DEVELOPMENT OF SAMPLE PREPARATION TECHNIQUE FOR ISOTOPE ANALYSIS OF FLUID INCLUSIONS BY SIMS

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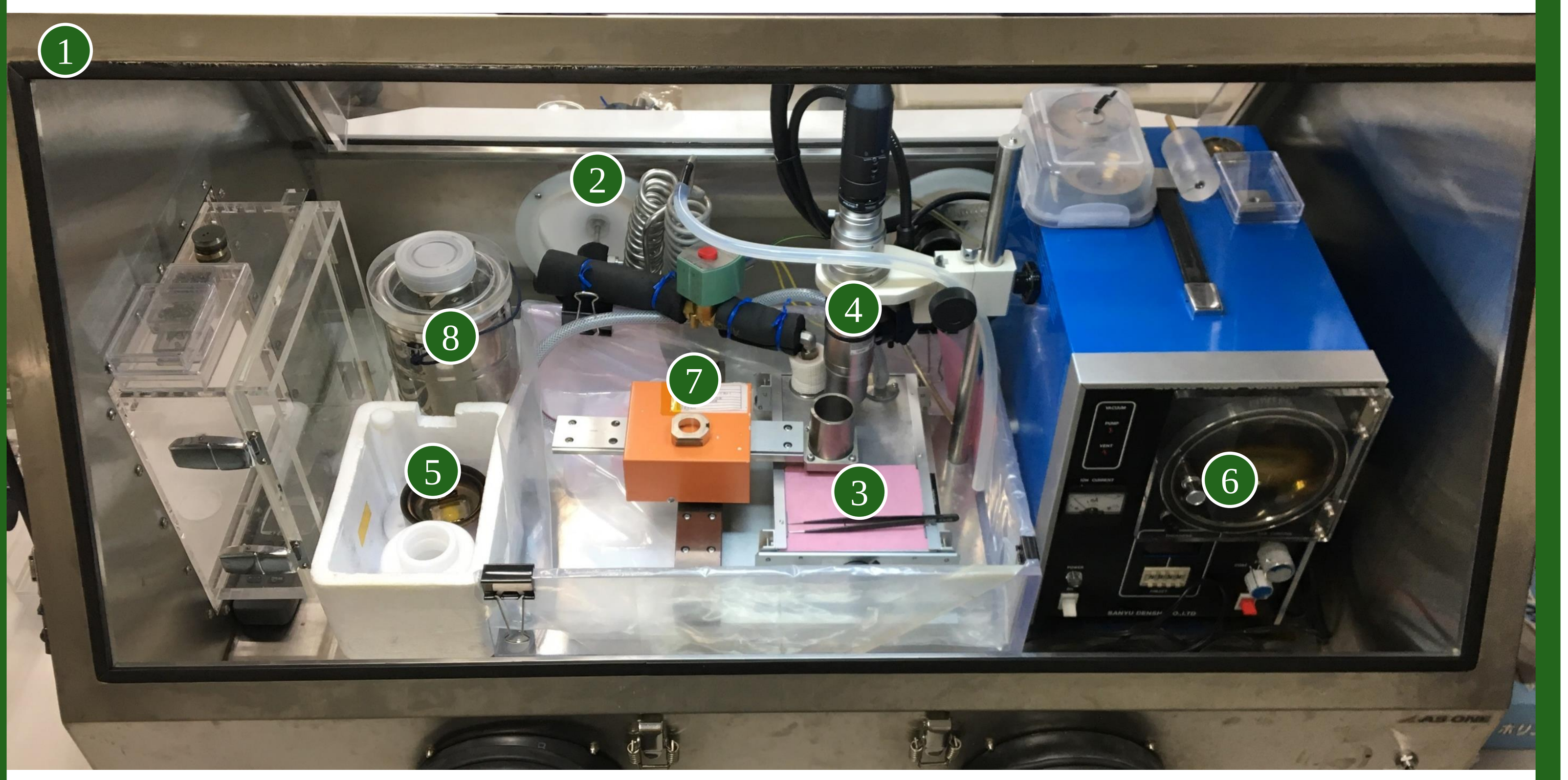
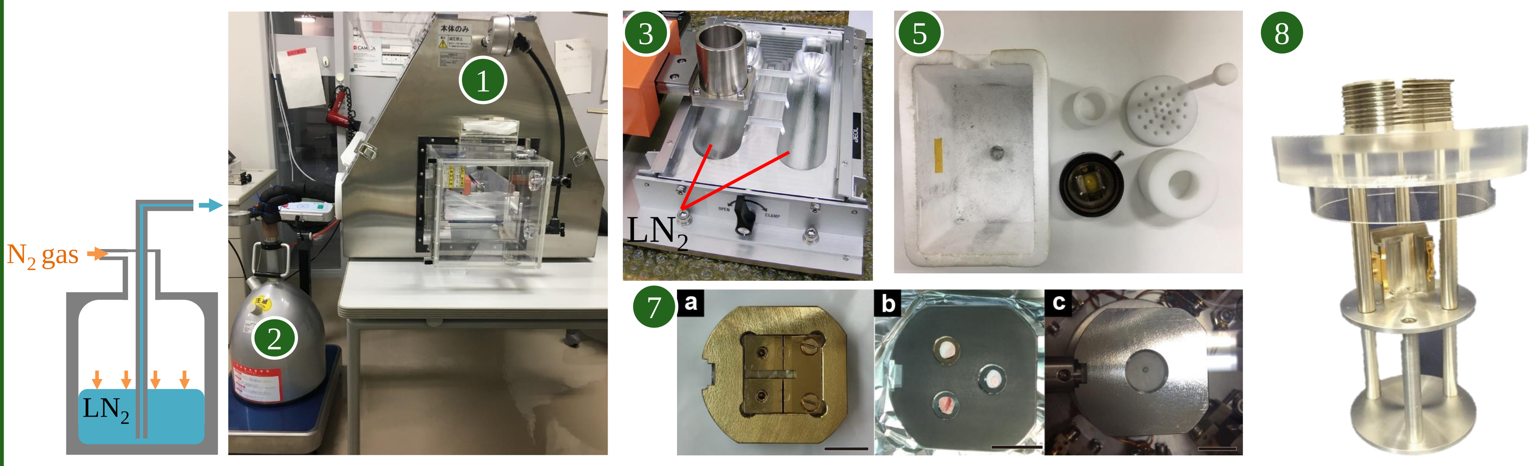
Fluid inclusions in halite crystals from meteorites provide direct information of extraterrestrial liquid water (Zolensky et al., 1999). In-situ isotope analysis of the fluid inclusions was realized by SIMS equipped with a cold-sample-stage (Yurimoto et al., 2014). However, the analytical precision was limited to 14 ‰ (1σ) for $\delta^{18}O$ because of severe electrostatic charging on the excavated area by ion beam to expose the fluid inclusion embedded in the halite crystal before SIMS analysis. In order to improve the analytical precision, we developed a cryogenic sample preparation technique to expose fluid inclusions on the sample surface including a cryogenic polishing, a cryogenic coating and cryogenic sample transfer systems. Here we demonstrate SIMS analysis of H_2O ice prepared by our cryogenic sample preparation technique developed in this study.

