

# EFFECT OF FRACTIONAL CRYSTALLIZATION ON $\delta^{25}\text{Mg}$ OF EVAPORATION RESIDUES OF CMAS LIQUIDS. A. V. Fedkin<sup>1</sup> and L. Grossman<sup>1,2</sup>, <sup>1</sup>Dept. of the Geophysical Sciences, <sup>2</sup>Enrico Fermi Institute, The University of Chicago, 5734 S. Ellis Ave., Chicago IL 60637.

**Introduction.** The chemical and isotopic evolution of CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CMAS) liquids during simultaneous crystallization and evaporation was studied theoretically in pure H<sub>2</sub> in [1] and in a closed system of solar composition in [2]. It was shown in [2] that the fraction of Mg evaporated that is calculated from the bulk isotopic composition of a residue using the Rayleigh equation may be an underestimate because of preservation of relatively unfractionated Mg due to fractional crystallization. In this work, the effects of ambient total pressure and cooling rate on the deviation of the model bulk isotopic composition from that calculated from the Rayleigh equation are explored.

**Method.** A CMAS liquid droplet of a given initial composition is assumed to be immersed in modified solar gas, which is a solar gas except for the amounts of elements and isotopes in the droplet. The activity-composition model of [3] is used to calculate vapor pressures of all species over CMAS liquids in modified solar gas at any temperature and ambient total pressure, as in [4]. Mg and SiO are found to be the dominant evaporating species, and the vapor pressure of each Mg isotope is calculated assuming no equilibrium isotopic fractionation between liquid and vapor. The evaporation flux,  $J$ , of each chemical and isotopic species,  $i$ , is related to its vapor pressure,  $P_i^{\text{vap}}$ , through the Hertz-Knudsen equation,

$$J_i = \frac{\alpha_i (P_i^{\text{vap}} - P_i^{\text{amb}})}{\sqrt{2\pi m_i RT}},$$

where  $\alpha$ ,  $P^{\text{amb}}$  and  $m$  are the evaporation coefficient obtained from [1], the ambient pressure and molecular weight, respectively. Changes in chemical and isotopic composition of the droplet are accompanied by complementary changes in the surrounding gas.

The activity model [3] is also used to calculate the equilibrium amounts and compositions of spinel, melilite and liquid at any temperature. The Mg evaporation rate from solids is assumed to be negligible compared to that from the liquid. All spinel equilibrates with the liquid except for a portion, calculated from the volume fraction of melilite, which is assumed to become trapped inside crystallizing melilite. We assume that 600 equal-sized, spherical melilite crystals form in the droplet. All melilite and the spinel trapped within it is assumed to be chemically and isotopically isolated from the liquid except for a fraction within a distance  $x = (D_{\text{Mg}} t)^{0.5}$  of the melilite crystal surfaces, where  $D_{\text{Mg}}$  is the diffusion coefficient of Mg as a function of akermanite content and temperature taken from [5], and  $t$  is the time step size. Allowance is made for the fraction of the surface area of the droplet occupied by

crystals, assumed equal to their volume fraction. This decreases the surface area available for evaporation, reducing evaporation rates. All liquid remaining at the solidus, 1500 K, is assumed to crystallize as clinopyroxene and anorthite. A high-temperature solid condensate assemblage of composition  $\delta$  (CMAS = 24.4, 15.1, 30.8, 29.8 wt%) is heated instantaneously to 1680 K, where it partially melts into a droplet of 0.25 cm radius and cools to 1500 K at a given rate. For each cooling rate, a time step is selected ~ the time required to cool by 1 K. At each time step, the chemical composition and temperature are used to calculate the amounts and compositions of melilite, spinel and liquid, the densities of all phases, the droplet radius and the fraction of the droplet surface area occupied by crystals. Then, the amounts of elements and isotopes evaporated are calculated from their fluxes and the droplet radius. These are subtracted from the amounts present in the droplet to obtain the liquid composition and added to the amounts present in the gas to obtain the gas composition, both for the next time step. Crystallizing melilite and spinel have the same isotopic composition as the liquid. The chemical and isotopic compositions of the isolated melilite and spinel, “the sequestered assemblage”, produced at each time step are cumulatively summed. The chemical composition of the combined liquid + equilibrated phases, “the equilibrating system”, are used to calculate the phase assemblage for the next time step.

