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# High-temperature condensation of iron-rich olivine in the solar nebula

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Received November 3, 1989; revised version accepted July 3, 1990

## ABSTRACT

Olivine is the most abundant mineral in many chondritic meteorites. It is also the first major Mg-silicate to condense from a solar gas upon cooling. The composition of olivine provides important information concerning its origin.

Results of calculations are presented for the Fe, Mn and Ni contents of olivine condensing from a gas with solar composition but variable oxygen fugacity. A basic computational method is described that takes into account the depletion of the gas in Mg and Si during condensation.

The first olivine that condenses from a solar gas has less than  $10^{-2}$  mol% FeO, independent of the oxygen fugacity of the otherwise solar gas. At lower temperatures when most of the Mg is condensed more FeO can be incorporated in forsterite by condensation if the oxygen fugacity is sufficiently high. The FeO/MnO ratio of the first condensing olivine is above 1000, decreasing with decreasing temperature and increasing oxygen fugacity to values of around 100 which are actually observed in fayalitic olivine rims in Allende. The Ni-content of condensed olivine is below  $10^{-7}$  mol%, even at high oxygen fugacities, indicating that condensation of NiO in olivine is a very unlikely process. Any Ni in olivine in the ppm range is, therefore, indicative of metal-olivine equilibration. Under increasingly oxidizing conditions ( $H_2O/H_2$  ratios of  $\sim 0.01$ – $0.1$ ) chromite is an early phase to condense, forming before forsterite.

Isolated olivine grains in Allende and olivine on the outside of chondrules have FeO-rich rims. Texture, composition and morphology of these rims indicate that they formed by condensation from a gas. Our calculations suggest that the gas was enriched by a factor of 100 in oxygen relative to solar-composition gas and that Mg was almost completely condensed when rim formation occurred. The sharp boundary between forsteritic and fayalitic olivine suggests an increase in oxygen fugacity and rapid formation of fayalitic olivine by condensation. Cr-enrichment at the rim interface with the underlying forsterite probably reflects stability of chromite under oxidizing conditions.

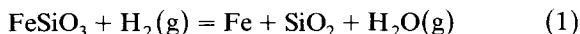
Conventional models of FeO-bearing silicate formation require oxidation of metal + silicate assemblages at temperatures as low as 400 K. It is shown here that diffusion at this temperature is so slow that the time needed for formation of the observed FeO-bearing phases would exceed the lifetime of the solar nebula.

Other oxygen-fugacity indicators reflect similar conditions. For example, the hercynite component of spinel in fine-grained Al-rich inclusions indicates equilibration with a gas of similar composition as that responsible for condensation of fayalitic olivine, suggesting formation of FeO-rich spinel by gas-solid reactions.

Mechanisms for producing oxidizing conditions in the solar nebula are briefly discussed.

## 1. Classical equilibrium condensation models

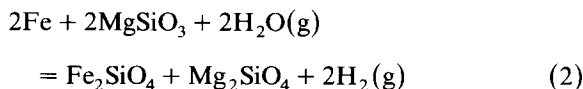
The origin of FeO-bearing silicates in the chondritic meteorites has been a central problem in cosmochemistry for almost four decades. The formation of FeO-bearing silicates in the solar nebula was first discussed quantitatively by Latimer [1] who considered the equilibrium:



and concluded that both  $FeSiO_3$  and  $Fe_2SiO_4$  were stable at  $T < 600$  K in the solar nebula. Although the relevance of reaction (1) to solar nebula chemistry would now be regarded as problematic, Latimer's central conclusion that FeO-bearing silicates are thermodynamically stable at low temperatures in solar-composition gas has been repeatedly verified by many subsequent calculations [2–9]. We also note that at about the same time as Latimer's work, Urey [10] pointed out that "At low tempera-

tures even with hydrogen and water present in cosmic proportions, iron would be stable as its oxides and silicates, and hence either all the water or all the metallic iron should have reacted.”

However, detailed calculations of the FeO content of ferromagnesian silicates in thermochemical equilibrium with solar gas were unavailable until the work of Larimer [3,4]. He considered the net thermochemical reaction:



and tabulated fayalite contents in olivine as a function of temperature and of the  $\text{H}_2\text{O}/\text{H}_2$  ratio in solar nebula gas. On the basis of the elemental abundances and thermodynamic data available at that time, Larimer concluded that FeO-bearing silicates containing ~18–28 mol% fayalite (which is the approximate range of olivine compositions in ordinary chondrites) would have formed at ~590–635 K in the solar nebula. Subsequently, Grossman [7] using updated elemental abundances [11] and thermodynamic data, recalculated that lower temperatures of ~510–530 K were required. Finally, the recent calculations by Saxena and Eriksson [9], who used the Cameron [12] elemental abundances and newer thermodynamic data, show that still lower temperatures of ~425 K are required to reach fayalite contents of ~20 mol% in olivine.

Thus, to summarize, three independent sets of thermodynamic calculations show that the formation of FeO-bearing olivines similar in composition (~18–28 mol% fayalite) to those found in carbonaceous and ordinary chondrites requires low-temperature equilibration of Fe metal grains and pyroxene with solar nebula gas. Furthermore, as both the elemental abundances and thermodynamic data used in the calculations have improved with time, it has become clear that the required low temperatures are in the 430–530 K range. The question of whether or not complete chemical equilibrium can, in fact, be attained at the low temperatures where the FeO-bearing silicates are calculated to be stable, is an important question which has not been quantitatively discussed in prior papers. Indeed, past studies of olivine condensation have implicitly assumed that complete chemical equilibrium will be reached (without

verifying the validity of this assumption). Therefore the kinetic constraints on reaction (2) will be discussed in a later section.

## 2. Olivine in Allende and other CV-chondrites

Olivine is the most abundant mineral in type 3 carbonaceous chondrites and it is a major mineral in most chondritic meteorites. The fine-grained matrix of Allende and other type 3 carbonaceous chondrites consists predominantly of FeO-rich olivine (~Fa<sub>50</sub>). However, an important constituent of most chondrules is FeO-poor olivine. The most refractory (i.e., MgO-rich) olivine with fayalite contents of 0.2–0.3 mol% [13] is found as isolated single grains in matrices of carbonaceous chondrites. They have a unique pattern of trace elements, most notably high contents of refractory elements such as Ca, Al, Ti, Sc. etc., suggesting an origin as condensates from the solar nebula [13,14].

Fayalitic olivine is often found together with forsterite, both minerals occurring in three different textural associations: (1) as rims surrounding forsterite grains, a few  $\mu\text{m}$  wide, with compositions of Fa<sub>35</sub>-Fa<sub>45</sub>; (2) as veins between and within grains of forsterite; and occasionally (3) as halos around metal grains within forsterite. Figure 1 gives an example of the first two types. Peck and Wood [15] have studied these two types of faya-

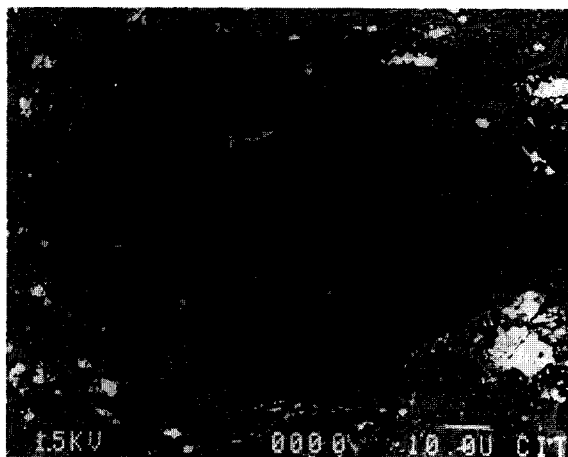


Fig. 1. Forsteritic olivine grain, surrounded by broad (10–20  $\mu\text{m}$ ) fayalitic rim. Note the sharp boundary between FeO-poor and FeO-rich olivine. Fayalitic veins transect forsterite core.