Cryogenic sample preparation system





1 Glove box

The glove box is purged by the N_2 gas evaporated from liquid nitrogen (LN_2) to prevent frost formation during sample preparation processes. The internal pressure of the glove box is kept about 0.5 kPa higher than the outside during operation to prevent invasion of water vapor.

2 LN_2 supplier

LN_2 is suppled to the inside of the glove box to keep low dew point and to cool cryo-polisher. The LN_2 is pushed out by the N_2 gas controlled by the mass flow controller in the range from 0 to 500 ccm.

3 Cryo-polisher

This cryo-polisher can polish the sample under low temperature. The polisher is cooled through the trench under the polishing table with LN_2 provided from the supplier. The temperature of the polishing table is controlled by LN_2 flow.

4 Optical microscope

This optical microscope (VK-X200, KEYENCE) is used to identify target fluid inclusions embedded in the host crystal and observe the sample surface. The microscope is incorporated into the cryo-polisher to reduce vibrations during observation.

5 Cryo-work station

Cryogenic samples cooled below the dew point in the glove box is treated in this work station in order to prevent frost formation. This cryo-work station contains LN_2 and is filled with pure N_2 gas evaporated from the LN_2.

6 Au ion coater

Gold coating is performed by an sputter ion coater (SC-701AT, SANYU DENSHI) to make conductive sample surface for SIMS analysis. The vacuum of the coating chamber is about 7 Pa for 40 seconds from the start and 10 nm thickness of gold is deposited for 1 min.

7 Cryo-holder

This sample holder for SIMS is made by machining from one metal block in order to prevent deformation at cryogenic temperature due to differences in thermal shrinkage between different materials.

