

MAGNESIUM AND SILICON ISOTOPIC COMPOSITIONS RECORDED DURING SIMULTANEOUS CRYSTALLIZATION AND EVAPORATION OF CMAS DROPLETS INTO AMBIENT SOLAR GAS.

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Introduction. Activity-composition models were used to calculate vapor pressures over CaO-MgO-Al₂O₃-SiO₂ (CMAS) liquids and, from these, the change in chemical and isotopic compositions of droplets having compositions of reasonable condensate precursors of Types A and B refractory inclusions during simultaneous cooling, crystallization and evaporation into pure H₂ [1]. In that work, melilite and spinel trapped within melilite crystals were assumed to be chemically and isotopically isolated from the liquid after melilite formation, but spinel surrounded by liquid was assumed to be in complete chemical and isotopic equilibrium with it. Evaporation rates of liquids were assumed to be so much greater than those of solids that the latter were ignored. In [2,3], techniques were developed for calculating both the vapor pressures over CMAS liquids in a gas of *any* composition, and the effects of ambient gas composition on the evaporation rate of a CMAS liquid. They were used to model the chemical and isotopic evolution of a completely molten droplet having the composition of a high-temperature condensate during cooling and evaporation in an 11-element, closed system of solar composition. In [2,3], as evaporation proceeded with falling temperature, ambient pressures of evaporating species were allowed to rise, causing retardation of evaporation rates, and $\delta^{25}\text{Mg}$ and $\delta^{29}\text{Si}$ of the ambient gas allowed to fall while those of the droplet rose. The present work combines the features of both studies [1,3], permitting calculation of the chemical and isotopic evolution of a CMAS droplet during simultaneous cooling, crystallization and evaporation into a "modified" solar gas, *i.e.* solar composition except for the amounts of elements and isotopes in the droplet.

Results. In the present work, several improvements combine to yield results differing from those in [1]. Because H₂O_(g) forms by reaction of ambient H_{2(g)} with MgO and SiO₂ in the droplet, P(H₂O) decreases with falling temperature. At each temperature step, P(H₂) was held constant in [1] but here the total number of atoms of H per liter are held constant. As a result, the P(H₂)/P(H₂O) ratio increases more with falling temperature in the present work than in [1], causing evaporation of slightly more Mg and Si in this study, all else being equal. In the present work, densities of liquid [4], melilite [5,6] and spinel [7] are allowed to vary with composition and/or temperature, while they were held constant in [1]. The largest effect of this is to make the surface area of the droplet ~8% larger in the

present study, leading again to more evaporation of Mg and Si than in [1], all else being equal. In [1], reduction of the surface area of the evaporating liquid due to crystallization was ignored, while in this work the fraction of the surface area occupied by solids is assumed equal to the volume fraction of crystals. This typically reduces the amount of evaporation by 10-20% compared to [1], and more than offsets the increase in the amount of evaporation due to different treatments of density and hydrogen speciation.

When a high-temperature condensate assemblage of composition δ (CMAS=24.4, 15.1, 30.8, 29.8 wt%) is melted into a droplet of 0.25 cm radius, and cooled at 2K/hr from 1693 to its solidus, 1500K, while immersed in modified solar gas at P^{tot}(H)=1.67x10⁻³ bar, relict spinel accounts for 33% of the Mg and melilite (X_{Ak}=0.22) begins crystallizing at 1688K (Fig. 1). If the droplet surface is assumed to be crystal-free (case #1), evaporation rates of Mg and Si are very high because of the high P(H₂) and, at this slow cooling rate, 66% of the Mg and 50% of the Si evaporate by 1657K. As a result, $\delta^{25}\text{Mg}$ and $\delta^{29}\text{Si}$ of the liquid increase continuously with falling temperature (Fig. 2). Melilite and the spinel trapped within it that precipitate from this liquid not only record a range of $\delta^{25}\text{Mg}$ from 3 to 36‰ and of $\delta^{29}\text{Si}$ from 1 to 24‰, but also preserve these isotopic compositions because these crystals do not re-equilibrate with the liquid. Meanwhile, the liquid undergoes a rapid decline in its MgO and SiO₂ contents, resulting in reverse zoning of melilite and in resorption of spinel not trapped inside melilite. X_{Ak} falls to <0.01 at 1659 and melilite stops precipitating at 1657K ("Mel out"). Evaporation of Si continues below this temperature, causing $\delta^{29}\text{Si}$ of the liquid to reach 31‰ by 1648K before exchange with the ambient gas causes it to decline. Without ongoing precipitation of SiO₂-bearing phases, however, no Si isotopic record of this stage of evolution is preserved. All spinel not encased in melilite is resorbed by 1642K ("Spn out"). While Mg evaporation continues below 1657K, and causes $\delta^{25}\text{Mg}$ of the liquid to reach 77‰ before exchange with the ambient gas causes it to decline below 1642K, no MgO-bearing solids that record this isotopic excursion survive. At this point, the liquid contains only ~0.05 wt% MgO and ~2.5% SiO₂. This liquid would probably crystallize to a mixture of calcium aluminates but a SiO₂-bearing liquid may persist with very low vapor pressures of Mg_(g) and SiO_(g). Assuming no calcium aluminates form, the ambient pressures

