

EVAPORATION KINETICS OF OXIDES OF RARE EARTH AND REFRACTORY TRACE ELEMENTS, AND THE CHEMICAL FRACTIONATION OF HIBONITE BY EVAPORATION; A. Hashimoto, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138, USA

Highly-enriched patterns of rare earth element concentrations in Ca,Al-rich inclusions have been interpreted as resulting from the condensation of gas that occurred in the primordial solar nebula [1,2]. It has been suggested that evaporation of volatile-rich starting materials such as carbonaceous chondrites would have produced similar effects [3] (except for the case of the Group II REE pattern, which requires at least one condensation event [2]). Which of these processes (or maybe both) was responsible for which kinds of CAIs? More importantly, can the patterns of chemical fractionation imprinted in CAIs provide detailed information on physical conditions in the nebula during evaporation and condensation? Consideration of gas-mineral equilibrium [4] cannot answer these questions, because it describes only final equilibrium states and does not distinguish condensation from evaporation.

To answer these questions, I have continued experimental studies on the kinetics of evaporation and condensation of oxides of planetary interest. Experimental methods were described in [5,6]. To assess kinetic effects, the "evaporation coefficient" defined by $\alpha_v = J_v/J_e$ and $J_e = P(2\pi MRT)^{-1/2}$ [7] is useful, where J_v is the evaporation rate obtained in vacuum (determined experimentally), and J_e is the theoretical maximum evaporation rate, which is equal to the incident rate of gas molecules onto a surface of their own condensed phase that is in equilibrium with the gas (the latter is calculated from the kinetic theory of gases; P is the equilibrium vapor pressure and M the molecular weight of the gas). If $\alpha_v = 1$, there is no kinetic effect; if $\alpha_v < 1$, evaporation and condensation are kinetically inhibited to the extent that this coefficient is smaller than unity. (α_v should never exceed unity, by definition.)

The first row of Table 1 shows evaporation coefficients of pure solid sesqui-oxides of REE (except Ce, Pr and Tb) and some other refractory trace elements (RTE: Sc, Y, Zr and Hf), determined experimentally. Those of Er and Tm exceed unity, implying that the thermodynamic data for their gases, used in calculating P , are in error. Excluding these and two other elements (Dy and Ho) whose oxide gas species have the largest assigned errors in dissociation energy, the elements fall into two groups: one with $\alpha_v \sim 1$, and the other with $\alpha_v = 0.5-0.6$. Thus, oxides of La, Nd, Eu^{3+} , Yb and Hf are not kinetically constrained in their evaporation and condensation. The reason for Sm, Gd, Lu, Sc, Y and Zr having small α_v is not yet understood. However, the fact that α_v has little or no temperature dependence (except for Lu, where α_v increases with temperature) indicates that the kinetic constraint is related only to entropy. Small α_v values of simple organic molecules have been attributed to inhibition of some rotational degrees of freedom of polymeric vapors in the activated state [8]. This cannot be true for oxides of REE and RTE, as then all of them would exhibit α_v values smaller than unity, which is not the case.

Using the evaporation coefficients determined, changes in the concentrations of REE and RTE during evaporation of various host phases can be calculated by assuming that α_v values obtained for the pure oxides do not change when they are mixed into hosts. This assumption is justified by experiments performed on pure oxides and compounds of Ca, Mg, Si and Al [6,9]. Additionally, one needs to know the activity coefficients (γ) of REE and RTE oxides in hosts. Those in hibonite have been determined [10] and are used in the present calculation. However, their values (*e.g.*, 1200 for $\text{EuO}_{1.5}$ and 24000 for $\text{YbO}_{1.5}$) appear to be too high; greater thermodynamic stability would be attained if pure REE oxides exsolved out of hibonite, for γ values this high. I have recalculated the activity coefficients, using the relationship between an activity coefficient and the depolymerization ability of cationic elements (Eu^{2+} or Sr^{2+}) in silicates and aluminates. The results are shown in the 2nd row of Table 1. The activity coefficient *ratios* between REE are the same as those in [10]. The values for RTE are order-of-magnitude estimates.

Assume C1-chondritic material is subjected to evaporation until only hibonite remains as a residue. By this time REE and RTE are enriched by 56x relative to C1, if they and Al have not yet begun to evaporate. Using this hibonite as initial material for further evaporation, the concentrations of REE and RTE in it have been calculated. The hibonite is assumed to evaporate nearly stoichiometrically, as is suggested by thermodynamic calculations and by my experiments. Results are shown in Figs. 1 (40% evaporation) and 2 (99.8%). Two evaporation mechanisms are considered. In the first, net evaporation occurs very slowly, as most of the vapor

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recondenses onto hibonite; the vapor and hibonite are in equilibrium at least temporarily, but the vapor is eventually removed from the system. This is so-called "Rayleigh distillation"; α_v is effectively unity for all the elements. The second corresponds to evaporation that is completely controlled by kinetics (i.e., "vacuum evaporation"); measured α_v values are used in the calculations.