8 Transfer vessel

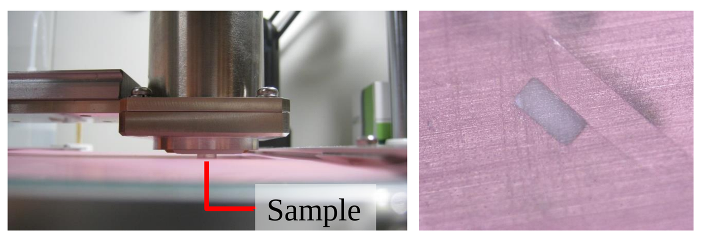
This transfer vessel is designed to transport the sample to the SIMS with keeping sample at LN_2 temperature. The vessel can hold a SIMS holder in the center of the vessel and pick up the holder by the cryo-loadlock using a connector compatible to the airlock system of SIMS instrument.

Procedure

1. Start up

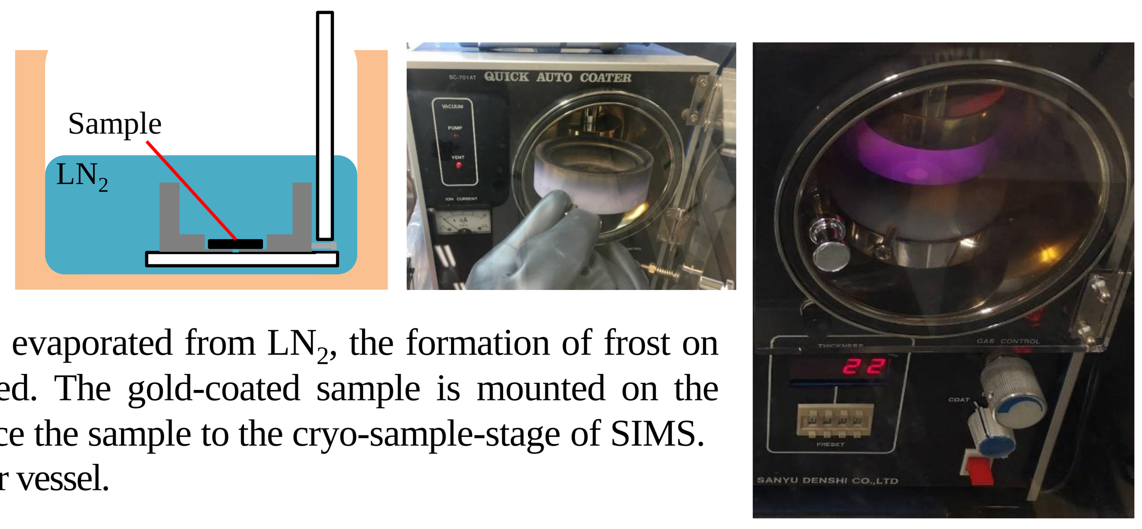
The atmosphere of glove box is replaced by N_2 gas generated from LN_2. The dew point in the glove box decrease at about −2.0 °C/min at N_2 gas flow to the LN_2 supplier of 200 ccm. After the N_2 gas replacement, the LN_2 from the LN_2 supplier was provided to the cryo-polisher to cooled down the polishing table. The cooling rate of the polishing table was about −2.0 °C/min at N_2 flow to the LN_2 supplier of 200 ccm. Since the LN_2 capacity of the LN_2 supplier was 7 kg and the consumption of LN_2 was about 2 kg/hr, LN_2 continues to be supplied for 3.5 hours.

