

Grain Formation through Nucleation Process in Astrophysical Environments. II

— *Nucleation and Grain Growth Accompanied by Chemical Reaction* —

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The process of homogeneous nucleation and grain growth is formulated, where the chemical reaction accompanying nucleation and growth is taken into account under the assumption that the rates of nucleation and grain growth are determined by one key molecular species. This theory is applied to the condensation of refractory minerals in a cooling gas of the solar composition. Condensation sequence of refractory minerals and their grain size are presented as a function of the cooling time of gas and the total gas pressure. The formation of refractory grains in sites of astrophysical interest is discussed.

§ 1. Introduction

Condensation of minerals in the cooling gas of various composition has been studied to understand the origin of meteorites and terrestrial planets,¹⁾ and also to investigate the composition of circumstellar and interstellar dust grains²⁾ on the basis of the chemical equilibrium theory. However this theory predicts only the temperature below which a bulk mineral is in a stable state. Formation of solid materials from a vapor takes place via formation of condensation nuclei. Consequently the condensation temperature is lower than that predicted by the chemical equilibrium theory because of the excess of the Gibbs free energy to form condensation nuclei.

The process of nucleation and grain growth was independently investigated by Yamamoto and Hasegawa³⁾ and Draine and Salpeter⁴⁾ on the basis of a classical homogeneous nucleation theory. This theory can predict the condensation temperature, number density and mean radius of grains formed, and has been applied to study the formation of dust grains in a variety of astrophysical sites such as novae,⁵⁾ late type stars^{6,7)} and comets.⁸⁾ This theory is formulated for a one component system in which a vapor is composed of one species. In order to study the condensation of minerals which are believed to be constituents of meteorites and interstellar dust grains, however, the process of nucleation and grain growth of minerals in a system of multi-component vapors is to be taken into account.

In this paper we formulate the process of nucleation and grain growth for a mineral whose composition satisfies the stoichiometric relation. In § 2 we formulate the process of nucleation and grain growth. Section 3 gives results of the calculations in a cooling gas of the solar composition. In § 4 results of the calculations and the condensation of refractory minerals in astrophysical sites are discussed. Conclusion is presented in § 5.

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§ 2. Formulation

First we generalize the formulation for the process of nucleation and grain growth presented by Kozasa et al.⁷⁾ Further the chemical reaction accompanying nucleation and growth is taken into account.

As a vapor becomes supersaturated through a certain process, grains with a stoichiometric composition condense homogeneously via the reaction,

$$\sum_i \nu_i A_i = \text{a condensate}, \tag{2.1}$$

where A_i 's represent the chemical species of reactants and products in the gas phase and ν_i 's are stoichiometric coefficients, which are positive for reactants and negative for products, respectively. We treat the chemical reaction accompanying nucleation and growth under the following assumptions:

- (1) The rates of nucleation and grain growth are controlled by one chemical species, which is referred to as a key species.
- (2) The key species is the species of the reactant that has the least collisional frequency onto a target nuclei. In the case that there are two or more kinds of minerals that are composed of the same elements and are thermodynamically stable in the nearly equal physical conditions, we assume (3) that a chemical composition of grains is nearly equal to the abundances of vapor species in a supersaturated state. Then the steady state nucleation rate J is written as

$$J = \alpha_s \Omega (2\sigma/\pi m_1)^{1/2} c_1 \exp[-4\mu^3/27/(\ln S)^2], \tag{2.2}$$

where α_s is a sticking probability of the key species (in the following calculations we set $\alpha_s=1$), Ω is a volume of a condensed material per one molecule of the key species, σ is a surface tension of a condensed material, m_1 is a monomer mass of the key species, S is the supersaturation ratio and c_1 is a concentration of monomer of the key species. The parameter μ is defined by $\mu=4\pi a_0^2 \sigma/kT$, where a_0 is given by $4\pi a_0^3/3=\Omega$, k is the Boltzmann constant and T is the temperature of gas.

