Recondensation reconsidered: effects in evaporation experiments and in natural settings. F. M. Richter1,2,3, P. E. Janney2,3, R. A. Mendybaev1,2, A. M. Davis1,2,3, and M. Wadhwa1,2,3,1Department of the Geophysical Sciences, 2Chicago Center for Cosmochemistry, 3Enrico Fermi Institute, The University of Chicago, Chicago, IL 60637, 4Isotope Geochemistry Laboratory, The Field Museum, Chicago, IL 60605. (richter@geosci.uchicago.edu)

Introduction. Recondensation of previously evaporated volatile species has been appealed to in many instances when the relationship between the elemental and isotopic fractionation of evaporation residues does not conform to some prior expectation, such as Rayleigh fractionation with a specified value for the kinetic isotope fractionation factor [1,2,3]. The Rayleigh equation applied to the isotopic composition of an evaporation residue is

$$R_{i,j} = R_0 f_j \alpha_{ij}^{-1}$$

where $R_{i,j}$ is the ratio of isotopes $i$ and $j$ in the residue, $R_0$ is the isotope ratio before evaporation, $f_j$ is the fraction of the initial amount of $j$ remaining in the residue, and $\alpha_{ij}$ is the isotope fractionation factor defined as $\alpha_{ij} = (J_i / J_j) / R_{i,j}$, where $J_i$ and $J_j$ are the molar evaporation fluxes of isotopes $i$ and $j$. It has often been assumed that $\alpha_{ij} \equiv \sqrt{m_j / m_i}$ where $m_i$ and $m_j$ are the molar masses of the dominant gas species in equilibrium with the condensed phase (e.g., 24.986 and 23.985 for $^{24}$Mg and $^{24}$Mg), although we [4] have previously argued that this need not be case (i.e., that $\alpha_{ij} \approx \sqrt{m_j / m_i}$) based on the isotopic fractionation we observed in laboratory produced evaporation residues. An important and recurring issue is whether laboratory residues may have been limited in their isotopic fractionation by slow diffusion in the residue and/or recondensation. Concerns regarding finite diffusion are easily dismissed given that rapidly quenched evaporation residues are demonstrably homogeneous. With regards the effect of recondensation on the isotopic fractionation of laboratory evaporation residues, we show that recondensation in a furnace of finite conductance has the previously unrecognized effect of shifting the actual isotope fractionation factor towards $\sqrt{m_j / m_i}$, (i.e., $\alpha_{ij} \rightarrow \sqrt{m_j / m_i}$) and thus recondensation will, if anything, increase the degree of isotopic fractionation. Thus the kinetic isotope fractionation factor determined from laboratory produced evaporation residues is actually an upper bound on the fractionation factor.

Recondensation during evaporation into a surrounding gas. Richter et al. [4] derived the following expression for the effective kinetic isotope fractionation factor $\alpha'_{ij}$ for evaporation into a surrounding gas of finite total pressure $P$, which can be used in connection with chondrules and CAIs:

$$\alpha'_{ij} - 1 = \left( \alpha_{ij} - 1 \right) \left( 1 - \frac{P_i}{P_{i,\text{sat}}} \right) + \left( \frac{D_i}{D_j} - 1 \right) \frac{P_j}{P_{j,\text{sat}}}$$

where $\alpha_{ij} = \gamma_i / \gamma_j \sqrt{m_j / m_i}$ is the kinetic isotope fractionation factor in the vacuum limit, $\gamma_i$ and $\gamma_j$ are the possibly distinct evaporation coefficients of the isotopes $i$ and $j$, $P_i$ is the pressure of species $i$ at the evaporation surface required to transmit the flux of $i$ from the surface through the surrounding gas of total pressure $P$, $P_{i,\text{sat}}$ is the saturation pressure of the dominant gas species containing $i$, and $D_i$ and $D_j$ are the diffusion coefficients of $i$ and $j$ in the surrounding gas. When the surrounding gas is dominantly hydrogen, the ratio $D_i / D_j$ will be sufficiently close to one that the second term on the right hand side of the expression for $\alpha'_{ij}$ is negligible. Thus as $P_i / P_{i,\text{sat}} \rightarrow 1$, $\alpha'_{ij} \rightarrow 1$ and isotopic fractionation is suppressed.

