

CONDENSATION OF THE HIGH-FEO SILICATES IN PRIMITIVE CHONDRITES: STILL A

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Introduction: The high FeO/FeO+MgO ratios, from 0.1 to 0.5, characteristic of olivine and pyroxene in chondrules and matrix of carbonaceous and unequilibrated ordinary chondrites present a serious challenge to understanding these phases as nebular condensates [1, 2]. In solar gas, all Fe condenses as metallic NiFe and almost all Mg and Si as pure forsterite and enstatite at temperatures above 1300K at most nebular pressures. The P_{H_2O}/P_{H_2} ratio gradually increases with decreasing temperature, eventually stabilizing FeO in the form of fayalite. This occurs at very low temperature ($T < 800K$) in solar gas, where the Fe-Mg interdiffusion coefficient, D , in olivine is so low that diffusion of Fe into the pre-existing forsterite crystals ceases before X_{Fa} exceeds 0.001, even in 0.1μ grains at very slow cooling [2]. Potential solutions have concentrated on increasing the f_{O_2} by increasing the (O-C)/H ratio of nebular regions, either by dust or water enrichment. Theoretical models of gravitational settling are unable to achieve dust enrichments of more than a factor of 120 [3], and those of inward migration of ice-bearing bodies are unable to achieve water enrichments greater than a factor of 10 relative to a system of solar composition [4]. This limits X_{Fa} to 0.019. In a further effort to find a solution to this problem, this paper investigates (1) the effect of a recent reassessment of the Fe-Mg interdiffusion coefficients in olivine [5, 6]; and (2) the possibility that nucleation kinetics prevented metallic Fe from condensing at its equilibrium condensation temperature, T_{cond}^{eq} [7].

New Diffusion Coefficients: The dependence of the Fe-Mg interdiffusion coefficient along the c-axis of olivine on temperature and X_{Fa} was measured in [8] at a constant f_{O_2} of 10^{-12} bar. Because the f_{O_2} of solar gas decreases with decreasing temperature, reaching 10^{-33} bar at 800K, the D s of [8] were modified in [1] and [2] to include the increase of $\log D$ with $1/6 \log f_{O_2}$ found in [9]. More recent measurements of D [5] over a range of f_{O_2} reproduce well those in [8] at $f_{O_2} = 10^{-12}$ bar and confirm the dependence on f_{O_2} found in [9] at $f_{O_2} > 10^{-15}$ bar, but find no dependence of D on $f_{O_2} < 10^{-15}$ bar. Accordingly, using the dependence of D on temperature and X_{Fa} for $f_{O_2} < 10^{-15}$ bar proposed in [6], *i.e.*, larger D s than used in [1, 2], the calculation of the fayalite concentration profile of an olivine grain of radius 0.1μ , whose surface is in contact with a gas of solar composition except for a water content 10x the solar value, was repeated in this study. For an absurdly

long, one million year nebular cooling time, the increased D allows diffusion to continue to 690K and the mean X_{Fa} of the grain to increase to 0.024, compared to values of 715K and 0.019 in [2]. Thus, elimination of the f_{O_2} -dependence of D at $f_{O_2} < 10^{-15}$ bar still does not explain the high X_{Fa} of olivine in primitive chondrites.

Supersaturation of Metallic NiFe: In 1967, Blander and Katz [7] pointed out that FeO contents of silicates condensing from solar gas would be much higher than those calculated at equilibrium if metallic Fe failed to nucleate at its equilibrium condensation temperature, T_{cond}^{eq} . To test the efficacy of this approach with modern thermodynamic data, the computer code of [10] was used for a condensation calculation in a solar gas at $P^{tot} = 10^{-3}$ bar, in which both metallic NiFe and Fe_3C were prevented from condensing. In this case, olivine condenses at 1418K, where its X_{Fa} is 4×10^{-4} . At 1338K, where 94% of the Mg is condensed as olivine, X_{Fa} is still only 5×10^{-3} and olivine begins to react with the gas to form orthopyroxene. The predicted X_{Fa} is plotted against temperature in curve (a) of Fig. 1, where it is compared to the same curve for solar gas at complete equilibrium. Below 1300K, X_{Fa} increases sharply with falling temperature, reaching 0.1 at 1230K, ~230K below the T_{cond}^{eq} of metallic NiFe. As foreseen [7], the temperature at which X_{Fa} of olivine becomes substantial is much higher when metallic Fe is prevented from condensing than at equilibrium, where X_{Fa} does not reach 0.1 until ~500K. Because the Fe-Mg interdiffusion coefficient in olivine is so much higher at these temperatures than those where FeO becomes stable in the dust- and water-enriched systems investigated above, even olivine grains of $r = 10\mu$ would have nearly homogeneous X_{Fa} at ~ the equilibrium values on curve (a) in a rapidly cooled nebula, *i.e.*, one that cools from 1340 to 1160K in 3300 yr. Fig. 1 also shows the FeO content calculated, using the code in [11], for a condensate liquid in a 1 bar solar gas when metallic NiFe and all other solid phases are suppressed. Because the liquid contains >25 wt % FeO by 1400K, any olivine that crystallizes from it will have a substantial X_{Fa} . Thus, supersaturation of metallic NiFe is a potential solution to the problem of how to make fayalitic olivine during condensation. The question that arises is whether kinetic barriers to nucleation of metallic Fe can delay its condensation by 230K, the minimum needed to allow X_{Fa} of condensate olivine to reach the levels seen in primitive chondrites.

