

UPDATE ON MEASUREMENT OF THE COMPOSITION OF RYUGU FLUID INCLUSIONS. M. Zolensky¹, A. Dolocan², R. Bodnar³, I. Gearba², J. Martinez⁴, J. Han⁵, T. Nakamura⁶, A. Tsuchiyama^{7,8}, J. Matsuno⁸, M. Sun⁷, M. Matsumoto⁶, Y. Fujioka⁶, Y. Enokido⁶, K. Uesugi⁹, A. Takeuchi⁹, M. Yasutake⁹, A. Miyake¹⁰, S. Okumura¹⁰, I. Mitsukawa¹⁰, A. Takigawa¹¹, T. Mikouchi¹¹, S. Enju¹², T. Morita⁶, M. Kikui⁶, K. Amano⁶, H. Yurimoto¹³, T. Noguchi¹⁰, R. Okazaki¹⁴, H. Yabuta¹⁵, H. Naraoka¹⁴, K. Sakamoto¹⁶, S. Tachibana^{11,16}, S. Watanabe¹⁷, Y. Tsuda¹⁶

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Introduction: Imaging using X-ray absorption contrast by synchrotron nano-computed tomography of a Ryugu pyrrhotite crystal (C0002-FC012 - from the second Hayabusa2 spacecraft touch-down site) revealed probable fluid inclusions in the center of a crystal of pyrrhotite, suggesting the parent fluids were trapped in the early stages of crystal growth on Ryugu's parent asteroid. We previously described the performance of Time-of Flight-Secondary Ion Mass Spectrometry (TOF-SIMS) depth profiling and high-resolution mapping at -120°C to expose and measure the composition of the trapped fluids in a frozen state in two Ryugu inclusions [1,2]. Here we report results from follow-on measurements of additional inclusions in the same pyrrhotite crystal, and the initial results of measurement of standards. The ultimate goal is to reveal the quantitative composition of the fluids that caused aqueous alteration, in particular the H₂O:CO₂ ratio, which will also facilitate cosmochemical modeling of the alteration process.

Measurements of Ryugu Fluids: TOF-SIMS measurements of four Ryugu fluid inclusions revealed that the ancient, trapped fluids on Ryugu's parent asteroid were saline aqueous solutions containing H₂O, CO₂, sulfur species, and nitrogen- and chlorine-bearing organic compounds identified by representative secondary ion species including O⁻, OH⁻, CO⁻, S⁻, Cl⁻, C₂⁻, C₂H⁻, and CN⁻. The inferred presence of CO₂ indicates formation of the sulfides, and by implication the Ryugu parent body, beyond the H₂O and CO₂ snow lines of the early solar system, i.e. > 3-4 au from the Sun [3]. In this work we made measurements of only a few planes exposed by sputtering. We later discovered that we should have measured the inclusions from top to bottom, as shown by our subsequent measurements of standards.

Standards: The next step in these analyses was the measurement of appropriate fluid standards, reported here. Artificial aqueous fluid inclusions in quartz were made at Virginia Tech (see [4] for technical details), with a known ratio of H₂O to CO₂ of 1:1. The surface of a quartz grain was carefully polished to bring promising artificial fluid inclusions to within 2 μm of the surface. Before freezing, the boundaries between water and CO₂ ice were apparent, as was a separate H₂O-CO₂ clathrate phase at that boundary. Thus, even before freezing the inclusions were compositionally heterogeneous, although the bulk compositions should all have been equal and constant.

H₂O:CO₂ Measurements: For the previous measurements in the pyrrhotite crystal we used CO⁻ as the molecular fragment to indicate the presence and apparent concentration of CO₂ [1]. However, host quartz in the standards contained major oxygen, which precluded reliance on the CO⁻ molecule. Therefore, we used the molecular fragment C⁻ to measure CO₂. Measurement of five standard fluid inclusions (entire inclusions rather than measurements of a few "slices") produced the following results. In four of the five standard inclusions the ratio H₂O:CO₂ varied by less than 10% relative, which was considered a success. The fifth inclusion produced a ratio 2x greater than the others, possibly due to leakage of CO₂. The next step is to measure standard inclusions with at least one additional, different H₂O:CO₂ ratio, which will permit construction of a calibration curve for determining actual H₂O:CO₂ ratios in fluid inclusions. In the course of this work we also verified that different species in the fluid inclusions freeze at different temperatures, resulting in frozen inclusions whose composition varies unpredictably as they are sequentially sputtered and measured by TOF-SIMS. This behavior necessitates that fluid inclusion contents must be measured *in-toto* in order to produce accurate bulk compositions.

References: [1] Zolensky et al. (2022) 53rd Lunar and Planetary Science Conference, Abstract 1451. [2] Nakamura et al., submitted to *Science*. [3] Tsuchiyama et al. (2021) *Science Advances* 7, 21 Apr 2021: no. 17, eabg9707. [4] Sterner and Bodnar (1984) *GCA* 48, 2659-2668.