Backscattered electrons.

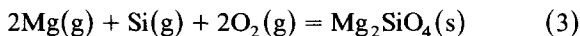
litic olivine in detail and on the basis of the significantly higher Al, Cr, and Ti contents of the fayalitic olivines relative to the matrix and forsteritic chondrule olivines they concluded that they formed by condensation from a gas phase. Based on textural observations and additional chemical arguments other observers [16,17] came to similar conclusions, i.e., formation of the FeO-bearing olivines in the rims and veins occurred at comparatively high temperatures. However, as noted earlier in section 1, this is not possible in a solar-composition gas because formation of FeO-bearing olivines with the composition  $Fa_{20}$  requires temperatures of  $\sim 425$  K [9] while more-fayalitic olivines, like those found in Allende, require even lower temperatures.

As originally shown by Palme and Fegley [18], a gas phase that is significantly more oxidizing than a solar composition gas is needed for the formation of FeO-bearing olivine at high temperatures in the solar nebula. In the present paper we calculate the conditions required for condensation of FeO-bearing olivine and show that an oxygen fugacity several orders of magnitude greater than that of a solar-composition gas is needed for condensation of the observed mineral assemblages.

### 3. Formation of FeO-bearing olivine at high temperatures

#### 3.1. Method of calculation

Condensation temperatures of minerals were calculated in the usual way [7]. For example, the condensation of forsterite was calculated by considering the reaction:



which has an equilibrium constant  $K_{FOR}$  given by the expression:

$$K_{FOR} = a_{FOR} / (p_{Mg}^2 \cdot p_{Si} \cdot p_{O_2}^2) \quad (4)$$

where  $a_{FOR}$  is the activity of forsterite and  $p_{Mg}$ ,  $p_{Si}$  and  $p_{O_2}$  are the partial pressures of Mg, Si and  $O_2$  in the solar gas.

Partial pressures of Si, Mg and  $O_2$  were calculated using a revised version of the METKON program previously described by Fegley and Palme [19]. Equilibrium constants were taken from Robie et al. [20]. The condensation temperature of forsterite, i.e., the temperature where the activity of

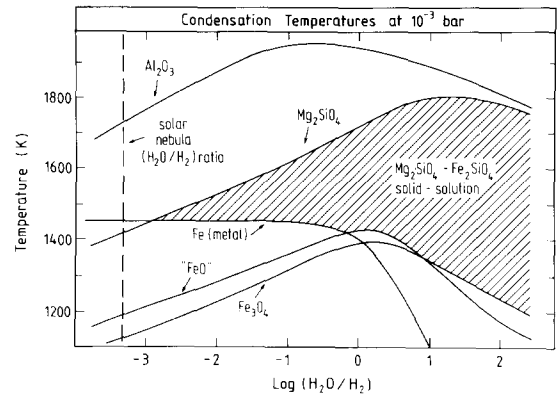


Fig. 2. Condensation temperatures of corundum, forsterite and various Fe-bearing phases (Fe-metal, wüstite, magnetite) as function of the oxygen fugacity of the nebula (expressed as  $H_2O/H_2$  ratio). The field for possible forsterite-fayalite solid solutions is indicated. The condensation curves for wüstite and magnetite are shown for comparison. They were calculated assuming no removal of Fe from the gas by condensation of metal. In the classical condensation model Fe would condense as metal and equilibrate at low temperatures with silicates to produce FeO-rich olivine and pyroxene. At more oxidizing conditions a solid solution of forsterite and fayalite would condense before Fe-metal. The amount of fayalite would increase with increasing  $H_2O/H_2$  ratios of the gas.

forsterite,  $a_{FOR}$ , is 1, was calculated from Eqn. (4). The same procedure was applied to a number of other minerals.

In Fig. 2, we have plotted condensation temperatures for corundum, forsterite and various Fe-bearing minerals at a total pressure of  $10^{-3}$  bar. With the exception of oxygen, the composition of the gas phase was solar. The  $H_2O/H_2$  ratio was allowed to vary independently, which is equivalent to adding additional oxygen atoms.

The solar  $H_2O/H_2$  ratio of  $5.1 \times 10^{-4}$  is indicated in Fig. 2. The corresponding oxygen fugacity ( $f_{O_2}$ ) as a function of temperature can be calculated from the equation  $\log_{10} f_{O_2} = 2 \log_{10} (H_2O/H_2) + 5.59 - 25598/T$  which is taken from Rubin et al. [21]. At this  $H_2O/H_2$  ratio and at a total pressure of  $10^{-3}$  atm, metallic iron condenses before forsterite. At lower pressures, the sequence is reversed [6,22]. For example, the condensation temperatures of forsterite and metallic iron at  $10^{-6}$  atm in solar-composition gas are 1234 K and 1205 K, respectively.

Oxygen fugacities higher than those in the solar nebula would, however, open up a gap between the condensation temperatures of forsterite and

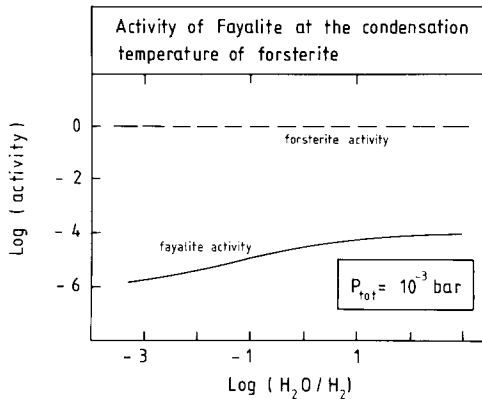


Fig. 3. Activity of fayalite at the condensation temperature of forsterite at increasing oxygen fugacities. The first condensing olivine has in all cases less than  $10^{-2}$  mole fayalite. Such FeO-poor olivines have never been found in meteorites.

metal. The condensation temperature of forsterite increases rapidly with increasing  $H_2O/H_2$  ratios, while that of Fe-metal stays constant over a wide range of  $H_2O/H_2$  ratios (Fig. 2).

Using a similar equation as (3) fayalite activities were calculated at the condensation temperatures of forsterite. In these calculations all O-, H- and OH-containing gas species for which thermodynamic data are available were considered. Calculated fayalite activities are several orders of magnitude below that of forsterite ( $a_{FOR} = 1$ ), at all  $H_2O/H_2$  ratios (Fig. 3). Fayalite mole fractions are not very different from activities, since the forsterite-fayalite solid solution is not far from ideality [23]. It is only at temperatures approximately  $300^\circ\text{C}$  lower than the forsterite condensation temperature that more FeO can be taken up by olivine. If, however, Fe condenses as metal, its partial pressure in the gas will be greatly diminished, preventing FeO-bearing silicates from forming. Figure 3 also demonstrates that forsterite would always be the first olivine to condense, even at very oxidizing conditions.

In order to calculate properly the activity of fayalite in olivine at any given temperature and oxygen fugacity, it is necessary to consider the reduction of the partial pressures of Si and Mg in the gas due to condensation of forsterite. To do this, we have chosen a relatively simple procedure which allows fast calculation of the activities of fayalite, Ni-olivine, and Mn-olivine (tephroite) in forsterite under a variety of different conditions.

The maximum nebular pressures of Mg and Si are designated as  $p_{Si}^0$  and  $p_{Mg}^0$ . These are the partial pressures before any condensation of Si and Mg. For example, in a gas of solar composition,  $p_{Si}^0$  is given by:

$$p_{Si}^0 = [A(\text{Si}) \cdot \beta_{Si} / A(\text{H}_2)] p_{\text{tot}} \quad (5)$$

where  $A(\text{H}_2)$  and  $A(\text{Si})$  are the solar abundances of Si and  $\text{H}_2$ ,  $p_{\text{tot}}$  is the total pressure, and  $\beta$  is the fraction of Si-metal atoms in the gas:

$$\beta_{Si} = p(\text{Si}) / [p(\text{Si}) + p(\text{SiO}) \dots] \quad (6)$$

$p_{Si}$ ,  $p_{SiO}$  etc. being the partial pressures of Si, SiO etc. Mg may be treated similarly.