The process of nucleation and grain growth is controlled by the growth of grains and the accompanying consumption of monomers of the key species. We take $t=0$ when $S=1$. This point is referred to as the equilibrium point and quantities at this point are represented by the subscript "e". The increase of S causes the nucleation rate to increase rapidly, while the accompanying consumption of monomers of the key species due to the growth of grains causes S and J to decrease. The grain growth and the consumption of the key species are respectively described by

$$dr/dt = \alpha_s \Omega \langle v \rangle c_1(t), \tag{2.3}$$

$$c_1(t)U(t) - c_{1e}U_e = - \int_0^t J(t')U(t')(4\pi/3\Omega)r^3(t, t')dt', \tag{2.4}$$

where $r(t, t')$ is a radius of grain which nucleates at t' and is measured at t . A specific volume $U(t)$ is defined so that $c_1(t)U(t)$ would be conserved if the amount of monomers were not depleted due to nucleation and growth. This factor is introduced

to take into account the change in the temperature and density in the course of nucleation and grain growth. The collision velocity $\langle v \rangle$ is given by $\langle v \rangle = (kT/2\pi m_i)^{1/2}$.

The supersaturation ratio S is generally expressed by

$$\ln S = -\Delta G_0 + kT \sum_i \nu_i \ln(P_i), \quad (2.5)$$

where ΔG_0 is the Gibbs free energy of formation of a bulk material per one monomer of the key species, and P_i is a partial pressure of the i -th species. By introducing new variables $X = \delta_1 \ln(P_i/P_{ie})$ and $Y_i = c_i(t)U(t)/c_{ie}U_e$, Eq. (2.5) is transformed into

$$\ln S = X + \sum_i \nu_i \ln(Y_i), \quad (2.6)$$

where $\delta_1 = \sum_i \nu_i$, c_i is the concentration of the i -th species, P_i is the total pressure and P_{ie} is the total pressure for which the condensed materials are marginally saturated with the vapor. When $1 - Y_i \ll 1$, Eq. (2.6) is reduced to

$$\ln S = X - \delta_2(1 - Y_1), \quad (2.7)$$

where $\delta_2 = \sum_i \nu_i^2 (c_{ie}/c_{ie})$.

By using X and Y_1 , Eqs. (2.3) and (2.4) are also transformed into

$$d\rho/dX = GY_1, \quad (2.8)$$

$$1 - Y_1 = (\Lambda_e^4/81) \int_0^X (\mu/\pi)^{1/2} \exp[g(X')] G(X') \rho^3(X, X') dX', \quad (2.9)$$

where ρ is a reduced radius defined by $\rho = 3r/\Lambda_e a_0$, and Λ is defined by the ratio of the saturation time $\tau_s = |dX/dt|^{-1}$ to the collision time given by $\tau_{col} = [\alpha_s 4\pi a_0^2 \langle v \rangle c_1(t)]^{-1}$. The function $G(X)$ is defined by

$$G(X) = \tau_s \langle v \rangle U(X)^{-1} / \tau_{se} \langle v \rangle_e U_e^{-1}, \quad (2.10)$$

which represents the change of the physical conditions in the course of nucleation and growth and satisfies the relation that $\Lambda(X) = \Lambda_e G(X)$. The function $g(X)$ is given by

$$g(X) = 2\ln(Y_1) - a^2/(\ln S)^2, \quad (2.11)$$

where $a^2 = 4\mu^3/27$.

The function $g(X)$ has a maximum due to the depletion of monomers at $X = X_c$ determined by $dg(X)/dX|_{X=X_c} = 0$. The nucleation rate J is proportional to $\exp[g(X)]$ and is sensitive to $g(X)$. When $\Lambda_c \equiv \Lambda(X = X_c) \gg 1$, the nucleation rate has a sharp maximum at immediate vicinity of X_c , which implies that the avalanche of nucleation takes place at X_c . We call this point the condensation point and quantities at the condensation point are represented by the subscript "c". It can be verified that, at X_c , the depletion of monomers is negligible and the nucleation rate has a sharp maximum for $\Lambda_c \gg 1$. Then by means of Eqs. (2.7)~(2.9) and (2.11), X_c is determined by

$$(\delta_2/108) \Lambda_c^4 (\mu_c/\pi)^{1/2} (X_c^9/a_c^6) \exp[-a_c^2/X_c^2] = (1 + 1/W_c)^{-1}, \quad (2.12)$$

where $W_c = \delta_2 a_c^2 / X_c^3$. The number density of grains formed is given by

$$N_{gr} = \int_0^t U(t') J(t') dt' / U \cong \int_0^\infty U(t') J(t') dt' / U$$

$$= \delta_2 (c_{1e} U_e / U) (\Lambda_c / 3) (\mu_c / 2)^{1/2} \exp(-1 - a_c^2 / X_c^2) / W_c. \quad (2.13)$$

When all the key species are consumed, the mean radius r of the grains is given by

$$r = a_0 (c_{1e} U_e / N_{gr} U)^{1/3}, \quad (2.14)$$

from the conservation of the total number of monomers. These approximation formulae fit well with the results of numerical calculations of Eqs. (2.5) and (2.6) if $\Lambda_c \gg 10$.

