NEW CLUES TO ANCIENT WATER ON ITOKAWA. Z. L. Jin[1*], M. Bose[1] and Z. Peeters[1], [1]Center for Isotope Analysis, School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287-6004. *Ziliang.jin@asu.edu

Introduction: Water is one of the key planet-building materials, apart from silicates and metals [1]. To analyze the H isotopes and estimate the water content in extraterrestrial samples, therefore has tremendous implications on our understanding of its origin in planets and distribution in the inner solar system. In the past few decades, numerous meteorites from Moon, Mars, and Vestoids have been studied to understand how inner planetary bodies derived their water and if the inner solar system contains primordial water. These studies suggest that water in the inner solar system, e.g. the Earth-Moon system, was delivered by water-rich asteroids and/or comets [e.g. 2-4]. However, these studies primarily focused on the hydrous minerals, e.g., apatite. Studies in nominally anhydrous minerals (NAMs) are scarce, despite the fact that the NAMs are the main components of high temperatures refractory phases, e.g., chondrules and the interior of the terrestrial planets, and can incorporate measurable amounts of hydrogen [5]. At present, knowledge about water in NAMs from asteroids is missing, and we intended to fill this gap in knowledge by studying regolith particles from asteroid Itokawa.

The spacecraft Hayabusa I of the Japan Aerospace Exploration Agency (JAXA) was sent to the S-type asteroid Itokawa and recovered more than 1500 particles in 2011 [6]. These are the only available particles in our inventory of extraterrestrial materials that originate from a well-characterized asteroid. NanoSIMS is characterized by high spatial resolution and has been used successfully to quantify water contents and D/H ratios in NAMs [e.g., 4, 7]. We conducted NanoSIMS measurements to measure water contents and H isotopic ratios on two Itokawa grains. To the best of our knowledge, these results are the first data on the water content of samples directly obtained from an asteroid surface.

Samples: Two low-calcium pyroxene (LPx) grains from Itokawa (RA-QD02-0057 and RA-QD02-0061) were chosen for this study. RA-QD02-0057 is one single phase LPx particle (Figure 1). RA-QD02-0061 is composed of multiple minerals, including LPx, plagioclase, troilite, and taenite (Figure 1). The troilite and taenite are micron-size subgrains within the multi-mineralic particle. Previous SIMS studies to measure oxygen isotopes measurements on these LPx grains show that these particles are depleted in ^{16}O relative to terrestrial minerals, which indicated that Itokawa is the most likely source of equilibrated ordinary chondrites [8]. RA-QD02-0057 is about 20×60 μm^2 and RA-QD02-0061 is about 40×60 μm^2 in size. Four terrestrial samples, namely, KH03-04, KH03-27, ALV-519 and SM-18 were employed as the standards for measurement of H_2O contents. KH03-04 is clinopyroxene with a water content of 220 ppm. The samples KH03-27 and SM-18 are orthopyroxene and have water contents of 367 ppm and 130 ppm, respectively. ALV-517 is a piece of basaltic glass and contains 1700 ppm water.

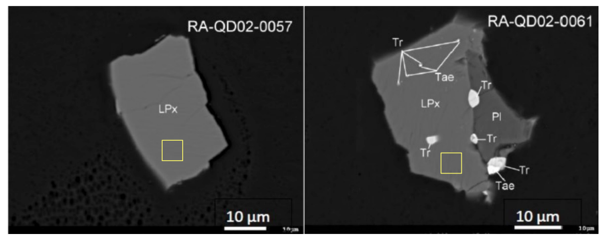

Figure 1: Backscattered electron images of Itokawa particles RA-QD02-0057 and RA-QD02-0061. The yellow squares show the NanoSIMS analyzed areas. LPx: low-Ca pyroxene; Tr: troilite; Tae: taenite; Pl: plagioclase.

Analytical method: The standards were first mounted in epoxy medium, polished by a 0.5 µm diamond film (non-water based protocol), removed from the epoxy, and pressed into indium. The allocated Itokawa particles were already mounted in epoxy discs (diameter=6mm), which were then pressed into indium mounts. All mounted samples were coated with a conductive gold layer (35 nm) and kept in a 50℃ oven for 24 hours. Then the samples were placed in the ultra-high vacuum (UHV) chambers of the NanoSIMS for 4 days.

D/H ratios and H_2O concentrations were measured by the Cameca Ametek NanoSIMS 50L at Arizona State University (ASU). A Cs+ primary beam of ~250 pA (D1-5 aperture, 100 µm diameter) was rastered on a 5×5 μm^2 surface on the grain. H^-, D^-, $^{12}C^-$ and $^{18}O^-$ were measured simultaneously. The electron gun (~1100 nA) was used in order to compensate for the charging of the sample surface. Prior to the data collection, the sample surface was presputtered for ~15 minutes to implant cesium and remove surface contamination. The counting time was set to 1ms/px and measurements on the standards and samples consisted of 240-480 cycles. The secondary ion signal from the internal 25 % of the rastered area was collected using electronic gating.

Results: H/O ratios of the standards with different water contents are shown in Figure 2. The calibration curve was used to estimate the water contents of the Itokawa LPx grains. The estimated water contents were corrected for contributions from galactic-cosmic-ray spallation. RA-QD02-0057 LPx grain has a water content of 971 ± 50 ppm (2σ), while RA-QD02-0061 LPx grain contains 683 ± 50 ppm water (2σ).