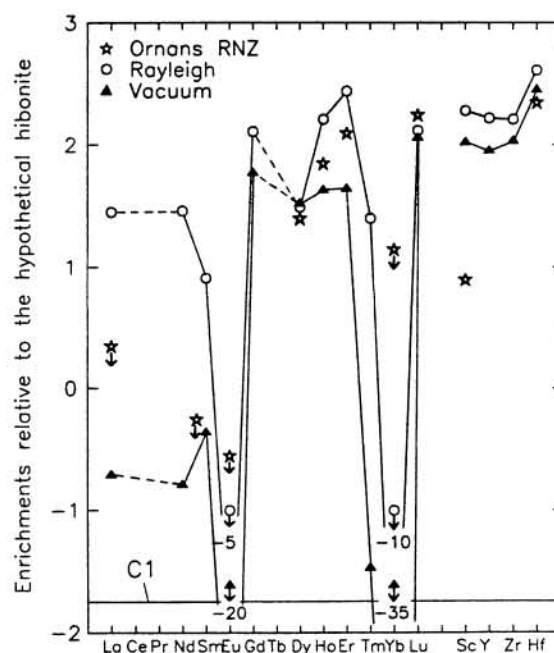
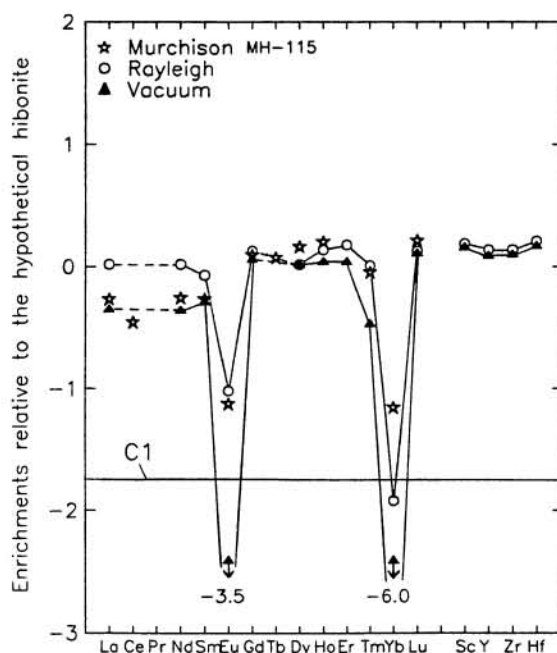
Results showed the γ values of Table 1 to be still too large: even heavy REE are depleted by both mechanisms, because the evaporation rates of REE are larger than that of Al if the values of γ in Table 1 are used. Since the absolute magnitudes of REE activity coefficients are the most uncertain among the parameters used (their activity coefficient *ratios* are fairly well defined), these are treated as a single free parameter. γ values uniformly reduced by 5 and 10 times for all REE and RTE except Sc were used in Figs. 1 and 2, respectively, to produce REE patterns similar to those in natural CAIs. The Rayleigh and vacuum evaporation mechanisms yield significantly different patterns, considering the relatively small differences in α_v between REE. This is again due to the fact that the volatilities of REE are very close to that of Al. The patterns of Ormans inclusion RNZ [11] and Murchison MH-115 [12] seem to be best approximated by a combination of the Rayleigh and vacuum evaporation mechanisms. This suggests that evaporation occurred under non-equilibrium, but not extreme non-equilibrium, conditions.

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Table 1. Evaporation coefficients (α_v) and activity coefficients (γ) of oxides in hibonite

	La	Nd	Sm	Eu ³⁺	Gd	Dy	Ho	Er	Tm	Yb	Lu	Sc	Y	Zr	Hf	Al	Ca
α_v^*	.95	.99	.60	1.0	.55	.34	.76	1.4	1.1	1.0	.56	.56	.54	.47	1.0	.35	1.0
γ^{**}	1.2	2.3	3.3	4.4	5.8	16	26	41	60	86	118	1	26	100	100	1.0	0.1

* Average of 3 to 4 data obtained at 1700-2200°C. ** Pure solid oxides taken as reference states.



Figs. 1 & 2. Enrichment factors (in \log_{10}) of REE and RTE in hibonite after evaporation at 2100 K (just below the hibonite m.p.) relative to the initial hypothetical hibonite enriched uniformly in these elements by 56X relative to C1-chondrites. Calculations (Rayleigh and vacuum evaporations), and natural CAIs [10,11] are compared. Residual volume fractions of the hibonite for the calculated patterns are 0.6 and 0.002 in Fig.1 (left) and 2, respectively.