**SUPPLEMENTARY MATERIALS**

**Discovery of argon in air-hydrate crystals in a deep ice core using scanning electron microscopy and energy dispersive X-ray spectroscopy**

Tsutomu UCHIDA1, Wataru SHIGEYAMA2, 3, \*\*, Ikumi OYABU3, Kumiko GOTO-AZUMA2, 3, Fumio NAKAZAWA2, 3, Tomoyuki HOMMA5, Kenji KAWAMURA2, 3, 4, Dorthe DAHL-JENSEN6

1 Faculty of Engineering, Hokkaido University, N13 W8 Kita-ku, Sapporo 060-8628, Japan

2 The Graduate University for Advance Studies, SOKENDAI, 10-3 Midori-cho, Tachikawa, Tokyo, 190-8518, Japan

3 National Institute of Polar Research, 10-3 Midori-cho, Tachikawa, Tokyo, 190-8518, Japan

4 Japan Agency for Marine Science and Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka 237-0061, Japan

5 Nagaoka University of Technology, 1603-1 Kamitomioka-machi, Nagaoka 940-2188, Japan

6 Centre for Ice and Climate, Niels Bohr Institute, University of Copenhagen, Juliane Maries Vej 30, 2100 Copenhagen K, Denmark

\*\* Present address: JEOL Ltd., 1-2 Musashino, 3-Chome Akishima, Tokyo 196-8558, Japan

**EDS background measurements**

**S1. EDS measurements for pure ice**

To prepare the pure ice samples, we froze ultrapure water and then prepared the sample the exact same way as for the core samples. Two thicknesses were prepared, 1 mm and 2.5 mm. The EDS spectra are in Fig. S1.

The largest peak in each sample is from O at 0.53 keV, which comes from H2O. Smaller peaks are from C (0.28 keV) and N peak (0.39 keV). Both samples also have a broad background signal from about 1 to 8 keV. As there is no significant difference in C, N and the broad background peaks between (a) and (b), we consider that these peaks arise from the surrounding environment, such as the adhesive material (the white material observed below the ice sample in the picture) and the N2 atmosphere. To remove the effects of these background signals from the sample spectrum, we used the differential spectrum analysis. Finally, the spectra show no signal around 2.96 keV that would indicate the Ar peak.

**S2. EDS measurement only for sample holder**

The sample holder was set in the SEM holder at room temperature and 120 Pa of N2 environment. The acceleration voltage was 20 kV. As the sample holder consists of a shuttle and an aluminium stub, the EDS spectrum shows various metal and other signals, including Al, Cu, Au, K, C, O, and Ni (Fig. S2). No peaks occur around 2.96 keV, which we identify as the Ar peak. Also, no peaks occur for Ag (L: 2.98 keV), which potentially could be confused with that of Ar. Thus, we confirmed that no signal corresponding to Ag was obtained, neither from the sample holder nor from the SEM chamber.



**Fig. S1**: EDS spectra of pure ice of thickness (a) 1 mm and (b) 2.5 mm. Inset SEM images show the measurement positions as a dashed circle. The SEM imaging position in the sample lies within the red-dashed circle as shown at right. The small white patches in the SEM image are from hoarfrost on the sample.



**Fig. S2**: EDS spectrum of the sample holder. The white dashed circle marks the measuring point.