§ 3. Result of calculations

We calculate the condensation temperature, i.e., the temperature at X_c and radius of grains condensed in the gas of the solar composition under the isobaric cooling. The elemental abundances of gas of the solar composition are taken from the table of Cameron.⁹⁾ Abundances of molecular species are assumed as follows in view of the calculations¹⁰⁾: All C, Si and Ti are in the form of CO, SiO and TiO respectively, and remaining O atoms are locked into H₂O. Elements Al, Ca, Mg and Fe are in atomic form. All hydrogen atoms which are not combined into other molecules are in the form of H₂. This molecular abundance is similar to that in the gas in chemical equilibrium at the temperature of 2000 K.¹⁰⁾ In the cooling of gas with these abundances, Al₂O₃, CaTiO₃, MgSiO₃ and Fe are expected to be the major condensates. MgSiO₃ is expected to be the major condensate of Mg-silicates from assumption (3) described in § 2.

P_{ie} is generally expressed in the Clausius-Clapeyron form,

$$\ln(P_{ie}) = -A/T + B, \quad (3.1)$$

where P_{ie} is in units of atm. Constants A and B are evaluated by fitting thermodynamic data in the range of temperature of interest. The thermodynamic data needed for the calculations are taken from JANAF table¹¹⁾ and the table of Robie and Waldbaum.¹²⁾ Numerical constants used in the calculations and the chemical reactions accompanying nucleation and growth are summarized in Table I. It should be kept in mind that we use the value of surface tensions of liquids. Generally the value of surface tension of solid is larger than that of liquid, but the cluster that is composed of a few tens to hundreds has a melting temperature lower than that for bulk.¹³⁾ Since the critical size of nucleus at the condensation point is of the same order of magnitude as the size of clusters, we use the value of surface tension of liquids. The surface tension of the compounds of oxides that is not available in the literature is estimated by the use of the surface tension factors.¹⁴⁾

Figures 1(a) and (b) represent the condensation temperature versus the cooling time defined by $\tau_r = |d \ln T / dt|^{-1}$ for total pressures of 10^{-5} and 10^{-7} atm, respectively. Figures 2(a) and (b) show the mean radius versus the cooling time.

Table I. Numerical constants and chemical reactions accompanying nucleation and growth used for calculations. References; 11) JANAF (1971), 12) Robie and Waldbaum (1968), 14) Boni and Derge (1956), 15) Kingery (1959), 16) Elliott et al. (1963).