2. Cryo-polishing



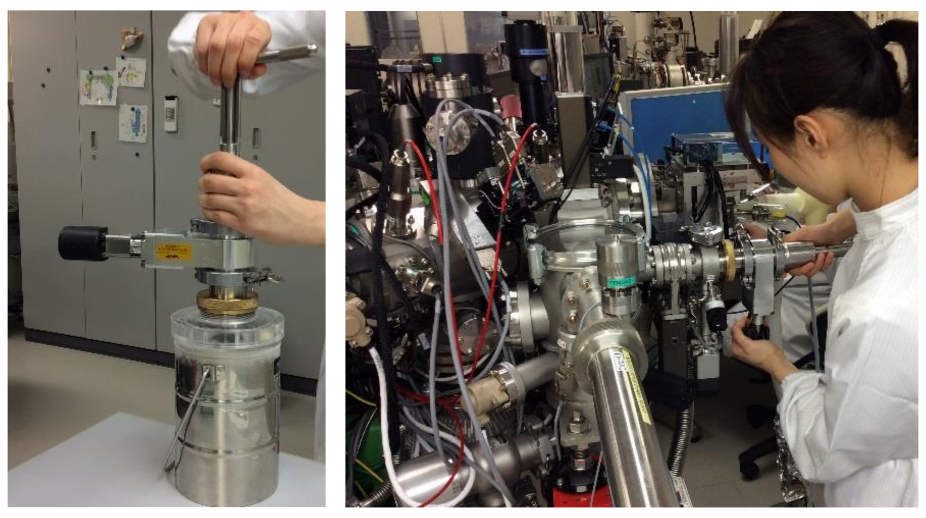
The frozen sample is polished to expose the fluid inclusions by polishing sheets of 40, 12, 9 um on the polishing table cooled down to −30 °C with checking the surface condition by the integrated optical microscope. The sample is finished by 3 um polish sheet.

3. Au coating & mount



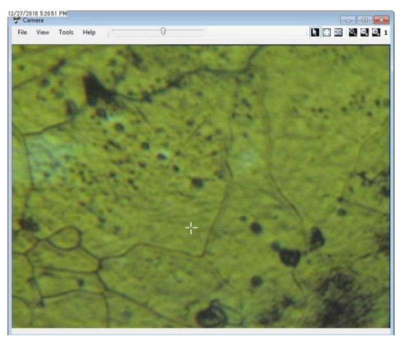
The polished sample is cooled by LN^2 in the cryo-work station to prevent sublimation of H_2O in the coating chamber vacuumed at several pascals during the gold coating. After the cooling, the sample on the coating stage is transported to the coater. Since the interior of the cryo-coating stage is filled with pure N_2 gas evaporated from LN_2, the formation of frost on the sample surface during transport is prevented. The gold-coated sample is mounted on the sample holder for cryo-SIMS in order to introduce the sample to the cryo-sample-stage of SIMS. The sample set on the holder is stored in the transfer vessel.

4. Transportation



The holder in the transfer vessel is transported to SIMS. The sample is picked up from the vessel by the cryo-loadlock chamber connected with the transfer vessel. After picking up the holder, a valve attached to the loadlock chamber is closed to shut off the outside air. The inside of the cryo-loadlock chamber is full of the N_2 gas evaporated from LN_2 in the vessel, frost formation on the sample is prevented. The loadlock chamber is quickly connected with SIMS. The attached valve the loadlock chamber is opened simultaneously with the start of vacuum by a roots pump. The holder is introduced to the cold-sample-stage of SIMS cooled at −190 °C. It takes 1 − 2 minutes for the installation of the holder to SIMS.

