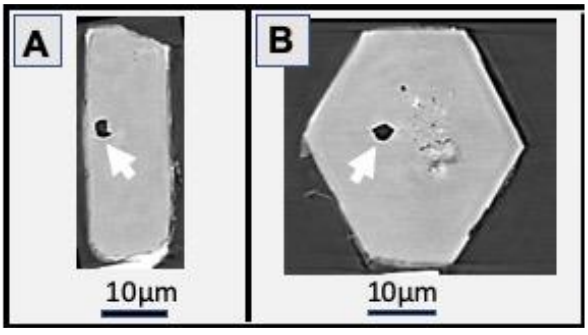
Results: The TOF-SIMS mapping showed that all analyzed fluid inclusions consist of water, CO_2, sulfur species, and organic material, with H^-, C^-, O^-, S^- and OH^- as the main fragments detected at these locations. In addition, various amounts of F^-, Cl^- and Ni^- were found, together with Na^+, 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 of more complex organic molecules containing H, C, N and O in these inclusions. Also trapped within the pyrrhotite crystal were several solid inclusions of chromite and other phases. None of these intruded into the fluid inclusions we analyzed.

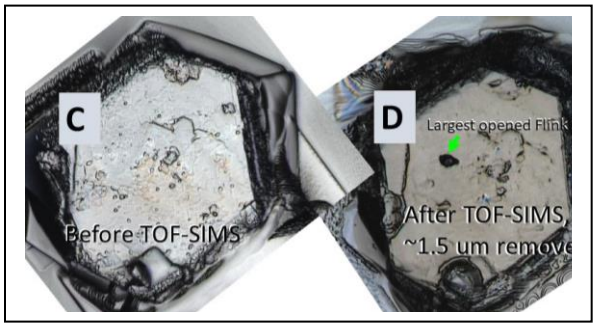
Figure 1E,F shows results for the largest fluid inclusion analyzed. Measurements are shown for the top and midplane of the inclusion. OH^- and CO^- are commonly identified secondary ion species of water and CO_2, respectively. With a similar localization to OH^-, S^- represents the sulfur species in the aqueous solution, likely dissolved in the fluid. The presence of CN^- indicates N-bearing organic compounds in the fluid. Given the spatial separation (both lateral and vertical) of the larger organic fragments such as C_2^-, C_2H^-, CN^- and C_3^- with respect to OH^- and CO^- we infer that the fluid contains a more complex organic compound of the form $H_xC_yN_z$, mixed with water and CO_2. The presence of Cl^- and F^-

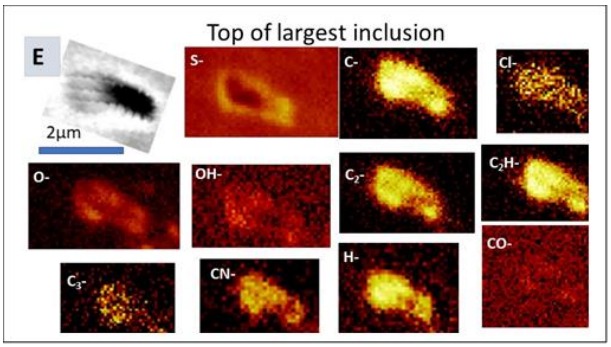
indicates that the trapped fluid was a brine. Differences in the distribution of each species within the inclusion, both within each map and between top and midplane maps, indicates stepwise freezing of different species–however the original fluid was probably homogeneous when trapped. Accurate bulk composition determinations will require TOF-SIMS measurements of specially-prepared standards and improved measurement of the electropositive species, work that is in progress.

We verified that the analyzed fluid inclusion did not contain solid inclusions of organics or OH-bearing phases such as phyllosilicates by performing SEM-EDS mapping of the opened inclusion following the TOF-SIMS. Only Fe and S were detected in the vicinity of the open inclusion.

Conclusions: TOF-SIMS measurements revealed that the ancient, trapped fluids on Ryugu's parent asteroid (possibly the parent of the Eulalia or Polana C-complex families [4]) were saline aqueous solutions containing H_2O, CO_2, sulfur species, and nitrogen- and chlorine-bearing organic compounds identified by representative secondary ion species including O^-, OH^-, CO^-, S^-, Cl^-, $C2^-$, C_2H^-, and CN^-. The inferred presence of CO_2 indicates formation of the sulfides, and by implication the Ryugu parent body, beyond the H_2O and CO_2 snow lines of the early solar system, i.e. > 3-4 au from the Sun [5].







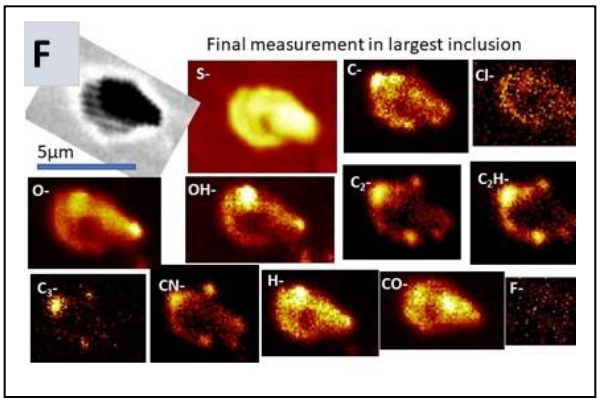


Fig. 1. A, B: Orthogonal "slices" through the XRCT scan of the pyrrhotite crystal. The target fluid inclusion (arrowed) is unconnected to the surface, located~1.5 µm from the upper surface shown at the left of the side view (A). Smaller fluid and solid inclusions are also visible. C, D: Optical profilometer images before and after TOF-SIMS. The largest opened fluid inclusion is arrowed. E,F: TOF-SIMS maps of the largest opened, frozen (-120 ºC), fluid inclusion indicating representative secondary ion species. E is near the top of the inclusion. F is midway down the inclusion. Note differences in scale bars.

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