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of $Mg_{(g)}$ and $SiO_{(g)}$ exceed their vapor pressures at 1638K and 1626K, respectively, causing Mg and Si condensation. When the MgO content of the liquid rises to 0.24 wt%, spinel resumes crystallization ("Spn in"), ultimately amounting to ~3% of all the spinel in the residue. Because its Mg is all derived from recondensation, this spinel has $\delta^{25}Mg = -13\%$. Although the SiO_2 content of the liquid ultimately reaches ~6%, melilite crystallization never resumes. Assuming all remaining liquid crystallizes in some form at 1500K, the final bulk SiO_2 and MgO contents are 19.5 and 6.2 wt%, respectively, similar to some Type A inclusions [8]. The weighted average of the isotopic compositions of the residual phases yields $\delta^{25}Mg$ and $\delta^{29}Si$ of 15‰ and 5‰, respectively, for the bulk inclusion, much higher than those of Type As [8]. In this model calculation, 70% of the initial Mg and 51% of the Si evaporated. A simple Rayleigh calculation suggests that a residue crystallizing after this much evaporation should have $\delta^{25}Mg = 25\%$ and $\delta^{29}Si = 8\%$, considerably more fractionated than the model inclusion. This discrepancy is due to a combination of factors, including preservation of crystals that precipitated from early liquids that had experienced only mild evaporation of Mg and Si at that stage; complete evaporation of Mg and failure to preserve isotopically fractionated Si by crystallization from later, highly evaporated liquid; and late exchange with and recondensation of isotopically light Mg and Si from the complementary ambient gas.

When allowance is made for the fraction of the surface area of the droplet occupied by crystals (case #2, not shown), the evolutionary path is significantly different for evaporation of the same starting composition under the same physical conditions. By 1500K, 61% of the initial Mg and 44% of the Si have been lost, but evaporation almost ceases below 1600K. Although the resulting decline in the MgO content of the liquid causes resorption of spinel and reverse zoning of melilite from $X_{Ak} = 0.22$ to $X_{Ak} = 0.04$, spinel is never completely resorbed and melilite never stops crystallizing in this case. Thus, melilite and the spinel trapped within it preserve the entire range of isotopic compositions of the liquid from which they crystallized, $\delta^{25}Mg$ from 4 to 26‰ and $\delta^{29}Si$ from 1 to 14‰. At 1523K, isotopically light Mg begins to recondense into the remaining liquid but chemical and isotopic consequences are minimal. If the remaining liquid freezes at 1500K, the bulk inclusion will contain 21.3 wt% SiO_2 and 7.7 % MgO, again similar to Type A inclusions. It will have bulk $\delta^{25}Mg$ and $\delta^{29}Si$ of 17‰ and 6‰, respectively, again much higher than those of Type As but significantly below the values expected for the amount of Mg and Si evaporated, 19‰ and 6.5‰, respectively. Note that, despite less Mg and Si evapora-

tion from this residue than in case #1, both $\delta^{25}Mg$ and $\delta^{29}Si$ are higher for this one. This is primarily due to the fact that more of the most heavily fractionated Mg and Si were preserved by crystallization in case #2.

Conclusions. For an object that underwent simultaneous fractional crystallization and evaporation, use of the bulk isotopic composition of an element to derive its fraction evaporated almost always yields an underestimate. The isotopic and chemical evolution of an evaporating droplet is strongly influenced by the fraction of its surface area occupied by crystals. Chemical compositions of Type A inclusions can be made by more extreme evaporation of δ than is required to make Type Bs, but Mg and Si isotopic compositions of natural samples seem to rule this out. Mg evaporation from liquid coexisting with spinel is a viable mechanism for spinel resorption, clear textural evidence for which is seen in refractory inclusions [9].

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