minerals	key species	Reaction	$A/10^4$ (K)	B	a_0 (Å)	σ (dyne/cm)	δ_1	δ_2
Al_2O_3	Al	$2\text{Al}_{(g)} + 3\text{H}_2\text{O}_{(g)} \rightarrow$	9.34518	46.6903	1.7179	690.	1.	1.030
		$\text{Al}_2\text{O}_{3(s)} + 3\text{H}_{2(g)}$						
CaTiO_3	TiO	$\text{Ca}_{(g)} + \text{TiO}_{(g)} + 2\text{H}_2\text{O}_{(g)}$	7.95682	42.0204	2.3711	494.	2.	1.042
		$\rightarrow \text{CaTiO}_{3(s)} + 2\text{H}_{2(g)}$						
MgSiO_3	SiO	$\text{Mg}_{(g)} + \text{SiO}_{(g)} + 2\text{H}_2\text{O}_{(g)}$	6.53088	39.1968	2.3193	400.	2.	2.599
		$\rightarrow \text{MgSiO}_{3(s)} + 2\text{H}_{2(g)}$						
Fe	Fe	$\text{Fe}_{(g)} \rightarrow \text{Fe}_{(s)}$	4.91725	26.9290	1.4114	1800.	1.	1.
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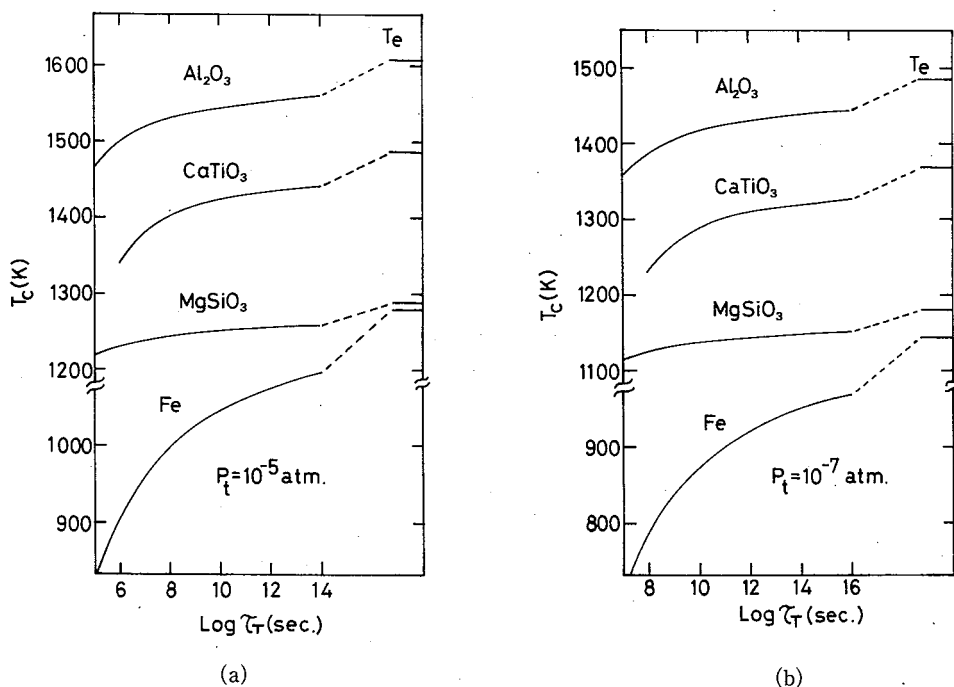


Fig. 1. (a) The condensation temperature of each mineral versus the cooling time for total pressure of $P_t = 10^{-5}$ atm.

(b) The same as (a), but for $P_t = 10^{-7}$ atm.

As the total pressure lowers and/or the cooling time becomes short, it can be seen that the difference between the equilibrium temperature T_e and the condensation temperature T_c increases and the mean radius decreases. This is explained in terms of the parameters Λ and μ as discussed below.

§ 4. Discussion

4.1. The process of nucleation and grain growth

The process of nucleation and grain growth is characterized by the parameters Λ

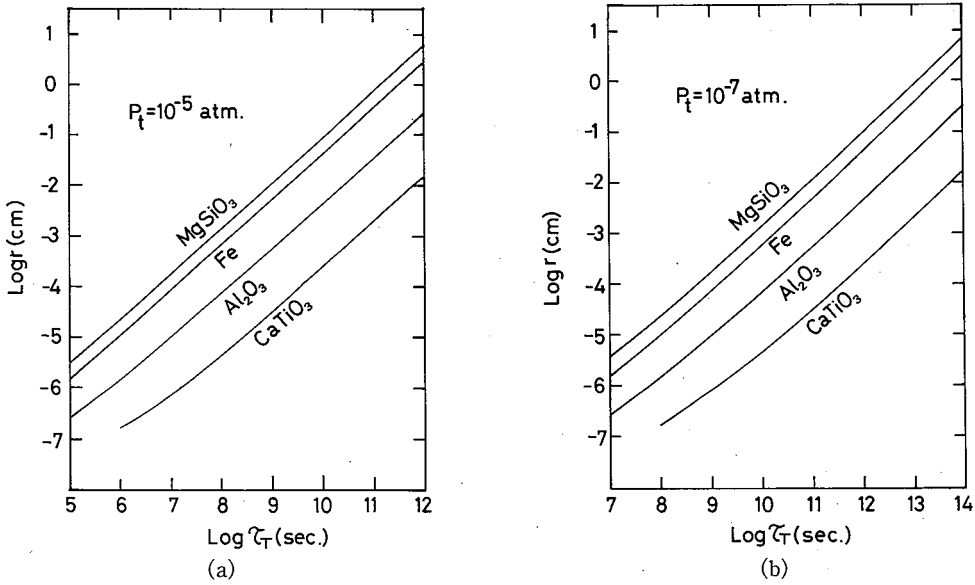


Fig. 2. (a) The mean radius of grains versus the cooling time for the total pressure of $P_t=10^{-5}$ atm. (b) The same as (a) but for $P_t=10^{-7}$ atm.

