ON THE TEMPERATURE DEPENDENCE OF THE KINETIC ISOTOPE FRACTIONATION OF TYPE B CAI-LIKE METALS DURING EVAPORATION. F. M. Richter, P. E. Janney, R. A. Mendybaev, A. M. Davis, M. Wadhwa, Department of the Geophysical Sciences, Chicago Center for Cosmochemistry, Enrico Fermi Institute, The University of Chicago, Chicago, Il 60637 (richter@geosci.uchicago.edu), Isotope Geochemistry Laboratory, The Field Museum, Chicago, IL 60605.

Introduction. Type B CAIs are often enriched in the heavy isotopes of magnesium and silicon, suggesting that a fraction of these elements was lost by evaporation [1]. Detailed comparisons between compositions calculated for a cooling solar composition gas and recent estimates of the bulk composition of Type B CAIs further suggests that evaporation played a significant role in that the Type B CAIs contain significantly less of the relatively volatile magnesium than calculated [2]. The silicon content, on the other hand, is not as useful a measure of evaporation because solids condensing from a solar composition gas in the temperature interval over which the typical mineral assemblages of the Type B CAIs are stable can have a large range in silicon content not much different from that of the CAIs themselves. For this reason we will focus on the behavior of magnesium during the evaporation of a Type B CAI-like melt.

The proposition that the elemental and isotopic compositions of the Type B CAIs have been measurably affected by evaporation can be quantitatively tested, given the right data and a realistic representation of the relationship between elemental and isotopic fractionation during evaporation. For example, given data on the heavy isotopic enrichment of magnesium and/or silicon of a set of Type B CAIs one could calculate the amount of magnesium and/or silicon that must have evaporated to account for the isotopic data and then check whether the observed composition of the CAIs, adjusted to take this loss into account, corresponds to plausible condensates from a solar composition gas (see [3] for such an attempt). A key issue is the appropriate relationship one should use for relating elemental and isotopic fractionations in the specific case of magnesium evaporation from a molten Type B CAI-like melt.

The kinetics of evaporation from a condensed phase into a gas of sufficiently low pressure is given by the Hertz-Knudsen equation,

\[ J_i = \frac{\gamma_i P_{sat}^{j}}{\sqrt{2 \pi m_i RT}}, \]

where \( J_i \) is the molar flux per unit surface area of \( i \), \( \gamma_i \) is the evaporation coefficient, \( P_{sat}^{j} \) is the saturation vapor pressure of the dominant gas species containing \( i \), \( m_i \) is the atomic mass of that gas species, \( R \) is the gas constant and \( T \) is temperature in Kelvin. The relationship between elemental and isotopic fractionation of the residue is generally assumed to be of the form

\[ \frac{R_{jk}}{R_{jko}} = f_k^{(\alpha_{jk}^{-1})}, \]

where \( R_{jk} \) is the ratio of isotopes \( j \) and \( k \) of element \( i \), \( R_{jko} \) is the initial ratio, \( f_k \) is the fraction of isotope \( k \) remaining in the residue, and \( \alpha_{jk} \) is the kinetic fractionation factor for isotopes \( j \) and \( k \) (see [4] for a detailed discussion of the conditions under which this sort of a fractionation equation will apply). The kinetic fractionation factor \( \alpha_{jk} \) is the ratio of the flux of the isotopes, thus from Eqn (1)

\[ \alpha_{jk} = \frac{\gamma_j}{\gamma_k} \sqrt{\frac{m_j}{m_k}}. \]

It is often implicitly assumed (as was done by [3]) that the evaporation coefficients of isotopes of the same element are the same and thus that

\[ \alpha_{jk} = \sqrt{\frac{m_j}{m_k}}. \]

We will show that the functional form given by Eqn. (2) is consistent with recent high-precision magnesium isotopic measurements of evaporation residues but that Eqn. (4) is not correct and will result in significant underestimates of the amount of an element that must be evaporated to account for a given amount of isotopic fractionation.

Experimental Results. The data presented in this section involve the magnesium isotopic composition of evaporation residues of samples run in a vacuum furnace at the University of Chicago for various lengths of time and temperatures ranging from 1600°C to 1900°C. All samples shown here had initial diameters of 2.5 mm. Details regarding sample preparation and the vacuum furnace can be found in [5], and the methods for purifying the magnesium and making the isotopic measurements with the multicollector ICPMS at the Field Museum are given in [6]. Figure 1 shows the magnesium isotopic composition of the evaporation residues for samples that were evaporated at various temperatures and it is apparent that the higher the temperature, the greater the fractionation associated with a given fraction of magnesium lost. Best fits through the data for each temperature give values for the fractionation factor \( \alpha \) and these are plotted in Fig. 2. Also shown in Fig. 2 are some earlier reported values for \( \alpha \) at different temperatures (the \( \alpha \) at 1500°C is from [5], those shown as open circles for T 1800°C are from [7] and [8]). We should at this point emphasize that the application of these data to Type B CAIs will involve temperatures never very much greater than 1400°C, and that significant evaporation of magnesium might continue to temperatures significantly below this (e.g., 1250°C when, depending on the composition, the system might still partially molten). We suggest that the kinetic fractionation factor that should be used for \( ^{25}\text{Mg} \) relative to \( ^{24}\text{Mg} \) under these circumstances is \( \alpha \approx 0.989 \) (from Fig. 2) not 0.9798, which corresponds to \( \sqrt{24/25} \). This difference in the kinetic isotope fractionation factor may at first sight seem rather minor, but in fact it has a significant effect when using the isotopic fractionation of evaporation residues to calculate the fraction of the element evaporated. This is shown in Fig. 3 by comparing \( \delta^{25}\text{Mg} \) as a function of the % magnesium evaporated when
calculated using $\alpha = 0.9890$ and $\alpha = 0.9798$. As an illustration of the significance of this for using the magnesium isotopic fractionation to estimate how much more magnesium there must have been in the precursor to a Type B CAI, we show that a sample fractionated by 6 ‰ per amu would have lost 40% of its magnesium if $\alpha = 0.9890$, but only 25% if $\alpha$ were 0.9798. This is a very significant difference given that the bulk magnesium compositions of Type B CAIs are only depleted by a few 10s of % relative to plausible condensed precursors.

**Conclusion.** High precision Mg isotopic measurements of vacuum evaporation residues of initially Type B CAI-like liquids are consistent with the functional form given by Eqn. (2).

The kinetic isotope fractionation factor ($\alpha$ in Eqn. 2) for magnesium evaporating from an initially Type B CAI-like melt is significantly different from the commonly assumed value of $\alpha = \sqrt{24/25} = 0.9798$. We find the kinetic fractionation factor to be a function of the temperature at which evaporation takes place, and for $T \sim 1400°C$ (a reasonable peak temperature for Type B CAIs according to Stolper, 1982) we recommend using $\alpha = 0.9890$.