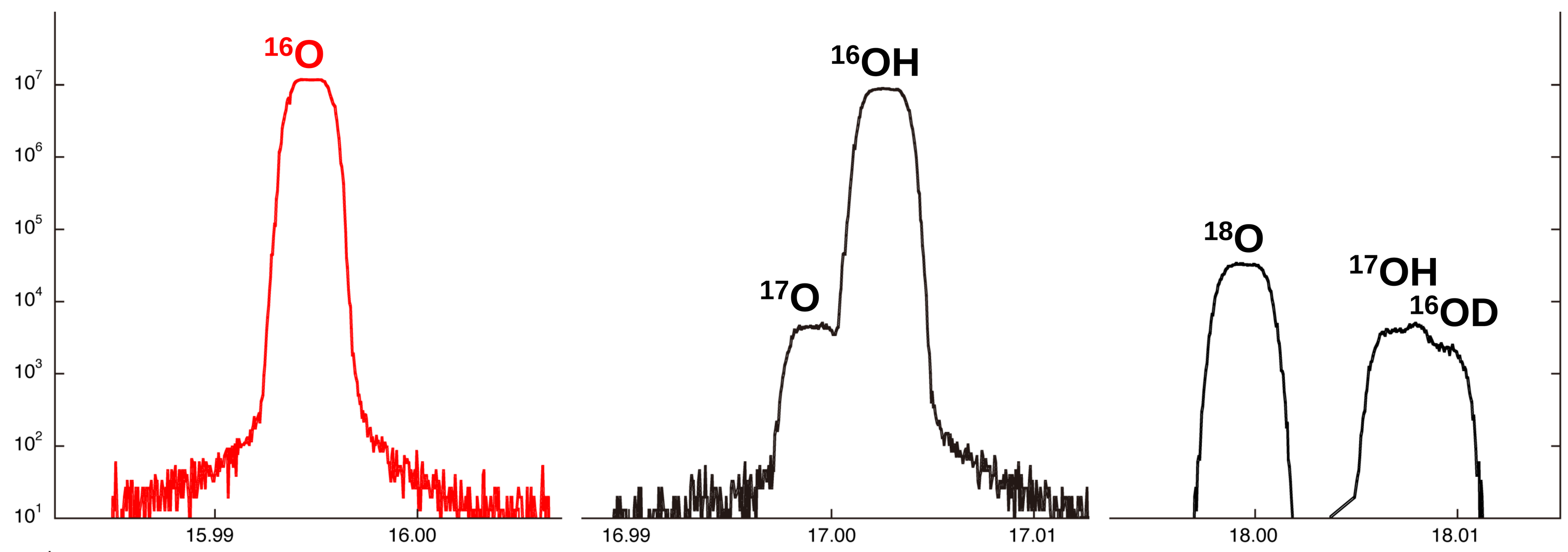
5. SIMS analysis

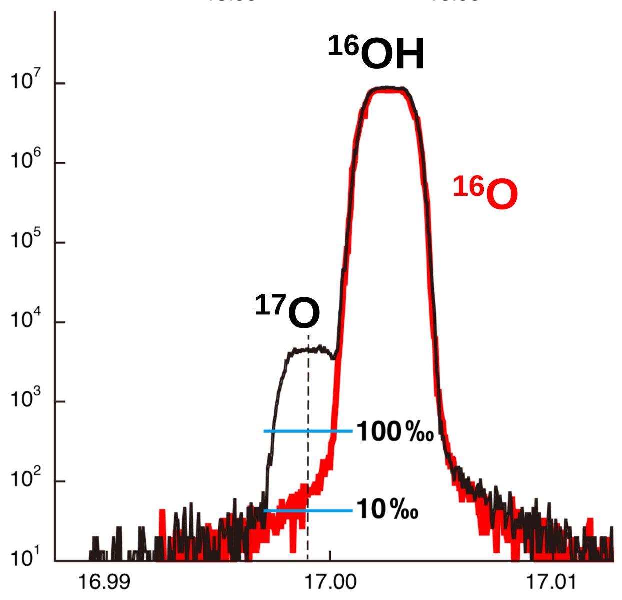


Ice on SIMS camera

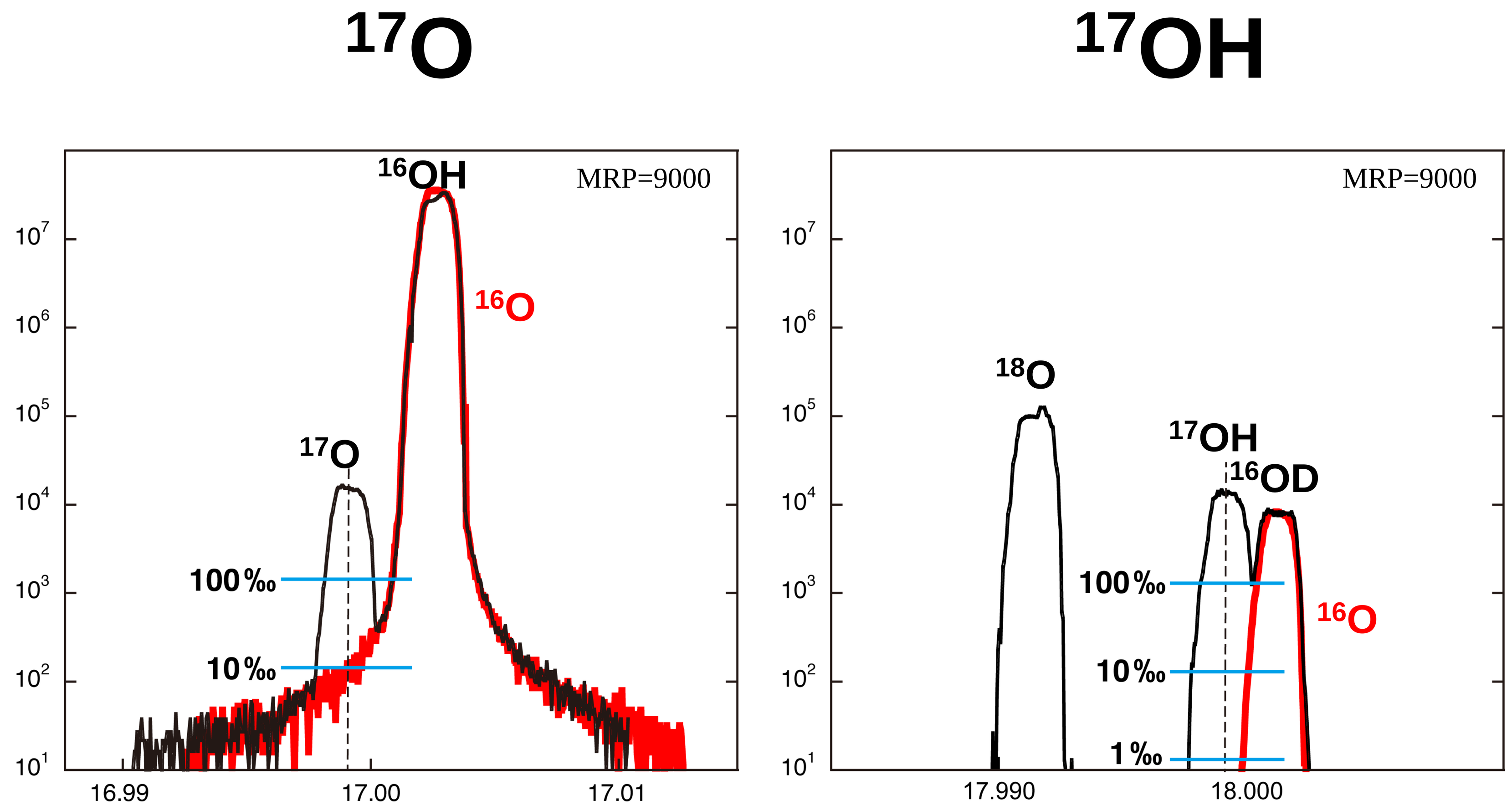
Left figure shows the optical image of the ice on SIMS. The yellow green area spread throughout the image is the surface of the ice after gold coating. Crystal boundaries of the ice are visible and the target position is clearly identified. The SIMS analysis of H_2O ice is performed by ims-1270 (CAMECA) using a Cs^+ beam as primary beam and a normal incident electron gun to compensate positive charging of the sputtered region due to primary beam irradiation.

Oxygen isotope analysis method for H_2O ice





Mass spectra of oxygen isotopes from H_2O ice were obtained by cryo-SIMS analysis. Upper figures shows mass spectra of $^{16}O^-$, $^{17}O^-$, $^{16}OH^-$, $^{18}O^-$, $^{17}OH^-$ and $^{16}OD^-$ with mass resolving power (MRP) = 5000. The intensity of $^{16}O^-$ was 1.0×10^7 cps, a tail was observed on both side of the peak. The intensity of $^{16}OH^-$ was similar to that of $^{16}O^-$ and three orders of magnitude higher than $^{17}O^-$.
The interference of $^{16}OH^-$ tail to $^{17}O^-$ was estimated to be more than 10‰ by overlapping $^{16}O^-$ peak (red) on $^{16}OH^-$. Yurimoto et al. (2014) corrected the contribution of the interference for $^{17}O^-$ by $^{16}O^-$-tail/$^{16}O^-$ ratio.



Upper figures show mass spectra of oxygen isotopes from H_2O ice using higher MRP and primary ion intensity. The contribution of interference from $^{16}OH^-$ to $^{17}O^-$ was similar to that of lower MRP condition (upper left). On the other hand, the tail effect of $^{16}OD^-$ to $^{17}OH^-$ was much smaller than the case of $^{16}OH^-$ because the intensities of $^{17}OH^-$ and $^{16}OD^-$ were similar (upper right). The contribution of from $^{16}OD^-$ to $^{17}OH^-$ was estimated to be less than 1‰. Isotope analysis using $^{16}OH^-$ and $^{17,18}OH^-$ signals would be effective for further high precision analysis of H_2O ice.

- A cryogenic polishing system was developed to expose fluid inclusions on the sample surface for the cryo-SIMS analysis.
- A cryogenic coating systems was developed to make sample surface conducive under cryogenic condition.
- A sample transfer system was developed to transport and introduce the cryogenic sample to SIMS.
- Oxygen isotope analysis using $^{16,17,18}OH$ signals instead of $^{16,17,18}O$ signals would be effective for H_2O ice because of the severe tail effect to ^{17}O for further high precision analysis.