The δD values of the LPx grains RA-QD02-0057 and RA-QD02-0061 normalized to D/H_{SMOW} (1.55×10^{-4}) are -61 ± 16 ‰ and -35 ± 12 ‰, respectively. The reproducibility of the D/H measurements on the standards is up to 9 %, and therefore the Itokawa D/H ratios show terrestrial ratios within errors.

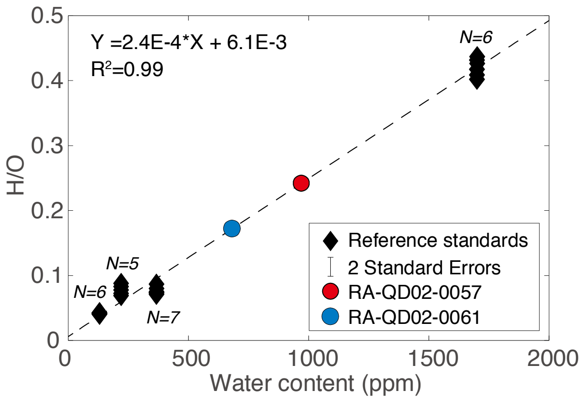

Figure 2: H_2O content vs. H/O for the standards and two Itokawa LPx grains (RA-QD02-0057 and RA-QD02-0061).

Discussion: The possible mechanisms that could modify the water contents and D/H ratios in Itokawa particles include: (1) terrestrial contamination due to adsorbed water, (2) cosmogenic ray spallation, (3) shock events, and (4) thermal metamorphism. In order to minimize terrestrial contamination, we cleaned and prepared the Indium mounts of Itokawa particles without water. They were stored in a desiccator purged with nitrogen at ASU before mounting and mounted in a class 10000 clean laboratory. By heating prior to analyses and long-term storage under dry, UHV conditions, the adsorbed water was significantly removed. During measurements, the pressure in the analysis chamber was constant at ~3×10^{-10} Torr, which indicates a low level of background hydrogen present during the analysis. All these factors have kept terrestrial contamination to a minimum.

Hydrogen could have been implanted into the samples by either solar wind or galactic-cosmic-rays. This process enhances the H/O ratio and therefore leads to a higher water content unless corrected. The hydrogen implanted by solar wind could be neglected due to the shallow implantation depths (< 60 nm) [9]. Galactic-cosmic-rays would be implanted into Itokawa up to a depth scale of meters and thus needs to be corrected. Using the previously reported 8 Ma exposure age of Itokawa [10], and the H and D production rates [7], we calculated that a very small amount of water, ~1ppm would be produced by spallation during the 8 Ma exposure to cosmic rays.

The parent body of asteroid Itokawa was proposed to have experienced impact events [6], which would possibly result in the dehydration and/or dehydrogenation of mineral grains. However, as shown in Figure 1, signs of deformation are absent for the particles studied here. We may thus consider that the shock impact had negligible effects on water in the Itokawa particles.

Finally, the parent body of Itokawa has experienced thermal metamorphism at temperatures of ~600 ℃ – 800 ℃ [6, 8]. Dehydration experiments on pyroxene have revealed a decrease in the OH concentration by heating samples between 700 ℃ and 1000 ℃ [11]. Thermal metamorphism experienced by Itokawa parent body would have reduced its water content. Consequently, the water contents of the two particles reported in this study (683–971 ppm) are lower limits and reflect values after the period of thermal metamorphism concluded, which was possibly when Itokawa got disrupted.

The δD values of phyllosilicates and chondrules in the LL3 ordinary chondrite Semarkona are +3300 ‰ – +4600 ‰ and +250 ‰ – +460 ‰, respectively [12]. In addition, the δD values of pyroxene grains in the LL3.1 ordinary chondrite Bishunpur range from -787 ‰ to +2090 ‰, with an average of +162 ‰ [13]. Compared to these previous results, the Itokawa particles from this study have relatively low δD values (-35 ‰ – -61 ‰). These low δD values could be achieved if water loss occurs during thermal metamorphism [14]. We can, therefore, envisage Itokawa to be a water-rich asteroid with high D/H ratios before the disruption.

References: [1] Lunine, J. I. (2006) *Meteorites and the early solar system II,* 309-319. [2] Hallis L. J. (2012*) EPSL, 359-360,* 84-92. [3] Sarafian A, et al. (2014) *Science, 346,* 623-626. [4] Barnes J.J. et al. (2014) *EPSL, 390,* 244-252. [5] Keppler, H. and Joseph R. S. (2006) *Water in nominally anhydrous minerals,* 193-230. [6] Tsuchiyama A. (2014) *Elements, 10,* 45-50. [7] Saal A. E. et al. (2013) *Science, 340,* 1317-1320. [8] Yurimoto H. et al. (2011*) Science, 333,* 11116-1119. [9] Thompson M. S. (2014) *Earth Planet Sp. 66,* 89. [10] Nagao K. et al. (2011) *Science, 333,* 1128-1131. [11] Ingrin J. et al. (1995) *J. Geophys. Res., 100,* 15489-15499. [12] Deloule E. and Robert F. (1995) *GCA, 59,* 4695-4706. [13] Deloule E. et al. (1998) *GCA, 62,* 3367-3368. [14] Suzuoki T. and Epstein S. (1976) *GCA, 40.* 1229-1240.