Forsterite begins to condense when the activity of forsterite,  $a_{FOR}$ , calculated from Eqn. (4) is unity. At temperatures below the forsterite condensation temperature, the actual nebular pressures  $p_{Si}$  and  $p_{Mg}$  will be lower than  $p_{Si}^0$  and  $p_{Mg}^0$ . If  $\alpha_{Si}$  is the fraction of Si atoms in the condensed state, then the partial pressure of Si ( $p_{Si}$ ) in equilibrium with forsterite is given by:

$$p_{Si} = p_{Si}^0 \cdot (1 - \alpha_{Si}) \quad (7)$$

and similarly for Mg:

$$p_{Mg} = p_{Mg}^0 \cdot (1 - \alpha_{Mg}) \quad (8)$$

Inserting Eqns. (7) and (8) into Eqn. (4) and considering that forsterite is in equilibrium with the gas ( $a_{FOR} = 1$ ), we obtain:

$$1 = K_{FOR} \cdot (p_{Mg}^0)^2 \cdot p_{Si}^0 \cdot p_{O_2}^2 \cdot (1 - \alpha_{Mg})^2 \cdot (1 - \alpha_{Si}) \quad (9)$$

Taking:

$$a_{FOR}^0 = K_{FOR} \cdot p_{O_2}^2 \cdot (p_{Mg}^0)^2 \cdot p_{Si}^0 \quad (10)$$

and substituting in (9) one obtains an equation for the two unknowns  $\alpha_{Mg}$  and  $\alpha_{Si}$ :

$$1/a_{FOR}^0 = (1 - \alpha_{Mg})^2 \cdot (1 - \alpha_{Si}) \quad (11)$$

Assuming that olivine is the only condensed phase, we can write:

$$\alpha_{Mg} = 2 \cdot \alpha_{Si} \quad (12)$$

Inserting this into Eqn. (11) yields a cubic equation for  $\alpha_{Si}$  (the fraction of Si atoms in the solid state) that can be solved easily. Knowing  $\alpha_{Mg}$  and  $\alpha_{Si}$  allows us to calculate the partial

pressures  $p_{\text{Si}}$  and  $p_{\text{Mg}}$  that are in equilibrium with olivine [Eqns. (7) and (8)].

In a gas of solar composition, enstatite condensation begins a few tens of degrees below the condensation temperature of forsterite. For example, at a pressure of  $10^{-3}$  atm and a solar  $\text{H}_2\text{O}/\text{H}_2$  ratio, forsterite would condense at 1429 K. If condensation of forsterite is neglected, enstatite would condense at 1426 K. Considering removal of Mg and Si by the condensation of forsterite yields a condensation temperature for enstatite of 1399 K.

The simultaneous condensation of olivine and enstatite can be considered in the same way as the condensation of olivine alone. Two equations result from this treatment:

$$1/a_{\text{ENS}}^0 = (1 - \alpha_{\text{Mg}}) \cdot (1 - \alpha_{\text{Si}}) \quad (13)$$

$$1/a_{\text{FOR}}^0 = (1 - \alpha_{\text{Mg}})^2 \cdot (1 - \alpha_{\text{Si}}) \quad (14)$$

From these equations,  $\alpha_{\text{Mg}}$  can be calculated easily as:

$$\alpha_{\text{Mg}} = 1 - (a_{\text{ENS}}^0/a_{\text{FOR}}^0) \quad (15)$$

and  $\alpha_{\text{Si}}$  from Eqn. (13). This is simply a reflection of the fact that equilibrium of forsterite and enstatite with a gas at a given temperature uniquely defines the partial pressures of Mg and Si. If, in addition, the oxygen fugacity is given, there is no degree of freedom left, in accord with the phase rule.

Knowing the partial pressure of Si in the gas, the activity of fayalite can be calculated:

$$a_{\text{FAY}} = (1 - \alpha_{\text{Si}}) \cdot p_{\text{Si}}^0 \cdot K_{\text{FAY}} \cdot p_{\text{Fe}}^2 \cdot p_{\text{O}_2}^2 \quad (16)$$

where  $K_{\text{FAY}}$  is the equilibrium constant for the formation reaction of fayalite. The partial pressure  $p_{\text{Fe}}$  is determined by the solar Fe-abundance and the oxygen fugacity, according to Eqns. (5) and (6).

The activities of Ni- and Mn-olivine can be calculated in exactly the same way. In order to convert the activities to mole fractions, it is necessary to know the solid-solution properties of the various types of olivine. It appears that there is no large deviation from ideality for all olivine solid-solution series. Schwerdtfeger and Muan [24] found ideal solid solution of  $\text{Fe}_2\text{SiO}_4$  and  $\text{Mn}_2\text{SiO}_4$ . Seifert and O'Neill [25] found only minor deviations from ideality for solid solutions of  $\text{Mg}_2\text{SiO}_4$  and  $\text{Ni}_2\text{SiO}_4$ .

The calculations presented above are relatively simple. They do not require complicated computer programs, such as a full condensation calculation. A similar approach can be applied to calculate the composition of the gas that is in equilibrium with any given mineral assemblage. This may be particularly useful for calculating the stability of various alteration phases in the refractory inclusions.

So far, we have discussed the general case of equilibrium between olivine, pyroxene and a gas phase, and we have shown that coexisting forsterite and enstatite uniquely define the partial pressures of Mg and Si in the gas at any given oxygen fugacity. Under these conditions it is possible to calculate the fractions of Si and Mg that have to be removed into the solid from a given initial gas composition.

In applying these results to the solar nebula, we shall make a simplification that does not affect the major conclusions that will be drawn from these calculations. There are several Ca, Al-containing silicates with higher condensation temperatures than forsterite (e.g., melilite, fassaite, anorthite) that are not considered here [7]. These minerals would, however, only tie up a comparatively small fraction of Si and Mg, since the solar atomic ratios of Si and of Mg to Al and Ca are around 10. We therefore neglect these phases. From the fraction of condensed Si ( $\alpha_{\text{Si}}$ ) and Mg atoms ( $\alpha_{\text{Mg}}$ ) one can in principle calculate the amount of pyroxene and olivine present in the solid condensate. This calculation is, however, sensitive to the fraction of Si that would have condensed with refractory minerals. Therefore, no efforts were made to quantitatively calculate the composition of the residual solid. The essential point is that we must know the partial pressure of Si in the gas phase in order to calculate the activity of  $\text{Fe}_2\text{SiO}_4$  that is in equilibrium with the gas. If forsterite and enstatite are stable phases then the Si-partial pressure is uniquely defined. The stability of forsterite and enstatite over a wide range of temperatures, pressures and oxygen fugacities in a gas of solar composition was shown by Lattimer et al. [26]. The condensation calculations for pyroxenes are more complex than assumed here, primarily because Ca which is contained in melilite and, perovskite is predicted to react with the gas to form a solid solution of diopside and clinoenstatite [9]. However, if the Ca-bearing minerals are not ex-

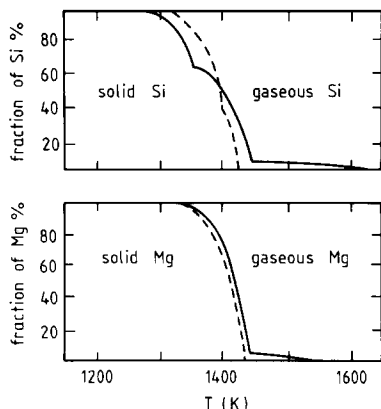


Fig. 4. Distribution of Si and Mg between gas and solid. Simplified calculations described in this paper are indicated by stippled lines. Complete condensation calculations by Lattimer et al. [26], solid lines, are shown for comparison. The kink in both Si-curves indicates beginning of enstatite condensation.

posed to the gas, because they are isolated inside Ca, Al-inclusions, Ca-free pyroxene would condense after forsterite. Indeed, enstatite is frequently observed to be associated with large forsterite crystals (see Fig. 7 and discussion in next section).