Recondensation during evaporation in a furnace of finite gas conductance. Richter et al. [5] derived the following expression for the effective kinetic isotope fractionation factor $\alpha'_{ij}$ for a residue evaporated in a furnace of finite gas conductance operating in the molecular regime.

$$\alpha'_{ij} = \gamma_i \gamma_j \frac{m_j / m_i}{\left( 1 - \frac{P_i}{P_{i,\text{sat}}} \right) \sqrt{m_j / m_i} + \frac{P_j}{P_{j,\text{sat}}}}$$

where $\gamma$ is the evaporation coefficient for the subscripted isotope and $G'$ is a geometric parameter determining the gas conductance $U_k$ of the furnace. $U_k = F_k / P_{k,\text{sat}}$, where $F_k$ is the total flux of a species $k$ and $P_k$ is the pressure at the evaporating source required to drive the flux of $k$ from the vicinity of the sample to a far-field vacuum. Recondensation is proportional to $P_d/P_{d,\text{sat}}$, thus when $G'$ is large (small), $P_d/P_{d,\text{sat}}$ will be small (large) for a given total flux and recondensation will be negligible (important). The quantity $\left( \gamma_i / \gamma_j \right) \sqrt{m_j / m_i}$ is the kinetic isotope fractionation factor in the limit of no recondensation (i.e., at large gas conductance $G' \rightarrow \infty$, and any departure of $\alpha'_{ij}$ from $m_j / m_i$ is due to $\gamma_i / \gamma_j \neq 1$). Figure 1 shows the dependence of the effective kinetic fractionation factor $\alpha'_{ij}$ on the gas conductance parameter $G'$. As the gas conductance becomes sufficiently small (i.e., significant recondensation), the term on the right side of the equation above approaches $\gamma_j / \gamma_i$ and the effective kinetic isotope fractionation factor tends to $m_j / m_i$. This occurs because in this limit, removal of each species from the system will be increasingly determined by its rel-
tive velocity, which is proportional to the inverse square root of its mass. Figure 2 shows a set of magnesium isotopic measurements made using the MC-ICPMS at the Field Museum (see [5] for details) on evaporation residues of different sizes that were run in the University of Chicago vacuum furnace at 1800°C for different amounts of time. The slope of the best fitting line through the data from the 2.5 mm and 6.0 mm samples corresponds to the quantity \( \frac{1}{\alpha} \), and confirms the theoretical expectation shown in Fig. 1 that the larger samples, which will have had more recondensation due to their larger total flux (the total flux being proportional to surface area) are the more isotopically fractionated with an effective kinetic isotope fractionation factor shifted towards \( \frac{m_j}{m_i} \). Similarly, we found that for a series of samples evaporated at 1700°C, 2.5 mm diameter samples were more fractionated than 1 mm diameter ones. The agreement between the calculated and observed effect of finite gas conductance on the isotopic fractionation of evaporation residues gives us confidence that the unexpected result we report here is real.

**Conclusion.** Evaporation into an unconfined surrounding gas will, for a sufficiently high pressure in that gas, reduce the isotopic fractionation of residues. If however the gas is contained in a small (i.e., small compared to the mean free path of the evaporating species) region of finite gas conductance the isotopic fractionation of residues will be enhanced rather than reduced. The former case should be kept in mind when interpreting isotopic mass fractionation effects in chondrules and CAIs. The latter case applies to laboratory-produced evaporation residues.


![Figure 1. Calculated magnesium isotopic fractionation of evaporation residues as a function of the fraction \( f \) of \( ^{24}\text{Mg} \) remaining in the residue and the gas conductance parameter \( G^* \).](image1)

![Figure 2. Magnesium isotopic fractionation of 2.5 mm and 6.0 mm diameter evaporation residues as a function of the fraction \( f \) of \( ^{24}\text{Mg} \) remaining in the residue. The corresponding kinetic isotope fractionation factors are given along with a red line showing the magnesium isotopic fractionation for \( \alpha = \sqrt{24/25} \). The net flux of magnesium is proportional to surface area, thus the 6 mm samples have a net flux of about a factor of 6 larger than that of the 2.5 mm samples. As a result the larger samples have more recondensation, and in agreement with the theory outlined above, they are the more fractionated for a given amount of magnesium evaporated.](image2)