and μ . The parameter Λ represents the physical conditions, while the parameter μ the barrier for nucleation. The number density as well as the mean radius of grains strongly depends on the parameter Λ , which is approximately proportional to $P_t\tau_T$. When the nucleation and grain growth occurs for large Λ , consumption of the key monomers due to the growth of grains causes the supersaturation ratio S to decrease rapidly. Thus formation of grains occurs explosively in the very narrow interval around X_c , whose width is approximated by $\Delta X \sim (a_c^2/X_c^3)^{-1}$. This leads to the smaller number density of the grains and the larger mean radius. The difference between the equilibrium temperature and the condensation temperature $\Delta T = T_e - T_c$ is approximately proportional to $\mu^{3/2}$ for a given material, which means that the high supersaturation ratio is needed for a material having large surface tension to condense.

In a cooling gas of the solar composition under the isobaric cooling, the mean radius r and the temperature difference ΔT are well approximated in terms of $x = \log(P_t\tau_T)$ and $y = \log(P_t)$ as

$$\log(r) = ax^2 + bx + cy + d, \tag{4.1}$$

$$\Delta T = [1 + 1/(e + fx + gy)](hy^2 + iy + j). \tag{4.2}$$

Since $\log(r)$ is approximately proportional to $\log\Lambda$ as derived from Eqs. (2.12) and (2.14), the dominant term in Eq. (4.1) is the second one. In Eq. (4.2) the dominant term is the constant j , which is proportional to $\mu^{3/2}/\delta_1 A$. Numerical constants a to j for mineral species calculated in the range of $P_t=10^{-3}$ to 10^{-11} atm are given in Table II, where P_t is in units of atm, τ_T in sec and r in cm. These approximation formulae are well fitted with the results of the calculations. The error is 15% for r and ± 1 K for ΔT for $10 < \Lambda_c < 1 \times 10^{10}$ except for iron. For iron Eqs. (4.1) and (4.2) hold within the error of 15% for r and ± 2 K for ΔT for $1 \times 10^2 < \Lambda_c < 1 \times 10^{10}$. As shown by

Table II. Numerical constants a to j for approximate formulae Eqs. (4.1) and (4.2) of mean grain size and temperature difference of each mineral.

	Al ₂ O ₃	CaTiO ₃	MgSiO ₃	Fe
a.	1.073×10^{-2}	1.408×10^{-2}	9.111×10^{-3}	9.135×10^{-3}
b.	8.010×10^{-1}	7.256×10^{-1}	8.414×10^{-1}	8.329×10^{-1}
c.	-6.873×10^{-3}	-7.458×10^{-3}	-7.670×10^{-3}	-1.838×10^{-2}
d.	-6.710	-7.657	-5.559	-5.702
e.	5.666×10^{-2}	5.872×10^{-2}	5.476×10^{-2}	4.911×10^{-2}
f.	-4.306×10^{-4}	-7.905×10^{-4}	-3.202×10^{-4}	-3.814×10^{-4}
g.	1.533×10^{-1}	7.020×10^{-2}	2.206×10^{-1}	1.847×10^{-1}
h.	9.947×10^{-3}	1.109×10^{-2}	8.652×10^{-3}	8.561×10^{-2}
i.	4.966×10^{-1}	5.176×10^{-1}	3.922×10^{-1}	2.867
j.	2.091×10^1	1.958×10^1	1.443×10^1	8.265×10^1

Eq. (4.1) and Table II the radius of grains is a good indicator of the physical conditions at the place where nucleation and grain growth occur. In the case that the total pressure varies with the temperature, the figures and approximations can be used to estimate r and ΔT by replacing τ_r by $\tau_{r_{\text{eff}}} = \tau_r |(T/A)d \ln P / d \ln T - 1|^{-1}$.

4.2. Condensation of refractory materials

Figures 1(a) and (b) and Table II show that Al₂O₃, CaTiO₃, MgSiO₃ and Fe grains condense in this order as a gas of the solar composition cools down. Note that condensation of metallic iron is always preceded by the condensation of Mg-silicates in contrast with the prediction of the chemical equilibrium theory, which predicts that the condensation temperature of iron is higher than that of Mg-silicate for $P_t > 4 \times 10^{-5}$ atm. The lower condensation temperature of iron is due to its large surface tension. For the same P_t and τ_r , the mean radius becomes small in the order of MgSiO₃, Fe, Al₂O₃ and CaTiO₃, whose result reflects the difference in the abundances of key monomers.

