UPDATE ON MEASUREMENT OF THE COMPOSITION OF RYUGU FLUID INCLUSIONS. M. Zolensky\textsuperscript{1}, A. Dolocan\textsuperscript{2}, R. Bodnar\textsuperscript{3}, I. Gehrba\textsuperscript{4}, J. Martinez\textsuperscript{5}, J. Han\textsuperscript{5}, T. Nakamura\textsuperscript{6}, A. Tsuchiyama\textsuperscript{7,8}, J. Matsuno\textsuperscript{9}, M. Sun\textsuperscript{10}, M. Matsumoto\textsuperscript{6}, Y. Fujioka\textsuperscript{6}, Y. Enokido\textsuperscript{9}, K. Uesugi\textsuperscript{9}, A. Takeuchi\textsuperscript{9}, M. Yasutake\textsuperscript{9}, A. Miyake\textsuperscript{10}, S. Okumura\textsuperscript{10}, I. Mitsukawa\textsuperscript{10}, A. Takigawa\textsuperscript{11}, T. Mikouchi\textsuperscript{11}, S. Enju\textsuperscript{12}, T. Morita\textsuperscript{6}, M. Kikui\textsuperscript{6}, K. Amano\textsuperscript{6}, H. Yurimoto\textsuperscript{13}, T. Noguchi\textsuperscript{10}, R. Okazaki\textsuperscript{14}, H. Yabuta\textsuperscript{15}, H. Naraoka\textsuperscript{14}, K. Sakamoto\textsuperscript{16}, S. Tachibana\textsuperscript{11,16}, S. Watanabe\textsuperscript{17}, Y. Tsuda\textsuperscript{16}

\textsuperscript{1}ARES, NASA Johnson Space Center, Houston TX 77058, USA (michael.e.zolensky@nasa.gov); \textsuperscript{2}Texas Materials Institute, Univ. of Texas, Austin, TX 78712, USA; \textsuperscript{3}Dept. of Geosciences, Virginia Tech, Blacksburg VA 24061, USA; \textsuperscript{4}Jacobs Engineering, NASA Johnson Space Center, Houston, TX 77058, USA; \textsuperscript{5}Univ. of Houston; Houston TX 77204, USA; \textsuperscript{6}Tohoku Univ.; Sendai 980-8578, Japan; \textsuperscript{7}Guangzhou Institute of Geochemistry, Guangzhou 510640, China; \textsuperscript{8}Ritsumeikan Univ.; Kusatsu 525-8577, Japan; \textsuperscript{9}JASRI/SPring-8, Sayo 679-5198, Japan; \textsuperscript{10}Kyoto Univ.; Kyoto 606-8502, Japan; \textsuperscript{11}The University of Tokyo; Tokyo 113-0033, Japan; \textsuperscript{12}Ehime Univ., Matsuyama 790-8577, Japan; \textsuperscript{13}Hokkaido University, Sapporo 060-0810, Japan; \textsuperscript{14}Kyushu Univ., Fukuoka 819-0395, Japan; \textsuperscript{15}Hiroshima Univ., Higashi-Hiroshima 739-8526, Japan; \textsuperscript{16}ISAS/JAXA, Sagamihara 252-5210, Japan; \textsuperscript{17}Nagoya Univ., Nagoya 464-8601, Japan.

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 \cite{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 H$_2$O:CO$_2$ 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 H$_2$O, CO$_2$, sulfur species, and nitrogen- and chlorine-bearing organic compounds identified by representative secondary ion species including O, OH, CO, S, Cl, C$_2$, C$_{3}$H, and CN. The inferred presence of CO$_2$ indicates formation of the sulfides, and by implication the Ryugu parent body, beyond the H$_2$O and CO$_2$ snow lines of the early solar system, i.e. $>3$–4 au from the Sun \cite{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 \cite{4} for technical details), with a known ratio of H$_2$O to CO$_2$ 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 CO$_2$ ice were apparent, as was a separate H$_2$O-CO$_2$ 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.

H$_2$O:CO$_2$ Measurements: For the previous measurements in the pyrrhotite crystal we used CO as the molecular fragment to indicate the presence and apparent concentration of CO$_2$ \cite{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 CO$_2$. 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 H$_2$O:CO$_2$ 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 CO$_2$. The next step is to measure standards inclusions with at least one additional, different H$_2$O:CO$_2$ ratio, which will permit construction of a calibration curve for determining actual H$_2$O:CO$_2$ 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-to-to in order to produce accurate bulk compositions.