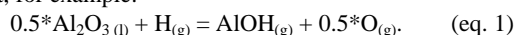


EVAPORATION AND THE ISOTOPIC COMPOSITION OF TYPE A AND B REFRACTORY INCLUSIONS. D.S. Ebel, L. Grossman¹, S.B. Simon, A. Davis¹, F.M. Richter, N.M. Parsad, Department of the Geophysical Sciences, 5734 South Ellis Ave., ¹also Enrico Fermi Institute, University of Chicago, Chicago, IL 60637 (debel@midway.uchicago.edu).

Calculations are described which predict the evolution of chemical compositions of non-ideal CaO-MgO-Al₂O₃-SiO₂ (CMAS) liquids undergoing open system evaporation into pure H₂ gas. This evaporation model is used to explain the degree of mass fractionation of Mg and Si isotopic compositions observed in refractory inclusions [1, 2].

Equilibrium Vapor Pressure: Assume an infinite reservoir of CMAS liquid, at fixed P(H₂) and temperature (T). For every gaseous species (see [3] for a complete list), a balanced chemical reaction can be written involving only that species, monatomic H and O, and a liquid oxide component, for example:



Determining the equilibrium constants, K , for these reactions from the Gibbs energies of the various species, and using Berman's model [4] for the activities, a , of CMAS liquid oxides, a mass-action law can be written for each gaseous species, e.g. from eq. 1:

$$P_{\text{AlOH}} = K(a_{\text{Al}_2\text{O}_3})^{0.5} P_{\text{H}} P_{\text{O}}^{-0.5}. \quad (\text{eq. 2})$$

Expressions in P_{H} and P_{O} can be written for $P(\text{O}_2)$, $P(\text{H}_2\text{O})$, etc. The dissociation constant for H₂ fixes P_{H} at a fixed $P(\text{H}_2)$. A mass-balance expression can be written expressing a "total pressure" of each element, for example,

$$P_{\text{Al}}^{\text{tot}} = P_{\text{Al}} + P_{\text{AlOH}} + P_{\text{AlO}} + \dots, \quad (\text{eq. 3})$$

resulting in 5 equations in 6 unknowns: P_{O} and $P_{\text{Ca}}^{\text{tot}}$, $P_{\text{Mg}}^{\text{tot}}$, $P_{\text{Al}}^{\text{tot}}$, $P_{\text{Si}}^{\text{tot}}$, $P_{\text{O}}^{\text{tot}}$. Finally, it is apparent that evaporated metal atoms cannot leave their oxygen behind in the liquid, so the sixth equation necessary to solve the system is

$$P_{\text{O}}^{\text{tot}} = P_{\text{Ca}}^{\text{tot}} + P_{\text{Mg}}^{\text{tot}} + 1.5P_{\text{Al}}^{\text{tot}} + 2P_{\text{Si}}^{\text{tot}}. \quad (\text{eq. 4})$$

Substitution of equations like eq.2 into eq.3, and of eq.3 into eq.4 results in a single, non-linear equation in P_{O} , which can be solved quickly by iteration, allowing calculation of the partial pressures of all gas species in equilibrium with the fixed liquid composition.

One may, alternatively, fix the total pressure of the system, P^{tot} , rather than $P(\text{H}_2)$. An initial estimate of P_{H} is chosen, and P_{O} determined as above. Then P_{H} alone is adjusted so that the sum of all partial pressures is equal to P^{tot} . A new P_{O} is computed with this new P_{H} , then a new P_{H} is computed, and so forth to a stable solution.

Evaporation Model: The process of open system evaporation can be approximated by calculation of the vapor pressure over the liquid at each of a series of small, equilibrium evaporation steps. Once the vapor composition over a particular liquid composition is determined, sufficient vapor of that composition is removed from the system such that one percent of the initial Mg is lost from the liquid. That is, the liquid composition is adjusted to reflect the loss of vapor having the computed composition. The new liquid composition becomes the initial composition for the next evaporation step.