An example of this type of calculation is shown in Fig. 4. Condensation of forsterite and enstatite leads to depletion of Si and Mg from the gas. The stippled line is calculated according to the method described above while the solid line represents results of more detailed calculations by Lattimer et al. [26]. The overall pattern is very similar in both cases with the effect of high-temperature minerals, such as melilite being rather small. The kink in both Si-lines indicates the onset of enstatite condensation. The difference between the two Si-curves can be neglected when calculating the activities of Fe, Ni, and Mn-olivine.

### 3.2. Results

The results of the calculations of the activities of Fe-, Mn- and Ni-olivine in forsterite for a total pressure of  $10^{-3}$  bar are given in Figs. 5 and 6. In Fig. 5, the 1% and 10% levels of fayalite activities are indicated. It is clear that an  $H_2O/H_2$  ratio of at least 0.1 is required to reach the 1% level of fayalite in forsterite by condensation from an otherwise solar gas. At still higher oxygen fugacities, a correspondingly higher fraction of fayalite

can be incorporated into forsterite. We have also indicated in Fig. 5 the temperatures where 90% of Mg is condensed. At all  $H_2O/H_2$  ratios these temperatures are above the 1% line of fayalite activity. A significant amount of fayalite would therefore form only after most of the Mg and Si is in the solid state. This is in accord with the observations, since fayalite rims always occur on the outside of forsterite grains (Fig. 1). However, this argument is only valid if condensation occurs in a closed system. As discussed in the next section there is some evidence for the contrary.

In Fig. 6 cross-sections through Fig. 4 at  $H_2O/H_2$  ratios of 0.1, 1 and 2 are given. The amount of FeO taken up by forsterite is limited by the condensation of wüstite or Fe-metal. At an  $H_2O/H_2$  ratio of 0.1 the maximum fayalite content that can be obtained by condensation is about 5%. However, olivine with more than 50% fayalite could condense at an  $H_2O/H_2$  ratio of 1, before wüstite would remove Fe from the gas.

We have mentioned before that, after some forsterite has condensed, enstatite would join forsterite as a stable phase. This is, however, only the case after a substantial fraction of Si and Mg is condensed. For example, at a pressure of  $10^{-3}$  bar and a solar  $H_2O/H_2$  ratio, 70% of the Mg and 30% of the Si would be condensed when enstatite

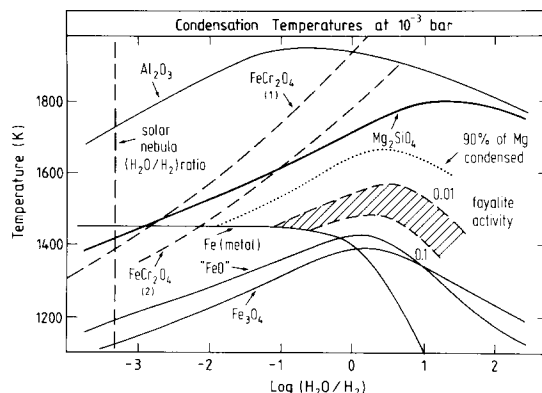
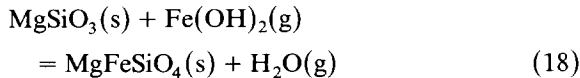
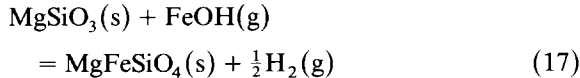


Fig. 5. Similar plot as Fig. 2. The dotted line indicates the temperature where 90% of Mg is in the solid state. Significant amounts of FeO can only be incorporated at lower temperatures. The 1% and 10% level of fayalite is shown. Condensation curves for chromite are also plotted. Two different sets of thermodynamic data were used: (1) free energy of formation data from Kubaschewski and Alcock [29]; and (2) Gibbs energy function data from Robie et al. [20] together with the enthalpy at 289.15 K by Kubaschewski and Alcock [29].

becomes stable at 1399 K. As high-temperature silicates and oxides would also remove Si and Mg, this is strictly only a lower limit. Kinetic constraints could further delay the onset of enstatite condensation. Enstatite is found on the outside of olivine fragments or chondrules (see Fig. 7). The texture is suggestive of enstatite replacement by fayalitic olivine by reactions exemplified by:



Such textures and the corresponding reactions have been described by Housley and Cirlin [27] and by

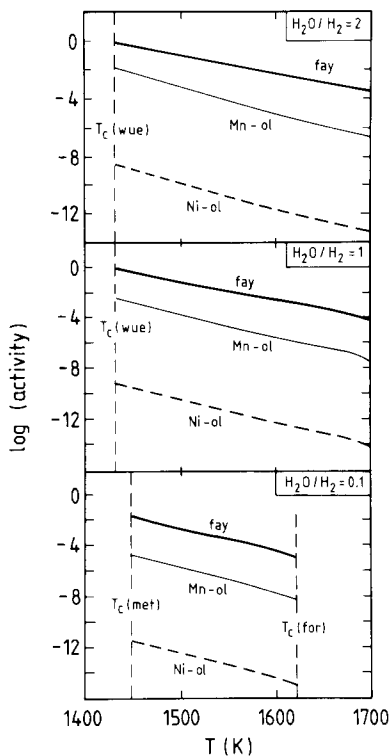


Fig. 6. Cross section through Fig. 4 at  $\text{H}_2\text{O}/\text{H}_2$  ratios of 0.1, 1 and 2 (solar ratio is  $5 \times 10^{-4}$ ). Fayalite stability is limited at low temperatures by the condensation of metal or wüstite ("FeO") and at high temperatures by condensation of forsterite. Fayalite contents of 10% or more require  $\text{H}_2\text{O}/\text{H}_2$  ratios of at least 1. FeO/MnO ratios decrease with higher oxygen fugacities and lower temperatures. The fraction of Ni, that can be incorporated into olivine by condensation is in all cases below the detection limit of conventional analytical methods.

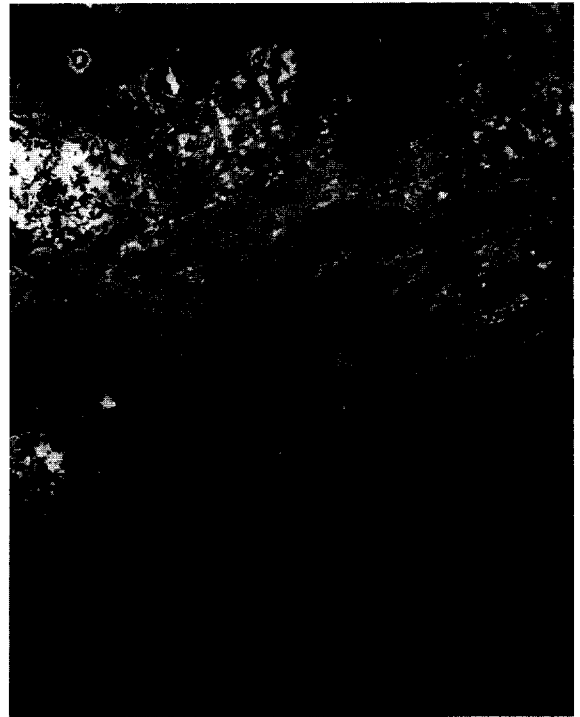


Fig. 7. Large elongated enstatite crystals on the outside of an olivine grain. Brighter phase in between enstatite is fayalitic olivine. The texture is suggestive of olivine replacing enstatite. Gaseous FeO has probably reacted with solid enstatite at high temperatures and elevated oxygen fugacities. Backscattered electrons.

