

FeO IN CHONDRITIC OLIVINE: IMPLICATIONS FOR f_{O_2} . L. Grossman^{1,2}, A. V. Fedkin¹, and S. B. Simon¹. ¹Dept. of the Geophysical Sciences, The University of Chicago, 5734 South Ellis Ave., Chicago, IL 60637 (yosi@uchicago.edu). ²Enrico Fermi Institute, Univ. of Chicago.

Introduction: How to condense olivine grains found in the matrices of, or that existed as precursors to chondrules in, carbonaceous and unequilibrated ordinary chondrites is a serious problem for condensation models because of the high FeO/FeO+MgO ratios, from 0.1 to 0.5, characteristic of olivine and pyroxene in these settings [1, 2]. Solar gas is so reducing (Fig. 1) that 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 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 0.1 μ grains that cooled through the fayalite formation interval, ~950 to 550K, in 1.3×10^5 yr [2], which would imply an absurdly long nebular cooling time in any event. 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. What is not generally recognized is the relative inefficiency with which dust enrichment enhances f_{O_2} . This is because most of the free oxygen added to solar gas by evaporation of the extra dust is simply locked up during cooling in condensates that form at temperatures that are still higher than those where iron oxidation becomes significant. As a result, very large dust enrichments are necessary, but theoretical models of gravitational settling are unable to achieve dust enrichments of more than a factor of 120 [3]. Water enrichment is more efficient, but models 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], limiting X_{Fa} to 0.019 in the same tiny grains for the same long time periods as above.

Subsequent Work: Since the last review of this subject [2], careful remeasurement of D in olivine [5] found that it is not dependent on f_{O_2} at $f_{O_2} < 10^{-15}$, where solar gas lies. Because the effect of this is to increase D by 2 to 6 log units over the temperature range of interest, X_{Fa} in olivine was recalculated in a gas that is solar in composition except for enrichment in water by a factor of ten [6]. Results are shown in Fig. 2, from which it can be seen that, if olivine grains were exposed to the gas for more reasonable time peri-

ods of 1.3×10^3 - 1.3×10^4 yr, X_{Fa} would reach 0.04-0.06 in 0.1 μ grains and 0.02-0.03 in 1.0 μ grains, still quite a bit less than observed in primitive chondrites.

The old idea that FeO would be much more stable in high-temperature silicates in solar gas if metallic iron failed to nucleate [7] was confirmed by [6], who used homogeneous nucleation theory to show that metallic Fe condensation could be delayed by 265K, to ~1200K at $P^{tot}=10^{-3}$ bar. Under these conditions, olivine would start to condense at 1418K, where it would be nearly pure forsterite, and would reach $X_{Fa}=0.20$ at 1200K. At these high temperatures, D is high enough that 10 μ grains would actually homogenize their compositions at these equilibrium X_{Fa} values even if the nebula cooled through this temperature range in only 5000 yr. The question was then addressed in [6] of whether it would be possible to prevent heterogeneous nucleation of metallic Fe near its equilibrium condensation temperature in view of the much higher equilibrium condensation temperatures of such phases as refractory siderophile element alloys and corundum. Critical supersaturation ratios calculated for each of corundum, W and Os show that each of these phases would have condensed at a higher temperature than the equilibrium condensation temperature of metallic Fe, even if they did so *via* homogeneous nucleation, making it unlikely that significant delay of metallic Fe condensation due to its supersaturation promoted high-temperature stabilization of FeO-bearing silicates in solar gas [6]. Even if a way could be found to delay metallic Fe condensation by this mechanism, this phase would probably nucleate heterogeneously on grains of forsterite as soon as the latter formed, once again preventing olivine from reaching high X_{Fa} .

FeO in Chondrule Olivine: Although a continuum of compositions exists between them, Types I and II chondrules are defined as having mean FeO/(FeO+MgO) atomic ratios <0.1 and ≥ 0.1 , respectively, in their olivine and pyroxene. The two types differ also in their total iron contents, with the mean Fe/Si ratios of Type Is being ~0.1 [8, 9] and those of Type IIs ~0.34 [10, 11], both relative to CI chondrites. The FeO contents of both types are important constraints on their origin, as they imply chemical communication with a gas whose log f_{O_2} was ~IW-1 or IW-2, i.e., 1 or 2 log units below the f_{O_2} of the iron-wüstite (IW) buffer, 5 or 6 log units more oxidizing than a system of solar composition (Fig. 1). Thus, if

oxidation of metallic Fe occurred during chondrule formation, water addition or some other means must still be found to enrich the nebula in oxygen relative to carbon and hydrogen. In Fig. 3 are shown results of equilibrium condensation calculations at high enough total pressure to generate olivine+MELTS liquid in systems that are solar in composition except for enrichment in water by amounts sufficient to stabilize significant FeO in the olivine. The purpose is *not* to demonstrate that chondrules are condensates but to show that water enrichments of at least several hundred would be needed in cosmic gases to yield the appropriate FeO contents at chondrule crystallization temperatures. A popular misconception is that the difference in X_{Fa} between the two chondrule types implies formation at significantly different f_{O_2} . This is not true. If liquids such as those in Fig. 3 were quenched after reaching the 1400-1650K interval, the mean X_{Fa} of their olivine would be 0.07-0.10, typical of Type I chondrules, at 240x water enrichment, equivalent to $\log f_{\text{O}_2} = \text{IW}-2.1$. The range of X_{Fa} would be 0.14-0.23, typical of Type II chondrules, with slightly less than double the water enrichment, to only 470x, equivalent to $\log f_{\text{O}_2} = \text{IW}-1.5$. Thus, only 0.6 of a log unit is necessary to produce the different olivine compositions in the two chondrule types at a given temperature. In fact, there need not be any f_{O_2} difference. If droplets that had equilibrated with gas enriched by a factor of 470 in water were quenched above 1650K, their olivine would have X_{Fa} characteristic of Type I chondrules but, if quenched below 1650K, the X_{Fa} would be typical of that in Type IIs. The difference in f_{O_2} implied by the different mean X_{Fa} of olivine in the two chondrule types is trivial. The real, persistent problem, and one deserving of much more attention because of the serious ramifications for the origin of chondrites, is how to generate an environment whose f_{O_2} can support the FeO content of *any* chondrule from solar gas, whose f_{O_2} lies 5 or 6 log units lower.

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