RAYLEIGH DISTILLATION CONSTRAINTS ON Mg ISOTOPIC COMPOSITIONS


For Mg, Ca, Ti, isotope fractionation effects in most terrestrial, lunar and meteoritic samples are extremely limited. By contrast, refractory inclusions show substantial isotope fractionation effects [1-3]. Isotope fractionation is of intrinsic interest: a) to identify kinetic isotope constraints in the condensation or distillation of materials in the early solar system; and b) to attempt to separate isotope fractionation effects from more general isotopic effects which can be attributed to specific nucleosynthetic components. Of particular importance are the FUN inclusions which show large isotope fractionation for Mg and O evidence for $^{16}\text{O}$ and deficits in $^{26}\text{Mg}$ after correction for mass fractionation [1,4]. In a recent report, Esat et al. [5] presented evidence for fractionation and isotope anomalies induced in Mg during laboratory distillation experiments.

We consider calculations which address these issues. Rayleigh distillation is an idealized process where the composition of the instantaneous distillate vapor ($v$) is related to the composition of the distillation reservoir ($r$):

$$\frac{dn_j}{dn_i} = \left(1 + a\right) \cdot \frac{n_i}{n_j}^v$$

If the reservoir remains well-mixed throughout a distillation process,

$$\frac{n_i}{n_j} = \left(\frac{f_j}{f_i}\right) \cdot \frac{n_i}{n_j}^0$$

where $f_j$ is the fraction of an index isotope ($j$) remaining in the reservoir, and $\left(\frac{n_i}{n_j}\right)^0$ is the initial composition. One usually assumes $a = \left(\frac{m_i}{m_j}\right)^{1/2} - 1$, where $m_i$ and $m_j$ are the molecular masses of the emitted species. Mass spectrometric data typically show isotope fractionation effects which are mass-dependent. This dependence is not calculable a priori. Several approximations or "laws" are in common use. Of these, the power law has been widely used

$$\frac{n_i}{n_j} = \left[1 + a\right]^{\left(\frac{m_i}{m_j}\right)} \cdot \frac{n_i}{n_j}^0$$

For Mg, one ratio, $^{25}\text{Mg}/^{24}\text{Mg}$, is typically used to calculate a fractionation factor [$F(^{25}\text{Mg})$, Table 1] and to normalize the second ratio (typically $^{26}\text{Mg}/^{24}\text{Mg}$) according to a chosen mass fractionation law. $^{26}\text{Mg}/^{24}\text{Mg}$ may then show deviations from the ratio obtained for a standard sample of normal composition. In Table 1, we show the $F(^{25}\text{Mg})$ in a Rayleigh distillation reservoir ($r$) as a function of the fraction of $^{25}\text{Mg}$ remaining in $r$. $F(^{25}\text{Mg})$ values substantially greater than unity are obtained for small values of $f(25\text{Mg})$. If the $^{26}\text{Mg}/^{24}\text{Mg}$ obtained for the reservoir by this (single stage) distillation were corrected for isotope fractionation using a Rayleigh-type fractionation law (i.e., Eq. 2), then for an initially normal composition, all corrected $^{26}\text{Mg}/^{24}\text{Mg}$ would be identical to normal, and $^{26}\text{Mg}=0$. If the power law is used to correct the data, deviations in $^{26}\text{Mg}/^{24}\text{Mg}$ ($\delta^{26}\text{Mg}$) from the normal value are obtained (3rd column of Table 1). These show a regular progression between $F(^{25}\text{Mg})$ and negative $\delta^{25}\text{Mg}$ indicating that in a Raleigh distillation, $^{26}\text{Mg}/^{24}\text{Mg}$ is enriched in the reservoir by a factor which is slightly less than the square of the factor for $^{25}\text{Mg}/^{24}\text{Mg}$. Esat et al. [5] stressed the importance of this artifact. We also calculate the artifacts produced, by the use of the power law, for the instantaneous vapor composition (subscript $v$) and for the integrated vapor condensate (subscript $c$), complementary to the reservoir. The instantaneous vapor is characterized initially by small positive $\delta^{26}\text{Mg}$ and is ~0.8°/oo offset from $\delta^{26}\text{Mg}$. The integrated
condensate is bounded by $\delta^{26}\text{Mg}<0.8^\circ/oo$ and zero. The regular behavior of $\delta^{26}\text{Mg}$ with $F(2^{5}\text{Mg})$ should be noted. If the FUN inclusions C-1 and EK-1-4-1 represent residues, then the negative $\delta^{26}\text{Mg}$ measured for C-1 and EK-1-4-1 are not consistent with this simple model, since EK-1-4-1 [$F(2^{5}\text{Mg})=20^\circ/oo$] has $\delta^{26}\text{Mg}=-3.5^\circ/oo$, which is more negative than that for C-1 by a factor of 2, while C-1 has $F(2^{5}\text{Mg})=30^\circ/oo$.

We may consider a model (I) in which we produce Mg fractionated by a single-stage Rayleigh process and then mix reservoirs obtained for different values of $F(2^{4}\text{Mg})$ with unfractionated, normal Mg to achieve a specified $F(2^{5}\text{Mg})$ for the mixture. Results are shown in Table 2 for mixtures which are characterized by $F(2^{5}\text{Mg})=20^\circ/oo$ and $30^\circ/oo$, the values for EK-1-4-1 and C-1. If the mixtures are corrected for mass fractionation, using the Rayleigh law, they all show $\delta^{26}\text{Mg}>0$ and a regular progression of $\delta^{26}\text{Mg}$ with $F(2^{4}\text{Mg})$. The observation of $\delta^{26}\text{Mg}>0$ follows from Eq. 2: on a plot of $2^{5}\text{Mg}/2^{4}\text{Mg}$ vs. $2^{9}\text{Mg}/2^{4}\text{Mg}$, there is a monotonic decrease in the slope of the line connecting the normal composition and the progressive compositions of the distillation reservoir. Model I cannot yield apparent deficits in $2^{6}\text{Mg}$. Use of the power law to normalize the mixture compositions results initially in small deficits in $2^{6}\text{Mg}$ ($\approx -1^\circ/oo$) which then approach $\delta^{26}\text{Mg}=0$ as $F(2^{4}\text{Mg})$ approaches 0.01; for lower $F(2^{4}\text{Mg})$, $\delta^{26}\text{Mg}$ becomes positive.

The basic conclusions are: a) residues of a Rayleigh process show only small artifacts of $\delta^{26}\text{Mg}$ if corrected by the power law unless extreme Mg fractionation is observed; b) the integrated condensates from a Rayleigh process have only positive $\delta^{26}\text{Mg}<0.8^\circ/oo$, if corrected with the power law; c) mixtures of single-stage Rayleigh distillation residues and of normal Mg will yield $\delta^{26}\text{Mg}>0$; this model is applicable for the case where only “surface evaporation” occurs; d) there is a general correlation of $F(2^{5}\text{Mg})$ and artifacts in $\delta^{26}\text{Mg}$ as shown by Esat et al. [5]; e) the detailed limits on $\delta^{26}\text{Mg}$ artifacts, produced by the models considered here, indicate that the results of Esat et al. [5] must be described by either a more complex process than considered here, or by a process which does not follow the Rayleigh distillation model with the fractionation assumed to be a function of $\text{m}^{1/2}$; f) the observed large excesses in $2^{6}\text{Mg}$ attributed to $2^{5}\text{Al}$ decay and the more general, large isotope anomalies for several elements cannot be considered to be artifacts.