Housley [28], who envisioned the reaction of solid metal with enstatite in a planetary environment [see reaction (2)]. However, in contrast to these authors, we believe that reactions such as (17) and (18) occurred at high temperatures in a solar gas with enhanced oxygen fugacity and gaseous Fe species such as FeOH and Fe(OH)<sub>2</sub>, which are predicted to be more abundant than FeO(gas) over the range of conditions considered. Reactions (17) and (18) would only produce olivine with a fayalite content of 50%. However, if the formation occurred at the high temperatures required for substantial FeOH and Fe(OH)<sub>2</sub> partial pressures, loss of gaseous SiO could enable the formation of olivine with lower fayalite content. It must be kept in mind that, although the calculations presented above predict the stable mineral assemblage in the oxidizing gas, they do not provide any information on how equilibrium was reached. Information

on the kinetics and mechanism may be obtained from textural observations such as disequilibrium between minerals (e.g., zonation), the FeO-content of coexisting enstatite, and laboratory experiments. However, the high temperatures postulated here would help to overcome limitations by kinetic constraints.

In Fig. 6, we also plotted the activities of tephroite ( $\text{Mn}_2\text{SiO}_4$ ) and Ni-olivine ( $\text{Ni}_2\text{SiO}_4$ ). Both, Ni- and Mn-olivine closely follow the condensation curve of the fayalite component. However, in detail, there is a significant variation in the FeO/MnO ratio, from more than 1000 at low oxygen fugacity and high temperatures to less than 100 at higher oxygen fugacities and lower temperatures. At an  $\text{H}_2\text{O}/\text{H}_2$  ratio of 0.1 the FeO/MnO ratio is in all cases above 500, while the lowest value reached for an  $\text{H}_2\text{O}/\text{H}_2$  ratio of 1 is 200; at an  $\text{H}_2\text{O}/\text{H}_2$  ratio of 2, an FeO/MnO ratio of 30 is obtained at 1450 K, corresponding to an oxygen fugacity half a log unit above the iron-wüstite buffer. The FeO/MnO activity ratios can directly be converted into mole fractions, since fayalite and tephroite mix nearly ideally with forsterite. Therefore, the observed ratio of 100 is within the calculated range. A detailed modeling of the FeO/MnO ratio would require consideration of the depletion of gaseous Fe and Mn by condensation of Fe and Mn, as well as the simultaneous condensation of other Fe-bearing phases, such as Ni-rich metal, wüstite or magnetite.

Figure 6 also demonstrates that the amount of Ni incorporated into olivine, even at rather oxidizing conditions, is extremely small, e.g., lower than a tenth of a ppm at a  $\text{H}_2\text{O}/\text{H}_2$  ratio of 2 as shown in Fig. 6 and assuming ideal solid solution of Ni-olivine and forsterite.

In Fig. 5 we have also indicated the condensation temperatures of chromite. Curve (1) was calculated from thermodynamic data for chromite given by Kubaschewski and Alcock [29]. Curve (2) was calculated from Gibbs energy function data for chromite listed in Robie et al. [20] and the enthalpy of formation at 298.15 K from [29]. It is clear from Fig. 5 that under increasingly oxidizing conditions chromite will eventually condense ahead of forsterite. Since the atomic abundance of Fe is more than 60 times higher than that of Cr, only a very small fraction ( $\sim 0.8\%$ ) of Fe will be tied up in chromite and its influence on the Fe-

budget can be neglected. The results of these calculations can be summarized as follows:

(a) The first condensing olivine is always forsterite, independent of the oxygen fugacity. The maximum activity of fayalite in these forsterites (along the forsterite condensation curve in Fig. 2) is  $10^{-4}$ .

(b) Substantial amounts of iron can only be incorporated in forsterite by condensation under more oxidizing conditions than those generally assumed for the solar nebula. This occurs at high temperatures ( $\sim 1350\text{--}1550$  K), which are about 200 K below the forsterite condensation point. To exceed 1% fayalite requires the condensation of more than 95% of Mg and Si in olivine and pyroxene and at least an  $\text{H}_2\text{O}/\text{H}_2$  ratio of 0.1, compared to that of  $5 \times 10^{-4}$  for solar gas.

(c) The FeO/MnO ratio is above 1000 for olivine condensing at high temperatures and relatively low oxygen fugacity. FeO/MnO ratios around 100, which are observed in Allende, require oxygen fugacities above the IW buffer and temperatures slightly above the condensation temperature of wüstite (Fig. 6).

(d) The amount of Ni that could enter olivine by condensation is extremely low. It never exceeds  $10^{-6}$  mol%, even at very oxidizing conditions.

(e) Under increasingly more oxidizing conditions, chromite ( $\text{FeCr}_2\text{O}_4$ ) will become an early phase in the condensation sequence, eventually condensing ahead of forsterite.

#### 4. Origin of fayalitic rims in Allende

The calculations described in the previous section show that high-temperature formation of FeO-rich olivine under oxidizing conditions in the solar nebula is a plausible model for the origin of the fayalitic rims surrounding isolated forsterite grains commonly observed in Allende (e.g., see Fig. 1). However, two other models for the origin of these rims, namely by reactions on the Allende parent body during metamorphism or by low-temperature reactions in the solar nebula, have also been proposed. In this section we discuss each of these three models and show that condensation under oxidizing conditions at high temperatures is the most plausible explanation for the observations.



#### 4.1. Arguments against parent-body reactions

Housley and Cirlin [27] and Housley [28] have proposed that fayalitic olivine in Allende formed during metamorphism by reaction of enstatite with Fe-bearing metal as exemplified by reaction (2). Alternatively, FeO-poor forsterite grains could also have equilibrated with more fayalitic matrix olivine grains. However, chemical compositions, isotopic compositions, and textural features observed for the fayalitic rims on forsterite grains argue strongly against rim formation on the Allende parent body. First we consider the chemical evidence. Recently Weinbruch et al. [17] have provided additional chemical and mineralogical data on forsterite cores, fayalitic rims and adjacent matrix. These authors demonstrate that FeO and MnO are correlated along concentration profiles from the forsteritic cores to the fayalitic rims of the isolated olivine grains despite a variation in absolute contents of FeO and MnO of more than 50. The observed increase of MnO with increasing FeO could not have been produced if the rims formed from Fe-metal + enstatite via reaction (2) because Allende metal does not contain Mn. Fayalitic halos around metal inclusions often found inside forsterite crystals in Allende were formed by metal-forsterite equilibration. As expected the fayalitic olivine around these forsterites is free of Mn [17].

Weinbruch et al. further noted that the FeO content of the fayalitic rims is always lower than the FeO content of the fayalitic matrix which surrounds the rims and is immediately adjacent to them. They also noticed that the Cr content of the rims is significantly higher than that of the matrix olivines. If formation of the rims were by equilibration of the isolated forsterite grains with matrix the FeO contents and the Cr contents of both types of olivine should have been equilibrated. Thus the chemical evidence is inconsistent with formation of the fayalitic rims and fayalitic halos via parent-body reactions.

Considering the textural evidenced, Peck and Wood [15], Hua et al. [16] and Weinbruch et al. [17], all reported that some fractured surfaces of broken chondrules have no fayalite-rich rims even though the chondrules are surrounded by fayalite-rich matrix olivines. These observations are inconsistent with formation of fayalitic rims inside the parent body. Also, the sharp boundaries generally observed between the fayalitic rims and

the forsteritic cores (e.g., Fig. 1) require rapid formation of the rim followed by fast cooling to preserve the steep compositional gradient of FeO. For example, Hua et al. [16] estimated that cooling rates would have to be faster than 2000 °C/day at 1200 °C and 10 °C/day at 900 °C in order to keep the steep compositional gradients observed at the fayalite-forsterite boundary. The fast cooling rate required to preserve this sharp boundary would not allow diffusive equilibrium with matrix olivine during the growth of the FeO-rich rim. In other words, it is impossible that a 20 μm rim with constant fayalite content could form by diffusion of FeO from nearby matrix olivine while a sharp increase in FeO from less than 1 to more than 30% within a few μm is retained (Fig. 1). During diffusive growth of the outermost layers of the rim, FeO would inevitably diffuse into forsterite producing a smooth FeO profile. Such profiles are indeed found in CO<sub>3</sub> chondrites and they can be reasonably well reproduced by diffusion calculations at temperatures of 740 to 800 K and cooling rates of 1 °C/million years as shown by Jones and Rubie [30]. Preservation of steep compositional gradients in Allende therefore constrains the thermal history of the Allende parent body, i.e., Allende must have cooled more rapidly through 770 K than CO<sub>3</sub> chondrites.