The "evaporated" increment is here assumed to contain CMAS oxides in proportion to their vapor pressures over the liquid. In a full kinetic treatment of evaporation

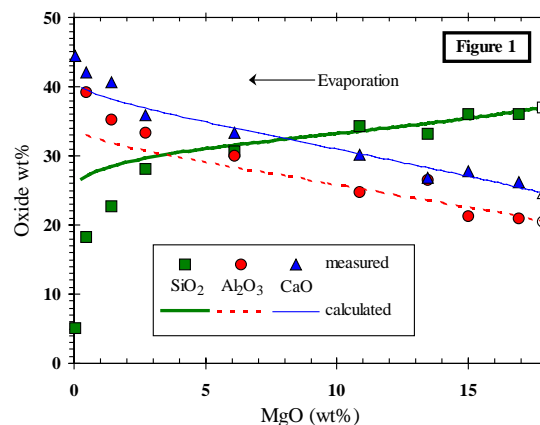
rates from a CMAS droplet into a CMAS-free gas, the Hertz-Knudsen equation states,

$$J_i = \alpha_i P_i / (2\pi m_i kT)^{0.5} \quad (\text{eq. 5})$$

in which k is the Boltzmann constant, T is in Kelvins and J , α , P and m are the flux from the droplet, the evaporation coefficient, the equilibrium vapor pressure and mass, respectively, of each evaporating species i . At all conditions investigated, the vapor pressures of Ca and Al species are $\sim 10^{-7}$ times those of Mg and Si, and $\text{Mg}_{(g)}$ and $\text{SiO}_{(g)}$ contain >99% of the Mg and Si in the vapor. The evolution of the SiO_2/MgO ratio in the droplet is, therefore, directly related to the relative loss rates of $\text{SiO}_{(g)}$ and $\text{Mg}_{(g)}$,

$$J_{\text{SiO}}/J_{\text{Mg}} = (m_{\text{Mg}}/m_{\text{SiO}})^{0.5} (\alpha_{\text{SiO}}/\alpha_{\text{Mg}}) (P_{\text{SiO}}/P_{\text{Mg}}). \quad (\text{eq. 6})$$

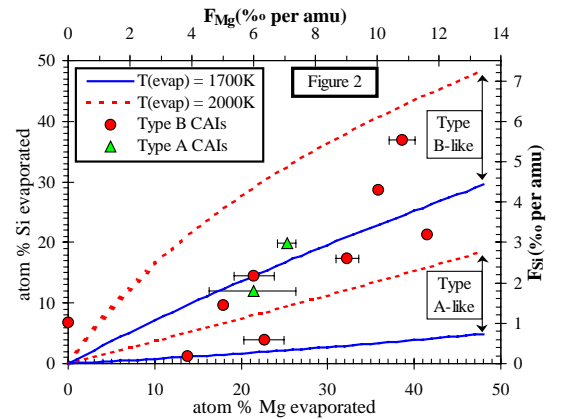
Little is known about the relative α values of different molecules evaporating from a liquid, but α for the congruent evaporation of forsterite varies by a factor of 5 with T , gas composition and crystallographic orientation [5]. Because of this uncertainty and the fact that measured activities [6] sometimes differ by several tens of percent from those predicted by the model [4] for CMAS liquids, we have taken the relative loss rates of SiO_2 and MgO simply as the calculated ratio $P_{\text{SiO}}/P_{\text{Mg}}$. The justification for doing so is the excellent agreement between model results and experimental observations seen in Fig. 1.



Comparison to Experiment: A bulk composition slightly more Mg- and Si-rich than Type B CAIs, 24.61 wt% CaO, 17.84 MgO, 20.51 Al₂O₃, 37.04 SiO₂ (open symbols in Fig.1) was melted and evaporated in 1.8×10^{-4} bar of flowing H₂ at 1773K using the facilities and methods of [7]. The evaporation calculation described above was performed for the same conditions and bulk composition. The concentrations of oxides measured in the experimental residue at different degrees of evaporation are compared in Fig. 1 with the evolution of the concentrations predicted by the evaporation model. Agreement between theory and experiment is excellent from 0 to $\sim 90\%$ Mg evaporation. Discrepancies at <3 wt% MgO remaining ($> \sim 90\%$ Mg

evaporated) could be due to either experimental problems or inadequacy of the model at extreme fractionations.

Isotopic Constraints: Heavy isotope enrichments of Mg and Si in non-FUN, coarse-grained CAI have been attributed [2] to partial evaporation. In Fig. 2, the degree of mass fractionation of Si, F_{Si} , is plotted relative to F_{Mg} for Allende samples 3675A, AL15-5, Egg-1, Egg-2, F2, F3, F6, F7, F11 and F12 of [2], and for Vigarano inclusions 1623-2 and 1623-8 from [8] for Si and [9] for Mg. All F_{Si} data are adjusted to an initial solar system F_{Si} of -0.28 ‰/amu [1]. Assuming $Mg_{(g)}$ and $SiO_{(g)}$ are the dominant evaporating species, the Rayleigh equation for kinetic isotope fractionation was used to calculate the percentages of each of the original Mg and Si that would have had to be evaporated from any starting material to account for F_{Mg} and F_{Si} , respectively, and the results are used to label the axes in Fig. 2. Most Type B inclusions underwent 15-35% evaporation of Mg and 5-25% evaporation of Si. The two type A inclusions lost 20-25% of their Mg and 10-20% of their Si.