The degree of supersaturation needed for homogeneous nucleation of a phase increases with its surface tension, σ , a parameter that is smaller and much more accurately known for liquids than solids. Equation (1) in [7] relates the critical supersaturation ratio, $S=P/P_e$, of a gaseous species to its equilibrium vapor pressure (P_e) over a liquid phase of the same composition, and to $T_{\text{cond}}^{\text{eq}}$, σ and nucleation rate of the phase, where P is the actual pressure of the species necessary to induce nucleation. Assuming that solid and liquid Fe have the same σ , this suggests that homogeneous nucleation of metallic Fe in solar gas at $P^{\text{tot}}=10^{-3}$ bar requires $S=750$, resulting in condensation of metallic Fe at $\sim 1200\text{K}$, 265K below its $T_{\text{cond}}^{\text{eq}}$. In this case, had olivine been able to nucleate near its $T_{\text{cond}}^{\text{eq}}$, it would have had $X_{\text{Fe}} > 0.1$ before metallic Fe formed. On the other hand, if grains of other phases were able to condense at temperatures above the $T_{\text{cond}}^{\text{eq}}$ of metallic Fe, they could have acted as heterogeneous nuclei to drastically reduce the degree of supersaturation needed for metallic Fe condensation. While the $T_{\text{cond}}^{\text{eq}}$ s of some relatively abundant phases are above that of metallic Fe, their surface tensions and thus their ability to have nucleated at temperatures above the $T_{\text{cond}}^{\text{eq}}$ of metallic Fe are unknown. In contrast, σ is known for solid Al_2O_3 [12] and for the liquid phases of some rare refractory metals, e.g. W [13], Os [14], and Re [15], the $T_{\text{cond}}^{\text{eq}}$ s of whose solids are above that of metallic Fe. If a nebular region were hot enough initially that each of these solids was vaporized, could any of them have nucleated at a temperature above the $T_{\text{cond}}^{\text{eq}}$ of metallic Fe? If so, grains of such phases could have acted as sites for heterogeneous nucleation of metallic Fe, allowing it to condense with minimal supersaturation, thus preventing high-temperature condensation of high-FeO silicates. Using the equation referred to above, the critical supersaturation ratios of each of Al_2O_3 , W, Os and Re were calculated in solar gas over a range of P^{tot} , and, from them, the temperatures at which they would homogeneously nucleate, assuming that solid and liquid metals have the same σ . S calculated for corundum is 270 and 1700 at 10^{-5} and 10^{-2} bar, resp., similar to values measured in [16]. Results are plotted in Fig. 2 as a function of P^{tot} . While the temperature of homogeneous nucleation of Re lies below the $T_{\text{cond}}^{\text{eq}}$ of Fe, each of Al_2O_3 , W and Os is so refractory that, even if its condensation were delayed by supersaturation, each would still nucleate homogeneously above the $T_{\text{cond}}^{\text{eq}}$ of Fe. It is thus likely that grains of other phases existed at the $T_{\text{cond}}^{\text{eq}}$ of metallic Fe, allowing it to condense with minimal supersaturation. A means of accounting for FeO contents of sili-

cates in primitive chondrites by condensation processes remains elusive.

If the stable form of oxidized iron, FeO-bearing olivine and pyroxene, can't form during nebular cooling, how did FeO-bearing silicates in primitive chondrites form? Primitive bodies would have accreted from FeO-poor silicates, metallic Fe, FeS and water ice. Because these bodies lacked excess H_2 , vapor plumes generated by impacts on them would have been oxidizing, thus possible formation environments of FeO-bearing silicates in chondrules and matrix of primitive chondrites.

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