**Results.** In the first case,  $P_{\text{H}_2} = 1\text{e-}3$  bar in the ambient, modified solar gas. Relict spinel occurs at 1680 K and, as the droplet cools at 5 K/hr, the liquid gradually evaporates, more spinel crystallizes and melilite starts crystallizing at 1673 K. By 1500 K, 36.8 % of the total Mg has evaporated, melilite (virtually all of which is sequestered) accounts for 10 % of the initial Mg, equilibrated spinel 21 %, trapped spinel 16 %, and the remaining liquid 16 %. As Mg evaporation proceeds,  $\delta^{25}\text{Mg}$  of the equilibrating system becomes progressively higher, reaching 10.7 ‰ by 1500 K. Because the sequestered assemblage preserves the isotopic composition of the liquid at each time step, its  $\delta^{25}\text{Mg}$  increases more slowly with falling temperature, reaching 6.9 ‰ by 1500 K.  $\delta^{25}\text{Mg}$  of the final, bulk residue, 9.08 ‰, is the weighted average of those of the sequestered assemblage and the equilibrating system which finishes crystallizing at 1500 K (Fig. 1a). Note that simple substitution of the fraction of <sup>24</sup>Mg remaining into the Rayleigh equation, using the inverse square root of the masses as the gas/liquid fractionation factor, yields bulk  $\delta^{25}\text{Mg} = 9.31$  ‰, a value 0.23 ‰ higher than the model result. Rayleigh distillation

assumes that the entire residue undergoes a uniform degree of evaporation. Thus, the above deviation is due to preservation in the residue of early crystals whose Mg is not as isotopically fractionated as that in late crystals that equilibrate with the most highly evaporated liquid.

At lower cooling rates, more Mg evaporates by 1500 K. Thus, in an identical calculation at 2 K/hr, 56.2 % of the Mg evaporates by the time the solidus temperature is reached. In this case, the fraction of the initial Mg in the sequestered assemblage and in the equilibrating system are 32.2 % and 11.6 %, resp. (vs. 26.6 % and 36.6 % at 5 K/hr). Relative to the *residual* Mg, however, 73 % is in the sequestered assemblage at 2 K/hr (Fig. 1b) and only 42.1 % at 5 K/hr. At 2 K/hr,  $\delta^{25}\text{Mg}$  of the sequestered assemblage rises to 12.4 ‰ by 1500 K.  $\delta^{25}\text{Mg}$  of the equilibrating system increases sharply from 1680 K to 1537 K where it reaches a maximum at 22.6 ‰ and then falls slightly due to partial exchange with the light isotope-enriched gas. As a result,  $\delta^{25}\text{Mg}$  of the bulk residue reaches 15.1 ‰ at about 1580 K and levels off. Substitution of the fraction of  $^{24}\text{Mg}$  remaining into the Rayleigh equation yields bulk  $\delta^{25}\text{Mg} = 16.8$  ‰, a difference of +1.7 ‰ from the model result. This difference is considerably larger than the difference at 5 K/hr.

The model bulk  $\delta^{25}\text{Mg}$  has been shown to deviate from that calculated from the Rayleigh equation by a greater amount at lower cooling rate. This is because decreasing the cooling rate increases the amount of Mg evaporation. As can be seen by comparing Figs. 1a and 1b, the greater the degree of evaporation, the greater is the proportion of the residual Mg sequestered in grains which preserve isotopic compositions of relatively early, partially evaporated liquids. In Fig. 2a,  $\delta^{25}\text{Mg}$  is plotted against the fraction of the total Mg evaporated for a series of model computations at different cooling rates but otherwise identical to those above, and compared to the Rayleigh fractionation curve for reference. The progressive departure of the model computations from the Rayleigh curve with decreasing cooling rate is clear. The degree of Mg evaporation also increases with increasing  $P_{\text{H}_2}$  at constant cooling rate. The results of a series of model calculations, identical to those above but at 3 K/hr and different values of  $P_{\text{H}_2}$ , are shown in Fig. 2b. The model calculations depart progressively from the reference Rayleigh curve with increasing  $P_{\text{H}_2}$ . Note that the departure of the model calculation from the Rayleigh curve is especially high at the highest  $P_{\text{H}_2}$ ,  $8.3\text{e-}3$  bar. In these models, high total nebular pressure is the cause of high  $P_{\text{H}_2}$  and high partial pressures of all other ambient species, including  $P_{\text{Mg}}^{\text{amb}}$ . High  $P_{\text{H}_2}$  increases  $J_{\text{Mg}}$ , causing  $P_{\text{Mg}}^{\text{amb}}$  in this closed system calculation to build up. At  $P_{\text{H}_2}=8.3\text{e-}3$  bar,  $P_{\text{Mg}}^{\text{amb}}$  becomes equal to  $P_{\text{Mg}}^{\text{vap}}$  above 1500 K. This, in turn, causes recondensation of Mg from the relatively light isotope-enriched gas, which has a larger effect on  $\delta^{25}\text{Mg}$  than on the MgO content of the bulk residue.

Because fractional crystallization probably occurred during evaporation of refractory inclusion melts [1], substitution of an inclusion's bulk  $\delta^{25}\text{Mg}$  into the Rayleigh equation will result in underestimation of the fraction of Mg evaporated by an amount which increases with decreasing cooling rate and increasing  $P_{\text{H}_2}$ .

**References.** [1] Grossman L. *et al.* (2002) *GCA* **66**, 145 [2] Fedkin A.V. & Grossman L. (2003) *LPSC XXXIV*. [3] Berman R.G. (1983) PhD thesis, UBC. [4] Grossman L. & Fedkin A.V. (2003) *GCA*. In press. [5] Morioka M. & Nagasawa H. (1991) *GCA* **55**, 751-759.