At present the thermal history of the primordial solar nebula is not well understood. Nakazawa¹⁷⁾ estimated the highest gas temperature and cooling time in the course of the formation of primordial solar nebula under assumptions that the gravitational energy of accreting gas is completely converted to the thermal energy and that the gas cools down radiatively after that. According to his estimation, at least in the inner planetary region of the primordial solar nebula, the temperature of gas rises high enough that primitive interstellar dust grains contained in the infalling interstellar gas evaporate completely. Around the orbit of the Earth, Nakazawa estimated the total gas pressure p_t to be of the order of 10^{-5} atm and the cooling time τ_r to be of the order of 10^7 sec around the temperature of 1000K. For these values of P_t and τ_r , we calculate the condensation temperatures of Al₂O₃, CaTiO₃, MgSiO₃ and Fe to be 1518, 1379, 1237 and 959 K and the mean radii to be 8.58×10^{-6} , 7.08×10^{-7} , 1.52×10^{-4} and 1.05×10^{-4} cm, respectively. At larger heliocentric distances, P_t would be lower and τ_r would be shorter. These physical conditions lead to lower condensation temperatures and smaller mean radii.

Dielectric grains of submicron size are considered to exist in interstellar space.¹⁸⁾ Main sources of interstellar grains are late type cool luminous stars, which lose mass

at the rate of 10^{-7} to $10^{-4} M_{\odot}/\text{yr}$ and have circumstellar dust shell.¹⁹⁾ One of composition of dust grains in the circumstellar shell of oxygen rich stars is silicates which are expected from their spectral features at 10 and 20 μm . According to the condensation theory, the composition of silicates is expected to be MgSiO_3 , if the gaseous abundance is similar to the solar composition. The temperature at the inner radius of circumstellar dust shell is estimated to be about 1000 K.²⁰⁾ Under the assumptions that the mass loss from these stars is driven by the radiation pressure on Mg-silicate grains and that the gas flow is in a steady state, it can be seen that the condensation distance of MgSiO_3 grains is just inside the sonic point, where the condensation temperature is about 1000 K and the total gas pressure is about 10^{-10} atm.⁷⁾ The condensation distance of grains such as Al_2O_3 and CaTiO_3 is inside the sonic point, while the condensation distance of Fe grains is far beyond the sonic point. Formation of Fe grains in this region would be actually very difficult because of its large surface tension, low gas density and rapid decrease of the gas density outside the sonic point. It is very interesting and important to investigate what kind of minerals iron vapor condenses into, since iron is considered to be locked in solids as suggested from the observations of interstellar depletion.²¹⁾

§ 5. Summary and concluding remarks

Condensation of refractory materials in a cooling gas of the solar composition is summarized as follows: (1) Main refractory materials Al_2O_3 , CaTiO_3 , MgSiO_3 and Fe condense sequentially in this order as the gas cools down, whose result differs from that predicted by the chemical equilibrium calculations as to the order of the condensation of Mg-silicates and iron. (2) As the total gas pressure becomes low and/or the cooling time of gas becomes short, the temperature difference between the equilibrium temperature and the condensation temperature increases and the mean radius of grains becomes small, and vice versa.

The temperature difference ΔT for iron is especially large, which is due to its large surface tension ($\sigma=1800$ dyne/cm). Blander and Katz²²⁾ pointed out that iron atoms are to be directly incorporated into pre-condensed Mg-silicate grains because of the barrier to nucleation. But it is known that impurities such as N, O, S and P dissolved into iron lower the surface tension of iron very much.¹⁶⁾ This effect and the resulting iron-bearing materials shall be discussed elsewhere.²³⁾

Finally we remark on the possibility of heterogeneous nucleation. In sequential condensations, it is possible that grains condensed at high temperature act as seed nuclei for the subsequent condensation, resulting in formation of core-mantle type grains. The heterogeneous nucleation rate depends on the interfacial tension between the core and mantle materials and on the physical conditions such as the number density of core grains, the vapor pressure of mantle materials and the cooling time of gas. At present the values of the interfacial tension between refractory materials of astrophysical interest are not well known. Condensation of refractory materials involving heterogeneous nucleation is a subject for the future investigation.

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