

O-ISOTOPE EXCHANGE KINETICS BETWEEN CAI MELT AND CARBON MONOXIDE GAS IN THE PROTOSOLAR DISK. D. Yamamoto^{1*}, S. Tachibana^{1,2}, N. Kawasaki³, M. Kamibayashi², and H. Yurimoto³,

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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, ¹⁶O-rich CO, and ¹⁶O-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 $P_{\text{CO}} = 0.1, 0.5$, 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 P_{CO} .

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 $P_{\text{CO}} = 0.1$ 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 ($f^{18}\text{O} = {}^{18}\text{O}/({}^{16}\text{O} + {}^{18}\text{O})$) 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 P_{CO} 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 $P_{\text{CO}} = 0.1$ Pa due to the relatively flat isotopic profiles, D was evaluated from the samples at $P_{\text{CO}} = 0.5$ and 1 Pa. The estimated D is $1.78 \times 10^{-11} \text{ m}^2 \text{ sec}^{-1}$, which is consistent with that estimated by O-isotope exchange experiments of CAI melt–H₂O ($1.62 \times 10^{-11} \text{ m}^2 \text{ sec}^{-1}$; [7]).

QMS analyses at 1420°C showed a peak at $m/z = 20$ with its partial pressure of $(\sim 0.4\text{--}1) \times 10^{-4}$ Pa, irrespective of P_{CO} , 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 $P_{\text{H}_2\text{O}}$ is ~3–4 orders of magnitude smaller than P_{CO} , 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 $f^{18}\text{O}$ 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 $f^{18}\text{O}$ profiles as a result of isotope exchange with H₂O with pressures of 4×10^{-5} and 1×10^{-4} Pa based on [7] and an experimental profile at $P_{\text{CO}} = 0.5$ 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 explain the $f^{18}\text{O}$ profiles. Considering the contribution of H₂¹⁸O, the net isotope exchange rate k_{net} is expressed as $(\alpha_{\text{CO}}J_{\text{CO}} + \alpha_{\text{H}_2\text{O}}J_{\text{H}_2\text{O}})/C_{\text{O}}$ where α_i 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 α_{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 α_{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-H₂O, and CO-H₂O) have been constrained. O-isotopic exchange timescales among CAI melt-CO-H₂O 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 H₂O. This suggests that CAIs should be heated for at least a few days at temperatures above melilite liquidus to form the homogeneous isotopic composition of melilite 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_2} greater than $\sim 10^3$ 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 $P_{H_2} > \sim 10^3$ Pa. Because CAI melt would crystallize under reducing condition, close to H₂O/H₂ ratio estimated from the Solar System abundance of elements [14], P_{H_2O} in the type B CAI forming region should be greater than ~ 1 Pa. The present results also suggest that H₂O, rather than CO, would control O-isotope exchange kinetics of chondrule melts during their formation [15].

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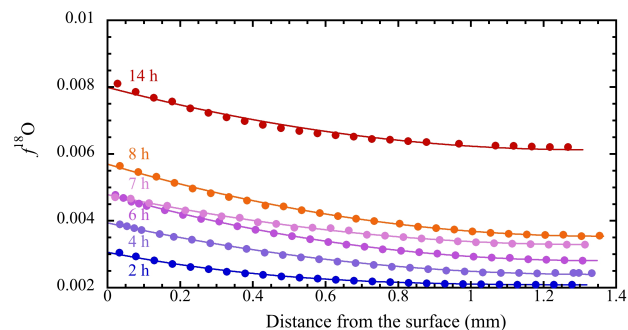


Fig. 1: Typical $f^{18}O$ profiles in samples heated at 1420°C and $P_{CO} = 0.5$ Pa for 2–14 h. Closed circles are experimental data, and solid curves are best-fitted results.

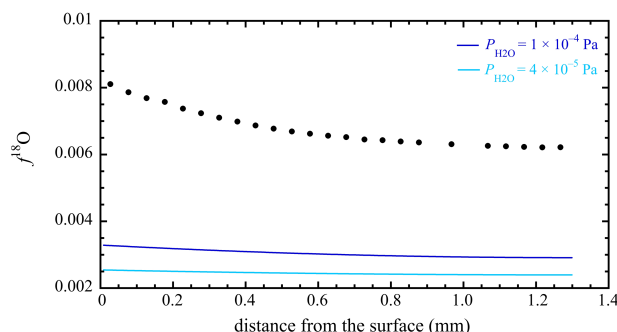


Fig. 2: Comparison between the experimental data of the sample heated at 1420°C and $P_{CO} = 0.5$ Pa for 14 h (closed circles) and model profiles as a result of isotope exchange with H₂O with pressures of 4×10^{-5} and 1×10^{-4} Pa (light and dark blue curves, respectively) calculated based on [7].

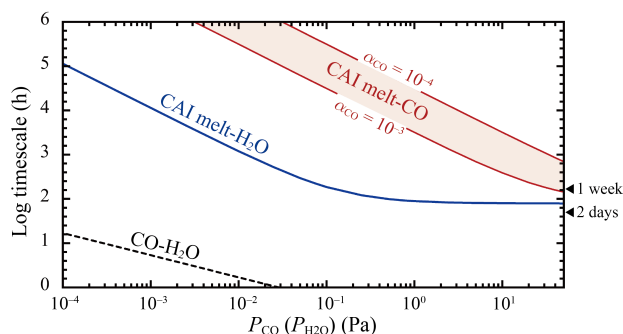


Fig. 3: Timescales of oxygen isotopic exchange between CO-H₂O gas (black dotted line; [8]), CAI melt-H₂O (blue solid line; [7]), and CAI melt-CO (red solid curves at $\alpha_{CO} = 10^{-3}$ and 10^{-4}) at 1420°C for a 1 cm-sized spherical melt as a function of P_{CO} (or P_{H_2O}).