ELEMENTAL AND ISOTOPE FRACTIONATION OF CHONDRULE-LIKE LIQUIDS BY EVAPORATION INTO VACUUM.

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Introduction. Laboratory data on the evaporation kinetics and isotope fractionation of evaporation residues of silicate liquids exposed to vacuum or low-pressure gas of solar or dust-enriched compositions provide constraints on processes that affected the evolution of primitive inclusions in meteorites. In earlier work we focused on evaporations of Type B CAI-like liquids [1,4]. Here we will re-examine the evaporation kinetics of sodium and potassium from a chondrule-like liquid, and the isotopic fractionation of potassium of the evaporation residues. The quantities that need to be determined are the evaporation coefficients γ_i in the Hertz-Knudsen flux equation $J_i = \dfrac{\gamma_i P_i^{sat}}{\sqrt{2\pi m_i RT}}$ and the kinetic isotopic fractionation factor α defined as the ratio of the isotopic composition of the evaporation flux to that of the evaporating source. The usual representation of the kinetic isotopic fractionation factor for the ratio of isotopes i and j of mass m_i and m_j is $\alpha = (m_j/m_i)^{\beta}$ with β having always been found to be ≤ 0.5. Experiments involving the evaporation of sodium and potassium from CAI-like liquids have been previously reported by [2], however we believe there are still a number unresolved issues that would profit from further experiments.

Experimental and analytical methods. A starting chondrule-like composition similar to that used by [2] (wt% ~ 58% SiO_2, 23% MgO, 5% FeO, 4% Al_2O_3, 2% CaO, 3.5% Na_2O, 3.5% K_2O) was evaporated into vacuum (P=10^{-6} Torr) at 1470°C for various lengths of time. The elemental composition of the evaporation residues was measured both at the University of Chicago by electron microprobe measurements over large portions of the samples and at Lawrence Livermore National Laboratory by solution ICPMS. The two methods gave very comparable results. A portion of the dissolved samples was put through an ion exchange column to separate the potassium for isotopic analysis using the GV Instruments ISOPROBE multicollector ICPMS at the Lawrence Berkeley National Laboratory.

Evaporation trajectories and rates. Figure 1 shows the trajectory in Na_2O-K_2O space of our residues along with those reported by [2] for their evaporations in 10^{-5} bars of air.
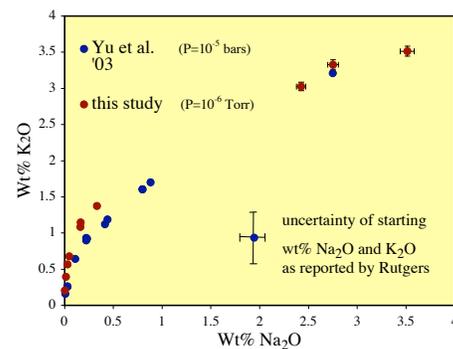

Figure 1. Trajectories in composition space defined by evaporation residues evaporated for different lengths of time into vacuum (our study) and into 10^{-5} bars air [2].

Figure 2 compares the evaporation rates of Na and K from our vacuum experiments with the lowest pressure experiments (10^{-5} bars air) from [2]. The evaporation rates of our shortest duration experiments were used together with a thermodynamic model for sodium and potassium vapor pressures integrated over the evaporation interval to calculate evaporation coefficients. We determined γ_{Na}= 0.09 and γ_K = 0.06. These values for the evaporation coefficients are

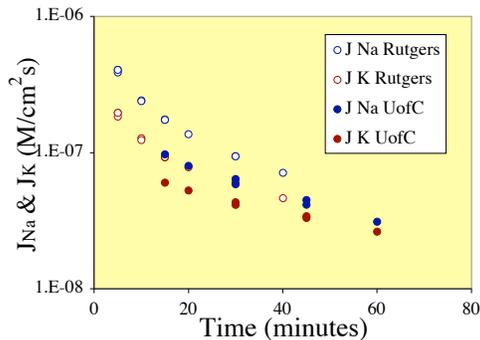about half the values reported by [3] based on their analysis of the data from [2].

Figure 2. Evaporation rates in moles per cm² per second for potassium (J_K) and sodium (J_{Na}) derived from our experiments and our estimate of the evaporation rates from the 10^{-5} bar experiments reported by[2] based on a reinterpretation of their published data.

K isotopic fractionation. A major motivation for our present study was to reexamine the isotopic fractionation of potassium in the evaporation residues of chondrule-like liquids. The earlier study [2] reported results from several sets of evaporation experiments done at different pressures and gas compositions. In all these experiments, the isotopic fractionations of the evaporation residues had unexpected features that if confirmed would require revising much of our understanding of kinetic isotope fractionations by evaporation. Only one set of the experiments reported by [2] (the P=10^{-5} bars air experiments) resulted in isotopic fractionations that more or less correspond to Rayleigh fraction behavior. However, as shown in Figure 3, the data imply a value for $\alpha_K \sim (39/41)^{0.56}$ or in other words, $\beta > 0.5$! All the other experiments reported by [2] resulted in isotopic fractionations that departed very significantly from the expectation of a Rayleigh fractionation process (see their Fig. 9). Figure 3 also shows the measured potassium isotopic composition of the evaporation residues from our experiments. In our case the isotopic data do correspond to a Rayleigh fractionation process but with a kinetic

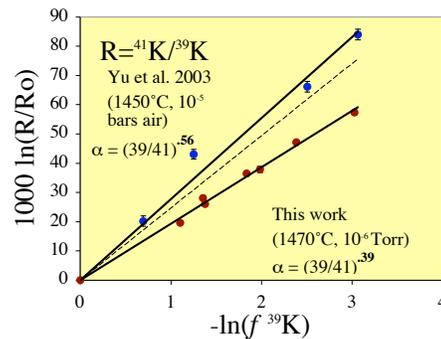isotope fractionation factor $\alpha_K = (39/41)^{0.39}$ (i.e., $\beta = 0.39$).

Figure 3. Isotopic composition of evaporation residues from our experiments (red symbols) and from [2] (blue symbols) plotted in such a way that a Rayleigh process would have the data fall on a line of slope $1000(\alpha-1)$. $f^{39}K$ is the fraction of original ^{39}K in the residue. The dashed line corresponds to $\alpha = (39/41)^{0.5}$.

Conclusions. Our new data on the evaporation coefficient of sodium and potassium are significantly less than one ($\gamma_{Na} = 0.09$, $\gamma_K = 0.06$) with the effect that the evaporation rates of these alkalis from a chondrule-like melt is significantly less than what one might expect by only taking into account their saturation vapor pressures. Similarly small evaporation coefficients have been found for silicon and magnesium evaporating from a CAI-like liquid [1]. The potassium isotopic fractionation of the vacuum evaporation residues corresponds to a Rayleigh fractionation process with $\alpha_K = (39/41)^{\beta}$ and $\beta = 0.39$. This value of the mass-dependence exponent β is similar to that of magnesium isotopes evaporating from a CAI-like liquid [4] ($\beta_{Mg} = 0.4-0.25$ in the temperature range 1900°C-1500°C).

References. [1] Richter F.M., Davis A.M., Ebel D. and Hashimoto A. (2002) *GCA* **66**, 521. [2] Yu Y., Hewins R., Alexander C.M.O'D. and Wang J. (2003) *GCA* **67**, 773. [3] Fedkin A., Grossman L. and Ghiorso M. (2006) *GCA* **70**, 206. [4] Richter F.M., Janney P., Mendybaev R., Davis A. and Wadhwa M. (2007) *GCA* **71**, 5544.