O-ISOTOPE EXCHANGE KINETICS BETWEEN CAI MELT AND CARBON MONOXIDE GAS IN THE PROTOTOSOLAR DISK. D. Yamamoto1,2, S. Tachibana1, N. Kawasaki3, M. Kamibayashi3, and H. Yurimoto1, 1Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, Sagamihara, Kanagawa 252-5210, Japan, 2The University of Tokyo, Hongo, Tokyo 113-0033, Japan, 3Department of Natural History Sciences, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan. *daiki@planeta.sci.isas.jaxa.jp

Introduction: Mass-independent O-isotopic variation observed in primitive Solar System materials would be a product of oxygen isotope exchange between three major isotopically-distinct oxygen isotope reservoirs (primitive solid materials, 18O-rich CO, and 18O-poor H2O) in the early Solar System [e.g., 1, 2]. Coarse-grained calcium-aluminum-rich inclusions (CAIs), the oldest high temperature mineral assemblages formed in the Solar System, are considered to experience multiple partial melting stages after condensation of their precursors [e.g., 3, 4]. Coarse-grained CAIs are suggested to have experienced gas-melt isotope exchange during the partial melting events [e.g., 5, 6], and would preserve information on high temperature processes in the earliest Solar System as their O-isotopic variation. We have shown the heating timescale and bulk O-isotopic composition of surrounding gas at the partial melting events, based on O-isotope exchange kinetics between CAI melt and H2O experimentally determined by [7] and that between H2O and CO gas [8]. Because O-isotope exchange kinetics of CAI melt-CO, which has not yet been investigated, could strengthen our conclusion or put further constraints on the thermal history of igneous CAIs, we performed O-isotope exchange experiments between CAI analogue melt and low pressure-CO gas.

Experiments: O-isotope exchange experiments between CAI analogue melt and low pressure-CO were conducted at temperatures of 1420 and 1460°C (above melilite liquidus of 1380°C; [7]) and PCO = 0.1, 0.5, and 1 Pa for 52 min–22 h using a high temperature vacuum furnace equipped with a gas flow system. The starting material is the same as used in [7], and its bulk chemical composition is close to that of average type B CAIs [9]. 18O-enriched CO gas (~98% 18O) was introduced into the furnace, of which flow rates were adjusted by a mass flow controller to maintain the desired PCO. The starting material and run products were polished to expose their cross section and analyze chemical and oxygen isotopic composition of glass by EPMA (JEOL JXA-8900L) at the University of Tokyo and SIMS (Cameca ims-1280HR) at Hokkaido University. Gas species in the furnace during heating were analyzed with a QMS (HORIBASTEC QL-SG01-065-1A), which is operatable at PCO = 0.1 and 0.5 Pa. We also analyzed gas species during heating in the presence of isotopically-normal CO gas for comparison.

Results and Discussions: The starting material and run products were spherical in shape with 2.5–2.7 mm in diameter, and consisted of glass and a small amount of spinel grains (~9–12 wt%). Oxygen isotope ratios (f18O = 18O/(16O + 18O)) of glass in all run products increase toward their surface, and that at the surface gradually increases with time (Fig. 1). The samples heated at higher PCO have a larger enrichment of 18O at the surface and steeper concentration gradient. The isotopic profiles were well fitted by a three-dimensional spherical diffusion model with a time-dependent surface concentration [10] (Fig. 1), and the diffusion coefficient D and the surface isotopic exchange rate k were obtained. Because of a low reliability of D at PCO = 0.1 Pa due to the relatively flat isotopic profiles, D was evaluated from the samples at PCO = 0.5 and 1 Pa. The estimated D is 1.78 × 10−11 m2 sec−1, which is consistent with that estimated by O-isotope exchange experiments of CAI melt–H2O (1.62 × 10−11 m2 sec−1; [7]).

QMS analyses at 1420°C showed a peak at m/z = 20 with its partial pressure of (0.4–1) × 10−4 Pa, irrespective of PCO, which was not observed in the presence of isotopically-normal CO. This result suggests that CO gas exchanges oxygen isotope with residual water vapor to form H218O vapor at 1420°C. This is consistent with the expectation that oxygen isotope exchange between CO and H2O is a very rapid process at such high temperatures (e.g., ~10 min at 1400°C in the solar nebula) [8]. Although P12O is ~3–4 orders of magnitude smaller than PCO, the effect of residual water vapor on the value of k should be taken into account because O-isotopic exchange between CAI melt and water vapor is effective [7]. It is expected that the f18O of H2O is equal to that of CO because of much higher abundance of CO compared with that of H2O and rapid isotope exchange between those gaseous phases [8]. Figure 2 shows the comparison between calculated f18O profiles as a result of isotopic exchange with H2O with pressures of 4 × 10−5 and 1 × 10−4 Pa based on [7] and an experimental profile at PCO = 0.5 Pa and 1420°C. The experimental profile shows 18O enrichment than the calculated profiles for the melt and the H218O molecules in the system, and the exchange with C18O is clearly required to explained the f18O profiles. Considering the contribution of H218O, the net isotope exchange rate knet is expressed as (αCO/CO+α12O/H12O)/CO where α is a
non-dimensional parameter that expresses isotopic exchange efficiency of colliding gas species \( i \) at the melt surface and \( J_i \) is the flux of gas \( i \), and \( C_o \) is the oxygen number density of the melt [7]. The values of \( \alpha_{CO} \) are in the orders of \( 10^{-3}–10^{-4} \), irrespective of the effect of water vapor, and are 2–3 orders of magnitude smaller than \( \alpha_{H_2O} \) (~0.28; [7]).

Combined with the results presented in this study, the kinetics of all isotopic exchange reaction processes during partial melting events of CAIs (i.e., CAI melt-CO, CAI melt-H\(_2\)O, and CO-H\(_2\)O) have been constrained. O-isotopic exchange timescales among CAI melt-CO-H\(_2\)O are compared in Fig. 3 as a function of \( P_{CO} \) and \( P_{H_2O} \) at 1420°C for 1 cm-diameter CAI melt. The order of isotopic exchange rates \( (k) \) always obeys the relation of \( k_{CO-H_2O} > k_{CAI-H_2O} > k_{CAI-CO} \), and oxygen isotopic exchange rate between CAI melt and disk gas is controlled by the reaction between CAI melt and H\(_2\)O. This suggests that CAIs should be heated for at least a few days at temperatures above melilitic liquidus to form the homogeneous isotopic composition of melilitic in type B CAIs [7] even if the effect of CO gas is taken into account. Open-system evaporation experiments suggest that such prolonged heating at maximum temperatures results in excess amounts of evaporation and associated isotopic fractionation for Mg and Si [11, 12]. At \( P_{H_2O} \) greater than \( \sim 10^6 \) Pa, recondensation of evaporated Mg and Si takes place, resulting in the reduction of evaporation amount [13]. The discrepancy between heating timescales inferred from the O-isotopic exchange rate and the melt evaporation rate is indicative of the formation of type B CAIs in semi-closed system at \( P_{H_2O} > \sim 10^6 \) Pa. Because CAI melt would crystallize under reducing condition, close to H\(_2\)O/H\(_2\) ratio estimated from the Solar System abundance of elements [14], \( P_{H_2O} \) in the type B CAI forming region should be greater than \( \sim 1 \) Pa. The present results also suggest that H\(_2\)O, rather than CO, would control O-isotope exchange kinetics of chondrule melts during their formation [15].