Mg-Si Relations: The curves in Fig. 2 illustrate calculated evaporation paths, at $P(H_2)=10^{-8}$ bar, at 1700 and 2000K, for two potential CAI precursor compositions. These initial bulk compositions (Table 1) are taken from the CMAS portion of the condensate assemblage in equilibrium with vapor in a system of solar composition at $P^{tot} = 10^{-5}$ bar, at 1320K (Type A-like) and 1310K (Type B-like) [3], and are somewhat more MgO- and SiO_2 -rich than the measured bulk compositions of Type A and B CAI's [10].

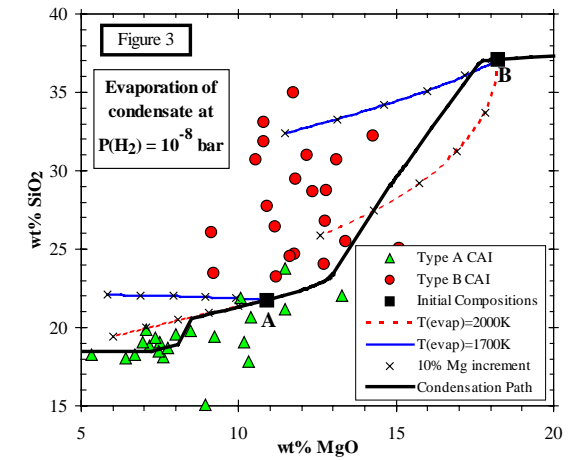
Table 1 (wt%)	CaO	MgO	Al ₂ O ₃	SiO ₂
Type A-like	29.74	10.90	37.58	21.79
Type B-like	19.76	18.24	24.92	37.08

Clearly, the relative amounts of Mg and Si evaporated from liquids depend strongly on the initial bulk composition and the evaporation T (T_{evap}). For each starting composition, there is a progressively greater fractional loss of SiO_2 for a given loss of MgO, with increasing T_{evap} . Also, for fixed T_{evap} , the fractional loss of SiO_2 for a given loss of MgO decreases with decreasing SiO_2 content in the initial composition.

The locus of bulk compositions of equilibrium condensates produced at different temperatures is plotted in Fig. 3, along with measured compositions of Type A and B CAIs, corrected to the solar CaO/Al_2O_3 ratio following [10]. In Fig. 3, A and B denote locations of the Type A-like

and Type B-like compositions discussed above. These represent, however, only two discrete points on a continuum of possible condensate assemblages along the condensation path. Also plotted in Fig. 3 are the evolutionary paths of the compositions of evaporation residues of A and B, calculated at 1700 and 2000K, demarcated in increments of 10% of the original Mg evaporated, to 50%. A large family of such paths exists, considering the continuum of possible initial condensate compositions and temperatures.

For a given degree of evaporation, at a given T_{evap} , the Type A-like composition changes much less than the Type B-like one. Most Type A and B CAI compositions are consistent with evaporation of up to 30% of the initial Mg and up to 10% of the initial Si, at 1700K, from condensate compositions intermediate between points A and B. The evaporation model thus suggests that the bulk compositions of Type A and B CAIs are consistent with the degree of Mg evaporation inferred from their Mg isotopic compositions, but predicts slightly less Si evaporation than do the Si isotopic data. The isotopic data are not, however, for the same CAI as the bulk composition data.



Conclusions: The amounts of Mg and Si evaporation required to produce the observed isotopic compositions of both Type A and B CAIs are broadly consistent with the amounts of evaporation necessary to move bulk chemical compositions of condensates into the field of the CAIs.

The precursor of each Type A and B inclusion could have formed by equilibrium condensation or evaporation in a nebular gas. Inclusions could subsequently have experienced open system evaporation, above their melting temperatures, in a gas highly depleted in Mg, Si, and O. This sequence of events is consistent with both major element oxide compositions, and Mg and Si isotopic compositions of CAIs.

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