Considering the isotopic evidence next, ion microprobe measurements of the oxygen isotopic composition of the forsteritic cores and fayalitic rims show a significant increase in δ<sup>17</sup>O and δ<sup>18</sup>O from core to rim [31]. Oxidation was obviously accompanied by a change in the oxygen isotopic composition. Although the oxygen isotopic composition of the rims is similar to that of the matrix, it is not consistent with a parent-body origin of the rims because of constraints imposed by the oxygen and iron diffusion coefficients. Measurements of Fe<sup>2+</sup> and O<sup>2-</sup> diffusion in San Carlos olivine [32,33] show that the oxygen diffusion coefficient is orders of magnitude lower than that of Fe. Thus diffusive equilibration of oxygen between the fayalitic matrix olivines and the isolated forsterite grains would necessarily smooth out the (observed) sharp gradient of FeO between the forsteritic cores and the fayalitic rims. Therefore, the similar oxygen isotopic compositions of the rims and of matrix olivines cannot be explained by a parent-body process.

#### 4.2. Arguments against low-temperature equilibration in the solar nebula

As noted earlier in section 1, the classical model for production of fayalitic olivines is by low-temperature equilibration of enstatite and Fe metal in the solar nebula [3–9]. However, reaction (2) can only be effective if it proceeds faster than nebular mixing of the grains to cooler regions or a corresponding local temperature decrease. In other words, if the time for reaction (2) to reach equilibrium ( $t_{\text{chem}}$ ) is less than or equal to the time for nebular mixing ( $t_{\text{mix}}$ ), then FeO-bearing silicates can be produced.

Considering  $t_{\text{mix}}$  first, it is conservatively set equal to the lifetime of the nebula,  $10^{13}$  seconds [34–36], which thus allows the maximum time available for the formation of FeO-bearing silicates. The characteristic chemical time constant  $t_{\text{chem}}$  obviously depends in part on the grain size and degree of physical contact of the Fe metal and pyroxene reactants [37]. A reasonable assumption for the lower limit of matrix grain size is  $1 \mu\text{m}$  [38]. Taking the time required for homogenization of the composite metal and pyroxene grain (by reaction to FeO-bearing olivine) as the characteristic chemical time constant yields the relationship  $t_{\text{chem}} \sim r^2/D$  where  $r$  is the radius of the spherical grains and  $D$  is the diffusion coefficient (with units of  $\text{cm}^2 \text{s}^{-1}$ ).

Although no data are available for the effective diffusion coefficients required to homogenize composite metal and pyroxene grains, these  $D$  values are almost certainly smaller than the diffusion coefficients for Fe-Mg interdiffusion in olivine (e.g., see [39] for a comparison of olivine and pyroxene  $D$  values). Following Cohen et al. [40], we take  $D = 6.3 \times 10^{-3} \exp(-28780/T) \text{ cm}^2 \text{ s}^{-1}$  for  $\text{Fe}_{0.87}$  from [41]. The corresponding  $t_{\text{chem}}$  values are then  $\sim 6 \times 10^{17} \text{ s}$  at 530 K and  $\approx 2 \times 10^{23} \text{ s}$  at 430 K. However, studies by Buening and Buseck [33] show that  $D$  is proportional to  $f_{\text{O}_2}^{1/6}$  so that diffusion under solar nebula conditions (430–530 K), which are approximately 40 orders of magnitude more reducing than those in the laboratory, will be even slower and thus  $t_{\text{chem}}$  will be even larger. In other words, the  $t_{\text{chem}}$  values for formation of olivines with  $\sim 20 \text{ mol}\%$  fayalite (as in the ordinary chondrites) are much greater than the solar nebula lifetime of  $10^{13} \text{ s}$  in the temperature range where these FeO-bearing olivines are ther-

modynamically stable. Extrapolation of the diffusion coefficients by Buening and Buseck [33] leads to significantly higher diffusion coefficients at low temperatures than those based on the work of Misener [41]. With these diffusion coefficients time scales of  $1.4 \times 10^{11} \text{ s}$  at 530 K and  $1.5 \times 10^{14} \text{ s}$  at 430 K would be obtained. However, considering the much lower oxygen fugacity in the solar nebula both times would still be several orders of magnitude above the lifetime of the solar nebula.

The kinetic inhibition of FeO-bearing silicate formation in the solar nebula is a robust conclusion because in reality the situation in the solar nebula was probably much less favorable for reaching chemical equilibrium than was assumed above. The Fe-metal grains and pyroxene grains were probably not in intimate contact (and also exposed to the nebular gas) over the entire nebula lifetime of  $10^{13} \text{ s}$ , accretion and/or coagulation probably produced larger grains (which have smaller surface to volume ratios and thus react more slowly with solar nebula gas) on relatively short time scales, and solid-state diffusion (bulk and grain-boundary) may have been quenched at these low temperatures. Thus, solid-state formation of FeO-bearing silicates at low temperatures in the solar nebula (e.g., via reaction (2) which has been frequently suggested in the literature) appears highly improbable.

But what about gas-grain reactions for forming FeO-bearing silicates in the solar nebula? Larimer and Anders [5] considered this problem and proposed that if the reaction rate for formation of FeO-bearing silicates is equal to the number of Fe atoms striking the grain surfaces, the minimum partial pressure of Fe required for addition of 1% Fe in  $t$  years is given by the relation:

$$P(\text{atm})10^{-11.77} \cdot a \cdot T^{1/2} \cdot t^{-1} \quad (19)$$

where  $a$  is the (spherical) grain diameter and  $T$  is the temperature. Taking  $a \sim 2 \times 10^{-5} \text{ cm}$  ( $0.2 \mu\text{m}$ ),  $T \sim 500 \text{ K}$ , and  $t \sim 3 \times 10^5 \text{ yr}$  ( $\sim 10^{13} \text{ s}$ ), the required Fe partial pressure is  $\sim 10^{-20.6} \text{ atm}$ . However, the Fe vapor pressure over Fe metal at 500 K is only  $\sim 10^{-35.4} \text{ atm}$ , about 15 orders of magnitude lower than required. Although Larimer and Anders noted that direct equilibration with Fe vapor was unrealistic at low temperatures, they also suggested that more volatile species such as  $\text{FeCl}_2$  would permit FeO-bearing silicate forma-

tion via gas-grain reactions at low temperatures. However, this is also inadequate.

Formation of  $\text{FeCl}_2(\text{g})$  in the solar nebula occurs via the net reaction:



Rearrangement of the equilibrium constant  $K_{19}$  for this reaction yields an expression for the partial pressure of  $\text{FeCl}_2(\text{g})$ :

$$P_{\text{FeCl}_2} = K_{19} \cdot P_{\text{HCl}}^2 \cdot a_{\text{Fe}} \cdot P_{\text{H}_2}^{-1} \quad (21)$$

where  $a_{\text{Fe}}$  is taken as the solar  $\text{Fe}/(\text{Fe} + \text{Ni})$  ratio of  $\sim 0.95$  independent of temperature. Then by using the appropriate thermodynamic data from the JANAF Tables [42] and the results of Fegley and Lewis [43] for the  $\text{HCl}$  partial pressure in the solar nebula,  $P_{\text{FeCl}_2}$  is  $\sim 10^{-47.0}$  atm at 500 K, which is even lower than  $P_{\text{Fe}}$ .

Thus, to summarize, both solid-solid and gas-grain mechanisms for the low-temperature formation of FeO-bearing silicates in the solar nebula are kinetically inhibited and thus are not able to account for the fayalitic olivines observed in the chondritic meteorites. This general conclusion applies to fayalitic rims, veins, and halos and also to matrix olivine.

#### 4.3. Formation at high temperatures in the solar nebula

The arguments reviewed above strongly suggest that the fayalitic rims in Allende did not form during metamorphic reactions on the parent-body or by low-temperature reactions in the solar nebula. It is much more likely that they formed by condensation from a gas phase at high temperatures. Condensation of FeO from a solar gas without an increase in oxygen fugacity was originally proposed by Blander and Katz [2] and more recently revived by Kozasa and Hasegawa [44]. These authors suggest that Fe metal condensation does not occur at the thermodynamically calculated temperature for  $\text{Fe}(\text{g})$ - $\text{Fe}(\text{solid})$  equilibrium because of nucleation constraints. Instead, the supersaturated Fe vapor continues to cool to lower temperatures where the primary condensation of FeO-bearing phases becomes possible in the absence of Fe metal formation.

However, this model has several serious drawbacks. First, the kinetic constraints to the homogeneous nucleation of Fe metal are only valid in the

absence of any pre-existing dust grains which could serve as heterogeneous nucleation sites for the Fe metal. The incomplete evaporation of presolar grains [45], the condensation of more refractory oxide, silicate, and metal phases [7,46], or a combination of both processes could have provided the necessary nuclei. For example, Kozasa and Hasegawa [44] calculated that the depletion time for gaseous Fe atoms by Fe metal condensation on pre-existing refractory metal nuggets, such as those commonly found in CAI's [46], is  $\tau_d = 2.7 \times 10^{10} (r_{\text{gr}}/1 \mu\text{m}) 10^{-5} \text{ bar}/P_1$  seconds at the Fe condensation temperature. Taking a typical nugget radius  $r_{\text{gr}}$  of  $1 \mu\text{m}$  and a nebular pressure  $P_1$  of  $10^{-3}$  bar yields  $\tau_d = \sim 2.7 \times 10^8$  s, or only  $\sim 3 \times 10^{-5}$  of the nebular lifetime. Thus, heterogeneous nucleation of Fe does not appear to be a problem. Furthermore, even if nucleation constraints do lead to the production of FeO-bearing silicates. Larimer and Anders [5] have noted that the Fe vapor must condense soon thereafter, and from then on the FeO-bearing silicates would be thermodynamically unstable at the solar  $\text{H}_2\text{O}/\text{H}_2$  ratio and would become reduced back to Fe metal and FeO-free forsterite.

Condensation from a high-temperature oxidized gas is left as the only alternative for explaining the origin of the fayalitic rims and veins. The chemical compositions, isotopic compositions, and textural features observed for different fayalitic olivines in Allende [13–17,31] and the thermodynamic calculations presented earlier indicate the following sequence of events for the formation of the FeO-rich olivines.

The forsteritic cores formed first. Their high content of refractory elements such as Ca, Al, Ti, Sc, etc. suggests an origin by condensation from the solar nebula [13,14]. However, their FeO content of  $\sim 0.2$ – $0.3\%$  is at least 20 times higher than predicted for condensation from a gas with the solar  $\text{H}_2\text{O}/\text{H}_2$  ratio. A more oxidizing gas is needed to produce even these low FeO levels which are similar to the lowest FeO levels found in forsterites in ordinary chondrites [47]. Additional evidence for the presence of a more oxidizing gas is provided by analyses of trace elements in blue-luminescing olivines [14] from Allende which show the presence of Mo, presumably as oxide, but not of other refractory metals at the same abundance level (thus apparently ruling

out the presence of submicroscopic metal grains). The presence of trace amounts of Mo oxides could be explained by condensation under oxidizing conditions [48,49] because Mo is more easily oxidized than the other refractory metals.

The fayalitic halos formed next, after the ambient oxygen fugacity increased. This increase could have reflected a change in time or in space. The fayalitic olivine halos surrounding embedded FeNi grains do not contain any Mn and probably formed by oxidation of metal. Weinbruch et al. [17] have noted that broad halos ( $\sim 30 \mu\text{m}$ ) are found in some forsterite grains. The same grains have sharp FeO concentration gradients at the core/rim interface. In these cases halo formation must have preceded rim formation; otherwise the sharp concentration gradients at the core/rim interfaces would not have been preserved during the metal-forsterite equilibration leading to the formation of diffuse halos.

A further increase in the ambient oxygen fugacity led to conditions where chromite became thermodynamically stable and chromite condensation occurred on the pre-existing forsterite grains. The Cr concentration profiles in some of the grains show Cr depletions as the core/rim boundary is approached, thus suggesting Cr was also diffusing out of the forsterites and was being incorporated into the chromites. Chromite formation in veins also occurred during this stage.

Another increase in the ambient oxygen fugacity then led to the formation of the fayalitic rims and veins. This increase also involved a change in the isotopic composition of the gas relative to that existing during the formation of the forsteritic cores. By this time, the majority of the Mg and Si has previously condensed as forsterite and enstatite.

This would limit the amount of fayalitic olivine that could be deposited by condensation on forsteritic cores. However, the assumption of a closed system may not be valid. As mentioned earlier, the oxidizing conditions which enable the condensation of fayalitic olivine are provided by a gas with a different oxygen isotopic composition. A new oxygen component implies addition of gaseous MgO, SiO, FeOH and  $\text{Fe}(\text{OH})_2$  from a different reservoir. Either grains were transported to a nebular region with an enhanced dust-gas ratio (mid-plane) or a new gas component arrived, at

the location of forsteritic grains. Hence, there is more than one reservoir involved making mass balance considerations questionable. The rapid condensation of fayalitic olivine that is required to retain sharp boundaries between forsterite and fayalitic rim may have been facilitated by supersaturation. The FeO/MnO ratio of the rim may in this case simply reflect the ratio in the ambient gas. However, condensation of rim olivine must have occurred before condensation of other FeO-bearing species. Otherwise the partial pressures of gaseous Fe species such as FeOH,  $\text{Fe}(\text{OH})_2$ , and FeO would be determined by the vapor pressure over these solids rather than by the iron abundance of the solar gas and their pressures would exponentially decrease with decreasing temperature preventing the formation of fayalitic olivine by gas-solid reaction. This situation implies high temperatures in the range of  $1400^\circ\text{C}$  at  $10^{-3}$  bar to  $1200^\circ\text{C}$  at  $10^{-6}$  bar (see Fig. 5).

In contrast to olivine, pyroxene did not become FeO-rich during these events because of the much slower  $\text{Fe}^{2+}$  diffusion in pyroxene relative to that in olivine.

The observed variations in the sharpness and widths of the fayalitic rims are due to variations in the ambient oxygen fugacities and in the thermal histories of the individual olivine grains. The inferred cooling rates of  $\sim 100^\circ\text{C}/\text{day}$  at  $\sim 1000^\circ\text{C}$  [16] are the same order of magnitude as cooling rates estimated for Type B CAI's [50,51], but are about 20–500 times less rapid than the cooling rates estimated for chondrules [52]. Thus, the required cooling rates are not unreasonably rapid when compared with those expected in other regions (or at other times) in the solar nebula.

Finally, it is tempting to postulate a similar high-temperature condensation origin for the fayalitic matrix olivines in Allende. Although this point will not be pursued further here we note that matrix olivine has similar dimensions or is even smaller than the width of the fayalitic rims, and thus could have reacted on a similar time scale.

## 5. Oxidizing conditions at high temperatures

### 5.1. Other oxygen-fugacity indicators

The increase in oxygen fugacity at elevated temperatures that was responsible for the formation of FeO-bearing olivines in Allende is also

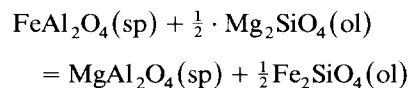
recorded by other oxygen-fugacity indicators. Fegley and Palme [48,19] showed that the Mo and W depletions observed in many Ca, Al-rich inclusions (CAI's) in Allende and other carbonaceous chondrites could be explained by condensation of refractory metal-rich alloys from an oxidized gas with an  $H_2O/H_2$  ratio of about 0.01 to 0.1 but could not be explained by condensation from a solar composition gas with the canonical  $H_2O/H_2$  ratio of about  $5 \times 10^{-4}$ . In a related study, Birschhoff and Palme [49] showed that scheelite ( $CaWO_4$ ) observed in Fremdlinge in CAI's could also be produced under similar oxygen fugacities at elevated temperatures in the solar nebula. However, formation of scheelite by the low-temperature oxidation of an Fe, Ni-alloy, containing much lower concentrations of W than in the refractory-metal-rich nuggets, is probably not possible because of the low-tungsten thermodynamic activity ( $W/Fe \sim 10^{-6}$  for typical CAI bulk compositions).

The FeO content of spinels in fine-grained CAI's in Allende is another indicator of oxidizing conditions at high temperatures in the solar nebula. Kornacki and Wood [53] pointed out that the FeO in fine-grained CAI's in Allende was probably the result of condensation under oxidizing conditions because the Co/Fe, Ni/Fe, and Au/Fe ratios in these inclusions are much lower than the chondritic ratios. This is what would be expected if the FeO entered the inclusions separately from Co, Ni, and Au; for example from an oxidizing gas. In contrast, if the FeO resulted from oxidation of a metallic phase, bulk inclusions should have chondritic Co/Fe, Ni/Fe, and Au/Fe ratios.

Kornacki and Wood [53] further noted that the absence of significant amounts of FeNi metal in fine-grained Allende CAI's is also incompatible with a low-temperature oxidation model for the origin of the FeO-bearing phases. They convincingly argue that at the low temperatures required for the production of FeO-rich minerals, which are well below 1000 K for solar-composition gas, solid-solid reactions such as those required for the production of  $FeAl_2O_4$ -bearing spinels would be kinetically inhibited. Thus, relict FeNi metal would be an expected phase in the FeO-bearing fine-grained inclusions and associations of metal + spinel should be common. However, neither the expected metal + spinel associations nor the relict

metal are observed in the fine-grained CAI's. This is a strong argument against the secondary formation of FeO-bearing minerals by low-temperature oxidation because even much more kinetically favourable gas-solid reactions postulated to destroy CAI minerals such as spinel and hibonite at much higher temperatures clearly did not proceed to completion. Otherwise the CAI's themselves would not be present.

Palme and Wark [54] pointed out that FeO incorporation into Mg-Al spinel in Allende fine-grained CAI's and in the outer parts of coarse-grained CAI's may have occurred simultaneously with the formation of fayalitic olivine. Because the distribution coefficients for the exchange reaction:



are close to unity [55], similar mole fractions of fayalitic olivine and hercynitic spinel should be expected if both phases were in equilibrium. The range of fayalite contents of olivine and hercynite content of spinels are indeed very similar as shown by Kornacki and Wood [53], i.e., both phases are in equilibrium and could have formed in the same environment and by the same process. Similar conditions are reflected in the FeO contents of spinels in the outer parts of CAI's, as noted by Palme and Wark [54].

### 5.2. Mechanisms for the production of oxidizing conditions at high temperatures

High-temperature oxidation in the solar nebula is apparently required to explain the formation of fayalitic olivines in Allende, the Mo and W depletions in CAI's in Allende and other carbonaceous chondrites, and the formation of FeO-bearing spinels in fine-grained Allende CAI's. Therefore it is important to consider the possible mechanisms which may have been responsible for the production of oxidizing conditions at high temperatures in the solar nebula.

One mechanism is hydrogen loss. The obvious problem with this model is the process by which hydrogen but not the other nebular gases would be lost.

Another, frequently proposed mechanism is the creation and subsequent vaporization of dust-rich regions. This is an attractive mechanism for several

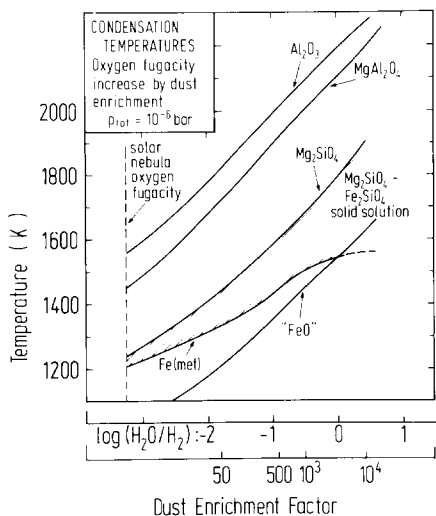


Fig. 8. Increasing the dust/gas ratio as a means to increase oxygen fugacity would simultaneously increase the partial pressures of all other elements. The results of such calculation are shown here. The forsterite-fayalite solid-solution is shifted to higher temperatures, suggesting that olivine in Allende may never have experienced an environment as reducing as that of the solar nebula.

reasons. First, the production of dust-rich regions is a natural consequence of dust settling to the nebular mid-plane during the initial stages of planetary accretion (e.g., see the review by Weidenschilling [56]).

Fegley and Palme [19] calculated the increase in the oxygen fugacity that would result from changing the dust to gas ratio. Large enrichments of about 500 times the solar dust to gas ratio are required to produce the observed Mo and W depletions, corresponding to a  $H_2O/H_2$  ratio of about 0.15, just above the  $H_2O/H_2$  ratio where fayalitic olivine begins to condense.

As dust is vaporized it would not only increase the oxygen partial pressure, but it would also lead to higher partial pressures of all other elements [ $p(Fe)$ ,  $p(Mg)$  etc.]. If dust enrichment occurred at a total pressure of  $10^{-3}$  bar, as considered by Bartholomay and Larimer [57], the olivine condensation curve would be above the liquidus for FeO-rich olivine. However, there is little evidence for a liquid origin of fayalitic rims. On the other hand, if dust enrichment occurred at lower total pressures, e.g., at  $10^{-6}$  bar as illustrated in Fig. 8, then FeO-rich olivine will condense below the liquidus. We note that lower nebular pressures of

$10^{-6}$  bar are suggested by recent solar nebula models [34–36]. More detailed calculations involving dust enrichment are not presented here because dust enrichment is not the only possible mechanism for increasing the oxygen fugacity. The exact mechanism is still unknown.

## 6. Conclusions

The origin of oxidized iron in chondritic meteorites is a fundamental problem in meteoritics. Conventional models of meteorite formation assume FeO incorporation into olivine and pyroxene at around 500 K. We and others [15–17] have presented evidence that, at least some, fayalitic olivine in Allende must have formed by condensation. Thermodynamic equilibrium calculations presented here define the nebular conditions that would enable condensation of fayalitic olivine: Temperatures of about 1400 K at  $10^{-3}$  atm. and 1200 K at  $10^{-6}$  atm. and oxygen fugacities several orders of magnitude higher than those conventionally assumed are required. Kinetic constraints on the formation of FeO-bearing silicates support the high-temperature formation of FeO-rich olivine. The conclusion is inescapable that conditions in the early solar nebula were, at least in some parts or at some times, rather oxidizing.

## Acknowledgements

The authors thank H. Kruse for his assistance with computer programming, and W. Boynton, G. Kurat, and S. Matsunami for useful reviews. Some of our stronger and clearer statements in favor of high-temperature oxidation were made in response to their reviews.

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